OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as "developed", "industrialized" and "developing" are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

by M. Gh. IVANUS CCI 89/104

17609

THERMOPLASTIC RUBBERS

Bucharest, 1988

1/76

CONTENTS

1. Introduction

1.1. Short history

Thermoplastic rubbers are a relatively new category of industrial products making a bridge between the rubber industry and the plastic industry.

The rubber and plastics industries have developed rather independently from each other for a long period of time, although polymer and rubber processing on the one hand and plastics processing, on the other, are a common factor. With the appearance in the 1950s of thermoplastic rubbers, the gap between them began to close mainly because the equipment is basically the same and the properties and performance of the resulting products are very similar to those of traditional elastomers. In the last 25 years, the number of types of thermoplastic rubbers has significantly increased and the products have captured a share of the markets traditionally belonging to elastomers and plastics.

In the first years following the marketing of thermoplastic rubbers it was believed that the new products would replace traditional elastomers; later, however, it was proved that such reports had been mere exaggerations and that thermoplastic rubbers add themselves to the existing range of rubber products.

At present, thermoplastic rubbers cannot wholly replace classical elastomers as their penetration into several markets for rubber products is still difficult. Obviously, they have not penetrated at all the tyre market, which is the largest one for elastomers, and will not do that for at least another decade.

Thermoplastic rubbers cannot displace, today or in the near future, the large quantities of thermoset rubber used in industrial rubber products although they have achieved success in replacing several hundred thousands tonnes of thermoset rubber polymers, natural and synthetic.

The thermoset rubber polymers can be developed in hundreds of individual compounds which, when combined, may result in products largely different in properties and performance. High performance products would however require lengthy research and development.

The cost/performance ratio is not to be ignored either. Even if the thermoplastic rubbers have very good performance, sometimes even better than thermoset rubber polymers, the starting raw materials for their production are generally more expensive than those for thermoset rubber compounds.

Given improved performance but higher raw materials cost for thermoplastic rubbers and higher processing costs (energy and labour intensive) for thermoset rubber compounds, the question is whether the former are or will be able to replace the latter.

The growth of thermoplastic rubbers is also related to the fact that they are manufactured in very large quantities and a limited number of grades which allows the use of highly automated, computer-controlled production systems.

Another advantage of thermoplastic rubbers is the constant and standardized quality of raw materials, irrespective of supplier, which provides consistent quality and increased competitiveness for the resulting products. By contrast, it is common knowledge that quality,batch-to-batch variations of rubber is a major shortcoming in rubber part fabrication.

The main advantages that favour the use of thermoplastic rubbers are their rubberiness, light weight, low temperature properties, skid resistance, good flow properties and design flexibility. (4).

1.2. Production capacities and consumption

The present market for thermoplastic rubbers is large and still growing. Worldwide, over 500,000 tonnes are sold and the total is expected to increase by 50,000 tonnes/year, mainly by replacing thermoset rubber parts and polymers.

In the USA, the thermoplastic rubbers consumption is about 200,000 tonnes/year and will probably increase by over 100,000 tonnes in the following years. The European and Japanese consumptions are also growing rapidly. This significant increase all over the world is due to the large range of applications for thermoplastic rubbers as well as to their specific properties.

The tables below indicate the total production and consumption of thermoplastic rubbers in the USA, Europe and Japan, taking into consideration the main types thereof:

Table 1.1.

Consumption of thermoplastic rubbers in some industrialized countries (thousand tonnes/year)

	1983	1985	1990
United States of America	150	175	275
Europe	200	230	320
Japan	75	90	150
Total:	425	495	745
Growth rate 1985-90: 8.5%			

Table 1.2.

Consumption of thermoplastic rubbers in the USA (thousand tonnes/year)

	1983	1985	1990
Styrene	80	90	125
Olefinic blends	30	35	70
Elastomeric alloys	2	7	25
Urethanes	25	30	35
Copolyesters	10	15	20
Total:	147	177	275

Table 1.3.

Production of thermoplastic rubbers in Europe (thousand tonnes/year)

	1983	1985	1990
Styrene	110	130	160
Olefinic blends	50	55	75
Elastomeric alloys	-	3	15
Urethanes	32	35	45
Copolyesters	-	4	14
Total:	192	232	309

Table 1.4.

Production of thermoplastic rubbers in Japan
(thousand tonnes/year)

	1983	1985	1990
Styrene	10	15	30
Olefinic blends	12	15	25
Elastomeric alloys	-	-	5
Urethanes	5	7	9
Copolyesters	2	3	7
PVC	25	30	40
Total:	54	70	116

A cursory look on tables 1.1 - 1.4 will indicate that the USA are now the largest consumer of thermoplastic rubbers with approximately 33% of the total consumption of the main industrialized countries; styrenic thermoplastic rubbers and olefinic blends have the highest consumption growth rate. The average yearly growth rate of thermoplastic rubber consumption in the next five years is very high (8.5%) and exceeds by far the growth rate of synthetic rubber and plastics consumption.

1.3. Short description of the present study

This technical information on thermoplastic rubbers was elaborated by a team of specialists within the Joint UNIDO-Romania Centre in Bucharest based on the technical literature listed as bibliography.

The study was so conceived as to cover the main aspects related to the production and development of thermoplastic rubbers. It is therefore made up of the following chapters, dealing with:

Chapter 1:	Short history of the development and marketing of thermoplastic rubbers; production capacities and consumptions in the main industrialized countries;
Chapter 2:	Technological types and marketed grades of thermoplastic rubbers; their physico-mechanical characteristics and applications;
Chapter 3:	Comparative analysis of the existing technologies for the production of graft copolymers, styrenic block copolymers and blends of natural or synthetic rubber with polyolefins;

Chapter 4: New trends in the production, development and utilization of thermoplastic rubbers;

Chapter 5: Health and safety aspects of thermoplastic rubbers;

Chapter 6: Economic aspects related to the production and use of thermoplastic rubbers.

Due to the rich content of information, the present study will hopefully be useful to the specialists in developing countries which intend to start a thermoplastic rubber production, as well as to those who are already involved in research and development or manufacturing of thermoplastic rubbers.

2. Thermoplastic rubber types and their applications

2.1. Thermoplastic rubber types

Thermoplastic rubbers are materials which soften reversibly and flow at elevated temperatures, but unlike thermoplastic resins, they 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 advantage, 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. (3).

Thermoplastic rubbers fall into three large categories, namely: graft copolymers, block copolymers and thermoplastic rubber blends.

Graft copolymer thermoplastic rubbers

This class of thermoplastic rubbers includes materials containing both rubbery and hard polymers; they are characterized by chemical bonds between the two polymers.

Heveaplus MG, which has been marketed for 25 years, is an example of graft copolymer thermoplastic rubber; it is obtained as a result of a chemical bond between natural rubber and polymethyl methacrylate (hard polymer).

Styrenic block copolymers

This class of thermoplastic rubbers is obtained through styrene block copolymerization with butadiene to produce styrene-butadiene-styrene thermoplastic rubber (SBS) or with isoprene to produce styrene-isoprene-styrene thermoplastic rubber (SIS) or with ethylene butadiene to produce styrene-ethylene-butadiene-styrene thermoplastic rubber (SEBS).

Thermoplastic blends

Thermoplastic blends are obtained by dry mixing the rubber with polyolefins; synthetic rubber - polyolefin blends are commercially available.

Table 2.1 below lists the trade names of the main types of thermoplastic rubbers as well as the names of the producing companies.

Table 2.1

Thermoplastic rubber types

Thermoplastic rubber type	Producer
A. Styrenic	
Cariflex	Shell
Kraton	Shell
Solprene	Phillips, Negromex Calatrava
Europene Solt	Enichem
JSR TR	Japan Synthetic Rubber
Finaprene	Fina
B. Olefinic blends	
Vistaflex	Essodrem
Kelton TP	DSM
Durtal TP	Himont
Leverflex	Bayer
Sumitomo TP	Sumitomo
Milastomer	Mitsui

From the US producers of olefinic blends, EPDM-PP blend, mention must be made of: BP Performance Polymers, Republic Plastres, Research Polymers, Telmon Apex, Ferro Corporation, Custom Compounders

2.2. Applications of thermoplastic rubbers

The main advantages that favour the use of thermoplastic rubber are its rubberiness, light weight, low temperature properties, [illegible] resistance, good flow properties and design flexibility.

The markets for which thermoplastic rubbers might profitably be accessed can be classified as follows:

(1) Replacement of vulcanised 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 the thermoplastic rubber 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 cross-linked PE;

(6) Good water and chemical resistance.

There is no doubt that the thermoplastic rubber 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. The thermoplastic rubber 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 thermoplastic rubber 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 thermoplastic rubbers 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.

The bumper cover is just one of several car components that can be made in thermoplastic rubber. 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 thermoplastic rubbers 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.

<u>Miscellaneous products in thermoplastic rubber</u>

Several products from the list given earlier have already been researched. These include rail pads 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 are an insurance against damage and the need for costly replacement.

The thermoplastic rubber sheeting 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 thermoplastic rubber by vacuum forming and other techniques (3).

The major markets for the styrenic thermoplastic rubber have been low cost footwear, hot melt adhesives, exterior automotive components and wire and cable. The worldwide consumption of styrenic thermoplastic rubber is over 200,000 tonnes and they have significantly displaced natural rubber and SBR in footwear. In addition, the hot melt adhesives have significantly displaced many rubber-based adhesives. In the wire and cable market they provide better heat resistance than PVC and are non-halogen.

The styrenic thermoplastic rubbers are similar to thermoset rubbers in that they can be readily compounded with fillers, extenders and additives. Numerous opportunities exist to compound styrenic block copolymers to reduce cost, improve performance, or achieve a different balance of cost/performance than is available in the heat polymer. Many applications have been developed in the footwear and mechanical rubber industries by the addition of non-black fillers and processing oils. These materials can also be flame retarded by addition of appropriate additives. This compounding flexibility provides the user of styrenic block copolymers with a method for increasing the value added and differentiating their products from those of potential competitors.

The styrenic thermoplastic rubbers are gaining acceptance as a replacement for both natural rubber and synthetic rubber in medical and surgical applications. They are proving to be cleaner materials with significantly lower levels of extractables than either natural or synthetic rubber compounds. It is easier to produce parts with reproductible dimensions and consistant performance characteristics than with natural or synthetic rubber. The rubber medical products field will continue to look extensively for alternative materials, and the styrenic thermoplastic rubber definitely will have a growth in this area.

The disadvantages of styrenic thermoplastic rubbers as replacements for thermoset polymers seem to dominate the future growth patern. They have weak heat resistance at temperatures above 80°C. They have low elastic recovery compared with thermoset rubbers. They have weak hydrocarbon resistance. Applications where these performance characteristics are required obviously will not be an opportunity for styrenic thermoplastic rubbers.

The olefinic blends (TPOs) are simple blends of EPDM rubber and may contain more plastic than rubber. The property of the blend is generally determined by the weight percentage average of the individual component properties. TPOs which have been commercialized since the early 1970s have found significant use, mainly in the automotive industry. TPO bumpers dominate the market for automotive bumpers in Europe and Japan and have made inroads against polyurethane products in the USA. The other major market for thermoplastic olefins is wire and cable. Other than the growth in use for car bumper covers, it is unlikely that TPOs will achieve further significant growth. As a replacement for conventional rubbers they have several advantages and disadvantages. They have the advantages of being thermoplastic, thus reducing production costs, and are colourable. The major disadvantages are: low hydrocarbon resistance and high compression set, significantl reduced properties at elevated temperatures, and the inability to be extruded into close tolerance profiles.

Thermoplastic urethanes have been in commercial production for over 20 years. There are two types: polyether urethanes and polyester urethanes. They are noted for excellent abrasion resistance and performance in speciality applications. The target markets include footwear, automotive components, wire and cable, adhesives, tubing and industrial products. Their market growth appears to have levelled off, and their future ability to displace thermoset rubber depends on overcoming several existing disadvantages: their prices in excess and their hydrolytic stability, inadequate for a number of industrial applications. These two characteristics make the urethanes less than desirable for many industrial rubber parts.

The copolyesters, while they are generally considered by the average rubber parts fabricator to be hard and stiff, have a unique position in the rubber products industry. They are used in automotive components such as rock and pinion boots and CV joint bellows, wire and cable, industrial hose and tubing and, to a limited degree, in special footwear. The copolyesters have several unique features which provide them with significant advantages for replacing rubber in industrial rubber products. They have excellent modulus, outstanding fluid resistance, high tear strength and excellent fatigue loss. The disadvantages are few: high hardness and high compression set make them less than desirable for many applications where flexible rubber products and a high degree of elastic recovery are required.

Perhaps the most effective way to establish the use of thermoplastic rubber 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 end pedal grips are just some of the possibilities.

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

2.3. The physico-mechanical properties of thermoplastic rubbers

2.3.1. Physical properties of the graft copolymers

The physico-mechanical properties of the graft copolymers are affected by several factors such as: chemical composition, grafting efficiency, molecular weight of the elastomer and polystyrene, compounding system etc.

Effect of composition

The composition of thermoplastic rubber is directly determined by the amounts of prepolymer and backbone polymer used in the reaction. Consequently, the physical and mechanical properties of the product are dependent on the content of prepolymer. Figure 2.1. illustrates the tensile stress - strain variation according to the level of polyisoprene and natural rubber.

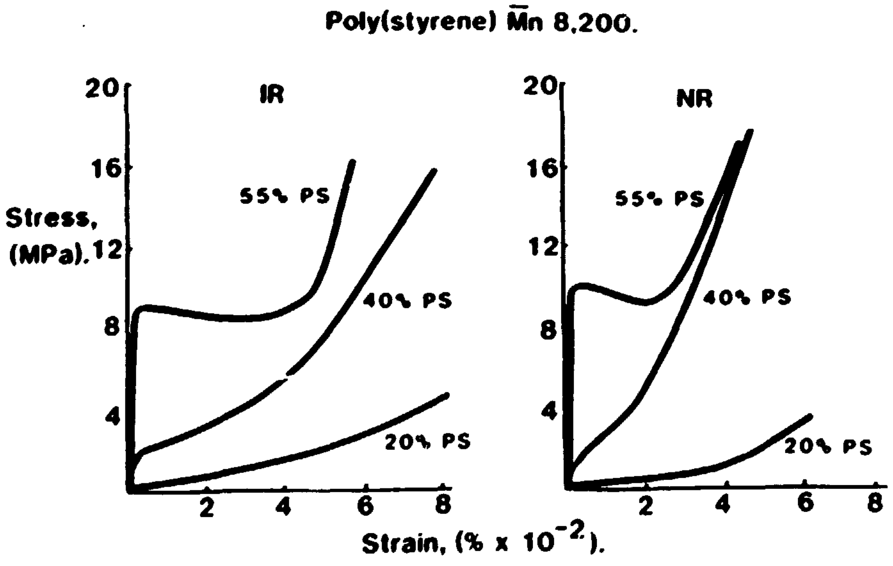


Fig. 2.1. Stress-strain curves of graft copolymers of poly(styrene) (Mn 8200) with Cariflex IR 305 poly(isoprene) and NR (SMR 5L).

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 polystyrene content is always higher for the NR graft copolymers in spite of the fact that the grafting efficiency is lower. Both types of graft copolymers show tensile yield phenomena above 40% w/w polystyrene and the yield becomes significant at 55% w/w polystyrene.

The tensile strengths of graft copolymers increase regularly with polystyrene content (Figure 2.2.) up to 45% w/w; above this level a decrease is noticed.

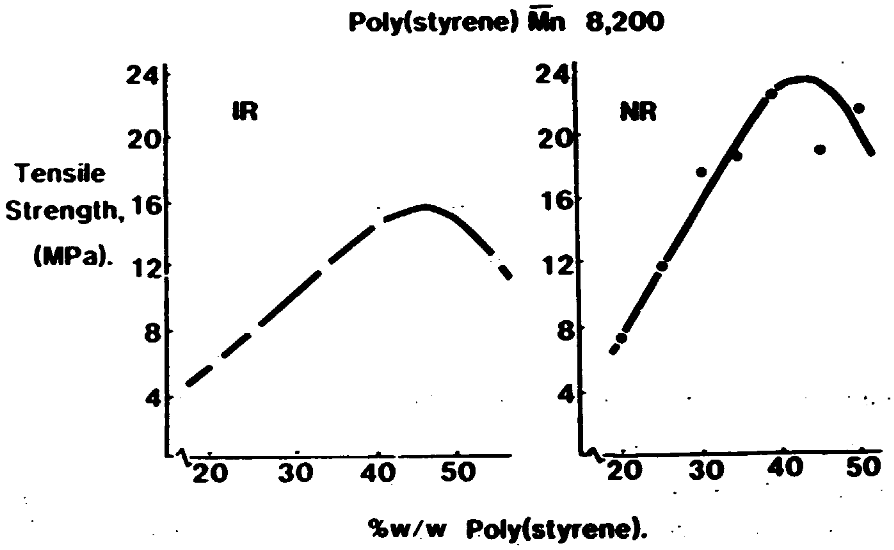


Fig. 2.2. Tensile strength x poly(styrene) content for graft copolymers of poly(styrene)($\overline{M}n$ 8200) with Cariflex IR 305 poly(isoprene) and NR (SMR 5L).

It can be noticed that, for both types of copolymers, there appears to be a decrease in tensile strength in the composition region where yielding becomes pronounced.

Effect of grafting efficiency

The dependence of tensile strength on polystyrene content leads to an expected dependence of tensile strength on grafting efficiency because both lead to changes in the average number of polystyrene chains attached to each polyisoprene backbone (Figure 2.3.).

This behaviour was experimentally confirmed by artificially reducing the grafting efficiency in a series of mixtures by incremental addition of linolenic acid to a constant amount of polystyrene (40%).

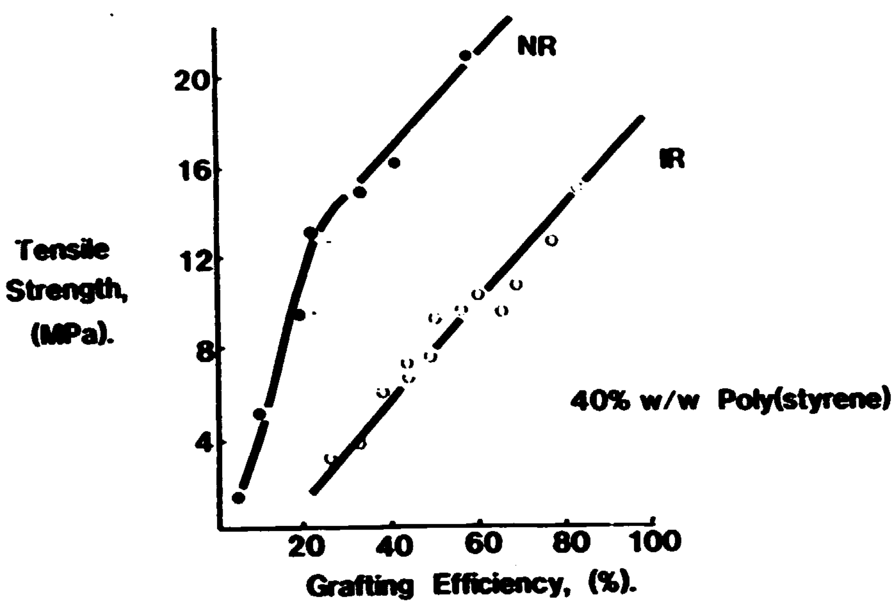


Fig. 2:3. Tensile strength v grafting efficiency for graft copolymers of poly(styrene) ($\bar{M}_n$ 7110) with Cariflex IR 305 poly(isoprene) and NR (SMR 5L).

The relationship between tensile strength and grafting efficiency for natural rubber is not linear. Tensile strength variation becomes linear, when natural rubber is used, only at grafting efficiencies above 25%.

The tensile strength relationships shown in Figure 2.3. 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 polyisoprene 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 25MPa could be obtained for natural rubber graft copolymers if the grafting efficiency could be increased to 80%.

Natural rubber and polystyrene molecular weight

The discussion of physical properties has so far centered around materials prepared from polystyrene of molecular weights in the region of 8000. At higher molecular weights there is a significant drop in tensile strength values of both the synthetic polyisoprene and natural rubber graft copolymers (Figure 2.4.).

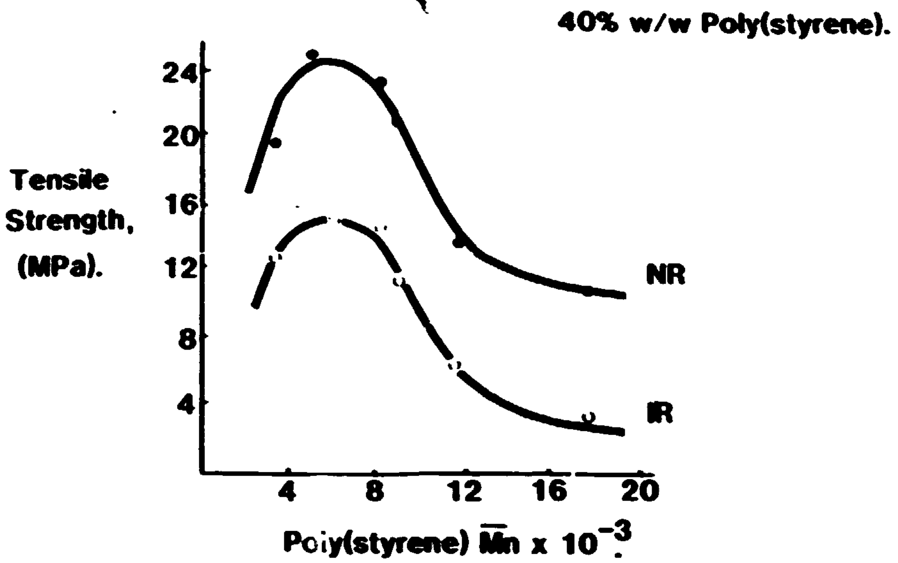


Fig. 2.4. Tensile strength as a function of poly(styrene) molecular weight for graft copolymers of poly(styrene) with Cariflex IR 305 poly(isoprene) and NR (SMR 5L).

The economics of the grafting process is closely related to the cost of the chemicals used to obtain the azodicarboxylate functional group of polystyrene. For a given weight % of polystyrene in the thermoplastic graft copolymer, this cost decreases as the molecular weight of polystyrene increases.

From a purely economic point of view it is attractive to work with polystyrene having a molecular weight higher than 8000, but the experimental results preclude such a course.

<u>Mastication history</u>

Mastication is an inevitable consequence of the preparation technique and directly influences the processability of thermoplastic rubbers obtained by grafting.

The grafting efficiency in Figure 2.5. indicate that the mastication results in scission of the backbone chains rather than removal of the side chains.

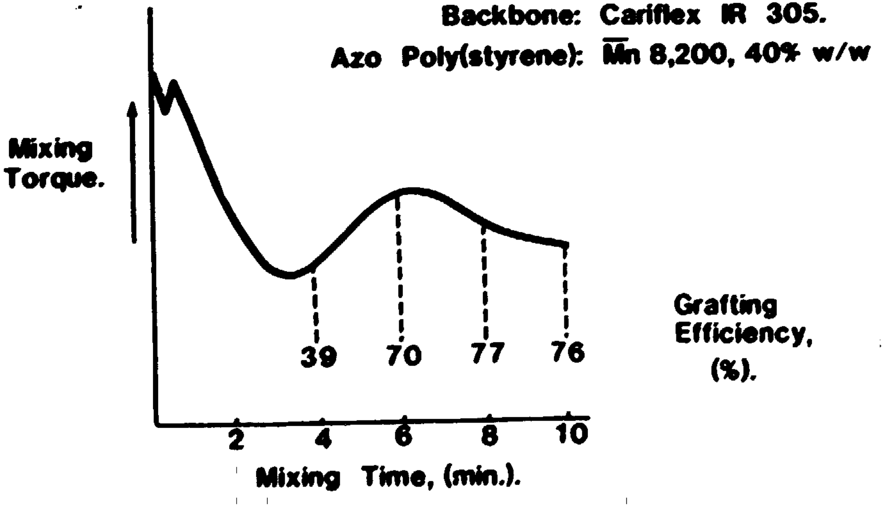


Fig. 2.5. Grafting efficiency v mixing time for the dry mix reaction of azodicarboxylate-functional poly(styrene) with Cariflex IR305 poly(isoprene).

If this scission is allowed to proceed too far the tensile properties can be adversely affected.

2.3.2. Physical properties of block copolymer thermoplastic rubbers

In styrene-butadiene block copolymers, most of the styrene units are concentrated at one end of the molecular chain. In the thermoplastic, the styrene units are grouped in different terminal polystyrene blocks of comparable length leaving no free polybutadiene chain ends. Furthermore, the polystyrene and polybutadiene blocks are linked in such a way as to form a symmetrical radial tetrachain structure, schematically represented below (Figure 2.6).

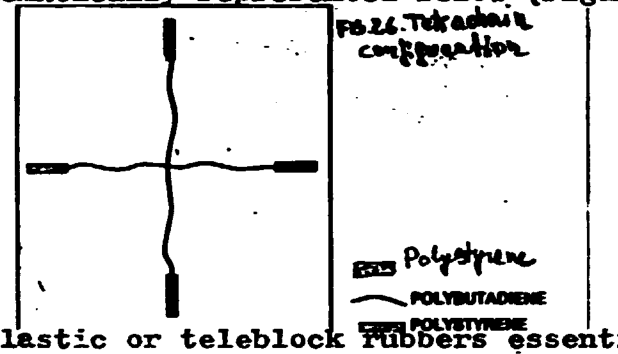
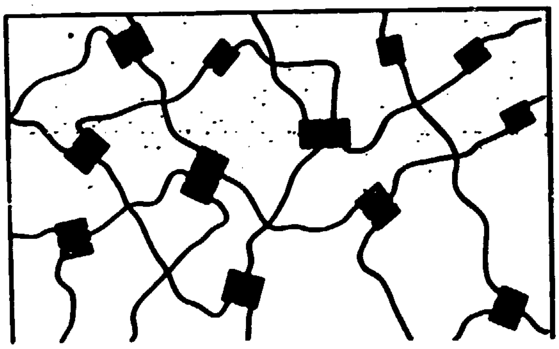


FIG 2.6. Tetrachain configuration

The thermoplastic or teleblock rubbers essentially differ from the normal block copolymers containing only one polystyrene chain end by the fact that a network structure is formed by the association of the terminal polystyrene blocks into rigid micelles (Figure 2.7).

FIG. 2.7.
Network structure of SOLPRENE thermoplastic rubbers



In the ordinary block copolymers, the free polybutadiene chain ends must be linked by vulcanization to form a network structure.

Polystyrene, being a thermoplastic material, undergoes a phase change as the temperature increases, resulting in a breakdown of the network structure as the glass transition temperature is passed ($T_G = 100^{\circ}C$). The structure can also be destroyed by dissolution in a suitable organic solvent.

A decrease of the temperature to below the glass transition point of polystyrene or the evaporation of the solvent will restore network structure.

This reversibility of the network formation is an important feature which determines to a large extent the applications and the processing technique of the thermoplastic rubbers.

Due to the association of the polystyrene segments in a network structure, these rubbers exhibit, in an uncured state, elastomeric properties similar to those of a reinforced vulcanizate.

The degree of "reinforcement" is a function of the styrene content. The effect of the molecular weight on the tensile properties is not significant at ambient temperature except for the very low molecular weight polymers. However, at higher temperature, the higher molecular weight teleblock copolymers exhibit better retention of tensile streng

The main types of thermoplastic rubbers produced by Phillips Petroleum Co. (Solprene) and Shell Chemicals (Cariflex) have the physico-mechanical properties given in Table 2.2 below.

Because of their molecular configuration, and especially their radial block structure, they combine economic processability with an attractive end-product performance in a wide variety of applications in both the rubber and plastics industries.

Shell thermoplastic rubber (Cariflex TR):

- Cariflex TR -11o1, straight, high molecular weight SBS;
- Cariflex TR -11o2, straight SBS;
- Cariflex TR -11o7, SIS;
- Cariflex TR -4113, easy-processing SBS;
- Cariflex TR -4122, easy-processing SBS;
- Kraton 21o4, medical uses and food packing;
- Kraton 21o9, medical uses and food packing;
- Kraton 32oo, general purpose;
- Kraton 32o2, general purpose;
- Kraton 32o6, general purpose;
- Kraton TOB-955, shoes and high quality house slippers;
- Kraton 5151 and
- Kraton TOB-956 } very hard, rubbery compound mainly for heel top-pieces;
- Kraton TOB-950
- Kraton TOB-954 } solid soling of walking shoes;
- Kraton 519, soft, solid sneaker soling;
- Kraton TOB-958, Wellington boot uppers.

Table 2.2

Solprene butadiene-styrene block copolymers

	Teleblock					Special copolymers			
	406	411	415	416	475	303	410	476	1205
Butadiene-styrene content	60/40	70/30	60/40	70/30	60/40	52/48	52/48	52/48	75/25
Block polystyrene, %	40	30	40	30	40	11	32	32	18
Naphthenic oil content	-	-	-	-	50	-	-	37.5	-
Mooney viscosity ML-4, at 100°C	-	-	-	-	-	45	47	37	47
Inherent viscosity, g/ml	1.25	1.50	0.95	0.90	0.75	-	-	-	-
Specific gravity	0.95	0.94	0.95	0.94	0.93	0.97	0.97	0.96	0.93
Hydrocarbon content, %	99	99	99	99	99	99	99	99	99
Colour	white non staining				very light non-staining	white non-staining		very light non-staining	white non staining
Vulcanization	no vulcanization required					50 min.cure at 145°C			
Tensile strength, kg/cm^2	260	210	260	180	160	175	155	150	175
Elongation at break, %	700	700	700	800	1300	-	550	500	-
Shore A hardness	-	80	-	70	55	-	-	-	-
Shore B hardness	35	-	35	-	-	-	-	-	-

The physico-mechanical properties of thermoplastic rubbers of styrene copolymer type, Cariflex, are given below:

- Styrene content,	% g in the main polymer	25 - 45
- Average molecular weight		12,000-30,000
- Content of volatile matter:		
- water,	% g	0.5
- solvent,	% g	0.2
- Ash content,	% g	not more than 0.02
- Tensile strength,	kgf/m^2	100 - 250
- Elongation modulus, 300%	kgf/cm^2	20 - 25
- Shore A hardness,	°Sh	60 - 80.

Characteristics of raw materials and auxiliary materials for the synthesis of thermoplastic rubbers of the styrenic block copolymer type

Butadiene

Butadiene may be obtained from the installations of extractive distillation with selective solvents of the butene-butadiene fraction which is produced in naphtha steam-cracking plants or by dehydrogenation of butane and/or butenes.

The typical composition of butadiene for thermoplastic rubber synthesis is given below:

- butadiene 1,3	min. 99.5% g
- propylene	max. 0.1% g
- isobutene + butenes	max. 0.2% g
- acetylene	max. 50 ppm
- sulphur	max. 50 ppm.

Styrene

Styrene may be synthesised by dehydrogenation of ethyl benzene which is obtained either by direct synthesis from ethylene and benzene or by separation from the BTX fraction.

The typical composition of styrene for thermoplastic rubber synthesis is given below:

- styrene	min. 99.7% g
- ethyl benzene	max. 0.3% g
- isopropyl benzene	max. 0.1% g

- alpha methyl styrene	max. 0.2% g
- xylene	max. 0.02% g
- acetylene	max. 50 ppm
- inhibitor	max. 2 ppm.

Isoprene

Isoprene may be obtained either by synthesis (from isobutene and formaldehyde, acetylene and acetone, isopentane dehydrogenation, etc) or by separation from cracked gasoline.

The typical composition of isoprene for thermoplastic rubber synthesis is given below:

- isoprene	min. 99.6% g
- piperylene	max. 0.1% g
- isobutylene + pentenes	max. 0.3% g
- cyclopentadiene	max. 0.0002 % g
- carbonyl, e.g. CH_2O	max. 0.0005% g
- water	max. 0.0001% g
- acetylenes, e.g. isopropylacetylene	max. 0.0003% g
- sulphur compounds	max. 0.0002% g
- nitrogen compounds	max. 0.0002% g

Extension oil

White, heavy oil, with the following characteristics:

- density, at 20°C	900 kg/m^3
- cinematic viscosity, at 50°C	min. 45
- ignition point	max. 200°C
- freezing point	-18°C

Topanol

Colourless crystals with melting point 66°C and density 1030kg/m^3.

Methyl cellulose

Viscosity 20 cp in 25% aqueous solution.

2.3.3. Physico-mechanical properties of thermoplastic natural rubber blends

The physico-mechanical properties of thermoplastic rubbers of this type depend on the following factors:

(1) the proportion of rubber and polyolefin;
(2) temperature;
(3) partial crosslinking;
(4) the nature of fillers and oils.

(1) Varying the proportions of rubber and polyolefin

There is a marked dependence of flexural modulus on the natural rubber/polyolefin ratio as shown in Figure 2.8, which gives mean stiffness values over different parts of the sheets produced in an edge gate mould.

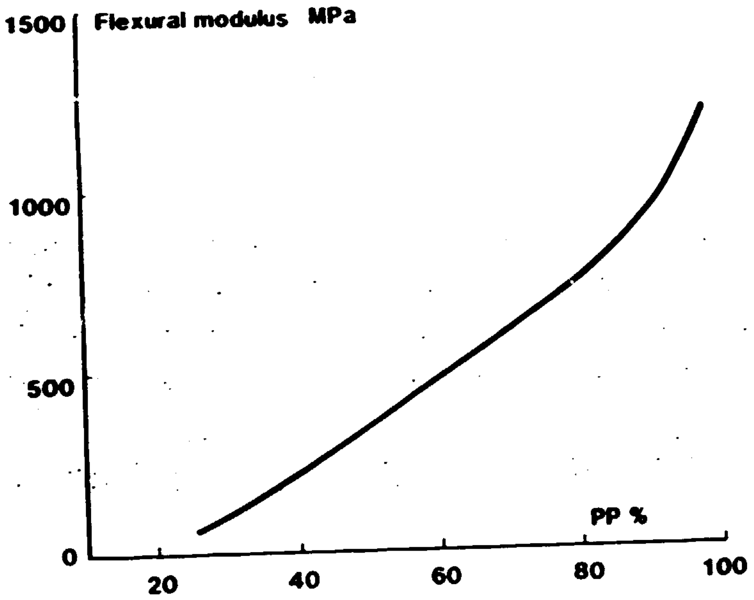


Fig. 2.8. Effect of PP content on flexural modulus at 23°C of unfilled TPNR injection moulded in Arburg 220 machine.

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 Figure 2.9 for sheet produced in a centre gate mould.

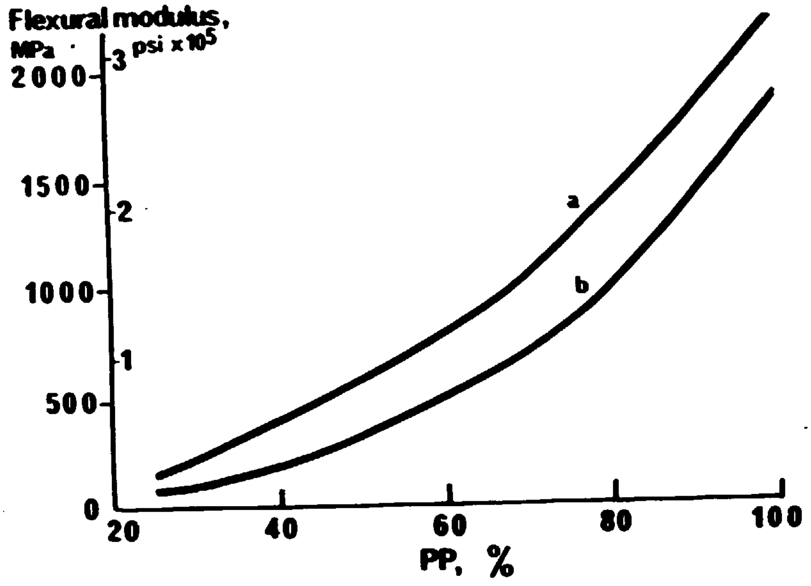


Fig. 2.9. Effect of PP content on flexural modulus at 23°C of unfilled TPNR injection moulded in REP B43K machine. a) and b) as in Figure 2.2.

Tensile strength increases with P.P. content while elongation at break generally decreases, particularly in the direction across flow lines, for filled material.

(2) Effect of temperature

Thermoplastic rubbers based on P.P. have higher softening points than the SBS and polyurethane types. This is shown by hardness/temperature curves in Figure 2.1o.

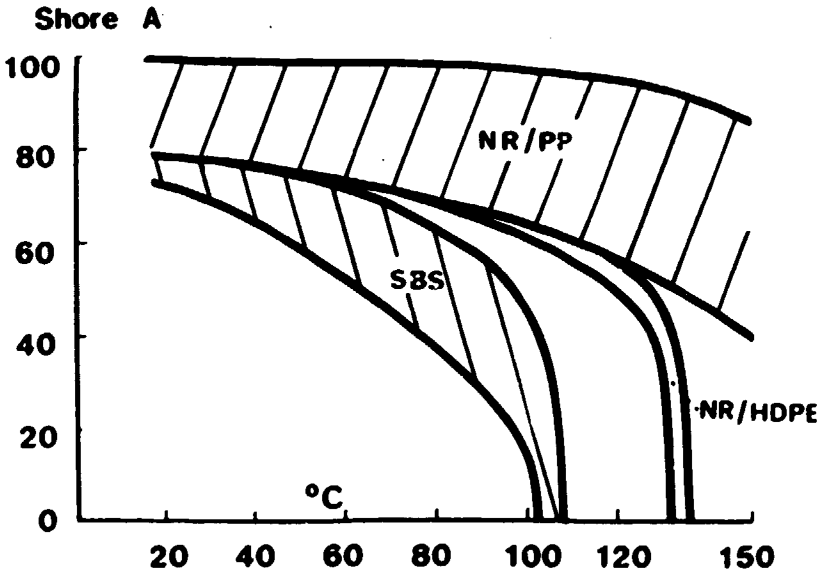


Fig. 2.10. Effect of temperature on hardness of TPNR and SBS copolymers.

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, thermoplastic natural rubbers 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 -40°C. This means that they must be stiff enough to prevent distortion at 70°C, but not become too stiff at low temperature that they cease to function as flexible impact absorbers.

(3) Effect of partial crosslinking

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

Figure 2.11 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 P.P. phase is almost certainly discontinuous since it is present in a low concentration. The effect of peroxide is less in the 65/35 blend.

The use of peroxide should be restricted to softer blends of thermoplastic natural rubbers 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.

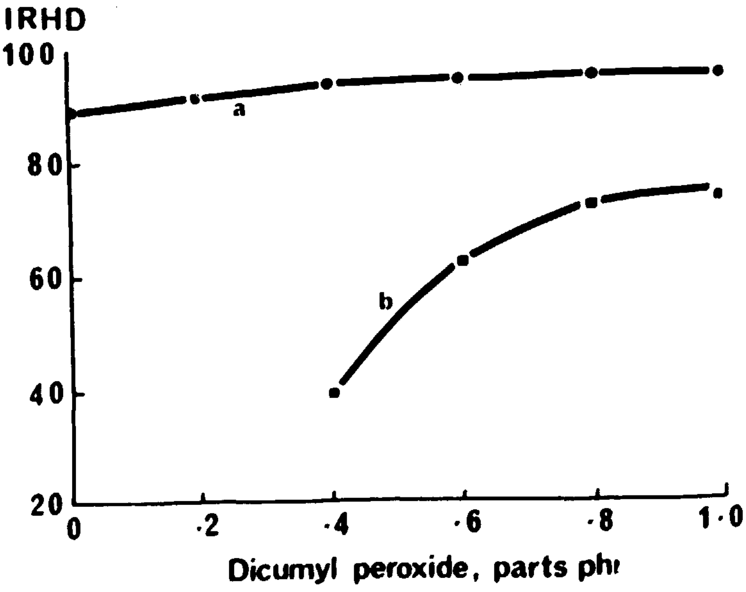


Fig. 2.11 Effect of dicumyl peroxide concentration on hardness of a) TPNR 6535. b) TPNR 8515.

(4) Compounding thermoplastic natural rubber blends with fillers and oils

Rubber/polyolefin blends, including TPNR, differ from the block copolymer thermoplastic rubbers in their ability to tolerate extension with oil 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 (Table 2.3.)

Table 2.3

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, MPa	14	17
EB, %	200	350
Density, kg/m^3	1.350	0.950

3. Technologies for the production of thermoplastic rubbers

The technological processes for the production of thermoplastic rubbers may be divided into two main groups, according to the type of technology used, i.e.:

a) Graft copolymers and block structure technologies, starting from natural rubber, synthetic polyisoprene rubber, polybutadiene rubber or other synthetic rubber types which are chemically bound to the hard polymer, namely polystyrene or polymethyl methacrylate.

From such processes characterized by phenomena of chemical binding between the elastic material (rubber) and the plastic one (polystyrene), there results a material which is not necessarily very elastic but nevertheless has elastic potential (1).

b) Rubber blends technologies, where the elastic material, natural or synthetic rubber, is mixed through physical methods with the plastic material, usually polyolefins such as low density polyethylene, high density polyethylene and polypropylene. The elastic material may be natural rubber or polyisoprene, polybutadiene and ethylene-propylene (EPDM) synthetic rubbers.

3.1. Graft copolymers and block structure technologies

3.1.1. Graft copolymers technologies

The product resulted from the chemical binding of natural rubber with polymethyl methacrylate (Heveaplus MG), which has been industrially produced for almost twenty years, is not a thermoplastic rubber, in the present day meaning of the term. Heveaplus MG cannot be directly processed by injection moulding or even compression moulding, due to its very high viscosity and its gel content (2).

Conventional mastication will confer a degree of processability to Heveaplus MG but the product does not have high strength or toughness unless it is subsequently vulcanized (6).

The modifications and improvements brought to the initial Heveaplus MG process have failed to produce a viable thermoplastic rubber. The major differences between Heveaplus MG and the styrene-diene thermoplastic rubber 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. Consequently, they would be expected to behave similarly in a phase-separating copolymer system with a poly(diene). However, there is no practical confirmation of that, due mainly to the difference in molecular architecture (graft versus block structure) (2).

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 MG process. The procedure involves the separate synthesis of hard polymer chains with reactive end groups and subsequent reaction of these end groups with the natural rubber backbone. (Figure 3.1.).

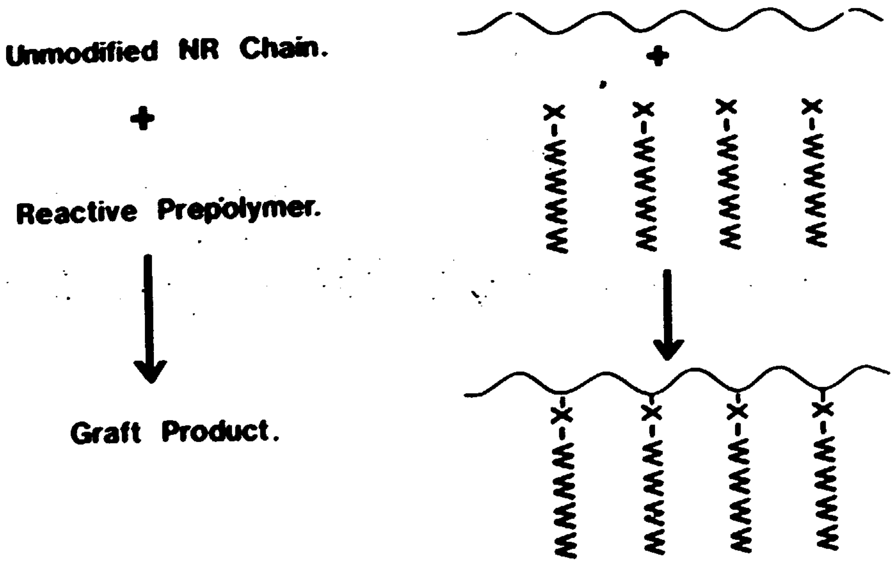


Fig. 3.1. method of grafting using reactive prepolymer.

The use of an air-stable prepolymer has clear advantages in the grafting process; the prepolymer can be prepared independently.(2).

The coupling reaction between the prepolymer and the poly (isoprene) backbone represents an "ene" addition of the azodicarboxylate group to an allylic double bond system. (Figure 3.2.).

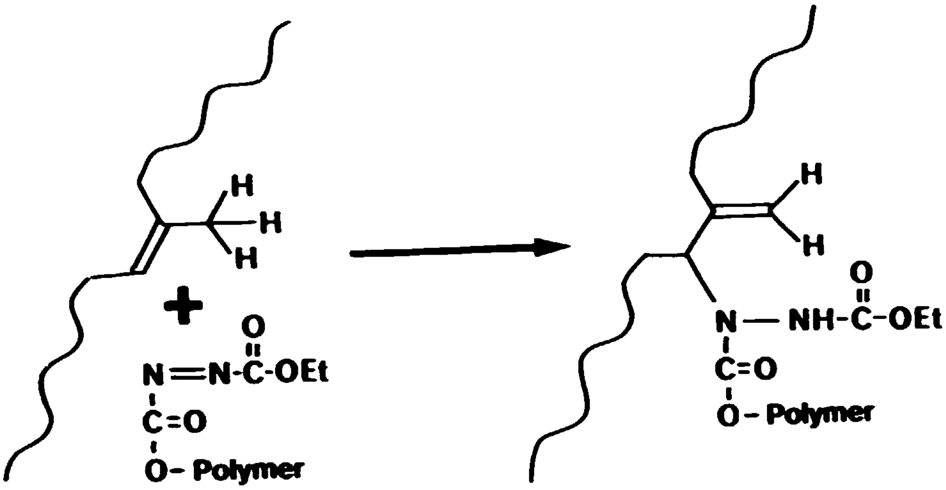


Fig. 3.2. 'ene' addition of the azodicarboxylate end group of the reactive prepolymer group to an allylic double bond system.

The reaction does not require the presence of a catalyst system and, compared to carbanion reactions, it is insensitive to impurities (either preexisting in the system or brought into it by raw materials). Thus, every double bond of the poly(isoprene) chain may be considered a potential reaction site. (2).

Figure 3.3. presents the direct synthesis of the azodicarboxylate-terminated polymer.

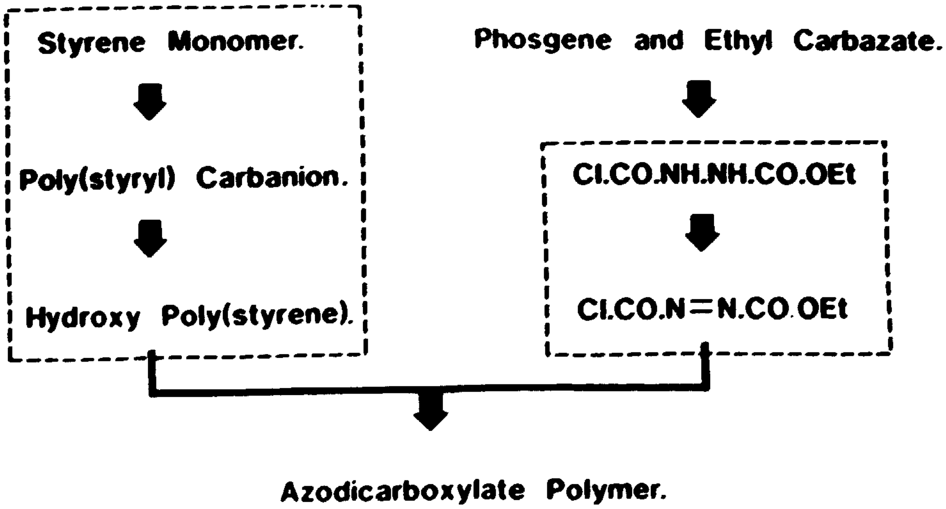


Fig. 3.3. direct synthesis of azodicarboxylate-terminated polymer by the reaction of hydroxypoly(styrene) with an azo-acid chloride.

The process consists in the preparation of a very highly reactive hydrochloric acid solution capable of reacting with the hydroxyl functional group of the polymer to give azodicarboxylate functionality. (2). The reactive intermediate is prepared by oxidation of 2-carbethoxyhydrazinecarbonyl with bromine in the presence of pyridine or t-butyl hypochlorite.

The reaction with hydroxyl functional poly(styrene) takes place in a solvent like toluene; the almost complete conversion of styrene monomer to azodicarboxylate-functional polymer is a one-step process involving successive addition of butyl lithium initiator, ethylene oxide and reactive azo acid chloride solution in a separate reactor to avoid contamination of the polymerization reactor with hydrogen chloride by-product. (8, 9).

Large scale application of experimental pilot-scale data is made difficult by the exotherm character of styrene polymerization reaction. Oxidation of 2-carbetoxyhydrazinecarbonyl chloride should be carried out immediately before reaction with polymer.

Polymerization can be made using either n-butyl lithium or sec-butyl lithium as reaction initiator; in the former case the molecular weight distributions are much higher.

Neutralization with carbonate, borax or sodium acetate is effective and so is water washing.

Reactions carried out in smaller reactors give higher azodicarboxylate functionalities (over 70%) while in the case of large scale reactors the figure is around 50%.

3.1.2. Direct mixing graft reaction

It has been observed that the functional poly(styrene) reacts with natural rubber or synthetic poly(isoprene) by direct mixing, in the absence of any diluent. For the reaction to take place, the temperature of the mixing operation should exceed the softening temperature of the poly(styrene) and the mix must be subject to higher shear for at least part of the mixing cycle. In other words, low shear and low temperature mixing does not result in graft copolymer formation. (8).

The reaction between poly(isoprene) of Cariflex IR 3o5 type and azodicarboxylate-functional poly(styrene) takes place at a temperature of 90°C and a mixing of 150 rpm; a sharp increase in mixing torque occurs between 4 and 8 minutes from mixing start (Figure 3.4).

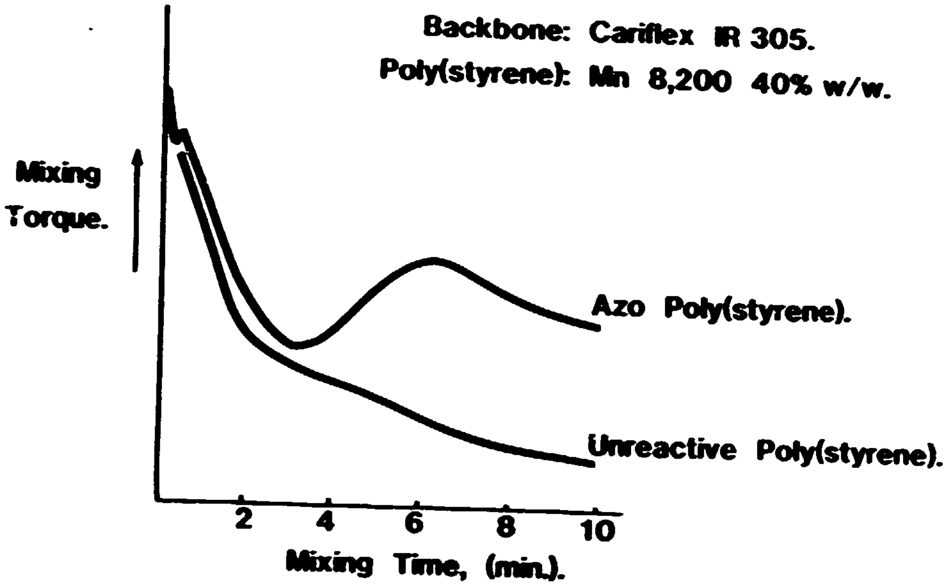


Fig. 3.4. Mixing torque v mixing time for Cariflex IR 305 poly(isoprene) with azodicarboxylate-functional poly(styrene) and non-functional poly(styrene) of the same mol. wt.

The overall duration of the mixing process is approximately 10 min. When the mixing operation is carried out with unreactive poly(styrene), the torque increase during the process is not observed.

When Cariflex IR 3o5 poly(isoprene) rubber is replaced with SMR 5L in the mixing process, a similar variation of mixing torque and mixing time is observed, as shown in Figure 3.5. The torque peak at intermediate mixing time is again noticeable, confirming graft copolymer formation. (10, 11).

The mixing torque versus mixing time variation curve is a consequence of the natural rubber very high initial viscosity, which then lowers; as the grafting reaction is developing, viscosity first lowers and then increases in the 2-8 minutes interval (10, 11)

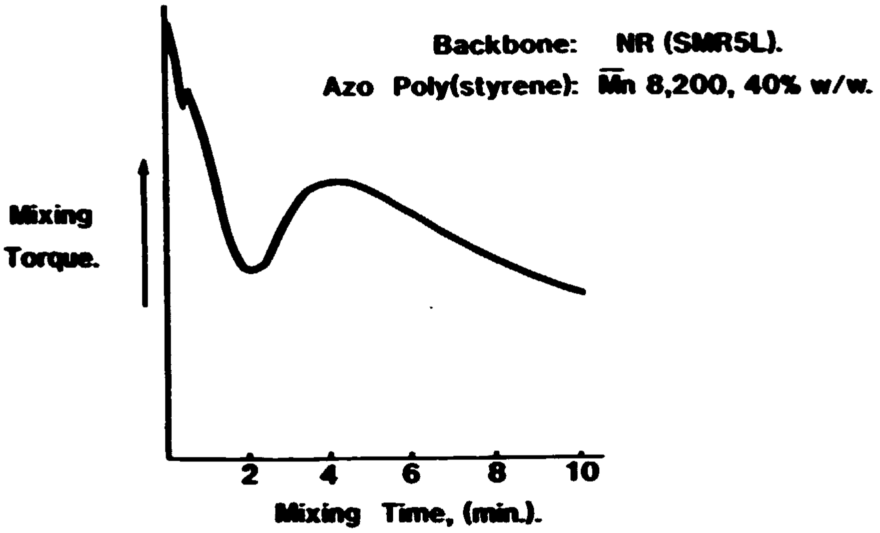


Fig. 3.5. Mixing torque v mixing time for the dry mix reaction of azodicarboxylate-functional poly(styrene) with NR (SMR 5L).

Mention should be made of the fact that grafting efficiency is lower for the reaction with natural rubber as compared to poly(isoprene) rubber and depends in both cases on the level of poly(styrene) in the mix. Grafting efficiency is summarized in Figure 3.6. in terms of bound poly(styrene) as a function of total poly(styrene) in the mix.

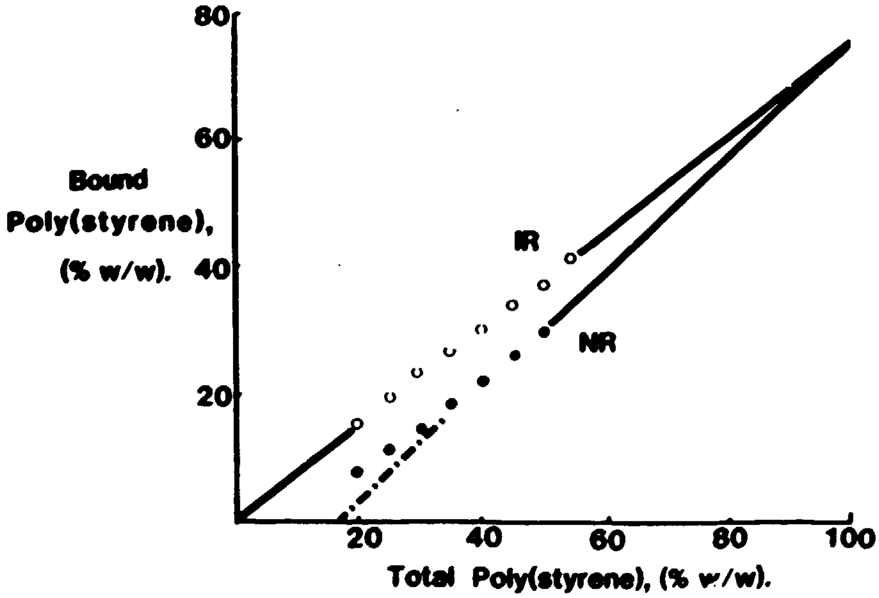


Fig. 3.6 Bound poly(styrene) as a function of total poly(styrene) for mixes of azodicarboxylate-functional polystyrene) ($\overline{M}n$ 8200) with Cariflex IR305 poly(isoprene) and NR (SMR 5L).

For the reaction with synthetic poly(isoprene) the amount of rubber-bound poly(styrene) increases linearly with increasing poly(styrene) level, the line extrapolated towards the lower values of poly(styrene) level passing through the origin of the axes.

In the case of natural rubber reaction, the amount of grafted poly(styrene) is lower for all experimental levels and the extrapolation is not precisely linear. This phenomenon is ascribed to interference of non-rubbers in the natural rubber.

At high poly(styrene) levels the natural rubber relationship approach 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 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 axodicarboxylate-functional poly(styrene) which is deactivated by non-rubbers.

The non-rubbers which interfere in the grafting process have not been clearly identified and the extent of their interference varies considerably.

The grafting efficiency for a particular batch of azodicarboxylate-functional poly(styrene) with different grades of natural rubber, as compared to Cariflex IR 3o5 is shown in the table below:

Backbone polymer	Grafting efficiency (%)
Cariflex IR 3o5	76
SMR 5L	48
SMR 10	46
SMR 20	33
SMR CV	31
SMR EQ	24
Acetone extracted SMR 5L	73

As it might be expected, acetone extraction of natural rubber before grafting removes the non-rubbers and results in a much better grafting efficiency, comparable to that obtained with Cariflex IR 3o5 synthetic poly(isoprene) rubber. However, acetone extraction is not practicable on industrial scale partly because of high cost and partly because of technological difficulties related to solvent recovery.

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 dispersed in mineral oil (Caloxol WSG) is more efficient and readily available for both the rubber industry and the plastics industry. (2, 10, 11).

Figure 3.7 illustrates the grafting efficiency for SMR 5L natural rubber in the presence of Caloxol, as compared to Cariflex IR 305.

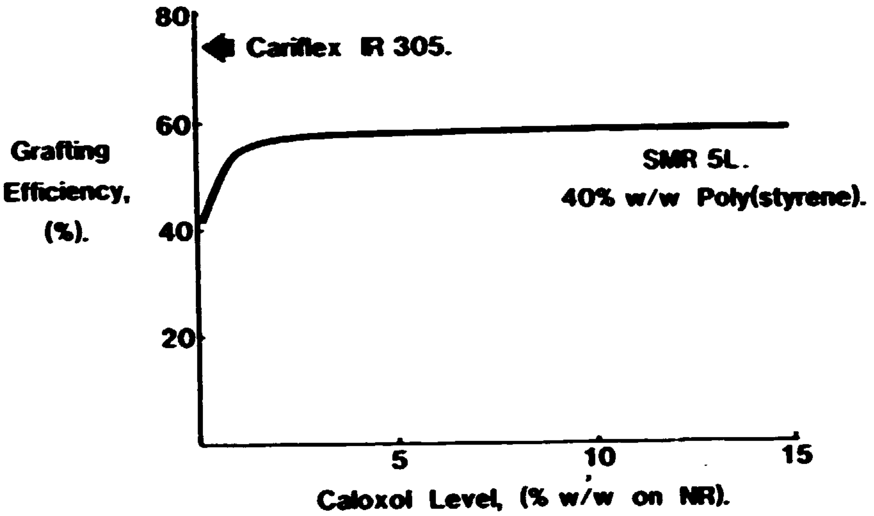


Fig.3.7 Effect of Caloxol WSG on the grafting efficiency of azodicarboxylate-functional poly(styrene) ($\overline{M}n$ 10 000) to NR (SML 5L).

The mechanism of operation of Caloxol is not entirely clear; its dessicating action is certainly important but other substances such as zinc oxide, carbonates and bicarbonates have also been reported to have an improving effect on natural rubber grafting efficiency. The latter observation has suggested that unsaturated fatty acids or their oxidation products are partly responsible for lowering of grafting efficiency in natural rubber. The hypothesis is supported by an experiment conducted with Cariflex IR 305 synthetic poly(isoprene) rubber to which linolnic acid was added; it was observed that grafting efficiency progressively decreases with the incremental addition of linolnic acid. (2).

The grafting process by direct mixing of the pre-polymer and natural or synthetic rubber seems to have essential economic advantage

3.2. Block structure technologies

The first reports on anionic polymerization date back to the years 1910-1911, when the first patents were issued. Matthews and Strange in 1910 and then Harries in 1911 described polymer preparation using sodium and potassium and possibly lithium as reaction initiator. (20).

The new "nontermination" concept that laid the foundation for living polymerization was actually put forth by Ziegler and coworkers.

The synthesis of elastomers reproducing natural rubber structure and properties was developed only after 1955, through the researches carried out at Firestone Research Laboratories under the sponsorship of the US Defense Department.

Szwarc rediscovered the living nature of anionic polymerization, thus proving beyond doubt its multiple possibilities. He could demonstrate that a poly(styrene)living chain accepts another monomer, such as isoprene producing a polystyrene-polyisoprene block-copolymer or butadiene producing a polystyrene-polybutadiene block-copolymer.

For alkadienes copolymerization with styrene in the presence of lithium alkyl, monomers activity in the polymerization reaction increases in the order styrene isoprene butadiene.

According to the speed of the initiation reaction the monomers can be arranged as follows:

styrene butadiene > isoprene .

Styrene polymerization begins only after most of the alkadiene has been used up.

The initiation reaction starts by the interaction of alkyl-lithium with alkyl-styrene and the subsequent increase of the chain is produced by diene polymerization.

The available experimental data ([illegible]) show that copolymers with ideal blocks can be produced only by sequential addition of monomers. When monomers are introduced concomitantly, the middle block will contain only a certain quantity of alkyl styrene.(20).

Industrial methods for the production of styrene-butadiene-styrene copolymers use cyclohexane or toluene as solvents since polystyryl lithium is not soluble in linear aliphatic solvents. However, recent researches have proved that hexane too may be used in such processes although polystyryl lithium is not soluble in it. Polystyryl lithium was dispersed in hexane, using 1% of SBS rubber as dispersion agent.

The microstructure of the soft block in SBS can be varied to produce SBS in which the middle block is from 100% 1,2 to 45% 1,2 or a mixture of varied composition.

Special techniques have led to obtaining butadiene-styrene copolymers with a low content of 1,2 vinyl. Such elastomers are known as solution SBR and their properties are in certain ways better than those of emulsion SBR.

Nonpolar monomer copolymerization in anionic system lends itself to experimental studies owing to the long life of active species. It could be thus proved that, although butadiene homopolymerization speed is low, the unexpectedly high level of butadiene in the initial copolymer is due to kinetic factors rather than to butadiene preferential absorption in active sites.

The production of thermoplastic rubbers of block copolymer type differs from both the production of classic elastomers (polyisoprene, polybutadiene) and the production of polystyrene mainly in the following:

- the use of two monomers - butadiene, and styrene - or isoprene and styrene; the level of styrene may vary considerably (8÷68%) from one type of thermoplastic rubber to the other;

- the use of different catalyst systems than those employed in isoprene or butadiene polymerization;

- both isoprene and butadiene polymerizations are continuous systems; styrene polymerization is generally produced batch-wise, while thermoplastic rubbers are produced using a mixed system: continuous for some steps and discontinuous for the others;

- certain thermoplastic rubbers of block copolymer type require extension with mineral oils (white oil) as they are destined for special applications.

The synthesis of block copolymers comprises the following steps:

(i) Synthesis of polystyryl lithium;

(ii) Synthesis of polystyrene-polybutadiene lithium diblock copolymer;

(iii) Coupling the active ends of the resulting diblock copolymer using a tetrafunctional coupling agent;

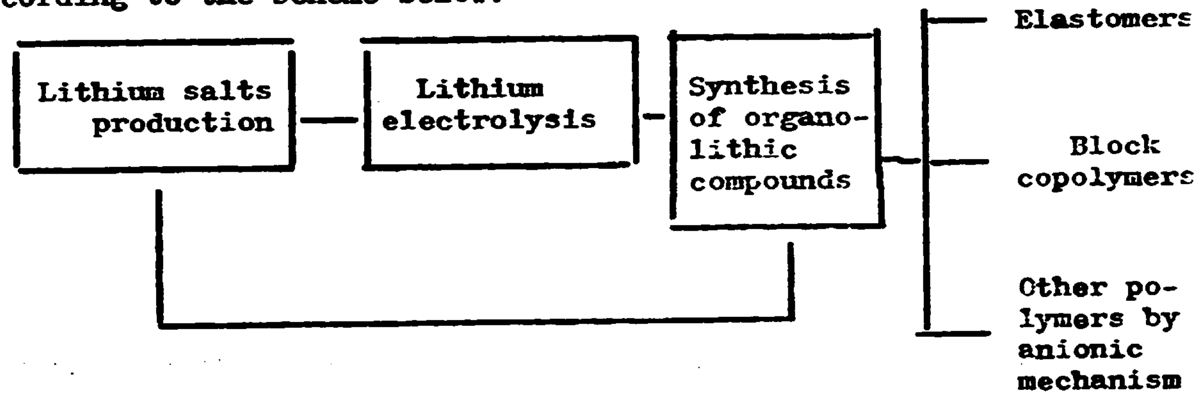
(iv) Stabilizing and extension;

(v) Solvent removal;

(vi) Polymer drying and granulation.

The synthesis of polystyryl lithium requires the previous preparation of organo-lithic compounds to be used as catalyst in the synthesis of polymers and copolymers, by an anionic mechanism.

The synthesis of organo-lithic compounds leaves a certain amount of nonreacted metallic lithium, as well as some lithium chloride; therefore, lithium chloride recycling after recovery is needed, according to the scheme below:



Kinetic studies on polymer synthesis by anionic mechanism using organo-lithic catalysts require rigorously controlled working conditions as well as the use of high purity solvents, monomers and catalysts.

Lower organo-lithic compounds: CH_3Li, C_2H_5Li are solid at room temperature, while n propyl-lithium, n butyl-lithium and amyl-lithiu are viscous fluids with very low vapour pressure. All organo lithic compounds - methyl lithium excepted - are soluble in aromatic or aliphatic hydrocarbons, as well as in ether.

Organo-lithic compounds reactivity with water, oxygen and carbon dioxide is especially high and prevents polymerization reactions with organo-lithic catalysts from taking place in the presence of such impurities.

3.2.1. Synthesis of organo lithic compounds

Lithium alkyls were first obtained by Schlenbach and Holtz, by the action of metallic lithium on mercury alkyls. Ziegler prepared various organo-lithic compounds by the same method, using lithium wire and successively treating it with alkyl-mercury to complete consumption. As organo-mercuric compound he used mercury diethyl, dipropyl and diphenyl at 60-65°C in benzene: (16, 17)

$$2Li + Hg(C_2H_5)_2 \longrightarrow 2C_2H_5Li + Hg$$

$$2Li + Hg(C_6H_5)_2 \longrightarrow 2C_6H_5Li + Hg$$

Later, Gilman continued Ziegler's researches; using various temperatures and various reaction media, he noticed that when the reaction temperature is lowered to room temperature, the reaction time increases to four days.

Although organo-mercuric compounds are relatively stable in water and oxygen, the higher sensitivity of organo-lithic compounds imposes the use of nitrogen during synthesis as well as the advanced drying of reactants.

K. Ziegler and H. Colonius were the first to show that in the Würtz synthesis an organo-lithic compound is obtained as primary product which, in the case of average reactivity metals, does not react further and the reaction is:

$$2Li + RX \longrightarrow LiR + LiX$$

Using this method, Gilman and coworkers obtained a large range of organo-lithic compounds and developed a working procedure for the production of such compounds with satisfactory yields.

Since not all organic chlorides react easily with lithium, some lithium compounds may be indirectly prepared from a more convenient lithium compound and the required organic halogenide:

$$C_6H_5Li + RX \longrightarrow RLi + C_6H_5X$$

Nobis developed the synthesis of organo-lithic compounds starting from organo-sodic compounds and the anhydrous lithium chloride:

$$RNa + LiCl \longrightarrow RLi + NaCl$$

Economic advantages may be derived from this method only if industrial production is coupled with the production of organo sodic compounds.

The earliest experiments aimed at obtaining organo lithic compounds were made without solvent, by the direct action of lithium on the halogenated derivative, at 150 250°C; however, the method failed to produce organo-lithic compounds. For instance, by the action of lithium on iodobenzene, only lithium iodide and diphenyl were obtained.

Later, various solvents, as well as some alkyl halogenides were used as reaction media. Unlike the synthesis of organo-magnesium compounds where any halogenated aliphatic alkyl (chlorides,bromides, iodides) may be used, in the synthesis of organo-lithic compounds alkyl iodides are excluded as they produce Würtz type condensation.

Ziegler investigated the influence of alkyl halogenides on the reaction yield when obtaining butyl-lithium in reaction systems without stirring; when butyl iodide is used, the reaction does not start even after a few days, while in the case of butyl bromide the reaction starts after ten minutes; on lithium the lithium bromide is deposited like a sponge - the reaction is consequently slow down and lasts about three days with 48% yield. When butyl chloride is used, the reaction duration is only 16 hours and the yield is 70%. (22).

Under vigorous stirring, the yields are the ones given below:

Alkyl halogenide	Yield, %
Butyl chloride	77.1
Butyl bromide	68.8
Phenyl chloride	48.7
Phenyl bromide	97.5

As it can easily be seen, in the aromatic series better yields are obtained with brominated derivatives, while in the aliphatic series the chlorinated derivatives produce better yields.

As for the solvent used in reaction, the first tests were made with ethyl ether, benzene and cyclohexane.

If ethyl ether is used, the reaction rate is high but the yield is 50-60%. This rather low yield can be explained by the fact that lithium aliphatic compounds are decomposed in ethyl ether solution and alcoholates result.

Ether reaction with organo-lithic compounds consists in the proton extraction by the carbanion followed by the spontaneous fragmentation of the resulting anion: (23)

$$R: + CH_3CH_2\text{-}O\text{-}CH_2CH_3 \text{ ——————— } RH + CH_3CH_2\text{ -}O\text{-}CH\text{-}CH_3 \text{ ——————— }$$

$$CH_3CH_2O + CH_2 = CH_2$$

Methyl-lithium is the only organo-lithic compound which is stable in ethyl ether.

By working at a temperature of -10°C, Gilman succeeded to increase to 75% the yield of organo-lithic compounds production in ethyl ether.

Higher yields are obtained with benzene and cyclohexane, but the reaction rate is slower than in the case of ethyl ether (e.g. 16 hours in benzene).

Subsequently, Gilman (25) suggested the use of petroleum ether as a reaction medium for producing organo-lithic compounds from alkyl halogenides and lithium. He pointed out the advantage of eliminating secondary reactions which take place in ethyl ether. Moreover, the resulting lithium chloride, being insoluble in petroleum ether, is easily removed by decanting and filtration. Gilman employed a petroleum fraction with a boiling point of 28-38°C and asserted that fractions with higher boiling points are less convenient. He obtained butyl-lithium at a 70% yield when using butyl bromide and a 75% yield when using butyl chloride.

For the preparation of butyl lithium Ziegler employed benzene as solvent; recently, heptane and cyclohexane have been used too.

Data to be found in literature indicate that the yield varies with the solvent, as described below:

Yield variation according to the nature
of the solvent

Alkyl halogenide	Solvent	Yield, %	Temperature, °C
Butyl chloride	benzene	77.1	65
Butyl chloride	petroleum ether	75	reflux
Butyl bromide	benzene	68.8	65
Butyl bromide	petroleum ether	70	reflux
RCl	ethyl ether	50-60	reflux
RCl	ethyl ether	75-90	-10

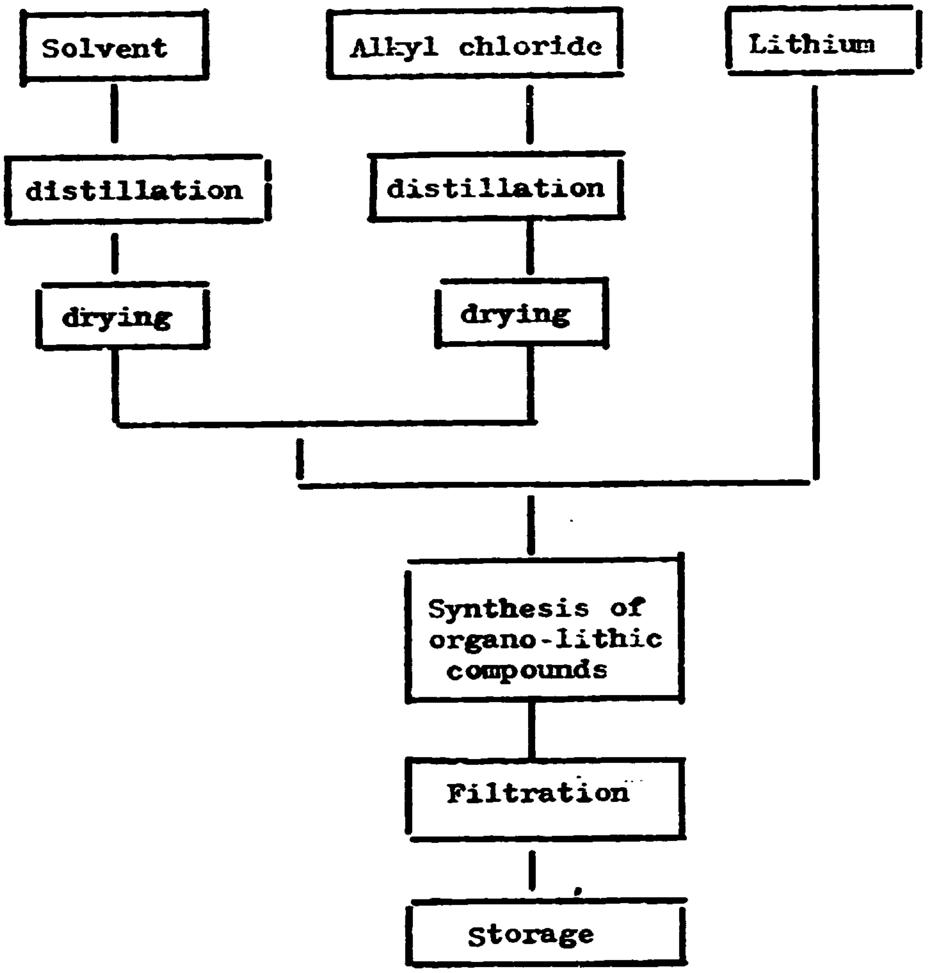
The reaction rate of butyl lithium synthesis is also influenced by the form of metallic lithium. As the reaction is a heterogeneous one between a liquid and a metal, it is more convenient to use lithium in dispersion so as to achieve a greater contact surface. In such cases argon and helium are recommended while nitrogen is not, because at temperatures over 25°C the increase of the contact surface may lead to the formation of lithium nitride, which slows down the reaction. Thus, working with heptane-dispersed lithium at 65°C, butyl-lithium is produced in a few hours with a 73% yield.

The reaction rate of organo-lithic compounds synthesis is also dependent on the level of sodium in lithium. A significant differenc in yields (about 15%) was noticed when synthesising butyl-lithium with metallic lithium having a sodium level of either less than 0.005% or 2%.

In the synthesis of tertiary butyl-lithium in pentane, 80% and higher yields were obtained when lithium under dispersion form with 2% sodium was used as against 35% when lithium with 0.5% sodium covered by copper was employed.

High purity butyl-lithium was produced by the vacuum technique from lithium and butyl chloride in benzene. Concentrated solutions of butyl-lithium were thus obtained, which were subsequently diluted by the same high vacuum technique.

The technological process for the production of organo-lithic compounds is shown in the scheme below:



From among the procedures for the production of organo-lithic compounds, the only industrially used one is the Gilman method, starting from metallic lithium, usually under the form of dispersion, and alkyl chlorides.

The Gilman method is the most convenient mainly because the intermediate synthesis of another organo-metallic compound is not needed. Moreover, metallic lithium is now readily available and so are alkyl halogenides which are produced in large quantities by the organic chemical industry.

The most frequently employed solvents are hexane and cyclohexane which are also used in anionic polymerization reactions. This choice is mainly due to the fact that such solvents are available in relatively large quantities and at a lower price than aromatic hydrocarbons on the European market.

Lower boiling point solvents (n-pentanes, i-pentane, petroleum ether) are not preferred owing to their high volatility (leading to instability of catalyst solutions concentration) and risk of self-ignition in contact with air (as a consequence of the solvent rapid evaporation and subsequent increase of solution concentration).

Lithium alkyl solutions delivered by specialized companies have concentrations ranging from 10 to 20%. On stability-related criteria, sec-butyl-lithium solutions concentration is usually at the lower limit of the interval and n-butyl-lithium solutions concentration at the highest limit. These concentrations seem to be the optimal ones as transport and storage are economical and the risk of spontaneous ignition is maintained within reasonable limits.

At present, the main suppliers of organo-lithic compounds are:

- LITHIUM CORPORATION OF AMERICA, producing:
    - metallic lithium as bars, wire and dispersion with various sodium levels;
    - phenyl-lithium (20% in a 70/30 mixture of benzene- ethyl ether);
    - sec-butyl-lithium (11% in n-hexane);
    - n-butyl-lithium (20% in n-hexane);
- FOOTE MINERAL CO. (Philadelphia, USA), producing:
    - metallic lithium as bars, wire and dispersion;
    - n-butyl-lithium;
    - tertiary butyl-lithium (20% in cyclohexane);
- METALLGESELLSCHAFT AG (Frankfurt, FRG), producing:
    - metallic lithium as bars and wire;
    - n-butyl lithium (15% in hexane, 20% in cyclohexane);
    - sec-butyl lithium (10% in i-pentane).

3.2.2. Synthesis of thermoplastic rubbers by the block-copolymer metho

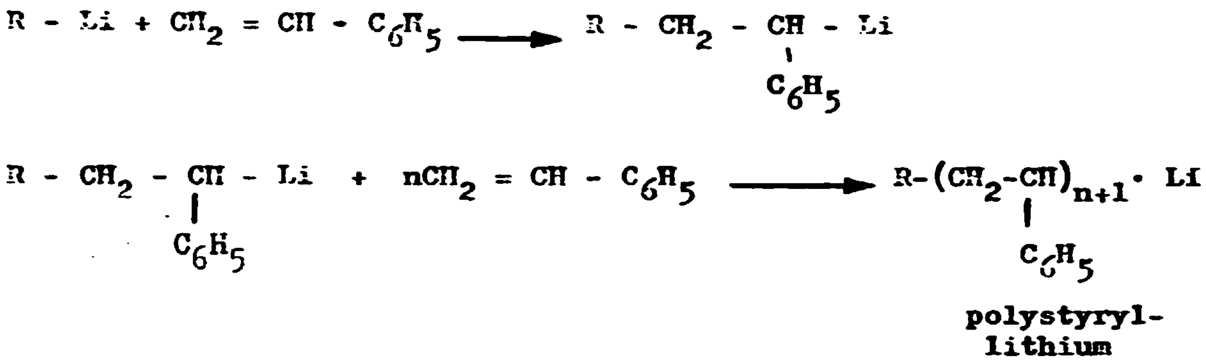
The synthesis of block-copolymers (isoprene-styrene-isoprene or butadiene-styrene-butadiene) consists of the following main steps:

i) synthesis of polystyryl-lithium;

ii) synthesis of the diblock copolymer;

iii) coupling the active ends of the resulted diblock copolymer with a tetrafunctional coupling agent.

Polystyryl-lithium is produced in a reaction medium formed by a solvent (toluene) in which, at moderate temperature (20-30°C), the organo-lithic compound and styrene react as described below:

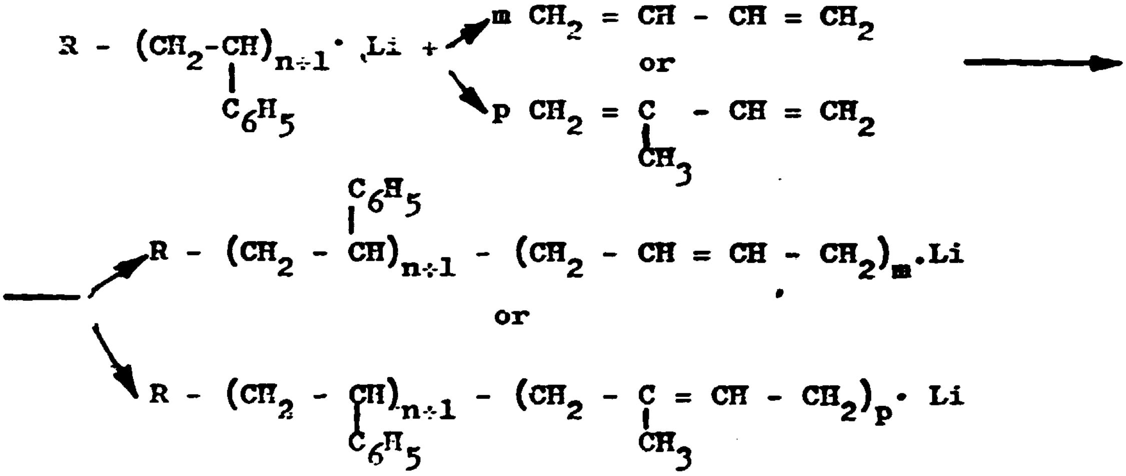


$$R - Li + CH_2 = CH - C_6H_5 \longrightarrow R - CH_2 - \underset{\displaystyle C_6H_5}{\underset{|}{CH}} - Li$$

$$R - CH_2 - \underset{\displaystyle C_6H_5}{\underset{|}{CH}} - Li + nCH_2 = CH - C_6H_5 \longrightarrow R-(CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}})_{n+1} \cdot Li$$

polystyryl-lithium

The diblock-copolymer synthesis takes place as described by the reactions:

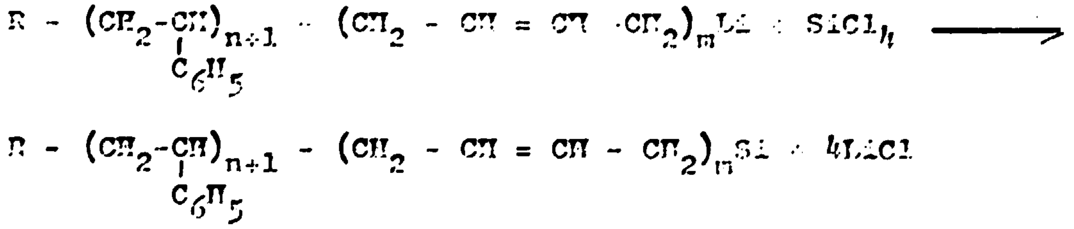


$$R - (CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}})_{n+1} \cdot Li + \begin{cases} m\, CH_2 = CH - CH = CH_2 \\ \text{or} \\ p\, CH_2 = \underset{\displaystyle CH_3}{\underset{|}{C}} - CH = CH_2 \end{cases} \longrightarrow$$

$$\longrightarrow \begin{cases} R - (CH_2 - \overset{\displaystyle C_6H_5}{\overset{|}{CH}})_{n+1} - (CH_2 - CH = CH - CH_2)_m . Li \\ \text{or} \\ R - (CH_2 - \underset{\displaystyle C_6H_5}{\underset{|}{CH}})_{n+1} - (CH_2 - \underset{\displaystyle CH_3}{\underset{|}{C}} = CH - CH_2)_p \cdot Li \end{cases}$$

As in media lacking reactive impurities the anionic polymerization initiated with lithium alkyls is carried out without interruption reactions, the previously synthesised polystyryl-lithium may be used to initiate diene polymerization.

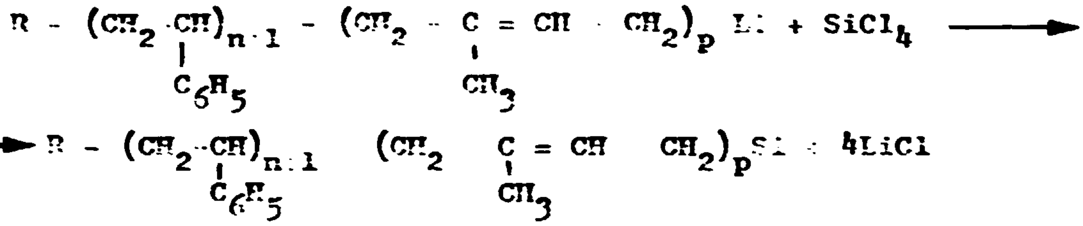
The diblock-copolymer is synthesised in a hydrocarbon solvent (benzene, toluene) in reaction vessels provided with stirring and heat recovery system (310 kcal/kg). The coupling reaction is produced by the contact of the resulting diblock-copolymer with a tetrafunctional coupling agent like silicon tetrachloride.



$$R - (CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}})_{n+1} - (CH_2 - CH = CH - CH_2)_m Li + SiCl_4 \longrightarrow$$

$$R - (CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}})_{n+1} - (CH_2 - CH = CH - CH_2)_m Si + 4LiCl$$

or



$$R - (CH_2 - \underset{C_6H_5}{CH})_{n-1} - (CH_2 - \underset{CH_3}{C} = CH - CH_2)_p Li + SiCl_4 \longrightarrow$$

$$\longrightarrow R - (CH_2 - \underset{C_6H_5}{CH})_{n-1} (CH_2 \; \underset{CH_3}{C} = CH \; CH_2)_p Si + 4LiCl$$

Lithium chloride resulting from the coupling reaction is dissolved in the solvent removal water so that the diblock-copolymer is not impurified with lithium chloride.

The resulted block-copolymer should be stabilized with stabilizing agents specific to the elastomers and plastics industry (e.g. topanol) and, whenever necessary, may be extended with oil.

The solvent-removal operation is aimed at eliminating both the non-reacted monomers and the solvent used in the previous reaction steps. Solvent-removal is made with warm water and low pressure vapour in stirred vessels to facilitate hydrocarbons evaporation and to prevent agglomeration of thermoplastic rubber particles.

After the solvent-removal operation the efluent under the form of vapours is directed to the solvent and monomer recovery step; the solid particles of thermoplastic rubber are subjected to water and volatile matter removal by extrusion in special equipments.

The main commercially available thermoplastic rubbers of this type are: Kraton (Shell), Solprene (Phillips) and Europrene (Anic).

3.3. Rubber blends technologies

This type of thermoplastic rubbers is obtained by the physical mixture of a natural or synthetic elastomer with plastics, usually polyolefins such as polyethylene and polypropylene. (26).

The physical properties of this material are similar to those of thermoplastic olefin rubbers such as ethylene-propylene rubber; consequently, they are competitors on a certain market section. (3).

To realize the place of thermoplastic rubbers as compared to traditional elastomers and plastics, Figure 3.8 below presents the hardness range of TPR, rubbers and plastics.

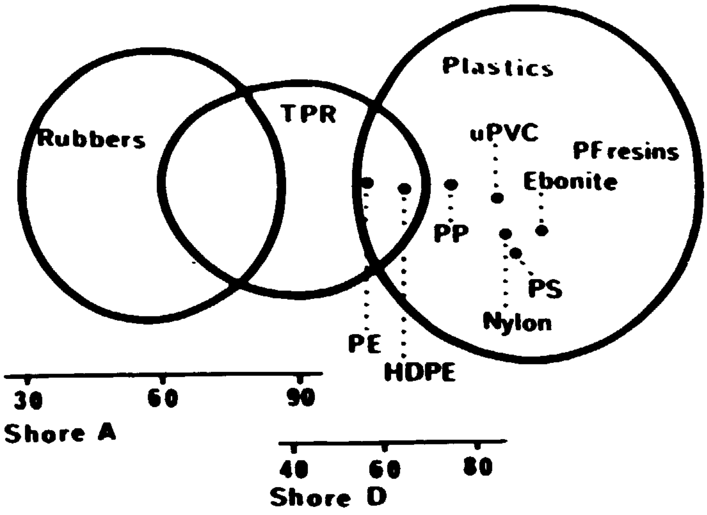


Fig. 3.8. Hardness range of TPR, rubbers and plastics.

The very large hardness range of natural rubber blends, graft copolymers or block-copolymers can be noticed. It may equally be seen that thermoplastic rubbers can be applied in the traditional fields of both elastomers and plastics. (3).

The block copolymers (SBS) types are available from hardness 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. (27, 28).

Thermoplastic rubbers of SBS copolymer type, with characteristics ranging from 50 to 70 Shore are likely to compete with vulcanized elastomers and plastified PVC in the shoe-making industry.

Thermoplastic olefin rubbers are mainly applied in the automotive industry for the production of bumbers, spoilers and other flexible panels requiring materials in the range 60 to 90 Shore.

Production of TPNR blends

Production methods for thermoplastic blends involve a fine dispersion of each of the two components which are to be blended so as to achieve phase adhesion and a unitary morphological structure.

The main stages of the technological process are:

- Mixing;
- Moulding;
- Extrusion.

Figure 3.9 below illustrates the main equipments composing a Frances-Shaw production line.

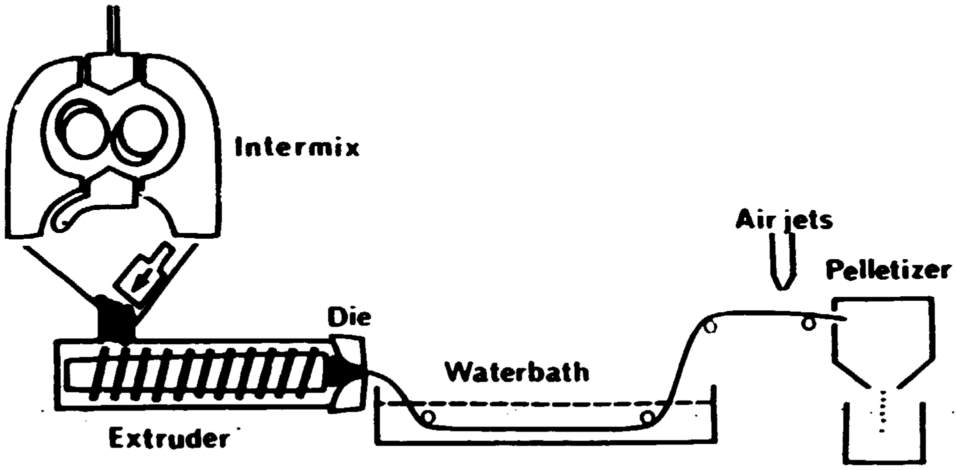


Fig. 3.9. Layout of the Francis-Shaw mixer/extruder.

Mixing

Natural rubber, mostly SMR L and polyolefin, usually polyethylene or polypropylene are mixed in a Banbury mixer and then a Shaw Intermix to achieve complete blending of components.

Temperature control during the mixing batch preparation is very important. Starting with a warm machine (80°-120°C) mixing soon raises the temperature to the melting point of polyolefins (135°C for HDPE and 165°C for PP). The batch should not be allowed to get too hot because degradation of natural rubber may occur if the temperature is allowed to exceed 200°C for more than five minutes. (3).

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

a) Add natural rubber, antioxidant, polyolefin (in either powder or pelletized form) and filler, if needed	0 minutes
b) Add crosslinking agent	3 minutes
c) Add antioxidant	5 minutes
d) Dump	6 minutes.

An organic peroxide or other crosslinking agent for natural rubber may be added during mixing. 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 micro-gelled 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 whole amount of polypropylene has melted; otherwise, intimate mixing of the two components cannot be achieved.

It may be noted that literature does not cite the necessity to delay the addition of peroxide in the case of EPDM/PP mixtures, because EPDM reacts more slowly than natural rubber with vulcanizing agents. (32, 33).

Treatment of the batch after mixing follows normal practice. While still hot, the batch is sheeted on a roll mill, allowed to cool and brought to a thickness of 8 mm. Passing it through the mill several times is not indicated, as the material cracks and becomes difficult to handle when the temperature falls below the melting point of the polyolefin. For subsequent processing, such as injection moulding, the thermoplastic rubber is granulated in a rotary type cutter, adding a partitioning agent in the case of softer grades to prevent particles agglomeration.

Moulding and extrusion

Thermoplastic rubbers can be moulded and extruded using machinery of the same type as those used in the plastics industry. For thermoplastic rubbers injection moulding is generally applied, as compression moulding was proved to be less satisfactory. (3).

The Arburg 220 series 35 tonne machine provided with reciprocating screw gives a maximum volume of about 60 cm^3 of thermoplastic material.

The extruder heaters should be 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.

As mentioned before, excessively high temperatures should be avoided during mixing and the same applied during moulding and extrusion.

A certain number of recyclings in the rejects extrusion process is possible, as shown in Figure 3.10.

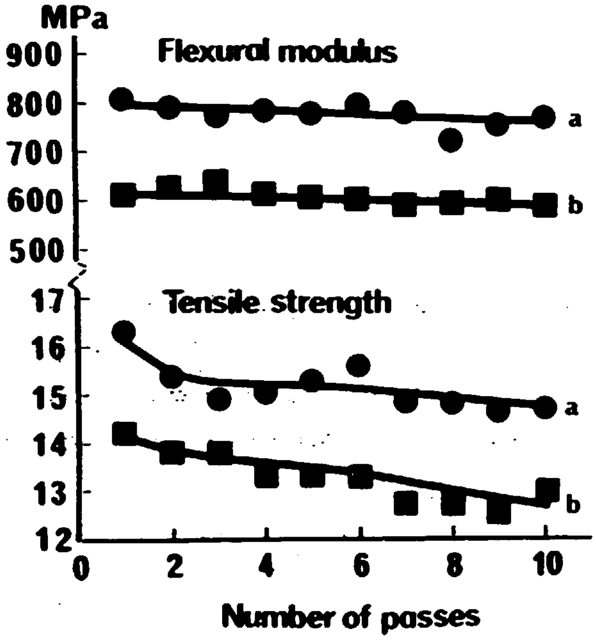


Fig. 3.10.
Effect of number of passes through REP B34K machine on flexural modulus and tensile strength of TPNR 6040 containing 40 php HAF black: a) along radial mould flow lines, b) across mould flow lines.

It can be concluded that up to ten recycles, the operation has only a small effect on modulus and tensile strength.

Rubber/polyolefin blends, including TPNR, idffer from the block-copolymer thermoplastic rubbers in their ability to tolerate extensio with oil. Practically, rubber/polyolefin blends only tolerate small quantities of filler for cost reducing purposes. For thermoplastic rubbers a temperature in excess of 160°C is required for introducing additives in the mixing operation.

1-2% of carbon black or titanium dioxide can be added to give protection against ultraviolet light, and coloured pigments may also be added. The abrasion resistance may be improved by adding 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.

Normally, amounts of 5 to 15% of oil are recommended to be mixed in thermoplastic rubbers of TPNR type in order to reduce hardness and also melt viscosity.

The table below shows the variation of physical properties with the filler content and the elastomer/polyolefin ratio:

	N.R/PP Ratio 40/60	N.R/PP Ratio 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

In conclusion, thermoplastic rubbers obtained by blending natural or synthetic rubbers with polyolefins, due to their specific characteristics, have found various applications with specialized consumers.

4. New trends in the production processes and utilization of thermoplastic rubbers

4.1. New trends in the production processes

Recent researches (5) have proved that any further developments in the manufacturing process of thermoplastic rubbers are economically viable if they are carried out either in latex or during rubber mixing.

Process modifications published in literature (5) fall into two main categories:

(i) The method of inserting pendent groups to functionalize rubber for purposes such as crosslinking, bonding, ageing, protection, etc. using sophisticated reagents;

(ii) The method using cheaper reagents for bulk modification to endow natural or synthetic rubber with new physico-chemical and mechanical properties thus making it competitive with higher priced materials.

As described in the previous chapter, by combining rubber with polystyrene (comb grafts), thermoplastic rubber is obtained, with the following advantages:

(i) The molecular weight of the polymer to be grafted can be accurately determined;

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

(iii) The reactivity of the azo-tipping group leads to an efficient grafting not only in solution but also in dry mixing;

(iv) The grafting method is applicable to all polymer that can be reactively tipped and even to mixtures of two or more polymers, so that a wide range of grafted polymers may be obtained.

Therefore, any azo-tipped polymer may be grafted to natural rubber in solution, provided that the common solvent be previously identified, which is not an easy task when widely disparate polymers are used.

Glass transition or melting temperature

For dry-mixing grafting, for thermoplastic properties and processability of the grafts, there are certain restrictions imposed by the glass transition (Tg) or melting temperatures (Tm) and by the solubility as a measure of compatibility between polymers.

For thermoplastic rubbers of graft or block copolymer type the Tg of the rubbery component should be below room temperature, while the Tg or Tm of the hard component should be above room temperature (35).

For retention of properties at high temperatures, Tg or Tm should be as high as possible and crystalline polymers are to be preferred since Tm is much better defined than Tg of a glassy polymer.

Since grafting of elastomers with olefins occurs at temperatures above Tg or Tm of the hard component, a practical limit is immediately placed on the values that these can assume. For components whose Tg and Tm are in the range 160-180°C, the temperature during the grafting process should not exceed 180-200°C (35).

Graft polymers are in a better position than block polymers from this point of view since the low molecular weight of the hard polymer chains depresses the normal Tg by almost 50%. Thus we can restrict consideration of hard polymers for grafting to those having a normal Tg between 70-230°C or Tm between 40-200°C.(35).

Solubility

Solubility is a parameter used to define compatibility of different polymers and is based on cohesive energy calculated from group molar attraction data.

It is not yet possible to predict accurately what the maximum difference is that would allow grafting but results in Table 4.1. suggest that it might be 1.3 cal$^{\frac{1}{2}}$cm$^{-3/2}$.

Table 4.1

Dependence of grafting to NR on difference in solubility parameters

Azo-polymer	$\Delta s^{x)}$	Grafting in solution	Dry mix grafting
Polyethylene	0.1	yes	yes
Polydimethylsiloxane	0.8	yes	no
Polystyrene	1.0	yes	yes
Polymethyl methacrylate	1.15	yes	yes
Polycaprolactone	1.3	yes	yes

x) Δs is calculated difference in solubility parameters taking for NR 8.1 cal ½ cm$^{3/2}$.

It is considered that the processability of the material becomes poor if the difference in solubility is larger than 1.3 - 2.0 (see Table 4.2). (5).

Table 4.2

Effect of solubility difference parameter on processability

Copolymer system	Solubility parameter difference ($cal^{\frac{1}{2}}$ $cm^{-3/2}$)	Processability
Block		
Polyalphamethylstyrene	1.6	good
Polystyrene	1.8	good
Polybis-phenol A-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. (5).

Solubility parameters difference from natural rubber versus Tg/Tm is presented in Table 4.3 below and Figure 4.1.

The preferred polymers would occupy the bottom right hand corner and they should have a reasonably right Tg or Tm for good retention of properties at high temperatures and a low solubility parameter difference for good processability.

Theoretically, it is possible to extend the upper limit of the diagram in Figure 4.1 by raising the solubility parameter of natural rubber through chemical modification; for instance, a 50% level of hydrochlorination would give 0.15 units increase or by a prior grafting to NR of a polymer with as high solubility parameter as feasible to give a pro-rata increase from 8.1 (e.g. polymethyl methacrylate 9.25).

Table 4.3

Solubility parameter difference from natural rubber versus Tg/Tm

Polymer	Solubility parameter difference ($cal^{\frac{1}{2}}$ $cm^{-3/2}$)	Tg(°C)	Tm(°C)
1. Nylon 6/6	5.5	-	265
2. Polyacrylonitrile	4.6	105	-
3. Polymethacrylonitrile	2.6	120	-
4. Poly (bis-phenol A-diphenyl sulphone	2.5	190	-
5. Polypivalolactone	1.4	-	240
6. Poly (bis-phenol A-carbonate)	1.4	-	220
7. Poly(2,6 dimethyl-1,4-phenylene oxide)	1.4	-	261
8. Poly(vinyl chloride)	1.35	81	-
9. Poly(2,2,4,4 tetramethyl 1,1,3-cyclobutanediol carbonate)	1.3	-	253
1o. Poly(ethylene sulphide)	1.3	-	210
11. Polycaprolactone	1.3	-	65
12. Polymethyl methacrylate	1.15	110	-
13. Polystyrene	1.0	100	-
14. Polyethylmethacrylate	0.9	65	-
15. Polyalpha methylstyrene	0.8	170	-
16. Poly dimethyl siloxane	0.8	120	-
17. Polypropylene	0.6	-	175
18. Polyethylene	0.1	-	140

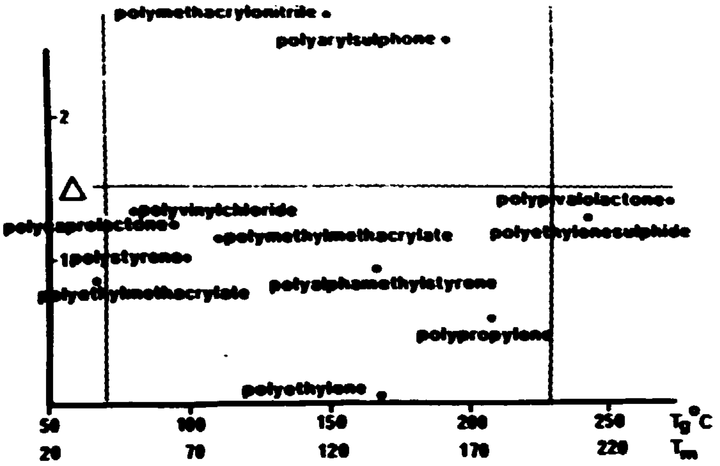


Fig. 4.1. A dry-mix grafting feasibility diagram obtained by plotting solubility parameter difference of the polymer and natural rubber versus T_g or T_m of the polymer.

Vulcanizates with labile or reversible crosslinks

An attractive alternative to the physically domain crosslinked thermoplastic rubber is a vulcanizate with heat labile, reversible crosslinks (Figure 4.2).

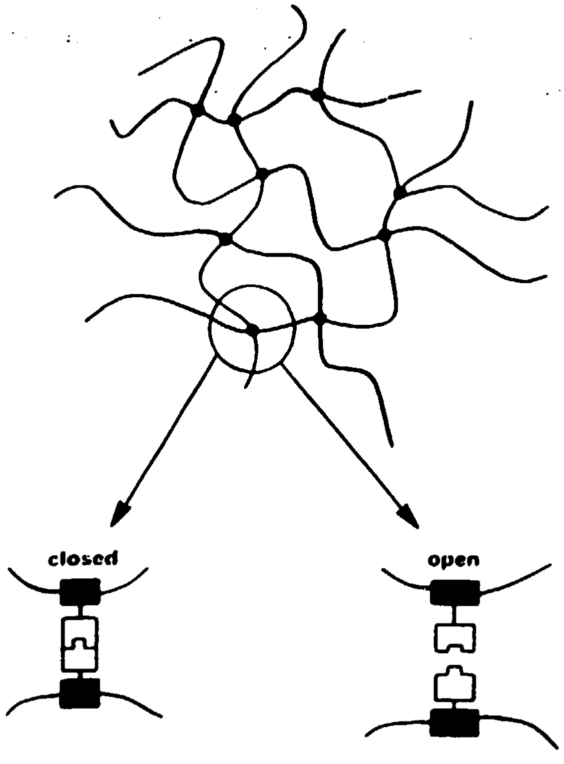


Fig. 4.2. Schematic representation of a thermolabile crosslink.

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.

Pendent amine groups were introduced along the polybutadiene chain by copolymerization techniques and crosslinked by quaternization with a bis-allyl halide (see Figure 4.3).

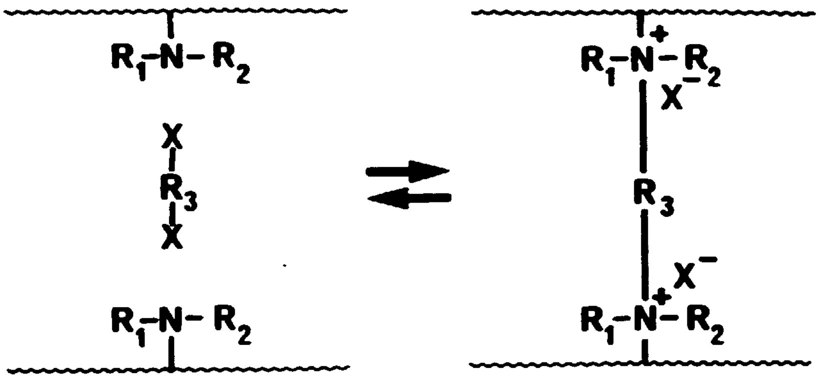


Fig. 4.3. A labile (heat or shear) quaternary salt crosslink.

This gave significant improvements in green strength without interferring 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 (5) in which natural rubber was first equipped with pendant hydroxyl groups some of which were transformed into crosslinks by reaction with a difunctional beta-keto ester (see Figure 4.4.).

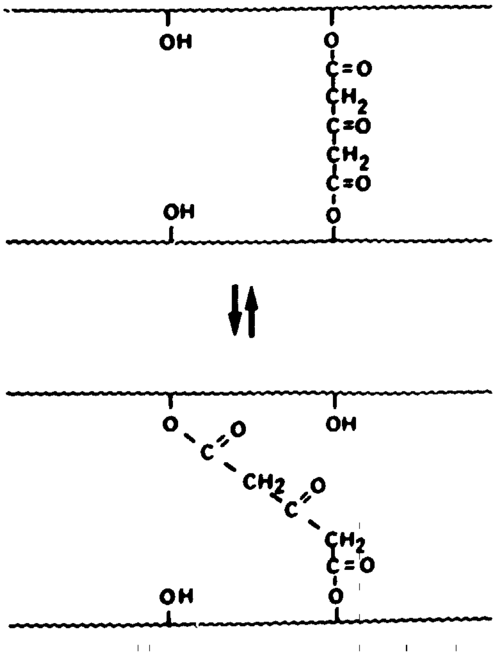


Fig. 4.4.
The keto-ester exchange reaction as the basis of a thermolabile crosslink.

Unfortunately, side reactions intervened at these temperatures leading to permanent crosslonk formation. The most attractive route left to a possible thermoplastic vulcanizate would be the synthesis of an azo-compound carrying a metal chelating substituent, such as acetyl acetonate residue.

A patent by Monsanto (B.Pat.1375416) claims some progress in this direction (see Figure 4.5.).

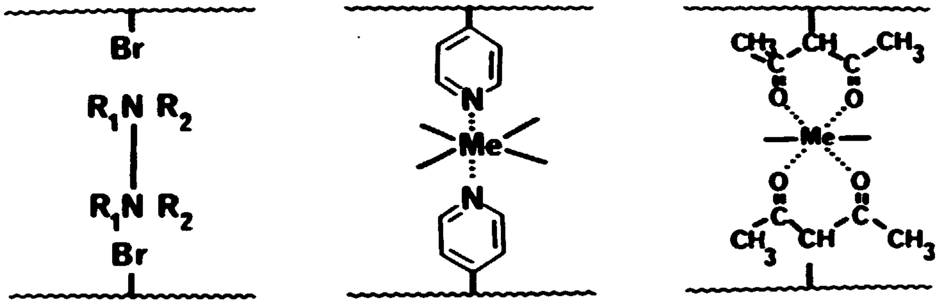
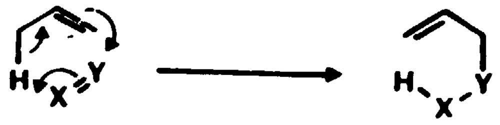


Fig. 4.5: Possible types of thermolabile crosslinks from chemically modified natural rubber.

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. (5).

In the field of minor modification levels, it was established that there is nothing better than the "ene" thermal addition process when reactions in solution are to be excluded, as shown in Figure 4.6



X = Y can be $-N{=}O$, $-N{=}N-$, $>C{=}O$, $>C{=}S$, $>C{=}C<$.

Fig. 4.6. The general 'ene' reaction.

Reactions of addition to the double bond have the following advantages:

- they are non-catalytic and therefore do not involve problems related to catalyst poisoning by non-rubbers, in NR;
- they are high efficiency reactions and do not induce side reactions such as crosslinking, degradation, cyclization or isomerization;
- they are versatile reactions allowing the modification of functional groups.

Of the "ene" reactions available, the addition of the azo functional groups seems to be the best (see Figure 4.7.).

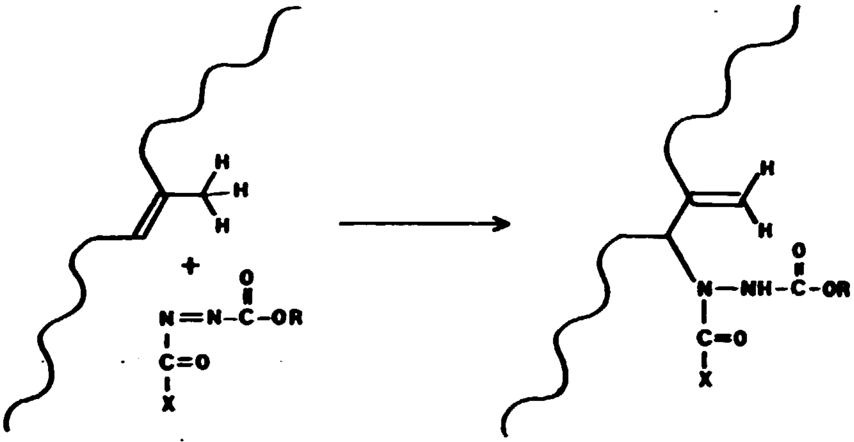


Fig. 4.7 The 'ene' reaction of azodicarboxylates with *cis*-1,4-polyisoprene.

The only disadvantage of this type of reaction is the very high cost of the resulting organic chemical complex (£ 8/kg).

There are two other functional groups that merit investigation in the field of "ene" reactions, i.e. carbenes and nitrenes, which attack most polymers by either double bond addition or C-H insertion reactions (see Figure 4.8).

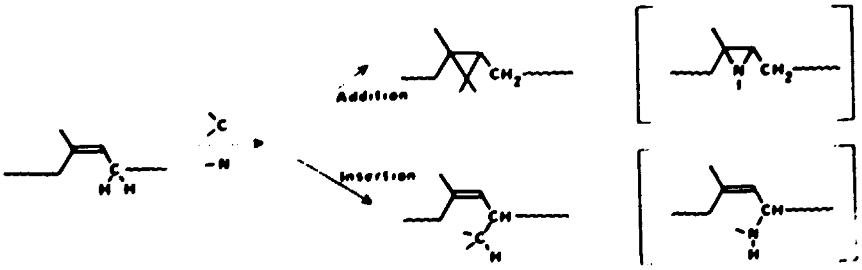


Fig. 4.8. The reaction of carbenes and nitrenes with natural rubber.

Carbenes are more difficult to generate in situ in other than solution reactions. However nitrenes can be generated by thermolysis of azido-compounds at temperatures of 120-160°C and are applicable to dry rubber reactions.

4.2. New trends in the utilization of thermoplastic rubbers

4.2.1. Thermoplastic rubbers in footwear

The footwear industry had in the past a relatively easy life in choosing its soling material - it used either leather or vulcanized rubber. However at the beginning of the 1960s, with the introduction of PVC soling compound, the scene changed considerably. Since PVC is thermoplastic, it could be processed by standard automatic injection moulding techniques. This led to a dramatic reduction in labour costs in comparison with those of vulcanized rubber and, as a result plasticised PVC compounds have captured a market share of around 25% in Western Europe.

Around 1970 another polymer system, namely polyurethane, was introduced to meet the requirements of the large platform units fashionable at that time. Polyurethanes, however, require the use of specialized technologies and machinery which could not be used for any other polymer system. These factors, in combination with fashion changes away from platform sole styles, have limited the growth of polyurethanes after the very promising start of the early 1970s. Currently their main appli n is in high cost soles for high severity applications, such as sports shoes, but they are also used in premium casual shoes, mainly produced by those manufacturers having a greater investment in equipment.

At about the same time (1972-74) thermoplastic rubbers based on styrene-butadiene-styrene block copolymers (SBS) were introduced.

Initially, the acceptance of those SBS elastomers was slow, which was partly attributed to their high cost, but largely a result of th lack of experience of both polymer manufacturers and end users as to their compounding potential and the selection of appropriate processing conditions. The situation has changed dramatically over 1980 and thermoplastic rubbers have now established a strong position in the footwear sector.

This progress is illustrated in Table 4.4. which gives the penetration of thermoplastic rubber in Western Europe.

Table 4.4.

% Share of West European Soling Market

Soling material	1980	1985	1990[x]
Vulcanized rubber	45	43	42
Plasticised PVC	27	26	25
Polyurethane	8	7	7
Leather	7	6	6
Thermoplastic rubber	11	16	18
Others	2	2	2
Total:	100	100	100

---

x) Author's estimation

The thermoplastic share of the market increased 5% in two years at the expense of the vulcanized rubbers and polyurethanes, while the high price of leather gave a further impetus to its steady substitution by PVC and TR.

The utilization of the compounding versatility of thermoplastic rubber combined with the development of new types has prompted further progress in various footwear markets. The following major areas in the solid soling sector will be of interest:

- Thin fashion dress shoe units/thin sole sheeting;
- Basic everyday walking shoes;
- Outdoor training/sport shoes.

Fashionable dress shoes have been the exclusive domain of clocked-out soles made from leather or high-styrene resin rubber sheet.

Nevertheless, for reasons of design flexibility and, to a lesser extent, cost, PVC injection moulded units have made substantial inroads into this market.

Thermoplastic rubbers have a different hardness/stiffness relationship from that of PVC, and a hardness of about 70-75 Shore A is adequate.

A comparison of thin dress shoe soling materials is represented in Table 4.5.

Table 4.5.

Comparison of thin dress shoe soling materials

Material type	Leather	T.R.	High styrene resin rubber	PVC
Hardness Shore A	95	70-80	85-90	75-85
Wear resistance	-	++	+	±
Flex resistance	+++	+	+	±
Slip resistance	--	++	++	--
Surface appearance	+++	+	++	++
Customer appeal	+++	++	++	-
Relative cost	250	100	105	85

Recently it has been shown that cycle times required for thermoplastic rubber compounds can be reduced to those for PVC compounds. Consequently, the cost differential for manufactured soles has become less than the 20% relative volume cost differential.

The development of thermoplastic rubber based solid sheet is in progress, and a formulation has been developed showing favourable properties compared with leather and high styrene resin sheet. A recent evaluation showed that laboratory produced thermoplastic rubber sheets can be processed into units and subsequently into shoes, without having to modify any of the conventional equipment.

4.2.2. The potential of thermoplastic NR/polyolefins blends in the shoe soling applications

Natural rubber/polyethylene blends show better flow properties when compared to natural rubber/polypropylene blends. A 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 (4).

Furhtermore, 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 4.6).

Table 4.6

Processing condition of thermoplastic rubber

Natural rubber	80	60	40	60	40	20
Polyethylene	20	40	60	-	-	-
Polypropylene	-	-	-	40	60	80
Dicumylperoxide	0.48	0.36	0.24	0.36	0.24	0.12
Barrel temperature, °C	200-240	165-185	160-180	210-280	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
Flexure modulus, MPa	-	-	61	-	255	-
Moulding quality	Poor	Good	Good	Poor	Good	Good

Another way of improving the flow properties is by incorporation of process oil. Table 4.7 shows the improvement of flow properties by addition of naphthenic oil, but this method is limited by its adverse influence on physical properties.(4).

Table 4.7

Effect of oil and silica on processability 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 temperature, °C	195	175	170	220
Injection pressure, kg cm^{-2}	100	100	70	100

Addition of reinforcing filler such as silica impairs the flow properties as higher melt temperature is required to facilitate flow. (4).

Effect of fillers on physical properties can be seen in the Table 4.8.

Table 4.8

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
M 100, MPa	3.9	4.7	5.8	4.6	4.1
Tear, N/2 mm	73	93	85	73	68
Abrasion (Du Pont), ml/1ooo rev.	1.9	1.2	1.2	-	3.2
Hardness, Shore A	89	92	94	91	92

To lower the hardness of TPNR, process oil is incorporated. Selection of the proper oil is important. Naphthenic oils compatible with the natural rubber were studied. The addition of oil besides lowering the hardness also reduces the tensile and tear strength, flexural modulus and abrasion (see Table 4.9).

Table 4.9

Effect of naphthenic oil

Oil, (w/w %)	0	10	30
Tensile strength, MPa	4.5	3.9	2.3
Tear strength, N/2 mm	73	67	40
Abrasion resistance (Du Pont), ml/1ooo 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%).

4.2.3. Thermoplastic rubber for carpet tile backing

Thermoplastic rubber is an ideal base material for highly filled compounds, to be used as an integral backing of self-laying carpet tiles.

The following is suggested as a starting formulation:

- Cariflex TR-4113 - 100 parts;
- Ground whiting - 500 parts;
- Naphthenic oil - 55 parts.

Stabilization of carpet tile backing compounds is not considered essential, but, if required, a 50/50 blend of dilauryl thiodipropionate and a hindered phenol type is recommended.

Fillers impart the high specific gravity required of backing for self laying carpet tiles and furthermore decrease compounds costs.

In general, whitings should be non crystalline. Particle sise must also be taken into account. For instance, as the particle size decreases, increasing amounts of processing oil will be absorbed by the whiting itself, and so adjustment of the oil level is necessary to accommodate this effect.

Barium sulphate can be used to obtain compounds of especially high specific gravity. Similar selection criteria should be used for whitings. Barium sulphate does tend to reduce tensile strength values slightly. Oil and whiting generally act in opposite directions on most of the properties of highly loaded compounds as can be seen from the contour diagrams shown in Figure 4.9. The compounds in the areas not covered by the contours are these in which difficulties in mixing or sheet processing may be encountered as the ratio of oil to whiting becomes too high or too low.

The type of compound recommended for carpet tile backing is in the region of 500 phr whiting and 55 phr oil.

Elongation at break gives an idea of "bendability" without breaking: 100% is considered an adequate minimum, and can easily be met with TR compounds.

The melt index figures are related to compound viscosity and thus give an indication of processability.

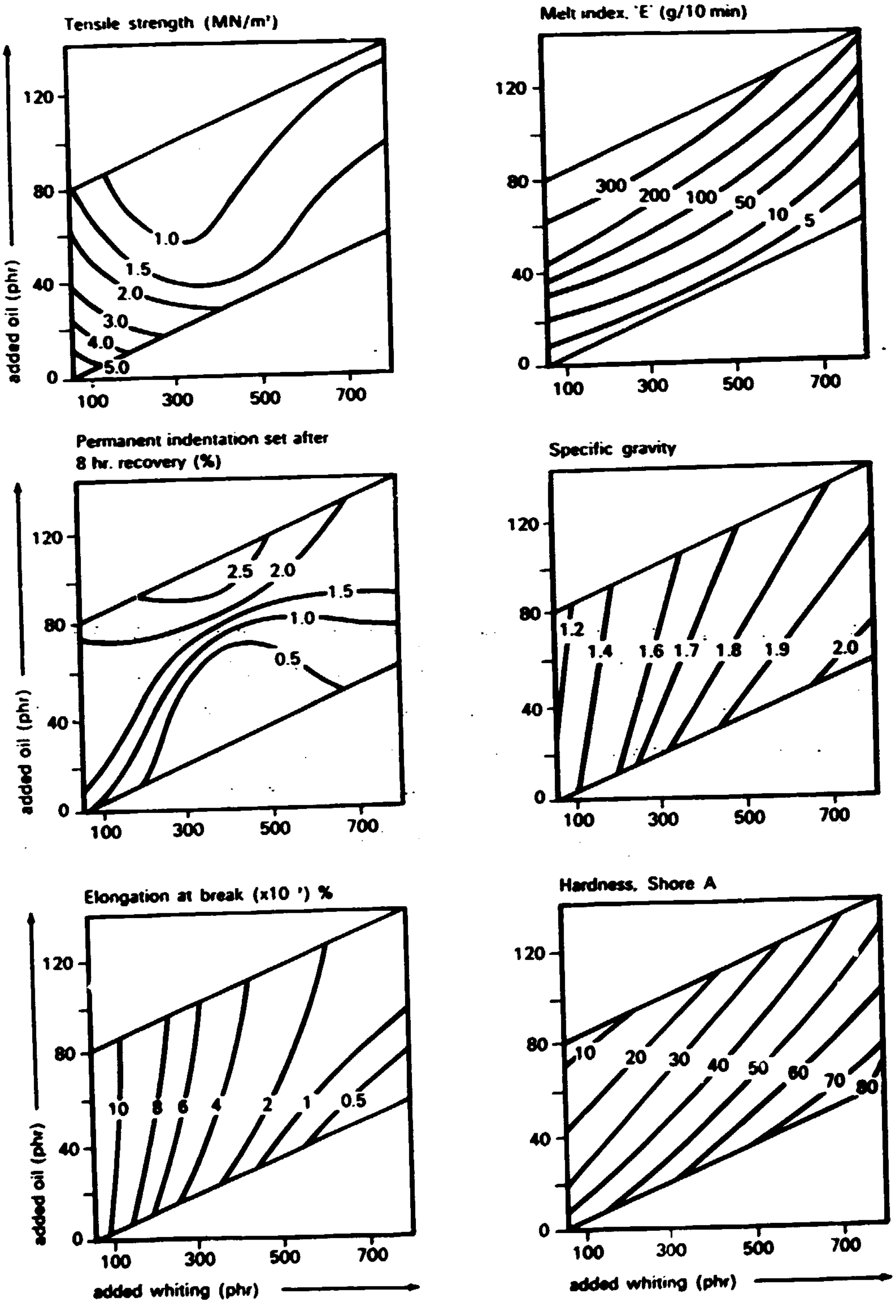
The specific gravity is seen to be mainly a function of the filler present.

Hardness is governed by both oil and whiting. The stiffness of the compound is naturally related to the hardness.

A production scheme for thermoplastic carpet tiles can be seen in Figure 4.10.

The internal mixer produces a large dump of material; a continuous mixer produces a strip. From these forms a sheet must be made.

Fig. 4.9. Effect of whiting/oil levels on the properties of carpet - tile backing compounds based on Cariflex TR-4113



Tensile strength (MN/m²)

Melt index, 'E' (g/10 min)

Permanent indentation set after 8 hr. recovery (%)

Specific gravity

Elongation at break (x10 ¹) %

Hardness, Shore A

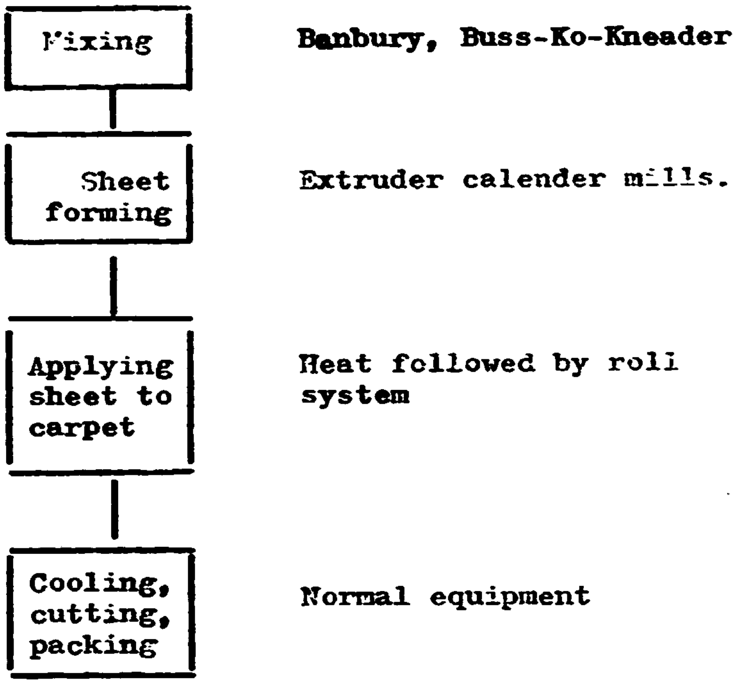


Fig. 4.10 Production scheme for TPR carpet tiles

There are two basic possibilities to applying sheet to carpet. Cold sheet can be fed with carpet to an "Auma" or "Rotocure" type of machine which presses them together around a heated drum by means of a robust belt.

The alternative route is essentially very simple; one uses an oven to warm up the sheet to about 140-160°C, followed by a pair of simple rolls to press the sheet on the carpet.

Alternative modern systems consist in a complete line of machinery to combine the sheet-forming and the sheet-application step. In other words, it is possible to feed such a compound to a bank on a simple two-roll system together with carpet (melt index 5kg/10 min and temperature 150°C).

4.2.4. Technological equipment

a) Block structure technologies

This process is characterized by phenomena of chemical binding between the elastic material (rubber) and the plastic one (polystyrene) and consists of the following steps:

i) synthesis of polystyryl lithium
ii) synthesis of the diblock-copolymer
iii) coupling the active ends of the resulted diblock-copolymer with a tetra-functional coupling agent.

For this process the main equipments for producing 20,000 t/y thermoplastic rubbers are shown below:

Type of equipment	Technological function	Capacity or dimensions	Materials	Potential suppliers
1. Stirring vessels	Preparation of the catalyst complex	5 m^3	s.s.*	Common suppliers for chemical equipment
2. Reactors with agitators	Synthesis of polysthyryl	10 m^3	s.s.	- " -
3. Reactors with agitator	Diblock-copolymer preparation	20 m^3	s.s.	- " -
4. Evaporator	Desolventation of the polymer solution	30 m^3	s.s.	- " -
5. Double screen extruder	Drying the thermoplastic polymer until 0,5% w water	2-4 t/h polymerfeed	c.s.**	Anderson - SUA French Oil - SUA Industrial Export Romania Neftehin - prom export - S.U.

Note: * s.s.: stainless steel
** c.s.: carbon steel

Elastic material, natural or synthetic rubber is mixed through physical methods with the plastic material, usually polyolefines such as low density polyethylene, high density polyethylene and polypropylene.

Such processes consist of the following steps:

i) mixing
ii) moulding
iii) extrusion.

The main equipment used for such processes is:

- intermix
- extruder
- die
- waterbath
- pelletizer

and the potential suppliers are:

SMTC Kaufman
55, rue du Pont VI - POB 204
F-76053 Le Havre Cedex, France
Telex: 190912 F

KRAUSS-MAFFEI AG
P.O. Box 500 340
D-8000 Munich 50, F.R.G.
Telex: 05 23 163

CRESPI SPA
Via Roncaglia, 13
I-20146 Milano, Italy
Telex: 332082

PLASTIMAC SPA
P.le G. Cesare 9
I-20145 Milano, Italy
Telex: 332215

POLYTAL
Strada Settimo 399/7
I-10156 Turin, Italy
Telex: 224075

BAKER PERKINS HOLDINGS
Westwood Works
Westfield Road
Peterborough PE3 6TA, United Kingdom
Telex: 32185

BETOL MACHINERY LTD.
187 Camford Way
Sundon Park
Luton, Beds, LU3 3AN, United Kingdom
Telex: 825233

KILLION EXTRUDERS, INC.
56 Depot Street
Verona, NJ07044, USA
Telex: 133560

PLASTIC STORK MACHINERY
P.O. Box 195
7550 Netherlands

STORK KUNSTSTOFF-MASCHINEN
Friedrichstrasse 35 a
D-5880 Lündenscheid, F.R.G.

INDUSTRIAL EXPORT
Bukarest, Romania

PAGANI. Machine per la lavoraziane
della materie thermoplastiche extruse
Via Marconi 23/25
Milano, Italy

5. Health and safety aspects of thermoplastic rubbers

Increasing attention is being given by industry to the health and safety aspects of chemical products. Regulations on these aspects vary from country to country and it is therefore not possible in this publication to make specific reference to them but it is recommended that the user be fully aware of existing regulations.

This technical information therefore describes only the possible hazards involved and the precautions that should be taken when handlin and processing thermoplastic rubbers.

The raw rubber contains additives to protect it during storage and transit and to confer specific characteristics (extender oil). It also contains traces of materials which are residues from the polymerization and finishing stages.

Thermoplastic rubbers, in common with all emulsion polymerized polymers, have by comparison a much higher level of residues, mainly organic acids, which are required for the polymerization and finishing of the product. Traces of free monomer and solvent may be present in the rubber depending on the polymerization process used.

At present time there is no evidence to suggest that the presence of these residues in thermoplastic rubbers constitutes a health hazard during handling or processing of the rubber compound, under normal safe working conditions.

The oils used are aromatic or naphthenic types depending on the final characteristics required. The oils differ in aromaticity and a general characterization is as follows:

- Aromatic oil - 60% wt aromatic content;
- Naphthenic oil - 30-60% wt aromatic content.

The aromatic oils contain polycyclic aromatic hydrocarbons of high boiling point (350-550°C) containing four or more aromatic rings, some of which are of a type known to pose a carcinogenic risk if contact with such oil is prolonged and under conditions of poor personal hygiene. Thus, a health hazard may exist depending upon the conditions of exposure when rubbers containing these oils are processed and handled.

The naphthenic oils are more highly refined and generally contain less polycyclic aromatic hydrocarbons than aromatic oils. Nevertheless, it is recommended that the same precautions be observed.

The use of protective clothing is recommended when processing thermoplastic rubber, especially in cases of prolonged contact. Overalls and undergarments should be laundered regularly and soiled gloves disposed of.

Repeated or prolonged skin contact with the oil extended types should be avoided especially when the rubber compound is hot or solvent wetted. When such contact does occur the skin should be washed with warm water and mild soap. Strong soaps, detergents and abrasive skin cleansers should be avoided.

The vapours or fumes that arise during the processing of general purpose rubbers can, in poorly ventilated areas, cause irritation. When this occurs the eyes should be irrigated with clean water.

Although ingestion of the rubber is not considered a hazard, it should be avoided. It is recommended that food, beverages and smoking should not be allowed in areas where the rubber is being handled or processed. The inhalation of fumes or vapours which are evolved when processing the thermoplastic rubbers, especially oil extended types, should be avoided. Efficient exhaust ventilation will solve problems arising from this source;when this is not available protective respirators should be worn. Washing facilities should be conveniently located near the working area to allow personnel to wash after handling the rubber, before eating.

First aid facilities should be readily and conveniently available, with qualified personnel in attendance. Where there is a need for further skilled medical assistance this should be sought immediately from a nurse or doctor.

During the processing of the raw rubber and in the subsequent stages of manufacture it is essential to observe the following safety precautions:

(a) avoid the inhalation of fumes and vapours from hot rubbers, compounds and vulcanizates;

(b) prevent skin contact with hot or solvent wetted rubber-compound surfaces by wearing appropriate protective clothing;

(c) observe the safety regulations for the chemicals used in rubber processing;

(d) maintain efficient ventilation especially where rubbers containing extender oils are being processed.

As a guideline and for further information on the atmospheric contamination by fumes and vapours, reference is made to the BRMA Code of Practice, where a value of 0.25 mg/m^3 is quoted.

The rubber should be stored in an adequately ventilated area where it will not be subjected to sunlight, extreme temperatures or naked flame.

Precaution should be taken to ensure the absence of sources of ignition in the storage and processing area. In the event of a small fire, this may be fought using carbon dioxide, dry chemical powders, foam, water spray, sand or earth. Large fire should be dealt with by foam or water fog.

Waste product can be disposed of by burying on an approved site or burning under controlled conditions. In many countries regulations exist regarding the disposal of waste products and it is recommended that these be referred to.

If the finished rubber article is intended for use in contact with food or in pharmaceutical applications, toys and other human contact areas the relevant regulations should be observed.

6. Some economic aspects related to the production and utilization of thermoplastic rubbers

The demand for thermoplastic rubbers is continuously growing as compared to traditional elastomers and plastics whose yearly growth rates are lower.

Today, about 500,000 tonnes/year of thermoplastic rubbers are produced and sold in the world; it is estimated that production will increase by another 50,000 tonnes/year as thermoplastic rubber products will further replace thermoset rubber parts and polymers. Various marketing studies point out that in the next years at least 100,000 tonnes of thermoset rubber parts will be replaced by thermoplastic rubber items.

The use of thermoplastic processing equipment will not only make the rubber industry more competitive, it will also put more pressure on the price of finished parts, and make the production of thermoset rubber parts significantly more cost competitive.

In the USA, thermoplastic rubbers consumption is 200,000 tonnes and will increase by over 100,000 tonnes in the next five years if natural rubber and EPDM rubber are approximately equal in price.

In Western Europe, the list price for ethylene-propylene rubber is considerably higher than current natural rubber prices and this leads to estimated selling prices of most grades of thermoplastic rubber at least 10% lower than thermoplastic olefin elastomers of equivalent hardness with similar rubber/polypropylene ratios, assuming all other manufacturing costs would be the same.

The European consumption of thermoplastic rubber is even larger then in the USA, and will show similar growth (250,000 tonnes/year) in 1989 and 300,000 tonnes/year in 1990.

The Japanese production is also growing rapidly.

In a natural rubber producing country the lower cost of natural rubber (not having export duties and freight changes) will, to some extent, be offset by higher costs of imported chemicals and polypropylene. However, lower labour costs in a developing country and other costs savings make for a much lower estimated production cost of thermoplastic rubber in SE Asia compared with Europe. Hence there is an excellent case for producing thermoplastic rubber to supply local manufacture in these countries. It is estimated that an economic price for locally produced thermoplastic rubber could undercut the price of imported thermoplastic olefin elastomers by 20-30%. Even production for export should be possible, provided the additional cost of exporting and shipping is not too high (3).

Some assessment regarding the economic status of thermoplastic rubber process is essential, but the novelty of the process makes this assessment difficult to achieve.

A target price for raw graft copolymers can be set at £ 1,000/tonne. This was a representative price for pure styrene-diene block copolymer at the time of the costing exercise. Taking a price for natural rubber of £ 600/tonne and assuming a graft copolymer composition of 35% polystyrene, an allowable cost of £ 1,750/tonne can be assigned for the azodicarboxylate functional polystyrene. If it is assumed that the materials cost for the synthesis of one tonne of azodicarboxylate functional polystyrene 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 polystyrene.

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 polystyrene of a molecular weight of 7500, was £ 107. The cost of all 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 polystyrene of £ 612, which is not far outside the target price of £ 600. This materials cost does not include the solvents used in the polystyrene synthesis. Their cost is in the region of £ 650 per tonne of polystyrene 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.(2).

Bibliography

1. O'Connor - Novel natural rubber-based blends, Monsanto Chemical Co., 1988.
2. D.S.Campbell - Production, Properties and Performance of Graft Copolymers, 1988.
3. D.J. Elliott - Thermoplastic Natural Rubber Blends, 1988.
4. Lim Hun Soo - The Potential of Thermoplastic NR in Shoe Soling Application, 1988 .
5. D. Barnard - Chemical Modification of NR - The Future, 1988.
6. xxx - Modern Plastics International, 1979, 9 (Nov.), 52.
7. DePaolo P.A. - Rubber World, 1980, 182 (April), 43.
8. xxx - Modern Plastics International, 1979, 9(July), 8.
9. xxx - Handbook of Thermoplastic Elastomers, Walker B.M.(Ed. Van Nostrand Reinhold Company, New York, 1979.
10. G. Forger - Plastics World, 1979, 37(Aug.) 4o.
11. xxx - British Plastics and Rubber, 1979, May, 16.
12. Schlenbach, Holtzber - Journal of American Chemical Society, 52, 1930.
13. Ziegler- - Liebigs Ann.Chem., 473/1928.
14. Wittig - Berichte 71, 19o3/1938.
15. Nobis - Chem. Eng. News 4, 40/1957
16. K. Ziegler, H. Colonius - Liebigs Ann.Chem., 479, 135/1930.
17. H. Gilman, E.A.Zoellner, W.M.Selby - J.Amer.Chem.Soc., 54, 1957/1932.
18. Ibidem - J.Amer.Chem.Soc., 55, 1252/1933.
19. H. Gilman - J.Amer.Chem.Soc., 57, 1o62/1935.
20. C.D.Neniţescu - Chimie organică, vol.I, 645, ed.II
21. H. Gilman - J.Amer.Chem.Soc., 62, 2327/194o.
22. K. Ziegler - Liebigs Ann.Chem., 479, 123/1930.
23. P.J.Reed, J.R.Urwin - Journal of Organo-metalic Chemistry, vol.39, 1972.
24. Weygan, Hilgetag - Organisch Chemisch Experimentierkunst, 743
25. V.P.Shatalov - Technical Synthesis of n-BuLi, Kim.Prom., 44(12), 8887-8/1967
26. D.S.Campbell, D.J.Elliott & M.A.Wheelans - NR Technology, 1978, 9, 21.

27. D.J. Elliott - UNIDO International Symposium, Phuket, Thailand, May, 1981.

28. T.D. Pendle - Block and Graft Copolymerization, vol.1, Ed. Ceresa, R.J., John Wiley and Sons, London, 1973.

29. J.C. Falk, R.J. Schlott, D.F. Hoeg & J.F. Pendleton - Rubb.Chem. and Technol., 1973, 46, 1044.

30. J.P. Kennedy, R.R. Smith - Polymer Science and Technology, vol.14, p.303 Ed.Sperling, L.H., Plenium Press, New York

31. P. Sigwalt, A. Polton & M. Miskovic - J.Polym.Sci.Poly.Symp., 1976, 56, 13.

32. A. Sundet, R.C.Thamm, J.M. Meyer, W.H. Buck, S.W.Caywood, P.M.Subramaniam, & B.C.Anderson - Macromolecules, 1976, 9, 371.

33. R.P.Foss, H.W. Jacobson, H.N. Cripps & W.H. Sharkey - Macromolecules, 1976, 9, 373.

34. W. Rahlwes, J.E.Rooyers & S. Bywater - Macromolecules, 1977, 10, 604.

35. D.S. Campbell - Brit.Polym. J., 1973, 5, 55.

36. M.F. Sloan & collab. - Tetrahedron Lett., 1964.

37. S. Krauss - Sci.Rev., 1972, C7, 251.

38. E.J.Buckler - Rubb.Chem. Technol., 1978, 51, 872.