Polymer Bulletin 57, 975–982 (2006)
DOI 10.1007/s00289-006-0661-9

Polymer Bulletin

Preparation and properties of urethane acrylate-epoxy interpenetrating polymer networks containing silica nanoparticles

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Received: 9 June 2006 / Accepted: 20 July 2006
Published online: 8 August 2006 – © Springer-Verlag 2006

Summary

In this study, interpenetrating polymer networks (IPNs) and IPN composite materials were prepared by in situ polymerization of urethane dimethacrylate (UDMA) and bisphenol-A diglycidyl ether epoxy resin (DGEBA) with or without silica nanoparticles. Dynamic mechanical analysis (DMA), three-point bending test, thermogravimetric analysis (TGA) and visible spectrometry were performed to evaluate the physical properties of the resulting IPNs and IPN composite materials. The IPNs showed high transparency and higher elastic modulus and strength than that of each homopolymer at ratio of UDMA/ DGEBA is 70/30. The IPN composites maintained high transparency in spite of the addition of silica nanoparticles. Moreover, elastic modulus and surface hardness of the IPN composites increased with increasing silica content.

Introduction

Organic-inorganic hybrid materials have been widely investigated in order to improve their matrix properties [1-5]. There have been many attempts using various techniques to develop high performance organic-inorganic hybrid materials, which combine the features of inorganic and organic substances [6-10]. Such hybrid materials have been investigated at various scales from the level of microscale order to molecular order [11-15]. Organic-inorganic hybrid materials obtained by combining organic polymers with inorganic compounds at the nanoscale or molecular level, are expected to exhibit high performance in all properties. The materials properties of conventional organic-inorganic hybrid materials produced by mixing or dispersing inorganic materials in organic polymers are mainly determined by the nature of the interface between the organic and inorganic components, as well as by the size and dispersibility of the inorganic filler material. In order to obtain high performance hybrid materials, the inorganic component must be dispersed minutely and homogeneously in the organic polymer matrix, and there must also be good adhesion at the interface between the inorganic and organic components.

Interpenetrating polymer networks (IPNs) are defined as combination of two or more polymer networks prepared in juxtaposition. The entanglement of multiple cross-linked polymers leads to forced miscibility compared to simple blends and the resulting IPN materials exhibit excellent size stability. These kinds of polymer combinations, in the greater number of cases, lead to the materials with better mechanical properties, thermal properties and a possibly synergistic combination of the properties of their components. These IPN materials draw attention as matrix materials of nanocomposites with organo-clay or silica, and their properties (morphology, mechanical property and so on) are widely investigated [16-19].

In this study, interpenetrating polymer networks (IPNs) composed of urethane dimethacrylate (UDMA) and bisphenol-A diglycigyl ether epoxy resin (DGEBA) and IPN composite materials with silica nanoparticles were prepared by in situ polymerization. Moreover, physical properties of the IPNs and the IPN composites, mainly on mechanical properties, were evaluated. The UDMA and DGEBA were selected with the expectation that the monomers show the high affinity for the silica nanoparticles and provide homogeneous IPNs by simultaneous polymerization. The aim of this study is to develop novel transparency composite materials with high mechanical performance.

Experimental

Materials

2-(methacryloyloxy)ethyl isocyanate (MOI, Showa Denko K.K.), bisphenol-A diglycigyl ether epoxy resin (DGEBA, Epikote 828, Japan Epoxy Resins Co., Ltd) and 2-methylhexahydrophthalic anhydride (MHHPA, purity:97%, Hitachi Chemical Co., Ltd) were used as received. Colloidal silica (12 nm in diameter) in ethyl acetate (30 wt%, EAc-ST) was provided by Nissan Chemical Co. All other solvents and reagents were purchased from Nacalai Tesque Inc., and were used without further purification.

Preparation of UDMA

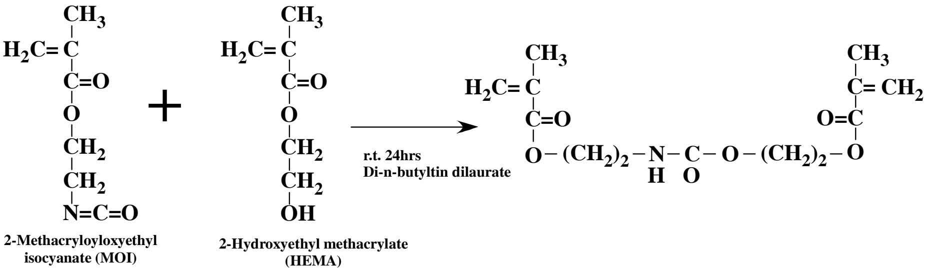
Scheme 1 depicts the preparation of UDMA. UDMA were prepared through the reaction of 2-hydroxyethyl methacrylate (HEMA) with MOI, as follows: A given amount of HEMA and di-*n*-butyltin dilaurate (DBTL) (ca. 250-500 ppm) catalyst were added dropwise to MOI with stirring in ice bath, and then the reaction was carried out at room temperature for 24 hours. The reaction between MOI and HEMA was confirmed by the disappearance of the peak attributed to the -NCO moiety (at 2272 cm^{-1}) in IR measurements.

Preparation of UDMA/DGEBA interpenetrating polymer networks

To prepare interpenetrating polymer networks (IPNs) materials, in situ polymerization of UDMA and DGEBA was carried out. A given amount of UDMA and DGEBA monomers were mixed and then di-*t*-butyl peroxide (1 wt% with respect to UDMA), MHHPA (equimolar amount with respect to DGEBA) and *N,N*-dimethylbenzylamine (0.1 wt% with respect to DGEBA) were added as curing agents. The mixture was poured into a mold made from aluminum plates clamped together and sealed with 2mm thick Tefron® gasket. The mold was heated in an oven at 130ºC for 12hrs to obtain IPN materials. The compositions (weight ratios) of the IPNs are summarized in

Table 1. An IPN obtained from mixture of 70wt% UDMA and 30 wt% DGEBA, for example, will be noted IPN (70/30).

As reference samples, UDMA and DGEBA single network materials were also prepared by similar method as UDMA/DGEBA IPNs.



Scheme 1 Preparation scheme of urethane dimethacrylate

Table 1 Compositions of UDMA/DGEBA IPNs

Sample Code	UDMA	DGEBA
P(UDMA)*	100	0
IPN (80/20)	80	20
IPN (70/30)	70	30
IPN (60/40)	60	40
IPN (50/50)	50	50
IPN (30/70)	30	70
P(DGEBA)**	0	100

* Homopolymer of UDMA
** Homopolymer of DGEBA

Preparation of UDMA/DGEBA IPN composite materials

To prepare UDMA/DGEBA IPN composites, a given amount of UDMA, DGEBA and curing agents were added to EAc-ST and then ethyl acetate was removed from the mixed solution with a rotary evaporator. The resulting mixture was poured into a mold, as described previously and polymerized at 130°C for 12 hours.

Measurements

FT-IR measurements were performed with Nicolet model AVATAR 320 spectrophotometer. FT-IR spectra were recorded in the 4000-400 cm^{-1} region by the ATR method and by the liquid film method with a Zn-Se crystal cell. Visible spectrometry was performed with a JASCO model V-520 spectrophotometer from 380 to 800 nm to evaluate the transparency of obtained materials. Dynamic mechanical analysis (DMA) measurements were carried out using a Seiko model DMS-200 viscoelastometer from 25 to 200°C at 1 Hz, at a heating rate of 2°C/min. To evaluate the surface hardness of IPN composites, its Vickers hardness was measured by Akashi model AVK-A Vickers hardness scale at room temperature. A 9.8N load was loaded on the sample for 15 seconds using the diamond indenter, after which the crosssectional area of the indentation which remained in the sample was measured. The mechanical properties of IPNs and IPN composites were evaluated by three-point bending test using TOYO BALDWIN Tensilon model UTM-4LH at 25°C. The size of specimen was 50mm × 10mm × 2mm. Atomic force microscope (AFM) analysis of IPN was carried out with NanoScope® IIIa from Veeco Instruments in tapping mode.

Volume contraction

The volume contractions of the IPN composites were calculated using the densities of before and after polymerization. The density of before polymerization was measured with a specific gravity bottle, and that of after polymerization by the Archimedes method using a Mettler Toledo solid densitometer. The volume contraction (*V. C.*) was calculated by the following equation.

$$V.\ C.\ (\%) = 100 \times (1 - \rho_m/\rho_p)$$

where ρ_m is the density of before polymerization and ρ_p is the density of the after polymerization.

Results and Discussion

Optical properties of UDMA/DGEBA IPNs

Table 2 summarizes the visible light transmittance data for the UDMA/DGEBA IPNs at 600 nm. The IPN showed high transparency, over 80 %T, until DGEBA content is 30 wt%, while, the transparency of IPN lowered to 15 %T, when the DGEBA content increased. This result indicates that miscibility or domain size change with the dependence on the content of DGEBA in IPN.

Table 2 Transmittance of UDMA/DGEBA IPNs at 600 nm

Sample Code	%T@600nm
P(UDMA)	89
IPN (80/20)	81
IPN (70/30)	88
IPN (60/40)	64
IPN (50/50)	49
IPN (30/70)	15
P(DGEBA)	86

Mechanical properties of UDMA/DGEBA IPNs

The mechanical properties of the UDMA/DGEBA IPNs at various UDMA/DGEBA ratios were evaluated by three-point bending test and the results are listed in Table 3. All UDMA/DGEBA IPNs indicate higher flexural modulus and strength than those of each single network. Moreover, these values increased with increasing UDMA content in IPNs and reached maximum at the ratio of UDMA/DGEBA is 70/30. This composition agrees with the composition showing highest transparency in prepared IPNs. It is inferred that the IPN structure entangled at molecular or nano level was formed at ratio of UDMA/DGEBA is 70/30, and as the result, the IPN (70/30) showed high mechanical performance. Figure 1 indicates loss factor tanδ variations vs. temperature for the IPN (70/30) and each single network. Poly(DGEBA) indicated maximum of tanδ around 140°C, while poly(UDMA) did not show tanδ in temperature range from 30°C to 200°C. The variation of tanδ for the IPN (70/30) was similar to that of poly(UDMA). It reveals that interactions exist between both phases in the IPN (70/30) and poly(DGEBA) chain segmental motions are hindered by poly(UDMA) [20]. This result also supports high mechanical performance and transparency of the IPN (70/30).

Table 3 Mechanical properties of UDMA/DGEBA IPNs

Sample Code	Flexural Modulus (GPa)	Flexural Strength (MPa)	Deflection (nm)
P(UDMA)	4.1	168	5.1
IPN (80/20)	4.2	173	3.8
IPN (70/30)	4.4	201	4.8
IPN (60/40)	4.4	184	3.6
IPN (50/50)	4.2	180	3.7
IPN (30/70)	3.6	165	3.6
P(DGEBA)	3.2	160	5.0

Morphology of UDMA/DGEBA IPN

Figure 2 depicts AFM image of the IPN (70/30). As can be seen from this figure, several dozen nanometer domains were observed in the the IPN. There are several reports with connected-globule bicontinuous phase structures in blend of thermoset/thermoplastic polymers, which brought about excellent mechanical properties [21-23]. In this combination, by the formation of the small globule particles, high transparency and mechanical properties seems to be accomplished.

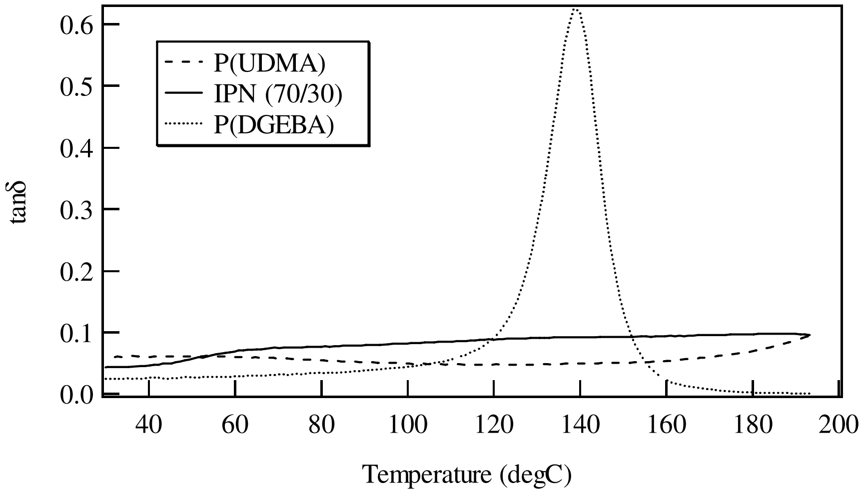


Figure 1 Temperature dependence of tanδ for IPN (70/30) and each homopolymer

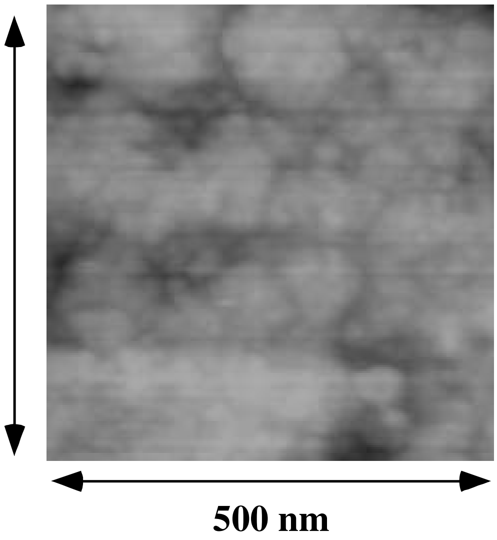


Figure 2 AFM image of IPN (70/30)

Optical properties of IPN composites

The IPN (70/30) showed excellent mechanical properties and high transparency, thence IPN (70/30) was used as matrix for composite. Table 4 lists the compositions (weight ratios) of the IPN composites and their transmittance. An IPN composite obtained from IPN (70/30) as matrix and 10 wt% silica particles, for example, will be noted IPN (70/30)-10. All the IPN composites evaluated in this study kept high visible light transmittance over 85% at 600 nm. It is difficult to maintain transparency when composite materials are prepared by conventional methods, in which the inorganic filler is simply mixed into the organic matrix. The present method was therefore thought to be an effective method for preparing highly transparent organic-inorganic nanocomposite materials.

Table 4 Compositions and transmittance at 600 nm of IPN composites

Sample Code	UDMA	DGEBA	colloidal silica	%T@600 nm
IPN (70/30)	70	30	0	88
IPN (70/30)-10	70	30	10	89
IPN (70/30)-20	70	30	20	88
IPN (70/30)-30	70	30	30	87

Mechanical properties of IPN composites

The mechanical properties of IPN composites were evaluated by three-point bending tests. These results are summarized in Table 5. With the increase of the SiO_2 content, the bending strength and deflection of the IPN composites decreased slightly. Elastic modulus increased drastically with increasing SiO_2 content, as the elastic modulus of IPN (70/30)-30 became 1.3 times of IPN (70/30) matrix. The variation of Vickers hardness (*Hv*) and volume contractions as a function of SiO_2 content in the IPN composites are also listed in Table 5. Vickers hardness of IPN composites also increased with increasing SiO_2 content in the same way the result of elastic modulus indicates, and became 1.1 times of the matrix. The volume contractions of IPN composites decreased with the increase in nanoparticle content, and the volume contraction was smaller (4.1% at 30 wt% nanoparticles) than that of the matrix (9.1%). It is considered that the effect of silica as a filler and homogeneous dispersion of silica component play important roles in the improvement of these properties.

Table 5 Mechanical properties and volume contraction (V.C.) of IPN composite

Sample Code	Flexural Modulus (GPa)	Flexural Strength (MPa)	Deflection (nm)	Hv (MPa)	V.C. (%)
IPN (70/30)	4.4	201	4.8	301	9.1
IPN (70/30)-10	4.9	179	3.4	312	7.4
IPN (70/30)-20	5.3	180	3.0	314	5.6
IPN (70/30)-30	5.8	162	2.7	331	4.1

Conclusion

As described above, in this study, IPNs and IPN composites were prepared with UDMA, DGEBA and colloidal silica. The IPN and IPN composite prepared at the ratio of UDMA/DGEBA is 70/30 were outstanding in terms of transparency; elastic modulus; flexural strength. These hybrid materials are therefore expected to be structural materials or engineering materials. More detailed characterization (thermal properties, morphology and polymerization kinetics) of the IPNs and IPN composites are currently being conducted.

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