We are IntechOpen, the world’s leading publisher of Open Access books
Built by scientists, for scientists

4,100
Open access books available

116,000
International authors and editors

125M
Downloads

154
Countries delivered to

TOP 1%
Our authors are among the most cited scientists

12.2%
Contributors from top 500 universities

WEB OF SCIENCE™
Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com
Abstract

Polyurethane is a versatile thermoplastic polymer with a range of characteristics (tensile strength, chemical resistance, thermal stability, and processability) as coating, elastomer, foam, and fiber for technical application. Epoxy resin, on the other hand, is thermoset having fine mechanical, chemical, and adhesion properties to be utilized as adhesives, coatings, and matrix for advanced composite materials. However, epoxy resins are rigid and brittle in nature and have poor crack resistance. To overcome these problems, polyurethane phase has been introduced in the epoxy network for toughening. Considerable research has been carried out to introduce a second reactive polymer in the matrix to generate interpenetrating polymer network (IPN). Consequently, mechanical properties, glass transition behavior, thermal resistance, and damping features of polyurethane have been enhanced by introducing epoxy to form polyurethane/epoxy interpenetrating polymer network structure. Different modifiers have been employed to modify the properties of polyurethane/epoxy IPNs such as montmorillonite nanoclay, fibers, fly ash, conducting polymers, etc. The polyurethane/epoxy cross-linked networks have shown a range of high-performance application in ion-exchange resins, aircraft, engineering materials, biomedical devices, and other commercial IPN products.

Keywords: polyurethane, epoxy, network, IPN, application

1. Introduction

Polyurethane (PU) has been used in several technical applications due to high tensile strength, chemical resistance, processability, and mechanical properties [1, 2]. In polyurethane, hydrogen bonding is sufficient to produce a physical link between polymer chains to enhance overall improved properties. Phase separation in PU has been found to influence by
hard and soft segment structures, molecular weight, polydispersity, and crosslinking ability. Epoxy polymers are tough and flexible with good corrosion and chemical resistance. The epoxy reactions are highly temperature dependent, epoxy oligomer/monomer-dependent, and energetic [3, 4]. Polymerizations can be typically carried out at or above ambient temperature (90–130°C). Solvent-free reactions are also used. Recently, there has been considerable interest in the development of mixtures with a second reactive polymer to generate interpenetrating polymer network (IPN) [5]. Interpenetrating polymer network is often considered as a novel type of polymer alloy, also known as polyblend. IPNs of polyurethane and epoxy have been reported by several investigators [6, 7]. In order to improve mechanical properties, thermal resistance, and damping properties of polyurethane, epoxy has been introduced in polyurethane systems to form polyurethane/epoxy IPN structure. Polyblends of linear polymers as well as grafted IPNs due to covalent bonding between the polymers have been established. Semi-IPN has also been developed from linear and crosslinked polymers [8].

Glass transition behavior and morphology studies have been used to explore the effective IPN. Generally, IPNs show excellent engineering properties due to synergetic effect induced by the compatibility of individual components in PU/epoxy IPNs [9]. Polyurethane/epoxy IPNs have been widely applied to foams, coatings, fibers, leather, and other applications [10].

2. Prolog to polyurethane

Polyurethane (PU) is one of the most important classes of thermoplastic polymers having versatile structural relevance. Polyurethane elastomers are segmented copolymers consisting of hard and soft segment domains [11]. Soft domains are consequential of a macrodiol, while hard segments are derived from diisocyanate (Figure 1). When a short chain compound commonly referred as chain extender is used, polyurethanes are considered as segmented. In shape memory polyurethane (an important class of PU), hard segments in polyurethane are also known as fixed phase, while soft segments are termed as reversible phase. In general, hard and soft segments are incompatible with one another to create microphase separation. This segregation is principally responsible for excellent mechanical and other physical properties. Phase separation between the segments has been found to influence by hard segment structure, soft segment structure, molecular weight, weight fraction, polydispersity, and crosslinking. Polyurethane exists in several forms such as rubbery materials, liquid, soft solids, and thermoplastic. Few types of polyurethanes also exist as thermoset materials. A wide range of potential applications of polyurethanes have been achieved due to tailoring the essential features of PU. General applications of PU range from foam mattress to medical implant to engineering components [12, 13]. The advantage of the choice of polyurethane in advance applications is the ease of synthesis, processability, tailorability, chemical nature of hard and soft segments, and phase separation properties. Hydrogen bonding phenomenon
also occurs in PU chains, which offers physical crosslinking points between polymer chains. Condensation polymerization of N-(4-hydroxybenzal)N′(4-hydroxyphenyl)thiourea and methylene diisocyanate (MDI) has been studied [14]. The polyurethanes were used as an effective adsorbent for toxic metal ions. Solution precipitation route was used to prepare conducting polyurethane [15]. Several blends of polyurethanes have been studied. For example, polyurethane/polyaniline (PU/PANI) blend has been studied with enhanced electrical properties [16]. The effect of moisture on glass transition temperature (T_g) of polyurethane has also been studied [17].

![Chemical structure of PU elastomer](http://dx.doi.org/10.5772/67678)

Figure 1. Chemical structure of PU elastomer.

### 3. Epoxy thermoset

Epoxy is generally illustrated by three-membered rings known as epoxy or oxirane or ethoxyline group. Epoxy resin is a prepolymer having more than one epoxide group. It is generally a low molecular weight compound. The most common type of epoxy resin is bisphenol-A epoxy resin (Figure 2). It is a type of epoxy resin produced by the reaction of epichlorohydrin with bisphenol-A in the presence of a basic catalyst. The properties of epoxy resin depend on the number of monomers in the epoxy chain [18]. Epoxy with low molecular weight usually has high viscosity and exists in the liquid state. High molecular weight epoxy occurs in solid state [19]. Depending upon the chemical structure of epoxy, they may have excellent electrical properties, thermal stability, UV stability, and weather ability [20]. In addition to linear epoxy resins, they can be cycloaliphatic, tri-functional, and tetra-functional epoxy resins [21, 22]. Various types of epoxy resins are shown in Figure 3.
Figure 2. Preparation of bisphenol-A epoxy.

Figure 3. Different types of epoxy resin.
Among these types, tetra-functional epoxy resin has high crosslinking density and high thermal resistance. Novolac epoxy resin is produced by the reaction of aromatic novolac resin with epichlorohydrin. It has high crosslinking density due to the bulk of epoxide groups. Because of crosslinking property, it has excellent chemical, thermal, and solvent resistance properties [23]. Another other phenomenon is hardening of epoxy resins. The thermosetting resins are hardened using extensive range of hardening agents. The properties of thermosets also depend on the specific combination of hardening agents and epoxy resins constituting a system [24]. Molecular structure of hardening agents affects the final structure and properties particularly the glass transition temperature of epoxy. The hardening agents are also of various types such as amine, anhydride, and catalytic hardening agents [25]. Different types of amine hardening agents have been employed in epoxies [26]. The reactions between amine hardener and the epoxy are generally nucleophilic addition. These hardeners provide excellent chemical, physical, and electrical properties to the epoxy systems [27]. Hardening can be performed at room temperature, or in the presence of light, or heat. Room temperature hardeners provide high tensile properties, electrical conductivity, thermal resistance, and low $T_g$ to epoxy systems [28]. Aliphatic polyamines, aromatic amines, and alicyclic polyamines are generally room temperature hardeners. Hardening time has been reduced using photocuring process, relative to heat curing or room temperature process [29].

4. Interpenetrating polymer network (IPN)

Interpenetrating polymer network (IPN) is a unique type of polyblend. IPNs can be simply defined as a mixture of two or more crosslinked polymeric networks [30]. The interpenetrating polymer network can be generated using physical or chemical interlocking between the polymer chains [31, 32]. IPNs can be considered as the crosslinking of one polymer component in the presence of another polymer component to form crosslinked polymer network. In this regard, fully formed interpenetrating polymer network and semi-interpenetrating polymer network have been identified [33]. Fully formed interpenetrating polymer network are acknowledged by the presence of crosslinks in both the network polymers, and the whole polymer components are crosslinked. Semi-IPN exists when one of the components is crosslinked and other is linear or non-crosslinked [34]. Semi-IPN is also referred to as pseudo-IPN. In in situ crosslinking, results in polymer chains are well interlocked. The full IPN and semi-IPN are shown in Figure 4. IPNs are sometimes confused with the polymer blends, block, graft, or crosslinked copolymers. However, there exist differences. An IPN can be distinguished from block copolymers as IPNs swell in the presence of solvents but does not dissolve. Moreover, IPNs exhibit characteristic morphologies. Polyurethane has been applied in elastomer, leather, foam, coatings, and fibers. Epoxy resin has been introduced in polyurethane systems to form epoxy/polyurethane interpenetrating polymer network structure. Various methods have been used to prepare and modify the properties of epoxy/polyurethane IPNs.
5. Polyurethane/epoxy interpenetrating polymer network

Due to high modulus, strength, and mechanical properties, epoxy resins have been used in high-performance structural composites. However, engineering applications of epoxy resins have been limited in several cases such as damping materials [35]. In contrast, polyurethane is a flexible and elastic polymer with low mechanical strength [36]. PU prepolymers have been prepared and incorporated into epoxy resin to form IPNs. The mechanical properties of PU/epoxy IPNs largely depend on the amount of polyurethane in the blend network. Jin et al. [6] investigated tensile properties of soybean oil-based PU/epoxy IPNs. The tensile strength and tensile modulus of PU/EP IPNs with 5–20 mass% PU were lower than pure epoxy. This means that the addition of PU turned epoxy to the rubbery elastomer increased the elongation at break by 13-fold as compared to pure epoxy. However, increasing the amount of epoxy increased tensile strength and tensile modulus drastically. IPNs basically integrate the structure and properties of these versatile polymers (epoxy and polyurethane). Integrated performance of epoxy/polyurethane networks have been improved by the structural modification. The glass transition temperature of PU/epoxy IPNs provides important information about the miscibility of the blend components and blend compatibility. Moreover, the glass transition temperature of PU/epoxy IPNs also provides information about the cure rate of the reaction. At the beginning of cure reaction, \( T_g \) of PU/epoxy IPNs is usually lower than that of neat epoxy. The cure rate of epoxy is usually slower than that of PU. Some of the epoxide groups remain unreacted and act as plasticizer leading to lower \( T_g \) values of IPNs at the beginning of the cure reaction. When reaction proceeds and an IPN is formed, this may result in an increase in \( T_g \) of IPNs. The increase in \( T_g \) can be attributed to the miscibility/formation of graft structure through the reaction of hydroxyl groups of epoxy with isocyanate [37].
6. Modified polyurethane/epoxy IPNs

Polyurethane/epoxy IPNs have been prepared by adopting several modifications. The reinforced PU and diglycidyl ether of bisphenol A (DGEBA) IPN composites have been prepared with aramid fibers. The mechanical properties have been found to improve [38]. The PU/epoxy IPNs exhibited higher tensile and Izod impact strength. Montmorillonite-filled polyurethane/epoxy IPN nanocomposites were prepared, and the influence of hydrogen bonding on free volume and miscibility of clay was studied [39]. Polyethylene glycol-based polyurethane and epoxy IPN composite filled with fly ash have also been studied [40]. Montmorillonite-filled polyurethane/epoxy nanocomposite has been prepared for electromagnetic interference (EMI) shielding and charge dissipation applications. The damping properties of the modified PU/epoxy IPN composites have also been studied [41]. T\text{g}, contact angle, interfacial, and mechanical properties have been investigated [42]. Recently, Kausar and Rahman Ur [43, 44] reported modified epoxy/polyurethane interpenetrating networks and their composites. Damping of vibration is a critical problem in the design of structural materials because excessive vibration may cause damage to the surroundings or the material components. To solve this problem, polymeric and composite IPNs with high damping properties around glass transition temperatures have been focused [45]. Chen et al. [46] prepared a series of castor-oil-based polyurethane/epoxy resin graft IPNs modified by hydroxy-terminated liquid nitrile rubber (HTLN). Figure 5 and Table 1 show the damping properties of HTLN-modified PU/epoxy IPN composites at 10 Hz. The glass transition temperature (corresponding to the peak of tan δ) was shifted to higher values with HTLN addition compared with that of pure IPNs. T\text{g} of 5% loaded composite was increased to 71°C relative to neat IPNs (68.2°C). The 5% HTLN-modified PU/epoxy also showed good damping properties.

![DMA curves of PU/EP IPN composites as a function of the HTLN content at 10 Hz [46].](http://dx.doi.org/10.5772/67678)
The tensile strength of polyurethane/epoxy IPN composites filled with montmorillonite (MMT) has been studied [8]. According to Figure 6, 1% MMT resulted in the maximum tensile strength of the composites. The tensile strength of all the filled composites increased by about 40% relative to pure PU/epoxy IPNs. The results were attributed to the large interface area and strong interfacial adhesion between the IPN matrix and MMT. Figure 7 shows the impact strength of MMT-filled PU/epoxy IPN composites. The impact strength primarily increased and then decreased with the increase in the MMT content. The impact strength reached higher values for 1 and 3% MMT contents. The results showed strong mutual interactions between the filler and matrix, and thus the impact strength of MMT-modified composites was improved.

<table>
<thead>
<tr>
<th>PU/epoxy/HTLN (%)</th>
<th>tan δ</th>
<th>Tₐ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/50/0</td>
<td>1.063</td>
<td>68.2</td>
</tr>
<tr>
<td>50/50/5</td>
<td>1.105</td>
<td>71.0</td>
</tr>
<tr>
<td>50/50/10</td>
<td>1.031</td>
<td>70.9</td>
</tr>
<tr>
<td>50/50/15</td>
<td>1.081</td>
<td>70.0</td>
</tr>
<tr>
<td>50/50/20</td>
<td>1.041</td>
<td>71.9</td>
</tr>
</tbody>
</table>

Table 1. DMA data of PU/EP IPN and HTLN-modified PU/EP IPN composites at 10 Hz [46].

Figure 6. Tensile strength of MMT-filled PU/EP IPN composites as a function of the MMT content [8].
7. Structure-property relationship in interpenetrating polymer network

The understanding of structure-property relationship in polyurethane/epoxy interpenetrating network is essential for a wide range of technical applications. Particularly, in the search of broadband damping materials, it is desirable to form IPNs with high loss region in shear or extension, covering the entire temperature and frequency range. Polyurethane/epoxy IPNs have been prepared for broadband damping materials. Epoxy and PU composites have been prepared to increase the crosslink density to improve polymer toughness. Epoxies have low toughness and poor crack resistance at room temperature due to high crosslinking density. Therefore, the literature focused on the matter of toughening of epoxies. Thermoplastic polymers/rubbers have been added to epoxy resins to improve the toughness of epoxy [47, 48]. Interpenetrating polymer network has been formed by the combination of crosslinked polymer networks in which at least one polymer is crosslinked in the immediate presence of the other. The mechanical properties of IPN structures are superior to the neat polymers. The presence of intermolecular hydrogen bonding between the hydroxyl group of epoxy and isocyanate group in PU plays an important role in interlocking network formation. IPNs of polyurethane and epoxy resin are very efficient for improving the fracture properties of the epoxy resin. Epoxy resin/polyurethane IPN nanocomposites with various contents of organophilic montmorillonite have been prepared through an in situ intercalation method [49]. The addition of PU to the epoxy matrix has remarkably increased the fracture toughness by 49% of pure epoxy, while the addition of clay improved toughness by 55% of
pure epoxy. The resulting IPN shows excellent physical strength and low density. The low
density may help in matching the specific acoustical impedance of the composite to the sea
water [50]. The material can be acoustically transparent at the operating frequency range
with high impact loading [51]. A successful operation of high-frequency sonar arrays needs
an acoustic window with minimal interference, acoustical signals, and sufficient rigidity.
To meet the demands of current designs of window materials, PU/epoxy composite materi-
als are desired [52]. During interpenetrating polymer network (IPN) formation, qualitative
control and relationship between temperature and polymerization kinetics are essential to
understand and manage. Furthermore, the relationship of IPN formation with monomer
type, concentration, temperature, and other reaction conditions should be considered for the
optimum design of high-performance systems.

8. Application of IPNs

As described in the preceding sections, polyurethane/epoxy IPNs are of interest because
they own enhanced glass transition temperature, impact strength, tensile strength,
and damping properties relative to the neat/individual polymers [7, 8, 37, 46–49]. These
properties are definitely superior to the polymer blends, which are usually obtained by
blending the polymers together. If two homopolymers are blended, in most of the cases
two distinct glass transition temperatures are observed. A major advantage is that the IPN
may display a broad glass transition temperature. In this regard, Zhang and Hourston et al.
[37] prepared a series of rigid interpenetrating polymer networks of rosin-based polyure-
thane and epoxy resin by a simultaneous polymerization technique. The chemical structure,
dynamic mechanical properties, and morphology of the materials were investigated using
relevant techniques. The PU/epoxy IPN showed a single broad glass transition over a wide
range of composition, with the tan δ peaks of the IPN shifting to a lower temperature. This
implies that the PU/epoxy IPN foam system was miscible over a wide range of composi-
tion. In other words, the single broad glass transition temperature indicated good compat-
ibility of the two polymers contributing to IPNs. As the epoxy graft content was increased,
tan δ peaks move toward the peak of neat epoxy. This broad glass transition temperature
is highly advantageous for energy absorption and vibration damping [53, 54]. In drug
delivery, IPNs have been used to maximize the therapeutic benefits of the drug. Moreover,
biologically active materials have been prepared when controlled release is desirable. The
physiochemical properties such as drug diffusivity, erosion rate, and controlled dissolution
can be tailored in vivo through selection of the materials, composition and crosslink density.
Another important application of IPNs is in dental applications. IPNs have been used as a
synthetic teeth and cavity filler. Moreover, the IPN offers a number of advantages such as
less temperature sensitivity and stronger bonding to the tooth. In engineering applications,
the IPN has advantage over homopolymers or homopolymer composites. Using IPNs, the
material properties can be tailored to a higher degree at different stages of polymerization.
However, IPN complexity may arise from processing conditions affecting the material prop-
nerties, kinetics, and thermodynamic instabilities driving phase separation. The use of these
IPNs has also been exploited in hydrodynamic machines such as water turbine pumps.
PU/epoxy IPNs have the ability to prevent the damage of cavitation corrosion. These IPNs are used to form cavitation corrosion resistant coating due to good adhesion to metals, abrasive resistance, water resistance, elasticity, toughness, and damping property. PU/epoxy IPNs have also been used in several applications such as thermally conductive adhesives in electronic components. The thermal conductivity of composites can be improved by using polyurethane/epoxy fully formed IPNs [55, 56]. To explore and implement more technical applications of PU/epoxy IPNs, fabrication processes, processing conditions, and developing trends must be focused in future.

9. Conclusions

The principal routes for the formation of IPNs are successive and simultaneous polymerization of the two polymer components. Polyurethane elastomers are segmented copolymers consisting of soft segment domains derived from a macrodiol and hard segment domains derived from a diisocyanate and chain extender. Usually, the two segments are incompatible, resulting in microphase separation, which is responsible for fine mechanical properties. Epoxy resins are well known for unique properties such as high mechanical strength, chemical resistance, and outstanding surface adhesion. However, they are rigid and brittle in nature, and have poor crack resistance, which prevent its engineering applications. To overcome these problems, toughening of epoxy resins with polyurethanes has been performed. Various factors affect the final properties of IPNs such as hard and soft segment structures, molecular weight, polydispersity, crosslinking, and phase separation. Consequently, the design of hard and soft segment structures affects the structure of PU prepolymer. The molecular weight of PU prepolymer also influences the formation of IPN structure. Phase separation is truly dependent on the content of polyurethane and epoxy contributing to the IPN network. Furthermore, the degree of crosslinking defines the glass transition temperature of the final PU/epoxy IPN. Two types of forces may form the IPN network in polymers, i.e., primary (chemical bond) and secondary (vander Waals). The presence of intermolecular hydrogen bonding between the hydroxyl group in epoxy and the isocyanate group in PU plays an important role in increasing network interlocking in IPN formation. Depending on the specific components selected for IPN formation, surface free energy of the blend system, and other structural parameters, there are several technical applications identified for epoxy/polyurethane systems.

Author details

Ayesha Kausar 1,2*
*Address all correspondence to: asheesgreat@yahoo.com
1 Nanosciences Division, National Center For Physics, Quaid-i-Azam University, Islamabad, Pakistan
2 Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan
References


