

Notice: This material may be protected by Copyright Law
(Title 17 U.S. Code)

PENNSTATE



TransactionNumber: 1497775



ILL Number: 91146011	Call #: TS1925.C87 2008 Location: EG
MaxCost: \$35IFM	
Billing Category: Exempt	

Penn State Interlibrary Loan - Article Request

Article Information

Journal Title: Current topics in elastomers research /

Volume: Issue:
Month/Year: 2009 Pages: 101-164

Article Author:

Article Title: Costa, Francis; Thermoplastic elastomers

Loan Information

Loan Title:

Loan Author:

Publisher:
Place:
Date:
Imprint:

Borrower Information

University of Minnesota
65 Wilson Library - ILL
309-19th Ave. South
Minneapolis, MN 55455

Odyssey: 206.107.42.151
Ariel: 160.94.230.141
Email: wilsill@tc.umn.edu

NOTES

/ 5/22/2012 11:30:58 AM (System) Billing Notes; FEIN #41-6007513

RETURN LOANS TO: Penn State University Libraries / Interlibrary Loan / 127
Paterno Library, Curtin Rd. / University Park, PA 16802

5 Thermoplastic Elastomers

*Francis R. Costa, Naba K. Dutta, Namita Roy Choudhury,
and Anil K. Bhowmick*

CONTENTS

5.1	Introduction	102
5.2	History and Growth	103
5.3	Generic Classification of Thermoplastic Elastomers	104
5.4	Polymer Synthesis	104
5.4.1	Block Copolymers	104
5.4.1.1	Styrenic Block Copolymer	104
5.4.1.2	Copolyester	108
5.4.1.3	Polyurethanes	109
5.4.1.4	Copolyamides (Thermoplastic Polyamides)	109
5.4.2	Blends and Elastomeric Alloys	110
5.4.2.1	Elastomeric Rubber-Plastic Blends	110
5.4.2.2	Thermoplastic Vulcanizates	112
5.4.2.3	Melt Processable Rubber	114
5.4.3	Crystalline-Amorphous Block Copolymers	114
5.4.4	Ionomers	115
5.4.4.1	Metal-Sulfonated EPDM	115
5.4.4.2	Zinc-Maleated EPDM	115
5.4.4.3	Sulfonated-Styrene(Ethylene-Co-Butylene)-Styrene Triblock Ionomer	116
5.4.5	Thermoplastic Elastomers from Waste Rubbers	116
5.4.6	Miscellaneous New Thermoplastic Elastomers	117
5.4.6.1	Protein-Based Thermoplastic Elastomers	119
5.4.6.2	Hybrid Molecular Structure with Peptide and Nonpeptide Sequences	124
5.5	Structural and Phase Characteristics	126
5.6	Thermodynamics of Phase Separation	131
5.7	Properties of Thermoplastic Elastomers	134
5.7.1	Factors Influencing the Properties	134
5.7.1.1	Constituents of Thermoplastic Elastomers	134
5.7.1.2	Molecular Weight	134
5.7.1.3	Relative Amount of Hard and Soft Segments	135
5.7.1.4	Effect of Processing	135
5.7.2	General Properties	135
5.8	Rheology	141
5.9	Processing	142
5.9.1	Drying	142
5.9.2	Extrusion: A Continuous Process	143
5.9.2.1	Screw Design	143
5.9.2.2	Die Design	144

5.9.2.3	Temperature Profile	144
5.9.3	Injection Molding.....	144
5.9.3.1	Injection Pressure and Rate	144
5.9.3.2	Screw Speed and Back Pressure.....	144
5.9.3.3	Mold Temperature and Cycle Time	144
5.9.3.4	Part Design and Mold Design Considerations	145
5.9.4	Blow Molding	146
5.9.5	Other Fabrication Methods	146
5.9.5.1	Thermoforming	146
5.9.5.2	Foam Preparation.....	146
5.9.5.3	Combining TPEs with Other Materials: Bonding and Overmolding	146
5.9.6	Regrinding of TPEs	147
5.10	Surface and Interface of TPEs	147
5.11	Blends of TPEs with Other Polymers.....	148
5.12	Novel Functional Nanomaterials Based on Thermoplastic Elastomers.....	149
5.13	Applications	150
5.14	Future	153
	References	154

5.1 INTRODUCTION

The emergence of thermoplastic elastomers (TPEs) provided a new horizon to the field of polymer technology. Their development and growth have reached a high level of commercial significance, and they have become an important segment of polymer science and technology in the last four decades. In the simplest way, TPEs can be defined as a class of polymers, which combine the service properties of elastomers with the processing properties of thermoplastics. TPEs consist of two structural units: (1) amorphous segment that is soft in nature and has a low glass-transition temperature (T_g) and (2) a crystalline and/or hard segment with high T_g that acts as physical cross-link for the soft segments. These two segments, i.e., soft and hard segments, must be thermodynamically incompatible to each other at service temperature to prevent the interpenetration of the segments. Therefore, a TPE possesses biphasic morphological structure. The hard segments that act as physical cross-links are thermally labile, and this allows TPEs to soften and flow under shear force at elevated temperature as in the case of true thermoplastics. TPEs bridge the gap between conventional rubbers and thermoplastics. The key factors responsible for their continuous acceptance and sustained growth are listed in Table 5.1.

TABLE 5.1
Advantages of Thermoplastic Elastomer over Thermoset Rubber Processing

Variables	Thermoplastic Elastomer	Thermoset Rubber
1. Fabrication	Rapid (s)	Slow (min)
2. Scrap	Reusable	High percentage waste
3. Curing agent	None	Required
4. Machinery	Conventional thermoplastic equipments	Special vulcanizing equipments
5. Additives	Minimal or none	Numerous processing aids
6. Remold parts	Yes	Impossible
7. Heating, sealing	Yes	No

Source: Walker, B.M. and Rader, C.P. (eds.), *Handbook of Thermoplastic Elastomers*, Van Nostrand Reinhold, New York, 1988.

5.2 HISTORY AND GROWTH

TPEs appeared in the market as commercial products in the late 1950s with the introduction of thermoplastic polyurethane (TPU, B.F. Goodrich Co.). This was preceded by activity in 1930s and 1940s that led to the introduction of TPU in Germany and polyvinyl chloride (PVC) in the United States. By the 1960s, TPEs were in their infancy. During this period enormous research efforts were devoted to the development of novel block copolymer TPE and a variety of blends of thermoplastic polyolefins (TPO) with elastomers. In 1965, the company Shell developed and introduced commercial styrene diene block copolymer, Kraton. The 1970s saw the emergence of commercial copolyester, Hytrel from DuPont and blends of polypropylene (PP) and ethylene-propylene–diene monomer (EPDM) rubber from Uniroyal. During this period, it was realized that TPE would have a bright and promising future in both the rubber and the plastic industries. Thus extensive research efforts were devoted toward their development and commercialization. As a consequence, the 1980s witnessed the growth of TPE to maturity. Table 5.2 illustrates the milestones for the commercialization of TPEs.

TABLE 5.2
Milestones for Commercialization of Thermoplastic Elastomer

Roots	
1933	Semon: Flexible PVC, Goodrich patent
1940	Henderson: PVC–NBR blends, Goodrich patent
1947	Commercial PVC–NBR blends, Goodrich
1952	Synder: Elastic thread from linear copolyester, DuPont patent
1954	PU Spandex fiber, DuPont patent
1955–1957	Schollenberger: PU TPE, patent and paper, Goodrich
1957	Bateman, Merrett: NR–PMMA grafts, BRPRA
TPE first decade of progress	
1958–1959	Tobolosky suggestion of crystalline and amorphous polyolefin copolymers
1959	Commercial PU elastic fiber, DuPont
1960	Commercial PU TPEs
1961	Ionomeric TPE, DuPont (Surlyn)
1962	Kontons α -olefin TPE research, Uniroyal
1962	Gessler patent on PP–CIIR blends, dynamically cured
1965	Commercial triblock TPEs, Shell (Kratons)
1967	California Institute of Technology and ACS, Polymer Group, Symposium on TPE theory
Second decade of progress	
1968	Radial styrenic block polymers, Phillips (Solprene)
1972	Polyolefin blends, Uniroyal (TPR)
1972	Copolyester TPEs, DuPont (Hytrel)
1972	SEBS TPEs, Shell (Kraton G)
Third decade of progress	
1978	A.Y. Coran's research on the melt–mixed blends of elastomer and thermoplastics with dynamic vulcanization
1981	Commercial melt–mixed blends of EPDM and PP, dynamically vulcanized, Monsanto (Santoprene)
1982	Polyamide TPE, Atochem (Pebax)
1985	Commercial blends of NBR and PP, dynamically vulcanized, Monsanto (Geolast)
1985	Single phase melt-processable rubber, DuPont (Alcryn)
1988	Functionalization hydrogenated styrenics TPEs, Shell (Shell FG)

(continued)

TABLE 5.2 (continued)

Milestones for Commercialization of Thermoplastic Elastomer**Fourth Decade of Progress**

1988–2006	Blends of TPEs with existing polymers for enhancement of properties. Academic research in various fields of TPEs worldwide New family of TPV having heat and oil resistance based on ACM and polyamide Development of crystalline–amorphous block copolymers (Engage), metallocene catalyzed TPEs, Polyolefin elastomer (POEs), application research on TPEs Protein-based block-copolymer
-----------	--

Source: Modified from Legge, N.R., *Rubber Chem. Technol.*, 62, 529, 1989.

5.3 GENERIC CLASSIFICATION OF THERMOPLASTIC ELASTOMERS

TPEs may be rationally classified into the following classes according to their chemistry and morphology:

1. Block Copolymers
 - a. Styrenic block copolymers
 - b. Thermoplastic copolyesters (COPE)
 - c. Thermoplastic polyurethanes (TPU)
 - d. Thermoplastic polyamides (COPA)
2. Blends and elastomeric alloys
 - a. Elastomeric rubber–plastic blends
 - b. Thermoplastic vulcanizates (TPVs)
 - c. Melt processable rubber
3. Crystalline–amorphous block copolymers
4. Ionomers
 - a. Sulfonated-EPDM rubber (S-EPDM)
 - b. Zn or Na salt of ethylene acrylic acids
5. Miscellaneous

A number of other polymers have the characteristics of TPE and some are available commercially, such as (1) 1,2-polybutadiene, (2) *trans*-polyisoprene (PI), (3) modified polyethylene (PE) (e.g., ethylene vinyl acetate [EVA] and ethylene ethyl acrylate [EEA]), (4) nonhydrocarbon elastomer-based TPEs, (5) metallocene elastomers/TPEs (MEs/TPEs), and (6) graft copolymeric TPEs.

Recently, a new method of nomenclature of TPEs was produced jointly by the International Organization for Standardization (ISO), the Society of Automotive Engineers (SAE), the Association of the Automotive Industries (VDA), Germany, and the producers of raw materials. Nevertheless, for this chapter the above-mentioned abbreviations for the TPEs have been utilized. Table 5.3 provides a list of significant suppliers of different generic classes of TPEs with respective trade names.

5.4 POLYMER SYNTHESIS**5.4.1 BLOCK COPOLYMERS****5.4.1.1 Styrenic Block Copolymer**

Triblock copolymers of ABA type, where B is the central elastomeric block and A is the rigid end-block, are well-known commercially available polymers [7,8]. The chemical structures of some common TPEs based on styrenic block copolymers are given in Figure 5.1. Synthesis of such ABA-type polymers can be achieved by three routes [9]:

TABLE 5.3
Significant Thermoplastic Elastomer Suppliers and Their Products

TPE Type	Supplier	Trade Name
Styrenic	Kraton Polymers	Kraton
	Alpha Gary	Evoprene
	Concept Polymers	C-Flex
	Dexco Polymers LP (Dow/Exxon)	Vector
	Fina Oil	Finaprene
	J-Von	J-Plast
	Nippon Zeon	Quantic
	Firestone (Bridgestone)	Stereon
	Kraiburg	Thermoplast K
	PolyOne	Synprene
	Enichem	Europrene
	BASF	Styroflex
	Technor Apex	Elaxar, Monoprene, Tekron, Tekbond
	Philips	K-Resin, Solprene
	Asahi Kasei	Tufprene, Asaprene, Asaflex
Polyurethane	BASF	Elastollan, Elastocell
	Akzo	Urafil
	Borealis	Daplen
	Noveon	Tecoflex, Tecothane, Carbothane, Tecophilic, Tecoplast, EstaGrip, Estane
	B.F. Goodrich	Estane, Estaloc
	Bayer	Texin, Baytec, Vulkollan, Desmopan
	A. Schulam	Polypur
	Morton Int.	Morthane
	DuPont	Hylene
	GLS Corp.	Versollan
	J-Von	J-Plast
	Discas Inc.	Prolastic
	K.J. Quinn	Q-Thane
	Dow	Pellethane, Isoplast
Copolyesters	DSM	Amitel
	DuPont	Hytrel
	General Electric	Lomod
	Eastman Chemical	Ecdel
	GE Plastics	Lomod
	Hoechst Celanese	Riteflex
	Toyobo	Pelprene
	Celanese	Gaflex
Polyamides	Wilden	Saniflex
	Atochem (now AtoFina)	Pebax
	ESM-American Garilon	Grilamid
	Huls	Vestamid
	DuPont	Zytel FN
TPOs or TEOs EPDM rubber/polyolefin	Dow Chemical	Pebax
	DSM	Sarlink
	Ferro Corp.	Feroflex
	Himont	Dytral/TP
	Montell	Hifax

(continued)

TABLE 5.3 (continued)

Significant Thermoplastic Elastomer Suppliers and Their Products

TPE Type	Supplier	Trade Name
	So.F.Ter. S.p.A.	Forprene
	Mitsui Petrochemicals	Milastomer
	Research Polymers Int.	Renflex
	Nippon Petrochemicals	Softlex
	A. Schulman	Polytrope
	Teknor Apex	Telcar
	Union Carbide	Flexomar
	Colonial Rubber	Solmel
NBR/PVC	A. Schulman/Mitsubishi	Sunprene, Sunfrost
	Polyone	Proflex
Thermoplastic vulcanizates	Advanced Elastomer Systems, LP	Santoprene, Geolast, Vyram, Dytron, Trefsin
	Teknor Apex	Uniprene
	DuPont	ETPV
	Zeon Chemicals L. P.	Zeotherm
Ionomer	DuPont	Alcryn
	Exxon	Iotek
	DuPont	Surlin

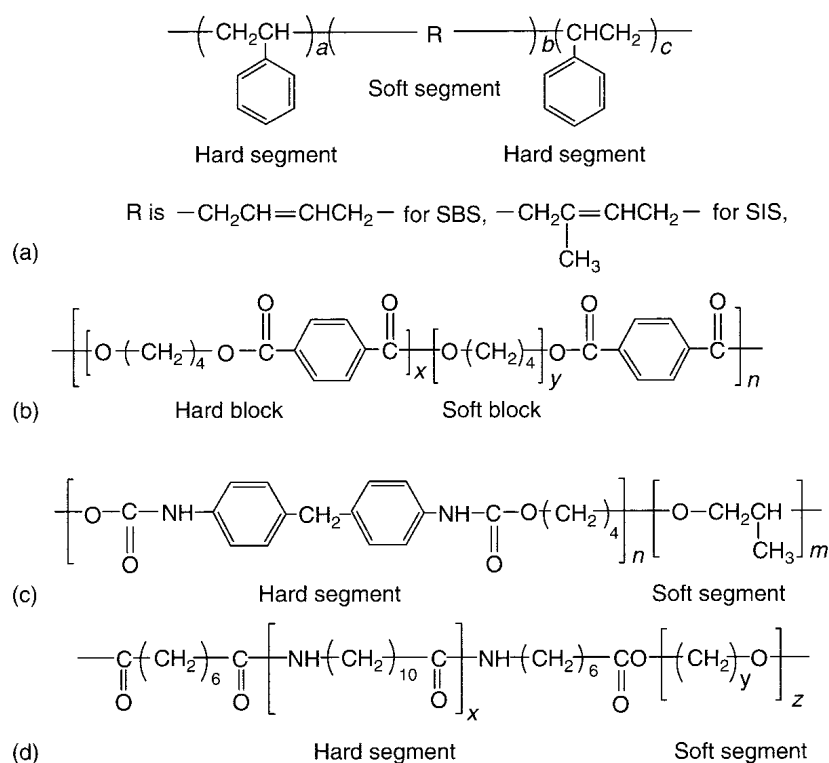
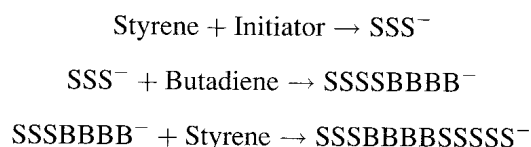


FIGURE 5.1 Chemical structure of block copolymeric thermoplastic elastomers (TPEs) (a) styrenic, (b) COPE, (c) thermoplastic polyurethane, and (d) thermoplastic polyamide.

1. Sequential monomer addition
2. Synthesis of AB diblock followed by linking or coupling reaction
3. Successive polymerization of monomers starting from a difunctional initiator

Linear triblock copolymers of the type styrene–butadiene–styrene (SBS) and styrene–isoprene–styrene (SIS) are produced commercially by anionic polymerization through sequential addition of monomers in the reaction chamber [10] as shown below:



Saturated styrene–ethylene–butylene–styrene (SEBS) and styrene–ethyl–propyl–styrene (SEPS) are produced by hydrogenating SBS and SIS block copolymers, respectively, before they are recovered from the solution [3].

Though living anionic polymerization is the most widely used technique for synthesizing many commercially available TPEs based on styrenic block copolymers, living carbocationic polymerization has also been developed in recent years for such purposes [10,11]. Polyisobutylene (PIB)-based TPEs, one of the most recently developed classes, are synthesized by living carbocationic polymerization with sequential monomer addition and consists of two basic steps [10] as follows:

1. Living polymerization of isobutylene (IB) by di- and trifunctional initiators to make the nearly uniform rubber mid-block
2. Sequential addition of a second monomer (e.g., styrene, *p*-terbutyl styrene, *p*-methyl styrene, indene, *p*-chloro styrene, isoprene, and α -methyl styrene) to make glassy outer-block

Poly(styrene-*b*-isobutylene-*b*-styrene) (PS-PIB-PS), triblock copolymers can be prepared via coupling of living PS-PIB diblock copolymers in a one-pot procedure [12].

Most common styrene-based block copolymers behaving as TPE show limited range of service temperature, below glass-transition temperature (T_g) of hard segment (around 100°C). For example, mechanical properties of these block copolymers are highly affected at elevated temperature and at T_g of polystyrene (PS) domains. This is often related to the lack of stereoregularity in polystyrene and the rubbery domains resulted from the anionic polymerization technique [13]. To solve this problem, several modifications have been proposed by researchers to enhance the T_g of the glassy domain; e.g., use of poly(α -methyl styrene) [14,15], poly(ethylene sulfide) [16] and syndiotactic poly(methyl methacrylate) (PMMA) (sPMMA) [17] as hard segments is well known. There have been some recent developments in this regard; like a triblock copolymer based on isobornyl methacrylate (IBMA) and butadiene has been synthesized, which shows T_g of the hard segment in the range of 170°C–206°C depending on the chain tacticity [18]. TPEs based on polyacrylates such as poly(methacrylate-*b*-dienes-*b*-methacrylate) [9] also show high T_g of the hard segment. Ban et al. have very recently reported a new approach to introduce crystalline PS domains in SBS-type triblock copolymer through a stereospecific sequential triblock copolymerization of S with B using a specialized catalyst. The introduction of syndiotactic or isotactic PS and elastic *cis*-polybutadiene block (instead of low *cis*-PB obtained in anionic SBS) causes improvement of several properties like satisfactory mechanical and chemical resistance at elevated temperatures [13].

Branched copolymers or star-block copolymers are new entrants in TPE family. There is a growing interest in the synthesis of star-block TPEs because of their unique mechanical and rheological properties. They can be represented by a general structural formula $(A - B)_n - X$, where X represents the core that holds the block copolymeric arms and n is an integer greater than 2. The arms comprise of inner soft rubbery segment (B) connected to hard glassy outer segments (A). The core (X) may be of different types, like calix[8]arene [19], cross-linked polydivinyl benzene [20], siloxane [21,22],

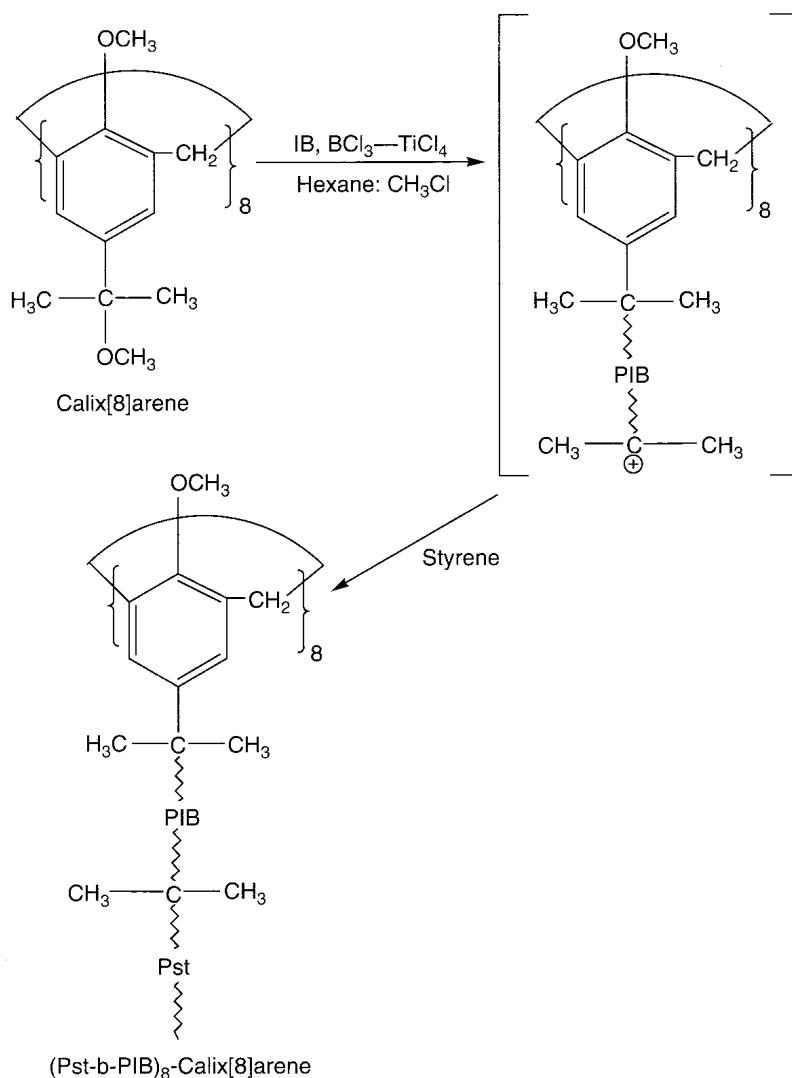


FIGURE 5.2 Synthesis of polyisobutylene (PIB)-based star-block thermoplastic elastomer (TPE). (From Jacob, S. and Kennedy, J.P., *Adv. Polym. Sci.*, 146, 1, 1999.)

etc. The synthetic procedure of star-block copolymers is well known for many years [20–27]. Different approaches are usually used to synthesize star-block copolymers such as anionic, cationic, free radical, condensation polymerization, and often combinations of them. However, the synthesis by anionic polymerization using living di- or triblock copolymer is the most popular method. Kennedy et al. have extensively reported the synthetic strategy (Figure 5.2) and characterization of PIB-based star-block copolymers [20,21,28]. They exhibit high tensile strength (18–26 MPa) and elongation at break (500%–600%). Star copolymer with 32% PS content shows tensile strength of about 26 MPa.

5.4.1.2 Copolyester

The first commercial polyester TPE (called thermoplastic copolyester, COPE) was introduced by DuPont with the trade name Hytrel, and at present it is the single-largest-volume TPE material which comes under the category of “engineering thermoplastic elastomer.” Polyester TPEs possess hard segments generally based on oligourethanes or aromatic polyesters and soft segments derived from aliphatic polyethers. By varying the concentration and the molecular weight of the soft segment, a wide range of products with different properties could be obtained. The segmented polyester–polyether block

copolymers are prepared readily and economically by melt transesterification. A mixture of phthalate ester, a low-molecular-weight diol, and a poly(alkylene ether) diol is heated to 160°C in the presence of transesterification catalyst [29]. This has been covered elsewhere in this book.

A disadvantage of the commercial poly(ether-ester) is a partial compatibility of the hard and soft segments. Even a poor compatibility reduces the crystallinity and mechanical stability of the hard segments and raises the T_g of the soft segments. Hard segments containing imide-building blocks should favor the microphase separation because of their high polarity and planarity of the aromatic imide group [30]. New TPEs prepared from polytetramethylene oxide (PTMO), 1,4-dihydroxybutane, and a bisimide dicarboxylic acid based on 1,4-diaminobutane and trimellitic anhydride show very good microphase separation. When PTMO of high polydispersity is used, good mechanical properties are obtained, which are better than those of classical TPEs based on PBT hard segments [30]. However, all poly(ether-ester-imides) crystallize slowly, which could be a hindrance for injection molding but allow their application as films.

Polyether-based thermoplastic copolyesters show a tendency toward oxidative degradation and hydrolysis at elevated temperature, which makes the use of stabilizer necessary. The problem could be overcome by incorporation of polyolefinic soft segments in PBT-based copolyesters [31,32]. Schmalz et al. [33] have proposed recently a more useful technique to incorporate nonpolar segments in PBT-based copolyesters. This involves a conventional two-step melt polycondensation of hydroxyl-terminated PEO-PEB-PEO (synthesized by chain extension of hydroxyl-terminated hydrogenated polybutadienes with ethylene oxide) and PBT-based copolyesters.

5.4.1.3 Polyurethanes

Polyurethane chemistry is a very broad field and encompasses a large number of chemical reactions of isocyanate with various active hydrogen-containing compounds [34]. TPUs are linear-segmented copolymers with alternating hard and soft segments. The soft segment is usually a high-molecular-weight macroglycol (polyether or polyester type) and the hard segment is formed by the reaction between a diisocyanate with a low-molecular-weight diol, such as 1,4-butanediol. Primarily, TPU linear polymers are synthesized by the condensation of diisocyanate with short-chain diol (chain extender) and polyester or polyether diol (polyol). The preparation of TPU can be done either by the one-shot [35] or the two-shot (prepolymer) [36] process. The latter involves preparation of a low-molecular-weight linear isocyanate-terminated prepolymer followed by its chain extension to produce the final TPU. There have been a number of patents and literatures available on synthesis of thermoplastic polyurethanes [37–41].

5.4.1.4 Copolyamides (Thermoplastic Polyamides)

Thermoplastic polyamide elastomers consist of a regular linear chain of rigid polyamide segments interspaced with flexible polyether segments. They are basically segmented block copolymers having general structure $(AB)_n$. The hard segments may be based on partially aromatic polyamide or aliphatic polyamide. Polyester amide (PESA) and polyether ester amide (PEEA) are prepared from the aromatic polyamide, while in the polyether block amide (PEBAX or VESTAMID) the hard segments are derived from aliphatic polyamide. In both PEEA and PEBA, the soft segment of aliphatic polyesters is linked to the hard segment by an ester group. The three principal methods for their preparation of thermoplastic polyamide elastomers [2] are as follows:

1. The Dow process consists of the formation of an acid-terminated soft segment, first by the esterification of polyoxyalkylene or other glycol, followed by the reaction of a diisocyanate and additional diacid to form PESA.
2. The ATO Chemie process involves the formation of an adipic acid-capped hard segment block of poly(11-aminoundecanoic) of molecular weight 800–1500, joined with a soft segment of polyol in a polyesterification process.

3. The Emser Industries process has no ester linkage, the bonds between the two segments being amides. An amine-terminated soft bis(3-aminopropyl)polyoxytetramethylene glycol is reacted with a dimer acid (Empol 1010) and caprolactum to form polyetheramide (PETA).

5.4.2 BLENDS AND ELASTOMERIC ALLOYS

5.4.2.1 Elastomeric Rubber–Plastic Blends

TPEs prepared from rubber–plastic blends have gained considerable interest in last two decades [3,42,43]. They provide the simplest way of achieving outstanding properties at low cost and with scope to tailor-make the properties by simple variation of the blend composition, viscosity of the components, and compounding ingredients. The first useful rubber–plastic blends were those obtained from nitrile rubber (NBR) and polyvinylchloride (PVC). There have been constant researches going on in this area to develop thermoplastic elastomeric blends with improved properties [44–46]. Elastomer–plastic blends containing large amount of elastomers have generally been prepared by melt mixing, which is easy and economical. The basic factors to be considered for the preparation of TPE of this kind are (1) high shear stress during mixing [47], (2) complete homogenization of the dispersed component particles, and (3) avoidance of local overheating and polymer degradation. Thus, mixing could be carried out in (i) a high-speed, two-rotor continuous mixer, (ii) a twin-screw extruder, or (iii) a single-screw extruder (length/diameter ratio, $L:D > 30$) [48].

TPEs prepared from rubber–plastic blends usually show poor high-temperature properties. This problem could be solved by using high-melting plastics like polyamides and polyesters. But, often they impart processing problems to the blends. Jha and Bhowmick [49] and Jha et al. [50] have reported the development and properties of novel heat and oil-resistant TPEs from reactive blends of nylon-6 and acrylate rubber (ACM). The properties of various thermoplastic compositions are shown in Table 5.4. In this kind of blend, the plastic phase forms the continuous phase, whereas

TABLE 5.4
Typical Properties of Thermoplastic Elastomers Developed
from Nylon-6–Acrylate Rubber Blends

TPE Composition	A	AB ₃₀	AC ₃₀	AS ₃₀
Nylon-6	40	40	40	40
ACM	60	60	60	60
HMDC	0.5	0.5	0.5	0.5
N770	—	30	—	—
China clay	—	—	30	—
Ultrasil VN ₃	—	—	—	30
Tensile strength (MPa)	12	11	11	15
Elongation at break (%)	114	94	115	183
Young's modulus	52	40	52	41
Tension set	35	25	28	23
Oil aging at 150°C in ASTM oil 3				
Volume swell (%)	3	5	7	2
Tensile strength (MPa)	12	13	11	16
Elongation at break (%)	70	62	60	113
Aging at 175°C for 72 h				
Tensile strength (MPa)	10	12	13	18
Elongation at break (%)	100	30	46	60

Source: Jha, A., Dutta, B., and Bhowmick, A.K., *J. Appl. Polym. Sci.*, 74, 1490, 1999.

the rubber phase remains as dispersed particles. The modulus, tensile strength, elongation at break, and hardness of these blends increase with increasing interaction between nylon-6 and ACM. The blends show excellent resistance to oil swelling at elevated temperature (e.g., 150°C), and their service temperature range can be extended up to 170°C–200°C without much deterioration of the mechanical properties. The mechanical properties of these blends are improved a lot with the addition of lower amounts of carbon black (i.e., 10–20 phr) and higher percentage of silica filler (30 phr). However, swelling properties are affected slightly on the addition of filler in such blends [51]. On dynamic vulcanization of such blends, hardness and modulus fall slightly, but tensile strength and elongation at break improve.

De Sarkar et al. [52] have reported a series of new TPEs from the blends of hydrogenated SBR and PE. These binary blends are prepared by melt mixing of the components in an internal mixer, such as Brabender Plasticorder. The tensile strength, elongation at break, modulus, set, and hysteresis loss of such TPEs are comparable to conventional rubbers and are excellent. At intermediate blend ratio, the set values show similarity to those typical of TPEs (Table 5.5).

Jha and Bhowmick [51] have reported the development and properties of thermoplastic elastomeric blends from poly(ethylene terephthalate) and ACM by solution-blending technique. For the preparation of the blend the two components, i.e., poly(ethylene terephthalate) and ACM, were dried first in vacuum oven. The ACM was dissolved in nitrobenzene solvent at room temperature with occasional stirring for about three days to obtain homogeneous solution. PET was dissolved in nitrobenzene at 160°C for 30 min and the rubber solution was then added to it with constant stirring. The mixture was stirred continuously at 160°C for about 30 min. The blend was then drip precipitated from cold petroleum ether with stirring. The ratio of the petroleum ether/nitrobenzene was kept at 7:1. The precipitated polymer was then filtered, washed with petroleum ether to remove nitrobenzene, and then dried at 100°C in vacuum.

Interesting TPEs can be derived from binary and ternary blends of polyfunctional acrylates, ACM, and fluorocarbon rubber (FKM) [53]. During the blend preparation, the liquid multifunctional acrylate monomer used is polymerized and forms the continuous matrix encapsulating the

TABLE 5.5

Properties of Thermoplastic Elastomeric Composition Based on Hydrogenated Styrene–Butadiene Rubber and Low-Density Polyethelene

Blend Composition	HL ₀	HL ₂₀	HL ₃₀	HL ₄₀	HL ₅₀	HL ₆₀	HL ₇₀
HSBR (pbw)	100	80	70	60	50	40	30
LDPE (pbw)	0	20	30	40	50	60	70
Transition temperature (°C)							
(i) α	–106	–107	–106	–104	–108	–105	–103
(ii) β	–18	–18	–21	–19	–20	–20	–21
(iii) γ	—	—	72	66	64	64	64
T_g of rubber phase (°C)	–28	–26	–31	–32	–32	–32	–32
Tensile strength (MPa)	5.7	7.0	8.4	8.6	9.0	10.5	11.4
Elongation at break (%)	957	743	735	600	580	560	555
Work at break ($\text{kJ} \cdot \text{m}^{-2}$)	12.1	13.9	15.5	15.8	15.8	16.8	19.3
Modulus (MPa)							
100%	1.5	2.7	3.3	3.8	4.7	5.7	6.2
200%	2.3	3.7	4.4	5.0	5.8	7.0	7.5
Set at 100% elongation (%)	2.0	6.3	7.5	10.0	12.5	15.0	17.5
Hysteresis ($\text{J} \cdot \text{cm}^{-3}$)	3.04	6.14	7.43	9.73	11.55	13.55	14.13

Source: De Sarkar, M., De, P.P., and Bhowmick, A.K., *Polymer*, 39, 1201, 1998.

TABLE 5.6
Mechanical Properties of Thermoplastic Elastomers Based on
Acrylate Rubber–Fluorocarbon Rubber–Polyacrylate Monomer

Blend Composition	AT30	AFT30	AFH30	AFD30
ACM	100	70	50	50
FKM	—	30	50	50
HDDA ^a	—	—	30	—
TMPTA ^b	30	30	—	—
DPHA ^c	—	—	—	30
Modulus (100%) (MPa)	4.3	7.8	4.7	—
Tensile strength (MPa)	8.5	9.2	6.5	12.8
Elongation at break (%)	450	138	270	52

Source: Kader, M.A., Bhowmick A.K., Inoue, T., and Chiba, T., *J. Mat. Sci.*, 37, 6789, 2002.

^a HDDA = Hexanediol diacrylate.

^b TMPTA = Trimethylolpropane triacrylate.

^c DPHA = Dipentaerythritol hexacrylate.

rubber matrix. This procedure generates a very fine morphology of the dispersed rubber phase. The TPEs obtained from such blends show very good mechanical properties (Table 5.6).

5.4.2.2 Thermoplastic Vulcanizates

This is a special class of TPEs resulting from the synergistic interaction of two or more polymers to give properties apparently better than those of simple blends [54]. This interaction can be brought about in an elastomer–thermoplastic system by cross-linking the elastomer and generating a fine dispersion of cross-linked elastomer particles in a continuous matrix of thermoplastics. In most cases, fully cross-linked droplets of 0.1–2.0 μm diameter are dispersed in thermoplastic matrix [55]. TPVs offer properties of cross-linked rubber, coupled with the processability of thermoplastics. There may be several combinations of conventional rubbers, like EPDM, natural rubber (NR), butyl rubber, and NBR, with conventional plastics, like PP, PE, polyesters, and polyamides, to form TPV compositions—the vulcanization of the elastomer phase being carried out under dynamic shear during mixing (dynamic vulcanization). This results in enhancement in the impact and failure properties of the blend. The conventionally used vulcanization systems, e.g., sulfur and accelerator, peroxide, and resin, are employed for carrying out dynamic vulcanization. Among nonconventional vulcanizing systems, hydrosilylation cross-linking system is commercially used, where a silicon hydride having at least two SiH groups is reacted with carbon–carbon multiple bond present in the elastomer component in the presence of a platinum-containing catalyst [56,57].

For the compatible elastomer–thermoplastic blends, melting of the two polymers is the first step followed by subsequent vulcanization of the elastomeric phase. A typical mixing cycle for dynamically vulcanized NR–PE blend (DVNR) in a Brabender mixer is as follows [58]:

- At 0 min add PE
- After 1–2 min add masticated NR
- In 2–3 min add ZnO and stearic acid
- In 3–4 min add accelerator
- In 4–5 min add sulfur
- After 5–6 min dump

For the elastomer–thermoplastic combinations, which are not technologically compatible, a uniform blend could be obtained by incorporating a suitable compatibilizing agent [59–61]. The effects of the type and amount of curing system for NBR-based or polyamide-based TPVs have been studied in details by Mehrabzadeh et al. [62]. Recently, Han et al. [63] developed a new method of EPDM-based or PP-based TPV using supercritical propane. In this method, PP and EPDM are first dissolved in supercritical fluid in certain concentrations to form homogeneous solution followed by the addition of peroxide curatives. The vulcanization of the EPDM phase was carried out by stirring the solution at 175°C and 650 bar pressure for 1 h. The polymer was then precipitated by reducing the pressure to below the cloud-point and subsequently reducing the temperature at constant pressure to the ambient temperature. The advantage of this method is that it provides much smaller size of the dispersed EPDM domains as compared to the melt blending technique.

However, when softening point of thermoplastic phase is very high, e.g., PET, nylon, polycarbonates, the conventional, that is, simple melt mixing of the components followed by dynamic curing with peroxide may not be very effective. In these cases, an indirect two-step masterbatch process can be used. Here, indirect means that the peroxide is premixed and dispersed in rubber phase; and a two-step masterbatch means that the dynamic vulcanizate is prepared first, followed by blending with the thermoplastic [55]. The flow diagram of preparation of TPV based on PET–rubber blend compatibilizer with EPR–g-glycidylmethacrylate is shown in Figure 5.3 [55].

A new TPV based on PP matrix in which a metallocene-type ethylene–octene (EO) copolymer is in dispersed phase has been synthesized and characterized by Fritz et al. [64]. The EO copolymers

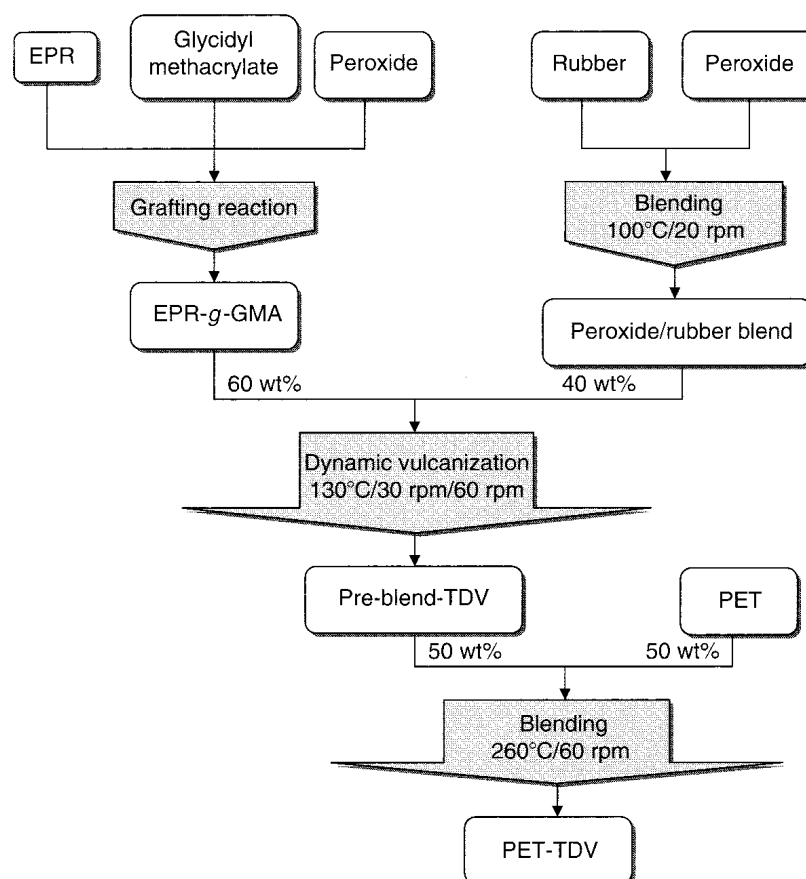


FIGURE 5.3 Flow diagram for the production of polyethylene terephthalate (PET)-based thermoplastic elastomer (TPE). (From Papke, N. and Kargar-Kocsis, J., *Polymer*, 42, 1109, 2001. Courtesy of Elsevier.)

are grafted with vinyl organosilanes, then blended with PP, hydrolyzed, and water cross-linked in a corotating, intermeshing twin-screw extruder. The resulting TPV grades are easy to process into articles showing an attractive range of properties. They can easily be colored to any desired shades. The reduced cost of ingredients is another advantage of the newly developed TPVs. High ultimate tensile strength and elongation at break values as well as a broad spectrum of different Shore A grades open up many fields of application. This new TPV differs from closely related members in TPV family (Santoprene) in the following aspects:

1. Replacement of EPM copolymers and EPDM ter-polymers by saturated metallocene-catalyzed EO copolymer
2. Modification of rubber phase cross-linking by the use of organosilanes

These two-phase polymers are generated in an optimized single-stage process using a corotating, close-intermeshing, twin-screw extruder.

5.4.2.3 Melt Processable Rubber

The melt processable rubber (MPR) blends are single-phase system. The single commercially available MPR is Alcryn, currently sold by Advanced Polymer Alloys. It comprises alloys of ethylene interpolymer and chlorinated polyolefins, in which the ethylene polymer component is partially cross-linked *in situ* [65]. Halogenated polyolefin is miscible with a large number of ethylene interpolymers that are used as intermediate in MPRs. These are designed specially to contain strongly proton-accepting functional groups, in order to promote hydrogen bonding with the alpha hydrogen atom of halogenated polyolefins.

The Alcryn product line is grouped into four series—1000, 2000, 3000, and 4000—differing in hardness and mechanical properties. For example, Alcryn series 1000 has general plastic-processing characteristics and excellent weather resistance and is not suitable for injection molding, for which series 2000 has been designed. Series 2000 has high flow and is excellent for complex extrusion and is not suitable for calendering. The 1000 series has the highest viscosity and the 2000 series has the lowest. The 3000 and 4000 series have intermediate viscosity.

5.4.3 CRYSTALLINE–AMORPHOUS BLOCK COPOLYMERS

The polyolefin elastomers based on olefins with distinct crystalline and amorphous blocks belong to a new class of TPEs. These kinds of polymers are basically copolymers synthesized from one major olefin, like ethylene or propylene and a second minor comonomer, like butene or octene, that is incorporated to create amorphous block in the polymer backbone. ENGAGE polyolefin elastomer based on ethylene and octene is commercially available, which is synthesized by using INSITE catalyst and process technology that allows extraordinary control of polymer structure, properties, and rheology [66]. The ethylene/octene ratio could be varied to produce a range of polymeric materials from rubber to TPE. For example, the polymers with 25%, 19%, and 14% octene content have DSC melting temperatures of 55°C, 76°C, and 95°C, respectively. These copolymers present a broad range of solid-state structures from highly crystalline lamellar morphologies to fringed micellar morphologies of low crystallinity.

Recently, Bhowmick [3] reported the properties and thermoplastic elastomeric behavior of a series of ENGAGE copolymers and their blends (Table 5.7). The copolymer with low octene content (Engage 8440) displays highest tensile strength, elongation at break, modulus and permanent set, while Engage 8150 exhibits excellent permanent set, tensile strength, and modulus. Blending of Engage 8150 with low-density PEs (LDPE) in a ratio of 70:30 improves the modulus at the compromise of set and elongation properties. All the above properties are, however, further improved with the addition of 0.6 phr dicumyl peroxide as a cross-linker in the dynamic vulcanization process.

TABLE 5.7
Properties of Different Blends with ENGAGE

Blend	T.S. (MPa)	E.B. (%)	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Permanent Set (%)
Engage 8150	16.5	991	2.31	3.10	3.79	6
Engage 8440	30.7	1012	6.00	6.58	8.02	24
Engage 8150/LDPE 70:30	16.8	918	3.56	4.11	4.86	11
Engage 8150/LDPE 70:30, 0.6 phr DCP	19.4	943	3.67	4.28	5.15	9
Engage 8150/EVA12 70:30	20.3	999	3.14	3.92	4.17	10
Engage 8440/LDPE 70:30	28.7	933	6.09	6.66	8.07	24
Engage 8150/EVA12 70:30, 0.6 phr DCP	18.9	783	4.07	5.45	6.82	9

Copolymerization of ethylene and styrene by the INSITE technology from Dow generates a new family of ethylene–styrene interpolymers. Polymers with up to 50-wt% styrene are semicrystalline. The stress–strain behavior of the low-crystallinity polymers at ambient temperature exhibits elastomeric characteristics with low initial modulus, a gradual increase in the slope of the stress–strain curve at the higher strain and the fast instantaneous recovery [67]. Similarly, ethylene–butylene copolymers may also be prepared.

5.4.4 IONOMERS

Ionic polymers are a special class of polymeric materials having a hydrocarbon backbone containing pendant acid groups. These are then neutralized partially or fully to form salts. Ionomeric TPEs are a class of ionic polymers in which properties of vulcanized rubber are combined with the ease of processing of thermoplastics. These polymers contain up to 10 mol% of ionic group. These ionomeric TPEs are typically prepared by copolymerization of a functionalized monomer with an olefinic unsaturated monomer or direct functionalization of a preformed polymer [68–71]. The methods of preparation of various ionomeric TPEs are discussed below.

5.4.4.1 Metal-Sulfonated EPDM

The preparation of metal-sulfonated EPDM consists of two steps: sulfonation of EPDM and neutralization of the free acid groups [69,72]. Typical diene monomers that can be sulfonated include 5-ethylidene-2-norbornene (ENB), end-dicyclopentadiene (DCPD) and 1,4-hexadiene. The free form of S-EPDM is prepared from EPDM by using a sulfonating agent, which is added to the hydrocarbon (aliphatic) solution of the former at room temperature. After about half an hour a chain-terminating agent (i.e., isopropanomethyl-6-*tert*-butylphenol) is added to terminate sulfonation reaction. The resultant polymeric sulfonic acid is separated through steam stripping, washed with water, and dried. Neutralization of S-EPDM can be carried out in one of the two ways. In the first case, the polymer is redissolved in a mixture of toluene–methanol or hexane–alcohol to which metal acetate solution in water or water–methanol is added to neutralize the polymer. In second procedure (direct neutralization), the resultant solution after sulfonation is treated with an alcohol or water–alcohol mixture or an aqueous solution of metal hydroxide or acetate [73].

5.4.4.2 Zinc-Maleated EPDM

Blends of ionomeric Zn-maleated EPDM rubber (Zn-mEPDM) and Zn-maleated PP (Zn-mPP) show behaviors typical of TPEs [74]. The composition ranges of 90–10 (Zn-mEPDM–Zn-mPP, wt%)

to 60–40 is found to be more suitable for this purpose. Zn-mEPDM is prepared by the addition of ZnO into maleated EPDM. The mixing processes depend on the ethylene content of maleated EPDM. The mixing of ZnO into maleated EPDM of low ethylene content is done on an open two-roll mill, while that in high ethylene-containing EPDM is done in a Brabender Plasticorder at a temperature of 70°C and at a rotor speed of 60 rpm.

5.4.4.3 Sulfonated-Styrene(Ethylene-Co-Butylene)-Styrene Triblock Ionomer

Weiss et al. [75] have synthesized Na and Zn salt of sulfonated styrene(ethylene-co-butylene)-styrene triblock ionomer. The starting material is a hydrogenated triblock copolymer of styrene and butadiene with a rubber mid-block and PS end-blocks. After hydrogenation, the mid-block is converted to a random copolymer of ethylene and butylene. Ethyl sulfonate is used to sulfonate the block copolymer in 1,2-dichloroethane solution at 50°C using the procedure developed by Makowski et al. [76]. The sulfonic acid form of the functionalized polymer is recovered by steam stripping. The neutralization reaction is carried out in toluene-methanol solution using the appropriate metal hydroxide or acetate.

5.4.5 THERMOPLASTIC ELASTOMERS FROM WASTE RUBBERS

Thermoplastic elastomeric compositions can also be obtained from the blends of recycled rubbers and plastics. Nevatia et al. [77] have developed recently thermoplastic elastomeric compositions from reclaimed rubber and scrap plastics. The physical and dynamic mechanical properties, rheological behavior, and phase morphology of such blends have also been reported extensively. The blends are prepared from reclaimed NR and scrap LDPE using dicumyl peroxide and sulfur accelerators as curing agent in an open two-roll mill at high temperature. A 50–50 rubber–plastic blend is found to be the best for processability, ultimate elongation, and set properties. A sulfur-accelerator system is found to be better than a peroxide system for dynamic cross-linking of such blends. The waste rubber can be used to replace virgin rubber substantially in many existing thermoplastic elastomeric blends without much loss in properties. Recently, Jacob et al. [78] have reported the replacement of virgin rubber by ground rubber EPDM vulcanizates in EPDM–PP thermoplastic elastomeric composition. The blends of virgin EPDM-waste EPDM–PP at a constant rubber/plastic ratio of 70:30 show typical TPE-like morphology with a finely dispersed rubber phase in a continuous PP phase. The virgin EPDM and the rubber component present in waste EPDM together constitute the rubber phase in the EPDM–PP blends. Although the addition of waste-EPDM to virgin-EPDM–PP blend causes an initial drop in the mechanical properties, TPEs with enhanced properties are obtained at higher loading of waste-EPDM. Table 5.8 shows the mechanical properties of various blend compositions.

Naskar et al. have reported replacement of 50% of EPDM by ground rubber tire (GRT) in a thermoplastic–elastomeric blend of EPDM–poly(ethylene-co-acrylic acid) blend [79]. It is believed that surface modification of GRT imparts better physical properties of the GRT–plastic composites through improved adhesion between the composites. Adam et al. [80,81] and Fuhmann and Karger-Kocsis [82] have reviewed different surface modification techniques of polymers. Grafting of maleic anhydride (MA) is well-established and commercially exploited technique for modification of polymers [83–85]. Recently, Ray et al. [86] have developed thermoplastic elastomeric composition based on MA-grafted GRT. GRT powder is maleated in an internal mixture using MA and dicumyl peroxide at 160°C. The blend is prepared by mixing maleated GRT and EPDM first in Brabender Plasticorder at room temperature using cam type rotor and 60 rpm rotor speed followed by the addition of this mix to acrylated high-density PE (HDPE) at 160°C in a Brabender Plasticorder at a screw speed of 30 rpm. In the final stage of mixing, DCP is added and mixed thoroughly. Physical properties of 60:40 (rubber/plastic) thermoplastic elastomeric composition based on EPDM and acrylated-HDPE, where 50% EPDM is replaced by rubber hydrocarbon of maleated GRT, are shown in Table 5.9.

TABLE 5.8

Mechanical Properties of Thermoplastic Elastomer Composition with Varying Waste-Rubber Loading at Constant Rubber/Plastic Ratio of 70:30 (w/w)

Blend Compositions	F ₀	F ₁₀	F ₂₀	F ₃₀	F ₄₀
R-EPDM ^a	70	63.0	56.0	49.0	42.0
W-EPDM ^{b,c}	0.0	22.7	45.4	68.0	90.7
	(0)	(7.0)	(14.0)	(21.0)	(28.0)
PP	30	30	30	30	30
DCP	1.2	1.2	1.2	1.2	1.2
Tensile strength (MPa)	4.83	4.30	4.20	4.20	5.50
Modulus (100%) (MPa)	3.51	3.77	3.32	2.99	3.79
Elongation at break (%)	220	183	215	216	239
Tear strength (kN/m)	30.2	25.8	26.4	24.5	29.0
Tension set at 100% elongation (%)	14	26	18	14	14
Toughness (J/m ²)	3323	2794	3079	3136	4039

Source: Jacob, C., De, P.P., Bhowmick, A.K., and De, S.K., *J. Appl. Polym. Sci.*, 82, 3304, 2001.

^a Raw EPDM.

^{b,c} Values in parentheses are the rubber content in W-EPDM. Ratios of W-EPDM to R-EPDM in different mixes were as follows (total rubber content in each case being constant at 70 parts): F₀,0:100; F₁₀,10:90; F₂₀,20:80; F₃₀,30:70; F₄₀,40:60.

5.4.6 MISCELLANEOUS NEW THERMOPLASTIC ELASTOMERS

In addition to the two-phase TPEs, two new technologies have emerged. They are the metallocene-catalyzed polyolefin plastomers (POPs, the name given to Exxon's EXACT product line) and polyolefin elastomers (POEs, DuPont Dow Elastomer's ENGAGE), and reactor-made thermoplastic polyolefin elastomers (R-TPOs). These new types of TPEs are often called metallocene elastomers—TPEs (MEs—TPEs) [87]. The new POPs and POEs are essentially very low-molecular-weight—linear low-density PEs (VLMW—LLDPE). These new-generation TPEs exhibit rubber-like properties and can be processed on

TABLE 5.9

Physical Properties of the 60–40 Rubber–Plastic Blends Containing Ground Rubber Tire and Maleated-GRT

GRT Type in the Blend Composition ^a	Tensile Strength (MPa)	Ultimate Elongation (%)	Young's Modulus (MPa)	100% Modulus (MPa)	Work of Rupture (kJ/m ²)	Tear Strength (kN/m)	Tension Set at 100% Elongation (%)	Hardness (Shore A)
GRT (acetone extracted)	8.2	152	36.6	7.8	4.5	56.6	24	82
GRT (unextracted)	7.1	203	22.3	6.2	5.3	60.8	26	80
m-GRT (acetone extracted)	10.3	158	41.2	9.9	5.9	62.5	24	85
m-GRT (unextracted)	9.0	190	37.2	8.5	6.2	62.0	26	82

Source: Naskar, A.K., Bhowmick, A.K., and De, S.K., *Polym. Eng. Sci.*, 41, 1087, 2001.

^a EPDM/GRT/acrylated-HDPE 30/68/40 (w/w).

conventional thermoplastic equipments. They are synthesized using metallocene-based catalyst and could be tailored to desired specific properties not achievable with the conventional TPOs available in the market from 1980s. Some of their characteristics are (1) low temperature toughness, (2) chemical resistance, (3) ozone and UV resistance, (4) wide service temperature range from -55°C to 120°C , (5) low density, (6) no plasticizer migration, (7) high tear strength, (8) good printability, etc.

TPEs can be obtained from many conventional homopolymerizing olefins, like propylene, ethylene, and 1-octene, using suitable metallocene catalyst or cocatalyst composition. A typical catalyst composition is metallocene of Ti, Zr, or Hf and methylaluminoxane (MAO) as cocatalyst. In this process, polymerization occurs along two propagation paths, wherein one path causes homopolymerization of the monomer stereoselectively into crystallizable blocks in the resulting polymer chain, and the other path creates irregular noncrystallizable amorphous blocks [88]. Tullock et al. [89] synthesized PP exhibiting elastomeric properties using bis(arene)Ti, Zr, and Hf catalyst with materials of heterogeneous composition. A complete review on propene-based elastomers by transition metal catalyst is available [90].

Graft copolymers are not as common as TPE family. It has already been demonstrated by Jacob et al. [91] that graft copolymer molecular architecture can enhance TPE properties. To achieve acceptable mechanical properties with graft copolymers, it is necessary to use a rubbery backbone with glassy branches at two or more branch points and a fairly high molecular weight of rubbery backbone and branches [92]. Kennedy et al. reported that graft copolymers with trifunctional branch points randomly distributed along the backbone can lead to TPEs with improved properties [91,92]. Weidish et al. [93] reported PS-PI multigraft copolymers with tetrafunctional branch architecture. The materials comprise of PI branches with two PS branches grafted at each of several tetrafunctional branch point per molecule. Multigraft copolymers, with 8%–67% PS and 7–9 branch points per molecules, show unoriented morphology and, thus, their mechanical properties do not depend on the direction of stressing. Materials between 8% and 37% PS exhibit the behavior of TPEs as indicated by large increase of stress at higher strain. While the materials containing 8% PS and eight branch points show a low tensile strength, multigraft copolymers with 22% PS and seven branch points reveal both high tensile strength and high elongation at break. With increasing PS content, strain at break decreases dramatically without corresponding increase in strength. Modern synthetic techniques [94,95] even allow to control backbone molecular weight, and number and placement of branch points along the backbone. The presence of two glassy PS branches at each branch point provides enhanced stress transfer between the rubbery matrix and PS domains as compared to triblock copolymers and trifunctional multigraft copolymers. Figure 5.4 shows PI backbone has

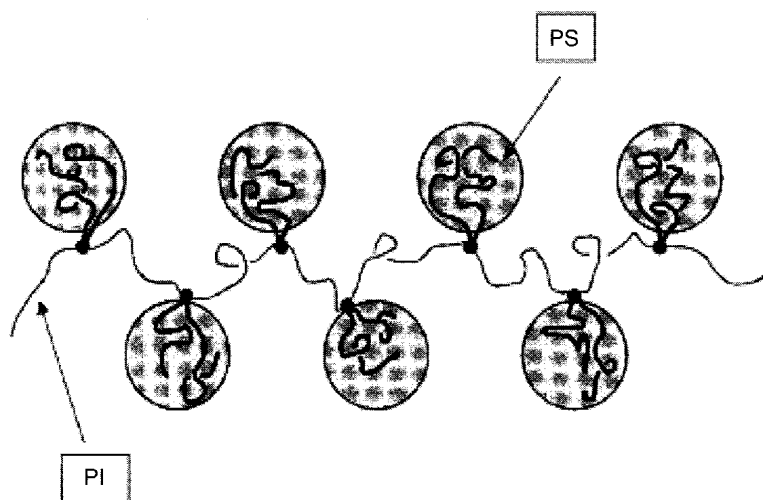


FIGURE 5.4 Polystyrene (PS) branches grafted on to the multiple branch points along the polyisoprene backbone.

multiple branch points connected with PS chains. In microphase-separated morphology, the junction points reside at the interface between PS cylindrical domains and the PI matrix [93]. Linear chain-branched PEs having crystallizable branches grafted on an amorphous and plastomeric copolymer backbone show TPE character. Recently, Markel et al. [96] have reported the synthesis and characterization of such TPEs. These are synthesized using mixed metallocene catalyst, for instance Cp_2ZrCl_2 and $(\text{C}_5\text{Me}_4\text{SiMe}_2\text{NC}_{12}\text{H}_{23})\text{TiCl}_2$ activated with MAO. Conceptually, the synthesis can be divided into two steps: (1) generation of vinyl terminated, crystallizable macromonomers and (2) incorporation of these macromonomers onto the copolymer backbone.

5.4.6.1 Protein-Based Thermoplastic Elastomers

TPEs traditionally have been synthesized with well-defined synthetic organic blocks of compositional dissimilarity that display phase-separated morphology and offer unique technical properties. However, the synthetic repertoire of the block copolymers has been so far limited to the tapered blocks of uniform sequence, which restricts preparation of controlled architecture of organizational and functional complexity of protein-based structural materials that exist in nature [97]. There is an increasing demand to develop biocompatible smart building blocks and functional molecular devices through self-assembly and natural functional materials, particularly peptides and proteins remain an inspiration for the quest. All the natural proteins are biopolymers based on unique linear arrangement of just 20 different unique amino acid monomers (Table 5.10) [98]. However, the self-organized folded proteins achieve a tremendous breadth of physical and chemical activities, ranging from exquisitely specific room temperature catalysis to the formation of unusually strong and tough biomaterials, such as collagen and spider silk. The complexity of the chemical structure of biopolymers and the general inability of amino acids to yield to standard synthetic protocol and physical processing methods restrict their production synthetically. However, the emergence of genetic engineering of synthetic polypeptides has recently enabled to synthesize protein-based analogues of conventional TPEs, artificially, by incorporation of two or more incompatible protein-based tandem sequences of different chemical, physical, and biological characteristics [99–102]. The resulting block copolypeptides would confer highly sophisticated chemical structure, unique self-assembly, functionality, and physiochemical properties to the resultant materials. This novel technique has opened up unlimited possibilities to synthesize new functional materials. Protein polymers can be designed to display a wide variety of properties including stimuli-responsive block copolymer assemblies; gelation under physiological conditions; film and fiber formation; adhesion to synthetic surface; controlled restorability; micelles for drug delivery; biological recognition; and chemical, enzymatic, and therapeutic activity.

A significant research has been dedicated in elastin-mimetic protein polymer and a versatile class of TPE based on block copolypeptide has been developed. It has been identified in early 1980s that the key structural feature that introduces elasticity to the protein of short repeat sequence contains proline and glycine residue. For example, the elastic proteins elastin and spider flagelliform silk are dominated by the pentapeptide repeats valine–proline–glycine–valine–glycine (VPGVG) [103,104] and glycine–proline–glycine–glycine–x (GPGGX) [105–107], respectively. Elastin is the major structural protein of those tissues, which required rapid extension and complete recovery (e.g., aorta, nuchal ligament). Thus significant focus has been placed on repeat sequence VPXYG [97,108]. It has been observed that the lower critical solution temperature (LCST) of this polypeptide can be manipulated by adjusting the identity of the fourth residue *Y*. In addition substitution of an ala residue for the consensus gly residue in the third position (*X*) of the repeat results in the change in the mechanical response of the biopolymer from elastomeric to plastic. The pentapeptide repeat residue has been the basis for the development of many ABA-type peptide-based triblock copolymer; some of them behave like hydrocarbon-based TPEs. Spontak and Patel [109] synthesized elastin-mimetic triblock polypeptides, ABA-type block copolymers using biological methods with a sequence based on the key elastin repeat sequence VPGVG that undergoes phase separation

TABLE 5.10
Standard Amino Acid Abbreviations

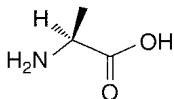
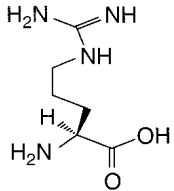
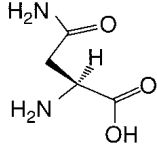
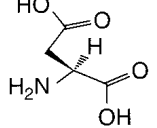
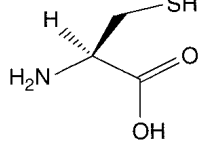
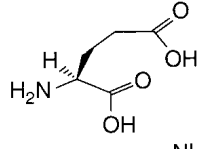
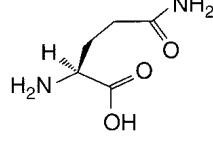
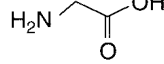
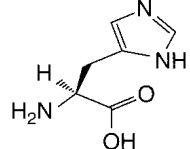
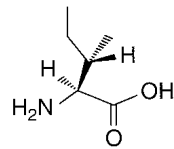
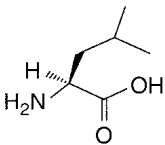
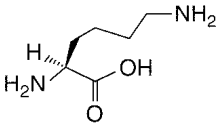
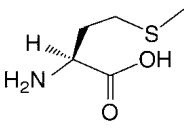
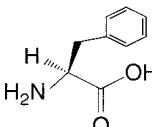
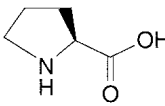
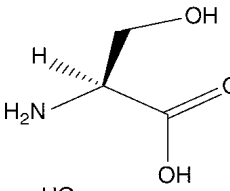
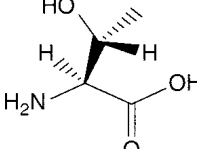
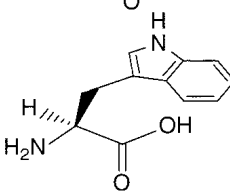
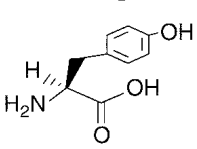
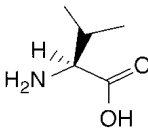
Amino Acid	Structure	3-Letter Code	1-Letter Code
Alanine		ala	A
Arginine		arg	R
Asparagine		asn	N
Aspartic acid		asp	D
Cysteine		cys	C
Glutamic acid		glu	E
Glutamine		gln	Q
Glycine		gly	G
Histidine		his	H
Isoleucine		ile	I

TABLE 5.10 (continued)
Standard Amino Acid Abbreviations

Amino Acid	Structure	3-Letter Code	1-Letter Code
Leucine		leu	L
Lysine		lys	K
Methionine		Met	M
Phenylalanine		Phe	F
Proline		Pro	P
Serine		ser	S
Theonine		Thr	T
Tryptophan		trp	W
Tyrosine		tyr	Y
Valine		val	V

above a critical temperature. The gel reliquifies upon cooling and thus behaves like TPE. The A blocks chosen in the polymer are more hydrophobic than VPGVG. These hydrogels are also ionically and thermally responsive (i.e., they undergo large volume changes as a result of these responses). By combining polypeptide blocks with different inverse temperature transition values due to hydrophobicity differences of the blocks, it is possible to produce amphiphilic polypeptides that self-assemble into hydrogels and exhibit TPE-like behavior.

Capello et al. developed a technology for successfully combining sequential block copolymers consisting of tandem repetition based on the natural repeating structure of silk (hard block) and elastin-like amino acid sequence blocks in a high-molecular-weight protein polymer using genetic engineering and biological production method [110]. This new class of TPEs was described as "ProLastins." They consist of silklike and elastin-like blocks and may be defined using the general formula $\{[S]_m[E]_n\}_O$, where "S" is the silklike block having the general amino acid sequence "GAGAGS," "E" is an elastic-like block having the general amino acid sequence "GVGVP," m is from 2 to 8 (but may be as high as 16), n is from 1 to 16 (but may have no limit as long as there is at least one silklike domain on both ends of each elastic-like domain). O was adjusted from 2 to 100 with respect to n and m to yield protein polymer of molecular weight ranging from 60,000 to 85,000 [111,112]. The compositions of ProLastins used in the study are described in Table 5.11 and their expected primary sequences of amino acids are shown in Table 5.12.

Thermal analysis and rheological investigation confirmed that "ProLastin" solution undergoes self-organization resulting in gelation due to nonreversible crystallization event and the process can be controlled by adjusting copolymer structure and conditions that affect crystallization of the protein polymer. Figure 5.5a shows the increase in viscosity as a function of time for three representative block structures. It is clearly demonstrated that the gelation time is a function of the presence of number of silklike blocks. ProLastic 816 solution (20% w/w) which contains eight silklike blocks starts gelling within 30 min. It has also been observed that higher temperature promotes gelation for the polymer (Figure 5.5b). It has also been demonstrated that hydrogen-bond disrupters such as urea affect the rate of crystallization, whereas, nucleating agents accelerate the gelation process. The suitability of the polymer gel for localized drug release has been examined in detail and predicted that ProLastin can be used as a framework on which to custom design and build functional protein-based biomaterial system for drug delivery.

Elizabeth et al. [108] reported an elastin-mimic polypeptide sequence that mimics triblock copolymers (ABA) with the sequence of the respective blocks as

$$\{VPAVG[(IPAVG)_4(VPAVG)]_{16}IPAVG\} - \{X\} - \{VPAVG[(IPAVG)_4(VPAVG)]_{16}IPAVG\} \text{ where } [X] = VPGVG[VPGVG]_2VPGEG(VPGVG)_2]_{30}VPGVG$$

TABLE 5.11
ProLastin Polymer Compositions

Polymer	Monomer Structure	Number of Repeats	Molecular Weight
ProLastin 27K (SELPOK)	$[S]_2[E]_4[EK][E]_3$	18	80,734
ProLastin 37K (SELP9K)	$[S]_3[E]_4[EK][E]_3$	12	60,103
ProLastin 47K (SELPSK)	$[S]_4[E]_4[EK][E]_3$	13	69,814
ProLastin 48 (SELP8)	$[S]_4[E]_8$	13	69,977
ProLastin 816 (SELP5)	$[S]_8[E]_{16}$	7	84,609

Source: Capello, J.W. Crissman, M. Crissaman, F.A. Ferrari, G. Textor, O. Wallis, J.R. Whitley, X. Zhou, D. Burman, L. Aukerman, E.R., and Stedronsky, J., *Controlled Release*, 53, 105, 1998, Table 1.

TABLE 5.12
Amino Acid Sequence^a of ProLastin Polymers

ProLastin 27K	Amino acids: 1000	MW: 80,734
MDPVVLQRRDWENPGVTQLNRLAAHPPFASDPM		
GAGAGS GAGAGS[(GVGVVP) ₄ GKGVP(GVGVVP) ₃ (GAGAGS) ₂] ₁₂ GA		
MDPGRYQDLRSHHHHHH		
ProLastin 37K	Amino acids: 749	MW: 60,103
MDPVVLQRRDWENPGVTQLNRLAAHPPFASDPM		
[GAGAGS(GVGVVP) ₄ GKGVP(GVGVVP) ₃ (GAGAGS) ₂] ₁₂ GAGA		
MDPGRYQDLRSHHHHHH		
ProLastin 47K	Amino acids: 884	MW: 69,814
MDPVVLQRRDWENPGVTQLNRLAAHPPFASDPM		
GAGSGAGAGS[(GVGVVP) ₄ GKGVP(GVGVVP) ₃ (GAGAGS) ₄] ₁₂ (GVGVVP) ₄		
GKGVP(GVGVVP) ₃ (GAGAGS) ₂ GAGA		
MDPGRYQDLRSHHHHHH		
ProLastin 48	Amino acids: 889	MW: 69,977
MDPVVLQRRDWENPGVTQLNRLAAHPPFASDPM		
GAGSGAGAGS[(GVGVVP) ₈ (GAGAGS) ₄] ₁₂ (GVGVVP) ₈ (GAGAGS) ₂ GAGA		
MDPGRYQLSAGRYHYQLVWCQK		
ProLastin 816	Amino acids: 953	MW: 84,609
MDPVVLQRRDWENPGVTQLNRLAAHPPFASDPM		
GAGS (GAGAGS) ₃ [(GVGVVP) ₁₆ (GAGAGS) ₈] ₁₆ (GVGVVP) ₁₆ (GAGAGS) ₃ GAGA		
MDPGRYQLSAGRYHYQLVWCQK		

Source: Capello, J.W. Crissman, M. Crissaman, F.A. Ferrari, G. Textor, O. Wallis, J.R. Whittedge, X. Zhou, D. Burman, L. Aukerman, E.R., and Stedronsky J., *Controlled Release*, 53, 105, 1998, Table 2.

^a Single amino acid abbreviations used.

This polypeptide is structurally identical to ABA-type triblock copolymer with a central hydrophilic elastomeric end-block capped with two hydrophobic plastic end-blocks and exhibits amphiphilic characteristics. The end-blocks of the polymer were chosen in such a way that their LCST would reside at or near room temperature. Thus the polymer exhibits phase separation, which is analogue to conventional TPEs, and offers TPE gels under physiological relevant conditions [104]. Glutamic acid residue is placed periodically in the elastomeric mid-block to increase its affinity towards the aqueous

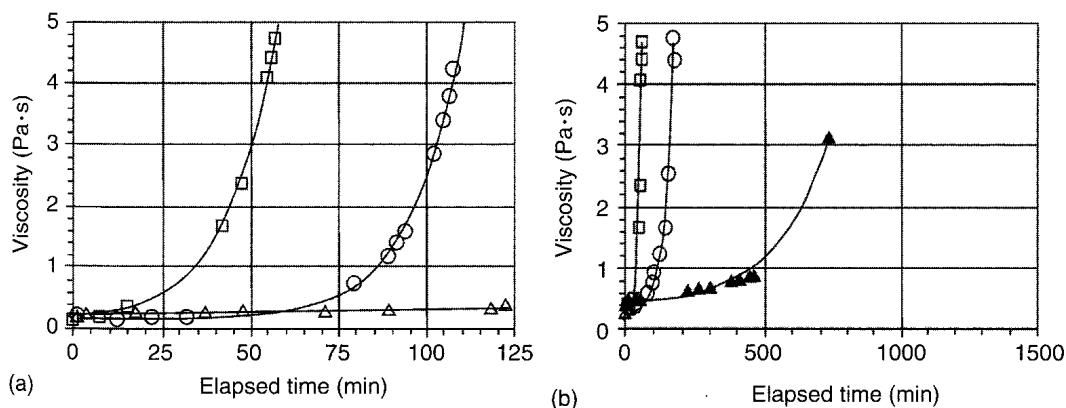


FIGURE 5.5 (a) Viscosity versus time plot of 20% solution of ProLastin 816 (□), ProLastin 47 (○), and ProLastin 27 (△). (b) Viscosity versus time plot of 20% solution of ProLastin 816.37 (□), 23 (○), 4 (▲).

solvent resulting in enhanced segregation between the two blocks above an LCST. Differential scanning calorimetry (DSC) and variable temperature (VT) ^1H - ^{13}C heteronuclear correlation through multiple quantum coherence (HMQC) nuclear magnetic resonance spectroscopy (NMR) confirm selective phase separation. The rheological behavior of the protein indicated that it behaved as gel at 25°C in that the G' exceeded that of G'' by nearly two orders of magnitude under these conditions. The morphology of the gel state was evaluated using cryo-high-resolution scanning electron microscopy (cryo-HRSEM), which exhibits microphase-separated morphologies with spherical micellar segregation of 20–30 nm in diameter. The underlying morphology of the protein aggregates within the gels can be more clearly observed from specimen in which vitreous ice has been etched from the surface via controlled sublimation.

Nagapudi et al. reported synthesis of high-molecular-weight recombinant protein ABA-type triblock copolymers that exhibit tunable properties that may find applications in novel scaffolds for tissue engineering and new biomaterials for controlled drug delivery and cell encapsulation [113]. They employed a modular convergent biosynthetic strategy which may greatly enhance the synthesis of triblock copolymer with significant flexibility in the selection and assembly of blocks of diverse size and structure. Development of large molecular weight ABA-type block-type protein-based biopolymers offers a unique opportunity to systematically modify microstructure on both nanoscale and mesoscale. They also demonstrated that through the rational choice of processing conditions, including solvent type, temperature, and pH, an array of TPE materials could be produced systematically from the ABA block copolymer that displays wide range of physical properties. Figure 5.6a shows the stress-strain relation for the films casted at different temperatures and pH from water or 2,2,2-trifluoroethanol (TFE) and significant difference in the films' stress-strain characteristics is clearly observed. TFE solvates both the blocks and renders the material plastic, whereas water preferentially dissolves the hydrophilic mid-block and generates elastomeric materials. Changing the pH of the solvent by addition of NaOH further enhances the elastic properties. Hysteresis behavior of the film cast from TFE and water is shown in Figure 5.6b. Petka et al. [114], Minich et al. [115], Breedveld et al. [116], Pochan et al. [117], and Nowak et al. [118] have recently reported the development of many different protein-based block copolymers that exhibit TPE-like behavior. The elastomeric behavior of the film cast from water is clearly observed from the figure. These functional materials expect to find applications in novel scaffold for tissue engineering and as new biomaterials for controlled drug delivery and cell encapsulation.

5.4.6.2 Hybrid Molecular Structure with Peptide and Nonpeptide Sequences

In protein-based biopolymers, particularly structural proteins, the conformational stability and precise chain sequences work together to hierarchically assemble three-dimensional complex fine structure from the linear macromolecules, which impart these materials with specific biological function. However, it is challenging to produce them in commodity volume, synthetically. Attempts to synthesize polypeptides with well-defined amino acid sequences, using synthetic protocol, have been plagued by unwanted side reactions, polydispersity, and poor organization. On the contrary, synthetic polymers can be manufactured in bulk at low cost. However, due to the lack of precise control over composition, architecture, and dimension, well-defined complex folding organization cannot be designed [119]. The access to a variety of synthetic building blocks in hydrocarbon polymers holds tremendous potential to create an improved class of nonnatural bioinspired polymers of hybrid molecular structure with peptide and nonpeptide sequences. These polymers can not only mimic the protein, structure, activity, and properties with novel backbone and side-chain chemistry, but also can be obtained at low cost, chemical diversity, and biological activity. The spectrum of polymeric materials and the wide range of possibilities of nonnatural sequence-specific block copolymers are unlimited [120–123].

Recently, synthesis of many compositionally and topologically different block copolypeptides has been reported [119,124]. In most cases, the copolypeptide block is composed of γ -benzyl

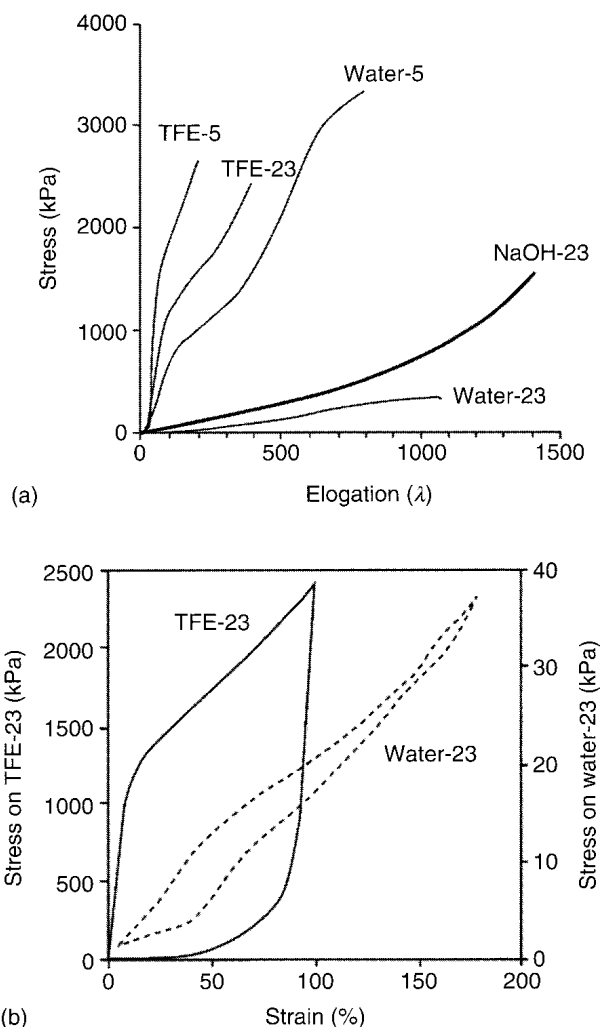


FIGURE 5.6 (a) Stress–strain relation for the films cast at different temperatures and pH from water or 2,2,2-trifluoroethanol (TFE). Significant difference in the films’ stress–strain characteristics is clearly observed. TFE solvates both the blocks and renders the material plastic whereas water preferentially dissolves the hydrophilic mid-block and generates an elastomeric material. Changing the pH of the solvent by addition of NaOH further enhances the elastic properties. (b) Hysteresis behavior of the film cast from 2,2,2-trifluoroethanol (TFE) and water. Significant difference in the films’ stress–strain characteristics is clearly observed. TFE solvates both the blocks and renders the material plastic whereas water preferentially dissolves the hydrophilic mid-block and generates an elastomeric material.

L-glutamate, β -benzyl L-aspartate, or *N* ϵ -benzyloxycarbonyl-L-lysine as the polymerization of these NCAs is the best controlled of all. The chemical nature of the synthetic block segment has been varied to a much greater extent using both hydrophobic [such as PS, polybutadiene, PI, poly(methyl methacrylate), poly(propylene oxide), poly(dimethyl siloxane)], and hydrophilic segment [poly(ethylene oxide), poly(vinyl alcohol), poly(2-methyl oxazoline), etc]. Highly-effective zero-valent organo nickel, such as 2,2'-bipyridyl Ni(1,5-cyclooctadiene) and cobalt complex initiators, which are able to eliminate significant competing termination and transfer steps from NCA polymerization to allow preparation of well-defined peptides, has recently been demonstrated by Deming et al. [125]. Recently, Seidel et al. [126] also reported the use of chiral ruthenium and iridium amido-sulfonamide complex for controlled enantioselective polypeptide synthesis. These new methods can now

be employed successfully to realize stereocontrol in NCA polymerization that has been difficult to achieve before.

Recently, unique vesicle-forming (spherical bilayers that offer a hydrophilic reservoir, suitable for incorporation of water-soluble molecules, as well as hydrophobic wall that protects the loaded molecules from the external solution) self-assembling peptide-based amphiphilic block copolymers that mimic biological membranes have attracted great interest as polymersomes or functional polymersomes due to their new and promising applications in drug delivery and artificial cells [122]. However, in all the cases the block copolymers formed are chemically dispersed and are often contaminated with homopolymer.

5.5 STRUCTURAL AND PHASE CHARACTERISTICS

TPEs demonstrate a number of unique properties as a result of their morphological features and have one feature in common—they generally exhibit a phase-separated system in bulk. One phase is hard at room temperature while the other phase is soft and elastomeric. The microphase or mesophase-separated morphology is made possible by the type of macromolecular architecture. TPEs should have rubber-like plateau, which is as wide and as flat as possible and that should be adjustable according to certain applications. The properties of TPEs are strongly sensitive to which phases are present and how they are spatially arranged (for instance, disperse versus co-continuous). Important parameters in this respect are crystallinity and crystal imperfection of the hard segment, composition of the amorphous phase, and continuity of different phases. There exist many important structural differences among the different block copolymers. Styrenics are represented by SES (S—PS, E—elastomer) or a branched structure of general formula $(S-E)_nX$ (n = multifunctional junction points). The remaining block copolymers TPU, TPA, and COPE have formulae $(H-E)$, H = hard block. An important structural parameter that affects the ultimate properties of such polymer is the block frequency distribution. The average block length depends on the composition as well as molecular weight of the starting materials. The hard segment length is very important in most of these materials because the extent of phase separation depends significantly on block length. Monte Carlo [127–129] simulation has also been used to derive hard segment molecular weight distribution, MWD under ideal and nonideal conditions. In general, longer average sequence length for hard segment block offers increased crystallinity and modulus. Other parameters of chain microstructure such as tacticity, *cis-trans*-isomerization, and copolymerization content also have very important influence on the performance of the TPE. These parameters are usually characterized by using NMR [130] and, in some polymers, by infrared spectroscopy (IR) technique.

In block copolymers, incompatibility does exist, but phase segregation is restricted to microscopic or mesoscopic dimensions and the equilibrium morphological state of the microphase is a highly organized domain structure. There is a critical molecular weight of each block below which phase separation is insufficient [131]. Phase separation also becomes more difficult as the number of blocks increases [132]. In linear triblock copolymer of the type ABA (where A is the hard and B is the soft segment), the free chain ends are associated together to form discrete microdomains of the hard phase (as are large number of particles of rigid glass polymer that are dispersed in a soft rubbery matrix), which eventually behaves as thermo reversible physical cross-links. Continuous three-dimensional network structure is obtained, as many flexible rubber chains emanate from each domain and terminate in the neighboring domain as shown in Figure 5.7. At temperature above the softening point of the glassy domains the material can be made to flow (Figure 5.8a). The lower bound of the service temperature of these materials is governed by the glass-transition temperature, T_g value of the continuous rubbery phase.

The morphology of the ABA-type linear block copolymers is strongly influenced by the volume fraction of the two components. For example, in PS-EB-PS-type block copolymer as the volume fraction of PS is increased, the shape of the dispersed PS phase changes from spherical (comprising body-centered cubic spheres of PS dispersed in continuous soft phase) to cylindrical form (hexagonal packed cylinders of PS) [10,133,134]. When the volume fraction of the two phases

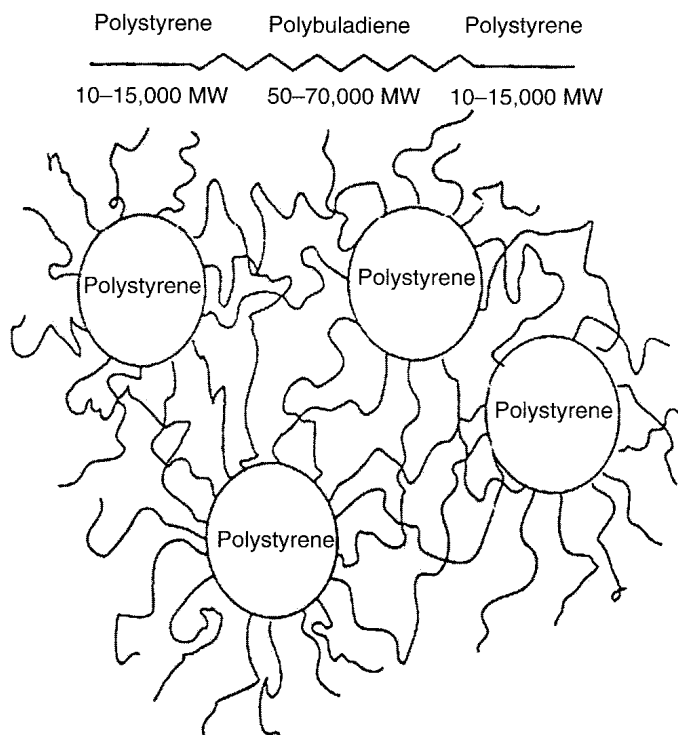


FIGURE 5.7 Phase separation in styrene–butadiene–styrene (SBS) triblock copolymer. The isolated spherical styrene domains form the hard phase, which act both as intermolecular tie points and filler. The continuous butadiene imparts the elastomeric characteristics to this polymer. MW = molecular weight. (From Grady, B.P. and Cooper, S.L., *Science and Technology of Rubber*, Mark, J.E., Erman, B., and Eirich, F.R. (eds.), Academic Press, San Diego, CA, 1994. With permission.)

becomes comparable a lamellar morphology is developed containing alternating layers of the components and the materials lose their TPE characteristics [134]. With the change in temperature, these various forms of morphology may undergo reversible transition from one to another [135,136]. For example, SIS triblock copolymer has cylindrical morphology of the dispersed phase at 150°C, which changes to spherical microdomains at 200°C [135]. In addition to dispersed glassy domain, multifunctional physical cross-links can be formed by regions of crystallinity, ionic attraction, or strong hydrogen bonding in case of functionalized materials.

There are several models for describing the microphase separation and domain morphologies, e.g., confined chain model [137,138] and mean field model [139–141]. However, these models are restricted to simple diblock or triblock copolymers. Suitable models for microphase separation in multiblock segmented copolymers, in particular, to those containing crystallizable components such as TPU or COPE are still lacking in wide scale. It is generally observed that in the melt state these materials have a homogenous mixed phase of the two segments. Upon cooling to below the melting temperature, the microphase separation is facilitated by the crystallization process of the hard segments and no phase separation precedes the crystallization process [142]. Recently, a new model has been proposed by Gabrielse et al. to describe the microstructure and phase behavior of block co-poly(ether–ester) TPEs [143]. Unlike previous concepts, which conclude into a distinct biphasic morphology of block co-poly(ether–ester) (a crystalline polyester phase and a homogeneous amorphous phase of polyether mixed with noncrystalline polyesters [142,144–147]), this new model proposes the amorphous phase as inhomogeneous and segmented into microphases. This effect is pronounced in co-poly(ether–ester) with a relatively large concentration of soft segment and relatively long soft-segment block lengths.

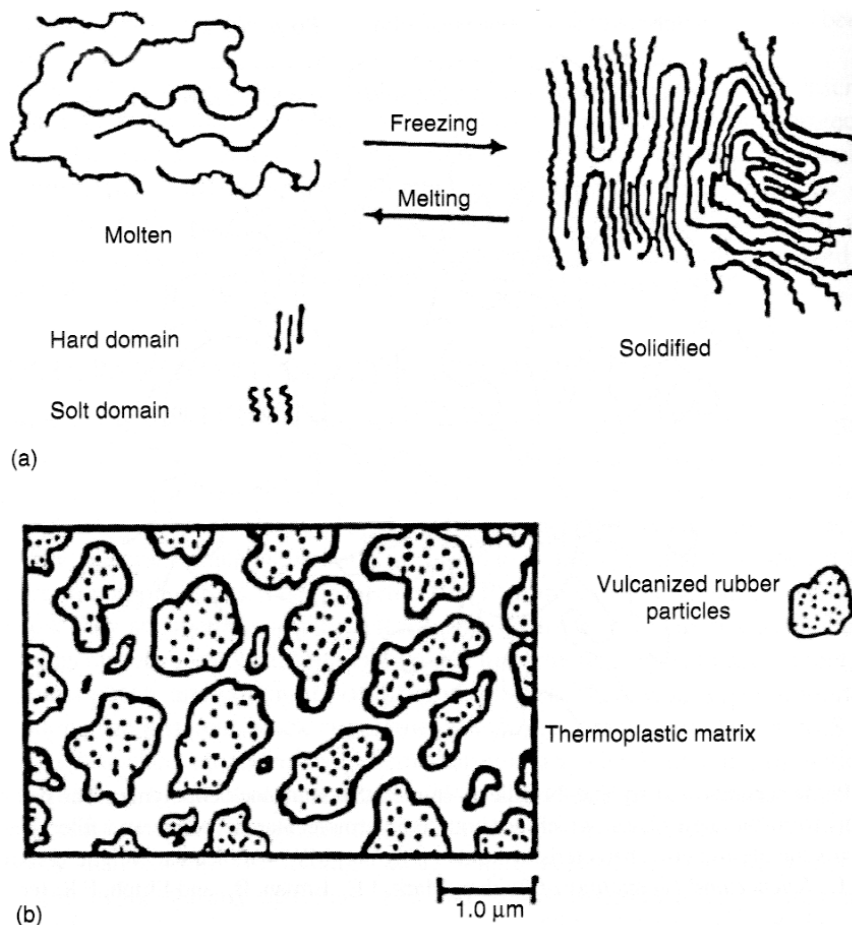


FIGURE 5.8 (a, b) Morphology of block copolymer thermoplastic elastomers (TPE) in molten and solidified rubber state. The transformation is reversible as the material passes through the melting point. Morphology of ethyl acrylate (EA) thermoplastic elastomers (TPE). The fine highly cross-linked rubber particles are distributed homogeneously throughout the thermoplastic matrix. (From Arnold, R.L. and Rader, C.P., *Handbook of Plastics, Elastomer and Composites*, C.A. Harper (ed.), McGraw-Hill, New York, 1992. With permission.)

Unlike the block copolymers, the blends and alloys consist of two or more polymer systems. The phase morphology in rubber-plastic blend changes as a function of blend composition, intrinsic viscosity of the components, and the mixing conditions. Blends with a greater disparity in the component melt viscosity show larger domains. In some cases, the lower viscosity of the plastic at mixing temperature accompanying high proportion of rubber in the mixes favors continuity in both the phases [148]. The mixing time is a determinant of particle size and shape. Sometimes morphological changes after mixing occur by simply coarsening of rubber-plastic emulsion due to melt agglomeration [149]. In elastomeric alloys, dynamic vulcanization offers a route to control the particle size by resisting agglomeration, as a result of which the size of the rubber particles is reduced. Figure 5.8b represents the morphology of dynamically cross-linked blends. It consists of finely divided particles of about 1 μm diameter of highly cross-linked EPDM in PP. Bhowmick and Inoue studied the structure development during dynamic vulcanization of hydrogenated nitrile rubber (HNBR)-nylon blends through light scattering technique [150]. They found that the size of the dispersed HNBR particle in a 50:50 blend passes through a minimum with increasing mixing time at constant temperature. The increase in gel fraction of the HNBR and delaying the addition of vulcanizing agent also increased the dispersed particle when mixing was carried out at same temperature and for same duration. Kresge [151] reviewed the morphological

changes that can result from processing blend compositions into finished product. Optimum dispersion of the rubber particles in plastic is achieved by matching the melt viscosities of the two phases and a closeness of their surface energies and significant interaction between them. For optimum properties, cross-linked rubber particles should be approximately 1–2 μm in diameter [140]. However, the MPR polymer blends are single-phase systems. Strong hydrogen bonding exists in MPR; thus miscibility is exhibited over the entire composition range and no phase separation occurs with the miscible blends of MPR polymer constituents [65,152,153].

Kader et al. [53] have described the morphology development of thermoplastic composition based on ternary blends of ACM, FKM, and polyfunctional acrylates (p-TMPTA). The changes in the blend morphology with varying compositions of ACM and FKM at a constant level of p-TMPTA are shown in Figure 5.9. The blends containing 70–30 ACM–FKM and p-TMPTA show phase separation. The dark phase in Figure 5.9a represents FKM, which forms a dispersed phase with elongated ellipsoid particle. On the other hand, ACM combines with acrylate to form the continuous phase (bright region). The sizes of the dispersed phase show polynodal distribution with varying particle dimension. It has been observed that at higher magnification, there is no sharp boundary between the dispersed phase and the matrix. Some of the ACM or polyacrylate are also included in the form of islands in the dispersed phase. This could be due to the miscibility of ACM–FKM blend [53]. With the increasing amount of FKM in the ternary blend of ACM–FKM–p-TMPTA to the level of 50–50–30 (w/w), the population of dispersed phase particles per unit area is increased with retention of phase-separated morphology (Figure 5.9b). When FKM concentration in such a ternary blend is increased further, more and more dispersed phase particles combine together and form macrophase leading to formation of co-continuous phase formation (Figure 5.9c). Figure 5.9d shows a transmission electron

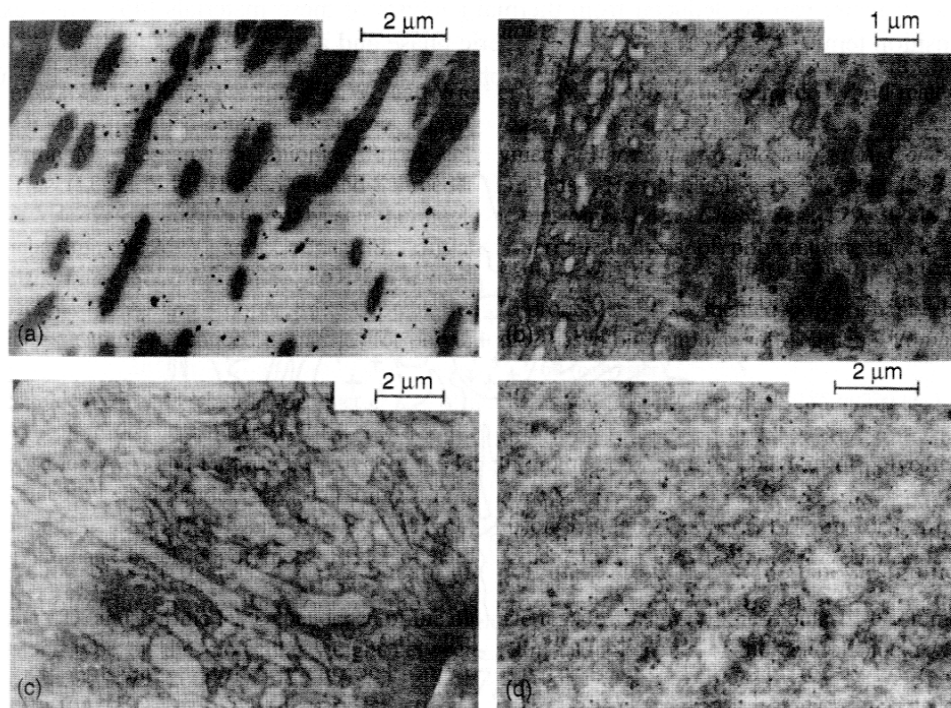


FIGURE 5.9 Transmission electron micrograph of (a) 70–30–30 (w/w) ACM–FKM–p-TMPTA blend; (b) 50–50–30 (w/w) ACM–FKM–p-TMPTA blend; (c) 30–70–30 (w/w) ACM–FKM–p-TMPTA blend; and (d) 100–30 (w/w) FKM–p-TMPTA blend. (From Kader, M.A., Bhowmick, A.K., Inoue, T., and Chiba, T. *J. Mat. Sci.*, 37, 6789, 2002. Courtesy of Springer.)

microscopy (TEM) photomicrograph of FKM-p-TMPTA blend. As the concentration of rubber (bright portion) is higher than that of the plastic, the blend behaves like a filled raw rubber.

Theoretical and experimental evidences on morphological features of ionomers show that salt groups in them exist in two different environments' multiplets and clusters [154,155]. The multiplets are considered to consist of small numbers of ion dipoles associated together to form higher multipoles—quadrupoles, hexa or octapoles, etc. These multiplets are dispersed in the hydrocarbon matrix and are not phase separated from it. In addition to acting as cross-links, they affect the properties of the matrix, e.g., T_g and water sensitivity. The clusters are considered to be small (<5 nm) microphase-separated zones rich in ion pairs in conjunction with ordered crystalline region, both of which are embedded in an amorphous matrix. There are few models that have been suggested for cluster morphologies. In one model, crystallites are represented as regularly folded section with disordered amorphous region acting as the third interconnecting phase (Figure 5.10a). They possess some properties of phase-separated systems. The proportion of salt group residing in the two environments in a particular ionomer is determined by the nature of the backbone, the total amount of salt group, and their chemical nature. Figure 5.10b represents a typical shell-core model for clusters [156,157]. It postulates that in the dry state a cluster of ~0.1 nm radius is shielded from surrounding matrix ion not incorporated in the cluster by hydrocarbon chain. The surrounding matrix ions that are separated from the cluster by hydrocarbon chains will be attracted to it by electrostatic forces.

The morphology is not very well defined in industrially produced TPEs, which are far from equilibrium. Prediction of precise morphology requires knowledge of sample history. Deviation from equilibrium morphology can also arise due to polydispersity in block length. There are various analytical methods to characterize the morphology of TPEs. TEM [158–161] IR [162–165], wide angle X-ray scattering (WAXS) and small angle X-ray scattering (SAXS) [166–170], small angle neutron scattering (SANS) [171], and NMR [172–175] techniques have been used efficiently and extensively by several authors for morphological characterization of TPEs. Further evidence for the two-phase structure can be deduced from thermal analysis of these materials [45]. They exhibit a glass-transition temperature (T_g) for the elastomeric phase and a melting endotherm corresponding to melting temperature (T_m) for the crystalline phase. Table 5.13 shows the T_g and T_m values for various TPEs.

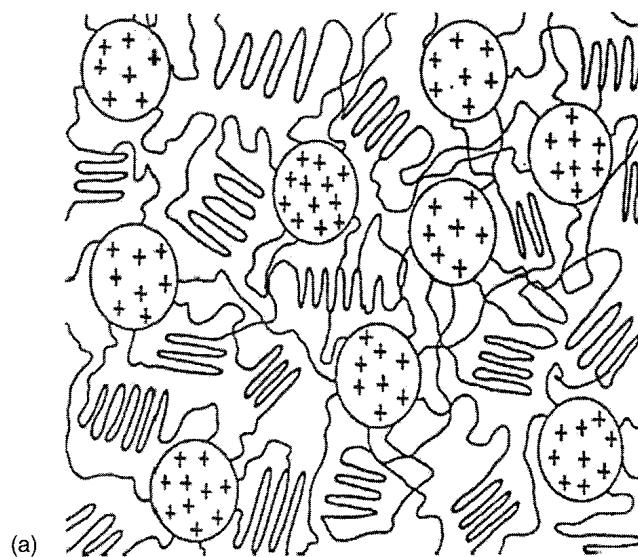


FIGURE 5.10 (a) Scientific representation of the three-phase structure of a dry ionomer, consisting of cation clusters, lamellae, and disordered regions. (From Cowie, J.M.G., *Polymer: Chemistry and Physics of Modern Materials*, Intertext, London, 1973.)

(continued)

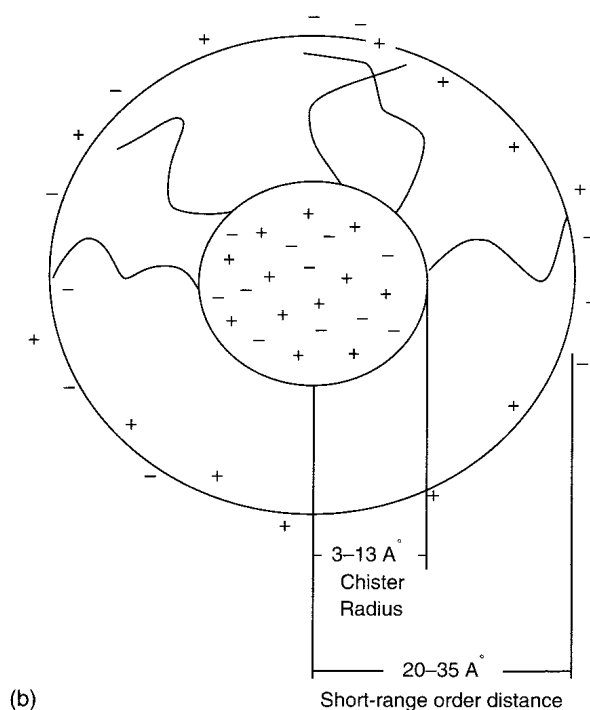


FIGURE 5.10 (continued) (b) Shell-core model for clusters. (From Macknight, W.J., Taggart, W.P., and Stein, R.S., *J. Polym. Symp.*, 45, 127, 1974. With permission of Wiley, New York.)

TABLE 5.13
Glass-Transition and Crystal-Melting Temperature^a

TPE Type	Soft Rubber Phase T_g (°C)	Hard Phase T_g or T_m (°C)
PS-elastomer block copolymer		
SBS	-90	95 (T_g)
SIS	-60	95 (T_g)
SEBS	-60	95 (T_g)
Polyurethane-elastomer block copolymer	-40 (polyether) -60 (polyester)	190 (T_m)
Polyester-elastomer block copolymer	-65 to -40	185 to 220 (T_m)
Polyamide-elastomer block copolymer	-65 to -40	120 to 275 (T_m)
Hard thermoplastic-elastomer blends ^b	-60	165 (T_m)
Alcryn	-40	—

Source: Holden, G., *Rubber Technology*, Morton, M., ed., Van Nostrand Reinhold, New York, 1987.

^a Measured by differential scanning calorimetry.

^b Values quoted are for polypropylene-EPDM blend.

5.6 THERMODYNAMICS OF PHASE SEPARATION

Phase separation between block components occurs since the dissimilar block components, such as homopolymers, are typically incompatible with one another as a result of positive heat of mixing. There is a fundamental difference between phase separation in a system of incompatible homopolymers

and that in a corresponding block copolymer system. In the latter, the two incompatible components are chemically bonded to one another and hence the segregated phases are restricted from growing indefinitely in size. As a result, the domain sizes are much smaller in block copolymer in comparison to that observed in a physical mixture of the two corresponding incompatible homopolymers. Most theories take into account four factors that influence the phase separation of block copolymers: the Flory–Huggins interaction parameter χ , the overall degree of polymerization N , architectural constraints, and weight fraction of one component. By controlling appropriately the segment nature and length of each constituent of the block in block copolymers, a wide variety of microdomain structures of high degree of richness and complexity in bulk as well in solution phase are possible. Their complex structure has significant effect on the static, dynamic, and other functional properties of the polymer. In the ordered state, the block copolymers form “microdomains” with long-range order. They can also form a homogeneous structure in which the two segments are molecularly mixed in the “disordered state.”

There are several theoretical models for describing microphase separation. The confined chain model presented by Meier [137] describes domain structure by random flight chains being constrained by barrier. The barriers represent the effect of the incompatibility between the components and the resulting restriction of the components to region of space. The mean field model developed by Helfand and Wasserman [140] discusses theoretical approaches of phase separation containing all the necessary parameters for a complete description in strong segregation limit (SSL). Three energetic contributions are reported in the theory. Thus during microphase separation a loss of system entropy occurs in various ways: (1) confinement entropy loss as a consequence of confinement of joint degree of freedom, (2) conformational entropy loss resulting from various numbers of polymer conformations that are not allowed as they produce a lower density near the domain than at the boundaries, and (3) enthalpy caused by mixing of A and B segments. With the growth of microdomains, the entropy loss increases until it balances the decrease in surface energy and a thermodynamically stable size is attained, e.g., spherical, cylindrical, or lamellar microdomains (actually, meso-domains with size ca. several tens of nanometers). Self-consistent mean field theory (SCFT) has been the most successful, in describing the phase behavior of high-molecular-weight polymers [176–179]. Using SCFT approximation, where thermal fluctuations are ignored, the phase diagram for conformationally symmetric diblock may be parameterized using only two parameters: χN —the segregation parameter, and f —the block length ratio, and is shown in Figure 5.11a. The

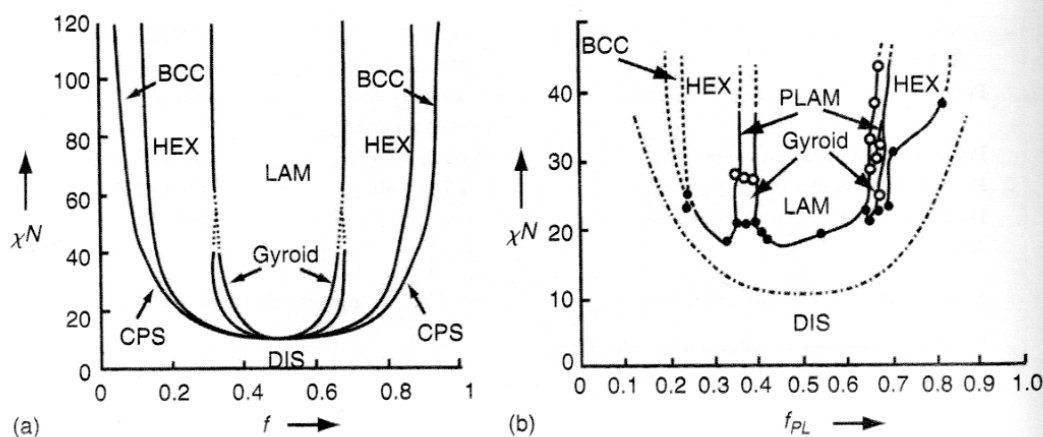


FIGURE 5.11 Theoretical (a) and experimental phase diagram (b) for block copolymers. Various self-organized morphologies can be obtained through variation of the block length, f and the segregation parameter, χN . (Adopted from (a) Foster, S., Khandpur, A.K., Zhou, J., Bates, F.S., Hamley, I.W., Ryan, A.J., and Bras, W., *Macromolecules*, 27, 6922, 1994. With permission. (b) Khandpur, A.K., Foster, S., Bates, F.S., Hamley, I.W., Ryan, A.J., Bras, W., Almdal, K., and Mortensen, K., *Macromolecules*, 28, 8796, 1995. With permission.)

experimentally observed phase diagram of a typical diblock copolymer, PS-PI, is also shown in the same figure (Figure 5.11b) [180,181]. The phase diagram exhibits several regimes of the phase segregation. For any fixed value of f , with increase in χN , one passes through a disordered regime, where the melt exhibits a disordered state, to a weak segregation regime (WSR), to an intermediate segregation regime, to finally the strong segregation regime (SSR). The sizes of the A- and B-rich domains in WSR are of the same order as the interfacial regions around the bonding points, and in SSR the domain size is much larger than the interfacial length. Thus, from the thermodynamic concept there are two limits: the strong segregation limit (SSL) and weak segregation limit (WSL). In SSL, the equilibrium state of the material consists of relatively pure phase of A separated from relatively pure phase of B (ordered state). In the WSL, the two phases are intimately mixed. The transition from the disordered state (WSL) to ordered state (SSL) is known as microphase separation transition (MST) or order-disorder transition (ODT) and the reverse is called microphase dissolution [179,182,183]. The rich polymorphism near the ODT in WSL, where $\chi N \sim 10$, is remarkable (Figure 5.11b). In SSL, at large values of χN , limited morphologies are stable. In diblock copolymers the microdomain structures formed can be controlled in a systematic fashion between 10 and 200 nm depending on the composition, molecular dimension, and architecture.

Microdomain structure is a consequence of microphase separation. It is associated with processability and performance of block copolymer as TPE, pressure sensitive adhesive, etc. The size of the domain decreases as temperature increases [184,185]. At processing temperature they are in a disordered state, melt viscosity becomes low with great advantage in processability. At service temperature, they are in ordered state and the dispersed domain of plastic blocks acts as reinforcing filler for the matrix polymer [186]. This transition is a thermodynamic transition and is controlled by counterbalanced physical factors, e.g., energetics and entropy.

Figure 5.12 schematically depicts the transition in "AB" diblocks. As the percentage of "A" hard block increases, the equilibrium morphology changes from body-centered cube (BCC) to hexagonally packed cylinder (HEX) to lamellar morphology (LAM) according to the sequence shown. Besides these simple morphology various complex minimal surfaces (gyroid, F-surface, P-surface), simple modulated lamellae (MLAM), and perforated lamellae (PLAM) are also observed in many specific diblock copolymers (Figure 5.11). However, this is also to note that the self-organization in block copolymer is a spontaneous process based on the information intrinsic to the assembling unit; and the complexity and multiplicity of the morphology increases with the number of blocks present in the copolymer. The complexity of the morphological states will increase even further if one of the synthetic blocks in the multiblock copolymer is replaced by protein-peptide segments (Figure 5.13) [123,187]. To understand the availability of the numerous morphological organizations available in multiblock complex materials, significant research efforts need to be dedicated in the area.

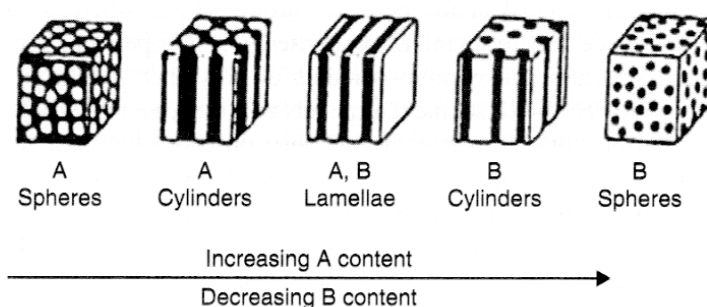


FIGURE 5.12 Change in the morphology of an A-B-A block copolymer as a function of composition. (From Walker, M. and Rader, C.P. (eds.), *Handbook of Thermoplastic Elastomers*, Van Nostrand Reinhold, New York, 1988.)

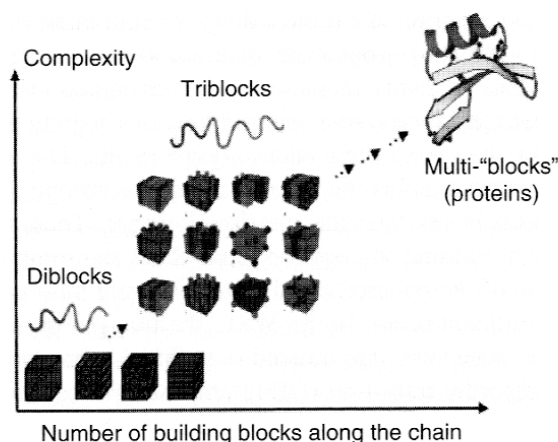


FIGURE 5.13 Complexity diagram for block copolymers. (Adapted from Morton, M., *Thermoplastic Elastomer: A Comprehensive Review*, Legge, N.R., Holden, G., and Schroeder, H.E. (eds.), Hanser, Munich, 1987 and Simon, P.F.W., Ulrich, R., Spiess, H.W., and Wiesner, U., *Chem. Mater.*, 13, 3464, 2001. With permission.)

5.7 PROPERTIES OF THERMOPLASTIC ELASTOMERS

5.7.1 FACTORS INFLUENCING THE PROPERTIES

Since TPEs typically consist of two incompatible phases at service temperature, the final properties of TPEs are influenced by the properties of the individual phases and the interface. It is therefore necessary to consider several factors, like the constituents' nature, their molecular weight and relative amounts, processing history, etc., to understand the properties of TPE. The influences of various factors on TPEs' properties are discussed below.

5.7.1.1 Constituents of Thermoplastic Elastomers

The constituents of the TPEs play a vital role in determining the properties. In triblock ABA-type copolymer, the change in the center-block or the end-block results in difference in properties. In SIS, where isoprene is the center-block, the tensile strength does not vary with the styrene content, whereas in SBS, it does so with the styrene content. Despite the fact that T_g s for butadiene and isoprene segments are different, no marked effect due to this difference is observed in room temperature properties of the triblock TPEs [188]. However, substitution of α -methyl styrene gives rise to a tougher polymer that is partly due to higher T_g values of this block. This emphasizes the major role of the hard phase on the mechanical properties of TPEs. For segmented TPEs, e.g., COPE, TPU, and for blends, changing hard segment type will affect the crystallinity of the hard phase. In TPUs, symmetric diisocyanates produce strong TPEs, whereas substituents on the aromatic ring tend to reduce the mechanical properties. The properties of polyether–polyester rubbers depend on the structure and relative amounts of polyether soft segments and polyester soft segments used [189]. The soft segment type also influences the driving force for phase separation and hence the physical properties. It has been observed that soft segments, which are capable of strain crystallizing, produce tough material with higher tensile strength and tear resistance. Improved phase separation does not necessarily lead to improved properties. Though polyester-based materials do not show complete phase separation as both polyether [190] and polybutadiene soft segments [191] do, yet the polyester-based materials show better mechanical properties. The reason is the poor interfacial adhesion [192].

5.7.1.2 Molecular Weight

The properties of TPUs, COPEs, and TPAs are also influenced by the molecular weight and molecular weight distribution, e.g., molecular weight influences the kinetics of phase separation,

which affect the mechanical properties. Increasing the molecular weight of the soft segment promotes phase separation in block copolymers during polymerization, which will reduce the fractional conversion. Soft segment with average molecular weight between 1000 and 5000 Dalton gives materials with optimum properties, below which adequate phase separation is not possible. Moreover, low-molecular-weight material does not allow strain crystallization of soft segment that imparts the strengthening process. The effect of hard segment block length is also important. The longer blocks lead to phase separation and better properties. Apostolov and Fakirov [193] studied the effect of block length on the deformation behavior of polyether esters by SAXS. The overall molecular weight of TPE has little effect on mechanical properties, provided it is greater than the threshold value. However, soft segment polydispersity does not remarkably alter the physical properties. Monodispersed hard segments give higher modulus and tensile strength presumably because of better packing of hard segments and improved phase separation [194].

Recently, Tong et al. [195] have shown that in methyl methacrylate-*b*-alkyl acrylate-*b*-methyl methacrylate (MAM) and SIS-type triblock copolymers, the ultimate tensile strength is inversely proportional to the molecular weight between the chain entanglements in the middle soft block at comparable proportion of the outer block.

5.7.1.3 Relative Amount of Hard and Soft Segments

The relative proportion of hard and soft segments is an important factor that decides whether the elastic properties of a TPE would be more close to those of cross-linked elastomer or of hard plastics. The material changes from a flexible elastic rubber to semirigid plastic with increasing hard segment content and at very high level of the hard segments the materials behave more like toughened plastic. Therefore, TPE features are obtained within certain composition range of the components. In case of multiblock-segmented block copolymers (like COPE, TPU, COPA, etc.), the performance characteristics of TPE depend on the weight fraction of crystallinity of hard phase and its T_m . Crystallinity affords a mean for rather large deformation in hard phase. The useful temperature range for a TPE is between T_m and T_g . Within this range it is elastomeric, below which it is brittle and above which the hard phase melts. Passage from T_g to T_m is reversible. The elastic properties of a TPE blend, e.g., Youngs and shear moduli are functions of elastic properties of the components. Strength of the hard phase represents limit for strength of such blend.

5.7.1.4 Effect of Processing

The conditions applied during processing and fabrication of TPEs strongly influence their morphological features and hence their final properties. ABA-type materials often show marked difference in the shape and orientation of the hard domains between the samples prepared by extrusion and film casting from solution. For example, SBS block copolymers when cast from solution usually show spherical shape of the dispersed PS domains with no orientation, whereas the same materials when extruded develop cylindrical nature of the PS domain with preferred orientation in the direction of flow. This results in highly anisotropic mechanical properties in the latter [133]. The rapid cooling of the melt after processing cycles freezes the structures induced in the melt by shear stresses. Arcozzi et al. [196] investigated the correlation between physical properties and processing condition on a styrene-butadiene block copolymer under different molding conditions. If unidirectional shear strains are frozen into the polymer as in injection and extrusion molding, the material will be anisotropic due to statistically fibrillar structure. If the shear strains applied are high enough, the domain structure is fine textured, an isotropic article will be produced, e.g., injection molding. If nondirectional shear strains are frozen into the material, the material will be isotropic.

5.7.2 GENERAL PROPERTIES

The majority of TPEs function as rubber at temperature as low as -40°C or even lower as measured by their brittle point. The upper temperature limit is determined by the maximum temperature at which it can give satisfactory retention of tensile stress-strain and hardness properties. Table 5.14a

TABLE 5.14a
Key Properties of Generic Classes of Thermoplastic Elastomers

Property	Styrenic	Copolyester COPE	Polyurethane TPU	Polyimide TPA	TPO	EA Two Phase	EA Single Phase	Ionomer
Specific gravity	0.9-1.1	1.1-1.3	1.1-1.3	1.0-1.2	0.89-1.0	0.94-1.0	1.2-1.3	0.95-1.95
Hardness, Shore	30A-75D	35A-72D	60A-55D	75A-65D	60A-75D	55A-50D	55A-80A	49A-90A
Low-temperature (continuous) limit (°C)	-70	-65	-50	-40	-60	-60	-40	-57
High-temperature limit (°C)	100	125	120	170	120	135	125	180
Compression set resistance at 100°C	P	F	F/G	F/G	P	G/E	F	G
Resistance to aqueous fluid	G/E	P/G	F/G	F/G	G/E	G/E	F/G	F/G
Resistance to hydrocarbon fluid	P	G/E	F/E	G/E	P	F/E	G/E	G

Source: Arnold, R.L. and Rader, C.P., *Handbook of Plastics, Elastomers and Composites*, Harper, C.A., ed., McGraw-Hill, New York, 1992. With permission.

Note: P, poor; F, fair; G, good; E, excellent.

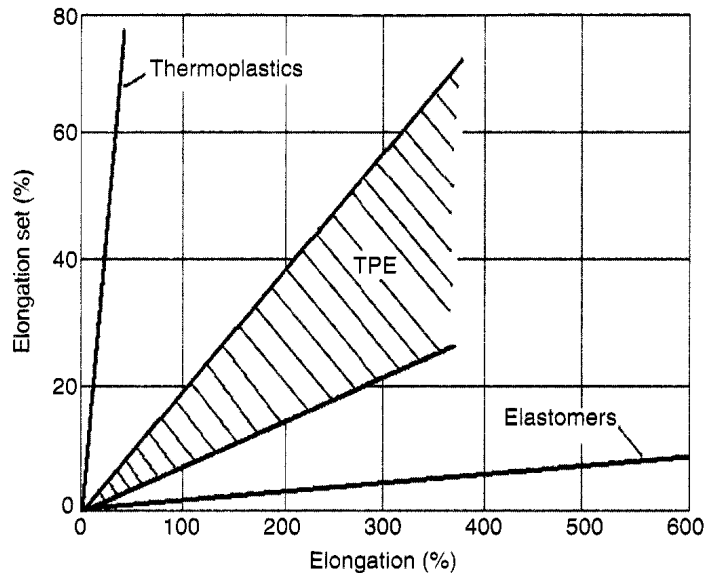


FIGURE 5.14 Elongation set properties of elastomers, thermoplastic elastomers (TPEs), and thermoplastics. (From Hofmann, W., *Kunststoffe*, 77, 767, 1987.)

reports various properties of different TPEs. The upper service temperature increases with cost. Styrenics with saturated soft block have higher heat resistance than those with diene soft blocks. Elastomeric alloys from saturated elastomer give better high-temperature performance characteristics than those from an unsaturated elastomer backbone. TPEs generally extend to high elongation and often in some cases with residual elongation or permanent set. Their set properties are in between elastomers and thermoplastics as shown in Figure 5.14. TPEs, toward the bottom of the curve scattered ranges, are close to elastomers and those toward the top are close to thermoplastics. Mullins effect or stress softening [197] occurs in most TPEs. Choudhury and Bhowmick [198] have observed a stress softening and strain hardening in NR-PE elastomeric alloys. This phenomenon occurs presumably because of two irreversible effects: (1) breakdown of weaker points of continuous hard or glassy phase and (2) orientation of the hard phase in the stretching direction. Pedemonte et al. [199] have reported similar stress softening and strain hardening behavior of thermoplastic block copolymers. A model proposed by the same authors explains that strain hardening is a result of interaction of rigid plastic domain.

In TPE, the hard domains can act both as filler and intermolecular tie points; thus, the toughness results from the inhibition of catastrophic failure from slow crack growth. Hard domains are effective fillers above a volume fraction of 0.2 and a size <100 nm [200]. The fracture energy of TPE is characteristic of the materials and independent of the test methods as observed for rubbers. It is, however, not a single-valued property and depends on the rate of tearing and test temperature [201]. The stress-strain properties of most TPEs have been described by the empirical Mooney-Rivlin equation

$$\sigma = (\rho RT/M_c + 2C_2/\lambda)(\lambda - 1/\lambda^2) \quad (5.1)$$

where

σ = stress

R = gas constant

T = temperature

C_2 = experimental constant

M_c = molecular weight between cross-links

λ = extension ratio

Swelling data and stress-strain results in SBS have shown that M_c is approximately the molecular weight between entanglements. Choudhury and Bhowmick [201] have shown in the case of different NR-based TPEs the following relation:

$$\sigma' \propto E \quad \text{and} \quad (1 + e_{\text{bmax}})^2 \propto 1/E \quad (5.2)$$

$$(1 + e_{\text{bmax}}) \propto M_c^{1/2} \quad (5.3)$$

where

M_c = the cross-link density of melt

σ' = stress

E = modulus

e_{bmax} = maximum elongation

When plastics act as a physical cross-link and strength properties are indirectly related to the modulus of hard phase and morphology of the blend, the filler effect is analyzed by the following equation:

$$E_F/E = (1 + 2.5\phi + 14.1\phi^2) \quad (5.4)$$

where

E_F/E = modulus of filler/modulus of unfilled elastomer

ϕ = volume fraction of filler

The above equations gave reasonably reliable M_c value of SBS. Another approach to modeling the elastic behavior of SBS triblock copolymer has been developed [202]. The first one, the simple model, is obtained by a modification of classical rubber elasticity theory to account for the filler effect of the domain. The major objection was the simple application of rubber elasticity theory to block copolymers without considering the effect of the domain on the distribution function of the rubber matrix chain. In the derivation of classical equation of rubber elasticity, it is assumed that the chain has Gaussian distribution function. The use of this distribution function considers that all spaces are accessible to a given chain. However, that is not the case of TPEs because the domain also takes up space in block copolymers.

Another comprehensive model [202] accounts for a possible contribution from trapped entanglement to the equilibrium elastic behavior, in addition to the factors considered by the other models. Inclusion of trapped entanglement causes the modulus to increase an order of magnitude than considering only the domains as cross-links. Hergenrother and Doshak [203] have reported the determination of the entanglement molecular weight of TPE (triblock copolymer) by tensile retraction measurement. Origin of rubber elasticity in EAs has been modeled by Kikuchi et al. [204] in the two-dimensional model with many rubber inclusions in ductile matrix. Finite element method (FEM) of the elastic plastic analysis on the deformation mechanism revealed that even at the highly deformed state at which almost whole matrix has been yielded by stress concentration, the ligament matrix between rubber inclusion in stretching direction is locally preserved within an elastic limit and it acts as an *in situ* formed adhesive for inter-connecting the two phase systems and also provides a key mechanism of strain recovery in the two phase systems.

The typical tensile behavior of TPE, with change in temperature, could be best represented by single parabolic curve, "Failure envelop." Figure 5.15 shows such a curve for NR-PE system. There are two extremes—one corresponds to an increase in strength with increase in breaking extension at higher temperature and low strain rates and the other showing high breaking strength and low extensibility. As the temperature rises in TPE, modulus and strength decrease due to softening of hard domain, in the vicinity of softening point, the properties decrease dramatically and

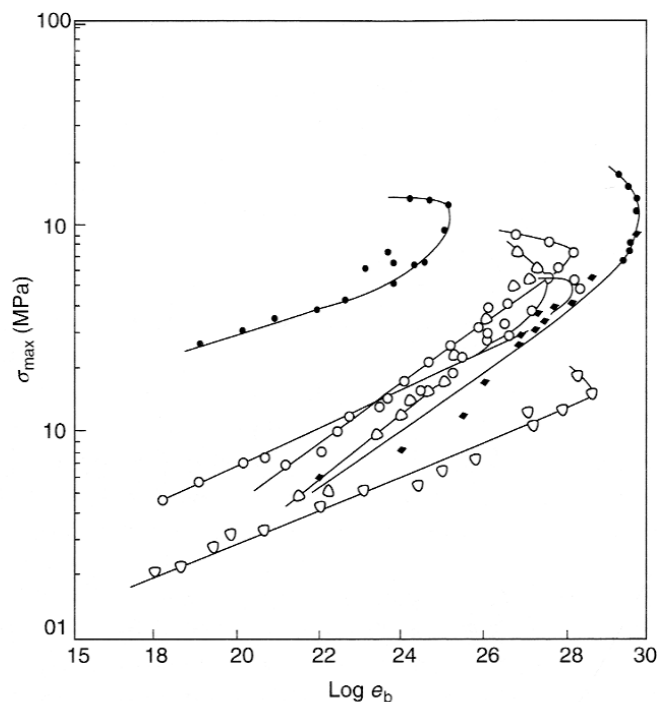


FIGURE 5.15 “Failure envelope” of various mixes: Δ , natural rubber–polyethylene (NR–PE) vulcanizate (peroxide cured); $\bullet$, NR–PE vulcanizate (sulfur cured); $\square$, NR–PE vulcanizate with CPE as compatibilizer; ∇ , EPDM–PE vulcanizate; $\circ$, EPDM–PP vulcanizate (sulfur cured); $\bullet$, NR–ENR–PE_m–PE. (From Roy Choudhury, N. and Bhowmick, A.K., *J. Mat. Sci.*, 25, 161, 1990. With permission from Chapman & Hall.)

the material cannot be used as TPE [205]. Additives could be added to alter this temperature, but they may influence the domain structure. Most of the TPEs are in the high rubber-hardness range (above 80 Shore A). Styrenics are available in the soft hardness range (below 55 Shore A). EA with 40 Shore A hardness has been developed. The tear strengths of COPE and TPU are excellent. COPE also offers high fatigue resistance. TPU offers very good abrasion resistance. In general, TPE will be less rubbery and more like a thermoplastic as hardness is increased. Most TPEs have fair to good compression set resistance at ambient temperature. The set properties of the styrenics and TPOs become poorer at elevated temperature. The set resistance will decrease with increase in hardness. Marasch has reported a new, relatively soft TPU (polyether-based), which is claimed to have rubber-like behavior in terms of recovery after deformation [206].

The resistance of a TPE to different chemicals is influenced greatly by its chemical similarity to the fluid. The nonpolar styrenics, TPOs, and EAs have high resistance to polar chemical. Their resistance to nonpolar hydrocarbon ranges from poor to fair. The polar COPE, TPA, and TPU have better resistance to hydrocarbon fluid, but poorer resistance to polar chemicals than that of conventional rubbers. They are also very susceptible to oxidation at elevated temperature. Antioxidant and other additives could improve the chemical resistance of these materials. The resistance to many oils and greases is high for more polar TPEs. Hydrolytic stability is poor for the polyester-based TPU and copolyamides because the ester and amide linkages can be attacked by water. The addition of small amount of 1%–2% of hindered aromatic diamide can increase the lifetime significantly in hot water or steam. Ionomers swell when exposed to water. The electrical properties of the generic classes of TPEs are listed in Table 5.14b.

The electrical properties of styrenics, TPVs, and TPOs are very good. Their nonpolar nature allows their use as a primary electrical insulation where temperature and fluid resistance are

TABLE 5.14b
Electrical Properties of Generic Classes of Thermoplastic Elastomers

Properties	Test Method	Styrenic Elexar 8421	COPE Hytrel 4056	TPU Texin 480AR	TPA Estamid 90A	TPO TPR 1600	EA, Two Phase, Santoprene 101-73/201-73	EA, Single Phase, Alcryn R12028-80A
Volume resistivity (ohm · cm)	ASTM D257	3.5×10^{16}	8.2×10^{12}	2.1×10^{12}	8.1×10^{10}	3×10^{16}	2×10^{16}	1.4×10^{10}
Surface resistivity (ohm)	ASTM D257	6.2×10^{16}	—	3.3×10^{13}	3.1×10^{12}	—	2×10^{16} (D275)	—
Dielectric constant								
60 Hz		2.4	—	6.34	10.3	2.21	—	—
1 kHz		2.4	5.1	6.08	9.3	2.22	2.95	11.1
1 MHz	ASTM D150	2.4	4.7	5.15	5.7	2.20	3.15	—
Dissipation factor								
60 Hz		0.0008	—	0.024	0.092	0.0005	—	—
1 kHz		0.0008	0.008	0.019	0.066	0.0008	0.0039	0.40
1 MHz	ASTM D150	0.0008	0.060	0.063	0.100	0.0001	0.0079	—
Dielectric strength, V/mil	ASTM D149	660	410	330	—	600	590	140

Source: Walker, B.M. and Rader, C.P. (eds.), *Handbook of Thermoplastic Elastomers*, Van Nostrand Reinhold, New York, 1988.

not very critical. These nonpolar TPEs are excellent starting materials because of their compatibility with wide variety of polymers, which provide low-cost and effective compounds. Polar TPEs, e.g., COPE, PU, and TPA, are also compatible with a wide variety of fillers, however, the modified compounds do not provide an outstanding balance of overall properties. Therefore, they have not made major penetration in stringent electrical applications compared to styrenics and TPVs.

5.8 RHEOLOGY

The melt rheological behaviors of TPEs are strongly dependent on shear rate, temperature, and the composition. TPEs exhibit wide variation in viscosity and elasticity. A wide variation in morphology (i.e., copolymers, physical blends, side-chain branching, etc.) results in semi-Newtonian to highly shear-thinning behaviors. There are fundamental differences in rheological responses between a conventional rubber and TPE. In the vicinity of T_g of a conventional rubber or T_g of the soft segment in TPEs, both are very resistant to stress and below this temperature they behave as a single-phase brittle glassy polymer. On increasing temperature, the hard domain starts weakening and flows. The melt rheology of TPE is thus related to that of hard segment and/or plastic materials. Vinogradov and coworkers [207] have reported the viscoelastic properties of SBS triblock copolymers at wide range of shear rate (hence shear stress) and their comparison with statistical copolymer and polybutadiene of comparable molecular weight. It was observed that SBS block copolymers show three distinct regions of melt flow behavior in the temperature range of 110°C–170°C. In the intermediate shear rate the block copolymers show pseudo-Newtonian flow behavior closely resembling the polybutadiene. At low and very high shear rates they show pronounced non-Newtonian flow behavior usually not observed in homopolymer or statistical copolymers. The block copolymers also show much higher melt viscosity and its dependency on temperature. The non-Newtonian behavior at low shear rate in SBS copolymer indicates its resemblance with filled polymeric system, where the dispersed filler particle shows structure formation [207]. Such unusual rheological behaviors are mostly attributed to the complex morphological features observed in triblock copolymers. The dispersed PS domains may undergo reversible breakdown or deformation under shearing at temperature close to the T_g of PS [133,207]. Such breakdown could further intensify with increase in temperature and shear rate causing significant lowering of viscosity of the material. The apparent viscosity depends strongly on the shear rate (and corresponding shear stress), which decreases sharply with shear rate (Figure 5.16). This implies that molding should be carried out at higher shear rate so that the low viscosity allows quick filling of the mold. Also parts could be removed rapidly from the mold. TPE viscosity is less sensitive to temperature than shear rate indicating the fact that input of mechanical energy is more effective during processing than the input of thermal energy. In an injection molding operation, higher injection pressure will have a significant impact on flow rate and fill time than a change in temperature. Wallace [208] has reported on the unique rheological characteristics of processing of MPR and polyolefin alloys in injection and blow moldings. Recently, Borgaonkar and Ramani [209] reported extrusion behavior of TPEs. Energy input to extrude and viscous dissipation are related to process parameters and polymer rheological characteristics. Metering zone temperature and revolutions per minute (rpm) are the most significant parameters to influencing melt temperature, extruder pressure, torque, and output.

The processing characteristics of TPE are intimately related to the ODT temperature or the MST temperature as the viscosity becomes lower above ODT. The styrene–diene triblock systems have ODTs above a reasonable processing temperature. Melt viscosities are usually higher in block copolymer than in homopolymer of the same molecular weight. Rheological measurements can give information of the ODT. Dynamic mechanical experiments are used as a macroscopic characterization of phase separation because highly phase-separated systems will have larger temperature difference between hard and soft segments and a feature plateau modulus. In one method, the

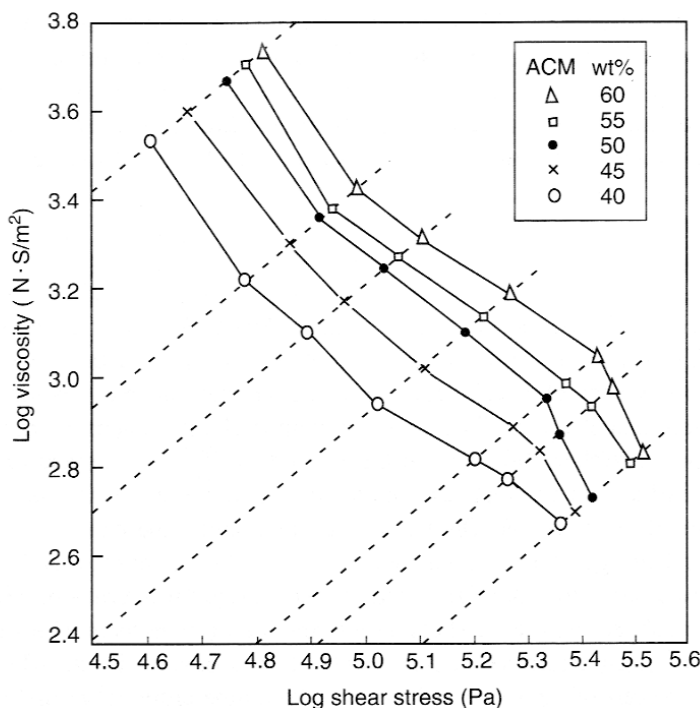


FIGURE 5.16 Viscosity-shear stress relationships for various compositions of nylon-6-acrylate rubber (ACM) blends at 240°C.

storage and loss moduli are measured as a function of frequency at different temperatures above and below ODT. The higher frequency data are put into one master plot by applying WLF equation [210]. Though WLF is not generally applicable to TPE as two phases make the material thermorheologically complex, entanglement dominates the response at higher frequency and microphase-separated nature has little influence on the rheological behavior [210]. However, below ODT, these properties are highly strain dependent. The critical frequency (ω_c) is first found out where the curves start diverging. Then, the dynamic measurements are carried out below ω_c . The temperature at which discontinuity occurs in the modulus marks the ODT as represented in the Figure 5.17. This method is based on different behaviors of storage and loss moduli at low frequencies for ordered ($G' \sim G'' \sim \omega^5$) and disorder ($G' \sim \omega^2$, $G'' \sim \omega$) systems. The most attractive property of TPEs is their ease of processing. They can be inexpensively processed into simpler or complex goods by a variety of methods. The extrusion and injection molding techniques are two of the most important processes for their fabrication. Other methods include blow molding, calendering, and solution fabrication. The saving in part fabrication cost by thermoplastic processing and from low specific gravity can often outweigh the difference in material cost of a TPE compared to a thermoset.

5.9 PROCESSING

5.9.1 DRYING

Moisture may cause both processing and aesthetic problems. So many TPE resins need to be dried before they are processed. A moisture content that is too high in molding or extruding can cause appearance of defects, such as splay marks and bubbles on the surface of the finished part. Besides, water may react with the polymer during processing, changing the physical performance of the final part. Hygroscopic polymers like polyamides, polycarbonates, polyesters, polyurethanes, etc., require careful drying prior to processing. Because of the chemical differences between SBCs,

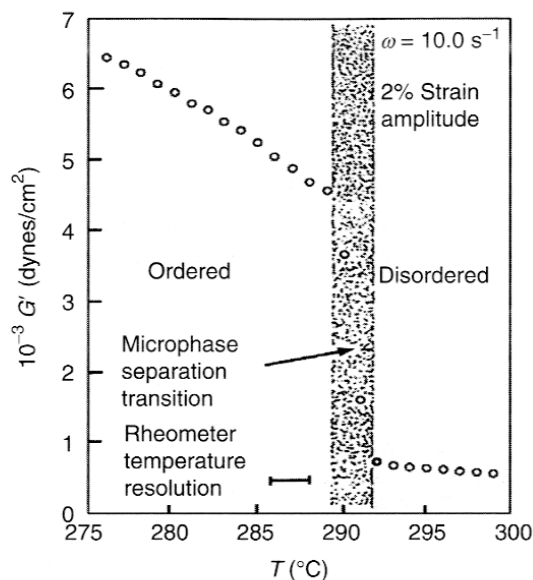


FIGURE 5.17 Temperature versus G' —the shear storage modulus at a frequency of 1.6 Hz for diblock copolymer poly(ethylene propylene)–poly(ethylethylene) (PEP–PEE). The order–disorder transition (ODT) calculated to be $291^{\circ}\text{C} \pm 1^{\circ}\text{C}$. (From Rosedale, J.H. and Bates, F.S., *Macromolecules*, 23, 2329, 1990. With permission of American Chemical Society.)

TPVs, TPUs, etc., different drying techniques are required. The drying of TPE is directly dependent upon the hygroscopic characteristics of the TPEs. TPVs, TPUs, thermoplastic polyesters, and TPAs are more hygroscopic than SBCs and recommended to be dried before processing using a desiccant drier. SBCs can be molded without drying. However, where aesthetic requirement is very stringent drying is a must [211].

5.9.2 EXTRUSION: A CONTINUOUS PROCESS

Extrusion can be used to manufacture a variety of TPE shapes, e.g., tubing, hoses, sheets, and complex profiles. A thermoplastic extruder with a screw length to diameter ratio L/D of 20:1 and preferably 24:1 to 32:1 is recommended for most TPEs since longer screw leads to better melting and mixing of polymers. Coextrusion of a TPE with a thermoplastic or another TPE is possible provided they are compatible and have melting points in the same range [212]. It is a cost-effective process by which soft TPE could be used as a sealing surface and a rigid hard plastic can act as a support. Crosshead extrusion is a popular technique of applying TPE insulating or jacketing layer on an electrical wire or cable or a cover over a reinforced hose.

5.9.2.1 Screw Design

The screw is the heart of the extruder, and screw geometry greatly affects the efficiency of extrusion. Extrusion of TPEs can be accomplished using general-purpose screws. Other aspects to be considered during extrusion are given below [213]:

1. Single-stage, three-zone, polyolefin-type metering screw
2. L/D ratio 24:1 minimum (for TPVs and SBCs)
3. L/D ratio 24:1 minimum for heavy wall extrusion (for TPUs)
4. L/D ratio 30:1 minimum for thin wall extrusion (for TPUs)
5. 2.5:1 to 3.1 compression ratio

6. Cooling at feed throat recommended
7. Screw cooling should be avoided
8. Dead or stagnation zones with that flat plate dies should be avoided

Screws having equal length of feed, compression, and metering zones are very popular in extruding TPEs. However, it is always advisable to use the suitable design for different goods. A variety of screw designs—polyolefin type, flighted barrier, pin mixing, and Maddock mixing—have been used. For even mold flow and clean melt stream, screen packs of 20–40–60 mesh are used.

5.9.2.2 Die Design

The main design criteria of most TPE dies are to ensure that changes in flow channel diameter from the extruder barrel bore to the die exit are equal. Most of the viscoelastic materials exhibit a die swell on exit from a die. TPEs tend to show die swell significantly lower than that of typical thermoplastics. This swell must be taken into consideration in designing dies and adjusting extrusion condition to achieve a perfect profile. The die swell normally increases with increasing hardness and shear rate and decreasing temperature.

5.9.2.3 Temperature Profile

The temperature has a strong influence on the viscosity of the melt, so its fluctuation should be kept in a narrow range to obtain good extrudate. The polymer melt temperature should be kept at about 30°C–70°C above the melting point of TPE. In general, the temperature profile for extrusion gradually increases from the feeding zone to compression zone and then gradually drops off in the metering zone. The die is kept at polymer melt temperature.

5.9.3 INJECTION MOLDING

Injection molding is the most widely used process for fabricating TPE parts [214]. It fully exploits the processing advantages of thermoplastics. Elimination of scrap and short cycles of this molding outweighs the higher material cost of TPE compared to a thermoset. TPEs can be molded in the same type of machine as used for conventional thermoplastics. Although ram injection molding has been successfully used for some TPEs, conventional reciprocating screw injection machines for these types of materials are recommended. The operating temperature for processing normally lies in the range of 20°C–50°C above the melting point of the TPE to allow adequate mold packing and minimum shrinkage. Good mold packing will give shrinkage as low as 1%–2.5% for most TPEs.

5.9.3.1 Injection Pressure and Rate

Too high or too low injection pressure will cause overfilling or incomplete filling of the mold, respectively. The typical injection pressure is kept in the medium range (34.5–103.4 MPa) for rapid mold filling. However, the hold pressure is kept at nearly half of the first stage injection pressure, for a period of 1–10 s to allow gate freeze off. The rate of injection depends mainly on the configuration of the part. Thicker parts require a slower speed whereas thinner sections require faster injection.

5.9.3.2 Screw Speed and Back Pressure

TPEs are quite fluid at shear rate above 500 s⁻¹. A moderate speed is always preferred. A screw-back pressure below 1.38 MPa is sufficient for homogenization.

5.9.3.3 Mold Temperature and Cycle Time

Mold temperature and cycle time vary with part thickness, part configuration, and hardness and the temperature is kept normally in the range of 40°C–60°C. Proper mold temperature will ensure

proper release of parts. The harder the TPE, shorter is the cycle time; thicker and complicated the part, longer is the cycle time. The cycle time contributes to the cost calculation of the molding application.

5.9.3.4 Part Design and Mold Design Considerations

In addition to the process parameters, there are large numbers of factors that decide the success of an injection molding operation. Mold design, product design, position, and size of gates, type and positioning of runners, etc., are extremely important factors to be taken care of. A detail consideration regarding these factors has been discussed below [213].

Mold Type

Two- and three-plate mold designs are commonly used for TPEs. Hot runner tools and stack molds may also be used. Molds made of metal with high thermal conductivities enable TPEs to achieve shorter cycle times when compared to lower thermal conductivity molds. For prototyping and limited-use tools, aluminum molds are suitable. Beryllium copper molds are preferred over steel for blow molds and some injection molds because of their higher heat conductivity. Prehardened steel (P20) injection molds are very durable and have low part cost for long run. Posthardened and ground molds have the highest durability for extended usage. TPEs can have a high coefficient of friction to most tooling materials and will tend to stick in nondrafted cavities and shrink onto long cores. TPEs release better from sand-blasted or EDM tool surfaces. Good results have been achieved with steel shot blasted surfaces. High draft (over 3° per side) may be helpful, or a release coating on the mold may be necessary. Teflon or molybdenum disulfide-type impregnated mold coatings offer some aid with softer TPEs.

Part Design

To meet the products' functional needs the wall thickness of the part can be varied. However, to obtain optimum processing cycles and reduce the chance of sink- and flow-mark formation, wall thickness should be kept as uniform as possible. Where variation in wall thickness is unavoidable, gradual transitions in the wall thickness should be provided to ease the polymer melt flow transitions. Part design, mold design, and gate location should work together to allow the material from heavier section into thinner walls for best appearance and process latitude.

Gate Design and Location

SBCs and TPVs are shear-thinning materials. Therefore, as such they are benefited from the flow restrictions at the entry of molds and this allows the provision for small diameter, short landed gates. For TPVs and SBCs, it is suggested that gates should be 20%–30% of the wall thickness of the part to be filled.

TPUs are not shear thinning and so gates with generous cross-sectional area allow the material to flow freely with minimum pressure loss. Usually, gate size should be 50% of the thickest section of the part. Fan gates and tab gates are the most, and pin gates are the least, suitable for TPU processing. The land length for gates should be kept as short as possible.

Common problems like insufficient filling–packing and poor dimensional control are often related to the gate size and design. Similarly, gate location is another important factor. They should be located in areas having heaviest cross-section of the part to assure fill-out and elimination of sink marks. Also their position should not facilitate the residual molded stress formation in the part, knit line formation.

Runners and Sprues

Full round, trapezoidal, or modified-trapezoidal runners are preferred for TPE processing, while half round runners give poor results. The length of the runners should be kept as short as possible. Hot runner systems using valve gates are typically used to reduce both gate freezing and cycle time. Cold slug catchers should be placed at all runner transition. The sprue should be as short as possible and polished in the direction of ejection. Hot sprue bushings are often used to reduce cycle time and

eliminate sprue sticking with softer grades of TPEs. For harder grades of TPEs tapered cone, “Z” pullers and “Christmas tree” sprue pullers are used depending upon grades and hardness [214].

5.9.4 BLOW MOLDING

By using injection and extrusion blow moldings, hollow and thin parts could be uniquely manufactured from TPEs [215,216]. Blow molding cannot be used for conventional thermoset rubber. Injection blow molding is a capital-intensive process whereas extrusion is the simpler process. The blow ratio (cavity diameter/parison diameter) of TPEs may be limited and parison diameter should be as large as possible related to mold cavity. Because of high viscosity at low shear rates, TPE melt retains their shapes in parison prior to blowing. The processing temperature, in the same range of extrusion or injection, is normally used. Cycle time is 10–240 s and could be reduced by rapid water circulation in the mold. Cakmak and Wang [217] reported that the tubular blown film of PP-EPDM elastomeric alloys exhibits complex superstructural behavior. The inner surface appears relatively featureless, while the outer surface exhibits bundle-like fibrillar structure probably due to rapid cooling of this surface during processing. The various technological advances in the blow molding of TPE have been discussed by Rader et al. [215].

5.9.5 OTHER FABRICATION METHODS

5.9.5.1 Thermoforming

TPEs in comparison to thermoset are also suited for thermoforming, which is a fast, low-cost production. The maximum draw ratio decreases with decrease in hardness. Draw ratio up to 0.1 can be attained with TPEs in the hardness range of 40–50 Shore D. The major limitations are to avoid undercut sharp corners, and adequate taper angle for rapid ejection of parts.

5.9.5.2 Foam Preparation

TPEs have been applied with considerable success in foaming extruded profiles, tubings, and sheeting with a thin solid skin over closed cell interior foam. TPVs could be foamed by water injection, compounded chemical blowing agent, and dry blended chemical blowing agents. SBC foams are made by dry blending chemical blowing agents and gas injection. Chemical foaming agent (azodicarbonamides) can reduce the bulk specific gravity of extrudates from 1.0 to 0.7 and physical blowing agents, e.g., fluorocarbons can lower down to even further about 0.3. Die swell in TPE foam extrusion is 10–50 times than that in dense TPE.

5.9.5.3 Combining TPEs with Other Materials: Bonding and Overmolding

TPEs are often employed to produce a resilient and soft ergonomic layer over a hard structural part. This could be done in a number of ways [213]. TPEs can also be overmolded onto an engineering material through insert molding or multiple-shot injection molding.

Bonding

TPEs can be bonded to other materials by adhesive, heat bonding, electromagnetic filling, radio frequency, heat-sealing lamination, friction and spin welding, and ultrasonic welding. For TPUs, the most widely used techniques are radio frequencies, and ultrasonic and hot stamping. A few typical applications include football bladders, valves, and conveyor belts.

Overmolding

Overmolding is the process by which two different materials are joined into one assembly without using secondary operations like gluing or welding. In case the materials are chemically compatible, chemical bonds may form between them and so mechanical interlocks are not required. There are two common techniques of overmolding—insert molding and multiple-shot injection molding.