Kirk-Othmer Encyclopedia of Chemical Technology.

THERMOPLASTIC ELASTOMERS

Thermoplastic elastomers (TPE) were introduced in the 1960s. They have shown rapid growth since then and have been the subject of many conferences, symposia, etc. In particular, the developments in this field have been covered fairly recently in two books: one being a comprehensive survey of the subject (1) and the other being a general introduction (2). Thermoplastic elastomers have many of the physical properties of rubbers, ie, softness, flexibility, and resilience; but in contrast to conventional rubbers, they are processed as thermoplastics. Rubbers must be cross-linked to give useful properties. In the terminology of the plastics industry, vulcanization is a thermosetting process. Like other thermosetting processes, it is slow and irreversible and takes place upon heating. With thermoplastic elastomers, on the other hand, the transition from a processible melt to a solid, rubberlike object is rapid and reversible and takes place upon cooling. Thermoplastic elastomers can be processed using conventional plastics techniques, such as injection molding and extrusion; scrap is usually recycled.

Because of increased production and the lower cost of raw material, thermoplastic elastomeric materials are a significant and growing part of the total polymers market. World consumption in 2000 was estimated to be $\sim$ 1,300,000 metric tons (3). However, because the melt-to-solid transition is reversible, some properties of thermoplastic elastomers, eg, compression set, solvent resistance, and resistance to deformation at high temperatures, are usually not as good as those of the conventional vulcanized rubbers. Applications of thermoplastic elastomers are, therefore, in areas where these properties are less important, eg, footwear, wire insulation, adhesives, polymer blending, and not in areas such as automobile tires.

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

1. Structure

Most thermoplastic elastomers are multiphase compositions in which the phases are finely dispersed. In many cases, the phases are chemically bonded by block or graft copolymerization. In others, a fine dispersion is apparently sufficient. In these multiphase systems, at least one phase consists of a material that is hard at room temperature (RT) but becomes fluid upon heating. Another phase consists of a softer material that is rubberlike at RT. A simple structure is an A—B—A block copolymer, where A is a hard phase and B an elastomer, eg, poly(styrene-*b*-elastomer-*b*-styrene). Other possiblities include multiblock A—B—A—B—A—··· structures and graft copolymers of hard A segments on a elastomeric backbone polymer B (4).

Most polymer pairs are thermodynamically incompatible and mixtures separate into two phases. This is true even when the polymeric species are part of the same molecule, as in these block copolymers. Poly(styrene-*b*-elastomer-*b*-styrene) copolymers, in which the elastomer is more than $\sim$ 2/3 of the total volume, should have a structure similar to that shown in Figure 1. Here, the polystyrene end segments form separate spherical

Table 1. Classification of Polymers According to Properties and Processing

Property	Thermoset	Thermoplastic
rigid	epoxy, melamine–formaldehyde, sheet molding compounds	polypropylene, high density polyethylene, polystyrene
flexible	highly vulcanized rubber	low density polyethylene, ethylene–vinyl, acetate copolymer, plasticized poly(vinyl chloride) (PVC)
rubbery	vulcanized rubber	thermoplastic rubbers

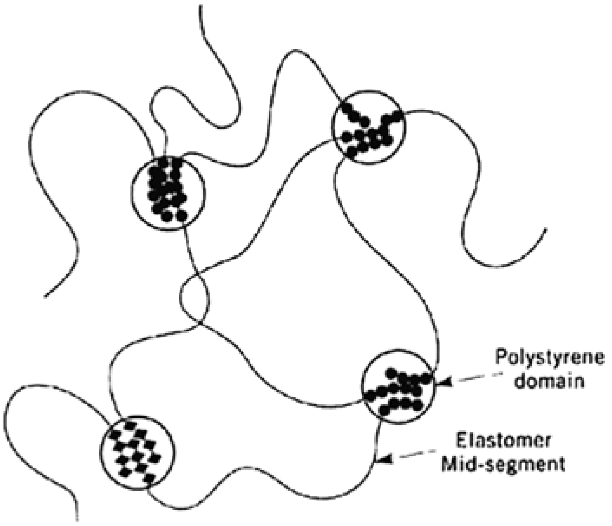


Fig. 1. Phase arrangement in poly(styrene-*b*-elastomer-*b*-styrene) copolymers

regions, ie, domains, dispersed in a continuous elastomer phase. Most of the polymer molecules have end polystyrene segments in different domains. At RT, these polystyrene domains are hard and act as physical cross-links, tying the elastomer chains together in a three-dimensional network. In some ways, this is similar to the network formed by vulcanizing conventional rubbers using sulfur cross-links. The main difference is that in thermoplastic elastomers the domains lose their strength when the material is heated or dissolved in solvents, which allows the polymer or its solution to flow. When the material is cooled down or the solvent is evaporated, the domains harden and the network regains its original integrity. This explanation of the properties of thermoplastic elastomers has been given in terms of a poly(styrene-*b*-elastomer-*b*-styrene) block copolymer, but it would apply to any block copolymer with the multiblock structure A—B—A—B—···, as well as to branched block copolymers $(A—B)_nx$ (where x represents an n functional junction point). In principle, A can be any polymer normally regarded as a hard thermoplastic, eg, polystyrene, polyethylene, or polypropylene, and B can be any polymer normally regarded as elastomeric, eg, polyisoprene, polybutadiene, poly(ethylene-*co*-propylene), or polydimethylsiloxane (Table 2).

Block copolymers with structures such as A—B or B—A—B are not thermoplastic elastomers, because for a continuous load-bearing network to exist, both ends of the elastomer segment must be immobilized in the hard domains. Instead, they are much weaker materials resembling conventional unvulcanized synthetic rubbers (5).

Table 2. Thermoplastic Elastomers Based on Block Copolymers

Hard segment, A	Soft or elastomeric segment, B	Structure[a]	References
polystyrene	polybutadiene and polyisoprene	T, B	5,6,7
polystyrene	poly(ethylene-*co*-butylene) and poly(ethylene-*co*-propylene)	T	6
polystyrene and substituted polystyrenes	polyisobutylene	T, B	8
poly(α-methylstyrene)	polybutadiene and polyisoprene	T	7
poly(α-methylstyrene)	poly(propylene sulfide)	T	7
polystyrene	polydimethylsiloxane	T, M	9
poly(α-methylstyrene)	polydimethylsiloxane	T	7,9
polysulfone	polydimethylsiloxane	M	10
poly(silphenylene siloxane)	polydimethylsiloxane	M	11
polyurethane	polyester and polyether	M	12,13
polyester	polyether	M	14
poly(β-hydroxyalkanoates)	poly(β-hydroxyalkanoates)	M	15
polyamide	polyester and polyether	M	16
polycarbonate	polydimethylsiloxane	M	17–19
polycarbonate	polyether	M	20,21
polyetherimide	polydimethylsiloxane	M	22
poly(methyl methacrylate)	poly(alkyl acrylates)	T, B	23
polystyrene	poly(alkyl acrylates)	T, B	23
polyurethane	poly(diacetylenes)	M	24
polyethylene	poly(α-olefins)	M	25,26
polyethylene	poly(ethylene-*co*-butylene) and poly(ethylene-*co*-propylene)	T	7,25
polypropylene (isotactic)	poly(α-olefins)	X	25
polypropylene (isotactic)	polypropylene (atactic)	X	25,26

[a] T = Triblock, A—B—A, B = branched, $(\text{A—B})_n x$, M = multiblock, A—B—A—B—···, X = mixed structures, including multiblock.

Besides the thermoplastic elastomers based on poly(styrene-*b*-elastomer-*b*-styrene) and similar styrenic block copolymers, five other block copolymers are of commercial importance: polyurethane/elastomer block copolymers, polyester–elastomer block copolymers, polyamide–elastomer block copolymers, polyolefin block copolymers, and polyetherimide–polysiloxane block copolymers. All five have the multiblock A—B—A—B—··· structure. The morphology of the polyurethane, polyester, polyamide, and polyolefin block copolymers is shown diagrammatically in Figure 2. It has some similarities to that of poly(styrene-*b*-elastomer-*b*-styrene) equivalents (Fig. 1) and also some important differences: (*1*) the hard domains are more interconnected; (*2*) they are crystalline; and (*3*) these long A—B—A—B—··· molecules may run through several hard and soft phases. The polyetherimide–polysiloxane block copolymers share some features of both types. As in the poly(styrene-*b*-elastomer-*b*-styrene) analogues, their hard domains are glassy (amorphous) rather than crystalline. However, these polymers have multiblock A—B—A—B—··· structure rather than A—B—A, and so again, each molecule may run through several hard and soft phases.

Not all thermoplastic elastomers are block copolymers. Thermoplastic elastomers based on graft copolymers, ionomers, and structures with core-shell morphologies have also been described (4) but have not achieved much commercial importance. Combinations of a hard thermoplastic with a softer, more rubberlike polymer (Table 3) are much more significant.

Usually, the components are mechanically mixed together, (25,26) although it is sometimes possible to produce the rubber component *in situ* during polymerization. Typically, the two components form

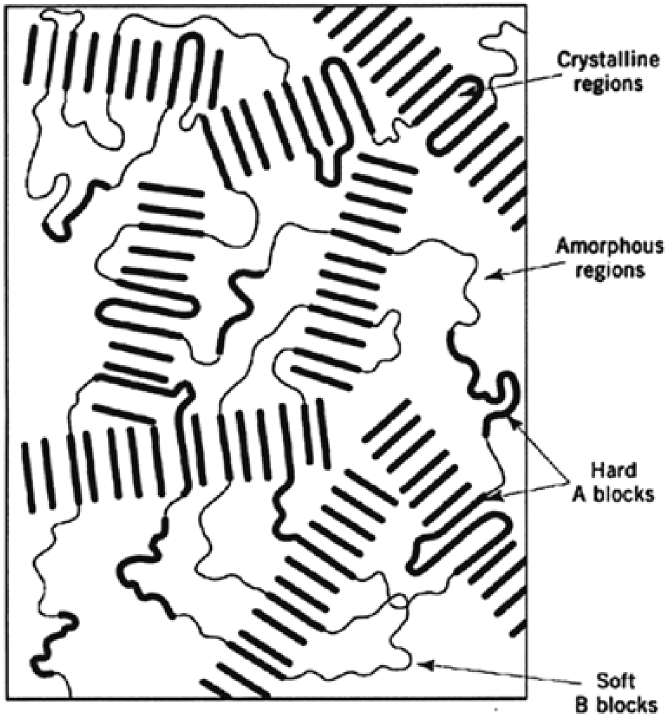


Fig. 2. Phase arrangement in crystalline block copolymers.

interdispersed multiphase systems and a diagrammatic structure for blends of this type is shown in Figure 3. Blends of polypropylene with ethylene–propylene–diene monomer (EPDM) were the first materials of this type (25,26). Blends with ethylene–propylene copolymer (EPR) are now more important commercially, and propylene copolymers often replace polypropylene homopolymer as the hard phase. In some cases, the elastomer phase is cross-linked while the mixture is being highly sheared (25–27). This process is often referred to as "dynamic vulcanization" (28) and gives a finely dispersed and cross-linked elastomer phase (Fig. 4.). Collectively, thermoplastic elastomers of both type (blends and dynamic vulcanizates) are referred to herein as hard polymer/elastomer combinations.

As noted above, a phase separated structure is normally formed in thermoplastic elastomers based on polymer blends, but there are exceptions. Some interpolymer alloys based on halogenated polyolefins are claimed to be single-phase systems (31).

Other hard polymer–elastomer combinations, in which the elastomer phase may or may not be cross-linked, include blends of polypropylene with nitrile (27), butyl (29), and natural (30) rubbers, blends of poly(vinyl chloride) (PVC) with nitrile rubber and plasticizers (31–33), and blends of halogenated polyolefins with ethylene interpolymers (31). Commercially important products (34,35) based on blends of styrenic block copolymers with oil and other polymers such as polystyrene or polypropylene are described later in this article. They can also be considered as hard polymer–elastomer combinations. The oils used in these products are usually hydrocarbons but blends with silicone oils have also been described (36).

Thermoplastic elastomers based on blends of a silicone rubber (cross-linked during processing) with block copolymer thermoplastic elastomers have also been produced (37,38). Other types that have been studied (4) include graft copolymers and elastomeric ionomers, but these so far these have not become very important commercially.

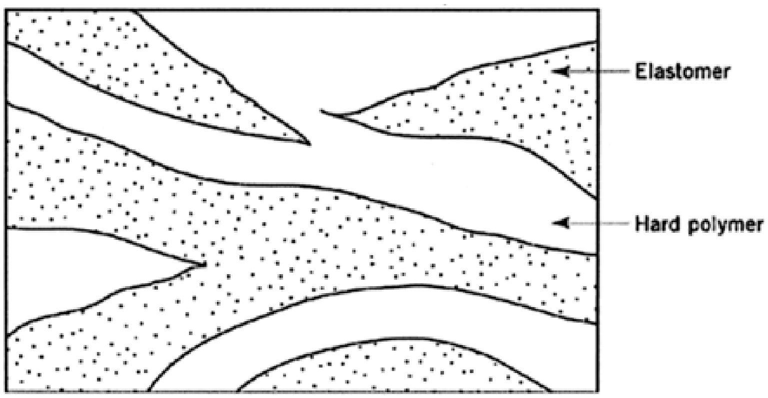


Fig. 3. Phase arrangement in hard polymer/elastomer blends.

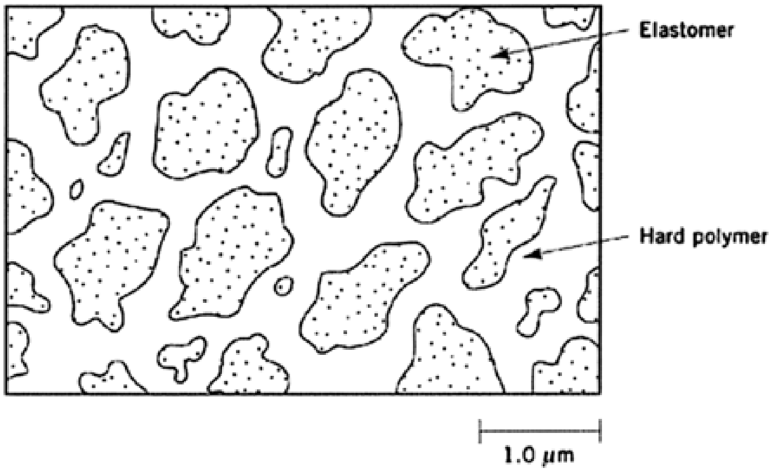


Fig. 4. Phase arrangement in hard polymer/elastomer combinations in which the elastomer phase has been dynamically vulcanized.

2. Property–Structure Relationships

With such a variety of materials, it is to be expected that the properties of thermoplastic elastomers cover an exceptionally wide range. Some are very soft and rubbery where others are hard and tough, and in fact approach the ill-defined interface between elastomers and flexible thermoplastics.

Since most thermoplastic elastomers are phase separated systems, they show many of the characteristics of the individual polymers that constitute the phases. For example, each phase has its own glass transition temperature (T_g), (or crystal melting point T_m if it is crystalline). These, in turn, determine the temperatures at which a particular thermoplastic elastomer goes through transitions in its physical properties. Thus, when the modulus of a thermoplastic elastomer is measured over a range of temperatures, there are three distinct regions (see Fig. 5).

At very low temperatures, both phases are hard and so the material is stiff and brittle. At a somewhat higher temperature the elastomer phase becomes soft and the thermoplastic elastomer now resembles a conventional vulcanizate. As the temperature is further increased, the modulus stays relatively constant

Table 3. Thermoplastic Elastomers Based on Hard polymer/Elastomer combinations

Hard polymer	Soft or elastomeric polymer	Structure[a]	Refs.
polypropylene	EPR or EPDM	B	25,26
polypropylene	EPDM	DV	25–28
polypropylene	poly(propylene/1-hexene)	B	26
polypropylene	poly(ethylene/vinyl acetate)	B	26
polypropylene	butyl rubber	DV	29
polypropylene	natural rubber	DV	30
nylon	nitrile rubber	DV	27
polypropylene	nitrile rubber	DV	27
PVC	nitrile rubber + DOP[b]	B, DV	31–33
halogenated polyolefin	ethylene interpolymer	B	31
polyester	EPDM	B, DV	26
polystyrene	S-B-S + Oil	B	34,35
polypropylene	S-EB-S + Oil	B	34,35

[a] B = simple blend, DV = dynamic vulcanizate.

[b] DOP = dioctyl phthalate. Other plasticizers can also be used.

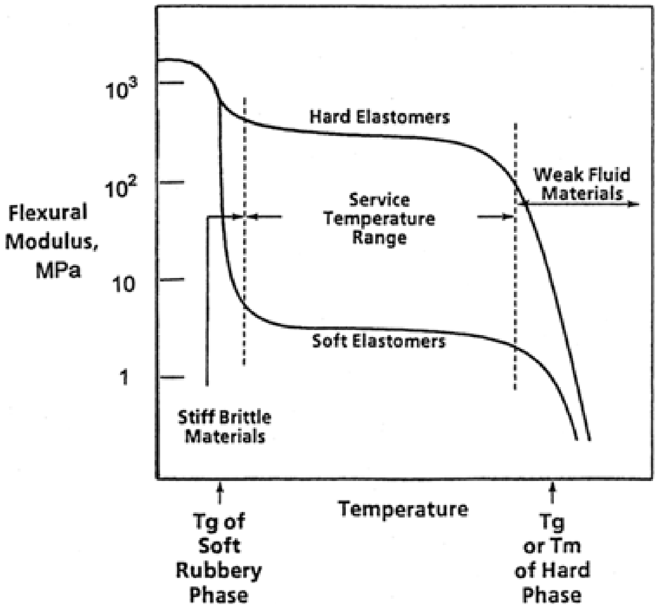


Fig. 5. Stiffnes of typical thermoplastic elastomers at various temperatures.

(a region often described as the “rubbery plateau”) until finally the hard phase softens. At this point, the thermoplastic elastomer becomes fluid.

Thus, thermoplastic elastomers have two service temperatures. The lower service temperature depends on the T_g of the elastomer phase while the upper service temperature depends on the T_g or T_m of the hard phase. Values of T_g and T_m for the various phases in some commercially important thermoplastic elastomers are given in Table 4.

Some of the parameters that can be varied in order to change the properies of thermoplastic elastomers include.

Table 4. Glass-Transition and Crystal Melting Temperatures

Thermoplastic elastomer type	Soft, rubbery phase T_g (°C)	Hard phase T_g or T_m (°C)
polystyrene / elastomer block copolymers		
S-B-S	−90	95 (T_g)
S-I-S	−60	95 (T_g)
S-EB-S and S-EP-S	−60	95 (T_g) and 165 (T_m)[a]
Multiblock copolymers		
polyurethane/elastomer block copolymers	−40 to −60[b]	190 (T_m)
polyester/elastomer block copolymers	−40	185 to 220 (T_m)
polyamide/elastomer block copolymers	−40 to −60[b]	220 to 257 (T_m)
polyethylene/poly(α-olefin) block copolymers	−50	70 (T_m)[c]
polyetherimide/polysiloxane block copolymers	−60	225 (T_g)
Hard polymer / elastomer combinations	–	
polypropylene/EPDM or EPR combinations	−50	165 (T_m)
polypropylene/butyl rubber combinations	−60	165 (T_m)
polypropylene/natural rubber combinations	−60	165 (T_m)
polypropylene/nitrile rubber combinations	−40	165 (T_m)
PVC/nitrile rubber/DOP combinations	−30	80 (T_m)

[a] In compounds containing polypropylene.

[b] The values are for polyethers and polyesters respectively.

[c] This low value for T_m is presumably the result of the short length of the polyethylene segments.

2.1. Molecular Weight

Compared with homopolymers of similar molecular weight, poly(styrene-*b*-elastomer-*b*-styrene) copolymers have very high melt viscosities which increase with increasing molecular weight. These effects are attributed to the persistence of the two-phase domain structure in the melt and the extra energy required to disrupt this structure during flow (5,6). If the styrene content is held constant, the total molecular weight has little or no effect on the modulus of the material at ambient temperatures. This findings is attributed to the modulus of the elastomer phase being inversely proportional to the molecular weight between entanglements in the elastomer chains and the fact that this quantity is not affected by the total molecular weight.

2.2. Proportion of Hard Segments

The tensile behavior of otherwise similar block copolymers with differing proportions of the hard segments shows a family of stress–strain curves (5,7,8,25). As the hard segment content is increased, the products change from very weak, soft, rubberlike materials to strong elastomers, then to leathery materials, and finally to hard flexible thermoplastics. This change from a soft to a hard material is associated with the increasing continuity of the hard phase. As the proportion of the hard phase is increased, the morphology changes from a dispersion of the hard phase in the soft phase, to a cocontinuous structure and finally to a dispersion of the soft phase in the hard phase (5). Styrenic block copolymers with a relatively high polystyrene contents have been commercialized as clear, high impact polystyrenes under such trade name as K-Resin (39) (Phillips Petroleum Co.), Kraton D1401 (Kraton Polymers), and Finaclear (Fina). Thermoplastic elastomers in general show similar behavior; ie, as the ratio of the hard to soft phase is increased, the hard phase becomes more continuous and the product in turn becomes harder.

2.3. Elastomer Phase

The choice of elastomer segment has a profound effect on the properties of block copolymers. In the styrenic block copolymers, four elastomers are commercially important: polybutadiene [9003-17-2], polyisoprene [9003-31-0], poly(ethylene-*co*-butylene) [9019-29-8], and poly(ethylene-*co*-propylene). Polyisobutylene have also been extensively investigated (8, 40) but the products have not been produced commercially. The corresponding styrenic triblock copolymers are referred to as S—B—S, S—I—S, S—EB—S, S—EP—S, and S—*i*B—S, respectively. Polybutadiene and polyisoprene both have one double bond per monomer unit. These double bonds are an obvious source of instability and limit the thermal and oxidative stability of the S—I—S and S—B—S block copolymers. In contrast, poly(ethylene-*co*-butylene), poly(ethylene-*co*-propylene) and polyisobutylene are completely saturated, and so S—EB—S, S—EP—S, and S—*i*B—S block copolymers are much more stable. Another important aspect is the modulus of the materials. It is postulated that the modulus of styrenic block copolymers is inversely proportional to the molecular weight between chain entanglements (M_e), as well as to the effects of the polystyrene domains acting as reinforcing filler particles (5,40). Values of M_e are as follows (40): polyisobutylene 8900, polyisoprene (natural rubber), 6100; polybutadiene, 1700; and poly(ethylene-*co*-propylene), 1660. The parameter M_e for poly(ethylene-*co*-butylene) is similar to that of poly(ethylene-*co*-propylene).

Because of these differences in M_e, S—*i*B—S block copolymers are the softest of all, S—I—S block copolymers are softer than the S—B—S analogues; the S—EB—S and S—EP—S analogues are the hardest (40).

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

Among the polyurethane, polyester, and polyamide thermoplastic elastomers, those with polyether-based elastomer segments have better hydrolytic stability and low temperature flexibility, whereas polyester-based analogues are tougher and have the best oil resistance (13). Polycaprolactones and aliphatic polycarbonates, two special types of polyesters, are used to produce premium-grade polyurethanes (13).

In the polyolefin based block copolymers, the elastomeric segment is typically a copolymer of ethylene and 1-octene. It is nonpolar and very stable, as is the polysiloxane elastomer segment in the polyetherimide–polysiloxane block copolymers.

In the hard polymer–elastomer combinations, the elastomer is most often a stable nonpolar rubber such as EPR or EPDM. Substitution of a polar rubber (such as nitrile rubber) and/or cross-linking improve the resistance to oils and solvents.

2.4. Hard Phase

The choice of the hard phase determines the upper service temperature and also influences the solvent resistance. In styrenic block copolymers, those based on poly(α-methylstyrene) [25014-31-7] have higher upper service temperature and tensile strength than analogues based on polystyrene [9003-53-6] (7); both are soluble in common solvents. Replacing the polystyrene end segments in S—EB—S by polyethylene (giving E—EB—E block copolymer) improves solvent resistance; the phases are not separated in the melt (7).

In polyurethane–elastomer, polyester–elastomer, and polyamide block copolymers, the crystalline end segments, together with the polar center segments, impart good oil resistance and high upper service temperatures. In the polyolefin block copolymers, polyethylene is the hard phase. The polyethylene in this phase has a relativly low T_m ($\sim$ 70°C) (25) and so these thermoplastic elastomers should have a low upper service temperature. The hard segment in the polyetherimide–polysiloxane block copolymers has a very high T_g, ($\sim$ 225°C) and so these thermoplastic elastomers have a very high upper service temperature.

Polypropylene is used as the hard phase in many hard polymer–elastomer combinations. It is low in cost and density and its T_m is quite high ($\sim$ 165°C). This crystalline polypropylene phase imparts resistance to solvents and oils, as well as providing the products based on it with relatively high upper service temperatures.

3. Synthesis

Block copolymers are synthesized by a variety of methods; most important are sequential (40–46) and step growth polymerization (13,14,16,47,48). In sequential polymerization, a monomer A is reacted with an initiator I$*$ (where $*$ denotes an active species capable of initiating polymerization) to give a polymeric chain A_n*, also terminated by an active species.

$$\mathrm{I}^* + \mathrm{A} + \mathrm{A} + \mathrm{A}\cdots \rightarrow \mathrm{A}_n^*$$

The active polymeric chain A_n* can initiate polymerization of another monomer B.

$$\mathrm{A}_n^* + \mathrm{B} + \mathrm{B} + \mathrm{B}\cdots \rightarrow \mathrm{A}_n - \mathrm{B}_m^*$$

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

$$\mathrm{A}_n - \mathrm{B}_m^* + \mathrm{A} + \mathrm{A} + \mathrm{A}\cdots \rightarrow \mathrm{A}_n - \mathrm{B}_m - \mathrm{A}_n^*$$

after which the functional group $*$ is deactivated.

In a variation of this process, polymerization can start in the center $*\mathrm{B}_m*$ segment, and A_n segments can then be polymerized onto each end. Alternatively, A_n—B_m* block copolymers can be joined together by a coupling agent that reacts with the functional group $*$:

$$2\,\mathrm{A}_n - \mathrm{B}_m^* + \mathrm{X} \rightarrow \mathrm{A}_n - \mathrm{B}_m - \mathrm{X} - \mathrm{B}_m - \mathrm{A}_n$$

In this example, X is difunctional and the product is linear. If the functionality of X is higher, the product is a branched $(\mathrm{A—B})_n\,x$ polymer.

In step-growth polymerization, the two segmental types (A_n and B_m) can first be produced separately as difunctional prepolymers. Each type of prepolymer has terminal groups that can react with the terminal groups of the other prepolymer, but not with themselves (eg, one prepolymer could be terminated with hydroxyl groups and the other with carboxylic acid groups). These reactions link the prepolymers together:

$$\mathrm{A}_n + \mathrm{B}_m + \mathrm{A}_n + \mathrm{B}_m + \cdots \rightarrow \mathrm{A}_n - \mathrm{B}_m - \mathrm{A}_n - \mathrm{B}_m\cdots$$

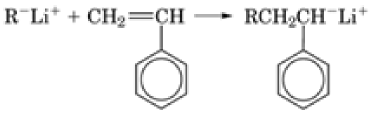
More commonly, a prepolymer A_m can react with two difunctional monomers B and C:

$$\mathrm{A}_n + m\mathrm{B} + m\mathrm{C} \rightarrow \mathrm{A}_n - (\mathrm{BC})_m - \mathrm{A}_n - (\mathrm{BC})_m\cdots$$

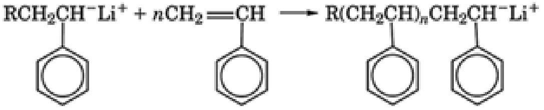
Thermoplastic elastomers that are hard polymer–elastomer combinations are usually not synthesized directly. Instead, the two polymers that form the hard and soft phases are intimately mixed on high shear equipment.

4. Commercial Production

The commercially available styrenic block copolymers are made by anionic polymerization (6,7,40–42). An alkyllithium initiator (R^+Li^-) first reacts with styrene [100-42-5] monomer:



This product acts as an initiator for further polymerization:



The product, referred to here as S^-Li^+, is able to initiate further polymerization. Similar products have been termed living polymers (45). Addition of a second monomer, such as butadiene [106-99-0], gives

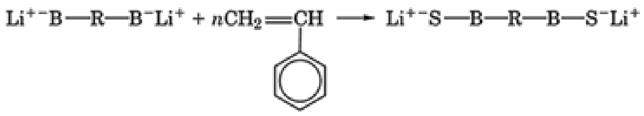
$$S^-Li^+ + nCH_2{=}CH{-}CH{=}CH_2 \rightarrow S{-}(CH_2CH{=}CHCH_2)_{(n-1)}CH_2CH{=}CH{-}CH_2^-Li^+$$

The product of this reaction, ($S{-}B^-Li^+$) may initiate a further reaction with styrene monomer to give $S{-}B{-}S^-Li^+$. This, in turn, can react with an alcohol, ROH, to give S—B—SH + LiOR. Alternatively $S{-}B^-Li^+$, may react with a coupling agent such as an organohalogen (46):

Other coupling agents include esters (46), chlorosilanes (41,46), and divinylbenzene (41). The last gives highly branched materials, whereas the others can give branched or linear products, depending on the functionality of the coupling agent. Another variation of anionic polymerization uses multifunctional initiators (6,7,40,41,45,46), in which the polymer chains grow outward from the center of the molecule. In the case considered here, a difunctional initiator ($Li^{+\,-}R^-Li^+$) first reacts with butadiene monomer:

$$Li^{+-}R^-Li^+ + CH_2{=}CH{-}CH{=}CH_2 \rightarrow Li^{+-}B{-}R{-}B^-Li^+$$

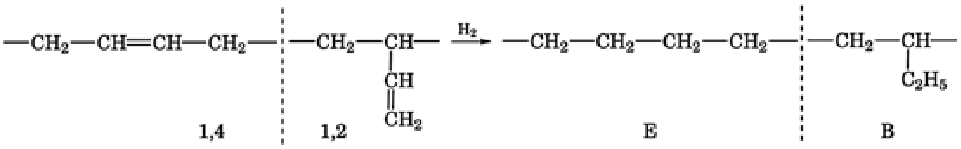
This product is a also a difunctional initiator and can polymerize styrene monomer:



and the final product can again react with an alcohol to give S—B—S, ignoring the minor amount of the R radical that is left at the center of the polymer.

All these polymerizations proceed only in the absence of oxygen or water, which react with the highly reactive propagating species. Polymerization is usually carried out in an inert, hydrocarbon solvent and under a nitrogen blanket. Under these conditions, polymers with narrow molecular weight distributions and precise molecular weights can be produced in stoichiometric amounts.

Only three common monomers, styrene, butadiene, and isoprene isoprene [78-79-5] are easy to polymerize anionically; therefore only two useful A—B—A block copolymers, S—B—S and S—I—S, can be produced directly. In both cases, the elastomer segments contain double bonds which are reactive and limit the stability of the product. To improve stability, the polybutadiene mid-segment can be polymerized as a random mixture of two structural forms, the 1,4 and 1,2 isomers, by addition of an inert polar material (a structure modifier) to the polymerization solvent; ethers and amines have been suggested for this purpose (41). Upon hydrogenation, these isomeric forms of polybutadiene are converted to a random copolymer of tetramethylene and 1-butene. This copolymer is usually referred to as poly(ethylene-*co*-butylene) and abbreviated as EB.



If the proportion of 1-butene segments is greater than ~ 35%, the polyethylene crystallinity in the EB segment is negligible and the product is an elastomer. The S—EB—S block copolymers produced in this way have excellent resistance to degradation.

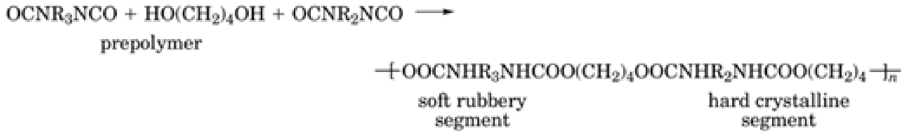
S—I—S block copolymers are usually polymerized in the absence of a structure modifier. Under these conditions, the polyisoprene segments are predominantly (>90%) polymerized in the 1,4 form. Upon hyrogenation, these segments are converted to what is essentially an alternating copolymer of ethylene and propylene (EP). Thus the final product is a stable S—EP—S block copolymer. In this case, the EP segments cannot contain ethylene sequences and so are completely free from crystallinity.

S—*i*B—S block copolymers are made by cationic polymerization (8,40,43). So far, they have not been produced commercially, although they should have excellent thermal stability (equivalent to S—EB—S and S—EP—S) and lower manufacturing costs (40).

Polyurethane block copolymer are produced from prepolymers by polycondensation (13,48). A relatively **high** molecular weight polyester or polyether with terminal hydroxy groups (a diol) first reacts with an excess of a diisocyanate.

$$\mathrm{HOR_1OH + 2\,OCNR_2NCO \rightarrow OCNR_2NHCOOR_1OOCNHR_2NCO}$$

This reaction continues to give a prepolymer in which the segments originally derived from the diol and the diisocyanate alternate, and which is terminated by isocyanate groups. This prepolymer, designated $\mathrm{OCNR_3NCO}$, cannot crystallize because it has an irregular structure (the high molecular weight diols are not a single species but have a broad range of molecular weights). It becomes the elastomeric or soft segment in the final polymer. It, in turn, reacts with a **low** molecular weight diol such as 1,4-butanediol and with more diisocyanate.



$$\underbrace{\mathrm{OCNR_3NCO}}_{\text{prepolymer}} + \mathrm{HO(CH_2)_4OH} + \mathrm{OCNR_2NCO} \longrightarrow -\!\!\left[\underbrace{\mathrm{OOCNHR_3NHCOO(CH_2)_4}}_{\text{soft rubbery segment}}\underbrace{\mathrm{OOCNHR_2NHCOO(CH_2)_4}}_{\text{hard crystalline segment}}\right]\!\!-_n$$

The segments derived from the condensation reaction of the **low** molecular weight diol with the diisocyanate have a regular structure and so can crystallize. They agglomerate into separate hard domains. The elastomeric chains are thus cross-linked to form a network similar in many ways to that given by the simple poly(styrene-*b*-elastomer-*b*-styrene) polymer described previously (5,6,12,40). However, the polymer is a multiblock A—B—A—B—··· rather than a simple A—B—A triblock, the hard domains are crystalline rather than glassy and the molecular weights and molecular weight distributions of the segments are not as well controlled. 4,4′-Diphenylmethane diisocyanate is the most common diisocyanate used in this application (13,48) but toluene and hexamethylene diisocyanates are alternatives.

Commercial polyester block copolymers are synthesized in a similar way (14,48) by the reaction of a relatively **high** molecular weight polyether diol with terephthalic acid (or its dimethyl ester) to give a prepolymer. This is then reacted with a **low** molecular weight diol (usually 1,4-butanediol) and more terephthalic acid. The segments derived from the polyether based prepolymer become the soft segment in the final product, whereas the terephthalic acid–1,4-butanediol copolymer forms the hard crystalline domains. Because the soft segments are derived from polyethers, these polymers are often known as polyether ester elastomers.

There are several types of polyamide block copolymers (16,48). Their synthesis is similar to that of the polyurethane and polyester equivalents. In some cases, only the soft segments are prepolymers; whereas in others, prepolymers are used to give both segmental types. Both polyesters and polyethers are used for the soft segments, and this choice affects the final properties of the product. Various polyamides, including those based on aromatic groups, may be used for the hard segments. These all have different melting points and degrees of crystallinity and so give products with a wide range of properties.

The polyolefin thermoplastic elastomers are produced using metallocene catalysts (44). These are typically based on cyclopentadienyl groups linked to a halide of a transition metal (eg, Ti, Zr, Hf). Under the right conditions, these polymerize mixtures of ethylene and α-olefin monomers (usually 1-octene) into polymers with long repeating polyethylene segments, rather than into random copolymers. These polyethylene segments form the hard phase in the polymer. There are also copolymer segments with pendant groups, usually arranged atactically. Because of their random atactic structures, these segments cannot crystallize. Instead, they are amorphous materials with low glass transition temperatures and so are soft and rubberlike at room temperature. They form the soft phase in the polymer.

The polyetherimide/polysiloxane block copolymers are synthesized by step growth polymerization (47). Many other synthetic methods for preparing block copolymers have been described (15,17–21,23–26) but are currently not believed to be commercially important.

The production of the hard polymer/elastomer combinations is more simple. The two polymers are mixed together under conditions of intensive shear. To achieve a satisfactory dispersion, both the viscosities (at the mixing conditions) and the solubility parameters of the polymers must be carefully matched (27,49). In some cases, grafting may occur. In a variation of this technique, the elastomer can be cross-linked while the mixing is taking place and these products are described as dynamic vulcanizates (27,28,49).

Many dynamically vulcanized compositions have been investigated (27). In some cases, the components are technologically compatibilized by use of a grafting reaction, but usually a fine dispersion of the two phases is formed that is sufficient to give the product the properties of a thermoplastic elastomer.

Table 5. Approximate Price and Property Ranges for Thermoplastic Elastomers[a]

	Price range (cents/lb)	Specific gravity	Hardness Shore A or D
Polystyrene–elastomer block copolymers			
S—B—S (pure)	85 − −130	0.94	62*A* − −65*D*
S—I—S (pure)	100 − −130	0.92	23*A* − −87*A*
S—EB—S (pure)	185 − −280	0.91	47*A* − −75*A*
S—B—S (compounds)	90 − −150	0.9 − −1.1	40*A* − −45*D*
S—EB—S (compounds)	125 − −225	0.9 − −1.2	5*A* − −60*D*
Multiblock copolymers			
polyurethane–elastomer block copolymers	225 − −375	1.05 − −1.25	70A–75D[b]
polyester–elastomer block copolymers	275 − −375	1.15 − −1.40	35*D* − −80*D*
polyamide–elastomer block copolymers	450 − −550	1.0 − −1.15	60*A* − −65*D*
polyethylene–poly(α-olefin) block copolymers	80 − −110	0.85 − −0.90	65*A* − −85*A*
	2000	1.2	70*D*
polyetherimide–polysiloxane block copolymers			
Hard polymer–elastomer combinations			
polypropylene–EPDM or EPR blends	80 − −120	0.9 − −1.0	60*A* − −65*D*
polypropylene–EPDM dynamic vulcanizates	165 − −300	0.95 − −1.0	35*A* − −50*D*
polypropylene–butyl rubber dynamic vulcanizates	210 − −360	0.95 − −1.0	50*A* − −80*D*
polypropylene–natural rubber dynamic vulcanizates	140 − −160	1.0 − −1.05	60*A* − −45*D*
polypropylene–nitrile rubber dynamic vulcanizates	200 − −250	1.0 − −1.1	70*A* − −50*D*
PVC–nitrile rubber–DOP blends	130 − −150	1.20 − −1.33	50*A* − −90*A*
halogenated polyolefin–ethylene interpolymer blends	225 − −275	1.10 − −1.25	50*A* − −80*A*

[a] These price and property ranges do not include fire retardant grades or highly filled materials for sound deadening.
[b] As low as 60A when plasticized.

5. Economic Aspects

Global consumption of thermoplastic rubbers of all types is estimated at about 1,300,000 t/yr (3). Of this, the market is estimated to be divided as follows: styrenic block copolymers, 50%; blends and thermoplastsic vulcanizates based on polyolefins, 29%; polyurethane block copolymers and polyester block copolymers, 16%; and others, 6%. Annual growth rate during the period 1990–2000 was estimated to be 7%. The ranges of the hardness values, prices, and specific gravities of commercially available materials are given in Table 5.

Table 6. Some Trade Names of Thermoplastic Elastomers Based on Styrenic Block Copolymers

Trade name (Mfr.)	Type	Elastomer segment	Notes
KRATONTM D (Kraton Polymers)[a]	linear and branched	B or I	General purpose, soluble. Also compounded products
VECTOR (Dexco)[b]	linear and branched	B or I	
SOLPRENE[c] (Phillips)	branched	B or I	
TAIPOL (Taiwan Synthetic Rubber Company	linear and branched	B or I	General purpose, soluble.
QUINTAC (Nippon Zeon)	linear and branched	I	
FINAPRENE (Fina)	linear	B	
COPERBO (Petroflex)	linear	B	
TUFPRENE & ASAPRENE (Asahi)	linear	B	
CALPRENE (Dynasol)	linear and branched	B	Not available as compounded products
KIBITON (Chi Mei)	branched	B	
EUROPRENE SOL T (Enichem)	linear and branched	B or I	
STEREON (Firestone)	linear	B	High polystyrene content
K-RESIN (Phillips)	branched	B	Very high polystyrene content. Hard and rigid
KRATON G (Kraton Polymers)[a]	linear	EB or EP	
SEPTON (Kuraray)	linear	EB or EP	Improved stability, soluble when uncompounded
TUFTEC (Asahi)	linear	EB	
CALPRENE H (Dynasol)	linear and	EB	
DYNAFLEX (GLS)	linear	B or EB	
MULTI-FLEX (Multibase)	linear	EB	
HERCUPRENE[d] (J-VON)	linear	B or EB	Only compounded products.
FLEXPRENE (Teknor Apex)	linear	B	
TEKRON (Teknor Apex)	linear	EB	
ELEXARR (Teknor Apex)[a]	linear	EB	Wire and cable compounds.
C-FLEX (Concept)[e]	linear	EB	Medical applications. Contains silicone oil

[a] Formerly produced by Shell.
[b] Joint venture of Dow and Exxon.
[c] No longer made in The United States. Similar products are produced by Taiwan synthetic rubber and Enichem.
[d] Formerly produced by J-PLAST.
[e] Now Consolidated Polymer Technologies Inc.

6. Applications

The applications of these thermoplastic elastomers are described in detail in (34) and (35). Trade names and suppliers of commercial thermoplastic elastomers of all types are given in Tables 6, 7, 8.

Table 7. Some Trade Names of Thermoplastic Elastomers Based on Multiblock Copolymers

Trade name (Manufacturer)	Hard segment	Elastomer segment	Notes
ESTANE (B.F. Goodrich) MORTHANE[a] (Morton International) PELLETHANE[a] (Dow) ELASTOLLAN (BASF) DESMOPAN and TEXIN (Bayer)[b]	polyurethane	polyether or amorphous polyester	Hard and tough. Abrasion and oil resistant. Good tear strength
HYTREL (DuPont) LOMOD (DSM)[c] URAFIL (Akzo) RITEFLEX (Hoechst) ECDEL (Eastman) ARNITEL (DSM)	polyester	polyester	Similar to polyurethanes but more expensive. Better low temperature flexibility. Low hysteresis, fairly high cost
PEBAX (Elf Atochem) VESTAMIDE (Huls) GRILAMID and GRILON (EMS America)	polyamide	polyether or amorphous polyester	Similar to polyurethanes but can be softer. Good low temperature flexibility. Expensive
ENGAGE & AFFINITY (Dow) EXACT (Exxon) FLEXOMER (Union Carbide)	polyethylene	poly(α-olefins)	Flexible and low cost. Good low tempreature flexibility. Limited at higher temperatures
SILTEM (GE)	poly(etherimide)	polysilicone	Fire resistant. Very high cost

[a] Including some with polycaprolactone segments.
[b] Formerly marketed by Mobay and Miles.
[c] Formerly GE.

6.1. Styrenic Block Copolymers

In all their commercial application, the styrenic block copolymers are never used as pure materials (34,35). Instead, they are compounded with other polymers, oils, fillers, resins etc to give materials designed for the specific end use.

6.1.1. Substitute for Conventional Vulcanized Rubbers

For this application, the products are processed by techniques and equipment developed for conventional thermoplastics, ie, injection molding, extrusion, etc. The S—B—S and S—EB—S polymers are preferred (small amounts of S—EP—S are also used). To obtain a satisfactory balance of properties, they must be compounded with oils, fillers, or other polymers; compounding reduces costs. Compounding ingredients and their effects on properties are given in Table 9. Oils with high aromatic content should be avoided because they plasticize the polystyrene domains. Polystyrene is often used as an ingredient in S—B—S-based compounds; it makes the

Table 8. Some Trade Names of Thermoplastic Elastomers Based on Hard Polymer/Elastomer Combinations

Trade name Manufacturer	Type	Hard polymer	Elastomer	Notes
REN-FLEX (D&S)[a]	Blend	polypropylene	EPDM or EPR	relatively hard, low density, not highly filled
HIFAX (Himont)				
POLYTROPE (Schulmam)				
TELCAR (Teknor Apex)				
FERROFLEX (Ferro)				
FLEXOTHENE (Equistar)[b]				
SANTOPRENE (AES)[c]	DV[e]	polypropylene	EPDM	better oil resistance, low compression set, softer
SARLINK 3000 and 4000 (Novacor)[d]				
NIPRENE (Teknor Apex)				
HIFAX MXL (Himont)				
TREFSIN (AES) and SARLINK 2000 (Novacor)[d]	DV	polypropylene	Butyl Rubber	low permeability, high damping
VYRAM (AES)	DV	polypropylene	Natural Rubber	low cost
GEOLAST (AES)	DV	polypropylene	Nitrile Ruber	oil resistant
ALCRYN (Advanced Polymer Alloys)[f]	Blend	halogenated polyolefin	Ethylene Interpolymer	single phase, oil resistant
SARLINK 1000 (Novacor)[d]	DV	PVC	Nitrile Rubber	oil resistant
CHEMIGUM (Goodyear)	Blend			
APEX N(Teknor Apex)	Blend			
RIMPLAST (Petrarch Systems)	blends of TPEs with silicone rubbers			medical applications

[a] A joint venture between Dexter and Solvay.

[b] Formerly quantum. Product is a blend of pp and EPR produced in the polymerization reactor.

[c] Advanced Elastomer Systems–a joint venture between Solutia (formerly Monsanto) and Exxon Chemical.

[d] Now a part of DSM.

[e] Dynamic Vulcanizate: a composition in which the soft phase has been dynamically vulcanized, i.e., cross-linked during mixing.

[f] Formerly DuPont

products harder and improves their processibility. In S-EB-S-based compounds, crystalline polyolefins such as polypropylene are preferred. Some work has been reported on blends of liquid polysiloxanes (silicone oils) with S—EB—S block copolymers (37,38). The products are primarily intended for medical and pharmaceutical-type applications. Compounds based on S—EB—S with hardnesses as low as 5 on the Shore A scale have been reported (50).

Large amounts of inert fillers, such as whiting, talc, and clays, can be added. Very dense fillers, such as barium or strontium sulfates, are used to make compounds intended for sound-deadening applications. In contrast, high levels of reinforcing fillers, such as carbon black, produce undesirable properties in the final product.

A large volume usage of S—B—S based compounds is in footwear. Canvas footwear, such as sneakers and unit soles, can be made by injection molding. Frictional properties resemble those of conventionally vulcanized rubbers and are superior to those of the flexible thermoplastics, such as plasticized PVC. The products remain flexible under cold conditions because of the good low temperature properties of the polybutadiene segment.

Table 9. Compounding Styrenic Block Copolymers

	Component				
Properties	Oils	Polystyrene	Polyethylene	Polypropylene	Fillers
hardness	decreases	increases	increases	increases	small increase
processibility	improves	improves	improves	improves, especially with S—EB—S	improves
effect on oil resistance	none	none	improves	improves	none
cost	decreases	decreases	decreases	decreases	decreases
other	decreases ultraviolet (uv) resistance		often gives satin finish	improves high temperature properties	often improves surface appearance

Compounds based on S—EB—S usually contain polypropylene, which improves solvent resistance and processibility and raises upper service temperatures. Compounds intended for use in the automotive industry are able to survive 1000-h air exposure at temperatures of 125°C with only minor changes in properties (51). Very soft compounds have been developed to replace foam rubber for interior trim parts. In this and similar applications, these soft compounds are usually insert molded over polypropylene or metal and then coated with flexible polyurethane paint (52). Other automotive applications include products intended for sound deadening, flexible air ducts, and gear shifter boots, as well as improving the properties of sheet molding compounds.

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

Commercial products have hardnesses from 5 on the Shore A scale (which is extremely soft) to 45 on the Shore D scale (almost leathery). Specific gravities usually range from 0.9 to 1.20; some products intended for soundproofing have specific gravities as high as 1.95. Processing is relatively easy. In general, products based on S—B—S are processed under conditions appropriate for polystyrene, whereas products based on S—EB—S are processed under conditions appropriate for polypropylene. Predrying is usually not needed and scrap is recycled.

6.1.2. Adhesives, Coatings, and Sealants

For these applications, styrenic block copolymers must be compounded with resins and oils (Table 10) to obtain the desired properties (53–56). Materials compatible with the elastomer segments soften the final product and give tack, whereas materials compatible with the polystyrene segments impart hardness. The latter are usually styrenic resins with relatively high softening points. Styrenic resins with low softening points are to be avoided, as are aromatic oils, since they plasticize the polystyrene domains and reduce the upper service temperature of the final products.

These resins and oils have low molecular weights, ie, typically <1000. This, combined with the relatively low molecular weights of the styrenic block copolymers, typically 40,000–150,000, allows solutions in common solvents to be formulated at high solids levels. Alternatively, the products can be applied as hot melts, with considerable advantages in terms of safety, production rates, energy consumption, and air pollution.

6.1.3. Blends with Other Polymeric Materials

Styrenic block copolymers are technologically compatible with a surprisingly wide range of materials and can be blended to give useful products (57,58). Blending can often be carried out on the equipment producing the final article. Blends of S—B—S with polystyrene, polyethylene, or polypropylene show improved impact and tear resistance. Both S-B-S and S—EB—S can be blended with poly(phenylene oxide) to improve impact resistance (59). S—EB—S can also be blended with the less polar engineering thermoplastics such as polycarbonates. An unusual feature of these block copolymers is their ability to enable useful blends to be made from incompatible polymers, eg, polystyrene or poly(butylene terephthalate) with polyethylene (60). Another development is the use of functionalized S—EB—S block copolymers as impact modifiers for more polar engineering thermoplastics such as polyesters and polyamides (58). The functionality is given by maleic acidanhydride groups grafted to the S—EB—S polymer chain. These functionalized S—EB—S block copolymers have also been found useful in the compatibilization of polyolefins with polyamides (61) and with poly(phenylene oxide) (62).

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

6.1.4. Blends with Asphalts

Blends with styrenic block copolymers improve the flexibility of bitumens and asphalts. The block copolymer content of these blends is usually $< 20\%$; even as little as 3% can make significant differences to the properties of asphalt (qv). The block copolymers make the products more flexible, especially at low temperatures, and increase their softening point. They generally decrease the penetration and reduce the tendency to flow at high service temperatures; and they also increase the stiffness, tensile strength, ductility, and elastic recovery of the final products. Melt viscosities at processing temperatures remain relatively low so the materials are still easy to apply. As the polymer concentration is increased to $\sim 5\%$, an interconnected polymer network is formed. At this point the nature of the mixture changes from an asphalt modified by a polymer to a polymer extended with an asphalt.

It is important to choose the correct grade of asphalt; those with a low asphaltene content and/or high aromaticity in the maltene fraction usually give the best results (63,64). Applications include road surface dressings such as chip seals (applied to hold the aggregate in place when a road is resurfaced); slurry seals; hot-mix asphalt concrete (a mixture of asphalt and aggregate used in road surfaces); road crack sealants; roofing; and other waterproofing and adhesive applications (64–66). Because of their lower cost, S—B—S block copolymers are usually chosen for this application; but in roofing and paving applications, the S—EB—S block copolymers are also used because of better long-term aging resistance.

6.1.5. Oil Gels

As noted previously, the styrenic block copolymers are very compatible with mineral oils. Blends with as little as 5% of an S—EB—S block copolymer (the remainder being 90% mineral oil and 5% wax) have been described for use as cable filling compounds (67,68). These fill the voids in “bundled” telephone cables and prevent water intrusion. Another potential application is toys, hand exercising grips etc (69).

6.2. Multiblock Copolymers

Replacement of conventional vulcanized rubber is the main application for the polar polyurethane, polyester, and polyamide block copolymers. Like styrenic block copolymers, they can be molded or extruded using equipment designed for processing thermoplastics. Melt temperatures during processing are between 175 and 225°C, and predrying is essential; scrap is reusable. These polymers are mostly used as essentially pure materials, although some work on blends with various thermoplastics (13,14,16,34,35,70–72) such as plasticized and unplasticized PVC and also acrylonitrile–butadiene–styrene (ABS) and polycarbonate has been reported. Plasticizers intended for use with PVC have also been blended with polyester block copolymers (70).

All three types of these block copolymers are relatively hard (from 70 on the Shore A scale to 70 on the Shore D scale) with specific gravities of 1.00–1.25. Applications (13,14,16,34,35) taking advantage of toughness, abrasion resistance, flexibility, and resistance to oils and solvents include belting, hydraulic hose, wheels, shoe soles, wire coatings, and automobile parts. The surface of these molded parts can be easily painted or metallized. Medical uses are a significant application for the polyurethane block copolymers with polyether elastomer segments (73). Blends with silicone rubbers have been described for these applications (37,38).

Table 10. Resins Used to Formulate Adhesives, Sealants, etc. from Styrenic Block Copolymers

Resin type	Segment compatibility[a]
polymerized C_5 resins (synthetic polyterpenes)	I
hydrogenated rosin esters	B
saturated hydrocarbon resins	EB
naphthenic oils	I, B
paraffinic oils	EB
low molecular weight polybutenes	EB
aromatic resins	S

[a] I indicates compatible with polyisoprene segments; B, compatible with polybutadiene segments; EB, compatible with poly(ethylene–butylene) segments; and S, compatible with polystyrene segments.

Another application is the use of a clear polyester thermoplastic elastomer as a replacement for glass bottles in medical applications.

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

The polyolefin block copolymers are lower in cost. Their suggested applications (74) include wire and cable insulation, replacements for PVC and styrenic block copolymers and blends with polypropylene, either to improve impact resistance or as the soft phase in a hard polymer–elastomer combination. Proceesing conditions are similar to those for polyethylene and thermal stability is excellent.

The polyetherimide–polysiloxane multiblock copolymers are relatively hard ($\sim$ 70 on the Shore D scale). Their main application is flame-resistant wire and cable covering (22,47), where they combine very low flammability with a low level of toxic products in the smoke. This unusual and vital combination of properties justifies their relatively high price, $\sim$ \$40kg, at a specific gravity of $\sim$ 1.2.

6.3. Hard Polymer/Elastomer Combinations

Substitution of conventional vulcanized rubbers is the main application for these materials (25–27,34,35). The first ones to be developed were simple blends of polypropylene and EPDM, made by conventional mixing of the two components (25,26,49). EPR has largely replaced EPDM in this application because of its lower cost. These simple blends had some limitation, because unvulcanized EPDM or EPR has almost no tensile strength or oil resistance. Thus only fairly hard products, ie, those containing small amounts of these elastomers, had satisfactory properties and so the first products of this type had hardness values in the Shore D range (although somewhat softer versions are now available). In later work, products based on dynamic vulcanization (27) were produced. In this process, the elastomer, typically EPDM, is simultaneously cross-linked and mixed into the hard polymer, typically polypropylene. The result is a very fine dispersion of vulcanized elastomer particles in a hard polymer matrix. The improved properties of the elastomer phase allow much higher levels to be used, giving quite soft products (as low as $\sim$ 35 on the Shore A scale). Compared to the mixtures of EPDM or EPR with polypropylene, the corresponding dynamic vulcanizates have lower compression set and better oil resistance. Natural (30) and butyl rubbers (29) have been used to replace EPDM in similar dynamically vulcanized products. Those based on natural rubber are low in cost and have properties intermediate between the EPDM-based dynamic vulcanizates and the simple EPDM-based mixtures. Those based on butyl rubber have low gas permeability and high damping, thus they can be used as vapor barriers or vibration isolators. An unexpected property advantage with those based on butyl rubber is that some grades show excellent adhesion when insert molded against such polar engineering thermoplastics as poly(butylene terephthalate) and polyamides (75). Specific gravities of these various combinations of polypropylene with EPDM, EPR, butyl, and natural rubbers are between ∼ 0.9 and 1.05. Molding and extrusion conditions are similar to those used for polypropylene, and the scrap is reusable. Important applications are wire insulation, appliance parts, and automobile exterior and interior parts (both painted and unpainted).

Even though vulcanized EPDM has some oil resistance, in contrast to unvulcanized EPDM that has virtually none, a rubber with inherent oil resistance should be even better. For this reason, more polar rubbers have replaced EPDM in applications where oil resistance is critical. Dynamic vulcanizates of nitrile rubber with polypropylene are the most important example. Commercial grades are somewhat harder than EPDM equivalents (between 70 on the Shore A scale and 40 on the Shore D scale) and are also more dense (∼ 1.0–1.1 specific gravity) (27,49).

PVC–nitrile rubber blends usually contain plasticizers such as dioctyl phthalate (DOP) (31). Similar dynamic vulcanizates appear to be less important commercially. These blends have excellent oil resistance as well as resistance to flex cracking and abrasion (31–35). Hardness ranges from ∼ 50–90 on the Shore A scale and specific gravity from ∼ 1.2–1.3. Processing is basically similar to that of plasticized PVC. Blends of halogenated polyolefins with ethylene interpolymers are claimed to give single-phase systems (31). They have a very rubberlike feel and are similar to the PVC–nitrile rubber combinations as far as processing, hardness and specific gravity are concerned. Like them, they have good oil resistance. All these products based on the more polar rubbers are often used in molded appliance, automotive, and similar rubber-like parts where oil resistance is needed at a reasonable cost.

7. Health and Safety

Most thermoplastic elastomers are stable materials and decompose only slowly under normal processing conditions. If decomposition does occur, the products are usually not particularly hazardous and should not present a problem if good ventilation is provided. Products based on PVC and halogenated polyolefins are exeptions, and care should be taken to avoid overheating these materials. Extra caution should also be exercised when processing polyurethanes, especially those containing polycaprolactone segments. In these cases the decomposition products may include isocyanates and caprolactam, both of which are potential carcinogens.

Of course, all materials that are processed in the molten state can cause burns if the hot material comes in contact with the skin. Care must be taken to avoid this, and it should be noted that molten material left in the barrel of an extruder or injection molding machine can “spit” unexpectedly. In all cases, it is recommended that the manufacturer’s Material Safety Data Sheet be consulted before working with any of these materials.

8. Reprocessing

Easy reprocessing is one of the great advantages that thermoplastic elastomers have over conventional vulcanized rubbers. The scrap can be reground and is usually blended with virgin material before being reworked. Regrinding is not difficult if it is remembered that rubber must be cut rather than shattered. This means that the cutter blades must be sharp and clearances minimized. Immediately after regrinding, softer products should be dusted with an antiblocking agent. It is usually best to dry the ground scrap before reworking it, and for the polyurethanes, polyesters, and polyamides, drying is a necessity. Thermoplastic elastomers can also be used to “sweeten” regrind; ie, they can be blended with reground scrap from conventional thermoplastics to restore impact strength and reduce brittleness. Many applications, eg, coextrusion, generate mixed scrap, which usually has very poor properties. Thermoplastic elastomers can often convert this into useful material (60–62).

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