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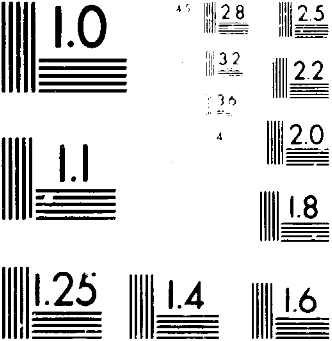

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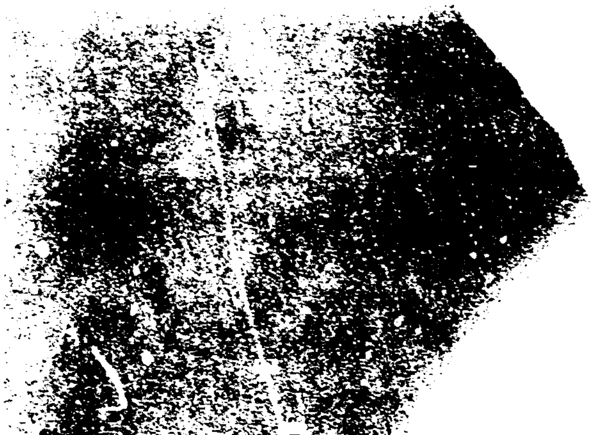

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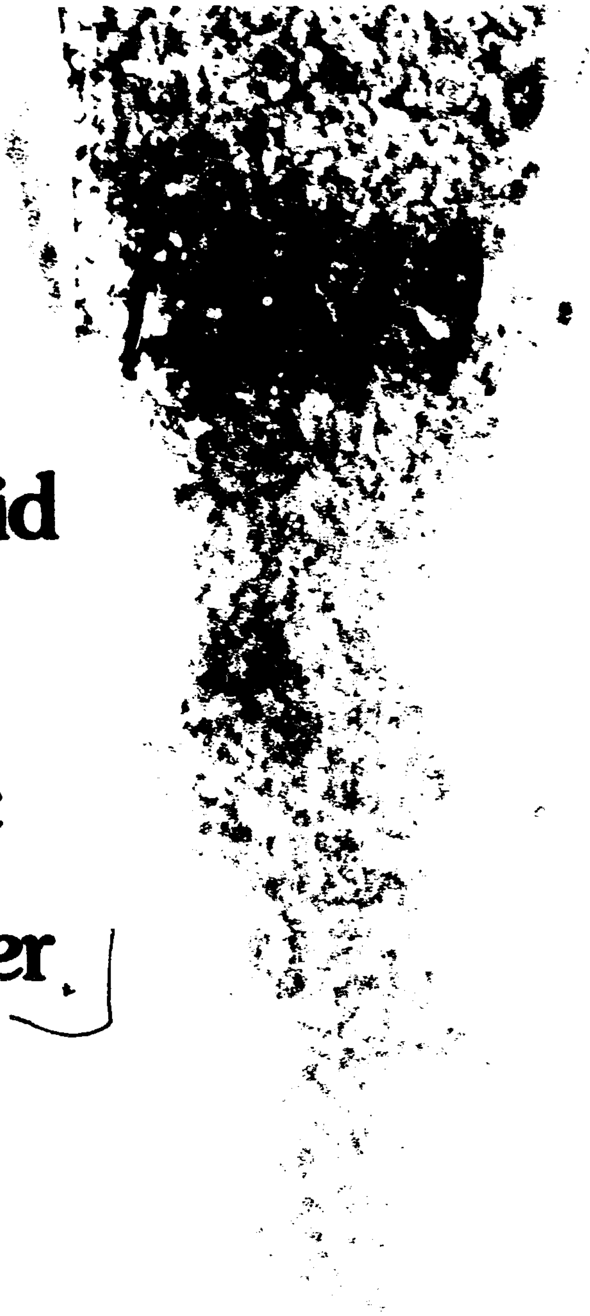

1981

Proceedings of a UNIDO-sponsored Symposium

13619

Powdered, Liquid and Thermoplastic Natural Rubber

Proceedings of a Symposium sponsored by the
United Nations Industrial Development Organisation
in association with
The International Rubber Research and Development Board

May 14-15,1981
Phuket, Thailand

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Malaysian Rubber Research and Development Board

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The papers collected in this volume were presented at a symposium sponsored by the United Nations Industrial Development Organisation (UNIDO) in collaboration with the International Rubber Research and Development Board (IRRDB), the Malaysian Rubber Research and Development Board (MRRDB), the Rubber Division of the Department of Agriculture, Thailand and the Rubber Research Centre (RRC), Thailand.

The symposium was held at the
Pearl Hotel, Phuket, Thailand
on May 14-15, 1981

BACKGROUND

During the 1970's it was widely forecast that the rubber industry would increasingly use rubber in new physical forms such as liquids or powders; and that thermoplastic rubbers would enable the industry to convert to simpler 'plastic-like' processing techniques.

It was to anticipate and meet such developments that the IRRDB in 1977 proposed to UNIDO a project to increase the competitiveness of natural rubber by the study of its production and properties in thermoplastic and free-flowing forms. The project was started in early 1979 and completed in March, 1981; it was supported by a special purpose contribution to the UNIDO fund by the Federal Republic of Germany.

The papers presented at the symposium describe the work carried out under the project by the contracting body, the MRRDB, at the laboratories of the Rubber Research Institute of Malaysia and the Malaysian Rubber Producers' Research Association with assistance from the Rubber Research Institute of Sri Lanka. Methods of production, technical properties, applications and economic aspects are dealt with. Also included are the views of experts from the rubber industry on the role of these new forms of rubber in the future, and an assessment of the possible viability of liquid natural rubber.

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Welcoming Address

by

Dr Slearmlarp Wasuwat

Director, Rubber Division, Department of Agriculture

Bangkok, Thailand.

Dr Herbert May, Tan Sri Dr B.C. Sekhar, IRRDB/UNIDO Delegates, Distinguished Guests, Ladies and Gentlemen:

On behalf of the Ministry of Agriculture and Cooperatives who authorized the Rubber Research Centre of Thailand to assist the UNIDO in organizing this important Symposium, we welcome all UNIDO/IRRDB officials, fellow participants, and attending guests to this gathering. The main reason why we are willing to assist this Meeting is because we consider it is a most important Symposium, the first of its kind in Thailand. Furthermore, the subjects to be presented and discussed and the future work to be done serve as a bridging or linkage between the prime or raw NR producers and the industrial users for which the IRRDB and UNIDO have played a major role now and will again in the future.

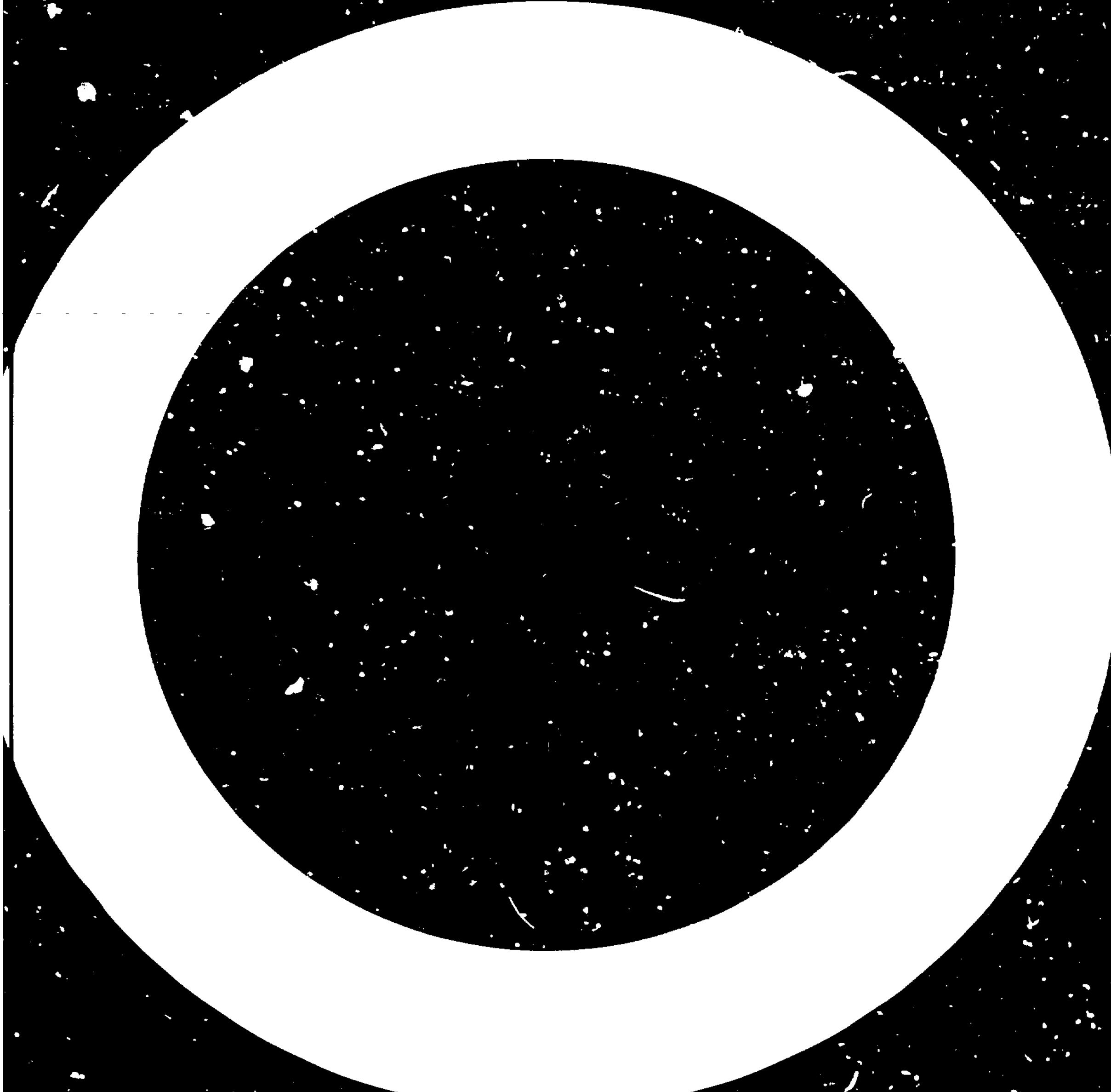
For NR producers in general and particularly the Smallholders in Thailand who are firmly supported by the RRC Thailand, to induce the new and better techniques of processing and utilization of NR adds to their economic and long term future. From the raw NR producers point of view, once they plant the rubber tree on the ground at least thirty years of their welfare have to depend on it. The more that we can ensure their future, the more they, as well as their neighbours, will produce more NR for us and the world.

On behalf of myself and my colleagues on the organizing committee, while we will do our best, this type of Symposium is relatively new for us and many errors or mishaps will occur. We would appreciate your advice and hopefully your sympathy because the language of communication is not our mother tongue. The majority of members of our organizing committee have never been trained abroad. Misjudgements and misunderstandings will happen; please kindly excuse them.

Lastly on behalf of my organization, the Rubber Division of the Department of Agriculture, which is responsible for all technical and development matters related to production, processing, utilization, and marketing of NR for Thailand, we will exert our best efforts to cooperate, coordinate and operate with all of you and the organizations with which you are concerned for the benefit of the world requirement for NR.

May I wish this Symposium great success.

Thank you.



Welcoming Address

by

Mr H. May

Head Chemical Industries Section, UNIDO

Ladies and Gentlemen,

On behalf of the Executive Director of UNIDO it is my honour and privilege to welcome you all here to participate in the UNIDO International Symposium on Powdered, Liquid and Thermoplastic Natural Rubber. UNIDO wishes to thank the Government of Thailand, Dr Slearmlarp Wasuwat and Dr Sribo Chaiprasit of the Rubber Research Centre for hosting this Symposium. To the IRRDB, UNIDO expresses its appreciation for this collaboration. Special thanks are also due to the MRRDB laboratories for the technical work well done. As many of you are aware, the UNIDO project was supported through a Special Purpose Contribution of the Federal Republic of Germany to the United Nations Industrial Development Fund. It is through the generous financial contribution from the FRG Government that the project was implemented during the last two years.

As you all know, the principal aim of this Symposium is to disseminate the results of the project 'Increasing the Competitiveness of Natural Rubber' and to explore their fuller exploitation and application particularly in rubber producing and other developing countries. The Symposium presents the results of two years work carried out on behalf of UNIDO by the MRRDB at its major laboratories in the UK and Malaysia.

I believe it is proper for me here to acknowledge the efforts of a distinguished pioneer and leader in the Natural Rubber field, Dr B.C. Sekhar who has played a key role in initiating the co-operation with UNIDO since his visit to UNIDO Headquarters, Vienna, in 1976 and maintained his keen interest in the present project throughout the implementation period. Dr Mullins must also be mentioned here for his important contributions to the design and formulation as well as the successful accomplishment.

The project started in February 1979 with its specific aims to:

a. Increase the competitiveness of Natural Rubber and to extend its range of industrial application;

b. Increase the co-operative efforts among the Natural Rubber producing countries in research and development;

c. Develop technologies in converting Natural Rubber into forms suitable for use in highly automated manufacturing processes normally used for conventional synthetic polymers;

d. Encourage increased production of Natural Rubber world-wide by strengthening the position of Natural Rubber technically and economically and by extending the range of applications.

In addition, there are two long-term objectives, namely one to increase the opportunities of employment and to encourage the local processing and manufacturing of Natural Rubber products, and the second, to conserve petroleum and natural gas which are the basic raw materials for the production of synthetic rubber and plastics.

This project has just been completed and you will hear the results of this work during the course of this Symposium.

We are pleased to learn that three new members have joined IRRDB during the past two years and also pleased to note that as a result of the success achieved in the first project, the IRRDB has now selected Rubber Composites as a first priority and Liquid Natural Rubber as second priority for a new IRRDB/UNIDO area of collaboration.

Further, in July 1980, UNIDO together with the Mexican National Council for Science and Technology sponsored an International Symposium "Natural Rubber towards the Year 2000". Proposals have emerged from this Symposium for UNIDO's action in support of IRRDB proposals. The first one was to support research and development work on Composite Rubber and the second on Liquid Natural Rubber. I am pleased to report that both of these proposals have been followed up by UNIDO and are under active consideration by the prospective sources of financing. Both these projects are designed for TCDC (Technical Co-operation among Developing Countries) which joins the efforts of developing countries in utilization of their natural resources and development of their industries.

UNIDO's work is guided by the Declarations and Plans of Action of Lima and New Delhi. According to the Lima target, the share of the developing countries' production in the manufacturing sector should reach 25 per cent of the total world production by the year 2000. To this end certain priority areas have been stressed in the New Delhi Plan of Action such as development and transfer of energy related technologies, development of human resources and increased industrial production. You will agree that Natural Rubber has an important role to play in fulfilling these targets.

I feel that the papers to be presented and the ensuing discussions will prove to be both beneficial and useful in helping us to identify further follow-up action and research work to be undertaken and how the results could be used. My colleagues from UNIDO and I will be happy to discuss with you during this Symposium concerning possible technical co-operation with your organizations.

I wish you every success.

INTRODUCTORY ADDRESS

by

Tan Sri Dr. B.C. Sekhar

Chairman, International Rubber Research and Development Board

This UNIDO/IRRDB Symposium signalizes a situation which is unique in several respects. Natural rubber (NR) is entering into partnership with petrochemically-derived plastics, and the days of "natural versus synthetic" are coming to an end, with the advent of NR/plastic blends. Energy has become a major factor affecting choice and use of materials across the world. Linked with the energy theme is the fact that the world may soon start to see a shortage of some materials; in the case of NR the future need is for more, not less.

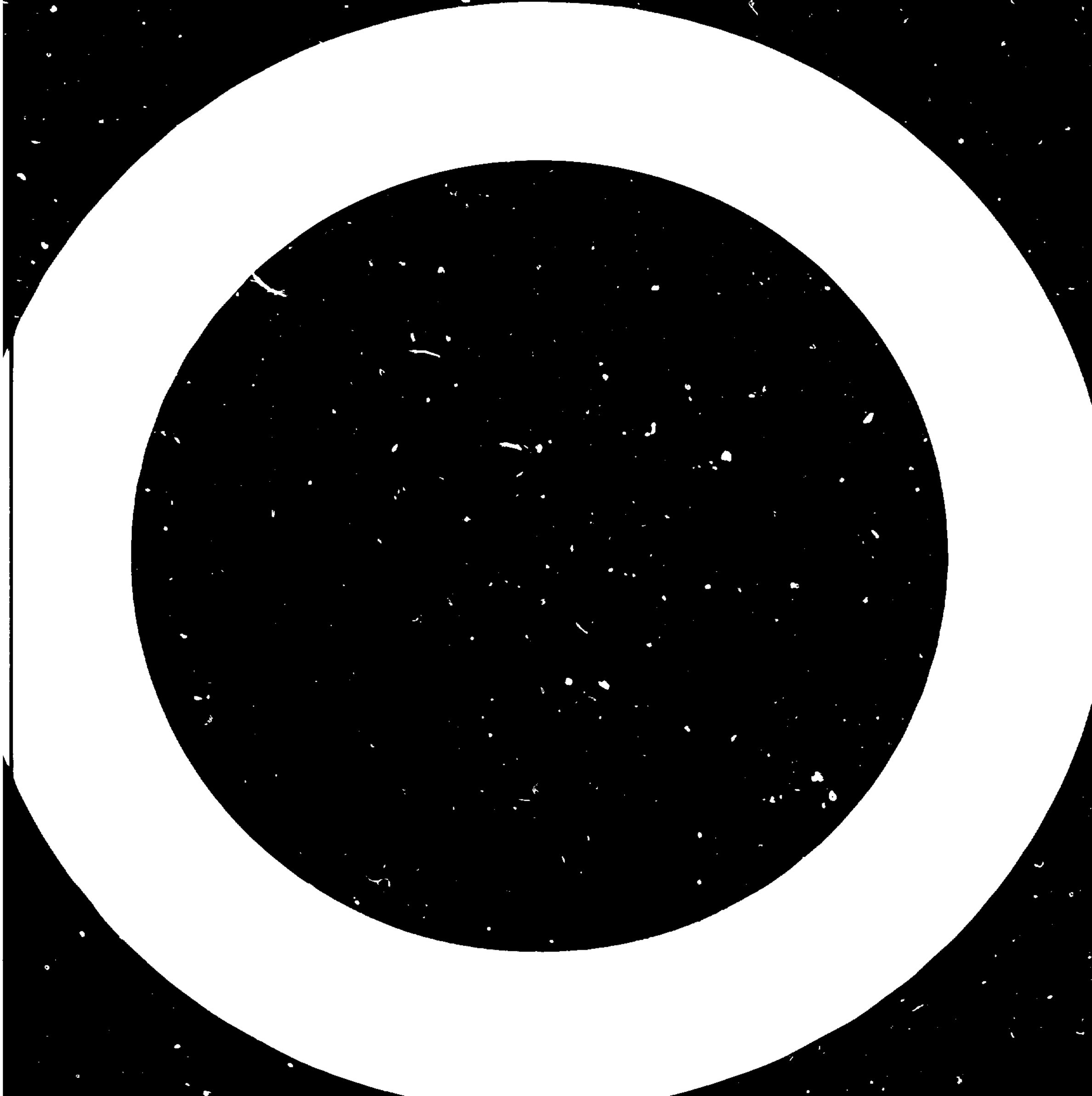
The Symposium is concerned to promulgate - to NR producing and all other developing countries - the outcome of the recently completed UNIDO/IRRDB Project on thermoplastic and powdered forms of NR. In choosing topics within this Project the features just noted were very much kept in mind. Powdered rubbers offer possibilities for energy saving during processing. Thermoplastic NR symbolizes the natural/synthetic partnership and is also relevant to the future materials supply situation.

Uniqueness also characterizes the IRRDB and also the way in which the IRRDB and UNIDO co-operated to set up this Project. The IRRDB itself is a form of "club" without, as far as I know, any parallels in other industries. It has no rules, and functions on the basis that decisions are taken only in a basis of mutual discussion among members of the "club" - the members do not compete with one another, but co-operate.

The overall purpose of the IRRDB is to help to optimize the totality of research and development in NR. To this end 1 per cent of the IRRDB's annual budget is now allocated to a special research fund. The linkage with UNIDO provided substantial extra muscle to give purpose to a number of promising ideas in the R & D pipeline. This linkage was unique in that the UNIDO Project did not follow the orthodox UN pattern, ie with engagement of outside experts. Instead, the Project team comprised scientists and technologists within IRRDB institutes who were able, by virtue of their substantial experience in relevant fields, to make rapid and effective progress, as we shall be hearing in the next two days.

This Project is only the start of intensive collaborative work among IRRDB members. Already, we have just completed a seed collection exercise in Brazil, which will provide germplasm for breeding work over the next 20-30 years. This long-term investment in NR's future has cost the IRRDB member institutes some £80 000. Next in the pipeline is work on NR-based composite materials and on liquid NR. For this, we are seeking further assistance from UNIDO.

Speaking as Chairman of the IRRDB and also as Chairman of the Malaysian Rubber Research and Development Board, I would like formally to thank UNIDO together with the Government of the Federal Republic of Germany, and especially to record our appreciation of the way in which Dr H May has assisted in the development of this fruitful co-operative exercise.



PROSPECTS FOR POWDERED, LIQUID AND THERMOPLASTIC ELASTOMERS

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INTRODUCTION

I am very pleased to have the opportunity to open a conference on powdered, liquid, and thermoplastic rubbers since I have been intrigued by them for thirty years. Each is in its way an approach to a very fundamental problem of the rubber industry. How do we deal with a very viscous material whose formulation into finished parts is an onerous task? The processing of rubber is still a very primitive technology where brute force is used instead of brain power. It requires labour intensive operations with massive energy consuming equipment. The scrap is not recoverable. Powders, liquids and thermoplasts each represent an attempt to capitalize on the more modern and efficient approaches of the plastics industry. Of the three I feel the use of powders likely to be limited since it is flawed by poor economics. The others are quite sound and should continue to grow strongly.

POWDERED RUBBERS

In the case of powders we are trying a one-for-one replacement designed to produce standard cured elastomers more effectively; with shorter mixing cycles in streamlined process lines. The assumption is that if the elastomer is in particulate form we can then use plastics processes. We dream of a plant where powdered rubber is discharged from hopper cars to storage silos. Rubber and compounding ingredients are metered into low cost intensive mixers. The dry compounds are then pneumatically conveyed to storage bins that feed mixer/extruders. Extrudates are continuously moulded and cured, inspected electronically, and stored. Meanwhile a small work crew sits in a spotless control room where scheduling, input, output, etc. are all organized by computer. Profits roll in and everyone is happy. Just contrast this with the inferno-like atmosphere of the typical rubber shop and you can understand the interest!

If it's all that good why doesn't it happen? I think the answer is that it's a mirage, with just enough substance to tantalize us and lead us on, but too far from reality to become a major factor. But there is enough there for certain specific situations, particularly for speciality rubbers.

For general purpose rubbers there are formidable economic and technical difficulties which make success improbable. First the world wide rubber industry has long been in difficult straits; 1980 was one of its worst years with production off 20-25%. Capacity is in excess and the companies cannot afford the expenses for research and development or for the new machinery. In addition the total costs for making and shipping powders are about equal to the savings.

The technological problems are probably all solvable. Bulk or baled rubber can be chopped or pelletized at a cost. Partitioning agents are reasonably effective in keeping particles separate, providing the rubbers do not flow; but most rubbers do! Fillers such as carbon black decrease flow by a gelling effect, but this limits flexibility in formulation. Chopping or pelletizing of solid rubber is probably the simplest approach. The equipment is available and possibly best used by incorporation directly in the processing line. When thus coupled with the extrusion/moulding process the problems inherent in shipping and storage are avoided. This must be the best way where economics justify a dedicated production line as for wire and hose.

Small particulate spheres of general purpose rubbers have been made directly by a variety of techniques. Spray drying of latex is effective if enough filler is present. Huls has patented a coating technique involving deposition of a siliceous coating during coagulation or isolation which yields free flowing particles if enough filler is present. A Du Pont patent teaches that silicic or aluminic acids afford tack-free coatings of a number of rubbers even in the absence of partioning agent or filler. Unfortunately the isolation of small particles requires energy to remove adherent and enclosed water and this must be accomplished under gentle conditions which do not allow massing. For best properties the polymerization chemicals, salts and dispersing agents should be removed from the polymer. I believe natural rubber is a better product for this process since there are no added dispersants.

The presumed benefits of powders are real. Tests have demonstrated shorter mixing cycles, lower power consumption in mixing, less heat development leading to more efficient equipment and lower labour requirements - all of these total greater productivity of capital. So it is a very desirable development if like black- or oil- masterbatch it costs the consumer nothing. But the industry is not in shape to make such a giveaway again. Unfortunately the sub-division of tacky general purpose rubbers can consume more energy than is saved because processing energy is so much less than product energy (Tables 1,2,3,4). Also we forget that most rubbers are in bale form to make isolation and shipping as economical as possible. We forget that the rubbers will need fillers, reinforcing agents, curing and stabilizing chemicals, plasticizers, etc,all of which must be available in a form for plastics style mixing. And we forget the shipping problem. It will be a very unusual rubber that can be shipped in hopper cars as powder or pellets without massing. And what is there to persuade the rubber producer and user to invest in new units to make, ship, store, convey and process the costly powders when he already has know-how and excess capacity? There is simply no driving force!

This pessimistic view for general purpose rubbers is confirmed by realities. Only a few organisations are working on a practical scale with powders, largely where new equipment is needed. Even the plastics industry has shown little interest in powders since pellets serve for most purposes. These are also very useful for the speciality rubbers which do not mass.

This leads us to the area where things are happening. Particulates are quite practical for products such as butadiene/acrylonitrile rubber, high-melting forms of polychloroprene, the fluoro-rubbers and the thermoplasts. With these, processors can get good mixes with one pass in a Banbury mixer or can mill mix in a quarter of the usual time. New equipment to use these is under development in Europe and America. Available products include powdered Hycar acrylonitrile rubber, pelletized

TABLE 1. ENERGY CONTENT OF SELECTED MATERIALS

Material	Specific Gravity	Energy Content by Weight (MJ/kg)	Volume (GJ/m^3)
Cast Iron	7.7	21	161
Sheet Steel	7.8	41	321
Zinc (die cast)	6.7	58	386
Copper	8.3	67	560
SBR	0.94	105	98
Aluminium (die cast)	2.4	215	515
Aluminium (sheet)	2.4	314	754

Source: Elastomerics (August 1978)

TABLE 2. ENERGY CONTENT OF SEVERAL SPECIFIC COMMERCIAL ELASTOMERS

Material	Specific Gravity	Energy Content by Weight (MJ/kg)	Volume (GJ/m^3)
HYPALON synthetic elastomer	1.18	116	137
NORDEL EPDM	0.86	170	146
VAMAC acrylic elastomer	1.03	151	156
NEOPRENE Type W polychloroprene	1.25	163	203
ADIPRENE polyurethane elastomer	1.06	209	222
HYTREL copolyester thermoplastic	1.18	207	244
VITON fluoroelastomer	1.60	477	763

TABLE 3. TYPICAL ENERGY REQUIREMENTS FOR PROCESSING RUBBER-LIKE MATERIALS

Process	Energy (for compound of Specific Gravity 1.0) (GJ/m^3)
One Pass Banbury Mix (from bale or chip form)	3 - 4
Mill Mix (from bale)	15 - 35
Warm-up Operation (of premixed compound)	2
Hot-Feed Extrusion	1 - 2
Cold-Feed Extrusion	2 - 3
Injection Moulding	?

TABLE 4. ENERGY UTILIZATION IN INJECTION MOULDING

Computed for a Rubber Compound
Based on Polychloroprene

Process Step	Energy Use (GJ/m^3)	Energy Use/Polymer Energy Content (%)
Mixing (Banbury)	2.8	1.4
Plasticizing	0.5	0.2
Injection and Packing	0.3	0.1
Curing	0.2	0.1
Total: (Raw Polymer to Moulded Part)	3.8	1.8

Viton fluoroelastomer, and small chips of adhesive polychloroprene. Naturally the thermoplastic elastomers are normally pelletized for easy fabrication in plastics equipment. But for general purpose rubber we are attempting to force fit an unsuitable product to an idealised standard. It would appear that there are more constructive solutions to the problem, namely the liquid and thermoplastic elastomers.

Liquids and thermoplasts are proven successes. Each type is enjoying large scale application in the low cost area because each gives better value in use than competitive products. There are also high priced specialities like the urethanes and silicones which offer sorely needed properties particularly in engineering type applications. Unfortunately we have not yet been able to make much headway where properties of a cured rubber appear essential - tyres, V-belts, or in the auto engine compartment.

LIQUID RUBBERS

In the field of liquids, polyurethanes are the major factor, especially in the form of isocyanate/polyol mixtures where sophisticated mixers permit precise control of stoichiometry and hence of properties in resilient foams, sponges, and in the RIM and LIM injection molding systems. Applications for these systems are so many that they are certain to grow as modified and improved products are developed. However for the outstanding abrasion resistance and toughness which have made the urethanes famous we must resort to prepolymers. These difunctional materials are made from long chain or macro diols and diisocyanates are chain extended and cured with aromatic amines or diols. The standards of excellence are still set with amine cures of products derived from polytetramethylene-ether glycol (PTMEG), polycaprolactone and esters like ethylene adipate. Their uses are myriad, and they have probably brought us closer to revolutionizing the tyre industry than any other approach; this in the form of the cast tire where the composite cord rubber structure is replaced by the multiblock elastomer. Despite many reputed advantages in manufacturing economy and performance the tyre industry has just not had the resources to mount a further change on top of the switch to radials.

For liquid elastomers to achieve major growth we need a wider range of properties like those of the solid rubbers. This requires new chain growth chemistry and new cheaper bifunctional oligomers. These are technically soluble problems but the economics are difficult. Attempts to achieve the objective through oligomerisation of dienes and olefins in the presence of telechelic agents have not yielded the requisite combination of bifunctionality and properties. Therefore in a practical sense we have seen mostly elaboration of the polyester and polyether themes using available cyclic ethers, glycols, and diacids.

An alternative approach to liquid elastomers has been the development of low molecular weight semi-fluid forms of presently available rubbers which are then cured by modifications of standard vulcanization chemistry. Most of the general purpose and specialty elastomers have been offered in such forms. Since the cured properties are in no way comparable with those of their high molecular weight counterparts, their acceptance has been limited and many have been withdrawn from the market. The problem is that a molecular weight low enough to produce a fluid is too low to yield a good network on curing; there is too high a concentration of loose ends. Here again the need is for functional groups at or near the chain ends. Another handicap is the cost and sheer difficulty of producing and shipping these very viscous substances on a large scale.

Because of all these factors the most original work has centred on a search for new reactants to replace the diisocyanates and on the study of capped isocyanate generators or other substances which can generate isocyanates on heating, - thus to avoid the problems of handling toxic isocyanates. These include adducts of isocyanates with phenols, oxiranes or other easily released groups and cyclic products like azlactones and isoxazolones.

In the grey area between elastomers and plastics a new form of liquid rubber has emerged from the technology of the impact toughened plastics. Elastomers such as natural rubber, dehydrochlorinated chlorobutyl, and EPDM are dissolved in monomers like styrene or acrylonitrile. On polymerisation with a peroxide catalyst a rubbery mass is produced even at monomer concentrations of 75%. At first thought you would expect an impact resistant plastic. However, if the plastic forming is sufficiently incompatible with the elastomer, the growing molecules of plastic become insoluble and precipitate as small particles. These are dispersed in and grafted to the now crosslinked elastomer which remains as a continuous phase reinforced by the plastic particles. There are probably other ingenious new ways of capitalizing on the processing advantages of liquids.

THERMOPLASTIC RUBBERS

We approach the ideal of converting our labour intensive processing industry into an efficient modern technology most closely with the class of thermoplastic elastomers. Although the thermoplasts are presently but minor offshoots of the total elastomer market (Table 5), this group is one of the fastest growing segments of the entire polymer field. Thermoplasts offer polymer scientists the opportunity to overcome many deficiencies of the large volume thermoset rubbers. Here too for the first time molecular structures can be designed to combine simple fabrication with desired physical and mechanical properties. The major uncertainty is the extent to which they will replace the thermosets. For this to happen low cost or high value-in-use products are needed with better compression set, with resistance to temperatures of 150°C or higher and with better solvent resistance.

TABLE 5. CONSUMPTION OF CONVENTIONAL AND THERMOPLASTIC ELASTOMERS IN USA*

	Consumption (tonnes)			
	1966	1969	1973	1978
Conventional elastomers	2 203 110	2 629 312	3 160 637	3 860 831
Thermoplastic elastomers	7 370	17 720	57 240	98 400
Total	2 210 480	2 647 032	3 217 877	3 959 231
TPE, % of total	0.33	0.67	1.78	

* Based on data from Rubber World.

Thermoplastic rubbers are usually block copolymers having a two phase microstructure. These blocks can be arranged in random or in ordered fashion in a copolymer molecule. Also we can have physical mixtures or chemically interacted mixtures of hard and soft polymers or even solutions of random or ordered copolymers in plasticizers. At the service temperature one of the blocks is viscous or rubbery; this is the soft segment. The other is of a glassy, crystalline or polar nature; this is the hard segment. It is the intermolecular association of the hard segments which provides the thermo-reversible physical crosslinks in the polymer. Ideally these melt cleanly at the processing temperature and permit easy processing. The family of commercial thermoplastic elastomers consists presently of five well established classes. I plan to skip by the first and oldest which is that of the internally or externally plasticised vinyl copolymers such as polyvinyl chloride and ethylene/vinyl acetate copolymers. More recently various forms of 1,2-polybutadiene including the syndiotactic have appeared as has ethylene/ethyl acrylate copolymer.

The four other major types are depicted in Figure 1. Thermoplastic urethanes were first developed in the 1950's by Goodrich and Bayer (Estane and Texin) and by Du Pont (Lycra elastic fibre). The ordered styrene block copolymers were introduced during the 1960's (Shell Kraton, Phillips Solprene) while the polyester elastomers were offered by Du Pont in 1972. The fourth class is that of the thermoplastic polyolefins which were introduced by Uniroyal as TPR. These are primarily blends of cured or uncured elastomer such as EPDM and a polyolefin plastic like polyethylene or polypropylene. An estimate of the present market shares and trends for each of the four is shown in Figure 2. Based on these projections total US consumption will be in the range of 300 000 tonnes in five years. There are at present over 100 manufacturers of well over 200 products in the field with world consumption about double that of the USA.

This dynamic growth is fueled by two main forces: economic and technological. Duplication of rubbery properties would greatly accelerate the growth. There is no doubt that the spiralling costs for energy and labour will dictate a new look at the economics of producing rubber goods. On the other hand the advantages of energy and labour efficient thermoplastic methods combined with the option of recycling scrap will counterbalance the higher cost of thermoplastic elastomers in the future to an even greater extent than now. It has been estimated that total costs including materials and energy of both formation and processing for a thermoplastic injection moulded boot are 60-75% of those for a conventional neoprene moulding at equal performance. This is despite a twofold differential in price for the elastomers! (Table 6).

Technological advances will undoubtedly broaden the versatility of thermoplasts. This trend is clearly evident from recent developments in the field. For example the copolyester elastomers - youngest in the family - are unlike any others. They offer a unique combination of properties and processing characteristics. To a greater extent than the urethanes, these polyesters bridge the gap between the yielding nature of rubber and the rigidity of plastics, making them truly engineering polymers.

As is typical of all breakthroughs the discovery of each of these major classes has led to proliferation within its own domain to develop the potential inherent in the primary invention. In fact starting with the original discovery of the plasticized vinyl polymers, then the thermoplastic polyurethanes, each discovery has opened up a new territory for exploration. Each has led to an utterly bewildering explosion of

TABLE 6. ENERGY BURDEN PER FINISHED PART INJECTION MOULDED FROM A THERMOPLASTIC AND A THERMOSET ELASTOMER

	Copolyester Thermoplastic	Polychloroprene Compound
Weight of finished part[1], kg	0.066	0.114
Compound product energy[2], MJ	14.8	15.7
Processing energy (includes mixing, forming, cooling/ curing), MJ	0.07	0.3
Energy equivalent or scrap[3], MJ	0.2	1.0
Total energy per part, MJ	15.1	17.0

[1] Parts designed for equivalent in-use performance

[2] Includes, where applicable, product energy of all fillers and plasticizers

[3] Lower value for thermoplastic reflects ability to grind and reuse runner and mould flash

patents and publications where all the new ideas are superimposed upon the older structure. The result is the proverbial haystack where the practical needle is increasingly hard to find.

Thus have the urethanes proliferated, eg Goodrich offers 15 different products in the Estane line; other manufacturers are similar. Research efforts with the urethanes have focussed on new soft segments which may be cheaper, more stable, or softer to give more rubbery products, or on new isocyanates to confer greater toughness, light stability or resistance to reversion. Antioxidants and other stabilizers are also sought. Recent advances include injection moulded foamed thermoplastic urethanes wherein a special compounding technique enables addition of the thermally sensitive foaming agent (a Goodrich discovery). A new urethane developed by American Cyanamide has improved solvent resistance since it is based on a glycol from polymerisation of thiodiethanol. Beatrice Foods is commercializing an old urethane block, the macroglycol from hexamethylene carbonate, originally discovered by Bayer. No new isocyanates have appeared in these structures since methylene dicyclohexyl diisocyanate and isophorone diisocyanate, but one manufacturer is contemplating production of para phenylene diisocyanate.

In the attractive practical world of the styrene-butadiene-styrene block copolymers, the ABA sandwich type thermoplasts, diversification has been primarily through structures or chemical types accessible by use of anionic polymerisation *via* 'living end' polymers. Other arrangements of the blocks have included star shapes and complex branched types for better shear resistance. This work has also led to elegant syntheses of ordered block copolymers, $(AB)_N$, $(AB)_NA$. Chemically the focus has been on glassy segments with higher softening points than polystyrene like alpha-methylstyrene and on soft segments less sensitive to oxidative degradation. Thence come the hydrogenation of the polybutadiene and polyisoprene blocks to form ethylene/butylene and ethylene/propylene copolymer segments and the search for other soft blocks like polyethers and polyacrylates. Other exotic sorts include polysiloxanes with hard segments of polystyrene, poly-(alpha-methylstyrene), bisphenol carbonates, and polysulfones. Many of the above are longer chain ordered polymers of the type ABABAB---- where the molecular weight of the recurring hard segment is relatively low to enable the products to process under practical conditions. Despite the many variations tried thus far I believe substantial practical progress is still possible as new approaches are devised. For example J.P. Kennedy has developed novel synthetic methods which extend the scope of the field to units accessible through cationic polymerisation.

This group of polymers enjoys a singular advantage in its ABA or in the star forms. The basic approach recognizes the need for low viscosity of the melt under processing conditions. This is realized by construction of a physically bifunctional molecule which when melted is disassembled and flows easily. On cooling the hard blocks resolidify and the rubber network is formed. End blocks of higher melting point, smaller size, and better phase separation might lead to duplication of the desirable features of thermoset elastomers.

From an industrial viewpoint the thermoplastic polyolefin blends are very attractive even with their limited range of properties With these TPO's we can use combinations of available plastics and rubbers as long as two phase systems are obtained. Edisonian work with commercial products combined with the growing understanding of the advantages and functioning of polyphase systems have spawned new impact resistant plastics, and the variety of thermoplastic polyolefin/EPDM products. Naturally the pursuit of compositions with better properties is feverish since an interesting discovery can be commercialized quickly with minimum capital investment. Natural rubber has potential in this field because of its reactivity and versatility.

There is a similar practical story for the copolyesters. Their unusual properties and the possibility of their manufacture in available equipment have stimulated great interest in alternate possibilities. They have also reawakened interest in the well ploughed field of condensation polymers by demonstrating the potentiality of polycondensation reactions as a source of products with interesting new characteristics. Patent and journal literature disclose many new hard and soft segments in these copolymers. These involve ringing the changes on polyethers and polyesters, use of polyesters to replace the polyether soft segment, and study of both lower and higher melting hard segments such as those based on naphthalene and terphenyl dicarboxylic acids. Some are crystalline, some glassy. Attention has also turned to the myriad possibilities of condensations involving polyamides, polyurethanes and other classes. It is in the area of polyetheresteramines- or polyamide elastomers- that the most recent competitive industrial research has centred. With the expiration of some older Du Pont patents dominating polyetheresteramides the search has been reopened. A variety of products have been made by one and two step condensations using available polyamide intermediates all with polytetramethylene ether glycol (PTMEG). Typical products include PTMEG with nylon 66 and analogs (Du Pont), laurolactam and dodecanedioic acid (Huls), 11-amino-undecanoic acid and adipic acid (ATO Chimie), hexamethylene diamine, dimethyl terephthalate and hexane diol (ANIC). Hardness, toughness and other properties are controlled by variation of the length of the polyamide blocks and their concentration relative to the polyether. Polyamide elastomers are believed to have morphology much like the ether-esters with large crystalline lamellae embedded in an amorphous matrix. In general, physical and mechanical properties are similar to those of the copolyesters. Chemical resistance is somewhat improved because of the relative inertness of the polyamide group to chemical cleavage. No doubt products of the general class will capture a share of the growing thermoplast market and will contribute to its continued growth. Obviously prospects for modified types with a spectrum of properties are manifold, even if the choice is limited to relatively inexpensive materials.

In all of these polymers the polyether segment has not been overlooked. While PTMEG still appears to be the best soft segment in terms of physical properties and ease of condensation, it is costly and is subject to oxidative degradation. Possible substitutes have included the obvious homo- and copolymers based on ethylene oxide, propylene oxide, tetrahydrofuran, amino terminated polyethers (BASF), and analogues. Degradation by light, heat and oxygen can be significantly lessened by replacement of the PTMEG with the butylene esters of long chain dibasic acids. Typical examples are the esters from dimer acids derived from oleic and linoleic acids or the octadecenyl succinic acid prepared by 'ene' reaction of maleic anhydride with octadecene-1 (Table 7). The copolyesters are surprisingly similar to their polyether based counterparts, but do show much higher resistance to oxidative and thermal degradation (Table 8).

TABLE 7. EFFECT OF DICARBOXYLIC ACIDS WITH LONG SIDE-CHAINS

	α-Octyl-succinate	Succinate	Docosenyl-succinate	Control
	40 4GT 13 4G-OS* 37 PTMEGT 10 PTMEG-OS*	40 4GT 8 4G-S* 42 PTMEGT 10 PTMEG-S*	57 4GT 43 4G-DS*	40 4GT 60 PTMEGT
$[\eta]$ (dL/g)	1.9	2.4	1.0	1.6
Stress at 100% (psi)	990	1010	1300	1210
Tensile strength (psi)	6450	5250	5600	4500
Elongation (%)	810	735	620	830
Tear strength (pli)	246	155	710	147
Shore D hardness	38	44	45	44
Melting point (°C)	157	151	171	172

* OS = α-Octylsuccinate
DS = 2-(2-Docosenylsuccinate)
S = Succinate

TABLE 8. SEGMENTED COPOLYESTERS[1] WITH DIMER ACID[2] SOFT SEGMENT

	Soft segment	
Original properties	Dimer acid	PTMEG
Melting point, DSC, (°C)	195	202
At 25°C		
M100, psi	2130	2190
M300, psi	2450	2410
TS, psi	6000	5000
EB, %	620	600
At 150°C		
M100, psi	450	500
TS, psi	2060	2250
EB, %	585	610
Heat aged at 150°C for	49 days	24 days
TS, psi	2450	Too degraded
EB, %	90	To test
Lifetime, days[3]	84	24

[1] 56D prepared with dimer acid or PTMEG soft segment and 1% 4,4'-bis-(α,α-dimethylbenzyl)diphenylamine

[2] Dimer of linoleic and linolenic acids

[3] To pass 180° bend test

With the above described condensation polymers we have a process and a group of products whose properties can almost be engineered at will anywhere between relatively rubbery elastomers and tough elastic plastics by variation of hard and soft segments. Just as the fluoropolymers are engineering materials with designable elastic properties and inertness, the copolyesters and amides can be regarded as engineering polymers with designable stress/strain properties as shown in Tables 9, 10.

Since these condensation polymers often contain crystallites of a fibre-forming nature immersed in a liquid environment, it is not surprising that some can be oriented. On monoaxial drawing extensive crystallite orientation occurs perpendicular to the draw direction. In a typical case the oriented polymer has highly directional properties. In the oriented direction 30% modulus is ten times that in the unoriented direction (Figure 3). Products of this sort clearly fill a gap between the stretchable elastomers and the deformation resistant plastics.

TABLE 9. 50% ALKYLENE-T/PTMEG-T COPOLYMERS, PROPERTIES AS A FUNCTION OF DIOL STRUCTURE

Diol	2G	3G	4G	5G	6G	10G
$[\eta]$ (dL/g)	1.3	1.7	1.8	1.6	1.5	1.3
Yield strength (psi)	-	-	-	700	-	-
Stress at 100% (psi)	1650	1700	1700	650	750	880
Tensile strength (psi)	6600	3310	7020	2230	1960	2250
Elongation (%)	675	660	755	880	750	640
Permanent set (%)	275	195	370	210	370	370
Tear strength (pli)	239	85	274	142	103	44
Shore D hardness	46	48	48	32	33	35
Compression set (%)	52	48	52	90	86	81
Clash-berg $T_{10,000}$ (°C)	-38	-36	-33	-50	-53	-51
Melting point (°C)	224	198	189	106	122	106

TABLE 10. 4GT/PTMEGT COPOLYMERS, PROPERTIES AS A FUNCTION OF 4GT CONTENT

4GT content (% w/w)	30	40	50	57.4	82
$[\eta]$ (dL/g)	2.0	1.8	1.8	1.7	1.8
Yield strength (psi)	-	-	-	1900	4120
Stress at 100% (psi)	855	1200	1700	1940	3540
Tensile strength (psi)	3570	4500	7020	6770	7900
Elongation (%)	900	830	755	660	535
Permanent set (%)	250	335	370	365	350
Tear strength (pli)	74	148	274	360	616
Shore D hardness	34	44	48	54	70
Compression set (%)	60	53	52	52	53
Clash-berg $T_{10,000}$ (°C)	-65	-52	-33	-7	>25
Melting point (°C)	152	172	189	197	212

Because they combine high modulus and substantial reversible deformation they possess greater capacity to do work or absorb energy than other materials (Figure 4). Thus a one gramme strip of oriented polyester can absorb the same energy as 50g of butadiene/styrene rubber or as a helical steel spring weighing 625g (Figure 5).

The major classes of thermoplastics rubbers are thus growing in scope and in commercial application. With the rapid growth in the market other products now under development will be ready to meet the emerging opportunities. New molecules are still sought while the established principles are applied to existing types. Of special interest is the effort to use commercial elastomers as loci for grafting thermoplastic groups or hard segments. Thus we have seen grafts of polyurethanes, polystyrene, polyamides and polyesters on natural rubber and a variety of synthetic rubbers such as EPDM and also some of rubbery chains on plastics. So far these 'comb' polymers have not been of practical utility. Despite interesting physical properties they are rather too difficult to process. This derives from the relatively high molecular weight necessary to assure an average of at least two hard blocks per chain. Similar behaviour has been observed with ionomers containing randomly attached ions. Typical are salts of carboxylic or sulfonic acids attached to chlorinated polyethylene, SBR, or EPDM as exemplified by Exxon's 'thionic' polymers. When the ionic interactions are strong enough to afford reasonable set resistance the polymers do not process easily.

Where are we? So far we have seen five types commercialized and growing;

1. Vinyl polymers with random glassy or crystalline segments, internally or externally plasticized.
2. Block copolymers with random crystalline segments
3. Block copolymers with random hydrogen bonded segments
4. Ordered block copolymers with glassy or crystalline hard segments
5. Blends of glassy or crystalline plastics with cured or uncured elastomers.

Other types can be visualised. Different chemical approaches remain which can yield new hard and soft segments as in ordered cationic polymerization. Also the ionomer principle which has been very successful in plastics has been barely scratched in thermoplastic elastomers and not yet commercialized except in the form of the various carboxylated latices, and also in a few thermoset solid rubbers.

We have seen that practically all the properties that we would want for most uses of elastomers are achievable in one thermoplast or another. Why is it that the products are not growing even faster? The answers are complex. Cost comes first of course. Where the thermoplasts are cheaper and the properties adequate they have swept the marketplace, as in coated fabrics of plasticized vinyl and shoe soles based on the SBS sandwich thermoplasts. There are also real property questions. We cannot yet get the resilience which fits an elastomer for tyres or V-belts. Nor have we yet seen that relative infusibility of a thermoset rubber that insures some integrity even after abuse such as is caused by the heat generated in a panic auto stop or an airplane landing. The long exposure to heat and oils under the car bonnet is too much for us so far.

These technical and economic problems are solvable. We have many degrees of freedom considering the variety of chemical species suitable for consideration as discretely separated tie points or hard segments. In addition to the glasses, crystals and ion clusters they include chemical groups or substances which dissociate on heating and recombine on cooling. From these we should be able to find a practical equivalent of the sulphur cross-link that will achieve the goal of stability at 150°C and processability at higher temperatures. Thus the highly polar pivalolactone segments in a 'comb' elastomer are high melting and show exceptional separation from hydrocarbon backbones even at relatively short chain lengths. The butylene terephthalate hard segments in a copolyester have surprising strength above 150°C but these products are too hard and stiff for many uses. More flexible soft segments with better phase separation might change this situation. More sophisticated design in the ABA block copolymer series might well afford the prime needs of easy processability and good high temperature resistance.

Thus the problems are typical. This time however as we search for the practical product in a world of bewildering complexity we are guided by an emerging understanding of what is really needed to reach the goal!

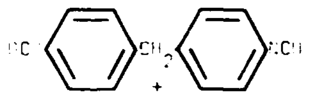
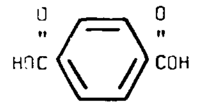
TYPE	SOFT SEGMENT	HARD SEGMENT (typical components)	STRUCTURE
Polyurethanes	polyether glycol polyester glycol (M.W. 1000-2000)	 + $HO(CH_2)_4OH$	$(AB)_n$
Styrene block copolymers	polybutadiene polyisoprene polyolefine	polystyrene	ABA
Polyetheresters	polyether glycol (M.W. 1000-2000)	 + $HO(CH_2)_4OH$	$(AB)_n$
Olefinic TPE	EPDM rubber	polyethylene polypropylene	Physical blend

Fig. 1.1 Technically important thermoplastic elastomers (TPE).

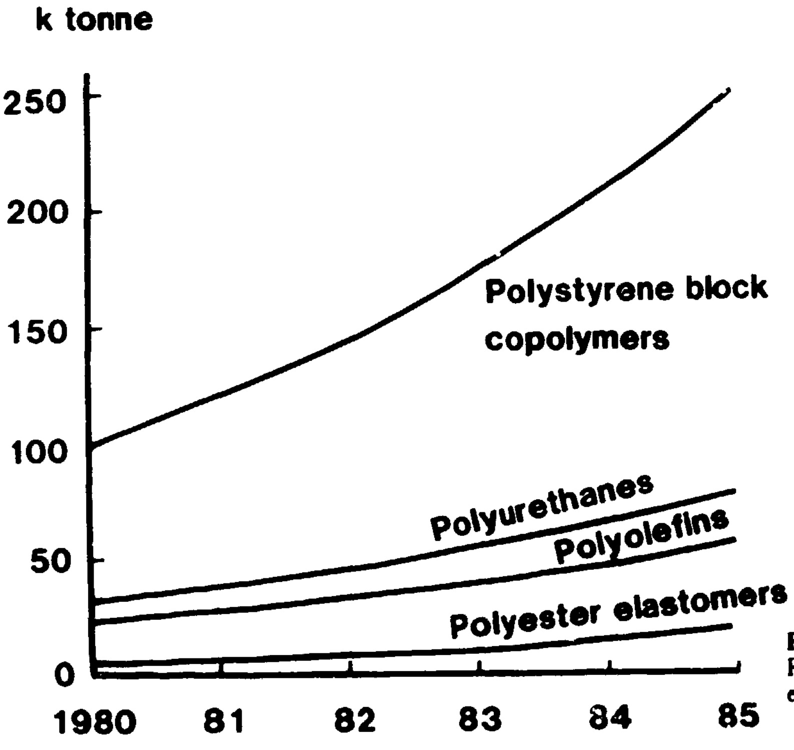


Fig. 1.2
Predicted growth of thermoplastic elastomers in the USA.

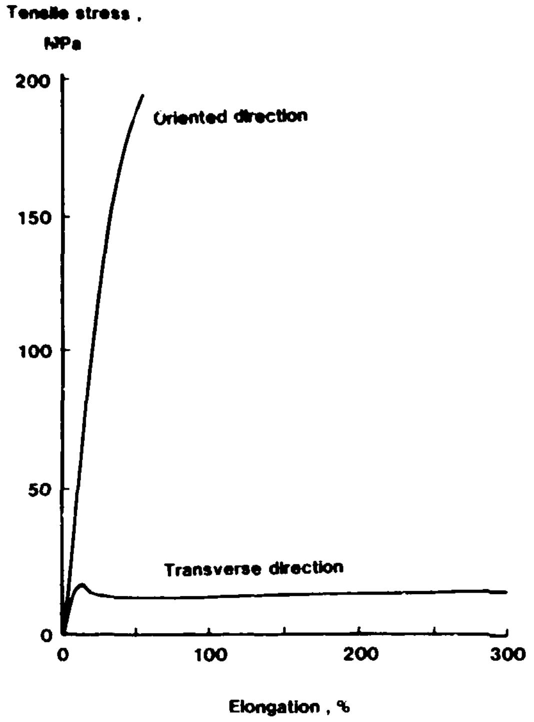
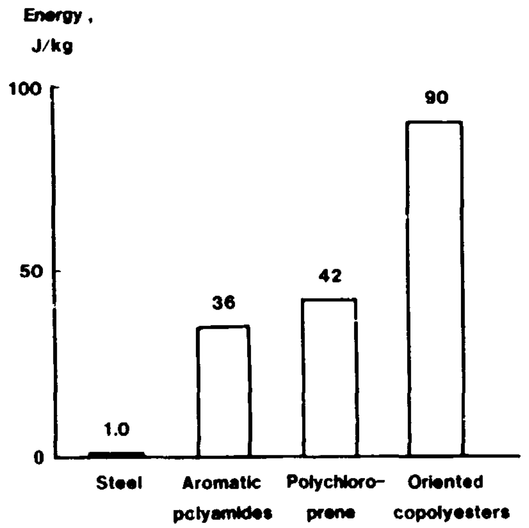


Fig. 1.3
Physical properties of oriented polyester elastomers.

Fig. 1.4
Energy absorption capacities of oriented polyesters.



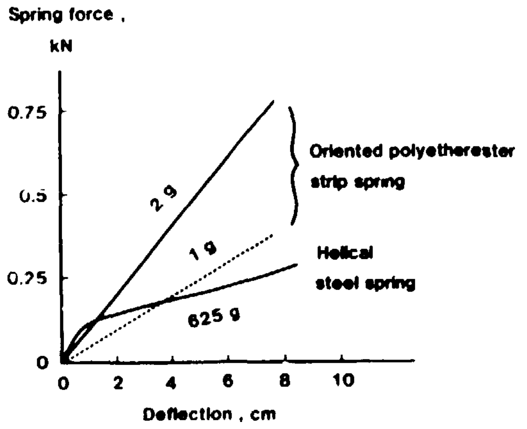


Fig. 1.5
Comparison of spring performance of steel and oriented polyetherester strips (equal lengths of spring, weights as indicated).

Thermoplastic Natural Rubber

Table 1

Types of thermoplastic rubber

	Approximate Shore hardness ranges available	Specific gravity	Typical values Tensile strength, MPa	Elongation at break, %
Block copolymers[1]	40A–95A	0·93–1·08	5–25	800
Thermoplastic polyurethane[2]	75A–70D	1·05–1·30	20–50	500
Thermoplastic polyester[3]	92A–72A	1·17–1·25	30–40	400
EPDM polyolefin blends[4]	70A–60D	0·88–1·05	4–18	200
NR polyolefin blends	80A–65D	0·91–1·05	6–20	200
Ionomer[5]	60D–65D	0·93–0·97	25–30	400

1. *eg Kraton* (Shell), *Solprene* (Phillips).
2. *eg Cyanaprene* (Cyanamid), *Pellethane* (Upjohn), *Estane* (B F Goodrich), *Plastothane* (Thiokol), *Roylar* (Uniroyal), *Texin* (Mobay).
3. *eg Hytrel* (Du Pont).
4. *eg TPR* (Uniroyal), *Somel* (Du Pont), *Vistaflex* (Exxon), *Uniprene* (International Synthetic Rubber), *Telcar* (B F Goodrich).
5. *eg Surlyn* (Du Pont).

THERMOPLASTIC NATURAL RUBBER BLENDS

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INTRODUCTION

Thermoplastic rubbers are materials which soften reversibly and flow at elevated temperatures, but unlike thermoplastic resins are resilient and flexible at normal temperatures, like vulcanized rubber.

There are several distinct types of materials which fit into this rather loose description, although within each type it is only the softer grades that comply with the accepted definition of an elastomer as a material capable of reversible extension to twice its original length.

In fact many of the harder grades of thermoplastic rubber have a tensile yield point well below 100% extension. All, however, have the commercially important advantages, compared with conventional elastomers, of 1) being processible on thermoplastics machinery, 2) not requiring a vulcanization step and hence 3) being free of the necessity to mix with a multitude of additives. Thus there are savings in time, energy and often capital costs of machinery, while scrap and rejects can be recycled. Production rates by injection moulding and extrusion are higher with thermoplastic as opposed to thermoset materials.

It is not surprising that thermoplastic elastomers are making inroads into markets previously held by vulcanized rubber products. At the same time they are being utilized by plastics converters for products with better performance than can be obtained with general purpose thermoplastics, such as PVC and polyethylene.

During 1980 when total consumption of both rubbers and plastics declined, sales of thermoplastic elastomers continued to rise towards a projected world-wide figure of about ½ million tons by 1985[1,2].

Table 1 gives some typical property values of four commercially important types of thermoplastic elastomers. The olefin types include blends of NR and crystalline polyolefins (TPNR)[3] and also the numerous EPDM/PP and EPDM/HDPE blends available. The olefins and the styrene-butadiene-styrene (SBS) types are similarly priced materials, while the polyurethanes and polyether-esters are much more expensive and are generally used in more specialist applications.

TABLE 1 TYPES OF THERMOPLASTIC RUBBER

One of the main points to note is the wide hardness ranges available. The block copolymer (SBS) types are available from hardnesses as low as unfilled NR to much higher values. The others range from approximately the hardness of a tread rubber to about that of high density polyethylene.

Figure 1 shows intersections of TPRs with conventional rubbers and plastics in terms of their hardness. It is mainly the wide hardness range which permits thermoplastic elastomers to be used in applications traditionally the preserve of rubber and also in entirely new markets. The SBS types, in the 50 to 70 Shore A range, compete with both vulcanized rubber and plasticized PVC in footwear, which is the biggest market outlet for them. The olefinic types have their greatest usage and future potential in automotive components such as bumpers, spoilers, and other flexible panels, requiring materials in the range 90 Shore A to 60 Shore D [4,5,6,7]. There are, however, many other markets open to thermoplastic elastomer blends including TPNR blends, and these will be discussed in a second paper.

In this paper an outline of the preparation and properties of TPNR will be given making comparisons where appropriate with other thermoplastic rubbers.

PREPARATION OF TPNR BLENDS

The ultimate goal of blending two or more polymers is usually a practical one of achieving materials that are commercially viable by virtue of having certain properties which cannot be obtained by other means or are obtained at lower cost than other means might provide. It is tacitly assumed that a fine state of division of each component is required and that the morphological structure and adhesion between phases are crucial factors affecting most properties.

Some studies of the morphology of NR/PP blends have been carried out under this project, but the emphasis has been on devising blending techniques using standard mixing equipment to obtain optimum properties.

Mixing

For this work the natural rubber, mostly SMR L, and polyolefin resin have been mixed in laboratory sized internal mixers (Banbury BR with a capacity of ca 1 litre and Shaw Intermix K2A, ca 25 litre).

Control of the temperature of the batch is important. Starting with a warm machine (80-120°C) mixing soon raises the temperature to the melting point of the resin (135°C for HDPE, 165°C for PP). High speed mixing is generally advantageous, but the batch should not be allowed to get too hot because degradation of the NR may occur if the temperature is allowed to exceed 200°C for more than a few minutes.

A typical mixing cycle in a BR Banbury with a rotor speed of 116 rpm is:-

0 minutes - add natural rubber, antioxidants, polypropylene and filler (if used)

5 minutes - dump.

The polypropylene may be in either powdered or pelletized form.

An organic peroxide or other crosslinking agent for the rubber may be added during the preparation. Normally only sufficient to partially crosslink the rubber is used and the procedure, which has been called 'dynamic crosslinking' to indicate that the reaction takes place during mixing, probably leads to formation of microgelled rubber dispersed in the melted polypropylene. In this case it is necessary to modify the mixing cycle by delaying the addition of crosslinking agent and antioxidant until the polypropylene has melted, otherwise intimate mixing of the two components cannot be achieved. A typical cycle for partially crosslinked TPNR is given below.

0 minutes - add natural rubber, polypropylene and filler (if used)
2-3 minutes - add crosslinking agent
5 minutes - add antioxidant
6 minutes - dump

The late addition of antioxidant is only necessary if the crosslinking agent being used is one, like a peroxide, which functions by a free radical mechanism.

It may be noted that the literature on dynamically crosslinked EPDM/PP blends[8,9] does not cite the necessity to delay the addition of peroxide, but this may be because EPDM reacts more slowly than natural rubber with vulcanizing agents.

Treatment of the batch after mixing follows fairly normal practice. While still hot it can be sheeted on a roll mill and allowed to cool as slab about 8 mm thick. Working it on a mill for more than one or two passes is not recommended because it crumbles and becomes difficult to handle when the temperature falls below the melting point of the polyolefin. For subsequent processing, such as injection moulding, the TPNR is granulated in a rotary type cutter, adding a little partitioning agent in the case of softer grades to prevent reagglomeration of particles.

Moulding and extrusion

TPNR blends can be moulded and extruded using plastics type machinery. For the evaluation of physical properties samples are usually prepared by injection moulding. Compression moulding is less satisfactory.

Full details of all the injection moulding conditions will not be described here. Several different machines have been used, all capable of giving a cylinder temperature of 220°C or more.

The Arburg 220 series 35 tonne machine used for this project has a reciprocating screw ram giving a maximum shot volume of about 60 cm^3 of material. The cylinder heaters were set within the following temperature ranges

Rear (feed end)	170-190°C
Centre zone	180-200°C
Front zone	190-220°C
Nozzle	190-220°C

and the mould was at 30-60°C.

For 2 mm thick samples the injection moulding cycle time can be as short as 20 secs.

Earlier it was mentioned that excessively high temperatures should be avoided during mixing and the same applies during subsequent processing. However, recycling of rejects is perfectly feasible as shown in Figure 2. This shows that up to ten recycles has only a small effect on modulus and tensile strength.

PHYSICAL PROPERTIES

Varying the proportions of rubber and polyolefin

Materials spanning a very wide range of stiffness can be obtained by varying the proportions of rubbery and hard phases. As mentioned earlier the fine structure of TPNR is not known in detail, but such evidence as does exist shows that both components probably exist as continuous phases, except in blends containing less than about 25% of either. It is well known that the microcrystalline or glassy domains in block copolymer types of thermoplastic elastomers are to a first approximation physically equivalent to the chemical crosslinks in vulcanized rubber. With TPNR blends the crystalline regions of the polyolefin provide stiffness while the amorphous rubbery phase gives flexibility.

There is a marked dependence of flexural modulus on the NR/polyolefin ratio as shown in Figure 3 which gives mean stiffness values over different parts of the sheets produced in an edge gated mould. As with other thermoplastics, especially those containing a crystalline phase, anisotropy due to flow during moulding occurs and this is reflected in values of the stiffness and other properties measured along and across flow lines as shown in Figures 4, 5 and 6 for sheets produced in a centre gated mould. Figure 4 shows flexural modulus for unfilled blends while Figures 5 and 6 give tensile strength and elongation at break respectively, for blends containing 30 parts of carbon black (high structure HAF grade). It can be seen that tensile strength increases with PP content while elongation at break generally decreases, particularly in the direction across flow lines, for this filled material.

It should be noted however that elongation at break is a very variable property. Cold drawing to very high elongations often takes place, especially in unfilled blends high in PP content, so that EB, and indeed TS, are somewhat irrelevant properties. In such cases yield stress is a more useful parameter to measure.

Effect of temperature on properties

Thermoplastic rubbers based on PP have higher softening points than the SBS and polyurethane types. This is shown by the hardness/temperature curves in Figure 7.

One of the requirements for vehicle body components is resistance to sagging and distortion during paint baking processes at 120°C, and cable covers for some classes of cables must withstand 140°C. With the possible exception of some of the softer grades TPNR will satisfy these requirements.

Another essential property of flexible bumper components is that they should be functional over a service temperature range from 70°C down to -30°C (or even -40°C according to some specifications). This means that they must be stiff enough to prevent distortion at 70°C, but not become too stiff at low temperatures that they cease to function as flexible impact absorbers.

The data in Figure 8 shows that TPNR 6040 (the numbers 60 and 40 after TPNR refer to the percentages of NR and PP, in that order) meets these criteria as well as, or better than, other materials that have been considered for these applications. PVC and polyurethanes exhibit greater stiffening at low temperatures than elastomer/polypropylene blends[5] and the data in Figure 9 show that a value of approximately 8 for the ratio of the stiffness at -30°C to the stiffness at 70°C is applicable to a whole range of NR/PP blends.

Effect of partial crosslinking

For blends containing more than about 65% natural rubber partial crosslinking of the rubber improves some physical properties.

Figure 10 shows the effect of the amount of added peroxide on hardness for two blends containing 85 and 65% NR respectively. Crosslinking has a pronounced effect in the softer blend in which the PP phase is almost certainly discontinuous since it is present in a low concentration. The effect of peroxide is less in the 65/35 blend.

Another property which is improved by peroxide is compression set. Thus an uncrosslinked blend containing 75% NR has a compression set of about 50% (tested at 23°C for 22 hours), but this is reduced to a set of 39% by the addition during its preparation of only 0.2% of peroxide.

Some grades of commercially available thermoplastic rubbers based on EPDM/PP are also partially crosslinked to upgrade properties such as compression set and there are patents, but as yet no commercial supply of blends in which the rubbery phase is fully crosslinked[10,11]. It is claimed that the latter retain thermoplasticity because the crosslinked rubber is dispersed as very small particles. It is well known that organic peroxides cause oxidative degradation of polypropylene at elevated temperatures and for the fully crosslinked materials alternative crosslinking systems such as a bismaleimide or an accelerated sulphur system were used.

It has been confirmed that in TPNR a peroxide initiates degradation of the polypropylene. The effect of different crosslinking systems on the melt flow index, which is inversely proportional to molecular weight was studied. It is evident from comparison of the curves in Figures 11 and 12 that when the rubber phase is crosslinked with sulphur there is simply a reduction in MFI over all NR/PP ratios, but when the crosslinking is accomplished with peroxide there are two superimposed effects, 1) a reduction in MFI, as with sulphur and 2) an increase in MFI due to a reduction in molecular weight of the PP, with the latter effect on MFI becoming more pronounced as the proportion of PP is increased.

It is concluded that the use of peroxide should be restricted to softer blends of TPNR containing more than 70% rubber. In harder blends partial crosslinking contributes little or not at all to the physical properties, and may damage the environmental resistance.

Alternative crosslinking systems can, of course, be used, but it should be remembered that they are likely to be either more expensive (the bismaleimide HVA-2 for example) or, in the case of accelerated sulphur systems, would involve the weighing out and mixing of numerous ingredients, which could increase significantly the cost of production.

Compounding TPNR blends with fillers and oils

Rubber/polyolefin blends, including TPNR, differ from the block copolymer thermoplastic rubbers in their ability to tolerate extension with oils and fillers. It is possible to add large volumes of filler and oil to block copolymers but not to blends.

Practical modification of blends is generally limited to relatively small amounts of filler for specific properties, although moderate amounts of cheap fillers may be used to reduce cost.

A temperature in excess of 160°C is required for mixing additives into TPNR and this will normally be carried out during its preparation in an internal mixer.

One or two percent of carbon black or titanium dioxide can be added to give protection against ultra violet light and coloured pigments may also be added at the mixing stage. Such low levels of filler have a negligible effect on physical properties, but rather higher levels can be useful in some cases. For example the abrasion resistance of light coloured TPNR might be improved by addition of precipitated silica and up to 50 parts of ground whiting can be used to reduce mould shrinkage or to improve extrusion with little effect on most physical properties.

The addition of mineral oil to TPNR will, of course, reduce its hardness and also reduce melt viscosity, which in some circumstances may be beneficial to processing, as referred to later. Normally only modest amounts of oil, eg 5 to 15%, are recommended, and oils having high viscosity are preferred because low viscosity oils have a tendency to bloom.

If higher levels of filler are used to reduce cost one of the chief attributes of TPNR, its low density, is lost. This is particularly relevant to automotive applications for which lightweight components are required in the interests of fuel economy.

Thus the highly filled compound shown in Table 2 has approximately the same stiffness as the lightly filled TPNR 3070 but its density is much higher. In order to be self supporting a flexible body panel, for example, would have to be made in the same thickness, and hence the same volume, whichever of the two materials were used. Therefore the TPNR 3070 would provide the lighter weight and, moreover, the material cost would be very little higher than one made from the filled TPNR 4060, because on a volume basis the latter is only slightly cheaper.

Table 2 Mean properties along and across mould flow

	NR/PP Ratio	
	40/60	30/70
HAF black	10	10
Soft clay	75	-
Talc	25	-
Flex modulus, MPa	620	690
TS, "	14	17
EB, %	200	350
Density, Mg/m^3	1.35	0.95

PAINTING PROCEDURES

Flexible components of USA cars, such as sight shields and facias, have for some years now been painted to match the metal finish of the car.

NR itself can readily be painted with flexible urethane paints after the rubber surface has been chlorinated to ensure good paint adhesion.

With TPNR certain problems had to be overcome before painting was satisfactory. Firstly a chlorinated TPNR surface did not always give good paint adhesion when the NR content of the blend was less than about 50%. Fortunately a flash primer (without chlorination) of the type used to prime EPDM and polyolefins overcomes this difficulty for all NR/PP blend ratios.

Secondly the frequently used techniques of electrostatic spray painting posed the problem of making the TPNR antistatic. The required conductivity can be achieved by incorporation of conductive carbon black or of high structure reinforcing grades such as N-347 black.

Figure 13 shows the effect of concentration of three grades of black on the resistivity of TPNR 6040 blend. The curves are of similar shape to those given by vulcanized rubbers containing these blacks and it is clear that in the antistatic region resistivity is very sensitive to concentration of black. The data show that low concentrations of the highly conductive Ketjen black EC can be very effective. However this black is very difficult to disperse in low concentrations so that resistivity is likely to be variable. The HAF-HS black also gives some variability when used at a concentration of 40 parts. Higher concentrations give more uniform resistivity but adversely affect flow properties and elongation at break. For these reasons selected proportions of the two blacks were tested and 40 parts HAF-HS with 5 parts Ketjen black EC was found to be the best compromise.

TPNR panels containing these amounts of black have been electrostatically spray painted with urethane paints of the brand currently used by the USA automotive industry. The painted panels were exposed in S. Florida under the conditions normally used for testing automotive body panels. After 2 years the 60° gloss retention was over 80% when the panels had been washed and lightly polished with auto wax.

AGEING AND WEATHERING

In comparison with vulcanized natural rubber TPNR blends are remarkably resistant to heat ageing. For example three days in hot air (100°C) will approximately halve the tensile strength of a typical vulcanized compound unless specially formulated with a heat resisting vulcanization system. Contrast this with the behaviour of TPNR 6535 which retains more than 90% of initial tensile strength after the same ageing conditions.

Undoubtedly this is due to the inherently greater oxidation resistance of polypropylene than polyisoprene and in fact the heat ageing resistance of TPNR is comparable with that of EPDM/PP blends in spite of the fact that EPDM is more resistant than NR to oxidation. However, even polypropylene cannot be classed as a highly inert polymer, in comparison with polyethylene for example. Specially protected grades of polypropylene are marketed for outdoor or elevated temperature usage.

The optimum protection system for TPNR is a combination of a phenolic or amine antioxidant, a synergist such as dilaurylthiodipropionate and a UV absorber. Various combinations of antioxidants selected from these three basic types were studied in TPNR 5050 in respect of hot air ageing and outdoor exposure (unpainted samples), the hot air ageing being extended to 7 days at 100°C.

Two important conclusions were drawn from the results. Firstly only relatively small differences were found in the effects of the antioxidants chosen and secondly the protection afforded by antioxidants was greatly diminished when a peroxide crosslinker was used during preparation of the TPNR. Thus the tensile strength of crosslinked TPNR 5050 after 7 days at 100°C was approximately 80% of initial value whereas that of the uncrosslinked TPNR 5050 was fully retained or even increased. A selection of the results are shown graphically in Figure 14.

For the weathering test disc shaped samples and moulded dumbells were placed outdoors in a South facing direction at an angle of 45°. All the samples prepared from the blend containing peroxide developed what appeared to be a white bloom, whereas those containing no peroxide were virtually unchanged after the 3 months exposure (Figure 15). It has been shown that the use of a sulphur crosslinking system does not cause the whitening during weathering.

The whitening is not a bloom of the type often found on rubber products since it is insoluble in acetone, benzene, chlorinated hydrocarbons etc. Examination of the surface by IR spectroscopy, scanning electron microscopy and X-ray analysis showed that the whiteness was caused by a porous surface layer of polypropylene devoid of NR to a depth of about 5 microns. Other measurements indicated that the PP at the surface is partially degraded and it may be concluded that oxidation is initiated by peroxide during hot mixing.

Many specifications for rubber products include a test for resistance to cracking in the presence of ozone. It might be expected that TPNR would fail this test because vulcanized NR is readily attacked by ozone, but this is not the case as shown by Figure 16. The vulcanized NR sample on the left has cracked, as expected since no antiozonant was added to the compound. The three TPNR samples (TPNR 4060, 5050 and 6040) also contained no added antiozonant but have not cracked after 7 days in an atmosphere containing 50 pphm ozone at 40°C due to the ozone resistant polypropylene phase and, probably, to the gradual relaxation of stress which occurs.

The ageing and weathering of TPNR has been dealt with at some length because it might be expected to compare unfavourably with EPDM/PP blends in this respect. However it has been shown that, provided the normal precautions are taken to protect against heat and sunlight by adding antioxidants, UV absorbers, pigments or painting, it will have an adequate service life.

In conclusion, therefore, TPNR has similar properties to synthetic olefinic thermoplastic rubbers and should find many applications in the growing market for materials which bridge the gap between conventional rubbers and plastics.

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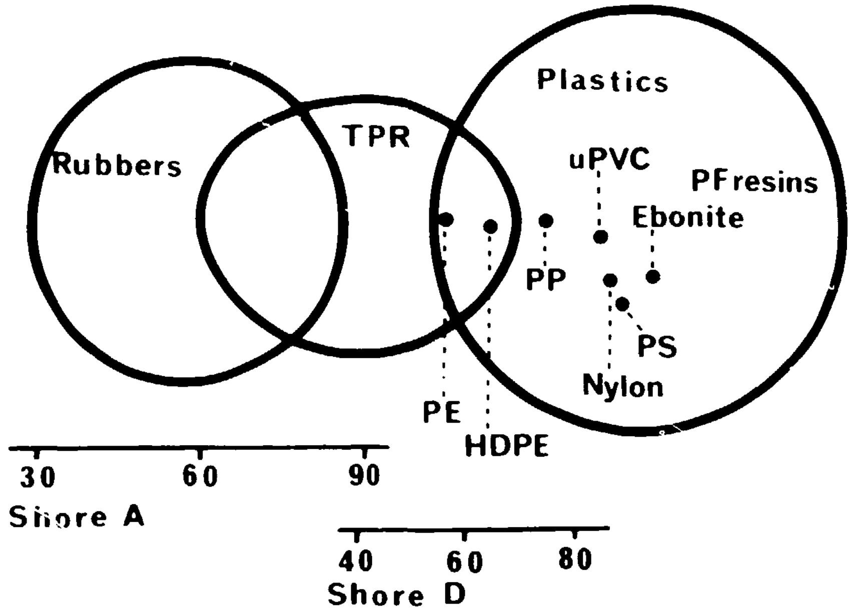


Fig. 2.1 Hardness range of TPR, rubbers and plastics.

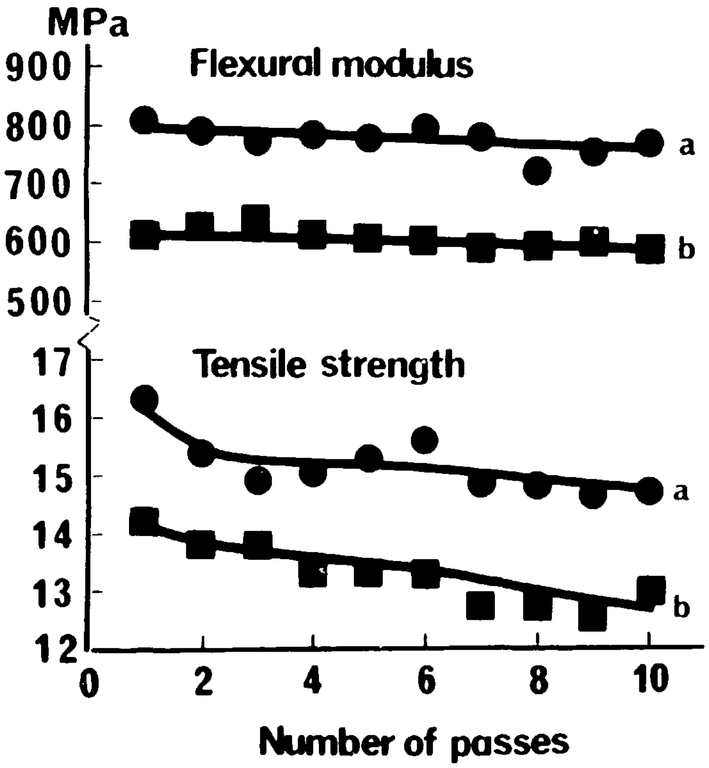


Fig. 2.2
Effect of number of passes through REP B34K machine on flexural modulus and tensile strength of TPNR 6040 containing 40 php HAF black; a) along radial mould flow lines, b) across mould flow lines.

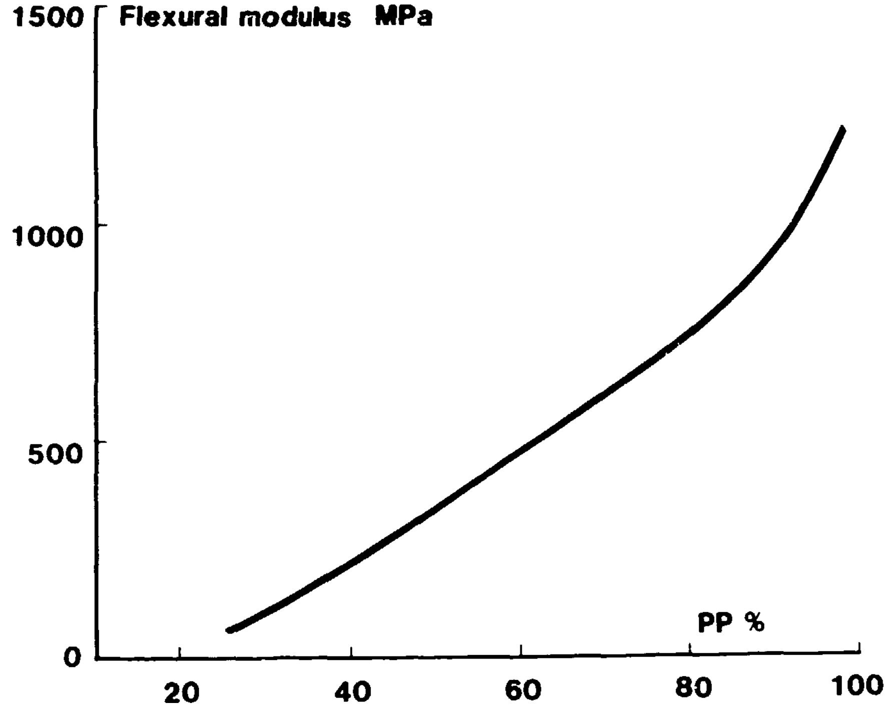


Fig. 2.3 Effect of PP content on flexural modulus at 23°C of unfilled TPNR injection moulded in Arburg 220 machine.

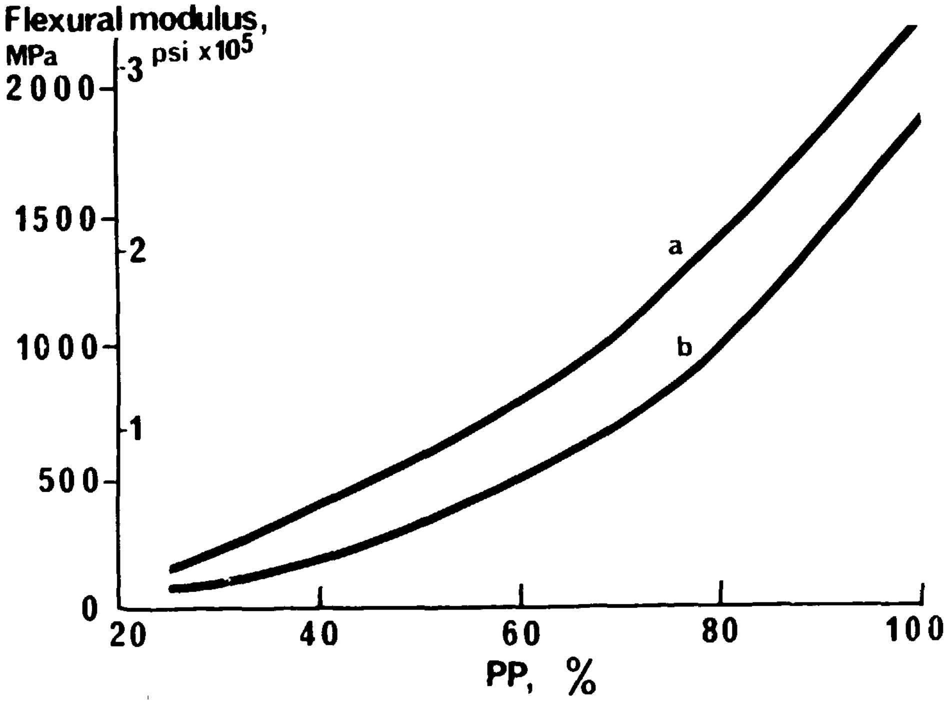


Fig. 2.4 Effect of PP content on flexural modulus at 23°C of unfilled TPNR injection moulded in REP B43K machine. a) and b) as in Figure 2.2.

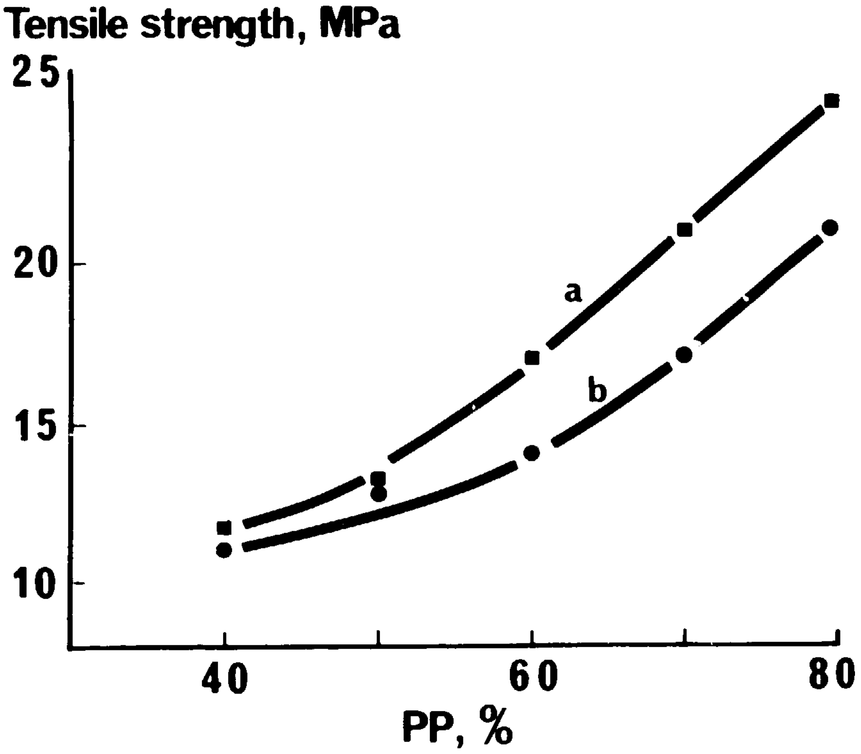


Fig. 2.5 Effect of PP content on tensile strength of TPNR containing 30 parts php HAF black.

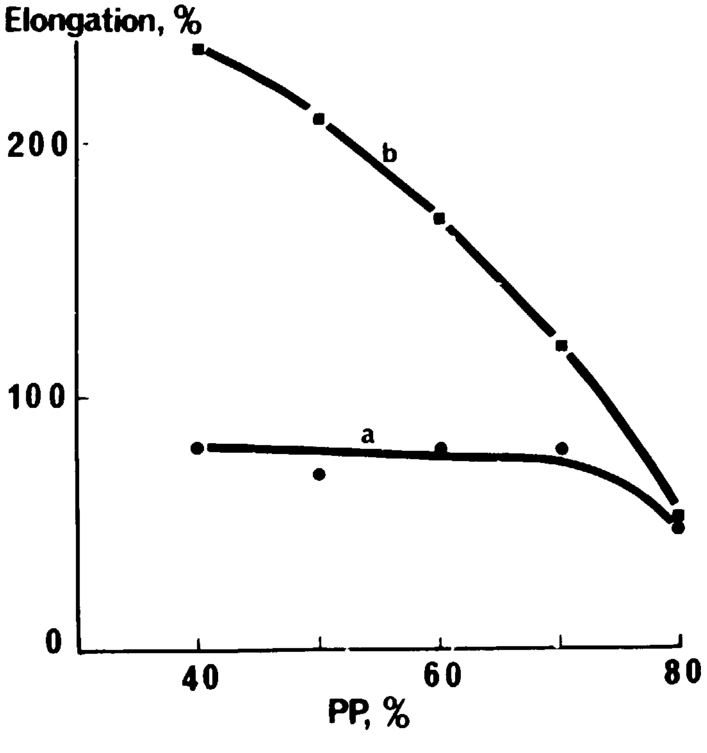


Fig. 2.6
Effect of PP content on elongation at break of TPNR containing 30 parts php HAF black.

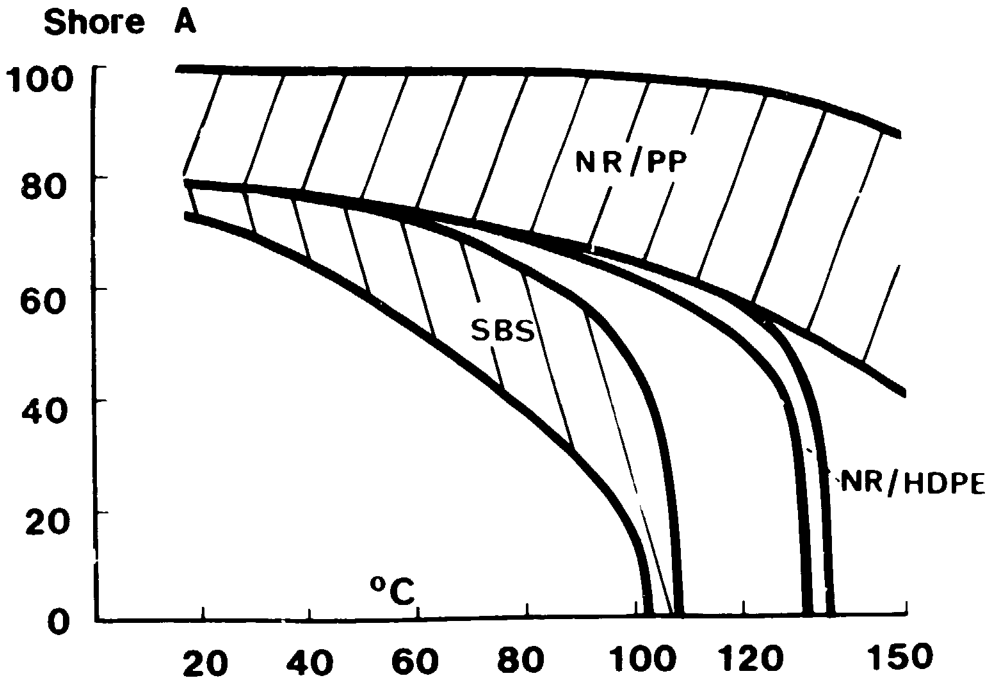


Fig. 2.7 Effect of temperature on hardness of TPNR and SBS copolymers.

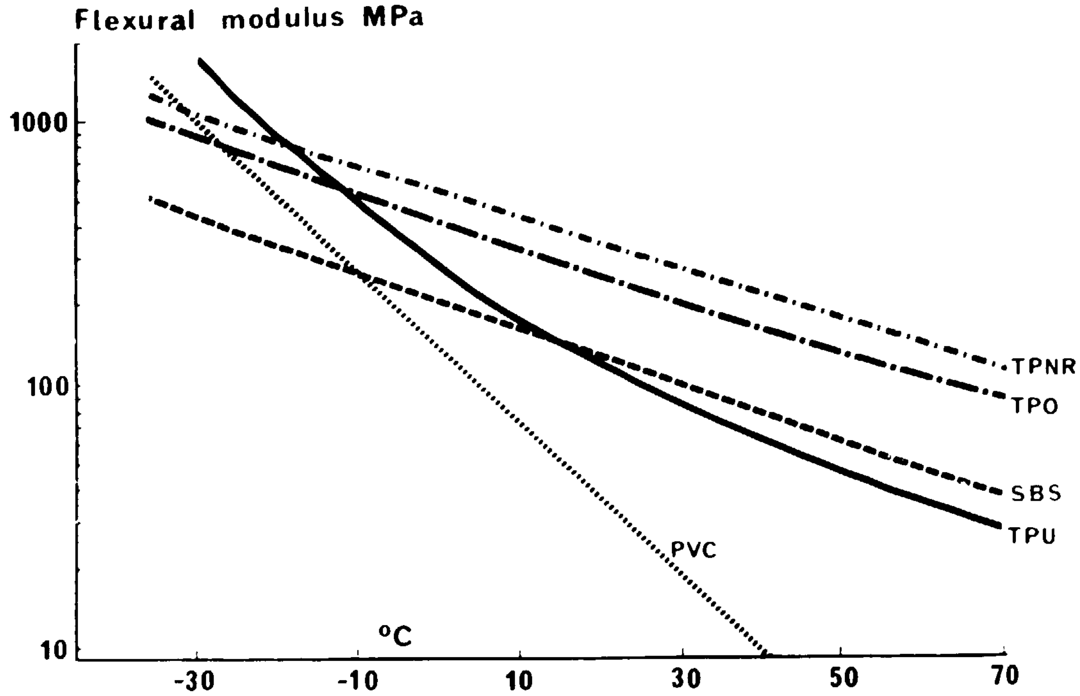


Fig. 2.8 Effect of temperature on flexural modulus of thermoplastic rubbers and PVC.

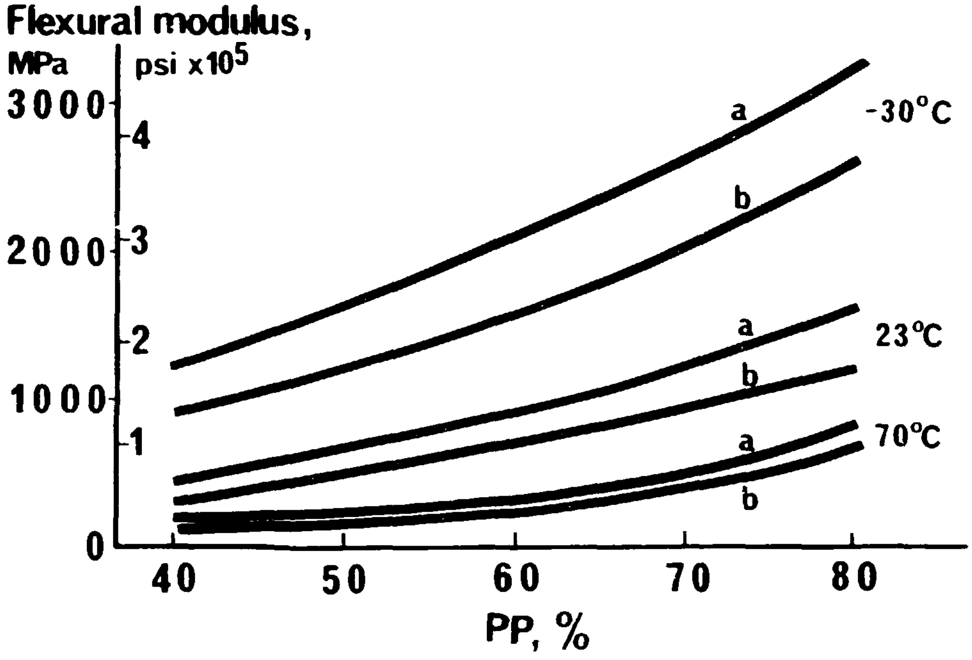


Fig. 2.9 Effect of PP content of TPNR containing 30 parts php HAF black on flexural modulus at 30°, 23° and 70°C.

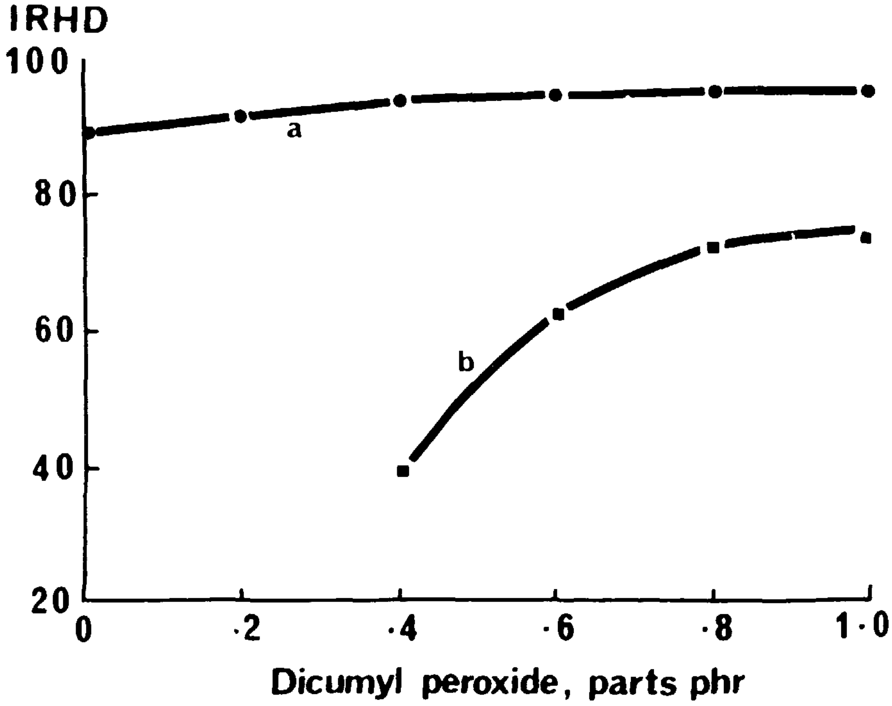


Fig. 2.10 Effect of dicumyl peroxide concentration on hardness of a) TPNR 6535, b) TPNR 8515.

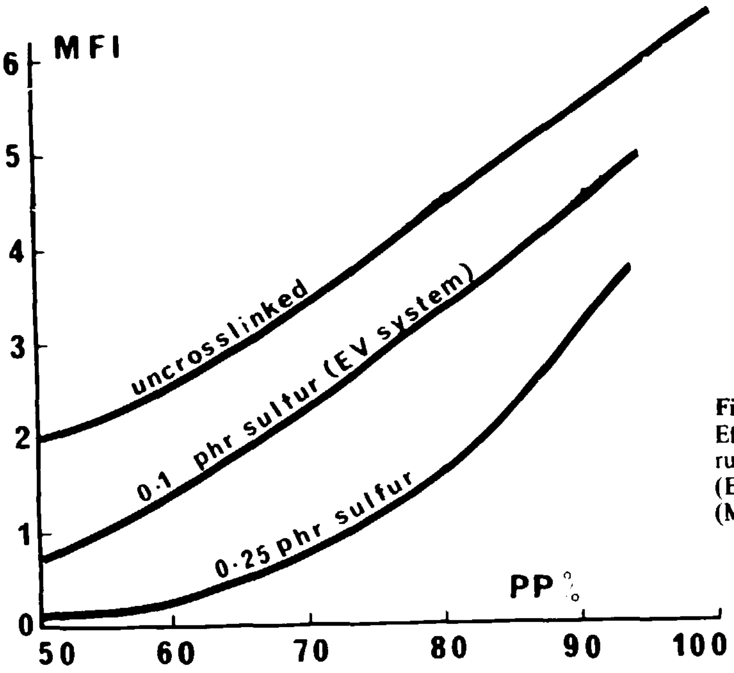


Fig. 2.11
Effect of partial crosslinking of rubber phase of TPNR with sulphur (EV system) on melt flow index (MFI) of blend.

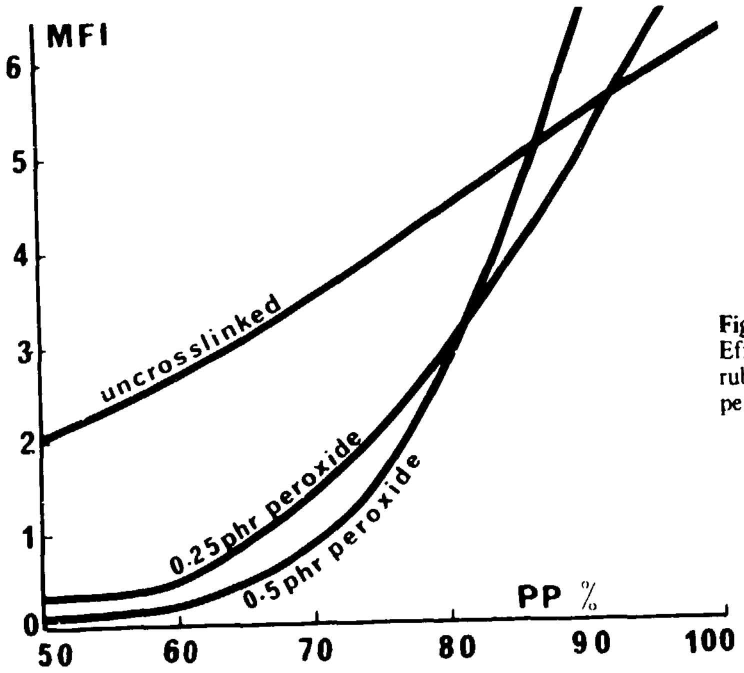


Fig. 2.12
Effect of partial crosslinking of rubber phase of TPNR with dicumyl peroxide on MFI of blend.

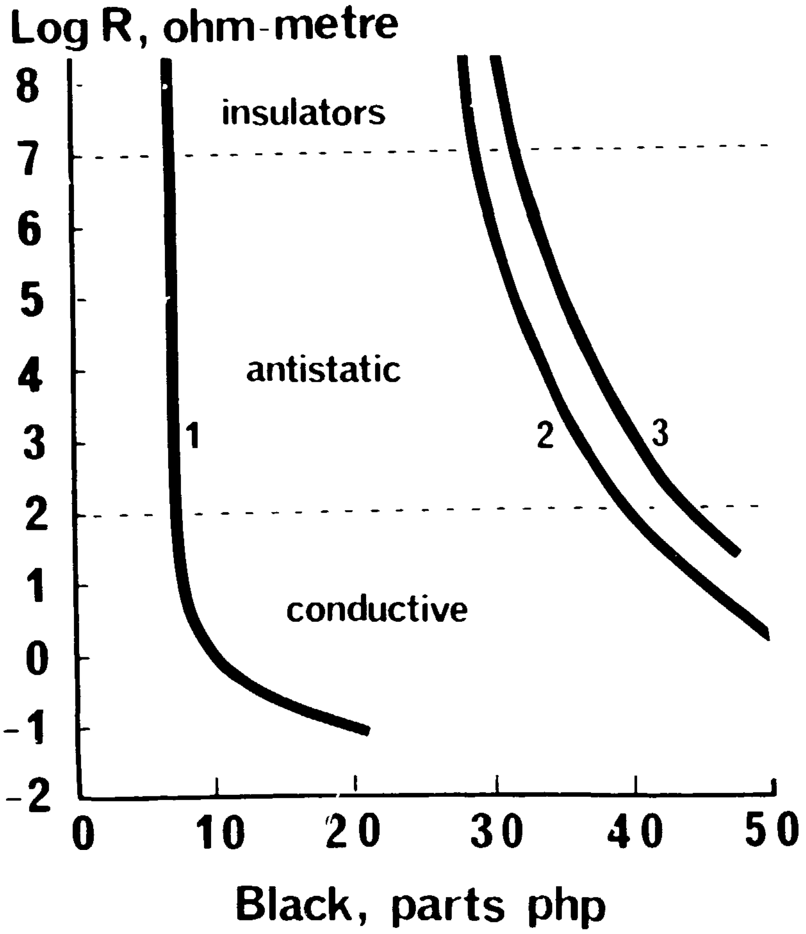


Fig. 2.13 Effect of carbon black on volume resistivity of TPNR 6040.
1, Ketjenblack EC; 2, Vulcan Xc72; 3, Vulcan 3H.

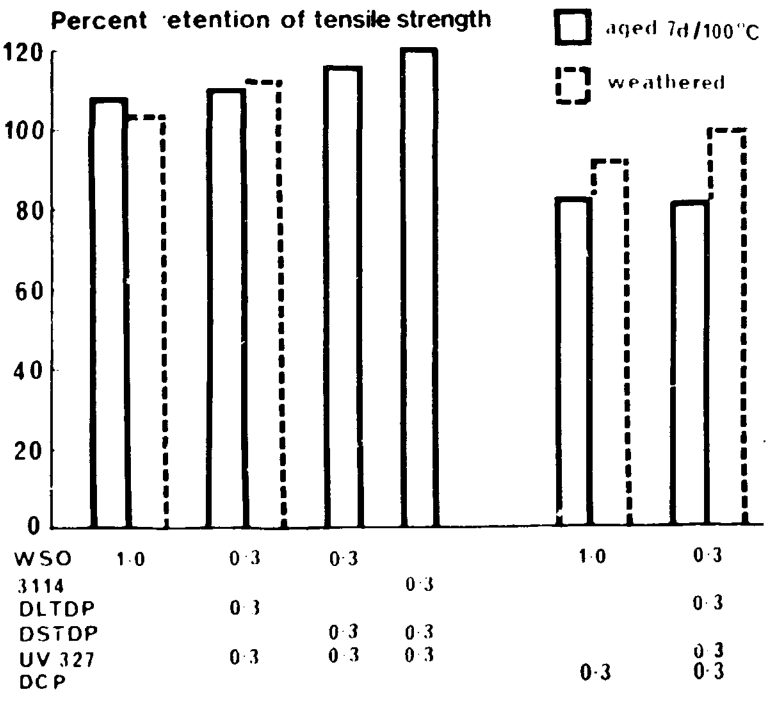


Fig. 2.14
Effects of ageing and weathering on tensile strength of uncrosslinked and peroxide-crosslinked TPNR 5050 containing various antioxidants.
WSO - Permanax WSO (Vulnax Int.) a high mol. wt phenolic antioxidant: 3114 - Cure-rite 3114 (B F Goodrich Chem. Corp.), a hindered phenolic antioxidant: DLTDP - dilaurylthiodipropionate: DSTDP - distearylthiodipropionate: UV327 - Tinuvin 327 (Ciba Geigy), a UV absorber:
DCP - dicumyl peroxide.

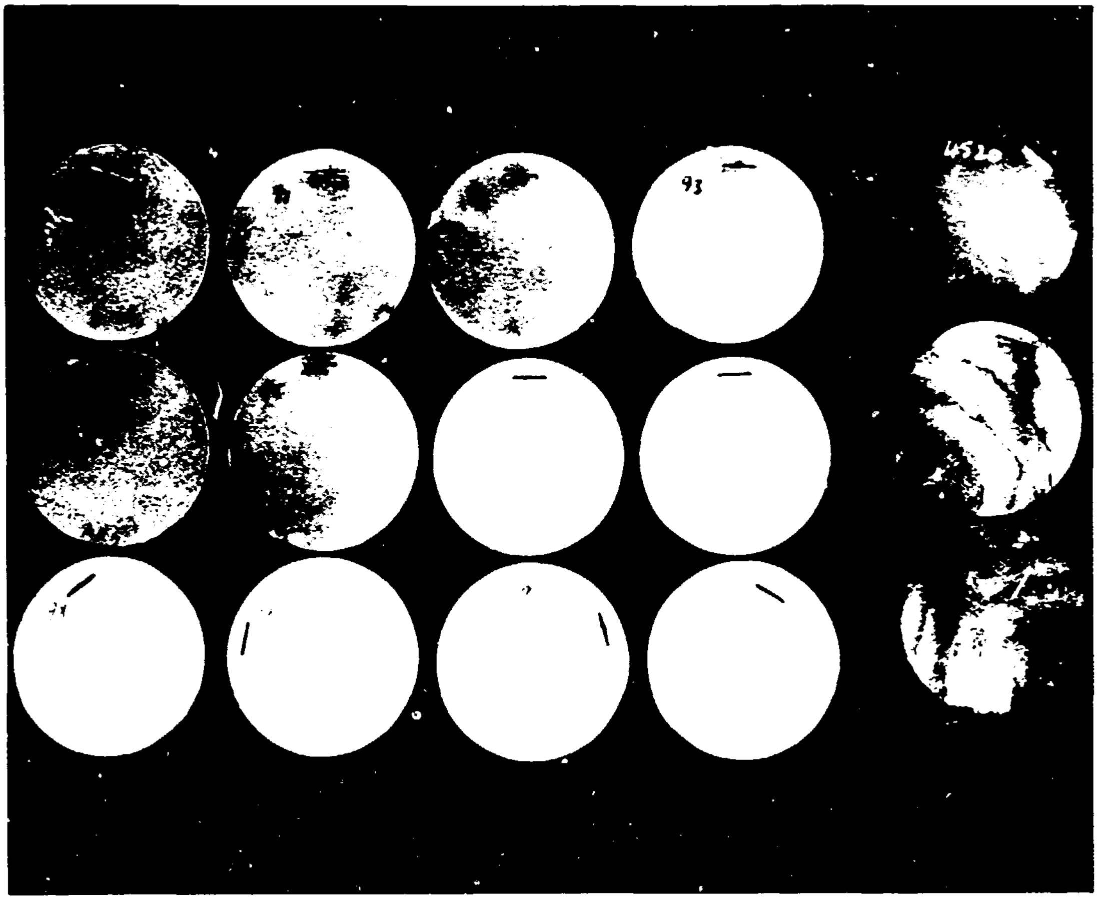
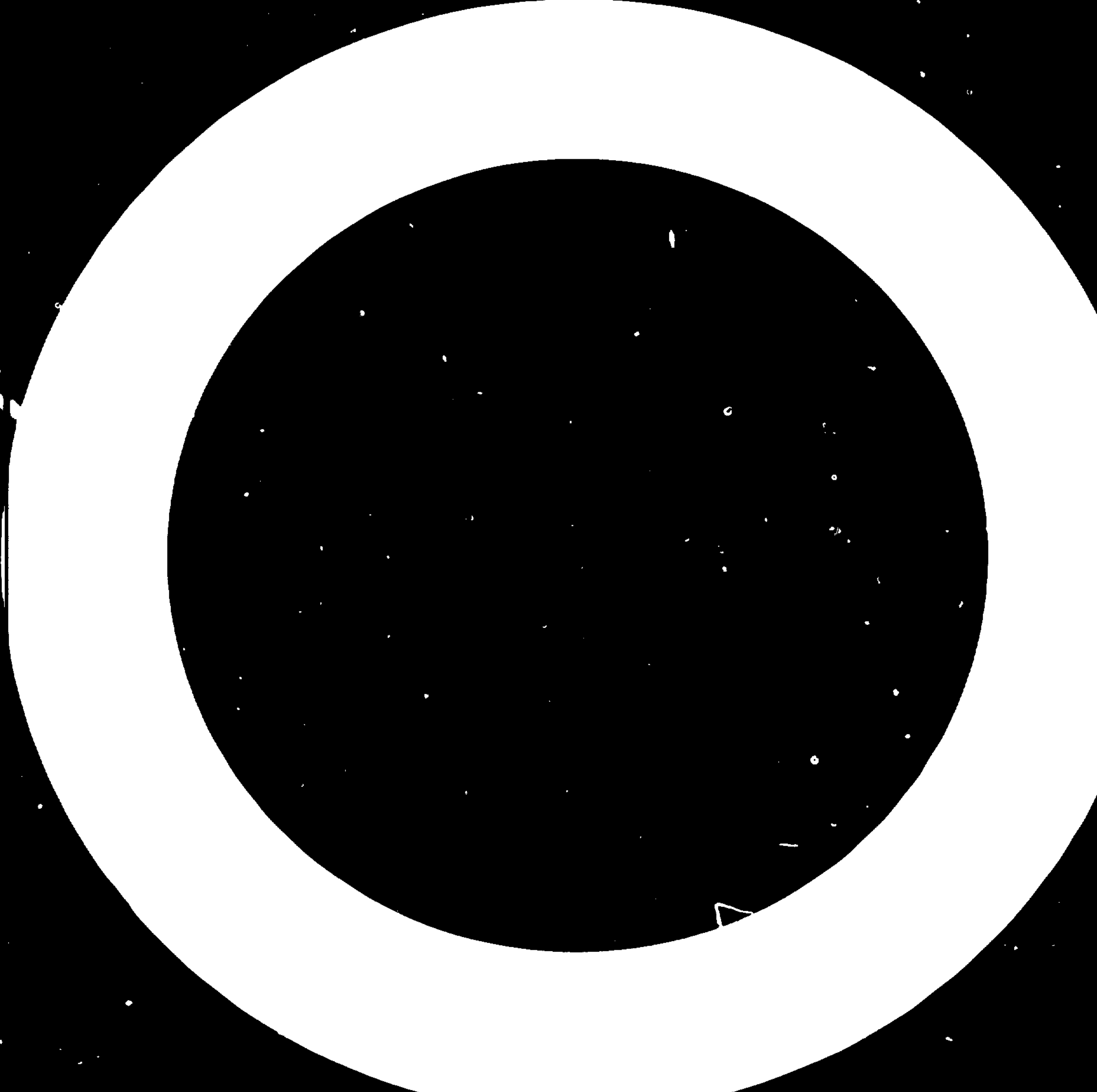


Fig. 2.15 Appearance of TPNR after weathering. The samples showing a white bloom are partially crosslinked with dicumyl peroxide.

Fig. 2.16 Effect of exposure to 50 pphm ozone at 40 C for 7 days, 20 per cent surface strain on (left to right) vulcanized NR; TPNR 4060; TPNR 5050; TPNR 6040. All samples contain carbon black, but no antiozonant.



INDUSTRIAL PROSPECTS FOR TPNR BLENDS

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ECONOMIC FACTORS

The prospects for TPNR, as for any new material, are dependent on both technical and economic factors.

The physical properties of TPNR are very similar to those of thermoplastic olefin elastomers (TPOE) and they are likely to compete in essentially the same markets.

It follows that the prospects of TPNR gaining a market share could well be decided by its availability and price.

It could be manufactured in any industrialized country where the basic raw materials are available. Compounders of rubbers and plastics with experience of blending different polymers would have no difficulty in making TPNR, in several hardness grades for example, which might be used 'in house' or sold to other product manufacturers. There are advantages in having the manufacturer of a semi-finished material such as TPNR close to the user. This is particularly so when a grade is being developed or selected for a new application and frequent liaison between supplier and user is necessary. On the other hand the marketing of a range of TPNR grades would not be so dissimilar to the marketing of the various grades of synthetic rubbers and plastics which almost from their inception have been shipped across the world.

A third possibility for TPNR, therefore, is for it to be made in countries where there is a strong incentive to add value to the indigenous material, in this case natural rubber.

In the USA natural rubber and EPDM rubber are approximately equal in price, so there appears to be little prospect in the immediate future at least, of TPNR costing less to produce than TPOE in USA.

In Western Europe the position is different. The list price for EPDM is considerably higher than current NR prices and this leads to estimated selling prices of most grades of TPNR at least 10% lower than TPOEs of equivalent hardness with similar rubber/polypropylene ratios, assuming all other manufacturing costs would be the same.

In a NR producing country the lower cost of NR (not having export duties and freight charges) will to some extent be offset by higher costs of imported chemicals and polypropylene. However, lower labour costs in a developing country and other cost savings make for a much lower estimated production cost of TPNR in SE Asia compared with Europe. Hence there is an excellent case for producing TPNR to supply local manufacturers in these countries. It is estimated that an economic price for locally produced TPNR could undercut the price of imported TPOE by 20-30%. Even production for export should be possible, provided the additional cost of exporting and shipping is not too high.

PRODUCTION METHODS

A number of companies in the UK have made production size batches of TPNR using, for example, a 3D Banbury (50 litres capacity).

The method is simply a scale-up of that given previously for preparations in smaller equipment. With high rotor speed and full ram pressure the heat build-up during mixing in a 3D Banbury is sufficient to raise the temperature to the required melting point of polypropylene in 3-4 minutes, and on a run of batches it would be necessary to use cooling water. The batch temperature should be precisely controlled and a quick response thermocouple measuring the actual batch temperature throughout the mixing cycle is desirable.

Care should be taken that no pellets of PP are allowed to remain on top of the ram, where they can easily get thrown when the ram is first lowered. Unmelted PP pellets, while not serious in TPNR because of the high temperatures used in further processing, can be very troublesome in normal rubber compounds that may follow TPNR in the mixer.

Production of polymer blends and compounds on a continuous basis using extruder blenders is well established, particularly in the plastics industry. Whilst this is a viable method for EPDM/PP blends it is less applicable to TPNR because NR is not widely available in the required chip or powdered form. A number of EPDM grades are shipped as pellets or friable bales, among these the high ethylene to propylene ratio grades which are the high green strength types preferred for making TPOE blends.

It has been reported that injection moulded and extruded products are being made from TPOE blends by the direct addition of mixtures of PP and EPDM pellets to the hopper. The machines can be fitted with segmented screws that blend as well as carry the material forward.

This method is obviously not suitable for bale NR, but new mixing machinery for rubbers and plastics is being developed and this opens up the prospects of TPNR being made on a continuous basis, with additional economies in terms of manpower and production rates.

One such mixing line, on which TPNR has been successfully processed, is Francis Shaw's mixer/extruder. The prototype equipment consists of a variable speed K2 Intermix dumping directly into an extruder to which various dies can be fitted.

The K2 was fed with pieces of NR cut from bale SMR L, pelletized PP, antioxidant and pigment. At a rotor speed of 125 rpm a good melt blend was obtained in less than 2 minutes. After dumping into the hopper the hot material was forced by the reciprocating ram into the extruder, which was fitted with a strand die.

The extruded strands of TPNR were led into a cooling bath and thence to a pelletizing machine. The whole process could be made virtually continuous by adjusting batch frequency to extruder throughput. The layout of the equipment is shown diagramatically in Figure 1.

The additional cost of granulating or powdering raw NR, together with higher freight charges make these forms less attractive starting materials for TPNR compared with sheet or block bales. However, in the producing countries a different situation exists and the direct processing of powdered rubber/PP dry blends by injection moulding or extrusion should be seriously considered.

APPLICATIONS OF TPNR

The markets for which TPNR might profitably be assessed can be classified as follows:

1) Replacement of vulcanized rubbers in products where high resilience and strength are not essential.

2) Replacement of flexible plastics such as plasticized PVC, EVA, LDPE and polyurethanes (PU).

3) Replacement of high impact polypropylene copolymers.

4) New applications, especially in the automotive industry.

The properties of TPNR which will enable its usage to grow in these markets are:

1) Better low temperature flexibility than PVC, PU etc.

2) Better high temperature properties than PVC, EVA, PE etc.

3) Better impact strength than polypropylene.

4) Lower density than PVC and PU; lower price than PU.

5) Lower production costs than vulcanized rubbers and crosslinked PE.

6) Good water and chemical resistance.

There is no doubt that TPNR will meet the quality requirements of a large number of products and the following list gives a few suggested uses.

Automotive: bumper covers, spoilers, filler panels, mudflaps, wheel trims, rub strips, mats. Wire covering, moulded plugs and connectors. Footwear. Battery tops. Pipe joints and closures. Grips for handlebars and tools. Water hose. Linings for chemical tanks. Rail pads. Sheeting, thermoformed products.

Automotive components

Automotive products are an important growth area for thermoplastic elastomers. There are two main reasons for this. Firstly, they are capable of replacing sheet steel, with a reduction in weight of the component, and secondly, components designed for passenger and pedestrian safety require the use of flexible impact resistant material. Most car manufacturers are now using some type of polymeric material for bumper covers. Depending upon the design of the bumper, whether it is a composite structure or is more or less self supporting, materials ranging in flexural modulus from about 250 to 800 MPa are required. TPNR has been studied for use in one particular bumper for which a flexural modulus of 250 MPa was specified.

Early experience showed that the specification could be met with TPNR 6040, but trial mouldings of the bumper indicated the need to modify the material in order to meet the exacting requirements of good mould flow and surface finish.

The melt viscosity of TPNR is generally higher than that the polypropylene it contains. This is no doubt due to the high molecular weight of NR even after it has been mixed at an elevated temperature.

In order to reduce the melt viscosity two approaches are possible (1) use of lower viscosity grades of polypropylene (or higher melt flow index grades, since MFI is inversely proportional to viscosity) and (2) addition of plasticizers.

Under the very high shear forces during injection moulding there may be a tendency for polymer mixtures to become unstable and there is some subjective evidence that the compatibility and stability of NR is greater with polypropylene copolymer grades than with the homopolymer.

Table 1 shows a number of recipes for the bumper material in which different grades of PP were compared. A subjective assessment of surface texture indicated the improvement obtained with PP copolymers.

Table 2 shows the effect of plasticization on MFI and surface texture. These formulations, especially those in columns 4 and 5, gave test mouldings having a uniform surface without flow marks and only slight marking persisted in moulded bumpers as shown in Figure 2.

The physical properties of the formulation in column 5 of Table 2 are included in the representative TPNR compounds in Table 3. This particular formulation was made to comply with the specification of a major car manufacturer.

TABLE 1 TPNR BLENDS USING PP HOMOPOLYMERS AND COPOLYMERS

SMR L	60	55	60	60	55	55
PP homopolymer[a]	40					
PP homopolymer[b]		40				
PP homopolymer[c]			40			
PP copolymer[d]				40	40	45
Atactic PP		5			5	
HAF black	2	2	2	2	2	2
Antioxidants	1.25	1.25	1.25	1.25	1.25	1.25
MFI of the PP[e]	0.5	4	8	4	4	4
MFI of the blend[e]	0.4	1.3	1.6	0.8	1.1	1.0
" " " "[f]	2.3	6.9	6.5	3.2	5.0	4.4
Flexural modulus, MPa	170	240	290	260	250	270
Surface texture	strain marks	flow marks	flow marks	slight flow marks	slight flow marks	slight flow marks

a Shell's PLZ 423

b ICI's GWM 22

c Shell's RM 6100

d Shell's KMT 6100

e At 230°C with 2.16 Kg load

f At 230°C with 5.0 Kg load

TABLE 2 PLASTICIZATION OF TPNR TO INCREASE MFI

SMR L	50	40		40	42
OENR (25% oil)			50		
PP copolymer [a]	50	60	50	60	60
FEF black	10	10	10	10	8
Petroleum jelly	5	15			
Mineral oil				12	8
Antioxidants/UV absorber	0.9	0.9	0.9	0.9	0.9
MFI ($230^{o}C/50N$), g/10 min	12	28	22	21	24
Flexural modulus, MPa	270	260	270	280	280
Surface texture	flow marks	slight flow marks		virtually no flow marks	

a. Grade RMT 6100 (Shell Chemicals)

The bumper cover is just one of several car components that can be made in TPNR. Spoilers and air dams require a stiffer grade such as TPNR 3070. Mud flaps require sufficient flexibility to withstand the occasional large deflection in bending.

There is always an incentive to use locally produced raw material if it is relatively cheap and a developing country having a car assembly industry could probably use TPNR for locally produced components, even when other materials are used for the same components in the major car producing countries of the West and Japan.

Miscellaneous products in TPNR

Several products from the list given earlier have already been researched.

These include rail pads (Figure 3) made in TPNR 4060 which have good impact strength and have better wear resistance than vulcanized rubber pads on certain types of railroad.

Impact resistance pipe fitments (Figure 4) are an insurance against damage and the need for costly replacement.

The TPNR sheeting shown in Figure 5 was produced on a plastics sheeting line which consisted of a long extruder (L/D ratio of 35/1) with a slit die, followed by calendering rollers. This sheet material has good chemical and abrasion resistance and is being evaluated for tank linings and for stair treads. Many other products can be made from sheet TPNR by vacuum forming and other techniques.

Perhaps the most effective way to establish the use of TPNR in a rubber producing country would be to begin in the competitive field of general mouldings where its attractive pricing and capability of giving high production rates could lead to increased profitability. Electric plugs, closures, gaskets and handlebar and pedal grips are just some of the possibilities.

In summary, a wide range of potential applications exist for TPNR blends. Commercial uptake in developing countries is a means of increasing overall markets and adding value to the basic raw material, natural rubber.

TABLE 3 TYPICAL PROPERTIES OF TPNR BLENDS

Colour	1 White	2 White	3 Black	4 Natural	5 Black	6 Natural	7 Black	8 Black
SMR L	70	50	50	55	42	35	30	15
Propathene GWM 101	30	50	50					
RMT 6100				45	60			
KMT 6100						65	70	
Propathene GWM 22								85
Sunpar 2280	15				8			
Ultrasil VN3	15							
Titanium dioxide	1	1						
Stockalite clay		85						
Zinc oxide	4							
Stearic acid	1							
TMTD	1							
Paraffin wax		3						
FEF black					8			
HAF black			1				10	1
Phenolic antioxidant		0.3		0.5		0.3		
Permanax CNS	0.5							
Flectol H			0.2		0.5		0.5	0.5
Irganox PS 800				0.2	0.2	0.2	0.2	0.2
Tinuvin 327				0.2	0.2	0.2	0.2	0.2
Density	1.02	1.28	0.91	0.91	0.94	0.91	0.95	0.91
MFI (230^{o}C/50N) g/10 min	2.7	5	6	10	25	10	7	20
Shore A hardness	80	95	96	96	97	98	99	100
Shore D hardness (instantaneous)	34	46	47	46	50	60	65	71
Flexural Modulus, MPa	-	160	300	290	260	600	700	800
Tensile Strength, MPa	8	11	12	11	11	16	18	
Tensile yield stress, MPa						17	18	23
Modulus at 50% extension, MPa	5	9	10	9	10	17	17	
Elongation at break, %	300	300	350	350	325	400	400	
Tear Strength, N/mm	40	75	80		92	150		

Notes:

Compound 1 is a flexible grade suggested as a wire insulation material.

Compound 2 is a higher density, low cost grade containing wax to assist extrusion or calendering.

Compound 3 is a low density black grade, and Compound 4 is a non-black grade with added protection against weathering.

Compound 5 is a high flow black grade suitable for complex injection mouldings for outdoor applications.

Compound 6, 7 and 8 are high modulus, impact resistant grades suitable for stiff non-brittle components in outdoor applications.

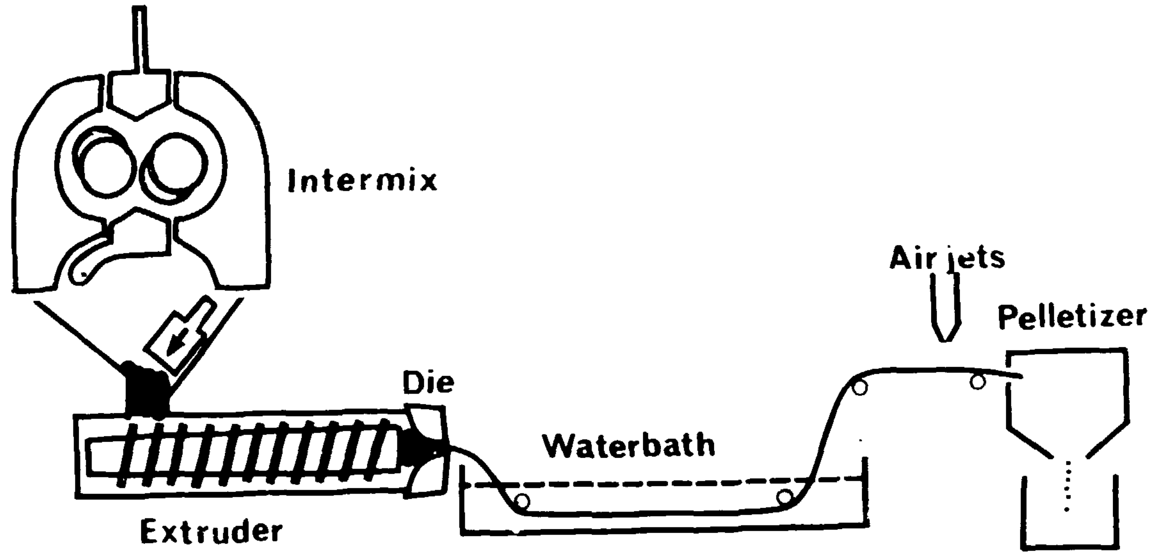


Fig. 3.1 Layout of the Francis-Shaw mixer/extruder.

Fig. 3.2 Car bumper moulded in a TPNR compound.

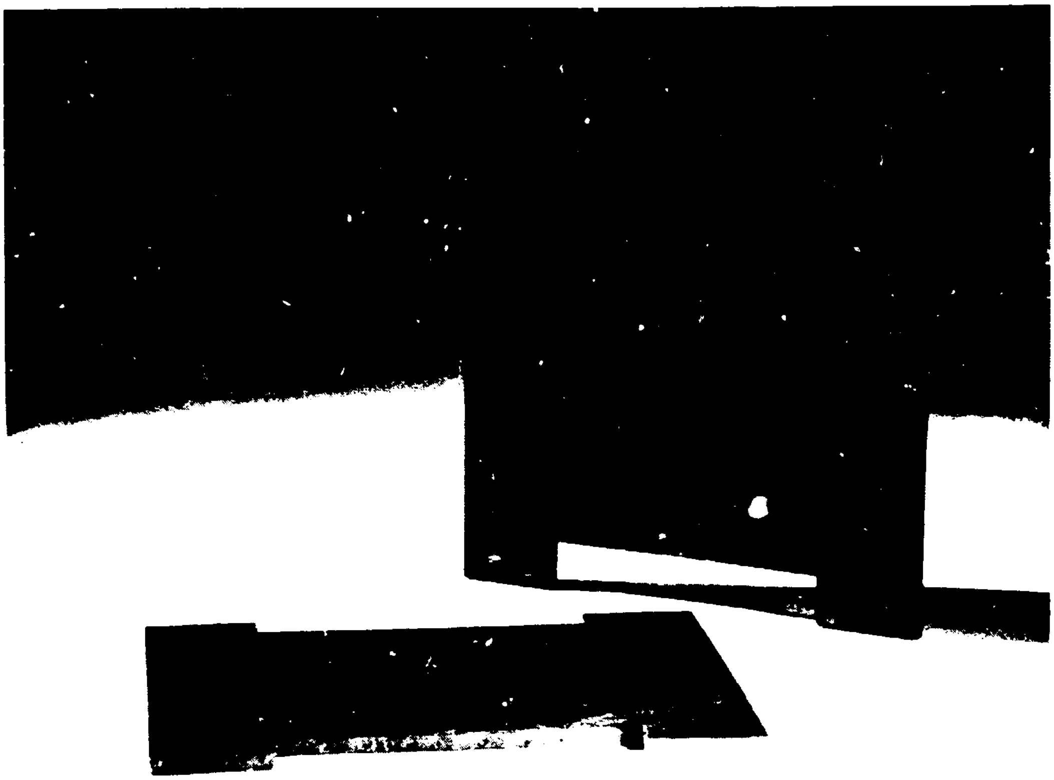


Fig. 3.3 Railway sleeper pads moulded in TPNR 4060.

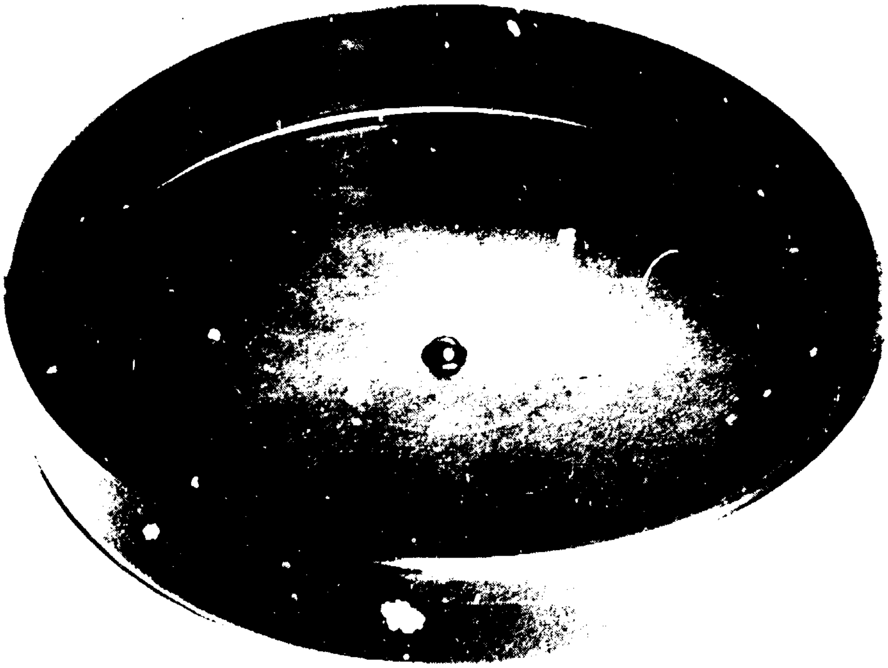
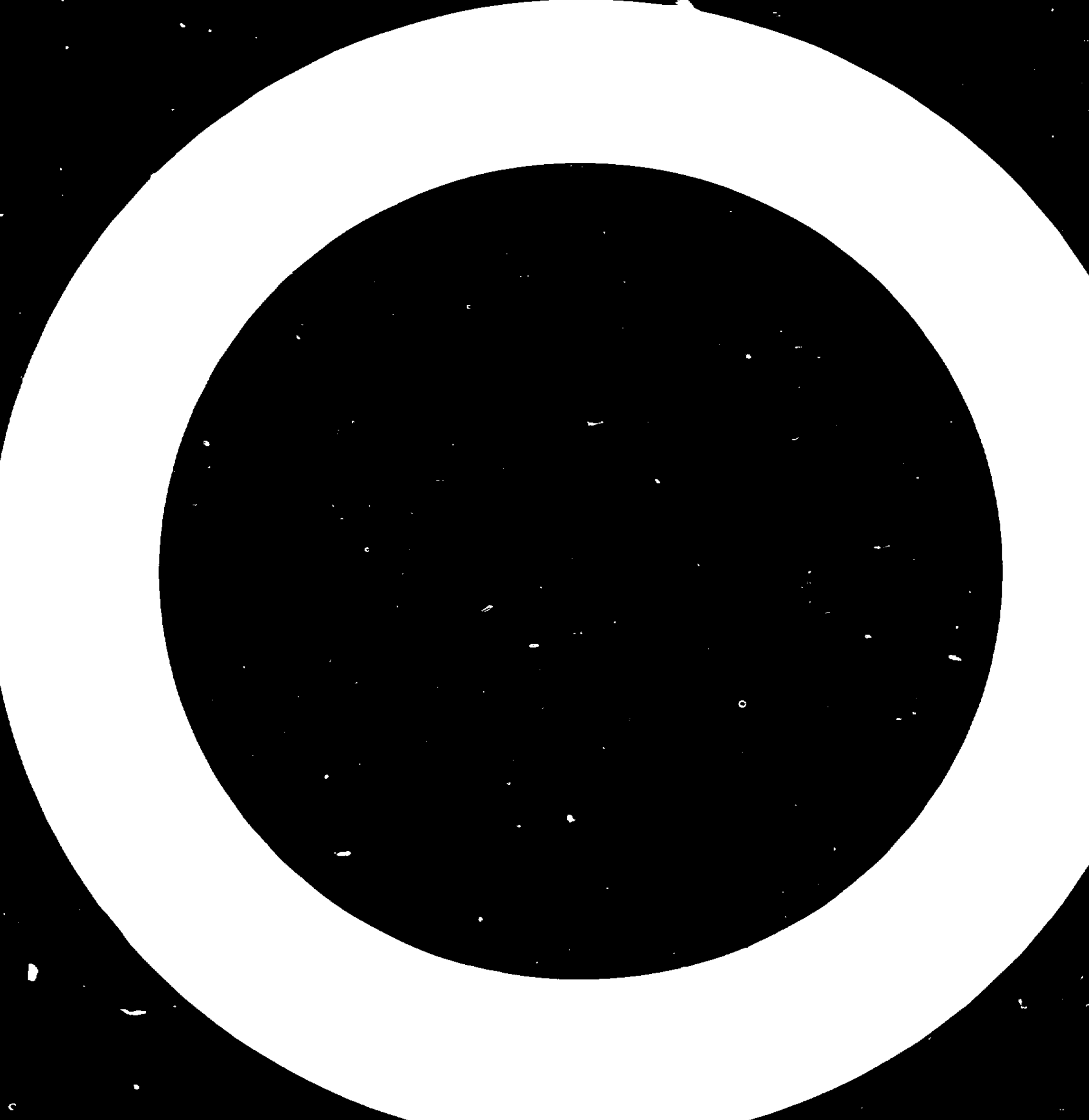


Fig. 3.4 Pipe closure moulded in TPNR 1585.

Fig. 3.5 TPNR 5050 extruded sheeting



THE POTENTIAL OF THERMOPLASTIC NR IN SHOE SOLING APPLICATIONS

by

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The consumption of thermoplastic rubber (TR) was estimated to be 230 000 tonnes in 1979.[1,2] Consumption of TR in footwear was 90 000 tonnes in 1979.[2] The type of TR used in shoe soling would be mainly styrenic TR such as Shell Kraton or Phillips Solprene or Anic Europrene material.

TRs are being used to a great extent at the expense of PVC and to some extent of vulcanized shoe sole. The main applications of TR in footwear are in men's and children's casual shoes. Other applications are heel top pieces and ski boots. However, TRs such as Kraton are not suitable for high severity sports applications such as tennis shoes etc.

The main advantages that favour the use of TRs are its rubberiness, light weight, low temperature properties, skid resistance, good flow properties and design flexibility.

This paper discusses some of our work on TPNR (a blend of NR and a polyolefin such as PP, PE, EVA) shoe soling applications. Comparisons are made against some of the established soling materials such as Kraton and PVC in the following properties such as processibility, abrasion resistance, flexibility, lightness, skid resistance, shrinkage. The two critical properties are wear and flex resistance.

PROCESSING

Our assessment on the flow properties of TPNR was carried out using a Nikko recipocrating screw, horizontal clamping, 144 ml shot capacity plastics injection moulding machine. A two cavity mould with two different flow paths were used (Figure 1). Because of the long runner system Cavity A has a more difficult flow path compared to Cavity B.

The optimum melt temperature for processing of TPNR is in the region of 190-220°C, low temperatures lead to poor flow and higher temperatures cause oxidation and tacky surfaces.

Our studies show that TPNR containing higher proportions of NR display poor flow properties (Table 1) as illustrated by the higher melt temperature required to achieve satisfactory mould filling. The amount of shrinkage increases with the increasing NR content.

NR/PE blends show better flow properties when compared to NR/PP blends. An NR/PE blend containing 60% by weight of natural rubber could be processed satisfactorily while in the NR/PP blend the proportion of NR is limited to 40% or less. Furthermore, NR/PP blends with a high proportion of PP are generally too stiff for soling. As the NR/PE blend shows the best promise for shoe soling applications our studies have been centred on blends containing equal proportions of each polymer (Table 2).

TABLE 1 PROCESSING CONDITION OF TPNR

(CAVITY A)

SMR 5L	80	60	40	60	40	20
Polyethylene	20	40	60	-	-	-
Polypropylene	-	-	-	40	60	80
Dicumyl peroxide	0.48	0.36	0.24	0.36	0.24	0.12
Barrel temperature, °C	200-240	165-185	160-180	210-230	190-210	160-180
Injection chamber temperature, °C	250	195	190	240	220	190
Injection pressure, kg cm^{-2}	105	105	100	105	105	100
Moulding quality	Poor	Good	Good	Poor	Good	Good
Flexural modulus, MPa	-	-	61	-	255	-

TABLE 2 BASE POLYMER

SMR 5L	50
Polyethylene	50
Dicumyl peroxide	0.36
Antioxidant	0.5

The two polymers were mixed and dispersed in a high shear internal mixer (Shaw K2 Intermix, 12 litre capacity). The conditions and cycle time used are given in Table 3.

TABLE 3 MIXING CONDITIONS USING K2 INTERMIX

Mixer body starting temperature		100°C
Rotor speed		25 rpm
Ram pressure		60 psi
Cycle time	0 min	NR + PE + fillers
	3½ min	Peroxide
	5 min	Antioxidant
	6 min	Dump

The dump temperature is in the region of 160 - 170°C.

Another way of improving the flow properties is by incorporation of process oil. Table 4 shows the improvement of flow properties by addition of naphthenic oil, but this method is limited by its adverse influence in physical properties.

Addition of reinforcing filler such as silica impairs the flow properties as higher melt temperature is required to facilitate flow.

TABLE 4 EFFECT OF OIL AND SILICA ON PROCESSIBILITY OF TPNR

	Oil (% w/w)			Silica (% w/w)
	0	10	30	20
Barrel Temperature, °C	165 - 185	145 - 165	140 - 160	190 - 210
Injection Chamber Temp, °C	195	175	170	220
Injection Pressure, kg cm^{-2}	100	100	70	100

PHYSICAL PROPERTIES

As with other soling materials such as Kraton and PVC, it is necessary to compound NR/PE with other ingredients to meet property requirements in soling applications. The copounding ingredients that we have studied are mineral fillers, plasticisers and other polymers.

Two fillers, namely silica and whiting, that are commonly used in compounding of TR were examined. Table 5 shows that the addition of silica improves the tensile, tear, abrasion of the blend while the addition of whiting reduces the abrasion resistance.

TABLE 5 EFFECT OF FILLERS ON PHYSICAL PROPERTIES

Filler, % w/w	0	20 silica	40 silica	30 whiting	60 whiting
Tensile Strength, MPa	4.5	5.7	7.5	4.7	4.4
M100, MPa	3.9	4.7	5.8	4.6	4.1
Tear, N/2 mm	73	93	85	73	68
Abrasion (Du Pont), ml/1000 rev	1.9	1.2	1.2	-	3.2
Hardness, Shore A	89	92	94	91	92

One limitation of a straight NR polyolefin blend is that it has high hardness.

To lower the hardness of TPNR, process oil is incorporated. Selection of the proper oil is important. Napthenic oils compatible with the natural Naphthene rubber were studied. The addition of oil besides lowering the hardness, also reduces the tensile and tear strength, flexural modulus and abrasion (Table 6). It was also observed that it would require a longer time to incorporate more than 20 parts of oil. However, the level of oil could be increased by using oil extended natural rubber.

TABLE 6 EFFECT OF NAPHTHENIC OIL

Oil, % w/w	0	10	30
Tensile Strength, MPa	4.5	3.9	2.3
M100, MPa	3.9	3.6	2.3
Tear Strength, N/2 mm	73	67	40
Abrasion Resistance (Du Pont) ml/1000 rev.	1.9	3.0	3.7
Flexural Modulus, MPa	29	22	10
Hardness Shore A	89	86	78

Another possible way of reducing flexural modulus and hardness without causing significant difference in tear and tensile properties is by substituting the polyethylene with EVA (vinyl acetate content 16%) (Table 7).

TABLE 7 EFFECT OF EVA IN PHYSICAL PROPERTIES

PE substituted by EVA, %	0	15	25
Tensile Strength, MPa	4.3	4.7	5.0
M100, MPa	3.8	4.8	3.5
Flexural Modulus, MPa	29	-	19
Tear Strength, MPa	73	60	60
Hardness, Shore A	89	86	84

SHRINKAGE

TPNR containing equal proportion of NR and PE gives acceptable mould shrinkage of about 1.5%. It is comparable to the PVC compound but higher than the Kraton compound. The typical range of TPNR is in the region of 1.5 - 3.0%, for PVC 1.5 - 2.5% for Kraton 0.4 - 1.0%.

In our factory trial with an international footwear company in Malaysia, the TPNR of formulation given in Table 8 was compared to Kraton 5152 and PVC compound used for the production of children's sneaker soles. TPNR as inferred from laboratory test results shows superior wear resistance over Kraton, and lightness and skid resistance over PVC (Table 9).

TABLE 8 FORMULATION OF TPNR SOLING COMPOUND

	parts
SMR 5L	50
EVA	15
Polyethylene	35
Dicumyl peroxide	0.36
Antioxidant CS	1.5
Silica	15
Naphthenic oil	10
T_iO_2	0.1

TABLE 9 TPNR VERSUS KRATON 5152 AND PVC

	TPNR	Kraton 5152	PVC
Tensile Strength, MPa	4.7	3.8	8.8
M100, MPa	4.0	0.9	6.1
Hardness, Shore A	86	64	81
S.G.	0.99	0.99	1.25
Dunlop Resilience, %	36	35	18
Stanley Skid Resistance	94	98	50
Tear, N/2 mm	60	47	118
Du Pont Abrasion, ml/1000 rev	1.1	3.4	1.3
Ross flex (2mm-6mm), kc	200	200	200

TPNR also shows a cost advantage over Kraton and PVC (Table 10). The TPNR compound is now being evaluated by this company as a possible replacement for their PVC compound and Kraton.

TABLE 10 COST COMPARISON OF TPNR, KRATON, PVC COMPOUNDS IN MALAYSIA*

	TPNR	Kraton 5152	PVC
Compound cost, M$/kg	2.85	5.90	3.20
S.G.	0.99	0.99	1.25
Volume cost index	100	207	142

* This cost comparison is not applicable outside Malaysia.

CONCLUSION

TPNR, a blend of natural rubber and polyolefin can be compounded to offer hard wear, flex resistance, light weight, good grip and flexibility acceptable as a soling material. It gives a cost advantage over Kraton and PVC compound particularly in Malaysia. However, as TPNR is a basically hard material, attempts are being made through compounding to achieve lower hardness.

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2. Thorstad, T. and Leclere, A., Scandinavian Rubber Conference, May 1980

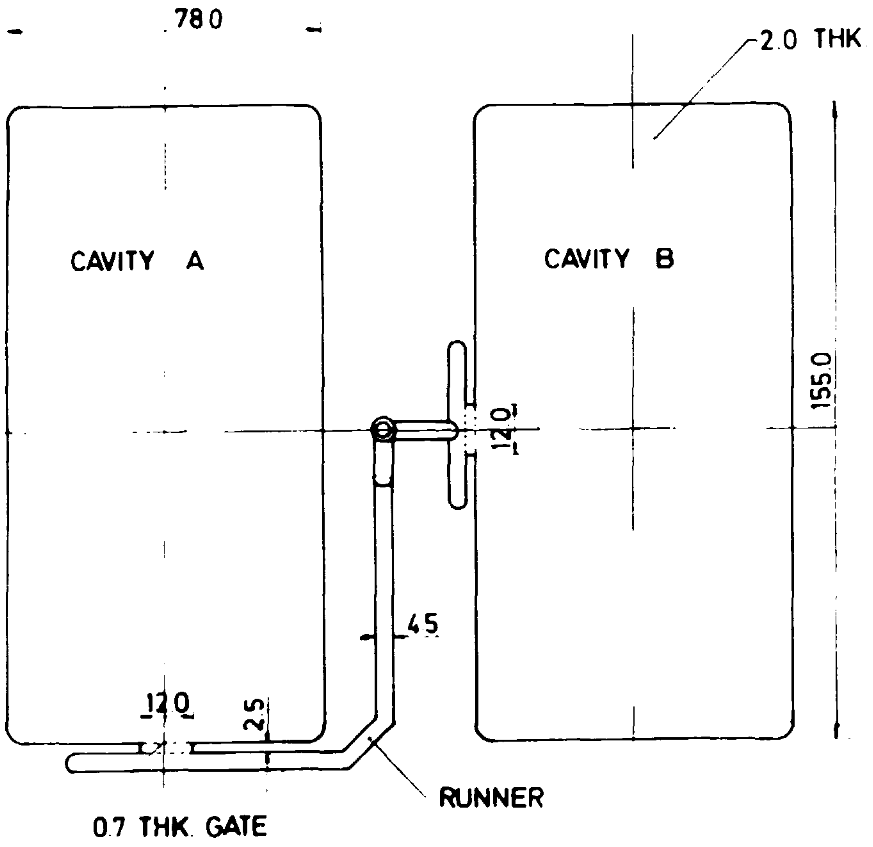

Fig. 4.1 Layout for mould to assess flow characteristics of TPNR.

PRODUCTION, PROPERTIES AND PERFORMANCE OF NR/POLY(STYRENE) GRAFT COPOLYMERS

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INTRODUCTION

Thermoplastic rubbers can be divided into two very general classifications. The first covers a wide range of materials obtained by blending a rubber with a hard polymer and is exemplified by the commercial synthetic rubber-poly(olefin) blends. Natural rubber (NR) analogues of these thermoplastic rubber blends can be prepared and are described elsewhere.[1,2] The other general class of thermoplastic rubbers is also constituted of materials which contain both rubbery and hard polymer but is characterised by the presence of chemical bonding between most or all of the hard polymer and the rubbery polymer. These latter materials need not necessarily be highly elastic but they have the potential of being so. The present paper will discuss an approach to the formation of this second class of thermoplastic rubber, using NR as a starting material.

Heveaplus MG

Composite materials with NR chemically bound to a second, hard polymer are not new.[3] A composite material of NR and poly(methylmethacrylate) (Heveaplus MG) has been in commercial production for nearly twenty years, but the material is not a thermoplastic rubber in the present day commercial meaning of the term. As prepared, Heveaplus MG is a tough material which will soften on heating but cannot be directly processed by injection moulding, or even compression moulding, because of its very high viscosity and its gel content. Conventional mastication will confer a degree of processability but the product of the mastication does not have high strength or toughness unless it is subsequently vulcanized. High strength and toughness cannot be obtained in conjunction with direct mouldability.

Numerous modifications to the Heveaplus process have failed to produce major changes in the properties of the materials. Many of the procedural modifications were tried before the thermoplastic rubber concept was being consciously pursued, but experience indicates that refinement of the Heveaplus process will not produce a viable thermoplastic rubber.

The deficiencies of Heveaplus MG do not lie in the chemical constitution of the rubbery component. Commercial styrene-diene thermoplastic rubbers with poly(isoprene) as the rubbery component have physical properties and processing characteristics generally comparable to those of the more common poly(butadiene) based materials. The two major differences between Heveaplus MG and the styrene-diene thermoplastic rubbers are the chemical nature of the hard polymer and the fundamental molecular architecture. Heveaplus MG has poly(methyl methacrylate) hard polymer in a graft structure whereas styrene-diene thermoplastic rubbers have poly(styrene) hard polymer in a block structure.

Poly(methyl methacrylate) and poly(styrene) are both glassy polymers, with similar glass transition temperatures. They would be expected to behave similarly in a phase-separating copolymer system with a poly(diene). There is, however, no direct confirmation that methyl methacrylate can replace styrene in a viable thermoplastic rubber system and this chemical difference between Heveaplus MG and the styrene-diene thermoplastic rubbers may be significant. The difference in molecular architecture (graft versus block structure) is almost certainly important.

GRAFT COPOLYMER THERMOPLASTIC RUBBERS

Several authors[4-8] have demonstrated experimentally that graft copolymers with elastomeric backbones and hard side chains can behave as thermoplastic rubbers although this type of system is not in commercial use. The detailed structure of such graft copolymers is important. They have a fairly large number of short hard polymer chains attached to each rubbery backbone whereas Heveaplus MG has a small number of very long hard polymer chains, and also a significant proportion of backbone chains which carry no graft chain at all.

Of the two known thermoplastic rubber structures (block copolymer and short chain graft copolymer) the short chain graft copolymer is clearly the more accessible from NR. The poly(diene) segments of block copolymer thermoplastic rubbers have an upper molecular weight limit of 1 x 10^5 imposed by criteria of processability. NR, even after extensive mastication, has a much higher molecular weight. This factor, conbined with the formidable chemical problem of ensuring attachment of one hard polymer segment at each end of the NR molecule precludes the possibility of constructing an exact replica of the block copolymer system from NR.

The experimental graft copolymer thermoplastic rubbers are prepared by polymerization of hard segment monomer from backbone initiation sites by living polymer techniques. The techniques give considerably greater control over the graft structure than can be achieved with the free radical reactions of the Heveaplus process. In principle, the living polymer grafting techniques are applicable to the poly(isoprene) backbone of NR but their sensitivity to the non-rubber constituents in NR precludes their use. We have therefore had to adopt an alternative and largely novel approach to the synthesis of graft copolymers of controlled structure. The procedure (Scheme 1) involves the separate synthesis of hard polymer chains with reactive end groups and subsequent reaction of these end groups with the NR backbone.

There are several literature reports of reactions of this general type where the reactive prepolymer is a polymeric carbanion and the backbone is a polymer which is inherently capable of combining with carbanions or has been suitably modified to do so.[9-14] Examples of the reaction sequence which involve air stable, isolable, reactive prepolymers are much less common.[15]

In seeking to apply this reaction sequence to the synthesis of a thermoplastic NR we defined the four criteria set out below. The criteria are not listed in any pre-conceived order of importance and there is a certain amount of interaction between them. The criteria are:

a. Reaction with unmodified NR. Direct reaction with the unmodified NR chain has economic attractions. A grafting process which depended on a prior chemical modification of the rubber could only be justified if the modification was cheap and led to a graft product which could command a substantial price premium in the market place. Reaction with the unmodified repeat unit of the NR chain is also likely to give a rate advantage in the grafting process by a simple concentration effect.

b. Reaction of a stable prepolymer. Use of an air-stable prepolymer has clear advantages in the overall organization of the grafting process. The prepolymer can be prepared independently. If appropriate it can be marketed as a reagent for use by processors who are concerned only with the preparation and use of the graft copolymer. An air-stable prepolymer is also a prerequisite for criterion c.

c. Reaction by direct mixing. A graft reaction which proceeds by direct mixing of the prepolymer and the NR seems essential on economic grounds. A reaction in NR latex is superficially attractive but becomes much less so on closer consideration and reaction with NR in solution will inevitably be expensive. This criterion of reaction by direct mixing sets a very serious constraint on the grafting process. For thermoplastic rubber behaviour the two polymer constituents must be thermodynamically incompatible and yet, the criterion demands reaction between the two with one of the reactants (the end group on the prepolymer) at a concentration of the order of 0.05 mole/lo. At the outset of the work there was no precedent for such a reaction.

d. Economic viability. Economic considerations strongly influence all three previous criteria but also become important in the synthesis of the reactive prepolymer. The criterion is difficult to apply strictly in the early stages of a research programme but it has been used to reject many avenues of work which we considered to be unreasonably complex in a chemical sense. Even so, the process which is to be described is not a simple one. The chemistry is sophisticated, and there is more than one operation involved in the overall synthesis.

The remainder of this paper will describe a graft copolymer synthesis which attempts to satisfy the above criteria. The discussion will be confined to a system using poly(styrene) as the hard polymer. For a number of experimental reasons, Cariflex IR305 will be widely used as a reference poly(isoprene) but the process is applied also to NR and comparisons between the two poly(isoprenes) will be made throughout.

PREPOLYMER CHEMISTRY AND SYNTHESIS

The chemistry which has been used for the coupling reaction between the prepolymer and the poly(isoprene) backbone is the 'ene' addition of the azodicarboxylate group to an allylic double bond system[16] (Scheme 2). The reaction does not rely on the presence of catalysts and, compared to carbanion reactions, it is relatively insensitive to impurities. Every double bond of the poly(isoprene) chain is a potential reaction site.

Our original synthesis of poly(styrene) with terminal azodicarboxylate functionality has been published.[17] The synthesis was a multi-stage operation involving changes of solvent and intermediate isolation of polymer. It was operated on scales up to 400g and provided supplies of azodicarboxylate-functional poly(styrene) for the initial trials of the grafting process, but it is totally unsuitable for production of larger amounts of the functional poly(styrene). A more direct synthesis is summarised in Scheme 3. The sequence involves the preparation, in solution, of a very highly reactive acid chloride which reacts directly with hydroxyl functional polymer to give azodicarboxylate functionality. The reactive intermediate is prepared by oxidation of 2-carbethoxyhydrazinecarbonyl chloride with bromine in the presence of pyridine or with t-butyl hypochlorite. The reaction with hydroxyl functional poly(styrene) takes place in the original polymerization solvent (toluene) and, in principle, the complete conversion of styrene monomer to azodicarboxylate-functional polymer is a one-pot process involving successive addition of butyl lithium initiator, ethylene oxide, acid and reactive azo acid chloride solution. In practice, reaction with the azo acid chloride solution is in a separate reactor to avoid contamination of the polymerization reactor with hydrogen chloride by-product. The reaction scheme has been applied on a scale of 1.5 kg using a simple batch polymerization reactor operating under dry nitrogen. The current limitation to the scale of operation is control of the polymerization exotherm for the styrene. Preparation and reaction of the azo acid chloride solution has presented no major handling problems on this scale. The major constraint is that oxidation of the 2-carbethoxyhydrazinecarbonyl chloride should be carried out immediately before reaction with the polymer.

The azodicarboxylate-functional poly(styrene) shows characteristic absorption bands in the infra-red and ultra-violet spectra. There is a strong carbonyl absorption at 1785 cm^{-1} which is clearly distinguished from the poly(styrene) overtones in polymers of number average molecular weight up to 2×10^4. There is also an absorption maximum at 407 nm which is well separated from shorter wavelength aromatic absorptions and which, by analogy with simple azodicarboxylate compounds, has an extinction coefficient of 34. The ultra-violet absorption maximum can be used, in conjunction with the number average molecular weight from gel permeation chromatographic analysis, to calculate the percentage functionality of the azodicarboxylate-functional poly(styrene). The calculated functionalities are reasonably precise up to poly(styrene) molecular weights of 2×10^4 provided the polymer sample is rigorously purified by reprecipitation to remove non-polymeric impurities. The accuracy of the molecular weight determinations represents a limiting factor in this calculation of percentage functionality.

A selection of results for preparation of 1.5 kg batches of azodicarboxylate-functional poly(styrene) is given in Table 1. The polymers were prepared using sec-butyl lithium as initiator. Similar results are obtained using n-butyl lithium but the molecular weight distributions are wider. The calculated azodicarboxylate functionalities are compared with grafting efficiencies under optimum conditions of grafting (see below). With one exception the agreement is reasonably good; the calculated functionalities giving a slight over-estimate of the grafting potential. The range of polymer functionalities is, however, wide and there have been several preparations which have produced polymer of less than 60% functionality. Some of the factors which have been responsible for the variations have been identified; in particular, the need to remove hydrogen chloride from the reaction solution before recovery of the polymer. Neutralization with carbonate, borax or sodium acetate is effective and water washing is also adequate. Small scale reactions following the same chemistry generally give higher azodicarboxylate functionalities. This is partly because it is practicable to use a larger molar excess of acid chloride reagent but also because the small scale reactions are generally carried out on dry, reprecipitated hydroxyl-functional polymer rather than on polymerization solution.

TABLE 1 ANALYTICAL DATA AND GRAFTING EFFICIENCY FOR AZODICARBOXYLATE-FUNCTIONAL POLY(STYRENES) PREPARED ON A 1.5 Kg SCALE

Polymer	$\bar{M}n$ (gpc)		Azo Functionality (%; u v)	Grafting Efficiency (%)
RPS 9	6550	1.09	75	71
RPS 10	6630	1.07	86	80
RPS 11	9300	1.07	71	61
RPS 12	11350	1.09	90	80
RPS 23	10100	1.13	85	70
RPS 37	7090	1.09	68, 84[a]	66
RPS 38	7190	1.06	72, 77[a]	68
RPS 40	7570	1.01	67, 93[a]	63

[a] Functionalities obtained for small scale reactions on samples of hydroxyl-functional polymer which had been isolated by precipitation into methylated spirits and dried.

In large scale reactions the efficiency of conversion of acid chloride reagent to azodicarboxylate functional polymer is seldom much better than 50%. The main outstanding problem in the synthesis is to improve this efficiency to the level of the small scale reactions.

The azodicarboxylate-functional poly(styrene) is isolated as a st yellow powder. It has been shown to retain its chemical identity and full grafting potential during 18 months storage at ambient temperature with no specific protection from the atmosphere.

DIRECT MIXING GRAFT REACTION

Azodicarboxylate-functional poly(styrene) reacts with NR or synthetic poly(isoprene) in solution to give graft copolymer.[17] The reaction has little interest as a potential commercial route to thermoplastic NR but it has been used to confirm the chemistry of the grafting process and the products have been extensively characterised. Of more immediate interest is the observation that the functional poly(styrene) reacts with NR or synthetic poly(isoprene) on direct mixing, in the absence of any diluent, provided two well defined conditions are satisfied. The temperature of the mixing operation must exceed the softening temperature of the poly(styrene) and the mix must be subject to high shear for at least part of the mixing cycle. Low shear, low temperature mixing followed by static high temperature treatment does not result in graft copolymer formation. The conditions for achieving grafting by direct mixing are, in fact, those commonly encountered in conventional internal mixers used for rubber processing. For experimental purposes the dry mixing process has been studied in a small internal mixer of 35 cc capacity‡. A torque transducer on the primary motor drive provides a continuous record of mixing torque and the shear conditions in the mixer are comparable to those required for carbon black dispersion.

‡ Hampden Test Equipment Ltd., Rothersthorpe Avenue, Northampton, England, NN4 9JH, UK.

When <u>Cariflex IR305</u> poly(isoprene) and azodicarboxylate-functional poly(styrene) are charged to the mixer at 90°C and mixed at 150 rpm initial mastication of the rubber backbone occurs, followed by a sharp increase in mixing torque (Figure 1). There is then a slow mastication at long mixing times. The overall time scale of the mixing process is approximately 10 min. When the mixing operation is carried out under the same conditions with poly(styrene) which does not have the azodicarboxylate functional group the torque increase at intermediate mixing times is not observed.

Analysis of the reaction product from the azodicarboxylate-functional poly(styrene) by gel permeation chromatography (gpc) shows two polymeric constituents, one at precisely the retention time of the poly(styrene) prepolymer and one at much shorter retention time, ie. much higher molecular weight (Figure 2). The main component, of high molecular weight, can be shown by double detection techniques to contain both poly(isoprene) and poly(styrene) constituents, ie. the main component is a graft copolymer. The low molecular weight component is poly(styrene) which, through lack of azodicarboxylate functionality, has failed to graft to the poly(isoprene). Direct comparison of the areas of the two peaks in the chromatogram gives the grafting efficiency of the poly(styrene). The grafting efficiency is defined as the percentage of the total poly(styrene) added to the mix which becomes bound to the poly(isoprene) backbone.

Determination of the grafting efficiency by gpc analysis at various stages along the mixing curve demonstrates clearly that the torque increase at intermediate mixing times is a consequence of graft copolymer formation (Figure 3). When the poly(isoprene) backbone is chemically clean (as is the case with <u>Cariflex IR305</u>) the optimum grafting efficiency is comparable to that obtained for reaction in solution. Also, with <u>Cariflex IR305</u> the grafting efficiency is independent of the total poly(styrene) content of the mix, offering further evidence that there are no non-rubbers in the synthetic poly(isoprene) which interfere with the grafting process. The grafting efficiencies agree well with the analytical estimates of azodicarboxylate functionality and we believe that the reaction of the azodicarboxylate groups with chemically clean poly(isoprene) is nearly quantitative.

The dry mixing process has been scaled up from the experimental mixer to the Laboratory Banbury (1.2 kg batches). The process shows exactly analogous behaviour when mixer motor current is monitored as a function of mixing time (Figure 4). There is a clearly distinguished load maximum after the initial rubber mastication. The time to reach the maximum in the load curve is dependent on mixing severity. Similar dependence on mixing severity was observed in the small scale reactions.

When <u>Cariflex IR305</u> is replaced by SMR 5L in the mixing process a similar variation of mixing torque and mixing time is observed (Figure 5). The torque peak at intermediate mixing times is again well defined and gpc analysis confirms graft copolymer formation. The torque maximum is at a slightly shorter mixing time for the NR reaction. This is almost certainly a consequence of the higher initial viscosity of NR, resulting in a more rapid rise in internal mix temperature and perhaps more rapid dispersion of the poly(styrene). Laboratory Banbury mixing on a 1.2 kg scale gives analogous behaviour.

The grafting efficiency for the reaction with NR is lower than for reaction with synthetic poly(isoprene) and is dependent on the level of poly(styrene) in the mix. Grafting efficiency information for a particular azodicarboxylate-functional poly(styrene) is summarised in Figure 6 in terms of bound poly(styrene) as a function of total poly(styrene) in the mix. For the reaction with synthetic poly(isoprene) the amount of rubber-bound poly(styrene) increases linearly with increasing poly(styrene) level, the line extrapolates accurately through the origin and to the measured grafting efficiency of 76% at a hypothetical 100% poly(styrene) content. This level of grafting efficiency reflects the less than 100% azo functionality of the poly(styrene) (cf Table 1). For the SMR 5L reaction the amount of grafted poly(styrene) is lower at all compositions and the relationship is not precisely linear. The difference is ascribed to interference of non-rubbers in the NR. At high poly(styrene) levels the NR relationship approaches linearity and extrapolation to 100% poly(styrene) gives the same maximum grafting efficiency of 76% as was observed for the synthetic poly(isoprene) reactions. Extrapolation of the linear section of the NR relationship to low poly(styrene) levels gives an intercept on the total poly(styrene) axis which can be interpreted as the total amount of azodicarboxylate-functional poly(styrene) which is deactivated by non-rubbers. Exactly analogous series of results have been obtained for reactions of poly(styrene) of different molecular weights and the intercepts on the total poly(styrene) axis can be shown to be equivalent to a constant molar concentration of interfering non-rubbers for any one batch of NR. For the SMR 5L rubber used in obtaining the results in Figure 6 this concentration is slightly over 2×10^{-3} moles per 100g of rubber. Assuming a molecular weight of 200 for the non-rubbers, this represents approximately 0.5% by weight. Extractable non-rubbers are normally present in NR to the extent of 5% or more by weight. Thus, only a small proportion of the non-rubbers is responsible for the interference. This conclusion is qualitatively supported by high pressure liquid chromatographic analysis of rubber extracts before and after the grafting reaction. Out of the very large number of individual non-rubber components only two or three showed any significant change as a consequence of the grafting reaction.

The non-rubbers which interfere with the grafting reaction have not been positively identified. They have been present in all samples of NR which have been used in the grafting process but the extent of their interference varies considerably. The grafting efficiencies for one particular batch of azodicarboxylate-functional poly(styrene) with different grades of NR are shown in Table 2 and compared with the grafting efficiency in synthetic poly(isoprene) and extracted NR. The performance of the NR bears no relation to conventional quality grading, and it has also been found that performance can vary substantially within a grade.

As might be expected, acetone extraction of the NR before grafting removes the non-rubbers and results in a grafting efficiency comparable with that obtained for synthetic poly(isoprene). This applies to all grades of NR. Extraction is not practicable on a large scale and some considerable effort has been expended in trying to evaluate simple additives which might counteract the effects of the non-rubbers. Pre-treatment of the rubber with low molecular weight azodicarboxylates gives some improvement but the effect is small at low levels of addition and becomes expensive at higher levels. Calcium oxide is both more effective and more accessible to the rubber and plastics processing industries. It is best used in the form of a dispersion in mineral oil, sold commercially as Caloxol W5G. Substantial improvement

TABLE 2 GRAFTING EFFICIENCIES OF AZODICARBOXYLATE-FUNCTIONAL POLY(STYRENE) ($\bar{M}n$ 8200) WITH DIFFERENT GRADES OF NR

Backbone Polymer	Grafting Efficiency (%)[a]
Cariflex IR305	76
Acetone extracted SMR 5L	73
SMR 5L	48
SMR10	46
SMR20	33
SMR CV	31
SMR EQ	24
DPNR	<10
RSS 1	<10

a. Measured for mixes with 40% w/w total poly(styrene)

in grafting efficiency is obtained at a level of 1% by weight on the rubber with only small additional improvement as the level is increased (Figure 7). We have used 3% w/w Caloxol as standard for much of our work with NR.

The mechanism of operation of the Caloxol is not entirely clear. Its conventional desiccating action is almost certainly important but other basic metal oxides, eg. zinc oxide, and also carbonates and bicarbonates have some improving effect on the grafting efficiency. The latter observation has suggested that unsaturated fatty acids or their oxidation products may be at least partly responsible for the lowering of grafting efficiency in NR. The hypothesis is supported, if not entirely proved, by the observation that incremental addition of linolenic acid to Cariflex IR305 grafting reactions progressively decreases the grafting efficiency. Corresponding additions of saturated fatty acid (stearic acid) have virtually no effect.

PHYSICAL PROPERTIES OF THE GRAFT COPOLYMERS

Many factors affect the physical properties of the graft copolymers obtained by the dry mixing process. In a way, this complicates the evaluation of the properties of the materials but it also gives the prospect of some degree of flexibility in the choice of product properties.

Effect of composition

An inherent feature of the whole prepolymer approach to the formation of graft copolymers is that the composition of the product is directly determined by the amounts of prepolymer and backbone polymer used in the reaction. As might be expected, the product properties change in a fairly systematic way as the proportion of prepolymer is increased. This is illustrated by tensile stress-strain curves over a range of compositions for both synthetic poly(isoprene) and NR graft copolymers (Figure 8). There is a general similarity in the behaviour of the two backbone polymers, but there are also some important differences. The modulus at any given elongation and poly(styrene) content is consistently higher for the NR graft copolymers in spite of the fact that the grafting efficiencies are lower. Both series of graft copolymers begin to show tensile yield phenomena above 40% w/w total poly(styrene) content and the yield becomes pronounced at 55% w/w poly(styrene). The incursion of a yield process is a clear indication of morphological changes occurring as the poly(styrene) content increases and can be interpreted as the onset of substantial continuity in the poly(styrene) phase above 40% w/w poly(styrene). The materials become increasingly susceptible to permanent plastic deformation above this poly(styrene) content.

The ultimate tensile strengths of the graft copolymers increase regularly with poly(styrene) content up to 40% w/w poly(styrene) (Figure 9). For the two series of polymers shown in the figure there then appears to be a decrease in tensile strength in the composition region where yielding becomes pronounced. Consideration of a wider range of results for different series of graft copolymers suggests, however, that in this composition region the measured tensile strengths become much less reproducible and the tensile strength maximum may not be real. As with the tensile modulus, the tensile strengths of the NR copolymers are consistently higher than those for corresponding materials derived from synthetic poly(isoprene).

Effect of grafting efficiency

The dependence of tensile strength on poly(styrene) content leads to an expectation of a dependence of tensile strength on grafting efficiency, because changes in poly(styrene) content and in grafting efficiency both lead to changes in the average number of poly(styrene) chains attached to each poly(isoprene) backbone. This expectation was confirmed experimentally by artificially reducing the grafting efficiency in a series of mixes by incremental addition of linolenic acid to mixes containing a fixed total amount of poly(styrene) (40%). The results for synthetic poly(isoprene) show a linear dependence of tensile strength on grafting efficiency over a wide range (Figure 10). This dependence corresponds fairly closely to the earlier results for the dependence of tensile strength on total poly(styrene) content when the results are normalised by equating 100% grafting efficiency to 40% w/w bound poly(styrene). The relationship between tensile strength and grafting efficiency for NR is not linear. Above a grafting efficiency of about 25% the relationship approximately parallels that for synthetic poly (isoprene) but the strength is enhanced by 11 MPa. This enhancement is almost certainly due to the effect of crystallization in stretched NR. At grafting efficiencies below 25% there is a much more rapid decrease in strength which can be interpreted as a decrease in crystallization at the point of failure due to inadequate restraint of the network chains by the relatively small number of poly(styrene) side chains.

The tensile strength relationships shown in Figure 10 illustrate clearly the importance of trying to achieve high grafting efficiencies in the process if high strength rubbery properties are to be obtained. Even at very high grafting efficiencies, the synthetic poly(isoprene) graft copolymers will not approach the very high tensile strength of pure styrene-diene block copolymers, but there is some reasonable expectation that tensile strengths in the region of 25 MPa could be obtained for NR graft copolymers if the grafting efficiency could be increased to 80%. This is still considerably less than the highest strengths recorded for styrene-diene block copolymers but compares favourably with strengths of conventional vulcanizates.

Hysteresis and set

The tensile strengths and moduli at high extensions are of limited significance in many practical applications of rubbery materials. Recovery from deformation is of much more practical significance and in this respect the graft copolymers have so far proved to be deficient to both conventional vulcanizates and pure styrene-diene block copolymers. The energy loss in performing a cycle to a fixed extension is high (Figure 11). The instantaneous permanent set is also high although in some cases this set is largely recoverable given sufficient relaxation time in the unstrained state. An improvement in hysteresis properties would be of benefit to the graft copolymers but it must not be assumed that the present level of performance is totally inadequate for practical applications. Styrene-diene block copolymers are not used in the pure state. They are compounded with oils, resins, and fillers and the elastic recovery properties of the compounds are often inferior to those of the pure block copolymers.

NR and poly(styrene) molecular weight

The discussion of physical properties has so far centred around materials prepared from poly(styrenes) of molecular weights in the region of 8000. At higher molecular weights there is a fairly pronounced drop in the tensile strength of both the synthetic poly(isoprene) and NR graft copolymers (Figure 12). We do not yet have a full understanding of the reasons for the effect but its existence is important. The economics of the grafting process is closely related to the cost of the chemicals used to construct the azodicarboxylate functional group on the poly(styrene). For a given weight % of poly(styrene) in the graft copolymer this cost decreases as the molecular weight of the poly(styrene) increases. From a purely economic point of view it is attractive to work at high poly(styrene) molecular weights but the experimental results preclude such a course. The same economic argument makes poly(styrene) of very low molecular weight unattractive and fortunately there is no conflict with the observed physical properties in this direction.

One other factor which strongly influences the physical properties of the graft copolymers is their mastication history. Mastication is an inevitable consequence of the preparative procedure and, to some extent, is essential to impart processability to the graft copolymers. The grafting efficiency results in Figure 3 indicate that the mastication results in scission of the backbone chains rather than removal of the side chains. If this scission is allowed to proceed too far the tensile properties can be adversely affected. The tensile properties which have been presented in this paper are for products obtained from a 10 min. mixing cycle. Shorter mixing times give products with significantly poorer mould flow characteristics but higher strength and extension of the mixing cycle up to 15 min gives a measurable deterioration in strength.

Compounding

The properties of the graft copolymers have been discussed strictly in terms of the raw polymers. In practice, the raw polymers would be compounded with oils, resins and fillers for different end uses. The present limited supply position for azodicarboxylate-functional poly(styrene) has severely restricted the systematic evaluation of compounding techniques and of compound properties. We have shown that compounding is feasible but the criterion for success in a compounding operation is the achievement of adequate service performance in a specific application at a competitive cost. We have not yet had sufficient material for applicational testing and our current evaluation of likely material costs is not sufficiently precise for detailed cost evaluation.

ECONOMIC STATUS

Some assessment of the economics of the grafting process is essential, but the novelty of the process makes this assessment difficult to achieve. In the following discussion some very sweeping generalizations are made and the final cost figures must be regarded as approximate. Prices are quoted in pounds sterling and are for commercial quantities of materials in Western Europe. They are inevitably somewhat out of date and are subject to geographical fluctuation but the conclusions are based on internal comparison rather than absolute accuracy.

A target price for raw graft copolymer can be set at £1000/tonne. This was a representative price for pure styrene-diene block copolymer at the time of the costing exercise. Taking a price for NR of £600/tonne and assuming a graft copolymer composition of 35% poly(styrene) an allowable cost of £1750/tonne can be assigned for the azodicarboxylate functional poly(styrene). If it is assumed that the materials cost for the synthesis of one tonne of azodicarboxylate functional poly(styrene) must be only about one third of the total allowable cost, a materials target price of £600 can be set for the preparation of one tonne of functional poly(styrene).

The price of styrene monomer at the time of costing was £325/tonne and the cost of n-butyl lithium initiator to convert one tonne of monomer to poly(styrene) of a molecular weight ($\bar{M}n$) of 7500 was £107. The cost of all the chemicals required to synthesise the azodicarboxylate end group, assuming 66% overall conversion from phosgene and ethyl carbazate, was £180, giving a total materials cost for one tonne of functional poly(styrene) of £612, which is not far outside the target price of £600. This materials cost does not include the solvents used in the poly(styrene) synthesis. Their cost is in the region of £650 per tonne of poly(styrene) and clearly, highly efficient solvent recovery would be essential.

The costing exercise is, of necessity, over-simplified, and does not even go as far as to include profit margins, but it serves to illustrate that the prepolymer approach to graft copolymer formation is not entirely beyond the bounds of commercial feasibility.

SUMMARY

We have developed a procedure for the preparation of styrene-diene graft copolymers which offers considerable control over the composition and structure of the graft copolymer and which is applicable to NR as well as to synthetic poly(isoprene). The products resemble styrene-diene thermoplastic block copolymers in their general properties but are structurally different and hence can be expected to differ in their detailed behaviour. Synthesis of the functional poly(styrene) prepolymer could still benefit from detailed refinement and scale increase to tonnage production would require substantial development work but the process is basically amenable to large scale operation. The grafting efficiency with NR could usefully be improved but this deficiency is offset to a considerable extent by the higher strength properties inherent in the NR products compared with those prepared from synthetic poly(isoprene).

The graft copolymers are deficient in elastic recovery when compared with pure styrene-diene block copolymers but the practical significance of this deficiency will only be fully assessed when sufficient quantities of the graft copolymers become available for systematic compounding and applicational testing.

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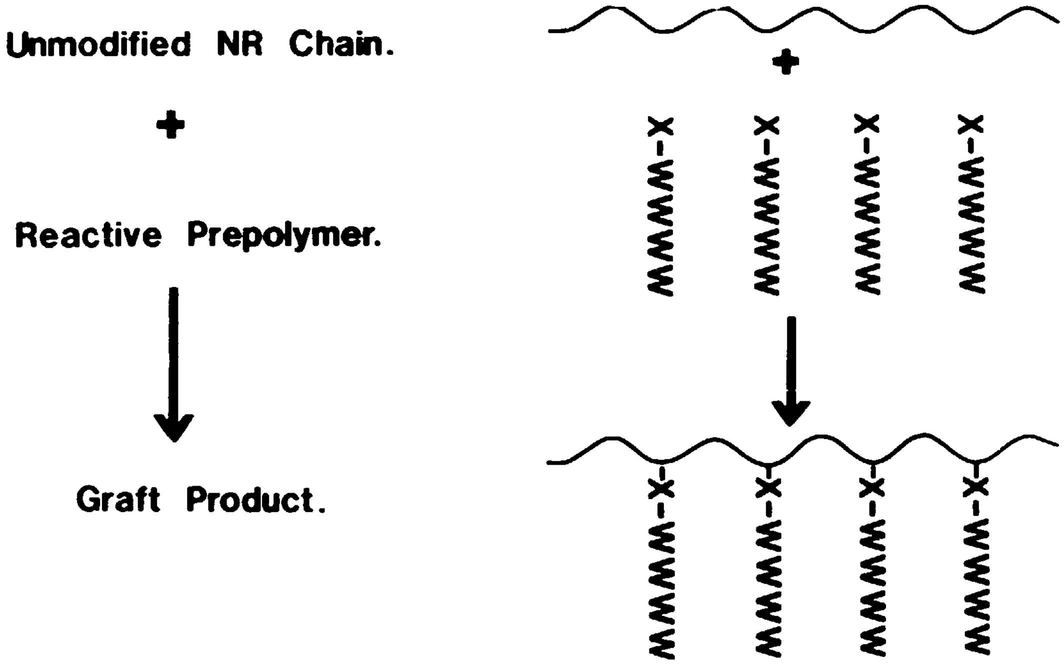
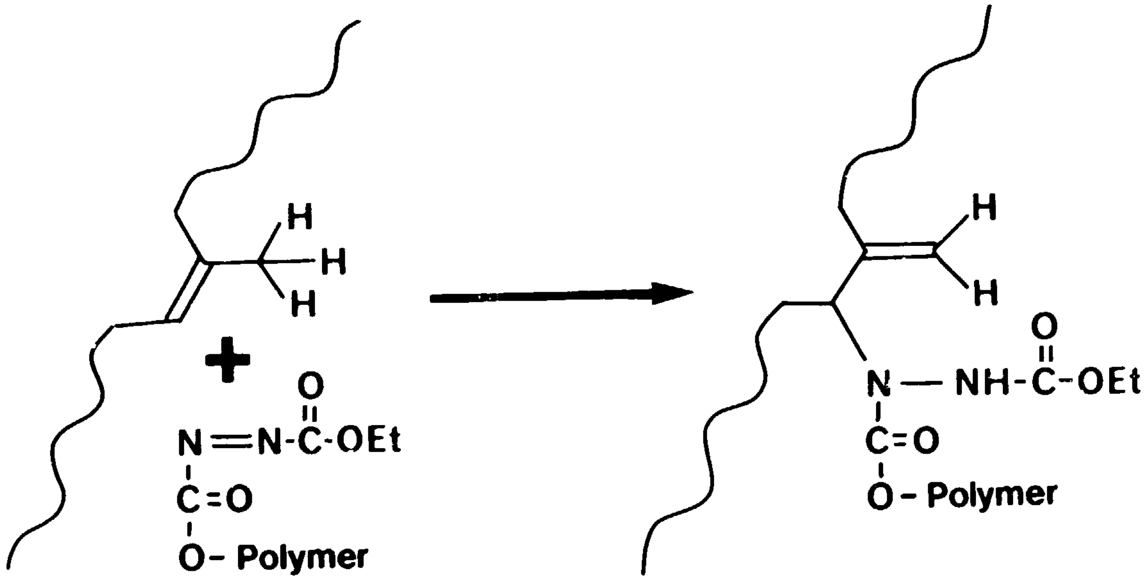
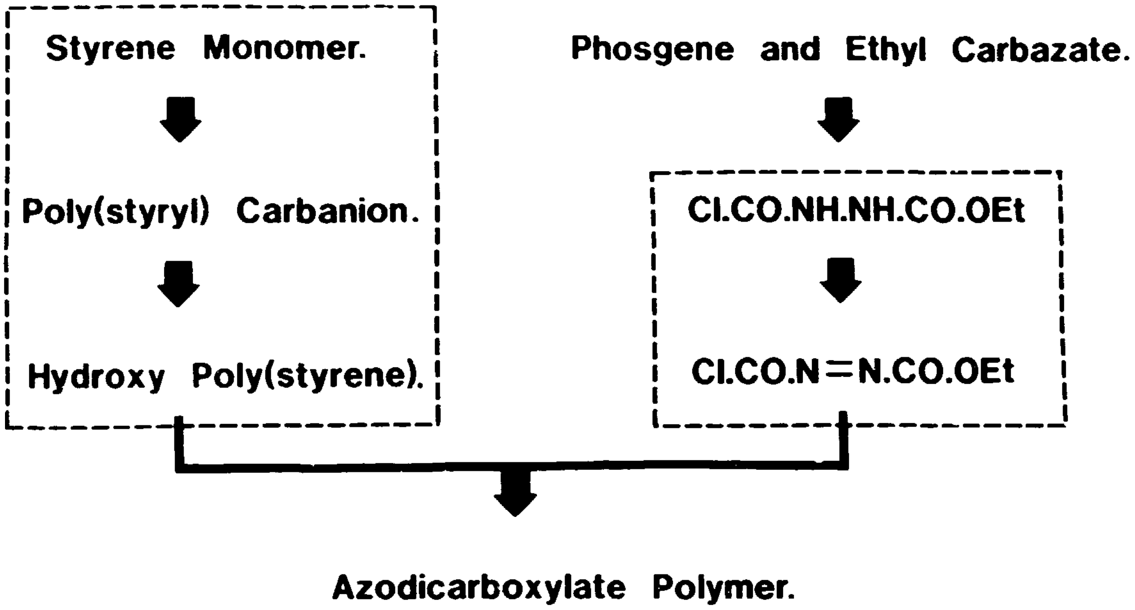


Scheme I : method of grafting using reactive prepolymer.



Scheme II : 'ene' addition of the azodicarboxylate end group of the reactive prepolymer group to an allylic double bond system.



Scheme III : direct synthesis of azodicarboxylate-terminated polymer by the reaction of hydroxypoly(styrene) with an azo-acid chloride.

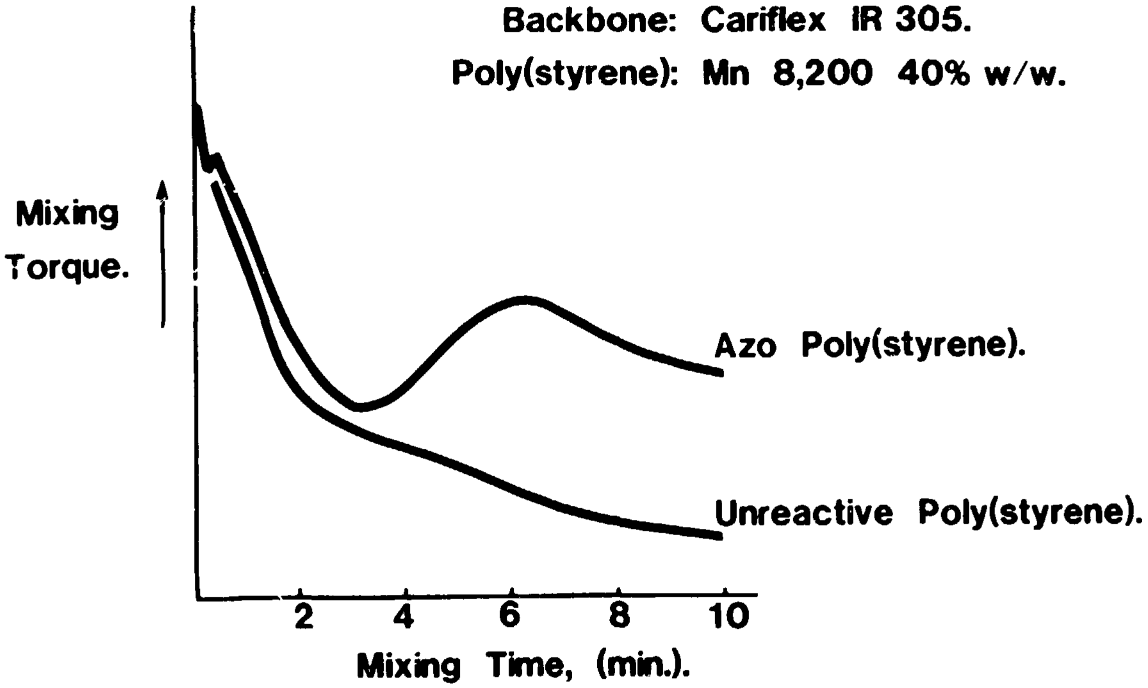


Fig. 5.1 Mixing torque v mixing time for Cariflex IR305 poly(isoprene) with azodicarboxylate-functional poly(styrene) and non-functional poly(styrene) of the same mol. wt.

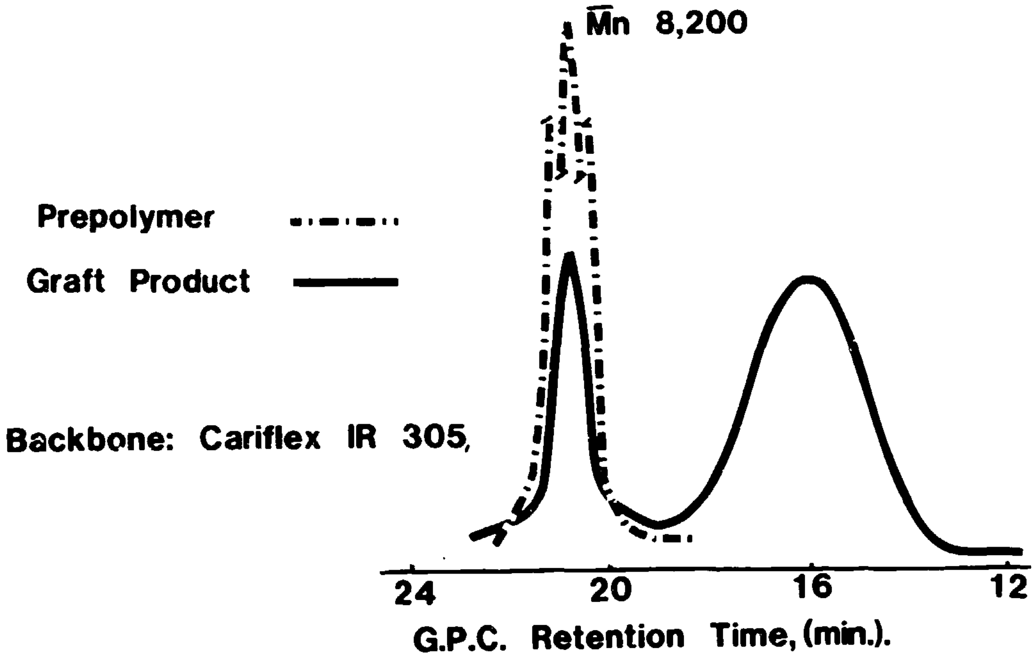


Fig. 5.2 GPC chromatograms for total dry mix reaction product of azodicarboxylate-functional poly(styrene) and Cariflex IR305 poly(isoprene) and for the poly(styrene) prepolymer.

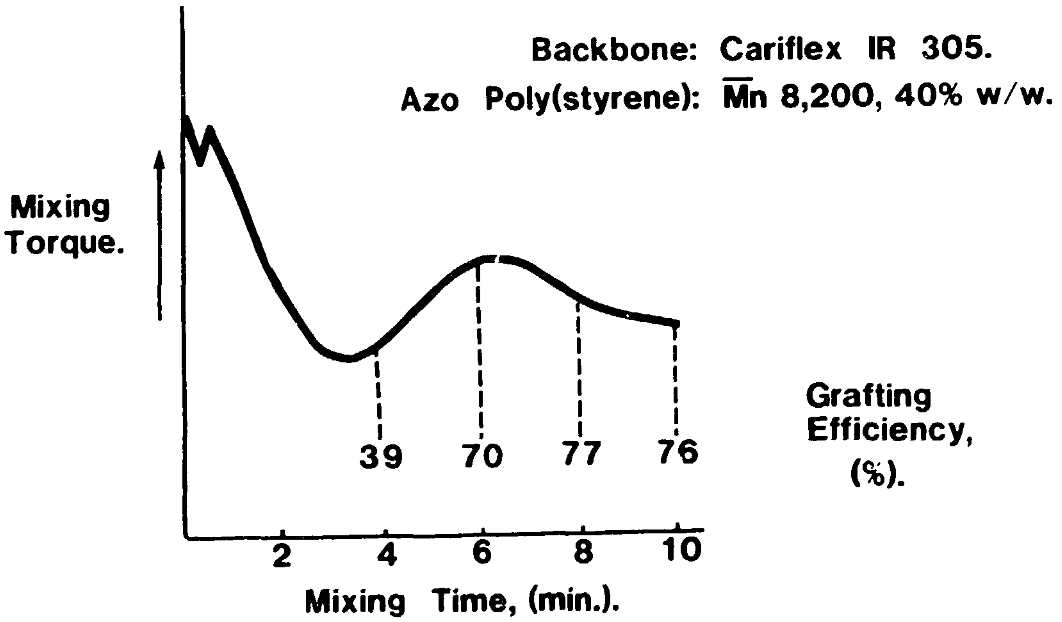


Fig. 5.3 Grafting efficiency v mixing time for the dry mix reaction of azodicarboxylate-functional poly(styrene) with Cariflex IR395 poly(isoprene).

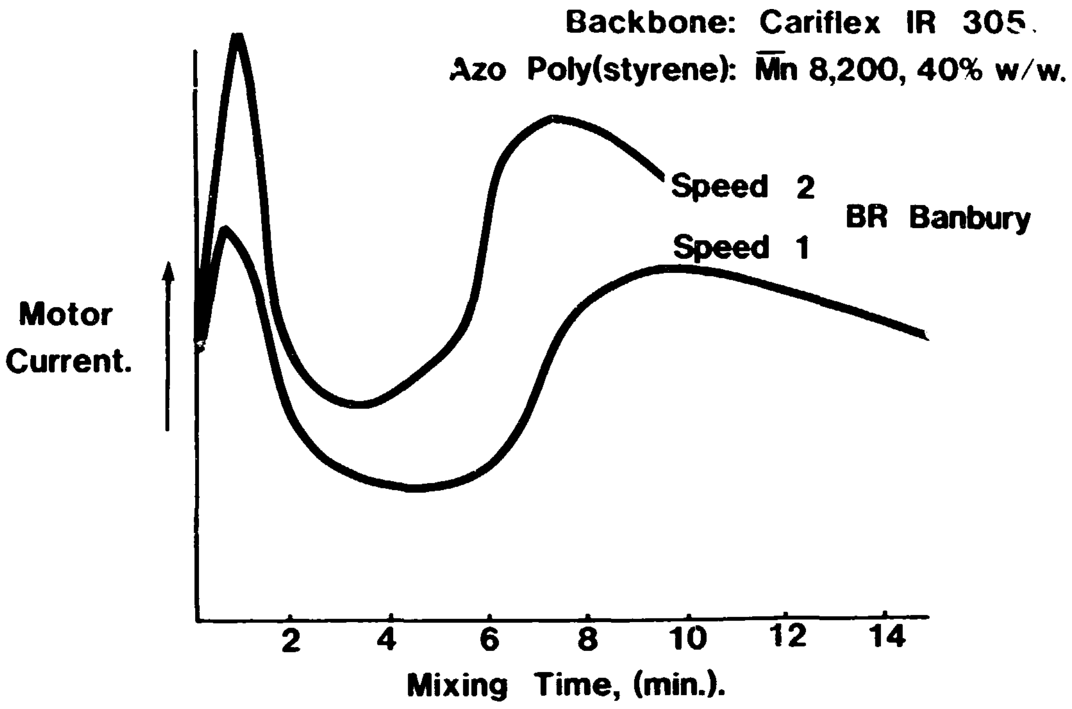


Fig. 5.4 Power consumption v mixing time for the reaction of azodicarboxylate-functional poly(styrene) with Cariflex IR305 poly(isoprene) in the laboratory Banbury.

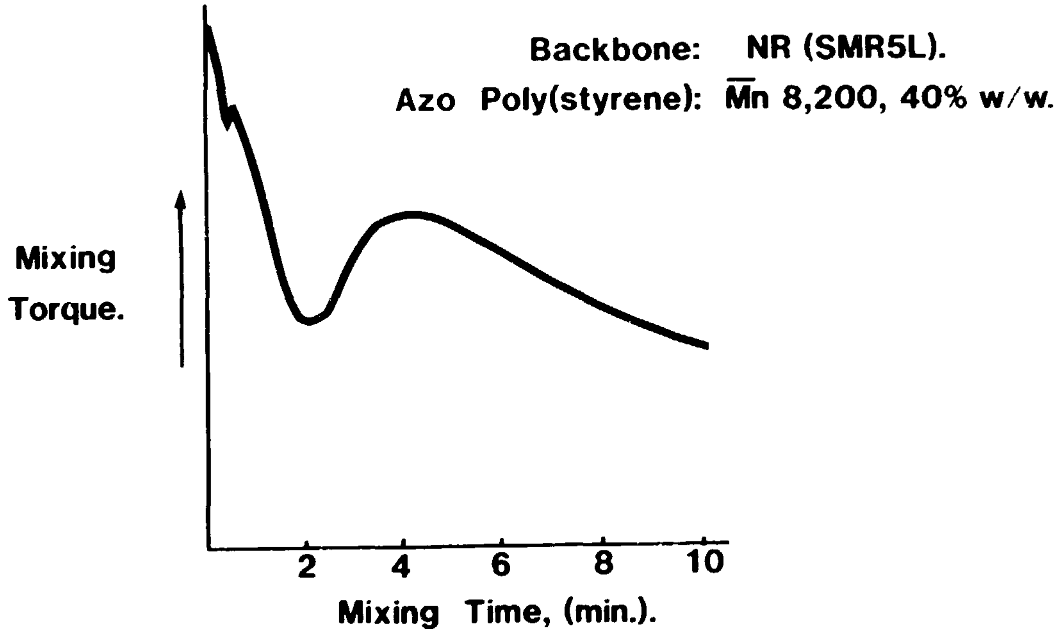


Fig. 5.5 Mixing torque v mixing time for the dry mix reaction of azodicarboxylate-functional poly(styrene) with NR (SMR 5L).

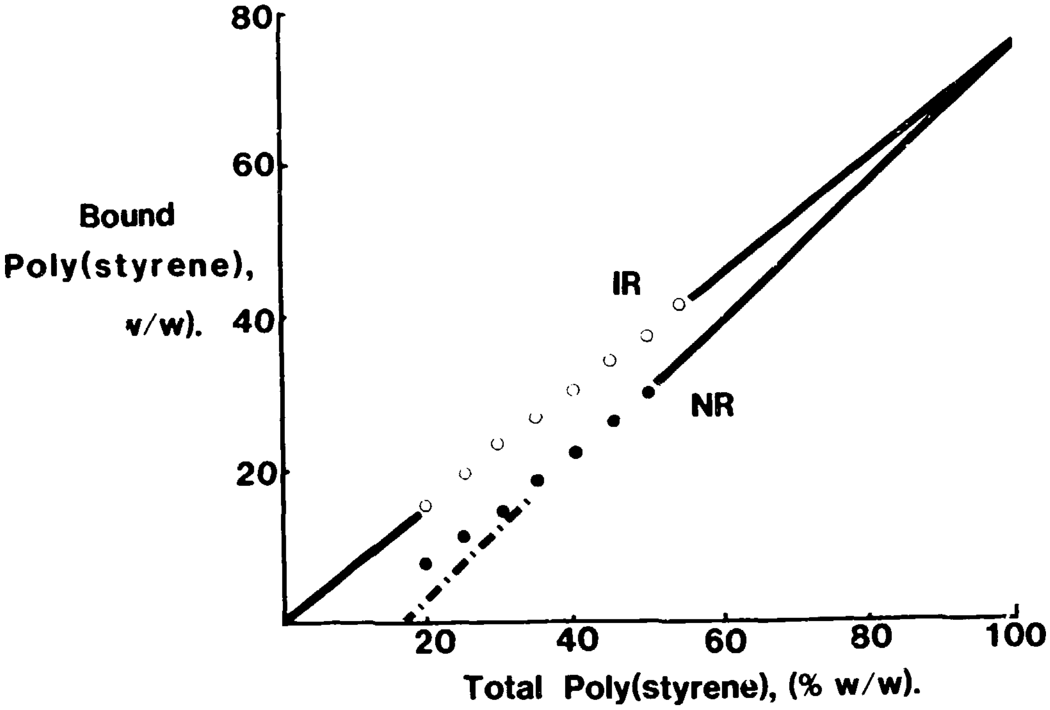


Fig. 5.6 Bound poly(styrene) as a function of total poly(styrene) for mixes of azodicarboxylate-functional polystyrene) ($\overline{Mn}$ 8200) with Cariflex IR305 poly(isoprene) and NR (SMR 5L).

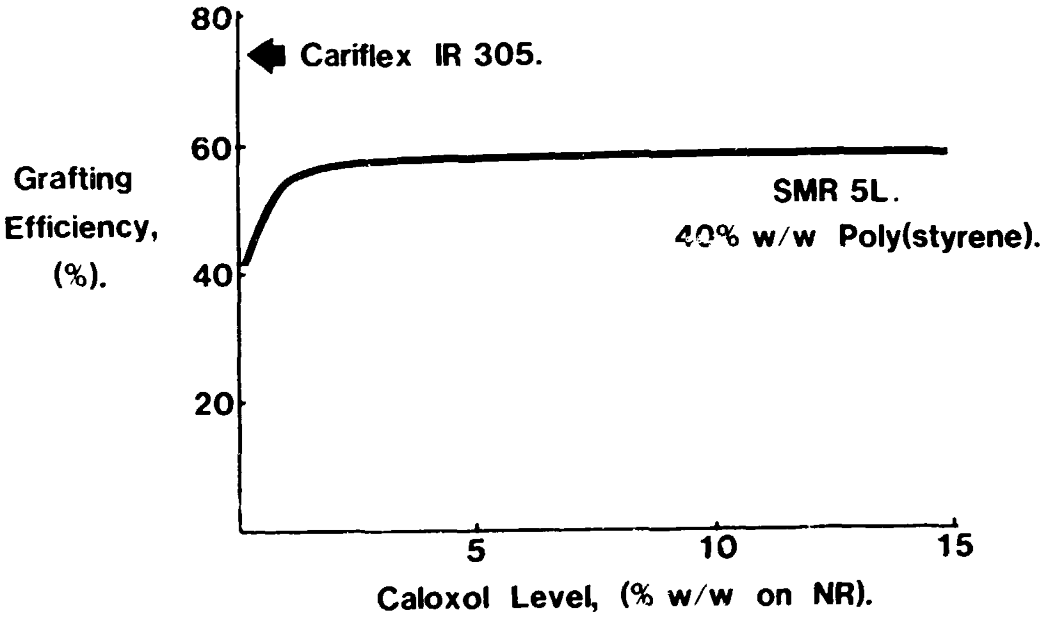


Fig. 5.7 Effect of Caloxol W5G on the grafting efficiency of azodicarboxylate-functional poly(styrene) ($\overline{Mn}$ 10 000) to NR (SML 5L).

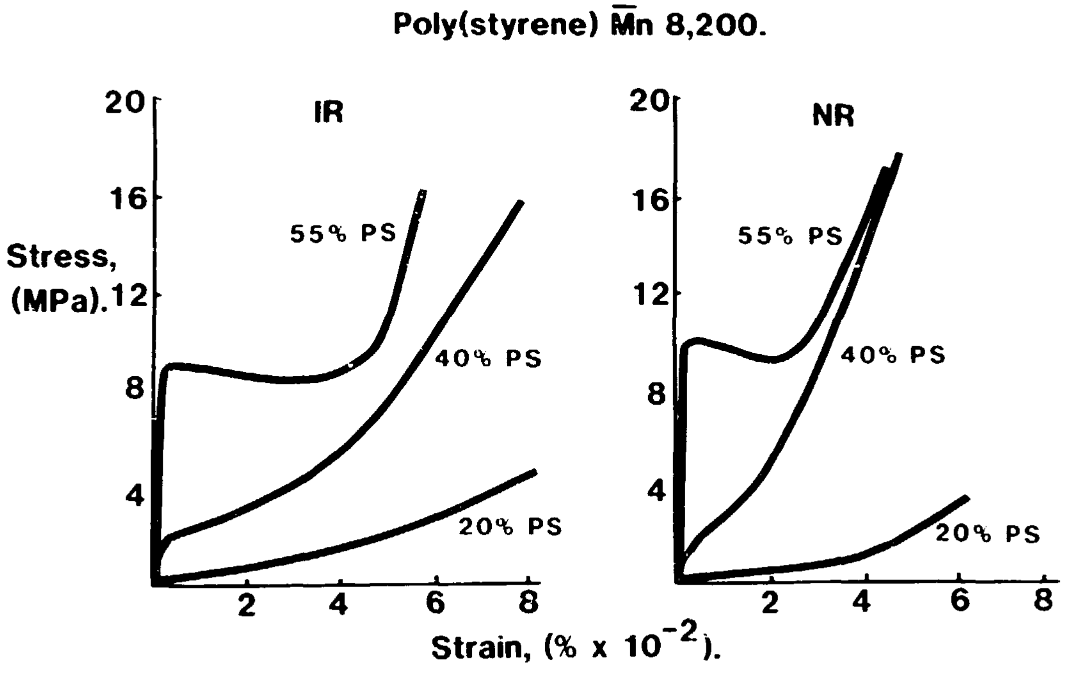


Fig. 5.8 Stress-strain curves of graft copolymers of poly(styrene) ($\overline{M}n$ 8200) with Cariflex IR305 poly(isoprene) and NR (SMR 5L).

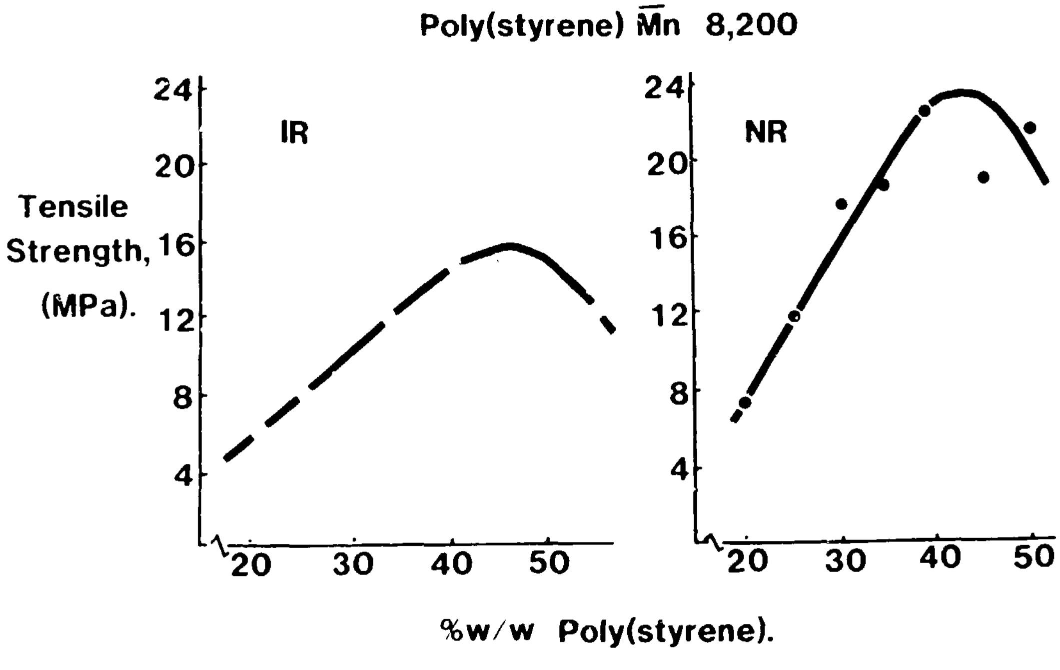


Fig. 5.9 Tensile strength v poly(styrene) content for graft copolymers of poly(styrene) ($\overline{M}n$ 8200) with Cariflex IR 305 poly(isoprene) and NR (SMR 5L).

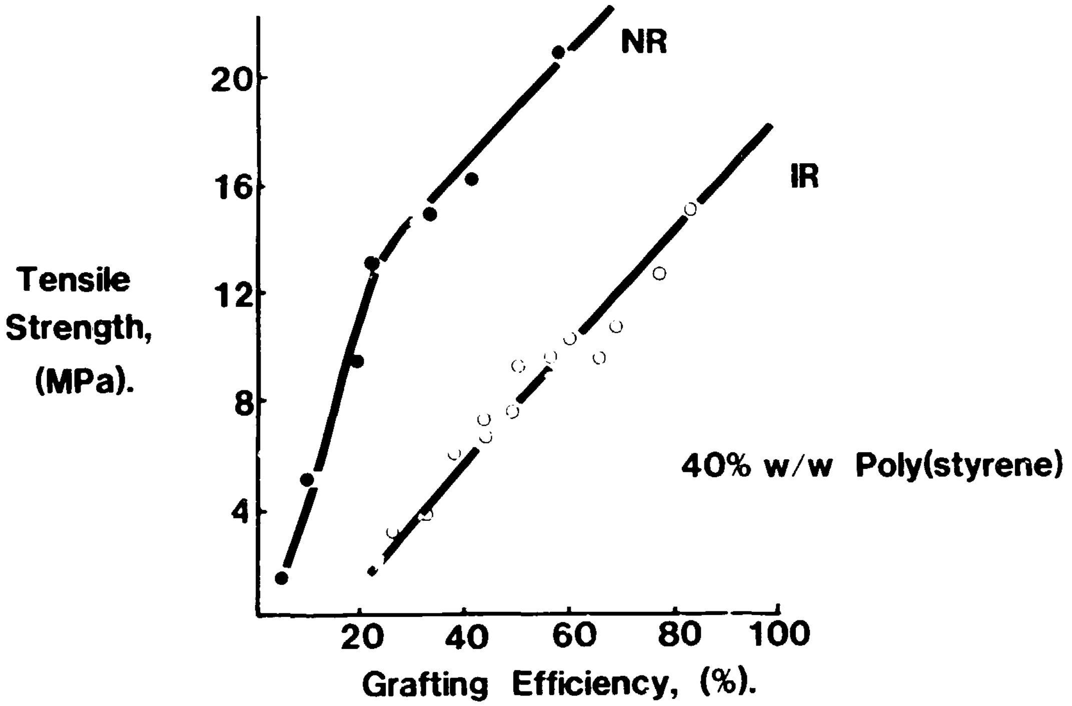


Fig. 5.10 Tensile strength v grafting efficiency for graft copolymers of poly(styrene) ($\overline{M}n$ 7110) with Cariflex IR 305 poly(isoprene) and NR (SMR 5L).

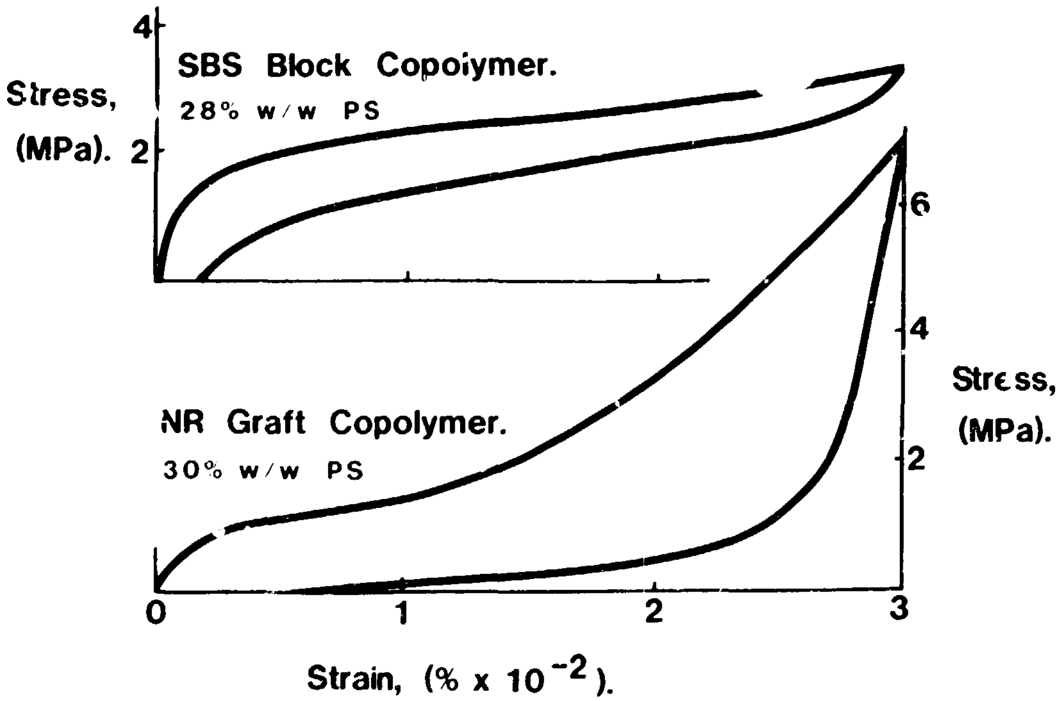


Fig. 5.11 Hysteresis loops for a styrene-butadiene block copolymer and for a graft copolymer of poly(styrene) ($\overline{M}n$ 6550) and NR(SMR 5L) of similar total poly(styrene) content.

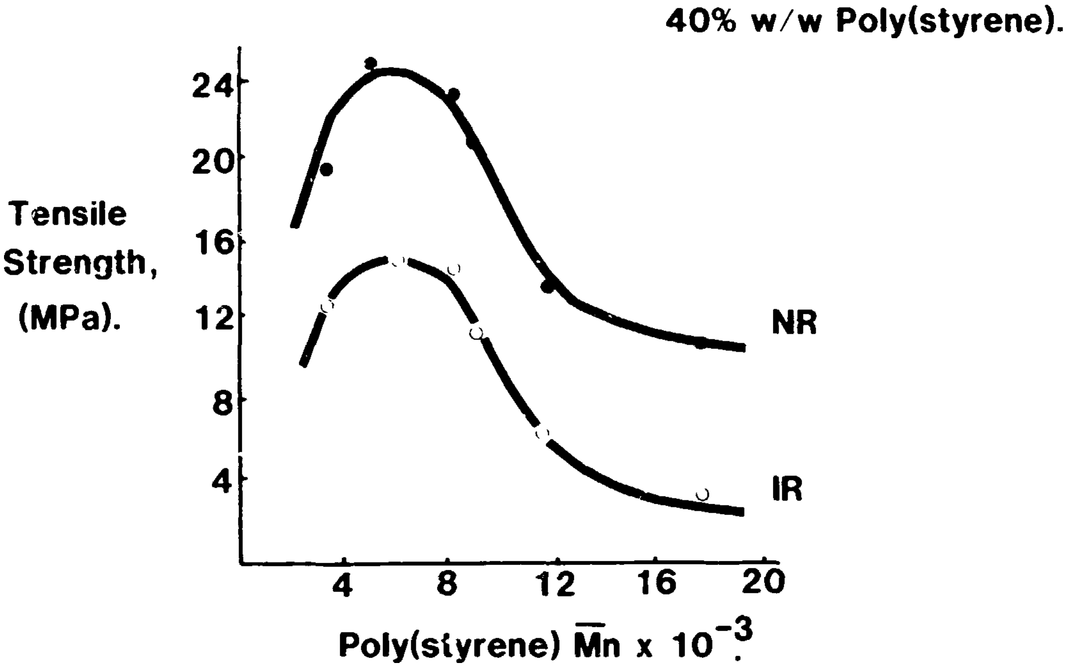
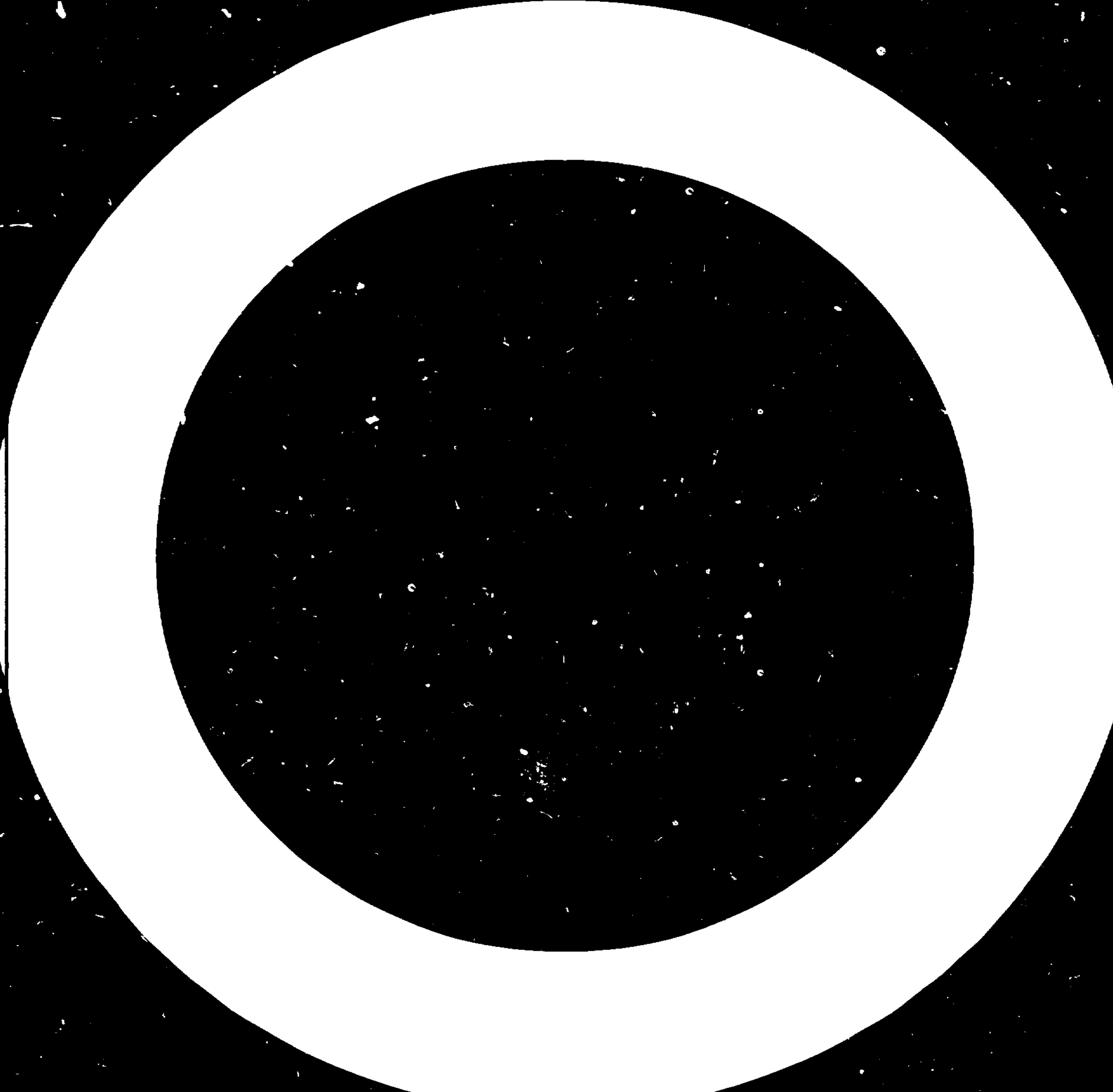


Fig. 5.12 Tensile strength as a function of poly(styrene) molecular weight for graft copolymers of poly(styrene) with Cariflex IR 305 poly(isoprene) and NR (SMR 5L).



CHEMICAL MODIFICATION OF NR - THE FUTURE

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MODIFICATION REACTIONS

It is evident that for any modification of NR to have a chance of being economically viable it must be capable of being carried out efficiently either in latex or during dry rubber mixing or curing. Even then we can recognise two distinct classes of modification:-

(1) One employs sophisticated (and therefore expensive) reagents which can insert pendent groups to functionalise NR for purposes such as crosslinking, grafting, bonding, ageing protection etc. Because of the cost the modification level must be low, around 1 mole % to give a spacing between pendent groups of 6800 molecular weight units, sufficient for the purposes mentioned above.

(2) The other uses relatively cheap reagents for bulk modification, 20-100 mole %, to endow NR with new physical and chemical properties, ie to upgrade it into a new material which can compete with higher-priced speciality synthetics.

Minor Modification Levels

In the first category we have over the last few years examined most reagents of any promise and have come to the conclusion that there is nothing better than the 'ene' thermal addition process when reactions in solution are to be excluded (Figure 1).

The 'ene' reaction possesses the following advantages:-

(1) It is a non-catalytic reaction and is therefore not relying on catalysts which can be poisoned by non-rubbers in NR (although non-rubbers may compete for the reagent in a stoicheometric manner)

(2) It is usually of high efficiency and does not induce side reactions such as crosslinking, degradation, cyclization or isomerization

(3) It is particularly suited to NR as it requires an electron-rich alkyl substituted double bond - an advantage over other elastomers

(4) It is versatile - can carry a varied selection of functional groups.

Of the 'ene' reactions available the activated azo addition seems to be superior to the others in terms of efficiency and versatility of spread of rates and synthesis of differently functionalised examples (Figure 2). Its only disadvantage is that like all complex organic chemicals it is expensive (typically £8/kg) and must therefore be used to effect minor modifications. Its application in grafting at around the 1 mole % level is an ideal example.

For the future then we see modification chemistry will still depend on the further exploitation of azo chemistry. However there are one or two other areas that merit exploration.

Carbenes and nitrenes will attack most polymers by either double bond addition or C-H insertion reactions (Figure 3).

Carbenes are difficult to generate in situ in other than solution reactions. However nitrenes can be generated by the thermolysis of azido compounds at temperatures of 120°-160° and are applicable to dry rubber reactions. Aryl sulphonyl azides are easily prepared and safe to handle and have been used to functionalise polymers with a variety of groups including isocyanates and hydroxyl, (Figure 4). We have examined the potential of this reaction in NR and found that a 1,3 cycloaddition of the azide to NR occurs at modest temperatures (100°-120°) before the nitrene is liberated. The resulting triazoline breaks down to give the aryl sulphonyl group bound to NR via a hydrolysis resistant imine bond (Figure 5).

This still provides the desired functionalisation and may offer a worthwhile alternative to the azo modification route.

Macro-modification levels

Here one must use cheap modifying reagents and chlorination, hydrochlorination and epoxidation are examples where the new properties imparted to NR could be worth the cost involved. All are well known reactions but as has happened in the epoxidation of NR reinvestigation in the light of modern analytical methods to control the reaction can lead to major improvements and a product which can challenge a speciality synthetic rubber such as nitrile in cost effectiveness.

For economic reasons it will be essential that modifications at this level be carried out in latex and this in turn will demand a much greater understanding of the course and locus of chemical reactions in this environment than currently exists. For example Figure 6 depicts the two extreme cases of competition between reaction and diffusion of a water soluble reagent in a latex particle resulting in a homogeneous or a surface modification. Epoxidation and chlorination exemplify these extremes.

Specific areas of importance include improved methods of stabilization of latex during chemical reactions and of introducing water insoluble reagents into the rubber phase. The surface modification only of latex particles to alter colloidal stability and processing characteristics is attractive. As the bulk level of modification is now small, more expensive reagents could again be contemplated - for example a water-soluble azo reagent could be used to introduce surface carboxylic acid groups.

Another approach to the modification of latex which should not be forgotten is that using biochemical methods. The growth of suitable bacteria or moulds could theoretically give by direct attack or via extra-cellular enzymes such modifications as isomerization, hydroxylation or epoxidation of the double bond, side chain methyl oxidation to hydroxyl, aldehyde or carboxyl group etc. Such reactions are well authenticated for steroids. For rubber the problem of physical contact may arise but as bacteria grow readily on oil droplets in the production of SCP this may not be insuperable. The biochemical production of hydrogen peroxide for epoxidation is attractive (Figure 7).

CHEMICAL AND PHYSICAL EFFECTS OF PENDENT GROUPS

The physical effects of pendent groups are now generally well understood. Most pendent groups are polar with respect to NR, especially those derived from azo chemistry. Because of this and the restrictive effect of large groups on segmental motion one would predict that T_g will be progressively raised and that oil resistance and air permeability will be improved. Such effects are well documented and can be induced to any desired level by extant modifications such as with ENPCAF or by epoxidation (Figure 8). Resistance to low temperature crystallization is an area where improvements might be also sought. Preliminary work suggests, however, that pendent groups are less effective than other chain irregularities such as crosslinks and are unlikely to be cost-effective.

Chemical effects have also been well explored. Reactive sites for crosslinking and grafting have been introduced. Pendent *p*-phenylenediamine residues are produced by the reaction of *p*-nitrosophenylaniline or quinonediimines with NR and impart powerful, non-extractable antioxidant activity. The benefits of rubber bound antioxidants were initially ignored by rubber manufacturers but there are now signs that they are beginning to be appreciated. There are even claims that such residues behave as good antiozonants which is surprising as they cannot migrate to the rubber surface. There is, perhaps, scope for a new investigation into improved protective systems, particularly non-staining antioxidants, introduced *via* chemical modification.

The same can be said for pendent groups tailored to give powerful bonding to specific substrates. The introduction of siloxane groups *via* the azo reaction enables NR to be bonded extremely well to glass and it is probable that other groups could be designed to give chemical bonding to steel, fibres, fillers *etc*.

CROSSLINKING

One of the obvious applications of modification at low level (1 mole % or less) is the crosslinking of NR through reactive pendent groups.

This has already been exploited in the *NOVOR* or urethane system in which pendent aminophenol groups introduced on NR by a nitrosophenol ene reaction are crosslinked by a diisocyanate (Figure 9).

It may be that the practical limit has now been reached in crosslink stability and reversion resistance and that the cost-effectiveness of alternative new vulcanizing systems would not merit their development.

Modification directed towards specialist crosslinking applications could be more fruitful. Thus, in latex products there is a question mark over sulphur systems using dithiocarbamates on toxicity grounds. *SILCAF*, a compound carrying a reactive azo group at one end and an alkoxy-silyl group at the other can be used to pre-vulcanize latex. The azo group adds to NR and the silyl group hydrolyses in the presence of water to form siloxane crosslinks (Figure 10).

Another application in latex is the addition of an azo-cinnamate. When thin, transparent articles such as surgeons gloves or condoms are made by dipping using the modified latex then photo-crosslinking occurs on exposure to light (Figure 11). This suggests a convenient continuous production line and both this and the previous application have the advantage that the vulcanizing agent becomes firmly bound to the rubber with no extractable residues.

Both applications work but need more development of the concepts to become suitable for industrial take-up.

Another aspect of crosslinking which could have a long term commercial significance is the use of our expertise in modification chemistry to build clean networks of known structure so that structure/property relationships can be firmly established, leading eventually to optimised design of vulcanizates for particular applications. Thus, in principle, difunctional azo reagents could be used to introduce crosslinks of specifically poly, di or monosulphide structure of, with monofunctional reagents, a variety of pendent groups, sulphidic or otherwise, and of course all combinations of the above. Crosslink length could also be explored as an influence on properties (Figure 12).

DEGRADATION

It is often useful to reduce the molecular weight of NR to give a lower plasticity raw rubber and indeed essential during mixing to get good processability. Both operations commonly use peptizing agents added to latex or to the internal mixer which work by catalyzing oxidative scission of the rubber. Such materials, often thiols, are difficult to control and may leave undesirable residues in the rubber to affect ageing or vulcanization.

It would be a useful development to have reagents available which bring about scission of the NR chain in a clean and controlled manner, and an added advantage if the cut chains were terminated with reactive groups (telechelic polymer) so that chain recombination and crosslinking could be performed if desired at a later stage.

Ozone is perhaps the most efficient scission reagent known capable of giving high yields of broken chains carrying terminal aldehyde or ketone groups. It is so reactive however that it is difficult to bring about random scission in latex or dry rubber. What would be an exciting development would be a complex or precursor of ozone which could be dispersed in rubber before liberating ozone itself.

One modification reaction that leads to a profound fall of molecular weight of latex rubber is in mechanism a close analogue of ozonolysis:- the reaction of nitrobenzene in the presence of UV light (Figure 13).

For rubber in solution this worked admirably leading eventually to a liquid rubber of MW ca 10 000 which was effectively terminated by carbonyl groups and chain extendable by a bis-hydrazide. In latex the system needs further development as efficiency is reduced by factors such as coagulation on the UV lamp.

The reaction of sydnones with NR occurs by a 1,3 dipolar addition, the product rearranging to give chain scission (Figure 14). The sydnone is dispersed in NR in an internal mixer and the rubber heated at 170°C. As seen in Table 1 peptization is efficient but sydnones are required which operate at lower temperatures before the process can be viable.

TABLE 1 REACTION OF p-CHLOROPHENYLSYDNONE WITH NR

Sydnone % w/w	Heating °C/hr	MW of NR
0	-	440 000
10	-	440 000
0	170/1	gel
1	170/1	114 000
3	170/1	77 000
5	170/1	18 000

THERMOPLASTIC NR

Graft copolymers

As seen in an earlier paper, comb grafts of NR and polystyrene behave as a thermoplastic rubber. The principle of preparing the grafts by the reaction of a functionally tipped polymer with NR has several advantages

i) The MW of the polymer to be grafted can be accurately determined

ii) The number and therefore average spacing of the grafted chains can be controlled

iii) The reactivity of the azo tipping group allows efficient grafting not only in solution but in dry mixing

iv) The method is theoretically applicable to all other polymers that can be reactively tipped, and indeed to mixtures of two or more polymers so that a very wide range of grafts, perhaps with unique properties, might be possible.

It is the latter statement that I wish to discuss in terms of the future possibilities for the modification of NR by grafting.

It is probable that any azo-tipped polymer will graft to NR in solution provided that a common solvent can be found, not always possible for a pair of widely disparate polymers.

For dry-mix grafting, for thermoplastic properties and for processability of the grafts there are certain constraints which need to be recognized. It is necessary to consider two separate properties of the polymers involved in the graft. Firstly their glass transition of melting temperature, T_g or T_m, and, secondly their solubility parameter - a measure of compatibility with other polymers.

T_g/T_m. For thermoplastic rubber behaviour a graft or block copolymer has to have a rubbery component whose T_g is well below room temperature and a hard component whose T_g or T_m must be above room temperature. For retention of properties at high temperatures T_g or T_m should be as high as possible and crystalline polymers would be preferred since T_m is usually much sharper and better defined than T_g of a glassy polymer.

However since dry mix grafting and subsequent processing of the graft must occur at temperatures above the T_g or T_m of the hard component a practical limit is immediately placed on the values that these can assume. If 180°-200°C is regarded as the upper temperature limit for mixing or processing NR then T_g/T_m must not exceed 160°-180°C. Fortunately, grafts are in a better position than blocks since the low molecular weight of the hard polymer chains depresses the normal T_g by as much as 50°C, and by rather less for the T_m of a crystalline material.[8] Compatibility leading to phase mixing can also reduce T_g or T_m slightly. Thus we can restrict consideration of hard polymers for grafting to those having a normal T_g between 70°-230°C or T_m between 40°-200°C.

Solubility parameter. This is a concept used to predict the compatibility of different polymers and is based on cohesive energy calculated from group molar attraction data[2]. It is of importance in two respects.

The first applies only to the dry-mix grafting technique, where to get reaction between the azo end of the hard polymer and NR, molecular contact must be made, implying a limited degree of phase mixing. This in turn implies that the difference in solubility parameters must be reasonably small. It is not yet possible to predict accurately what the maximum difference is that would allow grafting but results in Table 2 suggest that it might be 1.3 $cal^{\frac{1}{2}}\ cm^{-3/2}$.

TABLE 2 DEPENDENCE OF GRAFTING TO NR ON DIFFERENCE IN SOLUBILITY PARAMETERS

Azo Polymer	*	Grafting in Solution	Dry-Mix Grafting
polyethylene	0.1	yes	yes
polydimethylsiloxane	0.8	yes	?
polystyrene	1.0	yes	yes
polymethylmethacrylate	1.15	yes	yes
polycaprolactone	1.3	yes	no

* is calculated difference in solubility parameters taking that for NR as 8.1 $cal^{\frac{1}{2}}\ cm^{-3/2}$.

Obviously the data are very limited and more must be acquired.

However the second effect of solubility parameter difference impacts equally on block and graft copolymers and can be better authenticated. It concerns the processability of the material which becomes poor if the difference is larger than 1.3-2.0 (Table 3).

TABLE 3 EFFECT OF SOLUBILITY PARAMETER DIFFERENCE ON PROCESSABILITY

Copolymer system	S.P. Difference ($cal^{\frac{1}{2}}$ $cm^{-3/2}$)	Processability
Block polydimethylsiloxane -		
Bakelite C4 (polyalkylcarbonate)	0.5	Excellent
polyalphamethylstyrene	1.6	good
polystyrene	1.8	good
polybis-phenolA-carbonate	2.2	fair
polysulphone	3.3	poor
Graft		
NR-polystyrene	1.0	good
NR-polycaprolactone	1.3	poor
EPDM-polypivalolactone	1.7	poor

The effect is due to marked phase separation still existing in the polymer melt when the two components have disparate solubility parameters. The energy required to move a component from a domain through a viscous medium leads to very high melt viscosities.

Feasibility guidelines

Without taking any account of chemical feasibility (most things can be possible with sufficient research and development) limits can be placed on the number of polymers it is worth trying to graft to NR. They should give solubility parameters differing from that of NR by not more than 1.5 $cal^{\frac{1}{2}}$ $cm^{-3/2}$ and have a T_g between 70° and 230°C or a T_m between 40° and 200°C. Table 4 and Figure 15 present the position of these polymers for which data is available and we see from the latter that a Feasibility Rectangle is generated. The preferred polymers would occupy the bottom right hand corner, ie they should have a reasonably high T_g or T_m for good retention of properties at high temperature and a low solubility parameter difference for good processability.

In theory it should be possible to extend the upper limit of the rectangle. This could be done by raising the solubility parameter of NR through chemical modification, eg a 50% level of hydrochlorination would give 0.5 units increase, or by the prior grafting on to NR of a polymer with as high a solubility parameter as feasible (eg polymethylmethacrylate 9.25) to give a pro-rata increase from 8.1. Alternatively the solubility parameter of an interesting polymer could be lowered by affixing a block of a second polymer of greater compatibility with NR and azo tipping this block.

TABLE 4 SOLUBILITY PARAMETER DIFFERENCE FROM NR VERSUS T_g/T_m

Polymer	S.P. Difference ($cal^{1/2}\ cm^{-3/2}$)	T_g	T_m
		(°C)	
Nylon 6/6	5.5		265
Polyacrylonitrile	4.6	105	
Polymethacrylonitrile	2.6	120	
Poly(bis-phenolA-diphenylsulphone)	2.5	190	
Poly(bis-phenolA-carbonate)	1.4		220
Polypivalolactone	1.4		240
Poly(2,6-dimethyl-1,4-phenylene oxide)	1.4		261
Poly(vinyl chloride)	1.35	81	
Poly(2,2,4,4 tetramethyl-1,3-cyclobutanediol carbonate)	1.3		253
Poly(ethylene sulphide)	1.3		210
Poly(-caprolactone)	1.3		65
Poly(methyl methacrylate)	1.15	110	
Polystyrene	1.0	100	
Poly(ethyl methacrylate)	0.9	65	
Poly(α-methylstyrene)	0.8	170	
Poly(dimethylsiloxane)	0.8	-120	
Polypropylene	0.6		175
Polyethylene	0.1		140

Vulcanizates with labile or reversible crosslinks

We have always maintained that an attractive alternative to the physically domain-crosslinked thermoplastic rubber is a vulcanizate with heat labile, reversible crosslinks. This would be expected to have physical properties as good as a conventional vulcanizate at temperatures up to the point where the crosslinks break open (Figure 16).

Several attempts have been made to achieve this goal. The most successful aimed at low crosslink levels to improve green strength of polybutadiene. Pendent amino groups were introduced along the polybutadiene chain by copolymerization techniques and crosslinked by quaternization with a bis alkyl halide. (Figure 17).

This gave significant improvements in green strength without interfering with processability because, it was claimed, the crosslinks were shear and/or temperature labile.

Much higher degrees of crosslinking were obtained in the work of Campbell[4] in which NR was first equipped with pendent hydroxyl groups some of which were transformed into crosslinks by reaction with a difunctional β-keto ester. The ester crosslinks underwent a rapid ester exchange reaction with the remaining hydroxyl groups at temperatures of 180°C or so give a degree of thermoplasticity (Figure 18). Unfortunately side reactions intervened at these temperatures leading to permanent crosslink formation.

The most attractive route left to a possible thermoplastic vulcanizate would be the synthesis of an azo compound carrying a metal chelating substituent, eg an acetylacetonate residue.

By variation of the chelating group, metals to be chelated and ligands already attached to the metal it should be possible to vary the strength of the complex formed, ie the crosslink, so that adequate temperature reversibility might be obtained along with good physical properties and the resistance to creep at ambient temperatures that simple ionomers lack.

A patent by Monsanto (B.Pat. 1375416) claims some progress in this direction. Diene rubbers were prepared with pendent pyridine groups by copolymerization with vinyl pyridine. Complexes of nickel crosslinked the rubber, the crosslinks disappearing reversibly at 180°C. The physical properties claimed were reasonable, tensile strength being up to 3 MPa with good compression set (Figure 19).

With NR we cannot add pendent groups by copolymerization but our experience in modification chemistry should enable us to improve and extend this system.

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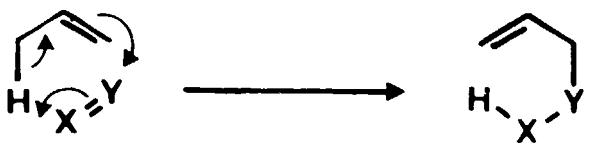

X = Y can be –N=O, –N=N–, $>C=O$, $>C=S$, $>C=C<$.

Fig. 6.1 The general 'ene' reaction.

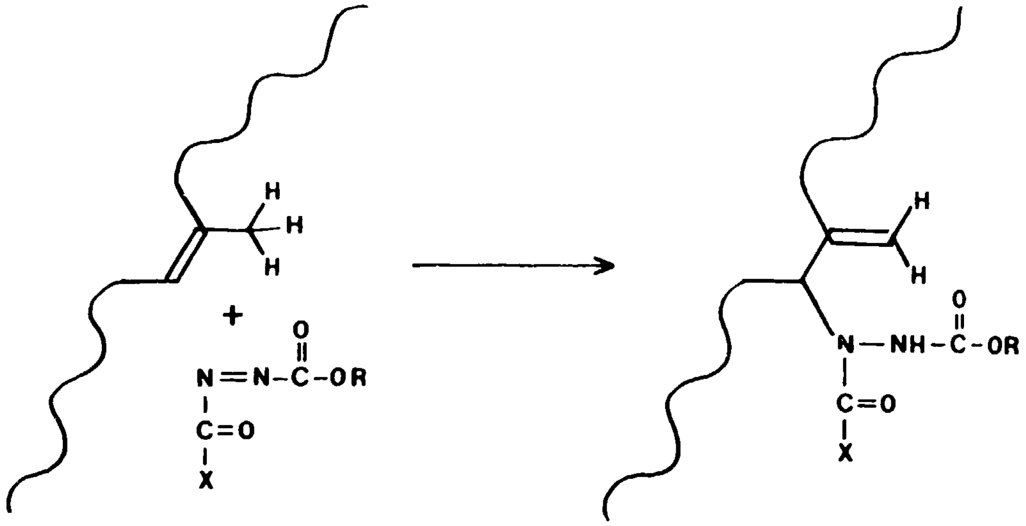

Fig. 6.2 The 'ene' reaction of azodicarboxylates with *cis*-1, 4-polyisoprene.

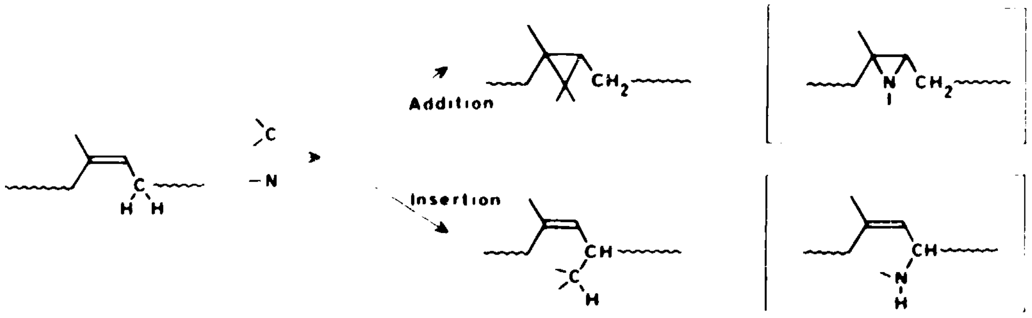

Fig. 6.3 The reaction of carbenes and nitrenes with natural rubber.

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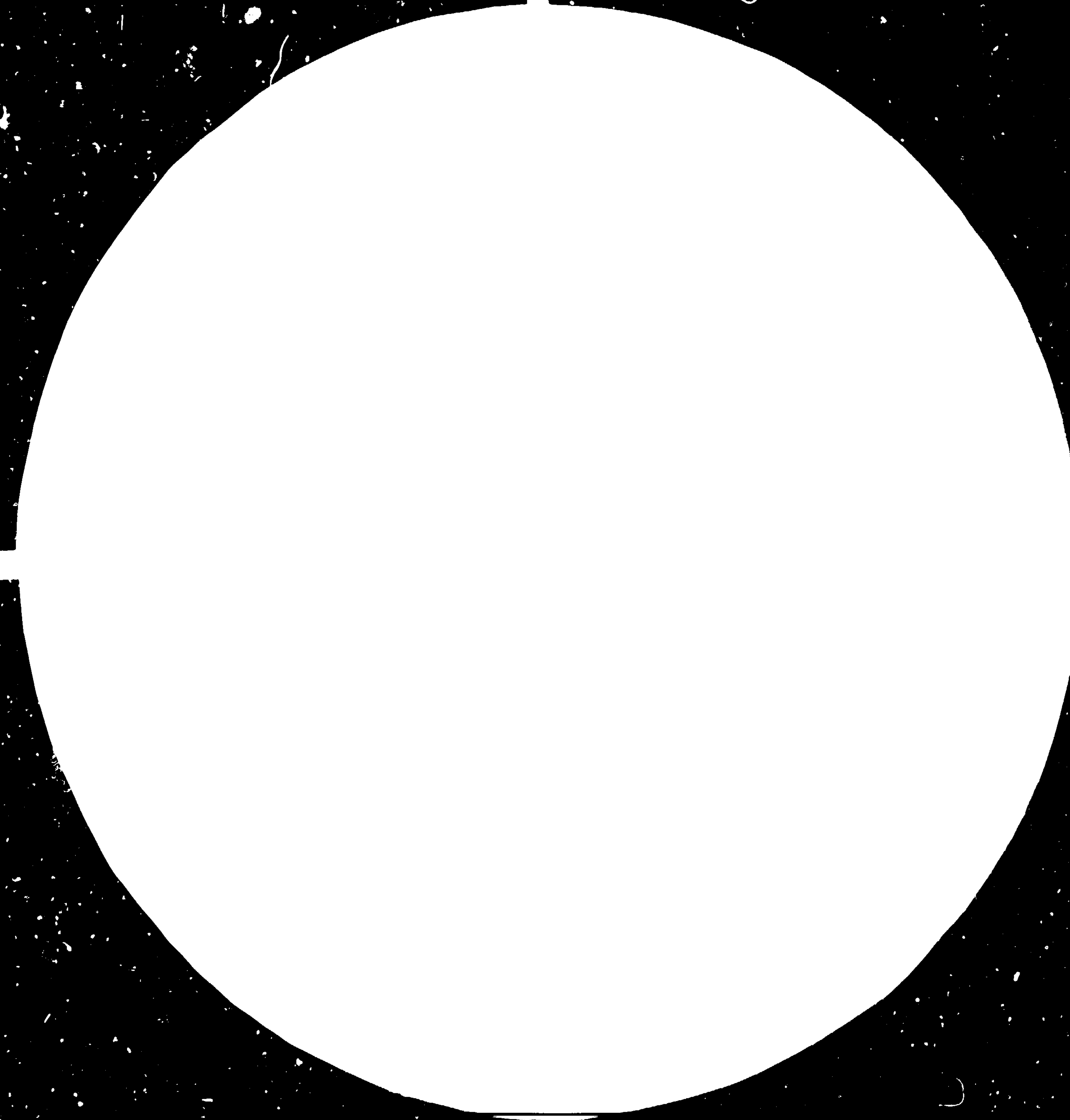

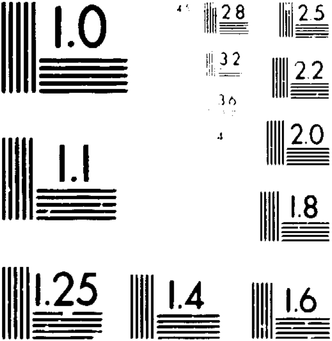
1.0
4.5
2.8
2.5
3.2
2.2
3.6
4
2.0
1.1
1.8
1.25
1.4
1.6

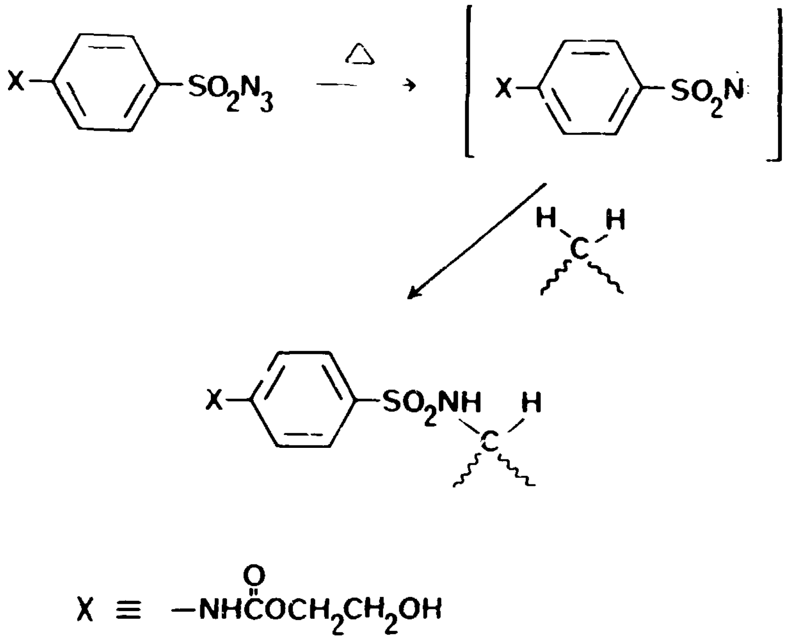

Fig. 6.4 Functionalisation using a substituted arylsulphonyl azide.

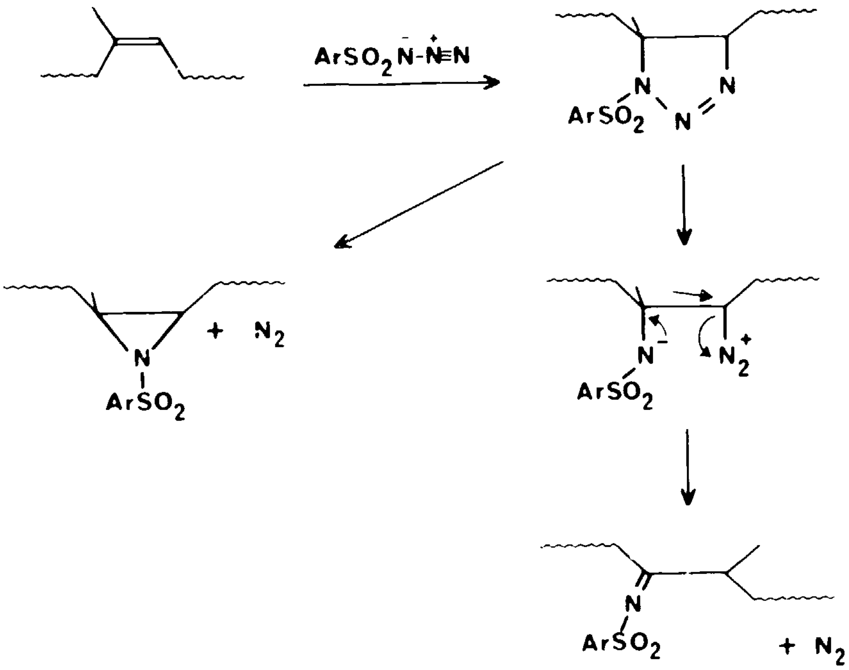

Fig. 6.5 Mechanism of reaction of an arylsulphonyl azide with natural rubber.

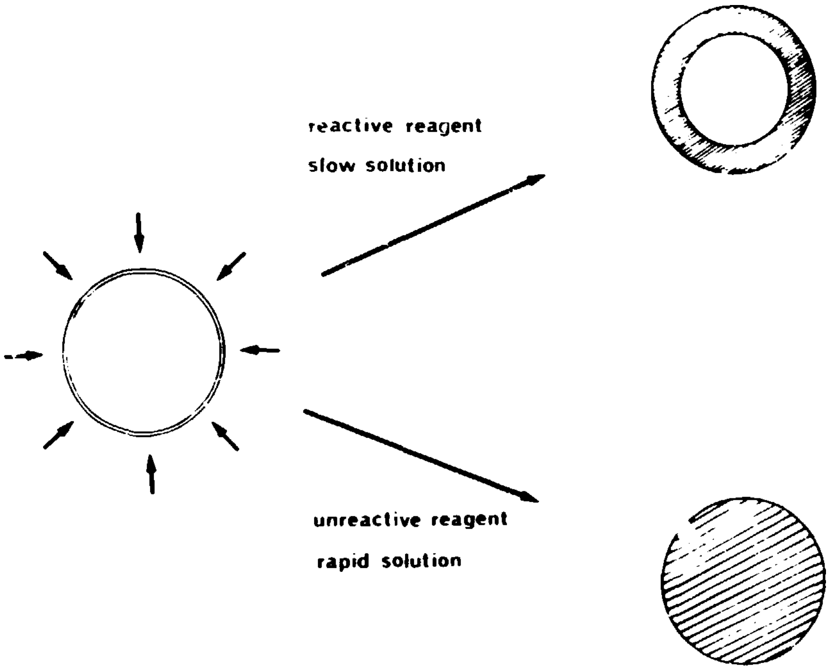

Fig. 6.6 The extremes of the locus of chemical reactions in latex.

$$\text{Glucose} + H_2O \xrightarrow[O_2]{\text{glucose oxidase}} \text{Gluconate} + H_2O_2$$

Fig 6.7 The enzymic production of hydrogen peroxide.

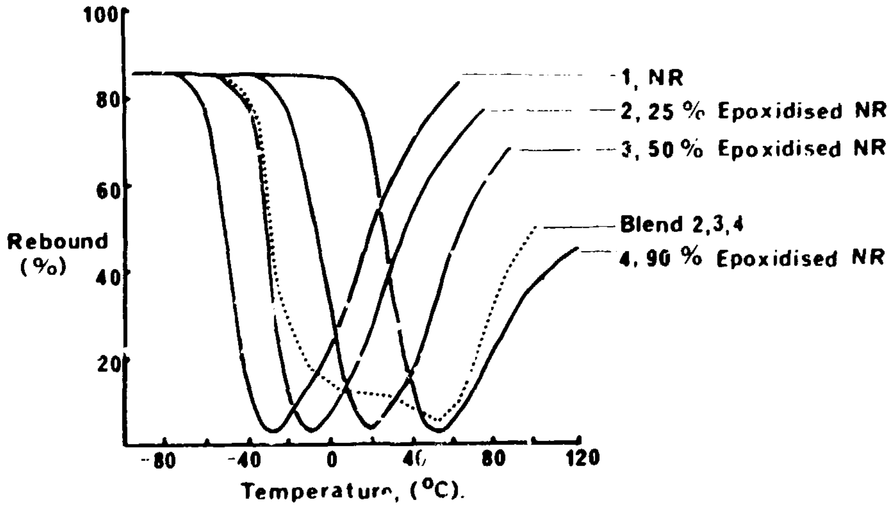

Fig. 6.8 The rebound resilience of natural rubber epoxidised to varying extents.

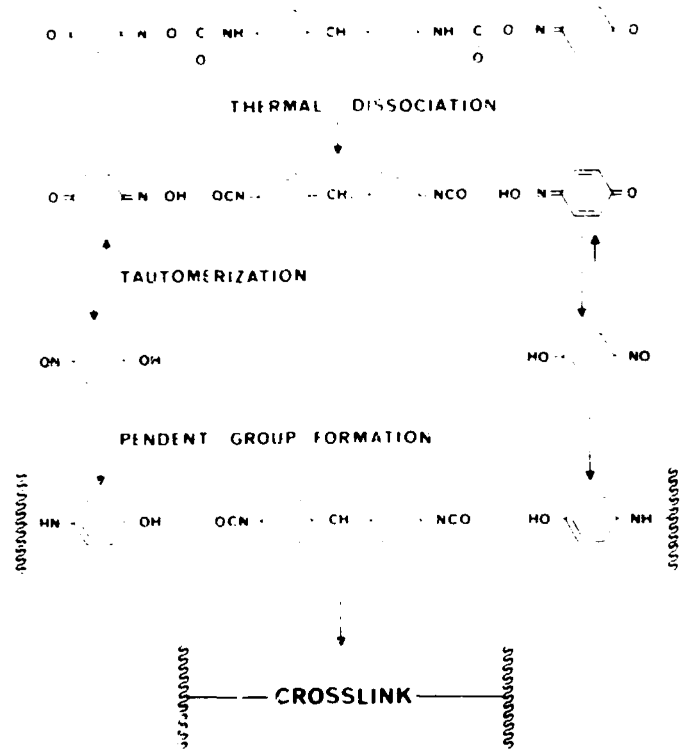

Fig. 6.9 The mechanism of NOVOR vulcanisation.

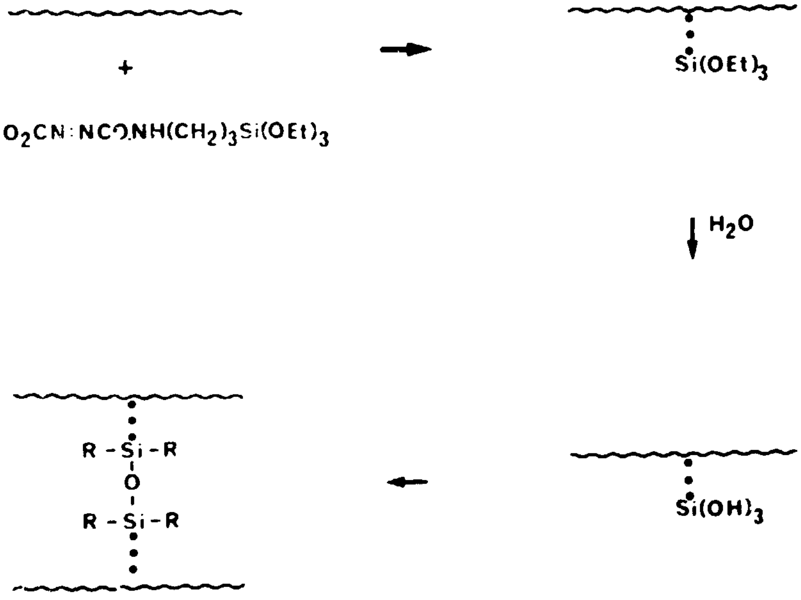

Fig. 6.10 The vulcanization of latex using an azosilane.

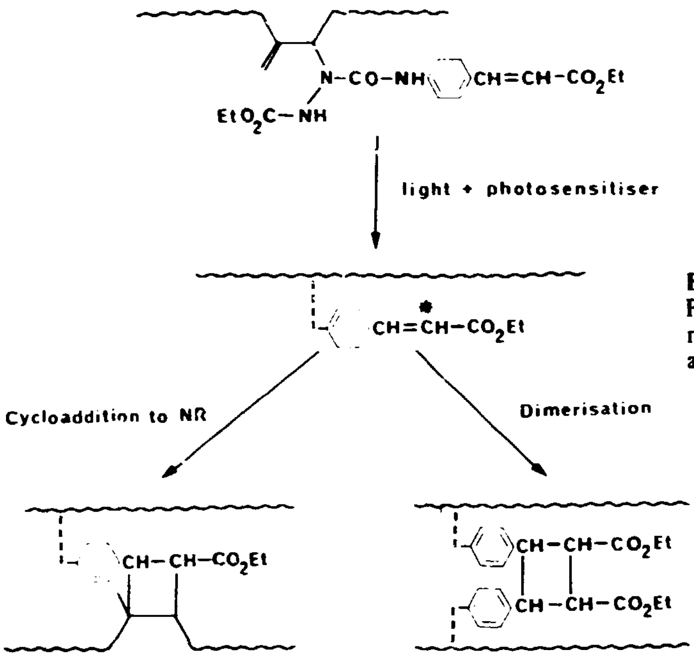

Fig. 6.11
Photochemical crosslinking of natural rubber *via* the addition product of an azocinnamate.

Azo—S—Azo

Azo—S_2—Azo

Azo—S_4—Azo

Azo—Azo

Azo————Azo

Azo—S_xR

Fig. 6.12
Bifunctional azo compounds to give tailored crosslinks of various structure.

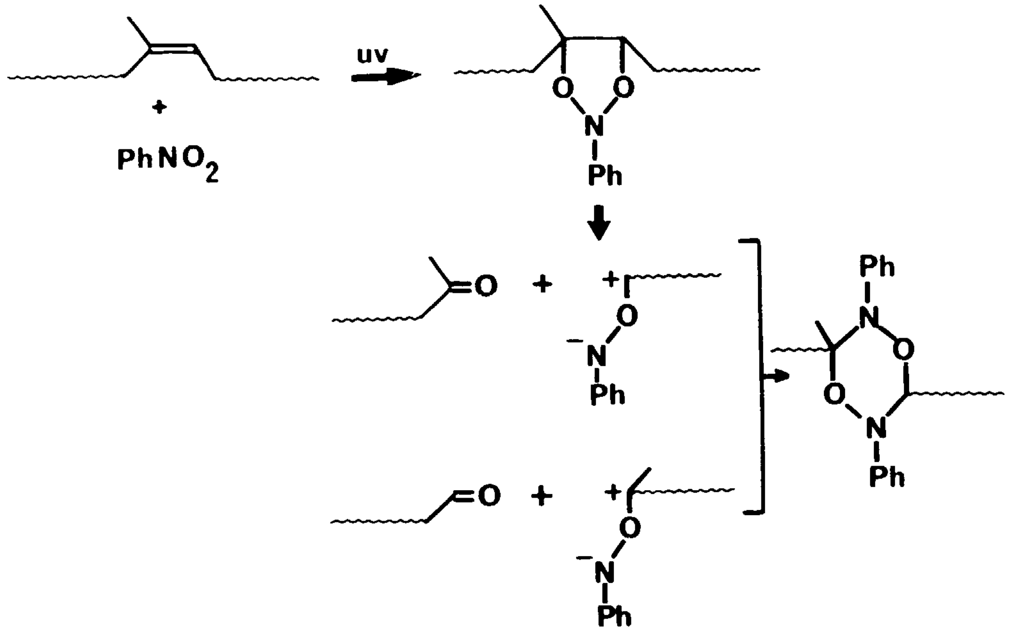

Fig. 6.13 The mechanism of chain scission of natural rubber by nitrobenzene and uv light.

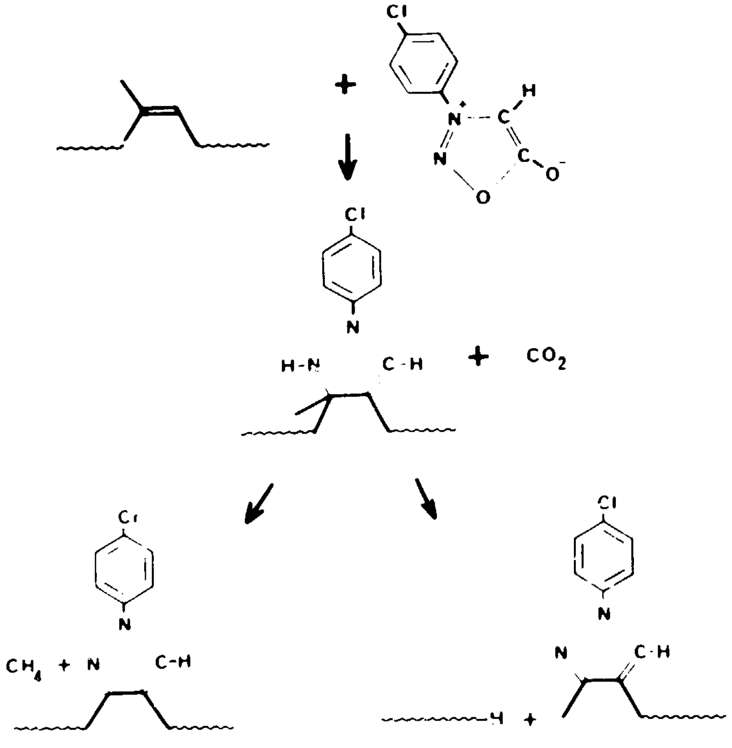

Fig. 6.14
The chain scission of natural rubber via reaction with *p*-chlorophenylsydnone.

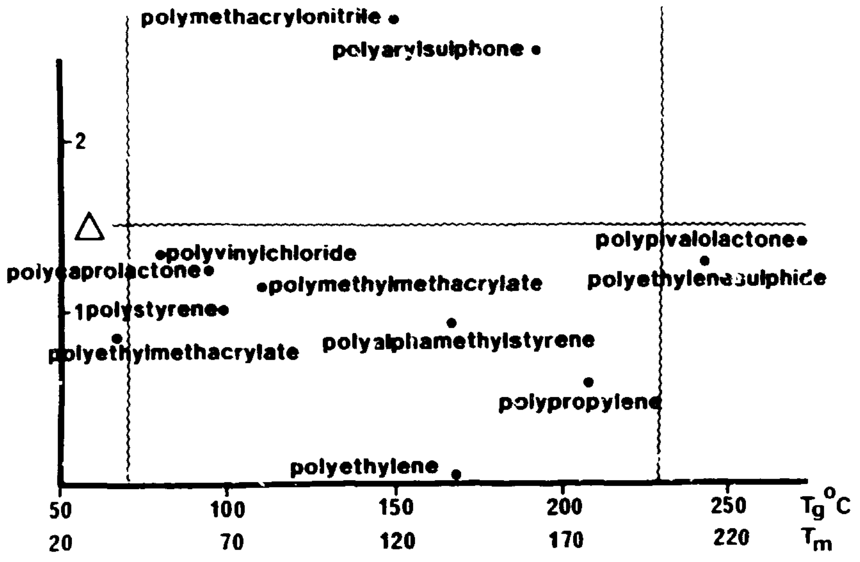

Fig. 6.15 A dry-mix grafting feasibility diagram obtained by plotting solubility parameter difference of the polymer and natural rubber versus T_g or T_m of the polymer.

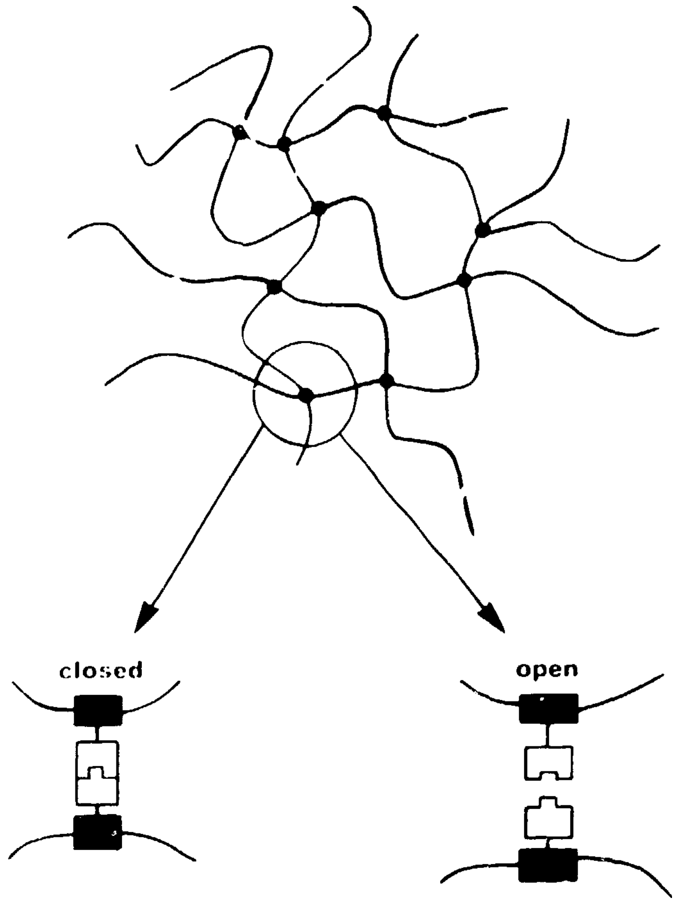

Fig. 6.16 Schematic representation of a thermolabile crosslink.

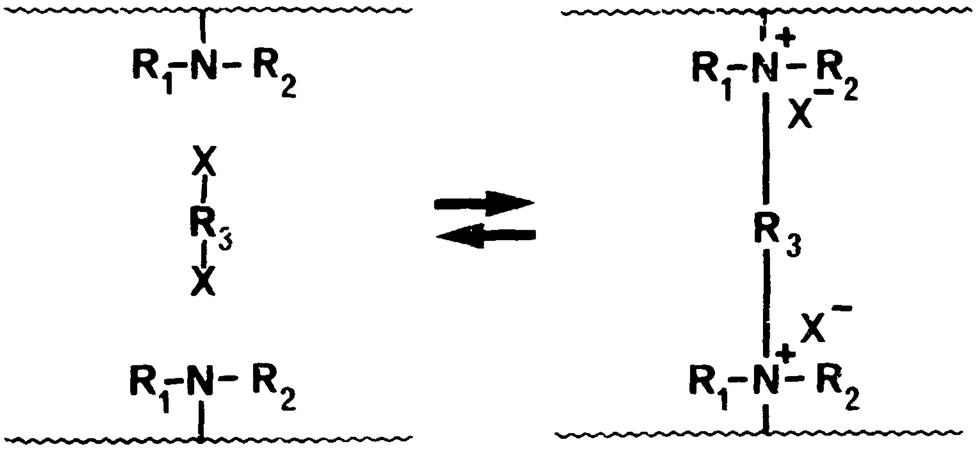

Fig. 6.17 A labile (heat or shear) quaternary salt crosslink.

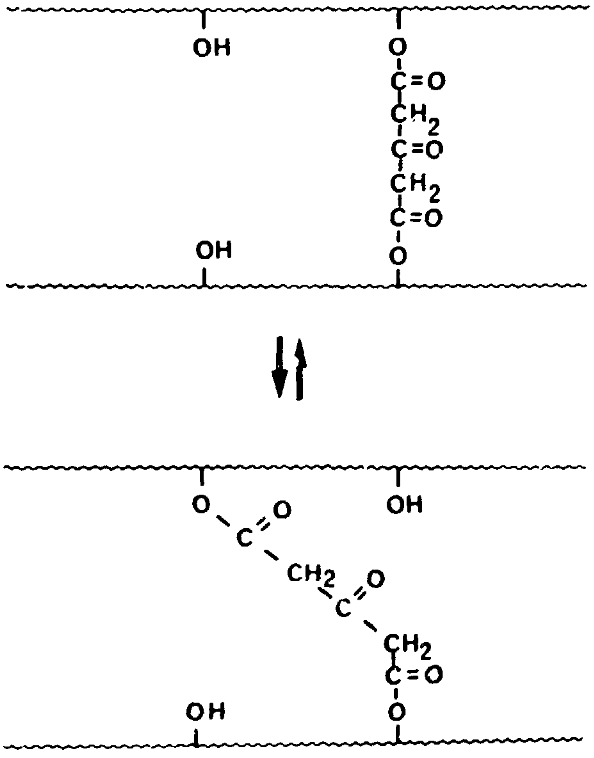

Fig. 6.18
The keto-ester exchange reaction as the basis of a thermolabile crosslink.

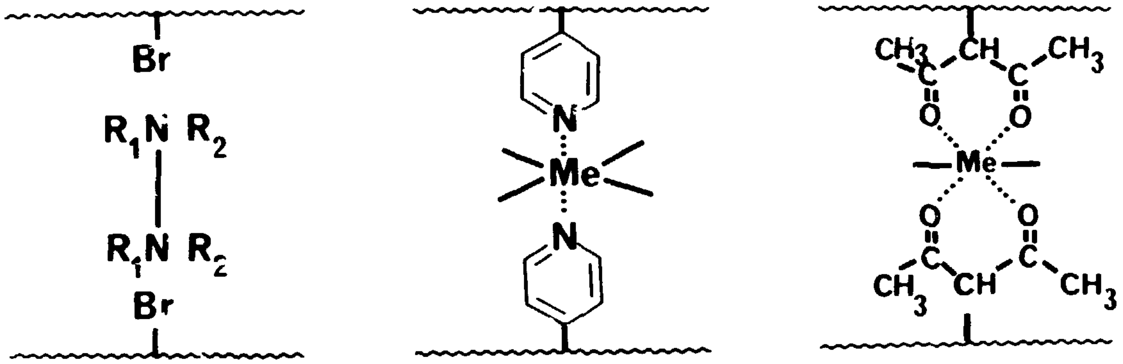

Fig. 6.19 Possible types of thermolabile crosslinks from chemically modified natural rubber.

Powdered Natural Rubber

POWDERED RUBBER PROCESSING
AN ESTABLISHED TECHNOLOGY WITH GREAT FUTURE POTENTIAL

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1 THE BAYER POWDERED RUBBER RANGE

Natural and synthetic rubber in powder form became commercially available a number of years ago. Bayer manufactures powdered polychloroprene and nitrile rubber materials, the products belonging to the two ranges being supplied under the trade names Baypren and Perbunan N.

The Baypren powdered rubber range consists of eight materials and includes normal grades having low to medium viscosity values and, correspondingly, slight to medium crystallization tendencies, precrosslinked grades, and sulphur-modified grades. The Baypren powdered rubbers are packed in the same way as the chip materials, ie in 25 kg bags, of which there are 40 to a pallet. In general they retain their ability to flow freely for more than six months, provided they are stored in a cool, dry place. This characteristic results from the presence of 5 ± 2% of an inorganic partitioning agent. Owing to the presence of the partitioning agent the powdered materials have higher Mooney viscosity values than the chip materials, but this has no influence on the vulcanization behaviour.

The Perbunan N powdered rubber range consists of eight materials also and includes a PVC-modified precrosslinked grade in addition to the main and special grades. The Perbunan N powdered rubber grades are packed in 25 kg plastic bags and the pallet weight is 450 kg. These materials also correspond to the polymers on which they are based and contain similar amounts of partitioning agent.

The maximum particle size of all the powdered rubber grades is 1.6 mm; the size of about 80% of the rubber particles is within the range 0.5 to 1.6 mm.

2 POWDERED RUBBER TECHNOLOGY

Our powdered rubber technology embraces the following operations:

Dry blending

Processing the powdered dryblend to homogeneous rubber compounds consisting of strips or pellets

Direct processing of the dryblend on injection moulding machines

Direct processing of the dryblend to extruded finished goods (this technique is still at the experimental production stage).

Dry blending is comparable with internal mixing in conventional rubber processing because it is common to all the processes which have been found suitable for powdered rubber. The subsequent operations represent alternatives to one another. A complete production sequence therefore comprises the basic dryblend operation, followed by one of the other above-mentioned operations.

In developing our powdered rubber technology we have cooperated with five German machinery manufacturers and one German handling equipment manufacturer.

2.1 DRY BLENDING

The production of a dryblend containing all the ingredients belonging to a compound formulation is the foundation of our entire powdered rubber technology. The purpose of dry blending is to produce a homogeneous powder, representing a mixture of all the ingredients belonging to a rubber compound, in a one step operation, in the shortest possible time, and in such a way that very little energy is consumed and the temperature of the materials therefore increases to only a very small extent.

For this purpose it was necessary to optimize a machine that was already being used at plants which process plastics in powder form, _eg_ PVC, in addition to rubber: the turbo-rapid mixer.

In modifying the turbo-rapid mixer to enable it to meet the technical and economic requirements of dry blending in the most satisfactory manner possible we studied a large number of parameters, including the shape of the chamber, the extent to which the volume of the chamber is filled, the impeller design, the tool speed, the shape and position of the baffle plate, the effects of heating and cooling, and the introduction of the powdery and liquid ingredients. Figure 1 shows a cross-section through a turbo-rapid mixer.

The finished mixture is a free-flowing powder with a mean bulk density of 0.5 ± 0.1 g/cm^3. Extensive development work resulted in machines with the sizes 100, 160, 250, and 400 (these figures represent the maximum volume of the chamber in litres), for which the following additional data can be given in Table 1.

TABLE 1 MACHINE DATA - TURBO-RAPID MIXERS

Mixer size (litres)	Average batch weight (kg)	Maximum drive capacity (kW)
100	30	30
160	50	37
250	80	55
400	120	75

The turbo-rapid mixers of these sizes give batches with average weights of 30, 50, 80, and 120 kg after net mixing times of 2 to 3 minutes. 1 to 1½ minutes must be allowed for the manual loading operation. The emptying time is negligibly short.

If the net mixing time is 2 to 2½ minutes the final temperature of a dryblend for vulcanizates with a hardness of 20 to 40 Shore A is 60 to 80°C. If the Shore A hardness is to be above 40 the net mixing time is about 3 minutes. In such cases the mixture contains a relatively small amount of plasticizer; it therefore absorbs less energy, with the result that the final temperature of the homogeneous powdery material is between 35 and 45°C. While the mixture is being produced the motor capacities of the machines just referred to are used to the extent of 60 to 70%.

2.1.1 Production of homogeneous rubber compounds from the dryblend powder

Especially where the production of mechanical rubber goods is concerned there are plants whose compounding capacity is inadequate and which therefore have to buy compounded stock from other firms. If it is intended to enlarge the existing capacity of a plant there are two alternatives: One can install either an additional internal mixing line or a powdered rubber processing line. In the case of the first alternative both the capital outlay and operating costs will be high. If a decision is taken in favour of powdered rubber technology the cost of investment will be considerably lower, less personnel will be needed to operate the machines, and energy will be saved. In view of these advantages we will first describe the processes by which the dryblend can be transformed into a homogeneous compound, which, like any other compound, can be converted into finished goods on all the rubber-processing machinery and equipment which happens to be available. Feed strip or pellets can be produced by three different machinery set ups.

2.1.1.1. Dryblend processing on special extruders. Special extruders which directly transform the dryblend into homogeneous feed strip or pellets are now supplied by the firms of Werner & Pfleiderer and Berstorff.

The dryblend is conveyed to the special extruder by a suitable metering unit either directly or from a silo in which it has been stored (Figure 2). The twin-screw section is relatively short, the pitch of the screws being such as to give a powerful feed effect. The free-flowing powder is compacted in this part of the extruder and fed to the longer single-screw section, where it is subjected to an EVK mixing action which improves the dispersion of the ingredients to the standard required for final processing. Depending on the type of extruder head in use, the material emerges as strip or pellets. The Werner & Pfleiderer machines are available in sizes of 90, 120, and 150 mm for outputs ranging from 200 to 1000 kg/h.

The sequence of operations which transforms the mixed ingredients into homogeneous pellets is shown in Figure 3. As an example it can be mentioned that a 150-mm machine which has been in use for almost two years converts Baypren powdered rubber dryblends into pellets at rates of 700 to 1000 kg/h.

The Berstorff special extruder represents a cascade consisting of two machines, a planetary extruder part and a separate final product warm-feed extruder (Figure 4). The dryblend is compacted and homogenized exclusively in the planetary part of the extruder, which consists of a stationary cylinder and a driven main spindle surrounded by eight to ten independent planetary spindles. The rotation of the main spindle forces the planetary spindles to rotate also. The planetary spindles are held in place by a special ring at the end of the cylinder. On entering the space between the main and planetary spindles the mixture of the ingredients is subjected to an intensive kneading action.

The Berstorff combination, which had been used for several years in the processing of plastics in powder form, especially of PVC, was modified to meet the requirements of powdered rubber technology. The type known as WE 140 has been used successfully for a large number of different rubber compounds. Depending on which of the types is used, the machine gives a throughput of 250 to 500 kg/h. The manufacturers intend to introduce additional types, which are to be known as WE 190 and WE 240. The type number indicates, not the screw diameter, but the distance in millimetres between opposite planetary spindles; this distance is thus 140 mm in the case of the WE 140 machine. Figure 5 shows as a schematic drawing how the dryblend is processed on a Berstorff planetary extruder unit.

2.1.1.2. Dryblend processing on mills fed by a single-screw compactor. Though less rational than the alternative procedures, dryblend processing on mixing mills to which the material is supplied by single-screw compactors minimizes the fundamental capital invesment necessitated by the introduction of powdered rubber.

For this procedure - irrespective of whether it is operated continuously or intermittently - the existing mill must be supplemented by a turbo-rapid mixer and a single-screw compactor. The net basic capital outlay, excluding the cost of the handling and aspiration systems and the total installation costs, is likely to be between 100 000 and 160 000 DM depending on the machine types and sizes. The existing mill serves to improve the dispersion of the compound to the standard required for final processing. To enable the work to proceed without interruption the mill should be divided into two zones and provided with a stockblender. The fully mixed strip leaving the mill should be passed through a cooling unit and deposited wig-wag-wise in open containers in readiness for final processing. If it is decided to operate the process continuously, as described before, it is important to adjust the throughputs of the machines to one another.

The sequence of operations embracing the turbo-rapid mixer, a single-screw compactor, and a mixing mill, is shown in Figure 6. If, for reasons of cost, it is decided to use an existing mill, the dryblend must nevertheless be compacted. If the dryblend were compacted on the mill itself this would create dust on a scale which would be hazardous to the personnel and would make it impossible to keep the mixing room clean.

The purpose of compacting, which is a new operation in rubber processing, is to compress the free-flowing dryblend, which has a mean bulk density of 0.5 ± 0.1 g/cm^3, until it has approximately the specific gravity of the compound required. This operation gives an inhomogeneous, but compact and continuous strip, which is afterwards homogenized on a mill. The strip is produced in a very inexpensive machine, which also requires very little energy, cooling water, and installation space. This machine, by which the dryblend is compacted, though not yet rendered homogeneous, was developed by Sikoplast, of Siegburg, in cooperation with us. It has a horizontal compacting screw with a special conical part and is available in two sizes with rated motor capacities of 11 and 35 kW for mean throughputs of 250 and 600 kg/h (Figure 7). The turbo-rapid mixer empties its contents batchwise into the feed hopper of the compactor, which is located at a lower level. The compactor can, however, be operated continuously if the outputs of the two machines are adjusted to one another.

2.1.1.3. Processing of dryblends in internal mixers or on mills.

Mills and internal mixers, which belong to the conventional equipment of rubber plants, are particularly suitable for soft compounds intended for soft printing rolls or use on coating machines when dryblends are processed by the direct method.

When such compounds are produced in the conventional way, ie in internal mixers, several stages or long compounding times are necessary because of the need to disperse the large amount of plasticizer homogeneously. If the ingredients of a compound are introduced into an internal mixer in the form of a dryblend, the number of internal mixing stages can be reduced to one or two, with a resultant considerable increase in the output of the internal mixing line. The savings that can be achieved in this way depend on the formulation of the compound, on how the compound of this type is normally produced at the present time, and on how modern internal mixer is. It is difficult to give a specific figure for the reason that, when the rubber is introduced into an internal mixer in the form of bales, the individual compounding stages are not of equally long duration. Nevertheless we know from practical experience that the capacity of an internal mixing line can be increased by about 20 to 40% by the interposition of dryblending.

A dryblend powder containing a high proportion of plasticizer is able to flow freely but does not form dust. If the ingredients of a compound are finally mixed, ie homogenized, on a mixing mill onto which they are introduced in the form of a dryblend, the total compounding time can be reduced, the quality of the product can be improved, and dust formation by compounding ingredients can be entirely prevented. In the manufacture of soft printing roll covers the use of powdered rubber together with the use of a new and inexpensive machine, the turbo-rapid mixer, in conjunction with an existing mill, simplifies and reduces the cost of producing a processable compound. If the dryblend has only a low plasticizer content, final compounding takes longer and dust formation is inevitable.

2.1.2 Direct processing of the dryblend on injection moulding machines

In connection with the direct processing of dryblends to moulded technical goods, which is also known as 'one-step moulding', we have been cooperating with Werner & Pfleiderer in the development of horizontal and vertical injection moulding machines. In connection with horizontal machines we are also cooperating with GKN Windsor, of Bischofsheim; the plasticizing units used with these machines are supplied by Berstorff, of Hanover.

The sequence of operations involved in the direct injection moulding of dryblends is shown in Figure 8. We have developed this two-stage procedure - production of a compound in a turbo-rapid mixer, followed by the final processing operation - mainly for use in the production of technical mouldings on horizontal and vertical injection moulding machines. The screw throughputs of rubber injection moulding machines are considerably smaller than those of extruders. The throughputs for screw diameters of 50 to 80 mm range from 20 to 80 kg per hour. If it would not be acceptable to increase the normal plasticizing times the entire free volume of the feed zone must be enlarged, and a suitable mixing and shearing screw fitted, so that direct feeding with dryblend is possible.

In this two-step procedure the kneading or mixing effects of internal mixers and mills have to be dispensed with. The screws of the plasticizing units of the injection moulding machines therefore have to provide the mixing and shearing effects needed to incorporate fillers and rubber chemicals into the powdered rubber particles and disperse them evenly. The horizontal and vertical rubber injection moulding machines made by Werner & Pfleiderer, of Stuttgart, are fitted with mixing and shearing screws based on the EVK principle, which were jointly developed by Werner & Pfleiderer and Bayer. The Werner & Pfleiderer mixing and shearing screw system is shown in Figure 9. A vertical Werner & Pfleiderer machine of the GSP type is shown in Figure 10.

The horizontal injection moulding machines supplied by GKN Windsor are fitted with plasticizing units jointly developed by Bayer and Berstorff, of Hanover. The mixing and shearing screws of these units represent a modification, designed by Bayer and Berstorff, of the Maillifer principle. The mixing and shearing system is shown in Figure 11. Figure 12 is a photograph of the GKN Windsor horizontal injection moulding machine with a Berstorff plasticizing unit.

The handling of the dryblend powder after it has left the turbo-rapid mixer and before it is fed to the injection moulding machine is most important to the success of the whole procedure. It would be unreasonable to expect the machine operators to feed the material by hand and, in any case, this would make it impossible to keep the building clean. A handling system has therefore been developed by Meyer, of Hennef, in cooperation with Bayer, in which the dryblend is fed by suction from a silo to a metering screw located above the feed opening of the injection moulding machine's plasticizing unit (see Figure 12). Disturbance-free handling is also fundamental to the entirely automatic operation of injection moulding machines without machine operators.

Practically speaking, every manufacturer of rubber goods would like to know whether existing rubber injection moulding machines can be modified so as to be suitable for this procedure, which is undoubtedly the most economical powdered rubber processing technique. In every case the circumstances must be carefully investigated. According to our experience machines with sufficient screw lengths and adequately powered plasticizing units can be modified if they are single-station machines. But the screw length should be at least 15 x D and not more than 20 x D, and the screw diameter D itself should not exceed 80 mm. As the drive motors of many existing rubber injection moulding machines are only just adequate for the demands made on them at present, one should be hesitant to assume that the drive motor will be adequate in any particular case.

2.1.3 Direct processing of the dryblend to extruded goods (techniques still at the experimental production stage)

If the direct processing of a dryblend on extruders is found to be practical it will, like one-step moulding, be an elegant one-step manufacturing procedure which permits correspondingly large savings. But the direct extrusion of a dryblend is considerably more difficult than the direct injection moulding of such a material. In this case the output and homogeneity of the mixture, the temperature of the material, and the dimensional stability of the extrudate must all be optimized at the same time; in other words a well dispersed compound must be produced at the highest possible rate, while remaining at the lowest possible temperature, and the dimensional stability of the extrudate must be extremely good. This procedure, which was envisaged as the final goal of our powdered rubber technology, is now being operated experimentally on industrial extruders.

All the familiar types of extruders are either entirely unsuitable for direct feeding with a dryblend powder or suitable only if the output is reduced to such an extent that the production becomes uneconomical. The practical trials are being conducted with the special Werner & Pfleiderer and Berstorff extruders as mentioned earlier. If the experiments are successful, these special extruders will be worthy of consideration in cases where the installation of a new extrusion line is planned. They will only be suitable for the direct processing of a dryblend powder, however.

With a view to enabling the use of modern cold-fed venting extruders which have already been installed to continue we are cooperating with Troester, of Hanover, in experiments under conditions similar to those of practice. It has already been found that the desired effect cannot be achieved simply by modifying an extruder of this type by, for example, fitting a mixing and shearing screw and extending the cyclinder. The feed systems available at present are not able to achieve the required output of strips or pellets when the extruder is fed with free-flowing dryblend. The concept which we are examining jointly with Troester represents a cascade system in which the feeding and compacting are separated from the homogenizing operations. This cascade system is represented schematically in Figure 13. The concept just referred to envisages the use of a twin-screw compactor with separate drive as an additional unit located above the feed opening of the extruder. The purpose of this unit is to draw in the dryblend, compact it, and feed it as an inhomogeneous, but continuous feed strip to the mixing extruder located below. The modern cold-feed venting extruder which is the next machine in the extrusion line must in all cases have a mixing and shearing screw and its length may have to be increased. We are not yet in a position to comment on the overall technological and economic potentialities of this concept.

3 ECONOMIC ASPECTS OF THE NEW TECHNOLOGY

The purchase of the plant needed for a conventional mixing room, and even the installation of an additional internal mixing line, entails such heavy capital expenditure that the burden is bound to be felt, even by a large firm, for a number of years. Such an investment may provide the production capacity that has been lacking hitherto, but the firm concerned is unlikely to be in a position to buy new processing machinery, such as extruders and injection moulding machines, at the same time.

The new powdered rubber technology provides a real alternative to such an investment. The plant's mixing capacity can be increased at very little cost, and, at the same time, the existing processing machinery can be modified very inexpensively or new equipment can be bought. In addition the new powdered rubber technology can be introduced in a number of stages, whereas a new mixing room must be provided, or an existing one enlarged, all at once.

The economic factors that must be taken into consideration differ considerably according to the country in which the factory is located or, in the case of a particular factory, according to the type, location and size of the undertaking. The conditions on which the following calculations are based have been averaged from those which existed in the Federal Republic of Germany in 1980. Assuming the validity of these figures, which cover such factors as the interest on capital, the depreciation period, maintenance costs, space requirements, energy consumption, and wages' costs, two examples of the savings permitted by the new technology will now be given. The assumptions on which both calculations are based are as follows:-

1 production methods recommended used as basis

2 hourly throughput

3 two-shift production

4 50% rubber content in compounds

5 powder rubber surcharge DM 0.40/kg

To start with we will compare a conventional internal mixing line, consisting of a 60 litre internal mixer, two 84 in. mills, and a batch-off unit with strip cutting device, with a dryblend mixing line, consisting of a 160 litre Papenmeier turbo-rapid mixer and a 150 mm Werner & Pfleiderer EVK extruder with twin-screw feed zone and strip extruding head. At an annual output of approximately 2 500 tonnes, produced on a two-shift basis, the saving permitted by the powdered rubber technology after allowance has been made for the fact that, at present, powdered rubber is more expensive than conventional forms of rubber is about 340 000 DM. Under the same conditions it will still be possible to save 170 000 DM a year after the conventional internal mixing line has been entirely written off.

The purpose of the second example is to indicate the considerably greater economic advantages which are possible when the powdered rubber is processed directly. I will assume that a technical moulding shop, equipped with 30 injection moulding machines, is supplied with conventionally produced feeding strips in one case and with freeflowing dryblends in the other, and that the other factors are the same as those on which our first example was based. Here again the amount of compound required annually is 2500 tonnes and there are two shifts a day. The compound strip is produced conventionally on the plant belonging to the internal mixing line. The production of a compound according to the powdered rubber technology is confined to the dryblending process, for which, again, a 160 litre Papenmeier turbo-rapid mixer is used. In the case of the powdered rubber technology one has to take into account the fact that the raw material is more expensive than conventional rubber and the capital outlay for new machinery or, in the case of modified machinery, for a new plasticizing unit with mixing screws and a dryblend feeding device. At interest rates of 8 and 16% the use of powdered rubber in this example permits annual savings of 540 000 and 510 000 DM. Even if the internal mixing line with which a comparison is made has been entirely written off, an annual saving of about 300 000 DM is still possible.

Finally, Figure 14 shows the future cost trends of a technical moulding shop with thirty rubber injection moulding machines as operated conventionally, in the one case, and according to the powdered rubber technology, in the other. This figure shows the trends of the costs of the two production processes as functions of the expected increases in the average wage of a skilled rubber worker. At the present average hourly wage of DM 25 it is clear that the total cost of production is likely to increase considerably more in the case of the conventional process than in that of the new process. Several factors favourable to the powdered rubber technology have been disregarded, however. These are the expected future increases in the cost of energy, the opportunities provided by the powdered rubber technolgy for reductions in curing times, and the fact that the prospect of operating injection moulding machines entirely automatically, ie without personnel, is considerably better when the machines are fed with dryblend than when they are fed with conventional mixed strips.

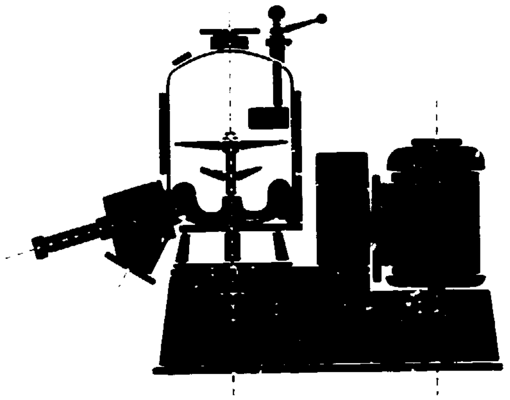


Fig. 7.1
Papenmeir turbo-rapid mixer (cross-section).

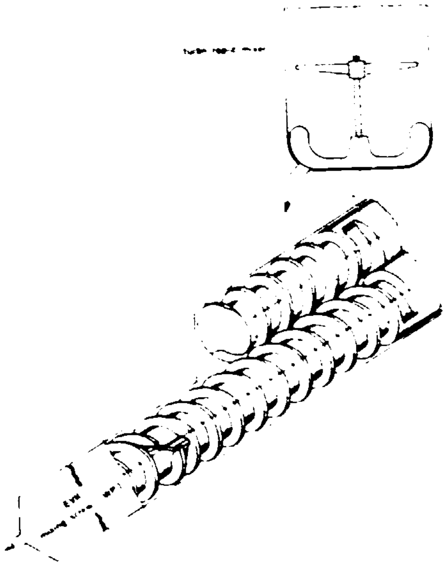


Fig. 7.2
EVK compounding extruder: Werner and Pfleiderer system.

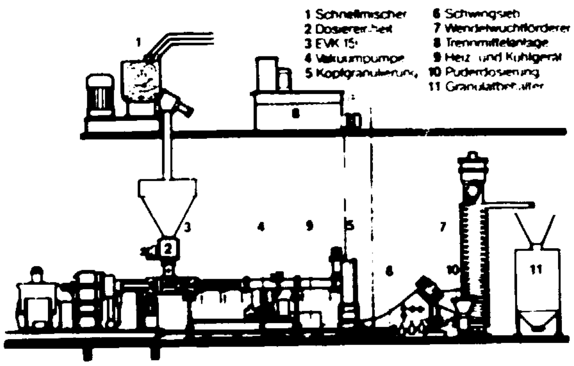


Fig. 7.3
Dryblend processing on a Werner and Pfleiderer special extruder.

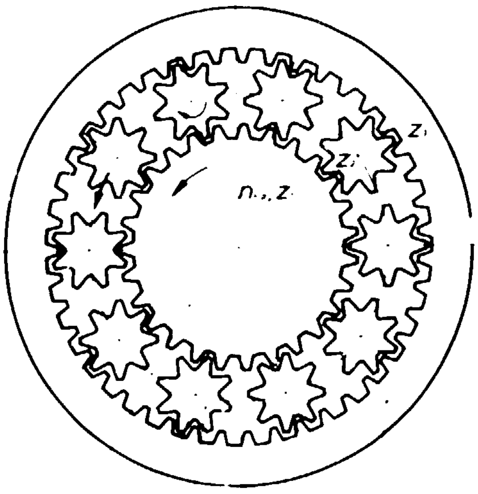


Fig. 7.4
Planetary extruder, Berstorff system.

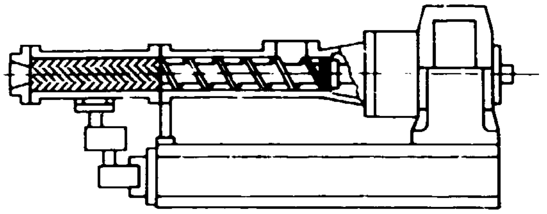


Fig. 7.5
Dryblend processing on Berstorff WE unit.

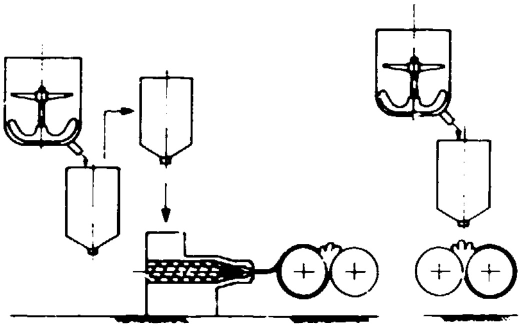


Fig. 7.6
Turbo-rapid mixer - single-screw compactor; mill processing sequence.

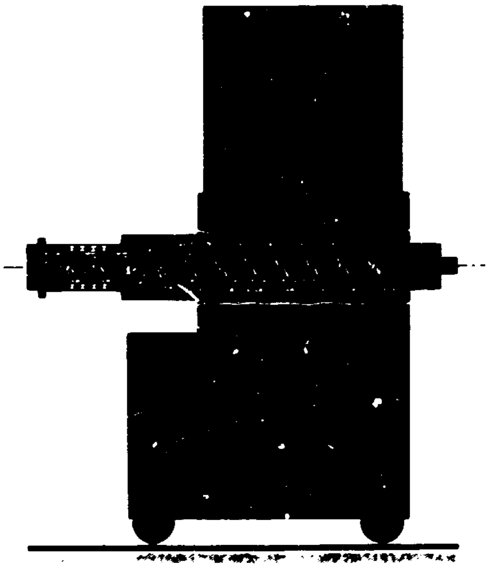


Fig. 7.7
Sikoplast single-screw compactor.

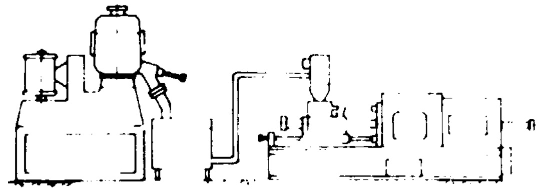


Fig. 7.8
Dryblend processing line (schematic drawing); one-step moulding on horizontal injection-moulding machine.

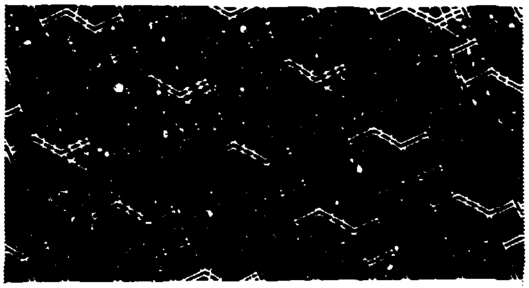


Fig. 7.9
EVK mixing and shearing system.
Werner and Pfleiderer.

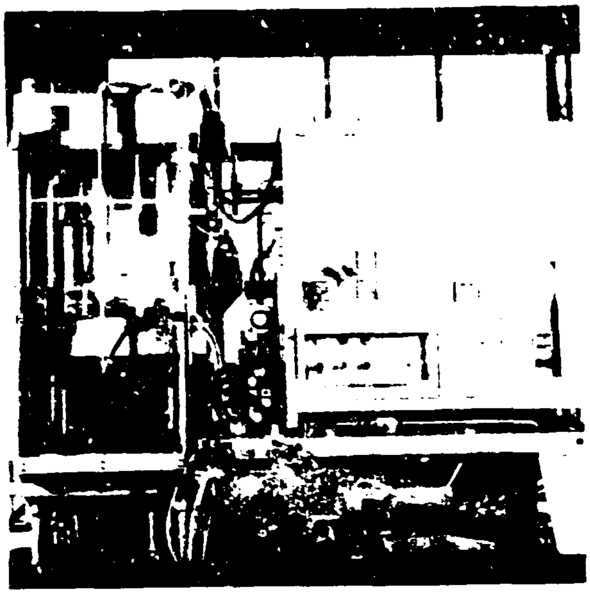


Fig. 7.10
Werner and Pfleiderer rubber injection-moulding machine, GSP type.

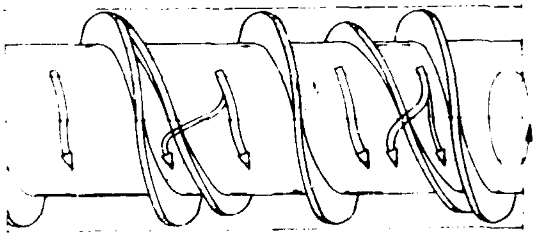


Fig. 7.11
The Berstorff mixing and shearing system.

Fig. 7.12
Horizontal GKN Windsor injection-moulding machine with Berstorff plasticizing unit.

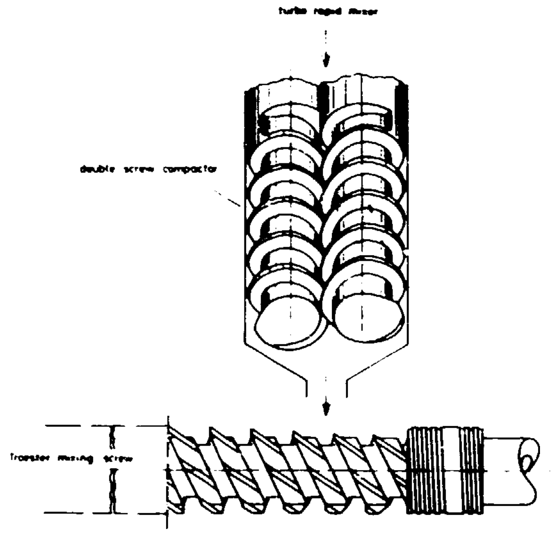
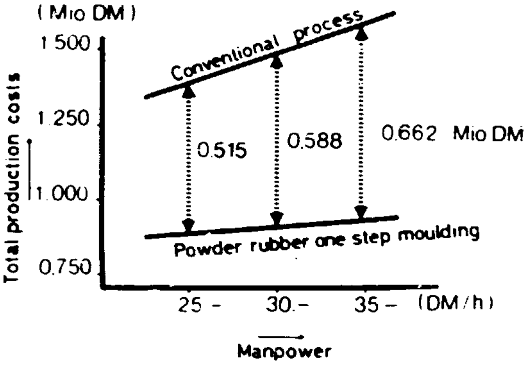


Fig. 7.13
Mixing extruder in combination with a twin-screw compactor, Troester system.

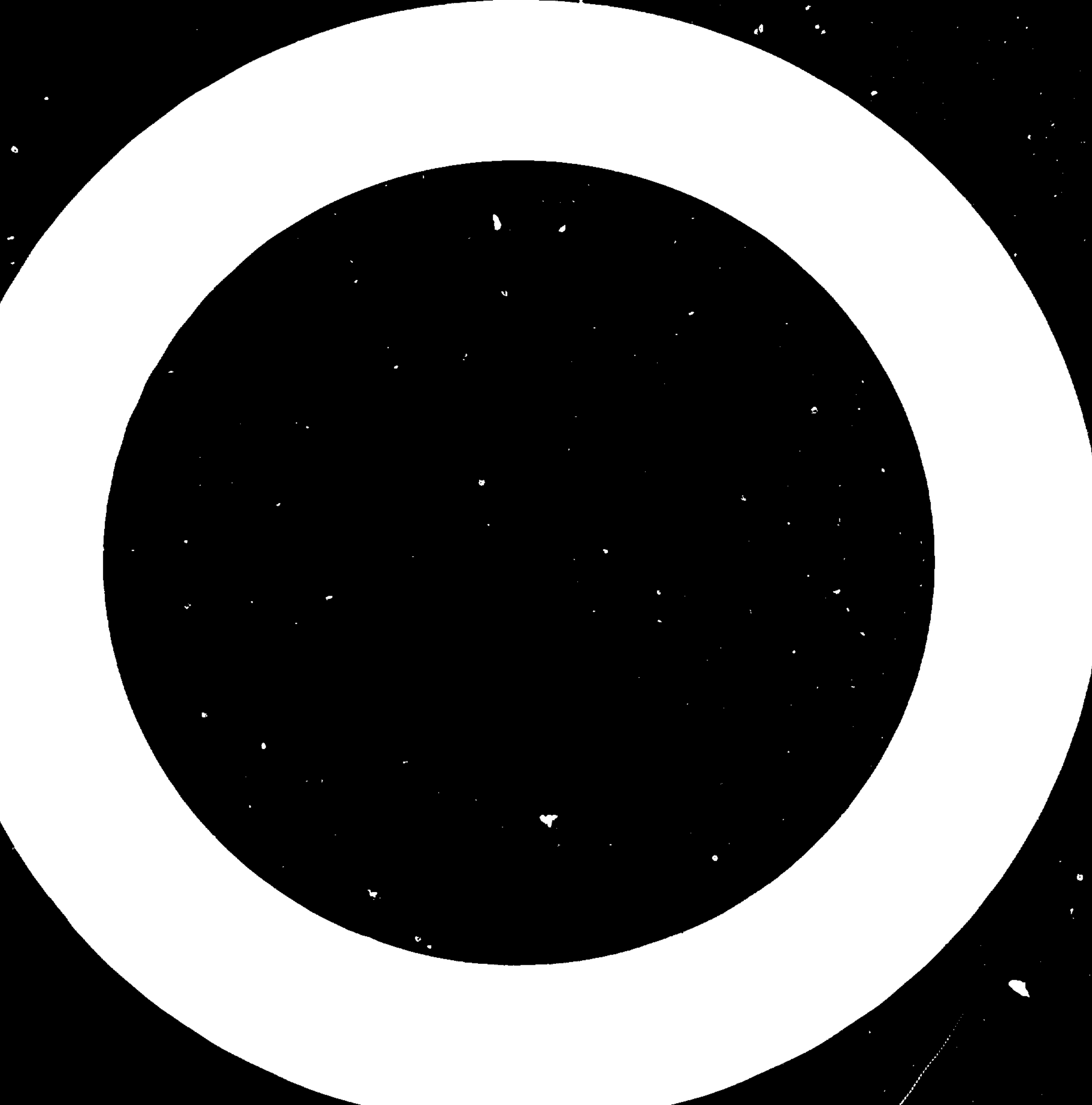


Future trend

Compa:sion conventional process vs
One step moulding

Moulded goods production with 30 injection - moulding machines

Fig. 7.14
Future trends of total produciion costs.



DEVELOPMENT OF POWDERED RUBBER MASTERBATCHES

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GENERAL SITUATION OF THE RUBBER INDUSTRY AND THE REQUIREMENT FOR NEW PROCESSING TECHNIQUES

The rubber industry is the oldest industry engaged in the processing of polymeric raw materials. Against this background it seems paradoxical that its methods, process routes, and mechanical equipment are too effort-wasting compared to other sectors of modern technology. This applies particularly to the indisputable lead in handling high polymer plastics. A long tradition has given rise to the generally known conservative attitude prevailing in the rubber-processing industry. Day-to-day routine in rubber processing is governed largely by practical experience. This situation is without doubt a characteristic of a still inadequate scientific knowledge of the raw material, rubber. Looking into the future, we may expect that a change in this situation will have to be brought about, particularly for economic reasons.

A starting point for a necessary reform is clearly evident. It is the simplification of the currently practised processing techniques. Modern plastics technology is pointing the way here. While its methods initially were adapted to the experience gained from the very much older rubber industry, plastics processing has in the meantime achieved a superior status of technology. The greatest handicap for transposing this to rubber technology is still the inevitable multistage process, caused by the requirement for the incorporation of highly active fillers and by the lack of a comparable thermoplastic behaviour. This situation is aggravated by constantly rising labour and especially energy costs. Changing this state of affairs means understanding the signs of the time.

The key to a change in this situation resides mainly in a change of the form in which the rubber is available. The variants that are eligible for this purpose form the subject of this symposium, namely, thermoplastic, low viscosity (liquid) or powdered rubbers! The pros and cons of these variants have already been the subject of a large number of publications. The utilisation of thermoplastic rubbers is limited in view of their poor hysteresis properties. Liquid rubbers exhibiting satisfactory final properties are not yet available. In addition, their introduction will call not only for entirely new equipment for their production but also for entirely new equipment and technologies for their processing.

On the other hand, powdered raw materials are based largely on conventional production units. Furthermore they can be advantageously processed even within the scope of conventional processing routes and lead to economically optimal single-step process. Following these considerations the provision of the usual high polymers in powdered form commands priority at least in the next decade.

Studies to realize a powder technology have so far largely concerned powdered nitrile rubbers because of their easy availability by simple grinding. A convincing breakthrough cannot be expected until the most important general purpose rubbers like NR, SBR and BR are also available in powder form. However, the general prerequisite for success in any case is an optimum economic route for powdered rubber production. An acceptable premium will be the decisive factor for the desired progress. Only if savings in rubber processing exceed additional costs for raw materials will powder technology make any sense.

Commonly used methods for powdered rubber production today are the spray drying of latices and cryogenic grinding of solid rubbers. Both techniques require additional energy. More economic results, however, can be expected by use of coagulation or precipitation techniques. The general difficulties to be surmounted reside not so much in the production of small particle sizes but rather in their preservation with a view to achieving excellent storage properties. Interfering factors are tackiness and cold flow of the individual particles. To overcome the interfering adhesion, dusting with inorganic or organic materials has been attempted in the past and the method of microencapsulation using special polymer compounds has been suggested. These methods entail the introduction of high portions of substances adversely affecting the rubber properties. In view of these problems a proposal for a new concept was offered by Huls some years ago.

PROPERTIES AND POTENTIALITIES OF POWDERED MASTERBATCHES

Our contribution to the solution of the key problems discussed above is based on the development of a special production process and offers the advantage of a new raw material concept. Our studies have shown that powdered rubber-filler masterbatches must primarily be regarded as an ideal basis for a successful introduction of powdered rubber technology. The results of our work indicate that this variant will not only avoid the difficulties in production and storage but also provide more ideal conditions for cost-saving and simplified processing techniques.

Preparation

For the production method, one of the preferred routes is illustrated by a simplified model reaction:

dispersing agent + coagulant ⟶ adhesion inhibitor.

Thus, rubbers and fillers in the form of stable aqueous dispersions are brought into contact with special deactivators. These will react together with the dispersion stabilizers used, forming insoluble products which subsequently serve as adhesion inhibitors. In this process step the batch is precipitated in a finely divided form. By a special drying method, free-flowing powders can be directly isolated. The proportion of by-products remaining in the rubber is extremely small and thus does not affect the quality of the vulcanizates.

This principle can be used in the production of the common general purpose rubbers, both by the solution or the emulsion process. In this connection it may be mentioned that caking problems due to cold flow of the individual particles are non-existent as a result of the optimum pre-distribution of fillers in the rubber phase. However, the creation of special surface structures that ensure the preservation of the free-flowing powder is also of importance (Figure 1).

The particle size distribution can be varied by different parameters of the production process. The distribution shown in Figure 2 can be regarded as an optimum and will also be used as the basis for the following tests. The bulk density is in the range of 500 g/l depending on the particle size, the particle size distribution and the type and amount of fillers, and thus comes up to the range of the known plastic powders (Table 1).

TABLE 1. BULK DENSITIES AND POURABILITIES

test method	powder batch	S-PVC Vestolit 7054	E-PVC Vestolit 6007	PE Vestolen A6016	PA Vestamid L1610
bulk density g/l DIN 53468	450	466	596	440	451
pourability (sec) ASTM-D 1895-69 nozzle 10mm	17.4	31.2	14.4	56.5	22.4

In spite of the higher volume, transportation costs compared to bale rubber are not impaired. This may be illustrated by the example in Table 2.

TABLE 2. TRANSPORTATION OF POWDERED VERSUS BALE RUBBER

20 ft Container (volume, 5.9 x 2.33 x 2.38 m, 32 m^3)

10 pallets at 900 kg	=	9 tonnes bale rubber
20 pallets at 750 kg	=	15 tonnes bale rubber
powdered rubber (0.5 g/cm^3) 32 x 0.5	=	16 tonnes powder batch

40 ft Container (volume, 12 x 2.33 x 2.38 m, 66 m^3)

21 pallets at 900 kg	=	18.9 tonnes bale rubber
42 pallets at 750 kg	=	31.5 tonnes bale rubber
powdered rubber (0.5 g/cm^3) 66 x 0.5	=	33 tonnes powder batch

The transport of free flowing powders allows the full use of the total volume. Furthermore no expensive pallets are necessary. Fork-lift trucks will be replaced by automatic conveying equipment.

Besides process factors, the molecular parameters of the rubbers as well as the amount and activity of the fillers govern the quality of the powder batch available in this manner. All carbon blacks and mineral products customary in the rubber industry can be used as fillers. The proportion of fillers has to meet the requirements and wishes of the customer. If optimum compounding variability is called for, the amount of fillers can be limited to a process dependent minimum. Further amounts can then be added in the course of processing. If, however, the emphasis is on the manufacture of large-scale series articles with only slight variation in compound composition, then, because of advantages in processing, the full amount of fillers should be present in the rubber phase of the powder batch.

Storage tests with the powder batch suitable for tread manufacture, were carried out in a silo of 160 cm diameter and 250 cm height. A height of 8 metres was simulated by the use of weights and increased temperatures were applied. The results obtained after several weeks of storage did not reveal any problems. The use of pneumatic conveying equipment turned out to be trouble-free with good efficiency. Automatic feeding devices could be used without difficulty on account of the favourable free-flowing properties. Even in conventional processing, the advantages of simplified handling afford a basis for considerable savings in labour. Automatic feeding to the mixing equipment as well as the reduction of feeding time permit an increase in the capacity of internal mixers.

Processing behaviour and technological properties

Further study of the properties of the powder batch presented here will open up possibilities for achieving far-reaching simplifications even of the conventional processing technology. For the characterization of the vulcanizates resulting from different procedures the test recipe is shown in Table 3.

TABLE 3. TEST FORMULATION

Powder batch	175 phr
100 phr SBR ML-4 ca. 110 75 " N-339 Black	
Stearic acid	1 "
ZnO	2.5 phr
4010 NA	1 "
Antilux	1 "
Gulfrex 125	50 "
Vulkacit CZ	1.1 "
Vulkacit D	0.25 "
Sulphur	1.9 "

This is a typical passenger tread compound based on a powder batch of 100 parts of E-SBR (ML-4 100) and 75 parts of N 339 carbon black.

The study of the processing behaviour was started with the usual two-stage Banbury mixing (Figure 3). Compared to the use of rubber bales an advantage is given by automatic handling of the elastomeric raw material. The energy graphs of the internal mixer as well as the discharge temperatures obtained with powder batches suggest a distinct reduction in mixing effort. As the tests have shown, even a single-stage process under simplified conditions will fully suffice (Figure 4).

In a test using a GK 160 Banbury a mixing time of 95 seconds was sufficient to obtain a final compound at temperatures of 119°C satisfying all criteria (Table 4).

TABLE 4. PHYSICAL PROPERTIES AND TYRE TEST DATA FOR POWDERED V BALE RUBBER

Equipment: Gk 160; two 84" mills + 200 mm 6-D extruder
mixing conditions: upside down; 190 kg; 30 rpm; 96 sec; discharge temp. 119°C
lab test: results - 20 min 150°C

		Banbury	1 mill	2 mill	extruded tread	control bale rubber
T.S.	MPa	16.5	18.8	17.4	16.9	17.8
EB	%	476	546	511	533	550
Mod 300	MPa	9.3	8.8	8.9	7.3	8.8
Tear	N/mm^2	36	39	43	38	35
Hardness	°Sh.A	65	64	62	62	61
Elast. 22°/75°C	%	26/40	26/39	27/41	29/43	29/43
Compound ML-4		85	63	63	64	63

Tyre test: dimension 175 SR 14 (2 cars Daimler Benz 230 autom.) - 10 000 km

	powder batch				control bale rubber			
Tyre	1	2	3	4	1	2	3	4
abrasion mm	2.54	2.53	2.54	2.51	2.47	2.52	2.52	2.52
$\bar{x}$		2.53				2.51		
index		99				100		
loss of weight g	520	450	540	500	560	450	495	500
$\bar{x}$		512				501		
index		98				100		

The use of powder batches thus permits the throughput of conventional mixing capacities to be increased by a factor of 2 or more without additional investment at correspondingly reduced energy and labour costs. However, the great variety of possibilities created by these powder batches are by no means exhausted in this way. The obvious target is to get rid of the need for heavy duty mixing machinery. Relatively cheap fluid mixers will prove satisfactory while at the same time reducing operating costs. Table 5 shows the time required for preparing the tread compound used here as the basis for the following testing.

TABLE 5. MIXING SCHEDULE USING A DIOSNA UNIVERSAL MIXER V 100

volume	100 l
rpm	212/min
charge weight	32 kg

powder batch	0 sec
addition of oil	5-60 sec
final mixing	30 sec
Total mixing time	90 sec
discharge temp.	25°C

The easy uptake of high amounts of oil leads to the conclusion that only oil-free powdered rubber filler masterbatches should be discussed as starting raw materials. This phenomenon of easy absorption of large amounts of plasticizer is due to the size and activity of the surfaces of the individual particles of the powder batch. These powder batches allow a powdered compound with invariably good pourability to be obtained. Using a simple fluid mixer, eg a 100-litre DIOSNA mixer (Figure 5), an hourly capacity of nearly one tonne final compound can be achieved. This is almost equivalent to the capacity of a 50-litre Banbury handling solid rubber in at least a two stage operation. Investment costs are less than 5% of the cost level of common mixing equipment. Energy costs are nearly negligible. Figure 6 illustrates the easy sheet formation as the final powdered compound is fed to a mill.

The effect of milling on vulcanizate properties is of technical and also scientific interest. A minimum mechanical frictional energy to obtain an optimum level of physical properties is necessary. Referred to our example a milling time of 1-2 minutes is required.

Spontaneous sheet formation provides the possibility of charging such powder compounds to common hot-feed extruders. This opens up the realization of a continuous rubber processing using conventional equipment (Figure 7).

The residence time on the preheating rolls will fully suffice to perform the required minimum shear. The utilization of the widely used extruder units without the usual preparation of the material in conventional mixers thus becomes possible. The results in Table 6 show the successful performance of such experiments.

TABLE 6. PROPERTIES OF POWDERED BATCH TREAD STOCK AFTER MILLING AND EXTRUSION

Equipment: three 84" mills + 200 mm 6-D extruder
lab test: results - 20 min 150°C

		sheeting mill	warm up mill	feeding mill	extruded tread	control rubber bales 3-step Banbury mixing
T.S.	MPa	16.4	16.1	15.6	16.0	17.6
EB	%	588	545	553	539	589
Mod 300	MPa	7.7	7.5	7.1	7.1	6.8
Tear strength	N/mm^2	52	43	42	42	42
Hardness	°Sh.A	62	61	59	60	59
Elast. 22°/75°C	%	27/39	28/45	28/45	28/45	32/47
Abrasion (DIN)	mm^3	150	156	160	157	161
sp. gr.		1.16	1.16	1.16	1.16	1.15

Tyre test: dimension 175 SR 14 (2 cars Daimler Benz 230 autom.) - 11250 km

	powder batch				control bale rubber			
Tyre	1	2	3	4	1	2	3	4
abrasion mm	3.31	3.40	3.27	3.38	3.29	3.29	3.15	3.26
$\bar{x}$		3.34				3.25		
index		97				100		
loss of weight g	655	620	780	750	680	720	650	740
$\bar{x}$		701				698		
index		99				100		

Use of special mixer-extruders

The most efficient utilization of the powder batch concept undoubtedly is the direct introduction of final powder compounds into special extruders (Figure 8). This requires an extruder screw design ensuring adequate shear action as pointed out before. This requirement is already being met by some special types that are commercially available. With this powder batch, satisfactory results have been obtained,for example, by the use of the EVK-system of Werner & Pfleiderer, the Maillefer-system of Berstorff and the MVX-system of Farrel. Table 7 shows the results of the direct extrusion of tread strips with an EVK 90 (Figure 9). The capacity was about 200 kg per hour.

With the use of suitable feeding devices for powder processing, such systems also afford the possibility of feeding the individual components directly into the extruder without premixing in a fluid mixer. On the laboratory scale it has been possible with the tread compound discussed, to effect direct feed of the individual components with full success (Figure 10).

TABLE 7. THE DIRECT EXTRUSION OF POWDERED BATCH TREAD STOCK

Equipment: EVK 90 (Werner & Pfleiderer)
24 D-screw; 180 kg/h, extrudate temp. 128°C
labour test results - 20 min., 150°C

		direct extruded tread	control, rubber bales 3-step Banbury mixing
Tensile strength	MPa	16.9	17.2
Elongation	%	511	561
Modulus 300	KPa	8.2	7.4
Tear strength	N/mm^2	40	42
Hardness	° sh.A	63	61
Elast. 22°/75°C	%	29/40	31/41
Abrasion (DIN)	mm^3	150	155
Compound ML-4		71	63

The approach to plastics technology is obvious. These powder batches also permit direct feeding to common automatic injection moulding machines that fulfill the requirement of sufficient shearing action. Tests with the powdered tread compound (according to Table 3) yielded moulded articles exhibiting fully satisfactory characteristics.

The advantages of the powder batch concept pursued by us - besides positive factors in production and storage - come out particularly well with the processing techniques demonstrated here. However, if compounds based on filler-free powdered rubbers with free carbon black are charged to the machines, much more mechanical frictional energy is necessary. This is understandable in view of the requirement of the additional step of incorporating the fillers into the rubber phase. As a consequence the demands made on the mixing and shearing zones become more stringent and the power requirements are incomparably higher.

The powder batches presented here allow to-day's processing technique to be cut down to a single stage process essentially without technical difficulty. This includes combination with continuous vulcanization facilities (UHF, LCM). The only disadvantage of the powder batch concept is the limitation in compounding regarding the amount of fillers. This can be easily overcome by the use of types with minimum amount of carbon black with the addition of further filler or by blending two types with minimum and maximum amounts of the same filler.

ADVANTAGES OF POWDERED RUBBER MASTERBATCHES

In view of the results presented it may be concluded that the advantages accruing from the use of powdered rubber masterbatches are much greater than the above mentioned disadvantages. The proven progress is summarized and explained as follows:

1. <u>No bale cutting necessary</u>

   The cutting of rubber bales represents a primary step in processing and requires capital, labour and time. Obviously, this operation is not needed with the use of powdered rubbers.

2. Use of automatic handling and feeding equipment

As a result of the pourability of the polymeric raw materials even conventional plants can be charged fully automatically. This cuts down sources of error and costs.

3. No premastication

Depending on the type of rubber used and the quality of the finished products the plasticization by mechanical degradation in the initial stage of the classical mixing process can be dispensed with. In this connection a number of the usual pre-batch operations could be abandoned.

4. Reduced mixing times in conventional plants

As shown by our studies, the capacity of internal mixers can be increased by a factor of three.

5. Reduced energy requirement

The reduction in mixing time consistently goes hand in hand with a reduction in energy consumption. The savings in this are greater than is to be expected from the reduction in mixing time since the peak load compared to bale rubber is reduced.

With the change-over to modern powder mixing equipment the energy requirement can be reduced to a fraction of the amount required with internal mixers!

6. Less maintenance costs of mixing equipment

Shorter mixing times and reduced energy usage will lead to less wear and tear. This greatly cuts down the sizeable expenditure otherwise required for maintenance.

7. Less heat generation of compounds

A result of the reduced energy consumption is the low conversion of mechanical work into heat. The discharge temperatures are reduced.

The problems especially with high loaded compounds are diminished.

8. Minimal impairment of the raw rubber

The reduction in shear forces is attended by a reduction in chain scissions due to mechanical tearing. Lower heat-up of the compounded material prevents undesirable gel formation.

9. Reduced scorching

High mixing temperatures shorten the incubation period in the subsequent vulcanization step. Mild mixing conditions thus reduce the danger of scorch and eliminate difficulties in moulding steps.

10. Use of faster curing systems

The reduction in scorching permits the use of fast-reacting accelerators with a view to increasing throughput rates in vulcanization equipment.

11. Lower investment in mixing capacity

The higher output achievable by the use of powdered rubbers will of necessity entail lower expenditure for mixing equipment.

12. Elimination of heavy mixing units

The powder state permits the replacement of expensive internal mixers by light and very low cost fluid mixers which moreover require only a fraction of the energy used today. With this technique the arguments given under 1 to 11 come into effect to an increased extent.

13. Optimum dispersion of ingredients

In powder mixers, the free flowing form of the rubber very rapidly permits a homogeneous dispersion of the finely divided additives and cross-linking agents within the micro-range. The most important requirement for the quality of the end-products is satisfied with greater certainty.

14. No expenditure for cooling energy

Since in powder mixing frictional energy is only produced to an insignificant extent, there is no expenditure for cooling devices.

15. Introduction of a continuous process

Powdered compounds can be fed direct to the usual moulding equipment such as transfer or injection moulding machinery, calendering or extrusion equipment. The latter may be combined with UHF vulcanizing units. Single-step process technology thus comes within the range of reality.

16. No pre-formation of pellets or feeding strips

With the direct processing of powdered compounds no labour and investment is necessary for the transformation of final compounds into feed strips or pellets for extrusion.

17. Simplified process control

The use of light machinery and the reduction of operations will of necessity lead to an easier and safer production procedure.

18. Increased degree of automation

The process technology simplified by the use of powdered rubbers and accomplishable on a continuous basis permits the use of most modern technical aids, especially of microprocessors. Besides further improved economy, this is a contribution to quality assurance.

19. Simpler quality control

As a result of the comparatively simpler mode of operation, the easier quality control associated therewith represents an obvious advantage (eg, use of T_{50}-test of ASTM).

20. Reduced labour cost

The reduction of process steps and the improvement in the degree of automation is of necessity attended by reduced operating effort. In highly developed countries this is a decisive factor.

21. Better ecology

The pourability of the compounds and automatic process control permit the use of closed systems. This is a contribution towards ecology and the humanization of job environment.

22. Economic operation of small production units

The reduction of energy and investment due to the use of rubber powders together with greatly simplified process technology permits the use of smaller production units of useful economic effect. This clears the way to an intermediate technology in production. Its particular importance to developing countries is obvious.

SUMMARY

Summarizing the results presented it may be concluded that the use of powdered rubbers, especially in form of the powdered batches developed by us, will lead to extraordinary technical and economic advances. As modernization of the existing machinery and equipment progresses, increasing profit can be derived from the powdered state of the batch. As has been shown, this product concept has already considerable advantages utilizing existing equipment. The many possibilities of different kinds of equipment and new developments in machinery will bring about drastic savings in the requirements and costs of rubber processing compared to common practice. Of particular advantage is the demonstrated possibility of a stepwise introduction of such powdered raw materials with a gradual transition from conventional techniques to the optimum continuous version (cf Figure 10).

In view of the large number of advantages argued a general switch-over to a rubber powder technology is most probably only a question of time. At the moment, the rubber industry lacks the initiative to a change over to such innovations. The poor overall earnings situation of this branch of industry in the past years along with a traditionally conservative attitude has so far revealed little mobility. For the moment, they tend to wait until the raw material manufacturers have made their decision. The latter in turn feel compelled to make investments only on market demand. In the near future, however, economic necessity will probably overcome this situation referred to commonly as chicken-and-egg syndrome. As an essential factor, the more and more precarious energy situation will strengthen endeavours along these lines. The impressive advantages regarding improved economics and better quality will undoubtedly pave the way for the rubber powder technology.

For its successful introduction the producers of natural and synthetic rubber have to provide the prerequisites by the provision of low-cost free-flowing elastomeric raw materials. We are firmly convinced that the powder batch development presented by us will be a contribution to prepare the ground for a successful future of the rubber industry.

Fig. 8.1
Surface structure of free-flowing powder.

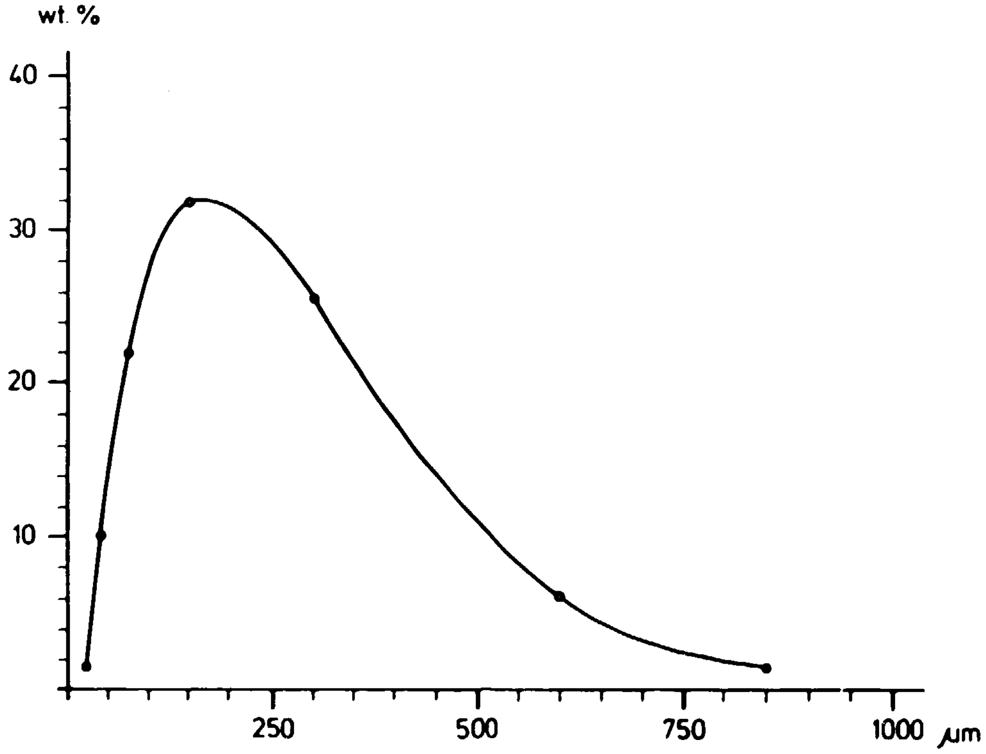


Fig. 8.2 Typical particle size distribution of a free-flowing rubber powder.

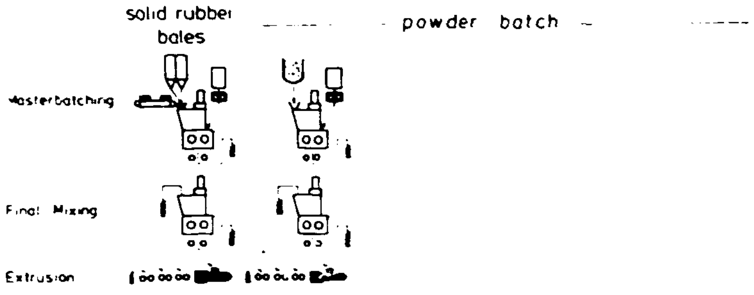


Fig. 8.3
Illustration of a two-stage Banbury mixing process using bale rubber (col.1) and powdered masterbatch (col.2).

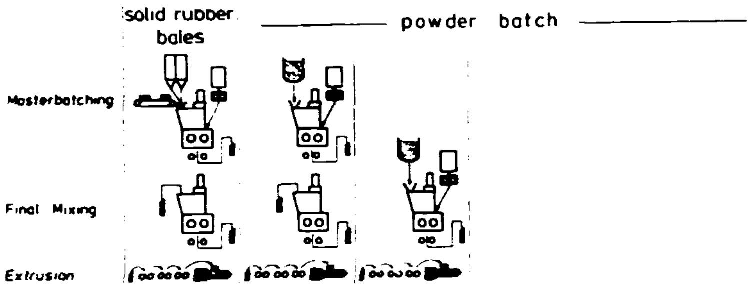


Fig. 8.4
A single stage Banbury mixing process (col.3) of powdered materbatch to replace two-stage process.

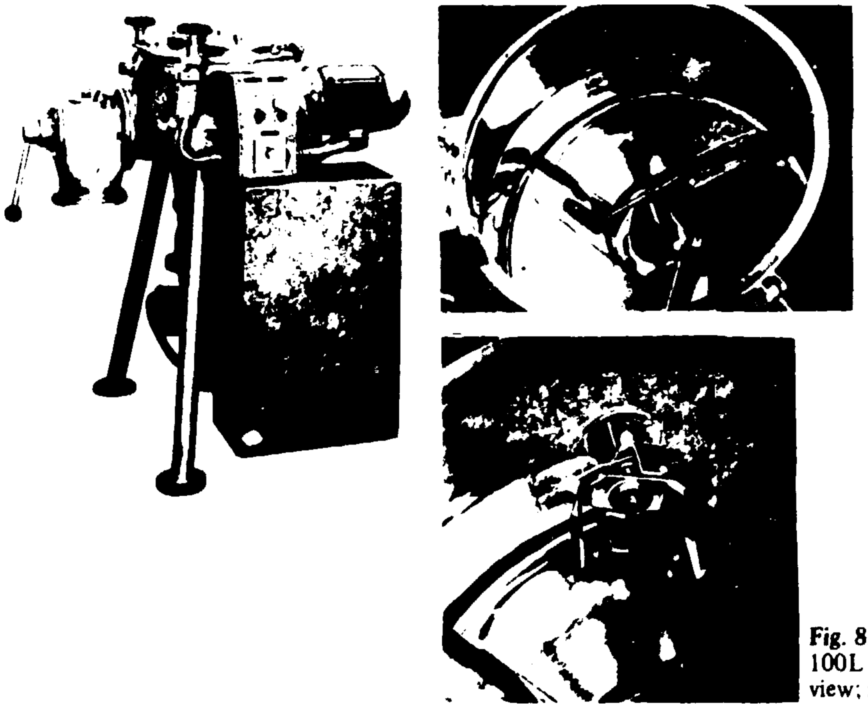


Fig. 8.5
100L DIOSNA mixer: left, general view; right, details of mixing unit.

Fig. 8.6
Direct feed of powder compound to mill giving rapid and easy sheet formation.

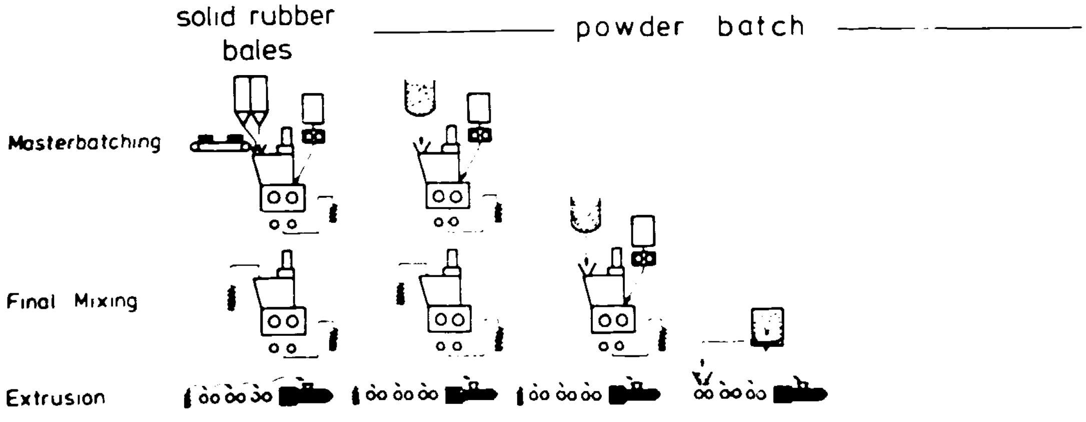


Fig. 8.7 Possible continuous process using conventional equipment, involving feeding powdered compound directly on to pre-heating rolls and the resulting sheet to an extruder (col.4).

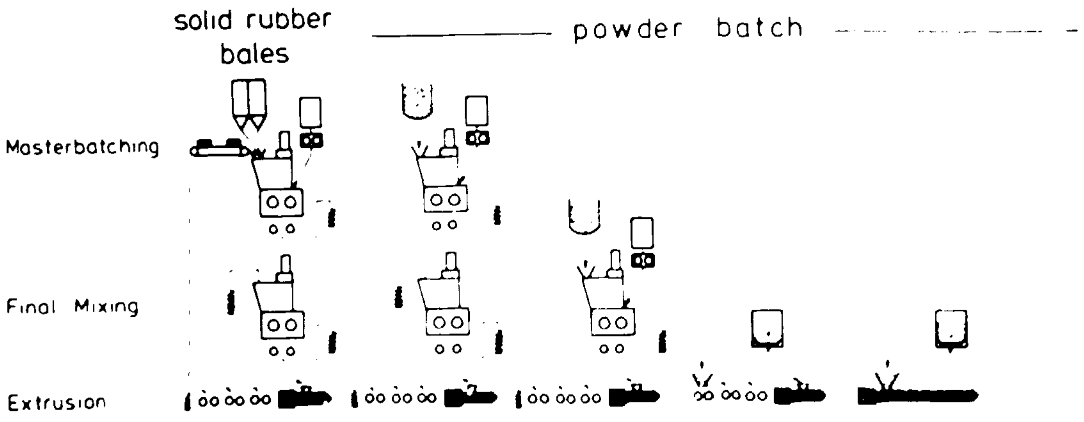


Fig. 8.8 The direct feeding of powdered compound to special mixer/extruders (col.5).

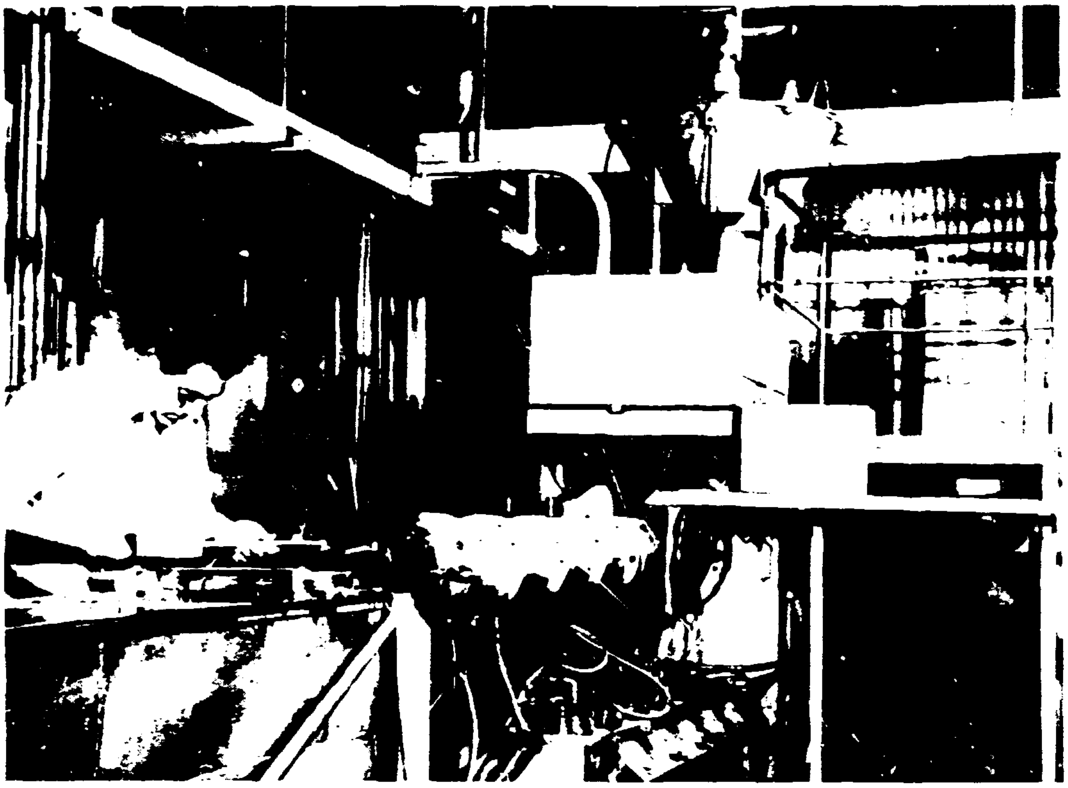


Fig. 8.9 Direct extrusion to tread strips with an EVK 90 unit.

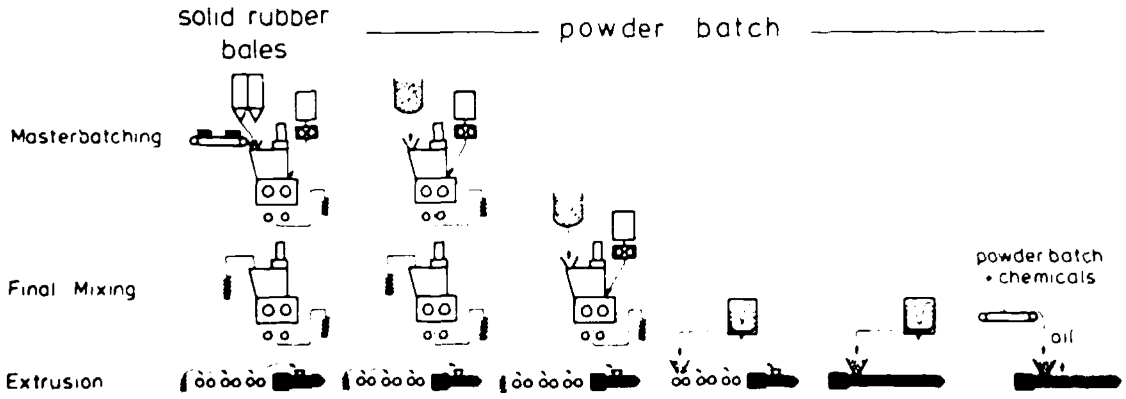
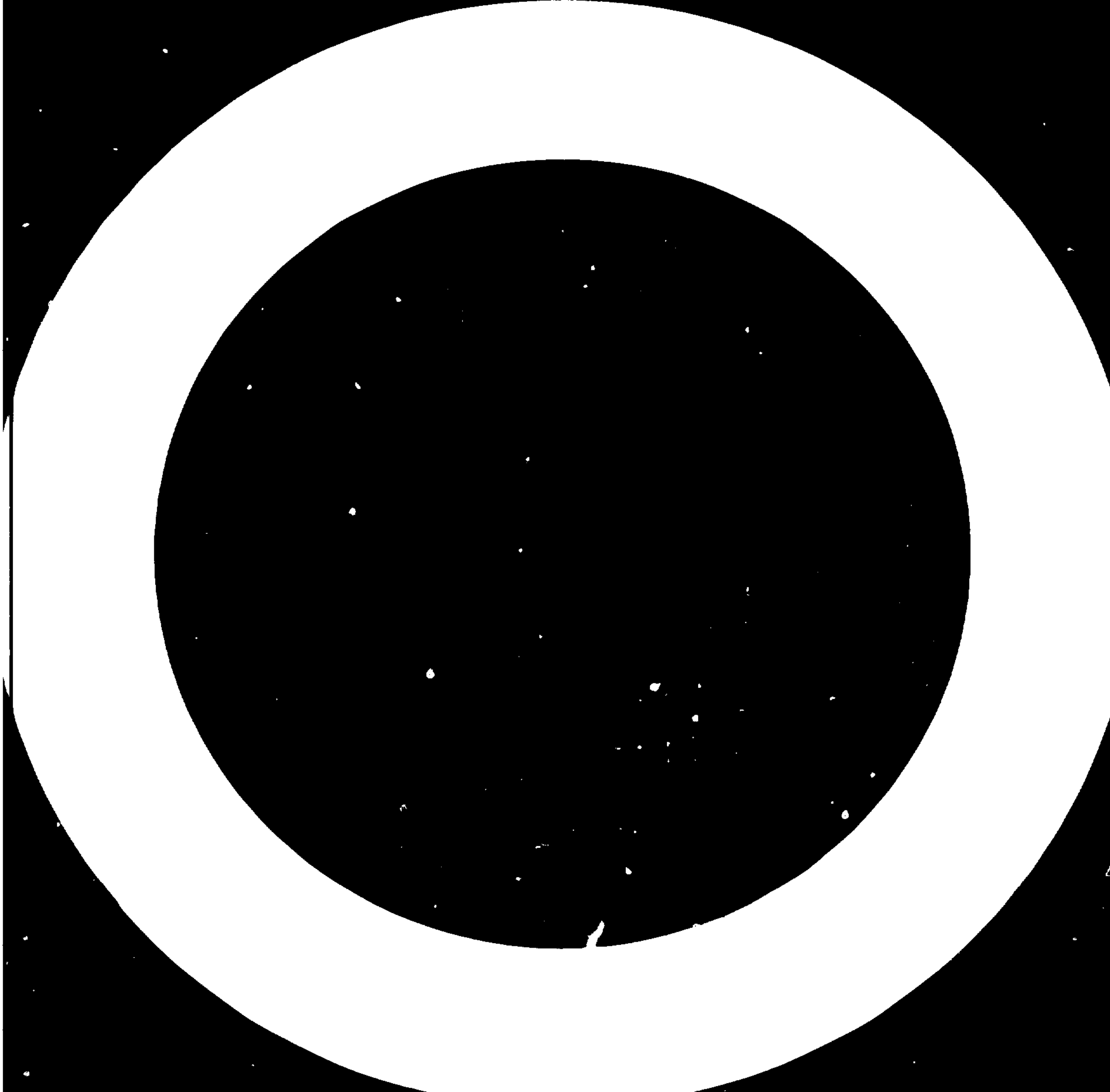


Fig. 8.10 Direct feed to mixer/extruder of powdered black materbatch and other ingredients of tread-stock compound without prior powder blending (col.6).



PREPARATION OF NATURAL RUBBER GRANULES BY LATEX FLOCCULATION

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INTRODUCTION

The rubber consuming industry is in search of greater simplification and automation of its operating processes. The transformation of solid elastomers, as it is currently performed, requires heavy and energy-consuming equipment, which usually works intermittently (hence large expenses in terms of manpower and operating cost). Besides, in industrialized countries, transformation techniques will have to progress towards improved working conditions and industrial health, which also implies progress in the field of operating processes.

As far as natural rubber is concerned, improvements of this kind are therefore foreseeable for the next decade. However, the use of new forms of high-molecular weight rubber (powdered elastomers) likely to bring about decisive improvements is countered by technical-economic difficulties met by rubber producers, transformers, and equipment manufacturers. The various facets of this problem have been studied by several authors [1-5]. Improvements in terms of packaging and consistency of rubber batches have already been achieved with the commercialization of small-dimension bales (compact rubbers and compacted granulated rubbers). However, the greater part of the work is still to be done in view of stringent technical and economic requirements. From a technical point of view, every change in operating conditions will result in a level of mechanical properties of vulcanizates close to that of the rubbers currently in use. From an economic point of view, the cost of elastomer enters by approximately 20-25% into the final production cost. Therefore, it is essential for the development of fine granular rubbers that the premium related to their production may remain lower than approximately 3-5% of the value of elastomers in bulk (depending on their use).

In 1972 a DELPHI enquiry[6] conducted in the USA stated that - subject to the above requirements - more than half of industrial mixes could be produced in continuous operation from granular elastomers in the 1980-1990 decade.

SPECIFIC PROPERTIES OF POWDERED RUBBERS

The advantage of a granular or powdered elastomer lies essentially in its easy utilization. The methods of transformation in continuous operation (injection, extrusion) should have a significant impact on manpower and energy, not to mention industrial health which becomes more and more important at the transformers' level.

If we come back to the technical point of view, one advantage that could be important comes from the lesser heating of the mixes during their utilization, which could make it possible to achieve a complete mixing in a single stage and to use more rapid vulcanizing processes. A 30 to 40% cut in the mixing operation cost could offset the maximum premium which granular rubber can stand. It is essential, at least in the first phase, that these forms of elastomers may be used with conventional equipment so as to defer new investment and to improve machinery progressively.

It is already expected that masterbatches consisting of powdered rubbers and filler (with possibly other ingredients) will be obtained. Encouraging results have already been achieved with special equipment, but the mechanical properties and, particularly, the dynamic characteristics in black-filled mixes still remain inferior to those of conventional rubbers. This is mainly due to some problems of filler dispersion within the powdered elastomer and to lesser mechanical-chemical shearing effects during mixing, which affects strengthening. It seems that granules 1-5 mm in diameter are more appropriate for operating with a traditional apparatus, whereas powders (less than 0.5-1 mm in diameter) are more suitable to be used with continuous-operation techniques and for the preparation of adhesive solutions. In the case of powders, the search for a very small granule dimension rapidly entails a high operating cost.

The main disadvantages of powdered rubbers result from their very nature. First of all, the packaging, storage and transport conditions for these products, which are considerably cumbersome in volume, increase their costs in comparison with conventional bale rubber.

Certain varieties of powdered rubber exist in the field of synthetic elastomers. As regards the studies on natural rubber, let us quote among many those conducted by IFC in co-operation with IRCV. At that time the economic balance sheet was not favourable because granule processing intended to avoid their re-agglomeration, added to packaging problems was prohibitive. At the present time, it seems that there is only one production located in Malaysia (Harrisons and Crosfield[5]), limited in tonnage and mainly attractive in the field of adhesives.

PREPARATION OF NATURAL RUBBER GRANULES

Several methods exist to obtain natural rubber in various forms, from coarse grains produced by simple shredding to fine powders made of grains approximately 1 mm in diameter. The techniques most commonly used consist in mechanically grinding bale rubber or latex coagulum, whether or not in the presence of products likely to prevent particles from reagglomerating during storage and transport. These grinding techniques can also be applied at low temperature, *eg* in liquid nitrogen. Generally, these mechanical processes, which require a currently reliable equipment, entail a non-negligible energy consumption.

Other processes of preparation from latex are also used: atomization of an aqueous dispersion of rubber on a heated wall or micro-flocculation by the addition of acids or electrolytes. Considering the tack specific to natural rubber, one of the main problems to be solved is the non-reagglomeration of elastomer particles, while avoiding the use of large quantities of partitioning agents which are detrimental to the rubber properties as well as from an economic viewpoint. Attempts are being made, particularly by RRIM, to substitute these separating agents with a superficial chemical treatment of rubber by halogenation. However, it is to be feared that this technique will yield relatively unstable rubbers.

Work of IRAP Relating to the Preparation of Granulated Rubbers

Within the framework of a study agreement with IRCA, an investigation was conducted on the use of fine silicas so as to avoid the irreversible reagglomeration of the rubber granules obtained by latex flocculation by means of aluminium sulphate[8]. In fact, fairly fine, compactable rubber granules were obtained in the form of bales, the latter thereafter remaining easy to disintegrate. However, a slowdown was observed in the vulcanizing rate as well as a decrease in mechanical properties (after ageing) in comparison with bale rubber.

Therefore, another method was searched for to eliminate rubber tack without the introduction of mineral filler into the granules or chemical treatment. Certain molecules, purely organic, were selected because of their compatibility with natural rubber, but it is not possible at the present time, for proprietary reasons, to disclose the chemical structure and the action of these new products (available at a moderate price). Advantages are expected of their use, such as:

- partitioning agents, permitting however, for transport purposes, a reversible compaction of rubber granules, either by compressing or by packing them in thermoretractable small bags
- regulating agents, controlling the vulcanizing rate of rubber and/or including chemical groups acting as antioxidants.

The granulated rubbers obtained from these products are prepared by latex flocculation in the presence of an aluminium sulphate. The partitioning agent is then introduced in a proportion of 2 to 3% with respect to dry rubber. This process yields rubbers which contain neither silica, nor halogens, nor mineral element except those present in the initial latex. They are compactable, but disaggregate easily.

After vulcanization, the rubbers have the properties shown in the Table. For adapted formulations, vulcanization kinetics are not changed compared with those of control rubbers.

TABLE MECHANICAL PROPERTIES OF POWDERED RUBBER AND A SMOKED SHEET CONTROL SAMPLE

	UNFILLED		BLACK FILLED	
Property	POWDER	SMOKED SHEET	POWDER	SMOKED SHEET
Tensile Strength, MPa	26.3	29.4	26.5	29.8
M300, MPa	-	-	11.3	12.5
M500, MPa	6.2	11.1	-	-
Elongation at Break, %	740	645	570	590
Tear Strength, MPa	4.2	6.0	10.5	11.8
Hardness, Shore °	39.5	44	66	63.5

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CRUSOE, THE POWDERED NATURAL RUBBER

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INTRODUCTION

The concept of powdered rubbers is not new. As early as 1920 patents relating to the production of powdered natural rubber were applied for, and although these were not entirely satisfactory, patents which were applied for a little later in 1927 did produce what might be termed 'particulate rubber', where the particulates were encapsulated in a small proportion of ethyl methylcellulose and a suitable caseinate. Since these patents there have been several attempts to produce powdered rubbers, particularly from spray dried latex, and a commercial plant was built in N. Sumatra in the mid-1930s. This plant did not, however, produce powdered rubber, the dried rubber was collected on a moving conveyor at the bottom of the chamber and then pressed into blocks.

In the late 1960s the Harrison & Crosfield Research Laboratory in the UK examined the feasibility of producing a free flowing product from natural rubber. Various production methods, including mechanical comminution of block rubbers, were considered. However, the spray drying technique was selected, primarily because of the ease of converting the latex into a dry product in a single stage operation. Initial pilot plant studies were carried out in the UK and, after some promising results, a patent was applied for and samples sent to potential customers who showed a keen interest in the product.

Following customer assessment of the UK produced powdered natural rubbers, a decision was made to construct a commercial plant in Malaysia with a production capacity of about 250 - 300 tons per month. The plant (Figure 1) was completed in April 1975, and although giving a similar product to that produced in the UK, there were a considerable number of inherent problems which had to be overcome; the major one being to improve the free flowing characteristics and to stop the process of re-agglomeration, which appeared to be more troublesome than with the product produced in the UK. Secondly, a market evaluation of the product had to be carried out to try and suit customers' requirements which necessitated considerable product development.

PRODUCTION OF POWDERED NR (CRUSOE RUBBER)

1 Process of Manufacture

The flow chart (Figure 2) shows the process presently in use. The features of the process of manufacture are:

(a) Creaming. Field latex which is ammoniated to 0.45% weight on latex is treated with laurate soap and hydroylamine neutral sulphate for both mechanical and viscosity stabilisation, respectively. The latex is then creamed for 14 to 36 hours to about 55% drc with sodium alginate as the creaming agent. The Zahn cup No. 2 viscosity of the creamed latex should, at this stage, be at least 23 seconds. Natural rubber latex as collected from the tree contains about 35% weight total solids and has a Zahn cup viscosity of about 16 seconds. We confirmed in our original trials in the UK that when a latex of this type is subjected to spray drying, it is not possible to carry out the spray drying procedure satisfactorily for more than about 90 minutes because of blockage around the atomiser caused by solid rubber deposits even if the latex is suitably stabilised. If the viscosity is raised to at least 23 seconds and spray dried under identical conditions, it is possible to continue the spray drying procedure for over 24 hours at least. In principle, only the lower viscosity limit is of importance, and in practice we have found that optimum results can be obtained by the use of latices having a viscosity of 23-30 seconds. The use of latices having a viscosity in excess of 30 seconds is possible, but it is not usually economically practical because of the practical difficulty of handling liquids of such high viscosity, and the expense of producing latices of that viscosity which would have a total solids content well in excess of 60%. It is, therefore, preferable to operate with latices having a viscosity of about 25 seconds. Viscosity increases with total solids content and it is possible to concentrate a natural rubber latex by centrifuging so its viscosity will reach at least 23 seconds and its solid content reaches at least 60% by weight. However, it was found preferable not to adopt centrifuging to increase the solid content of the latex due to the high capital cost of the centrifuge and of the relatively large rubber losses that occur in the production of concentrated latex by this method. Loss of rubber solids in the creaming process is about 2 - 2.5% as opposed to 5% in the centrifuging process.

(b) Spray Drying. The creamed latex having a viscosity of around 25 seconds and a solids content of about 55% [illegible] may be spray dried by conventional techniques. This involves atomising the rubber latex in a stream of hot gas which permits rapid heat and mass transfer. Atomisation is effected by controlled feeding of the creamed latex on to a 14.5 in. diameter inverted-bowl disc revolving at a speed of 6,400 rev/min. The air is heated to a temperature of around 200°C, into which Ultrasil VN3 is introduced immediately prior to entering the spray chamber; under these conditions the rate of drying is measured in seconds and micro-seconds. The majority of the rubber particles impinge and tend to agglomerate on the chamber wall; a rotating scraper arm sweeps down the product which falls in the form of soft lumps on to a conveyor at the chamber bottom. The fine VN3-rich rubber particles are carried away in the effluent air which passes through a cyclone to effect primary separation of the coarser particles. Recovery of the very fine particles is achieved in a bag filter or dust collector.

2 Particle Size and Screening

As previously mentioned, due to the design of the current spray dryer, a large number of rubber particles impinge and agglomerate on the chamber wall ; therefore, a relatively large particle size distribution of the rubber is obtained. This is undesirable for certain applications, and in order to produce a rubber powder of substantially uniform particle size, the product ex spray chamber is subjected to milling and subsequent screening. Rubber produced by spray drying is relatively porous, and by passing it through a hammer mill followed by screening, it is possible to obtain a final product having a reasonably uniform particle size.

3 Cooling and Post-dusting

The product is pneumatically conveyed to the end of the process line, where it is cooled and post-dusted. Further dusting is applied after screening to ensure that subsequent agglomeration will not take place and that uniform particle size will be maintained. In our original process we installed three storage silos and a small mill. The silos were meant to store the product until it had cooled to ambient conditions to ensure that it was completely free flowing before final packaging. This method of cooling proved, unfortunately, impractical, since by the time the product had cooled re-agglomeration had already taken place. The post-dusted product finally enters a sack filler where it is packed in four-ply paper bags, each being filled to a net weight of 20 kg. As they leave the process line, the bags are immediately stacked four layers high in a wooden pallet which has internal dimensions of 31" high, 42" long and 55" wide. The platform at the centre of the pallet separates the two layers from the one at the edge, the aim being to minimise compaction during storage.

4 Free-flowing Properties and Re-agglomeration

Following the commissioning trials in 1975, it was found that the plant in the original state was not able to produce a product which had the ability to remain free-flowing for an indefinite period of time. Initially the powder obtained ex-process lost its free flowing characteristics to form a re-agglomerated lump in just a matter of hours. Increasing the Ultrasil VN3 content from 6% to levels in excess of 10% did not prevent re-agglomeration. Initially the process of re-agglomeration was linked to the hygroscopic nature of the product, particularly on exposure to Malaysian ambient conditions which obviously had not been experienced during trials in the UK; the moisture content increased from a level of about 0.6 to about 2% in 48 hours. Whilst the rubber itself is inherently hydroscopic, there is ample evidence to show that this characteristic was enhanced by the presence of the Ultrasil VN3. It was, however, thought, though subsequently proved to be untrue, that the particle size ratio of the Ultrasil VN3 to rubber particles was not satisfactory for the VN3 to form an encapsulation around the rubber particles. A search was initiated to look for possible substitutes for VN3. A considerable number had already been evaluated in the UK and these were eliminated from the Malaysian trials. In all some 50-60 partitioning agents were examined, including Cabosil which is reported to have a particle size in the sub micron range which, it was believed, would effectively coat the latex particles in the chamber to prevent re-agglomeration. However, despite its small particle size Cabosil was not found to be a satisfactory partitioning aid; in fact re-agglomeration occurred considerably faster with this product than with Ultrasil VN3. Cabosil was also more expensive than VN3 and would have been uneconomical to use. Other silicas which are reported to have a particle size similar to VN3 and also reported to be hydrophobic, were only able to compare similarly with VN3 as a partitioning agent; costwise they were 3 - 4 times more expensive than VN3. Other partitioning agents such as talc, had to be used in considerably larger proportions to obtain free-flowing characteristics and gave an ash content far outside the required specification. The use of magnesium carbonate was also investigated but, apart from the possibility of explosion hazards in the spray chamber, similar re-agglomeration problems as with VN3 were experienced and hence experimentation with this material was discontinued. Ultrasil VN3 is, therefore, still being used despite its inability to maintain complete flowability for a long period. Only limited improvement to flowability has been achieved by adding further VN3 at the post-dusting stage. In view of this problem the process of post-dusting was, therefore, further investigated.

One of the problems of adding VN3 as a post-dusting agent was that the product became rather dusty. It was, therefore, decided to try a metal stearate as a damping product to prevent this dusting, and zinc stearate and calcium stearate were used for this purpose. These metal stearates were found to assist in reducing the dustiness and at the same time gave further improvements to the free flowing characteristics. The zinc stearate gave much improved free flowing characteristic properties but, unfortunately, was found to be unsuitable as a post-dusting agent due to its effect on the plasticity retention index of the rubber. Calcium stearate gave a reasonable product and did not unduly affect the PRI. The product on leaving the spray dryers is at a temperature of about 50°C, and in addition to post-dusting, it has been found necessary to first reduce the temperature to about Malaysian ambient, namely, 30° - 33°C, otherwise partial re-agglomeration will occur. A mechanised cooling system was installed so that both cooling and post-dusting could be carried out at the same time.

5 Product Specification

Two grades of Crusoe are currently being sold to the trade; these are Crusoe Standard and Crusoe NS. The Crusoe Standard contains hydroxylamine neutral sulphate. The specifications are shown in Table 1.

TABLE 1 SPECIFICATIONS[1] FOR CRUSOE RUBBERS (RAW POLYMER)

	Crusoe Standard[2]	Crusoe NS[3]
Ash content, max % w/w (at shipment)	8	8
Volatile matter, max % w/w (at shipment)	1	1
Plasticity retention index, min %	60*	60*
Mooney viscosity, ML1+4 at 100°C	70 ± 5	90 ± 10
Particle size	100% <4 mm* 60% <2 mm	100% <4 mm* 60% <2 mm
Colour coding marker	Black	Black
Packed in paper bags	20 kg	20 kg

[1] Testing for compliance shall follow ISO test method

* Not guaranteed

[2] Crusoe Standard is a spray-dried natural crumb rubber, viscosity-stabilized by the addition of hydroxylamine neutral sulphate to give a rubber of Mooney viscosity 70 ± 5.

[3] Crusoe NS is a spray dried natural crumb rubber. It is not viscosity stabilized and viscosity loads are therefore higher than those of Crusoe Standard at 90 ± 10.

For each type a fine particle inert silica is used as the partitioning agent and 0.15% of a non-staining, non-toxic rubber antioxidant is added at the latex stage.

The particle size of the final Crusoe product is mainly dependent upon the Ultrasil VN3 content. Increasing the VN3 injection at the spray chamber will bring about a reduction in particle size. With the final content of the partitioning agent at about 6%, the size distribution of Crusoe Standard and Crusoe NS is found to be within 5 - 6% of the 2 mm limit.

6 Powdered Rubbers

Low viscosity powdered rubbers can be produced by choice of clones or by peptisation with peptisers such as Renacit V11. Unfortunately with viscosities below 55 Mooney, the product is considerably more prone to re-agglomeration. Whilst it is possible to peptise latex grades of block rubbers at low levels of peptiser - additions of 0.01% being normal - it is is not possible in the production of powdered rubber to have the peptiser at this low level. Possibly this is due to the short drying time in the spray chamber which is inadequate for promoting the complete peptiser rubber reaction. At levels of 0.15% of peptiser there is always residual left in the powdered rubber and this residual peptiser does appear to cause some problems in re-agglomeration. Peptisation can, however, be carried out at the compounding stage and this will be discussed later.

7 Production Costs

Unfortunately, since making a decision to proceed with the commercial production of powdered rubber, there has been a three-fold increase in the cost of energy. This has resulted in increased drying costs, hence the spray drying technique does not have the same cost efficiency as was originally estimated; the high cost of processing is accounted for by the cost of fuel and electricity. The non-manufacturing items which increase the costs are packaging materials and freight which, due to the fact that the Crusoe is half the bulk density of block rubbers, increasing the shipping costs quite considerably. The current premiums for Crusoe over Harub SMR CV are FOB 13 p/kg and CIF 18 p/kg.

COMPOUNDING AND USE OF POWDERED NATURAL RUBBER

1 Rubber Solution and Adhesive Applications

Natural rubber has for many years been used as a base for adhesives, mainly because of its excellent green and cohesive strengths. Powdered natural rubber has shown considerable advantages in respect of dissolution times where the rubber has been let down in organic solvents, and dissolution times can be reduced to a quarter of those required to dissolve comminuted or sheet rubbers. There are also other economic advantages in using powdered rubbers for solution products:

- handling is greatly improved;
- weighing can be carried out easily and accurately;
- the laborious task of knife cutting the rubber to get accurate weighing and the need for bale cutting is completely eliminated, thus providing savings both in manpower and equipment.

Powdered rubber is ideal for adhesive manufacturers who are involved in producing small batches of specialist products. A further advantage in using powdered rubbers is that no pre-mastication is required and dissolution time is fast due to the fine particles of the rubber (Figure 3). Mixing machines for adhesives vary very widely, from the slow moving type to a mixer with a rapidly rotating stirrer. Due to the differences between machines the extent of comminution and molecular weight of the rubber dissolution times can vary greatly, taking anything up to 24 hours or more. When using a powdered natural rubber this mixing time can be as short as one hour, and reports from adhesive tape manufacturers inform us that mixing times are reduced from eight hours to one hour.

The correct Mooney viscosity of the rubber is very important to adhesive manufacturers. Normally to reduce the viscosity of a rubber it is necessary to either masticate the rubber for long periods on a mill with or without peptiser. With powdered rubbers this would tend to destroy the free flowing characteristics and would completely defeat the object of purchasing powdered rubber. Initially it was thought that the only satisfactory means of producing the correct viscosity would be at the time of production to select latices of a low Mooney type and stabilise the Mooney viscosity with the use of hydroxylamine. Recently, however, laboratory work has shown that it is possible to peptise powdered natural rubber in a turbo mixer at elevated temperature (80°C) in the presence of special peptising agents without destroying the free flowing characteristics. Due to the fact that spray dried powdered natural rubber remains unmasticated it generally has a much wider molecular distribution than milled rubber of equivalent Mooney viscosity. This affects the rubber solution in the following manner:

(1) The solution viscosity of the adhesive using a spray dried rubber will be higher than that using a milled rubber of similar Mooney viscosity. To eliminate the difference in solution viscosity, it is necessary to replace partially some of the powdered rubber with a low molecular weight polymer or to replace some of the solvent with a different type of solvent which is miscible with the main solvent but is of a type in which the rubber is not soluble, for example, methanol.

(2) Due to the presence of long chain molecules, the green strength or cohesive strength of the adhesive based on spray dried natural rubber is notably improved over that of a milled rubber of equal Mooney viscosity.

(3) A slight loss of tack will be experienced when using spray dried powdered rubber as compared to milled rubber, due to the presence of a partitioning agent. This deficiency can be alleviated with the use of increased levels of resins or resins of higher quality.

The particle size of powdered natural rubber, within limits, has little effect on the rate of dissolution of the rubber. Figure 4 shows that of a range of particle sizes between 0.7 and 2.8 mm, only the smaller particles initially dissolve more rapidly; total dissolution time of the range of different particles is similar. Applications which have shown particular advantages for powdered natural rubber are proofing, rubber/asbestos jointings, industrial tapes and surgical tapes.

2 Dry Rubber Processing

The largest potential usage of powdered rubber is in the non-adhesive sector. However, whereas the adhesive industry can utilise powdered rubbers with virtually no change in processing methods or formulations, a completely new area of technology is having to be built up around powdered rubbers for extrusion and moulded products. The advantages which are being looked for when using powdered natural rubber include lower capital equipment costs, increased production and simpler processing techniques, such as automatic fabrication, and, finally, higher quality finished products. Powdered natural rubber has been studied to assess its suitability for processing with conventional equipment and also for equipment more specifically designed to process powdered polymers. It has been shown that a pre-blend of powdered natural rubber compound can be mixed in an internal mixer in about half the time of a conventional rubber compound. A similar reduction in open mill mixing time can also be made by using a powdered pre-blended natural rubber.

It is in this latter type of mixing where Crusoe has been found to have considerable advantages. With rubber manufacturing plants which have a limited production, the use of an internal mixer is not normally economical due to its high cost and this, therefore, has meant that the factory always has to depend upon open mill mixers. Open mill mixers have shown various drawbacks:- the long time involved in mixing; wear on the mixer; the impossibility of keeping the factory hygienically clean for high-quality articles produced; the need to pre-cut the rubber bales which is costly and time-consuming, particularly in winter; and also the fact that it generally proves impossible to synchronise the operations of the open mill with those of the calender or sheeting mill.

When switching to Crusoe the consumer has found that he is able to eliminate the cutting and pre-mastication of the rubber; the size of the bag (20 kilos) has made weighing extremely simple; all the ingredients necessary for the mix can be introduced simultaneously into a turbo mixer with the result that dispersion is complete within less than five minutes and there is no escape of dust from the turbo mixer. The dispersed materials when placed upon an open mill rapidly form a sheet which can readily and safely be worked by a mill operator without any problems of dust. The consumption of energy is about 30% lower and productivity is considerably increased, since the mixing time using powdered natural rubber has been at least halved. The quality of the final products has been improved, with the result that it has proved possible to introduce increased quantities of filler and oil without detriment to the high standards of production set by the factories.

Mixing trials carried out on a Shaw K2A 30 litre internal mixer comparing powdered natural rubber with block rubbers, showed that Crusoe powdered natural rubber could be mixed successfully in an internal mixer with lower average power consumption and improved dispersion of ingredients (Table 2), particularly when an 'upside down' type mixing technique is used. It has been found very convenient and advantageous to fill polythene bags with a powdered pre-blend as discharged from the Turbo mixer, to the correct batch weight. The bag can be simply dropped directly into the internal mixer, or sealed and stored from moisture and air until used. The polythene acts as an additional plasticiser, and as long as the bag is made from thin gauge polythene no problems of dispersion will occur.

Efficient processing of powdered natural rubber starts with obtaining a satisfactory blend of the polymer and compound ingredients. This can be achieved by simply putting all the ingredients into a bag or stirring the ingredients together to effect a reasonable degree of success when the compound is mixed in the internal mixer. However, the optimum physical properties of the compound cannot be obtained by using this method and there is also the problem of dispersing liquid ingredients.

TABLE 2 K2A MIXING OF CRUSOE AND BALE NR

'Upside-down' cycle; 5 min mix at 25 rpm, 45 parts phr black

Rubber	Black	Peak Power (kW)	Mix Energy (kWh)	Dump Temp.* (°C)	Batch Viscosity	Black Dispersion (Cabot) rating)
SMR 5L	HAF	225	5.27	115	96	H2-4
Crusoe		110	4.87	119	89	E1-4
SMR 5L	FEF	198	5.25	118	85	H1-4
Crusoe		90	4.67	110	66	E1-3
SMR 5L	SRF	255	5.32	116	74	G1-4
Crusoe		90	4.28	102	55	C1-3
SMR 5L	MT	200	5.15	108	62	D1-3
Crusoe		75	4.05	96	46	B1-2

* Dependent upon starting temperature

A turbo powder mixer is essential to obtain adequate dispersion and optimum physical properties of the compound. A turbo mixer also has the advantages of breaking down and dispersing glomerates of both polymer and filler and of adequately dispersing the liquid ingredients. The method in which a powdered natural rubber compound is pre-blended does have an effect on the physical properties of the vulcanisates. The most important parameters are turbo mixer speeds. These have been found to be very critical. Table 3 shows the effect of different rotor speeds on a simple rubber compound using calcium carbonate as the filler. Pre-blend mixing time is important, but it has not been found to be as critical as rotor speeds. At slow rotor speeds the time of mixing, however, does appear to be very important (Table 4).

TABLE 3 TURBO-MIXING POWDERED RUBBER PRE-BLENDS AT DIFFERENT SPEEDS

	Rotor Speed	Tensile Strength (MPa)	Hardness (IRHD)
A	2' at 250 rpm. 5' at 500 rpm	16.2	70
B	2' at 400 rpm. 5' at 800 rpm	17.7	65
C	2' at 750 rpm. 5' at 1500 rpm	18.6	64
D	2' at 1000 rpm. 5' at 2000 rpm	16.7	53

Powdered natural rubbers offer alternative processing routes to the ones described above. By using what could be termed as 'mixer extruders' - these are continuous mixing and venting extruders, such as the Farrel Bridge MVX, Werner Pfleiderer EVK Extruder and the Farrel Bridge Continuous Mixer - turbo mixed material can be fed to these continuous mixers and the strip or diced product produced can be fed to conventional extruders for the production of hose or cables or other profiles, or fed direct to

TABLE 4 EFFECT OF TURBO-MIXING TIME VARIATION

Mixing Time (min)	Cure Time (min)	EB (%)	TS (MPa)	Hardness (IRHD)
4	5	690	15.7	55
5	5	730	16.7	54
6	5	730	17.1	53
7	5	720	17.9	55
8	5	760	18.1	53
9	5	700	16.2	56
10	5	690	16.5	57
12	10	680	14.7	59

injection moulding machines. Direct shaping of the profile by the continuous mixers is also possible if the extrudate is passed direct to continuous curing by the LCM or microwave method, and these techniques should offer considerable savings. Satisfactory compounds have been produced using powdered natural rubbers on the three machines mentioned above for high-quality hose extrusion, cheap flooring and high-quality rubber weathering strips. The physical properties of the compound taken direct from the MVX extruder is shown in Table 5. It has also been possible by using the MVX continuous mixer even to reduce the cost of the flooring compounds, since the quantity of rubber used can be lowered to a level below that which could normally be used in a Banbury to obtain suitable continuous calendered sheet for moulding.

TABLE 5 ENGINE MOUNT COMPOUND PROCESSED ON FARREL BRIDGE MVX

Physical Properties	
Hardness, IRHD	50
TS, MPa	23.3
EB, %	550
M 100, MPa	1.71
M 300, MPa	7.68
M 500, MPa	20.0

Formulation Crusoe NS, 100; Aromatic Oil, 3; SRFN 762 Black, 20; Stearic Acid, 2.3; IPPD, 1; Zinc Oxide, 10; PVI, 0.5; MBTS, 1; S, 2.2; Mooney Viscosity, ML 1+4, 100°C, 90; Optimum Cure at 150°C, 14 min.

The use of these continuous mixers with powdered rubbers is discussed at some length in the paper by M.A. Wheelans.

One particular development for the use of spray dried powdered natural rubber where its unique ability to absorb relatively large quantities of oil can be used to advantage, is for the manufacture of winter tyres. A compound has been developed which exhibits improved skid resistance on ice compared to other winter tyre formulations and with relatively good abrasion resistance (Table 6).

TABLE 6 CRUSOE WINTER TYRE COMPOUND

Crusoe (standard)	107
Zinc Oxide	3
Stearic Acid	2
Sulphur	2.25
Paraffinic Wax	3
Carbon Black SRFN 762	50
Dutrex 729	75
Santoflex 13	1
Flectol H	0.5
Santocure CBS	1.5
TMTM	0.2

	Crusoe Compound	Standard Compound 1	Standard Compound 2
Hardness, IRHD	32	64.5	48
Abrasion loss, Akron mm^3/500 rev	26	21	32
Skid test, Road Research Laboratory Pendulum Tester, -16°C	65	41	46

3 Soft Compounds and Sponge from Powdered NR

It is possible by using very simple processing techniques to produce solid natural rubber compounds which have a hardness level below 20 IRHD. It is also possible to utilise this technology to manufacture sponge and other microcellular types of rubbers without the necessity of long mixing cycles or the use of high levels of chemical peptisers to produce the low viscosity compound required in the manufacture of these materials. Micrograph studies of spray dried natural rubber have shown that there are voids present within each particle, so increasing its effective surface area; these factors, including the wide range of particle size analysis where particles range in size from 0.125 mm - 2 mm, give the spray dried natural rubber a unique ability to absorb relatively large quantities of oil (up to 200 parts phr) particularly in the presence of fillers. In order to produce very soft compounds, the mixing process is normally in three stages:

(1) All the dry ingredients, including the powdered natural rubber, are blended together. This is achieved by the use of the turbo mixer.

(2) The second stage is the addition of the process oil; this can be achieved either by adding the oil slowly into the powder blending machine, which must be running at a slow speed of not greater than 250 rev/min. By running the powder blender at this slow speed, all the natural rubber particles receive an even coating of oil. After completing the mix and discharging into a polythene bag, at least four hours should be allowed for the rubber to absorb the oil. By this procedure the resultant compound remains in a powder form and is dry to the touch.

(3) The final stage of the process is to use conventional rubber mixing

equipment to produce a fully homogeneous compound. As a good degree of dispersion of the compound and ingredients has already been achieved, mixing cycles can be kept very short. Mixing times on a two roll mill are usually around three minutes. Much longer cycles than this usually result in sticky, difficult to handle compounds, and internal mixing cycles are around 1.5-2 minutes. It is very important to keep both the mill and internal mixer temperatures as low as possible, as high temperatures will produce sticky, unmanageable compounds.

A wide range of different compounds can be produced by using the soft compound technique, ranging from highly filled, cheap compounds to technical compounds for demanding engineering applications. Accelerator levels must be based upon the level of rubber plus oil to achieve efficient vulcanization. All other ingredients should be used at normal levels based upon the level of rubber alone. Primary attention has to be paid to the type and loading of fillers and the ratio of filler to oil. Aromatic, naphthenic and paraffinic types of oil are all suitable, but the lighter aromatic and naphthenic oils tend to be absorbed by the rubber at a faster rate and are, therefore, preferable. The maximum loading of oil possible will vary depending upon the type of filler used. Fine particle size fillers such as silica and fine particle furnace blacks tend to have a higher oil absorbancy than more coarse types, and these tend also to impart a high level of hardness so they, therefore, require a higher loading of oil to achieve equally low hardness to the more coarse fillers. A typical soft compound is illustrated in Table 7.

TABLE 7 DETAILS OF A SOFT COMPOUND BASED ON CRUSOE RUBBER

Physical Properties	
Hardness, IRHD	20
TS, MPa	9.0
EB, %	640
M 100, MPa	0.10
M 300, MPa	0.57
M 500, MPa	2.39

Formulation Crusoe NS, 100; Calcium Carbonate (ppt), 60; Carbon Black (FEF), 20; Naphthenic Oil, 100; Zinc Oxide, 5; Stearic Acid, 2; Permanex WSL, 2; Antilux 654, 3; Sulphur, 2.5; MBTS, 1.0; DPG, 0.5; Optimum cure time at 150°C, 14 min.

The advantage of using this type of new technology is that the range of properties of natural rubber has been extended to a softness of below 15 IRHD. The important aspect of the process is that in achieving this low hardness there is very little breakdown of the polymer, so giving vulcanizates relatively good physical properties. The processing of these compounds does not necessitate the purchase of expensive equipment nor the acquisition of specialist skills. The process is essentially cheap and mixing times are rapid and simple in operation. These points are equally true of sponge and microcellular product manufacture, with the added advantage in cost as long as mixing cycles and/or high loadings of peptiser are necessary to achieve a sufficiently low viscosity compound to produce a good quality sponge article from conventional block rubbers. In order to obtain satisfactory compounds by this process, it is necessary to use the low particle size of natural rubber as produced by spray drying latex. It has been said that for normal compounding low particle size rubber is not required; particulate rubber of even up to 10 mm will satisfactorily process on MVX type machines. However, this new technology of producing soft natural rubber or sponge compounds necessitates the use of low particle size, where all the particles will be less than 4 mm and 60% of these particles will be 2 mm or less, in order for the compounds to remain easily mixable and free flowing. These very soft compounds have found a use in car door seal manufacture and for soft grommets. In the soft compound for car door seals it is required that the compound should also have good ozone resistance. A typical compound which will meet these requirements is shown in Table 8.

TABLE 8 A NON-STAINING OZONE RESISTANT COMPOUND

Physical Properties	
Hardness, IRHD	30
TS, MPa	6.01
EB, %	580
M 100, MPa	0.66
M 300, MPa	2.19
M 500, MPa	4.67

Ozone Test	
3 days preconditioning at ambient temperature	
Ozone conc., pphm	50
Extension, %	25
Temperature, °C	40
Time, d	3
Result	no crazing

Formulation Crusoe NS, 100; Carbon Black FEF, 40; Calcium Carbonate, 85; Naphthenic Oil, 100; Zinc Oxide, 5; Stearic Acid, 2; Antioxidant, 2; MBTS, 1.5; DPG, 0.5; Sulphur, 2.5; Vulcanox AFS50, 6; Okerin Wax, 5; Antilux 654, 5; Optimum cure at 150°C, 14 min.

The advantages of spray dried powdered natural rubber can be listed as follows:

1. Rapid mixing.
2. High filler/oil loadings possible.
3. Low breakdown of polymer required to produce a homogeneous mix.
4. Low capital cost of mixing and processing equipment.
5. Low manpower requirements.
6. Possibility of automated mixing systems.
7. Ability to produce very low hardness compounds.
8. Ability to produce high-quality sponge compounds very cheaply.
9. Possibility of producing very low-cost compounds having superior physical properties.

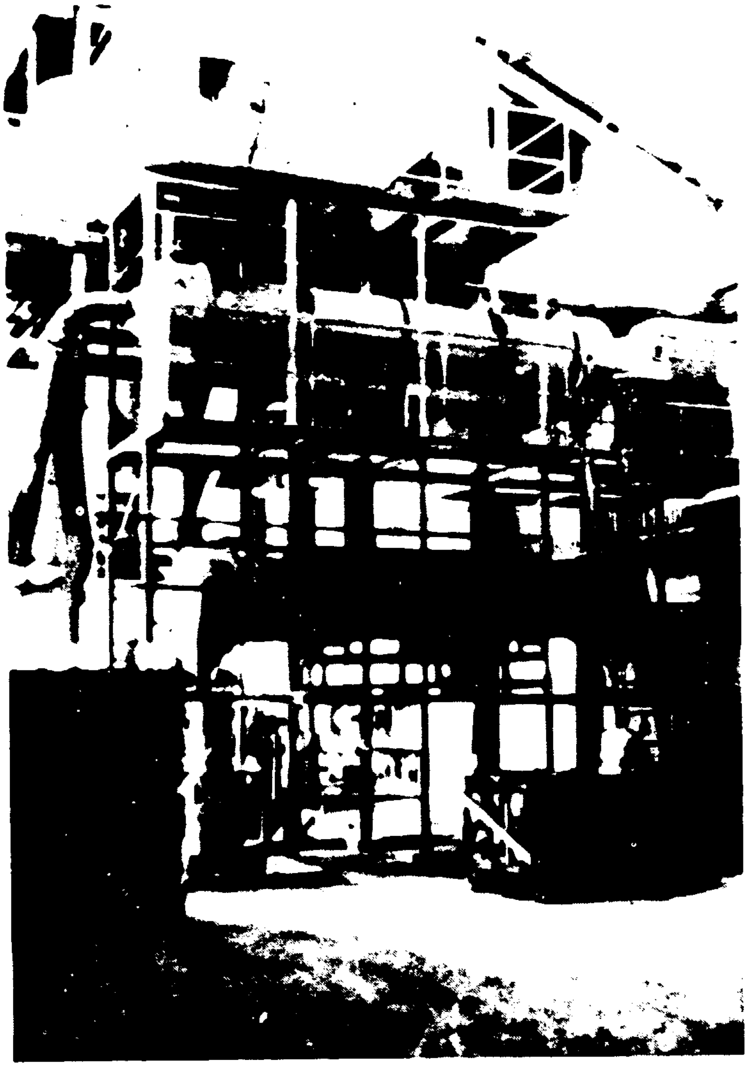

Fig.10.1
General view of the Crusoe spray-drying plant.

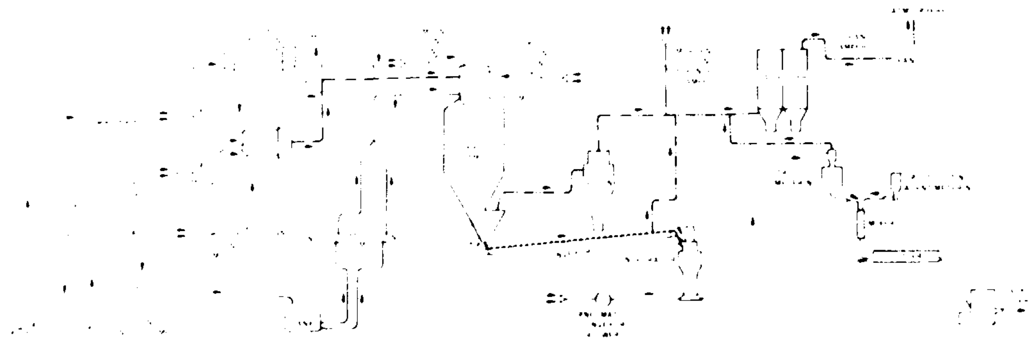

Fig.10.2 Flow diagram for the manufacturing process of Crusoe powdered rubber.

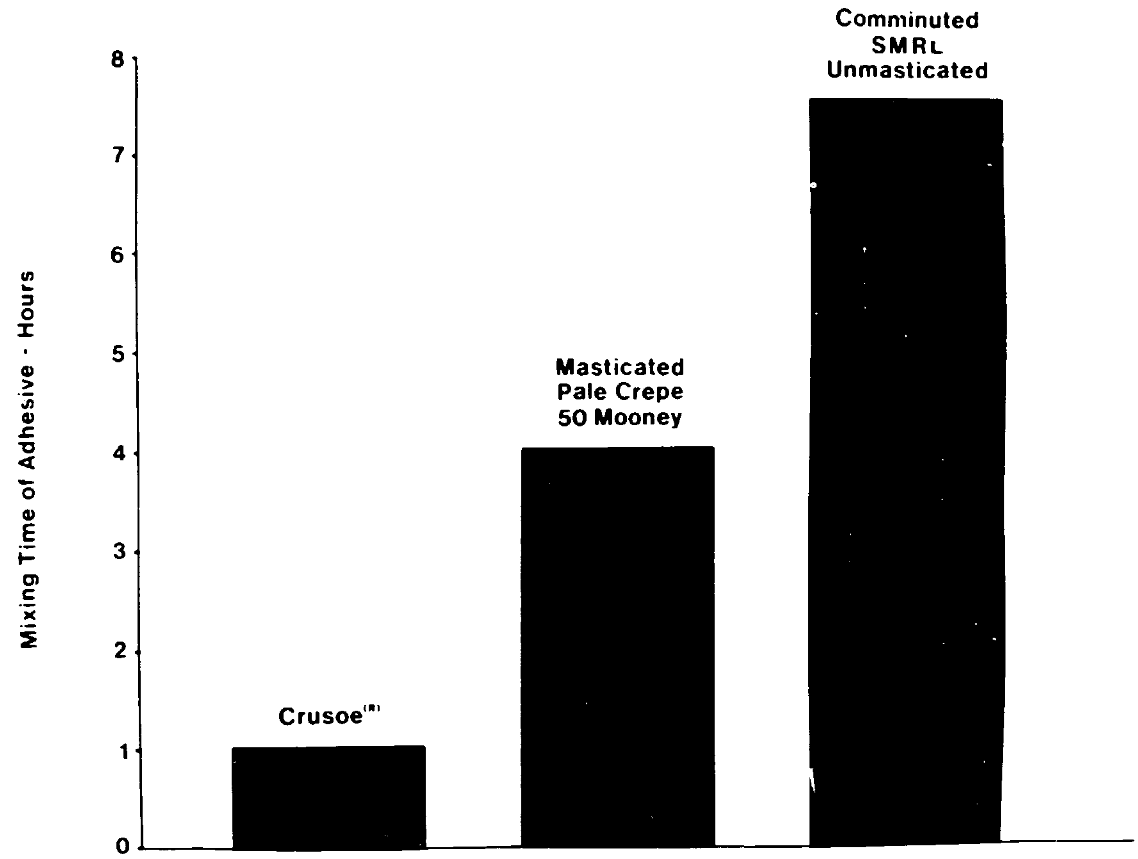

Fig. 10.3 Dissolution time of various natural rubbers in toluene in a laboratory mixer.

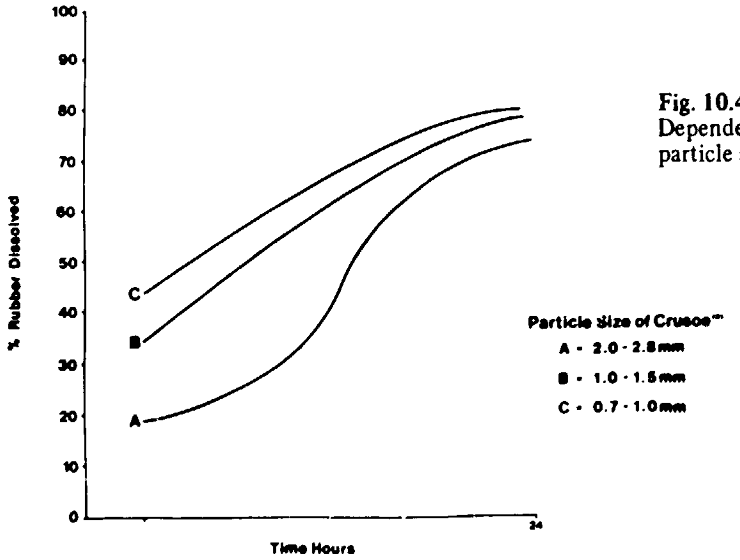

Fig. 10.4
Dependence of rate of solution on particle size for Crusoe rubber.

PREPARATION OF FREE-FLOWING NR CRUMBS

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INTRODUCTION

Natural rubber in particulate or powder form can be prepared in several ways. The most important of these in a commercial sense is the mechanical grinding of solid natural rubber, usually carried out in rubber consuming countries. It is, however, attractive to NR producing countries to consider adding value to their product by exporting particulate or powdered NR if this can be competitive with that obtained by grinding.

Natural rubber is produced by the tree in essentially particulate form as an emulsion (latex) and it would therefore be logical to exploit this fact by converting latex directly to a powder. Several methods do exist, namely spray-drying, encapsulation and flocculation. Spray-drying is the only extant commercial process.

All these methods have a number of disadvantages as compared to bale rubber, among which are the high content of partitioning agent, high cost and low bulk density of the material. This paper described a new and more promising method of producing natural rubber in particulate form as free-flowing crumbs.

PREPARATION

The process for the preparation of free-flowing crumbs from latex involves three steps. They are (i) coagulation and size reduction of coagulum, (ii) surface chemical treatment of discrete crumbs and (iii) drying of surface-treated crumbs.

0.7% of castor oil and 0.08% of sodium metabisulphite on drc are added to the field latex. The latex is then coagulated conventionally by the addition of formic acid. A pelletiser is used for the final size reduction of the coagulum into discrete crumbs. The untreated crumbs are prevented from agglomeration by the presence of a thin film of castor oil at the cut surfaces. The crumbs remain discrete when mechanically stirred in water. This allows homogeneous reactions on the surface of the crumbs to be carried out.

An advantage of the pelletiser as compared to other machines such as smooth roll crepers[1] and shredders is that the crumbs produced have a narrow particle size distribution. The disadvantage is that very little mechanical working is given to the coagulum in the pelletiser. This contributes to a longer drying time for the crumbs. However, by reducing the diameter of the holes in the die-plate from 4 mm to 2 mm, the drying time of the crumbs produced is shortened significantly.

Surface chemical treatment of the crumbs is via chlorination or bromination.

Chlorination is preferred to bromination because it is an easier and cheaper process. In chlorination, the reagents, sodium hypochlorite and hydrochloric acid are added directly to the crumbs dispersed in water whereas in bromination, bromine water is first prepared using sodium bromide, sodium bromate and sulphuric acid. The bromine water is then added to the crumbs dispersed in water. Addition of the brominating reagents directly to the crumbs dispersed in water, requires a significantly higher amount of sulphuric acid to attain a pH of 4, for the bromine to be generated.

The crumbs produced via the die-plate with holes of diameter 3 mm are chlorinated at 2% of chlorine on drc.

The surface-treated crumbs are dried in a through-air circulation batch drier. This is a standard drier used in the production of bale SMR. The drying time at 75°C is 19 hours and at 100°C is 6 hours. For the larger crumbs produced via a die-plate with holes of 4 mm diameter, the drying times are 38 hours at 75°C and 10 hours at 100°C.

CHARACTERISATION

Both chlorine and bromine are very reactive towards the carbon-carbon double bonds of the polyisoprene molecules. As such the rate of reaction between the reagents and the rubber molecules is significantly faster than the rate of diffusion of the reagents into the crumbs. X-ray analysis in the scanning electron microscope, using 30 kV electron energy show that the penetration depth of the halogen is of the order of 5 to 15 microns. When halogenated crumbs are soaked in toluene (approximately 1% w/w rubber/toluene), it is found that the non-halogenated rubber in the centre of the crumbs dissolves, leaving behind the thin halogenated skin. The intrinsic viscosity of the non-halogenated rubber in the centre of the particle is found to be comparable in value to the control non-halogenated crumbs. The free-flowing nature of the crumbs is due essentially to the surface halogenation. The dry non-halogenated crumbs agglomerate on storage or on slight compaction.

The amount of chlorine in the dry crumbs is about 0.35% by weight, from 2% by weight of chlorine originally used. The efficiency of the chlorinating process carried out is low, due possibly to the very low solubility of chlorine in water. However, at this level of chlorine, the dry crumbs show good resistance to agglomeration on storage and on compaction. At higher levels of chlorine, the plasticity retention index of the crumbs falls below 60% and the Mooney viscosity is also lower than the control, non-chlorinated crumbs.

Sieve analysis of the crumbs prepared via the die-plate with holes of 3 mm diameter show about 100% of particles less than 6 mm in diameter, about 75% less than 4 mm and about 2% less than 2 mm. The particle size distribution is narrow and can be regulated to a limited extent by using die-plates with holes of different diameters as shown in Table 1. For use in the new generation of continuous mixer extruder such as the Farrel-Bridge MVX or the Werner Pfleiderer EVK operation, this range of particle size is preferred where NR is concerned.

Two types of compacting trials were carried out. Several lots of approximately 1.6 kg of the free-flowing crumbs were compacted in a 16 x 23 cm section mould under a pressure of 54 g/cm^2 for 90 days at ambient temperature. This pressure is comparable to the pressure (45 g/cm^2) at the bottom of the fifth bale of free-flowing crumbs in a

TABLE 1 PARTICLE SIZE DISTRIBUTION

Particle Size	% by weight 3 mm die-plate	 4 mm die-plate
>6 mm	-	4
4-6 mm	25	65
2-4 mm	73	31
<2 mm	2	-

1-tonne SMR pallet. The compact bales have bulk densities around 650 kg/m^3 and are friable, ie they could be easily crumbled to revert to the particulate form again.

The second trial, involved compacting 32 g of crumbs to a bulk density of 627 kg/m^3 in a 5 cm diameter section mould under a pressure of 176 kg/cm^2. To obtain a compact minibale that could be handled, the sample dried at 100°C needs to be compacted under pressure for 24 hours. For the sample dried at 75°C, the time under pressure has to be increased to at least 72 hours. At lower drying temperatures, the free-flowing crumbs show a stronger resistance to agglomeration on storage and on compaction. Both the samples are reduced to a particulate form again after 2-3 minutes in a laboratory high speed powder blender.

The raw rubber properties of the crumbs are within SMR specifications for rubber prepared from latex material. The free-flowing halogenated crumbs have a higher optimum cure time and a higher scorch time as compared to SMR L. The vulcanizate properties of the crumbs are comparable to the control SMR L[1].

PILOT PLANT PRODUCTION

The layout of the pilot plant for the production of free-flowing NR crumbs is given in Figure 1. For each production run, about 830 kg of field latex (drc of about 30%) are coagulated in the separate sheet coagulation tank in the form of 10 cm thick slabs. The slabs are sliced by the coagulum slicer into strips of coagulum, each with cross-sectional area of 10 x 7.5 cm. The strips are directly and conveniently fed into the inlet of the pelletiser. The die-plate in the pelletiser has 160 holes, each of 3 mm diameter. The throughput of the pelletiser is about 38 kg per hour. The discrete crumbs from the output of the pelletiser are transferred along a chute into a holding tank. After one quarter of the coagulum has been fed into the pelletiser, the crumbs are scooped up by the bucket conveyor at the other end of the holding tank and dropped into the washing tank. From there, the crumbs are pumped up into the reaction tank. The chlorinating reagents are added to the crumbs dispersed in water. The mixture is mechanically stirred. After twenty minutes, the reaction is stopped and the serum is discharged. Water is then pumped into the reaction tank to wash the crumbs. After two washings, the chlorinated crumbs are discharged into the washing tank. From there, they are pumped out through a static screen into the stainless steel, two-tier boxes for drying. The crumbs are loaded to a depth of 9 cm per tier, two tiers per box. There are twenty-four boxes. Under such loading conditions, the capacity of the drier is about 0.25 tonne per batch.

The crumbs are packed in single layer polypropylene bags, each bag containing 20 kg of crumbs. Thirty bags are loaded in 5 layers into the standard 1-tonne SMR wooden pallet.

ECONOMIC ASPECTS

The major additional costs in the production and export of free-flowing crumbs as compared to bale SMR are due to the chlorinating reagents used, the longer drying time and the lower freight bulk density of the crumbs.

The chlorinating reagents are sodium hypochlorite and hydrochloric acid. Both chemicals are manufactured in Malaysia. Based on the use of 2% chlorine on drc, the cost is 9 cents per kg of rubber.

The crumbs could be dried at either 100°C or 75°C, in the pilot-plant's dryer. Compared with the drying of SMR at 110°C in the same dryer, the additional cost for drying the crumbs at 75°C is 9 cts per kg and at 100°C is 4 cts per kg.

Each standard 1-tonne SMR wooden pallet contains 30 polypropylene bags. Each bag contains 20 kg free-flowing crumbs. The packaging cost for the crumbs is 3 cts/kg higher than for the bale SMR. The additional freight and insurance for the material is 14 cts/kg.

The total additional cost for the free-flowing crumbs compared to bale SMR is 30-35 cts/kg. The amount compares favourably with the cost of mechanically grinding bale rubber in UK which is estimated at between £60 to £100 per tonne, ie approximately 30-50 cts/kg.

CONCLUSION

A pilot plant for the production of NR in particulate form as free-flowing crumbs is in operation. The throughput capacity of the plant is 0.25 tonne per day.

The free-flowing crumbs do not require any partitioning agent such as talc or silica to prevent agglomeration in storage or transport.

The free-flowing crumbs can be compacted to about 75 percent of the bale SMR bulk density and still be rendered friable on arrival at the consumer factory.

The free-flowing crumbs can be produced at comparable cost to particulate rubber obtained via mechanical granulation of bale rubber.

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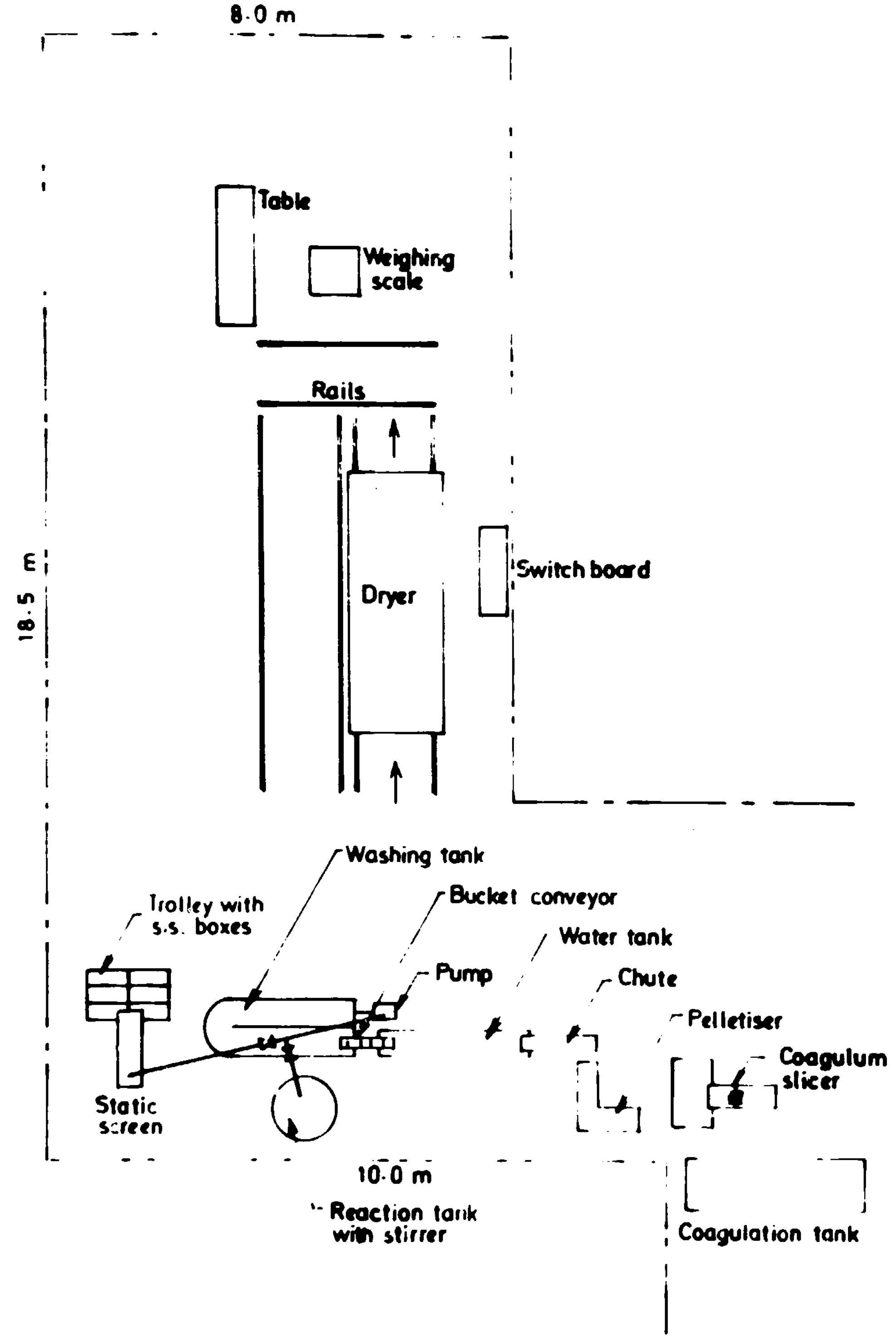
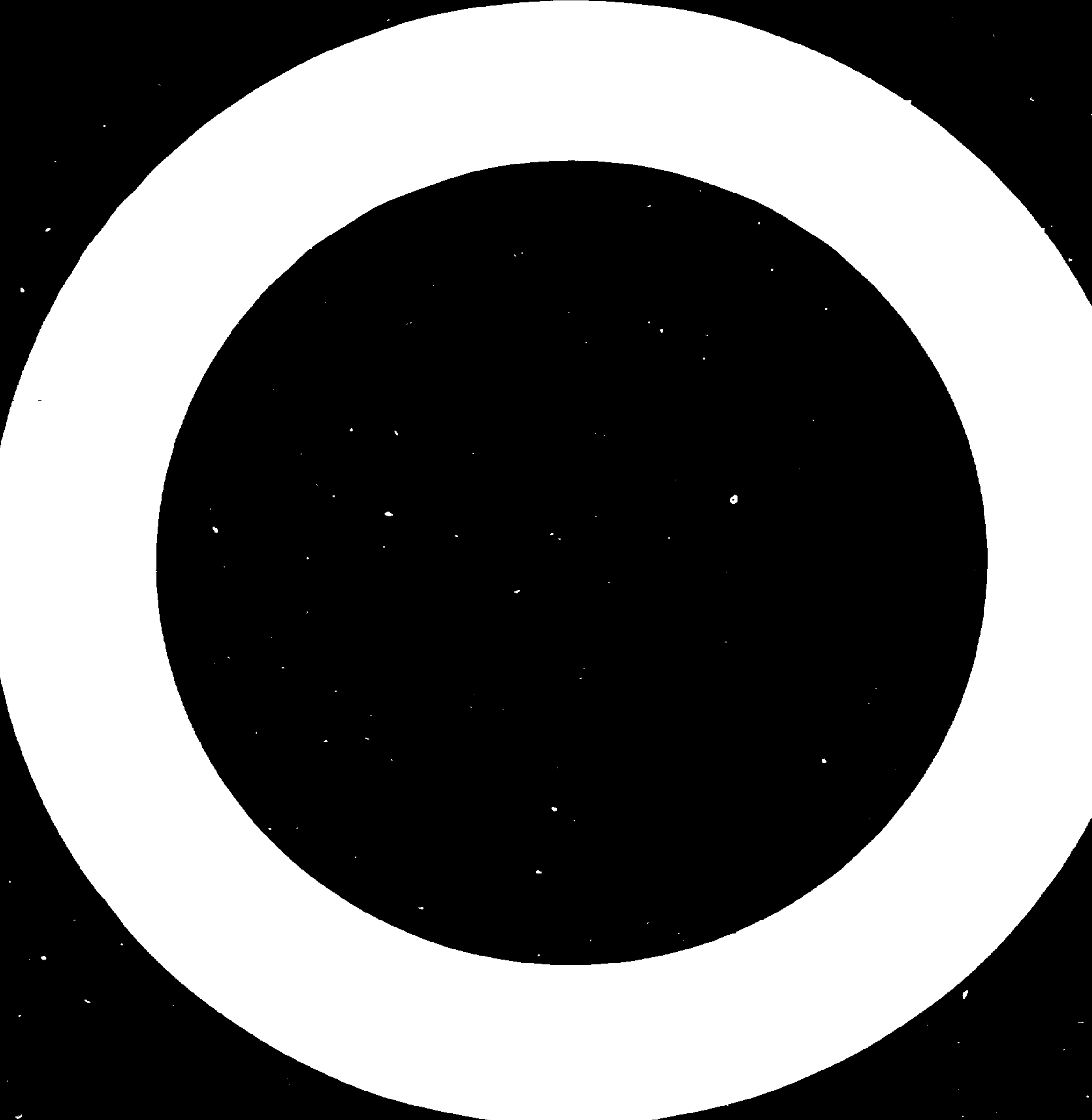


Fig. 11.1 Layout of free-flowing NR crumb pilot plant.



ROUTES TO POWDERED NR : GRANULATION OF NR

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1 INTRODUCTION

In 1980 it was observed[1,2] that the product costs (CIF landed in the UK) of spray dried powdered rubber (£842/tonne*), brominated rubber granules (£791/tonne) and talced rubber granules (£747/tonne) are significantly higher than the then current cost of SMR L bale rubber (£662/tonne). Differences between costs of the bale rubber and the various forms of rubber particles range from £84/tonne to £180/tonne and, even if there is no production cost premium on the granular forms of rubber the freight cost of rubber granules is £59/tonne higher than that for bale rubber. The talced rubber granules are the least costly of the three forms but they were not included in further discussion[1,2] on the ground that they have too short a storage life before agglomeration and loss of their free flowing characteristics. Spray dried rubber powder is too costly[1,2] for general purpose applications but it has a small market where its very fine particle size permits time saving in dissolution processes. Brominated granules are also regarded as expensive for general purpose applications.

Consideration of freight costs and the questionable ability of granulated rubber to travel without agglomeration led MRPRA to careful examination of the process and costs of granulation of bale rubber in the UK as typical of granulation in the country or place of final usage.

The market for particulate forms of natural and synthetic rubber is about 4500-5000 tonne/year in the UK (about 1% of the total usage). Most of this material is handled by three granulating companies but in spite of the market very little has been written about the granulation of natural or synthetic rubber. This lack of information prompted investigation into the process of granulation so that possible NR markets could be held or developed and not lost by default due to increasing information about particulate forms of synthetic rubbers. The granulating companies and users of their products acknowledge that there are problems with particulate rubbers including the difficulty of controlling amounts of partition agent (frequently talc) and agglomeration of particles. Excess of talc which is difficult to avoid and separation of this to the bottom of a bag or larger container can lead to inaccurate weighing of rubber for a rubber mix and serious inbalance of rubber/filler/curative ratios which cause variations in physical properties of vulcanizates. Questions have been raised about the effects on health of some grades of talc and alternative partition agents are considered. Other problems which are difficult to deal with are concerned with controlling dust and heat generation in the cutting chamber.

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*Converted from M¢/kg to £/tonne, M¢ 510 = £1.

1.1 Terminology

British Standard 2955, 1958 defines a powder as discrete particles with a maximum dimension of less than 1000 microns (1 mm). However, this standard recognises that certain industries regard particles larger than 1 mm as powders and, as the rubber industry is interested in rubber particles of 1-20 mm, this paper refers to free-flowing particles of this size range as powders. The term 'powder' is more appropriately used for spray dried material which is fundamentally very fine but agglomerated. The word 'granules' is used for bale rubber which has passed through the granulator or rotary cutting process.

2 GRANULATION STUDIES

2.1 Granulation with the Blackfriars Granulator

Granulation experiments have been carried out with a Blackfriars Engineering Co., Granulator Model 12 ASHD which was purchased under the UNIDO Project. This machine has a steel rotor with three rotating knives which cut with scissor action against two fixed knives in the steel casing, (Figure 1). The drive motor (18.75 kW) turns the rotor at 1500 rev/min. The knives were set as close as possible eg close enough to cut paper about 0.05-0.1 mm (2-4 x 10^{-3} in) thick. Before starting it was known that maximum cooling would be desirable and the machine was purchased with facilities for passing cold water through the rotor and the casing. A cold draught of air assists cooling and transports rubber granules pneumatically from below the cutting chamber to the top of a cyclone which separates rubber, partition agent (talc) and air.

Air flow rates were adjusted by pulleys on the 2.2 kW fan between the granulator and the cyclone so that the cyclone separated the talc away from the useful product allowing rubber to drop into an open bin while the dust collector sucked away the free talc. Successful operation of the cyclone depends on an open system. If the bin is too close to the exit of the cyclone it interferes with the air flow and causes the free, excess talc and rubber to flow together into the collecting bin.

Product bin temperatures of 21-24°C in winter and 27-29.5°C in summer are cool enough to give several days or even a few weeks freedom from agglomeration of NR when talc is used as a partition agent and storage bags are not greater than about 25-30 cm deep. This degree of storage stability has proved adequate for MRPRA's 'in-house' Fielder powder-blending operations.

2.2 Experimental Granulation Method

It is soon found that the granulation process is a delicate one that cannot be rushed. Overfeeding by exceeding the output rate or lack of partition agent easily causes overheating in the cutting chamber and individual particles are believed to mass together causing the cutter to go into a mastication action rather than a cutting one.

An experimental scheme was developed to monitor the weight of rubber and talc into the machine and out. For example, an experimental run would start with 0.5 kg pieces of SMR CV 60 being added at 1.5 or 2 min intervals with 25g (5%) talc being added steadily by hand in the following time interval. The change in weight of the granular product with time was graphically recorded from observations made of the product bin which rested on a balance. When overfeeding caused clogging of the cutting chamber of the machine detected by excessive ammeter readings or stalling, a lower rate of input was tried until a feed rate was found to permit continuous running. When satisfactory feeding rates were observed faster rates were tried. The operator soon develops an instinct to add more talc when ammeter readings rise.

2.3 Output Rates

General overfeeding becomes more frequent as the screen size is reduced and output rates are reduced (Table 1). Use of talc increases but bulk densities remain about the same. Larger granulators give a disproportionately greater output and a greater disparity between the outputs of large and small screens[3].

TABLE 1 EFFECT OF SCREEN SIZE ON GRANULE PRODUCTION

Screen size, mm	19.1	15.9	9.5	7.9	6.4	4.8
Overall output, kg/h	30.9	19.3	15.1	14.4	12.0	6.6
Output excluding over-run time to clear chamber, kg/h	34.3	20.5	20.1	15.9	14.1	8.0
Talc used, %	2.69	4.73	2.37	3.00	3.84	6.12
Bulk density, Mg/m^3	0.43	0.44	0.43	0.42	0.43	0.44

2.4 Characterization of Blackfriars Granules

2.4.1 Dependence of particle size distribution on screen size.

Representative samples of Blackfriars granules were analysed by sieving through standard test sieves for 10 min on an automatic shaker. Sieve analysis (Figure 2) shows that particle size distribution depends on screen size and that the Blackfriars granulator can conveniently give NR particles in the range of about 4-16 mm. A small percentage of particles as small as 2 mm diameter could be obtained by sieving the particles from a 4.8 mm (3/16 in) screen.

2.4.2 Dependence of talc level on particle size and screen size.

Sieved samples selected for ash analysis show (Figure 3) that as particle size decreases the level of talc increases. There is evidence that, for a given particle size defined by passing one sieve and being held on the next smaller sieve, the talc level also depends on the size of the Blackfriars screen. This implies that the longer a particle remains in the cutting chamber the more chance it has of picking up more talc, or having more talc hammered into it by the knife blades. When knife blades become blunt, particles remain longer in the cutting chamber and more talc is required.

Talc levels on particles of a given size range from the simple Blackfriars granulator are lower than observed with commercial granules usually obtained from more complicated machinery implying that the amount of talc carried by a particle also depends on the cutting machinery or process (Figure 4). This data helps to explain why it is difficult to control partition agent levels. Although the particles from the Blackfriars and the cyclone system have less talc around them and are less dusty than most commercial granules they probably have less storage resistance to agglomeration.

2.5 Examination of other partition agents

Twelve common, white rubber chemicals which could be used as partition agents have been examined to see whether a replacement for talc could be found in case it should be necessary on health grounds. It was also of interest to see whether variations in the partition agent would reveal a 'best' partition agent or further details of the mechanism of the granulation process. High levels of partition agent are expensive and tend to spoil the physical properties of rubber products. They also spoil the balance of the curing system if they are not correctly allowed for.

Test sieving of granules showed that, apart from cases of early agglomeration with fine silica (Hi-Sil 233), the pattern of particle size distribution is much the same for all the partition agents examined.

Samples having a natural distribution of particle sizes and fractionated samples having a limited range of particle sizes defined by sieving were chemically analysed by the standard SMR technique of ashing and maintaining furnace heat at 550 ± 25°C for 24 hours. The partition agents themselves were also 'ashed' by the same technique. Ash analysis data was then corrected for natural ash in the CV rubber used and the weight losses due to ashing the partition agents.

The output data for the Blackfriars granulator is linked in Table 2 with the amount of partition agent that needs to be used for the granulating process and also the amount of partition agent which remains attached to the rubber particle after being separated from excess agent by the draughts in the cyclone. Ranking in column 1 is based on 'overall output'. However, the correct output figure is difficult to assess accurately and is somewhere between the figures quoted for 'overall output' and 'output excluding over-run time' which takes account of the time required to empty the cutting chamber of granules after the last piece of rubber has been put in. Most of the experimental runs lasted for 60-70 min to produce 20 kg of product with an over-run time of about 9-12 min. The longer the production run the less important is the over-run time.

Considering the overall running time, talc is probably the best partition agent but it is only marginally better than zinc oxide, Hexafil clay and uncoated calcium carbonate. Talc is also one of the best agents because it can be used in low quantity. Significantly more zinc oxide (62% more), Hexafil clay (46% more) and calcium carbonate (15% more) need to be used.

TABLE 2 BLACKFRIARS GRANULATOR OUTPUT AND PARTITION AGENT REQUIREMENTS

	Overall output	Output excluding over-run time	Partition agent used for granulation	Partition agent found in granulate[3]	
Partition agent	kg/h	kg/h	%	w/w %	v/v %
Talc	21.8	25.3	4.84	1.29	0.52
Zinc oxide	21.5	25.4	7.84	4.84	0.94
Hexafil clay	20.6	24.9	7.07	1.80	0.75
Ppt.Calcium carbonate[1] (uncoated)	19.9	23.4	5.56	2.30	0.96
Stockalite clay	19.7	22.6	7.60	1.47	0.61
Silica (KS300)	19.3	22.3	8.26	0.90	0.48
Ppt.Calcium carbonate[2] (coated)	19.3	23.2	6.93	2.50	1.04
Calcium silicate	19.3	23.6	6.16	0.80	0.41
Aluminium silicate (Ultrasil AS7)	18.2	20.3	9.35	1.17	0.49
Zinc stearate	18.1	22.2	5.62	1.41	1.46
Calcium carbonate (Whiting)	16.6	19.3	11.09	2.50	1.01
Silica (Hi-Sil 233)	10.6	11.7	14.3	0.87	0.48

(1) Calofort U, (2) Calofort S, (3) Data for samples having a natural distribution of particle sizes using a 7.9 mm (5/16 in) screen.

Although excess quantities of partition agents can be collected and re-used, talc is economical in that about 3.75 times more talc is used than actually sticks to the rubber. Zinc oxide is more efficiently used in that only 1.62 times more needs to be used than finally sticks. By contrast 9.2 times more silica (KS300) and 16.4 times more Hi-Sil 233 are needed than stick to the rubber. The implication is that fine silica just flows through the machinery and into the dust collector without sticking to the rubber.

The percentage of talc by weight adhering to the rubber after passing through the cyclone is 1.29% which is significantly less than that for other relatively good partition agents. Less silica, less calcium silicate and less aluminium silicate than talc sticks to the rubber but these partition agents are less good than talc for output reasons. Silica, is a poor partition agent because re-agglomeration of granules occurs quickly. The highest volume % of partition agent attached to a volume of rubber is given by zinc stearate. High volume/volume % attachments are also given by calcium carbonate (whiting, precipitated, coated or uncoated) and zinc oxide. The volume/volume attachment of talc is quite low (0.52%) and that for silica and calcium and aluminium silicates is even lower.

This simple treatment pays no attention to important factors such as the particle size, shape or chemical nature of the partition agent but it is worth noting that some partition agents such as zinc oxide and precipitated coated calcium carbonate which adhere readily to the inner surface of the cyclone appear to give a good coating while the particles spiral down into the product bin.

3 ECONOMICS OF PRODUCTION OF GRANULATED RUBBER IN THE UK

The cost of a new factory with new buildings and up-to-date machinery is considered in a 'green field' site near to London or industrial centres of Manchester or Birmingham.

3.1 Processes

A flow chart (Figure 5) indicates the steps required for a simple granulation process ending with a spectrum of medium sized particles such as obtained through a 7.93 mm (5/16 in) screen (Figure 2). Particles of this size (about 62% in the range 4-8 mm diameter; 32% in the range 2.8-4 mm) are suitable for modern extruder mixers and conventional internal mixers. If smaller particles having a large proportion with a diameter of less than 2-3 mm are required for solution processes a more expensive and more sophisticated second granulator would be necessary.

If particles are required to pass stringent size specifications a mechanical sieve is required to separate over-sized and under-sized particles and return them to the granulator or reject them.

3.2 Products

The main features of the granules from a 7.93 mm sieve are summarised above. Particle size depends on sieve size; larger particles are a little cheaper and smaller particles more expensive because they spend more time in the cutting chamber. A medium size particle is chosen for examination here as being in between the extremes of about 4 mm and 12 mm which can be made by this method. The bulk density of granules is about 400-440 kg/m^3.

3.3 Capital Cost

Detailed capital costs for a building and machinery for granulating 250 tonne/month of NR are given in Table 3. A schematic factory layout is given in Figure 6.

TABLE 3 CAPITAL COST OF GRANULATED RUBBER PLANT IN UK

Approximate output: 10 tonne/day; 250 tonne/month

	£
Main building, 250 m^2 at £264/m^2	66 000
Bale cutter	8 000
Conveyor with weight sensor to feed bale slices to Blackfriars	3 500
Talc dispenser	9 000
Blackfriars 35 ASHD granulator	15 000
Pneumatic conveyor, cyclone	2 500
Filter bags	2 500
Centrifugal sifter	1 310
Bagging up equipment	4 500
Scales	800
Heat sealer for polythene bags	179
Shrink-wrap machine	365
Forklift truck	14 543
Office equipment	1 700
Installation (electrical and plumbing)	3 195
Total	133 092

The output of this hypothetical plant has been chosen to match the outputs of other hypothetical plants producing spray-dried powdered rubber, brominated granulated rubber, talced granulated rubber and SMR L control plants[2]. It has a relatively high potential output compared with the current output of the three existing UK factories already carrying out this type of operation and it would be capable of granulating two thirds of the quantity of their combined total annual production but not the finer 1-3 mm granule production.

3.4 Product cost

From Table 4 the total direct and indirect costs of granulated rubber are £794.78/tonne. Taking away the initial cost of the rubber (£660/tonne), the transport-in and port charge £10.97/tonne) and the transport-out or delivery charge (£25.00/tonne), the cost of the granulation process is £98.81/tonne or approximately £100/tonne of rubber granulated.

The cost of the granulation process quoted above (£98.81/tonne) contains no profit element for the granulator. It is reasonably consistent with prices charged for granulation by three UK granulating companies all of whom are believed to be using machinery which is about 6-8 years old. L. Stechler and Co charge £84/tonne for similar sized particles in bags and £132/tonne if the granules are packed in cardboard cartons. Transport is believed to be supplied by the customer. Telford Rubber Processors quote £67/tonne with extra for packaging and transport. Plascoat Systems quote £110/tonne for granules including up to 10% talc.

TABLE 4 PRODUCTION COSTS OF GRANULATED RUBBER IN THE UK

Output: 250 tonne/month for 12 months

Direct costs/year	£	% of total	£/tonne of rubber granulated
Rubber[a], 250 x 12 x £660	1 980 000	83.042	660.000
Partitition agent[b], 250x12x.02x£88	5 280	0.221	1.760
Bags[c,1]	17 300	0.726	5.767
Polythene wrappers,[c,2]	6 000	0.252	2.000
Pallets[c,3]	30 000	1.258	10.000
Electricity[d]	15 376	0.645	5.125
Water[e]	1 500	0.063	0.500
Transport in + port charges[f], 188 x £175	32 900	1.380	10.967
Transport out[g]	75 000	3.146	25.000
Labour[h]	37 195	1.560	12.398
Testing charges[i]	772	0.032	0.257
Total direct costs/year	2 201 323	92.325	733.774
Indirect, overhead costs/year			
Factory administration[j]	37 195	1.560	12.398
Building, machinery maintenance[k]	6 495	0.272	2.165
Building capital charge[l]	13 554	0.568	4.518
Machinery capital charge[m]	22 434	0.941	7.478
Working capital costs[n]	101 929	4.275	33.976
Factory heating[o]	1 346	0.056	0.449
Factory lighting[p]	63	0.003	0.021
Total indirect costs/year	183 016	7.675	61.005
Total direct and indirect costs/year	2 384 339	100.000	794.780

Note

Granulation process cost = £794.78/tonne less rubber, £660/tonne; less transport-in and port charge, £10.97/tonne; less transport-out or delivery charge, £25.00/tonne = £98.81/tonne of rubber granulated.

Notes and Assumptions for Table 4

Direct costs

a Rubber

Rubber is costed at £660/tonne, an average level for 1980.

b Partition agent

Partition agent is costed at a quantity of 2% on the weight of rubber processed. Although more is used some is recoverable.

c Packaging

c.1 Polythene or paper bags contain 25 kg of granulate.

c.2 One polythene wrapper per 0.5 tonne pallet.

c.3 One wooden pallet base per 0.5 tonne of granulate.

d Electricity

Electricity is costed at £0.03/kWh, times the working hours. The rating for the Blackfriars granulator is 94 kW.

e Water

Water is costed at £0.5 per 4546 l (1000 gallons).

f Transport

Transport-in to the granulating factory and port charges are costed at £160 for the journey and £15 for port charge for each 16 tonne container load, (10.94/tonne).

g Transport-out charges for granulated rubber delivered to the user are costed at £200 for an eight tonne load of granulated rubber (£25/tonne).

h Labour

One man is needed for feeding the bale cutter and another for packing bags of product on to pallets. A fork lift truck driver is necessary for unloading incoming pallets or crates and loading the product on to lorries. A skilled electrician or mechanic is necessary to run the complicated machinery. The main day shift requires a minimum of three men with a fourth who will be necessary from time to time. Labour is charged at £100/40 hour week. Employer's contributions to national insurance (13.7%) and pensions (15%) bring this sum to £128.7/40 hour week per man.

An annual output of 3000 tonne/year requires 375, 8h shifts at a production rate of 1 tonne/h. The main day shift can produce 240 x 8 = 1920 tonne/year leaving 1080 tonne to be produced in overtime or 1080/8 = 135, 8h evening shifts. 135, 8h evening shifts will require 135/5 = 27 weeks.

i Testing charges

One sieve test and one ash test per day is considered enough for routine quality control. One hour should suffice for this and this is charged at the labour rate of £128.7/40 £/h.

Indirect, overhead costs

j Factory administration

Administration cost is taken as equal to the labour charges.

k Building, machinery maintenance
The building and items in the relevant capital cost Table with mechanical and electrical working parts are charged at 5% for maintenance.

l Building capital charge
The annual charge is calculated by the 'discounted cash flow' method eg annual charge = investment x $\frac{i(1+i)^n}{(1+i)^n-1}$

where n is the number of years and i the interest rate.
The building is taken to have a life of n = 20 years, with i = 0.2 (ie 20% interest rate), as applicable in the UK in 1980.

m Machinery capital charge
The annual charge for this sum is costed as in note l above with n = 5 years and i = 0.2.

n Working capital costs
The working capital cost is calculated as a permanent debt of 20% of the value of three months working stock of NR, partition agent and packaging material.

o Factory heating
Factory heating is costed at £5.38/m^2 of floor space per year.

p Factory lighting
Lighting is costed at £0.25/m^2.

It is possible to visualize somewhat lower costs in the East if building, labour and electrical costs are lower and if lower capital charges can be considered for buildings, machinery and working capital. An in-house process would require lower packaging costs.

4 CONCLUSIONS

Granulation of NR is a feasible process and is carried out in industry to the extent of about 750-1000 tonne/year in the UK. There are still significant problems such as the difficulty of controlling the level of partition agent and the ability of the granules to resist agglomeration during storage and transport. These difficulties suggest an in-house process in which granules are moved to subsequent processes within a few days.

The cost of granulation in the UK is about £100/tonne of rubber processed and this is sufficiently high to make it difficult to recover the cost of subsequent processing.

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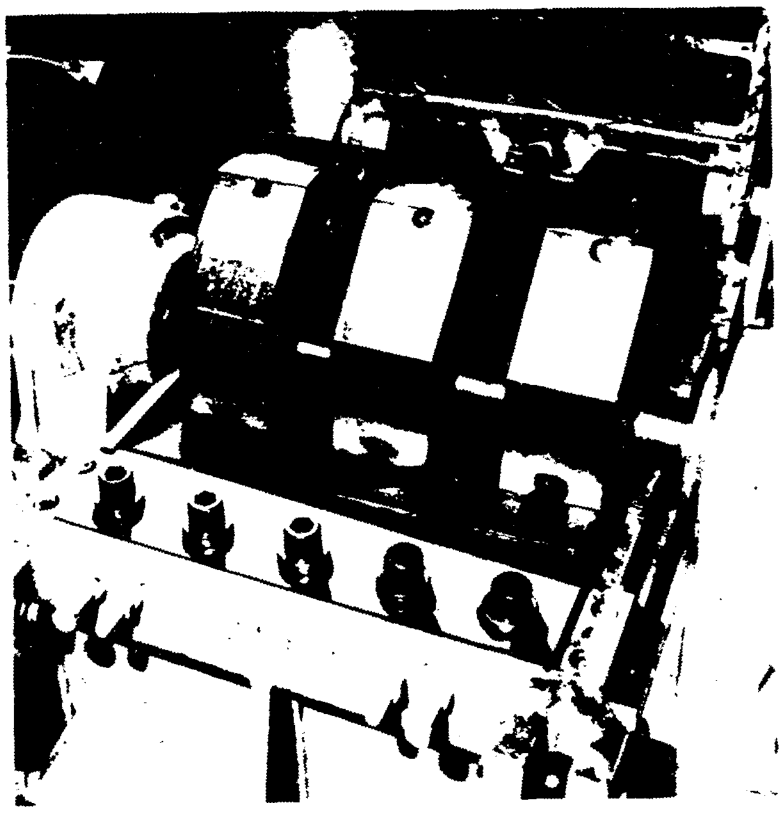


Fig. 12.1
Blackfriars granulator, showing scissor action of knives.

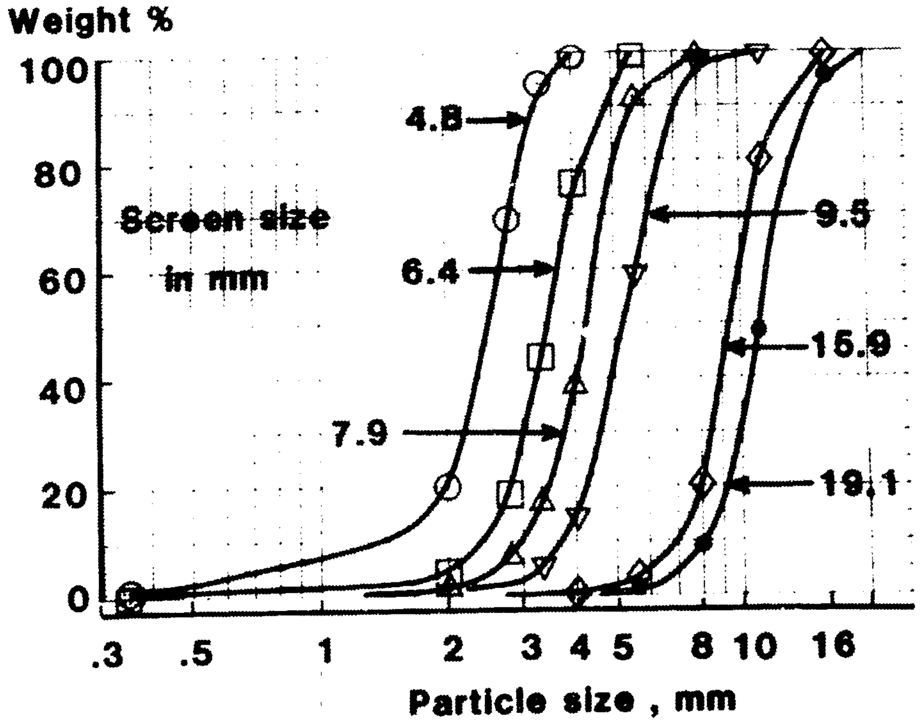


Fig. 12.2 Dependence of Blackfriars particle size distribution on screen size: screen size is indicated in mm.

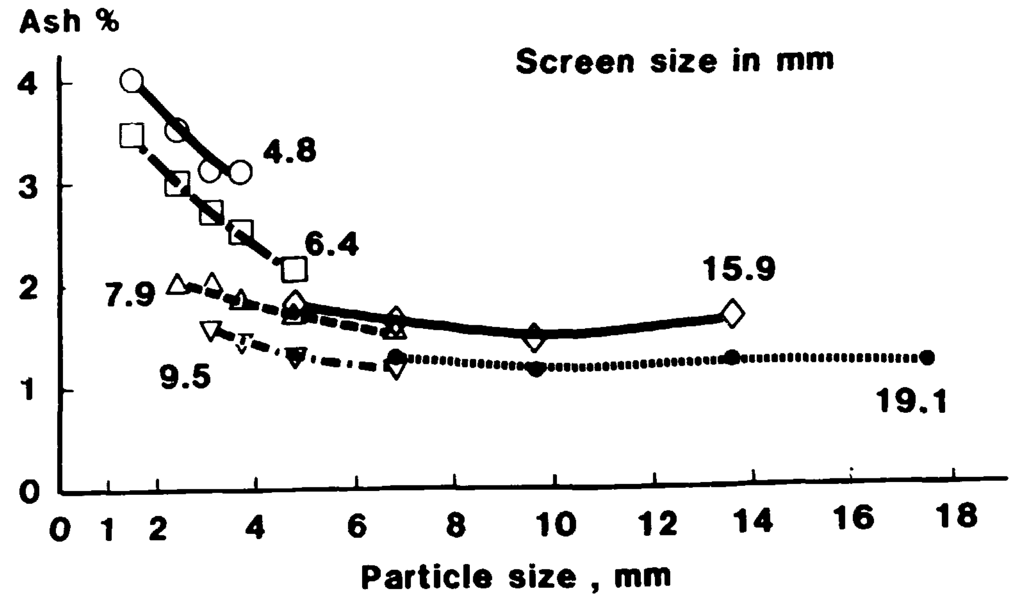


Fig. 12.3 Dependence of ash (talc) level on Blackfriars particle size and screen size.

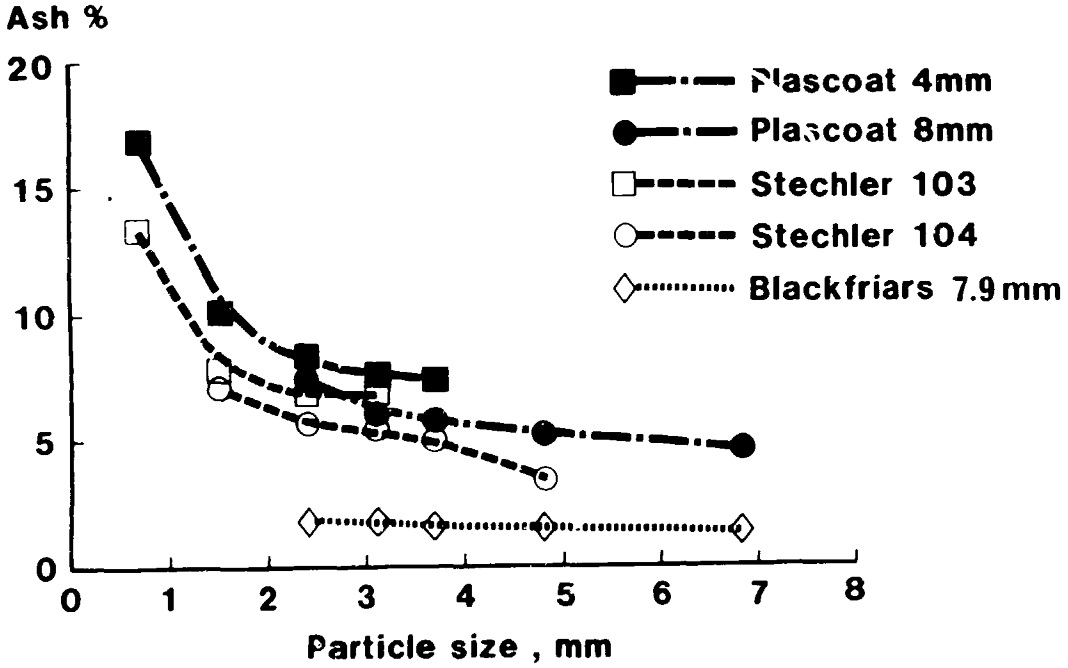


Fig. 12.4 Dependence of ash (talc) level on particle size and granulation system.

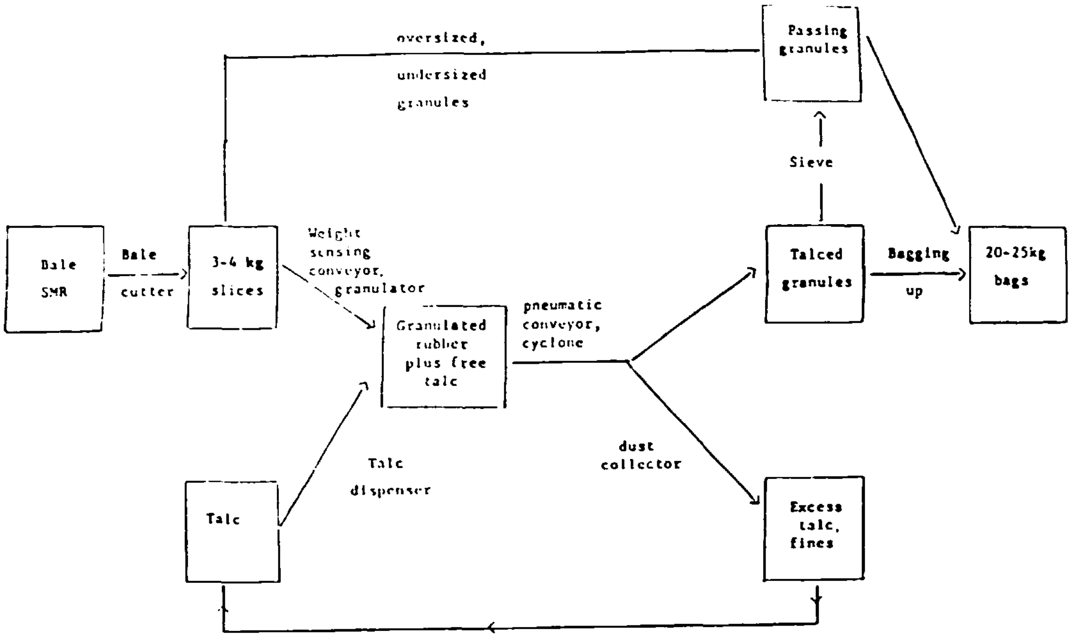


Fig. 12.5 Flow chart for granulation of bale rubber.

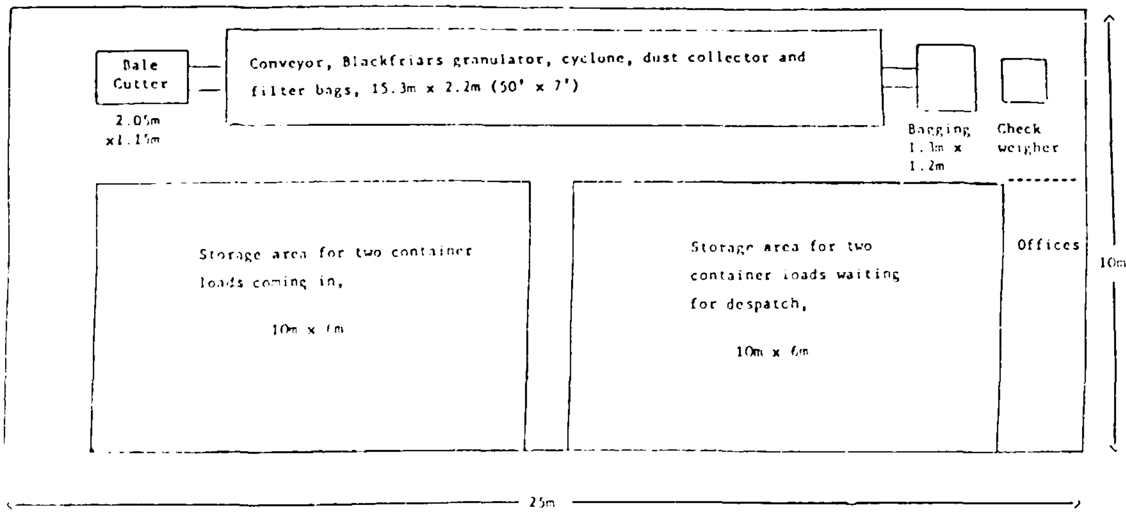
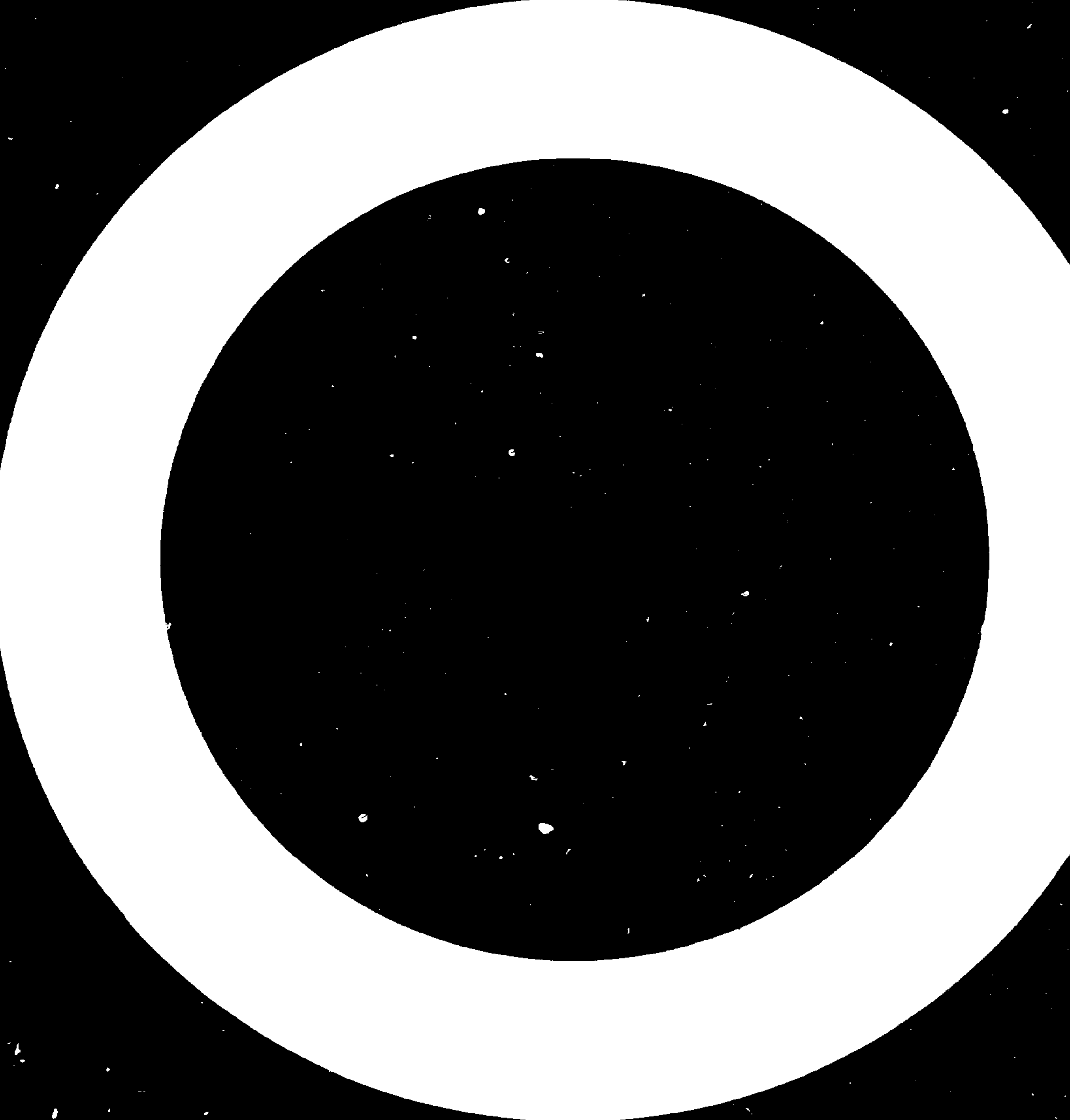


Fig. 12.6 Layout of granulated natural rubber factory (10 tonnes/day).



POWDERED NR : APPLICATIONS, PROCESSING AND ECONOMICS

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1 INTRODUCTION

Powdered rubber offers alternative processing routes to those used for mixing bale rubber in internal mixers. The powder process could start (Figure 1) with powdered rubber purchased from a supplier who makes a spray dried powder from NR latex (eg Harrisons and Crosfield's Crusoe), or one who granulates bale rubber. Alternatively bale rubber can be granulated 'in house' by the rubber manufacturer, with perhaps greater control over type and level of partition agent. The powdered rubber is then loosely mixed in a relatively cheap, low shear, one-stage mixing process in a powder blender with all the mix ingredients including sulphur and accelerators. This results in a loose powder blend which has then to be compacted and thoroughly mixed in further high shear rate processes.

Trials with powdered rubber in internal mixers have shown that in some cases savings in processing time and energy can be made.[1] Reduction of mixing costs by 38 per cent is claimed possible if a two-stage internal mixing process can be reduced to one stage. Greater savings are claimed to be made by using a powder blender to supply a powder mix direct to an extruder or injection moulder.

Unfortunately developments and expansion into markets in extrusion and injection moulding (also involving an extruder) of powdered rubber have been hampered because existing conventional extruders have not had the capacity to mix and extrude a powder blend with a good carbon black dispersion.[1-3] A new generation of continuous mixer-extruders has had to be developed especially for powdered rubber and has only just emerged in the last three or four years. The Farrel Bridge MVX[2,4,5] and the Werner and Pfleiderer EVK[6,7] machines are successful examples of these, but there are still very few of them in operation in the UK. Essential features of the new technology of these machines are continuous mixing at relatively low mixing temperatures, a means of compacting the powdered rubber, and use of a vacuum to withdraw air and volatile materials such as water which would normally evaporate off in the draught at the higher mixing temperatures in the internal mixer.

Direct shaping of hose products and direct covering of tyre bead wires with mixes having a Mooney viscosity up to 120 has been demonstrated with the MVX continuous mixer-extruder by Farrel Bridge[2,4,5,8]. If these or other extrusion products could be passed direct to a continuous curing process by the LCM or microwave methods the overall technique should offer useful savings.[1] At present it is more common for strip or diced product from a mixer-extruder to be fed to a conventional extruder for conventional production or continuous curing of hose, cables and profiles.[9] Strip or diced product can also be fed direct to existing conventional injection moulding machines or via mould blanking machinery to compression presses.

A major advantage for a developing country or an expanding rubber company with a shortage of mixing capacity is that a powdered rubber route could possibly be carried out with less capital expenditure than that necessary for an internal mixer and the associated cooling equipment and take-off mills, Evans.[10] The details of any financial advantages are critically dependent on whether the mixing advantages exceed the premium on powdered rubber or the costs of granulating.

1.1 APPLICATIONS

Current applications for about 2/3 - 3/4 of current powdered rubber production (4500-5000 tonne/year) include hydraulic hose (NBR, CR),[10] automotive hose (EPDM), cable covers (CSM) and extruded belting components (CR, EPDM).[9] Most of this powder is processed through the internal mixer but one Werner and Pfleiderer EVK machine is converting dry powder blend to cable belt components via the cold feed extruder.[9] The remaining 1/3 of production is used for compressed asbestos fibre gaskets, joints and similar products which are mixed in Z-blade mixers. These asbestos fibre products are the major users of powdered NR (750-1000 tonne/year).

Applications for Harrisons and Crosfield's Crusoe, finely powdered NR, include adhesives, surgical and industrial tape and mastics. The main advantage of powdered rubber in processing for these and compressed asbestos fibre products is the quick dissolution of very small 0.5-2 mm diameter particles in solvents.

1.2 THE UNIDO PROJECT

The wide objective of the UNIDO Project is to increase the competitiveness of NR with respect to synthetic rubbers and plastics, to extend its range of applications, to encourage increased production by strengthening its technical and economic position by developing new forms which will match present and future requirements.

In recent years the literature on powdered and granular forms of rubber has increased with glowing, but often far from precise accounts of how the advantages of the small particle form were derived. A certain lack of information in the NR producing countries concerning powdered NR manufacture and the granulation of NR made it desirable to examine the production and processing of small particle forms.

The more immediate objectives of the UNIDO Project with reference to powdered rubber have been to investigate, produce and then evaluate several different types of powdered (or granulated) NR with respect to their handling, processing and technical properties and to produce and evaluate rubber mixes made with them. Intentions have been to obtain first hand knowledge of the granulation of NR and use of granulated NR in new extruder-mixing and powder blending machinery so that, if the demand for powdered rubber increases or this new machinery becomes more widely used, appropriate advice can be given on use of NR without letting a possible market go to synthetic rubber by default.

The working plan carried out by MRPRA under the UNIDO Project and the major substance of this paper can be described under six broad headings:-

a <u>Granulation of NR in bale form</u>

The production of granulated NR from bale rubber and the examination of the most practical, though not novel granulating process is described at this conference in the paper 'Granulation of NR'.[11]

b Processing of powdered rubber

The evaluation of conventional internal mixer processing of NR particles granulated by the Blackfriars Rotary Cutter at MRPRA, and other commercial and experimental forms of powdered and granulated rubbers, has been combined with a study of the effects of processing on vulcanizate properties.

c Processing with new continuous mixing-extruding machinery

The pattern of applications and quantities used as quoted in section 1.1 above shows that powders and granules lend themselves to the extrusion process. Effort has therefore been concentrated on trials with recently developed mixing-extruding machinery, using an abrasion resistant hose or cable cover mix, because it is important to show that a high quality NR mix can be processed by this new class of machinery which is capable of playing a key role in the future of powdered rubber forms.

d Development of mix formulations for powdered NR

It is necessary to develop a working mix formulation for safe operation of any new machine or process. In the case of the new mixer extruders the complete mix including sulphur, accelerators and process aids must be included at the very beginning of the process. Experimental work was carried out to develop an abrasion resistant hose or cable cover mix for the MVX mixer-extruder process with due consideration for the resulting final mix viscosity, freedom from scorch during both the mixing-extruding process and subsequent processes and final vulcanizate properties.

e Examination of vulcanizates prepared from powdered rubbers

Consideration has also been given to expanding the range of finished products made from powdered rubbers to include general moulded goods. Test mix strips from extruder-mixers have therefore been injection moulded to show that they are suitable for feeding to injection machinery and to show that the quality of vulcanizates is comparable with that of control mixes and no loss of properties has been incurred by using either the small particle form or the new mixer-extruder process.

f Economics of granulation and processing

The economics of granulation have been considered. The costs of granulation thus obtained have then been used in an exercise to compare the costs of making strip for further processing by using conventional Banbury mixing of bale rubber and by using granulated rubber in a continuous mixer-extruder. This exercise has been extended to compare costs of subsequent cold feed extrusion and liquid curing of Banbury mixed strip with curing of a direct mixer-extruded profile.

1.3 TERMINOLOGY

British Standard 2955, 1958 defines a powder as discrete particles with a maximum dimension of less than 1000 microns (1 mm). However, this standard recognises that certain industries regard particles larger than 1 mm as powders and, as the rubber industry is interested in rubber particles of 1-20 mm, this report refers to free-flowing particles of this size range as powders. The term 'powder' is appropriately used for spray dried material which is fundamentally very fine but agglomerated. The word 'granulated' is used for bale rubber which has passed through the granulator or rotary cutting process. The more general word 'particulate' can be used for any powdered or granulated rubber in small particle form whatever the process of origin and is being encouraged in its use by some leading authors in the field.

2 PROCESSING OF GRANULATED RUBBER

Mixing of granulated and powdered rubbers has been studied in the conventional internal mixer, two new, commercial size mixer-extruders and an injection machine designed for the purpose.

2.1 MIXING IN THE INTERNAL MIXER

The 26 litre, Francis Shaw K2A mixer was used at low speed with a short, single-stage, 3 min, upside-down mixing cycle to compare two bale rubber control mixes with mixes based on Blackfriars granules of varying particle size. Mixes were based on 100 parts of SMR CV 60 adjusted to allow for the talc found by ash analysis. Table 1 shows that dump temperatures are not affected by the granular form of the rubber but peak power loads are significantly reduced. Granulated rubbers save between 4-12% of the mixing energy.

TABLE 1 EFFECTS OF PARTICLE SIZE AND TALC LEVEL ON PROCESSING, UNCURED RUBBER AND VULCANIZED RUBBER PROPERTIES

Particle (screen) size[1], mm	Bale	19.1	15.9	9.5	7.9	6.4	4.8
Talc by ash analysis[2], %	-	1.05	1.51	1.21	1.60	2.36	3.16
SMR CV 60[3], parts	100	101.06	101.53	101.22	101.63	102.42	103.26
K2A mixer; 25 rev/min							
Dump temperature[4], °C	114	105	110	115	115	115	115
Peak power, kW	149	103	97	91	90	94	98
Specific energy, kWh/litre	0.178	0.171	0.164	0.164	0.164	0.163	0.156
Uncured rubber properties							
ML 1+4, 120°C	69	68	66	64	64	62	63
MS t_5, 120°C, min	28.5	33	33	30.5	31	32.5	32
M_{HR}-M_L, 160°C	24.4	24.7	24.6	[illegible].4	25.0	25.0	25.1
Cabot black dispersion	G,H,1-5	H1-4	G1-3	[illegible]1-3	H1-4	H1-5	H1-4
Vulcanizate properties[5]							
Moulding weight, g	147.1	147.8	148.0	148.1	147.8	148.7	149.8
Density, Mg/m^3	1.140	1.149	1.145	1.146	1.145	1.150	1.158
Hardness, IRHD	66	66.5	67.5	67.5	66.5	66.5	66.5
Tensile strength[6], MPa	24.5	24.1	24.5	24.9	24.8	23.7	23.9
Elongation at break, %	539	535	538	537	551	538	533
M_{300}[6], MPa	10.6	10.9	10.7	11.0	10.5	10.5	10.6
Cabot black dispersion	F1-4	E1-3	F1-3	F1-4	G1-3	G1-3	G1-3

Notes. (1) As in Figure 2.[11] (2) Analysis of natural distribution of particle sizes. (3) Rubber plus talc to give 100 parts rubber; other mix ingredients: Dutrex 729 oil, 13; Zinc oxide, 5; Stearic acid, 2; IPPD, 2; N-330 HAF black, 56.5; CBS, 0.63; Sulphur, 2.6; Santogard PVI, 0.6. (4) By thermocouple probe in dumped mix. (5) Injection moulded, REP B43 K machine, optimum modulus cure 2.5-3 min, 180°C. (6) Mean of property values along and at 90°C to radial mould flow lines.

Wattmeter plots (Figure 2) for a bale control mix and a mix made with 7.9 mm granules show that the saving given by the granules is mainly due to the absence of the high power surge just before and just after the ram is lowered. The financial saving may well be greater than the 4-12% energy saving mentioned because the cost of peak power loads is disproportionately high. The high power surge is attributed to large pieces of bale control rubber being sheared between the rotors and casing when cold.

2.1.1 Effects of Particle Size and Talc Level on Uncured Rubber and Vulcanizate Properties

Table 1 shows that there is a small reduction in Mooney viscosity as particle size is reduced and possibly a small increase in scorch times. As a result of the small increase in talc level there is a small increase in density from 1.14-1.158 Mg/m^3 and a related increase in the average weight of an injection moulding from 147.1 - 149.8 g.

Hardness is marginally higher for mixes based on rubber particles. The means of tensile property values along and at 90° to radial injection mould flow lines are similar for bale control and granulate mixes in very narrow ranges leading to the conclusion that when the talc level is small and is allowed for there is no loss of tensile properties as a result of using rubber particles. Values for all properties are at a very high level considering the very short, 3 min, single stage mix cycle and the nature of the mix ingredients. Carbon black dispersions of the mixes after the 3 min mix cycle are disappointing in the range G 1-3 to H 1-4. These gradings are slightly improved by injection moulding to values of E 1-3 to G 1-3 and there are no real differences between the control mixes and the particulate mixes. However, it should be pointed out that the presence of talc complicates and spoils the assessment of dispersion.

2.2 PROCESSING WITH NEW MIXING-EXTRUDING MACHINERY

2.2.1 Trials with the Farrel Bridge MVX Machine

The Farrel Bridge MVX, mixing-venting-extruding, machine has an air operated reciprocating ram to prevent powder from bridging and to help feed the mixing chamber under pressure. The vacuum-vented mixing chamber consists of two delta rotors situated transversely above the relatively short (4-5D) hot feed extruder.[5] Three full scale trials have been carried out in conjunction with Farrel Bridge using their MVX 134/120 machine. Trials with Crusoe rubber were carried out in conjunction with Harrisons and Crosfield. Trials with SMR 10 particles were carried out jointly with Dunlop Hydraulic Hose Division who obtained the rubber granules from Plascoat Systems Ltd, Performance Polymers Division. Dunlop carried out the powder blending process with their own Fielder powder blender using a 3.5 min mix cycle, the final 2.5 min being carried out at high speed (1000 rev/min).

The first and most important conclusions are that the MVX is capable of continuously and safely mixing and extruding a range of Crusoe/N-765 SRF black mixes containing 25, 50 and 80 parts of black and convenient levels of oil (5, 10, 20 parts respectively) to give extrudates of good quality and appearance. It has given good extrudates with a highly loaded, Crusoe-based flooring mix. It has also safely and continuously mixed and extruded an abrasion resistant NR hose or cable cover mix as in Table 1 but based on granulated SMR 10 rubber of 4, 8 and 10 mm particle diameter (Figure 3) to give extrudates of good quality and appearance. This represents an advance in knowledge because NR particles of greater than 5 mm diameter had not previously been used. In most cases trials have been carried out with 400-500 kg of each powder blend and have exceeded one hour running times which would normally be long enough to reveal scorch and other problems.

2.2.1.1 Output and specific energy of mixing. As the MVX mixing section rotor speed increases, output increases as in Figure 4 and specific energy of mixing decreases as in Figure 5. This data suggests that high rotor speeds are economically desirable provided they do not cause over-heating and scorch or reduction in the quality or dispersion of the mix. The similarity and overlapping of output and specific energy data for mixes based on different particle sizes suggests that, as far as the mixing process is concerned, there is no obvious advantage in choosing a smaller or larger particle size. As large particles are cheaper than smaller ones industry is expected to use the largest particle that is satisfactory for its purposes.

The optimum output for SMR 10/HAF black mixes is about 250-300 litre/hour. (Figures 4 and 5). This is consistent with previously published data[4] and outputs for the Crusoe/SRF black mixes and the flooring mix for which similar specific energy data was also obtained. The range of values for specific energy of mixing of SMR 10/HAF black mixes in Figure 5 compares favourably with data for the same mixes based on SMR CV 60 and made with the economic, 3 min, single stage K2A mix cycles as quoted in Table 1. Thus the MVX should certainly save mixing energy compared with a two-stage internal mixer process. As the range of mixing energy used by the MVX (0.2-0.3 kWh/litre, Figure 5) is roughly comparable with the single stage internal mixer process (Table 1) it should also save the energy associated with the mill under the internal mixer and a warm-up mill which are not necessary with the MVX.

2.2.2 Trials with the Werner and Pfleiderer EVK Machine

The Werner and Pfleiderer EVK 90 machine[6,7] differs from the MVX in being smaller (90 mm diameter) and having a twin screw compacting and feed arrangement leading to a long (24.5D) vented extruder. The mixing mechanism relies on a long extruder screw with a number of shear dams which create intensive shear and which permit flow into neighbouring flight channels.[6]

Crusoe powdered rubber was blended in a 100 litre Fielder powder blender using a 3.5-4 min mix process and fed to the hopper of the EVK machine on a weigh belt which controlled the input rate. Figure 6 shows optimum outputs of 100-120 litre/h and the dependence of specific energy of mixing on output for Crusoe SRF black and calcium carbonate mixes.

2.2.3 Examination of Mixer-Extrudates from Full Scale Trials

Extrudates obtained under controlled conditions have been examined in the uncured state and then injection moulded for examination of their vulcanizate properties. Table 2 shows a set of data obtained from MVX extrudates based on SMR 10 granules of 8 mm diameter. It is typical of this set of data and other sets that MVX extrudates have higher Mooney viscosities and lower specific energies of mixing than relevant 4 min, single stage laboratory BR Banbury control mixes. This observation suggests that the MVX gives a shorter or less intensive masticating action and mix process than the laboratory Banbury and is consistent with lower mixing energy values already quoted. It also suggests that NR compounds for MVX work should contain more oil or other softeners than is usually employed.

Mooney scorch times of MVX extrudates are similar to, or a little lower than those of relevant Banbury control mixes. MVX and EVK extrudate temperatures are higher than conventional extrudate temperatures

TABLE 2 COMPARISON OF MVX EXTRUDATES WITH A BR BANBURY MIXED POWDER BLEND AND A SIEVED CONTROL MIX

	MVX Extrudates				Banbury	
					Powder blend[1]	Powder sieved[2]
SMR 10[3], 8 mm particles	105	105	105	105	105	105
MVX rotor speed, rpm	95	69	-	85	-	-
Output, litre/h	280	153	156	244	-	-
Extrudate T, °C	125	130	122	125	98[4]	102[4]
Specific energy, kWh/L	0.193	0.293	0.277	0.200	0.381	0.393
Uncured rubber properties						
ML 1+4, 120°C	95	87.5	86	81.5	68.5	67.5
MS t_5, 120°C, min	19.5	12	20	21.5	18.5	23
M_{HR}-M_L, 160°C	28.7	32.1	27.2	25.6	27.1	26.3
Vulcanizate properties[5]						
Density Mg/m^3	1.220	1.219	1.190	1.184	1.206	1.160
Hardness, IRHD	74	76	69	68	68	66
Tensile strength[6], MPa	18.6	20.4	21.1	21.8	21.0	23.7
Elongation at break[6], %	407	432	489	496	499	508
M_{300}[6], MPa	12.8	13.9	11.2	11.1	12.0	12.0
Cabot black dispersion	G,H1-4	G,H1-4	E1-4	E1-4		

(1) Powder blend as to the MVX. (2) SMR 10 granules sieved free of excess talc before mixing. (3) Rest of mix as in Table 1, except PVI, 0.4. (4) Banbury dump temp. 4 min mix cycle. (5) Injection moulded; REP B43K machine; optimum modulus cure, 2-2.5 min, 180°C. (6) Mean of property values along and at 90° to radial mould flow lines.

but lower than industrial internal mixer dump temperatures leading to the conclusion that it is wise to choose a safe curing system for continuous mixer-extrusion processes.

All the MVX and EVK extrudates produced under a range of rotor or extruder screw speeds and output rates which have been compounded with a sulphur/CBS/Santogard PVI cure system have proved safe enough for injection moulding with the REP B43K machine. All the extrudates derived from the Crusoe SRF black mixes gave a high level of vulcanizate properties which compared favourably with those of laboratory Banbury mixed controls made from the powder blends which went into the MVX. Although the extra processing by the REP machine may have masked some differences there were very few differences in vulcanizate properties to be detected between members of a series of injection mouldings which could be related to changes in MVX machine conditions of rotor speed and output.

All vulcanizates prepared from MVX extrudates derived from SMR 10 granules had a very high level of physical properties (Table 2) but they gave higher hardness and specific gravity than relevant control mixes which had been prepared direct from sieved SMR 10 granules. They also gave lower tensile strength and elongation at break than these control mixes. In most cases modulus at 300% elongation was higher. Observations of higher hardness, higher specific gravity, lower tensile strength, lower elongation at break and higher modulus are consistent with and are believed to be at least partly due to an excess of talc in the extrudates which had been sieved out of the laboratory control mixes. Average values for tensile strength and elongation at break measured along and at 90° to radial injection mould flow lines would pass BS 490:1972 Grade N17 belting specifications which were used as a criterion of quality for an abrasion resistant hose cover. Dunlop Hydraulic Hose Division expressed satisfaction with the quality of the rock drill hose prepared with about 1 tonne of experimental product.

2.2.4 Injection moulding

The Werner and Pfleiderer GSP 160 injection machine was used with an unvented EVK type screw for injection moulding of a Crusoe powder blend containing 50 pphr SRF black (mix B, Figure 6). Mouldings with a cross-section varying from 1.5-13 mm thick cured in 1.75 min at a mould temperature of 185°C, which is satisfactory but the dispersion of the carbon black was such that undispersed clusters or particles still contained air which formed blisters when the moulding pressure was released.

3 ECONOMICS OF PROCESSING GRANULATED RUBBER

One of the most important factors about powdered and granulated rubber concerns the question of whether the subsequent processing advantages outweigh the costs of producing the fine particle form and transporting it knowing that it has approximately twice the volume of bale rubber. Even if there is no production cost premium on the granular forms of rubber from Malaysia the freight cost of rubber granules is about £60/tonne higher than that for bale rubber. Spray dried rubber powder is available and has a small market where its very fine particle size permits time saving in dissolution processes but it is probably too costly for general purpose applications.

To help answer the question posed above, the economics of (a) Banbury mixing with bale rubber, (b) continuous MVX mixer-extrusion with granulated rubber and (c) liquid curing (LCM) of products from 'a' and 'b' have been examined by costing in a hypothetical 'green-field' factory with all modern facilities.

Granulation of bale rubber has been shown to cost about £100/tonne[11] which is reasonably consistent with prices charged by granulating companies. However, a slightly lower cost could be visualized if new buildings were not necessary and if a different set of capital charge assumptions was made.

3.1 COMPARISON OF THE COSTS OF MIXING WITH BALE AND GRANULATED RUBBER

This section compares the costs of production of a rubber strip by the classical Banbury mix process using bale rubber and the new continuous MVX mixer-extruder process starting with granulated rubber. The Banbury process is versatile in that it could start with bale rubber or granules but the MVX process must start with a dry powdered or granulated rubber blend made in a Fielder or similar powder blender.

The strip considered is to be suitable mainly for (1) feeding to extruders for further processing into products such as hose, cable covers, tyre beading or profiles but also for (2) feeding to injection moulding machines or (3) for use as moulding blanks for compression moulding. The MVX machine is capable of direct production of profiles or hose products, but this is the subject of a separate study. (Section 3.2).

Hypothetical factories are considered which will use 250 tonne/month of either bale rubber or rubber granules. The conversion to strip involves mixing in of fillers and curatives to the extent that about 5 500 tonne/year of rubber strip are produced, the general assumption being that such a rubber product contains about 50% of rubber. The actual production targets are 5 470 tonne/year of mix as in Table 1 from the Banbury/bale rubber process and the equivalent volume of 5 566 tonne/year from the MVX/granule process. The difference allows for the presence of 5% talc with the granules.

The choice of using 250 tonne/month of rubber granules is in balance with the output of the rubber granulating factory already considered.[11] However, this is rather a large general rubber goods factory for Europe if it turns out about 5 500 tonne/year of extruded goods.

3.1.1 Capital Costs of Mixing and Producing Strip, Banbury Process vs MVX

Table 3 sets out capital costs. Figures 7 and 8 give flow diagrams of the Banbury and MVX processes and Figures 9 and 10 show schematic factory layouts for area and building costing. Notes in Appendix 1 give further details of assumptions and methods of calculation.

The starting point is an F80 Banbury internal mixer which is sufficiently versatile to reach the annual production target (depending on shifts and hours worked), if it is used with 3 min or 6 min mix cycles. The basic Banbury mixer costs £135 000 and needs at least one, and most likely two, 1.5 m (60 in) mills (2 x £56 000) and ancillary machinery such as coolers, strip-cutters, conveyors and stackers. Automatic weighing and feeding is put in for modern practice but the quantities involved here are rather small for the expense involved. Small quantities of accelerators and curatives must still be weighed by hand. The Banbury production line costs about £1 231 000.

TABLE 3 CAPITAL COSTS OF MIXING, BANBURY PROCESS vs MVX, £

	BANBURY	Number of MVX Machines			
		3	2	2	1
Building[a]	660 000	719 136	668 448	668 448	617 760
F80, Banbury[b]	135 000	-	-	-	-
2, 1.52 m Mills[c]	112 000	-	-	-	-
MVX 134/120	-	384 000	256 000	-	-
MVX 240/150	-	-	-	296 000	148 000
Other machinery	98 000[d]	135 278[e]	95 278[e]	99 278[e]	57 278[e]
Automatic weighing	150 000	150 000	150 000	150 000	150 000
Miscellaneous[f]	76 124	77 488	69 088	71 288	61 788
Total	1 231 124	1 465 902	1 238 814	1 285 014	1 034 826

Notes a-f, see Appendix 1

There is no single figure for the output of the Banbury which varies depending on the type of mix employed and the mix cycle times. Therefore a range of Banbury outputs is considered depending on 3-6 min mixing cycles and a range of possible MVX mixing strategies needs to be considered in order to match these Banbury outputs. The capital costs of three and two smaller MVX 134/120 machines and two and one of the larger MVX 240/150 machines is considered in Table 3.

One MVX machine costs approximately the same as the F80 Banbury. If 2, MVX machines are required to match the Banbury output the MVX machine line costs are higher than those of the Banbury and its ancillary equipment. Space and building costs are also judged to be marginally larger for MVX lines. Only if a single MVX machine matches the Banbury output will capital costs for an MVX line be smaller than the Banbury line costs and this is considered very unlikely in the context of this cost exercise to produce strip for further processing.

3.1.2 Production Costs for Mixing and Producing Strip, Banbury Process vs MVX

Production costs for producing strip of non critical dimensions for further processing are compared in Table 4. Assumptions and methods of calculation are described in Appendix 2.

3.1.2.1 Banbury production costs. The most important and most likely process case under consideration in the first column of Table 4 is a Banbury mix cycle of 3 min followed by a second stage process during which mixed rubber is put on to a warm-up mill from which multiple strips can be cut. The cost as set out is about £748/tonne of mixed compound in strip form.

For achievement of adequate dispersion and viscosity, difficult, or more complex mixes may require longer mixing times (eg 6 min) or even 2, 3 min mix cycles followed by the second stage process. To allow for these two cases where the mixing time has doubled, the electricity, cooling water, labour and maintenance costs are considered to have doubled in proportion to the increased production time. These cases are accounted for in column 2 and the cost of strip becomes £803/tonne which is regarded as an upper limit for the Banbury mix process.

From the work described in Section 2.1, it is possible to envisage that a single stage, 3 min Banbury mix cycle is possible and would give adequate curative and black dispersion and satisfactory viscosity for further processing and that the second stage process of warming up would not be necessary. In this favourable case it is possible that strips could be cut from the mill under the Banbury and the capital costs of the second mill and the subsequent process line (£96 000) and about 10% of the factory space could be saved. This costing is not shown in Table 4 but it would lead to the minimum conceivable Banbury process cost of £729/tonne, thus saving about £19/tonne. However, it is unlikely that a factory could rely on such a simple process which is not very versatile and the most likely Banbury production cost for comparison purposes remains about £748/tonne.

3.1.2.2 MVX production costs. Production costs vary with the number of MVX machines, their size, their output and the number of shifts worked. They also depend on man-power per MVX machine. Details of costing involving either three or two of the smaller MVX 134/120 machines or two or one of the larger MVX 240/150 machines and the other variables are also given in Table 4.

The cost of rubber for the MVX process is higher than for the Banbury process by the amount for the cost of granulation and the presence of talc. Equal volumes of production output are considered but

TABLE 4 PRODUCTION COSTS OF MIXING AND EXTRUDING STRIP FOR FURTHER PROCESSING, BANBURY vs MVX;

Production targets : Banbury, 5470 tonne/year, MVX 5566 tonne/year

Banbury mix cycle, min	3	6	-	-	-	-	-
MVX Output, litre/h per machine	-	-	250	300	350	500	1 000
MVX machines: shifts/day	-	-	3S:3	3S:3	2S:3	2L:2	1L:2
Direct costs, £/year							
Rubber[a,b]	1 980 000	1 980 000	2 317 260	→			
Chemicals[c]	1 213 650	1 213 650	1 213 650	→			
Electricity[d]	51 400	103 000	56 814	47 348	41 953	51 541	27 354
Water[e]	26 661	53 323	31 667	26 391	22 619	15 835	7 918
Transport in, port cost[f]	32 900	32 900	-	-	-	-	-
Labour[g]	99 862	214 040	252 117	220 849	197 068	138 248	86 405
Testing[h]	28 532	61 154	45 839	40 154	49 267	34 563	34 563
Indirect costs, £/year							
Factory administration[i]	99 862	99 862	99 862	→			
Building capital[j]	135 535	135 535	147 679	147 679	137 270	137 270	126 861
Machinery capital[k]	190 974	190 974	249 705	249 705	190 720	206 168	139 459
Working capital[l]	159 683	159 683	181 923	→			
Maintenance[m]	74 271	148 542	86 853	86 853	74 838	77 038	63 922
Total direct and indirect costs, £/year	4 093 330	4 392 663	4 683 369	4 631 674	4 526 430	4 473 358	4 299 177
Cost of strip, £/tonne	748.32	803.05	841.42	832.14	813.23	803.69	772.40
Simplest assumption for labour saving:	Deduct labour above and substitute figures below.						
Labour (1 man to weigh + 1/MVX line)	-	-	91 679	80 309	73 901	51 843	34 563
Total direct and indirect costs, £/year	-	-	4 522 931	4 491 134	4 403 263	4 386 953	4 247 335
Cost, £/tonne	-	-	812.60	806.89	791.10	788.17	763.09
Processing costs							
3 men/MVX, £/year	866 780	1 166 113	1 152 459	1 100 764	995 520	942 448	768 267
Cost of strip £/tonne	158.46	213.18	207.05	197.77	178.86	169.32	138.03
1 man/MVX, £/year	-	-	992 021	960 224	872 353	856 043	716 425
Cost of strip, £/tonne	-	-	178.23	172.52	156.73	153.80	128.71

S = Small MVX 134/120; L = Large MVX 240/150.

For Notes a - m, see Appendix 2

owing to different densities due to the talc the output in tonnage is greater for the MVX process. Further details are in Appendix 1.

A key factor for calculations is the output in litre/hour because this determines the machine strategy and the number of working hours required to meet the annual volume production target. Costs such as electricity, water, labour, testing and maintenance are calculated depending on working hours to reach the production target.

The smaller MVX 134/120 machine is known by experimental work in Section 2.2.1 to give an output of about 250-300 litre/h (290-348 kg/h) with the NR mix (density 1.16 Mg/m^3) under consideration. At a feasible output of 300 litre/h, 3 MVX machines working 3 shifts/day are necessary to match the most likely Banbury output in column 1 and the associated cost of rubber strip is £832/tonne with 2 men to weigh and work the powder blender and 3 men per MVX machine. If the manpower can be reduced to one man for weighing and operating the powder blender and one man per MVX machine as suggested by Farrel Bridge the cost can be reduced to £807/tonne. Even at this optimistically low manpower level the cost of MVX strip is £59/tonne dearer than Banbury strip (£748/tonne).

During MRPRA's trials it was desirable, if not absolutely necessary to have a three man team on the MVX machine. One man fed the MVX, one operated it and one removed the product. It is not unreasonable to suppose a good element of automation in weighing with the 'push-button' weighing machinery costed here but one man must still weigh sulphur and accelerators. If this same man could operate the powder blender and if one can assume automatic feeding of the MVX the cost of £807/tonne appears to be possible but a cost between £807/tonne - £832/tonne seems more likely.

The maximum output observed with the MVX 134/120 machine was 330 litre/h (Figures 4 and 5). Thus, the other costs for the MVX 134/120 machine in column 5 of Table 4 are more speculative on account of the high output rates but, if an output of 350 litre/h is possible, the production costs could be reduced to £813/tonne for a 3 man MVX team or £791/tonne with a single MVX operator.

MRPRA has not had a trial with the bigger MVX 240/150 machine and the only production figure so far reported is 400 kg/h for a finished product. Production rates for a finished, dimensionally correct product can be expected to be less than for a strip of uncritical dimensions. Therefore calculations in columns 6 and 7 of Table 4 are based on 500 and 1000 litre/h, approximately as given by Farrel Bridge trade literature.

At a production rate of 500 litre/h the MVX 240/150 machine could produce rubber strip at about £804/tonne and, with only one man per MVX line this could perhaps be reduced to £788/tonne. At the highly speculative rate of 1000 litre/h with this MVX machine the cost of strip is about £772/tonne and this could possibly be reduced to £763/tonne if there is only one man working the MVX machine. Even under these highly optimistic production rate and labour conditions with one large MVX machine working only two shifts/day the cost of strip for further processing is £763/tonne which exceeds the most likely Banbury process cost of £748/tonne.

3.1.2.3 Comparison and discussion of production and processing costs, Banbury process vs MVX. Selected Banbury production costs are more simply reproduced at the top of Table 5 and compared with a range of possible MVX costs.

TABLE 5 COMPARISON OF PRODUCTION COSTS, BANBURY vs MVX

	Production cost, £/tonne	
Banbury mixing process		
3 min cycle with 2nd stage	748	(most likely cost)
3 min cycle without 2nd stage	729	(cheapest cost)
6 min cycle with 2nd stage	803	(upper cost limit)
MVX methods	3 men/MVX	1 man/MVX
3 MVX 134/120 machines		
Most likely output, 300 l/h each	832	807
2 MVX 134/120 machines		
Possible output, 350 l/h each	813	791
2 MVX 240/150 machines		
Output, 500 l/h each	804	788
1 MVX 240/150 machine		
Most optimistic output, 1000 l/h	772	763

This table shows that, at the most likely, three MVX 134/120 machine output rate for the natural rubber mix under consideration the production cost for strip exceeds even the upper limit for the Banbury production cost. Even with only 2, MVX 134/120 machines at an optimistic output of 350 l/h the production cost exceeds the upper Banbury cost.

The basic costs of possible MVX production lines and the factory space to house them are similar to those of Banbury mixer production lines and therefore any definite capital and space cost reductions are difficult to pinpoint with accuracy. When production rates of Banbury lines and MVX production lines are also similar, it follows that production costs are broadly similar.

By deducting rubber, chemical, transport-in and port costs from the production costs in Table 4 it is possible to arrive at the essentials of the processing costs which are simplified in Table 6. Here it is seen that the most likely Banbury processing cost for strip is about £158/tonne. Similar MVX processing costs could possibly be achieved if 2, small or large MVX machines operate at rather optimistic outputs with only one operator. Only when one large MVX machine operates at the highly optimistic rate of 1000 l/h does it seem possible that significant processing savings could be made but these are not enought to compensate for the granulation premium.

This means that MVX processing to the stage of making strip for further processing offers very little, if any, chance of making savings compared with the classical Banbury method. There is no evidence that any of the premium to cover the cost of granulation can be recovered.

Even if one MVX machine can equal the output of a Banbury line the capital savings in machinery and factory space are rather small in the context of the [illegible] areas of the general factory requirements. Even these savings [illegible] reversed by the extra storage capacity required by granulated [illegible]

It is of [illegible] to extract the cost of granulation from Table 4 which becomes £61.66/tonne of mixed product in strip form. This can be

TABLE 6 COMPARISON OF PROCESSING COSTS, BANBURY vs MVX

	Processing cost £/tonne	
Banbury mixing process		
3 min cycle with 2nd stage	158	(most likely cost)
3 min cycle without 2nd stage	139	(cheapest cost)
6 min cycle with 2nd stage	213	(upper cost limit)
MVX methods	3 men/MVX	1 man/MVX
3 MVX 134/120 machines		
Most likely output, 300 l/h each	198	173
2 MVX 134/120 machines		
Possible output, 350 l/h each	179	157
2 MVX 240/150 machines		
Output, 500 l/h each	169	154
1 MVX 240/150 machine		
Most optimistic output, 1000 l/h	138	129

compared with selected Banbury process costs for electricity and labour also extracted from Table 4 and reproduced in Table 7. The cost of granulation is now seen to exceed the combined costs of electricity and labour (£57.96/tonne) even when considering the 6 min Banbury mix cycle. Under these circumstances it is difficult to see how the premium on granulated rubber can be off-set by savings in labour or electricity.

TABLE 7 COMPARISON OF COST OF GRANULATION WITH ELECTRICITY AND LABOUR COSTS

	£/year	£/tonne	£/year	£/tonne
Cost of granulation	337 260	61.66		
Banbury process cycle, min	3	3	6	6
Electricity	51 400	9.40	103 000	18.83
Labour	99 862	18.26	214 040	39.13

3.2 COMPARISON OF THE ECONOMICS OF VULCANIZATION OF A PROFILE THROUGH A BANBURY/COLD FEED EXTRUDER/LCM BATH PROCESS AND AN MVX EXTRUDER-MIXER/LCM PROCESS

The hypothetical exercise in Section 3.1 compared the production costs of strip rubber for further processing produced by a conventional Banbury route starting with bale rubber and an MVX route starting with granulated rubber. This exercise is valid and realistic but it is a little unfair to the MVX machine and granulated rubber in that it ignores the fact that the MVX could have produced an accurate profile or vulcanizable product instead of just a strip having uncritical dimensions which could be used as feed stock for another process.

Although no company is known to be doing it yet commercially as in this present exercise, it is assumed now that the MVX 134/120 machine used in Section 3.1 produces a finished profile or product which is all ready for passing to the LCM bath for vulcanization. There are two points about this assumption which are not considered in detail. One is that the costs of expensive profile dies were not considered in Section 3.1 and the other is that the rate of production is not likely to be so high as in Section 3.1 if the product has to be dimensionally correct. However, these points are in favour of the granulated rubber and are neglected here for simplicity.

The main difference explored in this exercise is that the MVX directly produces a profile whereas the classical Banbury/warm-up mill process can only produce a strip of roughly controlled dimensions which needs to be put through a cold feed extruder to be shaped into a profile for vulcanization.

The LCM vulcanization plant is assumed to be adjacent to the Banbury plant or the MVX plant and rubber is assumed to be passed direct from the MVX to the LCM bath, but, for accounting purposes, the vulcanization plant is assumed to 'buy' its rubber from the strip manufacturing plant at costs indicated in column 5 of Table 4.

3.2.1 Processes and Products

In the cold feed extruder/LCM process (flow chart Figure 11) rubber strip via the bale source, the Banbury, the warm-up mill and strip cutting process is stored for quality control purposes. It is fed to a cold feed extruder and then, while still warm (90-100°C), it is fed directly into the liquid curing medium (LCM) salt bath at about 200°C in which vulcanization takes place. A cooling and washing bath at the end of the LCM bath cleans up the product and a haul-off machine removes it for pre-sale storage.

Two 150 mm (6 in), cold feed extruders are considered necessary for an output of 5470 tonne/year of an unspecified extruded product such as a profile. Two LCM baths are also necessary for this output. One man can run two extruders side by side and one man is necessary to look after the cured product from each LCM bath, eg a team of three men per shift.

In the MVX/LCM process the MVX machine produces a fully shaped profile which is passed while still warm (100-130°C) directly to the LCM bath as indicated in the flow chart, Figure 12. This saves the labour and space involved in storage for quality control and may make the conventional quality control unnecessary unless samples can be taken at intervals without spoiling the product or the continuity of the process. At least two MVX machines and two LCM baths are necessary for the 5566 tonne/year output.

One man is necessary to remove product from each LCM bath. For the present exercise a rather optimistic output of 350 l/h is assumed in order to keep the number of MVX and LCM machines down to two.

For this present exercise the details of the product are best left unspecified for lack of definite experience. The mix under consideration in Section 2 was designed as an abrasion resistant hose or cable cover. A hose up to 100 mm (4 in) diameter can be cured by the LCM bath so this could be a possible product. Profiles for window stripping or beadings for tyres are equally possible products.

3.2.2 Capital Costs

Detailed capital costs for buildings and machinery as in Figures 13 and 14 are given in Table 8.

TABLE 8 COMPARISON OF CAPITAL COSTS OF EXTRUSION AND VULCANIZATION FACILITIES FOR CONVERSION OF BANBURY STRIP INTO A CURED PROFILE AND VULCANIZATION OF A PROFILE STRAIGHT FROM THE MVX

	Banbury/cold feed extruder/LCM	MVX/LCM
	£	£
Main building	147 840	129 360
Two extruders	140 000	-
Two LCM baths	110 000	110 000
Pallets	10 000	10 000
Fork lift truck	14 543	14 543
Installation	13 227	6 227
Total	435 610	270 130

Costing scheme as Appendix 1

The building for the cold feed extruder/LCM process is bigger than that for the LCM bath by the amount necessary to house the two cold feed extruders. Costs are therefore higher and the machinery costs are also higher by the cost of the cold feed extruders.

On the other hand the working capital required by the MVX/LCM process (Table 9) is higher because the MVX extrudate is based on granulated rubber at a premium of about £101.45 above bale rubber price.

3.2.3 Production Costs

Detailed production costs are given in Table 9 with notes and assumptions in Appendix 3.

Direct costs such as the electricity, water and labour costs for the cold feed extruder/LCM process are higher than for the LCM process costs and so are most of the indirect costs but, in spite of this, the overall costs of the bale rubber/Banbury/ cold feed extruder/LCM product is about £16/tonne cheaper than the granulated rubber/MVX/LCM product because of the cheaper feedstock price.

Section 3.2 therefore indicates that the direct extrusion of a profile by the MVX machine and its direct vulcanization in an LCM bath is an economical step and it is cheaper than the cold feed extrusion and LCM curing of a similar product but the economies possible in this step do not offset the high premium of about £100/tonne which have to be paid for granulated rubber.

There is one last possible consideration. If the MVX/LCM bath process is 100% reliable it is possible that the 'other machinery' (cooling conveyors, stackers) in Table 3 and Figure 10 can be regarded as unnecessary and its associated capital and maintenance charges in Table 4 can be deleted. This would also allow a 20% reduction in factory space and associated capital charges leading to a reduction of the cost of a profile feed stock to the LCM being reduced from £791.1/tonne to £775.85/tonne.

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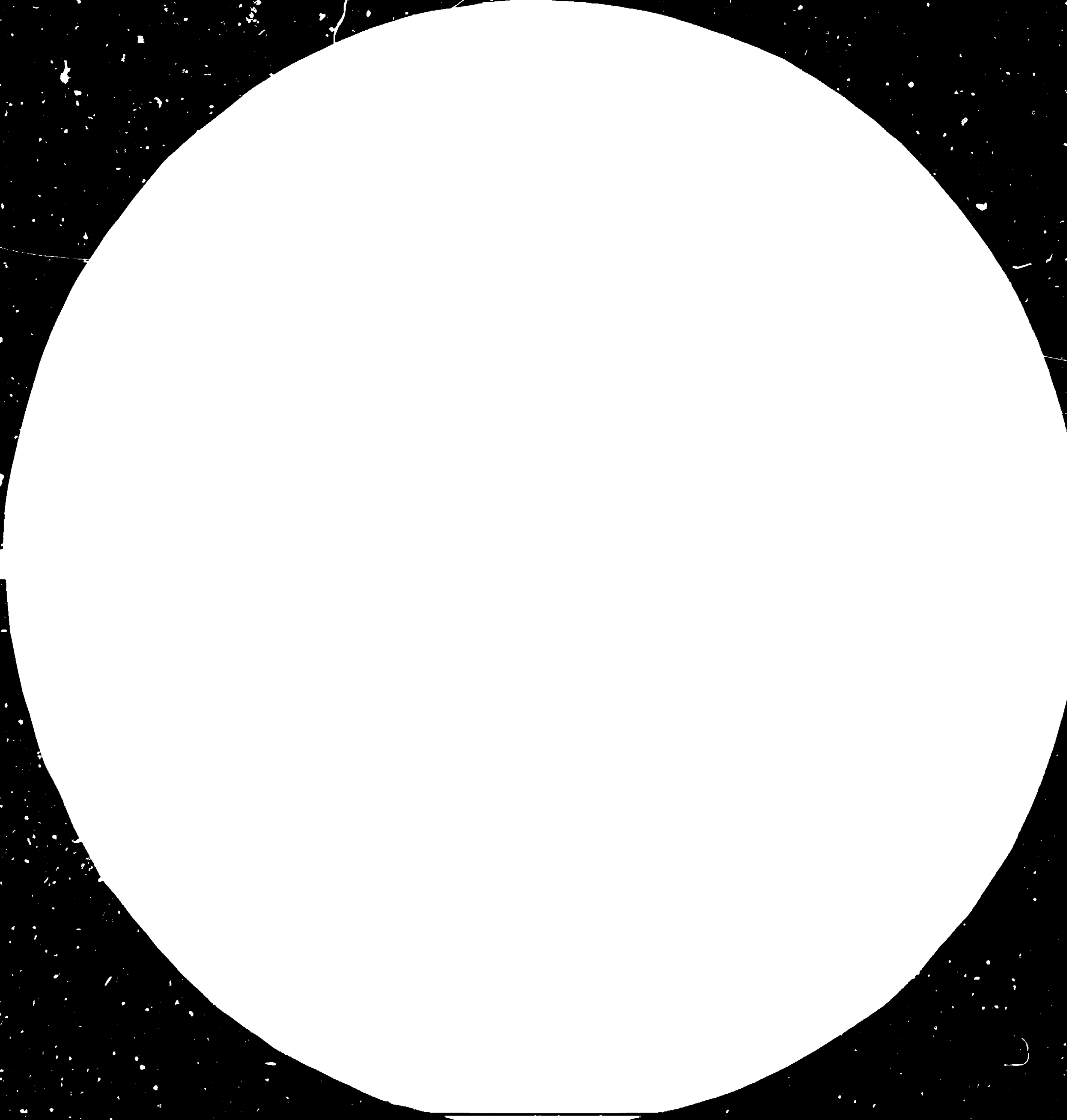

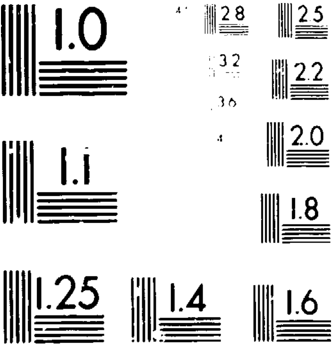

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS
STANDARD REFERENCE MATERIAL 1010a
ANSI and ISO TEST CHART No. 2

TABLE 9 COMPARISON OF PRODUCTION COSTS OF A VULCANIZED PRODUCT FROM A BANBURY/EXTRUDER/LCM PROCESS WITH THOSE OF AN MVX/LCM PROCESS

	Banbury/cold feed extruder/LCM	MVX/LCM
Direct costs/year	£/year	£/year
Rubber in strip form [a*]	4 093 310	4 403 263
Electricity[b]	86 949	48 945
Water[c]	26 329	18 095
Labour[d]	73 901	49 267
Indirect, overhead costs		
Factory administration[e]	73 901	49 267
Building capital charge[f]	30 360	26 565
Machinery capital charge[g]	96 225	47 071
Working capital costs[h]	204 666	225 540
Factory heating[i]	3 013	2 636
Factory lighting[j]	140	123
Machinery, building maintenance[k]	21 119	13 195
Total direct and indirect costs	4 709 913	4 883 967
Total costs, £/tonne	861.04	877.46

Difference = £16.42/tonne

* Rubber in strip form from the Banbury and warm-up mill to the cold feed extruder and an extruded profile from the MVX to the LCM bath are costed from Table 4, see also Appendix 3.

Substituting this reduced feed stock price in calculations as in Table 9 the cost of the MVX/LCM cured profile can be reduced to £862.21/tonne which is practically the same as that for the Banbury/cold feed extruder/LCM process. In this case the premium on granulated rubber has just been offset by the savings in other costs.

3.3 SUMMARY OF PROCESSING ECONOMICS

A summary of the granulation process[11] and the processing steps described in Section 3 is given in Figure 15 with value added costs for each step and cumulative costs. For simplicity, only a single value representing a cost range is taken from Table 4 but values chosen are the 'most likely' cost for the Banbury mix process and a rather optimistic figure for the output (350 l/h) of the MVX mixer-extruder process.

Figure 15 emphasizes the fact that the Banbury mix process and the MVX mixer-extruder process can produce strip for further processing at similar costs. If the MVX produces a profile or extruded product ready for direct vulcanization it is economical but the possible savings are not enough to offset the heavy premium on granulated or powdered rubber.

4 CONCLUSIONS

4.1 Background studies of commercial granulation and powdered rubber usage suggest that the present and near future demand for powdered and granulated rubber can be satisfied by existing sources.

4.2 The process of granulation has been studied with variations of the screen size and partition agent. Particles of varying size produced at MRPRA have been satisfactorily used for processing trials. Particles with a low level of partition agent have been produced and problems associated with controlling talc levels in industry have been identified.

4.3 Internal mixer processing studies have shown that rubber particles can lead to a small 4-12% saving in mixing energy compared with that required for a similar bale rubber process. Vulcanizate properties derived from mixes based on particles show no serious losses of physical properties provided the talc level is small and is allowed for. Variable talc levels can seriously upset vulcanizate properties by spoiling rubber/filler/curative ratios.

4.4 Full scale mixer-extruder trials with the Farrel Bridge MVX machine have shown that this new range of mixing machines can continuously and safely mix and give good quality NR extrudates over a range of processing conditions with a range of particle sizes from 2-10 mm diameter. Although the carbon black dispersion of these extrudates was disappointing they gave good quality vulcanizate properties compared with similar bale rubber control mixes. The new continuous mixing machinery is therefore quite satisfactory for use with NR with due care for black dispersion.

4.5 An abrasion resistant hose or cable cover mix was devised for use with the MVX machine. Compounding for this machine requires recognition that mixing times are short and that normal mastication steps or extended mixing times in conventional internal mixers have to be compensated for by accurate compounding for viscosity suitable for subsequent processing. Compounding for freedom from scorch is also important because the mixer extruder makes a complete mix including sulphur and accelerators and then extrudes it at somewhat higher extrudate temperatures than normal cold feed extruders. Dunlop Hydraulic Hose Division were well pleased with the quality of the tonne of extrudate derived from NR particles during MVX trials and the rock drill hose they made from it.

4.6 The cost of granulation in a hypothetical green-field factory is about £100/tonne of rubber granulated. It is possible that this could be reduced a little if new buildings were not costed and if lower assumptions for capital charges could be made.

4.7 The cost of a favourably quick MVX mixer-extrusion process with NR granules in a hypothetical factory to give a strip product suitable for subsequent processing is practically the same as that for a conventional bale rubber/internal mixer process leaving little or no opportunity for recouping the premium for granulation.

4.8 When the MVX machine produces a fully shaped profile ready for direct vulcanization in the LCM bath in a hypothetical factory it can lead to useful savings in plant and floor space but the cost of the vulcanized product is about the same as that for the product from the conventional bale rubber/internal mixer/cold feed extruder/LCM process. The direct MVX process is thus cheaper than the conventional process but it is not cheap enough to do more than just about compensate for the granulation cost.

4.9 The new continuous mixing-extrusion machinery offers an attractive alternative processing pathway to the internal mixer but the rather high cost of granulated rubber needs to be carefully considered with respect to the possible savings.

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Appendix 1

Notes and assumptions for Table 3

a **Buildings**

Building costs are £264/m^2.

b **Banbury internal mixer**

F80 Banbury, batch volume : theoretical maximum, 80 1; practical volume for batch weight calculations, 60 1.

c **Mills**

One 1.52 m (60 in) mill under F80 Banbury; second mill is a warm-up mill for second stage processing.

d **Other machines, Banbury line**

Other or ancillary machinery includes bale cutter (£8 000), batch-off machine, festoon cooler, strip cutter and stacker (£50 000) for main Banbury process line and a pallet unloader and mill feeder (£10 000) and strip cutter, cooler, conveyor and stacker (£30 000) for the second process line.

e **Other machinery, MVX lines**

For MVX lines other machinery includes one Fielder powder blender (£15 278) and a storage bunker, a powder conveyor, a cooling conveyor, pull rolls, an output conveyor and a stacker for each MVX line.

f **Miscellaneous**

Miscellaneous items include small weighing equipment (£7 000). pallets (£2 500), fork lift truck (£14 543), Monsanto rheometer (£11 020), Mooney viscometer (£8 865), dust extraction (£2 000), office equipment (£3 000) and installation at 5% of machinery costs.

Appendix 2

Notes and assumptions for Table 4

a **Rubber for Banbury**

Bale rubber costs 3 000 tonne x £660/tonne (average price for 1980).

b **Rubber granules for MVX**

The cost of granulated rubber for the MVX process is taken from a calculation as in Table 4, 'Granulation of NR'.[11] In this case the calculation allows for 5% talc which is more appropriate to the experimental work on the commercial granules.[11] With 5% talc the cost of granulation is £797.42 per tonne of rubber processed but an in-house process is considered here and the £25/tonne delivery charge can be deducted so the cost of granulated rubber for the MVX process is £772.42/tonne. The overall cost of the granulation process is now £101.45 if the initial cost of rubber (£660/tonne) and the transport-in and port charges (£10.97/tonne) are deducted.

The cost of granulated rubber for the MVX process is 3 000 tonne x £772.42 = £2 317 260. It can also be calculated as 3 150 tonne (including 5% talc) x £735.64/tonne of (rubber and talc mixture). This cost also includes transport-in and port charges.

c **Chemicals**

Chemicals, fillers, curatives etc are costed as for the mix given in Table 1.

d **Electricity**

Electricity is costed at £0.03/kWh, times the working hours to reach the production target. Kilowatt ratings were given by manufacturers.

e **Water**

Water is costed at £0.5 per 4 546 litre (1 000 gallons).

f **Transport**

Transport-in and port charges are included in the cost of granulation for the MVX processes.

g **Labour**

Labour for the main Banbury line consists of 5 men. Two men weigh; one man operates the Banbury; one man operates the mill and one man takes-off the product. Two men are required for the second stage process line; one man at the warm-up mill and the other at the take-off point.

The main calculation for MVX labour is based on two men for weighing, and three men/MVX machine line. A subsidiary calculation reduces the man-power level to one man for weighing and one to operate the MVX line.

Labour is charged at £100/40 hour week. Employer's contributions to national insurance (13.7%) and pensions (15%) bring this sum to £128.7/40 hour week per man. Saturday overtime is costed at 50% higher rates and Sunday overtime at double time.

The total labour cost is calculated on a combination of the shifts and extra hours work required to make up the annual production target.

h **Testing**

Testing is costed at two men's full time labour and involves testing every Banbury batch on the Rheometer. Other testing includes Mooney viscosity, Hardness and SG carried out less frequently.

Indirect, overhead costs

i Factory administration

Administration cost is taken as equal to the labour charges.

j Building capital charge

The annual charge is calculated by the discounted cash flow method eg annual charge = investment x $\frac{i(1+i)^n}{(1+i)^n-1}$

where n is the number of years and i the interest rate. The building is taken to have a life of $n=20$ years, with $i=0.2$ (ie 20% interest rate), as applicable in the UK in 1980.

k Machinery capital charge

The annual charge for this sum is costed as in note j above with $n=5$ years and $i = 0.2$.

l Working capital costs

The working capital cost is calculated as a permanent debt of 20% of the value of three months working stock of NR, partition agent and packaging material.

m Maintenance

The building and machinery items in the relevant capital cost Table with mechanical and electrical working parts are charged at 5% for maintenance. The term also includes factory heating costed at £5.38/m^2 of floor space per year and lighting costed at £0.25/m^2 per year.

Appendix 3

Notes and assumptions for Table 9

a Assumed feedstock price to Banbury/cold feed extruder/LCM process from Table 4 is £748.32/tonne (x 5470 tonne = £4 093 310). Assumed feedstock price to the MVX/LCM process is £791.10/tonne (x 5566 tonne = £4 403 263). The 'reduced' feedstock price to the MVX/LCM process if the single process to a finished profile is used without facilities to form strip for further processing is £775.85/tonne (x 5566 tonne = £4 318 381).

b-k The same methods of costing as used for Tables 3 and 4 are also used here.

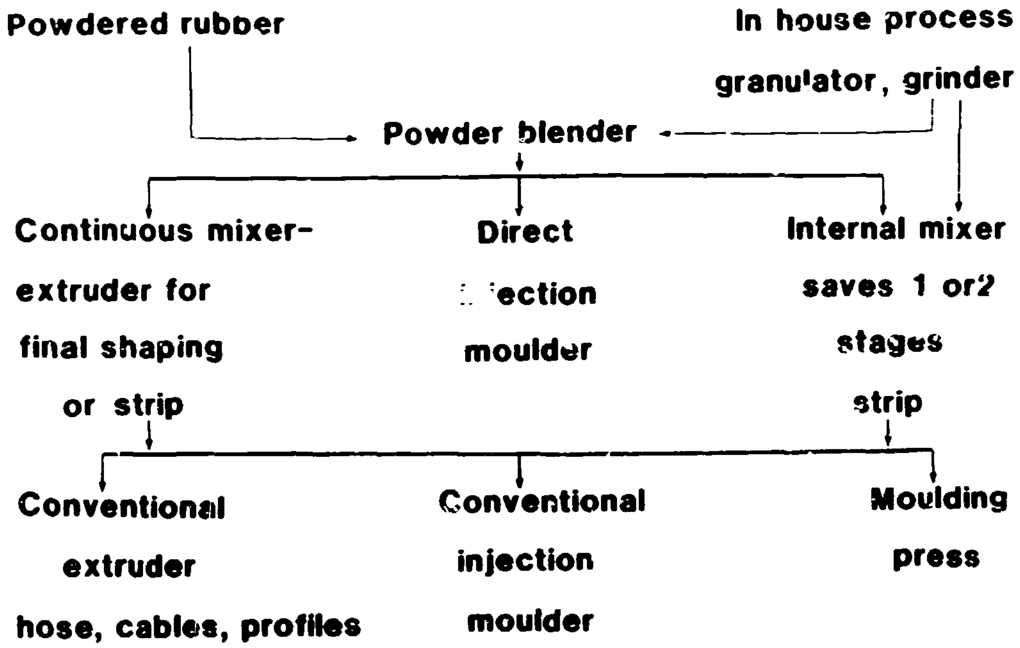

Fig. 13.1 A series of possible powdered rubber process routes.

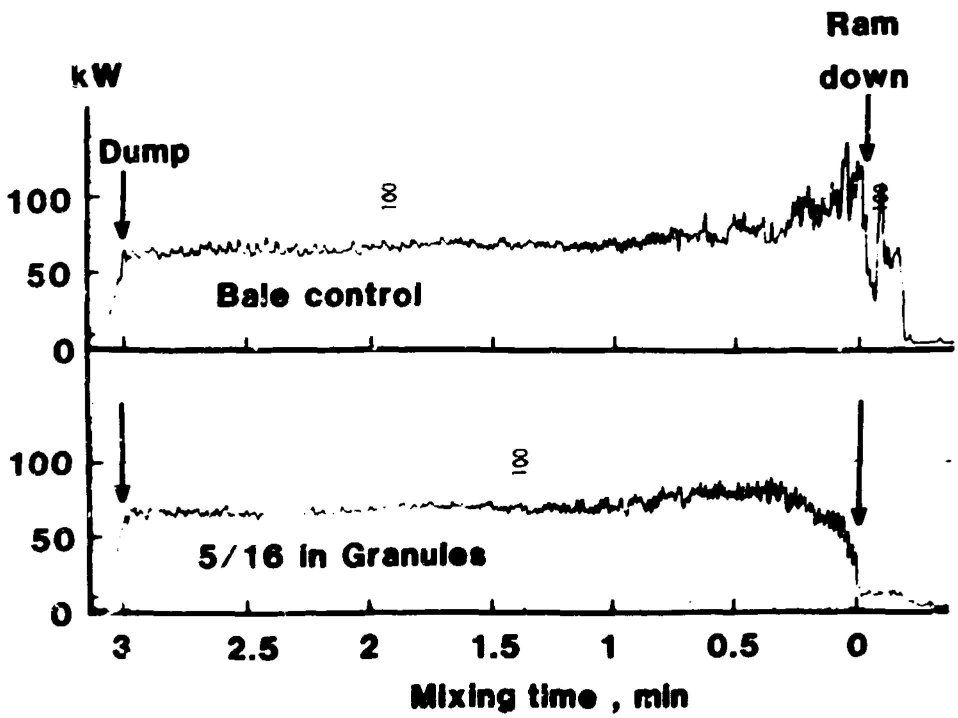

Fig. 13.2 Wattmeter plots of K2A mixes, based on bale SMR CV 60 and 7 9mm granules.

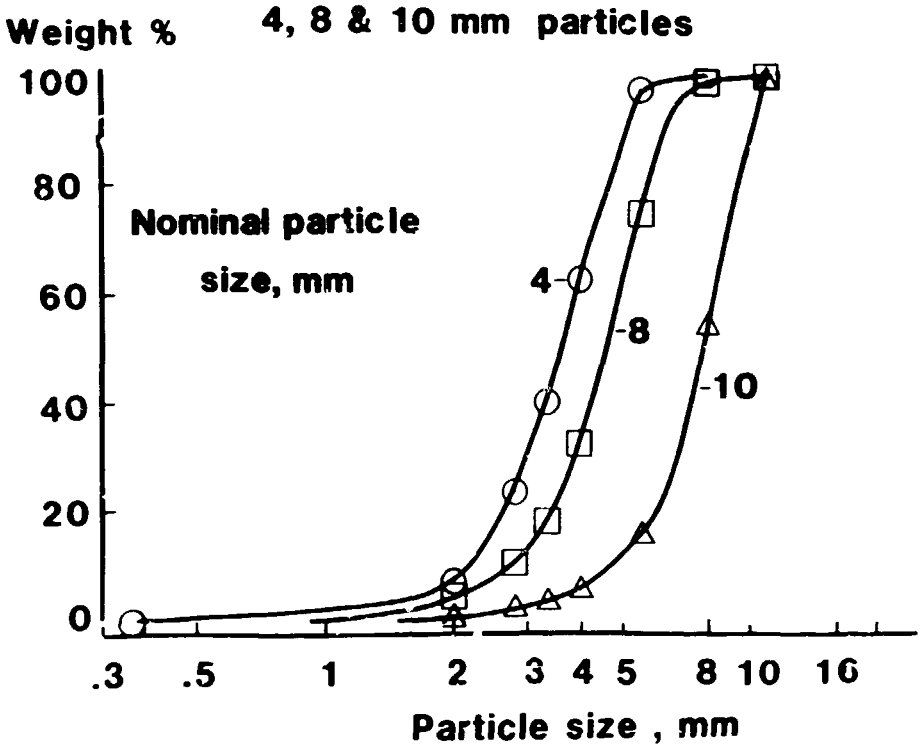

Fig. 13.3 Particle size distributi-- of Plascoat 4, 8 and 10mm diameter SMR 10 particles used for Farrel Bridge/Dunlop .rial.

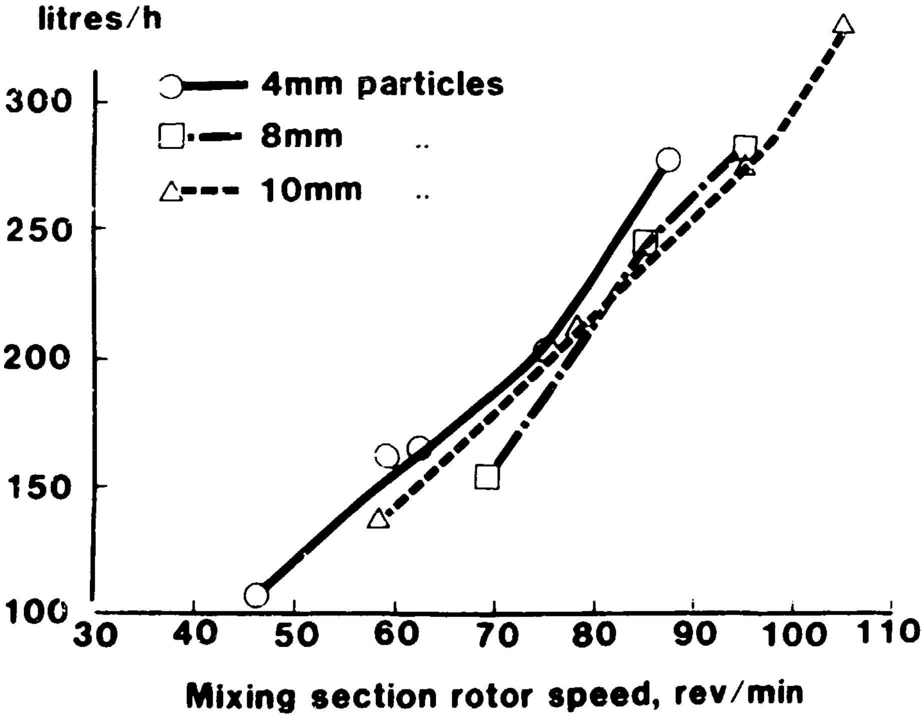

Fig. 13.4 Dependence of output on MVX mixing sect.on rotor speed, using different size SMR 10 particles.

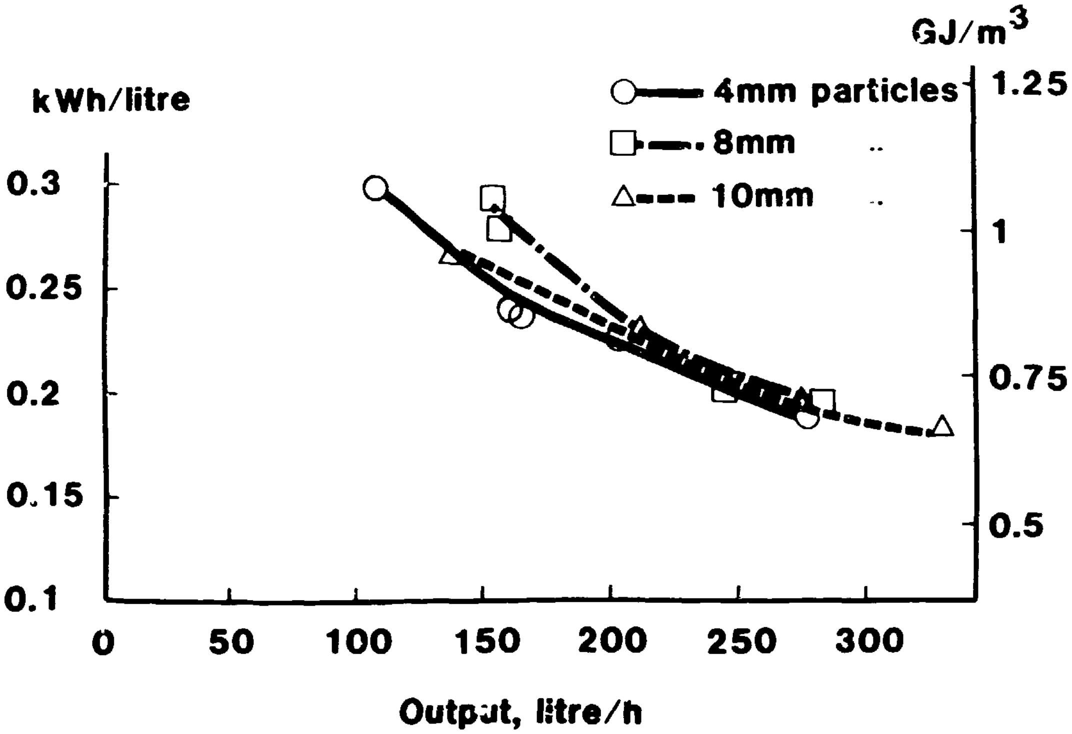

Fig. 13.5 Dependence of specific energy of mixing with the MVX on output for SMR 10 mixes of different particle sizes.

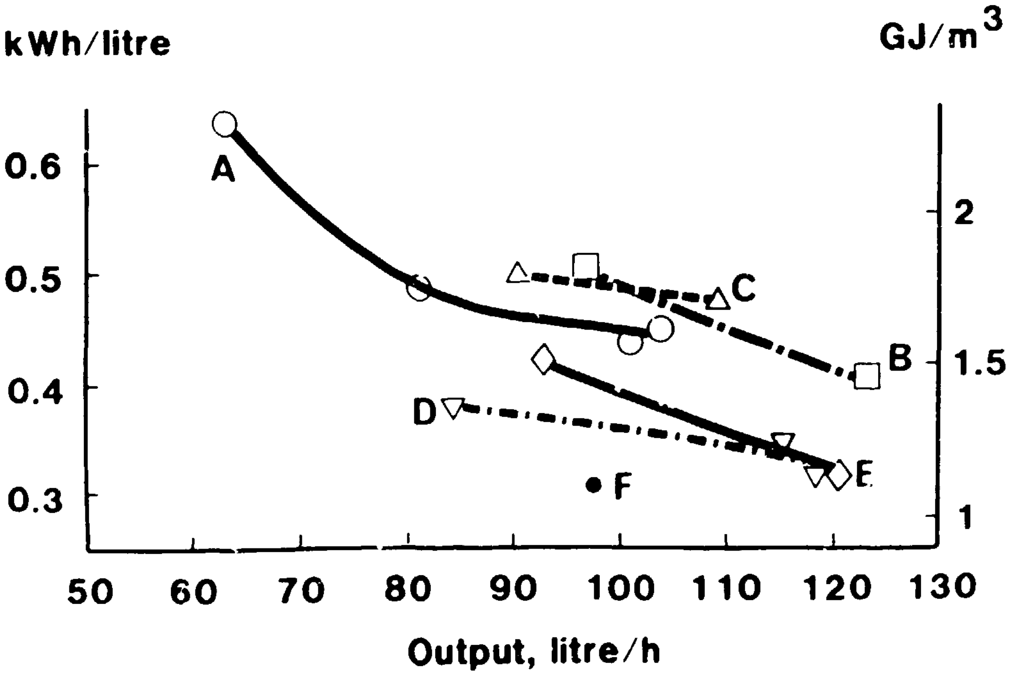

Fig. 13.6 Dependence of specific energy of mixing with the EVK on output for Crusoe mixes.

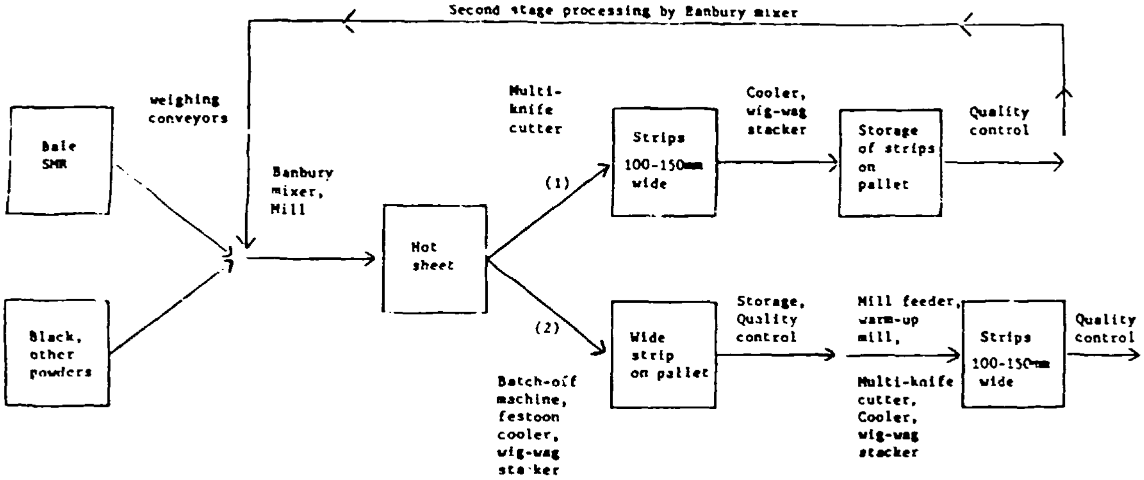

Fig. 13.7 Flow chart for production of narrow strips for further processing; 1), most direct process line with single - or double - stage Banbury mixing; 2), alternative line using warm-up mill to provide second-stage processing.

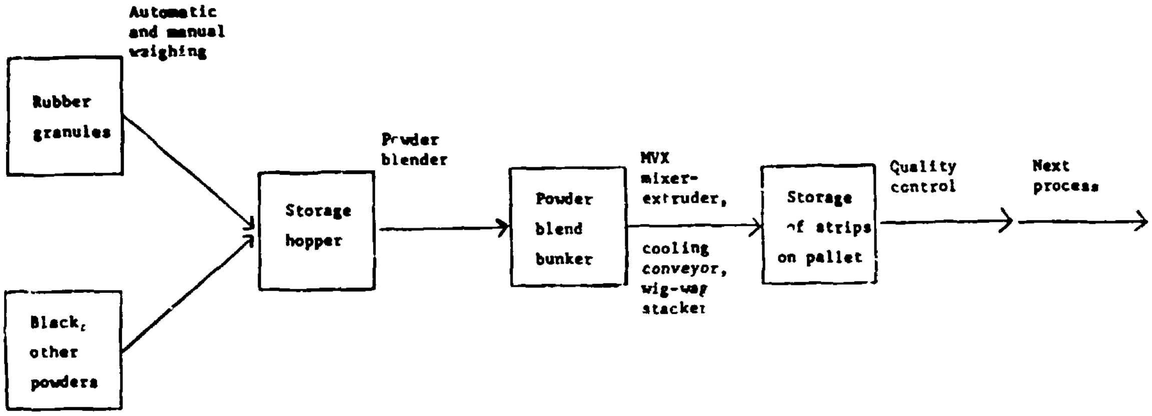

Fig. 13.8 Flow chart for production of narrow strip for further processing by the MVX mixer-extrusion process.

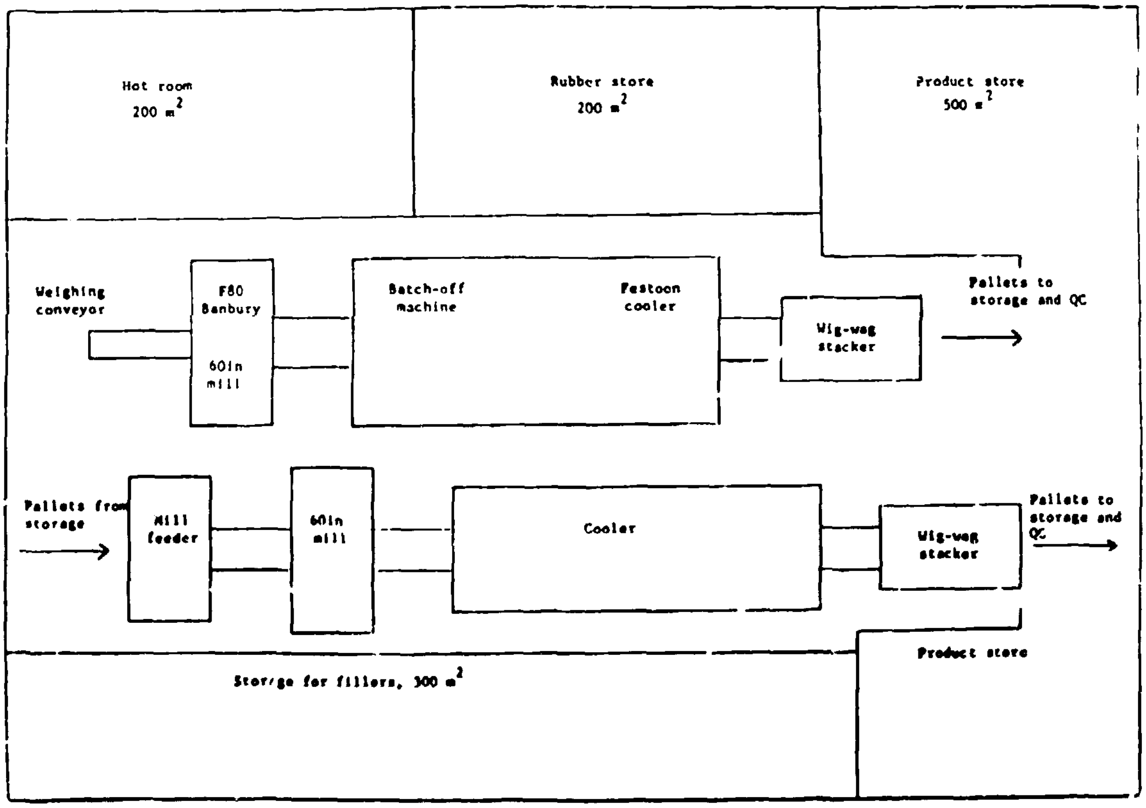

Fig. 13.9 Layout of factory producing rubber strip for further processing, using 10 tonne rubber/day.

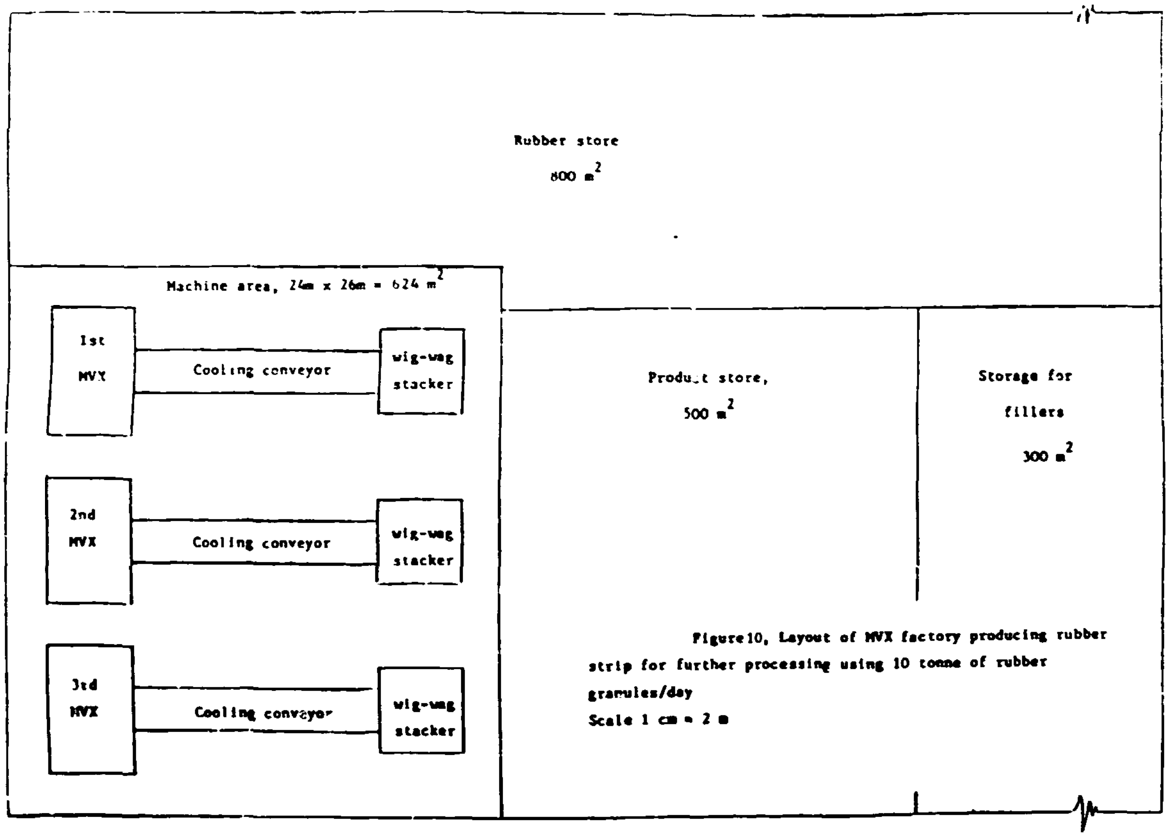

Fig. 13.10 Layout of MVX factory producing rubber strip for further processing, using 10 tonne of rubber granules/day.

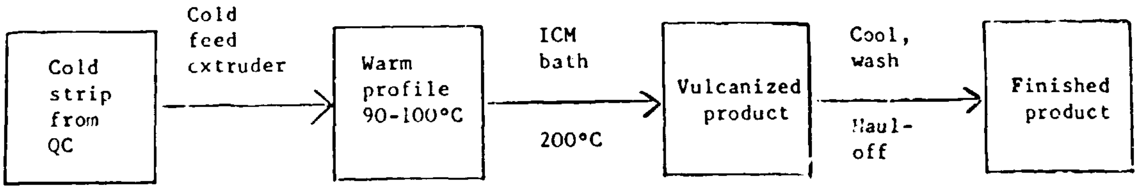

Fig. 13.11 Flow chart for Banbury strip to cold feed extruder and profile from this to LCM bath and finished product.

Fig. 13.12 Flow chart for profile from MVX machine to LCM bath and finished product.

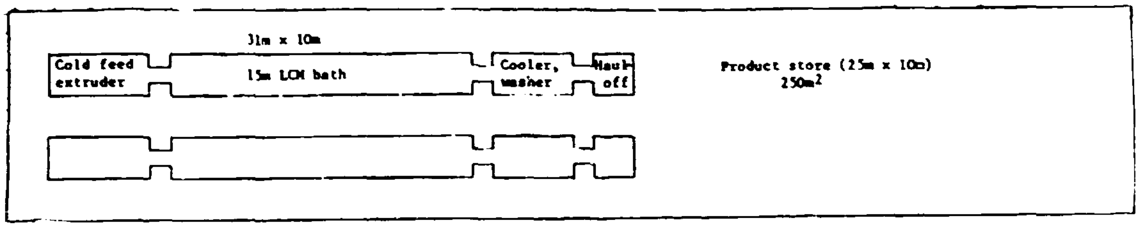

Fig. 13.13 Layout for two 152mm (6in) extruders and two 15cm LCM baths.

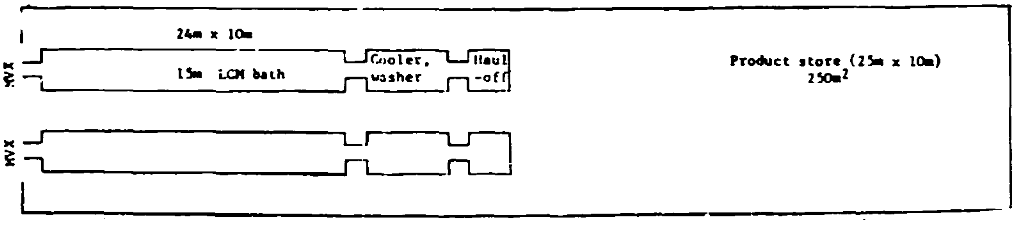

Fig. 13.14 Layout for two 15cm baths taking a profile direct from MVX mixer/extruder.

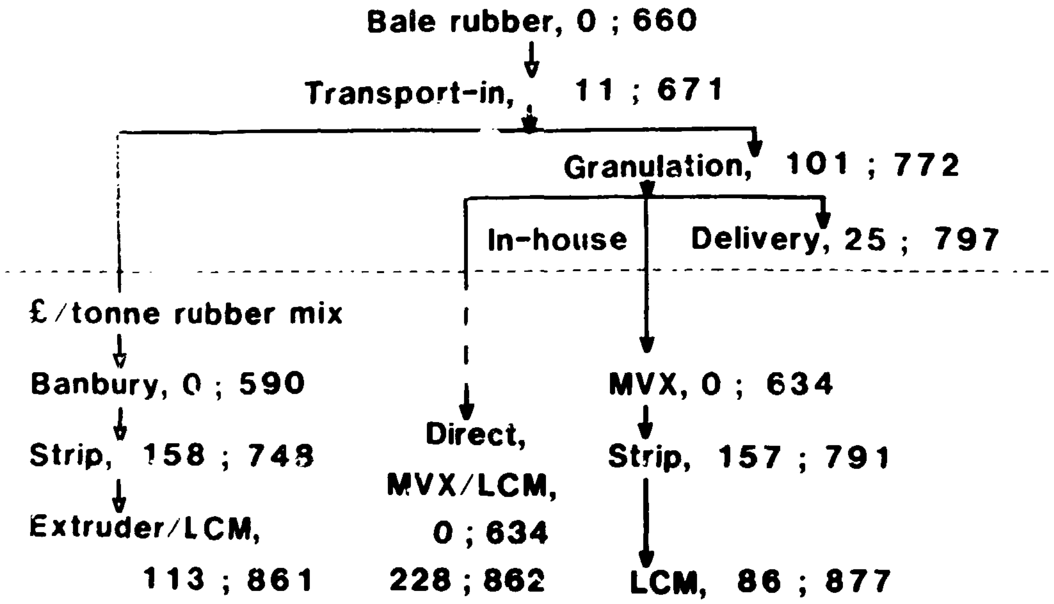

Fig. 13.15 Costs of bale and granulated rubber processes; value added, £/tonne; cumulative cost, £/tonne.

Liquid Natural Rubber

New Forms of Natural Rubber

CHEMISTRY OF LIQUID NATURAL RUBBER

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INTRODUCTION

Generally speaking, the technical and economic aims of research in the field of liquid elastomers are - using simplified operating procedures - to obtain vulcanizates with an elasticity and mechanical properties matching those of high molecular weight crosslinked rubbers.

TABLE 1 MAIN CHRONOLOGICAL STAGES IN LIQUID RUBBER DEVELOPMENT

Year	Development
1923	Depolymerized Natural Rubber by K.V. Hardman
1943	Polysulfide Rubber by the Thiokol Chemical Corporation
1944-1945	Strategic Applications of Solid Propellants by the Jet Propulsion Laboratory of California
1960	Telechelic Polymers Synthesis by C.A. Uranek

The first appearance of liquid elastomers on the market dates back to 1923. They were obtained on degradation of solid natural rubber by mechanical/chemical peptization and they found application in the field of adhesives. Twenty years later, the Thiokol Chemical Corporation produced the first synthetic liquid elastomers on an industrial scale : these were polysulfides with mercaptan ends which paved the way for new vulcanizing methods. In 1945, liquid rubbers began to be used extensively with the development of rocket solid propellants.

As early as 1960, the conventional macromolecule synthesizing processes - radical or ionic polymerization, polycondensation - gave birth to a second generation of synthetic liquid elastomers (Table 2); these telechelic polymers have a better definition in terms of structure and they have reactive chain ends which make it possible to obtain tridimensional networks (Figure 1).

TABLE 2 DIFFERENT WAYS OF SYNTHESIS OF TELECHELIC POLYMERS

Reactions	Initiators	End Groups
Polymerization		
Radical	Diazocompounds	Carboxyl Mercaptan Amine
	Peroxides	Hydroxyl Halogen Aziridine
Anionic	Alkaline metals Organometallics	Carboxyl Mercaptan Hydroxyl Halogen Epoxide
Depolymerization		
Thermal		Double bond
Chemical	Peptizing agents Ozone Redox systems	Hydroxyl Carboxyl

Nowadays, several of these products have found interesting industrial applications such as adhesives, cold vulcanizing mixtures, manufacture of flexible casts, binders used in propellants, coatings.

In the field of liquid rubber derived from natural polyisoprene, in addition to Hardman's work mentioned before, the studies conducted by MRPRA on rubber photochemical depolymerization, allowing short polyisoprenic chains with carbonyl ends to form in an oxidizing medium, are worth recalling. On the other hand, the ozonolysis of natural or synthetic polydienes made it possible to obtain oligomers of high steric regularity, which was difficult using conventional methods of polymerization.

The work described today was performed at the 'Institut Francais du Caoutchouc' (I.F.C.), and then continued and simplified at I.R.A.P. within the framework of a study agreement with the 'Institut de Recherches sur le Caoutchouc' (IRCA). This work led to the development of a method to obtain low molecular weight polyisoprenes from natural rubber latex at a moderate temperature; this method was the subject of a feasibility study on an industrial basis by the Agence Nationale pour la Valorisation de la Recherche (ANVAR).

STUDY OF THE REACTION

The action of an reducer-oxidizer couple upon the chains of rubber hydrocarbon can result, under particular conditions, in the cleavage of the chains, together with the forming on the so obtained oligomers of chemical functions derived either from the redox couple or from the reaction medium. The reagent used is composed of an ozidizer (organic peroxide, perhydrol, atmospheric oxygen) associated with a reducer such as sulphanilic acid or aromatic hydrazine. The depolymerization reaction can take place in an organic solvent or directly in the latex phase. For economic and operating reasons, we have more particularly developed the study of natural rubber latex processing by phenylhydrazine in an oxidizing medium (Figure 2).

The cis-1,4-polyisoprenic structure of the original rubber is fully preserved.

The tests were conducted on a scale giving 20 to 25 kg of liquid rubbers per operation.

Figure 3 shows the diagram of a depolymerized rubber preparation unit. The facility includes:

- an 'open top' reactor 1 used for stabilizing latex;
- two reactors 2 and 3 used in parallel for the depolymerization reaction. The reaction temperature is 50 to 70°C (122 to 158°F) and the flow of continuous air bubbling is 2 to 3 litres per minute;
- reactor 4 enables rubber to be precipitated and dried; it is fitted with a stirring system intended to effectively renew evaporation surfaces in an enclosed space maintained in a slight vacuum. The drying rate is about 2 kg per hour, the residual humidity is below 1%.

Main Parameters of the Reaction

We tried to find stabilizing agents to avoid using organic solvents for isolating liquid polyisoprenes from the reaction medium. The best results were obtained with sodium sulphonate para-anisidine (Vulcastab LS) used in the proportion of 1% with respect to dry rubber. Under these conditions, depolymerized rubber is caused to precipitate only by adding electrolytes or dilute formic or acetic acid.

The phenylhydrazine concentration and the time of reaction are the two parameters which - together with a good reproducibility - cause the molecular weights of polyisoprenes to vary from 3000 to 20 000 approximately (Figure 4).

Depending on these two variables, the intrinsic viscosity of processed rubbers can be followed; this value, in the case of the so called polyisoprenes under consideration enables their viscosimetric weight to be calculated.

Figure 5 shows that the change in viscosity - ie the rubber degradation rate - is fast for the first hours of the reaction, then slows down after 8 to 10 hours of treatment. In practice, we thus tried to obtain 15 to 20-hour reaction times by using quantities of phenylhydrazine suitable to the desired molecular weights.

CHEMICAL AND PHYSICAL-CHEMICAL STUDY

As far as the basic chemical composition is concerned, we observed no significant differences between a purified natural rubber and a depolymerized polyisoprene, except that the nitrogen content of the latter had slightly increased because of terminal groups.

An infra-red spectroscopic study shows first of all that the cis 1,4 structure of the initial rubber has not been modified by the treatment. which gives for a steadily regular structure of the chains. Moreover, the presence of combined phenylhydrazone groups at 1500, 1605 nd 1648 cm^{-1} could be observed.

HNMR confirmed the presence of cis-1,4 structure and allowed us to estimate that there was an average of 1.8 phenylhydrazone group per polyisoprene chain.

The presence of these functions can explain the brown colouration of the products obtained.

Gel permeation chromatography showed clearly - for every product tested - a monomodal distribution and the absence of oligomers of very low molecular weight. As for depolymerized rubber submitted to a correct purifying and drying process, the polydispersity index ranges from 1.7 to 3, a low value for macromolecules obtained by radical process (Figure 6).

The Process Producing Low Molecular Weights

Owing to atmospheric oxygen and temperature, phenylhydrazine forms a diazoic compound followed by radicals likely to attack methylenic groups and the dual linkages of polyisoprene chains. Hydro and endoperoxides are derived from macroradicals and their subsequent decomposition causes the chains to break up and leads to oligomers with terminal carbonyl groups which, in the presence of an excess of phenylhydrazine, are transformed into phenylhydrazones, which insures the stability of the obtained products (Figure 7).

From a strictly chemical viewpoint, the presence of aromatic hydrazone functions at the chain ends allows condensing reactions to take place via the mobile hydrogen carried by nitrogen. We thus aim at extending chains and crosslinking, which enables us to be closer to conventional vulcanization networks; this is observed with di-and trisocyanates, but it is not possible to determine whether the linkages obtained result from a topochemical reaction or from chain-end reactivity.

Chemical Modification of Chain Ends

Several possibilities have been studied to modify chain functionalities (Figure 8):

- For instance, a sulphonyl chloride, such as tosyl chloride, reacts almost quantitatively with the mobile hydrogen of phenylhydrazone groups. It is the same with organic acid chlorides which give the corresponding substitution derivative.

- Other reactions were studied with various acid dichlorides adipic, sebacic, fumaric, phthalic... Depending on the operating conditions, these are likely to react either through their two functions to give chain extensions or crosslinking, or through a single function, which allows the retention of an acid chloride function easy to transform into a carboxylic group. The latter transformation can be obtained by using an excess of acid dichloride and by operating in a basic medium under the conditions of an interface reaction; this results in a functionality of 1.95 carboxylate groups. No important change in the structure or in the molecular weight of the depolymerized rubber so treated is observed.

- The acid hydrolysis of phenylhydrazones provides for the regeneration of carbonyl groups.

- Controlled oxidation of reagents by a hypochlorite or hypobromite in an alkaline medium results in the formation of carboxylic acids with a 1 to 1.2 functionality.

These first experiments relating to the modification of chain ends will have to be carried on so as to increase the possibilities of functionalization and to have a better control of operating techniques and analytical methods. Therefore, much work remains to be done in this field.

Chemical Modifications along the Chain

In general, the capabilities of low molecular weight natural polyisoprenes rest on the problem of rubber chemical modification. So far, most modified rubbers have not found important outlets, mainly because of the technical-economic requirements and of the difficulties encountered to retain most viscoelastic properties of rubber. In the case of low molecular weight polyisoprenes, the problem of structure modification is not so critical and the technical conditions are more favourable.

Thus, some preliminary work has already been carried out in the field of depolymerized natural rubber (Figure 9):

- addition of trichlorfon (fireproofing, chelating molecules);
- addition of hydrochloric acid (adhesives);
- addition of maleic anhydride (adhesives surface-active agents);
- cyclization (photo-sensitizers).

Besides this work, a great number of chemical modifications have been completed on synthetic low molecular weight polyalkadienes; these modifications are shown on Figures 10 and 11 and are very easily applicable to depolymerized natural rubber.

These various modifications, and the second-step modifications by fixation of active substances on to the macromolecule (pharmacological drugs, antioxidants) result in products with a strong added value. We can mention, for example, the work we have initiated in the field of antioxidants linked to a molecular support. Figure 12 shows that the addition of N-phenylparaphenylenediamine to an epoxidized polyisoprene gives a high-molecular weight antioxidant. This macromolecular antioxidant makes it possible to reduce or suppress phenomena of migration into the mixture and to increase compatibility with the elastomer to be protected, which improves homogeneity; as for the volatility of these substances, which are often deemed to be toxic, it can be substantially decreased thanks to this technique.

Grafting - Applications to Elastomers

Chemical grafting of polystyrene on to depolymerized natural rubber provides a new field of application: thermoplastic rubbers.

The work which has been undertaken in this area is based upon the synthesis of copolymers grafted by radical initiation (Figure 13).

The elastomeric trunk is therefore a natural rubber of a 20,000 to 30,000 molecular weight. The operating method is relatively simple and inexpensive with respect to solvent and energy.

This approach to thermoplastic natural rubber is noticeably different from the study previously discussed in the Symposium whether on the mixtures of natural rubber and polypropylene or on copolymers obtained by mechanically/chemically grafting azo-polystyrene.

Two other grafting techniques can also be envisaged:

- de-activation of a living polystyrene anion in a chlorinated polyisoprene (Figure 14)
- grafting by metallation (Figure 15)

CONCLUSIONS

Depolymerized natural rubber prepared by chemical degradation in the latex phase can be considered as a new material in so far as the research work undertaken towards new applications is barely at the very first stage. Much work is still to be done: all the studies of chemical modifications conducted on high-molecular weight natural rubber, which did not bring about interesting outlets because of technical-economic requirements, are applicable to liquid rubber using an easier operating mode, since the transformations can even sometimes take place in the producer's facilities.

If a number of applications are already foreseen for non-modified liquid rubber (binders and coating products in the field of rubber ingredients, additives used in emulsions and paints, reactive plasticizers) then the very numerous possibilities of chemical modifications area prelude to the obtainment of compounds of a high added value aimed at other areas of application.

Therefore, a comprehensive research programme must be carried on showing a particular trend towards the field of modifications at the end of and along the chains, and towards an investigation on possible outlets for the new products obtained, namely thermoplastic elastomers.

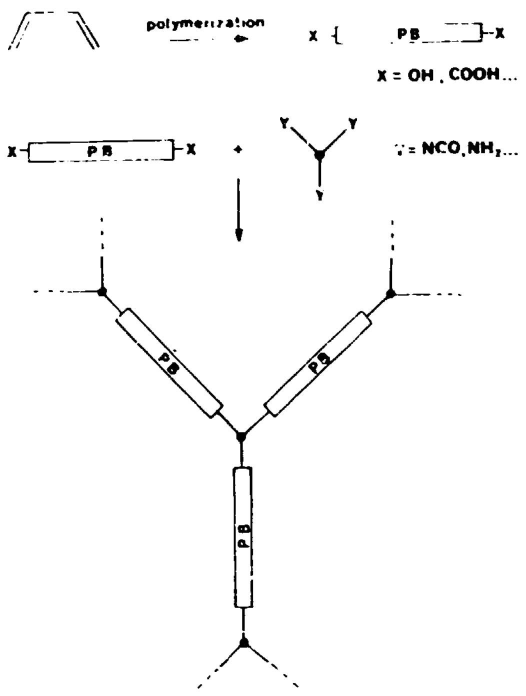


Fig. 14.1
Formation of three-dimensional networks from telechelic polymers.

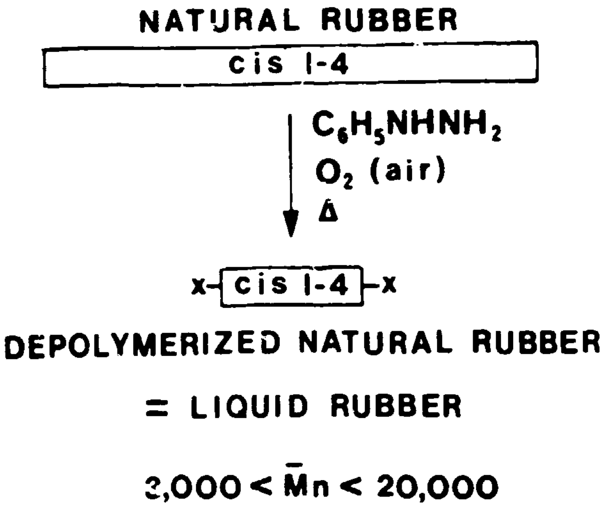


Fig. 14.2
Natural rubber depolymerization by phenylhydrazine in an oxidising medium.

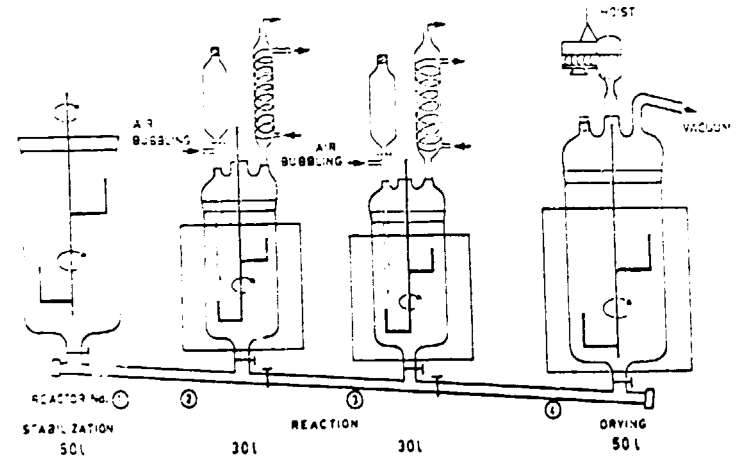


Fig. 14.3
Block diagram of pilot unit for the preparation of depolymerized natural rubber.

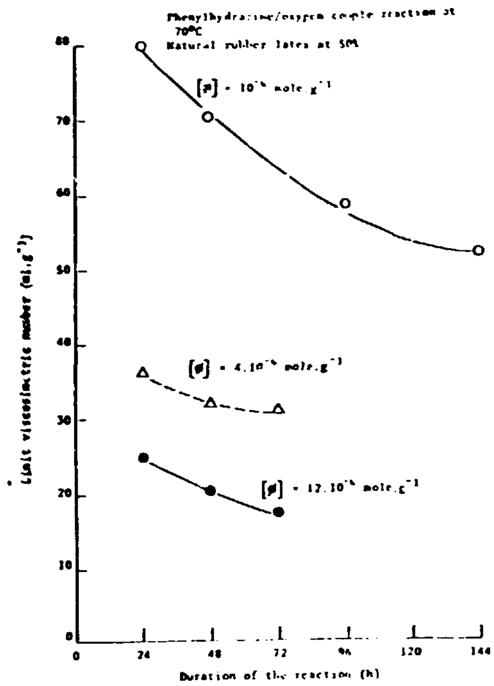


Fig. 14.4
Limit viscosimetric number v phenylhydrazine concentration and duration of reaction.

14.5

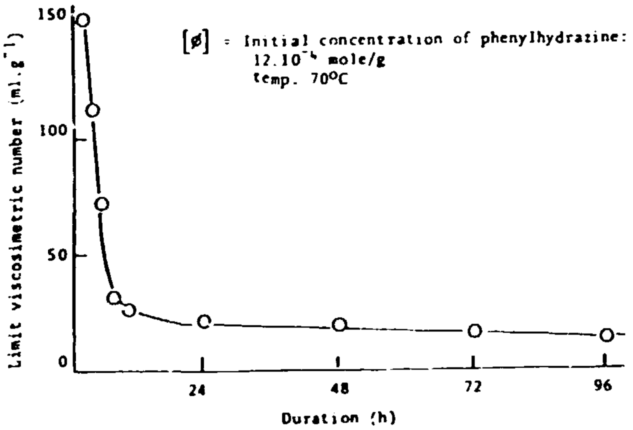


Fig. 14.5
Limit viscosimetric number v reaction duration.

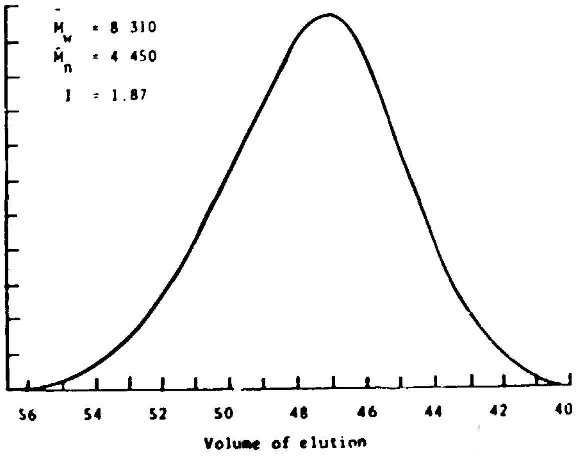


Fig. 14.6
GPC analysis of depolymerized polyisoprene.

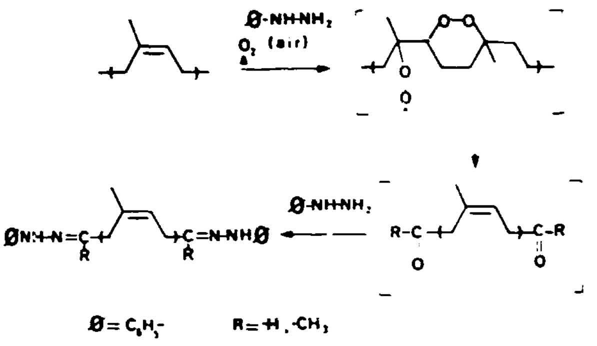


Fig. 14.7
Mechanism of formation of phenylhydrazone groups on ends of broken chains.

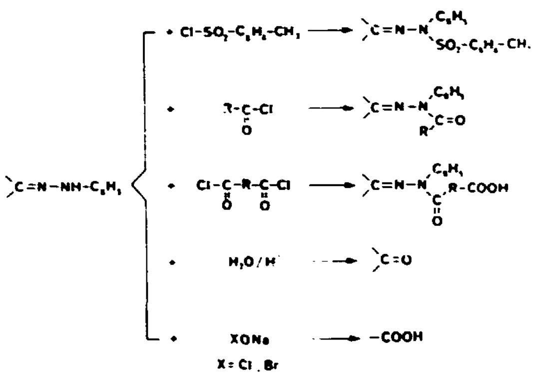


Fig. 14.8
Modification of the terminal functionality.

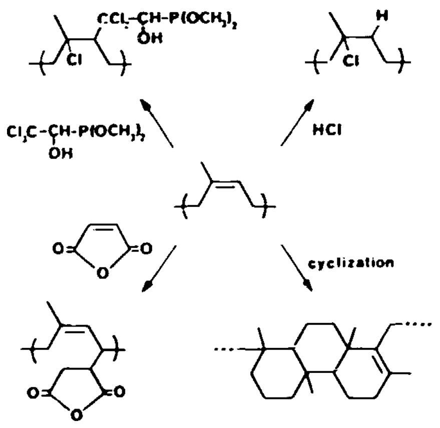


Fig. 14.9
Addition and cyclization reactions of depolymerized natural rubber.

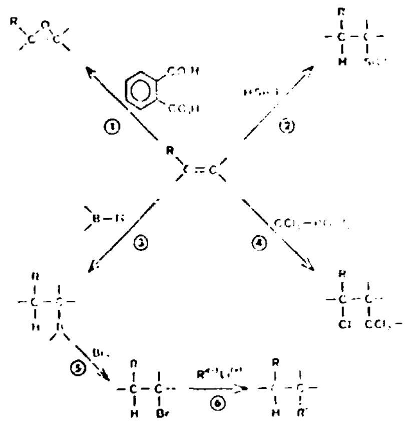


Fig. 14.10
Modification reactions of low molecular weight polyalkadienes.

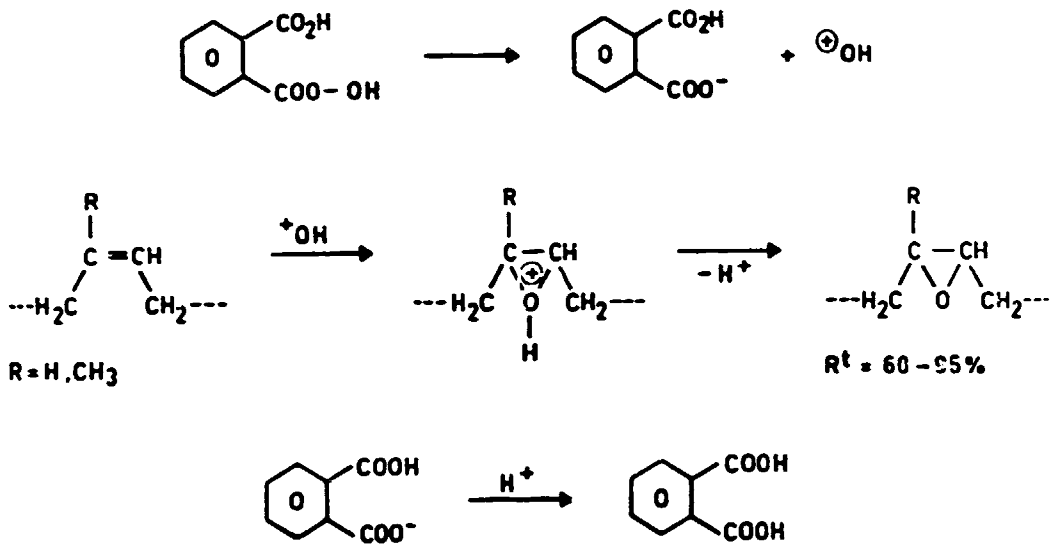


Fig. 14.11 Epoxidation of depolymerized natural rubber by per-phthalic acid.

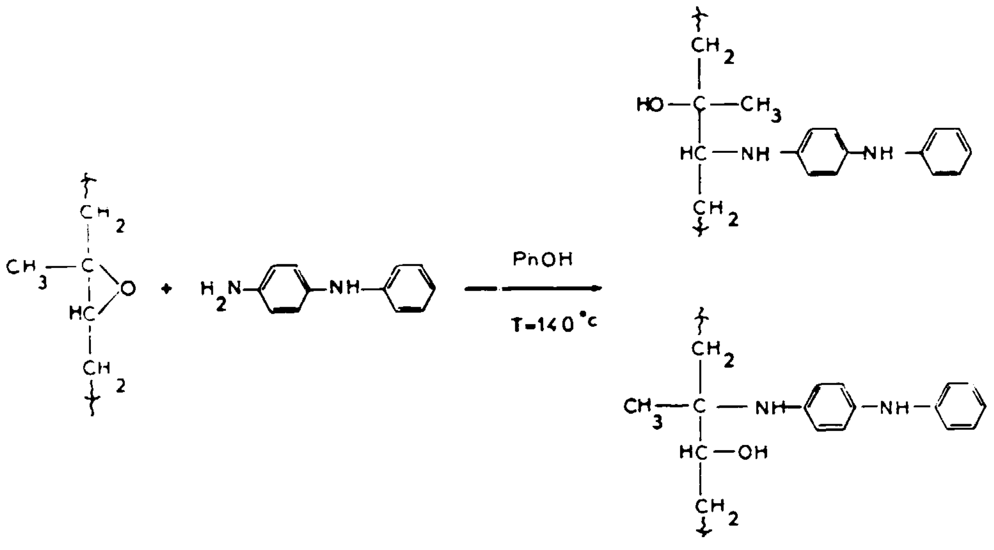


Fig. 14.12 Addition of N-phenylparaphenylenediamine to an epoxidised polyisoprene to yield a high mol. wt. antioxidant.

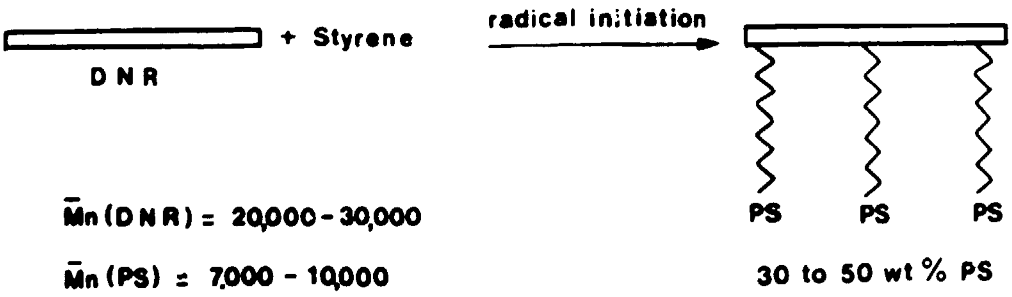


Fig. 14.13 Thermoplastic elastomer synthesis from depolymerized natural rubber.

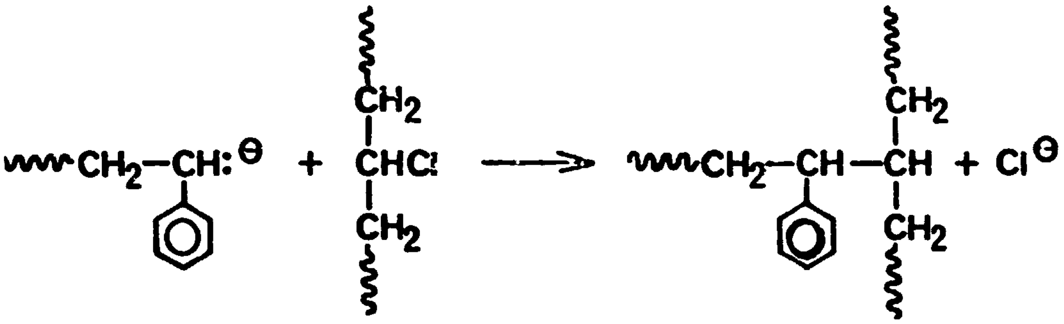


Fig. 14.14 Deactivation of a living polystyreneanion in a chlorinated polyisoprene.

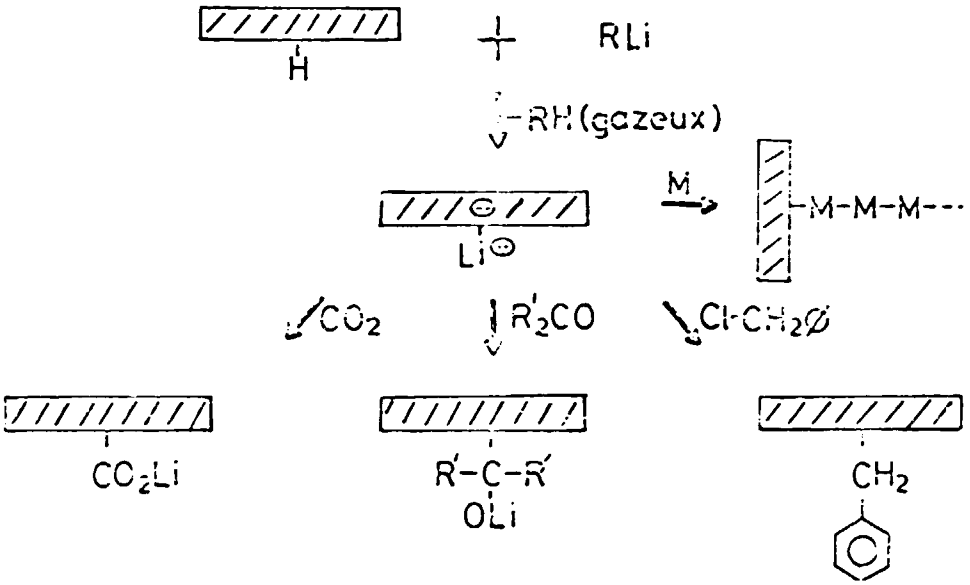
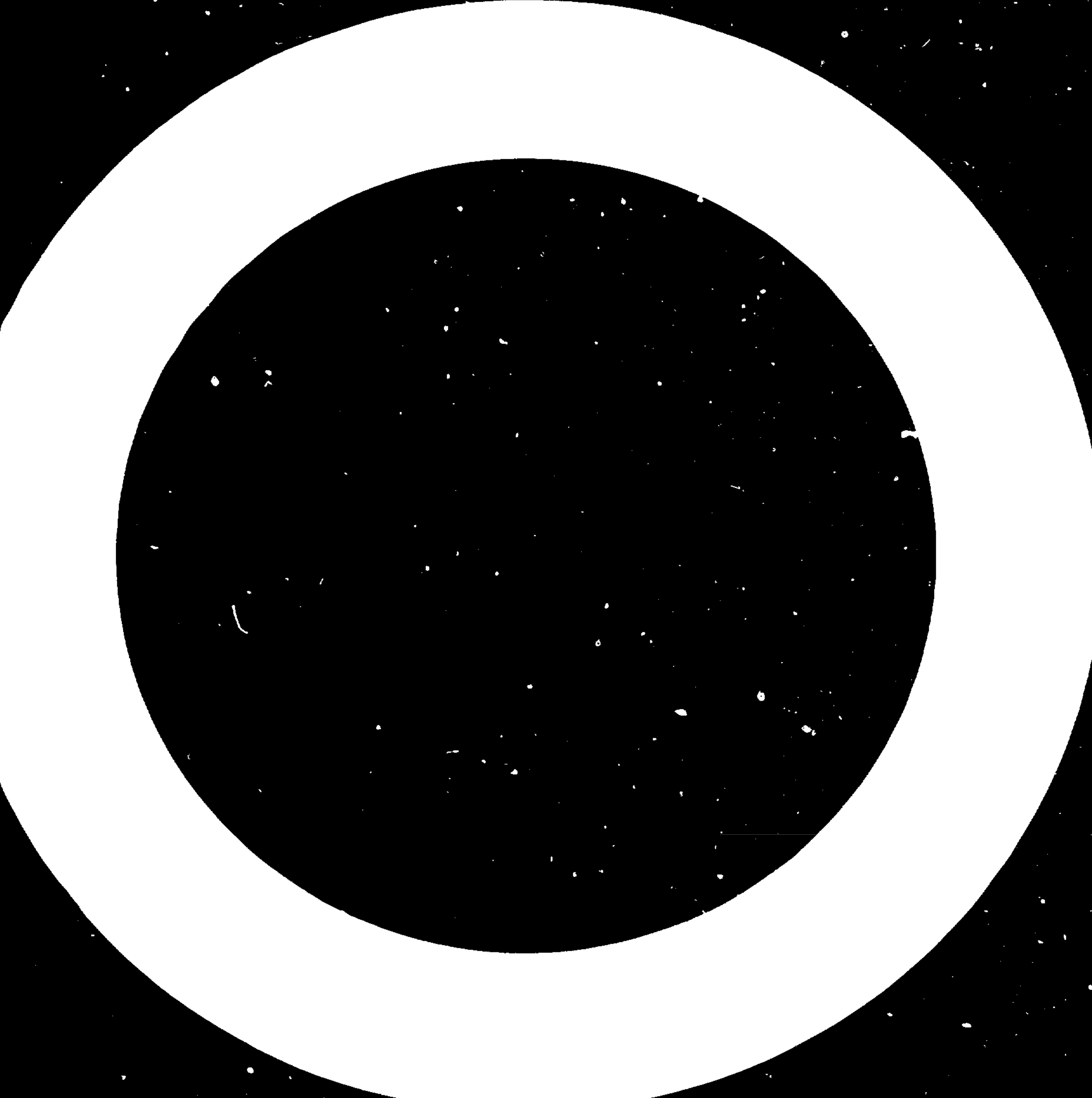


Fig. 14.15 Grafting by metallation.



PREPARATION AND APPLICATION OF NATURAL LIQUID RUBBER

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INTRODUCTION

Natural rubber depolymerised both by mechanical and chemical treatments and having a liquid form appeared in 1923.

Between 1945 and 1950, low molecular weight synthetic elastomers went into production for strategic applications. Now many kinds of these liquid rubbers with very low viscosities are in existence. Some years ago it was claimed that it was possible to pour some particular fluid rubbers to cast tyres with the typical properties of ordinary rubber like hardness, modulus, elongation at break, tear strength abrasion resistance etc. The tyres obtained no longer contained fabric or carbon black reinforcement.

At that time the French Rubber Institute (IFC) was beginning scientific work to produce liquid natural rubber which could be a competitor also in the processing of ordinary rubber goods. The results of these studies were patented in France (No 74/03052 on 30.01.1974) and abroad.

DEPOLYMERIZATION PROCESS FOR NATURAL POLYISOPRENE

The principle consists in using a redox couple on the polyisoprenic chain. The reactive chemicals are an oxidising agent, air is the most simple, and a reducing compound, typically phenylhydrazine. The depolymerization reaction is generally carried out in a latex medium. This method is the most simple and economical to commonly obtain molecular weights between 5000 and 20 000. Three parameters were particularly studied:

1. Nature of the latex stabilizing agent (anionic stabilizing agents are preferably used).
2. Influence of the quantity of phenylhydrazine.
3. Duration of the reaction.

It is possible to monitor these parameters to obtain the required molecular weight with a good reproducibility. The duration of the reaction is commonly 20 hours at 70°C. The intrinsic viscosity of depolymerized rubber decreases when the concentration of phenylhydrazine increases.

Four reactors in succession are used to prepare liquid rubber under these conditions (Figure 1).

The first is used to eliminate the ammonia and to stabilise the latex with Vulcastab LS. Reactors 2 and 3 are used to obtain depolymerization of the latex by means of phenylhydrazine under a continuous current of air. Reactor 4 is designed to precipitate and to dry the rubber. It is equipped so as to obtain an efficient renewal of the evaporating surfaces acting as a dynamic dryer within a slight vacuum.

The liquid rubber obtained by means of this process has the appearance of a fluid honey. Its ratio of polydispersity Mw/Mn established by gel permeation chromatography (Figure 2) is about 1.7 to 2.8. This value seems normal for products obtained from free radical methods.

REINFORCEMENT AND VULCANIZATION OF LIQUID RUBBER

Up to now it does not seem possible to reinforce and to cure properly this kind of rubber. This is partly due to the low shearing forces obtained during the mixing of liquid rubber and carbon black and also to the fact that it is not possible to create by curing the same network that is found in conventional vulcanized rubbers.

For example, a liquid rubber having Mn = 9,300, containing 50 phr of black N 330 and cured by carbamates has the processing and physical properties shown in Tables 1 and 2. It is possible to obtain similar properties on cured liquid natural rubber grafted with 40 or 50 parts phr of polystyrene or polymethylmethacrylate. Some grafting techniques permit different kinds of thermoplastic rubber to be obtained.

TABLE 1 MIXING A DEPOLYMERIZED RUBBER AND A NATURAL RUBBER CONTROL SAMPLE WITH CARBON BLACK

	Depolymerized Rubber		Rubber Control Sample (Smoked Sheet)
Formulation	Mn = 9 300	Mn = 20 000	
Rubber	100	100	100
ISAF Black	50 (A)	50	40
Zinc Oxide	5	5	3
Stearic Acid	1	1	2
Sulphur	5	5	2.5
Butyl Eight (B)	5	5	-
Santocure CLS	-	-	0.7
Phenyl β-Naphthylamine	-	-	0.75
Pine Tar	-	-	3
Mixing Conditions			
Kind of Blades	For sticky products (Sigma blades)		For rubbers
Rotation Rate, (rev/min)	64	64	64
Filling Coefficient, (%)	80	80	85
Torque (m/g)			
With Rubber Alone	Near zero		3200
With Plasticizer	-	-	500
After Addition of Black:			
Maximum Torque	700	900	3500
Stabilized Torque	300	350	2600

(A) Depelletised Carbon Black

(B) Liquid mixture of boosted dithiocarbamates

TABLE 2 MECHANICAL PROPERTIES OF DEPOLYMERIZED RUBBER VULCANIZATES

	Depolymerized Rubber		Natural Rubber	Arco cs 15
	Mn = 9 300	Mn = 20 000	(Smoked Sheet)	
Vulcanization				
Temperature (°C)	100	100	143	-
Time (min)	15	10	15	-
Properties				
Tensile strength (MPa)	10.5	15.3	28.6	10.5
Stress at 300% (MPa)	8.0	12.4	8.8	5.0
Elongation at break (%)	380	400	580	600
Tear strength (MPa)	6.0	7.5	11.1	-
Hardness, Shore (°)	70	73	62	57

Professor J C Brosse will detail in another paper all the aspects of the chemistry of liquid rubbers and consequently it seems more interesting now to record their different applications taking into account their present properties.

It is necessary to recall that there is a regular production and consumption of liquid natural rubber obtained by means of a mechanical-chemical process and of several types of liquid synthetic rubbers.

APPLICATIONS OF LIQUID NATURAL RUBBER

Moulds

Industry and arts require cheap and elastic moulds. Some of them are made from synthetic liquid elastomers, particularly fluid silicones, but it seems that the new form of liquid natural rubber described above can give an economical advantage for the same properties. They can be poured very easily and cured at room temperature. As it is not necessary to obtain the best mechanical properties, it is possible to add oil in the formulation to give it a higher fluidity and a lower price.

Printing Industry

It is possible to photocrosslink liquid natural rubber mixed with acrylic resins under certain circumstances. In this way thin elastic linings can be obtained which can reduce the price of printing process. The elasticity of these linings seems to be a technical advantage linked with a very simple and elegant process.

The photocrosslinking by uv radiation at 380 nm is obtained in one minute with a high pressure lamp of one kW.

Damping Properties of Rubber

Rubber antivibration mountings are increasingly used in many different industries. The rubber is recognised as a very good spring with low creep. However it would be interesting in some cases to increase the damping factor of these mounts. It seems possible to do this by incorporation in the recipe of a substantial quantity of vulcanizable liquid rubber.

Nonextractable Plasticiser

In the same manner it is possible to add to some compounds nonextractable plasticisers like vulcanizable liquid rubber. This process was successfully tested with acrylonitrile rubber. The finished article can swell during immersion into some solvents, but there is no extraction as observable with many traditional plasticisers.

It is a means to increase the service life of rubber in contact with solvents.

Low Shore Hardness Compounds

Pure gum compounds have generally a Shore hardness around 35. Some industries, especially the printing industry, may require very low Shore hardness for some rubber goods.

By using liquid rubber in the recipe as the greater part or all of the rubber content, it is possible with a particular mix to obtain regularly a Shore hardness under 10 while retaining sufficient mechanical properties.

Hard Rubber

Ebonite of good quality can be obtained by curing the liquid rubber with the required amount of sulphur, generally around 35 parts phr. The preparation and moulding of the recipe is largely cheaper than with conventional rubber. Generally speaking, it can be interesting to mould prototypes from flexible or hard rubber in order to study their general design.

Wire Industry

Production of electrical wire has been subject to considerable evolution for the last 30 years and now plastic materials are mainly used in these applications for technical and economical reasons and are replacing rubbers in many cases. It appears that compounds based on liquid rubber are used to fill the tubular cavity containing the isolated metallic wire itself. The manufacturers wish to use very cheap and easy processing materials which can contain extremely high proportions of non reinforcing filler. It is possible to obtain such compounds from liquid rubber which can be vulcanized at room or relatively low temperature, for example, 24 hours at 25°C or 4 hours at 80°C.

Adhesives

Liquid rubber with a molecular weight between 5 000 and 15 000 has naturally an excellent tack and it is not necessary to dry the adhesive layer because it contains no water or solvent. This is cheap and also good for health reasons. It can be used successfully, particularly in the tape and shoe industry.

The total market of adhesives represent 4% of the consumption of natural rubber and it seems that liquid rubber can be an interesting competitor in this market.

Coating of fillers

Many non-black rubber ingredients are coated with different oils, waxes or polymers. This coating is increasingly used by industry for health reasons and to save time during compounding operations. Different experiments were made to coat antidegradants and accelerators with 10 parts ph of liquid rubber. These coated ingredients are dispersed very rapidly in the compound. For a shorter time of mixing, the same weight of coated ingredients has the same effectiveness as the pure one with no dust during the mixing procedure. It seems that liquid rubber has a wide range of applications in this field because such coated ingredients have a good compatibility with many types of rubbers.

With the same technique it is possible to obtain encapsulation of pesticides or fertiliser used in high quantity for agricultural purposes. This encapsulation seems to give a more permanent activity of the chemical product which increases its practical value. It is necessary to underline that encapsulation of fertilisers was claimed to be a subject of interest in the submission for an IRRDB/UNIDO project on composite material and it appears that encapsulation with liquid rubber is very efficient and cheap.

Binder

Liquid rubber can be an interesting binder due to its excellent tack together with its easy processing. It is necessary to recall that of many solid propellants for rockets use binders made from synthetic liquid rubber. It seems possible to use liquid natural rubber for this particular application and Indian researches have been carried out in this field.

Thermoplastic Rubbers

As already pointed out it is possible to graft other polymers on liquid natural rubber to obtain thermoplastic rubbers under very regular conditions. This work could be made in the future part of the research conducted on natural thermoplastic rubber by IRRDB members. The rubbers so obtained have about the same properties as those discovered by MRPRA, however they have a lower range of Shore hardness and consequently match more precisely with ordinary cured rubber. The comparison of properties of different thermoplastic rubbers can be seen in Table 3.

TABLE 3 PHYSICAL PROPERTIES OF SOME THERMOPLASTIC RUBBERS

System	Shore Hardness (^{o})	M300 (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
Liquid Natural Rubber Grafted with Polystyrene 65:35	59	5.0	10.2	470
Natural Rubber blended with Polypropylene 65:35	85	-	9.6	310
Thermoplastic Synthetic Rubber, Cariflex 1101	73	1.0	35.0	900

CONCLUSION

The preparation of liquid rubber according to the IFC French patent is very simple, reproducible and economical because it is made directly from latex.

Some problems do exist to reinforce and vulcanize it so as to obtain the same properties as ordinary natural rubber and thus liquid rubber cannot be considered as general purpose natural rubber. However, its physical properties are sufficient for many applications.

The added value of liquid natural rubber is relatively high but there are compensations in view of the energy saving and the lower requirements for labour and heavy machinery. It seems interesting to develop research on these liquid natural rubbers to enlarge the market for natural rubber producers and to compete with liquid synthetic rubber.

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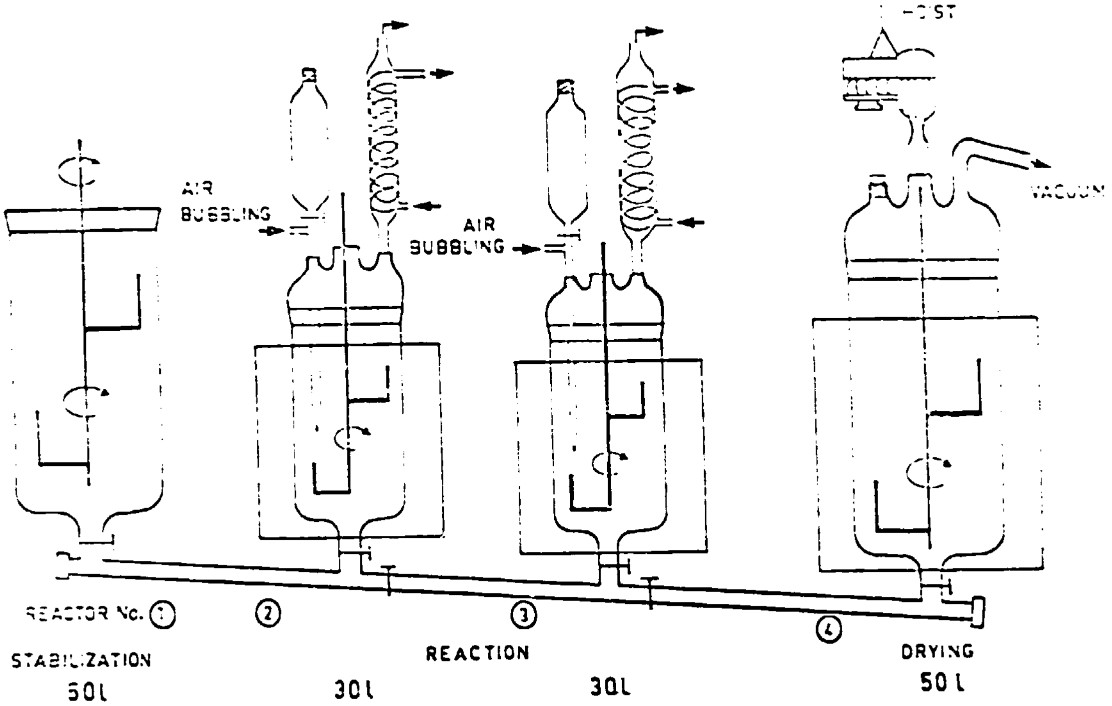

Fig. 15.1 Block diagram of pilot plant for preparation of depolymerized polyisoprene.

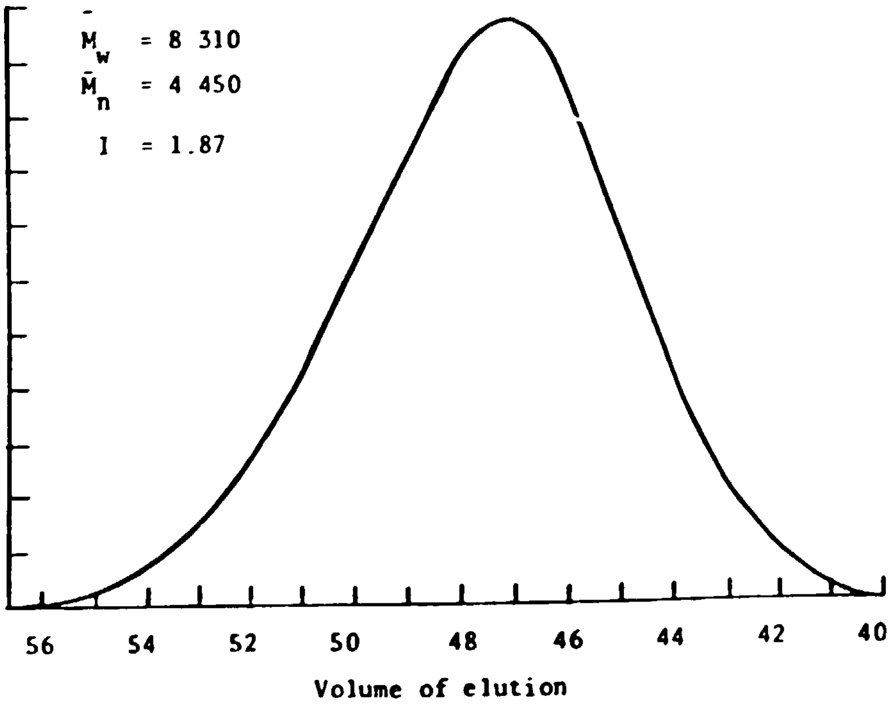

Fig. 15.2 GPC analysis of a depolymerized polyisoprene.

NEW FORMS OF NATURAL RUBBER : ECONOMIC ASPECTS

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INTRODUCTION

The traditional attitude towards the natural rubber (NR) producing countries - like that towards all developing countries which are major commodity producers - is that their function is solely to produce a basic raw material for export. It is the importing (ie 'consuming') countries which have been regarded as the right and proper places in which to convert the raw material into products, and these countries are of course mainly in the developed regions of the world.

Two factors are now operating against this pattern. First, many of the NR producing countries are undergoing fast economic growth which is generating a substantial domestic demand for rubber products, especially tyres. Secondly, there is growing acceptance of the need for commodity-producing countries to add value to their products by one form or other of further processing within the producing country. To quote from the Brandt Commission report: such countries 'can greatly increase their domestic value added, their employment and their foreign exchange earnings by expanding the processing of their raw materials'.

As far as domestic conversion of raw NR into products is concerned, the trend to greatly increased activity by NR producing countries - and developing countries generally - is well established (Figure 1), and the per caput consumption of NR in some of these countries is now at levels comparable with those in developed countries (Table 1). The primary impetus for this is import substitution, not surprising given the fact that only two Asian NR producing countries (India and Malaysia) have positive trade balances in rubber products. In addition, some of the countries intend to enter world trade with rubber products on a substantial scale.

TABLE 1 NR CONSUMPTION

	kg/head
Malaysia	3.1
Philippines	1.4
Sri Lanka	0.7
Brazil	0.6
Thailand	0.6
China	0.4
Indonesia	0.3
India	0.3
Developed countries	0.4-3.4

Domestic conversion of raw NR into products, whether for import substitution or for exports, is the obvious direct way of achieving added-value from NR. The value of NR in a car tyre, for example, is multiplied ten-fold in the finished product, with addition of other materials as well as labour.

There is another route to added-value : the production of NR in 'new forms', a term which will shortly need amplification. As will be demonstrated, the subject of NR in new forms is not to be considered as a separate, independent option. It is highly relevant to growth of rubber products manufacturing in the NR producing countries, and the main purpose of this paper is to develop the theme that the production of NR in new forms can have a strong synergistic relationship with rubber products manufacturing, the one reinforcing the other.

FORMS OF NR

NR is traded, domestically as well as internationally, either as a solid in bale form (TSR, RSS etc) or as liquid latex concentrate; in both cases the composition of the NR is essentially the same: rubber hydrocarbon plus some adventitious non-rubber substances.

Disregarding manufacture of products, value can be added to the raw material in one of three ways (Figure 2):

(i) The chemical composition can be changed so as to produce another kind of raw material and properties of which are different from those of orthodox raw NR and which are such as to command a price premium which exceeds the additional costs involved. The change can be effected either by chemical treatment or by blending with another polymer to produce a composite material. Although the term 'chemical modification' is normally reserved for the first route it is sensible to apply it to both since both methods involve a change in chemical composition.

(ii) The physical form can be changed, eg by converting NR into a particulate or liquid material. In this case, the attribute being sought is some improvement in the handling/processing behaviour of the raw material (eg suitability for newer processes being operated by consumers) which, as for (i), is adequate to command a sufficiently high premium.

(iii) For (i) and (ii) the new form is still a raw material requiring to be compounded, processed, shaped and (in some cases) vulcanized. Producers can consider another option: taking their raw material a stage further towards the final product, eg by marketing masterbatches containing carbon black (plus, perhaps, extender oil), or by marketing compounds, either complete (ie with all vulcanizing ingredients) or (more probably) partial.

The term 'new form' is ambiguous. The scientist will wish to restrict it to the development of novel ideas (eg a new chemical treatment) and there is certainly little element of technical novelty in the production of masterbatches or compounds. The economist examining options for the NR producing countries must regard all three approaches as involving new forms, on the basis that there is at present little activity on a real scale with any of them.

Chemical modification

Changing the chemical nature of NR has been a preoccupation of rubber scientists for many decades, and a number of modified forms of NR have been devised. Very few of these have achieved commercial use on any scale, post-1945 examples being cyclized NR, Superior Processing NR, graft copolymers of NR with polymethylmethacrylate. In no case has there been any fast take-off after the initial launch (Table 2). This comment is made, not to cast an aura of pessimism, but to emphasize the fact that there is obviously a severe problem in establishing a substantial and permanent market for any modified form of NR, and it will subsequently be necessary to identify the reason for this.

TABLE 2 EXPORTS OF MALAYSIAN SPECIALTY NRs

	Maximum level, tonnes
SP NR	5000
Oil-extended NR	++ 2000
Heveaplus MG	300
Cyclized NR	200

++ current level,
likely to increase?

The purpose of chemical modification must be recalled: it is to produce, at the right price, a material with some special set of properties. It is absolutely certain that the same, or essentially similar, set of properties will be possessed by a synthetic material; so to suppose that sometime somebody will devise a modified form of NR possessing radically unique and exceptionally valuable properties unattainable by a synthetic is to be completely unrealistic.

In practice, given the general nature of NR, all chemical modifications of NR can only aim to achieve some degree of improvement in properties such as resistance to environmental damage (eg improved ageing), or to convert NR into a thermoplastic rubber. It is relatively easy to put a value on such improvements, because such properties are also possessed in varying degrees by specialty synthetics such as polychloroprene rubber (CR), nitrile rubber (NBR), EPDM and synthetic thermoplastic rubbers (block copolymers of the SBS type of EPDM/polyolefin blends). In current (£ sterling) terms[*] all of these materials have prices clustering around the £1000/tonne level[+] against about £600/tonne for NR and general-purpose synthetics such as SBR. Therefore, to be economically viable a modification of NR must be able to be accomplished at a total cost plus profit not exceeding about £400/tonne.

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[*] Although costs and prices throughout this paper are in £ sterling the conclusions drawn are essentially independent of the choice of currency or country. Thus, the price gap between general-purpose and specialty rubbers is much the same in most Western countries save the USA where governmental policies concerning domestic oil prices plus different patterns of petrochemicals production produce prices that are lower than those elsewhere. For this reason, a modified NR which is economic for marketing in Europe or Japan might well find the USA an inaccessible market.

[+] There is another group of specialty synthetic rubbers which sell at very much higher prices (eg silicone rubbers, fluorinated rubbers) but their special properties are outside anything that a modified NR could sensibly aspire to.

It is impossible to generalize about the likely costs of utilities, labour and depreciation for modifications, save to say that even a simple process (eg blending in a mixer, reacting latex with chemicals at ambient temperatures) can easily add £100/tonne to the cost of NR exclusive of the cost of other raw materials. As a rough rule of thumb, it can be proposed that in the absence of detailed costings for a modification process, it is prudent to allow £200/tonne for all costs other than materials, recognizing that some allowance must be made for the element of extra profit that any commercial producer will require to cover the extra risk associated with a new venture.

On this basis, the need is to screen candidate chemical modifications in such a way as to eliminate (or disfavour) any for which the additional cost of other materials will increase the cost/tonne of modified material by more than around £200. The result of an analysis along these lines*, for several materials of contemporary interest, is shown in Figure 3. Several conclusions can be drawn. Modification methods involving very expensive reagents (over say £2000/tonne) are economically viable only if the extent of modification is at a very low level (a few moles per cent), limiting their use to situations where it is desired to modify, for example, a small proportion of the double bonds for subsequent treatment (eg crosslinking). Gross modifications with such reagents, aimed at changing the overall physical properties of NR, are clearly ruled out. For much less expensive modifying agents, eg the hydrogen peroxide/fatty acid combination used to prepare epoxidized NR, very high levels of modification are economically viable. In cases where the modifying material is either (i) very cheap relative to NR, eg HCl to make hydrochlorinated NR, or (ii) comparable in cost with NR and retained as part of the saleable end product eg thermoplastic blends and graft copolymers, then the raw materials economics look very favourable.

Thus, this analysis highlights four types of modified NR as deserving further scrutiny: epoxidized and hydrochlorinated NR, thermoplastic blends, thermoplastic graft copolymers. The last two require further comment.

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*The method of analysis, which is novel, involves evaluation of the following expression:

$$\text{raw materials cost per tonne of modified} = P(100 + r_1 r_2 m)/(100 + r_1 r_3 m)$$

where P = NR price; r = ratio of molar mass of modifying material(s) to that of isoprene (68); r_2 ratio of weighted price(s) of modifying material(s); r_3 = fraction of modifying material(s) permanently bound to NR; m = extent of modification, in moles of modifying material(s) per 100 moles of isoprene.

Thermoplastic NR

As a result of the recently concluded UNIDO/TRRDB project the NR producing countries now have available two distinct routes to thermoplastic NR (TPNR).

Thermoplastic blends of NR with a polyolefin have reached the take-off stage; the technology is well established and the economics are favourable. Requiring nothing more than orthodox rubber industry mixing equipment, and using cheap materials (polyolefins are currently considerably cheaper than NR), TPNR blends have properties so similar to those of all-synthetic blends as to suggest that they can be substituted in most applications, and indeed much interest has been roused among potential users eg in the European vehicle industry. Total production costs/tonne, including return on investment, are estimated to be in the range £600-£700, the lower figure applying to a developing country, the higher to an industrialized one (Table 3). At such costs the TPNR blend should be able to compete with synthetic counterparts costing £1000/tonne upwards.

TABLE 3 PRODUCTION COSTS OF TPNR BLENDS

	£/tonne	
	UK	NR producing country
NR	300	270
Polypropylene	250	250
other mtls	30	30
capital	80	25
labour	40	5
power	20	15
maintenance	5	5
	725	600

TPNR graft copolymers based on styrene are at a much earlier stage of development. Their production requires synthesis of a specially-capped polystyrene which is grafted to NR by simple dry mixing (Figure 4) and it is in the production of the former material where the economic problems lie. At the start of the UNIDO project a target was set: to reduce the raw materials cost per tonne of capped polystyrene to £600 (Table 4), at which point the subsequent NR/polystyrene mix was reckoned to be capable of competing with all-synthetic materials of the SBS type. By the end of the project this target had virtually been achieved (Table 5). Even so, it must be said that a great deal of chemical engineering development would be needed to establish full-scale production, and until this is done it is not sensible to be categorical concerning the economics.

TABLE 4 POLYSTYRENE GRAFT TPNR : TARGET PRODUCTION COST

	parts	cost £/tonne	contribution to cost
capped polystyrene	35	600	210
NR	65	600	390
	materials target :		600
	process target :		400
	total target cost:		1000

TABLE 5 POLYSTYRENE GRAFT TPNR MATERIALS COST REDUCTION

	£/tonne polystyrene	
	initial	now
styrene	325	325
n-Bu lithium	107	107
ethylene oxide	2	2
acetic acid	2	2
hydrazine	33	20
diethyl carbonate	47	28
phosgene	490	78
bromine	17	-
pyridine	168	-
t-Bu hypochlorite	-	50
	1191	612
solvents (90%) recovery)	125	65
	1316	677

Powdered NR

The use of powdered rubbers (NR or synthetics) has been promulgated, not on the basis that it will improve the properties of the end product, (which is not, generally speaking, the case) but because it is claimed to offer processing advantages. Specifically, powdered rubbers are claimed to simplify and thereby cheapen processing, being especially beneficial for continuous processing with the new generation of 'mixer-extruders'.

The world rubber industry has been talking along these lines for over a decade. Typical of the somewhat euphoric views that have been expressed, a Delphi study* by the Du Pont Company concluded that by 1980 powdered/granulated rubbers (the distinction is unimportant in the present context) would account for 50 per cent of world non-tyre rubber consumption. In fact, world consumption of powdered rubbers is currently not more than about 2 per cent, mostly synthetic. Given such a dramatic difference between performance and expectations, it is clearly of great importance that the NR producing countries should form a clear understanding of the present and likely future status of powdered rubbers so that they can steer a steady course between the twin dangers of either over-rating the future prospects for powdered rubber or failing to take advantage of what prospects there may be.

It is unfortunate that the period since the Du Pont and similar exercises of the early 1970s has been one of unparallelled poor growth in the Western rubber industry, with little opportunities for investment in new processes, to the extent that proponents of powdered rubbers may well argue that their basic belief in the merits of these materials remains unchanged, and that the rubber industry will witness fast growth in the use of powdered rubbers as soon as the world economy gets back on course. This, though, is too uncertain a position to serve as the basis for policy decisions.

Whatever means is employed to make a powdered rubber, it will cost more to make than the same material in bale form, and the question is: are the processing economics for powdered rubbers likely to be large enough, not merely to offset the extra cost/price, but to ensure a fast change-over from bales to powders? If this is not the case, then there will never be a large market for powdered rubbers.

The present position, elicited during the UNIDO/IRRDB project, is as follows. Using conventional processing equipment (internal mixers) there is a small saving in energy (reduction of peak power load) with powdered rubber and there may be a reduction in mixing times and perhaps also in the number of mixing cycles needed. The total savings do not appear large enough to warrant general use of powdered rubbers in mainstream products manufacturing. With open-mill mixing, the savings are said to be greater, but few manufacturers use this process on any scale nowadays.

With continuous mixing (powder blender following by mixer-extruder) the cost savings are potentially greater but they seem not to be as large as some have claimed and are associated mainly with a reduction in labour requirements rather than in energy. Capital costs are not reduced: powder processing equipment is neither simple nor cheap and a production line to handle 0.5 tonne/h by continuous powder processing costs the same (£0.25 million) as one to process the same quantity by normal batch mixing of bale rubber.

Since there is some usage of powdered rubbers, albeit modest, there must be some advantages to some users. It is reasonably certain that this is the case only in special circumstances, the rarity of which accounts for the modest usage. For example, manufacturers of solution-based NR adhesives

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*The Delphi method of technological forecasting involves submitting a series of questions to a panel of experts, circulating the answers to the panel, and repeating the process several times, expecting to find a convergence of views.

find that use of fine-particle NR powder greatly accelerates the process of dissolution, thereby saving costs. In another reported example, a belting manufacturer switched from buying his material from a custom compounder to mixing in-house with powdered rubber (synthetic) in a modern continuous line. He reports the process to be entirely economic compared with his previous method, and with better control of quality. In fact, the claimed improvements are just as likely to be associated with his change from external to in-house mixing rather than with the change to powdered rubber processing.

The present position with powdered NR is that there are 'custom granulators' in a number of consuming countries; they convert bales into granules, at a charge, typically, around £100/tonne. There is one commercial producer, in Malaysia, making fine-powder material direct from latex by spray drying. The UNIDO/IRRDB project has devised another route involving hardening the surfaces of the latex particles by bromination or chlorination to minimize reagglomeration. For powdered NR made in a producing country from latex the additional production cost is likely to be in the range £75-£125/tonne and if the material is to be exported to the West there is a further additional freight cost (ca £50/tonne) due to the lower density of powdered NR compared with bales. With present technologies, consumers in the West will find it cheaper to import bales and arrange for granulation (or do this themselves, which is still cheaper) than to buy powdered NR produced in an NR producing country (Table 6).

TABLE 6 POWDERED NR : COST BREAKDOWN

	£/tonne		
	factory cost	freight	total
in NR producing country			
spray-dried	125	70	195
brominated	70	70	140
talced	30	70	100
in consuming country			
custom granulator	70	30	100
in-house	60	0	60

It is quite certain that powdered NR exported from an NR producing country at a premium of at least £125/tonne would not be economic for use in mainstream products manufacturing with orthodox batch processing. Whether it would be economic at this time with the newer continuous processes is not certain; calculations performed within the UNIDO/IRRDB project suggest that it might just be, but it would be wrong to be categorical. And of course there may be special situations where use of such materials would pay off.

Masterbatches and compounds

There is a curious and significant difference between the plastics and rubber industries. The former, now very much the larger, has developed on the basis that the primary raw material marketed by the polymer producers reaches most converters, not as raw polymer, but as a ready-to-use compound. Manufacturers of rubber products, by contrast, mostly buy raw rubber from one source, the various chemicals, fillers etc from elsewhere, devise their own formulations, and carry out their own mixing ('custom compounders' do exist, but their throughput represents a small proportion of total rubber consumption). Of course, there is one difference between plastics and rubbers: vulcanization. It is not technically feasible to market, large-scale and over large distances, a fully compounded rubber; the shelf life is too short. There are various halfway houses. Marketing carbon black, oil, and carbon black/oil masterbatches has been a common practice with synthetic rubbers for many years. With NR, the marketing of such masterbatches is on a very small scale. Malaysia, for example, exports some 2000 tonnes/year of NR/oil masterbatches, and is starting operations with carbon black/NR masterbatches, using indigenous carbon black.

Given the intensely conservative nature of the rubber industry it would be wrong to suggest that trying to sell a substantial proportion of their NR in the form of masterbatches or partially-compounded products would be an easy way for the NR producing countries to add value to raw NR. It would not, and there are several problems. Consumers have always tended to argue that buying masterbatches or semi-compounds restricts their freedom of choice, that they can make up compounds more cheaply themselves. And there is the matter of tariffs: many of the countries which admit raw NR duty-free will charge import duties on 'semi-processed' materials, though these are generally not substantial (Table 7). Some, though not all, of the problems disappear if marketing is confined to within the borders of a country, and it is worthwhile to note the existence of one interesting concept: 'latex custom compounding'. Devised in Malaysia, this method involves making up an appropriate compound direct from field latex, for supply to relatively local consumers.

TABLE 7 IMPORT TARIFFS

	Raw NR	Masterbatches, compounds
USA	0	5
Canada	5	27.5
EEC	0	3
Austria	0	20
Norway	0	15
Spain	0	16
Sweden	0	0
Japan	0	12
Australia	0	0

PRODUCER ATTITUDES

There are evidently a number of recently-devised new forms of NR for which the technology is reasonably well established: TPNR blends, epoxidized NR, powdered NR. And there exist, of course, easy technical options relating to masterbatches and partially-compounded forms.

What should be the general attitude of the NR producing countries to such new forms? There is the cautious (some might call it negative) attitude of expressing interest in the hope that a few producing units here and there may think it worthwhile to add one or more of these materials to their output of exportable NR. This has been the pattern so far, with a few individual producers (almost invariably the larger estate groups) seeing some immediate advantage in undertaking production of a new line. This is not said in criticism of such producers, and indeed they should be complimented for their risk-taking activities, but it is not necessarily the best way to exploit the long-term potential of such materials, and it does not enable the NR producing countries to add value to their commodity on a substantial scale. It is easy to predict that, if this is the policy followed, usage of these new forms will never exceed a few thousand tonnes/year, as has been the case in the past with such materials (cf Table 2).

There is another possible attitude, which seeks to gain maximum added value from the new forms, by paying full recognition to the changing circumstances of the world rubber industry, and especially to the new status of the NR producing countries.

Integrated approach

In the introductory comments, the point was made that the production of new forms of NR should be regarded as synergistic with development of rubber products manufacturing in the NR producing countries. The view being advocated is that, unless the NR producing countries seek to integrate* production of new forms of NR with their own expanding rubber products sector, these forms will be limited to small-scale special products. This argument can now be expanded.

In rubber products manufacturing the NR producing countries have one very important comparative advantage over the industrialized world (apart from the obvious advantages of lower labour costs, direct access to lower-cost NR etc): their manufacturing sector is relatively new and is growing very fast (cf Figure 1 and Table 1). Since they are - and increasingly will be - investing in new processing facilities, and other rubber-related activities (eg rubber chemicals) they must ask themselves the question: what kinds of facilities, and should not the potential of the new forms of NR be borne in mind when planning these?

Powdered NR can serve as an example of the reasoning. From the earlier description there is obviously a fundamental hesitancy concerning the future growth of powdered rubbers in the industrialized world. Their economic advantages are evident only in conjunction with new types of continuous

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*Use of the word 'integrate' does not necessarily imply co-ownership of production facilities. It conveys the idea that production facilities within NR producing countries for new forms of NR should be established specifically to supply rubber products manufacturing operations which have been designed to use them.

processes. Established factories are unlikely to scrap existing processing machinery unless the economic advantages of switching from bales to powder are considerable (which they are not). Moreover, the high durability, slow obsolescence and high cost of processing machinery such as internal mixers act as a substantial barrier to replacement of old by new types of machinery. This is why the use of powdered rubber has grown so slowly in the West, given the relatively low level of investment in new factories in recent years. Since the NR producing countries are certain to be building a great number of new manufacturing units in future years it would make sense for them to think seriously about incorporating the new types of machinery, and to discuss how best concurrently to develop production facilities for powdered NR to use in the new machines.

The same argument applies to the TPNR blends, but with extra dimensions. These materials are likely to find their major use in applications such as automotive components. It would seem absurd for an NR producing country, building up an indigenous vehicle assembly and construction industry, to import synthetic thermoplastic rubber if it can obtain an equivalent material from its own resources. In this case, moreover, the requirement for materials such as polyolefins should be dovetailed with development of the local plastics industry. This point can be taken even further in the case of the TPNR graft copolymers: their production can really only be considered within the framework of a comprehensive petrochemicals/plastics industry. A similar argument applies to masterbatches and compounds, all of which require materials other than NR.

The argument is that integration of the production of new forms with products manufacturing can strengthen both activities. It can provide the springboard for rapid development in use of the new forms, it can give the expanding products sector in NR producing countries special and unique advantages over manufacturers in other countries. This approach can also serve to overcome another problem attending development of new forms of NR. Earlier, it was noted that establishment of reasonable-scale markets for these has always been difficult, and the reason for this is not hard to find. When an individual NR producer decides that a new form looks interesting enough to consider production the decision is usually made to produce a few hundreds of tonnes a year, entirely for export alongside with the producer's normal exports (TSR, RSS, latex). Interest is stimulated among a few consumers (often prematurely) and there quickly develops the 'chicken and egg' problem: consumers will not take the new form seriously until they see a substantial and therefore reliable source of supply, producers will not enter the market on a major scale until they see an assured market.

It is an axiom of marketing that success requires a large home market as the base: there are countless examples of the truth of this. Such a position could not be achieved for the new forms of NR until there had emerged a reasonably large products manufacturing sector in the producing countries, and the previous lack of this is undoubtedly the main reason for the disappointing market growth of earlier new forms. Emergence of a fast-growing products sector now introduces a new dimension, offering a take-off base for the new forms. Establishment of, for example, a large domestic market for powdered NR in an NR producing country (whether the products into which it goes are for local use or for export is beside the point) can serve as the stimulus for investment in proper-scale powdered NR plants, from which the subsequent spread of exports of powdered NR worldwide will become very much easier.

CONCLUSIONS

There are several contemporary new forms of NR of sufficient technical and economic promise to warrant very careful consideration of how best to undertake their large-scale and long-term development. If this is done piecemeal, on a small scale and by individual producing units, the likelihood is that the markets for these forms will remain relatively trivial, and the producing countries will derive little added value. Recognizing the synergistic relationship between new forms and the fast-expanding rubber products sector in NR producing countries, the view is put forward that full advantage will accrue to these countries only if production of the new forms is developed integrally with the products sector. Not only should this materially help the growth and proliferation of rubber products manufacturing, it should provide a sound basis for exports of the new forms worldwide.

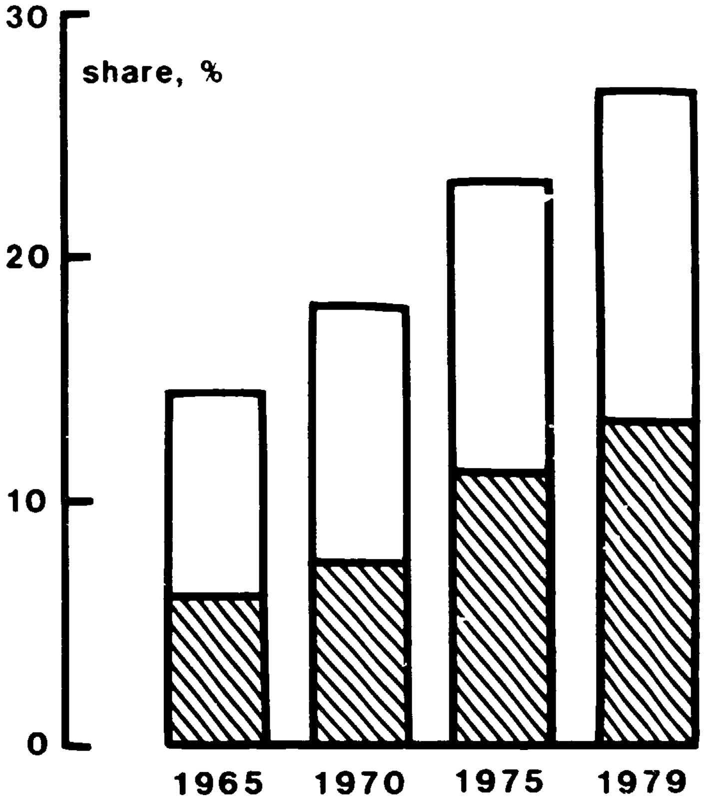


Fig. 16.1
Developing countries' share of NR consumption. The hatched areas are for the NR producing countries.

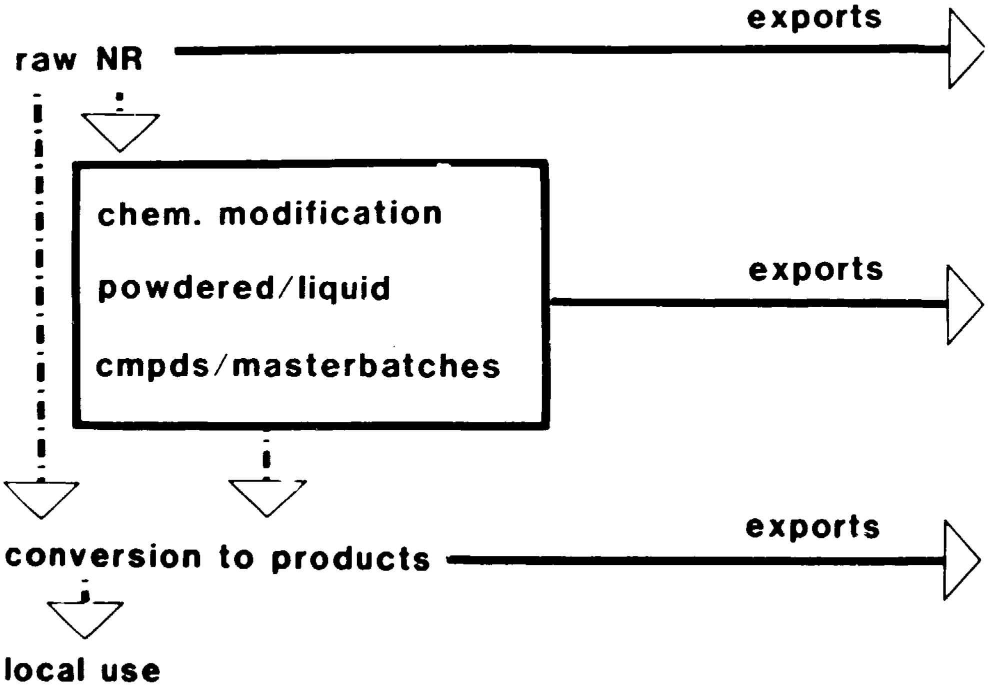


Fig. 16.2 Routes whereby NR producing countries can add value to raw NR.

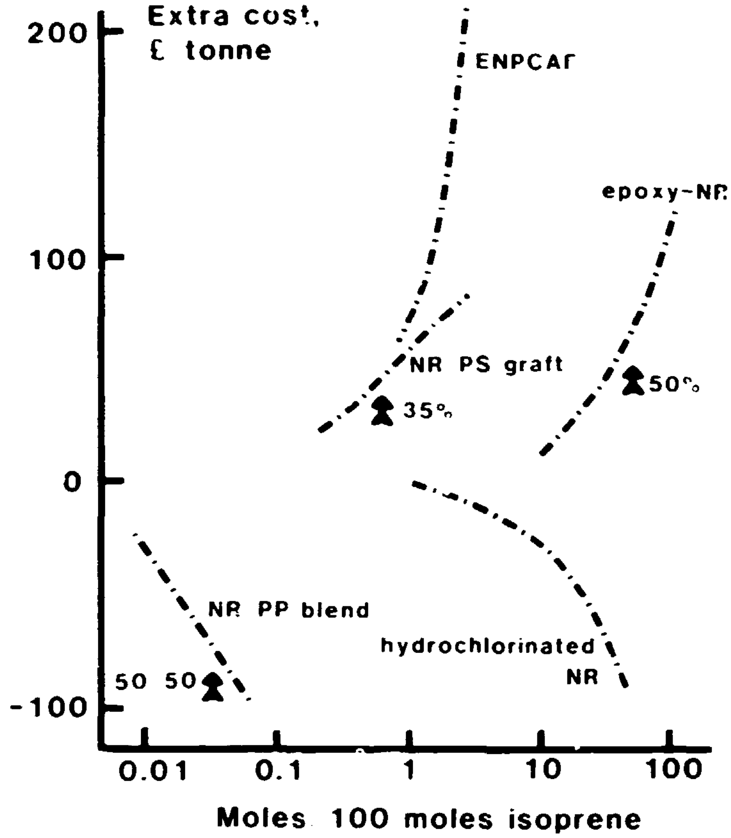


Fig. 16.3
Extra cost of raw materials per tonne of modified NR, for various modifications. The arrowed numbers are for normal levels of modification, eg. 50 per cent epoxidation, a 50/50 NR/polypropylene blend.

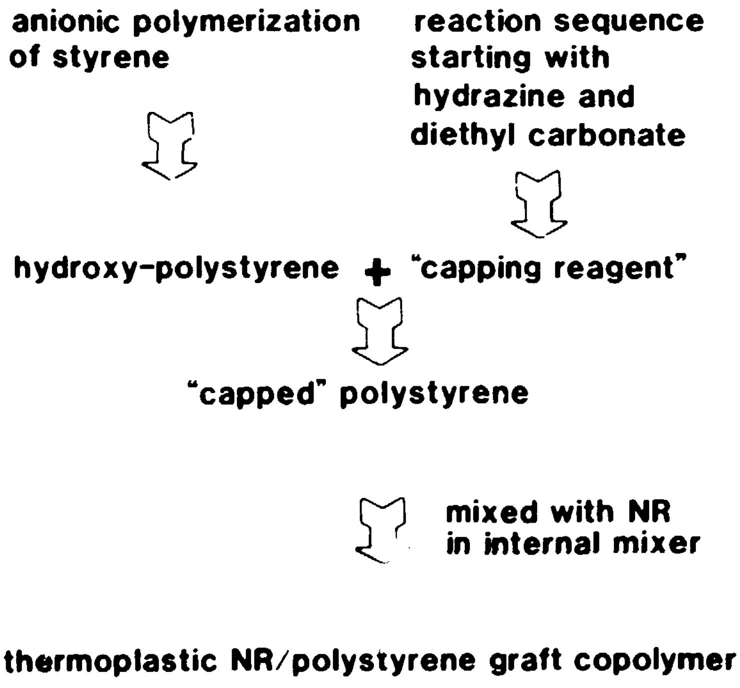


Fig. 16.4
Main stages in the preparation of a thermoplastic graft copolymer of polystyrene with NR.

APPENDIX I

RECOMMENDATIONS

After the symposium the following statement was issued by the organisers.

The Conference notes and resolves that:

1. UNIDO has taken appropriate follow-up action in the recommendations of the IRRDB for the second stage of collaboration on composites and liquid rubber. These are subject to final approval by the potential donor countries. The Symposium acknowledges the considerable support by the FRG Government in the first project completed. This conference now makes a special request to UNIDO and the FRG Government for their continued support to ensure that the projects on composites and liquid rubber are also successfully implemented.

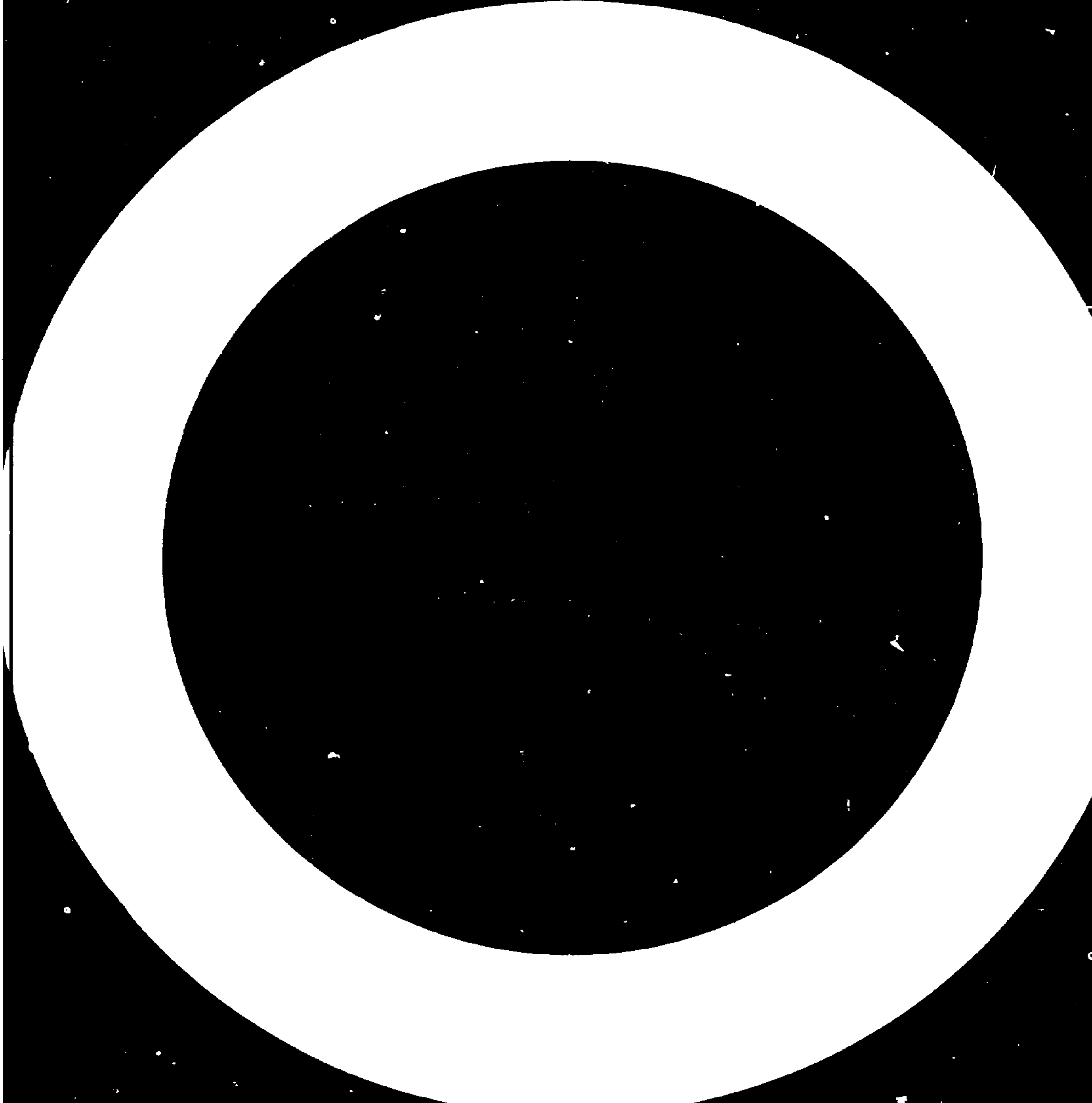
2. A training programme on an annual basis should be organized for rubber technologists from developing countries, and UNIDO is requested to organize that programme in consultation with potential host countries. (Definition of training courses to be discussed with Dr Sekhar and Dr Mullins).

3. In order to improve the technology in the processing and application of natural and synthetic rubber, technical co-operation under certain circumstances could be arranged with the IRRDB member countries for the benefit of other developing countries under the TCDC programme.

4. UNIDO's support will be appreciated to make expert services available on an urgent and a short-term basis to assist developing countries on the production, processing and application of natural and synthetic rubber upon specific requests of Governments.

5. In view of the commercial viability as shown by this project, UNIDO is requested to support advisory and fact-finding missions to interested countries to identify opportunities and to promote and assist in setting up local manufacture and processing of rubber blends in the rubber producing countries. The work would also involve both technical and economic considerations.

6. IRRDB should carry out demonstrations for high level managers from the rubber processing industry of developing countries at selected IRRDB laboratories. These demonstrations would include methods of making powdered rubber, rubber blends on semi-production scale, research and development techniques in chemical technology and application engineering.



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