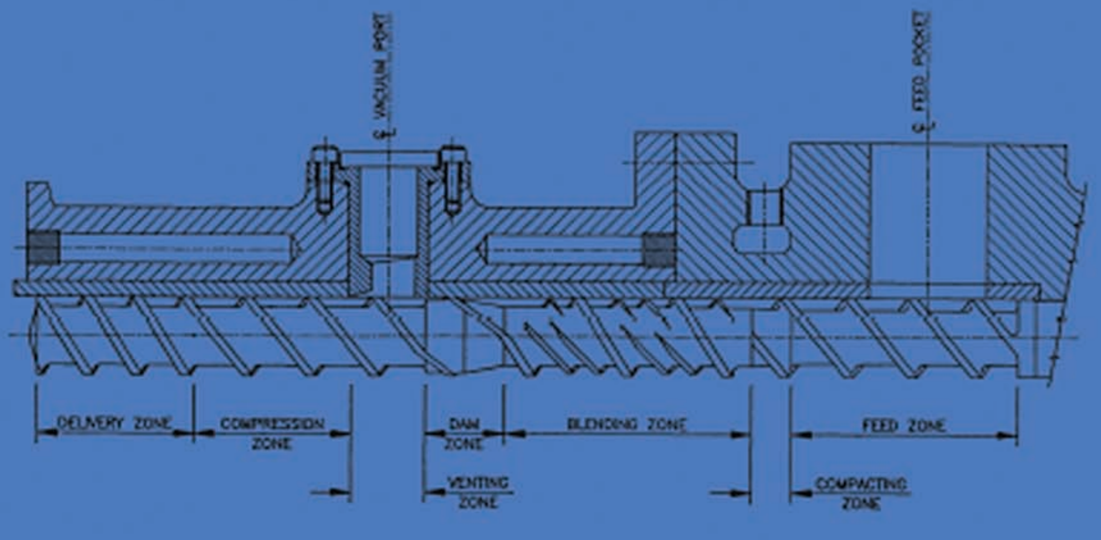
RUBBER PRODUCTS MANUFACTURING TECHNOLOGY



EDITED BY

ANIL K. BHOWMICK
MALCOLM M. HALL
HENRY A. BENAREY

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MARCEL DEKKER, INC. NEW YORK • BASEL

Library of Congress Cataloging-in-Publication Data

Rubber products manufacturing technology / edited by Anil K. Bhowmick, Malcolm M. Hall, Henry A. Benarey.
p. cm.
Includes bibliographical references and index.
ISBN 0-8247-9112-6 (acid-free paper)
1. Rubber industry and trade. I. Bhowmick, Anil K. II. Hall, Malcolm M. III. Benarey, Henry A.
TS1890.R84 1994
678'.2--dc20 93-43397
CIP

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Transferred to Digital Printing 2010

Publisher's Note
The publisher has gone to great lengths to ensure the quality of this reprint
but points out that some imperfections in the original may be apparent.

To

Asmit and Kumkum

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Preface

The last few decades have witnessed truly explosive development and growth in rubber products manufacturing technology. For example, a tire can be made today in a few minutes using sophisticated machinery without much manpower. Those who are involved in teaching, research, or business find that there is a dearth of immediate information on this subject. This book draws together and systematizes the body of information available and presents it in as logical a fashion as possible.

This book covers the compounding, mixing, calendering, extrusion, vulcanization, and manufacturing technology of a few important rubber products. Since most modern machinery, whether used in the mixing room or in the forming and shaping of products, and other modern manufacturing technology is self-controlling and monitored by computers, the use of computer-aided design and manufacturing, automation, and microprocessor has also been highlighted. Manufacturing process control is today's tool to combat excessive costs. Since a very large number of products are made using rubber, it was impossible to describe every form of manufacturing technology. However, the basic principles of manufacturing technology may be learned from this book. In a few cases, multiple authors were invited to contribute, to stress the importance of a subject. This volume contains material of interest to both scientists and technologists.

The various developments are described by experts in the field, most of whom have extensive industrial or working experience. Their contributions are expected to be of immediate relevance to those concerned with the applications of rubber. The editors are grateful to the contributors for the time and effort they were able to devote to this book.

During the preparation of the book, we received help from a large number of people from both industry and academics. We thank them all. In particular, we are thankful to Prof. K. L. Chopra, Director, IIT Kharagpur, and the faculty members and students of the Rubber Technology Center, IIT Kharagpur; Prof. Takashi Inoue, Tokyo Institute of Technology, Tokyo; Dr. E. Maekawa, Bando Chemical Company, Kobe;

Dr. K. Harada, JSR Company, Ltd.; and Dr. D. Banerjee, Mr. A. N. Bhattacharya, Mr. J. Chatterjee, and Dr. S. N. Chakravarty—all from the Indian Rubber Institute. We also thank various companies, authors, editors, and journals for permission to use diagrams and photographs from published sources and for other necessary assistance. We have acknowledged them in appropriate places in this book. If we have missed anyone, the slip is unintentional. Finally, we thank Mr. and Ms. J. M. Bhowmick and Dr. and Ms. S. K. Biswas for helping with the manuscript.

Anil K. Bhowmick
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1

Compound Design

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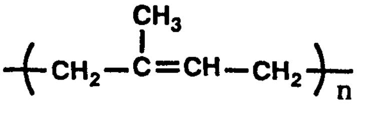
People are frequently surprised to learn that there are many different types of rubber, and that rubber articles are not always black. Confusion sets in when their request for a typical value for property *x* is met with the answer that no single value can be given because the property is dependent on the precise composition of the rubber compound. Their confusion is complete when they are shown a typical rubber formulation consisting of up to ten ingredients and told that one, present at a level of 0.1% by weight, is absolutely critical to service performance. Rubber technologists are therefore regarded as practitioners of a black art—a situation, one suspects, they are not really averse to.

Rubber technology is not a black art and it is hoped that this chapter, by describing the different types of rubber available, the compounding ingredients used, and how a rubber compound is designed, will help to dispel the myth. The reader seeking more information is directed to some basic texts for more details [1–4].

1.1 COMMERCIALLY AVAILABLE RUBBERS

1.1.1 Natural Rubber

Designation in ISO 1629: NR
Repeat Unit



$$\left(CH_2-\overset{\overset{\textstyle CH_3}{|}}{C}=CH-CH_2 \right)_n$$

General. Natural rubber can be isolated from more than 200 different species of plant; this includes some surprising examples such as dandelions. Only one tree source, *Hevea brasiliensis,* is however, commercially significant. Latex, an aqueous colloid of the rubber, is obtained from the tree by "tapping" into the inner bark and collecting the latex in cups. The latex typically contains 30–40% dry rubber by weight, and 10–20% of the collected latex is concentrated by creaming, or centrifuging, and used in the latex form. Historically, such latex has been exported to consumer countries, but it is expensive to ship a product with a high percentage of water, and consumer companies are increasingly siting their latex processing plants in the producer countries, where cheaper labor is an additional incentive. Latex technology is considered to be beyond the scope of this chapter and the reader is referred to the "Bible" on this subject by Dr. Blackley [5].

The remaining latex is processed into dry rubber as sheets, crepes, and bales. There is an international standard for the quality and packing for natural rubber grades, the so-called Green Book, published by the Rubber Manufacturers' Association. The following grades of natural rubber listed in the Green Book are sold to visual inspection standards only:

Ribbed smoke sheets
White and pale crepes
Estate brown crepes
Compo crepes
Thin brown crepes
Thick blanket crepes
Flat bark crepes
Pure smoked crepes

Under each category there are generally up to five divisions (e.g., 1RSS, 2RSS, 3RSS, 4RSS, 5RSS for ribbed smoked sheets); the higher the number, the lower the quality.

The Malaysian rubber industry has, however, played a pioneering role in producing natural rubber grades to technical specifications, and this system is being followed by other producer countries. Currently the following technically specified grades are sold by the producing countries:

SMR	Standard Malaysian Rubber
SIR	Standard Indonesian Rubber
SSR	Specified Singapore Rubber
SLR	Standard Lanka Rubber
TTR	Thai Tested Rubber
NSR	Nigerian Standard Rubber

Table 1 lists the SMR technical specifications.

Natural rubber is *cis*-1,4-polyisoprene, of molecular weight 200,000–500,000, but it also contains a small level of highly important nonrubber constituents. Of these, the most important are the proteins, sugars, and fatty acids, which are antioxidants and

Table 1 SMR Specification Scheme: Mandatory from October 1, 1991

Parameter	Latex			Sheet material:	Blend:	Field grade material			
	SMR CV60	SMR CV50	SMR L	SMR 5[a]	SMR GP	SMR 10CV	SMR 10	SMR 20CV	SMR 20
Dirt retained on 44 μm aperture (max), % wt	0.02	0.02	0.02	0.05	0.08	0.08	0.08	0.16	0.16
Ash content (max), % wt	0.50	0.50	0.50	0.60	0.75	0.75	0.75	1.00	1.00
Nitrogen (max), % wt	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Volatile matter (max), % wt	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
Wallace rapid plasticity P_0 (min)			35	30			30		30
Plasticity retention index, (min), %[b]	60	60	60	60	50	50	50	40	40
Lovibond color:									
individual value (max)			6.0						
range (max)			2.0						
Mooney viscosity, ML (1 + 4), 100°C[b]	60(+ 5, − 5)	50(+ 5, − 5)			65(+ 7, − 7)	[c]		[c]	
Cure[d]	R	R	R		R	R		R	
Color coding marker	Black	Black	Light green	Light green	Blue	Magenta	Brown	Yellow	Red
Plastic wrap color	Transparent	Transparent	Transparent	Transparent	Transparent	Transparent	Transparent	Transparent	Transparent
Plastic strip color	Orange	Orange	Transparent	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white

[a] Two subgrades of SMR 5 are SMR 5RSS and SMR 5ADS, which are prepared by direct baling of ribbed smoked sheet and air-dried sheet (ADS), respectively.

[b] Special producer limits and related controls are also imposed by the Rubber Research Institute of Malaysia (RRIM) to provide additional safeguard.

[c] The Mooney viscosities of SMR 10CV and SMR 20CV are, at present, not of specification status. They are, however, controlled at the producer end to 60 (+ 7, − 5) for SMR 10CV and 65 (+ 7, − 5) for SMR 20CV.

[d] Rheograph and cure test data (delta torque, optimum cure time, and scorch) are provided.

Source: MRPRA.

activators of cure. Trace elements present include potassium, manganese, phosphorus, copper, and iron, which can act as catalysts for oxidation.

Natural rubber is available in a granular form (powdered rubber), and oil-extended grades are also available.

Two chemically modified types of natural rubber—graft copolymers of natural rubber and polymethyl methacrylate, and epoxidized natural rubber—exhibit useful properties. The former are used in adhesive systems and for the production of hard compounds, while the latter probably has still to find its market niche.

As the name suggests, epoxidized natural rubber is prepared by chemically introducing epoxide groups at random onto the natural rubber molecule. This chemical modification leads to increased oil resistance and greater impermeability to gases, as well as an increase in the glass transition temperature T_g and damping characteristics; the excellent mechanical properties of natural rubber are retained.

A 50 mol % epoxidized natural rubber exhibits oil resistance only marginally inferior to that of nitrile rubber.

Natural rubber can strain crystallize, which results in its compounds exhibiting high tensile strength and good tear strength. Although crystallization can occur at low temperatures, compounding greatly reduces this tendency, which can be effectively prevented from crystallizing by using sulfur levels greater than 2.5 parts per hundred rubber (phr) to cure the compound.

Since the main chain of natural rubber contains unsaturation (residual double bonds), it, along with other unsaturated rubbers, is susceptible to attack by oxygen, ozone, and ultraviolet light; therefore, compounds require protection against these agencies.

Natural rubber is not oil resistant and is swollen by aromatic, aliphatic, and halogenated hydrocarbons.

Natural rubber can be crosslinked by the use of sulfur, sulfur donor systems, peroxides, isocyanate cures, and radiation, although the use of sulfur is the most common method.

The sulfur vulcanization of natural rubber generally requires higher added amounts of sulfur, and lower levels of accelerators than the synthetic rubbers. Sulfur contents of 2-3 phr and accelerator levels of 0.2-1.0 phr are considered to be conventional cure systems.

Natural rubber can yield a hard, rigid thermoplastic with excellent chemical resistance when cured with more than 30 phr of sulfur. Such a product is termed ebonite.

Natural rubber requires a certain degree of mastication (reduction in molecular weight) to facilitate processing, although the advent of constant viscosity (CV) and oil-extended grades has substantially reduced the need for mastication.

Peptizers are often used to facilitate breakdown of the rubber during mixing, although quantities of greater than 0.6 phr can cause a reduction in the final level of physical properties [6].

Uses. The uses of natural rubber are myriad, and a complete summary is not really possible. Its unique and excellent properties are utilized in tires, shock mounts, seals, isolators, couplings, bridge bearings, building bearings, footwear, hose, conveyor belts, plant linings, and many other molding applications.

Latices and solutions are used to produce adhesives, carpet backings, upholstery foam, gloves, condoms, and medical devices such as catheters. Natural rubber is also frequently used in blends with other elastomers.

1.1.2 Synthetic Rubbers

Unsaturated Homopolymers

Polyisoprene (Synthetic Natural Rubber).

Designation in ISO 1629: IR

Repeat unit (as for natural rubber)

General. Polyisoprene has the same empirical formula as natural rubber, hence closely approximates the behavior of its naturally occurring rival. It has the same cis structure as natural rubber, good uncured tack, high gum tensile strength, high resilience, and good hot tear strength. Although similar to natural rubber, it does exhibit some differences:

It is more uniform and lighter in color than natural rubber.

Because of a narrower molecular weight distribution, it exhibits less tendency to strain crystallize; hence green strength is inferior, as are both tensile and tear strength.

In general, synthetic polyisoprene behaves like natural rubber during processing, and it also requires protection against oxygen, ozone, and UV light as a result of unsaturation in the main chain. Oil resistance is poor, and resistance to aromatic, aliphatic, and halogenated hydrocarbons is lacking.

The absence of the nonrubber constituents, present in the natural rubber, leads to some differences in compounding, although, in essence, the principles are the same. An increased level of stearic acid is generally required for cure activation, and approximately 10% extra accelerator is necessary to achieve a cure rate similar to that of natural rubber; similar sulfur levels are, however, used. Polyisoprene and natural rubber can be cured by the same type of system.

Uses. Polyisoprene can be used interchangeably with natural rubber in all but the most demanding applications, and it is often used in blends with polybutadiene and styrene-butadiene rubber (SBR) in preference to natural rubber when improved processibility is required.

It is interesting to note that polyisoprene was more widely used in the USSR, presumably because of economy-based supply difficulties with natural rubber, and strategic considerations. This may, of course, change in the new political climate.

Polybutadiene

Designation in ISO 1629: BR

Repeat unit

$$-\left(CH_2-CH=CH-CH_2\right)_n-$$

General. Polybutadiene is produced by solution polymerization, and one important feature governing the performance of the resultant polymer is the *cis*-1,4 and 1,2-

vinyl contents. High *cis*-1,4 polymers (> 90%) have a T_g around −90°C, hence exhibit excellent low temperature flexibility, exceeded only by the phenyl silicones. They also exhibit excellent resilience and abrasion resistance. Since, however, the high resilience gives poor wet grip in tire treads, this rubber finds limited use as the sole base for such compounds.

As the 1,4 content decreases, and 1,2-vinyl content increases, the low temperature properties, abrasion resistance, and resilience become inferior.

The polymerization of butadiene results in a polymer with a narrow molecular weight distribution which can be difficult to process. Indeed, commercially available grades present a compromise between processibility and performance. Most polybutadiene rubbers are inherently difficult to break down during mixing and milling and have low inherent tack; moreover, the inherent elasticity of the polymer gives poor extrudability. Peptizers can be used to facilitate breakdown, hence aiding in processing.

The unsaturation present in the main chain necessitates protection against oxygen, UV light, and ozone. Oil resistance is poor, and the polymer is not resistant to aromatic, aliphatic, and halogenated hydrocarbons.

Polybutadiene-based compounds can be cured by sulfur, sulfur donor systems, and peroxides. Less sulfur and a higher level of accelerators are required than for natural rubber. The cure of polybutadiene by peroxides is highly "efficient" in that a large number of crosslinks are produced per free radical. Thus the resultant highly crosslinked rubber exhibits high resilience; this factor is utilized in the manufacture of "superballs."

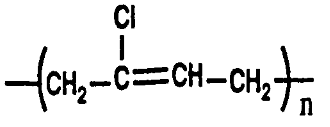
Compounds based on polybutadiene give optimum properties only at high filler and oil loadings.

Uses. Most polybutadiene is used in tire applications, and the majority of this use is in blends with other polymers, such as natural rubber and SBR, where polybutadiene reduces heat buildup and improves the abrasion resistance of the blend. The coefficient of friction on ice of snow tires is also improved by using higher levels of polybutadiene in the tread blend.

When polybutadiene is used in blends for other applications, the improved abrasion and low temperature flexibility conferred on the blend offer advantage, for example, in shoes and conveyor and transmission belts.

Polychloroprene

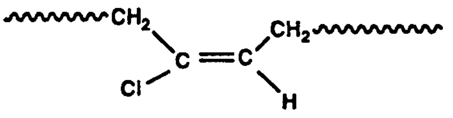
Designation in ISO 1629: CR
Repeat unit



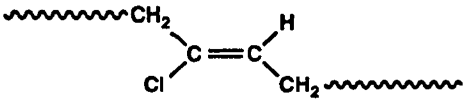
$$-\left(CH_2-\overset{\overset{\displaystyle Cl}{|}}{C}=CH-CH_2\right)_n-$$

General. This polymer is frequently, but incorrectly, referred to as Neoprene, which is a trade name.

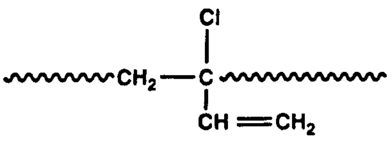
Polychloroprene is produced by emulsion polymerization, during which the following forms of addition are possible:



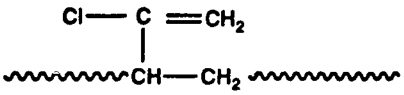
cis-1,4 addition



trans-1,4 addition



1,2 addition



3,4 addition

Since commercial production of a polymer based on the *cis*-1,4 form is impossible, commercial polymers are based on the *trans*-1,4 form, which has a crystalline melting point T_m of +75°C and a T_g of −45°C. Pure *trans*-1,4-polychloroprene thus crystallizes readily and would normally be considered to be of limited use for a rubber. Such a polymer, however, does not crystallize when dissolved in a solvent but will do so when the solvent evaporates. This feature is used to good effect in the production of contact adhesives.

The temperature of polymerization, however, influences how closely the polymer attains the *trans*-1,4 form. Raising the polymerization temperature from −40°C to +40°C increases the percentage of 1,2 and 3,4 forms, both of which reduce the stereoregularity, hence the tendency to crystallize. Thus chloroprene-based polymers that are intended to be rubbery are polymerized at higher temperatures. The 1,2 grouping in the main chain is the site of crosslinking reactions during cure. The ability to crystallize can also be controlled by copolymerizing chloroprene with small amounts of other monomers.

Two different mechanisms are used to control the molecular weight of the polymer during polymerization.

In the so-called G types, sulfur is copolymerized with the chloroprene to yield a product shown schematically as follows:

The G *types* are stabilized with tetraethyl thiuram disulfide (TETD), with the result that the G types can cure without further acceleration.

In the so-called W types, the molecular weight is controlled by the use of a mercaptan.

The following differences are apparent between the G and W types:

The *G type* can break down during mixing or milling via cleavage at the S_x group; this decreases molecular weight, hence reduces the elasticity, or nerve, during processing. The extent of breakdown is somewhat dependent on the exact grade, Neoprene GW being virtually unaffected by milling. Cleavage at the S_x group can also occur during long-term storage, and the G types therefore have the disadvantage of a limited storage life.

The G types do not require further acceleration during cure, but exhibit slightly inferior aging characteristics. Resilience and tack are generally better than with the W types.

The *W types* exhibit superior storage life and aging characteristics but require the addition of accelerators to achieve an acceptable rate of cure. They do not break down during mxing. During processing they are less prone to scorch, and they will accept higher loadings of filler. The cured compound generally exhibits a lower compression set and a greater ability to resist heat aging.

The chlorine atom in the repeat unit has a tendency to deactivate the double bond in the main chain. Thus polychloroprene tends to resist oxidation, ozone, and UV light to a higher degree than the other unsaturated rubbers, although it still requires protection if the maximum performance is to be obtained. Unfortunately, this deactivation of the double bond means that the polymer cannot be crosslinked by sulfur.

The chlorine atom also confers an increased level of resistance to oils: the oil resistance of polychloroprene is roughly intermediate between natural rubber and nitrile rubber, and is often sufficient for many applications. Polychloroprene is also self-extinguishing in flame tests.

Metal oxides are principally used for curing these materials; peroxides are generally not used. The most widely used cure system is based on a combination of the oxides of magnesium and zinc, the cured properties achieved being dependent on the ratio of the two; the most common MgO/ZnO ratio is 4.0:5.0. Since the zinc oxide tends to promote scorch, it is added late in the mixing cycle, whereas magnesium oxide is added early. One drawback of the MgO/ZnO cure system is that chlorine liberated during cure reacts with the oxides to yield the chloride, which is hydrophilic, and compounds containing this cure system can swell in hot water; even in cold water, swell can be progressive and eventually large.

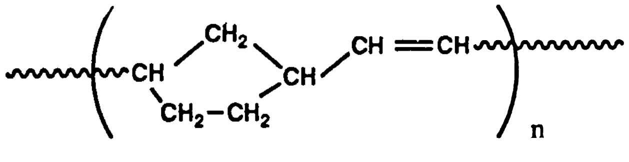
Lead oxide (PbO or Pb_3O_4) up to levels of 20 phr can be used to improve resistance to water because the chloride formed during cure is insoluble.

The W types require additional acceleration, and ethylene thiourea (ETU) gives the best balance of all properties. However, the use of this accelerator is increasingly being restricted as a result of fears of its effects on pregnant women, and now recently men. Diethylene thiourea, thiurams, and guanidines can also be used. Sulfur is sometimes used to increase the degree of cure in the W types, but its presence detracts from the aging performance of the vulcanizate.

Uses. As a result of its balance of strength, oil resistance, flammability, and increased resistance to ozone, aging, and weathering, polychloroprene finds widespread industrial use. Typical uses are V-belts, conveyor belts, wire and cable jacketing, footwear, wet suit applications, coated fabrics, inflatable products, hoses, extrusions, and many others goods. Adhesives are also a strong market area.

Polynorbornene

Repeat unit



General. The large ring structure in the main chain gives polynorbornene a high T_g of +35°C. Thus it is not rubbery at normal ambient temperatures and requires plasticization to achieve elastomeric behavior.

Polynorbornene exhibits some desirable advantages. It can be extended by large quantities of oils to give very soft vulcanizates (ca. 20 Shore A) with acceptable strength, and it gives high damping, which can be useful for vibration and noise reduction applications. However, since plasticization is required, particular care must be exercised in the choice of plasticizer if exposure to higher than ambient temperatures is anticipated.

Polynorbornene is not oil resistant, and solvents that can extract the plasticizer obviously will be detrimental to its performance.

The material can be cured by both sulfur and peroxides, but it requires protection against oxygen, ozone, and UV light.

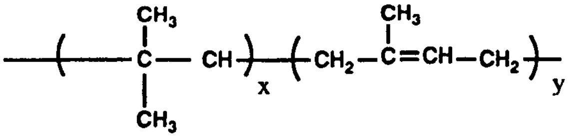
Uses. Roll covers and elements designed to utilize the high damping properties of this material are thought to be the major uses.

Unsaturated Copolymers

Butyl, Chlorobutyl, and Bromobutyl

Designation in ISO 1629: IIR, CIIR, BIIR

Repeat units



$$-\!\left(-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH\right)_x\!-\!\left(CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\right)_y\!-$$

General. Commercial grades of butyl rubber are prepared by copolymerizing small amounts of isoprene with polyisobutylene. The isoprene content of the copolymer is normally quoted as the "mole percent unsaturation," and it influences the rate of cure with sulfur, as well as the resistance of the copolymer to attack by oxygen, ozone, and UV light. Being saturated, however, polyisobutylene naturally confers on a polymer an increased level of resistance to these agencies when compared to natural rubber. Commercial butyl rubbers typically contain 0.5–3.0 mol % unsaturation.

The close packing of the isobutylene chain confers on the polymer a high degree of impermeability to gases but also results in a very "lossy" rubber. The high hysteresis loss can be utilized in some circumstances to provide a good coefficient of friction in wet conditions.

Chlorobutyl and bromobutyl are modified types containing 1.2 wt % chlorine or bromine, the isoprene unit being the site of halogenation. Introduction of the halogen gives greater cure flexibility and enhanced cure compatibility in blends with other diene rubbers. It also confers increased adhesion on other rubbers and metals.

Butyl rubber is not oil resistant.

Butyl and the halogenated butyls can be cured by sulfur, dioxime, and resin cure systems. In addition, the halogenated types can be crosslinked with zinc oxide and diamines. Peroxides cannot be used because they tend to depolymerize the polyisobutylene.

Because of the low level of unsaturation in the main chain, sulfur cures require the more active thiuram and dithiocarbamate accelerators to achieve an adequate state of cure.

Dioxime cures yield vulcanizates with good ozone resistance and moisture impermeability and, as such, are frequently used for curing electrical insulating compounds.

Resin cures utilize phenol formaldehyde resins with reactive methylene groups and a small added amount of either a chlorinated rubber (e.g., polychloroprene) or stannous chloride. If halogenated phenolic resins are used, the additional source of a halogen may not be required. Resin cures give butyl compounds excellent heat stability and are used to good effect where this property is required—for example, in tire curing bags, which must withstand service at 150°C in a steam atmosphere.

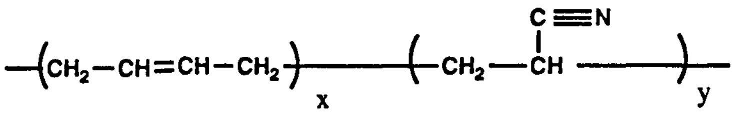
Calcium stearate is added to stabilize the chlorobutyl during processing.

Uses. The main applications of butyl rubber are in wire and cable applications, inner tubes, inner liners in tubeless tires, tire curing bladders, and pharmaceutical closures, the latter utilizing butyl's low impermeability to gases. Other applications include vibration isolation compounds, caulking and sealants, and sheeting for pond liners and roofing.

Nitrile Rubber

Designation in ISO 1629: NBR

Repeat units



$$-\left(CH_2-CH=CH-CH_2\right)_x-\left(CH_2-\overset{\overset{C\equiv N}{|}}{CH}\right)_y-$$

General. Nitrile rubbers are copolymers of butadiene and acrylonitrile produced by emulsion polymerization; "hot" and "cold" polymerized types are available. The "hot" polymerized types generally have higher green strength and are slightly harder to process than "cold" copolymers.

The introduction of acrylonitrile (ACN) into the polymer backbone imparts oil resistance and affects many other properties. Grades that vary in acrylonitrile content from 18 to 50% are commercially available, the percentage of acrylonitrile present forming the basis of the following grade descriptions:

Low	18-24% ACN
Medium low	26-28% ACN
Medium	34% ACN
Medium high	38-40% ACN
High	50% ACN

Many properties are influenced by the acrylonitrile content:

	Acrylonitrile content: 18% → 50%
Oil resistance improvement	→
Fuel resistance improvement	→
Tensile strength improvement	→
Hardness increase	→
Abrasion resistance improvement	→
Gas impermeability improvement	→
Heat resistance improvement	→
Low temperature flexibility improvement	←
Resilience improvement	←
Plasticizer compatibility	→

A typical T_g of an 18% ACN copolymer is $-38^\circ C$, and that of a 50% ACN copolymer $-2^\circ C$.

Carboxylated nitriles, hydrogenated nitrile, liquid nitriles, and blends with polyvinyl chloride (PVC) are also commercially available.

The carboxylated types (XNBR) contain one or more acrylic type of acid as a terpolymer, the resultant chain being similar to nitrile except for the presence of carboxyl groups, which occur about every 100-200 carbon atoms. This modification gives the polymer vastly improved abrasion resistance, higher hardness, higher tensile and tear strength, better low temperature brittleness, and better retention of physical properties after hot oil and air aging when compared to ordinary nitrile rubber.

Low molecular weight liquid nitrile grades are available, and these can be used as compatible plasticizers in the compounding of nitrile rubber. Such plasticizers can be partially crosslinked to the main chain during cure; hence they exhibit low extractability.

PVC/NBR polyblends can be produced as colloidal or mechanical blends, the former generally giving superior properties. Commercially available polyblends have PVC contents ranging from 30 to 55%. The polyblends have reduced elasticity, which gives improved extrudability, but they also exhibit superior ozone resistance, improved oil swell resistance, and tensile and tear strength; these properties, however, are achieved at the expense of low temperature flexibility and compression set. The ozone resistance of such polyblends is improved only if the PVC is adequately distributed and fluxed. Failure due to ozone attack can occur if proper distribution and fluxing are not achieved, but this is harder to do in mechanical blends.

Another method by which the ozone resistance of nitrile rubber can be improved is the removal of the double bonds in the main chain of the copolymer by hydrogenation. Hydrogenated nitrile rubbers also exhibit much greater resistance to oxidation and extend the useful service temperature range of nitriles up to ca. 150°C. Commercially available grades offer different degrees of hydrogenation, with residual double bonds ranging from ca. 0.8 to 6%.

Nitriles have good resistance to oil, aliphatic and aromatic hydrocarbons, and vegetable oils, but they are swollen by polar solvents such as ketones. The unsaturated main chain means that protection against oxygen, ozone, and UV light is required.

In compounding, choice of the correct grade is required if the required balance of oil resistance and low temperature flexibility is to be achieved.

Nitrile rubber can be cured by sulfur, sulfur donor systems, and peroxides. However, the solubility of sulfur in nitrile rubber is much lower than in NR, and a magnesium carbonate coated grade (sulfur MC) is normally used; this is added as early in the mixing cycle as possible. Nitrile rubber requires less sulfur and more accelerator than is commonly used for curing natural rubber. A cadmium oxide/magnesium oxide cure system gives improved heat resistance, but the use of cadmium, a heavy metal, will increasingly be restricted.

The hydrogenated nitrile grades that contain the lowest level of residual double bonds can be crosslinked only by the use of peroxides and radiation, while those with a level of residual double bonds greater than about 3.5% can be cured by sulfur.

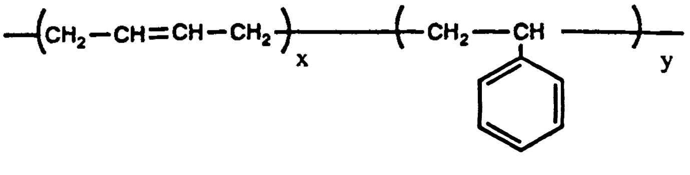
In addition to the normal sulfur cure systems, metal oxides can be used to cure the carboxylated nitriles.

The low temperature properties of nitriles can be improved by the use of suitable plasticizers (e.g., ester plasticizers).

Uses. Nitrile rubber, because of its oil resistance, is widely used in sealing applications, hose liners, roll coverings, conveyor belts, shoe soles, and plant linings. Nitrile rubber is also available as a latex.

Styrene-Butadiene Copolymers

Designation in ISO 1629: SBR
Repeat units



General. When the United States and Germany were cut off from the supplies of natural rubber during World War II, both countries sought to produce a synthetic alternative; SBR was the result, and at one stage it was the most commonly used synthetic rubber. It can be produced by both emulsion and solution polymerization techniques, with the emulsion grades being the most widely used. Emulsion polymerization yields a random copolymer, but the temperature of the polymerization reaction also controls the resultant properties. "Cold" polymerization yields polymers with properties superior to those of the "hot" polymerized types.

Solution polymerization can yield random, diblock, triblock or multiblock copolymers. It is important to note that the triblock, or multiblock copolymers, belong to that class of material termed *thermoplastic elastomers*, and only the random copolymer types are considered here.

Both random emulsion and solution polymerized SBRs contain about 23% styrene.

SBR continues to be used in many of the applications for which it earlier replaced natural rubber, even though it requires greater reinforcement to achieve acceptable tensile and tear strengths and durability. SBR exhibits significantly lower resilience than NR, so that it has a higher heat buildup on flexing, which restricts its use in truck tires, with their thicker sections. This inferior resilience (to natural rubber) is an advantage in passenger car tire treads because the higher hysteresis loss gives increased wet grip and this, combined with the good abrasion resistance that can be obtained from tire tread compounds, ensures for SBR a high volume use in tire production.

The oil resistance of SBR is poor, and the polymer is not resistant to aromatic, aliphatic, or halogenated solvents. Because of unsaturation in the main chain, protection is required against oxygen, ozone, and UV light.

Oil-extended SBR and SBR carbon black masterbatches are supplied by the polymer producers, and such grades give the advantage of reducing the necessity of further additions of filler and oil at the mixing stage.

SBR can be cured by the use of sulfur, sulfur donor systems, and peroxides. Sulfur cures generally require less sulfur (1.5–2.0 phr) and more accelerator than normally are required to cure natural rubber.

Uses. The major use of SBR is in tires, predominantly for car and light trucks; in the latter use it is frequently blended with NR and BR.

SBR also finds use in conveyor belts, molded rubber goods, shoe soles, hoses, and roll coverings.

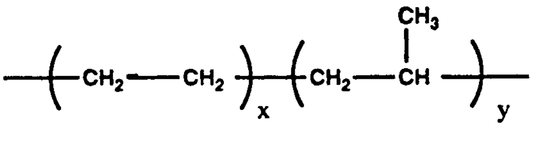
SBR is available as a latex, which is used in carpet backing and other applications.

Polymers Based on Ethylene

Ethylene Propylene and Ethylene Propylene Diene Methylene Rubbers

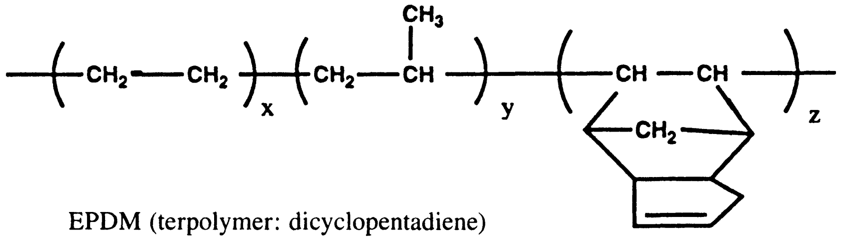
Designation in ISO 1629: EPM, EPDM

Repeat units

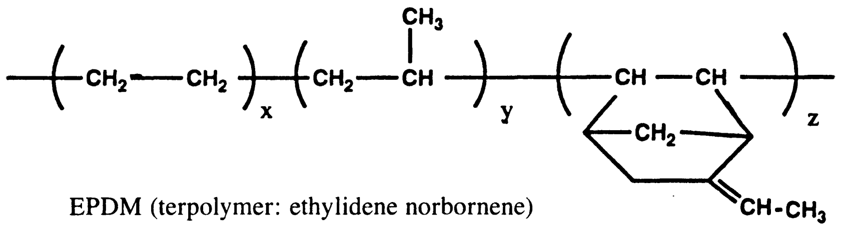


$$-\left(\mathrm{CH_2{-}CH_2}\right)_x\left(\mathrm{CH_2{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}}\right)_y-$$

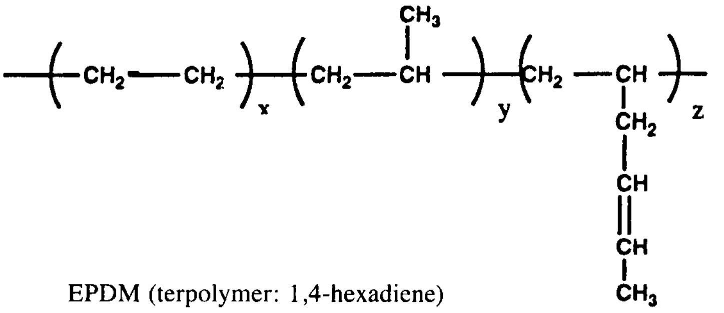
EPM



EPDM (terpolymer: dicyclopentadiene)



EPDM (terpolymer: ethylidene norbornene)



EPDM (terpolymer: 1,4-hexadiene)

General. The copolymerization of ethylene and propylene yields useful copolymers, the crystallization of both polymers being prevented if the ethylene content is in the range 45–60%; grades with higher ethylene contents (70–80%) can partially crystallize. The lower ethylene types are generally easier to process, while green strength and extrudability improve as the ethylene content increases. One disadvantage of the copolymer is that it cannot be crosslinked with sulfur because there is no unsaturation in the main chain. To overcome this difficulty, a third monomer with unsaturation is introduced; but to maintain the excellent stability of the main chain, the unsaturation is made pendant to it. The three types of third monomer used commercially are dicyclopentadiene, ethylidene norbornene, and 1,4-hexadiene. Generally 4–5% of the terpolymer will give acceptable cure characteristics, while 10% gives fast cures; dicyclopentadiene gives the slowest cure rate and ethylidene norbornene the highest.

Since the main chain of both EPM and EPDM rubbers is saturated, both co- and terpolymers exhibit excellent stability to oxygen and UV light, and are ozone resistant.

EPM and EPDM are not oil resistant, and they are swollen by aliphatic and aromatic hydrocarbons, as well as by halogenated solvents. They have excellent electrical properties and stability to radiation. Their densities are the lowest of the synthetics, and they are capable of accepting large quantities of filler and oil. They exhibit poor tack; and even if tackifiers are added, this property still is not ideal for building operations. Adhesion to metal, fabrics, and other materials can be difficult to accomplish.

The copolymers can be cured only by peroxides or radiation, while the terpolymers can be cured with peroxides, sulfur systems, resin cures, and radiation.

The dicyclopentadiene terpolymer can give higher states of cure with peroxides than the copolymer, although in peroxide curing of both the copolymer and terpolymer it is common practice to add a coagent, to increase the state of cure. Triaryl isocyanurate or sulfur is the most common coagent.

Bloom can be a problem in sulfur cures, so selection of the accelerator system is important.

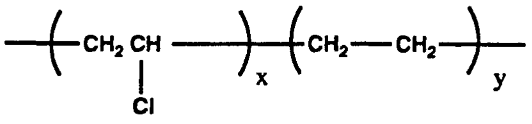
Resin cures utilize the same resins that are used for butyl rubber, but more resin (ca. 10–12 phr) and a halogen donor (10 phr), typically bromobutyl or polychloroprene, are required. Although heat stability is slightly improved by resin curing when compared to sulfur cures, the effect is not as marked as in the resin curing of butyl.

Uses. Wire and cable applications and extrusion profiles (e.g., seals for windows and car doors) probably form the major applications for EPM and EPDM rubber, although it is also used in a wide variety of other extrusion and molding applications. Washing machine door seals molded from EPDM are starting to replace NR as washer/dryers are becoming more common.

Chlorinated Polyethylene

Designation in ISO 1629: CM

Repeat units



$$-\left(\mathrm{CH_2}\,\underset{\overset{|}{\mathrm{Cl}}}{\mathrm{CH}}-\right)_x\left(\mathrm{CH_2}-\mathrm{CH_2}\right)_y-$$

General. Although polyethylene has a low T_g it is highly crystalline. Hence it is a thermoplastic and not a rubber at ambient temperatures. If the regularity of the main chain could be interrupted, and crystallization effectively prevented, a useful elastomer might result. The chlorination of polyethylene is one method by which crystallization can be prevented, and chlorinated polyethylene is commercially available; the degree of chlorination, however, determines how rubbery the modified polymer is. Polymers with a chlorine content of ca. 25% are still relatively crystalline, while those with a chlorine content greater than 40% become increasingly brittle as a result of interaction between the now highly polar polymer chains. The most desirable polymers, in terms of the absence of crystallinity and flexibility of the chains, are obtained when the degree of chlorination is around 35%.

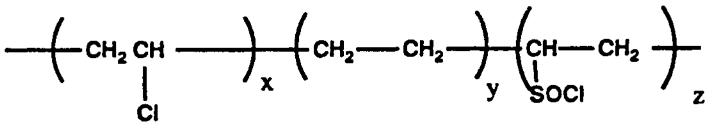
As with other polar polymers, these materials will resist oil, and the absence of a double bond in the main chain confers excellent stability to the deleterious effects of oxygen, ozone, and light. Because there are no double bonds in the main chains, these materials can be crosslinked only by the action of peroxides or radiation. It is recommended that metal oxides (of Mg and Pb) be added to act as acid acceptors during vulcanization; zinc oxide is not used because it decreases the stability of the polymer.

Uses. It is fairly true to say that the use of chlorinated polyethylene has not been large, possibly as a result of the greater ease with which the chlorosulfonated polyethylene (Hypalon), a closely related competitor material, can be cured. When selected, chlorinated polyethylene finds its major use in the wire and cable industry.

Chlorosulfonated Polyethylene

Designation in ISO 1629: CSM

Repeat units



$$-\!\left(CH_2\,\underset{\displaystyle Cl}{CH}\right)_x\!\left(CH_2-CH_2\right)_y\!\left(\underset{\displaystyle SOCl}{CH}-CH_2\right)_z$$

General. The level of chlorination in these materials varies, influencing the properties of the product in exactly the same manner as the closely related chlorinated polyethylene. The introduction of the chlorosulfonyl group in small amounts ($<$ 1.5%) gives greater choice in the methods used to crosslink to the polymer. However, in general, the properties exhibited by these materials are equivalent to those of chlorinated polyethylene.

Dupont recently announced the availability of a modified chlorosulfonated polyethylene based polymer trade-named Acsium. In this modified polymer the chlorine content is reduced, but an additional pendant alkyl group is used to restrict the ability of the polymer to crystallize. The result is a polymer with a lower T_g than the conventional CSM polymer.

In addition to the use of peroxides for crosslinking, metal oxides, polyfunctional alcohols, amines, and epoxide resin cure systems can be used with CSM rubbers. In the metal oxide based cure systems it is usual to add a weak acid, such as stearic acid, and accelerators, such as MBT, MBTS, or TMTD [see Table 16, below]; magnesium or lead oxides are generally used.

The most common polyfunctional alcohol used is pentaerythritol, but a base is also required to complete the cure system, magnesium and calcium oxide giving more controlled cure rates than stronger bases.

As with chlorinated polyethylene rubber, chlorosulfonated polyethylene exhibits good resistance to oxygen, ozone, and UV light. The polar nature of the polymer chain also confers oil resistance.

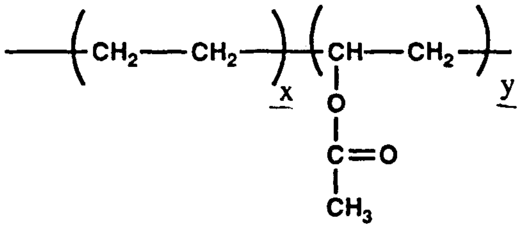
Uses. The excellent UV stability of chlorosulfonated polyethylene has led to a wide use as a roof sheeting material, and the ability to compound this material to slowly cure at ambient temperatures is an added advantage. Another sheeting application is pond liners. Wire and cable applications, coated fabrics and items made from them, hoses, and molded goods are other areas in which this material finds use.

Acsium is said to have been designed for use in synchronous drive belt applications.

Ethylene Vinyl Acetate Copolymers

Designation in ISO 1629: EAM

Repeat units



$$-\left(CH_2-CH_2\right)_x\left(\underset{\substack{|\\O\\|\\C=O\\|\\CH_3}}{CH}-CH_2\right)_y-$$

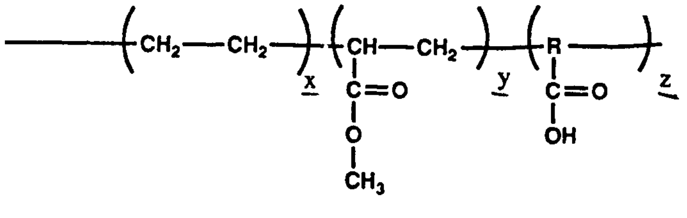
General. The copolymerization of ethylene with vinyl acetate (VA) is another method by which the crystallinity of polyethylene can be reduced and a rubbery polymer obtained. The final properties of the copolymer depend on the VA content: at a VA level of 50% the copolymer is entirely amorphous; elastomeric grades generally contain 40–60 wt % VA. The oil resistance of the copolymer, which is also dependent on the VA content, generally lies between that of SBR and that of polychloroprene.

The saturated main chain of the copolymer confers excellent resistance to oxygen, ozone, and UV light, but it means that these materials cannot be crosslinked by sulfur. Peroxides and radiation are the only methods by which crosslinking can be accomplished, and coagents are often required to achieve the required state of cure.

Uses. The main use of EVA is in wire and cable applications, although their electrical properties are inferior to those of EPDM.

Ethylene/Acrylate Rubbers: Vamac

Repeat units



$$-\left(CH_2-CH_2\right)_x\left(\underset{\substack{|\\C=O\\|\\O\\|\\CH_3}}{CH}-CH_2\right)_y\left(\underset{\substack{|\\C=O\\|\\OH}}{R}\right)_z-$$

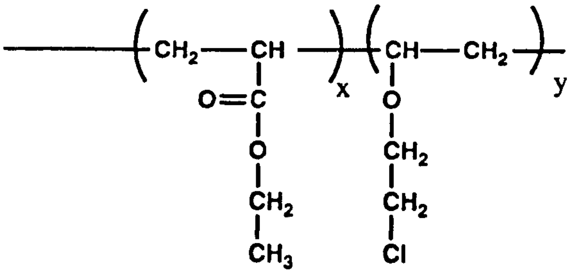
General. The terpolymer Vamac, produced by Dupont, exhibits properties generally comparable to those of an acrylate. The introduction of ethylene into the main chain gives low temperature performance similar to that of a polyoctyl acrylate polymer and oil resistance similar to that of a butyl acrylate polymer. In high temperature performance, Vamac is slightly inferior to the acrylates, but this deficit is compensated for by the generally higher physical strength.

Vamac is generally cured with diamines, with *N,N'*-diphenylguanidine (DPG) as an accelerator, but it is also possible to crosslink this material with peroxides.

Uses. Vamac finds use as a sealing material in automative applications and marine motor lead wire insulation. It has also been used as the base polymer for low flammability, halogen-free, cable jacketing compounds.

Acrylates

Designation in ISO 1629: ACM
Examples of repeat units



Ethyl acrylate (95%)

Chloroethyl vinyl ether (5%)

General. Although the chemical structure shown is used as an example, acrylates are a class of materials rather than one single type. These polymers are formed by the copolymerization of an acrylic ester and a cure site monomer, ethyl acrylate and chloroethyl vinyl ether, respectively, being illustrated here.

The choice of acrylic ester, hence its polarity, determines the low temperature flexibility and the heat and chemical resistance of the polymer; both alkyl and alkoxy acrylic esters are used as monomers. Within the alkyl acrylic esters, ethyl acrylate has the highest polarity, hence gives the best oil and heat resistance, but the worst low temperature performance. Low temperature properties improve as the alkyl acrylic ester changes from ethyl to butyl, and on to higher analogues, but this is at the expense of heat stability and oil resistance.

It is, of course, possible to copolymerize mixed alkyl acrylic esters to achieve a compromise in these properties. Alkoxy acrylic esters also confer improved low temperature properties.

One factor that has perhaps slowed the use of these materials is the perceived difficulties in their processing. The acrylates are soft and thermoplastic, and prone to scorch if tight process control is not in force in a factory.

The absence of main chain unsaturation confers good resistance to oxygen, ozone, and light, while the polarity contributes oil resistance to the copolymer.

The cure site monomer directly controls which cure systems can be used to vulcanize the rubber. Since cure behavior is determined by the cure site monomer, which can differ among suppliers and, presumably, grades, it is advisable to read the manufacturer's recommendation when choosing a cure system.

The first acrylates to be developed were cured by:

1. Amines (e.g., trimene base, triethylene tetramine, Diak No. 1, from Dupont).
2. Red lead and ethylene thiourea.

Of the amines, Diak No. 1 is the most efficient, since it does not volatilize during processing. Sulfur and sulfur-bearing materials act as retarders in this type of cure, also as a form of antioxidant.

Newly introduced polyacrylate rubbers can be cured with certain amines and are more responsive to a broad range of curative systems (e.g., alkali metal stearate/sulfur or sulfur donor, methyl zimate, and ammonium adipate).

Good, or best, compression set requires a postcure, although at least one manufacturer has introduced a new series of polyacrylates that only require a press cure.

The use of softeners and plasticizers presents a problem. TP90B, thioethers, and certain adipates can give low temperature flexibility to −45°C, but these agents are volatile at postcure temperatures; hence their effect is easily lost.

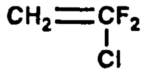
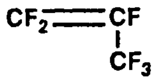
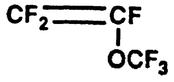
Uses. The main use for acrylates is in sealing applications, where improved heat stability over nitrile rubber is the benefit. Automotive transmission seals are probably the major use.

Fluorocarbon Rubbers

Designation in ISO 1629: FPM

General. The importance of fluorine in polymer chemistry has been known since the discovery of Teflon (polytetrafluoroethylene: PTFE) in 1938. Highly fluorinated polymers are very stable and have remarkable resistance to oxidative attack, flame, chemicals, and solvents.

The fluorine-containing compositional units generally used to produce commercial polymers are as follows:

$CH_2{=}CF_2$	Vinylidene fluoride
 $CH_2{=}\underset{\underset{Cl}{\vert}}{C}F_2$	Chlorotrifluoroethylene
 $CF_2{=}\underset{\underset{CF_3}{\vert}}{CF}$	Hexafluoropropylene
$CF_2{=}CF_2$	Tetrafluoroethylene
 $CF_2{=}\underset{\underset{OCF_3}{\vert}}{CF}$	Perfluoro(methyl vinyl ether)

Commercial polymers are understood to have the following compositions:

KEL F: a copolymer of vinylidene fluoride and chlorotrifluoroethylene. This material generally exhibits better resistance to oxidizing acids and better low temperature properties than other types.

Types such as Viton A: a copolymer of vinylidene fluoride and hexafluoropropylene.

Types such as Viton B: a terpolymer of vinylidene fluoride, hexafluoropropylene, and tetrafluoroethylene. This type has slightly improved thermal stability and fluid resistance when compared to the Viton A type.

Types such as Viton G: these grades are differentiated from the others by being peroxide curable, a condition that is achieved by the addition of a cure site monomer, said to be bromotetrafluorobutene. The grades are basically terpolymers, but the exact composition differs; for example, Viton G is said to be based on vinylidene fluoride, hexafluoropropylene, tetrafluoroethylene, and the cure site monomer; the hexafluoropropylene is said to be replaced by perfluoro(methyl vinyl ether) in the Viton GLT grade. As well as being peroxide curable, these grades exhibit superior resistance to aqueous media and steam. The GLT grade exhibits superior low temperature properties.

Kalrez: a copolymer of tetrafluoroethylene and perfluoro(methyl vinyl ether) plus a cure site monomer. This is the most thermally stable and chemically resistant polymer currently available, and one of the most expensive.

Aflas: a copolymer of tetrafluoroethylene and propylene.

Apologies are due to the other manufacturers of fluorocarbon rubbers, 3M (Fluorel), Montedison (Tecnoflon), and Daikin (Dai-EL), for facilitating the presentation by using the Viton trade name to illustrate part of the available spectrum of fluoroelastomers.

The resistance to heat and chemicals of the fluoropolymers is mainly dependent on the extent of fluorination and stability of the crosslinks. For example, most fluorocarbons have fluorine contents of 50–70%; more chemically resistant types have 65–69%; and Kalrez, which is almost completely fluorinated, has 70%. For comparison, fluorosilicones contain about 36% fluorine.

The fluorocarbons have the best heat stability of all rubbers. Kalrez, which exhibits the best performance, is capable of giving extended service life at temperatures exceeding 250°C. As a group, fluorocarbons resist aliphatic, aromatic, and chlorinated hydrocarbons, as well as most oils and mineral acids. They are also highly resistant to oxygen, ozone, and UV light.

There are several methods by which the fluorocarbons can be cured; the principal methods are summarized as follows.

Cure agent	Metal oxide acid acceptor	Comments
Diamine (e.g., hexamethylenediamine)	Magnesium oxide or calcium oxide	General-purpose cure system, fairly resistant to scorch. Best heat resistance, but not particularly resistant to acids.
	Red lead	Best acid and steam resistance, but exhibits strong tendency to scorch.
	Zinc oxide/dibasic lead phosphite	Least tendency to scorch, intermediate acid resistance.
Bisphenol A/ organophosphonium salt	Magnesium oxide/calcium hydroxide	Improved compression set, reduced fissuring, and shrinkage. Most common cure system for sealing applications.

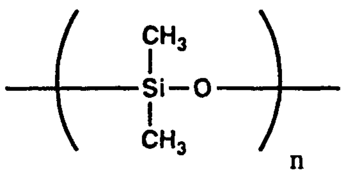
		Changes in the acid acceptor generally give the same trends as in the use of diamine cures.
Peroxide (not for all grades)	Acid acceptor required	Inferior compression set to the bisphenol cure. Improved resistance to amine-stabilized oils.

Only the large particle sized blacks, MT or Austin Black, and mineral fillers are used in the compounding of these materials.

Uses. The main uses of the fluorocarbons are in sealing applications.

Silicone Rubber

General. Silicone rubbers contain the following dimethyl siloxane unit:



$$\left(-\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{\mathrm{Si}}}-O-\right)_n$$

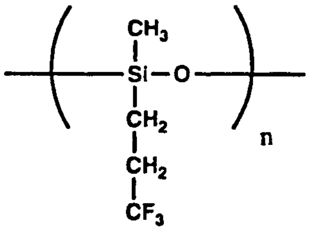
The millable gums, the only type considered here, generally contain 5000–9000 of the dimethyl siloxane unit.

Polymers that contain simply the repeat unit above are termed methyl silicones and are given the ISO designation MQ.

It is possible to replace a few of the methyl groups (< 0.5%) with a vinyl group, and the resultant vinyl methyl silicones (ISO designation VMQ) exhibit improved vulcanization characteristics and lower compression set.

The replacement of 5–10% of the methyl groups on the silicon atom with phenyl groups gives polymers that exhibit superior low temperature properties. Brittleness temperatures of approximately −117°C can be achieved, compared to the approximately −70°C for the VMQ types. The ISO designation for the phenyl-modified silicones is either PMQ or PVMQ depending on whether the grade is vinyl modified.

To improve the solvent resistance of the polymer, a fluoroalkyl group can be substituted on each silicon atom for one of the methyl groups, the resultant polymer having the following repeat unit.



$$\left(-\underset{\substack{|\\CH_2\\|\\CH_2\\|\\CF_3}}{\overset{\substack{CH_3\\|}}{\mathrm{Si}}}-O-\right)_n$$

ISO designation: FMQ or FVMQ

Silicone rubbers exhibit good resistance to heat aging and are considered to be usable up to 200°C. Although silicones do not exhibit high strength at room temperature, they do retain their properties at high temperatures to a much greater extent than other rubbers.

The long-term performance of silicones is generally excellent, although exposure to steam at high pressure, as well as aging in closed systems (oxygen essentially excluded), can lead to degradation via a hydrolysis reaction; this is especially true if acidic peroxide remnants have not been driven off during postcuring.

The oil resistance of silicone is roughly equivalent to that of polychloroprene, while the fluorosilicones approach the fluorocarbons in this respect.

Two further interesting points are noted: (1) upon burning, silicones form silica, which is an insulator, and thus cables insulated with silicone can function after short-term exposure in a fire situation; and (2) silicones are physiologically inert, and this property has led to their use in a wide variety of medical applications, including medical implants.

Because silicones are saturated, their resistance to oxygen, ozone, and UV light is excellent, but for this reason peroxides must be used for vulcanization.

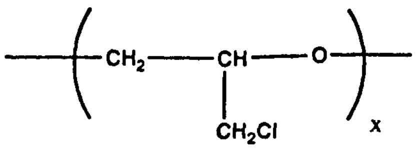
Silica fillers are generally used to reinforce these materials, carbon black being less reinforcing and its use somewhat specialized.

Uses. Silicones are widely used in many applications, such as pharmaceutical, medical, wire and cable, automotive, and aerospace, which utilize the excellent general inertness of these materials. They do, however, have a high price.

Other Saturated Rubbers

Epichlorohydrin-Based Rubbers

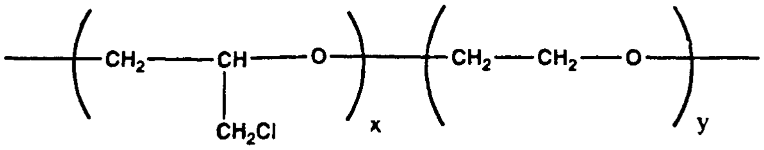
General. These rubbers are available as a homopolymer:



$$-\left(CH_2-\underset{CH_2Cl}{\underset{|}{CH}}-O\right)_x-$$

ISO Designation: CO

or as a copolymer with ethylene oxide:



$$-\left(CH_2-\underset{CH_2Cl}{\underset{|}{CH}}-O\right)_x\left(CH_2-CH_2-O\right)_y-$$

ISO Designation: ECO

or as a terpolymer with a small amount of unsaturated allyl glycidyl ether. There is no ISO designation for the terpolymer, but ETER is used by the American Society for Testing and Materials (ASTM). As with EPDM, this unsaturation is pendant to the main chain, which allows vulcanization with sulfur, while preserving the stability of the main chain. The ability to be cured by sulfur also allows the terpolymer to be used in blends with other polymers (e.g., nitriles).

As might be expected, the homopolymer having the highest polarity exhibits the best oil resistance, but this is at the expense of low temperature flexibility. The homopolymer also has a low permeability to gases. The unsaturated backbone gives these materials good resistance to oxygen, ozone, and light.

The main method of crosslinking the homopolymer and copolymer is by use of thioureas, and, because the cure reaction requires basic conditions, an acid acceptor is also added. Litharge, red lead, magnesium oxide, and dibasic lead phosphite are commonly used acid acceptors. The most commonly used thiourea is ethylene thiourea, but this compound has a tendency to promote mold fouling.

The Echo S cure system commercialized by B.F. Goodrich is said to give improved scorch safety and reduced mold fouling over the ue of thioureas. Inorganic acid acceptors other than those based on lead are recommended for use with the Echo S cure system.

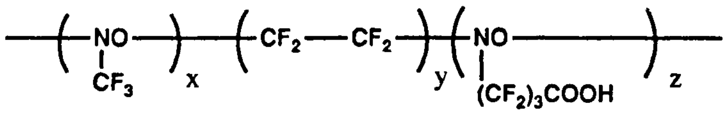
The terpolymers can be cured by the use of sulfur and peroxides as well as by the use of thioureas.

Uses. The main use of epichlorohydrin is in the automotive sector, for various seals and hoses.

Nitrosofluororubbers

Designation in ISO 1629: AFMU

Repeat units



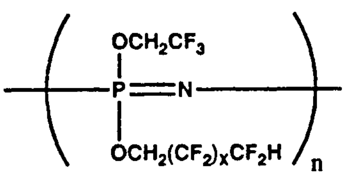
$$-\left(\underset{CF_3}{\underset{|}{NO}} \right)_x \left(CF_2-CF_2 \right)_y \left(\underset{(CF_2)_3COOH}{\underset{|}{NO}} \right)_z-$$

General. AFMU is a terpolymer based on trifluoronitrosomethane, tetrafluoroethylene, and perfluoro (nitrosobutyric acid) in which the latter acts as the cure site monomer. This material is included only for the sake of completeness, since it is an extremely expensive elastomer whose uses are restricted to highly specialized applications. The nitrosofluororubbers exhibit poor heat stability (ca. 150°C) for a fluorinated material and are difficult to crosslink; the vulcanizates do not exhibit good mechanical strength. Applications have been in the U.S. space program and areas that have utilized AFMU's reportedly excellent resistance to fire.

Polyphosphazene Rubber

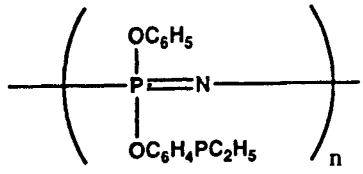
Designation in ISO 1628: FZ and PZ

Repeat units



$$-\left(\overset{OCH_2CF_3}{\underset{OCH_2(CF_2)_xCF_2H}{P}} = N \right)_n-$$

FZ



$$\left(\begin{array}{c} \mathrm{OC_6H_5} \\ | \\ -\mathrm{P{=}N}- \\ | \\ \mathrm{OC_6H_4PC_2H_5} \end{array} \right)_n$$

PZ

General. The 55% fluorine content of the FZ type is intermediate between the fluorosilicones and the fluorocarbons; thus, in general, the chemical resistance also lies between those two materials. As well as exhibiting a good resistance to chemicals, the FZ type of polymer gives superior low temperature performance when compared to the fluorocarbons.

The PZ type is thought to be commercially available as Eypel A (Ethyl Corporation). This material is not fluorinated but is claimed to give equivalent oil resistance to chlorosulfonated polyethylene and Vamac. It is self-extinguishing upon the removal of a flame and does not contain halogens—advantages indicating that wire and cable applications could be a potential market.

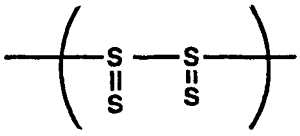
The FZ materials appear to be precompounded by the supplier, although it is understood that peroxides are the cure agent used.

The PZ materials can be crosslinked by peroxides, sulfur, or radiation.

Polysulfides

Designation in ISO 1629: OT and EOT

General. These materials are formed by the reaction of a dihalide with sodium polysulfide. The main chain of the polymer formed from this reaction contains the following grouping:



$$\left(\begin{array}{ccc} -\mathrm{S} & - & \mathrm{S}- \\ \| & & \| \\ \mathrm{S} & & \mathrm{S} \end{array} \right)$$

Four types of polymer are available from Thiokol, the only manufacturer of this type of material.

Thiokol A is produced from ethylene dichloride and sodium polysulfide. A high molecular weight polymer is obtained with predominantly hydroxyl end groups on the polymer chain. This type of polysulfide rubber was the first commercial grade but has, to a large extent, been superseded by the later FA type.

Thiokol FA is produced from a mixed dihalide, di-2-chloroethyl formal and ethylene dichloride, and sodium polysulfide. Here again a high molecular weight polymer (ca. 100,000) is produced with predominantly hydroxyl end groups on the polymer chain. The sulfur content of the resultant polymer is 49%.

Thiokol ST is produced from di-2-chloroethyl formal with a small percentage of 1,2,3-trichloropropane to provide a branch point for improving the cure state obtainable, hence the compression set. A much lower molecular weight polymer (ca. 80,000) is produced, with predominantly mercaptan (SH) end groups. The sulfur content of the resultant polymer is 37%.

Thiokol LP grades are liquid polymers used in sealant and mastic applications, and are formed by breaking down a high molecular weight polymer in a controlled manner. The liquid polymer again has mercaptan end groups.

The polysulfide grouping in the polymer confers an excellent resistance to solvents, with the sulfur content of the polymer determining the degree of swell.

The resistance of these materials to solvents, especially ketones, is good and is often the major reason for their use.

The resistance to ozone and UV light is excellent, although the use of 0.5 phr of nickel dibutyl dithiocarbamate (NBC) will improve ozone resistance further at high ozone concentrations.

Both Thiokol A and FA require peptization to ensure ease of processing, and this is normally accomplished by the addition of MBTS and DPG onto a two-roll mill maintained at 160°F prior to the addition of other ingredients.

The ST types do not require peptization.

The A and FA types can be cured by the addition of zinc oxide alone at ca. 10 phr. Further additions of sulfur, at up to 1 phr, act as accelerators, but these are needed only if very fast curing compounds are required.

Any one of the following systems may be used to cure the ST polymers.

Component	phr
p-Quinonedioxime	1.5
Zinc oxide	0.5
Stearic acid	0.5–3.0
p-Quinonedioxime	1.0
Zinc chromate	10.0
Stearic acid	1.0
Zinc peroxide	6.0
Stearic acid	1.0

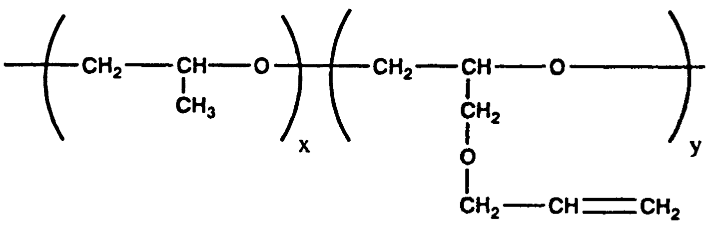
Uses. Polysulfide polymers are used in roller covering applications and hose liners, as well as in molded goods.

The sealants find use in the construction and aerospace industries.

Propylene Oxide Rubber

Designation in ISO 1629: GPO

Repeat units



Propylene oxide Allyl glycidyl ether

General. The only commercially available material in this class, Parel, is a copolymer of propylene oxide and allyl glycidyl ether.

The absence of any polar grouping gives this material superior low temperature performance when compared to the epichlorohydrin terpolymers, but this advantage is secured at the expense of oil resistance. The unsaturated nature of the main chain confers excellent resistance to oxygen, ozone, and UV light.

The only cure systems seen for this material are based on sulfur vulcanization.

Uses. Little comment can be made on the uses of this material. It is used in some moldings, where the advantages of heat resistance, low temperature performance, and oil resistance, roughly equivalent to the same properties of polychloroprene, can be utilized. It has been investigated for use in engine mounts.

Polyurethane Rubbers

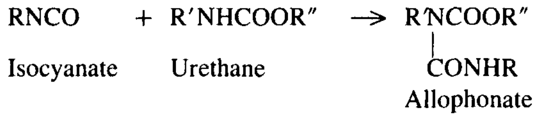
Designation in ISO 1629: AU and EU

General. Polyurethanes, as a class of materials, are one of the most versatile available. By varying the reactants, their amounts, and the reaction conditions, one can obtain millable elastomeric gums, hard rigid plastics, reactive liquids, and foams. The versatility is such that it is very difficult to provide a brief summary, and readers are directed to Reference 7 for further information.

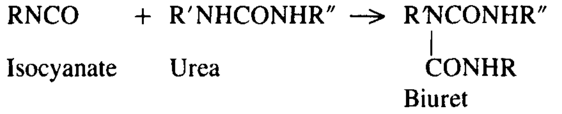
The basic reactions in polyurethane chemistry are:

$$\underset{\text{Isocyanate}}{\text{RNCO}} + \underset{\text{Alcohol}}{\text{R'OH}} \rightarrow \underset{\text{Urethane}}{\text{RNHCOOR}'} \qquad (1)$$

$$\underset{\text{Isocyanate}}{\text{RNCO}} + \underset{\text{Amine}}{\text{R'NH}_2} \rightarrow \underset{\text{Urea}}{\text{RNH}-\text{CONHR}'} \qquad (2)$$



$$\underset{\text{Isocyanate}}{\text{RNCO}} + \underset{\text{Urethane}}{\text{R'NHCOOR}''} \rightarrow \underset{\text{Allophonate}}{\text{R}'\underset{\substack{|\\ \text{CONHR}}}{\text{N}}\text{COOR}''} \qquad (3)$$



$$\underset{\text{Isocyanate}}{\text{RNCO}} + \underset{\text{Urea}}{\text{R'NHCONHR}''} \rightarrow \underset{\text{Biuret}}{\text{R}'\underset{\substack{|\\ \text{CONHR}}}{\text{N}}\text{CONHR}''} \qquad (4)$$

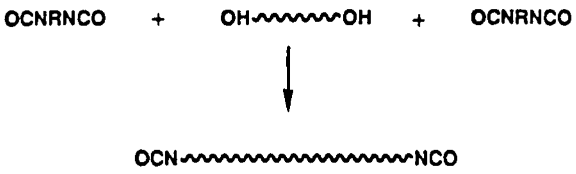
In reactions (3) and (4) the isocyanate is capable of reacting with the active hydrogen in a urethane or urea group, to give branching or crosslinking by the formation of an allophonate or a biuret group.

The most important reactions for the production of elastomers, however, utilize diisocyanates and polyols, and the elastomeric products formed can be castable polyurethanes, millable gums, thermoplastic polyurethanes, and polyurethanes of other types.

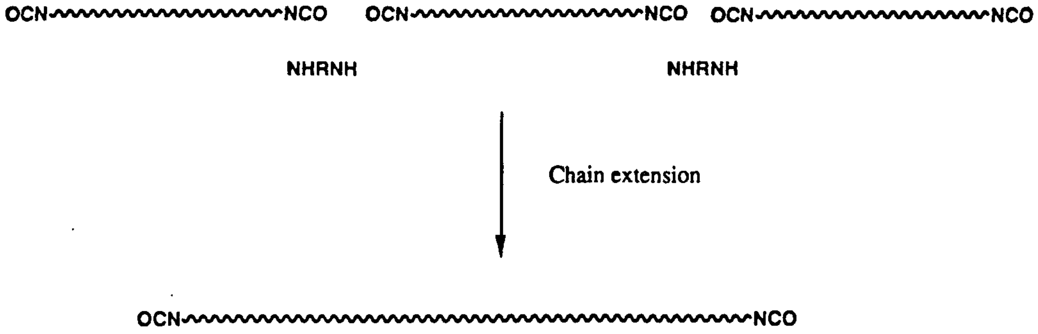
Castable Polyurethanes. These liquid systems can be produced either in a one-shot system (i.e., the diisocyanate, polyol, and chain extender reacted in a single stage) or, more usually, as a prepolymer, which is chain extended and crosslinked at a later stage.

In the prepolymer system, the diisocyanate and polyol (either a polyether or a polyester) are reacted to give a prepolymer, which may be either a liquid or a waxy solid. The reactant ratios used ensure the prepolymer contains isocyanate groups at the chain ends.

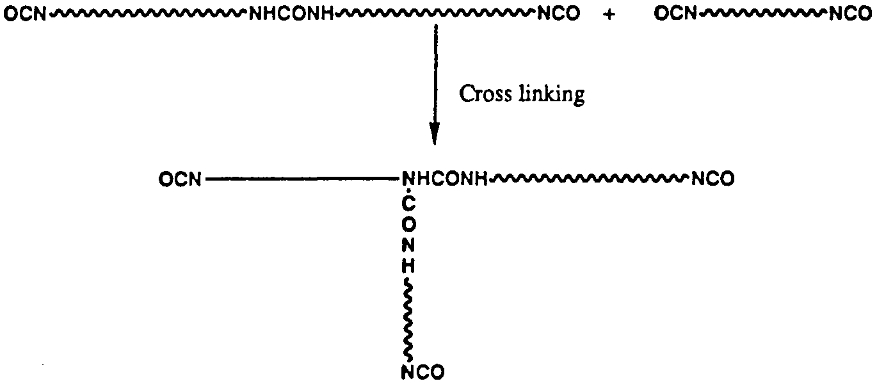
Isocyanate-terminated prepolymer



The prepolymer can, when required, then be chain extended to give a high molecular weight crosslinked product:

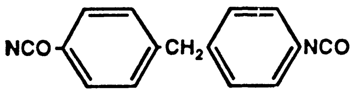


Crosslinking and branching can be promoted either by the use of a triol as a chain extender or by using less chain extender than is theoretically required; the unreacted isocyanate end groups then react with urethane groups in the main chain to form allophonate or biuret crosslinks.

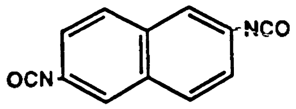


Crosslinking by biuret formation

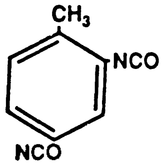
Typical diisocyanates that are used are:



MDI (diphenylmethane 4,4′-diisocyanate)



NDI (naphthalene 1,5-diisocyanate)



TDI (toluene diisocyanate)

$OCN(CH_2)_6NCO$

HDI (hexamethylene diisocyanate)

Typical polyols include:

$$HO(CH_2)_2\left(OCO(CH_2)_4COO(CH_2)_2\right)_n OH$$

Polyethylene adipate (a polyester)

$$OH\left((CH_2)_4O\right)_n H$$

Poly(tetramethylene ether) glycol (a polyether)

Typical chain extenders that are used are MOCA (4,4-methylene bisorthochloroaniline), butane diol or trimethylolpropane.

Variations can be made in the following compositional categories:

1. Type of diisisocyanate
2. Type of polyol and its molecular weight
3. Type of chain extender
4. Ratio of prepolymer to chain extender

By altering the foregoing components, it is possible to make products elastomeric or rigid and, by the inclusion of water or a blowing agent, cellular products can be obtained. Clearly, so many possible variations make general comments difficult, but the following are generally accepted.

1. Polyester polyurethanes generally give superior mechanical properties and chemical resistance, but inferior hydrolytic stability.
2. Polyether polyurethanes give superior low temperature properties and hydrolytic stability.
3. Diamine chain extenders give superior properties to diol-cured elastomers.
4. Mechanical properties are generally improved as the hardness increases.

Processing of liquid systems proceeds as follows:

Prepolymer
mix → degas → cast → cure (solid)
↓
postcure
Chain
extender

The mixing can be done by hand, or in low pressure mixer/dispensers, and in reaction injection molding (RIM) machines. In the latter operation, no degassing is required.

Millable gums. The diisocyanates and polyols are reacted to form high molecular weight hydroxyl-terminated millable gums. These millable gums are compounded and processed as conventional elastomers, both sulfur and peroxides being used to cure the polymers. Here again, polyether and polyester types are available, and the differences between these two types referred to above also apply here.

Thermoplastic Polyurethanes. Consider the polyurethane:

$$\mathrm{HO{-}R{-}\left(OCONHR'NHCOOR\right)_{n}{-}OCONH{-}R'{-}NCO}$$

When R is small, such as the tetramethylene group $(CH_2)_4$, and R′ is diphenylmethane, the polymers that result are rigid plastics, similar to polyamides.

If R is a polymeric ester or ether, of molecular weight 1000–3000, a flexible elastic material will result. By reacting MDI and active hydrogen components (polyether/ester and a short-chain glycol) in equivalent stoichiometric quantities, a linear polymer with virtually no crosslinks is obtained.

If U is used for the diisocyanate, G for the short-clain glycol, and a wavy line for the higher molecular weight flexible polyether or polyester, the resultant polymer can be represented as follows:

This is a copolymer of the $(AB)_n$ type, where the UGU sequences represent the urethane "hard segment" and the wavy line represents the "soft" flexible segment. Microphase separation of the hard segment occurs as shown in Figure 1.

The thicker lines represent the sequences of "hard" urethane segments, and the clusters of these effectively act as crosslinks, making the material perform like a conventional elastomer. When the temperature is raised high enough, the clusters disassociate and the material can be made to flow; when subsequently cooled, the clusters can re-form and the material again exhibits elastomeric properties. Thus these materials

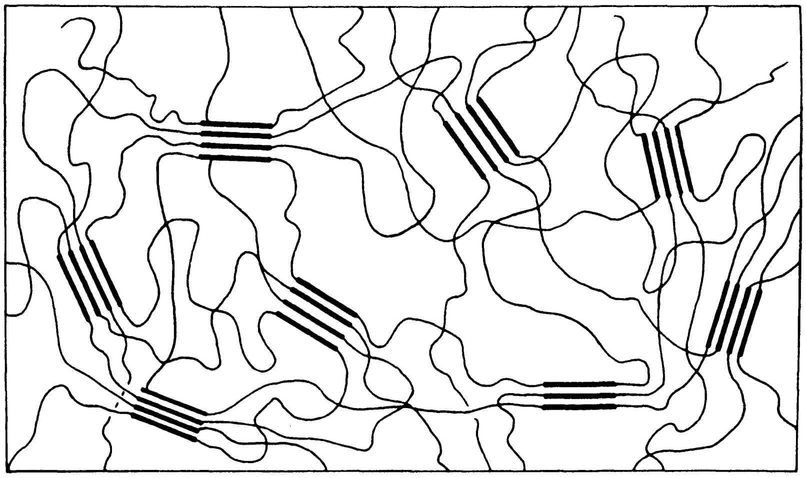


Figure 1 Schematic representation of thermoplastic polyurethane morphology.

show elastomeric behavior at room temperature but can be processed as thermoplastics. Hence the name of the material class—thermoplastic elastomers (TPEs).

Thermoplastic polyurethanes exhibit the same general properties as the cast and millable types; unlike the conventional rubbers, they do not require compounding.

Other Types of Polyurethane. These are listed but not discussed further.

1. One-component blocked, cast polyurethanes. Here reactive isocyanate end groups are prevented from reacting by a "blocking agent." Upon heating to cure temperatures, the blocking agent splits off and cure commences.
2. Cast systems to give rigid plastics.
3. Polyurethane foams and microcellular elastomers.
4. Spandex fibers.

Polyurethane elastomers are exceptionally tough and abrasion resistant; in addition, they resist attack by oil. The polyester types are susceptible to hydrolytic attack above ambient temperatures, and certain polyester thermoplastic polyurethanes have been known to stress-crack in cable jacketing applications when in contact with water at ambient temperatures; the latter effect has sometimes, incorrectly, been ascribed to fungal attack. Polyether types are far more resistant to hydrolytic attack. Certain polyurethanes can be attacked by UV light, and resistance to this agency is determined primarily by the isocyanate.

The polyurethanes are resistant to ozone attack.

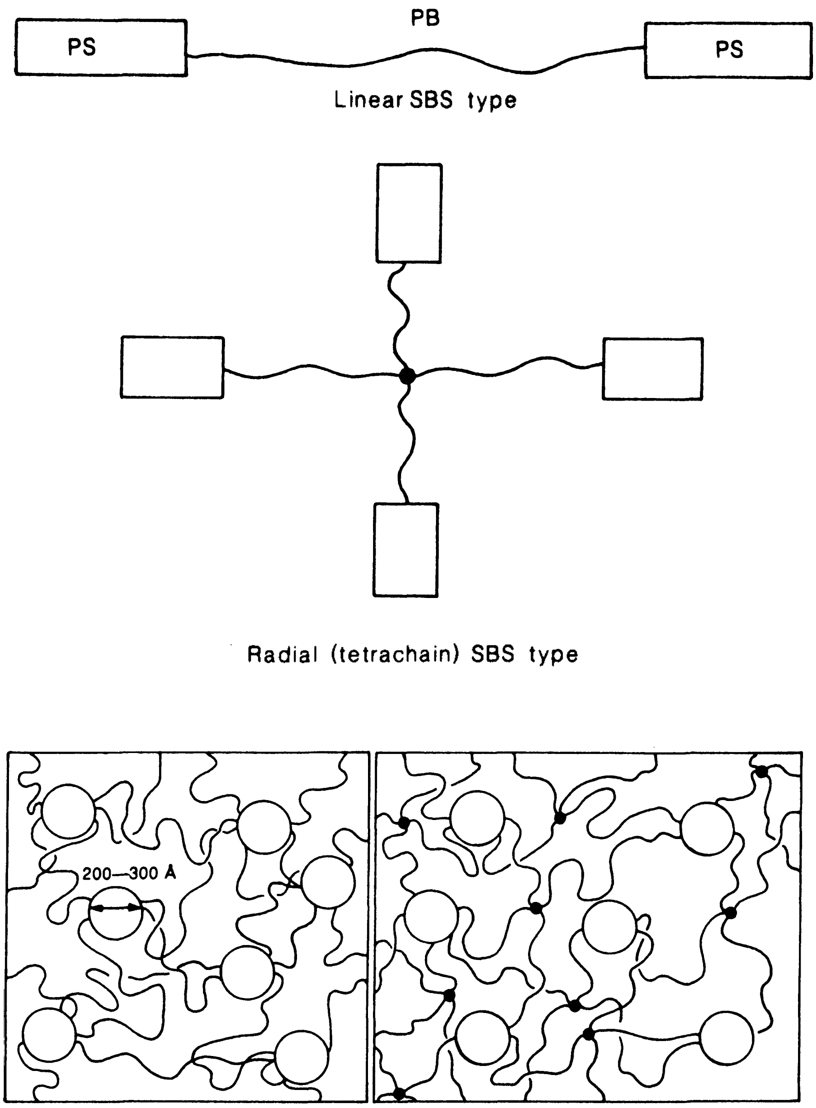
Uses. Polyurethanes are used in a wide variety of applications: seals, metal forming dies, liners, coupling elements, rollers, wheels, and conveyor belts are examples. The thermoplastic polyurethanes are used as cable jacketing materials, conduits, fabric coatings, in ski boots and other rigid boot soles, in automotive body components, and in gear wheels and other business machine parts.

Thermoplastic Elastomers

General. This unique class of materials has formed the basis for whole texts [8,9].

Thermoplastic elastomers exhibit elastomeric behavior at room temperature but can be processed as thermoplastics. Before one can understand the performance of these materials, an understanding of how they can give their unique properties of elasticity and thermoplasticity is required; this is best done by considering such block thermoplastic elastomers as styrene–butadiene–styrene (SBS).

It is possible to produce a block copolymer by the anionic polymerization of styrene and butadiene, as depicted in Figure 2: the polystyrene and polybutadiene are mutually incompatible; hence they phase separate to give the morphology shown. This simplified representation of the morphology shows spheres of polystyrene embedded in a continuous soft elastomeric polybutadiene phase. Here the polystyrene domains act as



Linear SBS type

Radial (tetrachain) SBS type

Linear type

Radial type

Figure 2 Simplified schematic representation of the structure of SBS block copolymers.

"pseudocrosslinks" and the polybutadiene conveys elasticity to the material. When heated above the T_g of polystyrene, the domains soften and disassociate, and the material can be made to flow. When cooled, the polystyrene domains re-form and elastomeric behavior returns.

The following features are therefore required for a material to act as a thermoplastic elastomer:

1. A structural feature that acts as a pseudocrosslink at room temperature but will disassociate at elevated temperatures
2. A soft elastomeric phase for the development of elasticity.

The materials listed in Table 2 are the major types of thermoplastic elastomer available commercially.

Before briefly discussing each type, it is necessary to consider the performance of thermoplastic elastomers and the problem of defining service temperature limits for them. The structural features that convey the ability to be processed as a thermoplastic are also responsible for a limiting factor in their use. Since it is the "pseudocrosslinks" that allow these materials to develop elastomeric behavior, any factor that interferes with the integrity of the pseudocrosslinks will weaken the material and allow excessive creep or stress relaxation to occur under the sustained application of stress and strain. Temperature is obviously one such factor.

A method commonly used to derive a maximum service temperature limit is the Underwriters Laboratories (UL) rating; here, a material is aged at various temperatures and a property, say tensile strength, is monitored. The maximum service temperature is then defined as the temperature at which the property being monitored decreases by 50% after 100,000 hours of aging. Thus for the thermoplastic FEP, the UL rating is 150°C. Another method by which the effect of temperature can be assessed is the heat distortion temperature, which has the advantage of assessing the effect of temperature while the material is stressed. For FEP the following limits are found:

Heat distortion temperature at 0.45 MPa, 70°C
Heat distortion temperature at 1.8 MPa, 50°C

Table 2 Major Types of Commercially Available Thermoplastic Elastomer

Major type	Subtype	Examples of trade names
Styrenic	SBS/SIS	Cariflex TR, Kraton
	SEBS	Kraton G, Elexar
Elastomeric alloys	EPDM/PP	Levaflex, Santoprene
	NR/PP	Vynamar
	NBR/PP	Geolast
	Chloro-olefin	Alcryn
Polyurethane	Ether/ester	Desmopan, Estane
Copolyether esters		Hytrel, Arnitel
Polyether amides		Pebax
NBR/PVC		Chemigum P83[a]

[a] Used as an additive to PVC to produce a TPE; this type is not discussed further.

It can therefore be seen that the UL rating is not an adequate method of assessing maximum service temperature if a material is to support stress or strain in service.

Figure 3 illustrates the dependence of the tensile strength of SBS block copolymers on temperature. In considering this plot, remember that tensile strength is a short-term measure of the ability of a material to resist stress and strain. One might ask the question, What would happen to the material if it were strained to 200% extension at 40°C and held there? The answer is that one would expect a high rate of stress relaxation, the rate being an order of magnitude higher than would be expected of a conventional elastomer. It is therefore unfortunate that except for Dupont with its Hytrel material, the manufacturers of TPEs do not include data on the creep and stress relaxation behavior at elevated temperatures. They tend to rely, instead, on the UL approach to determining maximum service temperatures; or at best, they furnish data on the variation of hardness and tensile strength with temperature. The maximum service temperatures quoted in the following descriptions therefore need to be treated with a high degree of caution. It is interesting to note, but not really surprising, that the major uses of TPEs are in applications that take advantage of their general toughness but do not call for the support of high applied stresses and strains.

Styrenic Block Copolymers

1. SBS/SIS Block Copolymers. In these block copolymers, the center elastomeric block is either polybutadiene or polyisoprene. The unsaturated nature of the midblock renders them susceptible to attack by oxygen, ozone, and light. The morphology of these materials was illustrated earlier, as was the dependence of their strength on temperature. Their ability to function at elevated temperatures is restricted. This drawback is best illustrated by noting that such block copolymers cannot be used as soling materials for athletic shoes worn in indoor sports arenas; the frictional heat developed by stopping and turning quickly, softens the material and causes excessive wear.

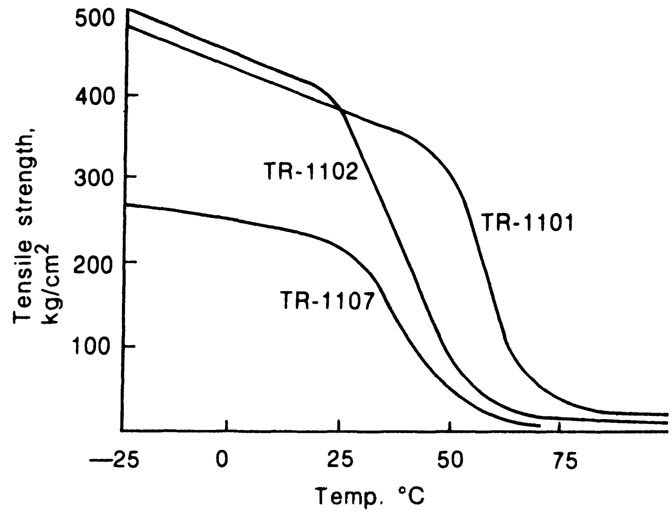


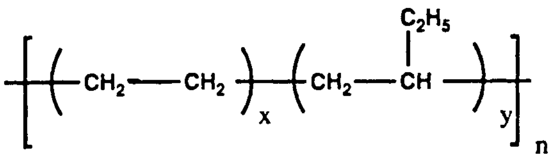
Figure 3 Dependence of the tensile strength of Cariflex TR grades on temperature. (Courtesy of Shell Chemicals, U.K.)

The styrenic thermoplastic elastomers are the only type to be fully compounded in the manner of conventional elastomers. In this case, however, the addition of carbon black or other fillers does not give reinforcement. Additions of polystyrene, or high impact polystyrene, and oil are used to vary hardness and tear strength, and fillers can be used to reduce the cost of the material. Other added polymers (e.g., EVA) can be used to increase ozone resistance. These materials also require antioxidants for protection during processing and service life, and poor UV stability restricts their use in outdoor applications.

While poor resistance to oil and solvents is a drawback in some applications, it is a positive advantage in solution processing applications (e.g., adhesive production).

Table 3 summarizes the SBS block copolymers. There may be some disquiet over the apparent use of these materials as glazing strips, given the quoted temperature range.

2. SEBS Block Copolymers. In this type of styrenic TPE the polybutadiene midblock used in the SBS types is replaced with ethylene butylene, which is saturated:



$$\left[\left(-CH_2-CH_2-\right)_x\left(-CH_2-\overset{\overset{\displaystyle C_2H_5}{|}}{CH}-\right)_y\right]_n$$

Ethylene butylene

Table 3 SBS Block Copolymers

Summary

Hardness range, 35 Shore A-40 Shore D
Maximum temperature, 65°C
Minimum temperature, $-70°C$

Advantages

Fully compoundable, especially for tack
Good wear characteristics in certain shoe sole applications
Ability to be solution processed
Good electrical properties
Wide hardness range

Disadvantages

Low maximum service temperature
Not resistant to oxygen, ozone, and UV light
Not oil or solvent resistant

Uses

Shoe soles, adhesives, plastics modification, bitumen modification, miscellaneous molded items [e.g., swim fins, black window glazing gaskets (U.K. $-30°C + 55°C$)]; not used in wire and cable

As expected, the materials exhibit the same morphology as the SBS types, but the saturated midblock confers resistance to oxygen, ozone, and UV light. Although it is said that improved phase separation gives improved stability to above ambient temperatures, the T_g of the polystyrene domains still restricts the use at high temperatures of the SEBS block copolymers.

The SEBS types are again fully compoundable, and Table 4 provides a brief summary. The properties exhibited by the SEBS compounds are also representative of those of the SBS-based compounds.

Elastomeric Alloys. These materials are generally produced by blending an elastomer with a crystalline plastic, polypropylene being the most common. Such blends rely on the crystal structures of the plastic to guarantee strength and on the elastomer to provide a degree of flexibility. In some blends the elastomeric phase can be partially crosslinked, and improvements in the final properties result if this is carried out dynamically (i.e., in a mixer).

The available hardness range of the elastomeric alloys is not as great as the styrenics, and at higher hardnesses the term "elastoplastic" might be considered to be more descriptive. This comment also applies to the other nonstyrenic thermoplastic elastomers, whose hardness range is even more limited than the elastomeric alloys.

1. Non-Oil-Resistant Types, EPDM/PP Blends, NR/PP Blends. The EPDM/PP blends are produced by blending EPDM and polypropylene; in certain types (e.g., San-

Table 4 Properties and Summary of SEBS Compounds

Typical properties				
Hardness	45A	55A	66A	95A
Tensile strength, MPa	6.5	7.5	10.3	11.0
Elongation at break, %	800	700	700	425
Tear strength, kN/m	28	21	48	78.8
Compression set, (%)				
24 h at 23°C		45		
24 h at 70°C		65		

Summary

Hardness range, 35 Shore A–40 Shore D
Maximum temperature, 65–80°C
Minimum temperature, −70°C

Advantages

Fully compoundable for tack
Ability to be solution processed
Good electrical properties
Resistant to UV light, oxygen, and ozone

Disadvantages

Low maximum service temperature
Not oil or solvent resistant

Uses

Wire and cable (U.S. automotive, not U.K.), adhesives, light-colored window glazing strips (U.K. −30°C to +55°C) toprene), the elastomeric phase is dynamically crosslinked. These materials exhibit excellent electrical properties, and they resist oxygen, UV light and ozone. They are not however oil resistant.

Table 5 summarizes the strength properties of Santoprene and lists the major characteristics of this type of thermoplastic elastomer.

Comparison of the heat-resistance properties of EPDM and NR indicates that a lower maximum service temperature should be expected for NR/PP blends, if aging is the criterion being used. The ozone resistance and UV stability of NR/PP blends is said to be greater than those of natural rubber, although at very high ozone concentrations some attack would be expected on the softer grades.

These materials are not oil resistant, but they do have good electrical properties. Table 6 summarizes the NR/PP blends.

2. Oil-Resistant Types, NBR/PP Blends, Chloro-olefinic Types. The blending of NBR and polypropylene gives a material that is oil resistant, and the commercially available example of this type, Geolast, is dynamically crosslinked. The ozone resistance is again said to be greater than that of nitrile rubber, but at high concentrations some attack would be expected on the softer grades.

The commercial example of the chloro-olefinic type is Alcryn, which is said to be a blend of a chloro-olefin with an elastomer. The nature of the elastomer has not been disclosed. Here again the material is oil resistant.

Table 5 Properties of Santoprene and Summary of EPDM/PP Blends

Typical properties				
Hardness	55A	73A	80A	40D
Tensile strength, MPa	4.4	8.3	11.0	19
Elongation at break, %	330	375	450	600
Tear strength, kN/m	19	28	34	64
Tension set, %	6	14	20	48
Compression set, %				
168 h at 25°C	23	24	29	32
168 h at 70°C	25	36	41	49

Summary

Hardness range, 55 Shore A-75 Shore D
Maximum temperature, +100°C
Minimum temperature, −50°C

Advantages

Resistant to UV light, oxygen, and ozone
Good electrical properties
Toughness

Disadvantages

Not oil resistant
Hardness range more limited

Uses

Electrical, boots and bellows, weatherstrips, body components, bumpers and sight shields in the automotive industry; wire and cable, window seals, and other mechanical goods

Table 6 Summary of NR/PP Blends

Hardness range, 60 Shore A–50 Shore D
Maximum temperature, 70°C
Minimum temperature, −40°C

Advantages

More ozone resistant than NR
Good electrical properties

Disadvantages

Not oil resistant

Uses

No current examples known

Table 7 presents a summary of both types.

Thermoplastic Polyurethanes (TPU). The morphology of this type of thermoplastic elastomer was given earlier.

The thermoplastic polyurethanes are available in a more limited hardness range than the styrenics, and they are characterized by excellent strength and toughness, and oil resistance. There are two major types available, polyester and polyether, the latter exhibiting superior hydrolytic stability and low temperature performance.

The electrical properties of the polyurethanes are not adequate for primary insulation applications, but their general toughness leads to their use as cable jacketing materials.

Table 8 summarizes these materials.

Copolyether Esters. These materials are segmented copolyether esters formed by the melt transesterification of dimethyl terephthalate, poly(tetramethylene ether) glycol, and 1,4-butane diol. As with the thermoplastic polyurethanes, one can describe a hard segment and a soft segment, the hard segments forming crystalline areas that act as "pseudocrosslinks," as depicted in Figure 4.

These materials are again strong, tough, and oil resistant, but they are available in a limited hardness range. Their hydrolytic stability is superior to that of the polyester

Table 7 Summary of Geolast/Alcryn

Hardness range
  Geolast, 60 Shore A–50 Shore D
  Alcryn, 60–80 Shore A
Maximum temperature, +120°C
Minimum temperature, −40°C

Advantages

Resistant to oxygen, ozone, and UV light
Oil resistance
Toughness

Uses

No current examples known

Table 8 Properties and Summary of Thermoplastic Polyurethanes

Properties			
Hardness	86A	95A(56D)	73D
Tensile strength, MPa	40	40	50
Elongation at break, %	450	400	250
Tear strength, kN/m	70	110	>120
Compression set, %			
24 h at 70°C	30	30	
70 h at 70°C	55	50	

Summary

Hardness range, 75 Shore A–75 Shore D
Maximum temperature, 120°C
Minimum temperature, −40°C

Advantages	*Disadvantages*
Resistant to oxygen and ozone	Limited hardness range
Oil resistant	Hydrolytic stability
Strong/tough	UV stability of some grades
	Electrical properties not adequate for primary insulation
	Cost

Uses

Cable jackets, conduits, fabric coatings, ski boots, and other boot soles; automotive: body components, bellows, and lock components; also hose jackets, protective bellows, mechanical parts, animal ear tags, and other uses

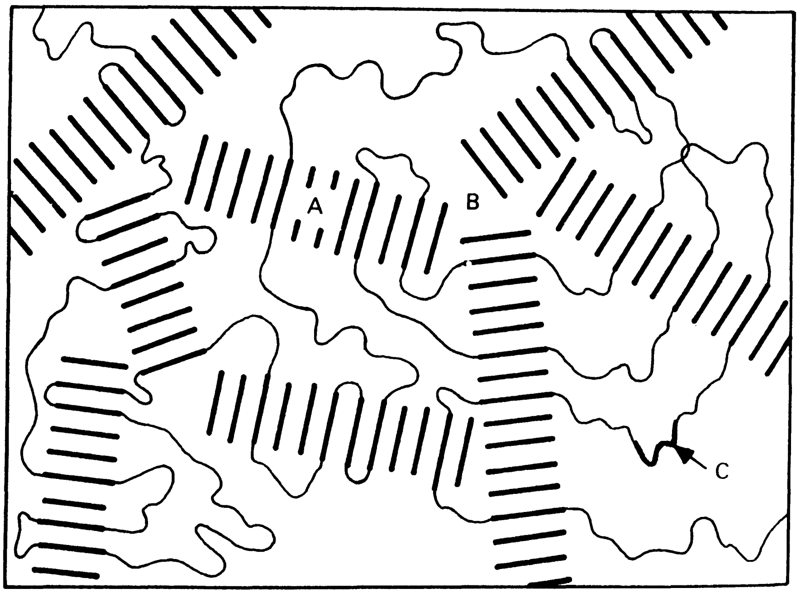


Figure 4 Schematic diagram of proposed 4GT segment (straight lines) and PTMEGT segment (wavy lines): A, crystalline domain; B, junction of crystalline lamellae; C, noncrystalline 4GT segment. Only one chain shown for simplicity. (Reproduced by R. J. Cella, *J. Polym. Sci., Polymer Symposia*, No. 42, Helsinki, Part 2, 1972. Courtesy of John Wiley & Sons, Inc.)

thermoplastic polyurethanes, but they do require additional protection in applications calling for a high degree of such stability. Table 9 gives representative properties of the copolyether esters.

Polyether/Polyamide Thermoplastic Elastomers. These materials exhibit the same type of morphology as the copolyether esters, the polyamide providing the hard segment and the polyether the soft elastomeric phase. The service temperature is lower than that of the copolyether esters, but apart from this difference they exhibit similar properties.

Table 9 summarizes both the copolyether esters and the polyether amides.

Uses. Although the tables summarizing the individual types of thermoplastic elastomer have given indications of their area of use, where known, it is interesting to look at the usage of TPEs in Europe, as given in Table 10 for the year 1987.

While the thermoplastic elastomers are generally more expensive than the conventional elastomers with which they sometimes compete (see Table 11), the price differential often can be overcome by reduced processing costs and design modifications.

Table 9 Summary of the Copolyether Esters and Polyether/Polyamides

Properties			
Hardness	40D(92A)	55D	72D
Tensile strength, MPa	25.0	38.0	38.0
Elongation at break, %	450	450	350
Tear strength, kN/m	122	154	
Compression set, 70 h at 100°C, %	60	56	

Summary

Hardness range, 85 Shore A–75 Shore D
Service temperature
  Hytrel −50 to +150°C
  Pebax −40 to +80°C

Advantages

Resistant to oxygen and ozone
Oil resistant
Strong/tough

Disadvantages

Limited hardness range
Hydrolytic stability
UV stability
Electrical properties not adequate for primary insulation
Cost

Uses

Cable jackets, hose jackets, tubing, seals; automotive bellows; mechanical parts: gear wheels, business machine parts

Table 10 Consumption of Thermoplastic Elastomers by End Use in Europe in 1987 (× 10^3 tons)

	Elastomers[a]						
End use	Styrenics	TPOs	EAs	TPUs	COPEs	PEBAs	Total
Automotive	2	44	1	2	1	2	52
Wire and cable	0	5	1	2	1	0	9
Footwear	54	0	0	10	1	1	66
Polymer modification	8	5	0	N	0	0	13
Hose and tube	0	2	1	2	1	1	7
General mechanical goods	0	5	3	4	1	1	14
Bitumen modification	18	0	0	0	0	0	18
Construction	0	0	N	N	0	0	1
Adhesives/coatings	13	0	0	11	0	0	24
Film/sheet	0	0	0	1	N	0	1
Other	5	N	N	N	2	N	7
Total	98	61	6	32	7	5	212
% of TPE use	46.2	28.7	2.8	15.1	3.3	2.3	

[a] TPO, EPDM/PP blends; EA, elastomeric alloys, apart from TPO; TPU, thermoplastic polyurethane; COPE, copolyether ester; PEBA, polyether/polyamide; N, negligible.

Table 11 Costs per Metric Ton

Material	Pounds sterling
SBS	ca. 1841
SEBS	ca. 2184
Santoprene	2636-2966
Alcryn	3500-4000
Hytrel	3500-6000
TPU	3400-4500
Natural rubber	600
Nitrile rubber	1700-2000
Polychloroprene	2400-2700

Data from 1992; £ = $1.55.

1.2 SUMMARY OF THE PROPERTIES OF ELASTOMERS

Tables 12 and 13 provide a summary of the properties of the different rubbers, apart from the thermoplastic elastomers. These tables should be read in conjunction with Sections 1.2.1-1.2.12.

1.2.1 Resistance to Service Temperatures and the Problem of Defining Service Temperature Limits

A distinction between the short- and long-term effects of temperature must be made when considering the temperatures to be encountered during service. Short-term effects are generally physical, hence reversible, whereas the long-term effects of elevated temperatures are mainly chemical. Long-term effects, which are irreversible, are generally termed "aging."

As the temperature is raised above ambient, mechanical properties (e.g., tensile and tear strength) decrease, the rate of decrease being dependent on the particular elastomer used and the compound formulation.

Long-term exposure to elevated temperatures, or aging, results in a permanent change in all the properties of a rubber compound. The rate of degradation, however, is also dependent on the environment and the compound formulation. In the absence of oxygen, compounds generally can function at higher than their normally accepted service temperature limits, whereas exposure to certain chemicals can drastically reduce the maximum service temperature.

The definition of a maximum service temperature for a rubber is therefore somewhat problematical, since it is dependent on the stresses and strains involved in an application, the service life required, the service environment, and the compounding ingredients.

The long-range elasticity characteristic of rubbers is due to the flexibility conferred by cooperative bond movements in the main chain. As the temperature is decreased from ambient, such cooperative bond movements become restricted and elasticity is progressively lost until, at the glass transition temperature T_g, they cease altogether and the chain becomes inflexible. The elastomer then exhibits the characteristics of a glassy polymer. The actual T_g of an elastomer is, however, dependent on the method used to determine it; for instance, if the method utilizes a dynamic property (e.g., tan δ), then the T_g measured is dependent on the frequency of the dynamic test. This, together with the increase in the flexibility of a compound at low temperatures that is possible through the addition of plasticizers, means that it is as difficult to define a lower temperature service limit as it is the upper.

Long-term exposure to low temperatures has no equivalent among the aging phenomena at high temperatures, but natural rubber and polychloroprene can exhibit an increase in "stiffness" with time when exposed to low temperatures above their T_g. This phenomenon is due to crystallization; with polychloroprene, the rate of crystallization is highly dependent on the polymer grade chosen, and with both rubbers the rate is dependent on the exact temperature and compound formulation.

This stiffening, like the stiffening due to the approach to T_g, is physical and reversible.

The values quoted in Table 12 for service temperatures are thus based on experience and should be used as guides only.

1.2.2 Environmental and Chemical Resistance

Chemical reagents and solvents can impair the structural integrity required for the retention of rubbery performance. It should be noted that a high molecular weight confers no special protection against chemical attack. The chemical reactivity of a polymer chain is dependent on the repeat unit(s) within it, but there are two conflicting requirements. Reactivity is required in the chain to allow the crosslinking reaction necessary to achieve rubbery performance; but ideally, in service, the chain should be inert. The chemical stability of the crosslinks and the additives in a rubber compound will obviously contribute further to the reactivity of a rubber compound.

Diene rubbers, those that contain a double bond in the main chain, are susceptible to attack by ozone, which can lead to surface cracking and eventually failure. They are also more easily attacked by oxygen and therefore generally have lower maximum service temperatures. Ions of copper, manganese, iron, nickel, and cobalt can further promote the oxidative breakdown of diene rubbers.

Table 12 Properties of the Major Rubber Tires[a]

	Natural rubber/ polyisoprene	Polybutadiene	SBR	Polynorbornene	Ethylene propylene polymers	Butyl rubbers	Polychloroprene	Nitrile	Polyurethanes	Polysulfides
ISO Designation	NR/IR	BR	SBR	PNR	EPM/ EPDM	IIR/CIIR/ BIIR	CR	NBR	AU/EU	TM
Maximum temperature, °C	80	80	80	80	120+	120	100	120+	80+	100
Minimum temperature, °C	−50	−70	−40	−20	−40	−25	−30	−30	−30 −40	−45
Physical properties										
Hardness range	30–100	45–80	35–95	15–95	30–95	35–95	35–95	30–95 (D)	10–95 (D)	20–80
Tensile strength (approx max), psi	4000	2500	3000	3500	3000	2500	4000	3000	4000	1500
Tear strength	E	G	F	G	F–G	G	E	F–G	E	P–F
Resilience	E	E	G	P–F	G	P–F	G–E	F–G	F–G	P–F
Abrasion resistance	E	E	G–E	G	G	F	G–E	G–E	E	P
Compression set resistance	G	F	G	G	G	F	F–G	G	G–E	P–F
Impermeability	F	F	F	G–E	F	E	F–G	G	P–F	E
Electrical resistivity	E	E	E	G	E	E	F	F	F	F
Low temperature flexibility	G–E	E	G	F–G	G	F	F	F–G	G	F–G
Environmental resistance										
Ozone resistance	P	P	P	P	E	G	F–G	P	E	E
UV resistance	P–F	P–F	F	F	E	G	G	P–F	F–G	G–E
Flame resistance	P	P	P	P	P	P	G	P	P–G	P

	Ethylene vinyl acetate	Propylene oxide	Chlorosulfonated polyethylene	Epichlorohydrin	Ethylene acrylic	Acrylates	Polyphosphazene	Silicone	Fluorosilicone	Fluorocarbon	Kalrez
ISO Designation	EAM	GPO	CM/ CSM	CO/ ECO		ACM	FZ	MQ/VMQ/ PVMQ	FMQ/ FVMQ	FKM	FKM
Maximum temperature, °C	120	130	120	130	150	160	175	200+	200+	225+	250+
Minimum temperature, °C	−30	−55	−30	−10 −40	−30	−30	−55	−55 −75	−55	−5+	−5
Physical properties											
Hardness range	40–90	40–90	40–95	40–90	40–90	40–90	35–90	25–90	25–90	55–95	55–95
Tensile strength (approx max), psi	4000	2500	3000	2500	2500	2200	2000	1250	1250	2500	250
Tear strength	F–G	F–G	F–G	F–G	P–F	P–F	P–F	P–F	P–F	F	F
Resilience	F	F–G	F–G	F–G	F–G	F–G	F–G	F–G	F–G	F	F
Abrasion resistance	G	F–G	G–E	F–G	F–G	F–G	F	P–F	P–F	F–G	F–G
Compression set resistance	G–E	F–G	F	F–G	G	G	G	G–E	G	G–E	G–E
Impermeability	G	–	G	E	F	F–G	F	P–F	P–F	G–E	G–E
Electrical resistivity	E	F	G	F	F	F	F	E	G	G	G
Low temperature flexibility	G	G–E	F	F–E	P–F	P–F	E	E	E	F–G	F
Environmental resistance											
Ozone resistance	E	E	E	E	E	E	E	E	E	E	E
UV resistance	E	E	E	G–E	E	E	E	E	E	E	E
Flame resistance	P–F	P	G	F–G	P–F	P	G	F–G	F–G	G–E	G–E

[a] The symbol + indicates that choice of polymer, cure system, or other variable can extend the range; D indicates that hardness range can be extended into the Shore D scale.

Table 13 Summary of the Resistance to Chemicals of the Major Types of Rubber

	Natural rubber/ polyisoprene	Polybutadiene	SBR	Polynorbornene	Ethylene proplyene polymers	Butyl	Polychloroprene	Nitrile	Polyurethanes	Polysulfides
Water	E	E	G-E	E	E	E	P-G	F-G	P-G	F
Steam (> 120°C)	P	P	P	P	G	G	F	F	P	P
ASTM oil no. 1	P	P	P	P	P	P-F	F-G	G	G	G
ASTM oil no. 3	P	P	P	P	P	P	F	G	G	G
Aliphatic hydrocarbons	P	P	P	P	P	P	G	E	G	E
Aromatic hydrocarbons	P	P	P	P	P	P	P-F	F-G	P-F	G-E
Halogenated hydrocarbons	P	P	P	P	P	P	P	F-G	F	G
Alcohols	G	G	G	G	G	G	F-G	F-G	F-G	G
Ketones/esters	G	G	G	G	G-E	G-E	F	P	P	G-E
Organic acids, dilute	G	G	G	G	E	G	E	G	P-F	G
Organic acids, concentrated	F	P	P	F	F	F	P	P	P	G
Inorganic acids, dilute	G	G	G	G	E	G	E	G	F	E
Inorganic acids, concentrated	F	G	G	F	G	G	G	F	P	P
Oxidizing acids, dilute	P	P	P	P	F	P	F	P	P	P
Oxidizing acids, concentrated	P	P	P	P	P	P	P	P	P	P
Alkalies	F	F	F	F	G-E	E	E	G-E	P	G
Animal and vegetable oils	P-G	F	F	F	G	G-E	G	G-E	G	G-E

	Ethylene vinyl acetate	Propylene oxide	Chlorosulfonated polyethylene	Epichlorohydrin	Ethylene acrylic	Acrylates	Polyphosphazene	Silicone	Fluorosilicone	Fluorocarbon	Kalrez
Water	G	G	G	G	E	P–F	F	G	G	E	G–E
Steam (>120°C)	F	P	P–F	P	P	P	P	P–F	P–F	P–F	G
ASTM oil no. 1	F–G	F	F–G	G	G	G	G–E	F–G	G–E	G–E	G–E
ASTM oil no. 3	F–G	F	F–G	G	G	G	G–E	F	G–E	G–E	G–E
Aliphatic hydrocarbons	F	F	G	G–E	G	E	E	P–F	E	E	E
Aromatic hydrocarbons	P	P	P–F	G	P–F	P–F	E	P–F	G–E	E	E
Halogenated hydrocarbons	P	P	P	G–E	P	P	G	F	G	G	G
Alcohols	G	G	G–E	G	P–F	P	P	G	G	F–E	G
Ketones/esters	F	F–G	F–G	P–F	P	P	P	G–G	P	P	G
Organic acids, dilute	G	F	E	F	P	P		G	G	F	E
Organic acids, concentrated	F	P	G	P	P	P		F	F	P	E
Inorganic acids, dilute	G	G	E	G	F	F		E	E	E	E
Inorganic acids, concentrated	F	F	G	F	P	P		P–F	F	E	E
Oxidizing acids, dilute	F	P	G	P	P	P		F	F		E
Oxidizing acids, concentrated	P	P	P	P	P	P		F	F	F–G	E
Alkalies	G	F–G	E	F–G	F	P		F	F	P–F	E
Animal and vegetable oils	G	F	G	G–E	G–E	G–E	G–E	F–G	G–E	E	E

The ultraviolet part of the electromagnetic spectrum can cause the degradation of the diene rubbers and those that contain carbonyl groups (e.g., polyurethane).

Certain types of elastomer—namely polyurethanes, silicones, acrylates, and EVA—are susceptible to hydrolysis, a reaction that leads to chain scission and consequent deterioration. The amine-crosslinked fluorocarbons can be attacked by steam, but it is the crosslinks that degrade rather than the main chain.

For all practical purposes, liquids that attack crosslinked rubbers either degrade the rubber or cause swelling through absorption. A swollen elastomeric network is much weaker and more susceptible to damage, although in certain sealing applications a small positive swell is beneficial for the retention of the sealing force. It appears that no account of the resistance to liquid media is complete without reference to the concept of solubility parameter δ, which is the square root of the cohesive energy density:

$$\delta = \left[\frac{L - RT}{M/D} \right]^{1/2}$$

where L = latent heat of evaporation
R = gas constant
T = absolute temperature
M = molecular weight
D = density

This concept predicts that a solvent with a solubility parameter similar to that of a polymer will swell or dissolve the polymer, depending on whether it is or is not crosslinked. Unfortunately, this concept does not always work. The solubility parameter of a fluorocarbon rubber lies in the range of 6.3–8.3, while that of hexane is 7.3. Hexane does not swell a fluorocarbon rubber, contrary to the prediction based on solubility parameters, because fluorocarbon rubber is polar and hexane is not. As a general rule, nonpolar solvents will swell nonpolar rubbers, and polar solvents will swell polar rubbers.

The degree of swell of a polar rubber immersed in oil is normally determined by the level of aromatics in the oil, the aniline point of the oil being a good guide to the level of aromatics; the lower the aniline point (typically 60–130°C), the higher the level of aromatics.

The solubility parameter becomes even less useful when compounded rubbers are considered, since the ingredients in a rubber compound can also reduce, or promote, swell; increasing the filler content of a compound will reduce swell in a solvent. The degree of crosslinking also affects the degree of swell; ebonite, a highly crosslinked natural rubber, exhibits much greater chemical resistance.

Liquid additives in a rubber compound can be extracted by liquids in contact with the rubber, which leads to the following possibilities:

1. Zero, or a positive swell, when immersed in a solvent, but shrinkage and hardening of the compound when the swelling medium is removed.
2. Zero, or a positive, swell but no shrinkage upon drying.
3. Negative swell upon immersion.

If the possibility of chemical degradation caused by contact with a liquid is included, other possibilities exist:

4. Zero swell, but chemical degradation occurs.
5. Positive swell and chemical degradation.

Since none of these possibilities is predictable by the use of solubility parameters, or any other simple rule, an empirical approach should be adopted when assessing the resistance of a rubber compound to liquid media. Reliance on swelling tests alone is inadvisable. Reference can, of course, be made to the polymer manufacturer's trade literature, ISO Technical Report 7620, and References 10 and 11 for guidance with respect to the likely effects. The chemical resistance values given in Table 13 should be regarded only as guides to likely performance.

Before leaving this subject, we note that liquid media can extract solid compounding ingredients, the loss of antioxidants being of particular concern here. It is rare, however, for compounded rubbers to be adversely affected by contact with solid reagents.

1.2.3 Mechanical Properties

Other terms—static stress-strain, and behavior under the short-term application of stress and strain—can also be applied to the mechanical properties of a given rubber to distinguish them from the dynamic (cyclic) tests and from creep and stress relaxation:

Mechanical properties include:

Hardness (a measure of the elastic modulus of a rubber)
Tensile stress–strain properties
Compression stress–strain properties
Shear stress–strain properties
Torsion stress–strain properties
Flexural stress–strain properties
Tear strength

Although tensile strength is widely measured on rubber compounds, it is generally only used as an indicator of the "quality" of a compound, since strains in this mode are rarely large enough to be truly of interest in actual service. Rubbers that crystallize upon stretching (e.g., natural rubber and polychloroprene) generally exhibit the highest tensile and tear strengths, but these properties, as with the other mechanical properties, are greatly influenced by compounding.

Rubber compounds exhibit extremely useful properties under compression, shear, and torsion, and these are widely exploited in many applications. The complex behavior of rubber under these deformation modes is dealt with comprehensively in References 12 and 13.

1.2.4 Long-Term Behavior Under Stress and Strain

Crosslinking of a rubber does not totally prevent the occurrence of flow due to the physical slippage of chains under an applied stress or strain. Two phenomena result: creep, which is an increase in length with time when the elastomer is held under a constant stress, and stress relaxation, which is a decrease in stress when the elastomer is held under a constant strain. Aging effects at elevated temperatures can cause chain scission or further crosslinking to occur, hence can alter the rates of both phenomena.

The widely used compression set measurement, and the less-used tension set, represent attempts to quantify the extent to which a rubber compound will exhibit creep and stress relaxation, but the former is also widely used as a method for checking the state of cure.

The creep and stress relaxation behaviors of a rubber compound are strongly influenced by the choice of cure system and the degree of crosslinking, among other factors.

1.2.5 Dynamic Properties

When a rubber compound is subjected to dynamic stressing, the response is a combination of an elastic response and a viscous response, rather than a purely elastic one, and energy is lost in each cycle. Reference 13 should be consulted for more detailed information.

Figure 5 shows the response of a crosslinked rubber to an applied strain. The resultant stress is considered to precede the strain by the phase angle δ; tan δ is called the "loss tangent" and thus is a measure of the energy lost within the material.

Figures 6 and 7 show the dynamic response (complex modulus and tan δ) of a natural rubber compound at different temperatures and frequencies in three-point bending. It can be seen that these dynamic properties are dependent on both factors, and these two effects can be related by the Williams-Landel-Ferry (WLF) equation.

The tan δ peak occurs at the T_g of the compound at the particular frequency of test, and its position is primarily dependent on the elastomer base of the compound. It is possible, within limits, to vary the position of the tan δ peak (e.g., by incorporation of low

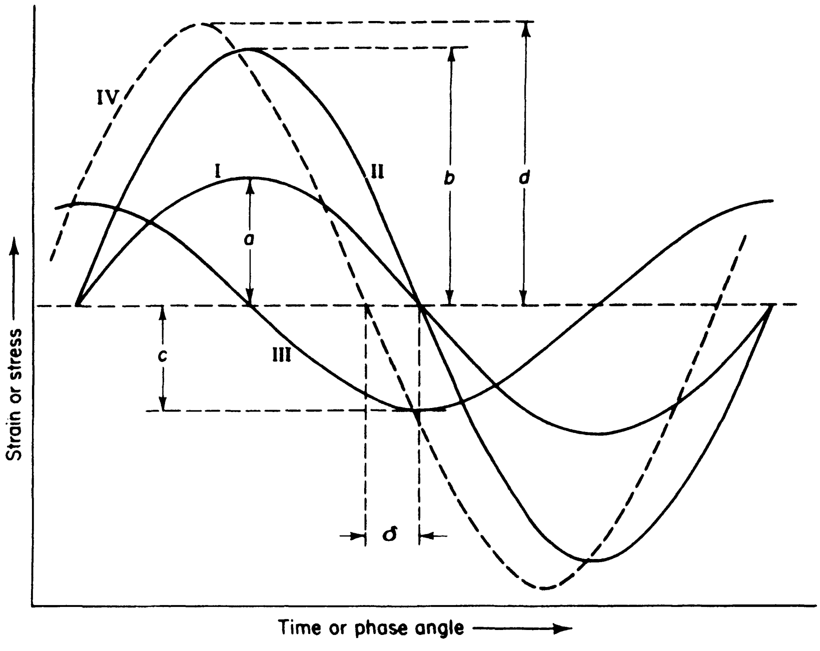


Figure 5 Sinusoidal chain and stress cycles. I, strain, amplitude *a*; II, in-phase stress, amplitude *b*; III, out-of-phase stress, amplitude *c*; IV, total stress (resultant of II and III), amplitude *d*. δ is the loss angle.

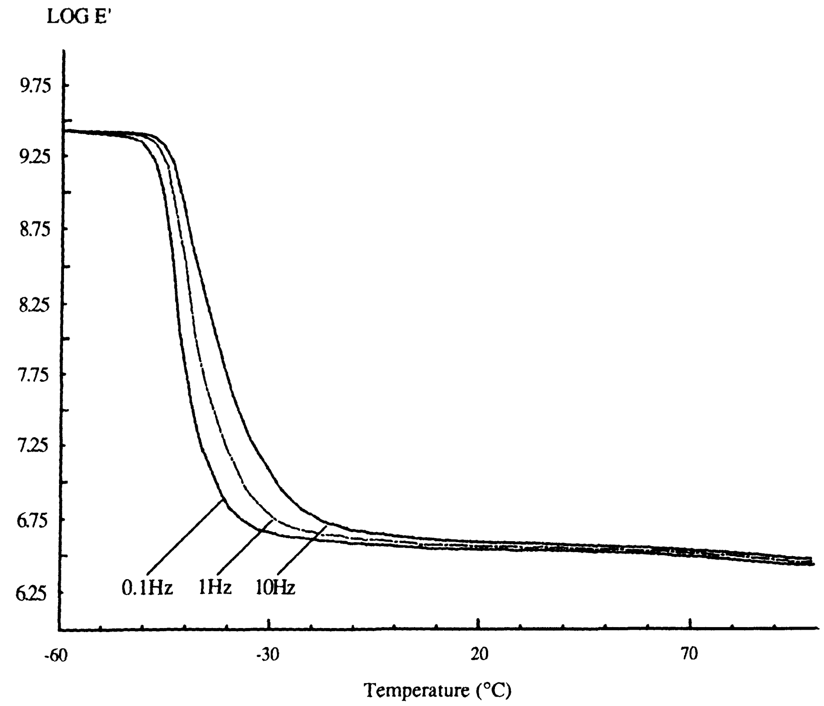


Figure 6 Dynamic modulus of a natural rubber compound versus temperature.

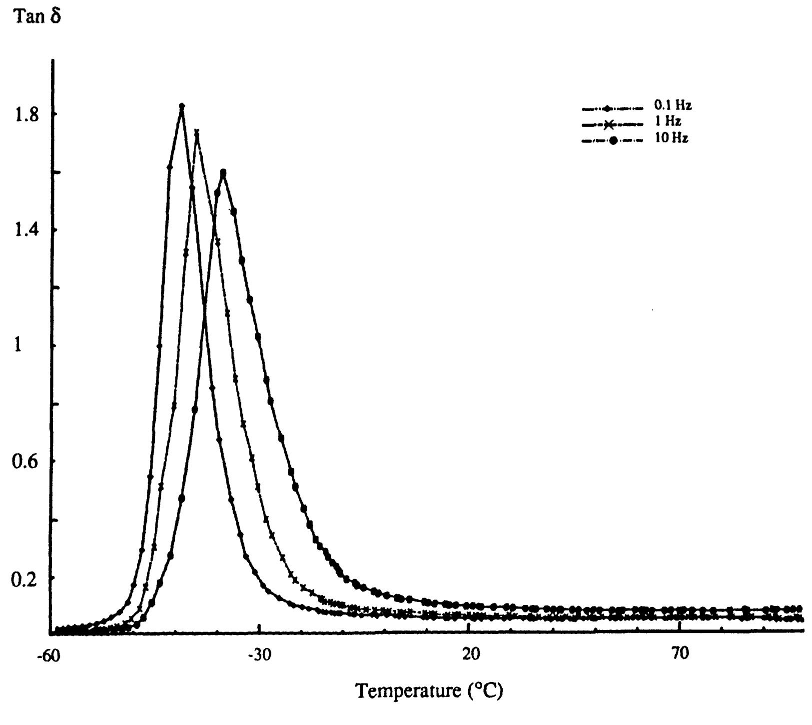


Figure 7 Values of tan δ of a natural rubber compound versus temperature.

temperature plasticizers) and the value of tan δ at ambient temperatures (e.g., by altering the filler loading and type). Blends of different polymers may exhibit more than one major tan δ peak or a broadening of the single peak, depending on the blend composition; blending is another method by which tan δ can be increased at ambient temperatures.

1.2.6 Fatigue Performance

Fatigue, in this context, is taken to mean the growth of cracks in a rubber compound undergoing cyclic deformation to moderate strains, although it can also result in a change of stiffness and a loss of mechanical strength.

The Malaysian Rubber Producers Research Association (MRPRA) [14,15] has undertaken valuable work on the fatigue of rubber strips in tension. The following expression was derived for strips cycled from zero strain:

$$N = \frac{G}{(2KW)^n} \frac{1}{C_0}$$

where N = fatigue life, in cycles to failure
G = cut growth constant
K = function of the extension ratio
W = strain energy per unit volume
C_0 = initial depth of cut (or intrinsic flaw)
n = strain exponent, dependent on the nature of the polymer

Elastomers generally show wide differences in tensile and tear properties, but the naturally occurring flaw size (C_0) does not differ widely among elastomers. The rate at which the crack propagates does, however, differ widely. The crystallizing rubbers exhibit good resistance to crack propagation, but this resistance is further enhanced by prestraining the part, since crack propagation is most severe if the part passes through zero strain. In the noncrystallizing rubbers, fatigue life is increased by increasing the hysteresis loss or damping (tan δ).

Fatigue resistance can be increased by the addition of reinforcing fillers, and the inclusion of antioxidants and antiozonants, where appropriate. In the sulfur-curable diene rubbers, resistance to fatigue at high imposed strains is increased by the use of conventional sulfur cure systems.

1.2.7 Friction and Wear Performance

Friction and wear are both considered here, since friction is a contributory factor in wear mechanisms; in tire applications, both factors are key performance characteristics. While the subject is dealt with only briefly here, further discussion of the subjects can be found in References 16–18.

The classical laws of friction do not apply to rubber; at high normal loads the coefficient of friction decreases with increasing normal load, and it is also dependent on velocity and temperature. Under certain conditions, where friction decreases with velocity, a "stick/slip" phenomenon can occur, with the coefficient of friction oscillating between two values. Aging, wear debris, humidity, and contact with liquids can all affect the frictional behavior.

In wet or lubricated conditions, the hysteresis loss, tan δ, of a polymer/compound assumes the major role in determining the coefficient of friction, and factors that affect tan δ, such as the level and type of carbon black, affect the coefficient. The deliberate modification of the surface layers (e.g., by chlorination of certain diene rubbers) provides a route by which the coefficient of friction can be altered; a lowering results in the example cited.

We have few useful data on friction; hence designers need to do laboratory testing where this aspect is of importance. Such tests, however, need to be relevant to the application, and the test techniques must be developed with care. In some instances, both friction and wear can be studied in the same experiment.

Wear, the general term used to describe loss of material from a body, is most commonly caused by rubber moving in contact with another surface. Wear can occur by three separate mechanisms:

Abrasive wear is caused by hard, sharp projections in the contact surface, which cut into the rubber.

Fatigue wear is caused by rough surfaces that do not have sharp projections; wear proceeds by the detachment of particles fatigued on a localized scale by dynamic stressing.

Adhesive wear is caused by contact with essentially smooth surfaces, rubber being detached by roll formation. This mechanism is associated with a high coefficient of friction between the surfaces.

In many applications all three wear mechanisms may be involved and which, if any, predominates will depend critically on the service conditions. Laboratory tests, which generally measure abrasive wear, are thus notoriously poor predictors of service life unless the wear mechanism involved in the application is mimicked as part of the test.

An example of this would be the comparison of a tire tread and the liner of a shot blast hose by use of the abrader of the German standardization organization (DIN). A tire tread with a low DIN abrasion loss wears well in service but would wear rapidly if used as hose liner. A very soft natural rubber compound, with a very high DIN abrasion loss, resists wear by shot blast media but would be rapidly worn if used as a tire tread.

It is difficult to usefully comment on the wear properties of polymers, apart from noting that they are influenced by friction and by the compounding ingredients used. Polybutadiene, carboxylated nitrile, and polyurethanes are noted for good abrasion resistance.

1.2.8 Electrical Properties

Electrical resistivity, dielectric constant, tangent of the dielectric loss angle (tan δ), and dielectric strength are key parameters which determine the usefulness of elastomers as potential insulators in wire and cable applications. The electrical properties of rubbers, apart from the dielectric constant, differ widely but can be further altered by compounding and as a result of the susceptibility of the polymer and/or the compound to picking up moisture; dielectric constant can be widely varied by the choice of additives.

Since some elastomers (e.g., nitrile) exhibit deficiencies in one or more of the key parameters, they do not find use as primary cable insulations. Silicone rubber is used in some cable applications where performance in a fire situation is important because when this material is burned, an insulating char is formed, and insulation, in the short term, is maintained.

While rubbers are normally considered to be insulating, black-filled vulcanizates may in fact be sufficiently conductive to be a hazard. Figure 8 shows the resisitivity of a natural rubber compound filled with superabrasion furnace (SAF) black.

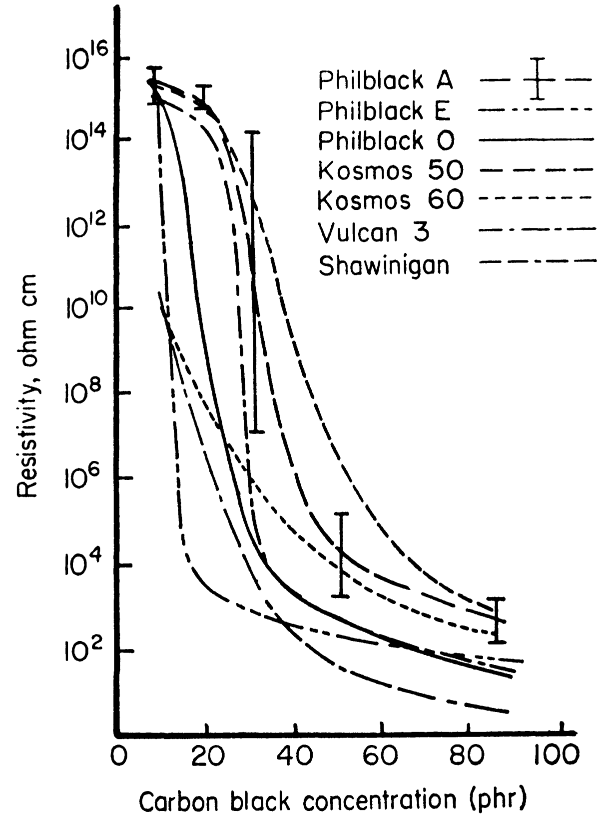


Figure 8 Effect of carbon black concentrations on resistivity.

Rubbers are frequently compounded to have antistatic properties by the addition of carbon black, and specially conductive blacks and metal powders can be used to produce truly conductive compounds. Resistivities as low as 5–10 Ω·cm can be achieved by the use of carbon black, and 0.02 Ω·cm by using metal powders. The following resistance ranges for products were suggested by Norman [19].

Product/characteristic	Resistance (Ω)
Insulating	$>10^{12}$
Elimination of static nuisance	10^{10}–10^{12}
Antistatic (no lethal currents)	5×10^{4}–10^{8}
Conductive	$>10^{4}$

1.2.9 Thermal Properties

Properties considered here are the specific heat, thermal conductivity, and thermal diffusivity. References 20 and 21 should be consulted for further details on these properties.

Specific heat is additive, so that this property can be calculated from a knowledge of the values for each ingredient.

Thermal diffusivity is a property that is becoming of increasing importance, since it governs the time-dependent temperature distribution in a rubber compound under non-steady-state conditions—for example, during processing. It is a parameter that is required in software packages that predict flow during molding operations and in software packages designed to calculate cure cycles for very large articles, such as dock fenders.

Differences in thermal diffusivity among rubbers are generally small and can be considered to be secondary, since the addition of fillers significantly alters this property.

The thermal conductivity of rubber compounds is important in controlling the heat transfer across the interface with metal during processing. It is of direct importance, however, only as a final compound property in heat insulation applications, where a cellular product would be produced, or in "potting" compounds, where heat loss from an electrical circuit is required. In both product applications the differences in thermal conductivity between rubbers are secondary to that of the ingredients used. In cellular insulations, the gas used to "blow" the product is also a significant factor.

1.2.10 Permeability

Gases, vapors, and liquids will permeate rubbers and their compounds in two stages. Initially, the gas or liquid dissolves in the polymer, and the dissolved gas or liquid diffuses through the polymer. The methods used to measure the permeability coefficient Q are detailed in References 20 and 21. The coefficient is related to the solubility coefficient S and diffusion constant D by:

$$Q = DS$$

For the air gases, Q is a constant, but for other gases and vapors it varies with presure and temperature. As with most other properties, the permeability of a compound is affected by the quantity and type of filler added.

Impermeability is an important characteristic in many applications, but in gas sealing applications it can lead to failure by explosive decompression. This phenomenon results when the external gas pressure is reduced faster than the dissolved gas can permeate out from the seal; failure will occur if the rubber compound cannot withstand the stresses resulting from expansion of the internally dissolved gas.

1.2.11 Adhesion, Corrosion, and Staining

In the many uses to which rubber is put, adhesion to metal, fabrics and fibers, and other materials is commonly required.

Rubber-to-metal bonds are normally achieved by the use of proprietary rubber-to-metal bonding agents applied to the metal, although sulfur-cured diene rubbers can normally be adhered to brass-coated metals without the use of this type of bonding agent. Achievement of a good bond may require chemical pretreatment of the metal, but in every case stringent in-process control procedures are essential.

Adhesion to fabrics and fibers normally requires the use of specially treated types (e.g., fabrics dipped in resorcinol-formaldehyde resin in a latex) and/or the use of additives that promote bonding.

In the examples above, the bond is achieved during vulcanization, but many proprietary adhesive systems are available to bond cured rubber to other materials. The particular adhesives that are used are dependent on the particular rubber/material combination, and the polymer manufacturer's recommendations should be followed. Surface pretreatments of either surface may be required, chlorination of the diene rubbers, and etching of PTFE respectively, being examples.

It is not commonly known that compounded rubber can promote the corrosion of metals with which it is in contact and that this corrosion may be accompanied by adhesion of the rubber to the metal. This phenomenon is dependent on the elastomer type and formulation used, and it should be considered in sealing applications. Acrylates and nitrile rubber compounds are two types that are known to exhibit this form of corrosion/adhesion. Further information can be found in References 22 and 23.

Rubber compounds can cause staining when they are in contact with organic finishes, but this phenomenon is primarily dependent on the ingredients used, not the base polymer.

1.2.12 Processibility

The term "processibility" is not well defined and is commonly used to describe several, often unconnected, desirable features it is hoped a polymer and compound will exhibit. Each processing stage must be considered separately.

The molecular weight average and distribution, and the degree and type of branching, are the principal factors that govern the processibility of an elastomer; that is: viscosity, die swell, quality of extrudate, milling characteristics, green strength, and tack. The processibility of a rubber compound is, however, further influenced by the level and types of filler and oil used, the presence of other process aids, the degree of mixing, and the level of scorch (premature cure).

1.3 COMPOUND INGREDIENTS

There are a wide variety of ingredients from which the rubber compounder can choose to modify the physical and chemical properties of an elastomer. The objective in using a particular ingredient might be one or more of the following:

1. To improve the physical properties of the rubber
2. To improve the processing properties of the rubber
3. To crosslink the rubber compound
4. To control the rate of cure
5. To prolong the service life of the rubber
6. To extend the service range of the rubber
7. To reduce the cost of the rubber compound

Unfortunately, however, any particular additive chosen may have a beneficial effect on one property but a detrimental effect on another.

Table 14 gives a typical rubber formulation and the function of the ingredients. In any one compound, two or more of the following types of compounding ingredient may be present:

A polymer
A vulcanizing agent
A cure activator
A cure accelerator(s)

Table 14 A Typical Compound Formulation

Ingredient[a]	Ingredient function	Amount (phr)
Natural rubber	Rubber	100.00
Whiting	Diluent white filler	100.00
HAF N330	Carbon black reinforcing filler	50.00
Naphthenic oil	Softener/process aid	20.00
Zinc oxide	Cure activator	5.00
Stearic acid	Cure activator	1.00
Santoflex 13	Antioxidant/antiozonant	1.00
Heliozone	Protective wax for ozone resistance	2.00
MBTS	Accelerator (primary)	1.00
DPG	Accelerator (secondary)	0.50
Sulfur	Vulcanizing agent	2.50

[a] For carbon black and accelerators, see Tables 16 and 18, respectively.

A filler (reinforcing, semireinforcing, or diluent)
A softener/process aid/tackifier
A plasticizer
A protective agent(s)
Miscellaneous ingredients: pigments, blowing agents, other

The following brief notes discuss each of the foregoing types and the salient features of their use.

1.3.1 Vulcanizing Agents

Various types of vulcanizing agent can be used to cure natural and synthetic rubbers, but the most common system for vulcanizing the unsaturated rubbers is sulfur.

The properties that result from a vulcanizate depend on the number and type of the crosslinks formed. The number of crosslinks formed will depend on the amount of the cure agent added and the cure time.

Increased amounts of cure agent will generally increase the number of crosslinks, with the following effects on the final properties of the elastomer:

Modulus/hardness, and resilience will increase.
Permanent set, elongation at break, and the degree of swell in a solvent will decrease.
Tensile strength and tear strength will generally go through a maximum and then decrease with an increasing degree of crosslinking.

With the same amount of cure agent, but a variation in the cure time, these effects will again be noticed as the cure time is increased. The magnitude of the effect will be reduced, but it is still possible to produce a significant effect on properties by under- or overcuring. The cure time chosen for any application is therefore a compromise with regard to the properties required of the end product.

Some cure systems can revert at the cure stage—that is, the number of crosslinks decreases if long cure times or high temperatures are employed at this point—and this reversion will cause a reduction in most properties.

Other cure systems exhibit an effect termed "marching modulus," which, not surprisingly, means that modulus continues to increase with increased cure time.

Sulfur

The rhombic form of sulfur, which is the type normally used, has a limited solubility in rubber at room temperature (ca. 0.8 phr). If the free sulfur level is above this, a surface bloom may form which can lower surface tack and cause "blotchiness" on cured articles. Insoluble sulfur, although more expensive and slightly more difficult to disperse, does not bloom; however, it converts back to the rhombic form if the temperature exceeds 100°C.

A magnesium carbonate surface treated grade of sulfur, sulfur MC, is available, and this is used in nitrile rubber, since the rhombic form is difficult to disperse in this rubber.

Unaccelerated sulfur cures are lengthy and do not yield a good property spectrum. Therefore the sulfur vulcanization of all unsaturated elastomers is modified by the addition of accelerators.

The properties that result from a sulfur-cured vulcanizate depend on the number and type of crosslinks formed. The effect of the number of crosslinks has been discussed, but the type of sulfur crosslink formed has an equally important role in determining the final physical properties.

Figure 9 illustrates the types of sulfur crosslink that can be formed during vulcanization by sulfur; the type of crosslink produced depends on the accelerator type and accelerator/sulfur ratio.

Typical numbers for S_x in polysulfide linkages in natural rubber are as follows:

Cure or system	Linkages
Unaccelerated rubber/sulfur cure	40–45
Conventional rubber/accelerator/sulfur	5–10
Efficient vulcanizing (EV) system	4–5
Sulfurless cure systems (sulfur donors)	< 4

The differences produced by different cure systems are best illustrated in Figure 10 by the work carried out by Moore on natural rubber.

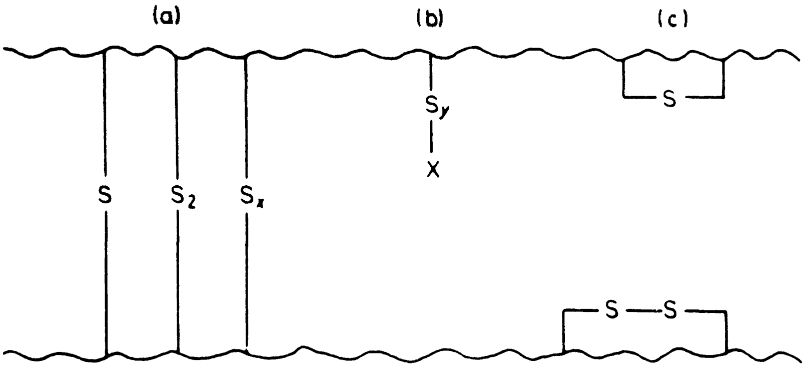


Figure 9 Types of sulfur crosslink: (a) monosulfidic, disulfidic, and polysulfidic; (b) pendant sulfur; (c) intramolecular linkages. Types (b) and (c) are wasteful of sulfur.

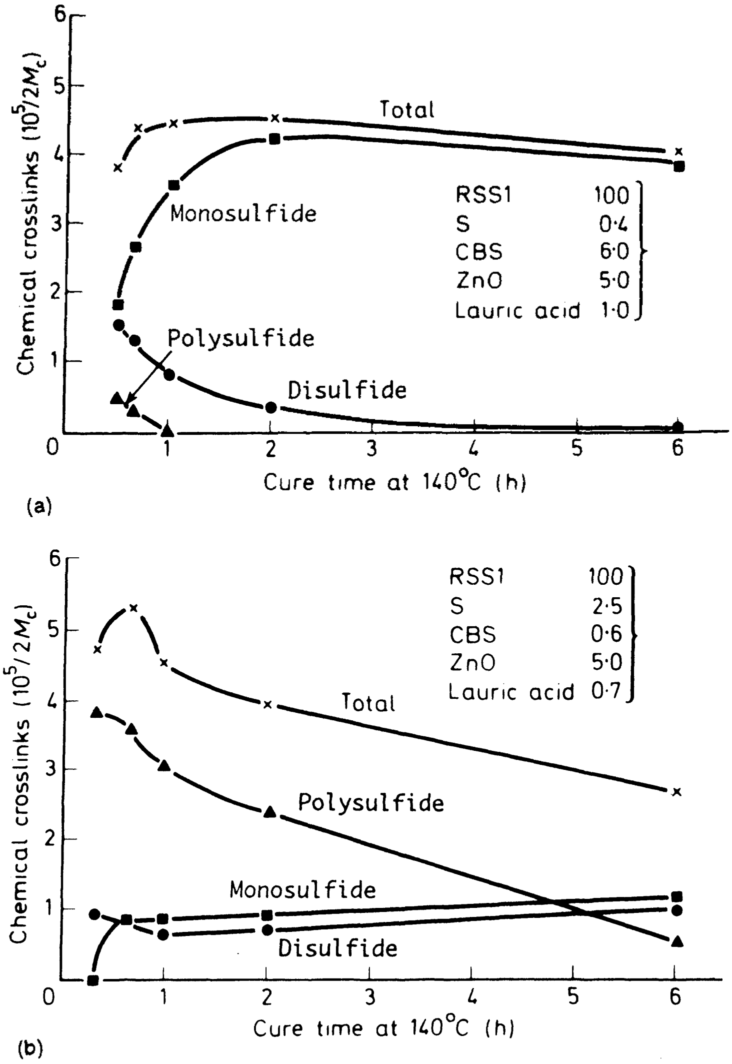


Figure 10 Variation of crosslink number and type for conventional (a) and EV (b) cure systems. (From G. C. Moore, *Chemistry of Vulcanisation, Proceedings of the Natural Rubber Producers Research Association Jubilee Conference, Cambridge 1964*, L. Mullins, Ed., London, McLaren & Sons Ltd., p. 184. Courtesy of MRPRA.)

Polysulfidic crosslinks will give better fatigue properties, but poorer compression set and aging properties. Monosulfidic crosslinks give better aging properties and compression set, but poorer fatigue properties. Semi-EV systems give intermediate properties.

If you have ever wondered why trucks shed their tire treads on highways, then consider the changes to the crosslinks of the conventional cure system in Figure 10. The reduced number of crosslinks and the change from polysulfidic to monosulfidic crosslinks drastically reduce the fatigue strength until eventually the tread separates.

Only unsaturated rubbers, or rubbers with pendant unsaturation, can be vulcanized with sulfur. For natural rubber, with a high level of unsaturation, vulcanization takes place readily, but in polymers where the unsaturation is low (e.g., butyl), vulcanization is slow, hence generally requires more active accelerators.

A conventional cure system for natural rubber would generally contain 2.0–3.5 phr of sulfur and 0.5–1.0 phr of an accelerator. Table 15 illustrates the different types of cure system for natural rubber.

As the level of accelerator is increased, the amount of sulfur must be reduced if a constant crosslink density is to be maintained; hence the number of atoms in the sulfur crosslink is reduced. The so-called efficient vulcanizing (EV) systems utilize accelerator levels of 3.0 phr plus (with low sulfur levels, ca. 0.2 phr), but at least one of the accelerators must be a "sulfur donor"; this feature of accelerators is discussed later, but we note here that sulfur crosslinks can be formed without the need for added elemental sulfur.

The synthetic rubbers require higher proportions of accelerators than natural rubber, with lower amounts of sulfur. It is also possible to use the EV and sulfurless cure systems.

Peroxides

It is possible to cure most unsaturated rubbers, and some of the saturated rubbers, by the use of covalent peroxides. Polychloroprene and butyl rubber are two unsaturated rubbers that cannot be cured by peroxides.

Upon heating, a covalent peroxide decomposes to form two radicals:

$$R-O-O-R \rightarrow 2R-O\cdot$$

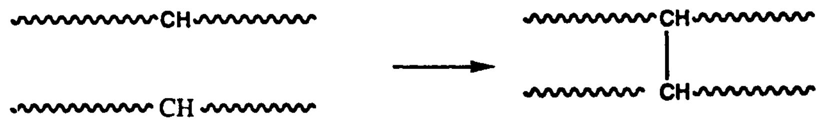
These free radicals are extremely reactive and stabilize themselves by dehydrogenating the polymer chain, during which process the free radical is transferred to the polymer chain.

Table 15 Examples of Cure Systems for Natural Rubber

Ingredient	Systems[a] A	B	C
Natural rubber	100.00	100.00	100.00
Zinc oxide	5.00	5.00	5.00
Stearic acid	1.00	1.00	1.00
Sulfur	2.50	0.75	0.20
Insoluble sulfur		1.75	
MBT	1.0	1.0	
TMTD			3.0

[a] A, conventional cure system; B, conventional cure system—no bloom; C, EV system.

Two polymer chains, containing a radical, can then react to form a C—C crosslink:



The C—C crosslink formed is more heat resistant than a C—S crosslink, and peroxide cures generally give better compression set properties. However, these advantages are offset by generally lower strength properties and a tendency for the surface of the rubber to become sticky if oxygen is not excluded during cure. Silicone rubber does not exhibit this latter disadvantage. Peroxide-cured vulcanizates can also exhibit a strong unpleasant odor.

Other compounding ingredients must be chosen carefully when peroxide cures are used. Acidic, or strongly alkaline, additives can interfere with the yield of free radicals and the rate of decomposition. Most fillers, and certain plasticizers, reduce the efficiency of peroxide curing, and this effect can be countered by an increase in the level of peroxide used. Process oils used should preferably be straight-chain aliphatics. Antioxidants can also inhibit the cure by peroxides.

The decomposition temperature of a peroxide is important in determining the cure temperature and the process safety; the rate of cure given by a peroxide is determined by its half-life at a particular temperature. Half-life is the time taken for half the amount of peroxide to decompose.

Number of half-lives	Peroxide decomposed (%) or cure state (%)	Residual peroxide remaining (%)
0	0	100
1	50	50
2	75	25
3	87.5	12.5
4	93.75	6.25
5	96.75	3.125
6	98.4375	1.5625
7	99.21875	0.78125

Thus, if the half-life of a peroxide at 160°C was 7 minutes, a 35-minute cure (5 half-lives) would leave approximately 3% unreacted. Such a cure time would be generally uneconomical, and peroxide-cured articles usually are given a short press cure, followed by a much longer postcure in an oven. As well as allowing unreacted peroxide to decompose, this postcuring serves to remove the decomposition products of the peroxides that might cause unnecessary odor and unwanted side reactions; for example, the decomposition products of peroxides containing carboxylic acid groups can catalyze the hydrolytic breakdown of silicones.

The half-life of a peroxide is also dependent on the polymer in which it is compounded. The following method can be used to provide a fairly accurate assessment of the half-life.

First a cure trace is obtained on a curemeter at the temperature of interest and allowed to proceed until a virtual plateau has been reached. Next a plot of log (maximum torque — torque at time t) versus time t is produced, and the slope m is calculated. The half-life is then:

$$t_{1/2} = \frac{-0.301}{m}$$

The amount of peroxide added to a compound determines the degree of crosslinking, but additives known as coagents can be used to further increase the degree of crosslinking at a constant peroxide level. The best-known example of a coagent is triarylcyanurate, but acrylates and sulfur can also be used.

Peroxides do not respond to accelerators, and the only method of increasing the cure rate is to increase the temperature of cure.

The peroxides normally used to cure rubbers are organic and can be divided into two general types:

1. Peroxides with carboyxlic acid groups (e.g., dibenzoyl peroxide). These exhibit low sensitivity to acids, low decomposition temperatures, and a high degree of deactivation by carbon black.
2. Peroxides without carboxylic acid groups (e.g., dicumyl peroxide, di-*tert*-butyl peroxide). These exhibit less sensitivity to acids, aliphatic substitution being preferable to aromatic, higher decomposition temperatures, and less sensitivity to oxygen.

Radiation Curing

The use of high energy radiation is another method by which crosslinking by free radicals can be initiated.

The use of electronic generators, such as the Van de Graaff generator, to produce electron beams of 0.5–10 MeV is the most common method of radiation curing, but colbat sources [^{60}Co] and resonance transformers can also be used.

Metal Oxides

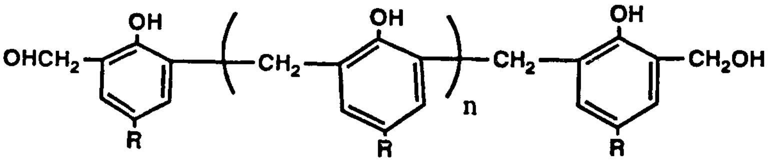
Crosslinking by the use of metal oxides is used to cure polychloroprene, chlorosulfonated polyethylene, polysulfides, and carboxylated nitriles. Metal oxides are also used as acid acceptors in rubbers containing halogens.

Commonly used metal oxides are magnesium oxide, zinc oxide, lead oxide, and red lead. The type of oxide used can influence the water and acid resistance of the rubber compound, especially in the case of polychloroprene. The particle size of the oxide influences the cure rate and degree of cure obtained, the fine particle sizes being preferred.

Metal oxide cures can be accelerated; the type of accelerator used and whether it is necessary depend on the particular polymer and metal oxide being used. These aspects have been discussed under each particular polymer type.

Resin Cures

Butyl, chlorobutyl, bromobutyl, and EPDM are elastomers that can be crosslinked with reactive phenol formaldehyde resins of the type:



It is understood that natural and nitrile rubber have also been crosslinked by this type of system, but no great advantages accrued.

In butyl rubber, the resins require activation by a halogen-containing material, polychloroprene normally being used in preference to $SnCl_2$. If some of the hydroxyl groups on the methylol group of the resin are replaced by bromine, the activation by an added halogen is not required. Chloro- and bromobutyl do not require the added halogen, but EPDM does.

Normally 5–12 phr of resin is used, and such cures give butyl rubber excellent heat resistance, the polymer being capable of service at temperatures some 60°C higher than temperatures obtainable from other cure systems. In EPDM, the service temperature is raised by about 30°C compared to the sulfur-cured varieties; this, combined with the low compression set and the good strength properties exhibited, makes resin cures an alternative to the peroxide curing of EPDM.

Typical resin cure systems for butyl rubber and EPDM are as follows:

Polymer	phr
Butyl rubber	
butyl	95.0
Neoprene W	5.0
zinc oxide	1.0
resin	3-6.0
EPDM	
EPDM	90.0
bromobutyl	10.0
resin	10–12.0

Diurethane Cure Systems (Novor Cures)

The diurethane cure systems are a fairly recently developed method of crosslinking natural and some of the synthetic rubbers, based on chemistry developed by MRPRA.

Generally the Novor cures combine the best features of conventional and EV systems, providing thermally stable crosslinks but with superior dynamic fatigue performance. The reversion resistance of the cure system is outstanding, and the physical properties obtained are also unaffected by cure temperature.

The ultimate heat and reversion resistance is gained by use of a pure Novor system, but small additions of sulfur produce a synergistic effect on modulus and a faster cure rate. The use of sulfur in the "80/20" system does not contribute to inferior aging.

Caloxol is added to the pure Novor cure system to remove water, which could deactivate the isocyanate cure agent; but steam curing can lead to surface hydrolysis.

Typical cure systems are as follows.

Ingredient	Pure Novor (phr)	80/20 system (phr)
Novor	6.7	4.2
ZDMC	2.0	
Caloxol	3.0	
Sulfur		0.4
TMTM		1.3
Santocure NS		0.08

For the accelerators ZDMC and TMTM, see Table 16.

Table 16 Major Types of Accelerator

Accelerator	Common abbreviation
Guanidines	
N,*N*′-Diphenylguanidine	DPG
N,*N*′-Diorthotolyl guanidine	DOTG
Orthotolyl biguanidine	OTBG
Triphenyl guanidine	TPG
Thioureas	
N,*N*′-Dibutylthiourea	DBTU
1,3-Diethylthiourea	DETU
N,*N*′-Diorthotolyl thiourea	DOTU
N,*N*′-Diphenyl thiourea	DPTU
Ethylene thiourea	ETU
Tetramethyl thiourea	
Trimethyl thiourea	
Thiazoles	
2-Mercaptobenzothiazole	MBT
Zinc-2-mercaptobenzothiazole	ZMBT
2,2′-Dibenzothiazyl disulfide	MBTS
2-(2,4-Dinitrophenyl)mercaptobenzothiazole	DMBT
4-Morpholinyl-2-benzothiazydisulfide	MBSS
Sulfenamides	
2-(4-Morpholinylmercapto)benzothiazole	MOR (MBS/MOBS)
N-*tert*-Butyl-benzothiazyl sulfenamide	TBBS (NS)
N-Cyclohexyl-2-benzothiazyl sulfenamide	CBS
N,*N*-Diisopropyl-2-benzothiazyl sulfenamide	DIBS
N-Dimethyl benzothiazyl sulfenamide	DMBS
N-Diethyl benzothiazyl sulfenamide	DEBS
N,*N*-Dicyclohexyl-2-benzothiazyl sulfenamide	DCBS
Aldehyde/amine condensates and related materials	
Acetaldehyde/aniline	AA
Butyraldehyde/aniline	BA

Table 16 Continued

Accelerator	Common abbreviation
Anhydroformaldehyde/aniline	MA
Heptaldehyde/aniline	HA
Anhydroformaldehyde/*p*-toluidine	MT
Hexamethylene tetramine	HEXA (HMT)
Dibutylamine	DBA
Cyclohexylethylamine	CEA
Polyethylene/polyamine	
Tricrotonylidene tetramine	
Thiurams	
Dimethyldiphenyl thiuram disulfide	MPTD (DDTS)
Dipentamethylene thiuram disulfide	DPTD (PTD)
Dipentamethylene thiuram tetrasulfide	DPTT
Dipentamethylene thiuram monosulfide	DPTM (PTM)
Tetrabutyl thiuram disulfide	TBUT (TBT/TBTS)
Tetraethyl thiuram disulfide	TETD (TET)
Tetramethyl thiuram monosulfide	TMTM
Tetramethyl thiuram disulfide	TMTD (TMT)
Dithiocarbamates	
2-Benzothiazyl-*N*,*N*,-diethyl dithiocarbamate	
Bismuth dimethyl dithiocarbamate	BMD (BDMC)
Copper dimethyl dithiocarbamate	CuDD (CuDMc)
Lead dimethyl dithiocarbamate	LDMC (PbDMC)
Piperidinium pentamethylene dithiocarbamate	PPD
Selenium diethyl dithiocarbamate	SEDC
Sodium dibutyl dithiocarbamate	SBUD
Sodium diethyl dithiocarbamate	SDED
Tellurium diethyl dithiocarbamate	TEDC
Zinc dibenzyl dithiocarbamate	ZBED (ZBEC/ZBD)
Zinc dibutyl dithiocarbamate	ZBUD (ZDBC)
Zinc diethyl dithiocarbamate	ZDC (ZDEC)
Zinc dimethyl dithiocarbamate	ZMD (ZDMC)
Zinc pentamethylene dithiocarbamate	ZPD
Xanthates	
Sodium isopropyl xanthate	SIX
Zinc dibutyl xanthate	ZBX
Zinc diethyl xanthate	
Zinc diisopropyl xanthate	ZIX
Others	
Dimorpholinyl disulfide	DTDM
2-Mercaptobenzimidazole	MB (MBI)
N-Oxydiethylene dithiocarbamyl-*N*′-oxydiethylene sulfenamide	OTOS
Zinc dibutyl dithiophosphate	ZDBP
Copper diisopropyl dithiophosphate	CuIDP

Amines

Polyfunctional amines are important vulcanizing agents for acrylate and fluorocarbon rubbers.

For acrylate rubbers, the amines frequently used are a reaction product of ethylene chloride, formaldehyde, and ammonia known as Trimene base, and triethylene tetramine. Trimene base is said to give particularly good resistance to aging at high temperatures. Vulcanization with one of these amines alone gives brittle products after long-term aging, but by the addition of small amounts of sulfur or accelerators (e.g., TMTD or MBTS: see Table 16), good heat resistance can be obtained. Amine-cured acrylates tend to stick and to have poor storage stability; skin irritations are another drawback.

In the fluorocarbon rubbers ordinarily diamines or polyamines give poor processing safety. Thus blocked amines, in which the inert molecule splits into active components at high temperatures, were developed. Hexamethylene diaminocarbamate and ethylene diaminocarbamate are examples.

Normal levels of addition of amines in fluorocarbon rubbers are 1–1.5 phr, but these should be increased to 1.5 – 2.0 phr if the compound contains mineral fillers. Metallic oxides are also required as activators and acid acceptors.

Dioximes

p-Benzoquinone dioxime can crosslink various elastomers such as natural rubber, SBR, and EPDM. However, it is of technical importance only in butyl rubber. The cure rate increases with the degree of unsaturation in the butyl, and the addition of sulfur raises the modulus and improves scorch safety. However, this advantage is at the expense of compression set and heat resistance.

To get the most efficient vulcanization, with good heat resistance, MBTS, lead oxide, and red lead can be added. The addition of zinc oxide raises the heat stability of the vulcanizate but decreases scorch safety.

1.3.2 Cure Activators

The characteristic of an activator is that relatively small additions to a compound considerably increase the degree of vulcanization. Often, almost no vulcanization will take place if the cure activators are omitted.

Organic accelerators almost always require the presence of organic and/or inorganic activators. Zinc oxide is probably the most important inorganic activator, but magnesium and lead oxide also find use. The fatty acids (e.g., stearic, palmitic, and lauric acids) are the most important organic activators; polyalcohols (e.g., ethylene glycol) and amino alcohols (e.g., triethanolamine) also find use and are often used to conteract the retarding effect of white fillers.

Activation by zinc oxide is dependent on the particle size used; normal grades require 3–5 phr, but grades having very small particle sizes can require as little as 1 phr for adequate activation. The latter grades would be preferred in transparent articles. The onset of vulcanization in sulfenamide-accelerated cures is further delayed if fine particle sized grades are used.

Basic zinc carbonate which is more soluble than zinc oxide can be used in the production of transparent goods.

1.3.3 Accelerators

There is such a wide variety of accelerators, that can be used singly, in combination, at different levels, and in different polymers, that it is a daunting task to try and present a brief summary of these critically important ingredients. The reader will therefore understand why we advise consulting the polymer manufacturers' trade literature for guidance in selecting a suitable cure system.

Accelerators are of most importance in the sulfur cure systems used to crosslink unsaturated rubbers, but their importance is belied by their low level of addition to a compound, typically 1-5 phr. Accelerators strongly influence not only the processing safety and cure characteristics of a compound, but also the final properties exhibited by the compound, including long-term service.

Figure 11 summarizes the principal manufacturing routes by which the commercially available accelerators are produced.

Table 16 summarizes the major accelerators available, together with their common abbreviation(s). In addition to these major types, there are accelerators available whose composition is undisclosed, as well as proprietary mixtures of different accelerators.

Guanidines

As a group, the guanidines exhibit very slow curing characteristics in unsaturated rubbers, and the vulcanizates offer inferior resistance to heat aging and UV light. They are, however, frequently used as a secondary accelerator with the thiurams, dithiocarbamates, and sulfenamides, but most commonly with the thiazoles, because such mixtures exhibit synergism—that is, there is more activity in the mixture than is represented by the sum of the two individual activities, as illustrated in Figure 12. The role of the guanidines as secondary accelerators is more restricted in butyl and EPDM rubbers.

Thioureas

The use of thioureas is restricted to being a secondary accelerator in the unsaturated rubbers, and even this use is rare except in polychloroprenes, where the thioureas have enjoyed wide use. Ethylene thiourea has been the most favored, because of the excellent balance of properties resulting from its use, but it is now becoming less used as a result of doubts over its safety, particularly with women.

Thioureas, and again principally ethylene thiourea, have been widely used as cure agents, as opposed to accelerators, for the crosslinking of epichlorohydrin.

Thiazoles

The thiazoles, together with the sulfenamides, can be considrered to be one of the most important groups of accelerators for the sulfur cure of unsaturated elastomers since, by correct choice of type and judicial incorporation with other accelerators, a wide range of cure characteristics and vulcanizate properties can be obtained.

The most common accelerators of the thiazole type are MBT and MBTS, whose structural formulas were shown in Figure 11.

The thiazoles give rates of cure and processing safety intermediate between those of the guanidines and thiurams, MBTS exhibiting a slightly better resistance to scorch than MBT. Used by themselves, thiazoles give good aging properties, but not a high extent of cure. For this reason they are commonly used in combination with guanidines, sulfenamides, thiuram, and dithiocarbamates; they can be classed as secondary accelera-

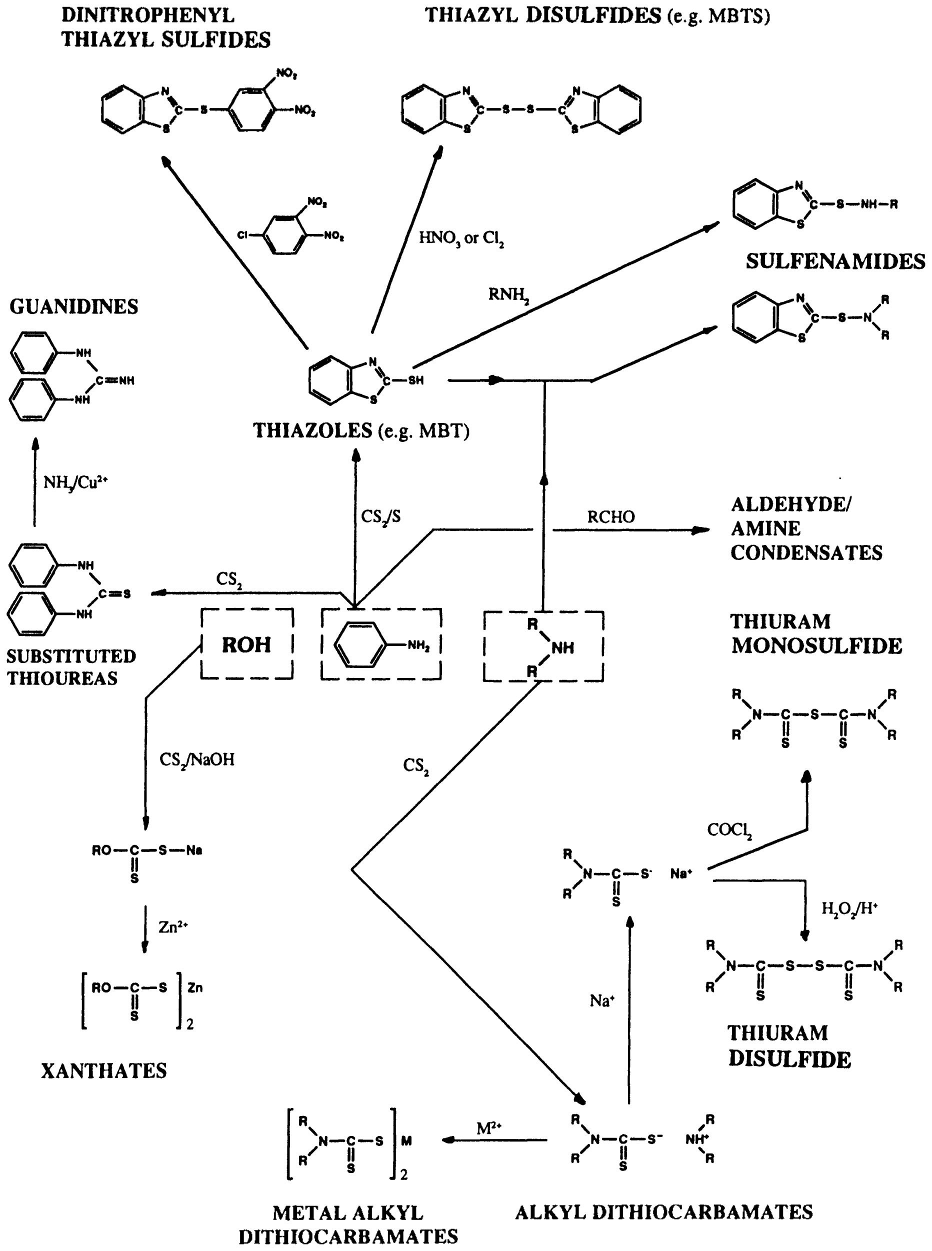


Figure 11 Principal manufacturing routes for accelerators. The speed of cure in natural rubber generally increases as one moves clockwise from the substituted thioureas/guanidines to the xanthates. (Figure compiled by B. Willoughby.)

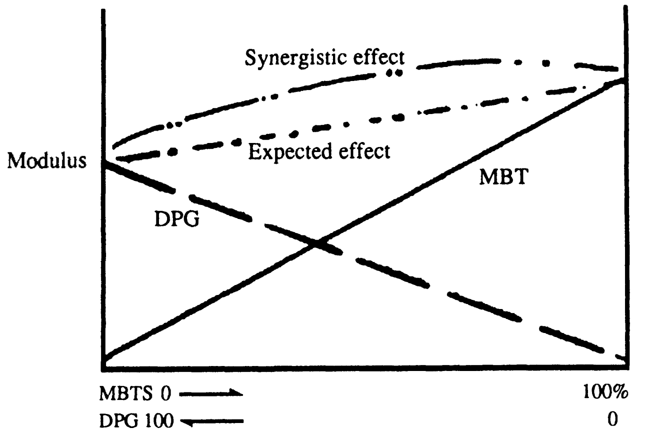


Figure 12 Example of a synergistic effect with accelerators.

tors when used with the latter three types. Only one accelerator, classed here as a thiazole, namely 2-(4)-morpholinodithiobenzothiazole (MBSS), is capable of acting as a sulfur donor in sulfurless cures.

Sulfenamides

Compared to the thiazoles, the use of sulfenamide accelerators in the sulfur vulcanization of unsaturated rubbers results in a longer scorch but a more rapid rate of cure.

The accelerators TBBS, MOR, and DCBS give greater processing safety than the most common sulfenamide accelerator, CBS, while TBBS gives the highest state of cure. The thiurams and dithiocarbamates can be used as secondary accelerators to increase the speed of cure, and sulfenamides can be used as secondary accelerators for the former types to increase the scorch time and to decrease the rate of cure.

Sulfenamides are used in semi-EV and EV cure systems, occasionally as the only accelerator, where levels of up to 5 phr may be required, or in combination with the thiurams and dithiocarbamates, where lower levels ($\leqslant$ 3 phr) are used.

The sulfenamides cannot be used to give sulfurless cures.

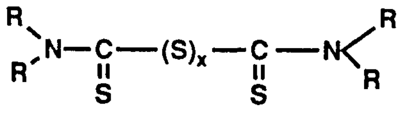
Aldehyde/Amine Condensates

The aldehyde/amine condensate accelerators vary from particularly fast accelerators, with low scorch times, to very slow accelerators. As a class of accelerators they are rarely used, and when selected they tend to be secondary accelerators. The curing of ebonites is one area of use.

Thiurams

The thiurams exhibit fast cure rates in unsaturated rubbers, hence are considered to be ultra-accelerators; they give a longer scorch time than the dithiocarbamates and thus find a much wider use as accelerators than the latter.

The thiurams have the following structure:



Where R is generally an alkyl group and x can be 1, 2, or 4. If x is greater than 2 it is possible to use the thiuram as a sulfur donor in a "sulfurless" cure system. If x is 1, sulfur must be used as the curing agent. In addition to sulfurless cures, the thiurams are used in conventional, semi-EV, and EV cure systems, both singly and in combination with the other accelerator classes.

Dithiocarbamates

A wide variety of metal and alkyl dithiocarbamates are available, but in solid unsaturated rubbers the zinc-based dithiocarbamates are the most technically important.

The dithiocarbamates are also classed as ultra-accelerators, but since they have very low scorch times and fast cure rates, they are used as only secondary accelerators with the slower acting accelerators.

Dithiocarbamates based on zinc, sodium, and ammonium-based alkyls are water soluble, hence find wide use as accelerators in latex applications, where their high activity is less problematical because the cure temperatures used are much lower. Similarly, they also find use in solution applications, where cure temperatures tend to be much lower.

The other metal-based dithiocarbamates listed in Table 16 are rarely used. Dithiocarbamates based on nickel are not used as accelerators, but as antidegradants in polychloroprene, chlorosulfonated polyethylene, and epichlorohydrin.

Xanthates

The xanthates, together with the ammonium-based alkyl dithiocarbamates, are the fastest accelerators known. They are seldom used in curing solid unsaturated rubber. In solution processing applications, adhesives, and sealants, however, it is possible to achieve cure at room temperature with these accelerators.

Others

Of the accelerators listed under "Others" in Table 16, dimorpholinyl disulfide and *N*-oxydiethylene dithiocarbamyl-*N'*-oxydiethylene sulfenamide are two types that can be used as sulfur donors, as well as being used in combination with the other types of accelerator.

1.3.4 Fillers

Fillers of many types can be added to rubber compounds to extend the range of physical properties, to reduce the cost of the compound, to modify the processing properties (e.g., to achieve a reduction in die swell), and to influence the chemical resistance of the compound.

In addition, fillers can pigment a compound, impart conductivity to it, and influence its aging characteristics.

A reinforcing filler can be defined as a filler that improves modulus, tensile strength, and tear and abrasion resistance. Remember, however, that this improvement of properties is not continuous: when the volume percentage of filler further increases, the point at which there is insufficient rubber to bind the filler together eventually will be reached. A noticeable decrease in strength would have become apparent well before this point.

Fillers can also be classed as semireinforcing or diluent.

The effect of a particulate filler on a rubber depends on the following factors:

1. *The surface area of the filler particles.* The surface area of a filler particle is directly related to the particle size; the lower the particle size, the higher the surface area. SAF, a highly reinforcing carbon black, has a particle size of 11–19 nm and a surface area of 125-155 m^2/g, whereas with SRF black, which is semireinforcing, the values are 61–100 nm and 17-33 m^2/g. Coarse inorganic fillers may have surface areas of around 1 m^2/g.

2. *The chemical nature of the particle surface.* The chemical nature of the particle can vary among different fillers. On the surface of carbon blacks there are chemically active sites that have a profound effect on the reinforcement obtained. If the carbon black is exposed to temperatures of 1600-3000°C, these active sites are destroyed, and reinforcement is lost. Thus both total surface area and surface activity of a filler are important requirements for the development of reinforcement.

The pH of the filler can influence the cure characteristics. Silica fillers tend to be acidic and to have $-OH$ groups on the surface which can deactivate accelerators, hence retard cure. This disadvantage can be overcome by increasing the level of accelerators or by inclusion of diethylene glycol, polyethylene glycol, or triethanolamine.

The reinforcing effect of several white fillers can be increased by the use of silane coupling agents, which react with chemical groups on the filler surface.

3. *Geometrical characteristics.* If carbon black is examined under an electron microscope, it is seen that the primary particles are fused into larger aggregates. The size, shape, and number of voids in this "aggregate" determine the "structure" of the carbon black, and this structure can influence the physical, and processing properties obtained.

Whereas the primary particles of carbon black are generally spherical, the shapes of inorganic or mineral filler particles exhibit much greater variation. The anisometry of the filler particle is an important characteristic, affecting the viscosity and modulus of the resultant rubber compound.

Porosity of the filler particle is another factor that influences the properties obtained. Silicas are generally more porous than carbon black, and thus silica fillers give higher viscosity compounds at equal volume loadings. In carbon blacks, increasing porosity can decrease the electrical resistivity obtained.

The general effects of the surface area and geometric factors of a filler are summarized in Table 17.

Table 17 Summary of the General Effect of Filler Properties on Compound Properties

Property	Increasing surface area (lower particle size)	Increasing structure or anisometry
Tensile strength	Increases	Decreases
Tear strength	Increases	Minor effect
Modulus	Increases	Increases
Abrasion resistance	Increases	Increases
Damping	Increases	Increases
Viscosity	Increases	Increases
Extrusion shrinkage	Minor effect	Decreases
Electrical conductivity (carbon black only)	Increases	Increases

Carbon Blacks

The most important types of carbon black used in the rubber industry are those produced by the oil furnace process and thermal blacks; channel blacks have virtually disappeared.

A wide variety of carbon blacks are available, and these are summarized in Table 18. At equal volume loadings the tensile, tear, hardness, modulus, abrasion resistance, and heat buildup properties of a compound decrease as one moves down the table, whereas flexibility, resilience, elongation at break, and processibility improve.

Silica and Silicates

Silica fillers are reinforcing white fillers that can be produced by two processes: precipitation from solution and combustion methods (fumed silica). Because the latter method yields a very fine particle size (ca. 10 nm; surface area ca. 190 m^2/g), which produces very high viscosity, stiff compounds, it is not as widely used as the precipitated type. The precipitation process yields a filler with a particle size of 10–40 nm (surface area ca. 150 m^2/g), and this type of process is the more commonly used.

Silica can give tensile and tear strengths equivalent to those obtainable from the use of carbon black, but the resilience, set, and abrasion resistance are generally inferior. Hot tear strength is reputedly superior to that obtainable with carbon black.

As mentioned earlier, diethylene glycol, polyethylene glycol, triethanolamine, or silane coupling agents are required to eliminate the cure-retarding effect of silica fillers.

Both aluminum and calcium silicates can be produced by the precipitation process; they are classed as semireinforcing white fillers. The calcium silicates, with surface areas of ca. 80 m^2/g, are slightly more reinforcing than the aluminum types, but the activity of these fillers is such that the reinforcement achieved is lower than that obtainable from a carbon black of equal surface area.

Table 18 Major Grades of Carbon Black

Abbreviation	Unsystematic common name	Particle size (nm)	Surface area (m^2/g)	ASTM D1765 designation[a]
SAF	Superabrasion furnace	11-19	125-155	N110
ISAF	Intermediate abrasion furnace	20-25	110-140	N220
CF	Conductive furnace	20-25	110-140	N293
SCF	Superconductive furnace	20-25	110-140	N294
HAF	High abrasion furnace	26-30	70-90	N330
HAF-LS	High abrasion furnace, low structure	26-30	75-105	N326
HAF-HS	High abrasion furnace, high structure	26-30	80-100	N347
EPC	Easy processing channel	26-30	95-115	S300
FF	Fine furnace	31-39	43-69	N440
FEF	Fine extrusion furnace	40-48	36-52	N550
GPF	General-purpose furnace	49-60	26-42	N660
SRF	Semireinforcing furnace	61-100	17-33	N762
MT	Medium thermal	201-500	6-9	N990

[a] N, normal curing, neutral, or basic blacks; first digit, particle size indication; second and third digits, arbitrary designations.

Clays

White clay based fillers are a useful compounding ingredient in rubber. They can be divided into "hard" and "soft"; the hard clays can be classed as semireinforcing fillers, their smaller particle size giving a greater effect on modulus than the "soft" types. The distinction between the two types is, however, somewhat blurred.

Calcination, or removal of combined water from the clay, can modify the properties imparted to the rubber, the effect on electrical properties being particularly noticeable.

Chemical treatments of the clay by amines or, more important these days, silane coupling agents, can result in improved reinforcement.

Calcium Carbonate

Ground calcium carbonate, whiting, has a coarse particle size (0.5–30 μm) and is used only as a diluent filler because of its low cost.

Precipitated calcium carbonate has a smaller particle size ($\geqslant$ 0.1 μm), which gives improved properties compared to the use of whiting. Stearate-coated grades, which give improved dispersability, are available.

As with all fillers produced from naturally occurring minerals, traces of metals such as Cu and Mn may be present. Thus care is required in the selection of the grade of filler if it is to be used in a rubber where these impurities might catalyze oxidative breakdown.

Other Types of Filler

Zinc oxide, in amounts larger than the approximately 5 phr used for cure activation, can act as a semireinforcing filler.

Barium sulfate is available as a ground filler (barytes) or as a precipitated filler (blanc fixe). Neither form reinforces, but the latter is widely used in the compounding of acid-resistant compounds. Barium sulfate is also opaque to X-rays.

Hydrated alumina is used as a flame retardant, but it tends to depress other physical properties.

1.3.5 Short Fibers

Another method of reinforcing a rubber compound is the inclusion of a short fiber, and the reader is directed to References (24–26) for further information on this subject.

Short fibers (20–30 μm in diameter, and up to 13 mm long) of polyester, Kevlar, nylon, and rayon are commercially available and can provide high reinforcement; the mechanical properties obtained depend on

Fiber type
Aspect ratio of the fiber
Fiber concentration
Orientation of the fiber in the product
Dispersion of the fiber
Degree of adhesion between the fiber and compound.

Cellulose fibers can also give reinforcement; Santoweb, produced by Monsanto, is probably the most important commercially. Santoweb is based on unregenerated cellulose treated to promote ease of dispersion and, in some cases, adhesion. The fibers are ribbon shaped (major axis diameter 16 μm, minor axis diameter 8 μm) and have an average length of 1.5 mm.

Certain grades of PTFE can be added to compounds, the PTFE fibrillating during processing.

Reinforcement by short fibers can give increased tensile strength and modulus, with a decrease in the elongation at break and swelling in solvents. Differences in properties in the longitudinal and transverse directions result if the fibers are highly oriented.

1.3.6 Reinforcing Resins

The two major types of reinforcing resin used in rubber compounds are the high styrene resins and the phenolic resins.

High styrene resins are copolymers of styrene and butadiene, with a styrene content of 50–85 wt %. These resins are primarily used in the compounding of natural and SBR rubber, and the main area of use is shoe soling applications. The high styrene resins increase hardness but, since they are thermoplastic, they achieve this without sacrificing processibility.

Phenolic resins are primarily used as reinforcing resins in nitrile rubber. If the phenolic resin is crosslinked during vulcanization, the hardness, tensile strength, tear strength, and abrasion resistance of the compound are increased. Before vulcanization, however, the phenolics act as process aids.

1.3.7 Softeners, Process Aids, and Tackifying Resins

The distinction between softeners, process aids, and tackifying resins is blurred, and many act as dual-purpose ingredients. Plasticizers also act as softeners and process aids but are dealt with separately here, the term "plasticizer" being reserved for an ingredient added for the purpose of lowering the T_g of a polymer.

The general reasons for adding softeners, process aids, and tackifies are as follows:

1. To improve the processing properties.
2. To modify the final compound properties (hardness and flexibility).
3. To alter the cost of the compound by allowing further increases in the filler level while maintaining a certain hardness.
4. To reduce power consumption during processing.

Petroleum Oils

All petroleum oils are a mixture of paraffinic, naphthenic, and aromatic hydrocarbons, and the precise composition of the oil determines its compatibility with a rubber, as well as the precise effects of the addition.

The viscosity gravity constant (VGC) and the refractive index (RI) of an oil are quoted by the manufacturers, and knowledge of these two parameters can be used to assess the composition of the oil. Table 19 summarizes the VGC and RI for various compositions of oil.

The composition of the oil also controls its compatibility with the various rubbers. The paraffinic oils are more compatible with EPDM and butyl rubber, while the more polar aromatic oils are compatible with the polar rubbers, polychloroprene, nitrile, and chlorosulfonated polyethylene. Most types of oil are compatible with natural, polybutadiene, and SBR rubbers.

Table 19 Viscosity Gravity Constant (VGC) and Refractive Index (RI) of Petroleum Oils

Type of oil	VGC	RI
Paraffinic	0.791-0.820	< 1.048
Naphthenic	0.851-0.900	1.048-1.065
Aromatic	0.951-1.000	1.053-1.065
Highly aromatic	1.001-1.050	> 1.065

The viscosity and volatility of the oil are important aspects in the choice of the grade of oil. Viscosity, as well as the type of oil, has an effect on the low temperature properties of the oil, hence the low temperature properties of the compound. Low molecular weight paraffinic oils are preferred where low temperature properties are important.

The volatility of the oil is important for permanence at high temperatures, which is dependent on the molecular weight and type of oil.

Process Aids

The major types of ingredient considered to be process aids are the fatty acids, metal salts of the fatty acids, and other fatty acid derivatives. There are numerous additives on the market that can have an appreciable influence on processibility. In addition to acting as lubricants for flow during molding, they can improve the dispersion of additives during mixing.

Liquid nitrile and EPDM are also available and can be used to increase processibility; they have the further advantage of being crosslinked into the polymer matrix during cure, hence are not extractable.

Tackifiers

Resins, pine tar, coumarone-indene resins, xylol-formaldehyde, and other hydrocarbon resins can be used to increase the "tack" of compounds in the uncured state, hence to improve building operations during manufacture.

Factices

Factices are vulcanized vegetable oils used as processing aids. Brown factice can give faster and smoother extrusions and can help to prevent collapse of extrudates during vulcanization in open steam. White factice is used in the manufacture of erasers, where it reduces the abrasion resistance of the compound.

1.3.8 Plasticizers

Synthetic plasticizers based on polyesters are the most important type of plasticizer commercially, although ether- and thioether-based types are also available.

The remainder of Section 1.3.8, on ester plasticizers, is due to Paul Clutterbuck of BP Chemicals, who has presented this material to section meetings of the Plastics and Rubber Institute. We are indebted to BP for allowing us to publish this in its entirety, since such excellent summaries are rare in the literature.

Ester plasticizers play a very important role in rubber technology. They are used to improve processibility, to improve low temperature properties, and to balance the swelling effects of fuels and oils with which rubber products are frequently in contact.

The use of ester plasticizers enables larger quantities of filler to be added to the rubber without the compound becoming too stiff to process. Because they reduce the compound viscosity, they also reduce the temperatures generated during processing, which substantially reduces the risk of premature vulcanization (scorch). The addition of ester plasticizers can also reduce compound costs and improve extrusion and calendering characteristics.

Ester plasticizers are particularly used in nitrile, polychloroprene, and chlorosulfonated polyethylene rubbers. However, smaller quantities are also used in other types of rubber, including chlorinated polyethylene, epichlorohydrin, polyacrylic, and fluorocarbon rubbers.

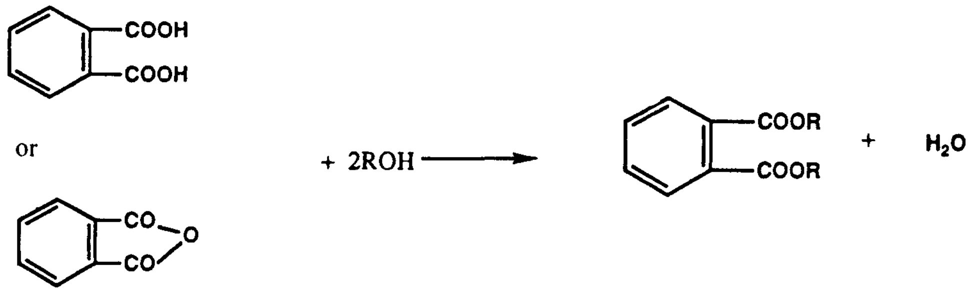
Selection of an ester plasticizer for a particular application can often be confusing because of the large choice available. However, ester plasticizers can be characterized by reference to their chemical constitution and end-product application. The considered use of high performance plasticizers can sometimes lead to cost savings and other technical advantages.

Nearly all ester plasticizers can be conveniently divided into the following five groups:

1. Phthalates (general-purpose plasticizers)
2. Low temperature
3. High temperature
4. Flame retardant (mostly phosphate)
5. Permanent (polyester)

Phthalates (General-Purpose Plasticizers)

Phthalates are organic esters of phthalic acid and alcohols. However, in practice phthalic anhydride is used instead of phthalic acid.



For general-purpose plasticizers, R ranges from normal butyl (C-4) to the isomeric branched decyl (C-10) group. The use of alcohols with mixed chain length is common.

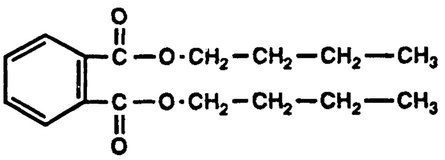
The following list shows phthalates that are currently commercially available or have been available in recent years.

Abbreviation	Phthalate
DBP	Di-*n*-butyl phthalate
DIBP	Diisobutyl phthalate
DHXP	Di-*n*-hexyl phthalate
DNHP	Di-*n*-heptyl phthalate
DIHP	Diisoheptyl phthalate
DOP	Di-2-ethylhexyl phthalate
DAP	Predominantly branched C-7—C-9 phthalate
DIOP	Diisooctyl phthalate
L79P	Predominantly linear C-7—C-9 phthalate
610P	Linear C-10—C-16
DNP	Diisononyl phthalate
810P	Linear C-8—C-10 phthalate
L711P	Predominantly linear C-7—C-11 phthalate
DIDP	Diisodecyl phthalate
L911P	Predominantly linear C-9—C-11 phthalate

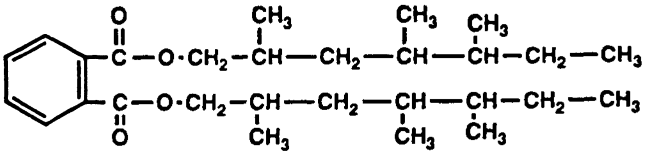
To explain how users can select the most appropriate material from this group, it is necessary to consider their chemical structure. Fortunately only two variables need to be considered:

The number of carbon atoms in the side chains
The degree of branching of the side chains

Carbon Number. The extremes for general-purpose phthalates are DBP and DIDP.



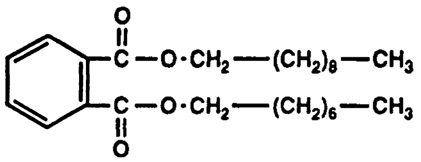
Di-*n*-butyl phthalate (DBP), C-4



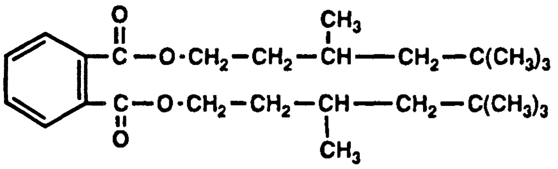
Diisodecyl phthalate (DIDP), C-10

When phthalates are made from alcohols with a spread of carbon numbers, performance depends on the average carbon number. Thus L79P behaves as a C-8 phthalate, and L911P behaves as a C-10 phthalate.

Chain Branching. The extremes found in practice are found in 810P and DNP.



Linear C-8–C-10 phthalate (810P), behaves as a C-9 phthalate



Highly branched C-9 phthalate, di-3,5,5-trimethylhexyl phthalate (DNP)

From these, the various phthalates can be set out on a grid according to carbon number and chain branching, as indicated in Table 20.

Increasing the carbon number gives:

1. Reduced compatibility
2. Poorer processibility
3. Higher oil solubility
4. Higher plasticizer viscosity
5. Reduced volatility
6. Reduced water solubility
7. Better low temperature flexibility

Table 20 Classification of Phthalates by Carbon Number and Branching[a]

Carbon number					
C-4	DBP				DIBP
C-5					
C-6	DHXP				
C-7	DNHP			DIHP	
C-8	610P	L79P	DOP	IOP	
C-9	810P	L711P		DINP	DNP
C-10		L911P		DIDP	

[a] Branching increases from left to right.

Increasing the branching gives:

1. Poorer low temperature performance
2. Increasing volatility
3. Lower stability to oxidation (except DNP)
4. Higher electrical volume resistivity in a compound (poorer conductivity)

Special Considerations. *L79P* is a phthalate of predominantly linear C-7–C-9 alcohols, average C-8. It gives rubber compounds with lower volatility and slightly better low temperature flexibility than branched C-8 phthalates such as DOP and DIOP.

L911P is the phthalate of predominantly linear C-9–C-11 alcohols, average C-10. Its high linearity and relatively high carbon number give it two main technical advantages:

Low volatility and good oxidative stability
Good low temperature performance, particularly when compounded to a fixed hardness

Low Temperature

Low temperature plasticizers are used to give improved flexibility and resistance to cracking at low temperatures. Compared to general-purpose phthalates, they are generally more difficult to process and have a higher volatility, more water solubility, and less compatibility.

Low temperature plasticizers are generally aliphatic diesters. They are made from linear dibasic acids with the general structural formula:

$$ROOC{-}(CH_2)_n{-}COOR$$

The most popular dibasic acids are adipic ($n = 4$), azelaic ($n = 7$), and sebacic ($n = 8$). Most aliphatic diesters are manufactured from branched-chain alcohols, such as 2-ethylhexanol or isodecanol. Linear alcohols are generally avoided, since their esters tend to crystallize at relatively high temperatures, giving storage and handling problems.

In selecting a low temperature plasticizer for any application, other factors such as cost and permanence, must also be considered.

DBS (di-*n*-butyl sebacate) is an excellent low temperature plasticizer for many elastomers. However, it has the disadvantage of poor volatility and very high cost.

DOS (di-2-ethylhexyl sebacate) has been regarded historically by many technologists as the rubber industry's low temperature standard. It is an efficient low temperature plasticizer that imparts low volatility, heat stability, and water resistance. However, the price of DOS has risen dramatically over the last few years, and more cost-effective replacements are now available.

DOZ (di-2-ethylhexyl azelate) provides a good balance of low temperature and permanence properties. It confers similar low temperature properties on DOS, but has slightly inferior permanence properties. During the last few years the price of DOZ has risen significantly, and more cost-effective replacements are now available.

DOA (di-2-ethylhexyl adipate) confers low temperature properties similar to those of DOS and DOZ with considerable cost savings. However, it has the disadvantage of relatively poor volatility.

DL79A (adipate of predominantly linear alcohols, average carbon number C-8) confers low temperature properties similar on DOS and DOZ with considerable cost savings. Its predominantly linear nature allows it to overcome some of the volatility disadvantages of DOA.

DIDA (diisodecyl adipate) provides a good compromise of low temperature and permanence properties but, unfortunately, has comparatively poor compatibility.

Bisoflex 102 [= Tricap = Harwick SC (triethylene glycol ester of linear acids, average C-9)] is an excellent low temperature plasticizer for NBR and CR rubbers. It confers superior low temperature performance than the adipates and sebacates. The heat aging properties of this material are significantly enhanced by the addition of a suitable phenolic antioxidant.

Bisoflex 111 [= TP95 (butyl carbitol adipate)] is an excellent low temperature plasticizer with good compatibility with a wide range of rubbers. Because of its relatively low volatility, it is effective over a wide range of temperatures.

Bisoflex 120 (aliphatic ester) is an efficient low temperature plasticizer for nitrile and polychloroprene rubbers. It imparts heat stability, low volatility, and water resistance. Bisoflex 120 is an excellent cost-effective technical replacement for DOS and DOZ.

Bisoflex 123 [= TP9B = BCF (butyl carbitol formal)] is an excellent low temperature plasticizer with good compatibility with a wide range of elastomers. Unlike most other low temperature plasticizers, it also provides resistance to fungal attack. However, it has very poor volatility and low resistance to water extraction.

Figure 13 summarizes the various characteristics of low temperature plasticizers.

High Temperature

High temperature plasticizers are primarily intended for use in synthetic rubber cable formulations, where excellent resistance to heat aging is a requirement. They are generally more difficult to process, less efficient than general-purpose phthalates, and generally characterized by their low volatility and good resistance to oxidation.

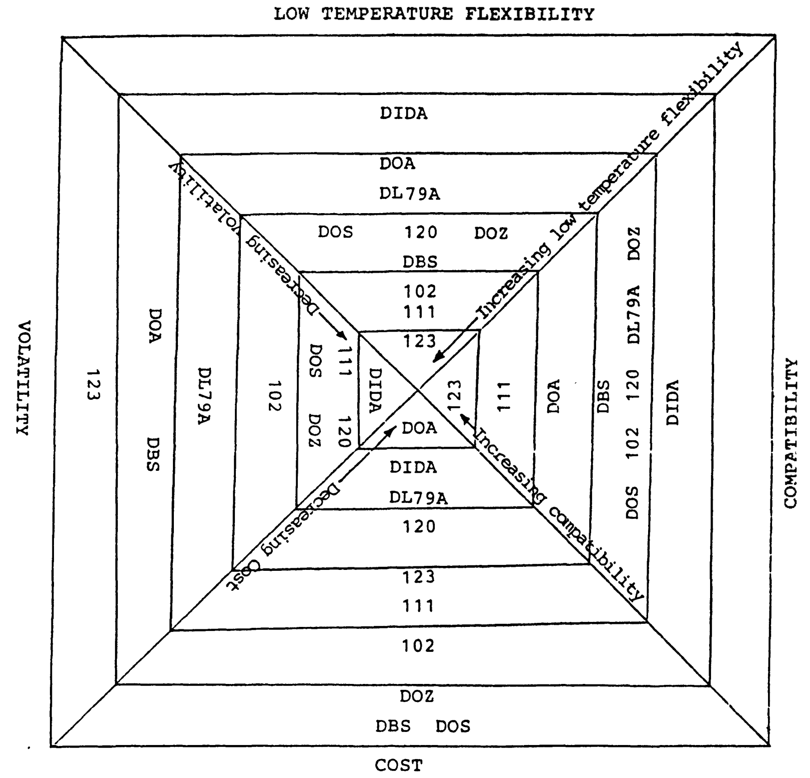
DTDP is the phthalate ester of tridecanol, which is a mixture of branched tridecyl (C-13) alcohols. DTDP is a good high temperature plasticizer that imparts low volatility and good resistance to extraction by water. However, compared to other high temperature plasticizers such as the trimellitates, DTDP has poor plasticizing efficiency, poor processing characteristics, and high viscosity.

Bisflex DUP is the phthalate ester of predominantly linear undecanol. DUP surpasses DTDP in heat aging performance, has greater plasticizing efficiency, and is more readily compounded with synthetic rubbers. It also imparts good low temperature properties.

TOT (tri-2-ethylhexyl trimellitate) surpasses DTDP and DUP in heat aging performance. TOT demonstrates particularly good resistance to marring (migration into other polymers) with a wide range of materials. Compared to other monomeric esters, TOT has excellent resistance to aqueous extraction.

TL79T is the trimellitate ester of predominantly linear alcohols, average carbon number C-8. It is marginally more efficient than TOT and gives slightly superior heat aging and low temperature performance. In common with other trimellitates, TL79T has good resistance to marring and excellent resistance to aqueous extraction.

T810T is the trimellitate ester of linear *n*-octanol and *n*-decanol. It is capable of withstanding even more extreme heat aging conditions than TOT or TL79T. It also confers moderate low temperature flexibility and is ideal for use in compounds that call for a combination of excellent high temperature and moderate low temperature proper-



Bisoflex 102 = Tricap = Harwick SC

Bisoflex 111 = TP95

Bisoflex 123 = TP90B = BCF

Figure 13 Characteristics of low temperature plasticizers.

ties. In common with other trimellitates, T810T has good resistance to marring and excellent resistance to aqueous extraction.

Note that DTDP, DUP, and the trimellitates listed above normally contain phenolic antioxidants to enhance aging characteristics.

Bisoflex OBC (pentaerythritol-type ester) is an excellent high temperature plasticizer that imparts low volatility and good resistance to oil extraction. The extreme low volatility, good oxidative stability, and high permanence of OBC make it a very useful plasticizer under severe service conditions.

Vulkanol OT (ether thioether) provides a good compromise between low temperature flexibility and good hot air resistance. It has good compatibility with many elastomers but has the severe disadvantage of being very expensive (more than double the price of other high temperature plasticizers).