Phase Separation of Poly(ether sulfone imide) Modified Epoxy Resin

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SYNOPSIS

Poly(ether sulfone imide)s (PEI) with molecular weight $M_n \sim 10^4$ were synthesized from 3,3',4,4'-benzophenone tetracarboxylic dianhydride and amine terminated poly(ether sulfone) having molecular weights ranging from $M_n \sim 400$ to $M_n \sim 4000$. Thus, the PEIs had the same molecular weight but various imide and ether sulfone contents. The PEIs were mixed with a stoichiometric mixture of diglycidyl ether bis-phenol-A (DGEBA)/diamino diphenyl sulfone (DDS). The effect of PEI on the curing reaction of DGEBA/DDS and the morphology of the polymer blend were studied by differential scanning calorimetry (DSC) and optical microscopy. In the DGEBA/DDS/PEI blend with a fixed PEI molecular weight and PEI concentration but with various imide content, the experimental data revealed the PEI with a higher content of ether sulfone had a lower T_g and a better compatibility with solvents and epoxy resins; the curing reaction rate of DGEBA/DDS/PEI was faster for PEI with a higher imide content; the DSC data of cured DGEBA/DDS/PEI showed two T_gs, indicating phase separation between PEI and cured epoxy resins; and the data of optical microscopy showed that the compatibility of PEI with epoxy resins increased with the content of ether sulfone in PEI. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Epoxy resin has been one of the most popular thermoset resins for several decades. Its good mechanical properties, excellent chemical resistance, high electrical resistance, and outstanding adhesion have allowed this class of materials to be used in a variety of composite materials. However, it also leads to low toughness and poor crack resistance of composite materials. Because of brittleness of epoxy matrix materials and reinforcements (glass and graphites), the damage tolerance to impact of epoxy based composites is poor. To enhance their fracture toughness, strengthened matrices, using elastomeric modifiers, have been explored during last two decades. The toughness can be increased by incorporating a second phase of dispersed rubbery particles into the crosslinked polymers.[1-6] The adhesion of rubbery materials to epoxy resins enabled the enhancement of their fracture toughness while lowering their glass transition temperatures (T_g) and improving thermal and oxidative stability. Recently, high-performance ductile thermoplastics have been used to tough epoxy resins.[6-11]

Several studies have been done on the overall compatibility and phase behavior in blends of thermoset resins with elastomers or thermoplastics.[7,10-17] Bucknall and Partridge[7] used polyethersulfone (PES) in epoxy resin to generate a high temperature thermoplastics-modified thermoset. Subsequently, different thermoplastics have been studied in epoxy resins by Bucknall,[15,16] McGrath and co-workers,[10,11] and Sefton and co-workers.[18] In these studies, the thermoplastics and thermoset resins were chosen to be thermodynamically compatible before curing; however, during the curing process, the increasing molecular weight of the thermoset component initiated phase separation to generate a heterogeneous cured material.

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Table I Molecular Weight, T_g, and Monomer Feed Mole Ratio of APES

Sample	M_n[a]	T_g (°C)	BPA	DCDPS	p-Aminophenol
APES-0430	432	193.1 (T_m)[b]		1.00	2.0
APES-0750	750	81.9	0.72	1.72	2.0
APES-1000	999	81.2	1.29	2.29	2.0
APES-2000	1973	96.1	3.55	4.55	2.0
APES-3000	2963	104.1	5.81	6.81	2.0

[a] M_n was determined by total amine values method (ASTM D-207).
[b] No T_g was observed for APES-043; 193.1°C is the melting point.

Phase separation between epoxy resins and dissolved rubbers has been extensively studied, especially in systems of diglycidyl ether of bis-phenol A (DGEBA) resins containing carboxyl-terminated butadiene acrylonitrile (CTBN)[13] and amine terminated butadiene-acrylonitrile (ATBN)[3] liquid rubbers. Rubber particles precipitated during curing increase the fracture toughness of the epoxy resin.[2,3,13,19–22] Using light-scattering technique, structural developments during curing in ternary mixtures of DGEBA/PES/diamino diphenyl methane (DDM)[23] and tetra functional epoxy resin/poly(ether sulfone)/dicyandiamide,[24] and a mixture of epoxy resin with liquid rubber (CTBN and ATBN)[25] were investigated by Inoue and coworkers.

The curing reaction rate is directly related to the probability of mutual diffusion of the reacting molecules. This probability generally decreases as the viscosity of the reacting mixture increases. Intuitively, one anticipates that this probability would also decrease when foreign, relatively inactive, substances are present in the reacting mixture. Therefore, the curing behaviors of a thermoset mixture are expected to depend on the type and amount of inert additives. As the chain length of the polymer in a thermoset increases on curing, the phase of thermoplastics component tends to separate. Thus, the reacting mixture forms a network structure, henceforth lowering the solubility of the thermoplastics, and a new morphology of the thermoplastics dispersed in the network structure develops. This morphology of the dispersed phase may be either as discrete particles or continuous structure depending on the amount and chemical structure of elastomer (or thermoplastics), the curing temperature, and the rate of chemical reactions. In either case, when phase separation has occurred, the probability of chemical reactions (as a result of molecular diffusion) between the resins and the curing agent is expected to decrease, because the intervening regions of the thermoplastics phase prevent diffusion by occupying randomly distributed macroscopic sites in the incompletely formed polymer network. This leads therefore to form a polymer matrix with lower crosslink density.

In the present work, poly(ether sulfone imide)s (PEI) with molecular weight M_n around $\sim 10^4$ were synthesized from 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) with amine terminated poly(ether sulfone)s (APES) with various molecular weights ranging from M_n = 400 to M_n = 4000. These PEIs were then blended with the stoichiometric mixture of DGEBA/diamino diphenylsulfone (DDS). The effect of imide content in PEI on the curing reaction of DGEBA with DDS and on the morphology during the curing reaction of DGEBA with DDS in the presence of PEI were observed by differential scanning calorimetry (DSC) and optical microscopy.

EXPERIMENTAL

Materials

Synthesis of APES

Samples of APES with molecular weights (M_n) of 430, 750, 1000, 1970, and 2960 were prepared. These APESs were synthesized by the reaction of bisphenol-A (BPA) with 4,4′-dichloro diphenylsulfone (DCDPS) and p-aminophenol in N-methyl-2-pyrrolidone (NMP) using K_2CO_3 as the base. Detailed procedure of the synthetic routes have been developed by Hedrick and coworkers and are given elsewhere.[26,27] Table I shows the feed mole ratios of monomers, the number average molecular weight, and the glass transition temperatures of these APES. Figure 1 shows the IR spectra of these APES. The absorption band at 3300–3600 cm^{-1} indicates the presence of amine group from lower molecular weight APES.

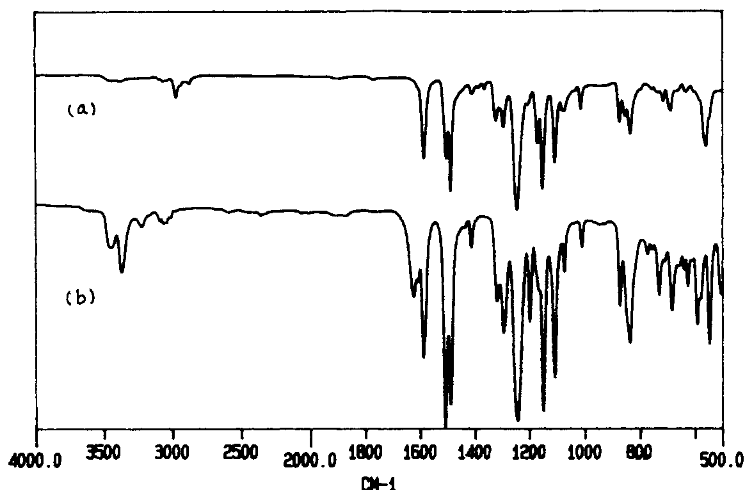

Figure 1 IR spectra of APES. (a) APES-3000; (b) APES-0430.

Synthesis of PEI

These APES listed in Table I were reacted with BTDA in *m*-cresol for the synthesis of PEI. Detailed procedures of the synthetic routes were developed by Lee[28] and D'Alelio[29] separately and reported elsewhere. Table II summarizes the feed ratios of reactants, the M_n, and T_g of these PEIs. The IR spectra of these PEIs are shown in Figure 2.

Epoxy Resin

The DGEBA, Epon 828, was purchased from Shell Chemical Co. Its $M_n = 380$, $T_g = 14°C$, and functionality = 2.[30] The DDS used as curing agent was purchased from Aldrich Chemical Co. and used without further purification.

IR Spectroscopy

Perkin-Elmer Fourier transform IR 1725X was used for the IR spectroscopy study of APES and PEI samples, which were synthesized in the present work.

Table II Molecular Weight, T_g, and Raw Material Feed Mole Ratio of PEI

Sample	M_n[a]	T_g	BTDA	APES
PEI-0430	—[b]	278.5	1.0	2.0
PEI-0750	12,250	219.7	1.719	2.0
PEI-1000	12,120	200.1	2.285	2.0
PEI-2000	11.867	182.8	4.548	2.0
PEI-3000	14,662	172.8	6.810	2.0

[a] M_n was determined by total amine values method (ASTM D-207).
[b] PEI-043 was not dissolved in a solvent; its molecular weight could not be determined.

DSC Measurements

DSC measurements were conducted in a Du Pont model 910 DSC. Indium was used for calibration. Hermetic cells were used for samples preparation. In all cases, a sample of approximately 10 mg was used.

T_g Measurements

T_g *of APES and PEI.* The T_g of APES and PEI were obtained from the nonisothermal scan of DSC with a heating rate of 10°C/min in nitrogen atmosphere. The T_g of APES and PEI are listed in Tables I and II, respectively.

T_g *of Cured DGEBA/DDS/PEI Blend.* Stoichiometric mixtures of DGEBA with DDS were mixed with 20 wt % of various PEI synthesized in our laboratory. The weight ratio of DGEBA/DDS/PEI was 60.3/19.7/20.0. The mixtures of DDS/PEI mixture were mixed with small amounts of water and were ground into fine powder. After complete mixing, the samples were then vacuum dried at 60°C overnight to remove water. The fine powder of DDS/PEI then mixed with DGEBA by stirring gently for 1 h at room temperature. Two samples of each DGEBA/DDS/PEI blend cured under different conditions were prepared for T_g measurement. One sample was cured at 150°C/3 h and the other sample was cured at 150°C/3 h and then postcured at 220°C/2 h. The T_g of the cured sample was obtained from the nonisothermal scan of DSC with a heating rate of 10°C/min in nitrogen atmosphere.

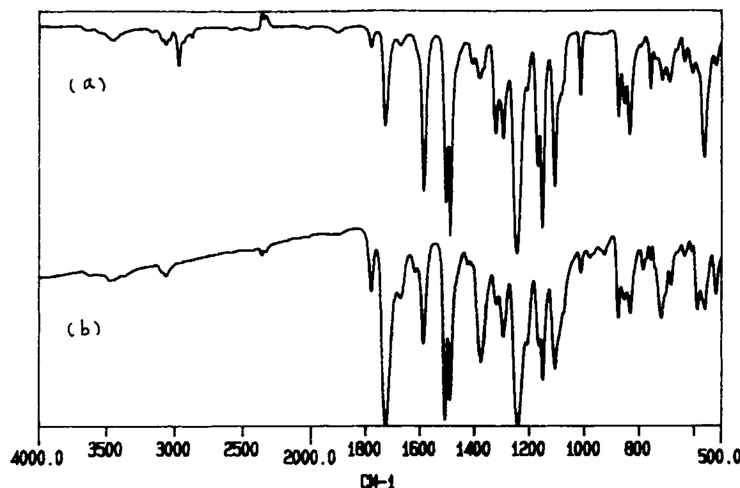

Figure 2 IR spectra of PEIs. (a) PEI-3000; (b) PEI-0430.

Isothermal Curing Measurements

For the study of curing reaction, the stoichiometric mixture of DGEBA/DDS was blended with 20 wt % of PEI. The procedure of sample preparation for curing measurement was the same as that described previously for T_g measurement except that these samples were freshly prepared and not cured before DSC isothermal scan. In the use of DSC for studying the curing kinetics of thermosetting resins,[31] one assumes that the amount of heat generated due to the curing reaction is directly proportional to the degree of curing α (or the extent of reaction) of the sample at that reaction time and then one relates the rate of curing $d\alpha/dt$ to the rate of heat generated dQ/dt by

$$\frac{d\alpha}{dt} = \frac{1}{Q_{\text{tot}}} \frac{dQ}{dt} \tag{1}$$

$$\alpha = \frac{1}{Q_{\text{tot}}} \int_0^t \left[\frac{dQ}{dt}\right]_T dt \tag{2}$$

In eqs. (1) and (2), the total heat of the curing reaction Q_{tot} is given by

$$Q_{\text{tot}} = Q_{\text{iso}} + Q_r \tag{3}$$

where Q_{iso} is the heat released during the isothermal DSC runs at 150°C for 3 h and Q_r the residual heat that is released when sample is heated to 350°C at a heating rate of 10°C/min after the completion of 3 h of isothermal curing at 150°C. After completion of the above curing process, the sample was then cooled to 150°C and then reran isothermally for 3 h on the cured sample to obtain the baseline.

Optical Microscopy

Nikon microphot-FXA with a Mettler FP82 heating stage was used to study the variation of the morphology of DGEBA/DDS/PEI blend during curing at 150°C. The blend of DGEBA/DDS/PEI was prepared by the same procedure as that described above for T_g measurements. The freshly prepared sample was degassed under vacuum for 10 min and then placed on a glass slide with a cover of another glass slide. Both slides were then clamped together. Two pieces of 0.01-mm-thick steel spacers were placed between top and bottom glass slides to control the sample thickness. This assembly was then transferred to a heating stage. The sample was subsequently cured at 150°C under nitrogen atmosphere. The morphologies of the blend at curing times of 0, 1, 2, 5, 10, 20, 40, 60, 120, and 180 min were observed by optical microscopy.

RESULTS AND DISCUSSION

Solubilities of PEI With Solvents

The solubilities of PEIs with various solvents were tested by dissolving 1 g of PEI in 2 mL of solvent. The results are shown in Table III. Because all polyimides had similar molecular weight, the variation among these PEIs was due to the contents of imide group and ethersulfone. From Tables II and III, we know that PEI-3000 had the highest ethersulfone content (lowest imide content) and best solubility with most of solvents. However, the solubility of PEI with solvents decreased with the imide content. This behavior was consistent with the T_g data of PEI (Ta-

Table III Solubility of PEI with Solvents

Solvent	PEI-043	PEI-075	PEI-1000	PEI-2000	PEI-3000
m-Cresol	+	+	+	+	+
NMP	−	+	+	+	+
DMSO	−	+	+	+	+
DMF	×	×	+	+	+
THF	×	×	×	+	+
Dichloromethane	×	×	−	+	+
MEK	×	×	×	−	−
Acetone	×	×	×	−	−
Diethyl ether	×	×	×	×	×

+, soluble; −, slightly soluble; ×, nonsoluble.
DMSO, dimethyl sulfoxide; DMF, N,N-dimethylformamide; THF, tetrahydrofuran; MEK, methyl ethyl ketone.

ble II). The T_g of PEI increases with imide content. From Tables II and III, it is obvious that increasing the content of ethersulfone resulted in an increase in the flexibility of PEI and an increase in solubilities of PEI with solvents and also a decrease in T_g of PEI.

T_g of Cured DGEBA/DDS/PEI Blends

Two samples of each DGEBA/DDS/PEI blend were prepared. One sample was cured at 150°C/3 h and the other sample at 150°C/3 h and then postcured at 220°C/2 h. Figure 3 is the plots of nonisothermal DSC scan with a heating rate of 10°C/min for DGEBA/DDS/PEI-1000 blend. Similar observations were also obtained for DGEBA/DDS/PEI-0430, DGEBA/DDS/PEI-0750, DGEBA/DDS/PEI-2000, and DGEBA/DDS/PEI-3000 blends. Table IV summarized the T_gs of these blends cured under two different conditions. Two T_gs were obtained for each measurements. The T_{g1} at lower scanning temperature corresponds to the T_g of cured epoxy resin, whereas the glass transition at higher scanning temperature (T_{g2}) corresponds to the T_g of PEI. These results indicated that phase separation occurred between PEI and cured epoxy resin. Comparing the samples that had been postcured at 220°C/2 h with those without being postcured, we found that both T_{g1} and T_{g2}, respectively, for epoxy resin and PEI were lower for samples without being postcured. The behavior of higher T_g for the postcured samples was due to the higher conversion of epoxy resin. From Table IV, we noticed that both T_{g1} and T_{g2} increased with PEI imide content for DGEBA/DDS/PEI blends. The increase of T_{g2} with increasing PEI imide content is due to the enhancement of rigidity in the presence of imide functional

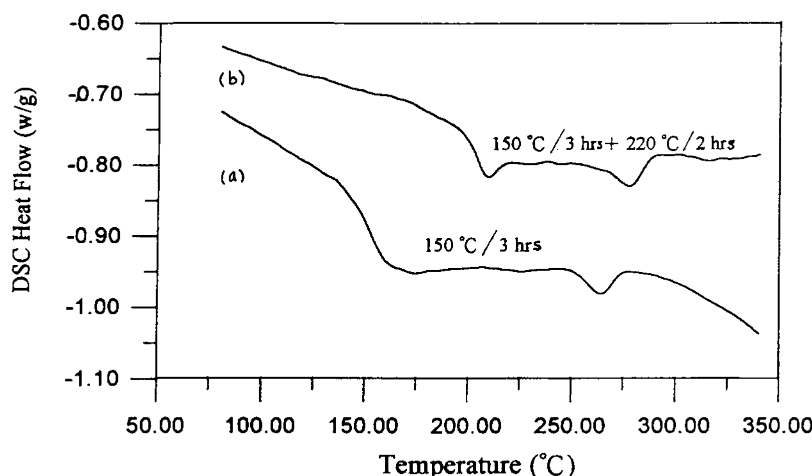

Figure 3 Nonisothermal DSC scan (10°C/min) of cured DGEBA/DDS/PEI-1000 blend. (a) Sample cured at 150°C/3 h; (b) sample cured at 150°C/3 h + 220°C/2 h.

Table IV T_g of Cured DGEBA/DDS/PEI Blends

Sample	Cured at 150°C/3 h		Cured at 150°C/3 h + 220°C/2 h	
	T_{g1} (°C)	T_{g2} (°C)	T_{g1} (°C)	T_{g2} (°C)
DGEBA/DDS	155		208	
DGEBA/DDS/PEI-0430	137	262	210	281
DGEBA/DDS/PEI-0750	160	282	204	296
DGEBA/DDS/PEI-1000	153	259	204	272
DGEBA/DDS/PEI-2000	144	219	198	260
DGEBA/DDS/PEI-3000	142	200	194	259

group. The increase of T_{g1} with imide content of DGEBA/DDS/PEI blend could be due to the higher conversion of DGEBA with DDS caused by the catalytic effect of tertiary amine of imide functional group (see the discussion in the next section). The anomalous behavior of lower T_{g1} and T_{g2} for DGEBA/DDS/PEI-043 blend than that of DGEBA/DDS/PEI-075 blend could be due to the lower conversion of DGEBA/DDS caused by the worse compatibility of PEI-043 with epoxy resin (see also the discussion in the next section). The behavior of higher T_{g2} of PEI (Table IV) in epoxy matrix than that of pure PEI (Table II) could be due to the lower mobility of PEI in the epoxy network matrix.

DSC Isothermal Curing Study

Stoichiometric samples for DGEBA/DDS system mixed with 20 wt % of PEI were cured in the isothermal mode of DSC measurements. Figure 4 is the DSC isothermal runs at 150°C (α versus curing time) of the stoichiometric mixture of DGEBA/DDS blended with 20 wt % of various PEIs in N_2 atmosphere. Table V shows the residue heat (Q_r), total heat (Q_{tot}), and final conversion (α_f) for DGEBA/DDS/PEI blends cured at 150°C/3 h. From these results, it is obvious that the curing reaction rate and the final conversion of DGEBA with DDS were lowered for DGEBA/DDS modified with PEI. The

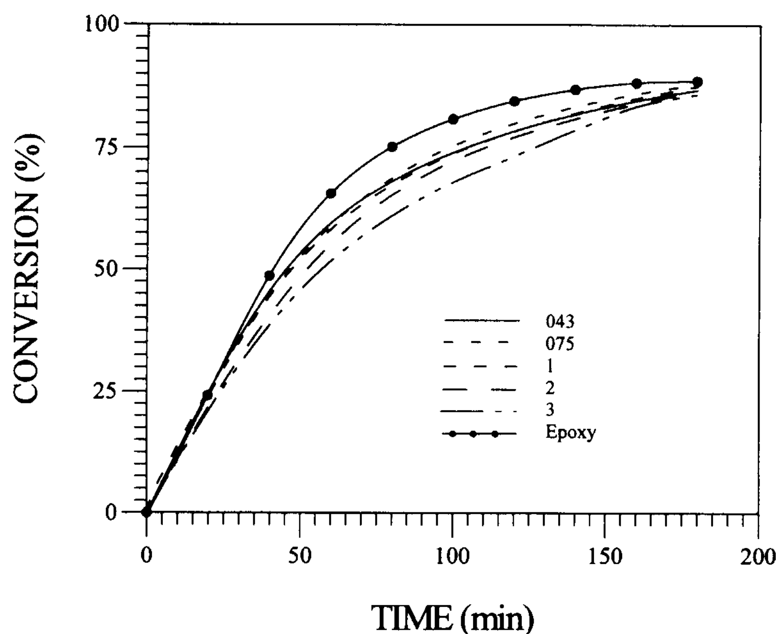

Figure 4 DSC isothermal curing of DGEBA/DDS/PEI blends at 150°C. (—— 043) DGEBA/DDS/PEI-0430; (- - - 075) DGEBA/DDS/PEI-0750; (– – – 1) DGEBA/DDS/PEI-1000; (— — 2) DGEBA/DDS/PEI-2000; (— - - 3) DGEBA/DDS/PEI-3000; (-•-•-•-•-) DGEBA/DDS.

Table V DSC Isothermal Curing Reaction Heat of DGEBA/DDS/PEI at 150°C/3 h

Sample	Q_{tot} (J/g)	Q_r (J/g)	α_f (%)
DGEBA/DDS	369.0	42.5	88.5
DGEBA/DDS/PEI-0430	331.6	43.7	86.8
DGEBA/DDS/PEI-0750	332.8	40.2	87.9
DGEBA/DDS/PEI-1000	332.4	41.2	87.6
DGEBA/DDS/PEI-2000	329.0	43.5	86.6
DGEBA/DDS/PEI-3000	328.0	46.2	86.5

presence of PEI caused phase separation between epoxy resin and PEI as curing reaction proceeded and resulted in a retardation of the curing reaction. However, for samples with a fixed PEI concentration, the curing reaction rate ($d\alpha/dt$) and final conversion (α_f) increased as the PEI imide content increased (or the ethersulfone content in PEI molecular chains decreased). The increase in the curing reaction rate and final conversion could be due to the catalytic effect of tertiary nitrogen from the imide group on the reaction between DGEBA and DDS.[32] The anomalous curing behavior of DGEBA/DDS/PEI-0430 blend could be due to the high incompatibility of PEI with epoxy resin oligomers retarding the curing reaction. The high incompatibility of DGEBA/DDS with PEI-0430 was shown by optical microscopic studies. Comparing the final conversion α_f data (Table V) and T_g data (Table IV) for DGEBA/DDS/PEI blends, we found good consistency in these two results, (i.e., higher final conversion with a higher T_g of the blend).

Morphology of DGEBA/DDS/PEI Blend Via Optical Microscopy

The morphology of the mixture of DGEBA/DDS oligomer with various PEI was observed at 150°C during curing by optical microscopy. Figure 5 shows the microscopies at various curing times for DGEBA/DDS/PEI-0430 blend at 150°C. The dark region is ascribed to the PEI-rich phase, whereas the bright region corresponds to the epoxy-rich phase. Initially, the PEI rich-phase domain and the epoxy-rich phase domain were distinctly separated. After 1 min of curing, a small amount of PEI-phase was melted and dispersed into epoxy-rich phase. As shown in Figure 5(a), the little dark spots were dispersed between the big dark spots and bright region. The number of little dark spots increased until 2 min of curing. The microscopies indicated that after 2 min of curing, both the PEI-rich phase and epoxy-rich phase were fixed and PEI-0430 was almost not compatible with the mixture of DGEBA/DDS during the whole period of curing. Figure 6 shows the microscopies at various curing times for DGEBA/DDS/PEI-0750 blend at 150°C. It is obvious that the mixture of DGEBA/DDS/PEI-075 blend was more homogeneous than that of DGEBA/DDS/PEI-043 blend. At the start of curing, little dark spots of PEI-rich region appeared in the microscopy. Around the PEI-rich region, there was the epoxy resin-rich phase and epoxy-rich and PEI-rich interdisperse region [Fig. 6(a)]. At the curing time of 1 min [Fig. 6(b)], the size of PEI-rich region decreased and a small amount of PEI was dispersed into the epoxy resin-rich region due to the melting of the mixture as the sample was transferred from room temperature to a heating stage at a temperature of 150°C. At curing time of 2 min, phase separation between PEI-rich and the partially cured epoxy resin phase became more distinct [Fig. 6(c)]. After 2 min of curing, the microscopy revealed that the structure of morphology was fixed and not varied with curing time [Fig. 6(c)–(j)]. Comparing Figures 5 and 6, we found that both the sizes of PEI-rich region and epoxy-rich region were smaller and the epoxy and PEI interdisperse region was larger for DGEBA/DDS/PEI-0750 blend than that of DGEBA/DDS/PEI-0430 blend.

Figure 7 shows the microscopies at various curing times for DGEBA/DDS/PEI-1000 blend at 150°C. Similar to the morphology of DGEBA/DDS/PEI-0750 blend in the early stage of curing reaction, the dark spots of PEI-rich phase of DGEBA/DDS/PEI-1000 blend melted and dispersed into the epoxy-rich phase as the sample was transferred from room temperature to a heating stage with a temperature of 150°C [Fig. 7(a)–(c)]. After 5 min of curing, the structure of morphology was fixed [Fig. 7(d)–(j)]. Comparing Figures 6 and 7, it is obvious that the epoxy phase and PEI phase interdisperse region of DGEBA/DDS/PEI-1000 blend

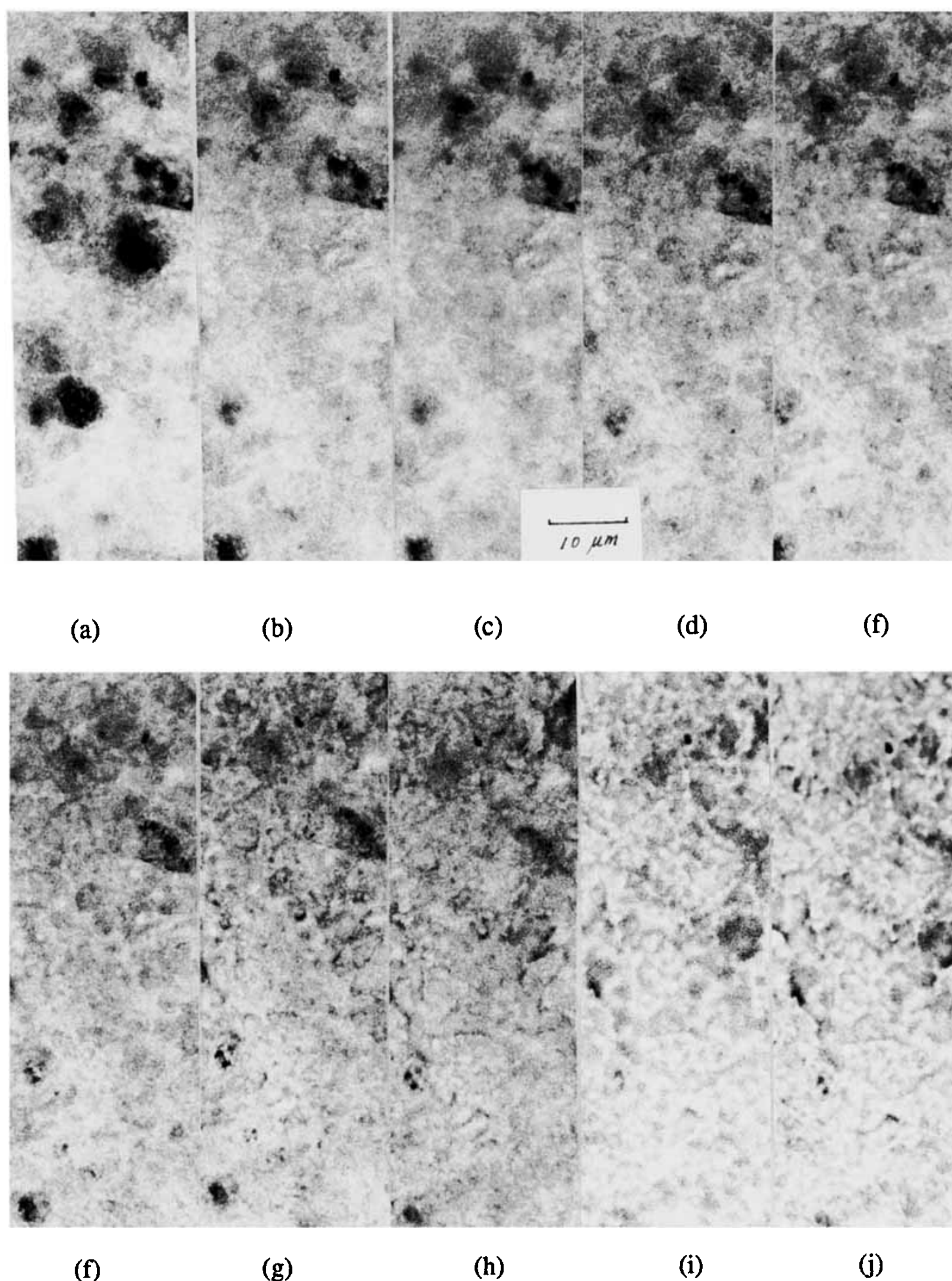

Figure 5 Optical microscopies (250×) of DGEBA/DDS/PEI-0430 cured at 150°C with various curing times: (a) 0.0 min; (b) 1 min; (c) 2 min; (d) 5 min; (e) 10 min; (f) 20 min; (g) 40 min; (h) 60 min; (i) 120 min; (j) 180 min.

was larger than those of previous two blends. Figure 8 presents the microscopies of DGEBA/DDS/PEI-2000 blend. Comparing with the optical microscopies of DGEBA/DDS/PEI-043, DGEBA/DDS/PEI-075, and DGEBA/DDS/PEI-1000 blends, the microscopies of DGEBA/DDS/PEI-2000 blend demonstrated that the mixture was more homogeneous than the previous mixtures. The epoxy resin-rich and PEI-rich phases were melted and interdispersed at the beginning of curing [Figs. 8(a)

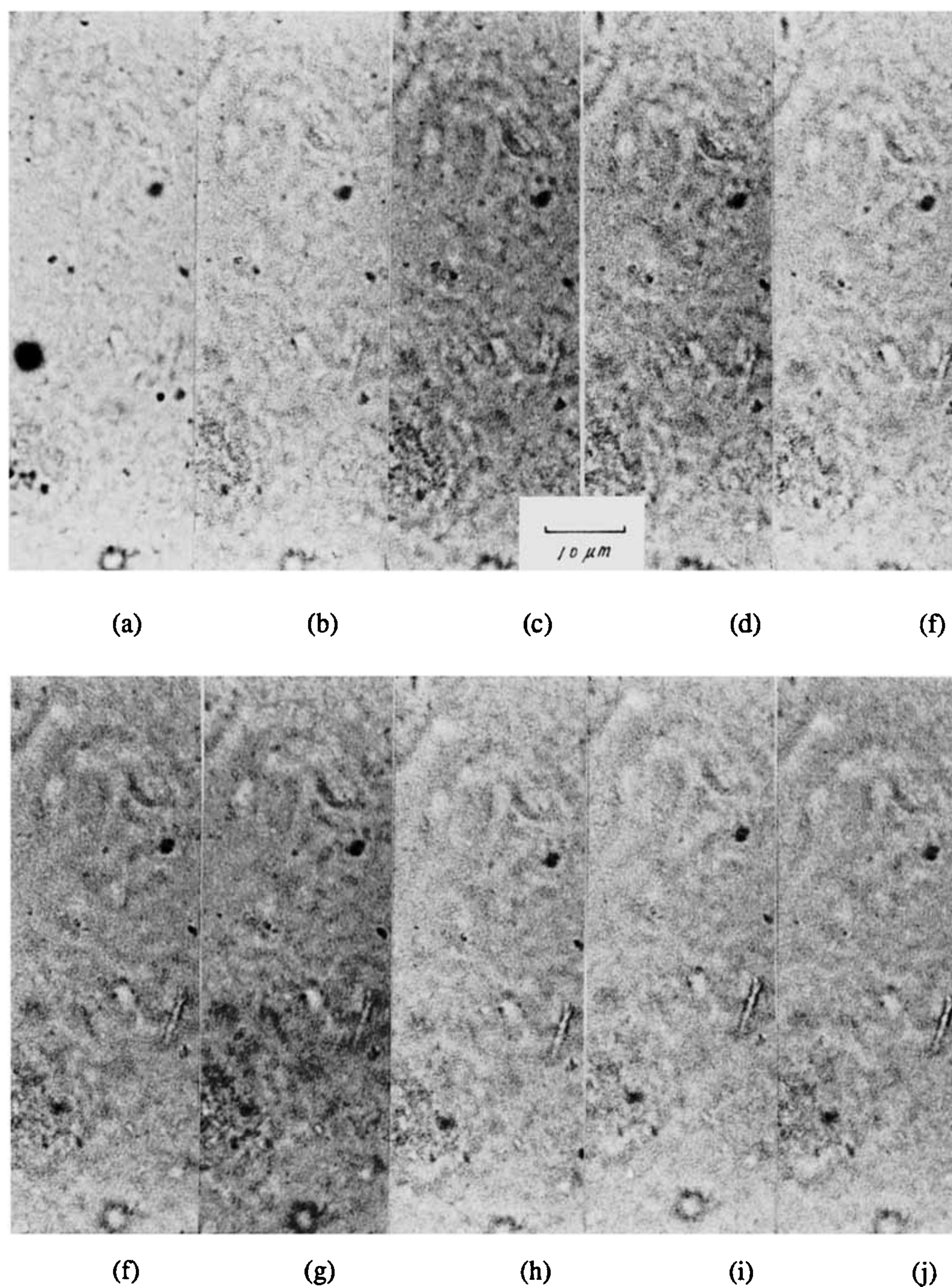

Figure 6 Optical microscopies (250×) of DGEBA/DDS/PEI-0750 cured at 150°C with various curing times: (a) 0.0 min; (b) 1 min; (c) 2 min; (d) 5 min; (e) 10 min; (f) 20 min; (g) 40 min; (h) 60 min; (i) 120 min; (j) 180 min.

and (b)]. However, little dark spots (PEI-rich phase) were still found in Figure 8(b). As the curing proceeded, the PEI-rich phase dark spots were moving [Fig. 8(b)–(f)]. After 20 min of curing, the size of PEI-rich phase was fixed and no more flow of the PEI-rich phase was found [Fig. 8(g)–(j)].

Figure 9 shows the microscopies at various curing time for the blend of DGEBA/DDS/PEI-3000 at 150°C. The curing morphology of the blend of DGEBA/DDS/PEI-3000 was similar to that of DGEBA/DDS/PEI-2000 blend. Both PEI-rich and epoxy-rich phases were melted and interdispersed

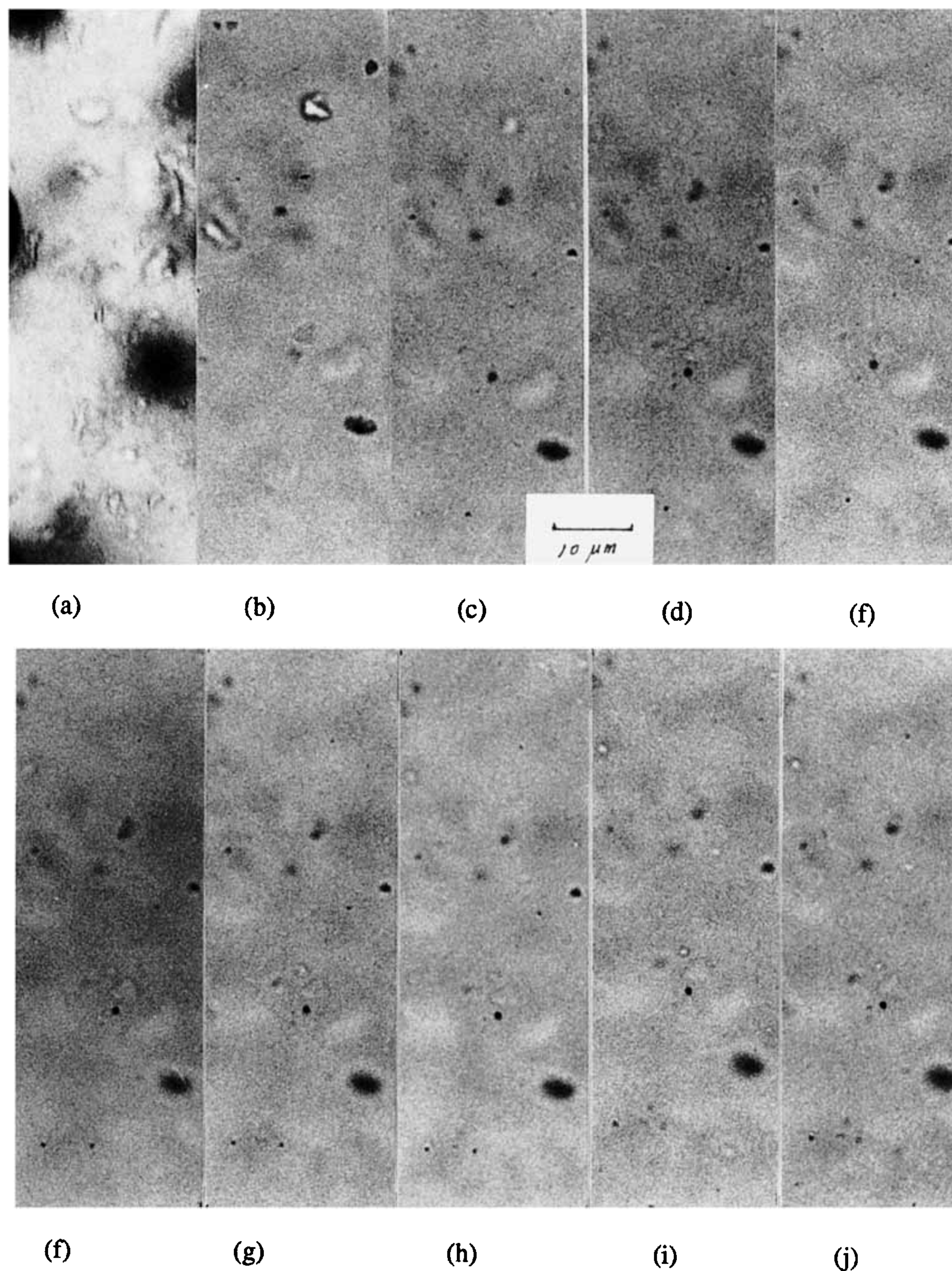

Figure 7 Optical microscopies (250×) of DGEBA/DDS/PEI-1000 cured at 150°C with various curing times: (a) 0.0 min; (b) 1 min; (c) 2 min; (d) 5 min; (e) 10 min; (f) 20 min; (g) 40 min; (h) 60 min; (i) 120 min; (j) 180 min.

at the early stage of curing as the mixture sample was transferred from room temperature to a heating stage at a temperature of 150°C [Fig. 9(a) and (b)]. The PEI-rich phase (dark spots) and epoxy rich phase (bright spots) were moving as the curing reaction proceeded till a curing time of 60 min [Fig. 9(b)–(h)]. After a curing time of 60 min, no more flow of PEI-rich phase was observed and the size of PEI-rich phase was fixed. Comparing Figures 8 and 9, we found that the size of PEI-rich phase was

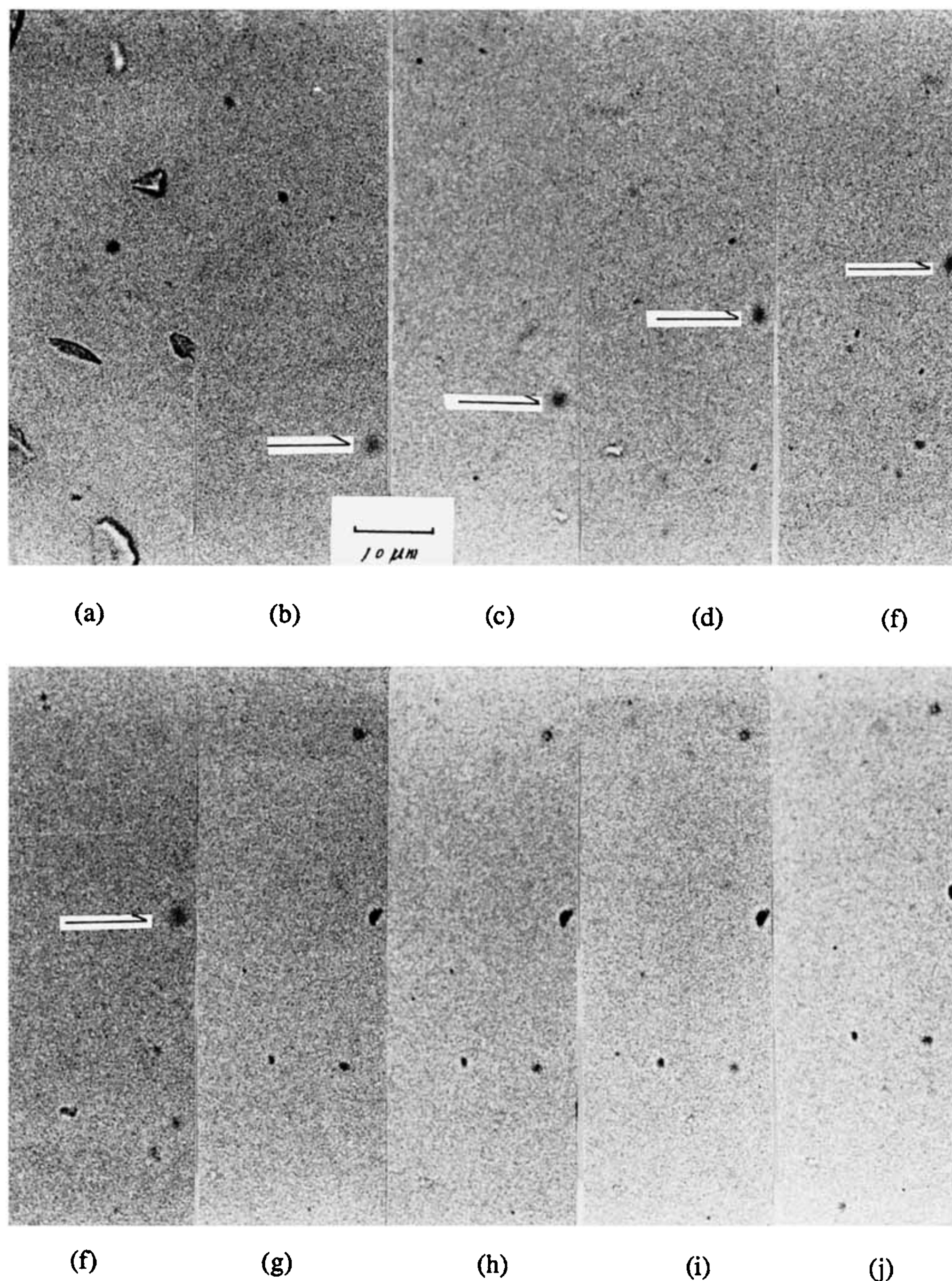

Figure 8 Optical microscopies (250×) of DGEBA/DDS/PEI-2000 cured at 150°C with various curing times: (a) 0.0 min; (b) 1 min; (c) 2 min; (d) 5 min; (e) 10 min; (f) 20 min; (g) 40 min; (h) 60 min; (i) 120 min; (j) 180 min.

smaller in DGEBA/DDS/PEI-2000 blend than that in DGEBA/DDS/PEI-3000 blend. The morphology of DGEBA/DDS/PEI-2000 blend was more homogeneous than that of DGEBA/DDS/PEI-3000 blend. The reason for these phenomena could be attributed to the lower molecular weight of PEI-2000 than that of PEI-3000.

From above observations, we may conclude that the compatibility of PEI with epoxy resins increased with the ethersulfone content in PEI. The domains

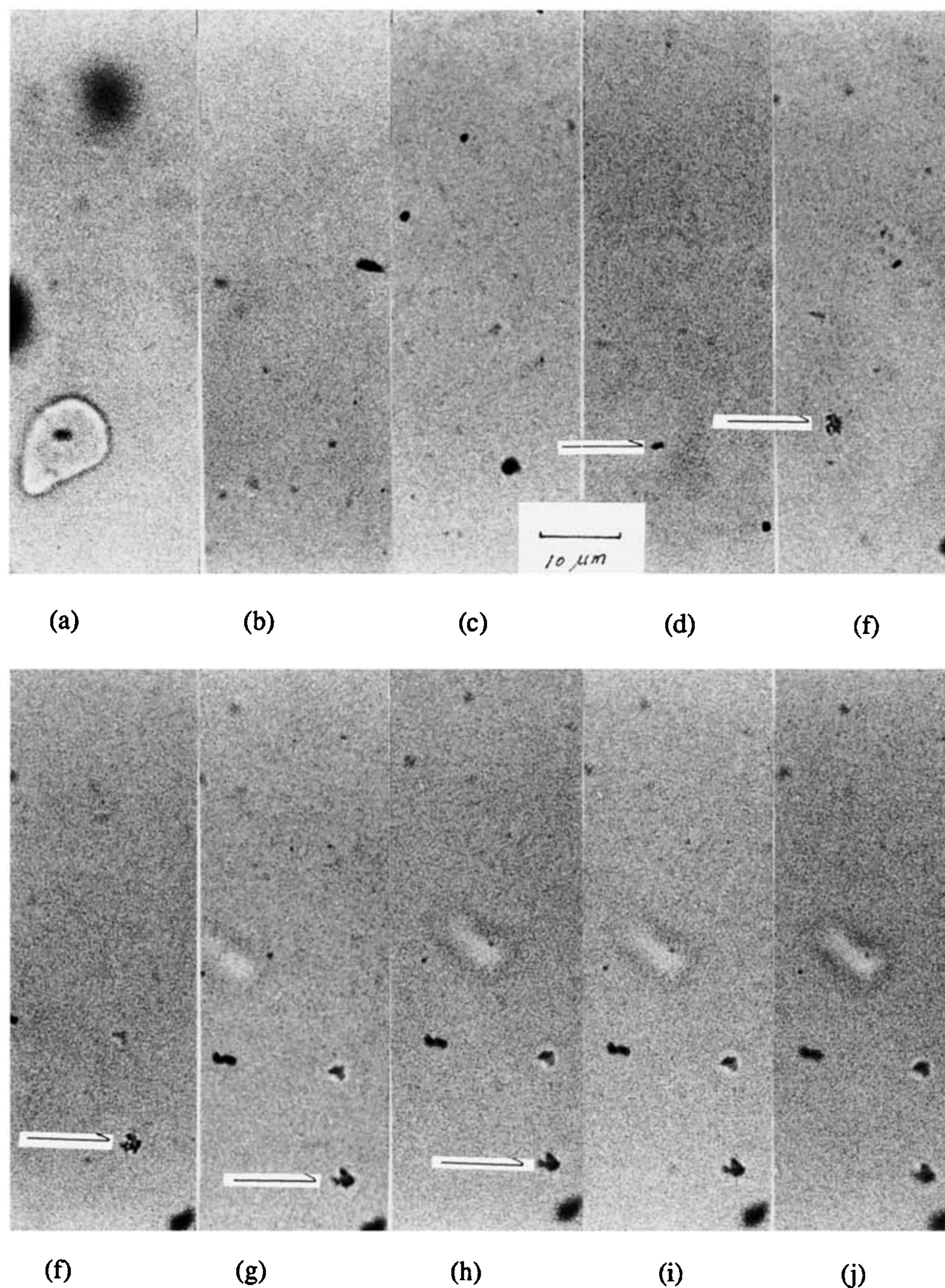

Figure 9 Optical microscopies (250×) of DGEBA/DDS/PEI-3000 cured at 150°C with various curing times: (a) 0.0 min; (b) 1 min; (c) 2 min; (d) 5 min; (e) 10 min; (f) 20 min; (g) 40 min; (h) 60 min; (i) 120 min; (j) 180 min.

of epoxy-rich and PEI-rich phase decreased, whereas the domain of epoxy-PEI interdispersed region increased and the time for the fixation of the phase-separated structure increased with the ethersulfone content in PEI.

Inoue and coworkers studied the curing process of DGEBA/PES/DDM blend[25] and tetrafunctional epoxy resin/PES/dicyandiamide blend[24] by light-scattering and SEM. Their results revealed a single phase mixture in the early stage of curing. As the curing

reaction proceeded, phase separation took place via the spinodal decomposition induced by the increase in epoxy molecular weight. In the present systems, phase separation started at the beginning. During early stage of curing, PEI melted and dispersed into the epoxy resins. The domain of epoxy and PEI interdisperse region increased with the ethersulfone content in PEI.

CONCLUSION

In the present work, the structure development of the curing of the thermoplastic/thermoset blend can be described by the following processes: onset of phase separation, interdispersion of PEI-rich and epoxy-rich phases, gelation, fixation of the phase-separated structure, and vitrification. We dealt with a DGEBA/DDS/PEI blend and investigated the curing kinetics by DSC and the phase separation process by optical microscopy. Two factors affected the curing reaction of DGEBA/DDS/PEI blend: phase separation between PEI and partially cured resin which caused the retardation of curing reaction and the catalytic effect of the tertiary nitrogen from imide group in PEI. The experimental results revealed that the curing reaction of DGEBA/DDS/PEI-0430 was highly retarded due to the high incompatibility between PEI and epoxy resins. The compatibility between PEI and partially cured epoxy resins increased with the ethersulfone content (or decreased imide content) in PEI. For the blends of DGEBA/DDS/PEI-1000, DGEBA/DDS/PEI-2000, and DGEBA/DDS/PEI-3000 that had a better compatibility with epoxy resins, the retarding effect of phase separation on the curing reaction of DGEBA with DDS was less than the catalytic effect of the tertiary nitrogen from the imide group of PEI.

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