

ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING

INDEX VOLUME

**Asphaltic Materials
to
Processing Aids
and
Index to all Volumes**

Copyright © 1990 by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

Reproduction or translation of any part of this work beyond that permitted by Section 107 or 108 of the 1976 United States Copyright Act without the permission of the copyright owner is unlawful. Requests for permission or further information should be addressed to the Permissions Department, John Wiley & Sons, Inc.

Library of Congress Cataloging in Publication Data:

Main entry under title:

Encyclopedia of polymer science and engineering.

Rev. ed. of: Encyclopedia of polymer science and technology. 1964—

"A Wiley-Interscience publication."

Includes bibliographies.

1. Polymers and polymerization—Dictionaries.

I. Mark, H. F. (Herman Francis), 1895—

II. Kroschwitz, Jacqueline I. III. Encyclopedia of polymer science and technology.

TP1087.E46 1985 668.9 84-19713

ISBN 0-471-80950-0 (Index Volume)

Printed in the United States of America

E

ELASTOMERS, SYNTHETIC

Elastomers are derived from natural rubber and synthetic polymers with rubberlike properties. They exhibit both long-range deformability on application of stress and essentially complete recovery on removal (1–4). These two properties are not shared by lower molecular weight solids, liquids, and gases, and metals, glasses, or ceramics. According to ASTM, an elastomer is “a natural or synthetic polymer which at room temperature can be stretched repeatedly to at least twice its original length and which after removal of the tensile load will immediately and forcibly return to approximately its original length” (5,6). In other words, an elastomer is “a macromolecular material which, at room temperature, is capable of recovering substantially in size and shape after removal of a deforming force” (7). Rubberlike behavior is exhibited exclusively by polymeric materials consisting predominantly of long-chain molecules, as only such macromolecules have the capacity of forming a sufficiently large number of arrangements in space to be able to alter their end-to-end separations when stress is applied (see ELASTICITY). Elastomers must be above the glass-transition temperature T_g to manifest high local segmental mobility. They must be amorphous in the unstressed state to exhibit high local segmental mobility, ie, the chains must be flexible and intermolecular (interchain) forces must be weak. Elastomers must possess a sufficient number of chemical or physical cross-links to form a continuous network in order to restrain chain slippage (4) (see CROSS-LINKING; NETWORKS). Some triblock copolymers, eg, styrene–butadiene–styrene (SBS), exhibit elastomeric behavior due to two-phase morphology, where the polystyrene domains act as thermally reversible physical cross-links as well as fillers. These materials exhibit permanent set when stretched to high elongations and allowed to relax (see ELASTOMERS, THERMOPLASTIC).

Bond rotations and segmental motion in a rubber take place at high frequencies at room temperature. A segmental jump changes the overall conformation of the macromolecule. An elastomer is essentially an entropy spring, in contrast to a steel wire, which is an energy spring that warms on retraction. In contrast, a strain-induced crystallizable elastomer cools on retraction. An ideal elastomer has a Young's modulus of about 10^5 – 10^6 N/m² (14.5–145 psi) and reversible elasticity of several hundred percent elongation. The force required to hold it at a constant length decreases as the temperature is lowered, ie, $(\partial U/\partial l)_T = 0$, where U is the internal energy and l the length.

Depending on their chemical structure and regularity, the chains of syn-

thetic rubbers may or may not be able to undergo crystallization on stretching. Natural rubber, by virtue of its regular chain structure, is capable of crystallizing on stretching. It exhibits a fiberlike structure at high elongation, providing high tensile strength. The interchain forces are not strong enough to stabilize this fiberlike structure on removal of the applied stress, and rubber chains retract to their thermodynamically stable configurations. *cis*-1,4-Polyisoprenes prepared with Ziegler-Natta catalysts exhibit this phenomenon of temporary crystallization, but less so than natural rubber (see ISOPRENE POLYMERS; RUBBER, NATURAL). Strain-induced crystallization plays an important role in determining the physico-mechanical properties of rubbers, such as tensile strength, tear strength, and fatigue resistance. *Trans*-polypentenamer, obtained by the ring-opening polymerization of cyclopentene with a tungsten hexachloride-trialkylaluminum catalyst, exhibits a crystallization behavior similar to that of natural rubber (8) (see POLYALKENAMERS). The preparation of synthetic amorphous rubbers that exhibit strain-induced crystallization has been an important goal of polymer chemists for a variety of industrial applications.

A rubber able to crystallize on stretching crystallizes, at least partially, on cooling without stretching. The temperature of crystallization is referred to as its crystalline melting point T_m . It is usually below room temperature; otherwise the rubber crystallizes and hardens on storage. This is occasionally observed with natural rubber stored at low temperatures.

Copolymers exhibit less tendency to crystallize than homopolymers. The melting point is decreased by copolymerization, and the ease of crystallization is much reduced; the strain-induced crystallizability may disappear. Polyethylenes of varying density are highly crystalline, but when copolymerized with propylene a noncrystallizable rubber is produced (see ETHYLENE-PROPYLENE ELASTOMERS). The T_g of a copolymer is dependent on the nature and ratio of the monomers. Polypropylene has a much higher T_g than polyethylene. Copolymerizing propylene with ethylene raises the T_g of the ethylene-propylene rubber (EPR) above that of polyethylene. Similarly, copolymerization of butadiene with styrene raises the T_g of SBR significantly above that of polybutadiene (see BUTADIENE POLYMERS).

A macromolecule is usually classified as a rubber at room temperature, where it exhibits deformability on the application of stress. However, at or near its T_g , the same material behaves as a glass, ie, a supercooled liquid. In contrast, polystyrene is glass-like (or plastic) at room temperature because it has a T_g of about 100°C; at 150°C, it is rubbery. Macromolecules with a T_g of -30 to -40°C, preferably lower, behave as rubbery materials at room temperature. A low T_g is a necessary but insufficient condition for high elasticity. The macromolecules must possess sufficient structural irregularity to prevent crystallization in the unstressed condition.

Vulcanizates that do not undergo strain-induced crystallization exhibit poor tensile and tear strengths. For instance, gum vulcanizates of emulsion SBR and EPDM have low tensile strengths of about 2–3 MPa (290–435 psi). To increase tensile strength, reinforcing fillers such as carbon black and silica are incorporated before vulcanization (qv). Finely divided fillers (qv) also improve abrasion resistance and prolong the life of the product, in addition to reducing the cost. An SBR vulcanizate containing 50 phr of carbon black may exhibit a tensile strength of 25–30 MPa (3625–4350 psi) at room temperature.

Nomenclature and Classification

In 1960, the International Institute of Synthetic Rubber Producers Inc. (IISRP) was formed with the objective of compiling a systematic listing of synthetic rubbers. In 1988, the Institute represented 51 producers in 19 countries. It publishes *Worldwide Rubber Statistics* annually and the *Synthetic Rubber Manual* once every 3 years. The latter gives testing standards, nomenclature, and data on commercial rubbers and latices.

The nomenclature of synthetic rubbers is based on ASTM D1418 (9–11): M denotes rubbers containing a saturated polymethylene chain and appears in many symbols for synthetic rubbers; N represents rubbers containing nitrogen, and O those with oxygen in the polymer backbone; R designates rubbers with an unsaturated carbon chain, eg, natural rubber and synthetic rubbers derived at least partly from conjugated diolefins. Rubbers with silicon in the backbone are designated by Q, and rubbers with sulfur by T. Rubbers with carbon, oxygen, and nitrogen in the macromolecule chain are described by U. Carboxylic groups substituted on the polymer chain are denoted by the letter X and halogen atoms by prefixes B or C for bromine or chlorine. The prefix P denotes the presence of vinylpyridine.

The chemical family is represented by prefix letters as follows (9): A, acrylate rubber; B, butadiene rubber; C, chloroprene rubber; I, isoprene rubber (synthetic); N, acrylonitrile rubber; S, styrene rubber (Table 1).

Table 1. Rubber Designations

Abbreviation	Rubber
ABR	acrylate–butadiene
BR	butadiene
CR	chloroprene
EPM	ethylene–propylene
EPDM	ethylene–propylene–diene ^a
IR	isoprene
IM	isobutylene
IIR	isobutylene–isoprene or butyl rubber
SBR	styrene–butadiene
SIR	styrene–isoprene
NBR	acrylonitrile–butadiene
NCR	acrylonitrile–chloroprene
PBR	vinylpyridine–butadiene
PSBR	vinylpyridine–styrene–butadiene
XNBR	carboxylic–acrylonitrile–butadiene
XSBR	carboxylic–styrene–butadiene
CIIR	chloroisobutylene–isoprene or chlorobutyl rubber
BIIR	bromoisobutylene–isoprene or bromobutyl rubber
MQ	dialkylsiloxane
GPO	poly(propylene oxide)
AU	polyesterurethanes
EU	polyetherurethanes

^a Nonconjugated diene; residual unsaturation from the diene is in the pendent group.

This system of nomenclature has its shortcomings. The letters used in designating the included elements or substituents often have no connection to the elements they represent. This aspect makes it difficult for those other than experts to recognize a rubber from its abbreviation.

Other systems are based on either the monomer(s), ie, source-based nomenclature, the structure, or trade names (12). A systematic IUPAC system for polymer nomenclature (11–16) is rarely used because the trivial naming system is fairly well entrenched (see NOMENCLATURE).

Synthetic rubbers may be subclassified as organic and inorganic rubbers according to elemental composition; the latter polymers are also referred to as semi-inorganic rubbers.

Organic rubbers contain carbon as the primary element of the polymer backbone. Examples are *cis*-1,4-polyisoprene, *cis*-1,4-polybutadiene, Li-polybutadiene (mixed *cis*-1,4, *trans*-1,4, and 1,2-structures), SBR, NBR, EPM, EPDM, butyl rubber, polychloroprene, polyurethanes, fluoroelastomers, propylene oxide rubber, epichlorohydrin rubbers, polysulfides, polyacrylates, polypentenamer, poly(alkyl vinyl ethers), and thermoplastic elastomers such as SBS.

Inorganic (or semi-inorganic) rubbers have heteroatoms in the backbone with hydrocarbon groups attached to some of the heteroatoms. Examples are solvent-resistant phosphazene elastomers made up of alternating phosphorus and nitrogen atoms in the backbone (17–22) such as phosphonitrile fluoroelastomer (PNF) ($T_g = -63^\circ\text{C}$) (see POLYPHOSPHAZENES).

Silicone rubbers possess alternating silicon and oxygen atoms in the backbone (23) and are usually high molecular weight linear polymers. These silicone elastomers have superior heat resistance and the lowest T_g of -110°C (24) of any rubber. Most silicone elastomers consist principally of silicon atoms substituted with methyl groups. For ease of vulcanization with a peroxide, about 0.5 mol % of the methyl groups are replaced by vinyl groups (23). The resulting vulcanizates exhibit low compression set (see SILICONES).

Polysilanes are another class of inorganic rubbers. The polymer chain is made up entirely of silicon atoms, each of which is substituted with a methyl group and a longer chain alkyl group such as *n*-butyl or *n*-hexyl (25). The glass-transition temperatures are between -50 and -60°C (26). Polysilanes are potential candidates for silicon carbide ceramics, photoresists for microelectronics, and photoinitiators for vinyl polymerization (see POLYSILANES AND POLYCARBOSILANES).

Development

Synthetic rubber holds a unique position among synthetic polymers, as it was developed to fill an important need of the modern world. The emergency resulting from the cut-off of natural rubber (NR) supplies to the United States during World War II contributed to rapid developments in research and manufacture of synthetic rubber.

Before World War I, research on synthetic rubber was emphasized for strategic as well as for economic reasons. In the United States, the expansion of the automobile industry created increasing demand for rubber. The world production

of NR, principally from plantations, rose from 44,000 tons in 1900 at about \$2.2/kg to 94,000 tons in 1914; the peak price was \$6.6/kg. Price fluctuations and recurring shortages spurred great interest in synthetic rubber in Europe as well as in the United States, which at that time was consuming about 75% of the world supply of rubber.

The history of discoveries of synthetic rubbers has been reviewed repeatedly (27–31). The early history of synthetic rubber is closely related to investigations of NR. Priestley, the discoverer of oxygen, coined the name rubber in 1770 because of its ability to erase pencil marks. In 1826, Faraday determined its empirical formula as C_5H_8 . The discovery of isoprene as a pyrolysis product of NR by Williams led to the synthesis of related dienes, the first station on the road to manufacturing synthetic rubber or elastomers. Other noteworthy developments were the discoveries by Mathews and Strange (32) in the UK in 1910 that isoprene and other dienes could be polymerized with sodium, and independently at about the same time by Harries (33) in Germany and Lebedev (34) in the USSR that butadiene underwent polymerization in a similar manner.

The first large-scale production facility for synthetic rubber was started in Germany during World War I to ease the shortage of rubber caused by blockade. 2,3-Dimethylbutadiene, because of the ease of synthesis from acetone, was selected as the most suitable monomer. However, the so-called methyl rubber was inferior to NR in physical properties and posed difficulties in processing and fabrication (see BUTADIENE DERIVATIVES, POLYMERIC).

In the 1920s, Staudinger (35) first proposed that macromolecules of rubber were long-chain molecules in which the isoprene units were connected by normal chemical bonds. This concept of giant molecules set the stage for a better understanding of macromolecules and contributed to accelerated efforts in the development of synthetic rubber during the 1920s and 1930s. Polymerization of butadiene was reduced to 12–14 h by the use of sodium catalyst and heptane or benzene solvent. I. G. Farbenindustrie AG chose the name Buna, derived from butadiene and natrium (sodium) for this material. Subsequently, the more efficient water-based emulsion polymerization was developed using alkyl naphthalene sulfonate acids as emulsifiers (36) and potassium persulfate as a catalyst (37). Buna S was a copolymer with styrene (31,38), Buna N the copolymer with acrylonitrile (39). The former was a general purpose rubber serving as a replacement for NR, whereas Buna N was oil-resistant. Today, Buna S is known as SBR and Buna N as nitrile rubber (see BUTADIENE POLYMERS).

In the United States, important contributions were made in the field of specialty rubbers with unusual resistance to swelling by hydrocarbon solvents or permeation of gases. Polymerization of ethylene dichloride and sodium polysulfide gave poly(ethylene polysulfide) (40–42), which was named Thiokol (see POLYSULFIDES). The second major U.S. contribution was polychloroprene, obtained by the emulsion polymerization of 2-chloro-1,3-butadiene (43–45). The polychloroprene rubber was commercialized by DuPont in 1932, well ahead of Buna N under the now-abandoned trade name Duprene, and was the first commercially successful synthetic elastomer derived from a diene (46,47); it was sold at \$2.20/kg. Several variations of this rubber are sold by DuPont under the trade name Neoprene. Polychloroprene shows superior resistance to swelling by oils

and hydrocarbon solvents compared with conventional diene rubbers and resists deterioration by heat, oxygen, ozone, and chemicals (see CHLOROPRENE POLYMERS).

The third U.S. contribution was the development of butyl rubber (48–52) by the Standard Oil Company of New Jersey (now Exxon). Isobutylene copolymerized with a small amount of a diene, such as butadiene or isoprene, provides just enough unsaturation sites in the rubber for sulfur vulcanization; ethyl chloride was the solvent, and AlCl_3 the Lewis acid catalyst (48,49). Subsequently, isoprene proved to be a better comonomer and methyl chloride a better solvent (51). Commercial production of butyl rubber was started in 1942; its extremely low gas permeability made it suitable for fabricating inner tubes of tires (see ISOBUTYLENE POLYMERS).

A rubber shortage developed during World War II, and the government invested about \$700 million for the production of monomers and rubbers. A giant new chemical industry was thus established in about 2 years time (1943–1944) (53,54). The present name for the rubber developed is SBR (styrene–butadiene rubber); the original designation was GR-S. Butadiene–styrene copolymers (GR-S) have several disadvantages compared to natural rubber (29): slower breakdown and softening during mastication and compounding, ie, greater processing difficulties; lower rupture strength as manifested by lower tear-strength values and lower abrasion resistance and higher crack propagation; and greater temperature rise during cyclic flexing due to poor dynamic mechanical properties.

Chemical agents were developed to promote the breakdown of the polymer chains, and new types of carbon-black reinforcing agents to enhance rupture strength and abrasion resistance (see CARBON). However, because of cyclic flexing, NR is preferred for truck and off-the-road tires (qv).

Milestones in SBR improvements include cold rubber, where hydroperoxide catalyst in conjunction with a reducing agent ("redox" recipe) allows polymerization around 5°C to produce much higher molecular weight rubber without any substantial amount of gel (55), and oil-extended rubber, which contains about 25–30% of an inexpensive, high boiling petroleum oil fraction added at the latex stage (56,57). Oil-extended rubbers are used in almost all passenger-car tire treads and as blends with other rubbers also in larger tires.

Other elastomers are made by the polymerization of diisocyanates with diols (58). The polyurethanes (qv) obtained can be used in a wide variety of applications (59,60).

So-called Alfin rubbers are made with the help of an Alfin (alcohol and olefin) catalyst, such as the sodium salt of a methyl *n*-alkyl carbinol and the sodium salt of propylene (61–63), which was used for the polymerization of butadiene and isoprene. The polybutadiene synthesized with this catalyst system is highly cross-linked, but polyisoprene prepared similarly is a soluble polymer. The heterogeneous Alfin catalyst system usually consists of allylsodium, sodium isopropoxide, and sodium chloride. Because of their high molecular weight, Alfin rubbers were difficult to process, although gum and tread stocks showed good properties (64,65).

In the early 1960s dihydroaromatic compounds such as 1,4-dihydrobenzene and dihydronaphthalene were found to be effective in reducing the molecular weight of polybutadiene, without affecting the yield or the microstructure (66–69).

Progress was reported in the preparation of the Alfin catalyst and the control of molecular weight (70), but the competition from polybutadiene and polyisoprene rubbers obtained with the aid of Ziegler catalysts prevented commercialization.

Stereospecific Polymerization

As early as 1929, Staudinger and coworkers (71) had recognized that each of the propagation steps in the growth of a polymer chain could give rise to stereoisomerism. By controlling the conditions of polymerization, two types of polymers could be prepared (72–75), eg, from vinyl isobutyl ether (76,77): a tacky, rubberlike amorphous product (75) or a nontacky solid that exhibited a crystalline x-ray diffraction pattern in the unstretched state and a sharp fiber diagram on stretching. Polymer-solvent interactions were different for the crystalline and rubbery polymers (78).

A new era in the synthetic rubber industry began in the mid-1950s when Goodrich (79), Firestone (80), and Goodyear (81) announced the synthesis of high *cis*-1,4-polyisoprene with properties matching those of natural rubber (79–81). This development had been made possible by utilization of the new catalyst systems discovered by Ziegler (82,83) in 1953 for producing linear polyethylene under low pressure. At Goodrich-Gulf, isoprene polymerized with a combination of a trialkylaluminum and titanium tetrachloride produced a rubbery material (Ameripol SN), which virtually duplicated the natural rubber molecule in microstructure and physical characteristics (84).

At about the same time, scientists at Firestone (80,85) accomplished the same objective by means of a different catalyst, namely, lithium metal or alkyl-lithium, although the *cis*-1,4 content of their polyisoprene (Coral rubber) was slightly lower than that obtained with a Ti-Al catalyst. In addition, Ziegler and coworkers (86) had investigated the addition reaction of lithium and alkyl lithium compounds with butadiene, isoprene, piperylene, and 2,3-dimethylbutadiene. Other industrial laboratories developed similar or modified catalyst systems (87). Within a few years, following systematic investigations for *cis*-1,4-polyisoprene synthesis with a $R_3Al-TiCl_4$ catalyst system, the preparation of *cis*-1,4-polyisoprene (Natsyn) on large pilot plant scale was reported by The Goodyear Tire & Rubber Company (88–92). Shell Chemical Company began the first commercial production of *cis*-1,4-polyisoprene (Shell Isoprene Rubbers; Cariflex IR) in the United States in 1959, using an alkyl lithium catalyst. In 1962, Goodyear started the first commercial production of Natsyn polyisoprene based on a modified AlR_3-TiCl_4 catalyst. Poly(*N*-alkyliminoalanes) in combination with titanium tetrachloride produces gel-free high molecular weight polyisoprene with a *cis*-1,4 content of 94–97% (93).

Lithium and alkyl lithium catalysts capable of producing polyisoprene of very high (>90%) *cis*-1,4 content do not give the same degree of stereospecific control for butadiene. Mixed structures, *cis*-1,4, *trans*-1,4 and -1,2, are obtained. However, trialkylaluminum and titanium tetraiodide give high *cis*-1,4-polybutadiene (94) with at least 85% *cis*-1,4 content. High *cis*-1,4-polybutadiene (95,96) is also prepared with a heterogeneous catalyst system based on organoaluminum and cobalt compounds. Other systems employ homogeneous catalysts prepared

from alkylaluminum halides and cobalt salts (97–99). Commercial high *cis*-1,4-polybutadiene shows low glass-transition temperature (-100°C), high resilience, ability to be blended with GR-S (SBR) and NR, and good abrasion resistance of its carbon-black-reinforced vulcanizates (100).

A Japanese manufacturer uses a soluble, three-component catalyst system, for instance, trialkylaluminum–nickel octanoate (or nickel naphthenate) and a Lewis acid (eg, boron trifluoride etherate) (101). The high molecular weight *cis*-1,4-polybutadiene obtained has a broad molecular weight distribution, no gel, and about 98% *cis*-1,4 content.

The basic discovery of Ziegler and coworkers (82,83) for polymerizing ethylene to linear, high molecular weight products was extended by Natta and his group (102–104) and others for the synthesis of entirely new polymer structures. Although initial efforts were directed to the preparation of stereoregular, crystalline homopolymers of simple α -olefins, attention turned to the preparation of elastomeric copolymers because of the low cost of the lower olefins in unlimited supply. Furthermore, elastomers with superior chemical and aging resistance were expected because of the absence of unsaturation.

A sulfur-cross-linkable rubber was prepared by a Dunlop team with the synthesis of a dicyclopentadiene–ethylene–propylene terpolymer (105). Independently, DuPont scientists found (106) that 1,4-hexadiene was a suitable diene monomer. The catalyst systems employed for ethylene–propylene copolymers and terpolymers include vanadium oxychloride, VOCl_3 , which is stable and inexpensive. Ethylene–propylene rubbers are reviewed in Refs. 107–111. Ethylene–propylene–diene terpolymers (EPDM) were introduced in the 1960s (see ETHYLENE–PROPYLENE ELASTOMERS).

Thermoplastic elastomers of the type polystyrene–polydiene–polystyrene, ie, poly(styrene-*b*-diene-*b*-styrene), were developed in the 1960s by Shell Development Company (112–114) and Phillips Petroleum Company (115,116). Typical examples are triblock copolymers SBS and SIS, where S represents polystyrene hard block (glassy) and B and I are high 1,4-polybutadiene and high *cis*-1,4-polyisoprene soft blocks (rubbery), respectively. These thermoplastic elastomers, generally referred to as ABA block copolymers, combine the good properties of vulcanized rubbers with the processing characteristics of thermoplastics. Thus they exhibit high tensile strength without curing or reinforcing fillers. They show heterophase morphology due to incompatibility of polymer blocks and are not chemically cross-linked; their scrap can be reprocessed (see ELASTOMERS, THERMOPLASTIC).

The elastic behavior of polyester–polyurethane thermoplastic rubbers (Estane materials) has been correlated (117,118) with that of SBS block copolymers. The thermoplastic elastomer behavior of Estane polymers is due to the presence of hard and soft phases and not to hydrogen bonding.

Economic Aspects

The rubber industry has not been very profitable in the 1980s. However, there seem to be signs for improvement in business of this mature industry, but without an increase in demand for its products (119,120). Data on production

and consumption of rubber are compiled by the International Institute of Synthetic Rubber Producers (IISRP) with 51 synthetic rubber producers from non-Communist countries. These companies produce more than 95% of the world's synthetic rubber. The 5-year forecast for worldwide total rubber (synthetic plus natural) consumption, including that for centrally planned economy countries (CPEC) is expected to show a significant increase in demand during the 1987–1992 period, with consumption increasing from 14.4×10^6 to 15.9×10^6 t, reflecting an increase of about 11% (Tables 2 and 3). In 1987, global rubber consumption increased 3.3% over that in 1986.

Table 2. Worldwide Rubber-consumption Forecast by Region, 10^3 t^{a,b}

Region	1986	1987	1988	1992
<i>Synthetic rubber</i>				
North America	2,444	2,523	2,485	2,561
Western Europe, Africa, Middle East	1,923	1,969	2,000	2,117
Asia and Oceania	1,401	1,492	1,550	1,737
Latin America	538	541	559	648
<i>Total</i>	<i>6,306</i>	<i>6,525</i>	<i>6,594</i>	<i>7,063</i>
<i>Natural rubber</i>				
North America	840	872	861	871
Western Europe, Africa, Middle East	1,060	1,085	1,105	1,160
Asia and Oceania	1,497	1,567	1,618	1,804
Latin America	234	247	259	296
<i>Total</i>	<i>3,631</i>	<i>3,771</i>	<i>3,843</i>	<i>4,131</i>
<i>Total</i>				
North America	3,284	3,395	3,345	3,432
Western Europe, Africa, Middle East	2,983	3,054	3,105	3,277
Asia and Oceania	2,898	3,059	3,168	3,541
Latin America	772	788	818	944
<i>Grand total</i>	<i>9,937</i>	<i>10,296</i>	<i>10,437</i>	<i>11,194</i>

^a Ref. 119. Courtesy of the International Institute of Synthetic Rubber Producers, Inc., Houston, Tex.

^b Excluding centrally planned economy countries.

Synthetic rubber (SR) accounted for 67.9% of total rubber consumption in 1987. The 5-year forecast projects an increase in global consumption from 9.75×10^6 to 10.78×10^6 t. This share of synthetic rubber is expected to remain the same during this period (Table 3). Worldwide SR consumption increased 3.1% in 1987 over that in 1986. In non-Communist countries (non-CPEC) as a group, SR consumption in 1987 accounted for 63.4% of total new rubber. That share is expected to decline steadily to 63.1% by 1992, when SR consumption is projected to exceed 7×10^6 t and natural rubber (NR) to exceed 4.1×10^6 t. The long-term forecast for consumption of different types of rubbers for various regions of the non-Communist world is shown in Table 4. The total rubber consumption in all Communist countries is projected to increase 16% to 4.7×10^6 t in 1992 (Table 3). China and other Asian Communist countries, including Vietnam and North Korea, will consume more NR than SR; however, SR consumption is increasing at a steady rate so that the share of SR in terms of total rubber consumed is

Table 3. Rubber Consumption Forecast, 10³ t^a

Area	1986	1987	1988	1992
Non-CPEC ^b				
synthetic rubber	6,306	6,525	6,594	7,063
natural rubber	3,631	3,771	3,848	4,131
<i>Total</i>	<i>9,937</i>	<i>10,296</i>	<i>10,437</i>	<i>11,194</i>
% synthetic	63.5	63.4	63.2	63.1
Eastern Europe				
synthetic rubber	2,875	2,920	2,980	3,300
natural rubber	391	390	390	375
<i>Total</i>	<i>3,266</i>	<i>3,310</i>	<i>3,370</i>	<i>3,675</i>
% synthetic	88.0	88.2	88.4	89.8
China and Asian CPEC				
synthetic rubber	270	300	320	420
natural rubber	420	450	470	600
<i>Total</i>	<i>690</i>	<i>750</i>	<i>790</i>	<i>1,020</i>
% synthetic	39.1	40.0	40.5	41.2
Total CPEC				
synthetic rubber	3,145	3,220	3,300	3,720
natural rubber	811	840	860	975
<i>Total</i>	<i>3,956</i>	<i>4,060</i>	<i>4,160</i>	<i>4,695</i>
% synthetic	79.5	79.3	79.3	79.2
Total world				
synthetic rubber	9,451	9,745	9,894	10,783
natural rubber	4,442	4,611	4,703	5,106
<i>Total</i>	<i>13,893</i>	<i>14,356</i>	<i>14,597</i>	<i>15,889</i>
% synthetic	68.0	67.9	67.8	67.9

^a Ref. 119. Courtesy of the International Institute of Synthetic Rubber Producers, Inc., Houston, Tex.

^b CPEC, centrally planned economy countries.

expected to rise to 41% in 1992 from 40% in 1987 and 39% in 1986. In the USSR and Eastern Europe, SR consumption in 1987 accounted for 88% of the 3.31×10^6 t total new rubber. This share is expected to increase to 90% in 1992, with the consumption of SR rising from 2.92×10^6 t in 1987 to 3.3×10^6 t.

Styrene-butadiene rubber (SBR) will continue to be the largest-volume SR produced and consumed in non-Communist countries (Tables 4 and 5), whereas polybutadiene rubber (BR) ranks second.

Worldwide SR production by region (excluding CPEC) is shown in Table 6 and by type in Table 7 for the period 1977–1986. Whereas EPDM production in 1986 was 64% higher than in 1977, the situation for synthetic polyisoprene was just the opposite, decreasing by 66%. The annual U.S. production of various rubber types for the period 1977–1987 is shown in Table 8 (122).

Following the pattern of many years, tires and tire products constitute 50% of rubber consumption (Tables 9 and 10). Overall, the percentage of total synthetic rubber use for tire and tire products in the non-Communist world decreased from 53.5% in 1980 to 50.2% in 1985 and 43.1% in 1987. A similar decrease took place in the percentage of NR consumption. Both SBR and BR remain the workhorses of the tire industry; butyl rubbers are used in inner-tire lining and tire tubes, whereas synthetic polyisoprenes are used in blends with SBR, BR, and NR. No

Table 4. Long-term Rubber Consumption (10³ t) Forecast by Area and Type^{a,b}

Rubber	North America		Western Europe		Latin America		Asia and Oceania		Africa and Middle East		Total	
	1987	1992	1987	1992	1987	1992	1987	1992	1987	1992	1987	1992
styrene-butadiene ^c	839	833	727	745	329	386	674	783	63	72	2,632	2,819
carboxylated styrene-butadiene	447	458	335	370	21	29	125	152	5	6	933	1,015
polybutadiene	422	424	240	257	109	131	270	309	19	21	1,060	1,142
ethylene-propylene-diene	204	216	170	195	11	16	107	126	2	3	494	556
polychloroprene	86	85	81	77	19	23	68	78	5	5	259	268
nitrile	68	66	81	85	13	17	51	66	3	4	216	238
other synthetics ^d	457	479	216	244	39	46	197	223	22	33	931	1,025
<i>Total synthetic</i>	<i>2523</i>	<i>2561</i>	<i>1850</i>	<i>1973</i>	<i>541</i>	<i>648</i>	<i>1492</i>	<i>1737</i>	<i>119</i>	<i>144</i>	<i>6,525</i>	<i>7,063</i>
natural	872	871	945	980	247	296	1568	1804	140	180	3,771	4,131
<i>Total rubber</i>	<i>3395</i>	<i>3432</i>	<i>2460</i>	<i>2953</i>	<i>788</i>	<i>944</i>	<i>3060</i>	<i>3541</i>	<i>259</i>	<i>324</i>	<i>10,296</i>	<i>11,914</i>

^a Refs. 119–121. Source: International Institute of Synthetic Rubber Producers. Courtesy of *Chemical and Engineering News*, American Chemical Society.

^b Excluding centrally planned economy countries.

^c Solid and latex forms of SBR.

^d Includes polyisoprene and butyl.

Table 5. Worldwide Rubber-Consumption Forecast, 10³ t^{a,b}

Rubber	1986	1987	1988	1992
synthetic				
SBR				
solid	2,341	2,381	2,408	2,554
latex	242	251	252	265
carboxylated latex	886	933	941	1,015
polybutadiene	997	1,060	1,070	1,142 ^c
ethylene-propylene	465	494	501	556 ^d
polychloroprene	258	259	260	268 ^e
nitrile, solid and latex	205	216	226	238
others ^f	912	931	936	1,025
Total	6,306	6,525	6,594	7,063
natural rubber	3,631	3,771	3,843	4,131
Total new rubber	9,937	10,296	10,437	11,194
% synthetic	63.5	63.4	63.2	63.1

^a Ref. 119. Courtesy of the International Institute of Synthetic Rubber Producers, Inc.

^b Excluding centrally planned economy countries.

^c 7.7% increase over 1987.

^d 13% increase over 1987.

^e <4% increase over 1987.

^f Includes butyl and polyisoprene rubbers.

nitrile rubber is used in the manufacture of tires and tire products; the use of polychloroprene is restricted to North America. Synthetic rubber is extensively used in nontire automotive, industrial, agricultural, and household sectors in a wide variety of consumer products.

Consumption of SR on a per capita basis in the period 1976 through 1986 (123) was highest in the United States, followed by Belgium, Canada, and the FRG:

U.S.	>	Belgium	>	Canada	>	FRG
102.2 kg		91.2 kg		90.6 kg		75 kg

The People's Republic of China and India had the lowest per capita consumption, 1.6 and 0.78 kg, respectively, for the same period.

World synthetic rubber capacities (excluding specialty rubbers) are shown in Table 11 for various types of rubbers. On a worldwide basis, SBR (solid, latex, plus carboxy latex) capacity outweighs the combined capacity of all other rubbers, both for 1987 and 1989. The order of worldwide capacities for various rubbers for both years is as follows:

SBR >> BR > IR > EPDM > IIR > CR > NBR

The increase in exports, spurred by improvement in product quality and plant efficiency by producers, accounted for a substantial part of the recovery in output in 1987 for most synthetic rubber produced in the United States. Besides competition from imported fabricated products (eg, tires), few new products made from elastomers are reaching the market. Growth in U.S. consumption of rubber is expected to remain slow.

Table 6. World Rubber Statistics: Synthetic Rubber Production by Area, 10³ t^{a,b}

	1977	1979	1981	1982	1983	1984	1985	1986	% Change, 1986/1985
Western Europe	1516	1694	1482	1396	1471	1607	1616	1630	0.1
North America	2753	2836	2235	1780	1900	2116	1886	1938	2.7
Latin America	283	338	393	404	381	399	455	443	(2.6)
Asia and Oceania	1105	1299	1171	1043	1105	1275	1254	1298	3.5
<i>Total</i>	<i>5657</i>	<i>6167</i>	<i>5281</i>	<i>4623</i>	<i>4857</i>	<i>5397</i>	<i>5211</i>	<i>5309</i>	<i>1.9</i>

^a Ref. 121. Courtesy of the International Institute of Synthetic Rubber Producers, Inc.

^b Excludes carboxylated latices. South Africa included under Asia and Oceania during 1973–1978. South Africa included under Latin America starting in 1980. South Africa included under Western Europe starting in 1983.

Table 7. Synthetic Rubber Production by Type, 10³ t^{a,b}

Rubber	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	% Change, 1986/1985
SBR, solid	2856	2914	3002	2586	2490	2184	2258	2388	2284	2308	1.0
SBR, latex	370	402	428	310	294	254	255	285	289	292	.0
BR	899	923	979	895	917	829	903	1004	978	1015	3.7
IR	219	222	242	219	168	129	120	146	110	132	1.2
CR	332	320	364	316	312	281	292	310	321	314	(2.2)
EPDM	294	319	344	308	365	318	373	443	453	483	6.6
IIR	403	415	457	395	426	370	372	^c	^c	^c	^c
NBR	197	213	239	211	204	175	189	238	213	214	.0
others	87	102	112	107	105	83	92	583	563	550	(2.4)
<i>Total</i>	<i>5657</i>	<i>5830</i>	<i>6167</i>	<i>5347</i>	<i>5281</i>	<i>4623</i>	<i>4854</i>	<i>5397</i>	<i>5211</i>	<i>5309</i>	<i>1.9</i>

^a Ref. 121. Courtesy of the International Institute of Synthetic Rubber Producers, Inc.

^b Centrally planned economy countries are excluded. Latices are included, except for SBR.

^c Included in others.

Table 8. Synthetic Rubber Production in the United States, 1977–1987, 10³ t^a

Rubber	1987	1986	1985	1984	1983	1982	1981	1980	1979	1978	1977	Annual change, %	
												1986–1987	1977–1987
styrene–butadiene rubber	850	792	735	958	904	876	1032	1074	1378	1395	1395	7	–5
polybutadiene	371	336	330	359	333	288	342	311	397	378	361	10	0
nitrile	69	59	53	67	55	45	66	63	75	73	70	17	0
ethylene–propylene	254	230	215	215	175	123	178	144	175	174	158	10	5
other ^b	638	596	505	556	468	498	404	423	509	453	432	7	4
<i>Total</i>	<i>2182</i>	<i>2013</i>	<i>1838</i>	<i>2155</i>	<i>1935</i>	<i>1830</i>	<i>2022</i>	<i>2015</i>	<i>2534</i>	<i>2473</i>	<i>2416</i>	<i>8</i>	<i>–1</i>

^a Ref. 122. Source: Rubber Manufacturers Association. Courtesy of *Chemical and Engineering News*, The American Chemical Society.

^b Includes butyl, polychloroprene, polyisoprene, silicone, and other synthetic elastomers. Some values are estimated.

Table 9. Rubber Consumption in Tire and Tire Products in 1987, %^{a,b}

Rubber	Western Europe	North America	Asia and Oceania	Latin America	Africa and Middle East	Weighted average
synthetic						
SBR solid	67.0	72.5	62.3	65.4	70.0	66.8
SBR latex	5.0	11.5	6.2	33.5	2.4	8.0
polybutadiene	72.0	73.9	54.7	81.0	80.0	66.8
ethylene-propylene	0.0	4.4	8.4	14.0	0.0	4.0
chloroprene	0.0	3.6	0.0	0.0	0.0	0.0
nitrile	0.0	0.0	0.0	0.0	0.0	0.0
other synthetics ^c	56.1	37.3	65.8	85.5	40.0	51.1
<i>Total synthetics</i>	<i>35.3</i>	<i>43.0</i>	<i>44.4</i>	<i>62.0</i>	<i>53.8</i>	<i>43.1</i>
natural rubber	66.0	72.3	50.1	77.3	66.0	61.6
<i>Total rubber</i>	<i>45.0</i>	<i>50.4</i>	<i>47.3</i>	<i>66.8</i>	<i>60.2</i>	<i>49.9</i>

^a Ref. 119. Courtesy of the International Institute of Synthetic Rubber Producers, Inc.

^b Excluding centrally planned economy countries.

^c Includes butyl and polyisoprene.

Table 10. Worldwide Tire and Tire Product Rubber Consumption by Polymer Type, Weighted Average, %^{a,b}

Rubber	1980	1985	1987
styrene-butadiene, solid	65.3	69.9	66.8
styrene-butadiene, latex	3.3	6.1	8.0
polybutadiene	77.8	74.9	66.8
ethylene-propylene	6.5	4.3	4.0
polychloroprene	1.1	0.0	0.0
nitrile	0.0	0.0	0.0
other synthetic ^c	N.A.	62.5	51.1
<i>Total synthetic</i>	<i>53.5</i>	<i>50.2</i>	<i>43.1</i>
natural	68.0	67.6	61.6
<i>Total rubber</i>	<i>58.5</i>	<i>59.8</i>	<i>49.9</i>

^a Ref. 121. Courtesy of the International Institute of Synthetic Rubber Producers, Inc.

^b Excluding centrally planned economy countries.

^c Includes polyisoprene and butyl rubber.

Product development in elastomers, particularly solution rubbers, is continuing, particularly in the United States, Japan, West Germany, Italy, and the United Kingdom. Increasingly, SBR is being adapted to solution polymerization techniques to provide a combination of low rolling resistance and high wet traction for passenger tire treads, features that have not been attainable by the widely accepted emulsion SBR without sacrificing good wear (abrasion resistance). At present, solution SBR probably accounts for less than 15% of total production of SBR in the United States. The widely used anionic polymerization techniques (124) permit control of copolymer composition and comonomer sequence distribution for styrene/butadiene, butadiene microstructure, *trans*-1,4/*cis*-1,4 ratio at constant vinyl content, molecular weight, and molecular weight distribution and chain architecture (linear or star).

Table 11. World Synthetic Rubber Capacities, 10³ t^{a,b}

Country or area	SBR-solid		SBR-rubber latex		SBR-carboxy latex		BR	
	1987	1989	1987	1989	1987	1989	1987	1989
Austria					6	6		
Belgium							65	65
Finland					7	65		
France	205	205	44	44	86	86	190	190
FRG	170	170	62	62	140	140	70	70
Italy	205	205	35	35	55	55	50	50
Netherlands	150	150	23	23	65	65		
South Africa	58	58	8	8	7	7	18	18
Spain	60	60			21	21	20	20
Sweden					32	32		
Turkey	32	32					14	14
United Kingdom	165	165	55	55	81	81	60	60
<i>Total Western Europe, Middle East, and Africa</i>	<i>1045</i>	<i>1045</i>	<i>227</i>	<i>227</i>	<i>500</i>	<i>565</i>	<i>487</i>	<i>487</i>
United States	976	976	74	74	447	462	403	423
Canada	20	20	19	19	37	37	63	63
<i>Total North America</i>	<i>996</i>	<i>996</i>	<i>93</i>	<i>93</i>	<i>484</i>	<i>499</i>	<i>466</i>	<i>486</i>
Argentina	54	54	12	5	6	9		
Brazil	246	286	4	4	21	23	55	68
Mexico	111	125	4	4	7	7	45	53
<i>Total Latin America</i>	<i>411</i>	<i>465</i>	<i>20</i>	<i>13</i>	<i>34</i>	<i>39</i>	<i>100</i>	<i>121</i>
Australia	3	35	4	4	12	17	10	10
India	39	50	1	1			20	20
Japan	680	680	85	85	137	137	258	258
Korea	155	155	15	20		20	30	55
Republic of China	120	120	18	18	8	8	40	40
<i>Total Asia and Oceania</i>	<i>1029</i>	<i>1040</i>	<i>123</i>	<i>128</i>	<i>157</i>	<i>182</i>	<i>358</i>	<i>383</i>
<i>Total Non-CPEC^c</i>	<i>3481</i>	<i>3546</i>	<i>463</i>	<i>461</i>	<i>1175</i>	<i>1285</i>	<i>1411</i>	<i>1477</i>
CPEC	1444	1549	161	171	^d	^d	400	420
<i>Grand Total World</i>	<i>4925</i>	<i>5095</i>	<i>624</i>	<i>632</i>	<i>1175</i>	<i>1285</i>	<i>1811</i>	<i>1897</i>

^a Ref. 121. Courtesy of the International Institute of Synthetic Rubber Producers, Inc.^b Excluding specialty rubbers.^c CPEC, centrally planned economy countries.^d Carboxylated latex included with SBR latex.

BIBLIOGRAPHY

"Elastomers, Synthetic" in *EPST* 1st ed., Vol. 5, pp. 406–482, by W. Cooper, Dunlop Rubber Company, Ltd.

1. P. J. Flory, ed., *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N.Y., 1953.
2. H. F. Mark, *Rubber Chem. Technol.* **61**(3), G73 (1988).
3. L. R. G. Treloar, ed., *The Physics of Rubber Elasticity*, 3rd ed., Clarendon, Oxford, UK, 1975.
4. J. E. Mark, *J. Chem. Educ.* **58**, 898 (1981).
5. *Compilation of ASTM Standards Definitions*, sponsored by ASTM Committee E8, ASTM, Philadelphia, Pa., 1976.
6. ASTM D2731, D-13; D2653, D-13; D2591, D-13; D1775, D13, American Society for Testing and Materials, Philadelphia, Pa.
7. ASTM D907, D-14, American Society for Testing and Materials, Philadelphia, Pa.
8. G. Natta, G. Dall'Asta, and G. Mazzanti, *Angew. Chem.* **76**, 765 (1964); *Angew. Chem. Int. Ed.* **3**, 723 (1964).

IR		EDPM		IIR		CR		NBR-solid latex		Total all types	
1987	1989	1987	1989	1987	1989	1987	1989	1987	1989	1987	1989
				85	85					6	6
										150	150
										7	65
		65	65	48	48	40	40	41	41	719	719
		41	41			60	60	48	49	591	592
		60	60					45	45	450	450
40	40	55	70					50	50	383	398
45	45									136	136
										101	101
										32	32
										46	46
		15	15	60	60	33	33	16	16	485	485
85	85	236	251	193	193	133	133	200	201	3,106	3,187
68	68	270	296	219	219	163	163	113	115	2,733	2,796
				120	120			25	25	284	284
68	68	270	296	339	339	163	163	138	140	3,017	3,080
								2	2	74	74
	13	10	10					14	23	350	427
								3	3	170	192
	13	10	10					19	28	594	687
										61	66
								2	2	62	73
67	67	135	165	75	75	75	85	75	75	1,587	1,627
		10	10					5	5	215	265
			10					16	19	202	215
67	67	145	185	75	75	75	85	98	101	2,014	2,246
220	233	661	742	607	607	371	381	455	470	8,844	9,200
1045	1045	120	150	120	210	200	220	89	95	3,579	3,860
1265	1278	781	892	727	817	571	601	544	565	12,423	13,062

9. *The Synthetic Rubber Manual*, 10th ed., International Institute of Synthetic Rubber Producers Inc., Houston, Tex., 1986.
10. *Rubbers and Latexes Nomenclature*, ISO Standard 1629, American National Standards Institute, New York, 1976; D1418-85, ASTM, Philadelphia, Pa., 1985.
11. H. Feurberg, *J. Polym. Sci. Polym. Lett. Ed.* **22**, 413 (1984).
12. N. M. Bikales and coworkers, *Macromolecules* **1**, 193 (1968).
13. R. B. Fox, *J. Chem. Ed.* **51**, 113 (1974).
14. Nomenclature of Regular Single-Strand Organic Polymers, *IUPAC Information Bull.* **29** (November 1972); *Macromolecules* **6**, 149 (1973).
15. M. L. Huggins, G. Natta, V. Desreux, and H. Mark, *J. Pure Appl. Chem.* **12**, 645 (1966).
16. K. L. Loening and co-workers, *J. Pure Appl. Chem.* **48**, 373 (1976).
17. U.S. Pat. 3,315,688 (June 2, 1970), S. H. Rose (to Horizon Research).
18. H. R. Allcock, *Angew. Chem. Int. Ed.* **16**, 147 (1977).
19. R. E. Singler, G. L. Hagnauer, and R. W. Sicka in J. E. Mark and J. Lal, eds. *Elastomers and Rubber Elasticity*, ACS Symposium, Series no. 193, American Chemical Society, Washington, D.C., 1982, Chapt. 11.

20. D. F. Lohr and J. A. Beckman, *Paper No. 34, 120th Meeting of Rubber Division, American Chemical Society, Cleveland, Ohio, Oct. 1981.*
21. D. F. Lohr and H. Penton in A. K. Bhowmick and H. L. Stephens, eds., *Handbook of Elastomers: New Developments and Technology*, Marcel Dekker, New York, 1988, Chapt. 16.
22. G. S. Kyker and T. A. Antkowiak, *Rubber Chem. Technol.* **47**, 32 (1974).
23. J. C. Caprino and R. F. Macander in M. Morton, ed., *Rubber Technology*, 3rd ed., Van Nostrand Reinhold Co., New York, 1987, Chapt. 13.
24. A. J. Barry and H. N. Beck in G. A. Stone and W. A. G. Graham, eds., *Inorganic Polymers*, Academic Press, New York, 1962, Chapt. 5.
25. R. West, *J. Organometal. Chem.* **300**, 327 (1986); *L'actualite Chimique*, 64 (Mar. 1986).
26. R. West, personal communication.
27. G. S. Whitby, ed., *Synthetic Rubber*, John Wiley & Sons, Inc., New York, 1954.
28. E. G. M. Törnqvist in J. P. Kennedy and E. G. M. Törnqvist, eds., *Polymer Chemistry of Synthetic Elastomers, Part 1*, Wiley-Interscience, New York, 1968, Chapt. 2.
29. M. Morton, *J. Macromol. Sci. Chem.* **A15**(7), 1289 (1981).
30. S. E. Horne, Jr., *paper presented at the Rubber Division American Chemical Society Meeting, Philadelphia, Pa., August 30, 1984; Rubber World*, Rubber Division 75th Anniversary Issue (1984).
31. H. Morawetz, ed., *Polymers: The Origins and Growth of a Science*, Wiley-Interscience, New York, 1985.
32. Br. Pat. 24,790 (filed Oct. 25, 1910; issued Oct. 25, 1911), F. E. Mathews and E. H. Strange; *Chem. Abstr.* **6**, 1542 (1912); Ger. Pat. 249,868 (July 30, 1912).
33. C. D. Harries, *Ann.* **383**, 184 (1911); *Ann.* **395**, 211 (1913); U.S. Pat. 1,058,056 (filed Nov. 4, 1911; issued Apr. 8, 1913) (to Farbenfabr. vorm. F. Bayer & Co.).
34. S. V. Lebedev and B. K. Merezhkovskii, *J. Russ. Phys. Chem. Soc.* **45**, 1249 (1913).
35. H. Staudinger, *Ber. Dtsch. Chem. Ges.* **53**, 1073 (1920); H. Staudinger and J. Fritsch, *Helv. Chim. Acta* **5**, 785 (1922).
36. U.S. Pat. 1,864,078 (filed Jan. 8, 1927; issued June 21, 1932); Ger. Pat. 558,890; U.S. Pat. 1,896,491 (filed Feb. 8, 1928; issued Feb. 7, 1933), M. Luther and C. Heuck (to I. G. Farbenindustrie); U.S. Pat. 1,924,227 (filed Sept. 21, 1928; issued Aug. 29, 1933); Ger. Pat. 558,585; U.S. Pat. 1,898,522 (filed Jan. 15, 1930; issued Feb. 21, 1933), W. Bock and E. Tschunkur (to I. G. Farbenindustrie).
37. Br. Pat. 292,103 (filed Jan. 13, 1927; issued Aug. 29, 1929) (to I. G. Farbenindustrie).
38. Ger. Pat. 570,980 (filed July 20, 1929; issued Feb. 27, 1933); U.S. Pat. 1,938,731 (Dec. 12, 1933), E. Tschunkur and W. Bock (to I. G. Farbenindustrie).
39. Ger. Pat. 658,172 (filed April 20, 1931; issued March 25, 1938); U.S. Pat. 1,973,000 (Sept. 11, 1934), E. Konrad and E. Tschunkur (to I. G. Farbenindustrie).
40. U.S. Pat. 1,890,191 (filed Dec. 13, 1927; issued Dec. 6, 1932), J. C. Patrick (to Thiokol); Br. Pat. 302,270 (filed Dec. 13, 1927; issued Aug. 15, 1929), J. C. Patrick and N. M. Mnookin (to Thiokol).
41. Swiss Pat. 127,540 (filed Oct. 20, 1926; issued Sept. 1, 1928); Br. Pat. 279,406 (June 28, 1928); Ger. Pat. 526,121 (filed June 30, 1928; issued June 2, 1931), J. Baer.
42. R. H. Gobran and M. B. Berenbaum in J. P. Kennedy and E. G. M. Törnqvist, eds., *Polymer Chemistry of Synthetic Elastomers, Part 2*, Wiley-Interscience, New York, 1968, Chapt. 8C.
43. U.S. Pat. 1,950,431 (filed Oct. 22, 1930; issued March 13, 1934), W. H. Carothers and A. M. Collins (to DuPont).
44. W. H. Carothers, I. Williams, A. M. Collins, and J. E. Kirby, *J. Am. Chem. Soc.* **53**, 4203 (1931).
45. A. M. Collins, *Rubber Chem. Technol.* **46**, G45 (1973).
46. C. A. Hargreaves, II, in Ref. 28, Part 1, Chapt. 4C.
47. P. R. Johnson, *Rubber Chem. Technol.* **40**, 650 (1976).
48. U.S. Pat. 2,356,127 (filed Dec. 29, 1937; issued Aug. 22, 1944), R. M. Thomas and W. J. Sparks (to JASCO).
49. U.S. Pat. 2,243,658 (filed Oct. 2, 1937; issued May 27, 1941), R. M. Thomas and O. C. Slotterbeck (to Standard Oil Development Company).
50. U.S. Pat. 2,356,128 (Aug. 22, 1944), R. M. Thomas and W. J. Sparks (to JASCO).
51. U.S. Pat. 2,356,129 (filed Aug. 30, 1941; issued Aug. 22, 1944), W. J. Sparks and R. M. Thomas (to JASCO).

52. R. M. Thomas, I. E. Lightbown, W. J. Sparks, P. K. Frolich, and E. V. Murphree, *Ind. Eng. Chem.* **32**, 1283 (1940).
53. R. F. Dunbrook in Ref. 27, Chapt. 2.
54. J. W. Livingston and J. T. Cox, Jr. in Ref. 27, Chapt. 7.
55. M. Morton and P. P. Salatiello, *J. Polym. Sci.* **6**, 225 (1951).
56. G. H. Swart, E. S. Pfau, and K. V. Weinstock, *India Rubber World* **124**(3), 309 (1951).
57. U.S. Pat. 2,964,083 (filed Nov. 20, 1950; issued Dec. 13, 1960), E. S. Pfua, G. H. Swart, and K. V. Weinstock (to General Tire & Rubber Company).
58. Ger. Pat. 728,981 (1942), O. Bayer, H. Rinke, W. Siefken, L. Orhner, and H. Schild (to Farbenfabriken Bayer).
59. J. H. Saunders and K. C. Frisch, eds., *Polyurethanes: Chemistry and Technology*, Vol. I, Wiley-Interscience, New York, 1962; Vol. II, 1964.
60. J. H. Saunders in Ref. 42, Part 2, Chapt. 8.
61. A. A. Morton, E. E. Magat, and R. L. Letsinger, *J. Am. Chem. Soc.* **69**, 950 (1947).
62. A. A. Morton, *Ind. Eng. Chem.* **42**, 1488 (1950); reprinted in *Rubber Chem. Technol.* **24**, 35 (1951).
63. A. A. Morton, *Rubber Age* **72**, 473 (1953).
64. J. D. D'Ianni, *Ind. Eng. Chem.* **40**, 253 (1948); J. D. D'Ianni, F. J. Naples, and J. E. Field, *Ind. Eng. Chem.* **42**, 95 (1950).
65. R. A. Stewart and H. L. Williams, *Ind. Eng. Chem.* **45**, 173 (1953).
66. Br. Pat. 943,625 (1953) (to National Distillers and Chemical Corporation).
67. V. L. Hansley and H. Greenberg, *Rubber Age* **94**, 87 (1963); *Rubber Chem. Technol.* **38**, 103 (1965).
68. U.S. Pat. 3,067,187 (Dec. 4, 1962), H. Greenberg and V. L. Hensley (to National Distillers and Chemical Corp.); Ger. Pat. 1,133,555 (July 19, 1962), H. Greenberg and V. L. Hensley.
69. H. Greenberg and L. Grininger, *Macromolecular Synthesis* **3**, 117 (1968).
70. U.S. Pat. 3,380,984 (filed Nov. 1, 1963; issued April 30, 1968) W. R. Birchall and E. A. Allgeier (to National Distillers and Chemical Corporation).
71. H. Staudinger, A. A. Ashdown, M. Brunner, H. A. Bruson, and S. Wehrli, *Helv. Chem. Acta.* **12**, 934 (1929).
72. C. E. Schildknecht, A. O. Zoss, and C. McKinley, *Ind. Eng. Chem.* **39**, 180 (1947).
73. C. E. Schildknecht, S. T. Gross, H. R. Davidson, J. M. Lambert, and A. O. Zoss, *Ind. Eng. Chem.* **40**, 2104 (1948).
74. C. E. Schildknecht, S. T. Gross, and A. O. Zoss, *Ind. Eng. Chem.* **41**, 1998 (1949).
75. C. E. Schildknecht, A. O. Zoss, and F. Grosser, *Ind. Eng. Chem.* **41**, 2891 (1949).
76. C. E. Schildknecht, ed., *Vinyl and Related Polymers*, John Wiley & Sons, Inc., New York, 1952.
77. J. Lal in Ref. 28, Part 1, Chapt. 5B.
78. M. S. Muthana and H. Mark, *J. Polym. Sci.* **4**, 531 (1949).
79. *Chem. Eng. News* **32**, 4913 (Dec. 13, 1954); **33**, 3472 (1955); U.S. Pat. 3,144,743 (filed Dec. 2, 1954; issued Dec. 17, 1963), S. E. Horne, Jr. (to Goodrich-Gulf Chem. Co. Inc.); Belg. Pat. 543,292 (Dec. 2, 1955); Br. Pat. 827,365 (filed Dec. 2, 1954; issued April 21, 1955), S. E. Horne, Jr., C. F. Gibbs, and E. J. Carlson (to Goodrich-Gulf Chem. Co. Inc.); S. E. Horne, Jr., J. P. Kiehl, J. J. Shipman, V. L. Folt, C. F. Gibbs, E. A. Wilson, E. B. Newton, and M. A. Reinhart, *Ind. Eng. Chem.* **48**, 784 (1956); paper presented at the Div. Rubber Chem., Am. Chem. Soc., Philadelphia, Pa., Nov. 1955.
80. *Chem. Eng. News* **33**, 3553 (Aug. 29, 1955); **33**, 3716 (Sept. 5, 1955); **33**, 5026 (Nov. 21, 1955); F. W. Stavely and coworkers, *Ind. Eng. Chem.* **48**, 778 (1956), presented at the Div. Rubber Chem., Am. Chem. Soc., Philadelphia, Pa., Nov. 1955; F. W. Stavely, *Rubber Chem. Technol.* **45**, G53 (1972).
81. *Chem. Eng. News* **33**, 4518 (Oct. 24, 1955).
82. U.S. Pat. 3,257,332 (filed Nov. 15, 1954; issued June 21, 1956), K. Ziegler, H. Breil, E. Holzkamp, and H. Martin (to K. Ziegler).
83. K. Ziegler, E. Holzkamp, H. Breil, and H. Martin, *Angew. Chem.* **67**, 426, 541 (1955); K. Ziegler, *Rubber Chem. Technol.* **38**(1), xxiii (1965); *Angew. Chem.* **76**, 545 (1964).
84. S. E. Horne, Jr., *Rubber Chem. Technol.* **53**, G68 (1968).
85. L. E. Forman in Ref. 42, Part 2, Chapt. 6.

86. K. Ziegler, F. Dersch, and H. Wollthan, *Ann. Chem.* **511**, 13 (1934); K. Ziegler and L. Jakob, *Ann.* **511**, 45 (1934); K. Ziegler, L. Jakob, H. Wollthan, and A. Wenz, *Ann.* **511**, 64 (1934); K. Ziegler, *Angew. Chem.* **49**, 499 (1936); K. Ziegler, H. Grimm, and R. Willer, *Ann.* **542**, 90 (1940).
87. A. A. Krotkov and co-workers, *Dokl. Nauk SSSR* **110**, 89 (1956); R. Ulrich, *Gummi Asbest.* **11**(5), 303 (1958); I. V. Garmanov, *Int. Symp. on Isoprene Rubber*, Nov. 22–24, 1972, Moscow.
88. W. M. Saltman, W. E. Gibbs, and J. Lal, *J. Am. Chem. Soc.* **80**, 5615 (1958).
89. U.S. Pat. 3,047,559 (July 31, 1962), R. H. Mayor, R. Leshin, and B. Wargotz (to The Goodyear Tire & Rubber Co.).
90. E. Schoenberg, D. L. Chalfant, J. B. Pyke, and R. H. Mayor, *paper presented at the Division of Industrial and Engineering Chemistry, American Chemical Society, New York Meeting*, Sept. 11, 1963.
91. E. Schoenberg, H. A. Marsh, S. J. Walters, and W. M. Saltman, *Rubber Chem. Technol.* **52**, 526 (1979).
92. C. T. Winchester, *Ind. Eng. Chem.* **51**, 19 (1959).
93. A. Mazzei, S. Cucinella, and W. Marconi, *Makromol. Chem.* **122**, 168 (1969).
94. *The Wall Street Journal*, East Ed. (April 26, 1956); Br. Pat. 848,065 (April 16, 1956) (to Phillips Petroleum Company); U.S. Pat. 3,050,513 (April 20, 1956), D. R. Smith and R. P. Zelinsky; Belg. Pat. 551,851 (filed Oct. 17, 1956; issued April 30, 1956).
95. U.S. Pat. 3,135,725 (filed May 31, 1957; issued June 2, 1964), E. J. Carlson and S. E. Horne, Jr. (to Goodrich-Gulf Chem. Co. Inc.).
96. Belg. Pat. 543,292 (1955) (to Goodrich-Gulf Chem. Co.).
97. S. E. Horne, Jr., R. G. Minchak, and H. Tucker, *paper presented at the Div. Ind. Eng. Chem.*, 1963.
98. G. Natta and L. Porri, in Ref. 42, Part 2, Chapt. 7A.
99. Belg. Pat. 573,680 (Dec. 6 and 24, 1957) (to Montecatini SpA).
100. J. N. Short, G. Kraus, R. P. Zelinsky, and F. E. Naylor, *S.P.E. Papers* **5**, 8 (1959).
101. U.S. Pats. 3,170,904, 3,170,905, 3,170,906, and 3,170,907 (Feb. 23, 1965), K. Ueda and co-workers (to Bridgestone Tire & Rubber Co.); U.S. Pat. 3,178,403 (Apr. 13, 1965), K. Ueda and co-workers (to Bridgestone Tire & Rubber Co.).
102. G. Natta, *Science* **147**, 261 (1965); *Rubber Chem. Technol.* **38**, xxxvii (1965); *Angew. Chem.* **76**, 553 (1964); *Chim. Ind. (Milan)* **46**, 397 (1964); G. Natta, A. Valvassori, and G. Sartori in Ref. 42, Part 2, Chapt. 7B.
103. Ital. Pat. 563,508 (April 20, 1956), G. Natta, G. Mazzanti, and M. Bruzzone (to Montecatini); Ital. Pat. 564,806 (April 20, 1956), G. Natta, M. Bruzzone, and G. Bonsini (to Montecatini); G. Natta, G. Crespi, and M. Bruzzone, *Chim. Ind. Milan* **42**, 463 (1960).
104. G. Natta, G. Crespi, E. DiGiulio, G. Ballini, and M. Bruzzone, *2nd International Synthetic Rubber Symposium*, London, October 11–13, 1961, Lecture N.13.
105. Br. Pat. 880,904 (filed July 17, 1957, Nov. 16, 1957; issued Oct. 25, 1961), S. Adamak, E. Dudley, and R. T. Woodhams (to Dunlop Rubber Co. Ltd.).
106. U.S. Pat. 2,933,480 (filed June 17, 1959; issued April 19, 1960), W. F. Gresham and M. Hunt (to E. I. du Pont de Nemours & Co.).
107. M. Bruzzone in S. Carra, F. Parisi, I. Pasquon, and P. Pino, eds., *G. Natta: Present Significance of His Scientific Contribution*, Editrice Di Chimica, Milan, Italy, 1982, pp. 68–124.
108. G. Natta, A. Valvassori, and G. Sartori, in Ref. 42, Part 2, Chapt. 7B.
109. G. Crespi, A. Valvassori, and U. Flisi in W. M. Saltman, ed., *The Stereo Rubbers*, Wiley-Interscience, New York, 1977, Chapt. 7.
110. F. P. Baldwin and G. Ver Strate, *Rubber Chem. Technol.* **45**(3), 709 (1972).
111. S. Cesca, *Macromol. Rev.* **10**, 1 (1975).
112. U.S. Pat. 3,265,765 (filed Jan. 29, 1962; issued Aug. 9, 1966), G. Holden and R. Milkovich (to Shell Oil Co.); S. Afr. Pat. 642,271 (1964), R. Milkovich (to Shell Oil Co.).
113. Br. Pat. 1,035,873 (1966), R. Milkovich, G. Holden, E. T. Bishop, and W. R. Hendericks (to Shell Oil Co.); U.S. Pat. 3,231,635 (Jan. 25, 1966).
114. N. R. Legge, *Rubber Chem. Technol.* **60**, G79 (1987); *Rubber & Plastics News*, 23 (May 15, 1989).
115. Br. Pat. 895,980 (filed May 11, 1959; issued May 9, 1962) (to Phillips Petroleum Co.).
116. U.S. Pat. 3,287,333 (filed Dec. 26, 1961; issued Nov. 22, 1966), R. P. Zelinsky (to Phillips Petroleum Co.).

117. S. L. Cooper and A. V. Tobolsky, *J. Appl. Polym. Sci.* **10**, 1837 (1966); *Textile Res. J.* **36**(9), 800 (1966).
118. U.S. Pat. 2,871,218 (filed Dec. 1, 1955; issued Jan. 27, 1959), C. S. Schollenberger (to BF Goodrich Co.); *Tech. Bull. Estane Sheet and Film*, BF Goodrich Co., Nov. 1964.
119. W. E. Tessmer, *Five-year Forecast for Global Synthetic Rubber Consumption*, International Institute of Synthetic Rubber Producers, Inc., Houston, Tex., February 23, 1988.
120. B. F. Greek, *Chem. Eng. News* **66**(12), 25 (March 21, 1988).
121. *Worldwide Rubber Statistics*, International Institute of Synthetic Rubber Producers, Inc., Houston, Tex., 1988.
122. *Chem. Eng. News* **66**(25), 42 (1988).
123. Ref. 121, Table 16.
124. S. L. Aggarwal, I. G. Hargiss, R. A. Livigni, R. J. Fabris, and L. F. Marker in J. Lal and J. E. Mark, eds., *Advances in Elastomers and Rubber Elasticity*, Plenum Press, 1986, pp. 17-36.

JOGINDER LAL
Lal Associates

ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING

VOLUME 5

**Dielectric Heating
to
Embedding**

A WILEY-INTERSCIENCE PUBLICATION

John Wiley & Sons

NEW YORK • CHICHESTER • BRISBANE • TORONTO • SINGAPORE

Copyright © 1986 by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

Reproduction or translation of any part of this work beyond that permitted by Section 107 or 108 of the 1976 United States Copyright Act without the permission of the copyright owner is unlawful. Requests for permission or further information should be addressed to the Permissions Department, John Wiley & Sons, Inc.

Library of Congress Cataloging in Publication Data:

Main entry under title:

Encyclopedia of polymer science and engineering.

Rev. ed. of: Encyclopedia of polymer science and technology. 1964—

"A Wiley-Interscience publication."

Includes bibliographies.

1. Polymers and polymerization—Dictionaries.

I. Mark, H. F. (Herman Francis), 1895—

II. Kroschwitz, Jacqueline I. III. Encyclopedia of polymer science and technology.

TP1087.E46 1985 668.9 84-19713

ISBN 0-471-88098-1 (v. 5)

Printed in the United States of America

ELASTOMERS, THERMOPLASTIC

Thermoplastic elastomers were introduced about 1960. They have many of the physical properties of rubbers, ie, softness, flexibility, and resilience, but in contrast to conventional rubbers, they are processed as thermoplastics. Rubbers must be cross-linked to give useful properties (see VULCANIZATION). In the terminology of the plastics industry, vulcanization is a thermosetting process. Like other thermosetting processes, it is slow and irreversible and takes place upon heating. With thermoplastic elastomers, on the other hand, the transition from a processible melt to a solid, rubberlike object is rapid and reversible and takes place upon cooling. Thermoplastic elastomers can be processed on conventional plastics equipment, such as injection molders; scrap is usually recycled.

Because of increased production and the lower cost of raw material, thermoplastic elastomeric materials are a significant and growing part of the total plastics market (1). However, because the melt to solid transition is reversible, some properties of thermoplastic elastomers, eg, compression set, solvent resistance, and resistance to deformation at high temperatures, are usually not as good as those of the corresponding vulcanizates. Applications of thermoplastic elastomers are therefore in areas where these properties are less important, eg, footwear, wire insulation, adhesives, polymer blending, and not in areas such as automobile tires (qv).

The classification given in Table 1 is based on the process, ie, thermosetting or thermoplastic, by which the polymer is formed into useful articles and the mechanical properties, ie, rigid, flexible, or rubbery, of the final product. All commercial polymers used for molding, extrusion, etc, fit into one of these six classifications; the thermoplastic elastomers are the newest.

Table 1. Classification of Polymers

Properties	Thermoset	Thermoplastic
rigid	epoxy resins, melamine-formaldehyde resins, sheet-molding compounds (SMC)	polypropylene (PP), high density polyethylene (HDPE), polystyrene (PS)
flexible	highly vulcanized rubber	low density polyethylene (LDPE), ethylene-vinyl acetate copolymer (EVA), plasticized poly(vinyl chloride) (PVC)
rubber	vulcanized rubber	thermoplastic elastomers

Structure

Thermoplastic elastomers are multiphase compositions in which the phases are intimately dispersed. In many cases, the phases are chemically bonded by block or graft copolymerization. In others, a fine dispersion is apparently sufficient. At least one phase consists of a material that is hard at room temperature but fluid upon heating. Another phase consists of a softer material that is rubberlike at RT. A simple structure is an A—B—A block copolymer, where A is a hard phase and B an elastomer, eg, poly(styrene-*b*-elastomer-*b*-styrene).

Most polymers are thermodynamically incompatible with other polymers, and mixtures separate into two phases (see COMPATIBILITY). This is true even when the polymeric species are part of the same molecule, as in these block copolymers. Poly(styrene-*b*-elastomer-*b*-styrene) copolymers, in which the elastomer is the main constituent, should have a structure similar to that shown in Figure 1. Here, the polystyrene end segments form separate spherical regions, ie, domains, dispersed in a continuous elastomer phase. Most polymer molecules have end polystyrene segments in different domains. At RT, these polystyrene domains are hard and act as physical cross-links, tying the elastomer chains together in a three-dimensional network. In some ways, this is similar to the network formed by vulcanizing conventional rubbers using sulfur cross-links. The main difference is that in thermoplastic elastomers, the domains lose their strength when the material is heated or dissolved in solvents. This allows the polymer or its solution to flow. When the material is cooled down or the solvent is evaporated, the domains harden and the network regains its original integrity. This explanation of the properties of thermoplastic elastomers has been given in terms of a poly(styrene-*b*-elastomer-*b*-styrene) block copolymer, but it would apply to any block copolymer with the structure A—B—A or (A—B)_n. In principle, A can be any polymer normally regarded as a hard thermoplastic, eg, polystyrene, poly(methyl methacrylate), polypropylene, and B can be any polymer normally

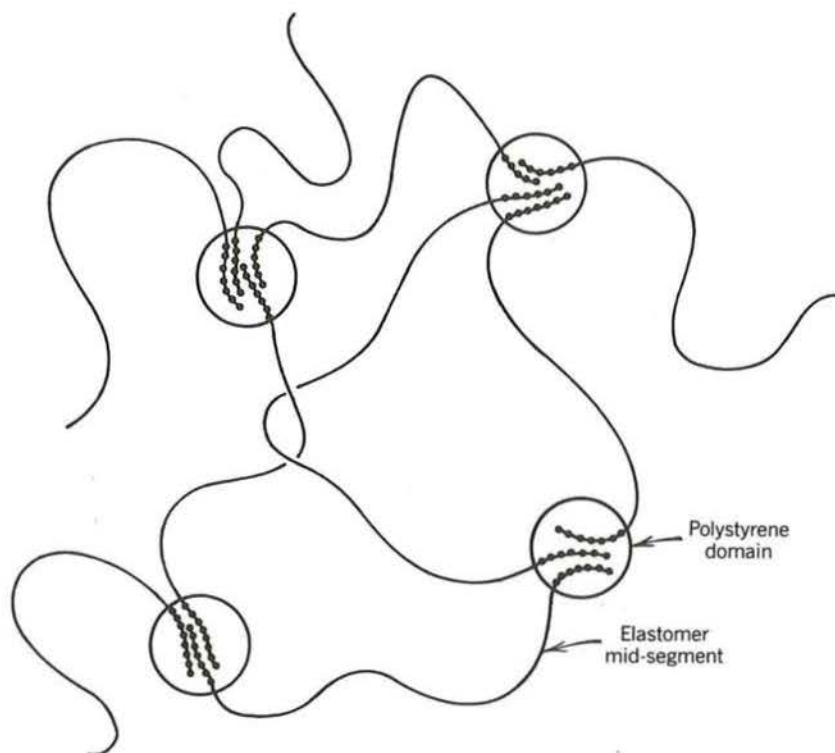


Fig. 1. Morphology of polystyrene-elastomer-polystyrene block copolymer (diagrammatic).

Table 2. Thermoplastic Block Copolymers

Hard segment, A	Soft or elastomeric segment, B	Structure	Refs.
polystyrene	polybutadiene, polyisoprene	A—B—A	2,3
poly(α -methylstyrene)	polybutadiene, polyisoprene	A—B—A	3
polystyrene	poly(ethylene-co-butylene)	A—B—A	4
polyethylene	poly(ethylene-co-butylene)	A—B—A	3
polystyrene	polydimethylsiloxane	A—B—A	5
poly(α -methylstyrene)	polydimethylsiloxane	A—B—A and (A—B) _n	3,5
polysulfone	polydimethylsiloxane	(A—B) _n	6
poly(silphenylene siloxane)	polydimethylsiloxane	(A—B) _n	7
polyurethane	polyester or polyether	(A—B) _n	8,9
polyester	polyether	(A—B) _n	10
polycarbonate	polydimethylsiloxane	(A—B) _n	11–13
polycarbonate	polyether	(A—B) _n	14,15

regarded as elastomeric, eg, polyisoprene, polybutadiene, polyisobutylene, polydimethylsiloxane (see Table 2).

Block copolymers (qv) with structures such as A—B or B—A—B are not thermoplastic elastomers, since for a continuous network to exist, both ends of the elastomer segment must be immobilized in the hard domains. Instead, they are much weaker materials resembling conventional unvulcanized synthetic rubbers (2).

The three commercially important block copolymers are poly(styrene-*b*-elastomer-*b*-styrene), thermoplastic polyurethanes, and thermoplastic polyesters.

Thermoplastic elastomers that are not block copolymers are finely interdispersed multiphase systems. Blends of polypropylene with ethylene-propylene rubbers (EPR) or ethylene-propylene-diene monomer (EPDM) are commercially important materials and are often grafted or cross-linked (see ETHYLENE-PROPYLENE ELASTOMERS). They are referred to here as polypropylene/ethylene-propylene copolymer blends (see also POLYMER BLENDS).

Property-Structure Relationships

Effects of variations in the structure of styrenic A—B—A block copolymers and similar materials were described in earlier work (2) and have recently been reviewed (3).

Molecular Weight. Compared with homopolymers of similar molecular weight, styrenic block copolymers have very high melt viscosities, which increase with increasing molecular weight (2). These effects are attributed to the persistence of the two-phase domain structure in the melt and the extra energy required to disrupt this structure during flow. If the styrene content is held constant, the total molecular weight has little or no effect on the modulus of the material at ambient temperatures. This is attributed to the modulus of the elastomer phase being inversely proportional to the molecular weight between entanglements in the elastomer chains and the fact that this quantity is not affected by the total molecular weight (2).

Ratio of Hard to Soft Segments. As expected, the modulus of styrenic block copolymers increases with the proportion of the hard polystyrene segments. The tensile behavior of otherwise similar block copolymers with a wide range of polystyrene contents shows a family of stress-strain curves (2,3,5). As the styrene content is increased, the products change from very weak, soft, rubberlike materials to strong elastomers, then to leathery materials, and finally to hard glassy thermoplastics. The latter have been commercialized as clear high impact polystyrenes under the trade name K-Resin (Phillips Petroleum Co.). Other types of thermoplastic elastomers show similar behavior, that is, as the ratio of the hard to soft phase is increased, the product in turn becomes harder.

Elastomer Segment. The choice of elastomer segment has a profound effect on the properties of the block copolymer. Polybutadiene and polyisoprene both have one double bond per monomer unit. These double bonds are an obvious source of instability, and limit the thermal and oxidative stability of the S—I—S and S—B—S block copolymers. In contrast, poly(ethylene-*co*-butylene) is completely saturated, and S—EB—S block copolymers are much more stable. Another important aspect is the modulus of the materials. It is believed that the modulus of these polymers is inversely proportional to the molecular weight between chain entanglements (M_e). Values of M_e are given below (16):

Polymer	M_e
polyisoprene (natural rubber)	6100
polybutadiene	1900
poly(ethylene- <i>co</i> -propylene)	1660

The M_e for poly(ethylene-*co*-butylene) is similar to that of poly(ethylene-*co*-propylene) (17), hence S—I—S block copolymers are softer than the S—B—S analogues; the S—EB—S analogues are the hardest.

Polyisoprene, polybutadiene, and especially poly(ethylene-*co*-butylene) are nonpolar. The corresponding block copolymers can thus be compounded with hydrocarbon-based extending oils, but they do not have much oil resistance. Conversely, block copolymers with polar polyester or polyether elastomer segments have little affinity for such hydrocarbon oils.

Among the polyurethane thermoplastic elastomers, those with polyether-based elastomer segments have better hydrolytic stability and low temperature flexibility, whereas polyester-based analogues are tougher and have better oil resistance (18).

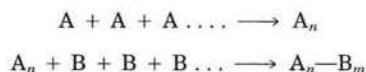
Hard Segment. The choice of the hard segment determines the upper service temperature and solvent resistance. In styrenic block copolymers, poly(α -methylstyrene) has higher upper service temperature and tensile strength than polystyrene (3,5); both are soluble in common solvents. Replacing the polystyrene end segments in S—EB—S by polyethylene (giving E—EB—E block copolymer) improves solvent resistance; the phases are not separated in the melt (3).

In thermoplastic polyurethanes and polyesters, the crystalline end segments (together with the polar center segments) impart good oil resistance and high upper service temperatures. Polypropylene is the hard component in commercial polymer-blend thermoplastic elastomers. It is crystalline and imparts solvent resistance and relatively high upper service temperature.

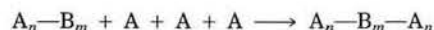
Synthesis

Block copolymers (qv) are synthesized by a variety of methods (19,20); most important are sequential polymerization and step growth.

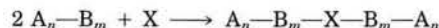
In sequential polymerization, a polymer $(A)_n$ is first synthesized in such a way that it contains at least one group per molecule which can initiate polymerization of another monomer B.



The product can be converted to a triblock copolymer by further addition of A



or alternatively, A_n-B_m can be joined together by a coupling agent

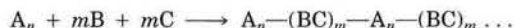


In the above example, X is difunctional and the product is linear. If the functionality of X is higher, the product is branched.

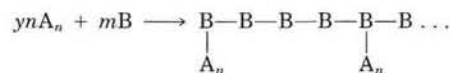
In step-growth polymerization, one or both segments can be produced separately as difunctional prepolymers. The products can then be linked together



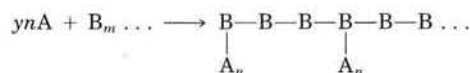
or react with more difunctional monomer.



It is also possible to attach polyA chains or A monomer, which can then polymerize further, at various points along the polyB chain to give grafts (see also GRAFT COPOLYMERS)



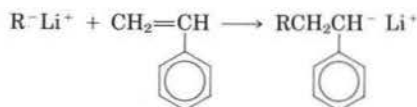
or



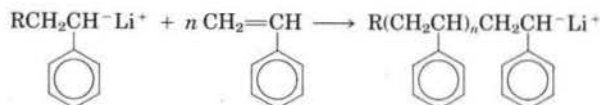
Thermoplastic elastomers that are polymer blends are not truly synthesized. Instead, the two polymers which form the hard and soft phases are intimately mixed on high shear equipment.

Commercial Production

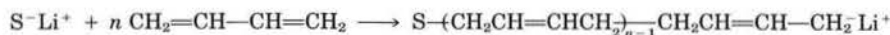
Commercially, the poly(styrene-*b*-elastomer-*b*-styrene) materials are made by anionic polymerization (qv) (19-21). An alkyl-lithium initiator (RLi) first reacts with styrene monomer:



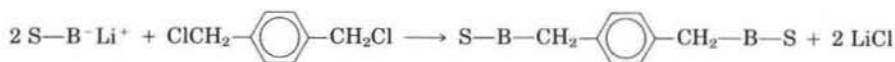
This product acts as an initiator for further polymerization:



The product, referred to here as S^-Li^+ , has been termed a living polymer (qv) (22) because it is able to initiate further polymerization. Addition of a second monomer, such as butadiene, gives

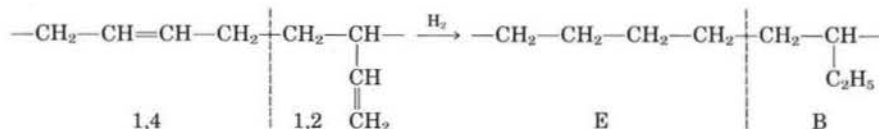


The product of this reaction ($\text{S}-\text{B}^-\text{Li}^+$) may initiate a further reaction with styrene monomer to give $\text{S}-\text{B}-\text{S}^-\text{Li}^+$. This, in turn, can react with an alcohol, ROH , to give $\text{S}-\text{B}-\text{SH} + \text{LiOR}$. Alternatively, $\text{S}-\text{B}^-\text{Li}^+$ may react with a coupling agent such as an organohalogen (19):



Other coupling agents include esters (19), chlorosilanes (19,20), and divinylbenzene (20). The last gives highly branched materials, whereas the others give branched or linear products, depending on the functionality of the coupling agent. These polymerizations proceed only in the absence of oxygen or water, which react with the highly reactive propagating species. Polymerization is usually carried out in an inert, hydrocarbon solvent and under a nitrogen blanket. Under these conditions, polymers with narrow molecular weight distributions and precise molecular weights can be produced in stoichiometric amounts.

Commercially, anionic polymerization is limited to styrene, butadiene, and isoprene, and therefore only two useful $\text{A}-\text{B}-\text{A}$ block copolymers, $\text{S}-\text{B}-\text{S}$ and $\text{S}-\text{I}-\text{S}$, can be produced directly. In both cases, the elastomer segment contains one double bond per molecule of monomer. These bonds are reactive and limit the stability of the product. To improve stability, the polybutadiene mid-segment is first produced as a random mixture of two structural forms, the 1,4 and 1,2 isomers, by addition of an inert polar material to the polymerization solvent; ethers and amines have been suggested for this purpose (20). Upon hydrogenation, these isomers give a copolymer of ethylene and butylene.



The $\text{S}-\text{EB}-\text{S}$ block copolymers produced in this way have excellent resistance to degradation (4) (see also **STYRENE-DIENE BLOCK COPOLYMERS**).

Thermoplastic polyurethanes are produced from prepolymers by polycondensation (19,20,23). A relatively high molecular weight polyester or polyether

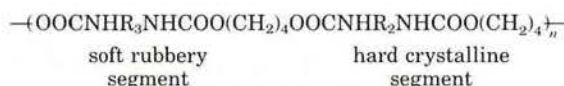
with terminal hydroxy groups (a polyglycol) first reacts with an excess of a diisocyanate.



Depending on the excess diisocyanate, this product reacts further with more polyglycol to give a prepolymer in which the segments originally derived from the polyether or polyester glycol and the urethane alternate and which is terminated by isocyanate groups. This prepolymer, designated OCNR_3NCO , becomes the elastomeric or soft segment in the final polymer. It, in turn, reacts with a low molecular weight glycol such as butanediol and more diisocyanate.



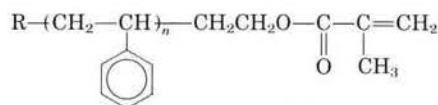
prepolymer



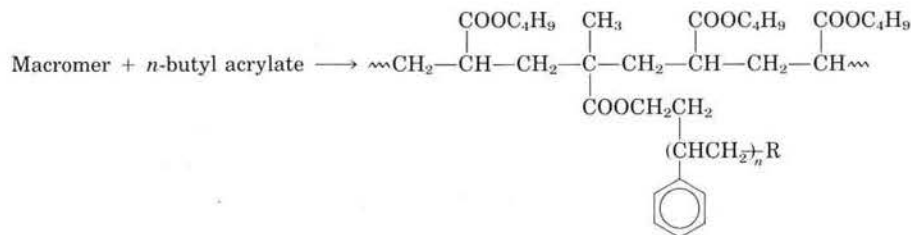
The segments derived from the condensation reaction of the butanediol and the diisocyanate agglomerate into separate phases, which are hard and crystalline. The elastomeric chains are thus cross-linked to form a network similar in many ways to that given by the simple poly(styrene-*b*-elastomer-*b*-styrene) polymer described previously (2,8). However, the polymer is a multiblock $(\text{A}-\text{B})_n$ rather than a simple $\text{A}-\text{B}-\text{A}$ triblock, and the molecular weights and molecular weight distributions of the segments are not as well controlled (see also POLYURETHANE, BLOCK COPOLYMERS).

Commercial thermoplastic polyesters are typically synthesized in a similar way by the reaction of a relatively high molecular weight polyetherglycol with butanediol and dimethyl terephthalate (10). The polyether chain becomes the soft segment in the final product, whereas the terephthalic acid-butenediol copolymer forms the hard crystalline domains (see also POLYESTERS, THERMOPLASTIC).

A family of reactive polystyrenes has recently been announced under the trade name Macromer (24). The polystyrene has a molecular weight of about 13,000 and is terminated by a methacrylate functional group.



Reaction of this polymer with a monomer such as *n*-butyl acrylate or 2-ethylhexyl acrylate gives a graft copolymer; the reaction is of the form $y\text{A}_n$ (Macromer) and $m\text{B}$.



With a styrene content of ca 30% or less, a structure resembling that shown in Figure 1 is obtained; it has the properties of a thermoplastic elastomer. The pendent polystyrene segments are the hard phase and the polyacrylate backbone is the continuous elastomer phase.

Many other synthetic methods for preparing block copolymers have been described (19,20), but are currently not believed to be commercially important.

The production of the thermoplastic elastomers that are not block copolymers is relatively simple. The components, ie, an elastomer, usually EPDM, and a hard thermoplastic, usually polypropylene, are blended together under conditions of intensive shear. In some cases, grafting may occur. In a variation of this technique, the elastomer can be cross-linked while the mixing is taking place, a process described as dynamic vulcanization (25).

A large number of elastomer-thermoplastic pairs made by the last technique have been investigated (26-33). In some cases, the components are chemically bonded (28), but usually a fine dispersion of the two phases is formed which is sufficient to give the product the properties of a thermoplastic elastomer.

Economic Aspects

The U.S. production capacity for thermoplastic rubbers is estimated at about 250,000 metric tons/yr (34), and world capacity at 500,000 t/yr. At present, the market is estimated to be divided as follows (35): styrenic block copolymers, 53%; polypropylene/ethylene-propylene copolymer blends, 29%; thermoplastic polyurethanes, 12%; and thermoplastic polyesters and others, 6%. Prices, production capacities, and specific gravities are given in Table 3.

Table 3. Prices, Productive Capacity, and Specific Gravities for Thermoplastic Elastomers

Elastomer	\$/kg ^{a,b}	Sp gr ^a	U.S. production capacity, 10 ³ t/yr ^b
<i>Styrenic block copolymers</i>			
Pure			
S-B-S	2.00-2.10	0.94	170
S-I-S	2.20-2.30	0.92	
S-EB-S	3.85-4.75	0.91	
Compounded			
S-B-S	1.40-2.40	0.93-1.1	
S-EB-S	2.10-2.65	0.9-1.2	
<i>Other block copolymers</i>			
polyurethane	4.40-5.50	1.1-1.25	35
polyester	5.15-7.15	1.15-1.25	7
<i>Copolymer blend</i>			
polypropylene/ethylene-propylene	1.65-2.75	0.90-1.0	35

^a Excluding fire-retardant grades or highly filled materials for soundproofing.

^b Ref. 34.

Applications

Trade names and suppliers of commercial thermoplastic elastomers are given in Table 4.

Table 4. Trade Names and Manufacturers of Thermoplastic Rubbers^a

Trade name	Manufacturer	Type ^b	Hard segment	Soft segment
<i>General purpose, soluble</i>				
Kraton D	Shell Chemical Co.	triblock (S—B—S or S—I—S)	S	B or I
Solprene 400 ^c	Phillips Petroleum Co.	branched (S—B) _n (S—I) _n	S	B or I
Stereon	Firestone Co.	triblock (S—B—S)	S	B
Tufprene	Asahi	triblock (S—B—S)	S	B
Europrene SOL T	Enichem	triblock (S—B—S or S—I—S)	S	B or I
<i>Improved stability^d</i>				
Kraton G	Shell Chemical Co.	triblock (S—EB—S)	S	EB
<i>Wire and cable</i>				
Elexar	Shell Chemical Co.	triblock (S—EB—S and S—B—S)	S	EB or B
<i>Hard, abrasion and oil resistant, multiblock^{e,f}</i>				
Estane	BFGoodrich Chemical Co.			
Texin	Mobay Chemical Corp.			
Pellethane	Upjohn Co. (now Dow Chemical Co.)			
Cyanoprene	American Cyanamid Co.			
Rucothane	Hooker Chemical Corp.			
Hytrel ^g	E. I. du Pont de Nemours & Co., Inc.		polyester	polyether
Gaflex	GAF		polyester	polyether
<i>Hard, low density blend^h</i>				
TPR	Reichhold-Cook		PP or PE	cross-linked EPDM
Santoprene	Monsanto Co.		PP	cross-linked EPDM
Ren-Flex	Research Polymers, Inc.		PP	EPDM
Polytrope	Schulman		PP	EPDM
Somel	Colonial		PP	EPDM
Telcar	Teknor-Apex		PP	EPDM
Vistaflex	Reichhold-Cook		PP	EPDM
Ferroflex	Ferro		PP	EPDM
ETA	Republic Plastics		PP	EPDM

^a Ref. 36. Courtesy of The American Chemical Society.

^b S = polystyrene; B = polybutadiene; I = polyisoprene; EB = poly(ethylene-co-butadiene).

^c Now withdrawn from the market.

^d Soluble when not compounded.

^e Except where noted otherwise, hard segment, polyurethane; soft segment, polyether or polyester.

^f High cost.

^g Similar to polyurethane, but better at low temperature.

^h Not highly filled.

Styrenic Block Copolymers. The applications of these block copolymers are described in detail in Refs. 37–39.

Substitute for Conventional Vulcanized Rubbers. For this application, the products are processed by conventional techniques, ie, injection molding, extrusion, etc, on equipment developed for conventional thermoplastics. The S—B—S and S—EB—S polymers are preferred. To obtain a satisfactory balance of properties, they must be compounded with oils, fillers, or other polymers; compounding (qv) reduces costs. Compounding ingredients and their effects on properties are given in Table 5. Oils with high aromatic content should be avoided because they plasticize the polystyrene domains. Crystalline hydrocarbon polymers such as polypropylene, polyethylene, or ethylene–vinyl acetate copolymer improve the ozone and solvent resistance of S—B—S.

Table 5. Effects of Compounding of Styrenic Block Copolymers^a

Component	Hardness	Processibility	Effect on ozone resistances	Remarks
oils	decreases	increases	none	reduces uv resistance
polystyrene	increases	increases	some increase	
polyethylene	increases	variable	increases	gives satin finish
polypropylene	increases	variable	increases	improves high temperature properties
EVA	small increase	variable	increases	
fillers	some increase	variable	none	improves surface appearance

^a Ref. 36. Courtesy of The American Chemical Society.

Large amounts of inert fillers, such as whiting, talc, and clays, can be added, whereas reinforcing fillers, such as carbon black, produce undesirable properties in the final product.

Probably the largest volume usage of S—B—S-based compounds is in footwear. Canvas footwear, such as sneakers and unit soles, can be made by injection molding. Frictional properties resemble those of conventionally vulcanized rubbers and are superior to those of the flexible thermoplastics, such as plasticized poly(vinyl chloride). They remain flexible under cold conditions because of the good low temperature properties of the polybutadiene segment.

Compounds based on S—EB—S usually contain polypropylene, which improves solvent resistance and processibility and raises upper service temperatures. Some compounds intended for exterior use in the automotive industry are hard but flexible and thus resistant to impact. They can be painted over a special primer to resemble metal. For other automotive applications (qv), such as flexible air ducts, softer compounds have been developed.

Other uses for which special compounds have been developed include materials intended for food contact, wire insulation, and pharmaceutical applications.

Commercial products have hardnesses from 35 on the Shore A scale (which is relatively soft) to 45 on the Shore D scale (almost leathery). Specific gravities usually range from 0.9 to 1.20; some products intended for soundproofing have

specific gravities as high as 1.95. Properties of representative grades are given in Table 6.

The processing is relatively easy. In general, products based on S—B—S are processed under conditions appropriate for polystyrene, whereas products based on S—EB—S are processed under conditions appropriate for polypropylene. Predrying is not needed and scrap is recycled.

Adhesives, Coatings, and Sealants. For these applications, styrenic block copolymers must be compounded with resins and oils (Table 7) to obtain the desired properties (40,41). Materials compatible with the elastomer segments soften the final product and give tack, whereas materials compatible with the polystyrene segments impart hardness. The latter are usually styrenic resins with relatively high softening points. Materials with low softening points are to be avoided, as are aromatic oils, since they plasticize the polystyrene domains and reduce the upper service temperature of the final products.

These resins and oils have low molecular weights, ie, typically below 1000. This, combined with the relatively low molecular weights of the styrenic block copolymers, ie, 30,000–150,000, allows solutions in common solvents to be formulated at high solids levels. Alternatively, the products can be applied as hot melts, with considerable advantages in terms of safety, production rates, energy consumption, and air pollution.

Blends With Thermoplastic or Other Polymeric Materials. Styrenic block copolymers are technologically compatible with a surprisingly wide range of materials and can be blended to give useful products (42). Blending can often be carried out on the equipment producing the final article. Blends of S—B—S with polystyrene, polyethylene, or polypropylene show improved impact and tear resistance. Similarly S—EB—S can be blended with a wide range of engineering thermoplastics, including poly(butylene terephthalate), poly(phenylene oxide), and polycarbonate. An interesting feature of these block copolymers is their ability to enable useful blends to be made from incompatible polymers, eg, polystyrene and polyethylene (43).

Special grades of styrenic block copolymers are useful modifiers for sheet-molding compounds (SMC) (qv) based on thermoset polyesters. They improve surface appearance, impact resistance, and hot strength.

Blends with styrenic copolymers improve the flexibility of bitumens and asphalts (44), eg, S—B—S/asphalt blends have low viscosity at processing temperatures, as well as remarkably elastic behavior at ambient temperatures. Such blends improve the flexibility and resistance to cyclic fatigue of built-up roofing membranes, particularly at low temperatures. The S—EB—S block copolymers offer similar advantages and also improve weather resistance. The S—B—S block copolymers are also excellent modifiers for asphalt-based crack sealants.

Polyurethane and Polyester Block Copolymers. Substitution of conventional vulcanized rubber is the main application for polyurethane and polyester block copolymers. Like styrenic block copolymers, they can be molded or extruded with equipment designed for processing thermoplastics. Melt temperatures during processing are between 175 and 225°C, and predrying is strongly recommended; scrap is reusable. They are used as essentially pure materials, although some work on plasticized polyester block copolymers has been reported (10,45). Both types give products that are relatively hard (from 70 on the Shore A scale

Table 6. Applications and Properties of Compounded Styrenic Block Copolymers

Product	Application	Properties					
		Hardness, Shore A or D	Tensile strength, MPa ^a	100% modulus, MPa ^a	Elongation, %	Melt flow, g/10 min ^b	Sp gr
Kraton D 2109	milk tubing	44A	6.5	1.7	800	15(G)	0.94
Kraton G 2705	medical	55A	7.6	1.7	700		0.9
Kraton D 3202	general	65A	5.9	3.3	500	14(E)	1.0
Kraton D 5119	footwear, direct-molded	47A	4	2.5	380	27(E)	1.09
Kraton D 5152	footwear, unit sole	47A	3.9	1.9	550	26(E)	1.0
Kraton D 5239	footwear, crepe look	36A	4.8	1.0	820	20(E)	0.98
Kraton G 7150	soundproofing	36D	4.8	3.5	250		1.94
Kraton G 7720	automotive, soft parts	60A	6.2	2.1	600		1.20
Kraton G 7880	automotive, bumper cover	42D	14.5	9	450		1.05
Elexar 8313	automotive, primary wire	54D	24	13	550		1.28
Elexar 8451	wire and cable, flexible cord	80A	14	4.1	500	22(G)	1.0
Elexar 8614	wire and cable, fire-retardant control cable	95A	14	9.7	500	3(G)	1.2

^a To convert MPa to psi, multiply by 145.^b Conditions E and G (ASTM D 1238).

Table 7. Resins for the Formulation of Adhesives and Sealants from Styrenic Block Copolymers

Resin type	Segment compatibility ^a
polymerized C ₅ ^b	I
hydrogenated rosin esters	B
saturated hydrocarbons	EB
naphthenic/paraffinic oils	I, B, EB
low molecular weight polybutenes	EB
aromatic	S

^a I = polyisoprene; B = polybutadiene; EB = poly(ethylene-co-butylene); S = polystyrene.

^b Synthetic polyterpenes.

to 70 on the Shore D scale) with specific gravities of 1.10–1.25. Properties of individual grades have been described in detail (10,9) (see Tables 8 and 9). Applications taking advantage of toughness, abrasion resistance, flexibility, and resistance to oils and solvents include belting, hydraulic hose, tires, shoe soles, wire coatings, and automobile parts. The surface of these molded parts can be easily painted or metallized. Medical uses, such as implants are a significant application for the polyurethane block copolymers with polyether elastomer segments (46).

Table 8. Properties of Thermoplastic Polyurethanes^a

Product	Properties				
	Hardness, Shore A or D	Tensile strength, MPa ^b	100% modulus, MPa ^b	Elongation, %	Sp gr
Estane 58133	55D	35	13	500	1.22
Estane 58013 ^c	86A	30	4.5	630	1.18
Estane 58880 ^c	80A	24	4.5	600	1.10
Texin 480A	86A	31	4.8	600	1.20
Pellethane 2102-90A	93A	38	10.7	500	1.20
Cyanoprene 9380	73D	35	27	320	1.24

^a Esters, except where otherwise stated.

^b To convert MPa to psi, multiply by 145.

^c Ether.

Table 9. Properties of Thermoplastic Polyesters

Product ^a	Properties				
	Hardness, Shore A or D	Tensile strength, MPa ^b	25% modulus, MPa ^b	Elongation, %	Sp gr
Hytrel 40xy	92A, 40D	26	7.5	450	1.17
Hytrel 55xy	55D	38	14	450	1.20
Hytrel 63xy	63D	39	17 ^c	350	1.22
Hytrel 72xy	72D	39	26 ^c	350	1.25
Gaflex 547	47D	32	11	450	1.18

^a xy denotes a two-digit identifier for the individual grades.

^b To convert MPa to psi, multiply by 145.

^c Yield point.

Some grades of polyurethane and polyester copolymers are used as hot-melt adhesives. Applications include shoe manufacture and as an adhesive interlayer in coextrusion (see FILMS, MULTILAYER).

Blended with plasticized poly(vinyl chloride) (10,47,48), polyurethane and polyester block copolymers give flexible products. Special grades of the polyurethane block copolymers give products with high abrasion resistance suitable for shoe soles.

Polypropylene/Ethylene-Propylene Copolymer Blends. Substitution of conventional vulcanized rubbers is the main application for these polymers (49). Hardness values are between 60 on the Shore A scale to 50 on the Shore D scale, and specific gravities between 0.88 and 1.04; fire-retardant grades have a specific gravity of ca 1.2. Properties are given in Table 10. Molding and extrusion conditions are similar to those used for polypropylene, and the scrap is reusable. The two most important applications are wire insulation and automobile exterior and interior parts (both painted and unpainted).

Table 10. Properties of Polypropylene/Ethylene-Propylene Copolymer Blends

Product	Properties				
	Hardness, Shore A or D	Tensile strength, MPa ^a	100% modulus, MPa ^a	Elongation, %	Sp gr
TPR 1600	67A	4.5	3.5	230	0.88
TPR 1900	92A	12.8	12.8	230	0.88
TPR 2800	87A	9.0	8.6	150	0.88
Telcar 340	91A, 41D	10.2	9.2	400	0.89
Somel 301	40D	11.5	10.6	230	1.02
Somel 601	50D	31	13.8	495	1.04
Santoprene 101-73, 201-73	73A	7.5	3.2	375	0.98
Santoprene 103-50, 203-50	50D	27	10	600	0.94

^a To convert MPa to psi, multiply by 145.

Polypropylene/ethylene-propylene copolymer blends can be used as impact modifiers for polyethylene and polypropylene (49), but are not compatible with more polar polymers such as polystyrene.

BIBLIOGRAPHY

1. B. M. Walker, *Paper presented at the Symposium on Thermoplastic Elastomers*, Philadelphia, Pa., May 4-7, 1982, the American Chemical Society Rubber Division, Washington, D.C., and the Society of Plastics Engineers, Inc., Brookfield Center, Conn.; *Chemtech* 13(10), 638 (1983).
2. G. Holden, E. T. Bishop, and N. R. Legge, *J. Polym. Sci. Part C* 26, 37 (1969).
3. M. Morton, *Rubber Chem. Technol.* 56, 1096 (1983).
4. G. Holden in L. M. Sperling, ed., *Recent Advances in Polymer Blends, Grafts and Blocks*, Plenum Press, New York, 1970, p. 276.
5. J. C. Saam, A. Howard, and F. W. G. Fearon, *J. Inst. Rubber Ind.* 7, 69 (1973).
6. A. Noshay, M. Matzner, and C. N. Merriam, *J. Polym. Sci. Part A-1* 9, 3147 (1971).
7. R. L. Merker, M. J. Scott, and G. G. Haberland, *J. Polym. Sci. Part A* 2, 31 (1964).
8. S. L. Cooper and A. V. Tobolsky, *Text. Res. J.* 36, 800 (1966).

9. S. Wolkenbreit in B. M. Waker, ed., *Handbook of Thermoplastic Elastomers*, Van Nostrand Reinhold, New York, 1979, Chapt. 5.
10. S. C. Wells in Ref. 9, Chapt. 4, pp. 104 and 105.
11. H. A. Vaughn, *J. Polym. Sci. Part B* **7**, 569 (1969).
12. R. P. Kambour, *J. Polym. Sci. Part B* **7**, 573 (1969).
13. D. G. LeGrand, *J. Polym. Sci. Part B* **7**, 579 (1969).
14. E. P. Goldberg, *J. Polym. Sci. Part C* **4**, 707 (1963).
15. K. P. Perry, W. J. Jackson, Jr., and J. R. Caldwell, *J. Appl. Polym. Sci.* **9**, 3451 (1965).
16. J. D. Ferry, *Viscoelastic Properties of Polymers*, John Wiley & Sons, Inc., New York, 1980, p. 374.
17. L. J. Fetters, Exxon Corp., Annandale, N.J., 1982, private communication.
18. Ref. 9, p. 217.
19. N. R. Legge, S. Davison, H. E. De La Mare, G. Holden, and M. K. Martin in R. W. Tess and G. W. Poehlein, eds., *Applied Polymer Science*, American Chemical Society, Washington, D.C., 1985, Chapt. 9, pp. 189–200.
20. P. Dreyfuss, L. J. Fetters, and D. R. Hansen, *Rubber Chem. Technol.* **53**, 738 (1980).
21. M. Morton, *Anionic Polymerization: Principles and Practice*, Academic Press, Inc., New York, 1983.
22. M. Szwarc, M. Levy, and R. Milkovich, *J. Am. Chem. Soc.* **78**, 2656 (1956).
23. D. C. Allport and W. H. Janes, *Block Copolymers*, John Wiley & Sons, Inc., New York, 1973, p. 20.
24. *Chemlink 4500, Technical Bulletin*, Sartomer Co., West Chester, Pa., 1984.
25. U.S. Pat. 3,037,954 (June 5, 1962), A. M. Gessler (to Esso Research & Engineering Co.).
26. A. Y. Coran and R. Patel, *Rubber Chem. Technol.* **53**, 141 (1980).
27. *Ibid.*, 892 (1981).
28. A. Y. Coran, R. Patel, and D. Williams, *Rubber Chem. Technol.* **55**, 116 (1982).
29. A. Y. Coran and R. Patel, *Rubber Chem. Technol.* **56**, 210 (1983).
30. U.S. Pat. 4,299,931 (Nov. 10, 1981), A. Y. Coran and R. Patel (to Monsanto Co.).
31. U.S. Pat. 4,355,139 (Oct. 19, 1982), A. Y. Coran and R. Patel (to Monsanto Co.).
32. U.S. Pat. 4,104,210 (Aug. 1, 1978), A. Y. Coran and R. Patel (to Monsanto Co.).
33. A. Y. Coran and R. Patel, *Rubber Chem. Technol.* **56**, 1045 (1983).
34. J. F. Auchter, *Rubber World* **185**(5), 21 (1982).
35. R. School, *Rubber Plast. News*, 49 (May 7, 1984).
36. J. K. Craver and R. W. Tess, eds., *Applied Polymer Science*, The American Chemical Society, Washington, D.C., 1975, Chapt. 29, p. 422.
37. G. Holden, *J. Elastomers Plast.* **14**, 148, (1982).
38. G. Holden in I. Rubin, ed., *Handbook of Plastics and Related Materials*, John Wiley & Sons, New York, Chapt. 67, in press.
39. D. J. St. Clair, *Rubber Chem. Technol.* **55**, 208 (1982).
40. G. Kraus, K. W. Rollman, and R. A. Gray, *J. Adhes.* **10**, 221 (1979).
41. *Bulletin SC:198-83*, Shell Chemical Co., Houston, Texas, 1984.
42. A. L. Bull and G. Holden, *J. Elastomers Plast.* **9**, 281 (1977).
43. C. R. Lindsey, D. R. Paul, and J. W. Barlow, *J. Appl. Polym. Sci.* **26**, 1 (1981).
44. E. J. van Beem and P. Brasser, *J. Inst. Pet. London* **59**, 91 (1973).
45. *Hytrel Bulletin HYT-302R(1)*, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1981.
46. M. Szycher, V. L. Poirier, and D. Demsey, *Elastomerics* **115**(3), 11 (1983).
47. *Hytrel Bulletin IF-HYT-370.025*, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1976; U.S. Pat. 3,718,715 (Feb. 27, 1973), R. W. Crawford and W. J. Witsiepe (to E. I. du Pont de Nemours & Co., Inc.).
48. H. W. Bonk in J. Agranoff, ed., *Modern Plastics Encyclopedia 1982–1983*, McGraw-Hill, Inc., New York, 1983, p. 120.
49. H. L. Morris in Ref. 9, Chapt. 2.

GEOFFREY HOLDEN
Shell Development Company