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Morphology and mechanical properties of polymer blends with photochemical reaction for photocurable/linear polymers

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Abstract

The relationship between morphology and mechanical properties were investigated in a binary blend of photocurable polymer (2,2-bis(4-(acryloxy diethoxy)phenyl)propane; BPE4) and linear polymer (polysulfone; PSU). The blend films are prepared by in situ photopolymerization of homogeneous mixtures of BPE4-monomer and PSU. The tensile strength and modulus reach a maximum in the blends having vague domain structures with a diffusion-phase boundary, at which the underdeveloped small BPE4-rich domains are wrapped with the PSU-rich matrix. The higher strength and modulus are caused by a strong interfacial adhesion between the BPE4-rich domain and the PSU-rich phase, which is brought about by incomplete phase separation in the PSU-rich phase. The tensile strength and modulus decrease as the bicontinuous structures clear due to deterioration of the interfacial adhesion. The mechanical properties also deteriorate in the blends with semi-IPN structures due to the lower conversion of BPE4. The composition dependencies on the tensile strength and the modulus for blends cured at optimum cure temperatures were found to give convex curves reaching maximums greater than those of pure components. © 2002 Published by Elsevier Science Ltd.

Keywords: Phase structure; Mechanical property; Viscoelastic phase separation

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1. Introduction

The physical properties of multicomponent polymers depend strongly on phase-separated morphologies. A bicontinuous two-phase structure in polymer blends provides polymers with mechanical properties such as high toughness, large extension, and excellent strain recovery [1,2]. Generally, a bicontinuous structure is demonstrated on spinodal decomposition, induced by temperature jump [3], solvent-casting [4], or shear [5] in polymer/polymer systems over a limited range (nearly 50 vol%) of composition, while a droplet structure is more evident at asymmetric composition. Tanaka has reported recently that in binary-blend systems having strong asymmetry with regard to molecular dynamics such as polymer/solvent systems [6–8], thermoset/thermoplastic polymer systems [2,9–16], and polymer/polymer systems having very different glass-transition temperatures [17], even minor polymeric components give network-like continuous phase-separated patterns. These systems undergo so-called viscoelastic phase separation in which viscoelastic effects play a dominant role in phase-separation behavior [6–8]. Numerous reports have been published regarding morphologies [10], phase-separation behavior [9,11–13], and mechanical properties [2,14–16] in polymer-blend systems associated with thermo-chemical reactions. The bicontinuous phase structure results in excellent mechanical properties in a small number of thermoplastic polymers [2].

Recently, photo-irradiation curing systems have found various applications in coatings, inks, and adhesives due to desirable features such as their lack of solvency, rapid cure, and cold cure. Photochemical reaction systems have advantages over thermal reaction systems in controlling phase structures, as cure temperature and light intensity can be varied independently [18]. However, there has been little investigation of the photo-polymerization curing associated with polymer blends [18–20].

We have investigated phase separation in and the functional properties of photocurable/linear polymer systems associated with photochemical reactions. Previously [21], we reported on the phase-separation behavior and morphology control in the binary blend of the 2,2-bis(4-(acryloxy diethoxy)phenyl)propane (BPE4) and polysulfone (PSU)

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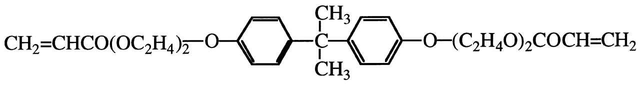
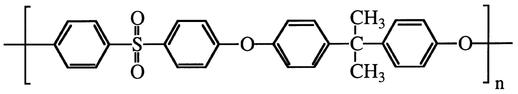
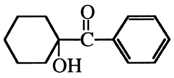


2,2-Bis(4-(acryloxy diethoxy)phenyl)propane (BPE4)



Polysulfone (PSU)



1-hydroxy cyclohexyl phenyl ketone (HCPK)

Fig. 1. Chemical structures of BPE4, PSU and HCPK.

system. It was found that network-like bicontinuous phase-separated structures are formed over a wide range of compositions of 5–70 wt% PSU via the viscoelastic phase-separation mode. The characteristic length scales of the network-like structures can vary from nanometer-scale (30 nm) to micrometer-scale (1 μm) under the preceding controlled conditions and blend composition. In this paper, we report on the relationship between phase-separated structure and mechanical properties in a binary blend BPE4/PSU system associated with a photochemical reaction.

2. Experimental

2.1. Materials

The sample of 2,2-bis(4-(acryloxy diethoxy)phenyl)propane (BPE4) supplied by Daiichi Seiyaku Kougyo Co. (Japan) was used as the photocurable monomer. The linear polymer was polysulfone (PSU, Udel P-3703) obtained from Amoco Chemicals. Purified PSU was obtained by precipitating it from dichloromethane solution (ca. 2 wt% concentration) with an excess volume of methanol. The weight-averaged molecular weight (M_w) of the purified PSU was 44,300, and the ratio between the weight-average and number-average molecular weights (M_w/M_n) was 1.90. The sample of 1-hydroxycyclohexyl-phenyl ketone (HCPK, Irgacure 184) obtained from Ciba Specialty Chemicals was used as the photoinitiator. To BPE4 was added 2 wt% (0.5 mol%) of HCPK (BPE4/HCPK) = (98/2 w/w). The chemical structures of BPE4, PSU, and HCPK are shown in Fig. 1.

2.2. Photo-polymerization

A typical procedure for photo-induced phase separation is as follows. BPE4 (5 g), including 2 wt% of HCPK (0.1 g), and PSU (5 g) were dissolved in dichloromethane (80 g) (for 50 wt% PSU composition). The samples were prepared by solvent-casting on glass slides and were kept in a Petri dish at room temperature (25 °C) overnight. These solvent-cast films were dried in a vacuum oven at 50 °C for 3 h. In this study, all coatings with 1–80 wt% PSU before the photopolymerization were transparent and homogeneous over a temperature range of 0–220 °C. The coating sandwiched between two glass slides containing spacers (PET films) with a thickness of 0.1 mm was heated at an appropriate temperature on a heat stage and then irradiated with ultraviolet (UV) light for 90 s using a high-pressure Hg-lamp (Spot Cure 250, Ushio Electric, Japan) under nitrogen atmosphere. The UV intensity at the surface of the coatings was ca. 10 mW cm^{-2} at 365 nm. The coating was further cured by photoirradiation at RT for 90 s under nitrogen atmosphere to ensure complete curing using a high-power UV light, a 3 kW metal-halide lamp (UE031, Eye graphics, Japan); the light intensity at 365 nm was ca. 75 mW cm^{-2}. The cured blend film was obtained by releasing the blend coating from the glass slide.

2.3. Measurements

Morphological observations were carried out by transmission electron microscopy (TEM) using a JEM-200CX (JEOL, Japan) and scanning electron microscopy (SEM) using a FE-SEM S-800 (Hitachi, Japan). For TEM observation, the cross-sections of the specimens were microtomed into ultrathin sections of ca. 50 nm and observed without staining. The fracture surface of broken blend film after the tensile test was examined by SEM. Phase separated-structure was also observed by SEM. The specimen was fractured in liquid nitrogen and the PSU-rich phase was etched out with dichloromethane. These fracture surfaces for SEM were coated with platinum at a thickness of 5 nm. All micrographs of electron microscopy were taken from the core region in the coatings (0.1 mm thickness).

The mechanical properties (tensile strength (yield strength), tensile modulus, and elongation at break) of the blend films were obtained from a uniaxial tensile test using an Autograph AGS-H (Shimadzu, Japan). A gauge length of 10 mm and a cross-head speed of 5 mm min^{-1} were used for this study. Measurements were performed at room temperature (25 ± 1 °C) with film specimens ($5 \times 50 \times 0.1$ mm^3).

The extent of the curing of BPE4 in blends was estimated by Fourier-transform infrared spectroscopy (FT-IR) using a FT-IR-550 (JSCO, Japan). Conversions were calculated from the area [$(A_{805})_{t=0}$ and $(A_{805})_t$] of absorption of the reactive acrylate functional groups at 805 cm^{-1} (CH_2=CH twisting) in the blends before and after photoirradiation [22]. The conversion (R_c (%)) of BPE4 is given by $[1 - (A_{805}/A_{1732})_t/(A_{805}/A_{1732})_{t=0}] \times 100$, where $(A_{1732})_{t=0}$ and $(A_{1732})_t$ are the area of the absorption of the no reactive ester functional groups at 1732 cm^{-1} (C=O stretching) in the blends before and after photoirradiation, respectively. FT-IR spectra of the blends were measured by the KBr method.

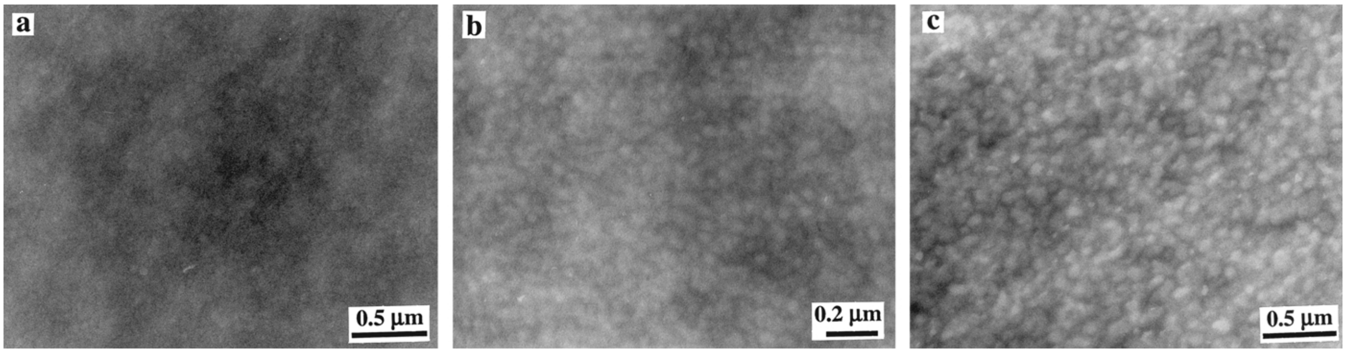


Fig. 2. TEM images of BPE4/PSU (5/5 w/w) prepared at (a) 120 °C, (b) 150 °C, and (c) 200 °C.

The PSU content in the blend with or without the etching with dichloromethane was measured by an electron probe microanalyzer (EPMA) using an EPM-810 (Shimadzu). The PSU content after the etching was obtained by $(I_{aet}/I_{bet}) \times 100$, where I_{aet} and I_{bet} are the intensities of the sulfur Kα line spectra at 5.373 Å with or without etching, respectively. A pentaerythrital (PET) was used as the analysis crystal, and the probe size was 5 μm.

Glass transition temperatures (T_g) of the cured blend films were measured by a dynamic viscoelastometer using a Solids Analyzer RSA-II (Rheometric Scientific, Inc.). The complex modulus E^* of films was measured at 1 Hz with a temperature sweep from 0 to 200 °C at a heating rate of 2 °C min^{-1}. T_g values of cured films refer to the maximum in the tan $\delta(=E''/E')$ peak, where E' is the storage modulus and E'' the loss modulus. In a homogeneous mixture of BPE4-monomer and PSU prior to photopolymerization, T_gs were obtained from a differential scanning calorimeter (DSC) measurement at a heat scan rate of 10 °C min^{-1} using a DSC-7 (Perkin Elmer).

3. Results and discussion

3.1. Morphology

In photocurable/linear polymer systems associated with photopolymerization, the resulting phase structures have varied significantly, ranging from the structure of a semi-interpenetrating polymer network (semi-IPN) to that of a droplet structure and a network-like bicontinuous structure as a result of controlling the blend compositions and preparation conditions such as the photocuring temperature and irradiation intensity [21].

The phase structures of the BPE4/PSU blends with 50 wt% PSU are shown in Fig. 2 (TEM images) and 3 (SEM images). In the TEM images, the dark part is the PSU-rich phase and the bright part the BPE4-rich phase. In the SEM images, the blend films were dissolved and etched out with dichloromethane, so the remaining phase should be a cross-linked BPE4-rich phase. In the blend cured at 200 °C, the PSU-rich phase appears as a continuous matrix phase in the TEM (Fig. 2c), and the BPE4-rich domains with a size of 0.08 μm are also connected to one another three-dimensionally in the SEM (Fig. 3c). The BPE4-rich domains were primarily wrapped with the PSU-rich matrix phase. Consequently, both the BPE4-rich and PSU-rich phases were found to be continuous, i.e. the structure was a bicontinuous structure. In the blends with 50 wt% PSU, bicontinuous structures were formed by the photopolymerization occurring above 130 °C. The bicontinuous structures became obscure in the TEM as the cure temperature decreased. At a cure temperature of 150 °C, the network-like structure was indistinct in the TEM image, and small globular BPE4-rich domains ca. 0.04 μm in size were wrapped with the PSU-rich phase in the SEM. Large amounts of BPE4 should be included in the PSU-rich phase, as this is the phase remaining after rinsing with

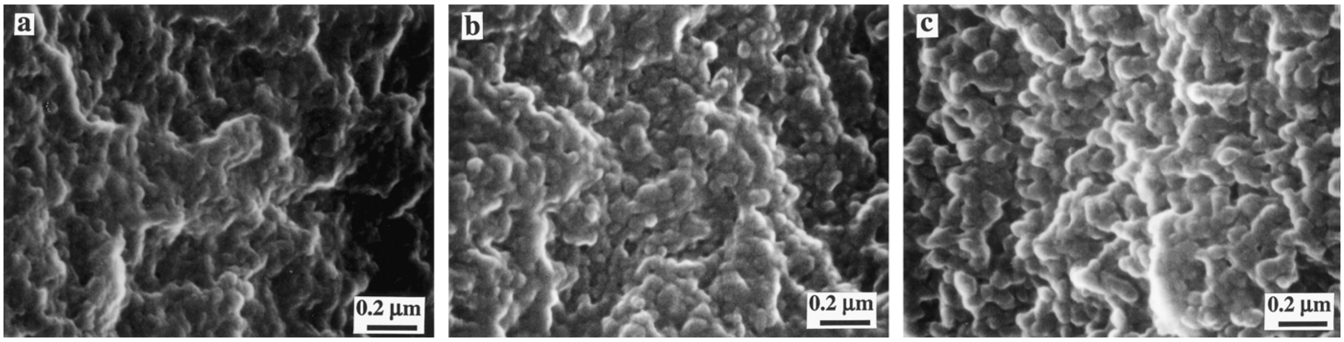


Fig. 3. SEM images of BPE4/PSU (5/5 w/w) prepared at (a) 120 °C, (b) 150 °C, and (c) 200 °C. The PSU-rich phase was rinsed out by etching with dichloromethane.

dichloromethane. From the EPMA measurement, the PSU content in the rinsed blends was found to decrease in the order 18, 15, 10, and 9%, respectively, with increases in the curing temperatures, 80, 100, 150, and 180 °C. The extent of phase separation in the PSU-rich phase has been reported to increase with the cure temperature [21], implying that BPE4 molecules are contained in the PSU-rich phase in blends cured at lower temperatures. Clear bicontinuous phase structures should result from the increased phase decomposition.

Only one glass transition temperature appeared in the blends cured below T_{g0} [21], where T_{g0} is the glass-transition temperature of a homogeneous mixture of BPE4-monomer and PSU before photopolymerization. The miscible semi-IPN structures would be given in the blends cured below the T_{g0}.

Two glass-transition temperatures were observed in the blends cured at a temperature of $T_{g0} - 130$ °C, with these temperatures characterizing the occurrence of a phase separation. At the cure temperature of 120 °C, small vague BPE4-rich domains were faintly observed in the TEM image (Fig. 2a), and underdeveloped small globular BPE4-rich domains completely wrapped with the PSU-rich phase were observed in the SEM (Fig. 3a). This vague structure appears as a vague domain structure with a diffusion-phase boundary that is generally apparent in blends with incomplete phase separation in the PSU-rich phase. In the vague domain structure, a thick semi-IPN layer should be formed at the phase boundary. At 50 wt% PSU, these vague domain phase structures were observed in the blends cured at an intermediate temperature of 80–120 °C. In contrast, there were no morphologies observed in the blends cured below 80 °C in the TEM. A partially phase-separated semi-IPN structure should be formed in the blends cured at a temperature of $T_{g0} - 80$ °C.

Fig. 4 shows the relationships between the resulting phase structures and controllable parameters (composition, cure temperature, and light intensity) in the binary blend of BPE4/PSU undergoing a photochemical reaction. The bicontinuous structures appear in the preparations at temperatures above $T_{g0} + 90$ °C (region IV) with a light intensity of 10 mW cm^{-2}, with the temperature increasing with the light intensity. The miscible semi-IPN structures were obtained by curing at temperatures below T_{g0}s (region I). The partially phase-separated semi-IPN structures were produced in the blends cured at a temperature of T_{g0}–$T_{g0} + 40$ °C (region II), while incompletely phase-separated blends having vague domain structures were obtained by curing at a temperature of $T_{g0} + 40$ °C $-$ T_{bi} ($T_{g0} + 90$ °C) (region III), where T_{bi} is the boundary cure temperature at which the bicontinuous structure appeared in TEM.

Bicontinuous phase structures were obtained by photopolymerization over a wide range of compositions of PSU (5–70 wt%). The characteristic length scales of the network-like bicontinuous pattern were controlled over a wide range of 0.03–1 μm by the preparation conditions and the blend compositions. The characteristic length scale became smaller with increases in the PSU composition and the irradiation intensity as well as with decreases in the cure temperature [21].

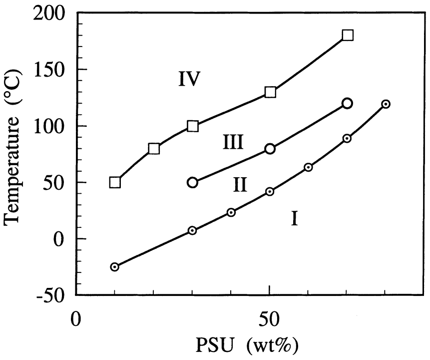


Fig. 4. Relationships between resulting phase structures and curing conditions for a binary blend of BPE4/PSU prepared by photopolymerization. Region I corresponds to miscible semi-IPN structures, region II to partially phase-separated semi-IPN structures, region III to vague domain structures, and region IV to bicontinuous structures. (⊙) glass transition temperatures (T_{g0}) of homogeneous mixtures of BPE4-monomer and PSU prior to photopolymerization.

3.2. Cure-temperature dependence of mechanical properties

Phase structures are easily controlled from miscible semi-IPN structures to bicontinuous structures by photocuring temperatures. We first investigated the cure-temperature dependence of the mechanical properties. Fig. 5 shows stress–strain curves of the blends with 50 wt% PSU cured at 25, 120, 180 °C, and the pure BPE4. The pure BPE4 film was photopolymerized at 120 °C. Each curve has a yield point around 8–10% at which the strength reaches a maximum. In the blend cured at 120 °C, the strength was somewhat higher than for the other blends cured at 25 and 180 °C, while the elongation at the break was inferior to that of the other blends. At a cure temperature of 25 °C, the strength was somewhat less than that of the pure BPE4.

Fig. 6 shows the cure-temperature dependence of the tensile strength (yield strength), tensile modulus, and

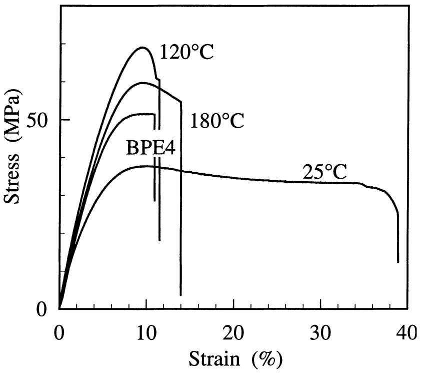


Fig. 5. Stress–strain curves for cured pure BPE4 film cured at 120 °C and blend films of BPE4/PSU (5/5 w/w) cured at 25, 120, and 180 °C.

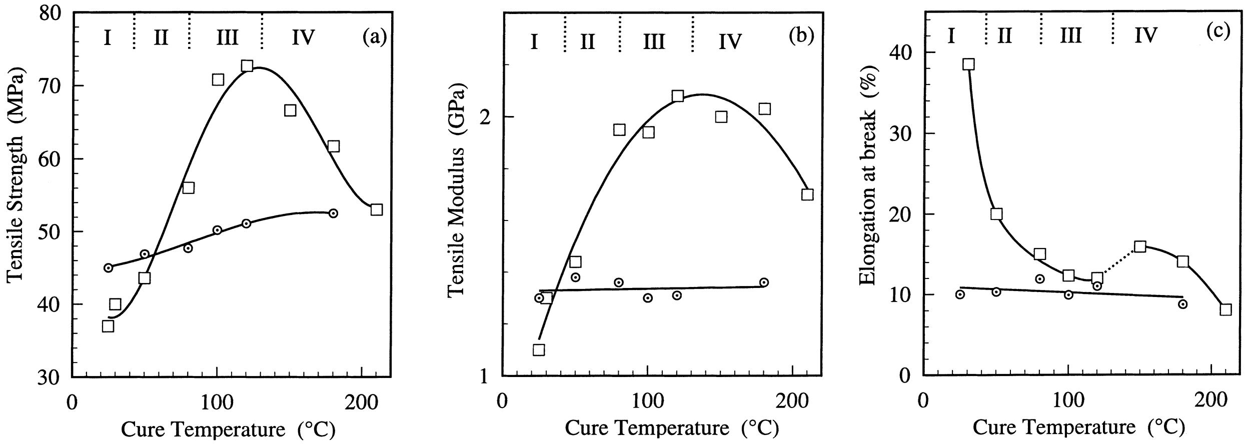


Fig. 6. (a) Tensile strength, (b) tensile modulus, and (c) elongation at the break for (□) blend films of BPE4/PSU (5/5 w/w) prepared by photopolymerization and (⊙) cured pure BPE4 as a function of the cure temperature. Phase structures in the blends were (I) miscible semi-IPN structures, (II) partially phase-separated semi-IPN structures, (III) vague domain structures, and (IV) bicontinuous structures.

elongation at the break for the blends of BPE4/PSU (5/5 w/w) prepared by photopolymerization. The tensile properties of the pure BPE4 cured at 25–180 °C are also given in Fig. 6. The mechanical properties varied widely depending on the curing temperature. The curves for the tensile strength and modulus reached a maximum at around 120 °C, which was slightly below the boundary cure temperature ($T_{bi} = 130$ °C), where a bicontinuous structure appeared. The maximum strength and modulus, which were 1.4–1.5 times higher than those of the pure BPE4, were reached in the blend with the vague domain structure.

The tensile strength and modulus of the blends cured below 120 °C gradually deteriorated as the cure temperature decreased. In particular, below 50 °C, the tensile strength and modulus decreased to less than those of the cured pure BPE4, likely due to the lower conversions of BPE4 in the blends cured at low temperature. The conversions of BPE4 in the blend films are shown in Fig. 7. In the blends with 50 wt% PSU, the conversion (65%) for those cured at 25 °C was somewhat lower than that (86%) for those cured above 120 °C. The conversions of BPE4 increased from 65 to 86% with cure temperatures up to 120 °C, and became saturated at around 86% above 120 °C. The cure-temperature dependence of the strength and modulus below 120 °C corresponds well to that of the conversion.

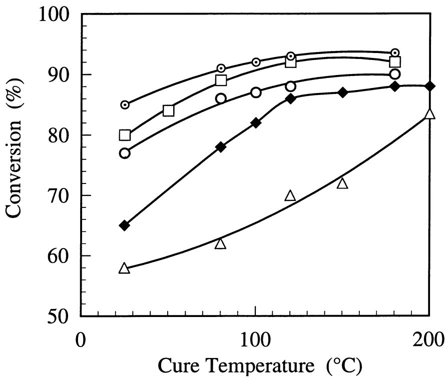


Fig. 7. Conversion of BPE4 in blends as a function of cure temperature: (⊙) PSU = 0 wt%, (□) PSU = 10 wt%, (○) PSU = 30 wt%, (◆) PSU = 50 wt%, and (△) PSU = 70 wt%.

The mechanical properties of the cured polymer blends are not only dependent on morphology, but are also influenced by the degree of curing. We investigated the effects of the degree of curing on the strength and modulus for pure BPE4 and the blend having the miscible semi-IPN structure. The pure BPE4 films with conversions below 85% were obtained by controlling a photoirradiation time of 10–60 s (at 25 °C, 75 mW cm^{-2}). The blends having the miscible semi-IPN with a conversion of 62–72% were obtained by the controlling of an irradiation time of 0.5–5 min under nitrogen atmosphere (at 25 °C, 75 mW cm^{-2}). The blend ($T_g = 63$ °C) irradiated for 2 min was further photoirradiated at 60 °C for 90 s at an intensity of 75 mW cm^{-2}. The conversion in the blend barely reached 76% by the postcuring period. The miscibility of the blend was verified by the glass transition behavior. All the blends exhibited one glass transition, as shown in Fig. 8c. The T_g for the pure BPE4 is also given in Fig. 8c. The T_gs increased linearly with the conversion of BPE4. The T_gs of the BPE4-rich phase for the phase-separated blends cured at a temperature of 50–120 °C are slightly higher than those for the miscible blends.

The relationships between the conversion and the tensile strength and modulus are shown in Fig. 8a and b, respectively. The tensile strength and modulus increased with the extent of curing. In the pure BPE4, when the conversion reached 85% or more, the strength and modulus were saturated at around 50 MPa and 1.4 GPa, respectively. The strength and modulus for the phase-separated blends are also plotted in Fig. 8a and b. The mechanical properties for the phase-separated blend correspond well to those for the miscible blend. The decrease in the mechanical properties of the blend cured at lower temperatures can primarily be ascribed to the lower extent of curing. The deterioration of the conversion in the blend cured at lower temperature is

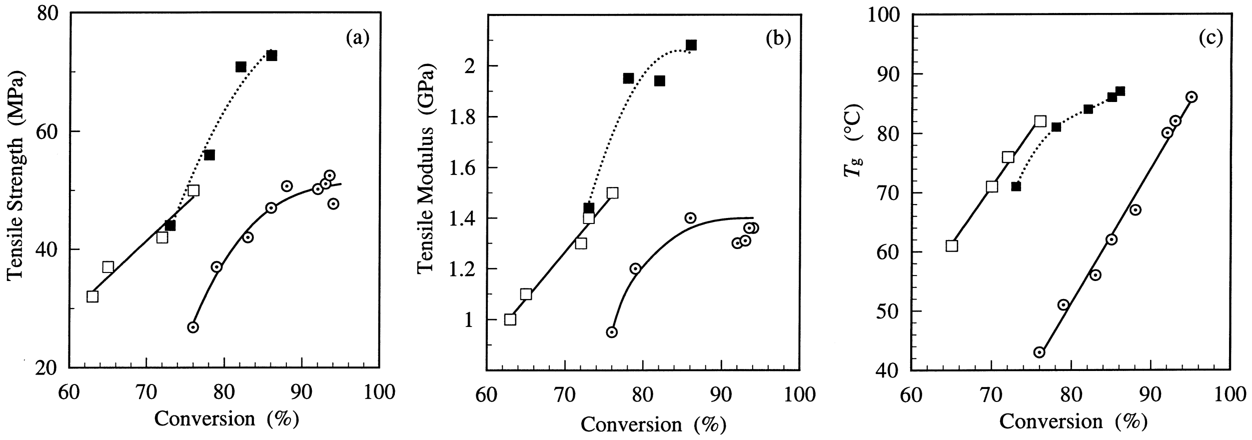


Fig. 8. Relationship between conversion and (a) tensile strength, (b) tensile modulus, and (c) T_g and T_g of the BPE4-rich phase for (□) miscible and (■) phase-separated blends of BPE4/PSU (5/5 w/w) and (⊙) pure BPE4.

likely inevitable, due to the interpenetrating phase formation during which the polymeric molecules penetrate the three-dimensional cross-linking network of BPE4. Photopolymerization of BPE4 is then blocked by the penetrating PSU molecules.

The fracture surfaces of the broken blend films after the tensile test were observed by SEM and are shown in Fig. 9. The fracture surfaces were flat and smooth, and appeared soft and weak for the blends cured below 100 °C (Fig. 9a), while ductile fracture behavior was observed in the blends cured above 120 °C (Fig. 9b and c). In the SEM images, the PSU-rich phase wrapped within the BPE4-rich domains exhibited a large extension in the blend cured at 180 °C, and the PSU-rich phase was stretched with and included small BPE4-rich domains in the blend cured at 120 °C. In particular, in the blends cured at a temperature of 120–180 °C, the PSU-rich phase was elongated and well-wrapped within the BPE4-rich domains. The improvements in tensile strength and modulus can be ascribed to the strong interfacial adhesion between the BPE4-rich domain and the PSU-rich matrix. The SEM images reveal that the interfacial adhesion for the blend cured at 120 °C is stronger than that for the blend cured at 180 °C.

Maximum strength and modulus were present in the blends having vague domain phase structures with a diffusion-phase boundary, which is brought about by incomplete phase separation. Bicontinuous structures appeared in the blends cured above 130 °C, after which there was a gradual clearing in the TEM image as the curing temperature increased. The clear bicontinuous phase structures were brought on by increases in the extent of the phase decomposition under the viscoelastic phase separation mode. The deterioration of tensile strength and modulus at a high cure temperature are caused by a decrease in the interface adhesion between the PSU-rich phase and the BPE4-rich phase due to a lowering of the PSU (BPE4) composition in the BPE4-rich (PSU-rich) phase.

The elongation at the break reached a maximum (ca. 38%) in the blend cured at 25 °C, and decreased to 12% as the cure temperature increased to 120 °C. The elongation at the break discretely improved from 12 to 16% in the blend cured at 150 °C. This jump temperature corresponds well to the T_{bi} (130 °C). In the SEM images, the fracture surface in the blend cured at 180 °C exhibited elastic deformation as compared with that cured at 120 °C (Fig. 9c), and BPE4-rich domains were sufficiently wrapped within the PSU-rich matrix in the blend cured at 150 °C (Fig. 3b). The elongations in the blends cured at 150 and 180 °C were improved ca. 1.4 times as much as that of the cured pure BPE4. The discrete improvement in elongation at the break is due to the continuous structure in the PSU-rich phase.

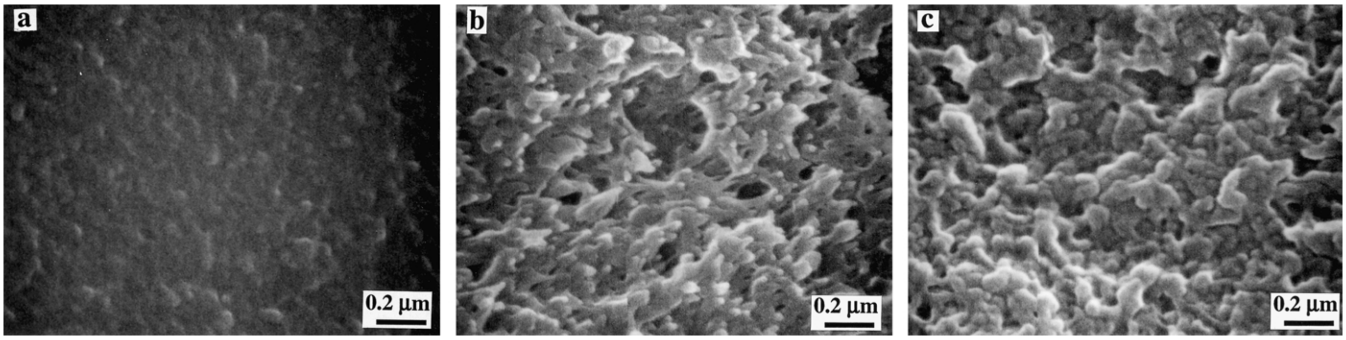


Fig. 9. SEM micrographs of the fracture surfaces after the tensile test for BPE4/PSU (5/5 w/w) cured at (a) 50 °C, (b) 120 °C, and (c) 180 °C.

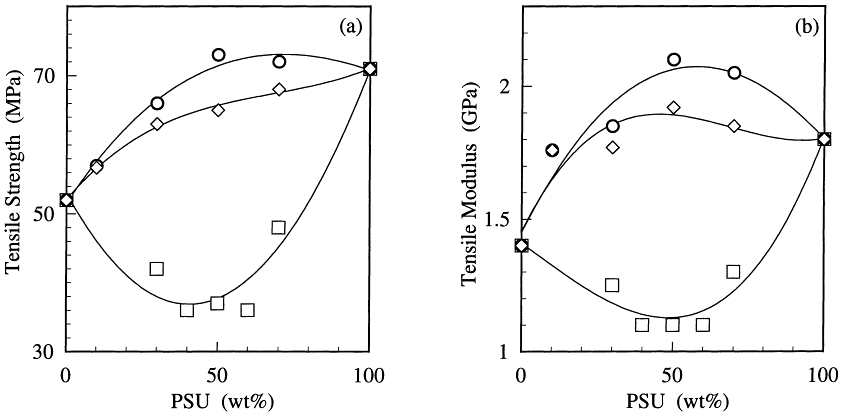


Fig. 10. (a) Tensile strength and (b) tensile modulus of BPE4/PSU blends as a function of composition when the blends were prepared at three different temperatures: (1) (○) the optimum cure temperatures (vague domain structures), (2) (□) below T_{g0}s (miscible semi-IPN structures), and (3) (◇) T_{bi}s + 30 °C at which clear bicontinuous structures appeared.

3.3. Composition dependence in mechanical properties

Fig. 10 shows the composition dependence of the tensile strength and modulus for the blend films prepared by photopolymerization at the three following temperatures: (1) the optimum cure temperatures at which the maximum strength and modulus were reached; (2) the temperatures below T_{g0}; and (3) T_{bi} + 30 °C, at which the network-like bicontinuous structures became clear. The optimum cure conditions are given in Table 1. In the case of blends cured at optimal temperatures, the composition dependence of the mechanical properties gave a convex curve with a maximum around 50–70 wt% PSU. It is notable that the maximums for strength and modulus were somewhat higher than those of the neat PSU, which is compounding as a reinforced component. It has been speculated that the PSU molecules might be oriented in a network-like structure, since an extension of the PSU-rich phase has been observed when the network-like structures are developed via viscoelastic phase separation [21]. A similar improvement in tensile strength has been observed in thermoset/thermoplastic polymers system induced by a thermal reaction [15].

At 30–70 wt% PSU, the optimal cure temperatures were just below the T_{bi}. In contrast, at 10 wt% PSU, the optimum cure temperature was 80 °C, which was 30 °C high than T_{bi} (50 °C). This difference is likely due to the low conversion of BPE4 in the blend cured at T_{bi} (Fig. 7). The conversion reached ca. 89% at 80 °C, at which time the mechanical properties of the pure BPE4 were saturated (Fig. 8). Consequently, a maximum improvement in mechanical properties was brought about in blends having vague domain structures with a diffusion-phase boundary.

The tensile strength of the blend with the clear network-like bicontinuous structure appears on the extrapolated line connecting the properties of the pure components, the modulus of which can be observed as being somewhat higher than that of the extrapolated value. The SEM micrographs show that the interfacial interaction had a high enough level of adhesion for an improvement in mechanical properties.

The mechanical properties of the blends with the

Table 1
Optimum cure conditions and mechanical properties for the BPE4/PSU blend

PSU (wt%)	T_{g0} (°C)	Optimum cure temperature (°C)	T_{bi} (°C)	Light intensity (mW cm^{-2})	Conversion (%)	Tensile property		
						Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
10	−25	80	50	10	89	58	1.76	10
30	7.5	100	100	10	87	66	1.85	10
50	42	120	130	10	86	73	2.10	12
70	89	150	180	10	75	72	2.05	7
10	−25	80	60	75	93	66	2.00	12
50	42	120	140	75	89	80	2.20	10
70	89	180	180	75	77	77	2.05	11
Pure BPE4 cured at 120 °C		T_g = 86 °C		75		51	1.30	11
Neat PSU		T_g = 198 °C		–		71	1.80	>100

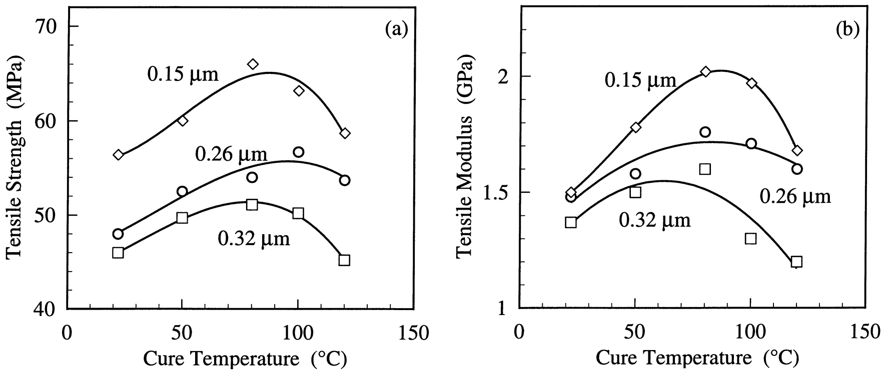


Fig. 11. (a) Tensile strength and (b) tensile modulus of blend films with 10 wt% PSU content having bicontinuous structures prepared by photopolymerization at three different irradiation intensities, (□) 1 mW cm^{-2}, (○) 10 mW cm^{-2}, and (◇) 75 mW cm^{-2}, as a function of cure temperature. The characteristic length scales of the bicontinuous structures were ca. 0.32, ca. 0.26, and ca. 0.15 μm by UV irradiation at 80 °C with intensities of 1, 10, and 75 mW cm^{-2}, respectively.

miscible semi-IPN structures decreased with PSU content, which reached a minimum around 30–50 wt% PSU. The minimum strength and modulus were 20–30% lower than in the cured pure BPE4 film due to the low conversion of BPE4 (see Fig. 7).

3.4. Characteristic length scale of bicontinuous structure

Characteristic length scales (BPE4-rich domain) of network-like structures become smaller as the light intensity increases [21]. Fig. 11 shows the tensile strength and modulus in the blend with 10 wt% PSU content prepared by photopolymerizations with three different light intensities, as a function of the cure temperature. The curves became higher with increases in the light intensity (with decreases in the characteristic length). Each curve reached a maximum at around 80 °C. The characteristic length scales of the network-like structure were ca. 0.32, ca. 0.26 and ca. 0.15 μm by photoirradiation at 80 °C with light intensities of 1, 10, and 75 mW cm^{-2}, respectively. The maximum strength (66 MPa) and modulus (2 GPa) in the blend photoirradiated with a light intensity of 75 mW cm^{-2} were ca. 30% higher than those (51 MPa and 1.6 GPa) of the blend cured with a light intensity of 1 mW cm^{-2}. The conversions of BPE4 in the blends cured at 80 °C were 87, 89, and 93% as the light intensities (at 365 nm) increased to 1, 10, and 75 mW cm^{-2}, respectively. Significant effects on the mechanical properties should not arise from differences in the conversions.

Similar improvements in the tensile strength and modulus were observed in the blends with 50 and 70 wt% PSU contents in response to photopolymerization with a high irradiation intensity of 75 mW cm^{-2}. Fig. 12 shows the mechanical properties of the blends photopolymerized with light intensities of 10 and 75 mW cm^{-2} as a function of composition. The optimum photoirradiation conditions are also listed in Table 1. The composition dependence of the properties also gave a convex curve with a maximum at around 50 wt% PSU. It is noteworthy that the tensile strength and modulus of BPE4 increased by 1.4–1.5 times in response to compounding with a small amount of PSU (10 wt%). This effect might have been caused by the bicontinuous structure being formed in the blend with a small amount of PSU.

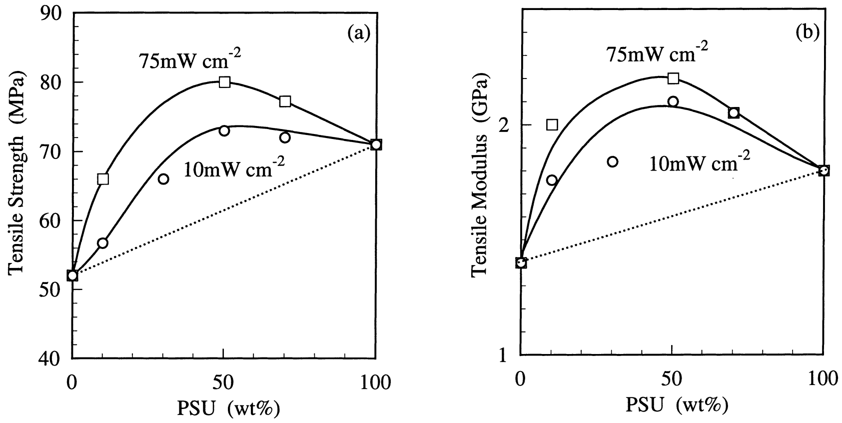


Fig. 12. (a) Tensile strength and (b) tensile modulus for BPE4/PSU blend films cured at the optimum cure temperatures with irradiation of (○) 10 mW cm^{-2} and (□) 75 mW cm^{-2} as a function of the PSU composition.

4. Conclusions

The maximum tensile strength and modulus were provided in a vague domain structure with a diffused phase boundary. The improvement in mechanical properties appeared to be caused by strong interfacial adhesion between two phases brought about by incomplete phase decomposition under the viscoelastic phase separation mode. One prominent finding of the present study is that the maximum strength and modulus of blends are greater than those of pure components. Improvements in mechanical properties have been achieved in blend compounds, including a small number of linear polymers. The tensile strength and modulus of the pure BPE4 film increased 1.4–1.5 times in response to compounding with 10 wt% of PSU. These improvements were likely due to bicontinuous structures being present in the blends with a small amount of polymeric materials. Furthermore, it was found that a small characteristic length ($<0.2\ \mu m$) results in an excellent improvement in mechanical properties, also increasing the transparency of the blend.

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References

[1] Quintens D, Groeninckx G, Guest M, Aierts L. Polym Engng Sci 1990;30:1474.
[2] Girard-Reydet E, Vigier G, Pascault JP, Sautereau H. J Appl Polym Sci 1997;65:2433–45.
[3] Nishi T, Wang TT, Kwei TK. Macromolecules 1975;8(2):227–34.
[4] Miyake Y, Sekiguchi Y, Kohjiya S. J Chem Engng Jpn 1993;26(5):543–50.
[5] Okamoto M, Shiomi K, Inoue T. Polymer 1995;36(1):87–91.
[6] Tanaka H. J Phys: Condens Matter 2000;12:R207–64.
[7] Tanaka H. Macromolecules 1992;25(23):6377–80.
[8] Tanaka H. J Chem Phys 1994;100(4):5323–37.
[9] Inoue T. Prog Polym Sci 1995;20:119–53.
[10] Jansen BJP, Meijer HEH, Lemstra PJ. Polymer 1999;40:2917–27.
[11] Oyanguren PA, Galante MJ, Andromague K, Frontini PM, Williams RJJ. Polymer 1999;40:5249–55.
[12] Chen J-L, Chang F-C. Macromolecules 1999;32(16):5348–56.
[13] Okada M, Sakaguchi T. Macromolecules 1999;32(12):4154–6.
[14] Harismendy I, Del Rio M, Marieta C, Gavalda J, Mondragon I. J Appl Polym Sci 2001;80:2759.
[15] Venderbosch RW, Meijer HEH, Lemstra PJ. Polymer 1994;35(20):4349–57.
[16] Pearson RA, Yee AF. Polymer 1993;34(17):3658–70.
[17] Tanaka H. Phys Rev Lett 1996;76(5):787–90.
[18] Tran-Cong Q. Structure and properties of multiphase polymeric materials. New York: Marcel Dekker; 1998. chapter 6.
[19] Tran-Cong Q, Nagaki T, Nakagawa T, Yano O, Soen T. Macromolecules 1989;22(6):2720–3.
[20] Harada A, Tran-Cong Q. Macromolecules 1997;30(6):1643–950.
[21] Murata K, Sachin J, Etori H, Anazawa T. Polymer 2002;43(9):2845–59.
[22] Decker C. Prog Polym Sci 1996;21:593–650.