

Preparation, morphology, and mechanical properties of modified-PU/UPR graft-IPN nanocomposites with BaTiO₃ fiber

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Abstract

Acrylate-modified polyurethane (PU) resin was used and then interpenetrated with unsaturated polyester resin (UPR), to form interpenetrating polymer networks (IPNs) and gradient IPNs cured at room temperature. The polymerization processes were traced through IR techniques, through which the phase separation in systems could be controlled effectively. Results of the morphology and miscibility of the multi-phase materials, obtained by TEM, indicate that the domains in these systems were constricted to the nanometer range. Thermo-mechanical analyzer (TMA) detection results showed that through interpenetration between networks; the glass transitional temperature ranges of systems can be linked up apparently. Mechanical characteristics showed that the IPNs obtained exhibit different types of characteristics varying from elastomer to brittle plastics. The systems were composited with BaTiO₃ fibers and the composite techniques were determined. Also, the morphology and mechanical properties were discussed in detail.

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1. Introduction

Polymer blends, as effective ways to develop and devise novel materials with excellent properties, have gained more and more emphasis in recent years. Interpenetrating polymer networks (IPNs), as a special sort of blends, refer to two or more than two kinds of polymer systems produced by interpenetration with each other, when at least one polymer is synthesized and/or crosslinked in the immediate presence of the other [1,2]. That is to say, IPNs belong to the class of “polymer alloys” composed of two chemically different components to form an intimate blend of two networks with special properties. Owing to the existence of large amounts of micro- or sub-micro-multi-phase structures, especially, the characteristics of a broadened glass transition temperature (T_g) ranges in partial IPNs, created by partial miscibility between components, IPNs have been made potential utilities as functional materials in many applied fields [3,4]. Through making use of permanent interpenetration and entanglement in the networks formed, one can constrain the phase separation, change the compatibility and improve

materials properties, especially the conventional mechanical properties, and thus can enlarge greatly their fields of application [5]. For example, previous research has indicated that the mechanical properties of polymers with interpenetrating network constructions are apparently superior to those of general polymers. Particularly, the phenomenon of interpenetration forming in networks makes the mechanical properties exceed those of the parent networks [6]. Many factors influence the mechanical properties. Compatibility is the most important [7]. Nanocomposite materials are new kinds of composites formed by dispersing one or more than one kind of particles in almost molecular level into the polymer matrix. The sizes of dispersed phase in nanocomposites are usually between conventional and microscopic ranges. Lot of transitional regions formed can bring material special physico-chemical properties [8–10]. Organic–inorganic hybrids, as a new class of nanocomposites, can combine the advantages of participating components and contribute to the composites many outstanding properties, such as mechanical, thermal, optical, electromagnetic, and biological properties [11,12]. Up to now, most reports on IPNs has focused on polyurethane (PU) based systems, the preparation methods, and the relationship between structure and property of the system formed. There are also many reports on

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their application [13,14]. However, reports on the preparation and properties of nanocomposites filled with inorganic powders or fibers, are relatively few.

In this study, IPNs and gradient IPNs are prepared based on modified PU and unsaturated polyester resin (UPR). The compatibility of systems with various PU/UPR compositions and with different techniques is discussed. The influences of crosslink density, weight ratios of soft/hard in system on mechanical properties of materials are studied. Barium titanate, one kind of substance with better piezoelectric characteristics, is selected to form the composites, and the morphology and mechanical properties are discussed.

2. Experimental

2.1. Raw materials and treatment

UPR (191[#]) and its curing agents are purchased reagents. The UP consists of a resin formed by phthalic anhydride, maleic anhydride, and propylene glycol. The weight ratio of UP and styrene monomer for the UPR used is 65/35. Benzoyl peroxide (BPO) and dimethyl aniline (DMA) are used as UPR's curing agent. TDI precursor formed by polyol and 2,4-tolylene diisocyanate (TDI content: 9%) and acrylate-modified polyurethane (modified PU) (hydroxyl value: 120, was dehydrated at 80 °C by reduced pressure for 1 h before use) are prepared by Chemical Factory of Harbin Institute of Technology. Dibutyltin dilaurate (DBTL) is used as catalyst and ethyl acetate is used as solvent to adjust the viscosity of the system.

2.2. Preparation of IPNs and gradient IPNs

A weighed amount of TDI precursor and UPR were added into the system formed by a weighed amount of curing agents and ethyl acetate (10 wt.%) and then kept stirring for 10–20 min. The weight ratio between the UP, BPO, and DMA used was 100:1:2. DBTL (0.1 wt.%) and modified PU were then added and stirred continuously for about 30 min until a homogeneous mixture formed. The viscous mass formed from above solution was poured into mold made of polycarbonate ester, and cured at 20 °C. A series of IPNs were synthesized in that way with –NCO and –OH ratios is 1.2:1.0 in PU network and PU (soft component)/UPR (hard component) ratios in system vary from 70/30 to 30/70. The gradient IPNs were obtained by casting components of every IPNs (from 70/30 to 30/70) in mold for about 60 min.

2.3. Preparation of barium titanate fiber

An amount of 23 wt.% of purified water was added into mixture of K₂CO₃ and TiO₂, which was in the molar ratio of 1:3 and mixed for about 1 h. The system obtained were placed on a platinum plate and dried at 80 °C for 72 h, calcined at 1000 °C for 100 h, then cooled down quickly to

room temperature and immersed in distilled water for about 1 week. The system was immersed in 1 mol L⁻¹ HCl solution for 1 week after stirring thoroughly, then filtered under vacuum and dried. Ba(OH)₂·8H₂O was then added into the above system with the same amount. All the components were poured into a hot reaction vessel with a weighed amount of water. The products were heated at 140 °C for 72 h and rinsed with hot water to neutral and dried.

2.4. Composite techniques

BaTiO₃ fibers and coupling agents (vinyl triethoxysilane) were added into IPNs during its formation. The mixtures were then grained for 25 min and dispersed for 20 min under supersonic treatment, then cast in mold. A series of composites were obtained by changing the amount of fibers added.

2.5. Test methods

The FTIR analysis was performed by a Nicolet-5DX FTIR spectrometer by casting the homogeneous systems composed of TDI precursor, modified PU, UPR, and curing agents onto a KBr crystal plate. The –NCO/–OH ratio and soft/hard component ratio were 1.2:1 and 60/40, respectively. The glass transition temperatures were determined using a thermomechanical analyzer (TMA) at heating rate of 10.0 °C/min. The temperature range was –50 to 150 °C. Phase morphology was examined by a Nippon Electron 1200-EX transmission electron microscope. The samples were ultramicrotomed into 100 nm thick sections and stained in OsO₄ solution for hours. Tensile strength, elongation at break of IPNs and gradient IPNs of small size dumb-bells were measured by Nippon Shimadzu DSS-10T-S tester at room temperature at a crosshead speed of 5 mm/min according to China Standard (GB4456-84). Data were taken as an average of at least five measurements.

3. Results and discussion

3.1. IR analysis

The FTIR spectra of IPNs at various reaction times are shown in Fig. 1. As shown in the figure, the intensity of the characteristic absorption peaks of –NCO at 2278 cm⁻¹, –OH at 3400 cm⁻¹, –NH at 3350 cm⁻¹, and –NHCO at 1528 cm⁻¹ decreases in all cases during the polymerization. In this study, the intensity changes of the absorption peak at 2278 and at 965 cm⁻¹ represent the change of –NCO group and –C=C– group, respectively [15]. Seen from some conversion data, collected in Table 1, of –NCO and –C=C– calculated from IR spectra, the disappearance of the –NCO absorption peak is a little faster than that of C=C absorption peak during early stages, but slower at later stages of the reaction. This indicates that during the forming of IPNs, although attempts are made to form the two networks

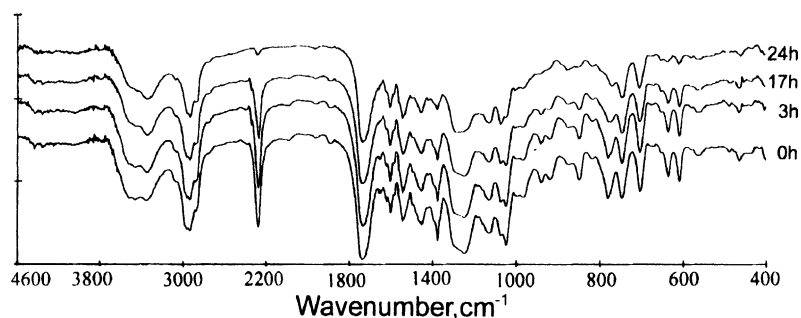


Fig. 1. IR spectra of IPNs at various reaction times.

simultaneously, the formation of PU was relatively fast at early stages. This is mainly because that the UPR polymerize through free radical mechanism and the initiation step tends to make it proceed slowly, before moving into the propagation step. Whereas, the hydrogen transfer polymerization of PU can undergo rapidly at early stages. But the last time of free radical reaction is much shorter. So the PU forms the continuous phase in system. Additionally, the acrylate-modified PU has unsaturated double bond in its molecular structures (besides the $-OH$ group to react with TDI). So it was expected to participate the polymerization of UPR, while forming its own network. Seen from the IR spectra, the react rate during the later stages of reaction is faster than that of polyaddition of the PU, so the system thus obtained belongs to graft-IPNs and the acrylate group is grafted onto PU network. The chemical crosslink structures formed lead to shorter distance between two networks and increase the extent of interpenetration, and thus decrease the domain sizes of the two phase, to nanometer scales. That can also adjust the component ratio in relative wide ranges without phase separation, thus lead to better miscibility and other improved integrated properties. The TEM and mechanical properties testing results can also illustrate the results further.

3.2. TMA testing results

The results of the thermomechanical analysis of IPNs and gradient IPNs are shown in Fig. 2. Two distinct T_g 's were observed. Since the T_g 's of pure PU and UPR are about -50 and 90°C , respectively, seen from Fig. 2, the two T_g values are near the respective homopolymer glass transitions, respectively, but shift inward apparently for the higher one,

Table 1

Conversion data of $-NCO$ and $-C=C-$ at various react time calculated from FTIR spectra

	T (h)		
	1/10	1	3
Conversion of $-NCO$ (%)	2.56	6.48	21.85
Conversion of $-C=C-$ (%)	1.82	11.35	16.76

especially for that of gradient IPNs. This is probably caused by the fact that, the interpenetration of UPR into PU network decrease the linkage movements of PU, so the IPNs exhibit higher T_g value than the PU. However, the increased distance between UPR molecule through the interpenetration into PU network increase the linkage movements of UPR. The larger increase extent than that of decrease induced by interaction between linkages makes the high T_g values of IPNs and gradient IPNs shift to lower temperature compared with that of the UPR. So, the IPNs, especially gradient IPNs, inevitably exist large amount of transitional regions in system. TMA results also show that the T_g can be broadened effectively through interpenetrating techniques.

3.3. Morphology measurement

TEM photographs of modified-PU/UPR IPNs with various component ratios are shown in Fig. 3. As shown in Fig. 3(a) and (b), the PU appears as the white phase and presents as the continuous phase in Fig. 3(b) with globules of the UPR dispersed within it. The globules are generated by first-stage phase separation led by immiscibility during polymerization. The fine structures in system are caused

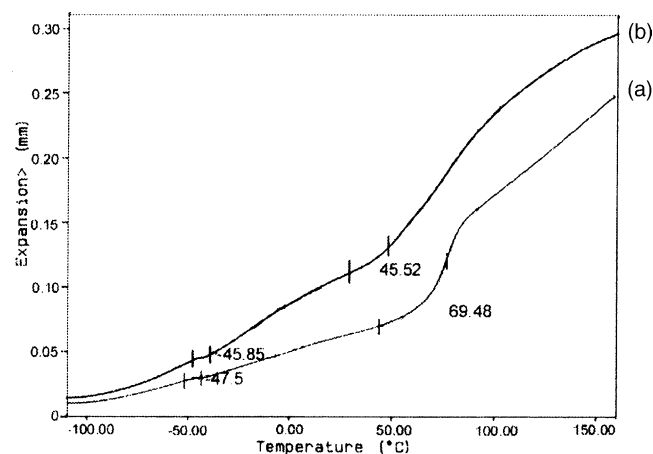


Fig. 2. Temperature-shape changing results of IPNs samples: (a) IPNs (soft/hard component ratio: 60/40 (w/w)); (b) gradient IPNs (soft/hard component ratio: 60/40–40/60 (w/w)).

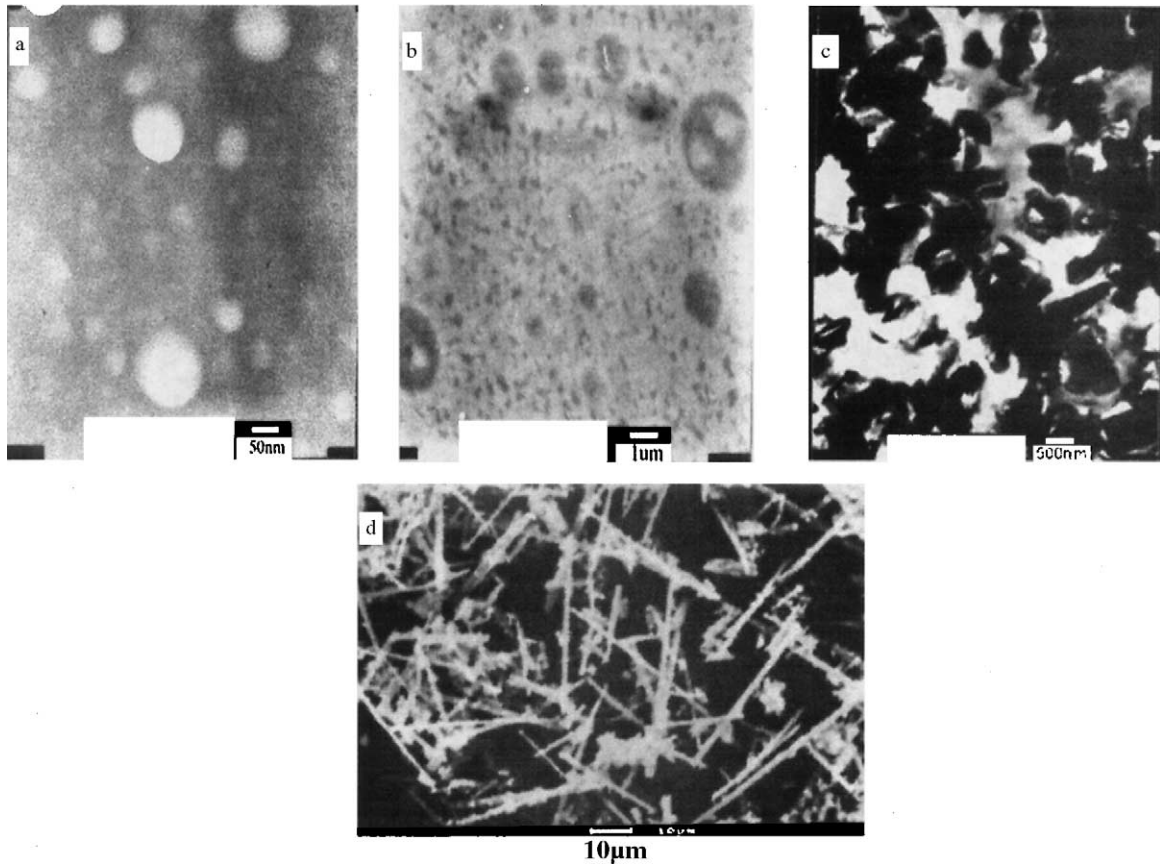


Fig. 3. Photographs of IPNs with soft/hard ratio (w/w) of (a) 40/60, (b) 60/40, (c) composites, and (d) BaTiO₃ fiber.

by second-stage phase separation after the polymerization. This is mainly because that, the increase of viscosity and crosslink density make the second-stage phase separation occur in narrow scales, and form small globules in nanometer sizes. Although the interpenetration and entanglement structures between the two networks increase the compatibility, the network formed later can just act as the filler of

the first formed one. However, through varying the component ratio and controlling the forming rate of the two networks to finish the polymerization process almost simultaneously, the extent of first-stage phase separation can be locked effectively, as shown in Fig. 3(a). SEM photograph of BaTiO₃ fibers and TEM photograph of composites with 25 wt.% BaTiO₃ are shown in Fig. 3(c) and (d),

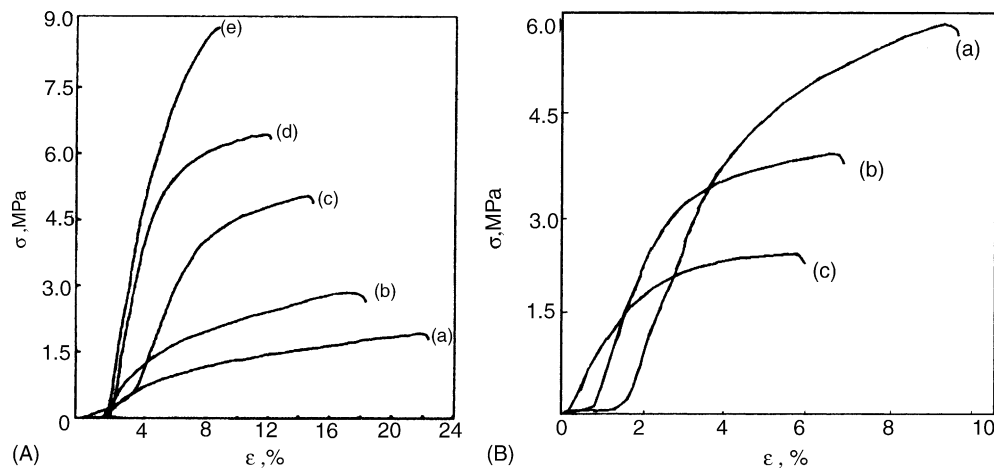


Fig. 4. Mechanical property of IPNs and composites: (A)—soft/hard ratio (wt.) (a) 70/30, (b) 60/40, (c) 50/50, (d) 40/60, and (e) 30/70; (B)—soft/hard ratio 40/60 (wt.), composite amount (a) 3%, (b) 10%, and (c) 25%.

respectively. As shown, the fibers are well dispersed in matrix with the original structures mostly.

3.4. Mechanical properties

Previous research of others has shown that [16], the compatible IPNs usually can contribute many remarkable properties to the system obtained. This is mainly caused by the large amount of interpenetration and entanglement structures formed. Fig. 4 shows stress–strain curves of IPNs. As shown in Fig. 4(A), the materials vary from elastomers to plastics with different soft/hard component ratios in the system. It is noteworthy that, while the soft/hard component ratios of IPNs are in a relative wide ranges from 40/60 to 60/40, the materials exhibit synergistic effects of elastomeric strength and brittle toughness. This is mainly because that the existence of interpenetration and entanglement structures in system attribute to reinforcement while the material are stretched and so improve greatly the mechanical properties of IPNs. The effect also provide valid means to gain novel materials with special properties and have significance to obtain functional materials with outstanding properties. Seen from Fig. 4(A), tensile strength increases with UPR in IPNs, whereas the elongation decreases. This is because that the first formed network commonly determines the mechanical properties of the system. The tensile strength of composites decreases with the increase of composite amount of BaTiO₃ fibers.

4. Conclusions

The analysis of IR spectra and materials selected suggest that the system obtained were graft-IPNs. TEM and TMA

testing results indicate that the domains of the systems were in nanometer scales by controlling the interpenetrating techniques. T_g 's of these IPNs shift inward effectively by interpenetration. The mechanical properties tests shows that the modified-PU/UPR IPNs exhibit characteristics varying from elastomer to brittle plastics. The soft/hard ratios, crosslinking density have influence on tensile strength and elongation of the system. The tensile strength and elongation at break of composites decrease with the increase amount of BaTiO₃ fibers.

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