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

D03625

Distr.
LIMITED

ID/WG.118/5
14 February 1972

ORIGINAL: ENGLISH

United Nations Industrial Development Organization

Expert Group Meeting on Future Trends in, and Competition between, Natural and Synthetic Rubber

Vienna, 27 - 30 March 1972

THE EXTENSION OF RUBBER TO PLASTICS MATERIALS [1]

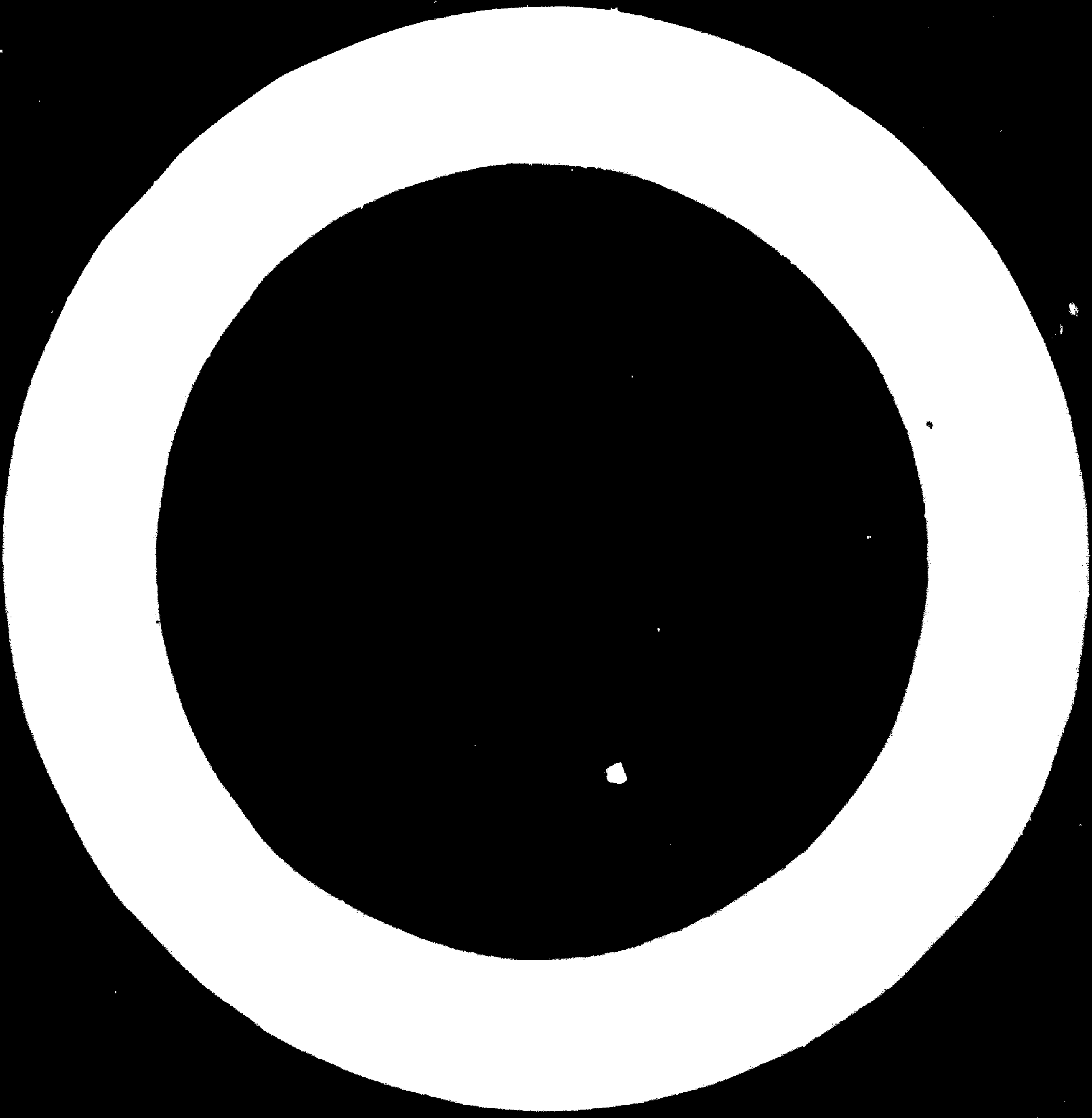
by

John F. Lontz
Research Associate
E.I. du Pont de Nemours and Company
Wilmington, Delaware
U.S.A.

---

[1] The views and opinions expressed in this paper are those of the author and do not necessarily reflect the views of the Secretariat of UNIDO. This document has been reproduced without formal editing.

CONTENTS



I. INTRODUCTION

1. In derived natural and synthetic forms, rubber as a class of elastomer materials is basically a polymer having molecular characteristics much in common with structural thermoplastic materials. These two classes of materials provide a broad spectrum of useful mechanical properties, often overlapping, ranging from elastic to rigid in nature, each with a varying degree of elasticity and energy-absorbing attributes when subjected to certain static and dynamic stresses, a feature often lacking with brittle plastics. Thus rubbers can serve to provide a toughening quality to brittle polymers which otherwise fail under stresses of rapid, high rate impact. Consequently, the extension of rubber to thermoplastics can serve a useful technological role in the ever-expanding needs for building materials, large conduits and piping, and myriads of utilitarian articles replacing, and in many instances being less expensive than, fabricated wood and metal products.

2. With the increasing technological prominence of rubber-plastics blends in view of the attractive economic merits made possible by the high production rates, an increasing investigative interest is developing toward understanding and defining the role the rubber compoent in rubber-plastics blends. These interests involve efforts in applying theoretical, analytical mechanics of strength and failure, too long neglected, physics of the macromolecular structure, and detailed view by means of high, three-

dimensional magnification techniques.

3. It is therefore the purpose of this presentation to highlight some of the salient features in understanding the role of rubberextended as a component into plastics, presaged by an analysis of the production statistics comparing the competitive positions for natural rubber and synthetic rubber for plastics blends with the expectation that the basic understanding of the role of rubber extension into plastics will proffer some new approaches and insight for the expanded, or at least sustained utilization of rubber with plastics.

II. TRENDS IN COMPETITIVE RUBBER-PLASTICS PRODUCTION STATISTICS

4. While the trends in the utilization of rubber have been expertly recounted by other participants in this current Expert Group Meeting in a more comprehensive manner, it is nevertheless of interest at this point to ascertain, or diagnose so to speak, the comparative trends for natural rubber vis-a-vis its synthetic counterpart based on annual world-wide statistics (1) and a selected instance of statistics derived for a special case of one highly industrialized national, namely, the United States of America (2). The latter is presented with deference, and acknowledgement of equal importance, to all other nationals solely for the purpose of analytical methodology; moreover, misconceptions or errors ensuing from this kind of an approach may be readily rectified with the detailed U. S. A. data (2) now available.

In particular, the assessment or evaluation of the annual figures is presented here in a special, restrictive manner to provide a scale or frame of reference which is termed as the Proportional Index (PI). This Index is intended to serve as a measure of the production, and obviously its utilization, in relation to the ever-expanding plastics technology and especially as a measure of the competitive ratios, considered individually, for natural rubber and synthetic rubber. It is expected that such an Index, applied as one criterion of assessing the trends for short periods, for instance five years, serving to predict the declines and advances for the two competing forms of rubber as adjuncts to plastics technology.

5. Based on the abbreviated statistical summation presented in Table I, Figure 1 presents graphically the general case of the annual Proportional Index as a ratio of the world production of total rubber, including both the natural and synthetic forms, to the world production of total plastics. The yearly trends of the Index are presented for a short increment of recent years for the (a) world-wide figures and (b) for the special case of the U.S.A. data. The marked decline of the Proportional Index for the former case is quite apparent, whereas that for the U. S. A. may appear less declining. A further assessment of the Proportional Index for the total natural rubber to the total rubbers, both natural and synthetic, is presented in Figure 2, which now illustrates a less severe decline in the yearly trends, a feature evident with

both the world and the U. S. A. data. The indices of course are just another manifestation of what is already apparent from the statistical data recounted in the straight, summary manner. A still further assessment is provided in Figures 3 and 4 dealing specifically with the Proportional Index for natural rubber to plastics and synthetic rubber to plastics, respectively. The higher Index for the case of synthetic rubber, as shown in Figure 4, compared to that for the case of natural rubber, as shown in Figure 3, shows and perhaps predicts that the synthetic rubber Index will undergo much less of a decline than that of natural rubber. It should be apparent by now that the Index, as a feature of analysis, is assessing the competition between rubber and plastics, on the one hand, and natural rubber with synthetic rubber on the other. It is now of interest to probe into a more specific case where rubber modification, and hence extension, of plastics is indeed an actuality.

6. An appropriate case to consider then is the Proportional Index for the yearly trend derivable for the case of styrene type of plastics such as that listed in Tables II and III from the readily accessable U. S. A. production figures (2). For this case, Figure 5 provides the Index based on rubber-modified polystyrene/polystyrene statistical data. In this case, the declining trend is not altogether firm despite the drop from 0.40 in 1964 to 0.33 in 1968 with a marked recovery from the low Index in 1967. The contributing factors are open to speculation. One rationale may relate to the improvements in

blending and formulating rubber-plastics polyblends prompted by basic, investigative efforts toward understanding the role of rubber in correcting some of the shortcomings of plastics with regard to durability, as well as providing broadened compositional range for a variety of blended candidates.

III. RUBBER TOUGHENING OF BRITTLE PLASTICS

7. Blends or mixtures of rubber and plastics for more than a century have been made and produced as forms of hard rubber with early dependence upon thermosetting technology involving phenolic resins. In early 1930 polymer chemistry was just emerging as a technological venture involving organic synthesis of monomers and their polymerization, including such diolefins as butadiene and chloroprene, one of the procursors to modern elastomers. At the same time some of the understanding of high molecular weight or macromolecular science along lines of physical chemistry was yet to be formulated. During this period the empirical efforts began to provide improvements in both the processing of rubbers and to up-grade the mechanical properties, notably hardness, tensile strength, tear strength, and abrasion. In effect, the plastic polymer components were blended into rubber materials for the purpose of enhancing certain ranges of durability for rubber materials.

8. Commencing in early 1940, polystyrene began to emerge as a plastics material along with several other high molecular weight

polymers having high stiffness and mechanical strength along with low cost processability by extrusion and injection-molding that started a new era in plastics manufacturing technology with high volume productivity and low materials costs. However, the principal shortcoming of polystyrene and its consequent copolymers was their extreme brittleness or lack of toughness, a feature also shared by another emerging polymer, namely polyvinyl chloride. By virtue of their basically low costs of starting monomers and economic processing into a broad range of applications generally replacing those conventionally served by rubber, the technology of plastics manufacture and fabrication soon began to compete and in some instances displace, with rubber. The transition was one in which the existing technologies in rubber, notably compounding, extrusion, sheeting, and so on, were applicable to plastics often with very little change in the equipment. Indeed, the plastics polymer science developed its own prestigious position and pursuits on the understanding of macromolecular chemistry, physics, and mechanics on par with that of the elastomer science. Thus in due course the early polymers accrued widespread acceptance despite their shortcomings with respect to to impact resistance, a deficiency gradually corrected along two lines of endeavors. The first of these was by blending polymers or copolymers with elastomer components as shown in Figure 6, while the second was by structuring polymer segments within the molecular chain or to the molecular chain as depicted in Figure 6. Eventually, the once brittle, single component polymers, polystyrene and polyvinyl chloride gradually were provided with a range of toughness and other properties designed to specific articles and applications. In effect, the energy-absorbing attributes for which the elastomer structure is uniquely constituted was advantageously combined to extend the utility of plastics in numerous ways.

9. The most prominent rubber-plastics blends that have acquired technological prominence are listed as illustrative categories in Table IV with a selected trade specifications pertinent to each category, in this case the well-established procedural designations of the American Society for Testing and Materials which have numerous counterparts among standards specified by other nationals. A number of these rubber-extended categories have in addition other derived tests for durability as well as dimensional specifications specific to sheeting, pipes and conduits, and so on, along with grades specific to flame resistance, outdoor weatherability, and chemical resistance, that continue to require modifications in the compositions of the rubber-plastics blends.

IV. CONCEPTS OF RUBBER-TOUGHENING

10. The brittleness of polystyrene (PS), acrylonitrile-butadiene-styrene polymer (ABS), and polyvinyl chloride (PVC) in their un-modified form is most commonly explained in terms of energy-absorption mechanisms and kinetics involving initatiation and propagation of cracks and internal stresses. Numerous investigators have investigated and followed in diverse ways the phenomenon of the onset of fracture and ultimate failure under impact. These diverse means included detailed examination

examination under high magnification, on the one hand, and by conceptual derivation of stress conditions using various models of a dispersed rubber phase in a plastic matrix on the other hand As a result numerous concepts or theories have been proposed, commencing with the general concept of the Griffith fracture criterion (6) expressed by the equation:

$$T = \sqrt{\frac{2 E \gamma}{\pi c}} ,$$

where T = tensile strength,
E = Young's modulus,
γ = energy required to produce a unit area of (new crack
c = critical crack length.

By applying known tensile and other constants in the above expression for the case of brittle plastics, where as a general rule the ductile absorbing energy is limited to the surface layer in the order of one micron, the equation provides a critical crack length in the order of 100 microns. A characteristic feature observed in the manifestation of the fractures of the brittle polymers has been the presence of craze patterns. The observations prompted several concepts as equations of state derived to account for the mechanism of failure and its alleviation by the presence of the disperse rubber phase. Some of these are recounted as follows.

11. *Energy Absorption by Rubber Particles*. The energy absorption induced by rubber on impact with attending stretching across the fracture of the brittle matrix, as depicted schematically in

Figure 8, does not fully account for the profound variations in actual, measured values of impact strength or resistance as the size and shape of the rubber particles are varied. A case in point is the effect of particle size and shape shown in Table V for a blend of polybutadiene-acrylonitrile rubber styrene-acrylonitrile polymer; the variations in particle geometry were obtained quite simply by appropriate mixing and blending conditions and by variation of applied shear during blending (7). The conditions were adjusted to produce dispersed rubber particle sizes below and above the 0.5 - 0.6 micron level in the initial rubber stock. The data in Table V indicate that significant toughening at the constant rubber level (20 percent) develops as the particle dimensions exceed 0.6 micron. Thus the general concept of energy absorption while substantiated in a qualitative way is seriously lacking for accounting for the quantitative variations evident in such cases as illustrated by the data presented in Table V.

12. <u>Hydrostatic Tension (Dilation) Concept.</u> In view of the apparent inadequacy of the direct energy absorption theory, a concept was proposed (8) on the proposition that the rubber particles generate hydrostatic tensile stress in the adjacent polymer matrix. Despite the elaborate development of a matrix (mathematical) solution involving shear moduli of the component spherical rubber and the polymer matrix, experimental tests of the concept failed to resolve the experimental inconsistencies noted in some cases (7). As was the case with the general energy

absorption concept the hydrostatic tension concept did not reconcile the calculated data with that obtainable by experiment with variations that could be effected by geometrical features. It might be properly surmised that the concept of hydrostatic tension could be adjusted with furrher elaborations that should include interfacial adhesion and its yielding criteria. This could be an appropriate exploitation with natural polyisoprene elastomers.

13. Craze Nucleation Concept. Another concept is that proposing the role of rubber particles as stress concentrators (9) by virtue of their multiplicity thereby dividing or redistributing the stress into a large number of small cracks, presumably restorable so long as the strain is within elastic limits. Thus more energy is needed to propagate a large number of cracks or near cracks with stress fields or vectors dispersed among each other negating part of the applied stress. Elaborations of this concept regard the rubber particles as serving to provide sites for craze formation (10) or the formation of tiny cracks ahead of the main crack producing a statistical branching effect such as depicted in Figure 9. As with the case for the hydrostatic tension concept, an elaborate equation of state is required, as indicated in the Appendix, to account for the stress distribution and its diminution based on the Goodier analysis (11) of stresses in a system composed of elastic spheres embedded in a solid matrix. The Goodier equation predicts that hard particles and voids provide higher stress concentrations, thereby providing stronger craze nucleation than rubber, and thus

hard particles and voids should toughen the plastics matrix to a greater degree than rubber. This has not been evident in some of the deliberate tests of the concept (7) and hence can be accorded a limited postulate stature. As with the hydrostatic tension concept, there is presumed to be some merit in augmenting the craze nucleation applying rubber particles cured to a range of hardness or cross-linking in which some optimal crack resistance range could be established by fairly simple experimental exploration.

14. Dynamic Crack Propagation. While this is phenomenologically related to the craze nucleation concept, this concept is an extension of the Griffith criterion. Once inititiated by the criterion, the crack then accelerates to a limiting velocity, approximately half the shear wave velocity, accompanied by branching of the crack and surface roughening. Calculations of the stresses ahead of a moving crack, made by Yoffe (12), indicated thatthe maximum stress swings out of the plane of the crack at high speeds as indicated graphically in Figure 9 . Tensile stress maxima exist in two planes ahead of the rapidly moving crack thereby directing the crack into either or both of the planes. In an isotropic solid, the cracks do not move faster than half the shear wave velocity (V_t) and hence the implications of the 0.8 and 0.9 V_t curves has yet to be resolved. In the case of the rubber-plastic system for the ABS compond, it is presumed that cracks propagate rapidly in the plastics matrix (V_t 0.5 being approximately 620 meters/second) and then into the rubber particle

(V_t 0.5 being approximately 29 meters/second) where branching would thus proliferate.

15. In retrospect, the concepts and premises involved provide no specific restrictions as to the chemical type of the dispersed rubber phase for modifying or toughening the impact resistance of brittle polymers. While the combinative concept of the Griffith criterion and the Yoffe concept of stresses developing out of the plane of the crack provides a working rationale, there is no suggestion here how the branching would mitigate against the use of natural rubber for the toughening phenomena. In this frame of reference it would seem that the exploitation of natural rubber in blends with synthetic plastics under certain conditions of planned integration of petro-monomer polymerization for proximal resources of natural rubber may proffer a significant outlet.

V. BLENDING AND COMPOUNDING

16. The blending of two phases of any two dissimilar materials, such as is the case with rubbers and plastics, has a long history of empirical practises often continued or sustained in existing technology by virtue of committed equipment or committed procedures. Rubber and plastics technologies have much in common with regard to compounding and blending with similar considerations of effectiveness and economics. With the advent of rubber extended compositions, newer appraches to efficient blending are becoming

increasingly evident. Combining the established and the the new, the following descriptive methods are available for producing rubber-plastics blends.

(a) mechanical mixing on conventional devices such as kneading (Banbury), milling, and extrusion,

(b) coagulation of mixtures of the rubber latex and the polymer dispersion or latex, and

(c) polymerization of one monomer in the presence of a polymer, with variations in the combinations of the constitutive components.

There is a paucity of data on the blend structure or dispersion evaluating the merits of each of the above blending methods. As a consequence, new explorations for unique merits of rubber extension would require some detailed comparisions comprising both property enhancement and the economic incentives.

17. <u>Milling operations.</u> Blending rubber with thermoplastics by mill-rolling is a common, large-scale production operation. As the two components are milled forming a smooth band, the blend is regarded as compatible, whereas a spongy, nervy or crentaed band or mill stock is an indication of incompatibility. Frequently, at this stage of processing the qualitative indication of homogenous dispersion is a practical assessment of the optimal ratios of the two materials if any does prevail. In this step much of the toughening effect can be maximized and samplings are taken for mechanical tests, as are generally specified in the trade, and definitve investigation of the fracture mechanisms.

18. Dynamic-Mechanical Measurements. A characteristic mechanical attribute of elastomers and polymers is their respective moduli over a span temperatures. The moduli can be determined throughout the broad temperature range by torsional oscillations in a pendulum arrangement to provide damping constants to calculate each temperature-designated modulus (13). The method provides a useful, definitive and analytical tool not only for obtaining a temperatur-dependent profile of the modulus but also in the characterization of the compatibility or homogeneity of blends of dissimilar materials (14). The temperature-dependent torsional constants can be used, for instance, to ascertain the manner in which the damping maximum of each of the two blend components can give rise to a different maxima frequently desired to vacate an undesirable maximum of an otherwise useful polymer ingredient.

19. Microscopic Characterization. The visual assessment of the rubber component in the plastic as well as the nature of adhesion and failure is indeed a valuable augmentation of the assessment in terms of practical milling and measured mechanical constants The recent development of scanning electron microscopy in an extended range of magnification provides a highly sophisticated tool for studying the discrete disposition of the rubber components in the optimal fabricated form as well as for ascertaining the nature of the failure criterion. It can be presumed that while current rubber/plastics technology has attained well established performance and endurance standards, the suitability of natural extension to polymer or plastics materials with the aid of detailed scanning

electron microscopy should enable its development into competitive blends for much-needed, world-wide items of construction.

VI. PERSPECTIVES

20. From the statistics of the trends in the extension of rubber into plastics, it is evident that the elastomeric attributes of natural and synthetic rubbers have acquired increasing merit and econometric importance. It is also evident that the synthetic form of the elastomer is outpacing the natural rubber as the compositional preference. This preference doubtlessly is occasioned by the well-integrated synthesis, polymerization, and formulating and blending technology, notably in countries that do not have indigenous sources of natural rubber and depend upon synthetic sources. The competitive displacement of the synthetic variety by the natural rubber form obviously presents problems of ready availability, shelf-life stability and uniformity, and numerous product standards yet to be defined, any one of which could impose economic disadvantages, besides costs of latex shipment or transfer with its non-renumerative aqueous phase. Despite these concerns, it is seen that the concepts of rubber modification or toughening of plastics as indicated in this presentation does not indeed preclude the utility of natural rubber for the same role.

21. It would thus appear that a major developmental effort is well justified for up-grading the proportionate share for natural rubber involving diligent study of indigenous technology expanded

with tandem synthetic, monomer technology perhaps even in some means of regionalization. As an econometric developmental effort this could entail evaluating the efficiencies and economics of such ventures as (a) latex modification for compounding with polyolefins and their related chemical analogs notably ABS and PVC polymers, (b) indigenous installation of balanced production capacity to provide independent source of monomers, and (c) development of integrated fabrication or conversion of the indigenous, stock rubber-plastics blends for indigenous needs of constructionforms for irrigation, flood control, sanitation, transportation, shelters, and myriads of utilitarian articles for minimal domestic usage. This in effect means a continued dispersal of monomer and polymer technology from high industrial complexes toward regional areas proximal to most economic transport or conveyance of rubber latex and its bulk stocks.

22. Finally, one important consideration that warrants study and appraisal and that relates to the possible conserving of fossil fuels, or even its excessive transhipment, as is needed to produce the tonnage of synthetic elastomers and polymers, both as a factor in the conservation of energy dissipated into oxides of carbon as well as as well as converting to condensed carbon form in a manner ofspeaking. This in itself could be considered a deserving endeavor for continued probing and study under the purview of the deliberations such as are now being experienced in the present Expert Group Meeting of the United Nations Industrial Development Organization.

VII. REFERENCES

(1) Statistical Yearbook (Annuaire Statistique) 1969, Twenty-first Issue, United Nations, New York, 1970.

(2) United States Tariff Commission, Synthetic Organic Chemicals, United States Production and Sales, Yearly Series.

(3) Current Industry Reports, Rubber: Supply and Distribution for the United States, U. S. Departm ent of Commerce.

(4) Thompson, M. S., Gum Plastics, Reinhold Publishing Corporation, New York, 1958.

(5) Multicomponent Polymer Systems, Advances in Chemistry(99) Series, American Chemical Society, Washington, D. C. 1971.

(6) Griffith, J. N., Trans. Roy. Soc. A 1921, 221, 163.

(7) Bragaw, C. G., Theory of Rubber Toughening of Brittle Plastics, Reference (5), 86 - 106.

(8) Newman, S. and Strella, S., Journal Applied Polymer Science, <u>1956</u>, 9, 2297.

(9) Schmitt, J. A. and Keskkula, H., Journal Applied Polymer Science, <u>1960</u>, III, 132.

(10) Matsuo, M., Polymer <u>1966</u>, 7, 421.

(11) Goodier, J. N., Transactions, American Society of Mechanical Engineers, <u>1933</u>, 55, A39, 39.

(12) Yoffe, E. H., Philosophical Magazine, <u>1951</u>, 42, 739.

(13) Nielsen, L. E., Journal of American Chemical Society, <u>75</u>, 1453, 1953.

(14) Kollinsky, R. and Markert, G., Demixing Phenomena in Copolymers, Reference (5), 175 - 188.

(15) Roberts, D. K. and Wells, A. A., Engineering, 1954, 178, 820.

(16) Cotterell, B., Applied Materials Research, 1965, 4 (4), 227; also International Journal of Fracture Mechanics, 1965, 1, 96

(17) Strella, S., Journal Polymer Science, A2, 1966, 4, 527.

APPENDIX

VIII. GRIFFITH FAILURE CRITERION (7)

23. In a homogenous system, a fracture of crack develops slowly until it attains a critical length postulated on the basis of measurable elastic constants. Rapid acceleration then ensues with the crack attaining a limiting velocity of approximately one half of the transverse wave velocity (15), at which point the total crack surface acquires an irregular fracture because of branching (16). For the critical crack length, Griffith (6) provides the expression:

$$T = \sqrt{\frac{2E\gamma}{\pi c}}$$

where T = tensile strength,

E Young's modulus (under tension),

γ = energy required to produce unit area of new crack,

c = critical crack length.

Rearranged for the purpose of computation, this expression takes the form for the critical length:

$$c = \frac{2E\gamma}{\pi T^2},$$

which immediately discloses the interplay of the modulus (E) with the tensile strength to the square power (T^2), a seemingly dominant contributor toward deiminishing the theoretical crack length.

24. For the case of brittle polystyrene (7) with the approximate values of:

$T \sim 5 \times 10^8$ dynes/cm^2,
$E \sim 3 \times 10^{10}$ dynes/cm^2, and
$\gamma \sim 2 \times 10^5$ ergs/cm^2,

a critical length of 50 or 100 microns is attained. Since ductile layers are limited to layers of approximately 1 micron, the Griffith relationship interms of the elastic or mechanical constants does pertain. In an actual breaking test with a molded sample of a styrene/acrylonitrile copolymer, it has been experimentally observed that crack roughening starts when c reaches 250 microns, which is compatible with the above calculated Griffith value.

IX. ANALYSIS OF DILATIONAL CONCEPT OF YIELDING

25. Commencing with the concept that the rubber particles generate a state of hydrostatic tensile stress with dilation and leading in turn to an increase in free volume which facilitates yielding instead of brittle fracture, one applies the Goodier analysis of stresses (11) in a system composed of an elastic sphere embedded in an elastic matrix. A simplification of the Goodier analysis is provided for the matrix stresses expressed by the equation (17):

$$HT = \frac{T}{3}\left[1 - \frac{5\,a^3}{2\,r^2} \times \frac{(1+\sigma_1)\,(1+3\cos 2\theta)(u_1 - u_2)}{(7 - 5\,\sigma_1)\,u_1 + (8 - 10\,\sigma_1)u_2)}\right]$$

where H = hydrostatic tensile stress,

T = simple tensile stress applied at radius $r =$,

r = distance from center of shphere,

a = sphere radius,

θ = angle between radius vector r and direction of T,

u_1 = shear modulus of matrix,

u_2 = shear modulus of rubber sphere,

σ_1 = Poisson ratio of matrix, and

σ_2 = Poisson ratio of sphere (not included).

Since the Poisson ratio of the sphere is not included in the expression, the generated value of HT becomes independent of σ_2. For a homogenous plastics matrix then, $HT = 0.33T$. Thus the magnitude of the hydrostatic tensile stress, HT, depends upon the relationship between u_1 and u_2 and the angle θ. Typical calculated values for the hydrostatic tension are summarized in Table VI, which provides the following assessments:

(a) inclusion of elastic component increases the hydrostatic tension above the 0.33T value of a homogenous matrix,

(b) a void as an artifact of softness increases the hydrostatic tension more than a rubber particle or sphere, and

(c) a hard inclusion increases the hydrostatic tension more than a void. The equation and calculated values make no provision for adhesion. The role of the chemical structure, such as the polyisoprene elastomers vis-a-vis synthetic homologs, may yet become quite significant in subsidiary dilational interaction.

TABLE I. RUBBER AND PLASTICS WORLD PRODUCTION (ABBREVIATED SUMMARY)

Units: Metric tons Reference (1)

Category	Year						
	1964	1965	1966	1967	1968	1969	1970
RUBBER							
Natural (NR)	2270	2380	2435	2490	2645		
Synthetic (SR)	3000	3235	3580	3695	4210		
Total (TR)	5270	5615	6015	6185	6855		
PLASTICS							
Total (TP)	12480	14360	16782	18225	21787		
PROPORTIONAL INDICES							
NR/TR (Figure 1)	0.43	0.42	0.40	0.40	0.39		
TR/TP (Figure 2)	0.42	0.39	0.36	0.34	0.32		
NR/TP (Figure 3)	0.18	0.16	0.15	0.14	0.13		
SR/TP (Figure 4)	0.24	0.23	0.21	0.20	0.19		

TABLE II. RUBBER AND PLASTICS U. S. A. PRODUCTION (ABBREVIATED)

Units: Metric tons Reference (1,2)

	Year						
Category	1964	1965	1966	1967	1968	1969	1970
RUBBER							
Natural (NR)	222	237	252	225	268		
Synthetic (SR)	669	710	768	750	874		
Total (TR)	891	947	1020	975	1142		
PLASTICS							
Thermosetting	1362	1492	1682	1621	1647	1728	
Thermoplastic	3295	3894	4581	4738	5895	6882	
Total (TP)	4657	5386	6263	6359	7542	8610	
PROPORTIONAL INDICES							
NR/TR (Figure 1)	0.249	0.250	0.247	0.231	0.235		
TR/TP (Figure 2)	0.191	0.176	0.163	0.153	0.151		
NR/TP (Figure 3)	0.048	0.044	0.040	0.035	0.036		
SR/TP (Figure 4)	0.143	0.132	0.123	0.118	0.115		

TABLE III. ANALYSIS OF TREND OF RUBBER EXTENSION - U. S. A.

POLYSTYRENE PRODUCTION

Units: Metric tons Reference: (2)

	Year						
Product Type	1964	1965	1966	1967	1968	1969	1970
Styrene Types (TS)	784	922	1068	1293	1314	1517	
(ABS and SAN)	-	-	164	168	231	265	
(Styrene)	-	-	918	972	1083	1252	
Rubber-modified (RMS)	310	291	389	338	400	507	
PROPORTIONAL INDICES							
TS/TP	0.24	0.24	0.23	0.27	0.22	0.22	
RMS/TS (Figure 5)	0.40	0.32	0.31	0.26	-.34	0.33	

TABLE IV. PLASTICS TYPES EXTENDED WITH RUBBER

Descriptive Category (Grade)	A. S. T. M. Specifications
A. Impact polystyrene	(D-703)*
(1). Medium impact	
(2) High impact	
(3) Very high impact	
(4) Heat-resistant impact	
B. ABS (Acrylonitrile-butadiene-styrene)	D - 1788
(1) Medium impact grade	
(2) High impact	
(3) Very high impact	
(4) Low temperature impact	
(5) Heat-resistantimpact	
C. Impact polyvinyl chloride (PVC)	D - 1784
(1) Medium impact	
(2) Very high impact	

*This test standard applies primarily to polystyrene un-modified but is generally applied to the impact grades.

TABLE V. EFFECT OF RUBBER PARTICLE SIZE AND SHAPE ON IMPACT PROPERTIES OF STYRENE-ACRYLONITRILE POLYMER MODIFIED WITH POLYBUTADIENE-ACRYLONITRILE RUBBER (*)

Particle Features	Izod Impact - ft lb/in	
	Average Value	Range
Spheroidal, 0.5 - 3.0	3.0	2.8 - 3.5
Spheroidal, 0.3 - 0.5	0.5	
Spheroidal, 0.5	0.5	
Elongated, 0.2 x 1.0	0.9	2.0 - 0.4
Elongated, 1.0 x 3.0 +	3.3	1.5 - 5.3
Elongated, 0.3 x 1.0	2.2	0.6 - 4.8
Elongated, 0.1 x 1.0	1.1	0.6 - 2.2

(*) 20 Weight percent. (7)

TABLE VI. HYDROSTATIC TENSION (HT) CALCULATED FROM GOODIER ANALYSIS (7)

Angle	Value of Hydrostatic Tension at Interface		
	$u_2 = 0$ (void)	$u_2 = 0.1u_1$ ("rubber")	$u_2 =$ hard inclusion
0°	- 0.45 T	- 0.32 T	+ 1.2 T
90°	+ 0.73 T	+ 0.67 T	- 0.1 T

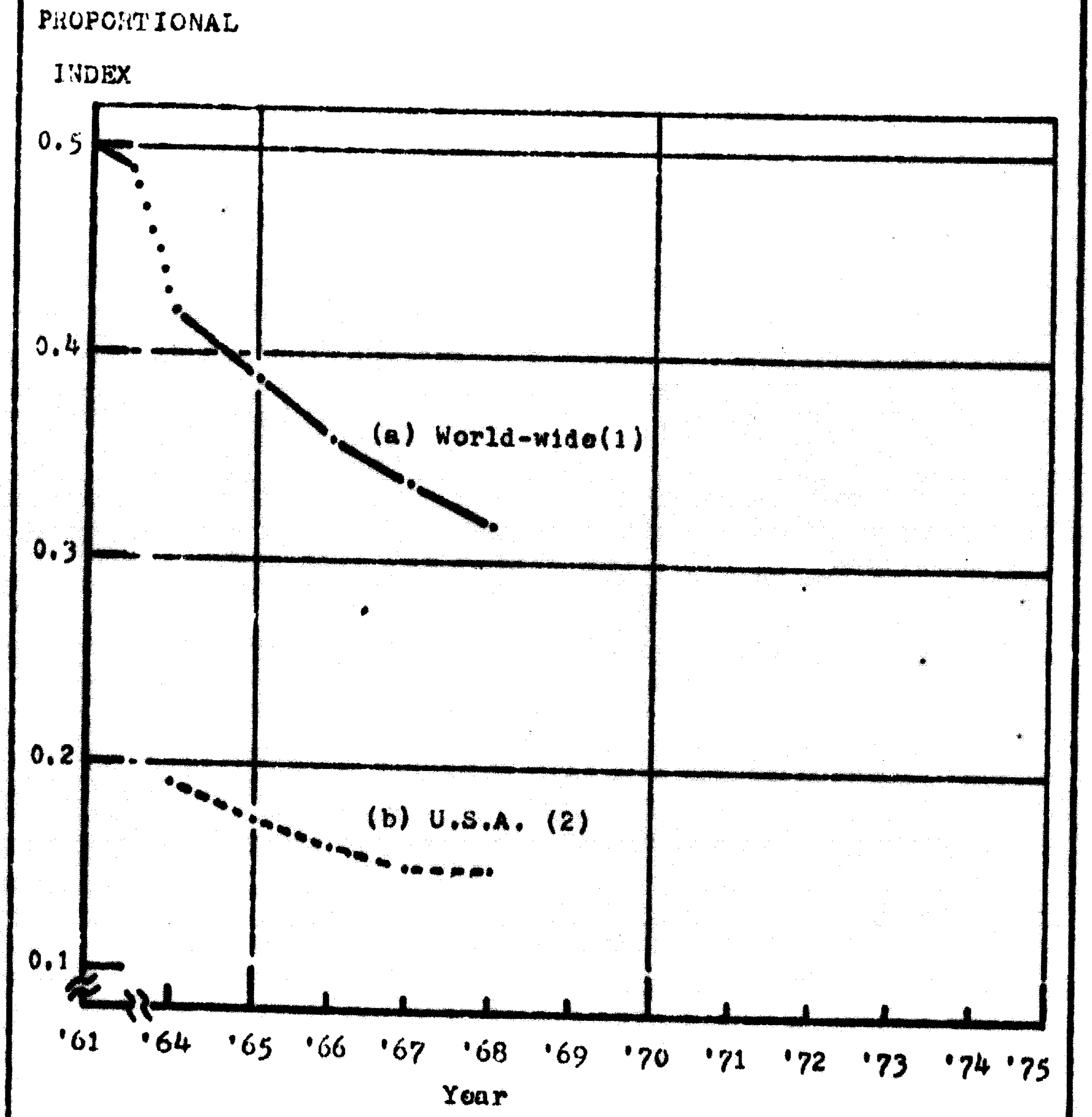


Figure 1. Proportional Index - Yearly Trend
Total Rubber/Total Plastics

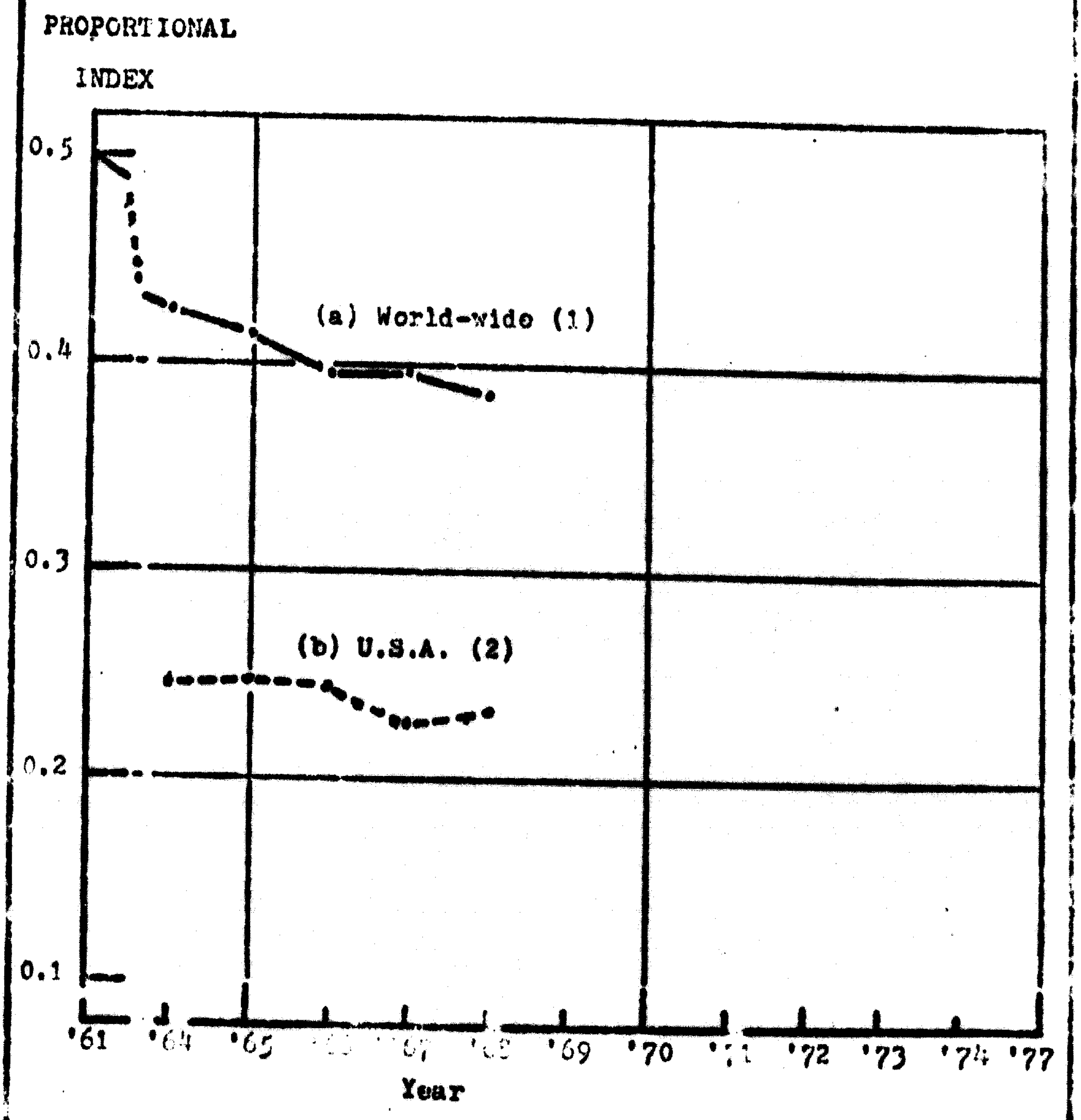


Figure 2. Proportional Index - Yearly Trend

Total Natural Rubber/Total Rubber

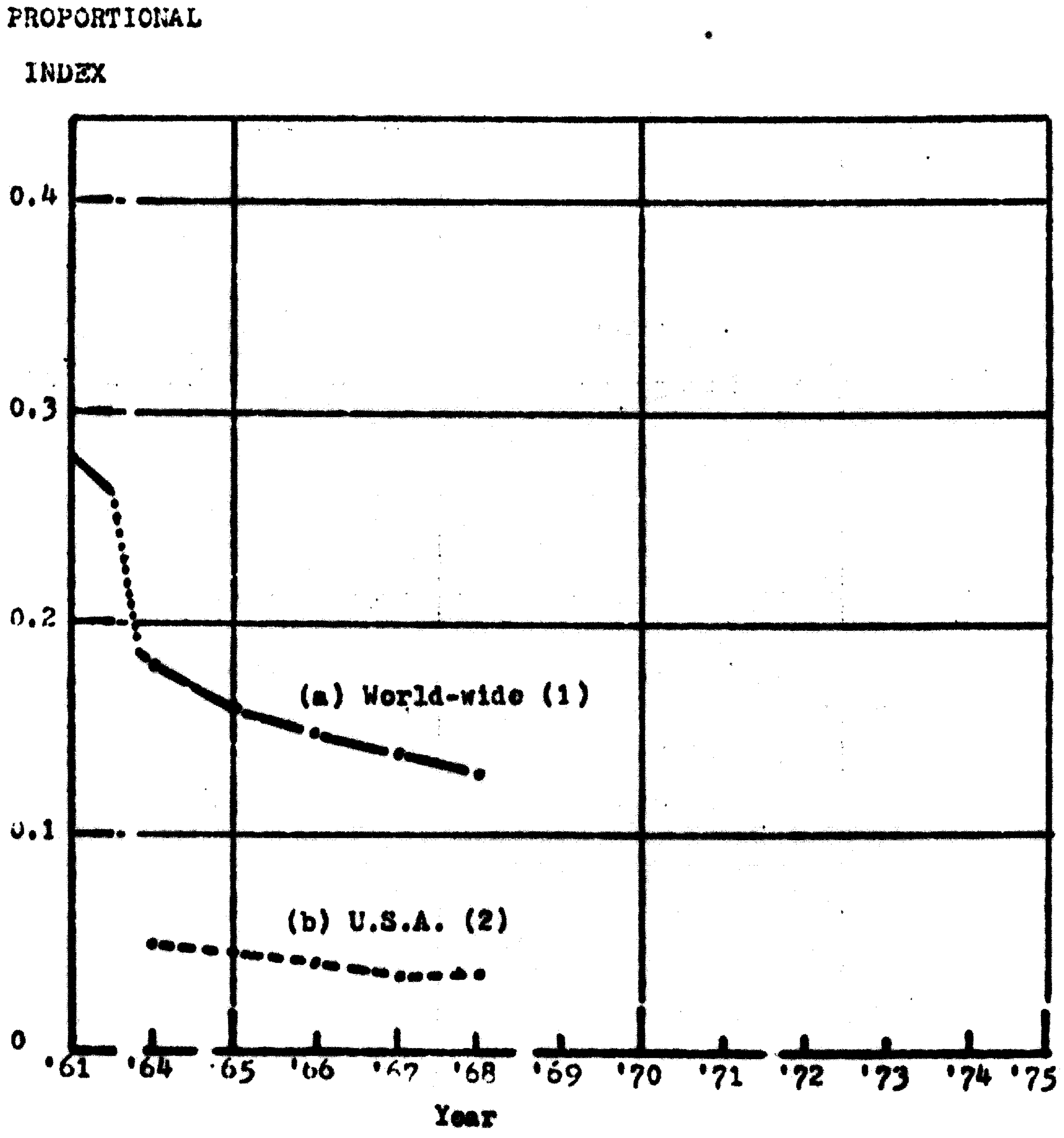


Figure 3. Poportional Index - Yearly Trend

Natural Rubber/Total Plastics

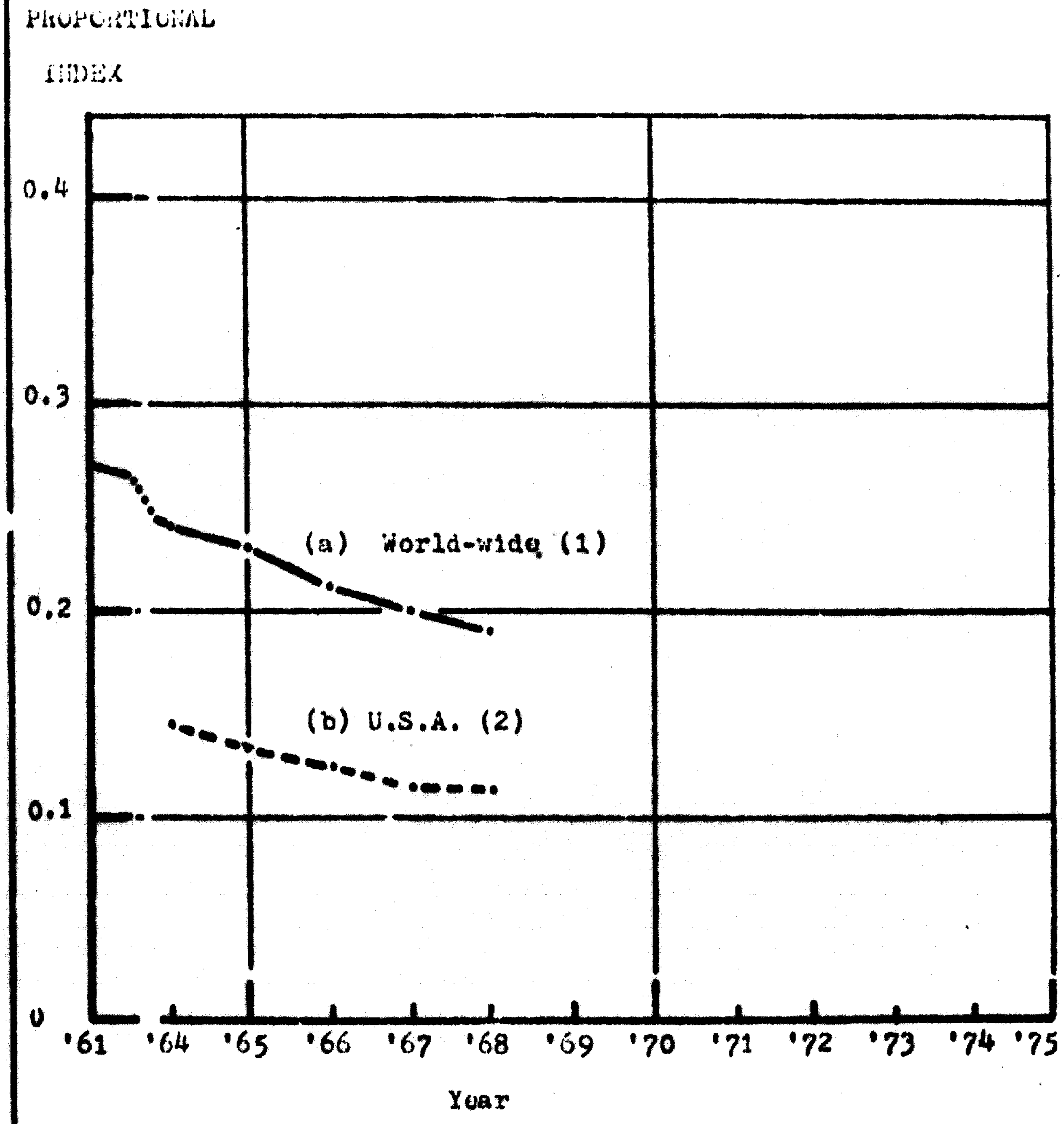


Figure 4. Proportional Index - Yearly Trend

Synthetic Rubber/Total Plastics

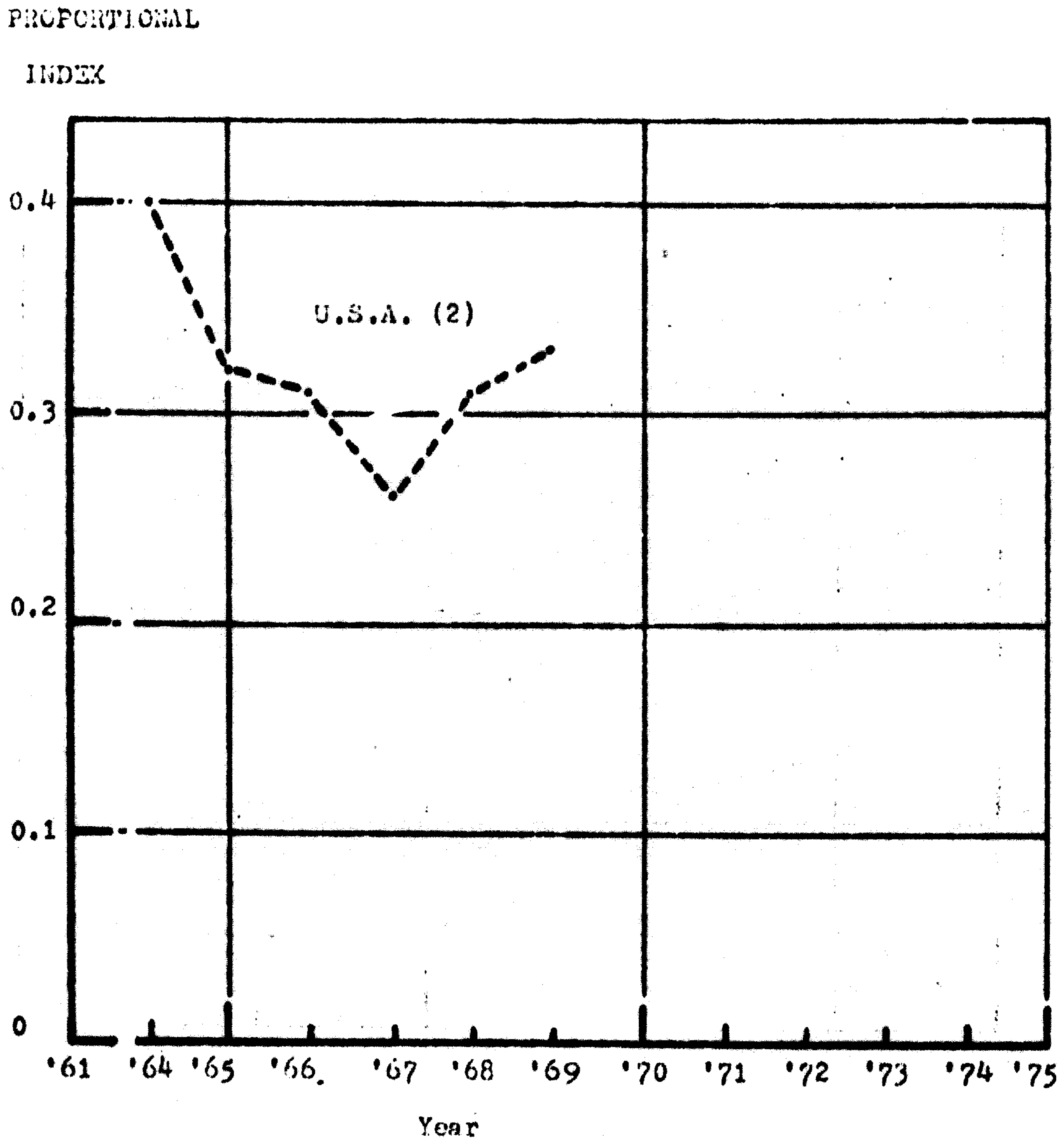


Figure 5. Proportional Index - Yearly Trend
Rubber-modified Polystyrene/Polystyrene

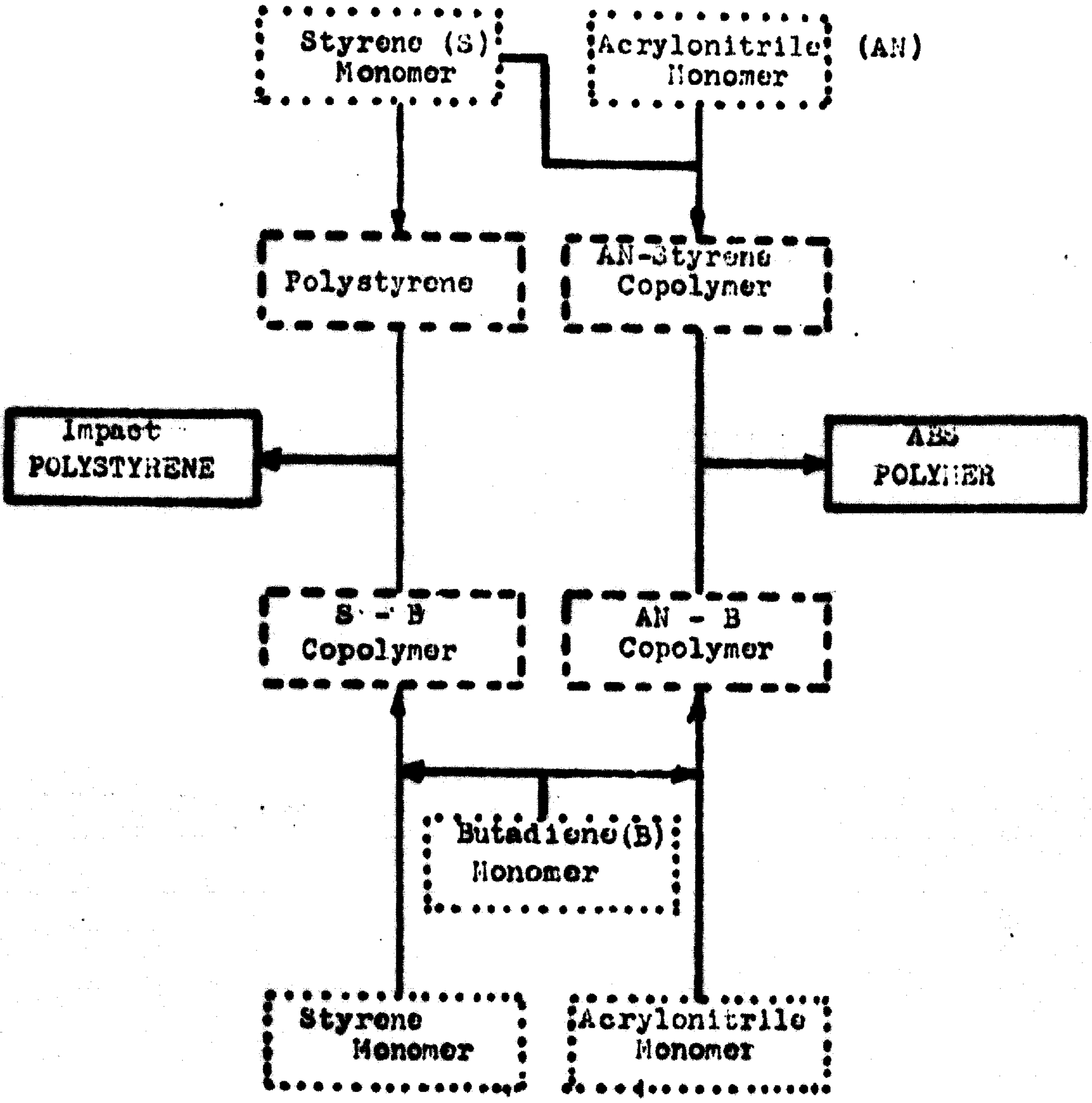
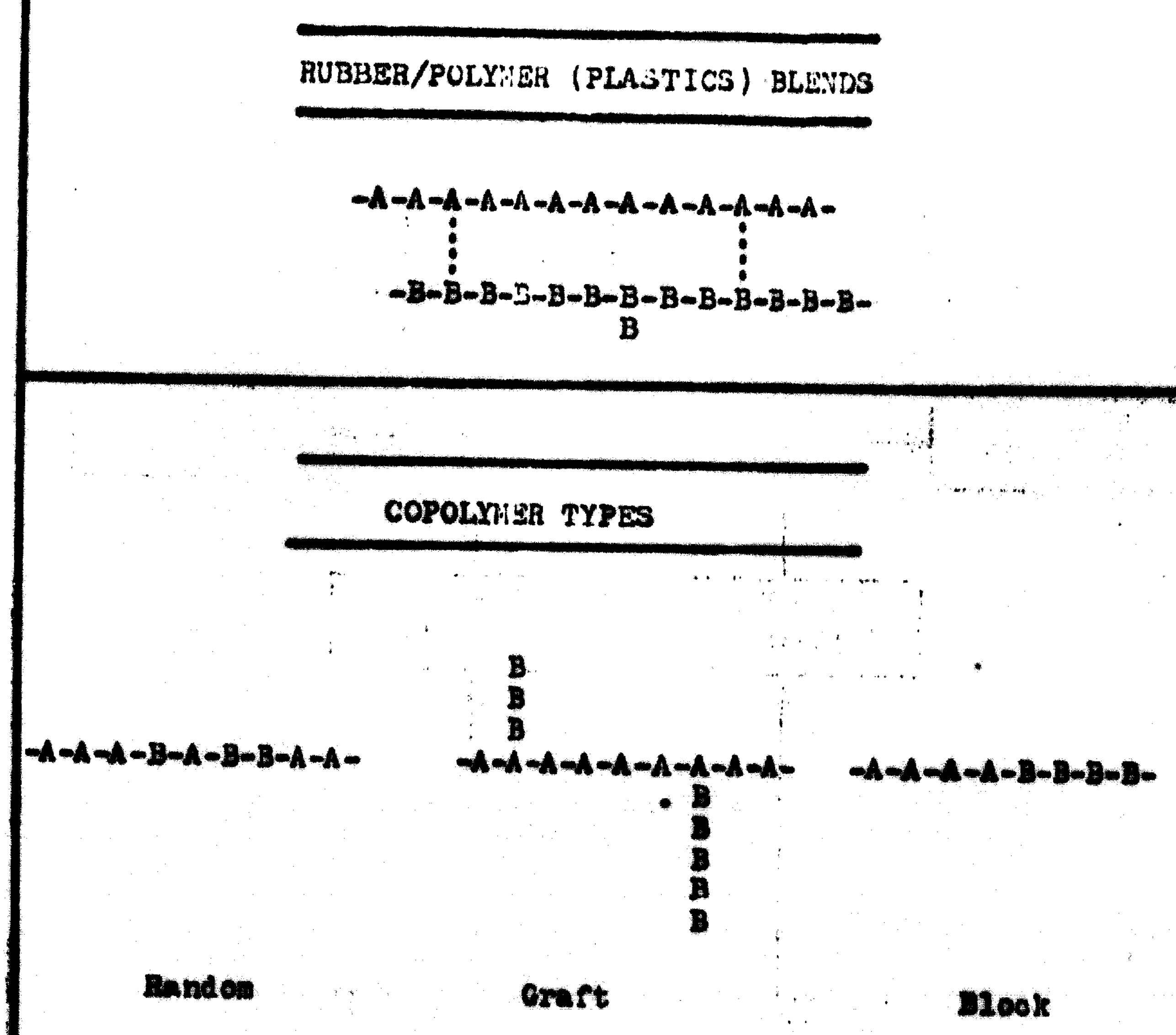


Figure 6. Typical Elastomer (Butadiene) Modification Styrene and Acrylonitrile Polymers. (4)



RUBBER/POLYMER (PLASTICS) BLENDS

COPOLYMER TYPES

Figure 7. Multicomponent Elastomer-Polymer Systems (4).

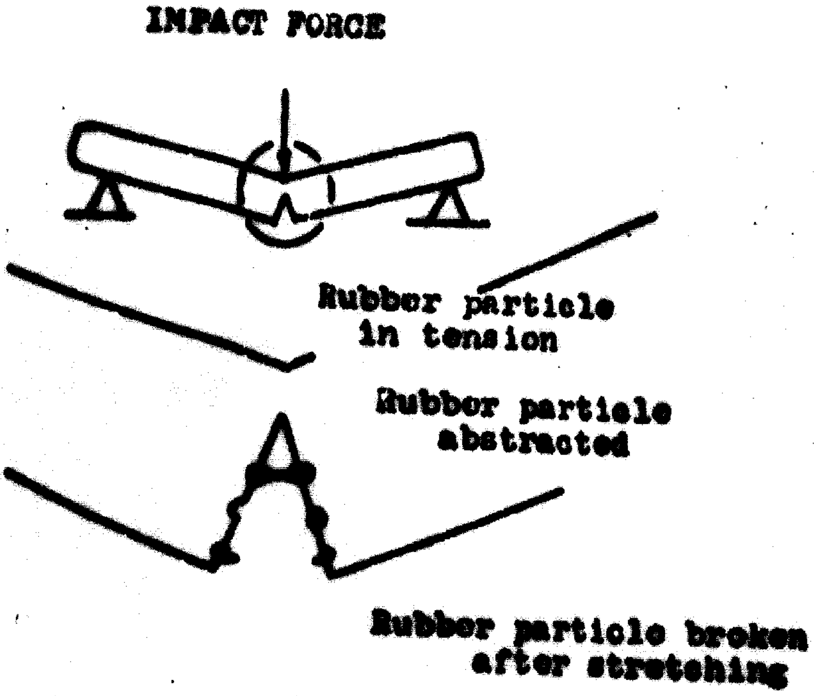


Figure 8. Impact Fracture with Rubber Modifier. (4)

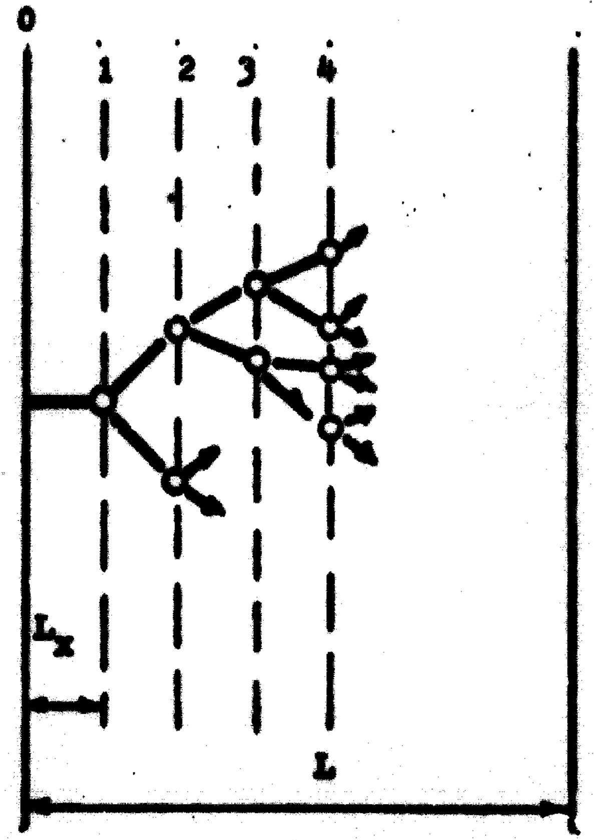


Figure 9. Craze branching model. (7)

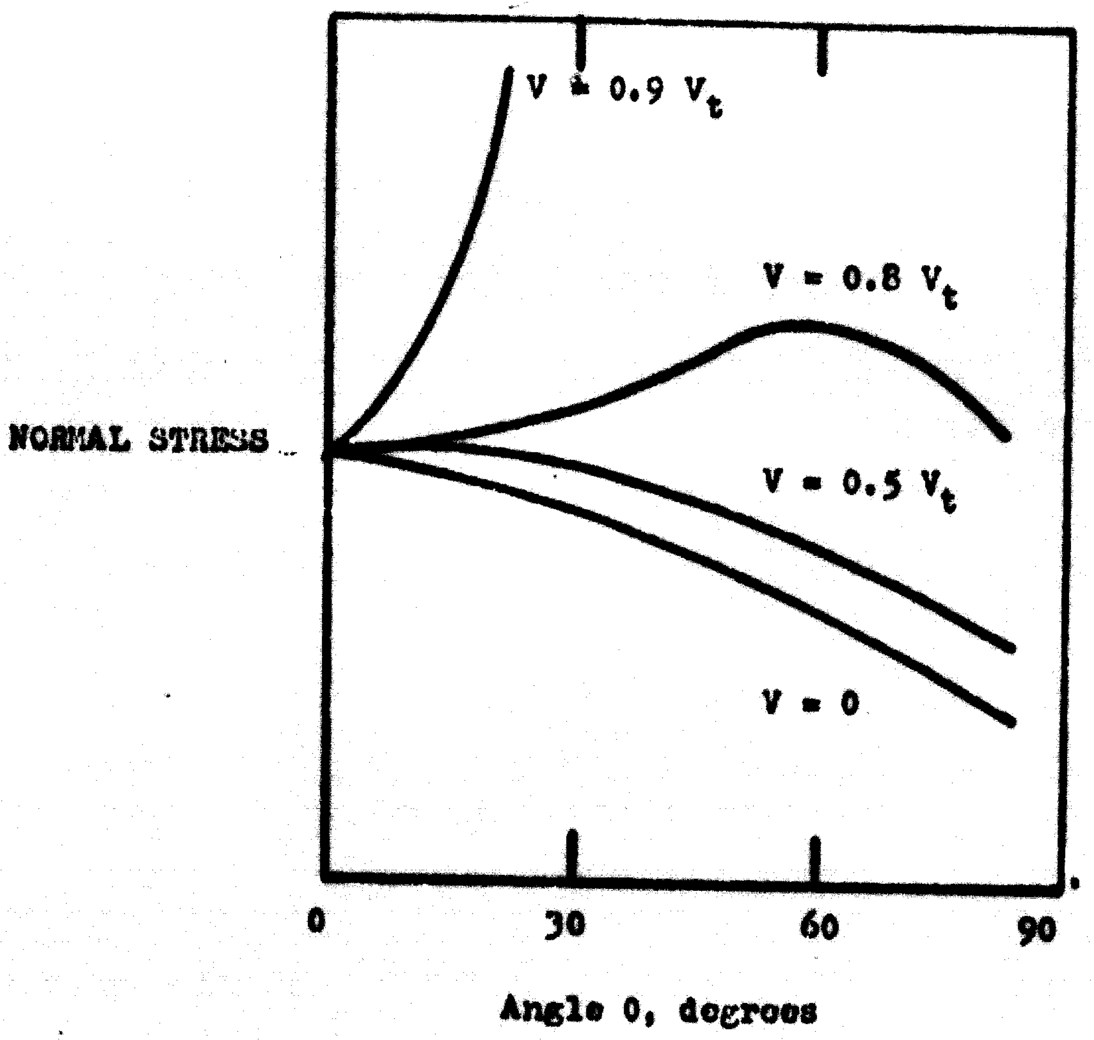
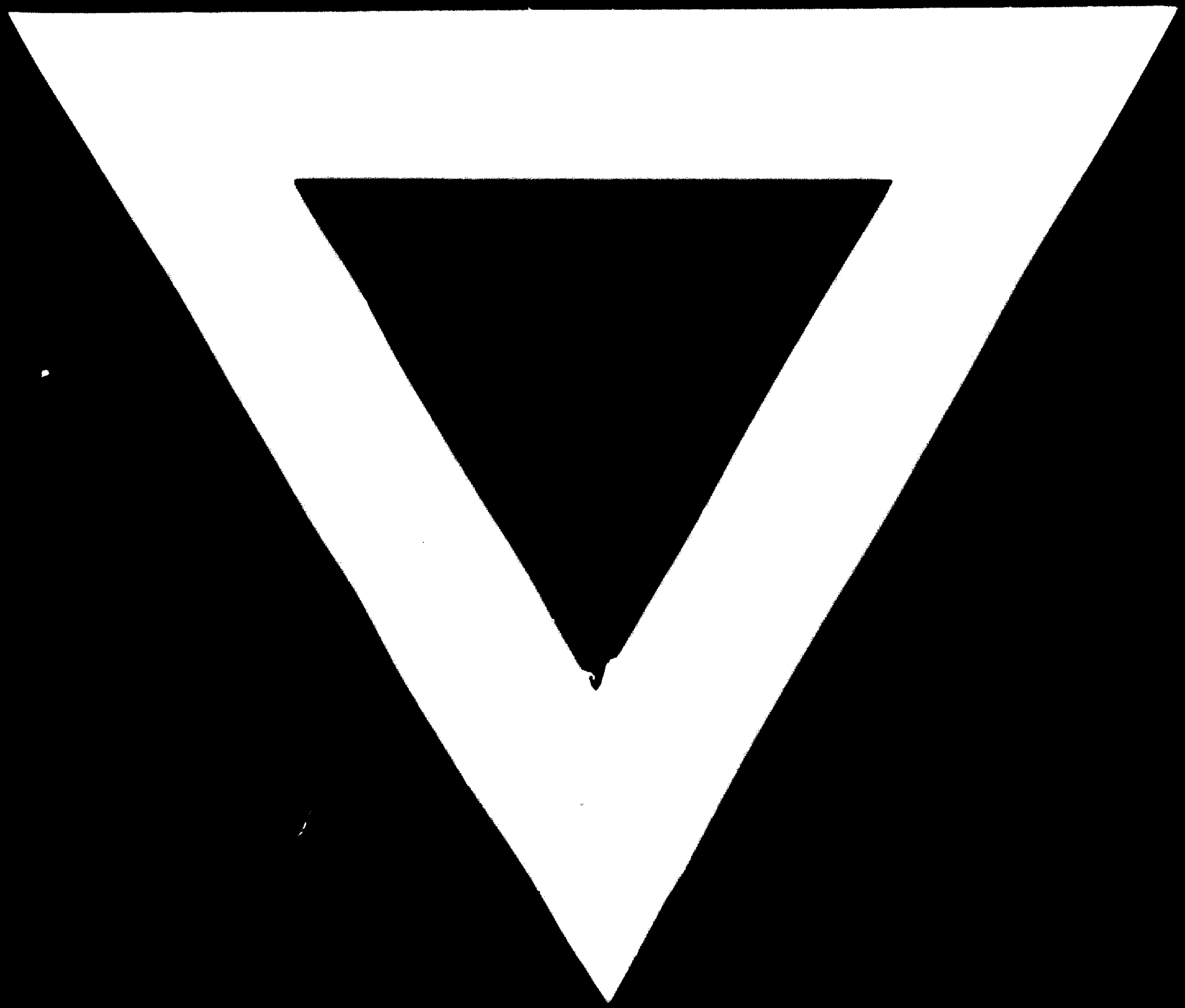


Figure 10. Effect of craze/crack speed on stress distribution.(12)



17.6.74