Microstructure and Thermal Properties of Silyl-Terminated Polycaprolactone–Polysiloxane Modified Epoxy Resin Composites

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ABSTRACT: With a direct nucleophilic addition between —OH groups of polydiol and —NCO of a silane, a blend of silyl-terminated polycaprolactone PCL-Si and silyl-terminated polydimethylsiloxane PDMS-Si oligomer, PCS-2Si, were firstly prepared, and then blended with a commercial epoxy resin (diglycidyl ether of bisphenol-A, DGEBA) to form a ternary composite. The formed ternary composites of different content of DGEBA were cured using a polyamidoamine as a curing agent and a sol–gel process at ambient temperature. The microstructures and properties of the cured composites were investigated by SEM, TGA, and energy dispersive spectroscopy. The results showed the compatibility between DGEBA and PDMS increased with increasing content of PCS-2Si, but higher content of PCS-2Si resulted in a slight enrichment of silicon in the surface of the cured film. TGA showed that incorporating PCS-2Si into epoxy resin altered the composites' thermal stability and degradation characteristics. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1105–1113, 2008

Key words: polycaprolactone; polysiloxane; epoxy; sol–gel process; morphology; thermal properties; composites; silicas

INTRODUCTION

A systematic and detailed study was made in the past to toughen the epoxy resin via blending or adding thermoplastic polymers to the thermoset epoxy resin. Among the modifiers, elastomer was favored due to its improved toughness, good solvent. These elastomers included carboxy-, amine-, or hydroxyl-terminated acrylonitrile butadiene rubbers, functionally terminated acrylates, polyurethane,[1–6] and so on. Compared with those elastomers, poly(dimethylsiloxane) (PDMS) had also been used to modify epoxy resin,[1,7–16] however in conventional introduction of siloxane into polymers through blending methods, pure PDMS had very little use as a toughening agent because of the poor compatibility between soft segments of PDMS and polar hard segments in epoxy which largely resulted from the lack of hydrogen bonding. This resulted in poor thermomechanical properties and had limited the use of larger silicone concentrations,[14,17–19] hampered their use in surface coatings.[16] To overcome this limitation, several techniques had been reported in the literature to improve the interaction between PDMS and epoxy matrices with improved thermomechanical properties and toughness, including the introduction of polar functionality to PDMS,[7,19] using silane coupling agents[20,21] and chemical incorporation of PDMS into the main chain of epoxy,[15] however, there still existed some drawbacks in these system, such as the swift decline of the thermomechanical properties' with an increase of the PDMS soft segment.

Introducing silica to form epoxy–silica hybrid through a sol–gel process had also improved the properties of epoxy resin such as toughness, impact strength, tensile strength, and thermal degradation.[23–26] Currently, two approaches of the sol–gel process to prepare epoxy–silica hybrids had been reported including (1) directly mixing epoxy resin with a silicone alkoxide such as tetraethoxysilane (TEOS), organofunctional silane,[23–32] (2) introducing trialkoxy silyl groups into an organic elastomer like polypropylene oxide and urethane[33–36] with organofunctional silane prior to the sol–gel reactions. Compared with the former method, the latter modified epoxy resins had shown a significant increase of mechanical properties such as elongation and peel strength, fracture energy[33–35] due to the presence of elastomer. Especially, tuning of the mechanical properties (i.e., strength from the epoxy and high impact resistance from the elastomer) could be easily achieved by adjusting the ratio and selection of the silylated oligomer and the epoxy resin, so this modified epoxy had appeared promising as new high performance and highly functional materials.

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In our studies, silyl-terminated polycaprolactone (PCL–Si) modified epoxy resin (DGEBA) had also shown excellent adhesion strength and fracture energy when used as an adhesive for coatings, especially, the modified systems had a significant improvement in acid-, and basic-resistance, thermal degradation when a suitable content of PCL–Si was used.[37,38] However, incorporating PDMS into epoxy resin through a sol–gel process has never been reported. It should be much interesting to comodify epoxy resin with PDMS and silica from sol–gel to obtain an optimal performance. Following the previous work,[36] silyl-terminated PDMS (PDMS–Si) was tentatively introduced in this study into epoxy resin through compatibilizing epoxy–immiscible PDMS with epoxy–miscible PCL segments, which were attached through sol–gel process between PDMS–Si and PCL–Si. In this work, the PCL–Si and PDMS–Si blend was prepared using direct nucleophilic addition between —OH groups of polydiol (polycaprolactone diol and α,ω-bis(3-hydroxypropyl)polydimethylsiloxane. The phase structure of modified epoxy resin was compared at different content of PDMS–Si/PCL–Si blend on the basis of scanning electronic microscopy (SEM). The effect of PDMS–Si/PCL–Si blend content on the thermal degradation performance and silicon element distribution of the modified system was also investigated by thermogravimetric analysis (TGA) and energy dispersive spectroscopy (EDS), respectively.

EXPERIMENTAL

Materials

The polycaprolactone diol (PCL 210, M_n = 1000, OH value = 114.1 mg KOH/g, Daicel, Japan), α,ω-bis(3-hydroxypropyl)polydimethylsiloxane (HPDMS, Tego® HSi 2311, OH value = 44.9 mg KOH/g, Degussa), DGEBA (epoxy equivalent ~500 g/Eq, Wuxi resin plant, China), Aradur® 250 (polyamidoamine type curing agent, amine value = 425–455 mg KOH/g, Huntsman, Germany), and isocyanatopropyltriethoxysilane (ICPTES, Shinetsu, Japan), dibutyltin dilaurate (DBTDL, 95%, Aldrich) were all commercial reagents. All other organic solvents, such as xylene, toluene, were analytical reagents, and directly used without purity. 50% (wt/wt) toluene solution of DGEBA was obtained before usage, and xylene/toluene (5/4 v/v) mixture was thoroughly dried with anhydrous $CaCl_2$ or $MgSO_4$.

Synthesis of silyl terminated polycaprolactone–polydimethylsiloxane oligomer (PCS-2Si)

Polycaprolactone diol (PCL 210) and polydimethylsiloxane diol (HPDMS) were mixed at a ratio of 50/10 (wt/wt), and introduced into a 250 mL round bottom flask equipped with a mechanical stirrer, a switchable inlet for argon and a vacuum connector. The mixture was first dried by heating at 100°C for 1.5–2 h under dynamic vacuum. After the temperature of the reactor was then lowered to 65°C under dynamic vacuum, argon was introduced. To this polydiol mixture 200 ppm catalyst DBTDL was added, and a stoichiometric weight of ICPTES was consecutively added drop by drop. After the addition was finished, the mixture obtained was maintained at 65°C under argon atmosphere until all isocyanate groups were completely disappeared through FTIR monitoring. After cooling the resultant to ambient temperature, and while strongly stirring, an amount of dried xylene/toluene (5/4 v/v) mixture was added to obtain a homogeneous 70% (wt/wt) of PCS-2Si solution.

Preparation and curing of modified epoxy resin films

To achieve the high compatibility of the oligomer in DGEBA, the prescribed amounts of epoxy resin solution, as shown in Table I, was premixed with the synthesized oligomer PCS-2Si, and kept at ambient temperature for a week with a continuous magnetic stirring. After then, to the mixture of DGEBA/PCS-2Si, the calculated amounts of Aradur 250 were added. Before casting on Teflon plate, these mixtures were thoroughly stirred. After completely evaporating the solvents, a series of polymer films containing DGEBA and PCS-2Si were obtained. These formed films were cured at ambient temperature for 3 weeks under about 60% relative humidity.

Characterizations

FTIR spectra were monitored with a Magna 750 FTIR Spectrometer. Thirty-two scans and 4 cm^{-1} resolution were used. After spreading out a dilute sample/THF solution on a KBr pallet and spontaneously

TABLE I
The Compositions of PCS-2Si Modified Epoxy Resins

Sample no.	PCS-2Si (g)	Epoxy resin (g)	Aradur 250 (g)
0	0	100.0	19.0
1	10.0	90.0	17.1
2	20.0	80.0	15.2
3	30.0	70.0	13.3
4	40.0	60.0	11.4
5	50.0	50.0	9.5
6	60.0	40.0	7.6
7	70.0	30.0	5.7
8	80.0	20.0	3.8
9	100.0	0	0

evaporating solvent to form a sample film, the IR was done. The morphology of the fractured surface of the sample with a thickness of 1–1.5 mm was carried out with scanning electron microscope (JSM 5600LV SEM). The samples were cooled in liquid nitrogen, fractured with a sharp blow, and the fractured section was coated with gold before examination. 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. The elemental composition of the fracture surfaces was obtained by EDS on a FEI Quanta 600 scanning electron microscope. Before EDS analysis, the sample film was crosscut, then ground and polished with superfine sandpaper of Grit No 600–800, washed with anhydrous ethanol. The thermal stability of the cured composites films was assessed by TGA using a TGA 951 thermal system. For the analysis, films were cut into small pieces, and about 10–20 mg of sample was taken and heated at a constant rate of 10°C/min in nitrogen atmosphere from 25 to 700°C.

RESULTS AND DISCUSSION

Synthesis of triethoxysilyl-terminated polycaprolactone–polydimethylsiloxane oligomer (PCS-2Si)

As previous reported[36], synthesis of silyl-terminated elastomers was directly carried out via nucleophilic addition between —OH groups of polydiol (polycaprolactone diol and α,ω-bis(3-hydroxypropyl)polydimethylsiloxane and —NCO groups of ICPTES (shown in Scheme 1). And DBTDL was chosen as a catalyst to ensure the complete reaction between the —OH and —NCO. Figure 1 shows the IR spectra of the ICPTES, PCL-210/HPDMS mixture and the resultant of PCL-210/PDMS-ICPTES after the reactive mixture was heated for 3.5 h at 65°C under Ar. It was clear that the broad —OH peak at 3400–3600 cm^{-1} of PCL-210/HPDMS and —NCO peak at 2271.7 cm^{-1} of ICPTES had disappeared, but 3378.7 cm^{-1} and 1731.8 cm^{-1} peaks assigned to —NH— and —OCO— of —OCONH— respectively, appeared. This indicated the reaction conversion was complete under the experimental conditions.

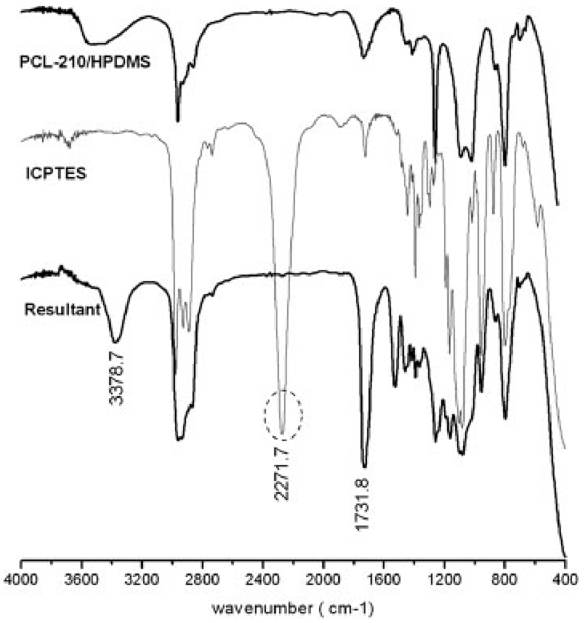
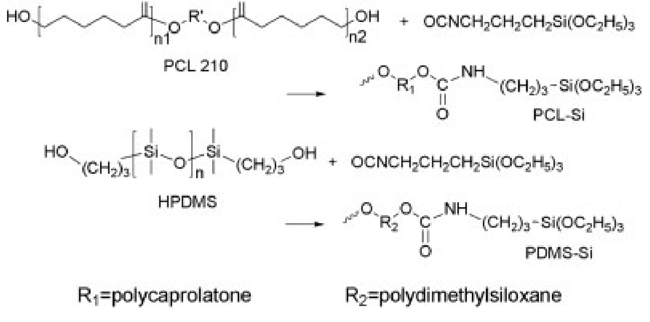


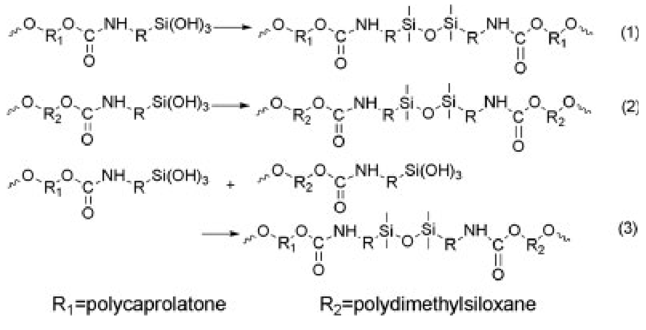
Figure 1 FTIR spectra of ICPTES, PCL-210/HPDMS mixture and the resultant.

Morphologies of the composites

Like PCL–Si modified epoxy resin,[36] here $—Si(OC_2H_5)_3$ of PCL–Si and PDMS–Si would proceed a sol–gel process to produce —SiOH, then condense to —Si—O—Si— as shown in eqs. (1) and (2) in Scheme 2, except the chemical reaction between active hydrogen of Aradur 250 and epoxy group in the composite. However, the —SiOH condensation between —SiOH of PCL–Si and that of PDMS–Si [Eq. (3)] should also take place except eqs. (1) and (2). Furthermore, the chemical reactions, such as —OH from epoxy resin reacting with $—Si(OH)_3$ and —CONH reacting with epoxy group might also occur. Therefore, it could be concluded that there



Scheme 1



Scheme 2

were at least four cured polymers in the composite: amine cured epoxy resin, self-condensed PCL–Si, self-condensed PDMS, and intercondensed PCL–Si/PDMS–Si. So many cured compositions made differentiate the morphologies of PCS-2Si modified epoxy from that of PCL–Si modified epoxy as shown in Figure 2, where indicated the morphologies change with the content of PSC-2Si increasing. Clearly, in Figure 2(A1–A4) ductile-fracture signs, and a bimodal cavity distribution with an irregular and a round shape were found. But Figure 2(A5–A7) showed brittle-fracture signs, and gave completely different morphologies, where the amount of round cavity suddenly decreased in Figure 2(A5), then disappeared in Figure 2(A6,A7).

Compared with PDMS–epoxy resin composites, where difference of solubility parameter value δ between PDMS and epoxy resin could easily cause microscopic and even macroscopic phase separation much easier or exude from the crosslinking matrix during curing procedure; the miscibility difference or morphology of epoxy resin–polycaprolactone depended much on the used curing condition, the blended composition, and even the type of curing agent,[39–45] but a homogeneous phase could be got usually between cured epoxy resin and polycaprolactone at lower blending temperature due to the presence of hydroxyl groups in the amine-cured epoxy, which was capable of forming hydrogen bonds with the PCL ester groups[42]. Similarly, that chemically blocked PCL–PDMS–PCL and pure PCL had a similar compatibility with epoxy resin at lower content (<10%) of PDMS had also been proved[19], so it could be thought here that the intercondensed resultant of silanol between PCL–Si and PDMS–Si would bring out an effect on epoxy in just the same way the self-condensed PCL–Si did, and that the morphology of irregular cavities in Figure 2(A1–A4) should be induced from the pull-out of the cured PCL–Si and intercondensed PCL–Si/PDMS–Si rubber phase, based on the result of the PCL–Si modified epoxy resin.[36] As to the formation and the change of the rubber phase, it could mainly come from the change of the solubility parameter δ value between rubber phase and epoxy resin. It could be understood that the δ value of PCL–Si would be decreased when —$Si(OC_2H_5)_5$ was chemically bonded to PCL, however, the change of δ value would directly affect the dispersion of the rubber phase and its particle size in epoxy phase,[33] so the miscibility and phase separation would be different from pure polycaprolactone blending epoxy resin during the process of curing reaction. Especially, with the advancement of the curing reaction, the silanol polycondensation reaction of ethoxysilyl groups of PCL–Si and PCL–Si/PDMS–Si would take place mainly around the aggregated PCL–Si and PCL–Si/PDMS–Si particles, that is, the crosslinked —Si—O—Si— structure was concentrated around the dispersed phase[36]. Therefore, the aggregated and grown rubber phase would undergo phase separation from irregular epoxy resin continuous matrix, meanwhile, epoxy resin dissolved in PCL via H-bonding also separated from the cured PCL-rich macrophase during curing, forming irregular fractures as shown in Figure 2(A1–A4), that was, a co-continuous morphology with strongly interpenetrating phase domains was formed according to the mechanism combining the Flory–Huggins and Hildebrand equations.[46] However, when PCS-2Si content increased up to 50%, there appeared the spherical particles on the surface of the composite in Figure 2(A5), that is, a combined morphology existed; this was thought to be a result of the phase inversion beginning, where cured PCS-2Si began to form a continuous phase, but cured epoxy to form a dispersion phase. Compared with the aggregated PCL–Si in Figure 2(A1–A4), where PCL was in dispersion phase and difficult to crystallize due to the stronger interaction between PCL–Si and epoxy, the aggregated PCL–Si in Figure 2(A5–A7) was a continuous phase, PCL of which was easy to crystallize, that is, the crystallinity of PCL would improve. Therefore, in the crystallized PCL combined with epoxy resin to form a brittle-fracture phase structure, the brittleness would enhance with increasing the content of PCS-2Si due to the change of crystallinity of PCL as shown in Figure 2(A5–A7).

Regarding the round cavity in Figure 2(A1–A4), it should be a consequence of the agglomeration of the PDMS particles formed from hydrolytic silanol polycondensation rather than aggregation of cured PCS-2Si that come from nucleation and growth (NG) mechanism.[39] This result had been proved with microdomain Si elemental analysis via EDS, of which the Si content in cavity was nearly four times higher than the other in PCS-2Si/Epoxy (1 : 1 wt/wt) cured at 50°C.[47] It was well known that PDMS had much lower solubility parameter δ value, that is, the greater δ value difference among epoxy, PCL–Si and PDMS made the self-cured PDMS–Si aggregate much easily, and then phase separation took place from the cured epoxy and cured PCL–Si. But increasing the content of PCS-2Si, that is, decreasing the content of epoxy resin, resulted in an increase in the number of urethanes per unit chain of polymeric resin, causing to strengthen the interaction between cured epoxy and condensed PDMS; that is, the improved interaction enhanced the miscibility between them, so the amount of cavity decreases, and even disappears as shown in Figure 2(A5–A7).

To provide direct evidence for the effect of phase inversion on the morphologies of the cured system with increasing contents of PCS-2Si, sample No. 3 and No. 7 films were selected for TEM analysis

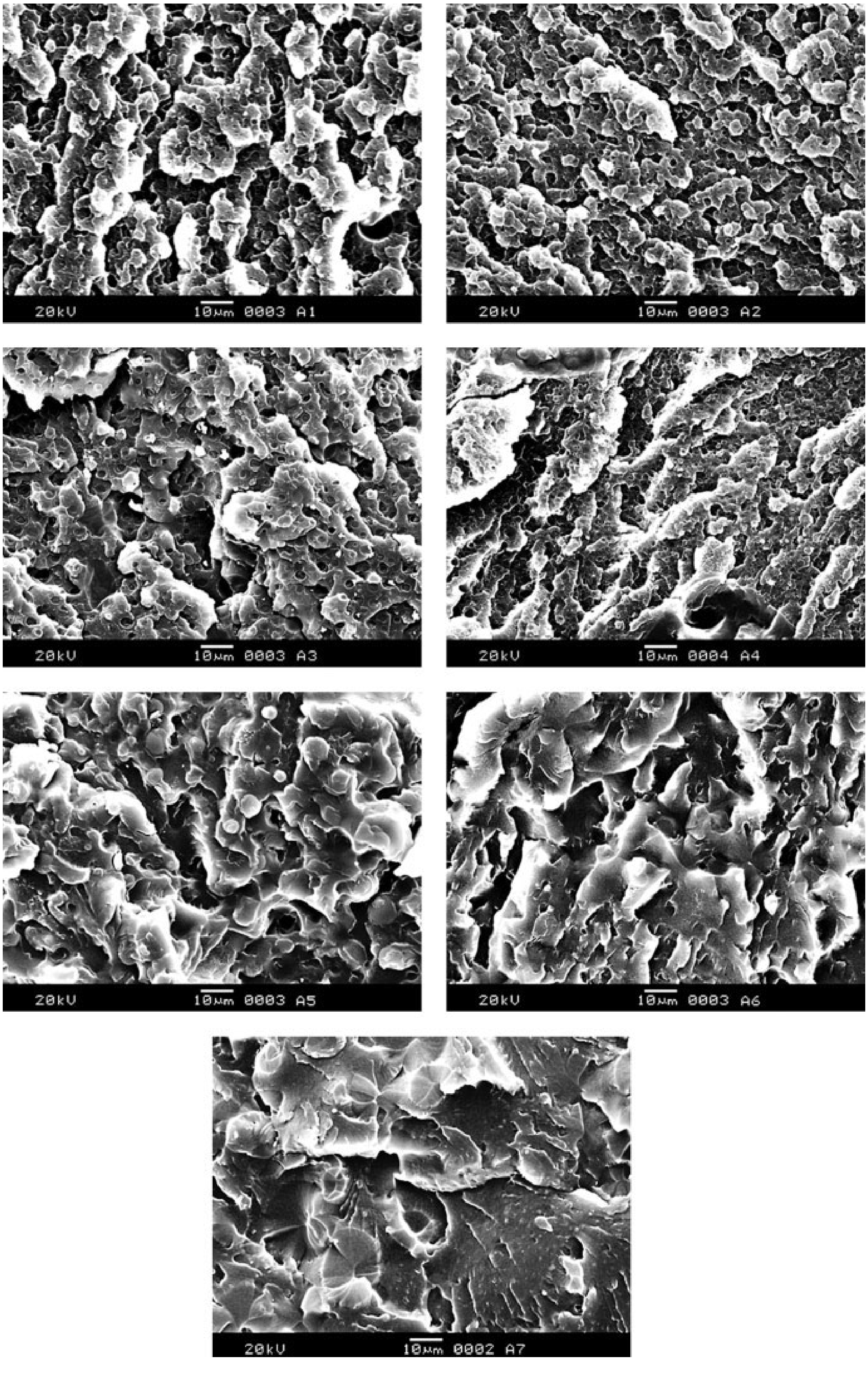


Figure 2 SEM micrographs of PCS-2Si modified epoxy resin with various PCS-2Si contents: (A1) 10%; (A2) 20%; (A3) 30%; (A4) 40%; (A5) 50%; (A6) 60%; (A7) 70%.

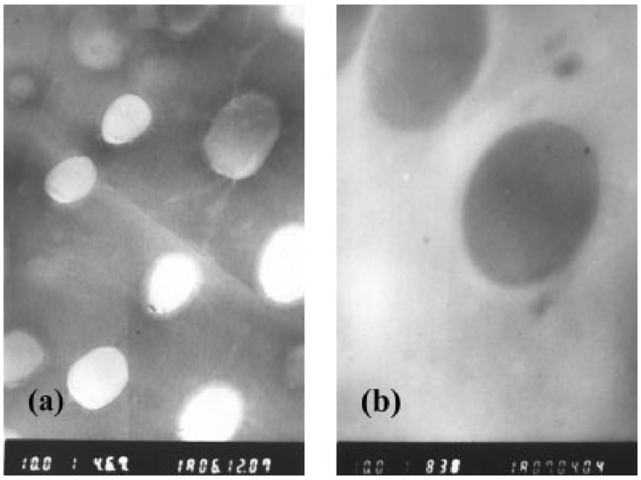


Figure 3 TEM micrographs of PCS-2Si modified epoxy resin with PCS-2Si content of (a) 30% and (b) 70%.

(seen in Fig. 3). In Figure 3(a), the white round particle (PDMS) constituted a dispersed phase, but black particles (epoxy resin) dispersed in continuous phase in Figure 3(b). Although there was nearly no clear phase separation between cured epoxy and cured PCL–Si or/and PCL–Si/PDMS–Si in this magnification size, some irregular white strips and faint particles could be still seen in Figure 3(a), indicating the presence of another phase, that was the —Si—O—Si— of PCL–Si and PCL–Si/PDMS–Si. And also, the interface of the continuous phase and the dispersed (strip and particle) was faint; this indicated that PCL–Si, PDMS–Si, and PCL–Si/PDMS–Si could have an interaction with epoxy resin.

Thermal properties of the composites

TGA was a technique used to measure changes in the mass of a sample as a function of temperature and/or time. The mass loss of the cured composites at different temperatures and the initial and the peak decomposition temperatures was evaluated from the respective TG and DTGA thermograms. Figure 4 shows the thermal decomposition of these polymers. The difference in degradation behavior of the epoxy resins containing various contents of PCS-2Si, which were difficult to distinguish just from TGA curves, could be clearly read from the DTGA (first derivative of thermal gravimetric analysis curve vs. temperature) thermograms. It revealed in DTGA that all mixtures had several peaks whose intensity depended on blend composition, which were attributed to several different degradation stages. The temperatures at the maximum weight loss rate ($T_{\max}$) and the value of the maximum weight loss rate ($R_{\max}$) for every stage of weight loss were read from the peak values of the DTGA thermograms, and listed in Table II.

For cured PCS-2Si, a three-stage degradation was observed: an early stage with a maximum rate at about 263.6°C, assigned to the simple depolymerization of urethane bonds; and a second stage with a maximum rate at about 392.8°C, assigned to the PCL chain scission,[48] the third stage at 492.6°C, assigned to the PDMS decomposition. Clearly, the urethane and PCL degradation temperature was higher than that of PCL in epoxy–PCL system; this relatively high thermal stability was explained with reference to the presence of —Si—O—Si— inorganic network

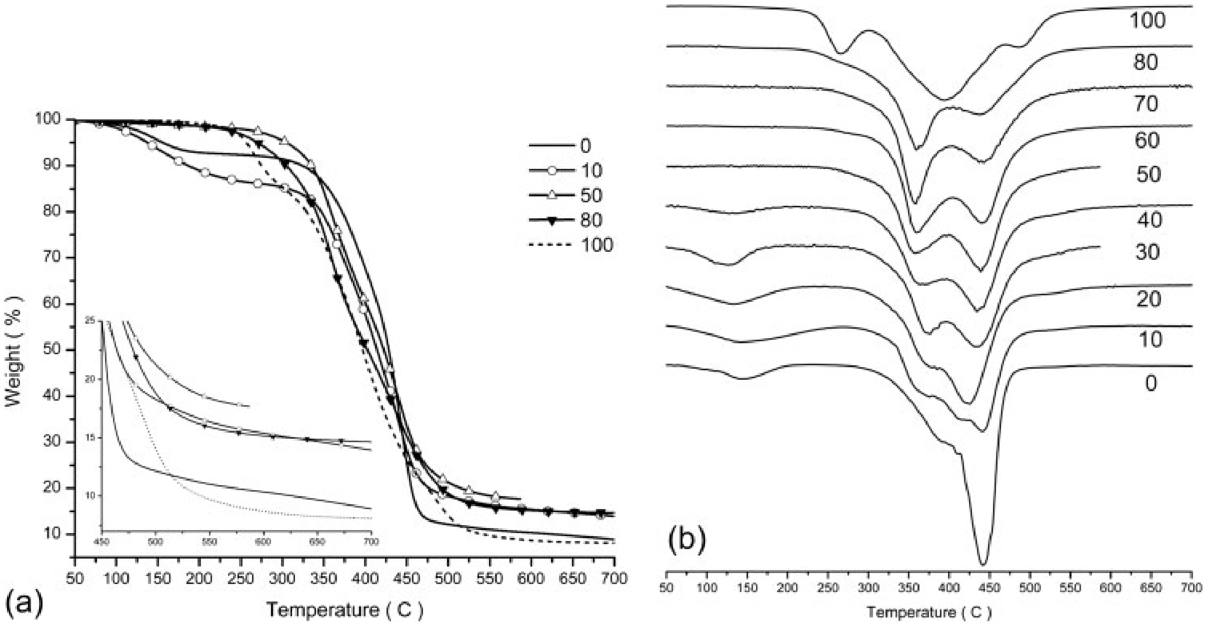


Figure 4 Dynamic thermograms of the modified epoxy resin materials (a) and first derivative curves of the dynamic thermograms of the materials (b) in nitrogen. (Numbers on the curves correspond to PCS-2Si content (wt/wt).

TABLE II
Thermal Stability and Degradation Data of the Modified Epoxy Resins from Thermogravimetrtic Analysis in Nitrogen

PCS-2Si content (wt %)	T^1_{max}(°C)	R^1_{max}(%/°C)	T^2_{max}(°C)	R^2_{max}(%/°C)	T^3_{max}(°C)	R^3_{max}(%/°C)	$T^{5\%}_{\mathrm{d}}$(°C)
0	144.8	0.094	389.5	0.46	441.7	1.21	155.8
10	142.0	0.11	361.2	0.38	410.2	0.56	137.6
20	132.9	0.12	366.6	0.45	426.5	0.72	123.4
30	125.5	0.13	369.4	0.53	439.0	0.61	124.1
40	130.1	0.05	363.6	0.48	442.2	0.64	230.2
50			361.4	0.53	439.4	0.64	304.9
60			358.6	0.64	440.4	0.59	308.5
70			358.9	0.71	443.1	0.46	298.0
80			359.0	0.62	445.0	0.41	270.2
100	263.6	0.29	392.8	0.56	492.6	0.25	256.7

come from PDMS and condensation of —Si$(OC_2H_5)_3$, because bond dissociation energy of Si—O was higher than that of C—C and C—O.

For unmodified epoxy resin, the weight loss mainly occurred in three stages: an initial weight loss followed a great final weight loss. The first decrease in weight occurred at 144.8°C, most likely corresponded to the thermal decomposition of the species related to the epoxy rings in structures, the second drop (shoulder) in weight at 389.5°C might correspond to the thermal decomposition of the remaining organic structure;[49] the third at 441.7°C was likely attributed to the carbonization of epoxy structure. But for modified epoxy, a very different degradation behavior was observed and different numbers of weight loss stages were found, where a gradual decrease of the T^1_{max} was observed when PCS-2Si content was up to 30% (seen in Table II), and their weight loss for neat epoxy, 10, 20, and 30% composite were 3.98, 5.48, 6.11, and 5.18%, respectively. The main factor for this decrease was thought to be the relative dilution of epoxy crosslinks in the structure with increasing PCS-2Si content[38], because a decrease in crosslink density would decrease the thermal stability[22]. Although introducing —Si—O—Si— in the composites could delay theoretically the degradation of the composite, the content of Si was too low to protect the organic component from heat. These also resulted in a slight increase of weight loss rate R^1_{max} from 0.11 to 0.13. Then, with increasing PCS-2Si content to 40%, the formed silica from heating was enough to serve as a heat barrier to protect the inner layer of the polymer, resulting in the great decrease of T^1_{max} to 0.05 and an increase of T^1_{max} to 130.1°C (seen in Table II), at which only 2.2% weight loss was obtained. Again, T^1_{max} completely disappeared upon addition of 50% PCS-2Si content in the first derivate curve of the materials. This change had a good consistence with the morphology change mentioned as above, where phase inversion began, but whether there existed a relation between them could not concluded here.

For PCS-2Si modified epoxy resins, the second and the third decomposition stages in DTGA thermograms were their main degradation, which were basically similar, and located at 300–500°C, corresponding to the cleavage of polymer chains. From the curves, it could be seen that the PCS-2Si content had no significant influence on the decomposition temperature, although there existed a slight difference of R^2_{max} and R^3_{max} due to the change of PCS-2Si content. Clearly, introducing PCS, PDMS, and condensed Si—O—Si into epoxy resins caused the second and third stage weight loss to shift to lower temperature, when compared with pure cured PCS-2Si and neat cured epoxy resin, that is, incorporating PCS-2Si into epoxy resin altered the composites' thermal stability and degradation characteristics. These phenomena were thought to be resulted from the presence of urethane bond in the phase structures, as urethane moiety had low thermal stability. From the curve of pure cure PCS-2Si, the urethane bond was much easily decomposed than PCL, epoxy, and PDMS did when heated. Compared with pure cured PCS-2Si, where there only existed the —Si—O—Si— network, with a relatively lower crosslinked density, the network density of modified epoxy was higher because of the presence of much dense crosslinked network, such as —Si—O—Si—, epoxy–amine and H-bond, so the heat energy from urethane bond decomposition of the composite had a relatively lower dispersion rate than that of pure cured PCS-2Si, that is, the heat could not disperse immediately, causing the molecular chain in the structure to take scission at a lower temperature. Of course, the decrease of T^2_{max} and T^3_{max} might also be the consequence of the decrease of the crosslinked network density of the composite with increasing the content of PCS-2Si. The effect from urethane bond and —Si—O—Si— decomposition could be found in Figure 4(b), where the peak width of T^2_{max} and T^3_{max} gradually increased with the increased loading of PCS-2Si.

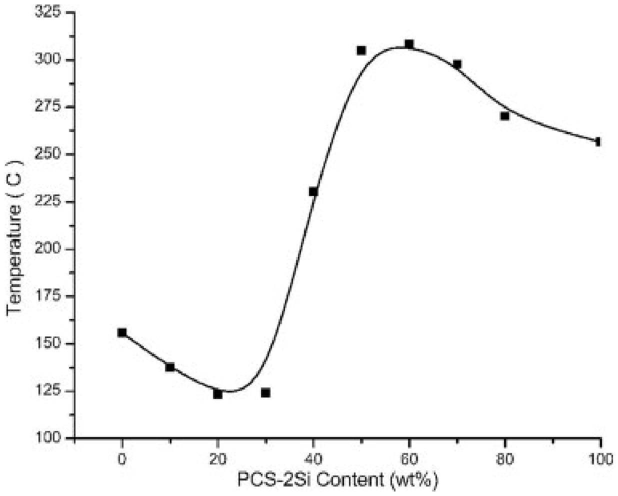


Figure 5 Thermal degradation temperature at 5% weight loss versus PCS-2Si content in modified epoxy resin.

The temperature $T_d^{5\%}$, at which 5% weight loss occurred, was also investigated to further assess the thermal stability of the composite materials with various contents of PCS-2Si as shown in Figure 5. It could be found the composite containing 50–60% (wt %) PCS-2Si had a highest temperature value at 5% weight losses. The reason, it was thought here, could be concluded when the effects were integrated from crosslinked density, urethane decomposition, silica's protection and so on as above.

EDS analysis of cured films

EDS was a useful tool to analyze the elemental distribution. Here, sectional Si distribution of cured film was selectively analyzed with EDS via scanning from the top layer to bottom layer as shown in Figure 6, where Si content was shown as pale dot. It was interesting to note that the cured film had a homogeneous Si distribution when the PCS-2Si was added at a lower content as shown in Figure 6(A1,A2). But when PCS-2Si content was increased up to 60%, the film had a slight ladder-like distribution of Si contents, where Si content gradually decreased from the top to bottom as shown

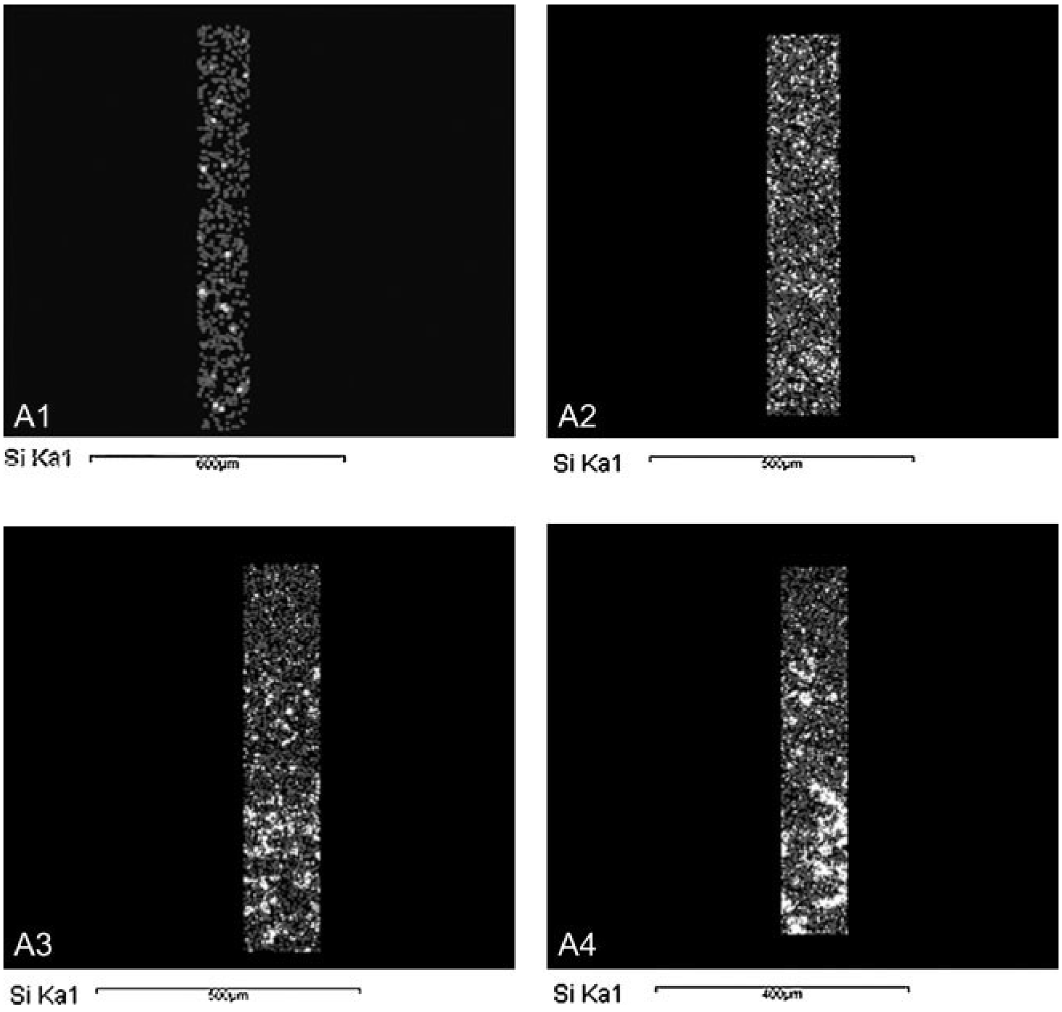


Figure 6 Relative Si distribution status in cured film at different PCS-2Si: (A1)10%; (A2) 50%; (A3) 60%; (A4) 70%.

in Figure 6(A3,A4). From these, it could be concluded that the PDMS did not rise up to the top layer of viscous epoxy resin during sample preparation and curing at lower content of PCS-2Si. Instead, it spread generally over the whole specimen. The fixation of the PDMS was therefore due to the chemical linkage between PCL–Si and PDMS–Si (as shown in Eq. (3) in Scheme 2), and to the H-bond between —CONH of PDMS–Si and —OH of epoxy. The slight inhomogeneous distribution of Si element, that is, a slight enrichment, at a higher content of PCS-2Si was thought to be the effect of low surface tension and surface energy of PDMS, although there also existed chemical and H-bond interaction.

CONCLUSIONS

A blend of PCL–Si and silyl-terminated polydimethylsiloxane (PDMS-Si), that was PCS-2Si, was prepared using direct nucleophilic addition between —OH groups of polydiol and —NCO of a silane, and characterized by FTIR. A series of epoxy resin composites containing different contents of PCS-2Si were prepared by the sol–gel process and amino-glycidyl reaction. The morphology and thermal stability of the composite system was characterized as a function of PCS-2Si content. It was shown that the compatibility between epoxy and PDMS increased with increasing content of PCS-2Si, but higher content of PCS-2Si would result in a slight enrichment of silicon in the surface of the cured film. Likewise, synergic effects from urethane bond, —Si—O—Si— bond and others resulted in incorporating PCS-2Si into epoxy resin to alter the composites' thermal stability and degradation characteristics, but the composite containing 50–60% (wt/wt) PCS-2Si had a highest temperature value at 5% weight loss, reaching to 308.5°C.

References

1. Hou, S. S.; Chung, Y. P.; Chan, C. K.; Kuo, P. L. Polymer 2000, 41, 3263.
2. Longuet, L. B.; Bonnet, A; Pichot, C.; Sautereau, H.; Maazouz, A. J Appl Polym Sci 1999, 72, 849.
3. Sankaran, S.; Chanda, M. J Appl Polym Sci 1990, 39, 1459.
4. Oprea, S.; Vlad, S.; Staciu, A.; Macoveanu, M. Eur Polym Mater 2000, 36, 373.
5. Mahesh, K. P. O.; Alagar, M. J Appl Polym Sci 2003, 87, 1562.
6. Mahesh, K. P. O.; Alagar, M.; Anandakumar, S. Polym Adv Technol 2003, 14, 137.
7. Rey, L. J Mater Sci 1999, 34, 1775.
8. Alagar, M.; Thanikaivelan, T. V.; Ashokkumar, A. J Polym Comp 2000, 21, 739.
9. Chojnowski, J.; Cypryk, M.; Fortuniak, W.; Rozga-Wijas, K.; Scibiorek, M. Polymer 1993, 2002, 43.
10. Wu, C. S.; Liu, Y. L.; Chiu, Y. S. Polymer 2002, 43, 4277.
11. Kambour, R. P. J Appl Polym Sci 1981, 26, 861.
12. Lin, S. T.; Huang, S. K. J Polym Sci Part A: Polym Chem 1996, 34, 869.
13. Hsiue, G. H.; Wang, W. J.; Chang, F. C. J Appl Polym Sci 1999, 73, 1231.
14. Shih, W. C.; Ma, C. C. M. J Appl Polym Sci 1998, 69, 51.
15. Ahmad, S.; Gupta, A. P.; Sharmin, E.; Alam, M.; Pandey, S. K. Prog Org Coat 2005, 54, 248.
16. Matsukawa, K.; Hasegawa, K.; Inoue, H.; Fukuda, A.; Arita, Y. J Polym Sci Part A 1992, 30, 2045.
17. Ahmad, S.; Ashraf, S. M.; Nusrat, S. N.; Hsanat, A. J Appl Polym Sci 2005, 95, 494.
18. Zafar, F.; Sharmin, E.; Ashraf, S. M.; Ahmad, S. J Appl Polym Sci 2005, 97, 1818.
19. Konczol, L.; Doll, W.; Buchholz, U.; Mulhaupt, R. J Appl Polym Sci 1994, 54, 815.
20. Alagar, M.; Kumar, A. A.; Prabu, A. A.; Rajendran, A. Intl J Polym Mater 2004, 53, 45.
21. Anand, A.; Alagar, P. M. J Macromol Sci Part A: Pure Appl Chem 2005, 42, 175.
22. Ahmad, S.; Ashraf, S. M.; Sharmin, E.; Mohomad, A.; Alam, M. J Appl Polym Sci 2006, 100, 4981.
23. Lu, S. R.; Zhang, H. L.; Zhao, C. X.; Wang, X.Y. J Mater Sci 2005, 40, 1079.
24. Macan, J., Brnardic, I.; Orlic, S.; Ivankovic, H.; Ivankovic, M. Polym Degrad Stab 2006, 91, 122.
25. Ochi, M.; Matsura, T. J Polym Sci Part B: Polym Phys 2005, 43, 1631.
26. Innocenzi, P.; Kidchob, T. J Sol–Gel Sci Technol 2005, 35, 225.
27. Khramov, A. N.; Balbyshev, V. N.; Voevodin, N. N.; Donley, M. S. Prog Org Coat 2003, 47, 207.
28. Chiang, C. L.; Chang, R. C.; Chiu, Y. C. Thermochim Acta 2007, 453, 97.
29. Vreugdenhil, A. J.; Woods, M. E. Prog Org Coat 2005, 53, 119.
30. Prezzi, L.; Mascia, L. Adv Polym Technol 2005, 24, 91.
31. Bauer, F.; Glasel, H.; Hartmann, E.; Langguth, H.; Hinterwaldner, R. Int J Adhesion Adhesive 2004, 24, 519.
32. Hass, K. H.; Rose, K. Rev Adv Mater Sci 2003, 5, 47.
33. Okamatsu, T.; Ochi, M. Polymer 2002, 43, 721.
34. Okamatsu, T.; Kitajima, M.; Hanazawa, H.; Ochi, M. J Adhes Sci Technol 1998, 12, 813.
35. Okamatsu, T.; Kitajima, M.; Hanazawah, H.; Ochi, M. J Adhes Sci Technol 1999, 13, 109.
36. Liu, P. G.; He, L. H.; Ding, H. Y.; Liu, J. N.; Yi, X. S. J Appl Polym Sci 2005, 97, 611.
37. Tang, Z. F.; Liu, P. G.; He, L. H.; Liang, X. Q.; Lin, B. F. J Mater Eng (Cai Liao Gong Cheng) 2005, 7, 47 (in Chinese).
38. He, L. H.; Liu, P. G.; Ding, H. Y. J Adhesion Interface 2006, 7, 32.
39. Chen, J. L.; Chang, F. C. Polymer 2001, 42, 2193.
40. Remiro, P. M.; Cortazar, M.; Calahorra, E.; Calafei, M. M. Polym Degrad Stab 2002, 78, 83.
41. Yin, M.; Zheng, S. Macromol Chem Phys 2005, 206, 929.
42. Chen, J. L.; Chang, F. C. J Appl Polym Sci 2003, 89, 3107.
43. Remiro, P. M.; Cortazar, M. M.; Calahorra, M. E.; Calafel, M. M. Macromol Chem Phys 2001, 202, 1077.
44. Chen, J. L.; Huang, H. M.; Li, M. S.; Chang, F. C. J Appl Polym Sci 1999, 71, 75.
45. Ni, Y.; Zheng, S. Polymer 2005, 46, 5828.
46. Ratna, D. J Adhes Sci Technol 2003, 17, 1655.
47. Song, J. X. Preparation and Properties of Polycaprolactone/Polysiloxane/Epoxy Resin Composites, Master's Dissertation, Guangxi University, China, 2007.
48. Yeganeh, H.; Lakouraj, M. M.; Jamshidi, S. J Polym Sci Part A: Polym Chem 2005, 43, 2985.
49. Copuroglu, M.; O'Brien, S.; Crean, G. M. Polym Degrad Stab 2006, 91, 3185.