Advances in Elastomers: Their Blends and Interpenetrating Networks-State of Art, New Challenges and Opportunities

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Abstract Elastomers are becoming an inevitable part of day to day life. The materials based on elastomers have tremendous applications in almost all areas of life. The present chapter deals with a brief account on various types of elastomers, elastomeric based blends and interpenetrating networks (IPNs). Various classes of elastomers, and blends are addressed by giving importance to the interfacial compatibility of different phases. Topics such as immiscible rubber blends, rubber/thermoplastic blends (micro and nano structured), rubber-thermoset blends (micro and nano structured), interphase modification and compatibilization, Interpenetrating Polymer Networks (IPNs), micro and nanofillers in rubbers have been very briefly discussed. Finally the applications, new challenges and opportunities of these elastomeric based blends and IPNs are also discussed.

1 Introduction

Elastomers are an important class of polymers having randomly distributed chains connected by cross links in their molecular structure. Irregularity of the chains due to the difference in geometrical arrangement prevents them from having crystalline

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nature. Among the two isomers, the cis configuration gives best elastomer properties even though the double bond restrains motion of the bonded carbon atoms. The trans configuration contributes to a regular planar zig–zag conformation that is crystallizable. A fully saturated hydrocarbon polymer can be elastomeric if substituents are in atactic configuration, or if it is a random copolymer where the segments cannot co-crystallize. The elasticity of this class of polymers is due to the random coil conformation of the macromolecular chains. This is because of the high thermodynamic stability of random coil compared to the fully extended chain. The assumption of a random coil conformation allows prediction of structural characteristics including end-to-end distance, radius of gyration, contour length, persistence length and characteristic ratio [1].

1.1 Classification and Compounding of Elastomers

Based on the applications, elastomers can be classified into two categories general purpose and special purpose elastomers. General purpose elastomers are applicable for a wide range of aspects as the name indicates. Natural rubber (NR) which is chemically cis-1,4-polyisoprene is the most significant among the general purpose rubbers. It is obtained from *Hevea brasiliensis* tree, and often used after compounding with vulcanizing agents, antioxidants and fillers. NR has high abrasion or wear resistance, electrical resistance, chemical resistance to acids, alkalies and alcohols and damping or shock absorbing properties and applied quite extensively in manufacturing large truck tyres, off-the-road giant tyres and aircraft tyres. Styrene-butadiene rubber (SBR) is a synthetic copolymer made of styrene and butadiene useful for many purpose. Its chemical resistance is similar to that of NR, however, it exhibits an excellent abrasion resistance than polybutadiene and natural rubber which makes it a suitable material for automobile tyres [1, 2].

Ethylene propylene diene monomer (EPDM) is another synthetic rubber having outstanding heat, ozone and weather resistance due to their stable, saturated polymer backbone structure. It is non-polar in nature and has good electrical resistivity, as well as resistance to polar solvents, such as acids, alkalies, phosphate esters, many ketones and alcohols. It is mainly used as a standard lining material for steam hoses, automotive weather-stripping and seals, radiator, electrical insulation and roofing membrane. The chlorinated rubber, polychloroprene (CR) was one of the first commercially successful synthetic rubbers. This rubber is known by the trade name Duprene or Neoprene. CR is commonly used as hose covers (resistant to oil and ozone), insulating CPU sockets, in bearings and seals for construction application and in automotive industry (waterproof seat covers). The compound is designed to have excellent low temperature, flex, ozone, and weather resistance [3].

Thermoplastic elastomers are another class of elastomers which can also be accommodated under general purpose category. Styrenic block copolymers (SBCs) are the largest volume and lowest priced category of thermoplastic elastomers. Their major applications include footwear, adhesives and sealants. SBCs can also be compounded to produce materials that enhance grip, feel, and appearance in applications. Polyolefin thermoplastic elastomers (TPOs) are an important part of the TPEs, which consist of polyolefin semi-crystalline thermoplastic and amorphous elastomeric components. TPOs are co-continuous phase system with the hard phase providing the strength and the soft phase providing the flexibility. In addition to the two most important processing methods injection moulding and extrusion, TPOs are also fabricated by calendaring, thermoforming, negative thermoforming and blow molding. TPOs ingredients generally include ethylene-propylene random copolymer (EPM), isotactic polypropylene (iPP), and other fillers and additives.

Special purpose elastomers have specific applications in various fields. For instance the poly (isobutylene-co-isoprene) rubber generally known as butyl rubber (IIR) has many applications requiring an airtight rubber. This synthetic rubber is a copolymer of isobutylene and isoprene monomer units and has a very low permeability and good electrical and shock dampening properties. The major applications of butyl rubber are in tyre inner tubes and hoses. Halogenation of IIR generates halogenated butyl rubber (XIIR) having improved air impermeability and cure reactivity required for tyre inner liner applications and to generate adhesion between the tyre inner liners and its body. The two kinds of halo butyl rubber are chloro butyl rubber (CIIR) and bromo butyl rubber (BIIR) [2–4]. Nitrile rubber with acrylonitrile content of 31–35 % can withstand a temperature range of −40 to 107 °C. It is considered to be the major oil, fuel, and heat resistant elastomer. It is useful in non-latex gloves, in dehusking rollers, where they give much longer life and greater dehusking capacity than any other polymers. Silicone rubber is well known as an electrical and thermal insulator since it contains strong silicon oxygen bonds. It has good weatherability and can maintain useful properties over a wide range of temperatures [5]. Fluoroelastomers also have excellent resistance to fuel, oil, acid and chemicals and good resistance to gas penetration and radiation and flame retardancy. Polyurethane and polysulfide rubbers are other special functional elastomers of which the latter have high resistance to petroleum solvents, organic solvents (esters, ketones etc.), aromatic fuels, oils, greases, sunlight, ozone and UV rays. Hence they are used as static seals for aircraft, building and marine industries where no other material serves the purpose.

During the processing of rubber, the raw polymer can be softened either by mechanical work termed mastication or by chemicals known as peptisers. Under processing conditions various rubber chemicals, fillers and other additives can be added and mixed into the rubber to form the rubber compound. The batch mixers like two roll mills and internal mixers allow high shear mixing. Internal mixers overcome the slowness of mill mixing by ensuring rapid mixing and large output. The internal mixers used in the industry vary in rotor, throat, chamber and floating weight design. In addition to this calenders and extruders are also used for compounding the rubber.

Vulcanization or crosslinking is the formation of three dimensional elastic networks along the polymer backbone or macromolecules to decrease its plasticity, cold and hot flow and also to improve its end-use properties like strength, elasticity and stability [6]. Materials initiating the formation of crosslinks between polymer chains are known as vulcanizing agents (e.g. Sulphur). The properties that result from a vulcanizate depend on the number and type of the crosslinks formed. Activators like zinc oxide, increases the rate of vulcanization to more than threefold. In chloroprene rubbers (CR), a combination of zinc and magnesium oxide is often used even though it can be vulcanized in the presence of zinc oxide alone. This is because magnesium oxide gives enough scorch resistance [7]. The cure behavior of peroxide vulcanization and sulphur vulcanization is different and leads to different properties in the cured compounds. The obtained rubber product can be called as mixed vulcanizate. If mixed vulcanization is just defined as vulcanization which leads to both sulphidic and C–C crosslinks, then the use of sulphur as co-agent in peroxide vulcanization, can be considered as mixed vulcanization [8, 9].

1.2 Blends

Polymers are often mixed together to achieve superior properties which arise from the individual systems. Blending of two or more elastomers is carried out for several purposes, such as improving the physical and mechanical properties of the first elastomer, obtaining good processing characteristics of rubber compound and/or decreasing the compound cost [10]. Since the macromolecular chains are very larger in size the entropy of mixing should be negligible and this is the reason why most of the blends are immiscible in nature. Depending on the interactions between the individual polymers the blends can be miscible and partially miscible as well. Elastomers can be compounded themselves as well as can be mixed with thermoplastics and thermosets. A brief discussion on the different types of blend systems is given in the following subsections.

1.2.1 Immiscible Rubber Blends

The phases of an immiscible blend can be co-continuous, or one phase will be dispersed within a continuous matrix of the other. The former morphology is favored by equal concentrations and equal viscosities. Most blends consist of discrete particles in a continuous phase, with the latter usually the lower viscosity component, is present at a sufficient concentration. During mechanical mixing, domains of the lower viscosity material deform and encapsulate the higher viscosity phase, to produce a “globular” morphology. However, for an immiscible blend the morphology is never at equilibrium (which would correspond to macroscopic phase separation). Upon improving the compatibility of the blend components, smaller and/or more interconnected phases forms and both of these can potentially improve the properties. This can be achieved through the use of compatibilizing agents or chemical modification of the components. Compatibilizers are surfactants that modify the interfacial tension to decrease the dispersed particle size.

1.2.2 Rubber/Thermoplastic Blends: Micro and Nano Structured

A rubber—thermoplastic polymer blend can be obtained either when rubber-rich mixtures form soft thermoplastic elastomers, or when plastic-rich blends produce rubber toughened thermoplastic. Rubber toughened thermoplastics with flexible and high impact properties can be used as economical alternatives for ordinary plastic materials. Thermoplastic elastomers have replaced conventional rubber in a variety of applications including appliance, automotive, medical, engineering, etc. They are made by copolymerization and by blending thermoplastics with rubber component. In most cases, thermoplastic elastomers are block copolymers consisting of soft and mobile 'rubbery' blocks with a low glass transition temperature (Tg), and rigid or hard 'glassy' blocks with a high melting temperature (Tm) and/or high Tg. Rubber/thermoplastic based nano-blends can be a new class of nanocomposites, which are particle-filled polymers for which at least one dimension of the dispersed particles, is in the nanometer range [11]. Thermoplastic elastomer nanocomposites (TPE nanocomposites) based on PA6/NBR/Cloisite 30B were fabricated through a direct melt mixing process in an internal mixer by Mahallati [12]. Excellent improvement in mechanical properties like tensile strength, elongation at break, and modulus was observed on incorporation of the nanofillers in the rubber/thermoplastic based nano blends. Manufacturing methods of rubber/thermoplastic based micro blends includes injection molding, compression molding, extrusion, blow processing, calendaring etc.

1.2.3 Rubber-Thermoset Blends: Micro and Nano Structured

Thermosets can be toughened by rubber particles with mainly two different morphologies which are either the use of 'core–shell rubber particles' or initially 'miscible reactive rubbers'. Emulsion polymerization is the route to the preparation of core–shell rubber particles having alternate rubbery and glassy layers. One of the most important classes of thermosetting polymers is the epoxy resins as their applications can cover a wider spectrum. They are extensively used in various fields of coating, high performance adhesives and engineering applications. Cured epoxy polymers are characterized by high chemical and corrosion resistance simultaneously having good mechanical and thermal properties. Epoxy resins are reactive monomers, which are commonly cured with amine to form thermosetting polymers. Jansen et al. [13] reported the preparation of thermoset rubbery epoxy particles as novel toughening modifiers for glassy epoxy resins. They used two types of liquid epoxy resin with an aromatic backbone; diglycidyl ether of bisphenol A (DGEBA) and diglycidyl ether of bisphenol F (DGEBF). Brittle thermoset materials can be toughened successfully by blending with proper liquid rubbers in small amounts or by incorporating preformed rubber particles directly.

Boyonton and Lee [14] applied a synergistic combination of liquid carboxyl-terminated butadiene acrylonitrile rubber and solid rubber particles of different sizes, the latter obtained from recycled automobile tyres. They found no significant improvement in the fracture toughness of the composite when solid rubber alone was used. However, when the combination with liquid rubber modifier was employed, they got higher fracture toughness for the hybrid epoxies than that of those toughened with liquid rubber alone. This synergistic effect is explained in terms of crack deflection and localized shear yielding. Furthermore, they observed a slight improvement in the fracture toughness as the size of the solid rubber particles increased. Although the combination of both reactive liquid rubber and solid rubber particles as toughening agents had been practiced previously, the usage of solid rubber particles obtained from the recycled rubber tyres provides relatively low cost and created higher-value products for recycled solid rubber.

1.2.4 Interphase Modification and Compatibilization

Elastomers are generally immiscible with each other and their blends undergo phase separation with poor adhesion between the main matrix and dispersed phase. The properties of such blends are often poorer than the weight average property of individual components. In fact, the main objectives of blending are to combine the performance characteristics of two or more polymers, to develop high performance products. These can be accomplished by compatibilizing the blend, either by adding a third component, called compatibilizer, or by enhancing the interaction of the two component polymers, chemically or mechanically. The role of compatibilizer is in reducing the interfacial energy and improving the adhesion between two or more polymer phases, achieving finer dispersion during mixing and stabilizing the fine dispersion against agglomeration during processing and throughout the service life. Since most blended polymers are immiscible, in many cases additional compatibilization process is required to obtain maximum synergy. The compatibilization process could be reactive or non-reactive. There are several excellent techniques for the compatibilization of polymer blends. However, compatibilization of rubber based blends is more difficult because of crowd and complex compound matrix [15].

Fillers can also compatibilize blends to a greater extent. Most commonly used fillers in blends include carbon black, silica, aluminum trihydrate, aluminum oxide, clay, calcium carbonate, talc, mica, zinc oxide, magnesium oxide, calcium, magnesium silicate etc. In the rubber industry, carbon black is consumed more than three times with respect to other fillers and is one of the well-known ingredients of a tyre [16]. Carbon black (size of 10–30 nm) and precipitated silica (size of 30–100 nm) still remain the conventional fillers due to difficulty in dispersing them at nanometer level. Silica with the general formula SiO_2 or $SiO_2 \cdot xH_2O$ is a naturally occurring mineral such as sand, quartz, quartzite, perlite, tripoli and diatomaceous [17–19]. They can be amorphous or crystalline forms. Its white color is a significant advantage in competition with carbon blacks. Silica with a specific surface area in the range of 125–250 m^2/g is designated as “reinforcing”, while products with a specific surface are in the range of 35–100 m^2/g are “semi-reinforcing”. Clay platelets bound together by Van der Waals forces have better compatibilizing action in polymer blends. Isomeric substitution (for e.g. tetrahedral Si^{+4} by Al^{+3} or octahedral Al^{+3} by Mg^{+2} or Fe^{+2}) within the layers generates negative charges that are counterbalanced by alkali and alkaline earth cations (typically Na^{+1} or Ca^{+2}) situated inside the galleries (gaps between the layers). Fillers can also change one or more of optical properties and color, improve surface characteristics and dimensional stability, change thermal, magnetic and electrical properties, improve mechanical properties, durability, and rheology, chemical reactivity and biodegradability [6, 20].

1.3 Interpenetrating Polymer Networks

Interpenetrating polymer networks (IPNs) have been studied extensively since their advent in the 1960s. In the beginning, the concept of a double network was introduced by Tobolsky and coworkers. Double-network rubber refers to an elastomer that has been crosslinked twice, the second time in a deformed state. These result in materials with unusual and enhanced properties which have been termed ‘‘double network elastomers”. The deformation employed may be uniaxial tension, biaxial tension, torsional, bending etc. Interpenetrating polymer networks (IPNs) are defined as a combination of two or more polymers in network form. IPNs come next to the class of polymer blends, blocks and grafts. IPNs involve the polymerization of one monomer in the immediate presence of the other, and the crosslinking of one or both the polymers. In most cases IPNs provide intimate mixing of phases, smaller domain sizes, better mechanical properties and damping properties than the corresponding blends, which are physical mixtures of two polymers. The mechanism of phase separation and morphology of simultaneous and sequential IPNs, are different and in most cases simultaneous IPNs leads to better phase mixing, especially when gelation point is reached at the same time.

IPNs have different applications and are the commercially successful form of polymer blends, probably owing to the crosslinked structure that provides better thermal stability, mechanical properties, chemical resistance etc. Though IPNs are traditionally used as damping materials, impact resistant materials, adhesives, etc., more recently they are used in combination with nanoparticles to produce nanocomposites for use as responsive hydrogels, medical implants, porous scaffolds or catalyst supports. The number of publications in this research area has shown a regular increase and is about 400 per year, currently. The interesting and unique properties of IPNs emerge when the deliberately introduced crosslinks outnumber the accidently introduced grafts in the polymerization stage. However, some amount of graft is usually present in all IPNs and contributes to the IPN performance in a favorable manner. In IPNs the two separate glass transitions (Tg) for each polymer, with or without inward shift can occur or one broad Tg intermediate to the Tgs of the individual polymers or one sharp Tg intermediate to the Tgs of the component polymers can be obtained, depending on the extent of compatibility or phase mixing.

Kong and Narine studied about the sequential IPNs of polyurethane (PU) using canola oil based polyol and polymethyl methacrylate (PMMA) and compared it with those castor oil based PU/PMMA IPNs [21]. Also the domain sizes found in interpenetrating networks are smaller than corresponding blends, which supports this concept of forced miscibility due to crosslinking. Most IPNs and related materials show phase separation. Dongyan et al. [22] reported the synthesis and applications of castor oil based PU/PMMA simultaneous IPNs containing $BaTiO_3$ fibers. The synthesis resulted in graft IPNs and the TEM analysis showed that the domain sizes were in nanometric scale. The mechanical studies of the nanocomposites showed a change from elastomeric behavior to brittle nature, due to the addition of $BaTiO_3$. Copper nanoparticles with 10–20 nm diameter in polyvinyl alcohol (PVA)/polyacrylamide (PAAm) IPNs resulted in hydrogels which can be tuned for drug release or tissue engineering applications [23]. The study showed that the complexation of PVA and PAAm with Cu^{2+} resulted in low aggregation of Cu nanoparticles and thereby controlling and stabilizing the dispersion and distribution of nanoparticles in the polymer network. There are many products like optically smooth surfaces, toughened plastics, adhesives, damping materials, ion exchange resins, impact modifiers etc. based on IPNs or related materials [24].

2 Conclusion

Elastomers, both synthetic and natural are very important class of polymers having great commercial importance. In general they could be classified as general purpose or special purpose based on their functional properties and end-use applications. New polymerization techniques such as controlled radical polymerizations, atom transfer radical polymerizations etc. will be very useful to synthesize new class of elastomers having controlled architecture and functional properties. The various types of elastomer blends and interpenetrating networks are gaining tremendous importance in recent years. Both blends and IPNs provide broad spectrum of property profile for a given application. They have very attractive cost/performance ratio on a commercial point of view. However, the morphology control of both blends and IPNs for the manipulation of ultimate properties is still a challenging task.

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