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Thermoplastic Elastomers

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1. Introduction

An elastomer is defined by mechanical response not by chemical structure. Elastomers comprise a diverse range of chemical structures although they are characterized as having weak intermolecular forces. An elastomer will undergo an immediate, linear and reversible response to high strain to an applied force. This response has a mechanical analogy with a spring according to Hooke's Law. Non-linear, time dependent mechanical response is distinguished as viscoelasticity according to the parallel spring and dashpot model. Time dependent irreversible response is a viscous response according to a dashpot model. An ideal elastomer will only exhibit an elastic response. Real elastomers exhibit a predominantly elastic response, however they also exhibit viscoelastic and elastic responses especially at higher strains.

The chemical structure and molecular architecture of elastomers is tightly related to elastomeric mechanical response. High strain requires a polymer with high molar mass preferred. Many materials can exhibit an elastic response, that is immediate, reversible and linear strain with stress, however only a polymer can exhibit additionally high strain. High strain is due to uncoiling of random molecular coils into more linear conformations. The limit to elastic response is when molecules are in fully extended conformations. This mechanism is due to uncoiling of chain segments. Molecules do not move relative to each other, there are reversible random coiling not translational motions.

Reversibility and immediate response is obtained with macromolecules that have flexible chains with weak intermolecular forces. Rigid groups such as benzene, bulky side-chains such as isopropyl, polar groups such as ester and hydrogen bonding groups such as hydroxy are not desirable if a polymer is to be an elastomer. This description supposes elastomeric properties at ambient temperatures, since at elevated temperatures above the glass transition temperature many polymers become elastomers.

At high extensions and when under strain for longer times viscous flow occurs, known as creep when over longer times. Chemical cross-linking prevents viscous flow, the movement of molecules relative to each other. Elastomers are cross-linked after moulding or shaping to fix molecules into their relative positions. Once cross-linked the unstrained shape of an elastomer cannot be altered and the elastomer cannot be reprocessed or recycled. The permanence brought about by cross-linking and the need to perform a cross-linking reaction on elastomers are disadvantages for their applications.

2. Thermoplastic elastomer

A thermoplastic elastomer has all the same features as described for an elastomer except that chemical cross-linking is replaced by a network of physical cross-links. The ability to form physical cross-links is the opposite to the chemical and structural requirements of an elastomer just described. The answer to this dilemma is that thermoplastic elastomers must be two-phase materials, and each molecule must consist of two opposite types of structure, one the elastomeric part and the second the restraining, physical cross-linking part. Thermoplastic elastomers are typically block copolymers.

The elastic block should have high molar mass and possess all of the others characteristic required of an elastomer. The restraining block should resist viscous flow and creep. One restraining block can be used per macromolecule, giving a diblock copolymer (AB), or one restraint block at each of the elastomer can be used giving a triblock copolymer (ABA). Specific polymers will be described in the context of these general principles in the following sections. To provide an example of thermoplastic elastomer block copolymer structures the monomers butadiene and styrene are chosen.

Elastomer Type	Soft phase, T_g (°C)	Hard phase, T_g or T_m (°C)
SBS	-90	95 (T_g)
SIS	-60	95 (T_g)
SEBS	-55	95 (T_g) and 165 (T_m) ^a
SIBS	-60	95 (T_g) and 165 (T_m)
Polyurethane elastomers	-40 to -60 ^b	190 (T_m)
Polyester elastomers	-40	185 to 220 (T_m)
Polyamide elastomers	-40 to -60 ^b	220 to 275 (T_m)
Polyethylene-poly(-olefin)	-50	70 (T_m) ^c
Polypropylene/poly(ethylene-propylene)	-50	50 to 70 (T_m) ^c
Poly(etherimide)-polysiloxane	-60	225 (T_g)
Polypropylene/hydrocarbon rubber ^d	-60	165 (T_m)
Polypropylene/nitrile rubber	-40	165 (T_m)
PVC-(nitrile rubber+DOP)	-30	80 (T_g) and 210 (T_m)
Polypropylene/poly(butylacrylate)	-50	165 (T_m)
Polyamide or polyester/silicone rubber	-85	225 to 250 (T_m)

Notes:

^aIn blends containing polypropylene

^bThe values are for polyester and polyether respectively

^cThe values are presumably the result of the short length of polyethylene and polypropylene segments

^dEPDM, EPR, butyl rubber and natural rubber

Source: Holden, 2011; Drobny, 2007

Table 1. Glass transition and crystalline melt temperatures of major TPEs

Polymerisation of butadiene via 1,4-addition gives the elastomer poly(1,4-butadiene). This polymer is a hydrocarbon with low intermolecular forces, no rigid or bulky groups and a relatively flexible chain, except for the double bond between carbons 2-3. The cis stereoisomer of the double bond is preferred over trans since this decreases chain regularity.

The transform is more regular and crystallinity can occur, which will prevent elastomeric response. Poly(butadiene) would need to be cross-linked to be a useful elastomer. Polystyrene is a glassy polymer with glass transition temperature ≈ 100 °C so it will resist flow and creep at ambient temperatures, but it can flow and be moulded at temperatures above T_g . A diblock copolymer of butadiene and styrene will provide the combination of properties required for a thermoplastic elastomer when the butadiene content is higher. Poly(butadiene-*b*-styrene) (BS) has two separate phases, a continuous polybutadiene phase with dispersed poly(styrene) phase. The matrix phase gives the overall elastomeric response while the dispersed islands are the restraining physical cross-links. Glass transition and crystalline melt temperatures for major TPEs are given in Table 1.

3. Thermodynamics of elasticity

Elastomers extend and contract by conformational change from a compact random coil to extended chain. The random coil can have many possible conformations resulting in a high entropy. A fully extended chain can only have one conformation resulting in low entropy. The extended chain will spontaneously contract into a random coil since the entropy of the process is favourable. Enthalpy is not a contributor for an ideal elastomer since intermolecular forces are minimal. Entropy is overcome by a mechanical force deforming the elastomer. Thermodynamic equations are applied to elastomeric deformation and recovery. By analogy with an ideal gas, elastomers that conform to the thermodynamics are called ideal elastomers. As in the case of real gases, real elastomers deviate from ideality.

Deviations of elastomers are the result of:

- At high extensions elastomer chains become fully extended between cross-links, chemical or physical, and as the distribution of chains become fully extended the stress-strain response becomes non-linear.
- At high extensions the extended chains can pack closely forming crystals that cannot be further extended. Crystallisation appears as stress whitening and it is only maintained with the deforming force since the intermolecular interactions are too weak to prevent entropy-controlled recovery.
- Molecular entanglements prevent free molecular uncoiling and therefore cause deviation from a linear elastic response. Often entanglement caused deviations are more pronounced in a first extension-recovery cycle that differs from subsequent cycles when performed together.
- In compression deviations from ideality are caused by the finite size of the molecules and the limited free volume available for molecules to occupy.

The aim of this review is to compile the updated knowledge on thermoplastic elastomers in general, practically their structures, syntheses, processing methods, mechanical properties and applications.

4. Structure of thermoplastic elastomers

Thermoplastic elastomers (TPEs) are defined as a group of polymers that exhibit instantaneous reversible deformation (to be an elastomer). Most of the TPEs consist of continuous phase that exhibit elastic behaviour and dispersed phase that represents the

physical crosslinks. If the dispersed phase is elastic then the polymer is a toughened thermoplastic, not an elastomer. Elastomer reversibility must have physical cross-links, therefore these crosslinks must be reversible. Physical crosslinks do not exist permanently and may disappear with the increase of temperature.

Generally, thermoplastic elastomers can be categorized into two groups: multi-block copolymers and blends. The first group is copolymers consist of soft elastomers and hard thermoplastic blocks, such as styrenic block copolymers (SBCs), polyamide/elastomer block copolymers (COPAs), polyether ester/elastomer block copolymers (COPEs) and polyurethane/elastomer block copolymers (TPUs). TPE blends can be divided into polyolefin blends (TPOs) and dynamically vulcanized blends (TPVs).

Thermoplastic elastomers are known as two-phase system consisting of rubbery elastomeric (soft) component and rigid (hard) component. The soft phase can be polybutadiene, poly(ethylene-*co*-alkene), polyisobutylene, poly(oxyethylene), poly(ester), polysiloxane or any of the typical elastomers while the hard phase are polystyrene, poly(methyl methacrylate), urethane, ionomer - poly(ethylene-*co*-acrylic acid) (sodium, Mg, Zn salt), ethylene propylene diene monomer, and fluoropolymers. The structure representing a styrenic TPE is shown schematically in Figure 1.

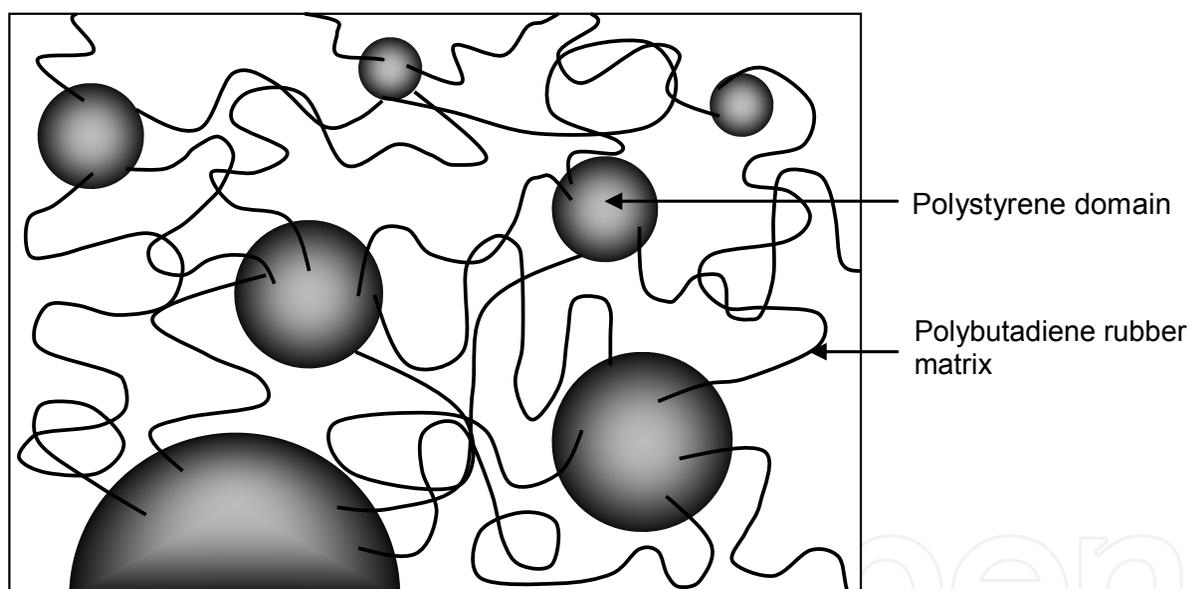


Fig. 1. Schematic of a styrene-butadiene-styrene block copolymer

5. Synthesis of thermoplastic elastomers

TPEs are two phase polymers, however they can be synthesised in one reaction step or in two or three steps to create each phase separately.

5.1 One-step methods

One-shot method is a commonly used industrial technique to prepare polyurethanes. The urethane reaction involves a diisocyanate (hard segment) and a diol (soft segment) (see Figure 2). Generally two diols are required, a chain extender or short chain diol and an

elastomeric hydroxyl terminated polymer. Examples of a diisocyanate are methane 4,4'-diphenyl diisocyanate (MDI), 2,4- and 2,6-toluene diisocyanate (TDI) and 1,6-hexane diisocyanate (HDI). A chain extender may be 1,4-butanediol. When MDI and butanediol react they form a polyurethane with alternating monomer units connected by urethane groups, though other functional groups also form as by products of the reaction. This polyurethane is not elastomeric and it constitutes the hard phase of a typical TPU. Hydroxyl terminated elastomers include polyethers: poly(oxyethylene), poly(oxybutylene), polyesters: poly(ethylene succinate), poly(butylene succinate), poly(ethylene adipate), poly(butylene), hydroxyl terminated polybutadiene and hydroxyl terminated poly(butadiene-co-acrylonitrile).

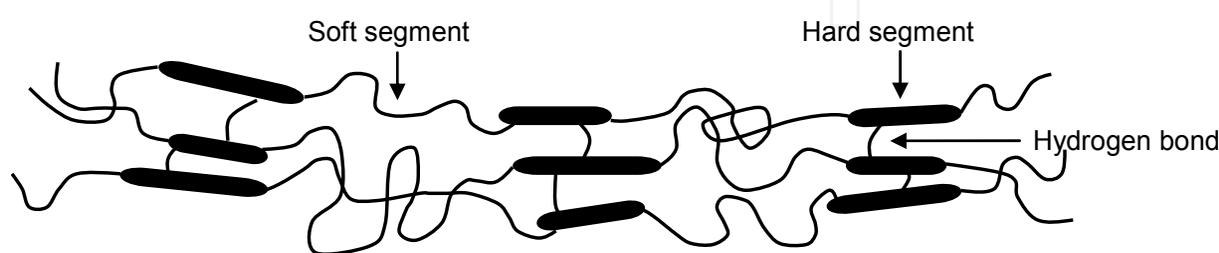


Fig. 2. Schematic representation of TPUs composed of alternating hard segment and soft segment structures

These polymeric diols react with isocyanate and are linked into the TPU as a complete elastomer block. The hard and soft (elastomeric) chain segments phase separate with the hard segments as a dispersed minor phase, since the soft segments must form a continuous phase if elastomeric properties are to be displayed. The reactivity difference between the $-OH$ groups of the polyol and the chain extender with different isocyanate groups affect the sequence of hard segments in the polymer chain. Thus, polyurethanes obtained by using this method have a more random sequence. However, the polymer is highly crystalline due to the favoured reaction between polyol and diisocyanate before extended polymer growth has occurred.

A chain growth polymerisation can be used to form a TPE in one step. An example is a poly(ethylene-co-butene) with a high butane content, polymerised using a single-site metallocene initiator. This polyethylene can undergo phase separation due to crystallisation, crystals are the physical crosslinks, and the highly branched structure will exhibit elastomeric properties. It may need to be blended with a less branched polyethylene to increase the physical cross-links. Alternatively it can be partially cross-linked by dynamically vulcanising by extrusion with a peroxide initiator. While chemical cross-links are formed this type of polyethylene can still be processed as a thermoplastic. Dynamic Vulcanization can be applied to poly(ethylene-co-propylene) rubber (EPR) that may be blended with a thermoplastic polyethylene to provide a binding crystalline phase.

5.2 Two-step methods

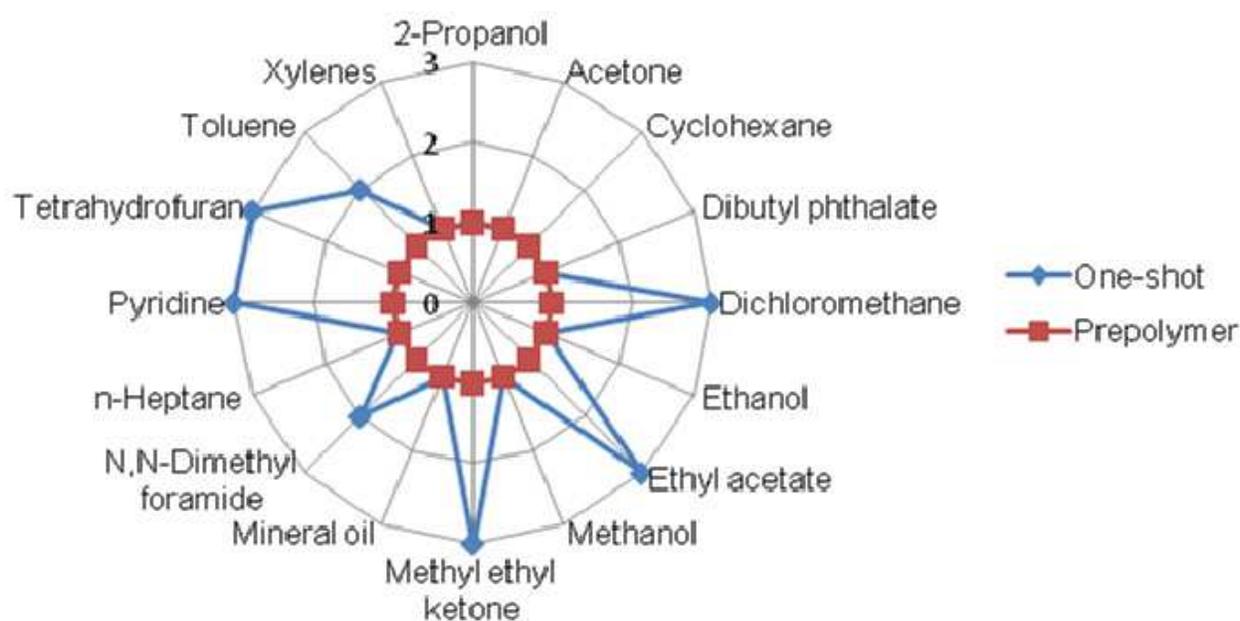
TPU can be synthesised by a two-step method, which is known as prepolymer method. The reaction may be carried out in two steps where excess diisocyanate is added to the polymeric diol to form an isocyanate terminated pre-polymer with excess diisocyanate

monomer that is then reacted or chain extended with the monomeric diol to form the segmented TPU structure. The polymeric diol can be a biopolymer or biodegradable polymer such as castor oil. Comparison has been made between poly(butylene succinate) and poly(butylene adipate) as the soft phase in TPU (Sonnenschein et al., 2010). The succinate derived TPU exhibited higher soft phase glass transitions and more hard phase to soft phase interactions than the adipate derived TPU, due to higher carbonyl content and hence polar interactions in the succinates. Abrasion resistance was a function of overall hard phase volume fraction.

Sequences are found to be more regular in the polymer obtained via prepolymer method compared to the one shot method. The structural regularity leads to a better packing of hard segments where physical cross-linking points are easier to form. Hence, a two-step method gives a product of better mechanical properties than a one-step method does (Table 2). Again, the solubility of these two products is different. The polyurethanes obtained from one-method are soluble in some of the common solvents, but the polyurethanes from the prepolymer process could not be dissolved in any common solvents (Figure 3).

Properties	One-shot	Prepolymer
Elongation at break (%)	550	559
Hardness Shore A	80	82
Modulus at 100% (MPa)	5.6	6.6
Tensile strength at break (MPa)	14.0	11.9
T_g (°C)	-35	-34

Table 2. Comparison of properties of TPUs made from one-shot and prepolymer methods



Source: Herbert & Nan, 2010

Fig. 3. Solubility results of TPUs made from one-shot and prepolymer methods in various solvents at room temperature (1: not soluble; 2: soluble after a few days; 3: soluble)

Dynamic vulcanization is a widely used method to prepare thermoplastic elastomers comprising partially or fully cross-linked elastomer particles in melt-processable thermoplastic matrix. Thermoplastic vulcanizates are prepared by melt-mixing the elastomer and thermoplastic in an internal mixer or in a twin-screw extruder. After a well-mixed blend has formed, in the second step, vulcanizing agents such as cross-linkers or curatives are added. Vulcanization of the rubber polymer takes place during the continuation of the mixing process under conditions of high temperature and high shear. According to the earlier investigation (Aubert et al., 2004) the best combinations of elastomer and thermoplastic are those in which the surface energies of the two components are matched, the entanglement molecular weight of the elastomer is low and the thermoplastic is at least 15% crystalline. The most common used compositions are based on dynamically vulcanized ethylene propylene diene monomer (EPDM) and polyolefins. Others blends include butyl and halobutyl rubbers and polyolefin resins, polyacrylate rubber and polyolefins (Soares et al., 2008) and butadiene-acrylonitrile rubber and poly(vinyl chloride) (Passador et al., 2008).

Anionic polymerization remains as an important technique to for the preparation of well-defined styrene butadiene triblock copolymer. Poly(styrene-*b*-butadiene-*b*-styrene) (SBS) is an example of a tri-block copolymer, though di-block copolymers are also formed from the same monomers. Styrene is first initiated with butyllithium and polymerised until all of the styrene has reacted. The polystyrene has an anionic end group with lithium counter-ion. Butadiene is added and the polymerisation continues forming a butadiene block. After all of the butadiene has reacted, more styrene is added and the polymerisation continues until all styrene has reacted. Then the polymerisation is terminated by addition of a protic substance such as methanol or water. Termination may be carried out after the second polymerisation step to give a di-block copolymer. The size of blocks is determined by the concentration of initiator and the amounts of monomers added at each step. Molar mass distribution is characteristically low for anionic polymerisation so the macromolecular architecture is accurately controlled.

Carbocationic polymerization has a more complex system than the anionic polymerization described above. It has been used to produce block copolymers with polyisobutylene mid-segments, or poly(styrene-*b*-isobutylene-*b*-styrene) (SIBS). This polymerization involves a three-step progression: (i) controlled initiation, (ii) reversible termination (quasi-living systems), and (iii) controlled transfer. The initiators have two or more functionalities. The polymer segments are produced sequentially from monomers as in anionic polymerization. The initiator is reacted with isobutylene at the first stage. The product is a difunctional living polymer. It can initiate further polymerization when more styrene monomers are added. After termination, this gives the block polymer SIBS. Polyisobutylene is the only mid segment that can be produced by this method while there are many aromatic polymers that can form the end segments.

6. Processing methods

Thermoplastic elastomers are technologically very attractive because they can be processed as thermoplastics, this is their main advantage compared with cross-linkable elastomers. They can be re-melted or devitrified and shaped again. Hence, they are generally processed by extrusion and injection moulding, which are the most common processing methods used

by thermoplastics. A disadvantage is that TPE have an operating temperature below that at which the hard phase becomes dimensionally unstable.

Several factors need to be taken into account during the processing of TPEs, including viscosity or rheology of the two-phase polymer, temperature at which the hard phase can be processed, thermal stability since the complex structures will potential have several weak chemical links, thermal conductivity since the hard phase is surrounded by soft phase, crystallinity in the hard phase that must be melted with excess enthalpy, and moisture that may cause hydrolysis at processing temperatures.

6.1 Extrusion

Extrusion is a high volume manufacturing process for fabricating parts from thermoplastic elastomers. This processing technique is essential in the melting of raw materials and shaping them into different continuous profiles. The most common extrusion methods are film and sheet extrusion, blow film extrusion, cast film extrusion, coextrusion, tubing extrusion and extrusion coating. The end products made by extrusion are pipe/tubing, wire insulation, film, sheets, adhesive tapes and window frames.

Basically, the extrusion process involves heating a thermoplastic above its melting temperature and forcing it through the die. The extruder is a heating and pressurizing device involves one or more screws operating in a heated barrel. The key determinant of an extruder's performance is the screw. It has three main functions to perform: feeding and conveying the raw material feed; melting, compressing and homogenizing the material; and metering and pumping it through the extrusion die at a constant rate. Raw thermoplastic elastomer material is fed into the barrel of the extruder and comes into contact with the screw. As a melt delivery device, the rotating screw forces the polymer forward into barrel which is heated at a desired temperature. After leaving the screw, the molten travels through a screen pack/plate breaker, where the contaminants in the melt are removed. Breaker plate also creates back pressure in the barrel which is needed for uniform melting and proper mixing of polymer. After that, the molten enters the die, where the cross section of the extruded product is determined.

6.2 Injection molding

Injection molding is by far the most used processing technique of producing parts from thermoplastic elastomers due to its high productivity. Injection molding machines and molds are very expensive because of the high pressures required and complexity of the process control. However, the shortcoming of this technique is balanced by its ability to produce a complex finished part in a single and rapid operation.

The principle of injection molding is very simple. The plastic material is fed into the injection barrel by gravity through hopper. Upon entrance into the barrel, the polymer is heated to the melting temperature. It is then forced into a closed mold that defined the shape of the article to be produced. The mold is cooled constantly to a temperature that allows the molten to solidify and the mold is opened, the finished product is ejected and the process continues.

The injection molding process is capable in producing a variety of parts, from the smallest components to entire body panels of car in a single molding operation. Other part designs

obtained from injection molding include threads, springs, storage containers, mechanical parts and automotive dashboards.

6.3 Compression molding

Compression molding was among the first method of molding to be used to produce plastic parts. However, it is by far less used than injection molding. Generally, this method involves four steps. First of all, the raw polymer materials in pellets or powder form are placed in a heated and open mold cavity. The mold is closed with another half of the mold and at the same time, pressure is applied to force the materials into contact with all mold areas. The materials soften under high pressure and temperature, flowing to fill the mold. The part is hardened under pressure by cooling the mold before removal so the part maintains its shape.

There are six important considerations that should be bear in mind, they are the proper amount of material, the minimum energy required to heat the material, the minimum time required to heat the material, the proper heating technique, the force needed to ensure that shots attains the proper shape, the design of the mold for rapid cooling. Compression molding of TPEs usually requires longer heating and cooling time due to their high melting points. Separate platens can be used to solve this problem where one is hot press that is electrically heated and another one is cold press that is water cooled. The part is hot pressed under pressure and then transferred immediately to the cold press to chill it under pressure. The hot press is usually preheated to reduce the total cycle time.

6.4 Transfer molding

Transfer molding is a process which the polymer is melted in a separate chamber known as pot then forced into a preheated mold through a sprue, taking a shape of the mold cavity. The mold is cooled down before opening. Thermoplastic elastomers usually have high viscosity and longer transfer time is needed. The temperature of the mold should be maintained at above melting temperature of the polymer to avoid premature cooling or freezing before the completion of transfer. The important variables during the process of transfer molding are the type of polymer, melting point of the polymer, pot hold time, transfer pressure, transfer rate and the mold cooling time.

6.5 Blow molding

Blow molding is a manufacturing process that is used to produce hollow plastic parts. There is a wide variety of materials can be used in this process, including but not limited to high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), Poly(vinyl chloride) (PVC) and Poly(ethylene terephthalate) (PET). The basic process begins with the melting of thermoplastic and extruding it through a die head to form a hollow tube called a parison. The parison is then clamped between two mold halves, which close around it and the parison is inflated by pressurized air until it conforms to the inner shape of the mold cavity. Lastly, the molds open and the finished part is removed.

Basically, there are three types of blow molding used to form the parison. In extrusion blow molding, plastic is melted and extruded using a rotating screw to force the molten through a die head that forms the parison. Injection blow molding is part injection molding and part

blow molding where the molten plastic is injection molded around the core pin and then the core pin is transferred to a blow molding station to be inflated. There are two stretch molding techniques. In one-stage process, the preform is injection molded which is then transferred to the blow mold where it is blown and ejected from the machine. In the two-stage process, preform is injection-molded, stored for a short period of time, and blown into container using a reheat blow machine.

6.6 Thermoforming

Thermoforming is a process which uses heat and pressure or vacuum to transform thermoplastic flat sheet into a desired three-dimensional parts. The sheet is drawn from large rolls or from an extruder and then transferred to an oven for heating to its softening temperature. The heated sheet is then transferred to a preheated, temperature-controlled mold. Vacuum is applied to remove the trapped air and deform the sheet into the mold cavity, where it is cooled to retain the formed shape. After that, a burst of reverse air pressure is applied to break the vacuum and assist the formed part out of the mold. The principal factors in this process include the forming force, mold type, sheet prestretching, the material input form and the process phase condition. These factors have a critical effect on the quality and properties of the final products.

6.7 Calendaring

Calendaring is a process where a large amount of molten plastic is fashioned into sheets by passing the polymer between a set of rollers. The rollers are hot and keep the polymer in its semi-molten state. This allows the molten to be rolled many times until the desired thickness is reached. The sheet is then rolled through cold rollers to enable it to go hard and then wound up into rolls. Calendar for thermoplastics generally operates in four-roll units made up of three banks, each bank being wider than the preceding one. The advantages of calendar over extruder are the possibility of calendar to produce embossed films, sheets and laminates and the higher output than extruder. Examples of the final products are cling film, shrink film, clear, translucent rigid sheets for blister packaging and opaque flexible film.

7. Plasticisers

Plasticisers are the additives added to polymeric materials to improve their flexibility and durability by spacing them apart. A plasticiser-polymer mix contains more free volume than a pure polymer, thus, the plasticised polymer need to be cooled to a lower temperature to reduce its free volume which defines glass transition temperature of the polymer. There are many types of plasticisers can be used to modify the thermoplastic elastomers and enhancing their utilities. Each of the plasticisers has a compatibility with a specific type of polymer. Among them, ester plasticisers have a well known function in the TPEs due to its exceptional ability to provide improved low-temperature by plasticising the soft phase while allow the hard phase to stay intact for strength and high temperature properties. Some examples of ester plasticisers are phthalate esters which are used in situations where good resistance to water and oil is required, adipic esters which are used for low temperature or resistance to UV light and trimellitic esters which are used in automobile interiors and where resistance to high temperature is required. TPU tend to be internally

plasticised by choice of monomer combination. For polyolefin elastomers, it is important to identify plasticisers which have low glass transition temperature and high boiling temperature and which are compatible over a broad temperature range with both rubber and polyolefin plastic components.

8. Additives

Common additives in TPEs include those materials added during or after polymerization to prevent their degradation, during monomer recovery, drying and compounding, and also storage.

8.1 Antioxidants

Among the additives, antioxidants are used to prevent oxidation and degradation. Primary or free radical scavenging antioxidants, which have reactive hydroxyl and amine groups, inhibit oxidation via chain terminating reactions. Secondary antioxidants inhibit oxidation of polymers by decomposing hydroperoxides.

8.2 Nucleating agents

Nucleating agents are generally used to enhance the formation of nuclei for the growth of crystal in the polymer melt. A higher degree of crystallinity and a more uniform crystalline structure in the hard phase can be obtained by adding a nucleating agent in the polymer. Nucleating agents can be classified as inorganic additives (talc, silica), organic compounds (salts of mono- or polycarboxylic acids) and polymer. Nucleating agents may be used to enhance crystallinity of a hard phase segment.

8.3 Colorants

Colorants are often referred to as dyes and pigments. Generally, dyes are soluble in water while pigments are not. The colours from dyes are produced from the light absorption and they are transparent. Pigments produce colours from the dispersion of fine particles throughout the resin. Inorganic pigments are thermally stable than organic pigments. They are less transparent and resistant to migration, chemicals and fading. Some examples of inorganic pigments are oxides, sulfides, hydroxides, and other complexes based on metal.

8.4 Flame retardants

Most thermoplastics are flammable, burning easily when heated to high temperature. Flame retardants are added to polymer to delay the ignition and burning of polymer. Char-formers form a foamy porous protective barrier on the polymeric material to shield it for further combustion. Flame retardants acting in the condensed phase deposit a layer on the surface of polymer to prevent it from the heat source while flame retardants acting in gas phase interrupt the combustion chemistry of the fire.

9. Composites

Various fillers and reinforcements have been introduced into thermoplastic elastomers to enhance their processability and mechanical properties, as well as to reduce material costs.

Most common fillers used in TPEs include cubic and spheroidal fillers (calcium carbonate, silica, carbon black), fibrous fillers (glass fibers, aramid fibers), platy fillers (kaolin, mica, talc) and nanofillers (carbon nanotubes, nanoclays, nanosilica). Reinforcing TPEs with fillers such as silica, clay, carbon black, carbon nanotubes, natural fiber results in better thermal and mechanical properties of the composites.

Carbon black composites with polyether polyurethane exhibited a percolation threshold of 1.25 % v/v and significant conductivity at 2 % v/v carbon black content (Wongtimnoi et al., 2011). Electric field induced strain was observed due to an increase in dielectric constant. Polyester thermoplastic elastomers reinforced by mica showed significant increment in the flexural, thermal and electrical properties with an increase in the filler concentration. The improved thermal properties are attributed to the small and uniform crystallite size distribution with the addition of mica (Sreekanth et al., 2009). Composites containing silica and poly(styrene-*b*-ethylene-co-butylene-*b*-styrene) (SEBS) block copolymer-based thermoplastic elastomer showed an improvement in the mechanical properties such as tear strength due to the strong interaction between the fillers and polymer matrices where the silica particles are wetted by the polymer (Veli et al., 2009). Polypropylene/natural rubber (PP/NR) and poly(propylene-ethylene-propylene-diene-monomer) (PP/EPDM) reinforced by kenaf natural fibre with maleic anhydride polypropylene (MAPP) as a compatibilizer agent has significantly increased the tensile strength, flexural properties and impact strength as compared to unreinforced thermoplastic elastomer. The improvement achieved in mechanical properties was due to the interaction both matrix system and kenaf fibre (Anuar & Zuraida, 2011).

10. Morphology

The disperse hard-phase in TPE self-agglomerates after processing to form reinforcing domains within the elastomeric matrix. The morphology contribution to elastomeric properties has been investigated using a semi-phenomenological approach (Baeurle et al., 2005). The authors describe an extended domain model for the size and distribution of hard phase within the elastomer and the contribution to stress relaxation times. Relaxation was modelled using a stretched exponential function to correlate stress decay due to multiple length-scales and time-scales. Behaviour under stress for long times resulted from plastic flow, chain pull-out from hard domains and finally disruption of the hard domains.

Transmission electron microscopy (TEM) is one of the most powerful equipment to characterize the structure and morphology of thermoplastic elastomers. It is often used to interpenetrate polymer networks (IPNs), morphology and crystallinity of hard blocks, structural evolution of segmented copolymers under strain and blends. The morphology of the IPNs transformed from SBS by using γ -radiation as shown by TEM is a homogeneous and sponge-like network (Robert et al., 2003). Sometimes, TEM is associated with other techniques, particularly small-angle X-ray scattering (SAXS), wide-angle X-ray scattering (WAXS), small-angle neutron scattering (SANS), and atomic force microscopy (AFM) to provide more information on the microstructure of TPEs. TEM and SANS have been used to examine the morphology of tough-semi- and full- IPNs with SIS crosslinkings and PS at different content (Bhavna & Robert, 2001). TEM showed similar structure for both samples which are different in total of PS content, while for SANS, the plot of intensity against the scattering vector q showed that both structures are significantly different with the tough

IPNs (lower PS content) having two types of domains. The morphology of natural rubber (NR)/high density polyethylene (HDPE) reinforced with carbon black composite was examined using TEM, SAXS and SANS (Kazuhiro et al., 2005). TEM image showed that NR and HDPE were phase-separated in the blends and carbon black nanoparticles were located in the NR domains. This phenomenon can be explained by the chemical groups on the surface of carbon blacks which chemically absorb olefin well.

11. Elastomer polymer blends

Elastomers are often used in blends with other polymers. When the elastomer is the minor component it will constitute a disperse phase. A disperse phase elastomer will be a toughening additive for the matrix phase that could be a thermoplastic or a thermoset polymer.

When the elastomer is the major component it will be a matrix phase and the overall blend will be an elastomer. The disperse phase blended polymer will contribute to physical cross-links that will prevent creep and assist with reversibility of elastomer deformation.

12. Mechanical properties

12.1 Stress-strain

When tested under a tensile stress-strain condition, TPE behave as elastomers until the yield stress after which they can undergo plastic flow, part of which may be viscoelastic (time-dependant recovery) and part will be permanent set. The pre-yield region represents an elastomeric response where the physical cross-links are not deformed. The stress-strain curve of SBS is shown in Figure 4.

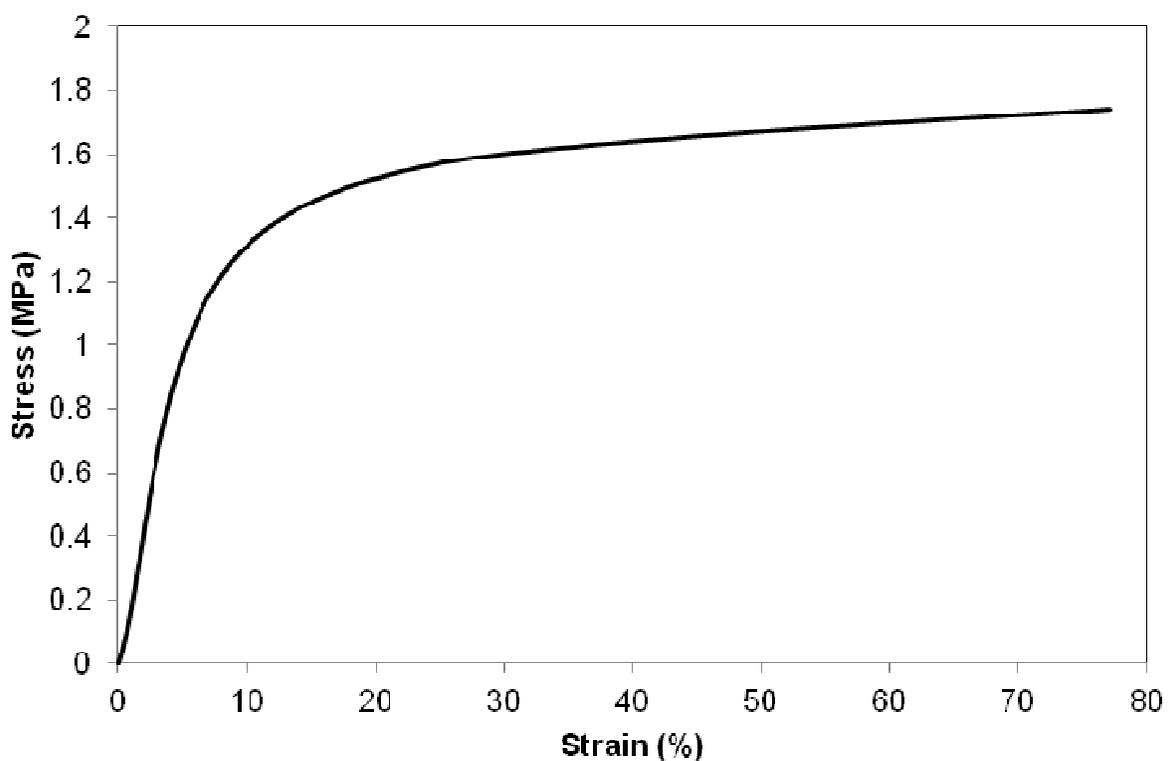


Fig. 4. The stress-strain curve of SBS

12.2 Dynamic mechanical analysis

Dynamic mechanical analysis (DMA), uniaxial tensile and microscopic properties were used to observe properties and transitions at lower temperatures to the glass transition of the elastomer phase (Adhikari et al., 2003). Two distinct transitions were detected at the lower temperatures evaluated, an elastomeric to ductile thermoplastic transition, and a thermoplastic to brittle transition. A typical DMA curve of SBS is shown in Figure 5. Scanning electron microscopy (SEM) revealed an associated change in deformation mechanism.

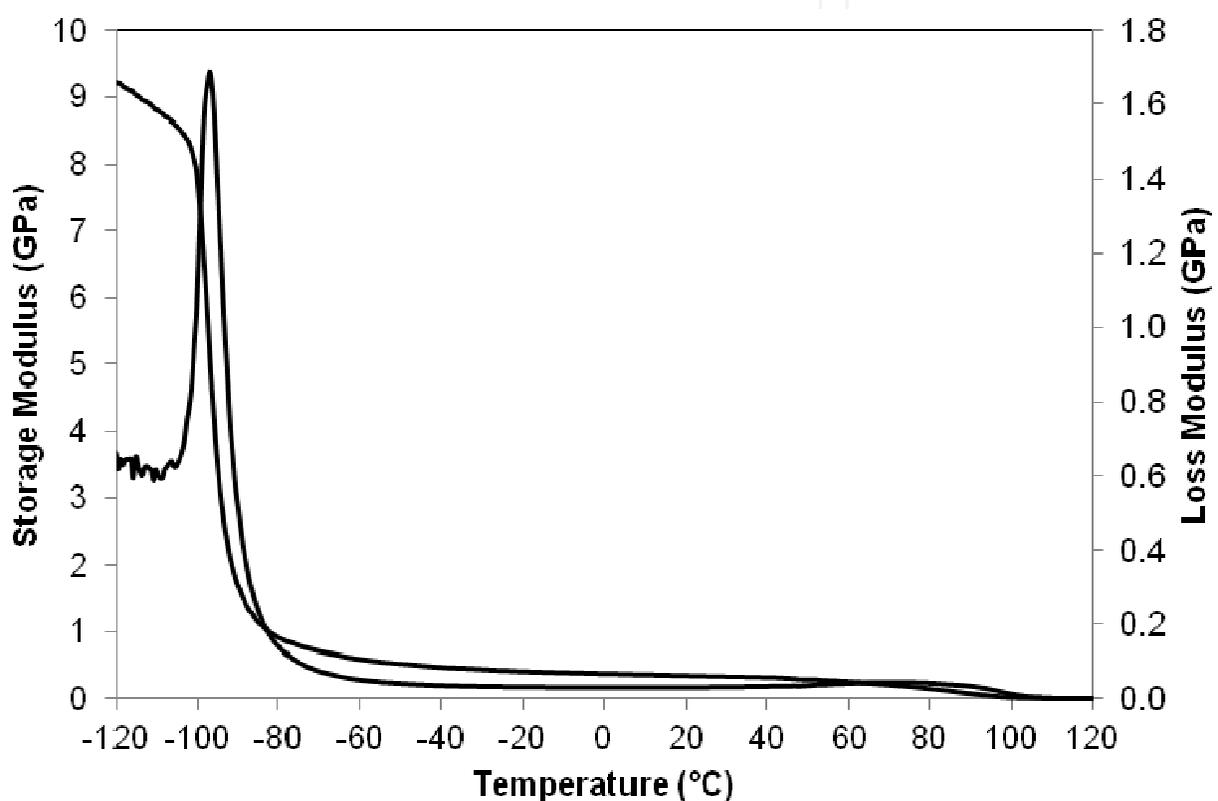


Fig. 5. The storage and loss modulus curves of SBS

12.3 Creep and recovery

Creep is a problem for TPE because there are only physical crosslinks that can dissociate and flow, chemical crosslinks are permanent and creep will be low. TPEs soften and melt with increasing temperature, showing creep on extended use. Creep resistance and tensile strength are generally directly related. A softer TPE will creep more and have less tensile strength than a harder TPE. Recovery should be elastic with some viscoelasticity, permanent set is not suitable in TPE. The deformation behaviour of TPEs during creep flow can be divided into three strain regimes: linear regime at low strains where the recovery from creep is complete; the transient regime, where the viscosity shows a maximum; flow regime where steady state morphology is formed. Creep and recovery curve of SBS is shown in Figure 6.

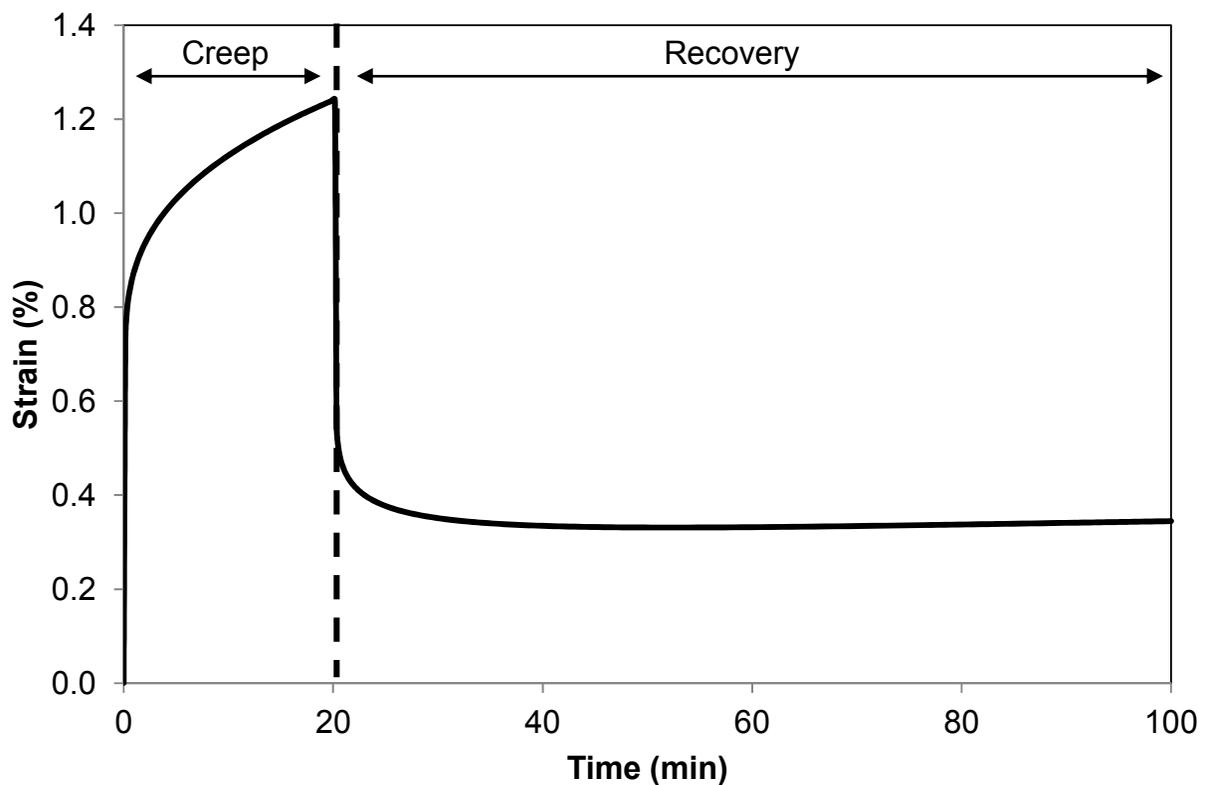


Fig. 6. The creep and recovery curve of SBS

12.4 Stress relaxation

Stress relaxation is a technique can be used as a physical method to determine the domain structure of the TPEs by studying the time-dependent deformation behaviour of the segmented block copolymer. There is no stress relaxation occurs in ideal elastomer.

12.5 Strain hardening

At high strain, strain hardening takes place and converts TPE from elastic behaviour to leathery or stiffer characteristic so that elasticity is lost while tensile strength and modulus will be increased. In time, the recovery of the deformation occurs suggesting that the part where deformation occurs is viscoelastic.

12.6 Tear strength

Tear strength which describes how well the elastomer resists tearing. TPE is stretched and the amount of force required is recorded. Peel strength is a measure of how well a TPE has bonded to a rigid substrate.

13. Applications

Thermoplastic elastomers have been widely used in automotive sector, medical devices, mobile electronics, household appliance sector and construction to replace conventional vulcanized rubber.

- Automotive: windshield seal (SEBS), wire/cable (SEBS, TPU), fibre reinforced soft touch surface for interior (TPO), gaskets (TPV) and spoiler (SEBS)
- Medical devices: syringe (TPV), medical tubing (TPO), medical wrapping and packaging (TPU)
- Mobile electronics: wire/cable (SEBS), earplugs (TPV), cell phone (TPV).
- Household appliance sector: sporting goods (TPU), footwear soles (SBS), toys (SEBS), adhesives (SIS)
- Construction: gaskets (SEBS)

The only constraint of TPEs is the physical reversible crosslinks need to be disrupted by heat to mould, but they may be disrupted during use.

14. Future directions

Thermoplastic elastomer structure, performance and specialty applications are interconnected with block copolymer molecular characteristics. Block continuity, molar mass, molar mass distribution and stereochemistry must be controlled. New polymerisation techniques and initiators are expanding the choice of monomers that can be polymerised under controlled conditions. This allows monomer selection and molecular architecture to provide elastomers with chemical resistance, self-healing, abrasion resistance and unique mechanical performance to be prepared for special applications.

Further thermoplastic elastomers can be prepared by creating blends of an elastic polymer with a dimensional stabilising polymer. Inclusion of ionomers as a physically cross-linking phase can be extended with carboxylates, sulfonates and phosphates with various metal ions. In conjunction with polyfluorocarbon elastomers chemical resistance can potentially be improved.

Nanocomposites are being formed with elastomers where the nanoparticles form self-assembled clusters or bridges to provide physical cross-links. Nano-particles have traditionally been used to modify elastomeric properties. Such modification will be expanded through increasing knowledge of nano-composite preparation and morphologies. Carbon black is a much used nano-fillers that is now being assisted or replaced by carbon nanotubes, graphenes and silicas with a diversity of surface modifications. Carbon blacks are known to form reversible clusters and to binder elastomer molecules within the clusters. Nano-silicas remain in multi-particles aggregates while forming reversible agglomerates that enhance absorption of elastic energy. Now carbon nanotubes and graphenes have been found to create reversible networks at low volume fraction.

15. Conclusions

The characteristics of an elastomer require that there is a mechanism to provide reversible deformation. Only the elastic component of the three-component viscoelastic model must be active. The viscous contribution resulting from molecules sliding past each other, this results in irreversible flow, is eliminated by cross-linking in a thermoset elastomer. Physical crosslinks are present in a thermoplastic elastomer as a second vitrified or crystalline phase. The viscoelastic component can be reduced by minimising chain stiffness and intermolecular interactions in the continuous elastic phase. Thermoplastic elastomers offer

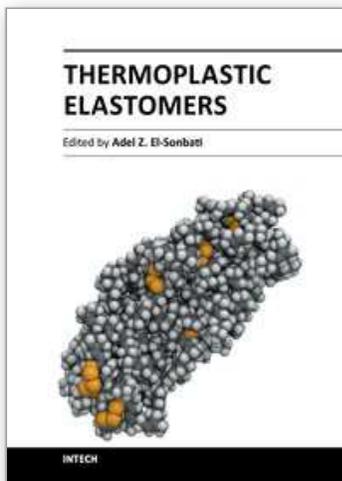
ease of processing the same as thermoplastics without the need for a separate curing reaction. Waste material can be reprocessed and production rates will be fast consistent with a thermoplastic. Upper application temperature limitations exist dependent upon the glass transition or melting temperature of the hard phase. Stress resistance is limited to the yield stress of the hard phase since permanent deformation will follow distortion or flow of the hard phase. Thermoplastic elastomers are enhanced by fillers, with nano-fillers having particular relevance when small amounts can support the hard phase. In the soft phase fillers will modify the elastic response. Structural diversity is found in thermoplastic elastomers with many chemical structures such as polyurethanes and polyolefins available as both thermoset and thermoplastic elastomers.

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Thermoplastics can be used for various applications, which range from household articles to the aeronautic sector. This book, "Thermoplastic Elastomers", is comprised of nineteen chapters, written by specialized scientists dealing with physical and/or chemical modifications of thermoplastics and thermoplastic starch. Such studies will provide a great benefit to specialists in food, electric, telecommunication devices, and plastic industries. Each chapter provides a comprehensive introduction to a specific topic, with a survey of developments to date.

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