Improvement in mechanical properties by photopolymerization induced, phase separation and controlled morphology, in polymer blend of photcurable/linear polymers.

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Abstract

Relationships between morphology and mechanical properties have been investigated in a binary blend of photo-curable polymer (2,2-bis (4-(acryloxy diethoxy) phenyl) propane; BPE4) and linear thermoplastic polymer (polysulfone; PSU). The blend films are prepared by in-situ photo-polymerization of homogeneous mixtures of BPE4-monomer and PSU. The maximum tensile strength and modulus are observed in films having vague network-like bi-continuous structures with diffused phase boundary, which are obtained by photo-irradiation at around the temperatures where network-like structures appeared. A strong interfacial interaction between two phases is observed in the fractural surface from SEM observation. The composition dependencies of tensile strength and modulus for the blends cured at the optimal cure temperatures gave synergestic properties, which are higher than that of pure components. Improvement in mechanical properties decreased with increasing the curing temperature above the optimal cure temperature due to the decreasing interfacial interaction. Mechanical properties are reduced in the blends with semi-IPN structures due to the low conversion of BPE4. However, the mechanical properties of these blends, with semi-IPN structures, can be improved exceptionally by annealing and post photo-curing in a high temperature regime, which bring high conversion and bi-continuous phase structure at nano-scale.

Keywords: Phase Structure; Mechanical Property; Photochemical Reaction;

1. INTRODUCTION

Physical properties of multi-component polymers strongly depend on phase-separated morphologies. A bi-continuous two-phase structure in polymer blends provides polymers with mechanical properties such as high toughness, large extension and excellent strain recovery [1-6]. Generally bi-continuous structure is observed on spinodal decomposition, induced by temperature jump[7], solvent casting [8], or due to shear [9,10] in polymer/polymer systems over limited range (near 50 vol %) of composition, while droplet structure is more evident at asymmetric composition. Tanaka reported recently that in binary blend systems having a strong asymmetry in molecular dynamics such as polymer/solvent systems[11-14], thermoset/thermoplastic polymers systems [1-5,15-22], and polymer/polymer systems having very different glass transition temperatures [23], even minor polymeric component gives network-like or sponge-like continuous phase-separated patterns. These systems undergo so-called viscoelastic phase separation in which viscoelastic effect play dominant role in phase separation behaviour [11-14]. Numerous reports have been published on morphologies, phase separation behaviour [1,16-20,24-25] and mechanical properties [1-5,21,22] in polymer blend systems associated with thermo-chemical reaction. The bi-continuous phase structure brought about excellent mechanical properties with small amount of thermoplastic polymers [1-5].

Recently photo-irradiation curing systems have found various applications in coatings, inks and adhesion due to desirable features such as non-solvent, cold and yet rapid cure. Photochemical reaction systems have advantages over thermal reaction systems in controlling the phase structures, since cure temperature and light intensity can be varied independently [26]. However little has been investigated on photo-polymerization curing associated with polymer blends [26-29]. In the previous report [30], network-like bicontinuous phase separated structures have been obtained in binary blend of photocurable polymer (cured bisphenol-A diacrylate; BPE4) and linear polymer (polysulfone; PSU) system associated with photochemical reaction over a wide range of composition of 10-70 wt% PSU via viscoelastic phase separation. The characteristic length scales of the network-like structures vary from nanometer-scale (30 nm) to micrometer-scale (1 µm) depending on the blend composition and the preparation conditions. This paper reports on relationships between phase-separated structure and mechanical properties (tensile strength, Young's modulus and elongation) in a binary blend of photocurble/linear polymers associated with photochemical reaction.

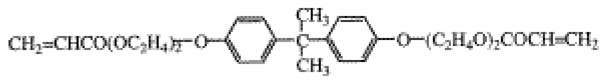
2. EXPERIMENTAL

2.1 Materials

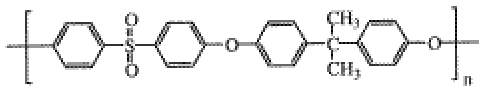
The sample of 2,2-Bis(4-(acryloxy diethoxy)phenyl)propane (BPE4) supplied by Daiichi Seiyaku Kougyo Co. (Japan) was used as photocurable monomer. Linear polymer was polysulfone (PSU, Udel P-703) obtained from Amoco Chemicals. Purified PSU was obtained by precipitation from dichloromethane solution (ca. 2 wt% concentration) with an excess volume of methanol. The weight average molecular weight (Mw) of the purified PSU was 44300 and the polydispersity was 1.90. The sample of 1-hydroxycyclohexylphenyl ketone (HCPK, Irgacure 184) obtained from Ciba Specialty Chemicals was used as photoinitiator. 2 wt% (0.5 mol%) of HCPK was added in BPE4, (BPE4/HCPK)=(98/2 w/w). The chemical structures of BPE4, PSU and HCPK are shown in Fig. 1.

2.2. Photo-polymerization

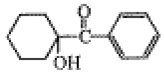
A typical procedure for photo-induced phase separation is as follows. BPE4 (5g), including 2wt% of HCPK (0.1g), and PSU (5g) were dissolved in dichloromethane (80g) (for 50 wt% PSU composition). The solution was cast on a glass slide kept in a Petri dish at 25°C (RT) overnight, and then the coating film was dried in a vacuum oven at 50°C for 3hrs. The complete evaporation of solvent was confirmed by TGA measurements, which showed that residual solvent in cast films was below 0.1 % by wt after drying. In this study, all coatings with 1-80% by wt PSU before the photopolymerization were transparent and homogeneous over a temperature range of 0-200°C. The coating sandwiched between two glass slides containing spacers (PET films) with a thickness of 0.1 mm was heated at appropriate temperature on a heat stage and then irradiated with ultraviolet (UV) light for 90-120 sec using a high-pressure Hg-lamp (Spot Cure 250, Ushio Electric, Japan) under nitrogen atmosphere. UV intensity at the surface of the coatings was ca.10 mW cm^{-2} at 365 nm; this is the line spectrum at which the photopolymeriztion of



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



Polysulfone (PSU)



1-hydroxy cyclohexyl phenyl ketone (HCPK)

Figure 1 - Chemical structure of a photocurable monomer (BPE4), linear polymer (PSU) and photoinitiator (HCPK)

BPE4 by using HCPK as photoinitiator proceed predominantly. Phase separation takes place with the increase in the molecular weight of BPE4. Increase in molecular weight decreases miscibility of one component in the other. Furthermore, vitrification and gelation due to the in-situ cross-linking of BPE4 simultaneously suppress the process of the phase decomposition. The coating was further cured by photo-irradiation under nitrogen atmosphere at RT for 1-2 min to ensure complete curing using a high power UV light, a 3 kW metal-halide lamp (UE031, Eye graphics, Japan); light intensity at 365 nm was ca.75 mW cm^{-2}. Additional photo-irradiation at RT virtually does not affect the earlier formed phase morphologies, since the post curing of the coating was done at temperatures well below the glass transition temperatures (Tg) of the coating. In case of 50% by wt PSU, T_gs before the post curing were above 50°C. The cured blend films were obtained by removing the blend coatings from glass slide.

2.3 Measurements

Morphological observations were performed 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. Fractural surfaces of blend films after a tensile test were observed by using SEM. Also, in morphological observation of phase structure, specimens were fractured in liquid nitrogen and PSU-rich phase was etched out with dichloromethane. The fractural surfaces were coated with platinum at a thickness of 5 nm.

Mechanical properties (Tensile strength (yield strength), Young's modulus and Elongation at break) of the blend films were obtained from a uniaxial tensile test using an Autograph AGS-H (Shimazu, 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°C) with film specimens (width=5 mm, length=50 mm and thickness=0.15 mm). The extent of curing of BPE4 in blends was estimated by fourier-transform IR (FT-IR) using a FT-IR-550 (JSCO, Japan). The ratio of the area between the CH_2=CH twisting vibrations of the reactive acrylate functional groups at 805 cm-1 and the C=O stretching vibrations of the non- reactive ester functional groups at 1732 cm-1 was used to calculate conversions [31]. Glass transition temperatures (T_g) of partial cured coatings and homogeneous mixtures of BPE4-monomer and PSU were obtained from a differential scanning calorimeter (DSC) measurement at a heat scan ratio of 10°C min^{-1} under nitrogen atmosphere using a DSC-7 (Perkin Elmer).

Dynamic mechanical measurements at 1Hz were carried out on dynamic viscoelastometer using a Solids Analyzer RSA-II (Rheometric, Inc.) with temperature sweep from 0°C to 200°C at a heating rate of 2°C min^{-1}. T_g values of cured films refer to the maximum in tan δ peak.

3. RESULTS AND DISCUSSION

3.1. Morphology

In photocurable/linear polymers systems associated with photopolymerization, resulting phase structures have been widely varied from a semi-interpenetrating polymer network (semi-IPN), to a droplet and a network-like bicontinuous structure by controlling on blend compositions and processing conditions such as temperature and irradiation intensity. Fig. 2 shows the relationships between resulting phase structures and controllable parameters (composition, cure temperature and light intensity) in the binary blend of BPE4/PSU with photochemical reaction. Semi-IPN structures should be obtained by curing at temperatures well below T_gs of homogeneous mixtures of BPE4-monomer/PSU. Network-like bicontinuous structures appeared in the samples prepared at temperatures above T_g+80°C with 1mW/cm^2 light intensity, which increased with light intensity. Phase structures became vague and non-distinct at the intermediate temperature range of T_g-T_g+80°C. Droplet structures were observed in extremely asymmetric blend compositions, which were blow 20% by wt PSU or above 70% by wt PSU. PSU-rich domains were dispersed in BPE4-rich matrix in the blends below 20% by wt PSU, while BPE4-rich phase became islands in PSU-rich matrix in the blends above 70% by wt PSU content. It was note worthy that phase inversion took place at the extremely asymmetric composition of 2-5% by wt PSU and bicontinuous phase structures were obtained over wide range of compositions of PSU (5-70% by wt). [Figure 2]

Figure 3 shows TEM and SEM images for BPE4/PSU (9/1 w/w) blend cured at 120ºC. In TEM image, the dark part is PSU-rich phase and the bright part is BPE4-rich phase. A minor component (PSU-rich phase) appeared as a network-like continuous interconnecting structure. In SEM image, PSU-rich phase was rinsed out by etching with dichloromethane. Small globule particles of BPE4-rich were connected to one another forming three-dimensional network. Consequently, both of BPE4-rich and PSU-rich phases are continuous. Characteristic length scale of the network-like bicontinuous pattern was controlled with a wide range of 0.03-1μm by the preparation conditions and the blend compositions. Characteristic length scale became smaller with the increase of PSU composition and irradiation intensity and with the decrease of cure temperature [30].

3.2. Effect of cure temperature on mechanical properties

Resulting phase structures have been easily controlled from semi-IPN structures to bicontinuous structures by proper choice of photocuring temperatures. Figure 4 shows the dependence of tensile strength (Yield strength), modulus (Young's modulus) and elongation at break for the blend films of BPE4/PSU (5/5 w/w) prepared by the photo-polymerization on cure temperture. Mechanical properties varied widely depending on the curing temperature. Tensile strength and modulus gave the maximum when cured at around 120 °C, which corresponds to the boundary cure temperature (T_{bi}) for network-like bicontinuous structure to be formed.

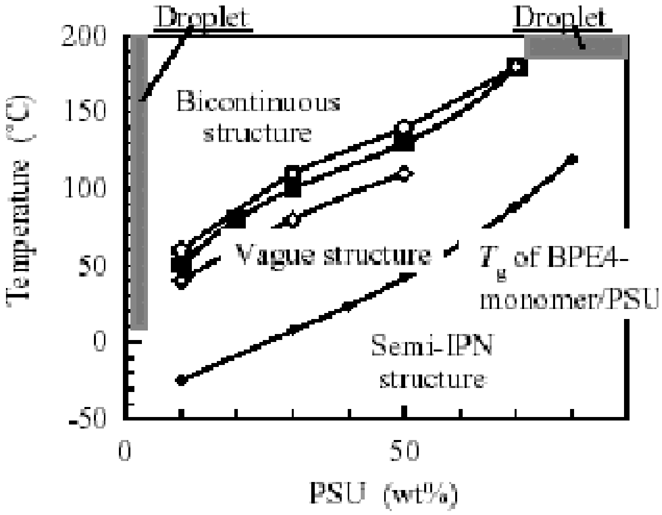
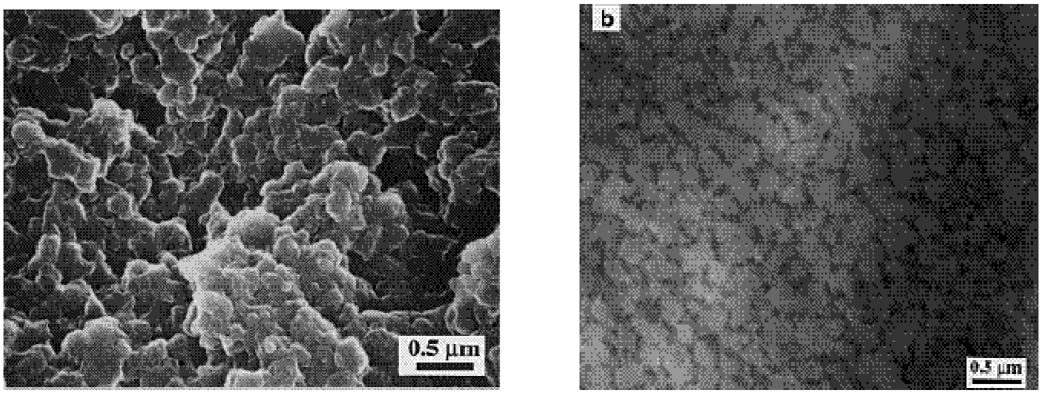


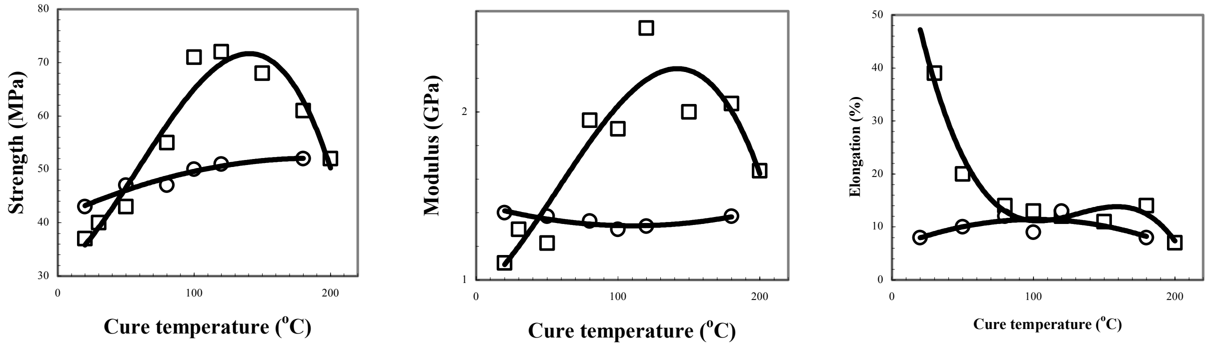
Figure 2 – Relationships between PSU content and T_{bi} for the BPE4/PSU system prepared by photopolymerization with light intensities (◊) 1mW cm^{-2} ,(■) 10mW cm^{-2} , (o)75mW cm^{-2} ; T_{bi} is the curing temperature at which the network like bi-continuous phase separated structure appeared. (•) T_g BPE4-monomer and PSU homogeneous mixtures (T_{go})



(a) (b)

Figure 3 - Network-like bicontinuous morphology of BPE4/PSU (9/1 w/w) cured at 120°C with a light intensity of 10mW cm^{-2}: (a) TEM image and (b) SEM image, in which PSU was etched out with dichloromethane.

The maximum strength and modulus were 1.4-1.5 times higher than those of the cured neat BPE4. Whereas the elongation at break became the maximum cured at 25°C, and drastically decreased with increasing the cure temperature. Stress-Strain curves of the blends cured at 25°C, 120°C, 180°C and the cured neat BPE4 (cured at 120°C) are shown in Figure 5. Each curve has the yield point around 8-10%, at which the strength became the maximum. The elongations at break were improved ca.1.4 times as that of the cured neat BPE4 by blending with PSU even cured at 100°C and 180°C. However, the improvement



(a) (b) (c)

Figure 4- (a) Tensile strength, (b) Modulus and (c) elongation at break for (□) blend films of BPE4/PSU (5/5 w/w) prepared by photopolymerization and (o) cured neat BPE4, as a function of cure temperature.

in elongation at break would be limited by the three-dimensional cross-linking formation of BPE4.

The tensile strength and modulus of the blends with semi-IPN structures cured below 50°C were inferior to those of the cured neat BPE4. It should be due to low conversion of BPE4 in the blend film. The conversions of BPE4 in the blend films are given in Figure 6. The conversion (65%) in the blend cured at 25°C was fairly lower than that (85%) of the phase separated blends cured above 100°C regardless of sufficient photoirradiation of 6.8 mW cm^{-2}. The tensile strength and modulus were improved with the conversion of BPE4 up to 120°C, at which the conversion was saturated. The reductions of strength and modulus and the improvement in elongation in the blends cured at low temperatures below 120°C would be caused by the low conversion of BPE4. The conversion should be inevitably reduced by the invasive formation, which the polymeric molecules penetrate into the three-dimensional cross-linking network of cured BPE4-phase such as the semi-IPN structures. Figure 7 shows temperature dependence of storage modulus (E') and tan δ for the blend films with 50 wt% PSU content cured at temperatures of 25-210°C. Only one glass transition appeared as tan δ peak at around 70°C for the film cured at 25°C, at which semi-IPN structure should be formed. Tan δ peak at 70°C is considerably lower than the predicted Tg (120°C) from the Fox relationships. It should be also ascribed to lower conversion of BPE4, which reduced not only in mechanical properties but also in heat-resistance. A main tan δ peak and a shoulder peak appeared in the blends cured at temperature between 50°C and 100°C, at which the phase decomposition should proceed incompletely.

The phase structures of the blends with 50 wt% PSU content are given in Figure 8. Significant and distinct morphologies could not be obtained in the blends cured below 100°C in TEM images. The phase structure was vague in the blend cured at 120°C, at which the strength and modulus became the maximum. Domain structure appeared in the blends cured above 150°C and became gradually clear as the curing temperature increased. The clear phase structure with clear boundary should reduce the interfacial interaction between BPE4-rich and PSU-rich phases resulting in decrease in mechanical properties. In the blends cured above 120°C, two distinct Tgs were observed on tan δ curve. The T_gs in low temperature region were saturated at around 89°C, which corresponds to T_g of BPE4-rich phase. The saturated composition of BPE4-rich phase are found to (BPE4/PSU)=(98/2) calculated from the Fox relationship, where T_gs of cured BPE4 and PSU were 87°C and 198°C, respectively

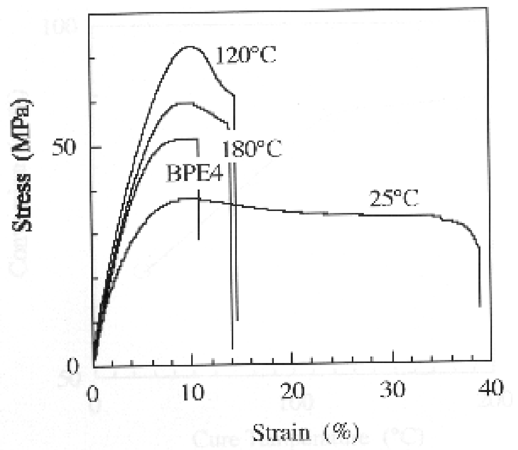


Figure 5- Stress-strain curve for cured neat BPE4 film and blend films of BPE4/PSU (5/5 w/w) cured at 25°C, 120°C, 180°C

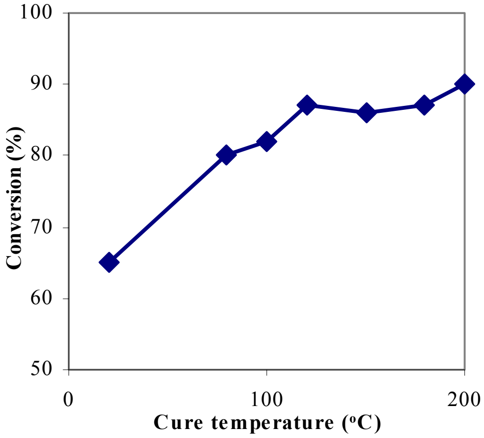


Figure 6 - Conversion of BPE4 in with 50 wt% PSU content as a function of cure temperature.

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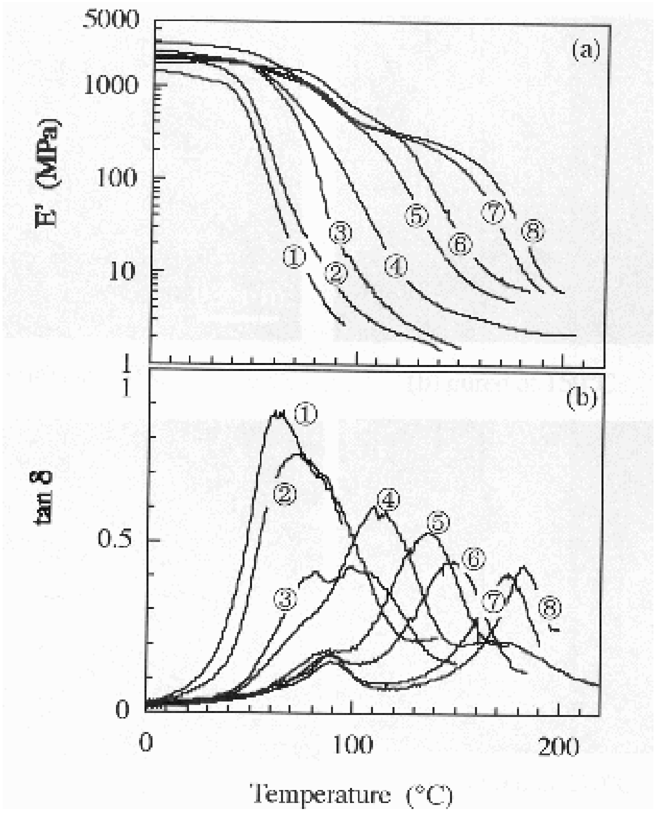


Figure 7- Temperature dependence of (a) storage modulus (E') and (b) tan δ for BPE4/PSU (5/5 w/w) cured at (1) 25°C, (2) 50°C, (3) 80°C, (4) 100°C, (5) 120°C, (6) 150°C, (7) 180°C and (8) 210°C; frequency = 1Hz

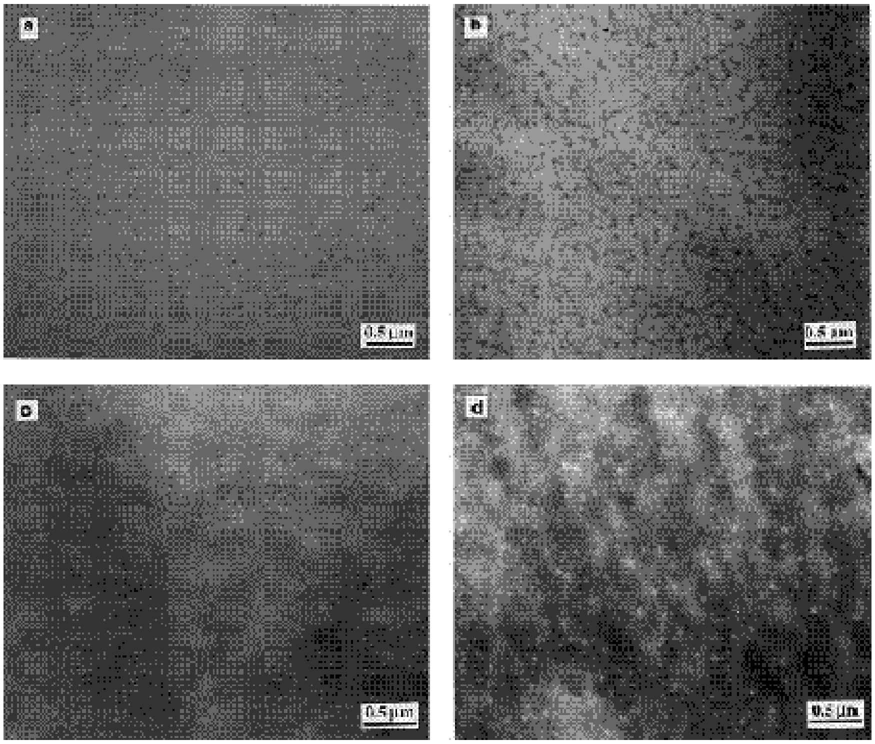


Figure 8- TEM micrographs for the blends of BPE4/PSU (5/5 w/w) cured at(a)120°C, (b)150°C, (c) 180°C, (d)210°C

Whereas the T_gs of PSU-rich phase in high temperature region increased with the curing temperature. The T_gs and calculated composition were given in Table 1. It was found that the phase decomposition proceeded as the curing temperature increased. Simultaneously, the mechanical properties gradually decreased with increasing in the curing temperature above 120°C.

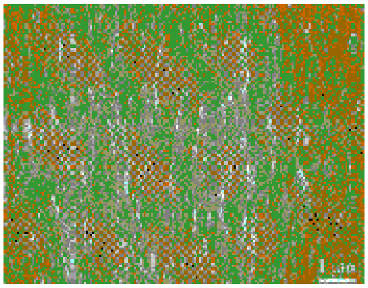
The fractural surfaces, after the tensile test, were observed by SEM and given in Figure 9. At curing temperature of 120°C, the domains of BPE4-rich were covered over PSU-rich phase with sufficient interfacial interaction as compared with the domains in the blend cured at 180°C. Strong interfacial interaction should provide the excellent strength and modulus in insufficiently phase separated blends with the vague structures.

3.3. Composition dependence in mechanical properties

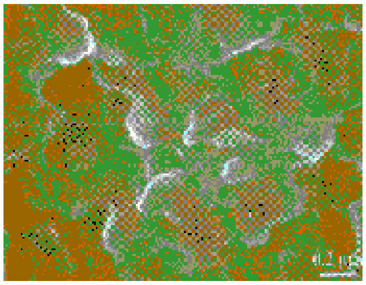
Figure 10 shows the composition dependence of the tensile strength and modulus for the blend films prepared by the photopolymerization at three different temperatures; (1) the optimal cure temperatures in which the maximum strength and modulus were given, (2) the temperatures below Tg of the homogeneous mixtures of BPE4-monomer and PSU, and (3) Tbi+30°C, at which the network-like bicontinuous structures became clear. The optimum cure conditions are given in Table 2. In the case of the blends cured at the optimal temperatures, the composition dependency in mechanical properties gave

Table 1
Tan δ peak temperatures (T_g), conversion of BPE4 and calculated compositions of BPE4-rich and PSU-rich phases for BPE4/PSU (5/5 w/w) cured at 25–210 °C (T_g of neat PSU is 198 °C)

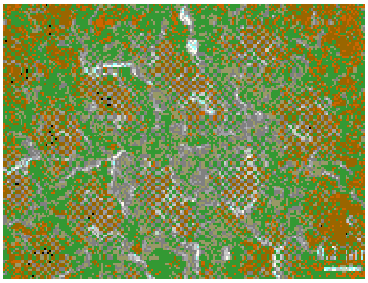
Curing temperature (°C)	T_g of cured BPE4 (°C)	Conversion (%)	T_g of BPE4/PSU (5/5 w/w)		Conversion (%)	Calculated compositions from the Fox relationship			
			BPE4-rich phase (°C)	PSU-rich phase (°C)		BPE4-rich phase		PSU-rich phase	
						BPE4 (%)	PSU (%)	BPE4 (%)	PSU (%)
25	62	85	61		65	–	–	–	–
50	67	88	71	85	70	96	4	83	17
80	80	92	81	99	78	97	3	80	20
100	82	93	84	109	82	98	2	71	29
120	86	94	86	136	85	98	2	52	48
150	86	94	89	148	87	97	3	38	62
180	86	95	89	174	88	97	3	16	84
210	87	95	89	182	89	98	2	11	89



(a) cured at 25°C

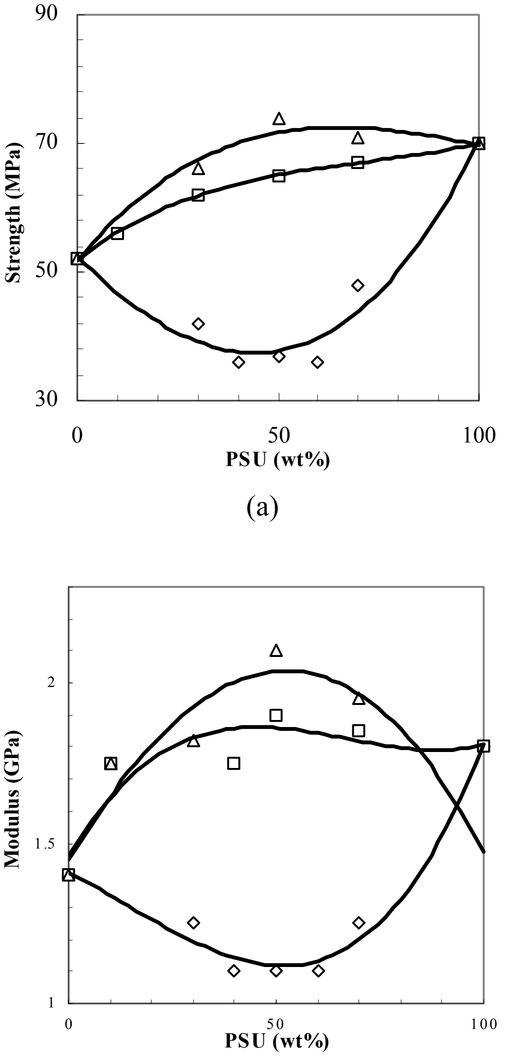


(b)cured at 120°C



(c) cured at 180°C

Figure 9- SEM micrographs of fractural surfaces after tensile test for BPE4/PSU (5/5 w/w)



(a)

(b)

Figure 10- (a)Tensile strength and (b) Young's modulus of BPE4/PSU blends as a function of composition, which is prepared at three different temperatures: (1)Δ the optimum cure temperatures (vague structures), (2)□ below T_gs of the homogenous mixtures of BPE4-monomer and PSU (semi-IPN structures) and (3)♦ the temperature +30°C at which network-like structure become clear.

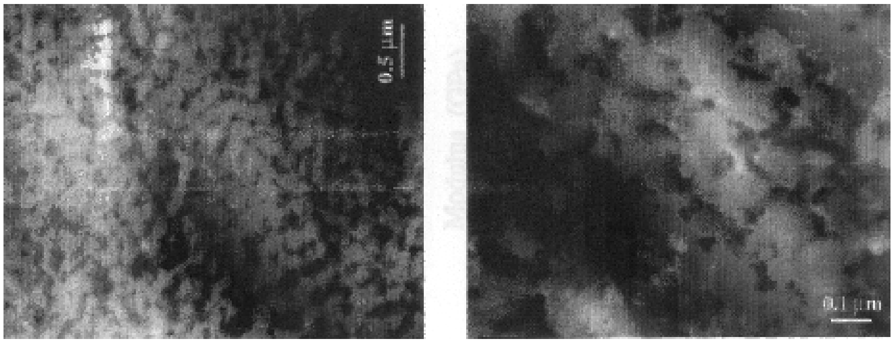
Table 2: The optimum cure temperature and mechanical properties for BPE4/PSU systems

PSU	Tg before irradiation	Optimal cure temperature	Cloud point	Light intensity	Conversion	Tensile properties		
						Tensile strength	Modulus	Elongation
Wt%	°C	°C	°C	mW cm^{2}	%	Mpa	Gpa	%
10	-25	80	80	10	93	57	1.76	10
30	7.5	100	100	10	90	66	1.85	10
50	42	120	130	10	88	73	2.10	15
70	89	150	180	10	55	69	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	72	77	2.05	11
Cured BPE4	62	-	-	-	-	52	1.40	10
Neat PSU	198	-	-	-	-	71	1.80	>100

convex curves with the maximum around 50-70 wt% PSU. It is notable that the maximum of the strength and modulus were slightly higher than those of the neat PSU, which is compounding as reinforced component. It is speculated that PSU might be oriented in the network-like structure, since the extension of PSU-rich phase has been observed to form into the network-like structures on the temporal change of the phase structure via viscoelastic phase separation mode.

Tensile strength of the blend with the clear network-like bicontinuous structure was coincided with the extrapolated line connected the properties of the cured neat BPE4 and the neat PSU, while the Young's modulus of which appeared above the extrapolated line. Interfacial interaction should be acting on the improvement in strength more efficiently as compared with that of modulus, due to large deformation. Whereas the mechanical properties of the blends with the semi-IPN structures decreased with PSU content, which were the minimum values around 30-50 wt% PSU. The minimum of strength and modulus were 20-30% lower than that of the cured neat BPE4 film.

The optimal cure temperatures were nearly boundary temperatures at which the phase structures appeared. At 10 wt% PSU, the optimal cure temperature was 80°C, which was 30°C high than T_{bi}. Since the conversion of BPE4 became low at T_{bi} (see Figure 6). TEM images of the blend with 30 wt% PSU contents are given in Figure 11. Phase boundary in the network-like structure cured at the optimal cure temperature was diffused. Whereas the network-like structure with clear and sharp phase boundary appeared in the blend cured at Tbi+30°C. It was found that the maximum improvement in mechanical property was brought in the vague network-like bicontinuous morphology with the diffused phase boundary.



(a) PSU= 10wt% cured at 80°C (b) PSU=30wt% cured at 100°C

Figure 11 - TEM images of BPE4/PSU: (a) at 10 wt% PSU, cured at 80°C and (b) at 30wt% PSU, cured at 100°C.

3.4. Characteristic length scale of bicontinuous structure

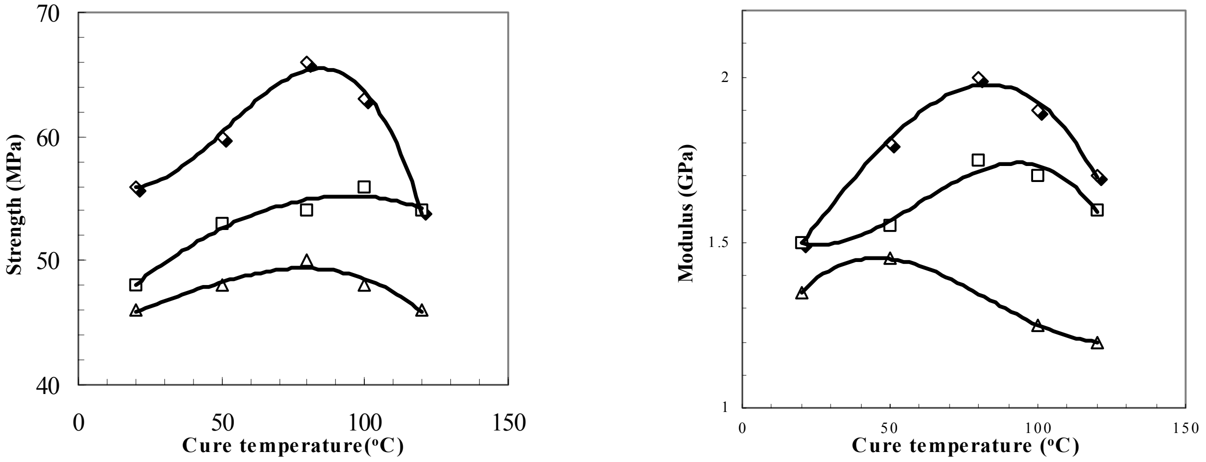
Characteristic length scale of the network-like structures becomes smaller as the irradiation intensity increases. Fig. 12 shows tensile strength and modulus of the blend with 10 wt% PSU content prepared by the photopolymerizations irradiated with three different light intensities. Both curves of strength and modulus became higher with light intensity (with decreasing of characteristic length). Each curve gave the maximum value by the curing at around 80°C temperature was diffused. Whereas the network-like structure with clear and sharp phase boundary appeared in the blend cured at T_{bi}+30°C. It was found that the maximum improvement in mechanical property was brought in the vague network-like bicontinuous morphology with the diffused phase boundary.

The conversions of BPE4 in the blends cured at 80°C are 88%, 93% and 93% as the light intensities increased of 1 mW cm^{-2}, 10 mW $cm^{-2}$and 75 mW cm^{-2}, respectively. Significant effect in mechanical properties should not be generally arisen from the difference of the conversion. The maximum strength and modulus cured at 75 mW cm^{-2} were 30% higher than those of the blend cured with a light intensity of 1 mW cm^{-2}.

Similar improvements in tensile strength and modulus were observed in the blends with 50 wt% and 70 wt% PSU contents with high irradiation intensity of 75 mW cm^{-2}. Figure 13 shows the mechanical properties of the blends photopolymerized with light intensities of 10 mW $cm^{-2}$and 75 mW cm^{-2}as a function of composition. The optimum photoirradiation conditions are also given in Table 2. The composition dependency in mechanical properties was improved higher as the irradiation intensity increased. It is note worthy that the tensile strength and modulus of neat BPE4 were remarkably improved 1.4-1.5 times higher by compounding with a small amount of PSU (10 wt%).

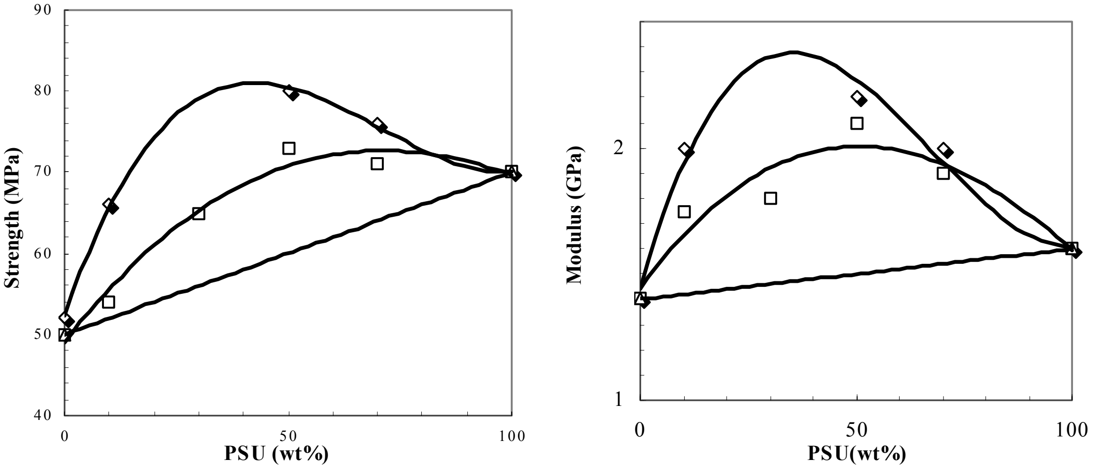
3.5. Effect of annealing of the blend with semi-IPN structure

In the blend films with the semi-IPN structure, no improvements in mechanical properties have been



(a) (b)

Figure 12- (a) Tensile strength and (b) tensile modulus of blend films at 10 wt% PSU content with network like phase structures prepared by photopolymerization with three different irradiation intensities of (□) 1mW cm^{-2}, (Δ) 10mW cm^{-2}, (◊) 75mW cm^{-2}. , as a function of cure temperature. The characteristic length scale of the network like structures were *ca.* 0.32µm, *ca.* 0.26µm, *ca.* 0.15µm by UV irradiation at 80°C with intensities of 1mW cm^{-2} , 10mW cm^{-2} , 75mW cm^{-2} respectively.



(a) (b)

Figure 13- (a) Tensile strength and (b) modulus for BPE4/PSU blend films cured at the optimal cure temperatures with inrradiation intensities of (□) 10mW cm$^{-2,}$, (◊) 75mW cm$^{-2.}$, as a function of PSU composition.

obtained except for the elongation at break due to low conversion of BPE4 in the blends. We try to improve in mechanical properties of blends having semi-IPN structures by means of increasing the conversion of BPE4 by annealing and post photocuring at high temperature region.

The homogeneous mixture of BPE4-monomer/PSU (5/5 w/w) was irradiated with UV light at an intensity of 10 mW cm-2 at 22°C under nitrogen atmosphere. A transparent cured blend film with the IPN-like structure was obtained. This transparent film was annealed in an oven at temperatures of 80-200°C for 1hr. Furthermore the annealed blend film was photoirradiated at 150°C with UV light at an intensity of 75 mW cm^{-2} under nitrogen atmosphere again.

Fig. 14 shows the effect of annealing temperature on tensile strength and modulus of resulting blend films. Tensile strength and modulus became the maximum annealed at around 150°C. The maximum strength was 1.7 times higher than that of the blend film with the semi-IPN-like structure, which was prepared by no-annealing and post photocuring at 25°C with light intensity of 75 mW cm^{-2}. This maximum of strength was almost the same as that of the blend prepared by the optimal cure temperature. The maximum modulus was ca.1.5 times higher than that of the blend with the semi-IPN structure. However this maximum modulus was ca.20% lower than that of the blend prepared at the optimal cure temperature. Conversions of BPE4 in the blends are also given in Table 3. The conversions became higher from 52% to above 90% by annealing above 120°C. The small improvements in strength and modulus obtained by annealing below 100°C should be attributed to the lower conversion of BPE4.

Morphologies of the blends annealed at 80°C, 150°C and 200°C are shown in Figure 15. Morphology was vague with diffused phase boundary by annealing at 80°C. However, in which case, the mechanical properties did not improve sufficiently due to the low conversion of BPE4 in spite of the good interfacial interaction. Bicontinuous morphology appeared in the blend annealed at 150°C, in which

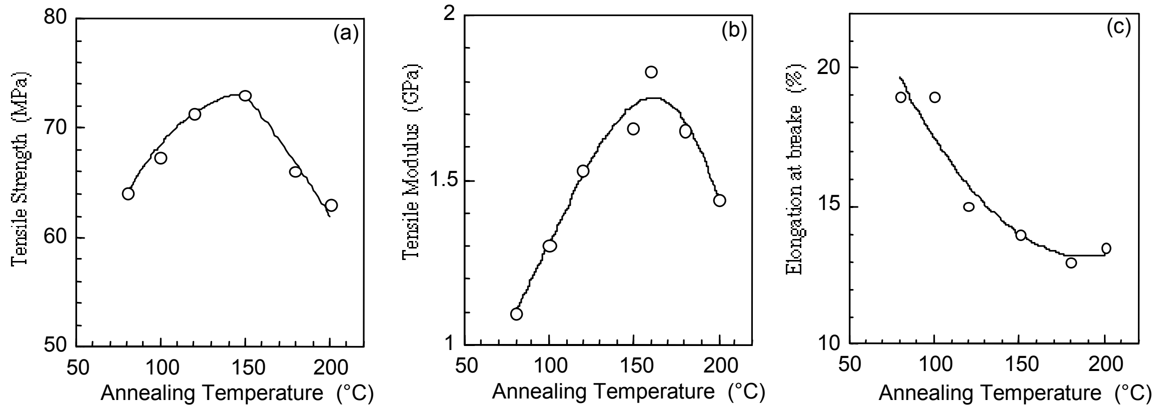
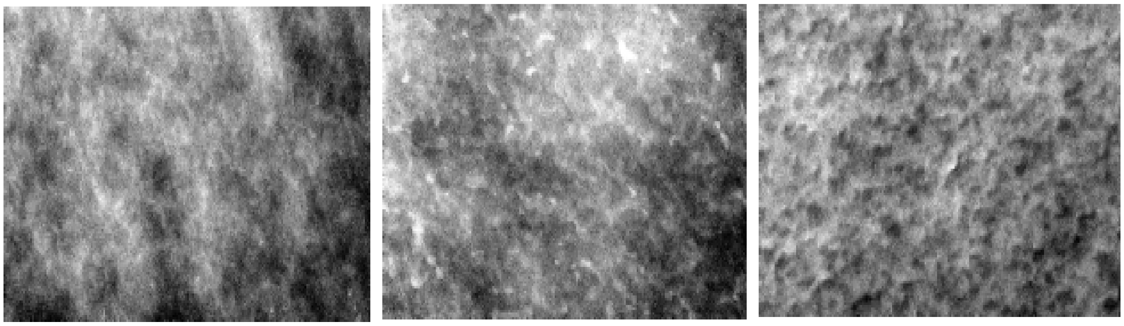


Figure 14- Effect of annealing temperature on: (a) tensile strength, (b) modulus and (c) conversion of BPE4 in the blends of BPE4/PSU (5/5 w/w). The blend film with semi-IPN structure was prepared by curing below T_g, and then annealed at the optimal annealing temperature for 1 hrs. The annealed films were additionally photocured at optimal temperature for 90 sec. with 75 mW cm^{-2} intensity.



(a) annealed at 80°C

(b) annealed at 150°C

(c) annealed at 200°C

Figure 15- TEM images for BPE4/PSU blends after annealing. The blend films with semi-IPN structure were prepared by curing below T_g, and then annealed at (a) 80°C, (b) 150°C and (c) 200°C for 1hrs. The annealed films were additionally photocured at optimal temperature for 90 sec. with 75 mW cm^{-2} intensity

maximum in properties of strength and modulus were observed. The characteristic length scale of the bicontinuous structure is ca.100 nm. Whereas droplet morphology was obtained in the blend annealed at 200°C, the PSU-rich phase became the island with a size of 100 nm dispersed in BPE4-rich matrix. The droplet structures in the blends annealed high temperature region should restrained the improvement in the mechanical properties.

Figure 16 shows the tensile strength and modulus of the blends at 30-70 wt% PSU with annealing as a function of composition. The semi-IPN films obtained by the curing below Tg were annealed at the optimal temperature for 1hr and then post photocured was done at the same temperature of annealing for

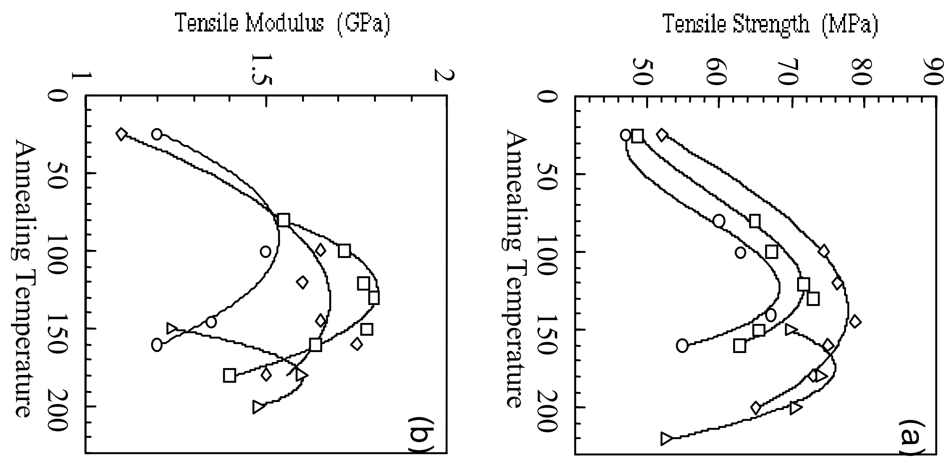


Figure 16 - Effect of annealing temperature on (a) tensile strength, (b) tensile modulus for BPE4/PSU: The first step cure temperature was –5°C for 30(o) and 40 (□) wt% PSU and 24°C for 60(◊) and 70 (Δ) wt% PSU. The post cure temperatures were130°C for 40 wt%, 160°C for 60 wt%, and 180°C for 70wt%

Table 2: The optimum annealing temperature and mechanical properties for BPE4/PSU systems

PSU	Tg of BPE4 monomer and PSU	First step cure temp	Optimum annealing temp	Post curing temp	No annealing and post cureing at RT					After annealing and post curing				
					Conversion	Tg	Strength	Modulus	Elongation	Conversion	Tg	Strength	Modulus	Elongation
Wt %	°C	°C	°C	°C	%	°C	MPa	GPa	%	%	°C	MPa	GPa	%
30	74	-5	130	120	55		42	1.25	14		84.5,152	67	1.60	9
40	22	-5	140	130	53	56	38	1.11	17		88.5,164	72	1.65	12
50	42	22	150	150	52	58	37	1.30	38	90	85.5,157	72	1.67	12
60	63.5	25	150	160	50	79	36	1.10	40			79	1.75	10
70	85	25	180	180	43		48	1.30	45			75	1.60	12

90 sec with 75 mW cm^{-2} intensity. The mechanical properties of un-annealed films, which were prepared by post photocuring of semi-IPN films at 25°C for 90 sec with 75 mW cm^{-2} intensity, are shown in Figure 10. The optimum annealing conditions are given in Table 3. The composition dependence of the mechanical properties gave convex curves with the maximum at around 60 wt% PSU. The curve of the strength was almost coincided with that of the blend prepared by the optimal cure temperature, while the curve of modulus was fairly lower than that of the blend obtained from the optimum curing.

The mechanical properties of the blends with semi-IPN structures can be improved by annealing and post photocuring at high temperature region. However semi-IPN morphologies were turned into the bicontinuous structures by the optimal annealing.

4. CONCLUSIONS

The maximum tensile strength and modulus were obsereved in the vague network-like bicontinuous phase structure with diffused phase boundary. The improvement in mechanical properties was brought by strong interfacial interaction. Most prominent feature of the present study is the maximum mechanical properties of the blend became higher than that of pure components. Reinforcing effect should due to the orientation of linear polymer components in the continuous network-like structure. These improvements will be further dominated by using mesogen polymers, which are easy to orientate.

Improvements in mechanical properties have been achieved in the blends compound with small amount of linear polymer. Tensile strength and modulus of the neat BPE4 film were improved 1.4-1.5 times higher in the blend with 10 wt% PSU content. Furthermore, it is found small characteristic length provide excellent improvement in mechanical properties, which also retains the transparency in the blend. We believe this investigation gives guidelines for developments of high performance polymeric materials.

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