

Epoxy Resin Containing the Poly(sily ether): Preparation, Morphology, and Mechanical Properties

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ABSTRACT: The poly(sily ether) with pendant chloromethyl groups (PSE) was synthesized by the polyaddition of dichloromethylsilane (DCM) and diglycidylether of bisphenol A (DGEBA) with tetrabutylammonium chloride (TBAC) as a catalyst. This polymer was miscible with diglycidyl ether of bisphenol A (DGEBA), the precursor of epoxy resin. The miscibility is considered to be due mainly to entropy contribution because the molecular weight of DGEBA is quite low. The blends of epoxy resin with PSE were prepared through *in situ* curing reaction of diglycidyl ether of bisphenol A (DGEBA) and 4,4'-diaminodiphenylmethane (DDM) in the presence of PSE. The DDM-cured epoxy resin/PSE blends with PSE content up to 40 wt % were obtained. The reaction started from the initial homogeneous ternary mixture of DGEBA/DDM/PSE. With curing proceeding, phase separation induced by polymerization occurred. PSE

was immiscible with the 4,4'-diaminodiphenylmethane-cured epoxy resin (ER) because the blends exhibited two separate glass transition temperatures (T_g s) as revealed by the means of differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). SEM showed that all the ER/PSE blends are heterogeneous. Depending on blend composition, the blends can display PSE- or epoxy-dispersed morphologies, respectively. The mechanical test showed that the DDM-cured ER/PSE blend containing 25 wt % PSE displayed a substantial improvement in Izod impact strength, i.e., epoxy resin was significantly toughened. The improvement in impact toughness corresponded to the formation of PSE-dispersed phase structure. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 505–512, 2003

Key words: synthesis; blends; morphology; toughness

INTRODUCTION

Epoxy resins are a class of important thermosetting polymer materials, and are widely used as high-performance materials, adhesives, matrices of composite materials, and electronic encapsulating materials.^{1,2} Due to high crosslinking density, epoxy resins are inherently of low impact resistance, and thus much effort was made to improve toughness. One of the successful modification routines is to incorporate dispersed toughener phase in the cured polymer matrix to form fine phase structure via reaction-induced phase separation.^{3–15,17–32} The effective modifiers could be elastomers^{3–13} or thermoplastics. Liquid rubbers such as carboxyl-terminated butadiene–acrylonitrile rubber (CTBN), amine-terminated butadiene–ac-

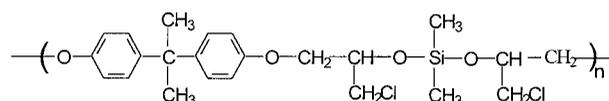
rylonitrile rubber (ATBN)^{3–9} have been exploited to improve toughness of epoxy resins. However, the presence of unsaturated structure in butadiene moieties is prone to thermal instability and low oxidation resistance. In comparison, organosilicon polymers (e.g., polysiloxane) are more advantageous modifiers,^{6,10–13,15} which possess some excellent properties, such as thermal stability, moisture resistance, and good electrical properties. However, polysiloxanes have poor compatibility with the precursors of epoxy resin due to the big difference in solubility parameter,¹⁶ which is essential to prepare elastomer-modified epoxy resins. Therefore, structural modification of polysiloxanes is necessary to solve this problem. More recently, much attempt was made to toughen epoxy resins with high modulus, high glass transition temperature (T_g) thermoplastics, especially for epoxy resins of higher crosslinking density, for example, tetraglycidyl 4,4'-diaminodiphenylmethane, novalac epoxy resins.^{17–32}

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polymers. Nishikubo et al.³³ first reported the synthesis of poly(silyl ether)s (PSE) through direct polyaddition of bis(epoxide)s with dichlorosilanes with quaternary onium salts as catalysts under mild reaction condition. In their work, several types of dichlorosilanes including dichlorodiphenylsilane (CPS), 1,2-bis(chlorodimethylsilyl)ethane (CMSE), cyclopentamethylenedichlorosilane (CPMCS), and bis [(2-(chlorodimethylsilyl) ethyl)benzene (CMSEB) were used to synthesize poly(silyl ether) of high molecular weight with high yield. However, dichlorodimethylsilane has not been used for preparing the polymer. In this work, we present the synthesis and characterization of the poly(silyl ether) via the polyaddition of diglycidylether of bisphenol A with dichlorodimethylsilane (DCM) with tetrabutylammonium chloride (TBAC) as a catalyst. The purpose to prepare the polymer is to enhance the compatibility of the organosilicon containing polymer with the precursor of epoxy resin by introducing the ether moiety of bisphenol A. The thermosetting polymer blends were prepared through *in situ* polymerization of diglycidylether of bisphenol A (DGEBA) and 4,4'-diaminodiphenylmethane (DDM) in the presence of PSE. The miscibility, phase behavior, and mechanical properties in blends of epoxy resin with the PSE before and after curing were addressed.

EXPERIMENTAL

Materials and preparation of samples

Diglycidyl ether of bisphenol A (DGEBA) was purchased from Shanghai Resin Co., Shanghai, China, and had a quoted epoxide equivalence of 185–210. The curing agent, chemical grade, was 4,4'-diaminodiphenylmethane (DDM), which was obtained from Shanghai Reagent Co., China. Chromatography grade dichlorodimethylsilane (DCM) was purchased from Shanghai Reagent Co. The quaternary ammonium salt, tetrabutylammonium chloride (TBAC), was used without further purification. Solvents such as toluene, chloroform, and hexane were purified in the usual way.

The poly(silyl ether) was synthesized by the polyaddition of dichlorodimethylsilane (DCM) and diglycidylether of bisphenol A (DGEBA) with quaternary onium salts as catalysts. The typical procedure is as follows. DGEBA (5.8864 g, 0.015 mol), DCM (1.9322 g, 0.015 mol), and TBAC (0.0783 g) was dissolved in toluene (20 mL). The solution was charged into a 500 mL three-necked round flask equipped with a reflux condenser and a mechanical stirring bar. The reactive system was cooled down to 0°C using the mixture of water and ice. The reaction was allowed to perform at 0°C for 1 h and at 30°C for 23 h. The solution was diluted with chloroform (10 mL), washed twice with 5 mL of water to isolate the inorganic salt and some amount of chloroform was evaporated. The polymer

was precipitated by hexane. The precipitated product was redissolved in chloroform and precipitated by hexane again. The polymer as prepared was dried in a vacuum oven at 60°C. The yield of the polymer was 72% (5.6 g). It has a molecular weight of $M_w = 19,000$ with $M_w/M_n = 2.7$ determined by GPC (Waters 510) relative to polystyrene standard in tetrahydrofuran (THF).

DGEBA/PSE blends were prepared by solution casting from chloroform at room temperature. The total polymer concentration was controlled within 5% (w/v). To remove the residual solvent, all the blend films obtained were further desiccated *in vacuo* at room temperature for 1 week. To prepare DDM-cured epoxy resin/PSE blends, PSE was first dissolved in the most possibly small amount of dichloromethane and then the solution was added to DGEBA at ambient temperature. The mixture obtained were heated up to 100°C with continuously stirring to remove the most of CH_2Cl_2 and degassed in vacuum at 100°C for 1 h to remove residual solvent. The curing agent, DDM, was added to system with continuously stirring until a homogeneous ternary mixture was obtained. The ternary mixture was poured into a Teflon mold and cured at 80°C for 2 h, 150°C for 2 h, plus 180°C for 4 h for postcuring.

Measurements

The Fourier transform infrared (FTIR) spectrum was measured on a Nicolet 750 spectrometer at room temperature. The thin films of polymer films were cast onto a NaCl window from a chloroform solution of 2 wt %. The films were sufficiently thin to be within a range where the Beer-Lambert law is obeyed. Sixty-four scans at a resolution of 2 cm^{-1} were used to record the spectra. The $^1\text{H-NMR}$ spectrum was recorded on an EM360 NMR (60 MHz) instrument in CCl_4 with Me_4Si (TMS) as an internal reference. A Perkin-Elmer Pyris 1 differential scanning calorimeter (DSC) was used to determine thermal transitions. The instrument was calibrated with standard Indium. The sample weight was about 12 mg, and a heating rate of 20°C was used in all cases. The T_g was taken as the midpoint of the heat capacity change. Dynamic mechanical tests were carried out on an MFIFA Multifunctional Internal Friction Apparatus (torsion pendulum, Laboratory of Internal Friction and Defects in Solids, Chinese Academy of Science, Hefei, China) at a frequency of 5.0 Hz and a heating rate of 3.0°C/min from ambient temperature until the sample became too soft to be tested. To investigate the morphologies of the DDM-cured epoxy resin/PSE blends the samples were fractured under cryogenic conditions using liquid nitrogen. The fractured surfaces so obtained were immersed in chloroform at room temperature for 30 min. PSE phase was preferentially etched by the solvent while epoxy matrix phase remains unaffected.

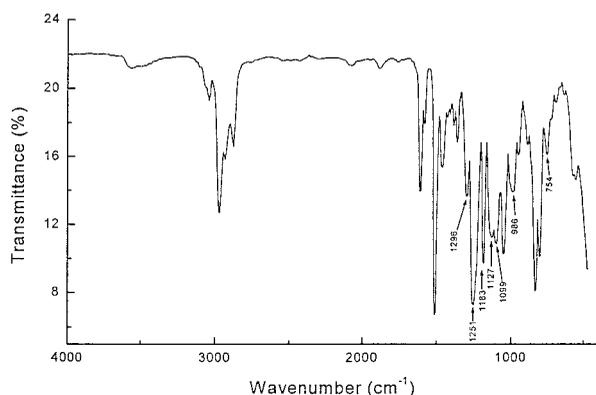


Figure 1 FTIR spectrum of PSE.

The etched specimens were dried to remove the solvents. All specimens were examined with a Hitachi 650 scanning electron microscope (SEM) at an activation voltage of 25 kV. The fracture surfaces were coated with thin layers of gold of about 100 Å. Notched Izod impact test was carried out on an impact test machine according to ASTM D638 at room temperature. At least five successful determinations were made to obtain average values.

RESULTS AND DISCUSSION

Synthesis and characterization of poly(silyl ether) (PSE)

The synthesis of the poly(silyl ether) (PSE) through direct polyaddition of bis(epoxide)s with dichlorosilanes with quaternary onium salts as catalyst was first reported under mild reaction condition by Nishikubo et al.³³ In their work, several kinds of dichlorosilanes including dichlorodiphenylsilane (CPS), 1,2-bis(chlorodimethylsilyl) ethane (CMSE), cyclopentamethylenedichlorosilane (CPMCS), and bis [(2-(chlorodimethylsilyl) ethyl)benzene (CMSEB) were used to give PSEs of a high molecular weight with a high yield. However, dichlorodimethylsilane has not been used for preparing the polymer. In this work, the poly(silyl ether) with a pendant chloromethyl group was synthesized by the polyaddition of diglycidylether of bisphenol A with dichlorodimethylsilane (DCM) with tetrabutylammonium chloride (TBAC) as a catalyst. The PSE of high molecular weight ($M_n = 19,000$) was obtained in 72% yields under the same condition. Shown in Figures 1 and 2 are FTIR and $^1\text{H-NMR}$ spectra of the product. In the FTIR spectrum, the absorption bands at 1251, 1099, and 754 cm^{-1} were ascribed to Si-CH_3 , Si-O-CH_2 and C-Cl stretching vibrations, respectively. The bands at 1183, 1127, 986 cm^{-1} were characteristic of the vibrations of Si-O-CH_2 , Si-O structural units. Figure 2 shows the $^1\text{H-NMR}$ (in CCl_4) spectrum of PSE together with the assignments. The proton signals were observed at $\delta = 0.20$ (s, 6H, Si-CH_3), $\delta = 1.55$ (s, 6H, C-CH_3 in

bisphenol A skeleton), $\delta = 3.60$ (d, 4H, $\text{C-CH}_2\text{-Cl}$), 3.95 (s, 5H, $\text{C-CH}_2\text{-Ph}$), $\delta = 4.25$ (m, 4H, O-CH-C-Cl), and $\delta = 6.50\text{--}7.5$ ppm (t, 8H, aromatic protons). From the results of FTIR and $^1\text{H-NMR}$, it is seen that the poly(silyl ether) with pendant chloromethyl groups (PSE) was synthesized by the polyaddition of dichloromethylsilane (DCM) and diglycidylether of bisphenol A (DGEBA) with tetrabutylammonium chloride (TBAC) as a catalyst.

Miscibility and phase behavior

The as-prepared poly(silyl ether) (PSE) was exploited to modify epoxy resin. To carry out the *in situ* curing reaction of DGEBA and DDM in the presence of PSE, miscibility (or solubility) of all components is essential. All the DGEBA/PSE blends cast from chloroform were transparent at ambient and elevated temperature (up to 150°C). This observation indicates that all the DGEBA/PSE blends present a single, homogeneous, and amorphous phase, i.e., phase separation did not occur at least on a scale exceeding the wavelength of visible light. The DGEBA/PSE blends were subjected to thermal analysis. DSC curves of the DGEBA/PSE blends are shown in Figure 3. It can be seen that each blend displayed a single T_g , intermediate between those of the two pure components and changing with the blend composition. From the transparency and glass transition behavior, it is judged that DGEBA/PSE blends are completely miscible in the amorphous state. Figure 4 summarizes the plot of T_g s of the blends as a function of weight fraction of PSE. There are several theoretical and empirical equations to describe the dependence of glass transition temperature on blend composition. Herein, the Gordon-Taylor equation³⁴ was applied to account for T_g -composition relationship of this system:

$$T_g = T_{g1} + k(W_2/W_1)(T_{g2} - T_{g1}) \quad (1)$$

where T_g is the glass transition temperature of the polymer blend, and T_{g1} and T_{g2} those of components 1

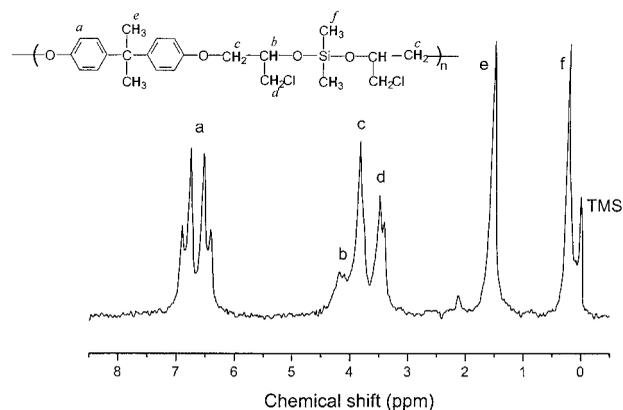


Figure 2 $^1\text{H-NMR}$ spectrum of PSE.

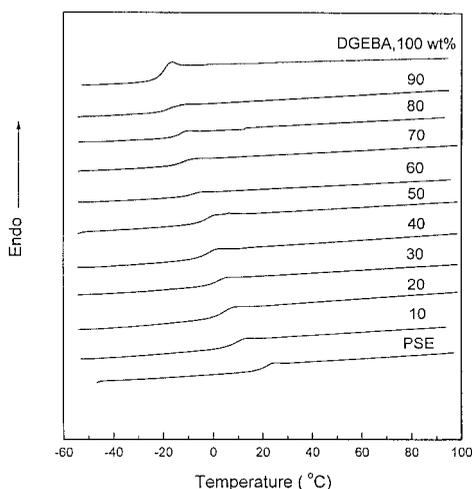


Figure 3 DSC curves of DGEBA/PSE blends.

and 2, respectively. W_1 and W_2 are the weight fractions; k is an adjusting parameter related to the degree of curvature of the T_g -composition curve. Application of the Gordon-Taylor equation to the experimental data yielded a k value of 0.35, fitting the experimental data quite well.

It has been proposed that k can be taken as a semi-quantitative measure of strength of the intermolecular interaction between components of blends.^{35,36} For instance, in blends of poly(ϵ -caprolactone) with chlorinated polyethylene, poly(vinyl chloride) (PVC), and chlorinated PVC, k increases from 0.26 to 1.0 with an increase of the amount of the intermolecular hydrogen-bonding between α -H of the chlorinated polymers and the carbonyl of PCL. When such an approach is used for the DGEBA/PSE blends, we noted that the k -value (0.35) is quite small compared with other DGEBA blend systems,²⁸⁻³³ suggesting that the intermolecular interactions between DGEBA and PSE are relatively weak. It should be pointed out that the

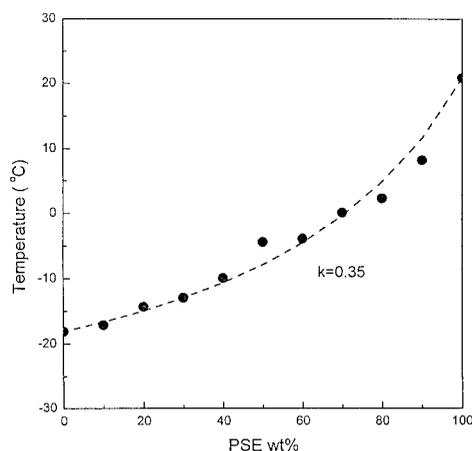


Figure 4 Plot of glass transition temperatures as a function of PSE content for DGEBA/PSE blends. The dash line is drawn from the prediction of glass transition by Gordon-Taylor equation with $k = 0.35$.

miscibility of the DGEBA/PSE blends can be considered to be due mainly to a non-negligible entropy contribution, as the molecular weight of DGEBA is rather low.

After DDM, the curing agent, was added to the binary DGEBA/PSE system, a homogeneous ternary mixture composed of DGEBA, DDM, and PSE was formed. After curing under the standard condition, the ternary mixtures were converted into the binary blends, i.e., *in situ* formed blends of epoxy resin (ER) with PSE. The DDM-cured epoxy/PSE blends with PSE content up to 40 wt % were thus obtained. It was observed that all the initially transparent mixtures of DGEBA/DDM/PSE gradually became cloudy as the reaction proceeded. This observation suggests the occurrence of phase separation induced by the polymerization. With DDM adding to the DGEBA/PSE mixture and curing at an elevated temperature, a series of structural changes involving chain extension, branching, and crosslinking occurred in succession. As the curing reaction proceeds, the molecular weight of system greatly increased and three-dimensional networks were formed. The increased molecular weight gives rise to the decrease of entropy contribution to miscibility. On the other hand, the occurrence of crosslinking caused dramatic changes in the chemical and physical nature of the system. Both the factors result in the phase separation between crosslinking epoxy and PSE. All DSC curves of the cured blends displayed two separate T_g s, which are ascribed to those of the epoxy-rich phase and PSE-rich phase, respectively. Shown in Figure 5 are the T_g plot of the control epoxy, PSE, and their blends as functions of PSE contents. For the control epoxy and PSE sample, the T_g s were observed at 165 and 20.9°C, respectively. It is seen that the T_g s of the epoxy-rich phase decreased slightly, whereas those of the PSE-rich phase increased slightly with increasing PSE concentration. The depression in T_g of the cured epoxy phase and the enhancement of

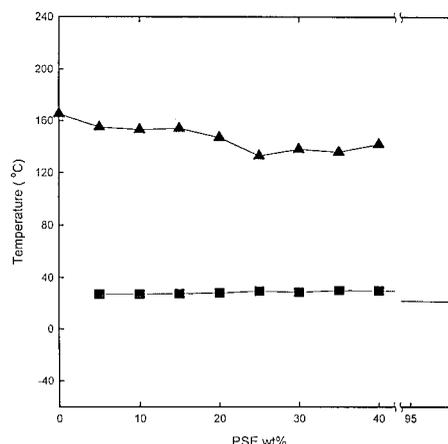


Figure 5 Glass transition behavior for the DDM-cured ER/PSE blends: (▲) T_g of the epoxy-rich phase, (■) T_g of the PSE-rich phase.

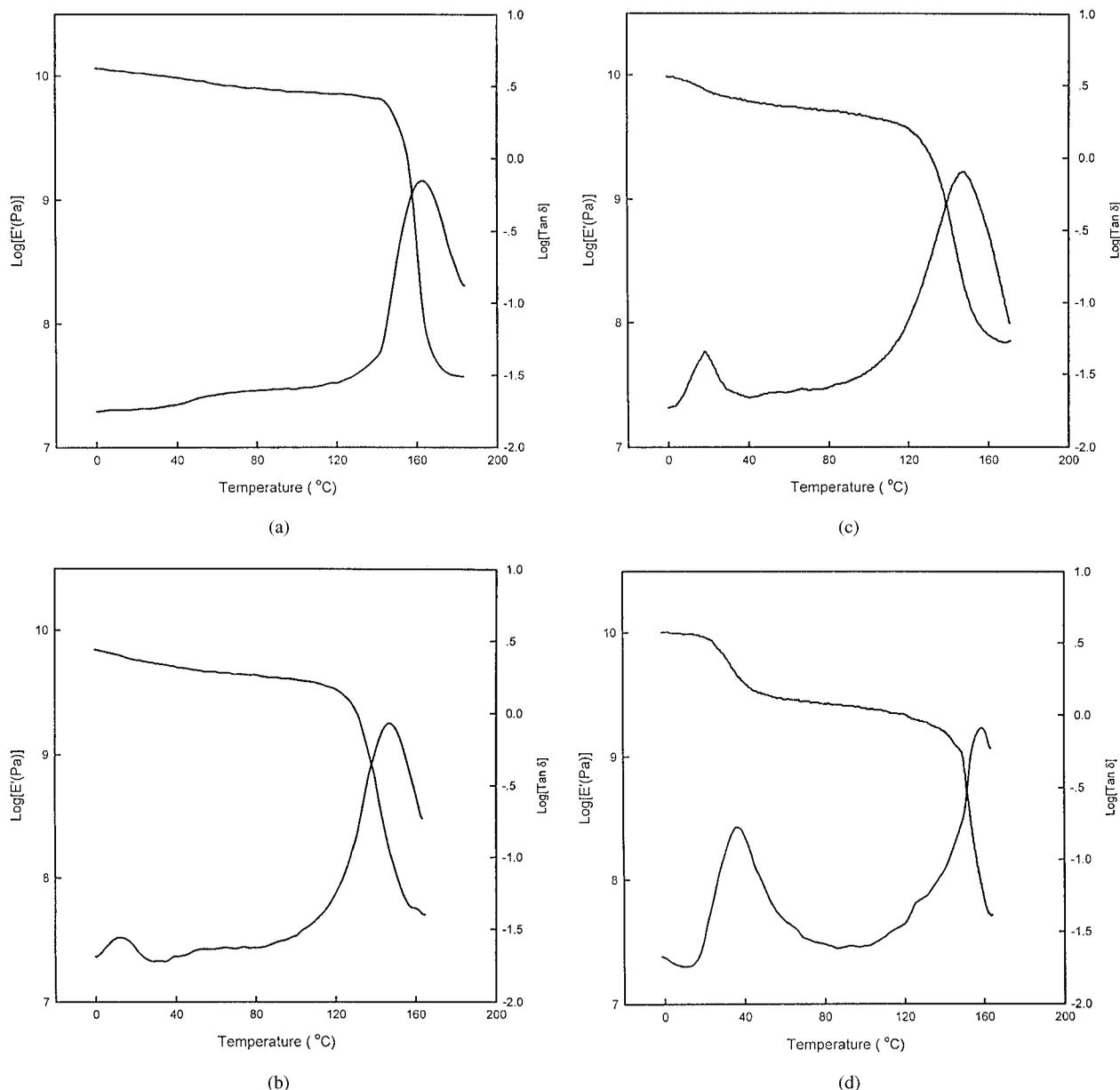


Figure 6 Dynamic mechanical properties of (A) 100/0; (B) 90/10; 80/20; and (D) 70/30 ER/PSE blends.

the PSE-rich phase could be due to the incomplete phase separation between crosslinked epoxy and PSE.

Figure 6 shows dynamic mechanical spectra of epoxy as well as 90/10, 80/20, and 70/30 epoxy/PSE blends. The dynamic mechanical spectrum of DDM-cured DGBEBA [Fig. 6(a)] exhibits exist a well-defined relaxation peak centered at 163°C, which is ascribed to the glass–rubber transition of the polymer. The dynamic mechanical spectra of the 90/10 [Fig. 6(b)], 80/20 [Fig. 6(c)], and 70/30 blends clearly display two peaks on internal friction ($\tan \delta$) vs. temperature curves, which correspond to the T_g s of ER and PSE phases, respectively. It is observed that the dynamic storage modulus (E') of all the blends decreased after the PSE-rich phase underwent a glass–rubber transition at ca. 20°C, which is typical of elastomer-modified

epoxy systems. The DMA results presented here further indicate that DDM-crosslinked epoxy resin is immiscible with PSE, i.e., the blends had a two-phase structure, which is in a good agreement with that from DSC results.

The morphology of the ER/PSE blends were investigated by SEM. Figure 7 presents SEM micrographs of chloroform-etched fracture surfaces of the blends frozen by liquid nitrogen. The heterogeneous morphology was observed in all the cases, which supports the results of DSC and DMA. It can be seen from Figure 7(a)–(c) that the spherical feature was uniform dispersed in the continuous matrix after PSE phase was rinsed by chloroform. The spherical phase was attributed to PSE phase, whereas the continuous phase was ascribed to the cured epoxy matrix. It is observed that

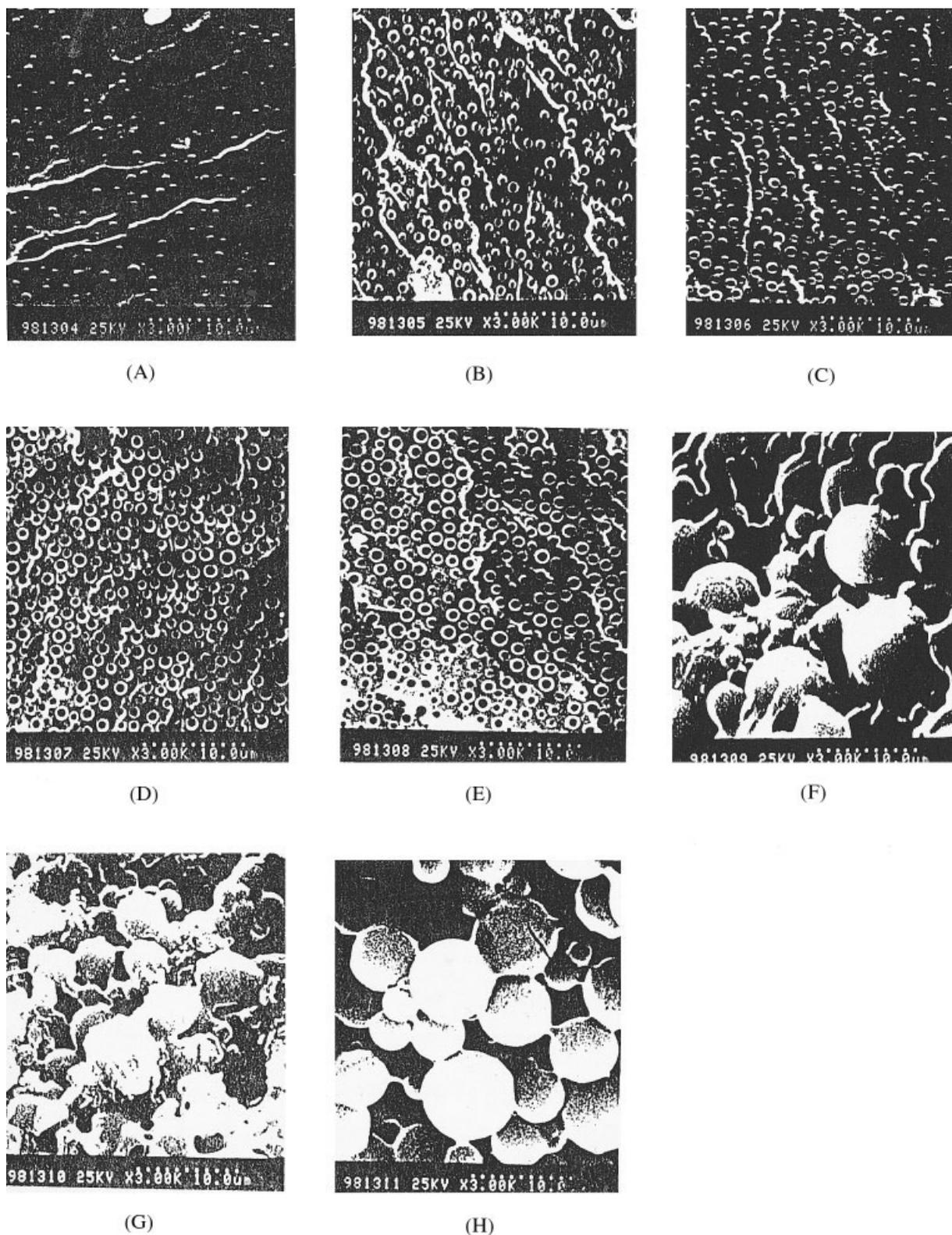


Figure 7 SEM micrographs of (A) 95/5; (B) 90/10; (C) 85/15; (D) 80/20; (E) 75/25; (F) 70/30; (G) 65/35; and (H) 60/40 DDM-cured ER/PSE blends.

the average size of the PSE spherical particle increases with increasing PSE content until 25 wt %. For the blend containing 5 wt % of PSE, the discrete PSE particles were uniformly dispersed in the continuous

cured ER matrices with the average size smaller than $1.0 \mu\text{m}$ in diameter [Fig. 7(A)]. With increasing PSE content, the average size of PSE-rich phase particles gradually increased up to $1.5 \mu\text{m}$ in diameter for

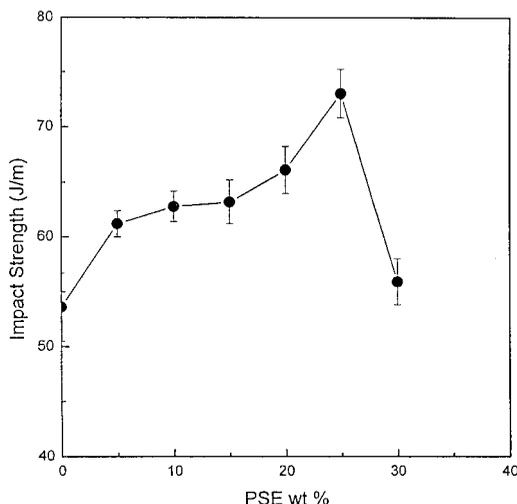


Figure 8 Izod impact strength as a function of PSE content for the DDM-cured epoxy/PSE blends.

ER/PSE 75/25 blends [Fig. 7(B)–(E)]. However, the 70/30, 65/35 blend displayed remarkably different morphologies [Fig. 7(F)]. It can be seen that PSE domains began to interconnect, and exhibited irregular shapes. At the same time, there appear the spherical particles on the surface of the etched blends with broad distribution of size. The spherical particles should be responsible for cured epoxy phase after PSE phase was dissolved by chloroform. Therefore, the phase inversion occurred while PSE content is 30 wt %. With increasing PSE concentration, totally phase-inverted morphology was observed for the 60/40 DDM-cured ER/PSE blend. The average size of spherical epoxy particle remains almost unvaried with increasing PSE content, in marked contrast with some other thermoplastics-modified epoxy systems.^{25,28,29,37} In phase separation induced by polymerization, morphology can be determined by two competitive processes, i.e., phase coarsening and polymerization. For thermoplastics-modified epoxy systems, the size of epoxy particles decreases with increasing thermoplastics concentration, which was attributed to the deceleration of phase separation and coarsening and incomplete curing reaction due to the inclusion of thermoplastics of high viscosity.³⁷ In the present system, the fact that the average size of spherical epoxy particle remains almost unvaried with increasing PSE content suggests the inclusion of PSE to epoxy did not cause significant increase in the viscosity of the reactive system, which facilitates processing.

Izod impact toughness

The mechanical property of the blends was investigated based on the Izod impact test at room temperature. Figure 8 summarizes the results of the impact test for the control epoxy and DDM-cured ER/PSE blends. It was noted that epoxy was significantly

toughened by incorporation of PSE as in other epoxy/modifiers blend system.^{3–15} The impact strength of blends increased with increasing PSE concentration until the content of PSE is up to 25 wt %. The 75/25 ER/PSE blend exhibited an improvement of impact toughness by about 50% in comparison with the control epoxy. The improvement in impact strength is comparable with those of other elastomer-modified epoxy systems.^{3,12} It is seen that there is a dramatic decrease in impact strength (IS) when the PSE content is more than 25 wt %. The improvement in impact toughness in a certain range suggests that the morphology plays a very important role in toughening of resins. As mentioned above, the cured epoxy blends with PSE contents less than 25 wt % exhibited PSE-dispersed phase structure. It is the very phase structure that yields a better toughness in this system. When the PSE content exceeds 25 wt %, phase inversion of the cured blends occurred. As a consequence, the fracture behavior of the phase-inverted blends depends predominantly on the tearing of the PES phase and thus gives low values of impact strength.

CONCLUSIONS

Poly(sily ether) with pendant chloromethyl groups (PSE) was synthesized by the polyaddition of dichloromethylsilane (DCM) and diglycidylether of bisphenol A (DGEBA) with tetrabutylammonium chloride (TBAC) as a catalyst. The miscibility in blends of epoxy resin with PSE after and before curing was investigated on the basis of DSC, DMA, and SEM results. The PSE is found to be miscible with diglycidyl ether of bisphenol A (DGEBA), the precursor of the epoxy resin. The miscibility is considered to be due mainly to entropy contribution. The DDM-cured epoxy resin/PSE blends was judged to be incompatible, as revealed by the appearance of two separate T_g s. Phase separation-induced polymerization occurred with the curing reaction proceeding. SEM showed that all the epoxy/PSE blends are phase separated and exhibited PSE- or epoxy-dispersed morphology depending on blend composition. The mechanical test showed that the epoxy/PSE blend containing 25 wt % PSE displayed a substantial improvement in Izod impact strength; the improvement in impact toughness was ascribed to the formation of PSE-dispersed phase structure.

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