

Nanoclay Reinforced Polyurethane-Epoxy Blend: A Review

K Natarajan¹, Anu K S²

¹Professor, ²Research Scholar, R.V. College of Engineering, Bangalore, India.

Abstract:

This paper presents a broad review on the recent advances in the research and development of nanoclay reinforced polyurethane-epoxy blend that are used in various applications such as drug delivery systems, anti-corrosion barrier coatings, UV protection gels, lubricants and scratch free paint, superior strength fibres and films, crack injections, etc. An overview of nanoclays or organoclays is presented with emphasis placed on the use of nanoclays as the reinforcement phase in polymer matrices for preparation of polymer/layered silicates nanocomposites, which are characterized by X-ray diffraction, Infrared spectroscopy and differential scanning calorimetry. Hence, this review offers a comprehensive discussion on synthesis, characterization and applications of polymer nanocomposites.

Keywords:

Polyurethane, epoxy resin, nanoclay/organoclay, interpenetrating networks.

Introduction:

Organically modified layered-silicates or nanoclays have become an attractive class of organic-inorganic hybrid materials because of their potential use in wide range of applications such as in polymer nanocomposites, rheological modifier in paints, inks, greases and cosmetics, adsorbent for toxic gases, effluent treatment and drug delivery carrier. The generic term, layered silicates, refers to natural clays as well as synthesized layered silicates such as montmorillonite, laponite and hectorite [1]. Clays especially can increase the barrier properties by creating a tortuous path that retards the progress of the gas molecules through the polymer matrix [2]. The nanoscale clay particles can be dispersed to a scale of few nanometers in the polymer matrix, and such dispersions are produced by shear or chemical reactions or a combination of both [3]. During the past decade, polymer-clay nanocomposites consisting of inorganic nanolayers of montmorillonite and organic polymers have attracted a great deal of attention in material science because of their superior engineering properties compared to neat polymer [4–6]. Furthermore, it is

discovered in some current research that the encapsulation of inorganic materials inside polymer can result in better particle dispersion in the polymer matrix, strong physical or chemical bonding between polymer and nanoparticles.

Polymer blend may also be defined as intimate mixtures of two kinds of polymers with no covalent bonds between them [7], or that are not bonded to each other [8]. Blending of polymer, therefore, are excellent methods for modification and improvement of polymer properties [[9, 10]. Blend display widely varied behavior from brittle to strong and flexible [11]. Due to the higher surface area available with nanofillers, polymer nanocomposites offer the potential for enhanced mechanical properties, barrier properties, thermal properties and flame retardant properties when compared to conventionally filled materials. This review concerns about polyurethane- epoxy blend with montmorillonite reinforcement.

Epoxy:

Epoxy resins are low molecular weight, oligomeric or polymeric compounds consisting of more than one epoxy group. They are liquids with high viscosity that undergo a cross-linking process and transform to insoluble and hard plastics. Cured epoxy resins are characterized by high chemical and corrosion resistance, good mechanical properties as well as acceptable thermal stability [12]. Epoxy resins are widely used for high performance composites, especially in aerospace, military and sports industries [13]. Epoxies are stronger, stiffer, tougher, more durable, more solvent resistant, dielectric properties and have a higher maximum operating temperature than polyester thermosets; rubber polymers are added to epoxy resins to increase toughness [14, 15].

The applications of epoxy resins are extensive and include coatings, adhesives and matrices for high performance composite materials containing carbon and glass fibers as well as electronic packaging. However, their field of applications is seriously limited by their poor resistance to crack propagation, low impact strength and small elongation at break, i.e. their brittleness [16-19]. The improvement of toughness, thermal stability and resistance to moisture and weather are essential in order that the epoxy resin can be used for high performance advanced composites. Hence, it is proposed to modify the epoxy resin in the form of an intercross linked polymer network having flexible and rigid molecular segments.

The inter-penetrating network (IPN) structure having a different polymer skeleton can be considered as an attractive method, since an intercross linked network mechanism provides matrix materials with a single glass transition temperature (T_g), when compared with polymer blends. This can be achieved by the incorporation of polyurethane and suitable filler into epoxy resin which improves the flexibility and thermo-mechanical properties due to its superior chain rigidity, high T_g , excellent thermal and thermo-oxidative stability and negligible tendency to absorb water.

Interpenetrating polymer networks:

Interpenetrating polymer networks (IPNs) are defined as a combination of two or more polymers in a network form, in which one of the polymers is cross-linked or synthesized in the presence of the other. Interpenetration or permanent entanglements usually lead to improved compatibility between the blend's component, which means a decreased degree of phase separation. Morphology, which plays a major role in affecting IPN properties, is controlled by the chemical compatibility of the polymers, interfacial tension, cross-linking densities of the networks, polymerization method, and IPN composition [20-22].

However, most IPNs do not interpenetrate on a molecular scale but may instead form finely divided phases of only tens of nanometers in size. Many IPNs exhibit dual phase continuity and the crosslink density (related to chain length between cross-links) plays a major role in determining the domain size of IPNs. Generally, it is well accepted that the presence of short chain segments between cross-links can form smaller domains, which may increase the miscibility between IPN components. However, in some cases, strong evidence suggests that the cross-links' density might lead to the decrease of the miscibility between polymer components [23].

Interpenetrating polymer networks can produce materials which may have completely different properties from the base components. Such IPN systems, composed of two different polymers, might exhibit advantages of both components with minimized drawbacks. Moreover, it is possible to adjust the structure of an interpenetrating polymer network such that an enhancement in the epoxy resin properties can be achieved.

Polyurethane:

Polyurethanes are a unique class of polymer materials with a wide range of physical and chemical properties. Polyurethanes are characterized by the presence of urethane linkages, although other groups such as ether, ester, and amide may be present in the polymer molecule. polyurethanes possess more complex chemical structures that typically comprise three monomers: a diisocyanate, a macroglycol (which is an oligomeric macromonomer) and a chain extender [24].

Polyurethane polymers were introduced by Otto Bayer and his coworkers in 1937 in the I.G. Farben laboratories in Leverkusen, Germany [25]. Polyurethane polymers are formed through step-growth polymerization. A urethane linkage $-RNHCOOR'$ is produced by reacting an isocyanate group $-N=C=O$ with a hydroxyl (alcohol) group $-OH$, in the presence of a catalyst. The step-growth polymerization is catalyzed by tertiary amines, such as dimethylcyclohexylamine, and organometallic compounds, such as dibutyltin dilaurate or bismuth octanoate. The choice of catalysts is furthermore governed by the urethane (gel) reaction, such

as 1,4-diazabicyclo[2.2.2]octane. The physical and chemical character, structure and molecular size of these compounds influence the polymerization reaction as well as the processability and resulting physical properties of polyurethane [26].

Polyurethanes (PU) are versatile polymeric materials that offer wide range of applications such as adhesives, elastomers, coatings for textiles/paper, foot wear, furniture/ foams, packaging material, and for automotive finishes [27, 28]. The ease of processing with relatively low tooling and manpower costs, as well as flexibility for long and short production runs, makes polyurethanes desirable for various applications [29]. Despite what is claimed in the literature, polyurethanes found a niche in biomedical applications mainly because of their interesting mechanical properties rather than for their biological response. Indeed, most of the studies related to the use of polyurethanes as biomaterials state that they are both “biocompatible” and “hemocompatible” despite the fact that several publications have clearly demonstrated that PUs degrade in the human body and are not more blood compatible than the other materials currently used in vascular surgery[25]. The bio-compatible products of PU range from nasogastric catheters, peritoneal dialysis infusion pumps to implanted pacemaker parts [27]. PU coatings are applied on different surfaces, to improve their appearance and lifespan. Due to their excellent properties which might be modified by structural elements, polyurethanes have been used to improve the toughness of epoxy resins. Polyurethane/epoxy resin graft interpenetrating polymer networks (IPN) with combined advantages of both polymers were first reported by Frisch et al [12].

Montmorillonite clay:

During the last two decades, a great number of studies have been devoted to the application of natural clays as additives for polymers and composites preparation. Attempts of specific additive incorporation such as with Montmorillonite, hectorite, vermiculite, saponite, illite and kaolinite were reported upon [30].Clays are inexpensive materials, which can be modified by ion exchange, metal/metal complex impregnation; pillaring and acid treatment to develop catalysts with desired functionality. Nanoclay can be obtained by simply the ion exchange reaction of hydrophilic clay with an organic cation such as alkyl ammonium or phosphonium ion [31]. The inorganic ions, relatively small (sodium), are exchanged with more voluminous organic onium cations. The ion-exchange reaction has two consequences: first, the gap between the single sheets is widened, enabling organic cations chain to move in between them and second, the surface properties of each single sheet are changed from being hydrophilic to hydrophobic or organophilic [32].

Montmorillonite (MMT) is a soft, natural clay that belongs to the smectite mineral family. It is named after Montmorillon, a place in France where MMT was discovered. MMT is composed of two tetrahedral sheets sandwiching a central octahedral sheet. The particles are plate-shaped with an average diameter of approximately one micrometer [33, 34]. The layers are continuous in the

x- and y-directions, and stacked one above the other in the z-direction. Chemically, MMT is hydrated sodium calcium aluminum magnesium silicate hydroxide $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$. Potassium, iron, and other cations are common substitutes, too. Similar to many other clays, montmorillonite swells upon addition of water.

However, some montmorillonites expand considerably more than other clays due to water penetration into the interlayer spaces and the concomitant adsorption. The amount of expansion is largely due to the type of exchangeable cation existing in the sample. The presence of sodium as the predominant exchangeable cation can result in the clay swelling to several times its original volume. Montmorillonite is known for its adsorbent quality; it has proven effective as an adsorptive of heavy metals, toxins, and hazardous chemicals [35-38] or moisture from air and gases. MMT is also widely used in the cosmetic and paper industries, and in pharmacology for a variety of applications such as stabilization of suspensions and emulsions, viscosity modifier, adhesion to the skin, and tablet making [39], drug carrier [40,41] or a part of a drug delivery system [42,43] for controlled drug release [44], and for tissue engineering [45].

Synthesis of polyurethane:

Three types of polyurethanes (PUR) were prepared using 4,40-diphenylmethane diisocyanate (MDI) and polyols: PUR based on PEG 400 (designated PUR 400), polyoxypropylene diol POPD 1002 (PUR 1002) and polyoxypropylene diol POPD 2002 (PUR 2002). Polyols were purified by means of azeotropic and vacuum distillation with toluene to eliminate water. First, 50 g of polyol and 0.25 cm³ of dibutyltin dilaurate were stirred for 5 min under vacuum and cooled to below 10°C to slow down the exothermic reaction between isocyanate and hydroxyl groups and finally MDI was rapidly added. The reaction was performed in a nitrogen atmosphere with vigorous mixing for 10 min and the temperature was maintained below 15°C until the mixture demonstrated an increased viscosity. All prepared polyurethanes had an isocyanate index equal to 1.05. The appropriate calculated amounts of MDI were the following: 27 g for PUR 400, 13.5 g for PUR 1002 and 6.6 g for PUR 2002.

Preparation of modified epoxy resins:

Polyurethanes in the amounts of 5, 10, and 15 wt % were mixed with epoxy resin at room temperature using a homogenizer for 15 min at a rotational speed of 2400 rpm. The mixtures were then placed in a vacuum oven to eliminate air bubbles. Finally, the curing agent was added, and the mixing continued for an additional 5 min before pouring the obtained compositions into a mold with standard geometries prior to mechanical tests. The curing process was carried out at room temperature for 48 h and postcuring took place in an air circulating oven for 3 h at 80°C.

The epoxy–MMT composites were prepared using 1, 2, and 3 wt% of Cloisite 30B (MMT). 10 g of MMT was added to 40 cm³ of acetone to disperse the nanoclay and then poured in a preheated epoxy resin (40°C), followed by mechanical stirring for 15min at 2500 rpm. After homogenization, the epoxy-based mixtures were placed in a vacuum oven to remove air bubbles and the residual solvent. Finally, the curing agent was admixed and the mixtures were poured into the cavities of the mold. Curing and postcuring were carried out under the same conditions as described for epoxy/PUR compositions.

Preparation of epoxy nanocomposites modified with polyurethane:

Compositions containing 1 and 2 wt% Cloisite 30B and different amounts of PUR were prepared. First, the solvent dispersion with a specific amount of MMT was mixed with epoxy resin for 20 min prior to the PUR incorporation and mixture homogenization. After degassing in a vacuum oven, the curing agent was added and the compositions were placed in the mold. Curing and postcuring processes were carried out as described previously.

Characterization:

The FTIR results showed that chemical reactions have occurred between the hydroxyl groups of the epoxy resin and the isocyanate groups of the polyurethane modifier, explaining the improvement in the fracture toughness of the polymer matrix. Moreover, SEM micrographs have indicated that the concomitant addition of 1% MMT and 10% PUR based on polyethylene glycol 400 (PUR 400) gave a more stratified elongated structure between epoxy resin and modifier as indicated by the rough surface and the presence of larger domains. However, the incorporation of PUR 1002 to epoxy nanocomposite (1% MMT) showed a rather different structure with elongated domains, which could be associated with the increase in the impact strength and KC values. The DSC results showed a slight decrease in the T_g with the addition of MMT, most probably due to a reduction in the cross-linking density of the polymer matrix. The XRD analysis has confirmed the formation of intercalated structure for the compositions containing only MMT and an exfoliated structure for the related nanocomposites.

Applications of polymer clay nanocomposite:

1. In drug delivery system:

Among different class of polymers used in biomedical field, polyurethanes are very attractive ones [46- 48]. This is because of their relatively good biocompatibility, their excellent physical and mechanical properties, and the ease of tailoring them for special end use.

Commercial medical-grade polyurethanes, such as Biomer[®], Elasthane[™], and ChronoFlex[®] AR [60], are typically synthesized from 4,4'-methylenebis(phenylisocyanate) (MDI). Carcinogenic and mutagenic aromatic diamines have been reported as degradation products from polyurethanes incorporating aromatic diisocyanates. To avoid the potential release of toxic degradation products to the extracellular matrix, it is desirable to synthesize new medical-grade polyurethanes from less toxic intermediates. In order to synthesize polyurethane elastomers with acceptable physical, mechanical properties and good cyto- and blood compatibility, epoxy-terminated polyurethane prepolymers based on poly(ethylene glycol) (PEG) and poly(tetramethylene ether glycol) (PTMEG) and HDI were prepared and cured with equivalent amount of hexamethylene diamine (HAD). It was expected that increased hydrophilicity due to presence of extra hydroxyl groups generated from ring opening of epoxy groups via reaction with HDI could improve surface hydrophilicity and increase blood compatibility. Increasing surface and bulk hydrophilicity of PTMEG based prepolymers via addition of PEG based epoxy-terminated polyurethane [49].

2. In vehicle structure:

The polymer nanocomposites are manufactured commercially for diverse structural vehicles applications. The opportunities of clay Nanocomposite lay in the increased stiffness and reduced density, which will lead to thinner wall stock and lower part weight. Additionally improved scratch resistance and reduced thermal sensitivity can be achieved. The incorporation of carbon nanofibers in sheet moulded compounded body panels, improves surface quality and can be used for improved toughness and thinner panels [50].

3. Rheological modifier:

Rheological modifiers control the flow properties of liquid systems such as paints, inks, emulsions or pigment suspensions by increasing the medium viscosity or impart thixotropic flow behavior to liquid system. Organoclay is used in the ink formulation. It helps to adjust the consistency of printing inks to the desired values, avoiding pigment sedimentation, providing good colour distribution, obtaining desired film thickness, reduction in misting, control of tack, water pickup and dot gain control by incorporation of small amount of organically modified layered silicates. Thickening lubricating oils with organoclays can produce specially high temperature resistant lubricating greases. Organoclay also gives good working stability and water resistance to the greases. The performance of cosmetics is enhanced by the use of organoclays and they allow good colour retention and coverage for nail lacquers, lipsticks and eye shadows. They have been tested to be nonirritant for both skin and eye contact.

4. Wastewater treatment:

Organoclays exhibit a synergistic effect with many commonly utilized water treatment unit processes including granular-activated charcoal, reverse osmosis, and air strippers. Organoclays have proven to be the technology of choice for treating oily wastewaters.

5. Food Packaging:

The excellent barrier characteristics of nanoclay reinforced polymer blends have resulted in considerable interest in nanoclay composites in food packaging applications, both flexible and rigid. Specific examples include packaging for processed meats, cheese, confectionery, cereals and boil-in-the-bag foods, also extrusion-coating applications in association with paperboard for fruit juice and dairy products, together with co-extrusion processes for the manufacture of beer and carbonated drinks bottles. The use of nanocomposite packaging would be expected to enhance considerably the shelf life of many types of food.

6. Fuel Tanks:

The ability of nanoclay incorporation to reduce solvent transmission through polymers such as polyamides has been demonstrated. Available data reveals significant reductions in fuel transmission through polyamide-6/66 polymers by incorporation of nanoclay filler. As a result, considerable interest is now being seen in these materials as both fuel tank and fuel line components for cars.

7. Films:

The presence of filler incorporation at nano-levels has also been shown to have significant effects on the transparency and haze characteristics of films. In comparison to conventionally filled polymers, nanoclay incorporation has been shown to significantly enhance transparency and reduce haze. Similarly, nano-modified polymers have been shown, when employed to coat polymeric transparency materials, to enhance both toughness and hardness of these materials without interfering with light transmission characteristics. The ability to resist high velocity impact combined with substantially improved abrasion resistance was also demonstrated.

8. Environmental Protection:

Water laden atmospheres have long been regarded as one of the most damaging environments, which polymeric materials can encounter. Thus an ability to minimize the extent to which water is absorbed can be a major advantage. Available data indicate that significant reduction of water absorption in a polymer could be achieved by nanoclay incorporation. Similar effects could also be achieved with polyamide-based nanocomposites. Specifically, increasing aspect ratio diminishes substantially the amount of

water absorbed, thus indicating the beneficial effects likely from nanoparticle incorporation compared to microparticle loading.

Hydrophobicity enhancement would clearly promote both improved nanocomposite properties and diminish the extent to which water would be transmitted through to an underlying substrate. Thus applications in which contact with water or moist environments is likely could clearly benefit from materials incorporating nanoclay particles.

9. Flammability Reduction:

National Institute of Standards and Technology in the US has demonstrated the extent to which flammability behaviour could be restricted in polymers such as polypropylene with as little as 2% nanoclay loading. In particular heat release rates, as obtained from cone calorimetry experiments, were found to diminish substantially by nanoclay incorporation. Although conventional microparticle filler incorporation, together with the use of flame retardant agents would also minimize flammability behaviour, this is usually accompanied by reductions in various other important properties. With the nanoclay approach, this is usually achieved whilst maintaining or enhancing other properties and characteristics.

Conclusion:

Nanoparticles have a higher specific surface area in comparison to microparticles; this facilitates better adhesion between particles and polymer matrix. The addition of MDI based PUR results in a greater improvement of epoxy resins mechanical properties than in the case of TDI application. Hybrid composites containing 1 or 2 % MMT and 5 to 15 % PUR (both MDI and TDI based) exhibit improved mechanical properties in comparison to neat epoxy resin. For optimum strength enhancement the loading level of 1 % MMT and 15 % of MDI-PUR synthesized from polyethylene glycol is intercepted with two mechanisms involved in the improvement: exfoliation of nanoclay depicted with X-ray diffraction, and formation of chemical bonding between hydroxyl groups of epoxy resin with isocyanate groups from polyurethane confirmed with infrared spectroscopy as well as differential scanning calorimetry. Furthermore, polyurethane modifier acts as a compatibilizer for epoxy resin and montmorillonite mixtures and promotes the exfoliation process of the latter.

Taking into account all results obtained from mechanical tests and structural analyses, it might be assumed that the obtained EP/PUR/MMT hybrid composites are formed from grafted EP/PUR interpenetrating polymer networks and exfoliated montmorillonite acting as nanofiller.

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