Morphology of Epoxy Resin Modified with Silyl-Crosslinked Urethane Elastomer

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ABSTRACT: Silyl-crosslinked urethane elastomer modifying epoxy resin has drawn much interest. Here the triethoxysilyl-terminated polycaprolactone elastomer (PCL-TESi) modifying diglycidylether of bisphenol A epoxy resins (DGEBA) system was chosen, and then the effect of the type of curing agent on the phase structure of the studied epoxy resin system was investigated. The modified systems were obtained with different phase structures by varying the formulations of the curing agent. It was experimentally shown that with the addition of aminosilane (KBE-9103), the crosslinked density was greatly increased. The cured system also showed from SEM and TEM analysis that addition of KBE-9103 increased the compatibility between the PCL-TESi and DGEBA, which made the ductility of the system decrease, but also indicated from TEM that addition of much KBE-9103 made the reacted silicone particles coagulate each other. The state of phase separation from TEM in the cured system was theoretically explained. These would serve the deeper studies of the mechanism of silyl-crosslinked urethane elastomer modifying epoxy resin in the future. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 611–619, 2005

Key words: epoxy resin; triethoxysilyl-terminated polycaprolactone elastomer; compatibility; phase structure
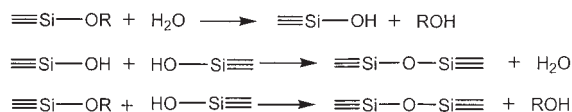
INTRODUCTION

Much attention has been paid to improving the toughness of epoxy resin while maintaining its nature, that is, excellent heat resistance, mechanical properties, and adhesion properties. Among these studies, reactive elastomers such as carboxyl-terminated acrylonitryl rubber (CTBN) were one of the most successful techniques,[1–5] but the existence of unsaturated bonds in the butadiene components of the elastomer limited the application at high temperature.[6] Recently, some saturated liquid rubbers such as polysulphide,[7] acrylate,[8–10] and polyurethane[11,12] were reported as replacements for CTBN. However, most of the reported rubber-toughened epoxy formulations suffered from the problem of heat cure, and also, these systems generally showed high viscosity, so that these disadvantages would limit the wide usage of epoxy resin as a surface coating and adhesive onto intricate structures. In order to solve these problems, modifying epoxy resin with silyl-terminated elastomers such as polypropylene oxide[13] and urethane[14] was developed recently. These systems were reported to have excellent peel strength and fracture energy. In contrast with the common epoxy-amine curing system, the curing processes of the silyl elastomer-epoxy modified system had a sol-gel process, as depicted in Scheme 1. Because the hydrolytic silanol condensation reactions

initiated by water were relatively humidity dependent, but relatively temperature independent, the silyl elastomer-epoxy modified system has been considered to be a potential route to ambient film forming. Also, the polymer/silica hybrid, which combined the superior properties of both the organic and inorganic polymer,[15] gave the films formed from the modified epoxy resin some good properties in terms of adhesion to steel and organic coatings, flexibility, and better acid and solvent resistance.

In our studies, the selected bisphenol-A type epoxy resin (diglycidylether of bisphenol A, DGEBA) had been tentatively modified with synthesized triethoxysilyl-terminated polycaprolactone elastomer containing urethane linkage (PCL-TESi). It was interestingly found in our primary studies that the modified material, that is, PCL-TESi/DGEBA, had excellent adhesion strength and fracture energy when used as an adhesive for coatings, but also that the components of the modified systems, especially the type of the selected curing agent, greatly affected their mechanical properties. Before intensively probing the effect of phase structure of these silyl elastomer-epoxy systems on their bulk mechanical and adhesion properties and understanding the toughening mechanism, here the effect of the components of the modified systems on their morphological properties was first investigated. The morphology of the cured epoxy resin films was evaluated by scanning electron microscopy (SEM) and presented, based on different components of PCL-TESi, epoxy, and curing agent. The synthesis of PCL-TESi was also introduced.

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$\equiv$Si—OR + H$_2$O $\longrightarrow$ $\equiv$Si—OH + ROH

$\equiv$Si—OH + HO—Si$\equiv$ $\longrightarrow$ $\equiv$Si—O—Si$\equiv$ + H$_2$O

$\equiv$Si—OR + HO—Si$\equiv$ $\longrightarrow$ $\equiv$Si—O—Si$\equiv$ + ROH

Scheme 1

EXPERIMENTAL

Materials

The epoxy resin used was a commercial grade of diglycidylether of bisphenol A (DGEBA, E-20, Wuxi Resin Plant, China). 50% (*w/w*) butanone solution of E-20 was obtained before usage. Polycaprolactonediols (PCL-210: M_n = 1000, OH value = 114.1 mgKOH/g; and PCL-220: M_n = 2000, OH value = 56.5 mgKOH/g) purchased from Daicel Chemical Ltd Co. were used as the diol component in the urethane oligomer. Isocyanatopropyltriethoxysilane (ICPTES), 3-triethoxysilyl-N-(1,3-dimethyl-butylident) propylamine KBE-9103 (Shin-Etsu Chemical Co.), 2,4,6-tri-(dimethyl)-amino-methylphenol (DMP), dibutyltin dilaurate (DBTDL), and others of analytical grade were used as received. KB-2, a mixture of modified aliphatic and aromatic amines (amine value = 450 mgKOH/g, Chenhua Chemical Co., China), was used as a curing agent for DGEBA. Like most amino curing agents, KB-2 could cure DGEBA at ambient temperature, even at a lower temperature. All organic solvents were directly used without further purification except where noted with "dried," where the solvent was thoroughly dried with anhydrous CaCl$_2$ or MgSO$_4$ before usage. The structures of some of the above are shown as Scheme 2:

Synthesis of silyl-terminated urethane elastomers PCL-TESi

PCL-TESi-210: 50 g of PCL-210 was introduced to a 250 ml round bottom flask equipped with a mechanical stirrer, a switchable inlet for argon, and a vacuum connector. PCL-210 was first dried by heating at 100°C for 1.5 – 2 hr under dynamic vacuum. Later, the temperature of the reactor was lowered to 65°C under dynamic vacuum. Then argon was introduced; to this polydiol, a mixture of a stoichiometric weight of

ICPTES (25.8 g) and a certain amount of catalyst DBTDL was added, and the obtained mixture was maintained at 65°C under argon atmosphere until all isocyanate groups completely disappeared through FT-IR monitoring. After cooling to ambient temperature, by strong stirring an amount of "dried" xylene/butyl acetate (5/4 *v/v*) mixture was added to obtain 70% (*wt*) of PCL-TESi-210 solution.

PCL-TESi-220: A similar procedure to PCL-TESi-210 was done, except for the amount of ICPTES. 13.0 g of ICPTES was used here. 60% (*wt*) of PCL-TESi-220 solution was obtained.

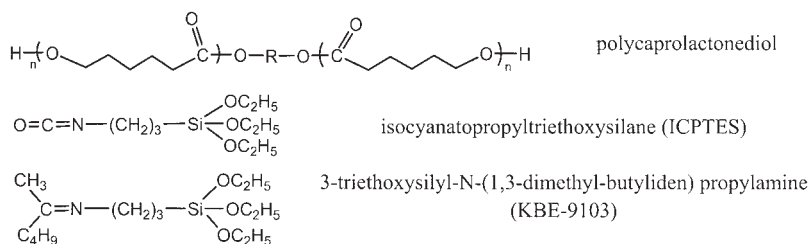### Preparation and curing of modified epoxy resin films

To achieve the high compatibility of the oligomer in DGEBA, the epoxy resin solution was pre-mixed with the synthesized oligomer PCL-TESi, and kept at 30°C overnight.

To the mixture of 15 g of DGEBA/PCL-TESi, the prescribed amounts of DMP, DBTDL, KB-2, and KBE-9103 were added, as shown in Table I. After thorough stirring, these mixtures were cast on a Teflon plate to obtain polymer films after completely evaporating the solvent. These formed films were cured at ambient temperature for 3 weeks under about 60% relative humidity.

As shown in Scheme 1, in the KBE-9103, the N$\equiv$C group was transformed to NH$_2$ much more easily when it reacted with H$_2$O. This induced chemical had both amino and ethoxysilyl groups, and also made DGEBA react with the resultant easily at a lower temperature. The amino and ethoxysilyl were able to react with the glycidyl groups of DGEBA and the ethoxysilyl group of the PCL-TESi, respectively. Thus, KBE-9103 acted as a reactive coupling agent between DGEBA and PCL-TESi.

Characterizations

FTIR spectroscopy was carried out with a Magna 750 FTIR Spectrometer. The resolution was 4 cm^{-1} with 32 scan times. Sample film was prepared by spontaneous evaporation of a diluted sample/THF solution spread out on a KBr pallet.

H$\{$O$\cdots\cdots$C$\}$—O—R—O$\{$C$\cdots\cdots$O$\}$H   polycaprolactonediol

O=C=N—(CH$_2$)$_3$—Si$\langle$OC$_2$H$_5$ isocyanatopropyltriethoxysilane (ICPTES)

C=N—(CH$_2$)$_3$—Si$\langle$OC$_2$H$_5$ 3-triethoxysilyl-N-(1,3-dimethyl-butyliden) propylamine (KBE-9103)

Scheme 2

Run no.	Composition before curing (phr)				Silica (wt %)[a]
	PCL-TESi-210	PCL-TESi-220	KBE-9103	KB-2	
1	10	—	0	21.6	0.63
2	10	—	7.6	16.2	1.73
3	10	—	13.7	11.9	2.59
4	10	—	19.7	7.6	3.42
5	10	—	25.8	3.3	4.24
6	10	—	30.3	0	4.84
7	—	15	0	21.6	0.55
8	—	15	13.7	11.9	2.44
9	—	15	21.2	6.5	3.44
10	—	15	30.3	0	4.61

0.55 phr of DMP and DBTDL were added for DGEBA, respectively.
[a] Calculated from reactant stoichiometry.

The swelling measurement was carried out as ref. 16. The cast film samples (8×8 mm^2) were cut off and thoroughly swollen in "dried" toluene at ambient temperature until the weight m_s of the swollen ones was unchanged. Later, samples were dried under dynamic vacuum for 24 hrs at ambient temperature and weighed again (m_d). Swelling (Q) was calculated as:

$$Q = \frac{m_s - m_d}{m_d}$$

Transmission-electron microscopy (TEM) specimens were stained with OsO$_4$ and sectioned with a diamond knife at ambient temperature. Electron micrographs were taken with an H-800 TEM at an accelerating voltage of 20 KV.

Scanning-electron microscopy (SEM) was carried out with a JSM 5600LV on samples of sheets with thickness of 1 mm, which were fractured at liquid nitrogen temperature. Fractured surfaces were coated with gold before examination. All photo signs were digitized.

RESULTS AND DISCUSSION

Synthesis of triethoxysilyl-terminated polycaprolactone elastomer containing urethane linkage (PCL-TESi)

Synthesis of silyl-terminated elastomers was usually carried out in two methods. One was by transesterification reaction, in which tetraethyl orthosilicate was directly reacted with polyol under an acid catalyst.[17]

The reaction was driven via evolution of alcohols. The second was a nucleophilic addition reaction,[14,18,19] where the isocyanate group (—NCO) terminated oligomer was first obtained via the reaction of hydroxyl of the oligomer and isocyanate, such as isophorondiisocyanate (IPDI), then the terminated —NCO group further reacted with aminosilane, producing an alkoxysilane terminated urethane oligomer. To avoid using isocyanate, here PCL-TESi was directly synthesized via nucleophilic addition between the —OH group of polycaprolactonediol (PCL-210 and PCL-220, structure shown as Scheme 1) and the —NCO group of ICPTES (shown as Scheme 3).

It was reported the catalyst could play a great role when —OH groups of oligomer reacted with —NCO of ICPTES.[16] To ensure the complete reaction between them, here DBTDL was chosen. Figure 1 shows the IR spectrum of the resultant mixture of PCL-210 and ICPTES after the reactive mixture was heated for 3.5 hrs at 65°C under Ar. It was clear that the reaction conversion was complete under the experimental conditions, due to the non-existence of 2270 cm^{-1} assigned to the —NCO group.[16] Although the resulting —OCONH— group could further react with the —NCO of the ICPTES to form a branched polyurethane, the relatively lower reaction temperature utilized here would restrain the addition between —OCONH- and —NCO, and the reaction could be neglected, due to the activity of the —OCONH- being lower than that of the —OH group and the larger steric effect exerted on the —OCONH- group, which would make the —OCONH-/-NCO reac-
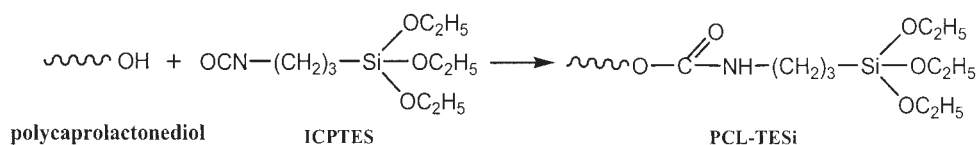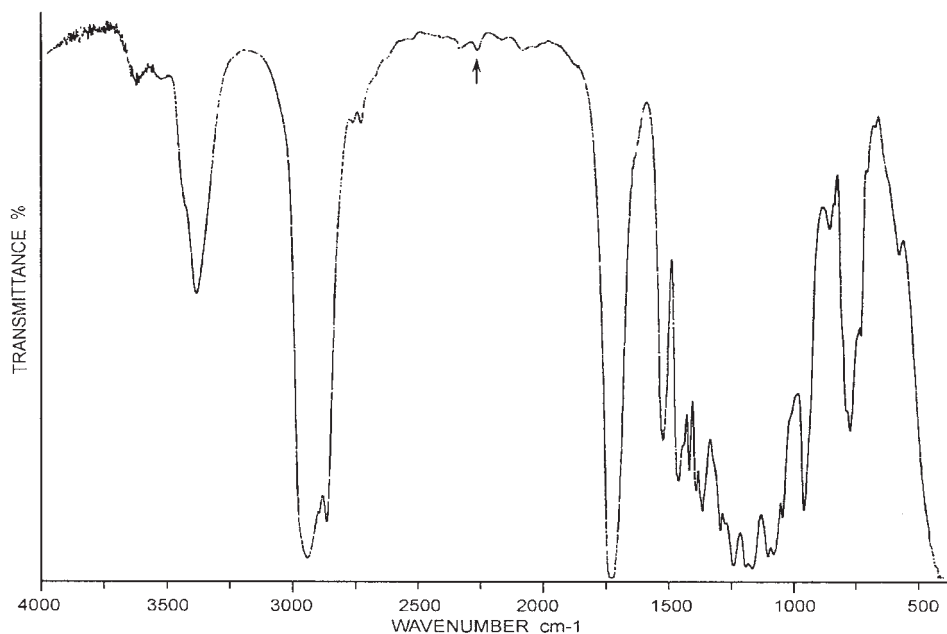

Scheme 3

Figure 1 FT-IR spectrum of PCL-TESi-210.

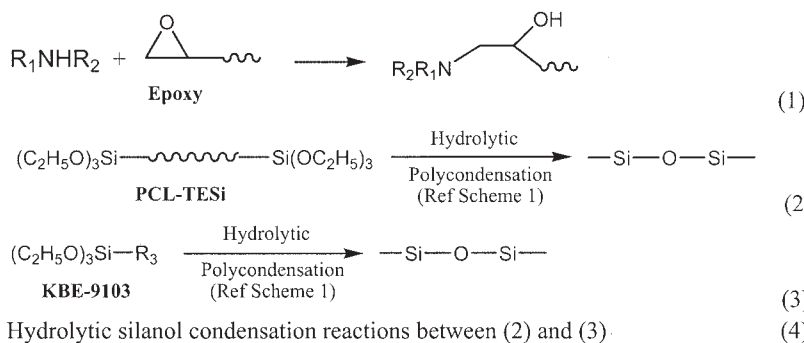tion proceed under higher temperature than that needed for the —OH group.[20]

Chemistry of the curing procedure of PCL-TESi/ DGEBA systems

From Table I, it was clearly found there were many chemically active groups in the mixture of the PCL-TESi/DGEBA-curing agents system, such as —Si(OC$_2$H$_5$)$_3$, amino, and epoxy, so the network produced would be complex due to multiple crosslinking reactions. Since, as mentioned above, KB-2 and the resultant KBE-9103 much more easily reacted with epoxy at ambient temperature, and also the hydrolytic polycondensation reactions (catalyzed by water) could occur easily as Scheme 1, it was easily understood that the reactions of both the amine-epoxy and hydrolytic polycondensation reactions of —Si-(OC$_2$H$_5$)$_3$ should

occur predominately. Among the hydrolytic polycondensation reactions, it should contain the reactions between the —Si(OC$_2$H$_5$)$_3$ groups of PCL-TESi and that of KBE-9103 besides PCL-TESi selves and KBE-9103 selves, when KBE-9103 was used. In addition to these organic reactions, urethane-epoxy reactions might occur (Scheme 4), and the potential for other reactions to take place also existed. The complexity might be further enhanced when the effects of relative humidity on both the organic and inorganic reactions taking place were considered.

Effect of the KBE-9103/KB-2 formulation on the crosslinked networks density of the cured systems

Solvent swelling properties of the cured systems directly reflect their crosslinked network densities. Figure 2 shows the dependence of the swelling value Q

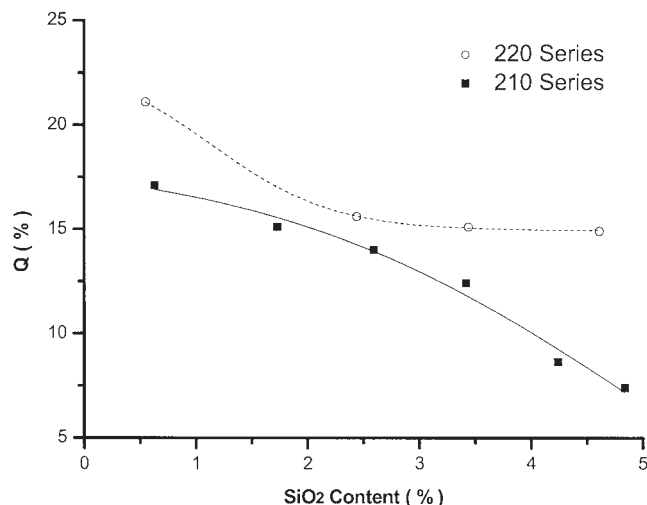$$R_1NHR_2 + \overset{O}{\triangle}\!\!\!\!-\!\!\sim \longrightarrow R_2R_1N\!\!-\!\!\overset{OH}{\underset{}{|}}\!\!\sim \tag{1}$$

Epoxy

$$(C_2H_5O)_3Si\!\!-\!\!\sim\!\!\sim\!\!-\!\!Si(OC_2H_5)_3 \xrightarrow[\substack{Polycondensation \\ (Ref\ Scheme\ 1)}]{Hydrolytic} -Si\!\!-\!\!O\!\!-\!\!Si- \tag{2}$$

PCL-TESi

$$(C_2H_5O)_3Si\!\!-\!\!R_3 \xrightarrow[\substack{Polycondensation \\ (Ref\ Scheme\ 1)}]{Hydrolytic} -Si\!\!-\!\!O\!\!-\!\!Si- \tag{3}$$

KBE-9103

Hydrolytic silanol condensation reactions between (2) and (3)   (4)

$$(R_1NHR_2 \quad = \quad KB\text{-}2,\ KBE\text{-}9103,\ or\ PCL\text{-}TESi\ )$$

Scheme 4

Figure 2 The dependence of the Q value versus the calculated SiO_2 content in the cured systems.

versus the calculated SiO_2 content of the cured systems. Clearly, Q decreased with increase of the SiO_2%, especially for the PCL-210 series. This indicated with increasing silica contents, a significantly decreasing coefficient of solvent expansion and total volume shrinkage; at the same time, increasing stiffness could be achieved in the systems.

Also, the Q value of the PCL-220 series was bigger than that of the PCL-210 series at the same SiO_2 content. This was consistent with the change of the molecular weight of PCL, which induced the change of the volume of the crosslinked networks.

Effect of the KBE-9103/KB-2 formulation on the change in morphology of the cured systems

It was reported that the coupling agent containing —NH_2 and Si-OR groups had a great effect on the morphology in the cured epoxy system.[13,21] To investigate the morphological change of the cured system with the addition of the KBE-9103, the SEM observation results of the fractured surfaces are shown in Figures 3 and 4 for the PCL-210 series and the PCL-220 series, respectively. Clearly, increasing KBE-9103 content greatly affected the change of the ductile of the cured epoxy resin. It was easily found that Figure 3a (using less KBE-9103) showed relatively smooth surfaces; Figures 3b–f showed conversely cavities and some deformed regions that might result from the coarseness of the fractured surface. These suggested the change of fracture behavior from ductile to brittle, that is, figure 3a showed ductile-fracture signs, and the rest showed brittle-fracture signs, especially using pure KBE-9103 for curing.

Some compared trends are also shown in Figure 4 for the PCL-220 series. Interestingly, one observed many thin and long strips that were parallel to each other and were homogeneously distributed (Figs. 4g and i), which suggested the crack might start from one elongated particle but stop as it met another elongated particle nearby.[22] Despite this, how to form the structure was still not explained in these cured systems.

Figure 5 depicts the magnification of the previous fractured surface (Fig. 3) and intensively shows the change of the fracture behavior. It clearly reveals the presence of some cavities from Figures 5a–e, but strips in Figure 5f. Larger and deeper cavities were generally characteristic of rubber-modified epoxy resins; these cavities represented the initial position of the rubber particles, which were pulled out or broken during the fracture process. From the morphological change of these cavities in Figure 5, it was shown the cavitation degree induced from the pull-out of the rubber phase (PCL-TESi) greatly decreased from Figure 5a to 5e, and even almost disappeared in Figure 5f, indicating the existence of a complete plastic deformation. These indicated that the interfacial energy between PCL-TESi and epoxy resin increased with increasing KBE-9103 content, due to the compatibilization of KBE-9103 for PCL-TESi and epoxy resin.

The change of the size of the deformed regions and cavities was also observed in Figures 3 and 5. The fractured surfaces were more deformed when higher contents of KBE-9103 were used in the cured system, but the biggest size of the cavities seemed to be found in Fig. 5d. This was probably a consequence of the agglomeration of the —Si-O- particles formed from hydrolytic silanol polycondensation as shown in Scheme 4. A detailed reason is explained below.

Effect of the KBE-9103/KB-2 formulation on the phase structure of the cured systems

To provide direct evidence for the effect of the formation of —Si-O- particles on the morphologies of the cured system with increasing contents of KBE-9103, here TEM analysis was used, and the phase structure was observed to confirm the interaction among PCL-TESi, KBE-9103, and the epoxy matrix, and the distribution of the dispersed phases. The relation between the content of KBE-9103 and the phase structure of the cured epoxy resin systems is shown in Figure 6. In system 1 (Fig. 6a), there was nearly no coagulation of any particles in this magnification size, indicating good compatibility between the cured DGEBA and the crosslinked PCL-TESi phase formed from silanol polycondensation, although the phase separation should take place with the advancement of the curing reaction.[23] The phenomenon might be due to the following: (1) relatively low content of PCL-TESi in the epoxy resin matrix; (2) the chemical interaction between —CONH- of PCL-TESi and the glycidyl groups of DGEBA as shown in Scheme 4. But from Figures 6b to f, we could see that the white DGEBA constituted the continuous phase and the black —Si-O- constituted a
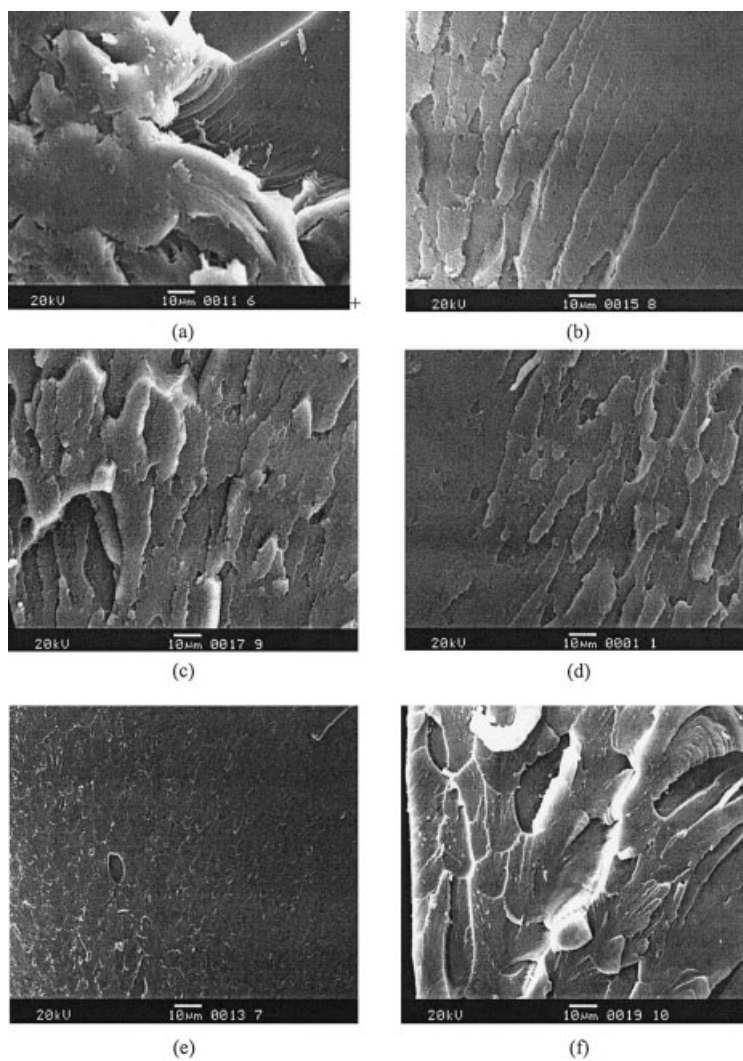
Figure 3. SEM of fracture surfaces of the PCL-TESi/DGEBA systems (PCL-210 series): (a) Run No 1, (b) Run No 2, (c) Run No 3, (d) Run No 4, (e) Run No 5, (f) Run No 6 in Table I.
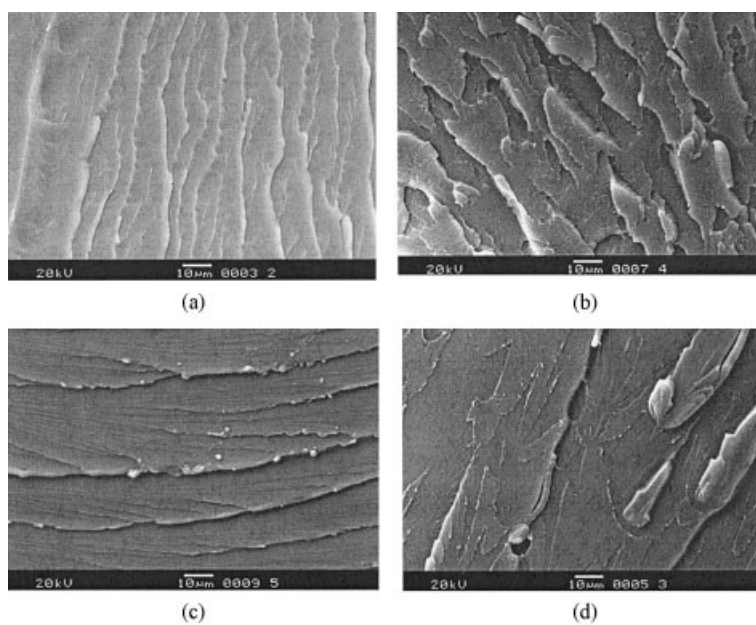

Figure 4. SEM of fracture surfaces of the PCL-TESi/DGEBA systems (PCL-220 series): (a) Run No 7, (b) Run No 8, (c) Run No 9, (d) Run No 10 in Table I.
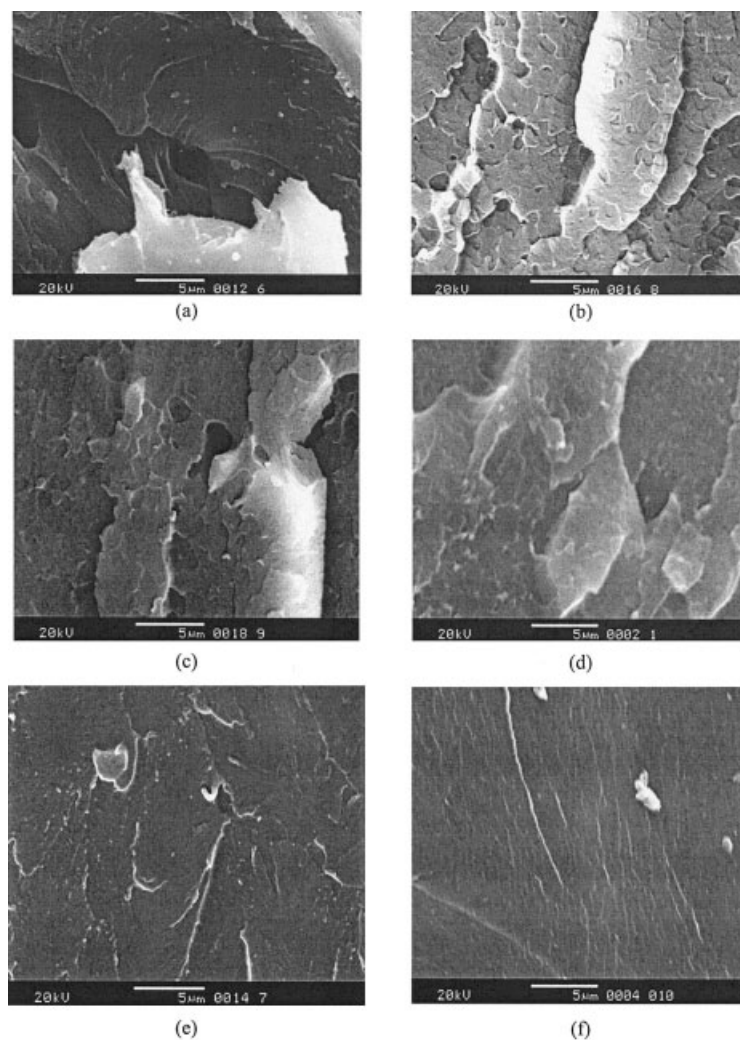
Figure 5 SEM of fracture surfaces of the PCL-TESi/DGEBA systems (PCL-210 series): (a) Run No 1, (b) Run No 2, (c) Run No 3, (d) Run No 4, (e) Run No 5, (f) Run No 6 in Table I.

dispersed phase, and that the dispersed phase became more visible when increasing the content of KBE-9103. The interface of the continuous phase and the dispersed was faint; this indicated that the KBE-9103, the amine of which could react with epoxy groups, acted as a good compatibilizer for the cured system.[13,21] These phenomena indicated there would be much more hydrolytic silanol polycondensation, which resulted in the coagulation of -Si-O- particles and induced the phase separation, that is, the formation of the dispersed phase, when KBE-9103 was added.

On the other hand, it was interestingly shown in Figures 6c2 and d that the crosslinked Si-O-Si structure was mainly concentrated in the interfacial area, and the interphase containing the high concentration of the organic polymer was clearly observed around the dispersed phase. This could not be seen in the others. According to the mechanism combining the Flory–Huggins and Hildebrand equation that the rubber phase would undergo phase separation with the advancement of the curing reaction in the rubber

toughening epoxy resin system[23] when a small amount of KBE-9103 was added in this studied system, that the silanol polycondensation reaction of ethoxysilyl groups between PCL-TESi and KBE-9103 would take place around the aggregated PCL-TESi particles was mainly thought due to the difference of solubility parameters and molar volumes of KBE-9103 and PCL-TESi. But increasing the amount of the KBE-9103, which favored the mixing process of KBE-9103 and PCL-TESi, made the silanol polycondensation reaction of the ethoxysilyl groups between PCL-TESi molecular and KBE-9103 occur much more easily and predominate besides the interaction of ethoxysilyl groups of KBE-9103 selves. And these reactions made the size of the separated particles become smaller. This might explain the reason that the size of the dispersed phases, that is, the coagulated —Si-O- particle became big, then small, with the change of content of KBE-9103 in Figure 6. It could be found that among these particles, the size of the dispersed phase in Figure 6d was the biggest; this induced the biggest cavities size
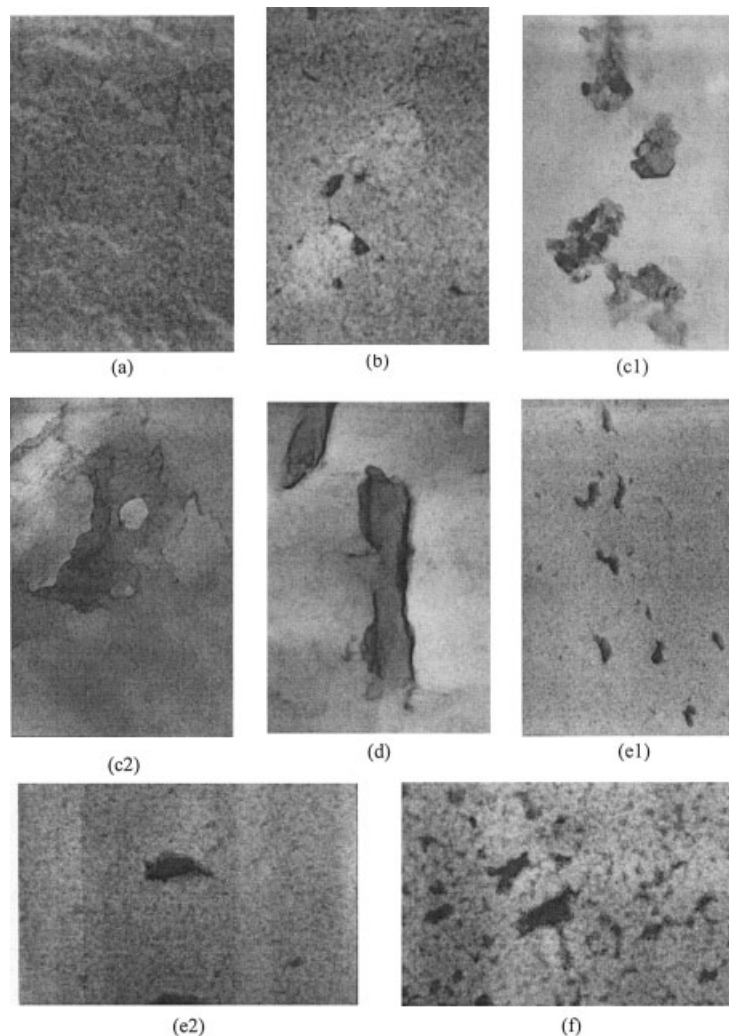
Figure 6 TEM of PCL-TESi/DGEBA systems (PCL-210 series): (a) Run No 1; (b) Run No 2; (c1), (c2) Run No 3; (d) Run No 4; (e1), (e2) Run No 5; (f) Run No 6 in Table I (Magnification: 100,000 ×, except (c1) and (e1): 50,000 ×).

when fractured as described above. The same trend could be observed for the PCL-TESi-220/DGEBA series.

CONCLUSION

The results obtained in the present study led to the following conclusions. A silyl-terminated elastomer based on polycaprolactonediol was synthesized and used as a modifier in epoxy resin. Further, the modified epoxy resin systems were cured with different curing agents at different concentration.

The solvent swelling property results indicated that increased addition of KBE-9103 decreased the swelling of the cured resin matrix and increased the stiffness of the system. Also, internal cavitation of the modifier particles was decreased with increasing KBE-9103, as seen from the SEM analysis results. The TEM results demonstrated the phase structure was greatly changed with addition of KBE-9103, which resulted

from the coagulation of the reacted silicone particles with each other.

Therefore, a modified epoxy resin with excellent toughness and strength could be obtained by controlling the phase structure of the cured PCL-TESi/ DGEBA after adjusting the formulation of the curing agent (KB-2 and KBE-9103) and the modifier. More detailed information about these is being studied and will be presented in the future.

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