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Preparation and Properties of IPN Materials Containing Bisphenol A Acrylate and an Epoxide Hybrid Unit

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Abstract

Interpenetrating polymer networks (IPNs) were prepared by photo and thermal polymerizations of diacrylate, diepoxide and hybrid monomer mixtures, in which the functional groups in each monomer were linked by bisphenol A hard segment. Dynamic mechanical analysis, tensile tests, thermogravimetric analysis, hardness analysis and visible spectrometry were performed to evaluate the properties of the IPNs and their precursors. The IPNs obtained, containing a small amount of diepoxide, indicated the highest mechanical properties at a ratio of hybrid/diacrylate of around 1:2. This composition also agreed with the composition showing highest surface hardness and transparency. In addition, the influence of microwave irradiation on curing time was also studied.

Keywords

Interpenetrating polymer network, mechanical properties, thermal properties, epoxide, acrylate, hybrid

1. Introduction

Co-polymers, polymer blends and interpenetrating polymer networks (IPNs) are interesting in connection with their applications, including adhesives, nanocomposites, coatings and printing inks [1–5], since they can include at least two diverse characteristic chemical units in materials and represent cooperative specificity [6]. Among such a material, IPN materials containing epoxy and acrylate components, in particular, have been expected to represent unique physical properties, i.e., the IPNs can be expected to have both epoxy characteristics, including strong adhesiveness and heat-stability, and acrylate characteristics, including flexibility and easiness of processing [7–9]. Thus, so far various types of IPNs have been synthesized using monomers such as diacrylate, dimethacrylate, and diepoxide of bisphenol, phthalic acid ester and urethane types, respectively. Unfortunately, how-

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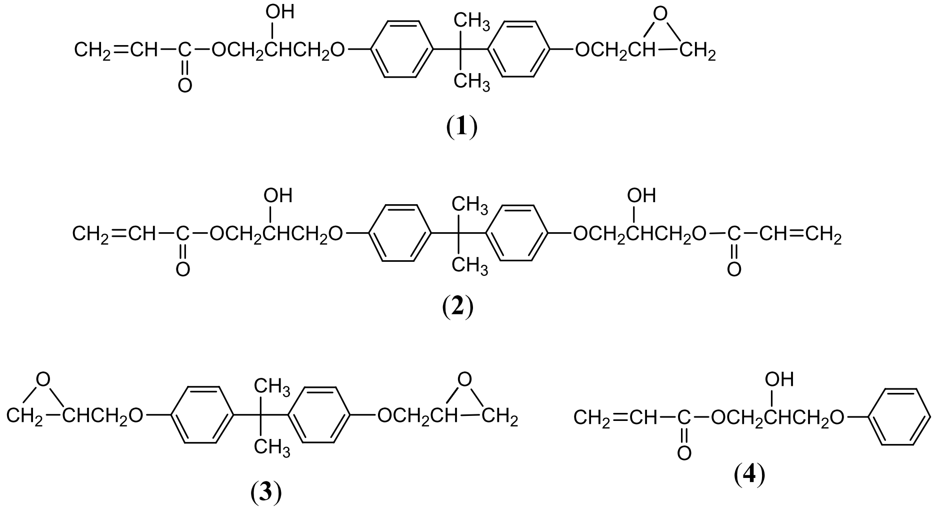

(**1**)

(**2**)

(**3**)

(**4**)

Scheme 1. Structures of compounds **1**–**4**.

ever, synthesis of IPN using epoxide–acrylate hybrid monomers linked by a hard core segment and characteristics of its IPN have not yet been studied up to now.

In the present study, we prepared IPNs by photo and thermal polymerizations of monomer mixtures containing hybrid (**1**), diacrylate (**2**) and diepoxide (**3**) linked by bisphenol A hard segment and diluent (**4**) (Scheme 1) and report a synergistic effect of mixtures on the IPN preparation. In addition, influence of microwave power on preparation of IPNs has also been examined.

2. Experimental

2.1. Materials

Commercial grade bisphenol A diglycidyl ether (**3**) (DIC) and phenylglycidyl ether (NOF) were used without further purification. Initiators, including Irgacure 651 and 500 (Chiba Japan), and 2-ethyl-4-methylimidazole (Kanto Chemicals) were used as given. Deuterated solvent $CDCl_3$, used for NMR, was purchased from Acros Organics.

Bisphenol A diacrylate (**2**) was prepared according to a similar manner as described in the literature [7] by adding triethylbenzylammonium chloride (TEBAC) (1.03 g) to a solution of **3** (173 g, 1.00 equiv) and acrylic acid (86.4 g, 1.20 equiv) at 60°C in the presence of a small amount of hydroquinone (0.22 g) and further continuous reaction for 2 h at 80°C. Complete esterification was confirmed by the residual acid value of 43.11 (calcd. 43.05) in a titroprocessor and no detectable epoxy equivalent. After the reaction, toluene (600 g) and water (300 g) were added to the reaction mixture, and the toluene layer was separated using a 1.0-l separatory funnel. Purification of the product was performed by vacuum evaporation of toluene from the organic layer in the presence of hydroquinone (0.22 g) and following a vacuum filtration of the residue using a filter paper (Whatman No. 5); yield 205 g (98%, based on **3**). The product was purified by column chromatography using a Silica Gel 60 N (Kanto Chemicals) as a stationary phase in ethyl acetate/n-hexane (2:3, v/v) at ambient temperature. Epoxy equivalent and acid value for **2** were estimated to be 420 (calcd. 419) and 0, respectively. IR (neat) for **2**: 3480 ($\nu_{\text{O–H}}$), 1730 ($\nu_{\text{C=O}}$), 1640 cm^{-1} ($\nu_{\text{C=C}}$). ^{1}H-NMR (CDCl$_3$, TMS, ppm) for **2**: 1.64 (s, 6H), 2.57 (d, $J = 4.0$ Hz, 2H), 4.04 (m, 4H), 4.29 (m, 2H), 4.38 (m, 4H), 5.89 (d, $J = 12.0$, 2H), 6.17 (dd, $J = 8.0$, 16.0 Hz, 2H), 6.46 (d, $J = 12.0$ Hz, 2H), 6.82 (d, $J = 8.0$ Hz, 4H), 7.14 (d, $J = 8.0$ Hz, 4H).

Monomers M4–M9 were synthesized in a similar manner as above, by changing the feed molar ratio of acrylic acid to **3** as shown in Table 1. As a typical example, the synthesis of M5 is as follows. Acrylic acid (36.0 g, 0.500 equiv) was added drop-wise to **3** (173 g, 1.00 equiv) containing hydroquinone (0.22 g) at 60°C in a 500-ml round-bottom flask equipped with condenser, stirrer, thermometer and dropping funnel. Then, TEBAC (0.53 g) was added to the solution, and the solution was gradually heated to 80°C and maintained for 2 h. After the reaction, toluene and water were added into the reaction mixture, and following isolation and purification of the products were similar to above; yield 205 g (98%, based on **3**). Epoxy equivalent and acid value were estimated by titration to be 420 (calcd. 419) and 0, respectively. **2** and M4–M9 are transparent pale yellow viscous oils. IR (neat) for M4–M9: 3480 ($\nu_{\text{O–H}}$), 1730 ($\nu_{\text{C=O}}$), 1640 ($\nu_{\text{C=C}}$), 914 cm^{-1} ($\delta_{\text{C–O–C}}$). ^{1}H-NMR (CDCl$_3$, TMS, ppm) for M4–M9: 1.64 (s, CH$_3$), 2.57 (d, $J = 4.0$ Hz, OH), 2.74 (dd, $J = 4.0$ Hz, O–CH$_2$–C), 2.89 (t, $J = 4.0$ Hz, O–CH$_2$–C), 3.34 (m, CH), 3.95 (m, O–CH$_2$–C), 4.04 (m, O–CH$_2$–C), 4.18 (m, O–CH$_2$–C), 4.29 (m, CH), 4.38 (m, O–CH$_2$–C), 5.89 (d, $J = 12.0$, =CH$_2$), 6.17 (dd, $J = 12.0$, 16.0 Hz, =CH), 6.46 (d, $J = 16.0$ Hz, =CH$_2$), 6.82 (d, $J = 8.0$ Hz, aromatic ring), 7.14 (d, $J = 8.0$ Hz, aromatic ring).

Table 1.
Composition of monomers

Monomer	Feed composition (g)		TEBAC (g)	Yield (%)
	3	Acrylic acid		
2	173 (1.0)	86.4 (1.2)	1.03	98
M9	173 (1.0)	64.8 (0.9)	0.95	95
M8	173 (1.0)	57.6 (0.8)	0.85	95
M7	173 (1.0)	50.4 (0.7)	0.74	98
M6	173 (1.0)	43.2 (0.6)	0.64	98
M5	173 (1.0)	36.0 (0.5)	0.53	98
M4	173 (1.0)	28.8 (0.4)	0.43	98

Numbers in parentheses denote the molar equivalent. TEBAC, triethylbezylammonium chloride, used as esterification catalyst.

Mono-acrylate (**4**) was also quantitatively prepared according to a method similar to that for **2**. That is, TEBAC (1.03 g) was added drop-wise to a solution of acrylic acid (86.4 g, 1.20 equiv) and phenylglycidyl ether (150.1 g, 1.00 equiv) containing hydroquinone (0.22 g) at 60°C, and the reaction was further continued for 2 h at 80°C. Complete esterification was confirmed by the acid value of 47.30 (calcd. 47.19) and negligible epoxy equivalent value. Purification of the product was followed to the procedure of **2**; yield: 205 g (96% based on phenylglycidyl ether). Both epoxy equivalent and acid value of **4** were confirmed to be 0. IR (neat) for **4**: 3480 ($\nu_{\text{O–H}}$), 1730 ($\nu_{\text{C=O}}$), 1640 cm^{-1} ($\nu_{\text{C=C}}$). ^{1}H-NMR ($CDCl_3$, TMS, ppm) for **4**: 3.09 (br. s), 4.04 (m, 2H), 4.32 (m, 1H), 4.36 (m, 2H), 5.85 (d, $J = 12.0$, 1H), 6.15 (dd, $J = 12.0$, 16.0 Hz, 1H), 6.44 (d, $J = 16.0$ Hz, 1H), 6.93 (d, $J = 4.0$ Hz, 2H), 7.29 (d, $J = 4.0$ Hz, 2H).

2.2. Preparation of Pre-IPNs and IPNs

Monomer M5 and diluent **4** (20 wt%), for instance, were mixed and degassed by heating at 40°C for 3 h. Then, Irgacure 651 (1 wt% with respect to the total amount of M5 and **4**) and 2-ethyl-4-methylimidazole (1 wt% with respect to the total amount of M5 and **4**) were added into the degassed monomers as a radical initiator and a curing reagent, respectively, and photopolymerization, which could induce only a polymerization of acrylate units in the monomers, was carried out to get a precursor of IPN (pre-IPN) at ambient temperature for 1 h using high-pressure mercury lamp (Ushio UI-501C, 100 W) in the mold made from Tefron plates clamped and sealed with 2-mm-thick Pyrex glass (Edmund Optics) which was coated with polypropylene film to avoid a sticking to the specimen. Pre-IPNs were then cured by thermal polymerization of epoxy units using the imidazole in an oven at 100°C for 5 h to obtain IPN materials. IPN(**3**) was obtained according to a method similar to M4–M9, but IPN(**2**) was prepared only by photopolymerization without heating in an oven, since **2** and diluent **4** have only acrylate units. Preparation of IPNs aided by microwave was carried out using a microwave oven (Hitachi MRO-N55) at 500 W power for the given time.

2.3. Measurements

^{1}H-NMR spectra were recorded on a Jeol EX-400 (400 MHz) spectrometer at 20°C in $CDCl_3$, in which TMS was used as an internal standard. FT-IR spectra were measured in the 4000–400 cm^{-1} region on a Jasco FT/IR-230 spectrometer in neat or KBr pellet for the structure determination of reagents and monomers and Varian 3100 FT/IR spectrometer for an attenuated total reflection measurement of pre-IPNs and IPNs materials at ambient temperature. Transmittance (T) of polymer was recorded using a film sample with thickness of 50 ± 1 μm on Ocean Optics S2000 spectrophotometer. The refractive index (n_D) of pre-IPNs and IPNs was measured with a Atago Abe Refractometer, in which the matching oil used in this system is 1.6570.

The composition of **1**–**3** in M4–M9 was determined by high-performance liquid chromatography (HPLC) on a HPLC instrument equipped with a Jasco 880-PU pump and Tosoh RI-8020 detector (Column: Shiseido C-18, 5 μm, 4.6 × 250 mm) in acetonitrile/water (3:2, v/v) at a flow rate of 1 ml/min at ambient temperature. The retention time of **1**, **2** and **3** was 9.15, 11.52 and 15.07 min, respectively. The samples for the evaluation of acid value and epoxy equivalent were prepared in 0.1 M HCl dioxane and 0.1 M alcoholic KOH acetone solutions, respectively, and the value and equivalent were measured on a Kyoto Electronics AT-510 titroprocessor.

Dynamic mechanical analysis (DMA) was carried out using a TA Instruments RSA-III viscoelastometer from 25 to 250°C at 1 Hz at a heating rate of 5°C/min. For the measurement of surface hardness of materials, Vickers and Shore D hardnesses were evaluated. Vickers hardness was measured by a Matsuzawa Seiki MXT70 digital micro-hardness tester at ambient temperature. A 9.8 N load was loaded on the sample for 15 s using the diamond indenter, after which the cross-sectional area of the indentation which remained in the sample was measured. Shore D hardness was measured using Ueshima UF shore's durometer. The mechanical properties were evaluated using an Instron model 4507 at 25°C. The size of specimens was 30 mm × 2.0 mm × 2.0 mm for the tensile test. Thermogravimetry (TG) was performed at a heating rate of 10°C/min with a Seiko TG/DTA220 under a nitrogen stream (30 ml/min).

3. Results and Discussion

3.1. Preparation of Monomers, Pre-IPNs and IPNs

Monomers M4–M9, containing various amounts of **1**, **2** and **3**, were prepared by changing a reactant ratio of acrylic acid to **3**, and hybrid monomer **1** is increasingly produced with decreasing acrylic acid additive until the feed composition of **3**/acrylic acid is 1:0.4 as shown in Table 2. The monomers obtained are high-viscosity liquids, with a viscosity of 3600 and 500 Poise for **2** and M5, respectively, at ambient temperature; therefore, mono-acrylate **4** was added into the polymerization system as a reactive diluent to reduce the viscosity. Monomers **1**–**4** are soluble in tetrahydrofuran, methanol and toluene, but insoluble in water. No detectable amount of free acrylic acid in acid titration and coincidence between experimental and calculated values in epoxy equivalent by both titration and HPLC experiments, as well as ^{1}H-NMR and IR spectra, confirmed that side-reactions including etherification, trans-esterification, hydrolysis and hydration did not occur in these acrylations under the experimental conditions, indicating the production of only **1**, **2** and **3** in the molar ratios shown in Table 2.

Preparation of pre-IPNs was carried out by photopolymerization of acrylate units in M4–M9 with Irgacure 651 as a radical initiator under UV irradiation at ambient temperature, in which the pre-IPN obtained from M9, for instance, will be denoted pre-IPN(M9) hereafter. AIBN and Irgacure 500 were also used as an initiator, but they were not appropriate for the present polymerization reaction because of a gas evolution and low initiator efficiency, respectively. Pre-IPN(M4)–pre-IPN(M6) are too soft and ductile as compared with other Pre-IPNs because of a higher content of unreacted epoxy units in the specimens.

Table 2.
Composition and epoxy equivalent of monomers

Monomer	Monomer composition			Epoxy equivalent		
	1	**2**	**3**	Observed by HPLC	Observed by titration	Calculated
2	0	100	0	0	0	0
M9	19.7	80.3	0	2408	2385	2384
M8	32.3	64.2	3.5	1173	1160	1156
M7	38.5	51.5	10.0	753	755	747
M6	47.3	37.2	15.5	568	546	538
M5	50.2	26.6	23.2	420	429	419
M4	53.0	12.4	34.6	330	324	319
3	0	0	100	173	173	170

Monomer composition was determined by HPLC. The calculated epoxy equivalent values were estimated assuming complete acrylation using pure reactants.

IPN materials were prepared not only by heating in an oven at 100°C but also by microwave irradiation in the presence of the imidazole as a cured reagent. Figure 1 shows the dependence of conversion of epoxy moiety on curing time in the concentration of the imidazole of 0.5 and 1.0 wt% for the polymerization of pre-IPN(M5), in which the conversion of epoxy polymerization was determined by monitoring a decrease of the absorption at 914 cm^{-1} due to an antisymmetric stretching of the epoxy group in the IR spectrum. After 5 min of reaction in 1.0 wt% imidazole, the conversion of epoxide in pre-IPN(M5) is about 3 and 97% for the heating in an oven and microwave irradiation, respectively. In 0.5 wt% imidazole, the conversion was completely 100% after 20 min of microwave irradiation, whereas it was only 4% after the same heating time in an oven, and it takes about 500 min to go up to 100% conversion. Such an appreciable reduction in curing time by microwave irradiation seems to be due to a rapid elevation of the temperature of the system by microwave power, i.e., 1 and 3 min to go up to 100°C for microwave irradiation and heating in an oven, respectively, in addition to some microwave effect which has not been confirmed yet.

3.2. Optical Properties

Table 3 represents the visible light transmittance data for IPNs at 470 and 600 nm. The IPNs show high transparency, over 87% T at 600 nm and 82% T at 470 nm, until **3** content in the total amounts of **1**, **2** and **3** is around 35 wt%, and IPN(M8) provides the highest transparency in the IPNs containing hybrid unit **1**, while, the transparency of the IPNs lowers with increasing **3** content, and it becomes 83.8% T in a single epoxy network. This result suggests that miscibility or domain size change with the dependence on the content of **3** in the IPNs. In addition, transparency of the IPNs is little influenced by the concentration of the imidazole, but

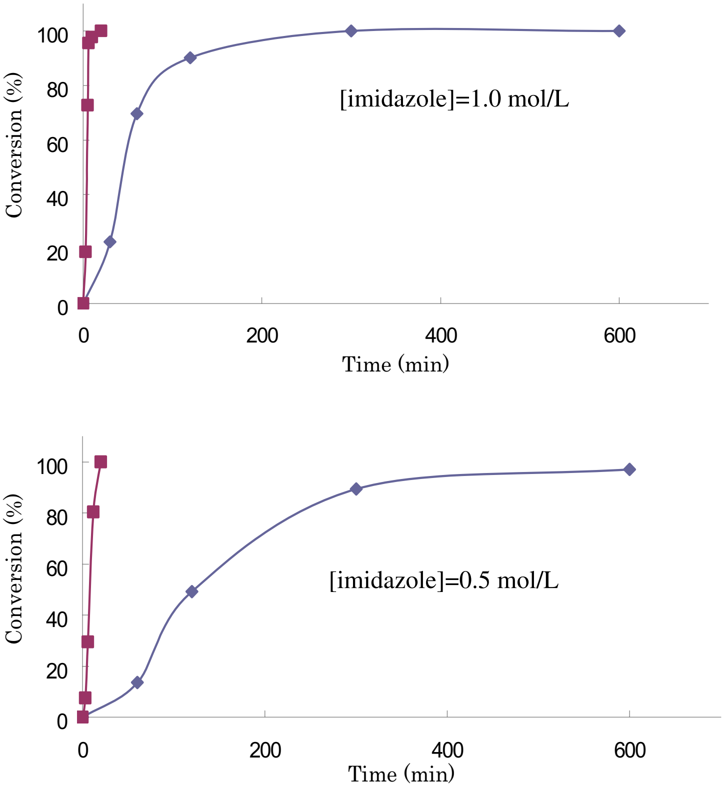

Figure 1. Time–conversion curves for epoxy polymerization of pre-IPN(M4) with 2-ethyl-4-methylimidazole by (left curve) microwave irradiation and (right curve) heating in an oven at 100°C. Polymerization condition: [imidazole] = 1.0 and 0.5 wt% with respect to the total amount of M4 and **4**. This figure is published in colour in the online edition that can be accessed *via* http://www.brill.nl/dmp

lower by microwave irradiation, as seen in Table 3, probably because of an overheating due to a rapid elevation of temperature under the irradiation.

Table 4 summarizes the refractive index (n_D) of monomers, pre-IPNs and IPNs. It is evident that the n_D depends little on the composition of **1**, **2** and **3** in each monomer mixture, pre-IPNs and IPNs, respectively, i.e., n_D remains nearly the same among M4–M9, pre-IPN(4)–pre-IPN(M9) and IPN(4)–IPN(M9). Moreover, their n_D values are fairly higher than those of methyl methacrylate (MMA) and poly(MMA), i.e., 1.414 and 1.492, respectively, due to the aromatic ring in the bisphenol A unit. It is noted that the polymerization brings about an increase of n_D as generally known, but the variation is very small as compared with other related materials, e.g., increase of n_D by polymerization is only about 1.5% for the present specimens as seen in Table 4, but 5.5, 3.4 and 6.1% for MMA, styrene and propyleneoxide, respectively [10, 11]. A small change of n_D between pre-IPNs and IPNs also coincides with the small increase of n_D by polymerization.

Table 3.
Transmittance of IPNs

IPN	Curing method	Curing agent (wt%)	Transmittance	
			At 470 nm	At 600 nm
IPN(**2**)	Heating	1.0	97.6	98.2
IPN(M9)	Heating	1.0	92.8	94.6
IPN(M8)	Heating	1.0	94.8	96.9
IPN(M7)	Heating	1.0	92.3	93.7
IPN(M6)	Heating	1.0	91.3	91.8
IPN(M5)	Heating	0.5	90.5	91.4
IPN(M5)	Heating	1.0	88.1	89.9
IPN(M5)	Microwave	0.5	74.2	77.6
IPN(M5)	Microwave	1.0	72.6	76.4
IPN(M4)	Heating	1.0	82.8	87.5
IPN(**3**)	Heating	1.0	73.1	83.8

Table 4.
Refractive index of monomers, pre-IPNs and IPNs

Monomer		Pre-IPN		IPN	
Sample	Refractive index	Sample	Refractive index	Sample	Refractive index
2	1.547			IPN(**2**)	1.571
M9	1.549	Pre-IPN(M9)	1.572	IPN(M9)	1.573
M8	1.551	Pre-IPN(M8)	1.578	IPN(M8)	1.577
M7	1.552	Pre-IPN(M7)	1.573	IPN(M7)	1.575
M6	1.553	Pre-IPN(M6)	1.574	IPN(M6)	1.574
M5	1.553	Pre-IPN(M5)	1.577	IPN(M5)	1.578
M4	1.555	Pre-IPN(M4)	1.573	IPN(M4)	1.577
3	1.567			IPN(**3**)	1.565

3.3. Mechanical Properties

Tables 5 and 6 list the mechanical properties including stress at break and Young's modulus which can be characterized by tensile test for pre-IPNs and IPNs, respectively, at various **1**/**2**/**3** ratios. For pre-IPNs, the stress and Young's modulus tend to decrease with decreasing acrylate content in the network polymers because of a flexible unreacted epoxide. On the other hand, all IPNs containing hybrid monomer **1** exhibit higher Young's modulus than that of each single network, as well as the corresponding pre-IPNs. Moreover, Young's modulus increases with increasing **1** content in IPNs and reached maximum at the ratio of **1**/**2**/**3** was 32.3:64.2:3.5. This composition agrees with the composition showing highest transparency in the IPNs over all specimens studied as already shown in Table 3. It is interpreted that the IPN

Table 5.
Mechanical properties of pre-IPNs

	Stress at break (MPa)	Young's modulus (MPa)
Pre-IPN(M9)	65.7	1448
Pre-IPN(M8)	53.0	1395
Pre-IPN(M7)	51.3	1377
Pre-IPN(M6)	36.4	1319
Pre-IPN(M5)	13.6	305
Pre-IPN(M4)	1.4	7

Table 6.
Mechanical properties of IPNs

	Stress at break (MPa)	Young's modulus (MPa)
IPN(**2**)	70.6	1472
IPN(M9)	82.1	1717
IPN(M8)	85.3	1748
IPN(M7)	78.4	1680
IPN(M6)	75.0	1658
IPN(M5)	69.5	1646
IPN(M4)	69.2	1640
IPN(**3**)	52.8	1265

structure entangled uniformly with the best toughening effect on acrylate–epoxy network in IPNs is surely formed at the nano-level at this composition ratio, and it results in high-mechanical performance for IPN(M8).

Figure 2 indicates typically a variation in loss factor $\tan\delta$ *vs.* temperature for some IPNs and each single network. All curves show $\tan\delta$ as a single peak, but no bimodal curve which is often observed in a blend of epoxy and acrylate polymer [12]. This should be attributed to the uniform structure of the present IPNs probably by the contribution of the hybrid unit **1** and, thus, the phase separation between the two networks would not take place in all cases, which gives rise to single peak. Absence of the phase separation in the IPNs is also supported by the comparable solubility parameters (δ) calculated for **1**, **2** and **3**, i.e., $\delta = 16.16$, 16.49 and 15.84 $\text{cal}^{0.5}\ \text{cm}^{-1.5}$, respectively [13], as is also known in IPN of epoxy resin and poly(methyl methacrylate) (PMMA) [14, 15]. As seen in Fig. 2, the maximum of $\tan\delta$ for IPN(M4), IPN(M6) and IPN(M8) lies in the temperature range from 99°C to 110°C, indicating a small variation of chain segmental motions for these IPNs.

IPNs obtained represent generally high-surface hardness, and Shore D hardness is too high to detect the value for all IPNs as listed in Table 7. For Vickers hardness

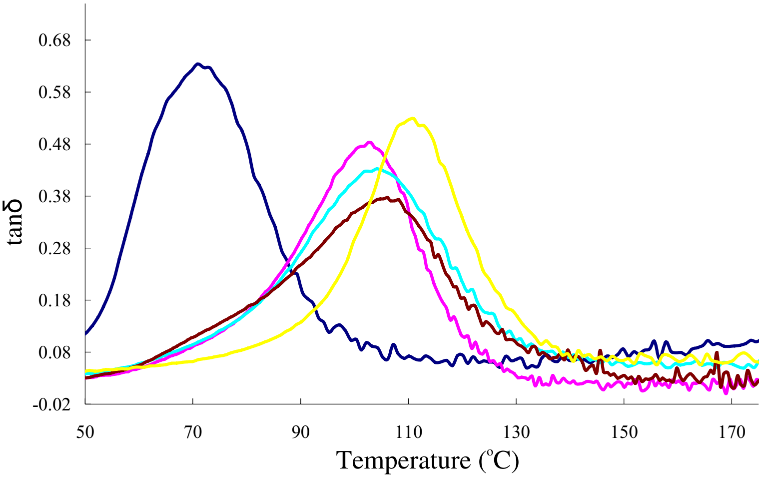

Figure 2. Temperature dependence of tan δ for (peaks from left to right) INP(**2**), IPN(M8), IPN(M6), IPN(M4) and IPN(**3**). This figure is published in colour in the online edition that can be accessed *via* http://www.brill.nl/dmp

Table 7.
Surface hardness of IPNs

	Vickers hardness (HV)	Shore D hardness (HS)
IPN(**2**)	19.1	>90
IPN(M9)	21.2	>90
IPN(M8)	21.9	>90
IPN(M7)	21.7	>90
IPN(M6)	20.9	>90
IPN(M5)	20.2	>90
IPN(M4)	19.9	>90
IPN(**3**)	18.0	>90

of IPNs, it increases with increasing the content of **1** in IPNs and reached maximum at the ratio of **1**/**2**/**3** is 32.3:64.2:3.5, corresponding to IPN(M8). The hardness of IPN(M8) is also higher than that of the single networks of IPN(**2**) and IPN(**3**), 1.1–1.2 times the hardness of the single networks. It is indicated that acrylate and epoxy networks can be toughened by a hybrid network, and IPN(M8) exhibits better comprehensive surface hardness than that of each single network, which must be related to better interpenetration between the two networks. While the Vickers and Shore D hardnesses of pre-IPNs decrease monotonously with decreasing acrylate content because of the soft epoxy units remained unreacted in the pre-IPNs as collected in Table 8.

Table 8.
Surface hardness of pre-IPNs

	Vickers hardness (HV)	Shore D hardness (HS)
Pre-IPN(M9)	18.9	>90
Pre-IPN(M8)	18.4	90
Pre-IPN(M7)	15.9	85
Pre-IPN(M6)	13.9	81
Pre-IPN(M5)	8.8	70
Pre-IPN(M4)	4.1	40

Table 9.
Glass-transition temperatures of IPNs

	T_g (°C)
IPN(**2**)	70.9
IPN(M9)	99.3
IPN(M8)	103.2
IPN(M7)	104.2
IPN(M6)	108.1
IPN(M5)	106.1
IPN(**3**)	111.1

3.4. Thermal Properties

The glass transition temperature (T_g) estimated from the DMA of these IPNs is summarized in Table 9. It has been known in the network of epoxy and urethane acrylate resin that the PMMA segments linking with urethane acrylate oligomer may be not easy to diffuse into the epoxy domains leading to less interpenetration between the two networks, which results in two T_g [16]. In the present case, however, it is evident that over the monomer composition range of IPNs studied, there is only one T_g, indicating the excellent compatibility for acrylate/bisphenol A/epoxy units in the IPNs as already seen in Fig. 2. The T_g of IPN(M4)–IPN(M9) is located in between the T_g of each single network, but their T_g values are much higher than that of the single acrylate network (70.9°C), and slightly lower than that of the single epoxy network (111.1°C) and PMMA (111°C) [17]. T_g tends to increase with increasing the amount of **1** in the IPNs.

TG charts and 10 and 50% weight loss temperatures for pre-IPNs and IPNs are shown in Figs 3 and 4 and Table 10. As clearly seen in Fig. 3 and Table 10, 10 and 50% weight loss temperatures for pre-IPNs tend to decrease with increasing unreacted epoxy content in the network, and accordingly the TG charts change from one step to two step degradation curves as is known for epoxy acrylate oligomers con-

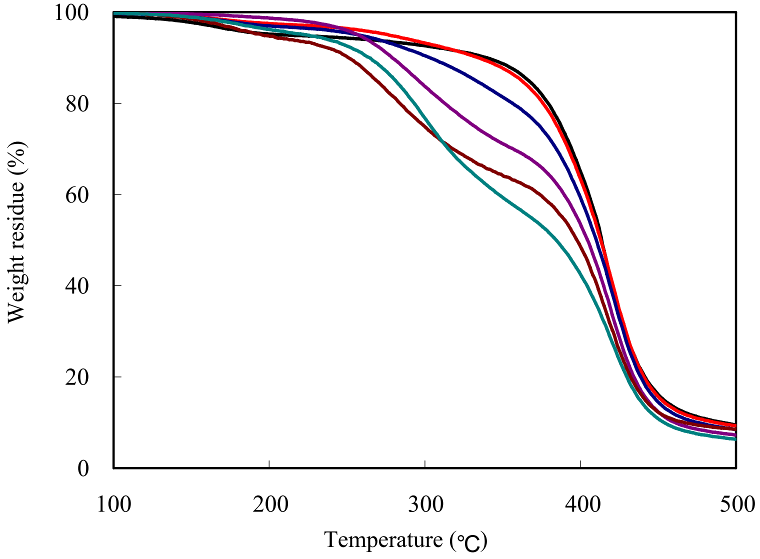

Figure 3. Weight loss *vs*. temperature for pre-IPNs M9–M4 (top to bottom). This figure is published in colour in the online edition that can be accessed *via* http://www.brill.nl/dmp

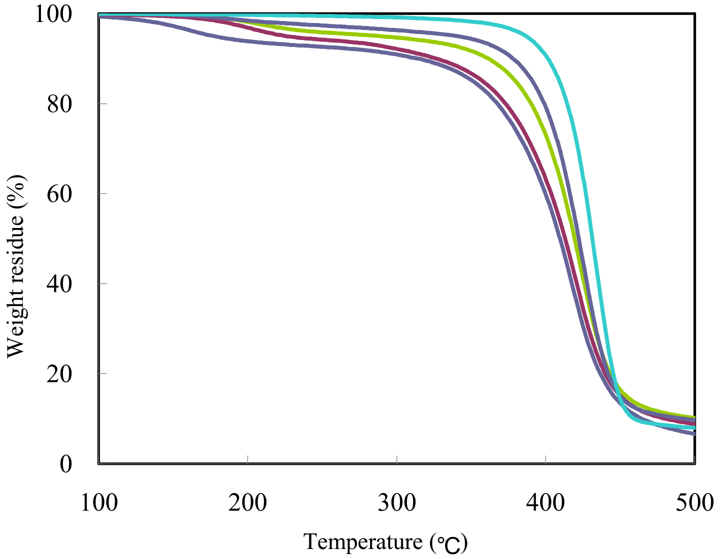

Figure 4. Weight loss *vs*. temperature for IPNs **3**, M4, M6, M8, **2** (top to bottom). This figure is published in colour in the online edition that can be accessed *via* http://www.brill.nl/dmp

taining pendant alkoxysilane group [18]. In such a two-step degradation, the weight lost in the first step corresponds approximately to the weight of the epoxy content in the specimen. This means that the weight loss at the first stage of degradation originates from the elimination of unreacted pendant epoxy unit in the IPNs. Contrary

Table 10.
Weight lodd temperatures of pre-IPNs and IPNs

	10% weight loss temperature (°C)	50% weight loss temperature (°C)
Pre-IPN(M9)	340.1	413.4
Pre-IPN(M8)	334.7	411.6
Pre-IPN(M7)	304.3	409.9
Pre-IPN(M6)	279.1	404.4
Pre-IPN(M5)	250.6	397.4
Pre-IPN(M4)	264.9	318.6
IPN(**2**)	356.2	415.2
IPN(M9)	332.9	411.7
IPN(M8)	327.7	412.7
IPN(M7)	327.9	413.4
IPN(M6)	361.4	418.7
IPN(M5)	370.5	420.2
IPN(M4)	378.7	421.5
IPN(**3**)	400.8	431.2

to the pre-IPNs, the 10% weight loss temperature of IPNs increases with increasing the content of epoxy unit in the specimen, and it is lower than that of single epoxy network because of a high-heat resistance of polyepoxide itself.

4. Conclusions

IPNs were synthesized with hybrid (**1**), diacrylate (**2**) and diepoxide (**3**) monomers linked by bisphenol A. The IPN prepared at a ratio of **1**/**2** of about 1:2 containing small amount of **3** was outstanding in terms of Young's modulus, surface hardness and transparency. These hybrid materials are, therefore, expected to be structural materials or engineering materials. Moreover, curing time was much reduced by microwave irradiation.

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