Chapter 19

Elastomeric Fibers

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19.1 Introduction

Only a few of the plethora of commercial natural and synthetic polymers can be made into useful fibers. This is because a polymer must meet certain requirements before it can be successfully and efficiently converted into a fibrous product. Some of these important requirements are: (i) the polymer must have long, linear, and flexible chains; (ii) the side groups of the polymer chains should be polar and small in size; (iii) the polymers should be dissolvable in a common organic solvent or meltable for extrusion; and (iv) the polymer chains should be capable of being oriented or crystallized under elongational and shear flow conditions during the extrusion process.

Elastomeric fibers are typically synthetic fibers containing at least 85 wt% of a segmented polyurethane (Oertel, 1994; Rubin, 1990). In general the fibers are characterized by high elastic recovery (up to 99% recovery) and high extensibility (up to 500%), to an extent that depends on their exact chemical composition and fabrication method used to produce them. Unlike rubber fibers that are produced as monofilaments, these relatively thin elastomeric fibers are used in modern style and high comfort clothing. Elastomeric fibers were first produced commercially in 1930 by DuPont Company and marketed under the tradename of Spandex$^{®}$ (or Elastane$^{®}$). Current producers of elastomeric fibers include RadicGroup (RadiciSpendex^{TM}), Dow Plastics Co (Pellathane$^{®}$), Hysoung Company (Creora$^{®}$), and DuPont Company (Lycra$^{®}$ Spandex). The special properties of elastomeric fibers include superior oxidation resistance, excellent resistance to dry-cleaning solvents, good dyeability, excellent retention of properties after exposure to ultraviolet light, excellent resistance to body oils, and excellent toughness that avoids the need for fiber protection during knitting. In a number of elastic textile applications, these characteristics of modern elastomeric fibers make

them the materials of choice in elastic textile applications, replacing rubber fibers and creating new markets such as active sportswear, medical textile, and comfort stretch garments. As will be described later in this chapter, it is worthy to note that the characteristic properties of elastomeric fibers can be tailored to specific applications by varying the chemical composition, the polymerization and fiber production method used.

Recent advancements in production techniques have spurred new and successful uses in manufacturing textile products for a number of functional application areas. As already mentioned elastomeric fibers can be elongated for more than 100% regardless of any crimp, and when stretched and released, retracts quickly and forcibly to substantially its original length. The fibers are either composed of homopolymers, such as polybutadiene and polyisoprene or made by copolymerizing two or more monomers, using either block or graft polymerization techniques. Typically, one of the monomers forms the hard or crystalline segment that functions as a thermally stable component which softens and flows under shear, as opposed to the chemical crosslinks between polymeric chains in a conventional, thermosetting rubber. The other monomer forms the soft or amorphous segment that contributes the rubbery characteristic. The fiber properties can be controlled by varying the ratio of the monomers and the lengths of the hard and soft segments. Block copolymerization techniques are used to create long-chain molecules that have various sequences or block copolymers of hard and soft segments while graft polymerization methods involve grafting one polymer chain to another as branches. The grafting techniques just mentioned offer more possibilities to varying the resulting copolymer composition and properties because both the backbone monomer and the grafted branches can be made to be rubbery, glassy (i.e., hard), or some relative composition of both.

There are four traditional thermoplastic elastomer types that can be used to produce elastomeric fibers, i.e., polyurethanes, polyester copolymers, styrene copolymers, and the olefinics. Mechanical properties of fibers produced from the first two types are generally better than those of the last two. Recent thermoplastic elastomers used in fiber manufacture may be divided into two classes of high-performance materials, namely thermoplastic polyamide (nylon) elastomers and elastomeric alloys. The latter consists of polymer alloys of an olefinic resin and rubber while the polyamide thermoplastic elastomers are low-density, high-elongation materials with good solvent and abrasion resistance. Although elastomeric alloys are based on olefins, their proprietary manufacturing methods give them better properties than conventional thermoplastic olefins.

To illustrate the science and technology of elastomeric fibers that may provide a basis for future progress in this important technological field, the chemical structure, fiber formation and the relationship between structure and properties of a few representative examples of elastomeric fibers such as polyurethane, styrene block copolymers, polyolefin, and elastomeric polymer alloys are described in the following sections of this chapter. Because of space limitations, a number of published papers and monographs in this field has been omitted but the interested reader might find this in the references of the cited bibliography.

19.2 Polyurethane Fibers

As already mentioned, polyurethane fiber (Spandex® or Elastane®) is a synthetic fiber known for its exceptional elasticity (or stretchability). Spandex® is stronger, lighter, and more versatile and durable than rubber. In fact, Spandex® fibers can be stretched to

almost 500% of their length. The Spandex® fiber technology was invented in 1959, and when first introduced, it revolutionized many areas of the clothing industry and found a number of important replacement applications for rubbers previously used in many applications. Spandex® is the preferred trade name in North America, while Elastane® is most often used elsewhere. Two well-known trademarks for Spandex® or Elastane® are Invista's brand names Lycra® and Elaspan®. Spandex® fiber is round in cross section, thus offering extra elasticity and good elongation. The material has superior resistance to degradation caused by sunlight, perspiration and chlorine, making it ideal for various kinds of active wear and swimwear.

The special elastic property and wide industrial application of Spandex® fibers is a direct result of the material's polyurethane (PU) chemical structure that is a multiblock copolymer comprised of alternating soft polyester or polyether and hard polyurethane-urea segments. These two segments undergo microphase separation into hard and soft phases, respectively, below and above their glass transition temperatures. This microphase separation is responsible for the excellent elastomeric properties of PU. By varying the structure, molecular weight of the segments, and the ratio of the soft to the hard segments, a broad range of physical properties can be obtained. The materials can be hard and brittle, soft and tacky, or anywhere in between. Figure 19.1 depicts schematically the structure of PU elastomer as multiblock hard segments (urethane) and soft segments (polyester or polyether diol). The TEM shows how these two segments can phase-separate into nanoscale morphology. The very small dark particles in the micrograph are the hard segments and the bright matrix is the soft segments (Madbouly, Otaigbe *et al.*, 2007).

Various types of diisocyanates can be used to synthesize PU (Madbouly and Otaigbe, 2008). The diisocyanates can be either aromatic or aliphatic with different chemical reactivities.   The aromatic diisocyanates are more reactive than aliphatic ones, which can only be used if their reactivities match the specific polymer reaction and special properties desired in the final product.   For example, polyurethane fibers made from aliphatic isocyanates are stable to light (Oertel, 1994; Szycher *et al*., 1983; Schollenberger and Stewart, 1972; Brauman *et al*., 1981), while fibers made from an aromatic isocyanate will undergo photo-degradation (Schollenberger, 1958; Adams *et al*., 1950; Hepburn, 1992).

The soft segments used in polyurethane elastomers are typically dihydroxy terminated long chain macroglycols with low molecular weight (M_w = 500 to 5000 g/mol) such as, polyethers, polyesters, polydienes and polyolefins. Polyester-based urethanes have relatively good material properties, but they are susceptible to hydrolytic cleavage of the ester linkage while polyether based urethanes have relatively high resistance to hydrolytic chain scission. Caprolactones offer a good compromise between the polyether and polyester types. Polyethylene oxide (PEO)-based urethanes exhibit poor water resistance due to the hydrophilic nature of the ethylene oxide.   Polypropylene oxide (PPO) has also been widely used because of its low cost and reasonable hydrolytic stability (Frisch and Dieter, 1975). Abrasion resistance of the urethanes is outstanding among elastomers, low-temperature flexibility is good, oil resistance is excellent up to approximately 82 °C, and load-bearing capability ranks with the best of the elastomers. Additives can be used to improve dimensional stability (or heat resistance), reduce friction, or to increase flame retardancy and fungus resistance (or weatherability).

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The low molecular weight diol and diamine chain extenders play a very important role in polyurethanes properties and applications. Without a chain extender, a polyurethane formed by directly reacting diisocyanate and polyol generally has very poor physical properties and often does not exhibit microphase separation. Thus, the introduction of a chain extender can increase the hard segment length to permit hard-segment segregation, resulting in excellent mechanical properties such as an increase in the modulus and an increase in the hard-segment glass transition temperature (T_g) of the polymer fiber. Polyurethane chain extenders can be categorized into two classes: aromatic diol and diamine, and the corresponding aliphatic diol and diamine. In general, polyurethanes that are chain-extended with an aliphatic diol or diamine produce softer materials than do their aromatic chain-extended counterparts (Dieterich, 1993). The chemical structure of Spandex® is very complicated because it has both urea and urethane linkages in the backbone of the main chain as depicted in the following structure.

x = 40 or so
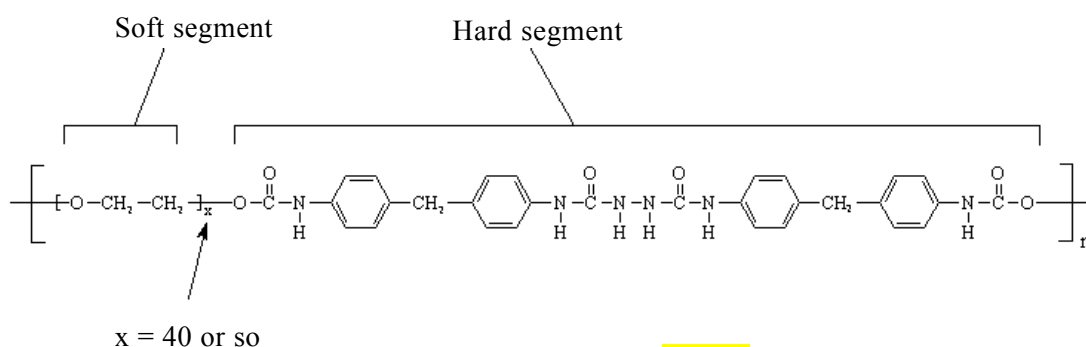
Chemical structure of Spandex®

19.3 Production of polyurethane fibers

19.3.1 Solution dry spinning method

Spandex$^{®}$ fibers are traditionally produced using four different methods namely; (i) melt extrusion, (ii) reaction spinning, (iii) solution dry spinning, and (iv) solution wet spinning. The first step of these four methods involves the chemical reaction of the monomers to produce a prepolymer. The resulting prepolymer undergoes further reaction, in various ways, and is subsequently drawn out to produce a long fiber. Solution dry spinning is used to produce the main industrial products of Spandex$^{®}$ (i.e.; up to 90% of the world's Spandex$^{®}$ fibers are dry-spun from solution). Figure 19.2 shows a schematic diagram for the solution dry spinning method. In this method the production of the prepolymer is done initially by mixing polyol with a diisocyanate (DIC) monomer. The reactants are mixed in a reaction vessel and under the right conditions they react to form a prepolymer. Because the ratio of the component materials produces fibers with varying characteristics, it is strictly controlled. A typical ratio of polyol to diisocyanate may be 1:2. The prepolymer is further reacted with an equal amount of diamine to increase the molecular weight in a chain extension step as already mentioned. The resulting solution is diluted with a solvent to produce the spinning solution. The solvent (e.g., THF) helps to make the solution thinner and more easily handled so that it can then be pumped into the fiber production cell. The spinning solution is pumped into a cylindrical spinning cell where it is cured and subsequently converted into fibers. In this cell, the polymer solution is forced through a metal plate with small holes called a spinneret. This production step causes the solution to be aligned into strands of liquid polymer. As the strands pass through the cell, they are heated in the presence of nitrogen and solvent gas, making the liquid polymer to chemically react and form solid strands. Specific amount of the solid

strands are bundled together as the fibers exit the cell to produce the desired thickness. Compressed air device is normally used to twist the fibers together. Each fiber of Spandex® is made up of many small individual fibers that adhere to one another due to the natural stickiness of their surfaces. The fibers are then treated with a finishing agent such as magnesium stearate or another polymer such as poly(dimethyl siloxane). These finishing materials prevent the fibers from sticking together, an important desirable requirement in textile manufacture. After this treatment, the fibers are passed through a series of rollers onto a spool or bobbin.

19.3.2 Electrospinning method

The polyuretane (PU) fibers can also be produced via the electrospinning process (Predicini and Farris, 2003). This method has been known since 1934. In this method fiber properties depend on electric field uniformity, polymer viscosity, electric field strength and distance between the nozzle and collector. The idea of electrospinning process is based on an external electrical field applied to charged polymer fluids or melts. This external electric field leads to electric charges on the polymer surface that overcomes the surface tension, and consequently a jet is produced. This electrical force can also lead to a very thin jet as it travels. In the case of polymer fluid, the common organic solvent is evaporated extremely fast (millisecond time scale) to produce electrically charged nanofibers. The technique is valid only for charged polymer solutions or melts with sufficient molecular entanglements. In electrospinning process, a charged droplet of solution suspended at the end of a capillary deforms into a conical shape, or Taylor cone, when subjected to a Coulumbic force (Taylor, 1969). The Taylor cone is formed due to a balancing of the repulsive nature of the charge distribution on the

droplet's surface and the surface tension of the liquid (Reneker *et al.*, 2000). As the charge is increased above a critical voltage, a stable jet is discharged from the tip of the Taylor cone. A jet of low molecular weight fluid breaks up into small droplets, a phenomenon termed electrospraying, while a polymer solution with sufficient chain overlap and entanglements does not break up but undergoes the so-called bending instability that causes a whiplike motion between the capillary tip and the grounded target (Hohman, 2001). The instabilities of the electrically forced jet in the electrospinning technique have been studied (Shin, 2001). One theoretical model for interpreting the relationship between bending instability, electric field, and solution flow rate has been reported (Shin, 2001).   It is this bending instability that accounts for the high degree of single fiber drawing, resulting in submicrometer size fibers.

Figure 19.3 shows a schematic diagram of the electrospinning process. The resulting electrospun nonwoven fiber mats have a high specific surface area, high porosity, and small pore size. This process normally produces fiber with diameters of nanometers to submicrometers. Fibers with ranges of diameters less than 1000 nm are very difficult to obtain from other conventional fiber production techniques. The nanofibers obtained by the electrospinning process can be used for many applications such as filtration devices, membranes, optics, vascular grafts, protective clothing, molecular templates, and tissue scaffolds (Bhattarai *et al*., 2004; Kim *et al*.; 2004; Ma *et al*., 2005).

The morphology of PU fibers strongly depends on the chemical structure, molecular weight and the percentage of hard and soft segments. Linear and branched PU will produce different fiber morphologies. For example, linear PU (M_w = 42,000 g/mol and M_w/M_n = 1.56) based on poly(tetramethylene oxide) polyester (soft segment) with

2000 g/mol and 35 wt% hard segment produces fibers with average diameters of 5.5±1.8

μm (Figure 19.4a). In contrast, a highly branched PU fiber (M_w = 91,900 g/mol and

M_w/M_n = 5.78) based on poly(tetramethylene oxide) polyester (soft segment) with 2000

g/mol and 30 wt% hard segment produces fibers with average diameters of 4.0±1.5 μm as

shown in Figure 19.4b. The two types of PU-fibers shown in Figure 19.4 were obtained

using electrospinning method at 20 kV, 10 ml/h volumetric flow rate, and 20 cm from the

syringe needle to the collecting target (McKee *et al*., 2005). Although there is a

significant change in the morphology of the two samples both of them can be used to

obtain nonwoven fiber mat of approximately 10 x 10 cm^2 without any bead defects

(McKee *et al*., 2005).

The rheological behavior of the linear and branched PU fiber solutions in THF

(10 wt% PU) is considerably different. Although the viscosities of the solutions of the

two different fibers show Newtonian behavior over the entire range of shear flow, the

zero-shear viscosity of the linear PU ((M_w = 42,000 g/mol) solution is more than two

times higher than that of the branched one (M_w = 91,900 g/mol) (i.e., 420 and 160 cP,

respectively) as clearly shown in Figure 19.5. The lower value of zero-shear viscosity of

the branched PU fiber solution is attributed to the fact that the branched polymer chain

has small hydrodynamic volume compared to that of the linear PU fiber solution (McKee

et al., 2005).

The tensile stress-strain properties of the two fibers just described are compared

with that of linear PU films in Figure 19.6a. The measurements were made according to

ASTMD3368 using an Instron® tensile tester operating at a crosshead displacement rate

of 15 mm/min (McKee *et al*., 2005). Clearly, Figure 19.6 shows that different mechanical

properties can be obtained for the three different samples (i.e., the branched PU fibers

shows the highest degree of elongation at break compared to that of the linear PU fibers and film). The branched PU fibers can be elongated up to 1300% strain at break, while the linear fiber and film reached 970% and 830% strain-at-break, respectively. The high value of elongation of the electrospun fibers is related to the increased tear resistance of the fiber mats compared to that of the neat PU film. The interconnected network of the electrospun fibers hinders tear propagation, resulting in higher elongation prior to break (McKee *et al*., 2005). It is also clear that the microporous character of the electrospun fibers is a direct reason for the very low Young's modulus of the electrsospun fibers (i.e., 1 and 4 MPa for branched and linear PU fibers, respectively) compared to that of the linear PU film (17 MPa).

The hysteresis or extension and recovery characterization of polyurethane elastomeric yarn was investigated by (Blazhaitis et al., 1970) as shown in Fig. 19.6b). The hysteresis loop of the fifth cycle (curves 3 and 4) shows that the losses are very small. The performance loss of high-elastic yarn in the recovery after extension are considerable in the first 3-4 cycles after which the loss becomes stable and less marked.

19.4 Polyester copolymer fibers

The poly(ether ester) (PEE) fiber is one of the most important materials that can be used for a number of potential applications. Poly(ether ester) is multiblock (or segmented-block) copolymers of the (AB) type comprising semicrystalline polyester (hard) segments and noncrystalline polyether (soft) segments. Their excellent characteristics as thermoplastic elastomers as well as their morphology are well studied, particularly in the case of PEE based on poly(buty1eneterephthalate) (PBT) and poly(tetramethy1ene oxide). Fiber formation from the melt of a copolymer based on PBT

and PEG 1000 was studied by [Gogeva *et al.* 1990]. The characteristics of the starting polymer, the processing conditions and the properties of the final fibers were considered [Gogeva *et al.* 1990]. The surface of the fiber was investigated by SEM as shown in Figure 19.7. The processing of this fiber from the melt was carried out at a spun rate of 800 m/min and stretching of approximately 3.64 times at a rate of 1195 m/min at 80 $^{\circ}$C. Clearly, a regular structure with a period of about 390 nm is observed perpendicular to the fiber axis (Figs. 16.7a and 16.7b). The fracture surface of the fiber (Figs. 16.7c and 16.7d) confirms the elastic nature of the copolymer.

19.5 Styrene copolymers elastomeric fibers

The styrenics are the lowest priced thermoplastic elastomers. They are block copolymers produced with hard polystyrene segments interconnected with soft segments of a matrix such as polybutadiene, polyisoprene, ethylene-propylene, or ethylene-butylene. These elastomers are commercially available from Shell (Kraton[®]) in several molding and extrusion grades ranging in hardness from 28 to 95 Shore A. Tensile strength of these materials is lower, elongation is higher than that of styrene butadiene rubber SBR or natural rubber, and weather resistance is about the same. The weather resistance characteristics can be improved by the addition of resins such as polypropylene or ethylene-vinyl acetate. The styrenic elastoplastics resist water, alcohols, and dilute alkalies and acids. They are soluble in, or are swelled by, strong acids, chlorinated solvents, esters, and ketones. They also have excellent low-temperature flexibility up to -120°F.

19.5.1 Styrene– butadiene–styrene (SBS) triblock copolymer fiber

Styrene–butadiene–styrene (SBS) triblock copolymer is a typical microphase-separated thermoplastic elastomer. When the polystyrene concentration is relatively low, the domains are spherical; with increasing concentration, the domains become cylindrical and then lamellar (or plate-like). Such well-developed morphology requires careful sample preparation. In general, the morphology is irregular and its degree of complexity depends on the thermal and mechanical history of the preparation, as well as, the interactions between each block (Helfand and Wasserman, 1976). Thermodynamic theories reported by Liebler, 1980; and Matsen and Schick, 1994, explains miscibility of block copolymers and the resultant morphologies. The rubbery butadiene chains interconnect glass polystyrene domains which act as reinforcing fillers or physical crosslinks. A typical TEM of SBS film morphology is shown in Figure 19.8 (Yang *et al*., 2006). Note that solution casting from toluene was used to obtain the SBS film depicted in Figure 19.8. The polybutadiene (PB) domains can be selectively stained by OsO_4 vapor, the bright and dark regions in the TEM micrograph represents the PS and PB domains, respectively. Cylindrical SBS morphology can be clearly seen in Figure 19.7. This morphology can be easily modified not only by varying the concentration of the blocks but also by controlling the processing conditions such as type of solvents used for casting films, method of extrusion, annealing temperatures, and blending with suitable homopolymers (Gohil, 1986). A difference in the interaction between blocks of a polymer ultimately affects its morphology. This is evident from the morphological changes in block copolymer films prepared from solvents having different solvent powers (Gohil, 1986).

Fong and Reneker, 1999 produced SBS electrospun fiber (Kraton D1101, 31 wt% PS with M_w and M_w/M_n 151,000 g/mol and 1.12, respectively) from a mixture, of 75 wt% tetrahydrofuran and 25 wt% dimethylformamide with 14 wt% polymer concentration. Tetrahydrofuran is a good solvent for both polystyrene and polybutadiene blocks, and the addition of 25% dimethylformamide improves the stability of the electrospinning jet. The electrospinning apparatus used by Fong and Reneker had a high voltage power supply (160 microamperes at 30 kilovolts). They applied positive high voltage through a copper wire to the SBS solution inside a glass pipette and placed a grounded copper sheet 30 cm below the tip of the glass pipette. Several glass microscope slides covered by films of evaporated graphite were placed on the copper sheet. The pipette was tilted a few degrees from the horizontal so that surface tension maintained a small droplet of the solution at the tip without dripping. As the electrical potential was gradually increased to 24 kilovolts, a jet was created. The jet, formed by electrical forces, followed a complicated stretching and looping trajectory as it dried and solidified. The resulting electrically charged nanofibers were collected on films of graphite for electron microscopy, or on a rotating drum covered with aluminum foil to produce a nonwoven elastomeric fabric. The mass flow rate of the polymer solution, carried by the jet, was around 50 mg/min (Fong and Reneker, 1999).

Typically, diameters of SBS electrospun nanofibers are about 100 nm. The aligned SBS nanofibers can be elongated to more than three times their original lengths without breaking. Figure 19.9 shows SBS nanofibers as the sample was observed between crossed polarizers, and then rotated. In the upper picture, fibers A-A and B-B are bright. Turning the sample clockwise by about 45° causes these nanofibers to become dark, as shown in the bottom picture. The bright and dark segments in the looped

nanofiber move along the loops and remain approximately parallel to each other as the sample is rotated. These observations show that the electrospun nanofibers are birefringent. Both the elongational flow (Mackley and Keller, 1975; Perkins *et al*., 1997) and the rubberlike strain of the molecular network may contribute to the birefringence of Figure 19.9.

In addition to the smooth nanofibers, very thin nanofibers with small beads are sometimes obtained in practice. Beads form, while the jet is still fluid, if the force that tends to extend the nanofiber is reduced, for example, by the neutralization of the excess charge on the fibers with ions created in air by a corona discharge. Surface tension in the small fiber creates a pressure that forces the solution into the beads (Fong and Reneker, 1999; Yarin, 1993). An electron micrograph of an example of a beaded fiber reported by Fong and Reneker is shown in Figure 19.10. This figure shows beads with diameters of about 60 nm that were elongated in the direction of the fiber axis. The distance between the beads is around 100 nm.

19.6 Polyolefin elastomeric fibers

The market for polyolefins manufactured with metallocene technology is growing exponentially as they are increasingly meeting commercial expectations. The continued success of the polyolefins is due to producers positioning themselves for success through consolidation and the introduction of new products. Metallocene-catalyzed polymers represent a significant advance in polymer synthesis and production. Unlike other catalyzed polymers, the structure and molecular weight of metallocene-catalyzed polymers are relatively easy to control. These characteristics enable production of precisely structured polymers in large, regulated amounts. Global

demand for metallocene-based polyolefins was several billion pounds in 2000, according to a new study by Houston-based Chemical Market Resources Inc. (CMR). North America and Europe accounts for 47 percent (or 1.075 billion pounds) and 25 percent (or 579 million pounds) of that demand, respectively.

Thermoplastic olefin (TPO) elastomers are available in several grades, having room-temperature hardnesses ranging from 60 Shore A to 60 Shore D. These polyolefin-based materials have the lowest specific gravities of all thermoplastic elastomers. They are uncured or have low levels of crosslinking. Material cost is mid-range among the elastoplastics. These elastomers remain flexible down to -50 °C and are not brittle at approximately -70 °C. They are autoclaveable and can be used at service temperatures as high as 135 °C in air. The TPOs have good resistance to some acids, most bases, many organic materials such as butyl alcohol, ethyl acetate, formaldehyde, and nitrobenzene. They are attacked by chlorinated hydrocarbon solvents.

19.6.1 Polybutadiene elastomeric fibers

Polybutadiene is one of the first types of synthetic elastomer, or rubber, to be invented. It is good for uses that require exposure to low temperatures. Tire threads are often made of polybutadiene copolymers. Belts, hoses, gaskets and other automobile parts are made from polybutadiene because it can withstand cold temperatures better than other elastomers. Syndiotactic 1,2-polybutadiene (s-PB) elastomeric fibers produced using electrospinning technique from dichloromethane solutions (CH_2Cl_2) have been recently reported (Hao and Zhang, 2007). Dichloromethane is the best common solvent which can be used to produce nanofibers of s-PB via the electrospinning technique. The other solvents have very poor fiber forming ability. The effects of processing variables

(including applied voltage, tip to target distance, and the feed rate of the solution to the capillary tip and solution properties like solvent, viscosity, concentration, conductivity, and surface tension) on electrospun fiber morphology have been extensively investigated in the literature for a variety of polymeric systems (Reneker and Chun, 1996; Megelski *et al*., 2002; Lee *et al*., 2002). It has been shown for a number of polymer/solvent systems that increasing the solution concentration or viscosity decreases the number of bead defects and increases the overall fiber diameter of the electro-spun fibers (Zong *et al*., 2002a). Moreover, researchers have electrospun polymer solutions with varying concentrations and viscosities to yield fibers with various structures and textures (Zong *et al*., 2002b; Jun *et al*., 2003). Figure 19.11 depicts the SEM morphologies of *s*-PB nano-elastomeric fibers obtained from electrospinning of different concentrations of CH_2Cl_2 (Hao and Zhang, 2007). Clearly, the figure shows that the concentration of *s*-PB in CH_2Cl_2 can significantly affect the morphology and fiber formation. When the concentration of s-PB is ″ 3 wt% no good fibers can be produced. For 1 wt% s-PB, half spheres porous structure with about 15 mm diameters can be clearly seen in Figure 19.10a. Morphologies like fiber-beads have been observed for 2 and 3 wt% s-PB samples. Typical *s*-PB elastomeric fibers can be seen for ≥ 4 wt% *s*-PB in Figures 19.10d-f.

19.7 Elastomeric polymer alloy fibers

This class of thermoplastic elastomers consists of mixtures of two or more polymers that have received a proprietary treatment to give them properties significantly superior to those of simple blends of the same constituents. The two types of commercial elastomeric alloys are melt-processable rubbers (MPRs) and thermoplastic vulcanizates (TPVs). MPRs have a single-phase while TPVs have two phases. Thermoplastic

vulcanizates are essentially a fine dispersion of highly vulcanized rubber in a continuous phase of a polyolefin. Critical to the properties of a TPV are the degree of vulcanization of the rubber and the quality of its dispersion. The crosslinking and fine dispersion of the rubber phase gives a TPV with high tensile strength (7.58 to 26.89 MPa), high elongation (375 to 600%), resistance to compression and tension set, oil resistance, and resistance to flex fatigue. TPVs have excellent resistance to attack by polar fluids, fair-to-good resistance to hydrocarbon fluids, and a maximum service temperature of 275°F. Elastomeric alloys are available in the 55A to 50D hardness range and with ultimate tensile strengths ranging from 5.5 to 27.5 MPa. Specific gravity of MPRs and TPVs respectively range from 1.2 to 1.3 and 0.9 to 1.0. Commercial applications of elastomeric alloys include automotive protective boots, hose covering, electrical insulation, seals, gaskets, medical tubing and syringe plungers, architectural glazing seals, and roofing sheet. Fibers from these materials are described in the following two sections.

19.7.1 Olefinic/EPDM alloy fiber alloy

Commercial olefin-based thermoplastic elastomers obtained by dynamic vulcanization with EPDM rubber (density 0.94 g/cm^3, hardness 40D) has been used to produce monofilaments through the traditional melt spinning extrusion technique (Spiridonov, *et al.,* 2005). The elementary steps for producing elastomeric fibers from this material is depicted in Figure 19.12 with the following descriptions: (1) Extruder with a constant value of compression ratio is used to melt the elastomeric belts; (2) One or more spinning gear pumps receive the molten polymer and send it through the spinning pack to homogenize the product; (3) Quenching of the extruded filaments into a cooling water tank; (4) Stretching the fibers through the rollers sets; (4) Immersing the

fibers in hot water bath; (6) Stretching the fibers again; (7) Relaxation of the fibers; (8) Stretching again; and (9) Winding of the fibers through the winding machine. Extrusion dies of 10 and 16 mm in diameter are typically used for this process. The stretching ratio is set from 2:1 to 7:1. The fibers with a stretching ratio 1:1 are obtained without a stretching step right after the cooling tank. The monofilament diameters obtained from this process typically range from 2 to 5 mm.

Figure 19.13 illustrates the stretching ratio dependence of stress at break for olefinic/EPDM elastomeric fiber alloy. Obviously, the stress increases exponentially with increasing value of stretching ratio. However, the percent elongation decreases strongly with increasing stretching ratio as shown in Figure 19.14. This behavior is related to the orientation of the polymeric chains of the fiber parallel to the stretching force (Roff and Scott, 1971; Fried, 1995). When the fibers are stretched the polymeric chains are oriented partially and consequently the fibers maintain their elastic behavior. The stretching ratio of these fibers can reach up to 7:1, after this value the fiber starts to break. At a stretching ratio value of 6:1 a so-called 'rough and peel' surface structure of the fiber is observed. The diameters and cross-sectional area of the monofilaments are also changed significantly with increasing stretching ratio, i.e.; the fiber diameters and the cross-sectional area decrease strongly with increasing stretching ratio as shown in Figures 19.15 and 19.16, respectively.

19.7.2 PU/PAN alloy fibers

Another example of thermoplastic polymer alloys that can be used to produce nanofibers is a mixture of crosslinkable elastomeric polyester urethane (PEU) with a thermoplastic polyacrylonitrile (PAN) (Fang *et al.*, 2007). Crosslinking either a polymer

phase or interlocking both polymers to form a so-called ''interpenetrating network'' has been an established strategy to compatiblize an immiscible polymer blend (Brown, 2002). In addition, a slightly crosslinked elastomer has been found to be more effective in toughening a thermoplastic material than its noncrosslinked counterpart (Lee, 1993).

Electrospinning of PEU/PAN polymer blend without any crosslinking reaction has also been used to produce fibrous structures (Fang *et al.*, 2007). When the overall concentration of PEU/PAN blend was kept at the same value in dimethylformamide (9 wt % dimethylformamide), the ratio between the PEU and the PAN is found to influence the fiber morphology. As illustrated in Figure 19.17, three different PEU/PAN ratios (PEU/PAN = 2:1; 1:1; 1:2 w/w) resulted in different fiber morphology. When the PEU/PAN ratio is 2:1, the PEU concentration is 6 wt%. Electrospinning of such a polymer solution resulted in a fibrous product, though the fibers tended to stick together to form an interconnected web structure (Fang *et al.*, 2007). This suggests that the addition of PAN to the PEU solution has facilitated the formation of nanofibers in electrospinning. When the PEU concentration is reduced to 4.5 wt% (PEU/PAN ratio = 1:1), individual fibers containing a small amount of fiber beads are produced. Further reduction of the PEU concentration to 3% (wt) (PEU/ PAN ratio = 1:2) leads to nonsticky and uniform fibers (Fang *et al.*, 2007). The fiber diameter from the different PEU/PAN ratios is in the range of 200–300 nm. By comparison, the pure PAN nanofibers electrospun with the same overall concentration have fiber diameters in the range of 354-664 nm (Figure 19.17d). The PEU/PAN ratio also influences the fiber diameter by slightly decreasing it with an increase in the PEU component, even if the same overall polymer concentration is used. The change in the fiber diameter can be attributed to the effect of the PEU/PAN ratio on the solution properties.

The crosslinked PEU/PAN fibers just described were prepared by Fang *et al.*, 2007 by adding a crosslinker (Imprafix VP LS 2323, Bayer Mat. Sci. Germany) and catalyst (Imprafix TH LSG, Bayer Mat. Sci., Germany) (2.5 wt% each based on the weight of PEU) to the PEU/PAN solutions prior to electrospinning. As soon as the crosslinker and catalyst are added to the PEU/PAN solutions, the PEU chains starts to crosslink (Fang *et al.*, 2007). The presence of the crosslinker and catalyst has a little effect on the fiber morphology. As shown in Figure 19.18, the crosslinked PEU/PAN fibers have similar fiber morphology to the noncrosslinked fibers, except that the crosslinked fibers from the PEU/PAN (2:1) solution are less interconnected than the noncrosslinked fiber mat. The presence of the crosslinker leads to a fiber diameter increase when the solution contains a higher composition of PEU (i.e., PEU/PAN, 2:1 and 1:1). In contrast the fiber diameter is observed to decrease slightly when the PEU composition is low (i.e., PEU/PAN = 1:2) (Fang *et al.*, 2007).

The tensile stress–strain curves for the noncrosslinked and the crosslinked electrospun fiber mats with PEU/PAN =2:1 ratios are shown in Figure 19.19. With the same PEU/PAN ratio, the tensile strength of the crosslinked fiber mats is more than 50% greater than that of the noncrosslinked fiber mats, and the crosslinked fiber mats have a higher elongation-at-break than the noncrosslinked ones (Fang *et al.*, 2007). The crosslinking reaction leads to 79% increase in the tensile strength and 29% increase in the elongation at break for this composition ratio (PEU/PAN ratio = 2:1). These results indicate that the crosslinking reaction enhances the interaction between PEU and PAN chains.

19.8 Conclusions and outlook

This chapter surveys the current science and technology of elastomeric fibers with enhanced benefits in a number of applications in the textile and allied industry. In general, the quality of elastomeric fibers has shown significant improvements since they were first developed. Strict quality control tests, according to industry standards, on the starting materials and final products are essential to ensure production of a consistent end product with prescribed properties. Future advances in polymer (fiber) science and engineering will help continue their improvement. For example, researchers have found that by changing the starting raw materials and the fiber production method in a clever way they can develop fibers which have even better properties such as stretching and weathering characteristics. Other characteristics of elastomer fibers can be improved by using various fillers and polymer additives. Because of the desirable characteristics of elastomeric fibers, it is likely that increased research and development attention will be focused in the future on these complex but important industrial materials. For example, it is likely that advanced textile fabrics will be produced which incorporate the versatile Spandex® fibers with conventional fibers such as in the commercially available polyamide/spandex fiber blends described above. Industry efforts to improve cost-to-performance ratio of elastomeric fibers and products made from them may spur discovery of new manufacturing processes that will focus on producing fibers faster and more efficiently.

Acknowledgements

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