

Properties of Alkoxysilane Functionalized Polycaprolactone/Polydimethylsiloxane-Modified Epoxy Resin Composites: Effect of Curing Temperature and Compositions

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ABSTRACT: A series of epoxy resin composites containing different contents of alkoxysilane functionalized polycaprolactone/polydimethylsiloxane (PCS-2Si) were prepared after curing with polyamidoamine curing agent at different temperatures. The effects of PCS-2Si content and curing temperature on morphologies, solvent resistance, and surface properties of the composites were studied. The scanning electron microscope results showed that increasing the PCS-2Si content and curing temperature caused the changes of miscibility between epoxy and modifier, leading to different morphologies. Other data from solvent swelling and surface tension of composites

cured at the same temperature illustrated that the modified epoxy resins with higher content of PCS-2Si had less crosslinked networks, but lower surface tension. At the same time, the composites cured at higher curing temperature generally had more resistance to chemicals and higher surface tension due to the formation of highly crosslinked networks. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 811–817, 2009

Key words: polycaprolactone; polydimethylsiloxane; epoxy resin; morphology; solvent swelling; chemical resistance; surface properties

INTRODUCTION

As thermoset polymers, epoxy resins—which are characterized by low shrinkage, ease of cure and processing, excellent moisture, solvent, and chemical resistance, and good adhesive strength—are widely employed as the matrix material for high-performance materials. However, their shortcomings are low fracture energy, low thermal stability, low pigment holding ability, poor hydrophobicity, and weathering and impact strength, which restrict their wide application in the field of coatings and paints.¹ To improve these properties, while at the same time retaining other properties, a second component such as the thermoplastics of PEEK, polyester and polyurethane, and the familiar reactive liquid rubber have been reported.² Recently, the introduction of siloxanes as modifiers to epoxy resins is attracting more researchers in this field.^{1,3,4} Some unique characteristics of siloxane structures, such as low surface tension, good low temperature flexibility, nonflammability, and high resistance to thermal oxidation, could perhaps render them useful as epoxy modi-

fiers. But, there arise the questions of functionality and also the miscibility or solubility of such hydrophobic non-polar materials in the typically aromatic-based epoxy precursor. Several techniques were reported in the literature, including using silane coupling agents^{5,6} and chemically incorporating polydimethylsiloxane (PDMS) into the main chain of epoxy to form the interpenetrating network,^{1,7} but there still existed some drawback in these modified systems, such as the thermo-mechanical properties declining swiftly with an increase of the PDMS soft segment.

In our previous paper,⁴ alkoxysilane-functionalized PDMS was tentatively introduced into epoxy resin through compatibilizing epoxy-immiscible PDMS with epoxy-miscible polycaprolactone (PCL) segments, which were attached to each other through a sol-gel process. It was experimentally shown that the compatibility between epoxy and PDMS increased with increasing content of alkoxysilane-functionalized PDMS/PCL (PCS-2Si). Compared with conventional epoxy resin, the thermal stability and degradation characteristics of the modified systems were greatly altered due to the incorporation of PCS-2Si into epoxy resin. To follow up on this work, here some properties of these systems, such as morphologies, solvent resistance, and

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TABLE I
List of Raw Materials Used in the Preparation of the Composites

Designation	Chemical description	Suppliers
PCL	Polycaprolactone diol, PCL 210, OH value = 114.1 mg KOH/g	Daicel, Osaka, Japan
HPDMS	α , ω -Bis(3-hydroxypropyl)polydimethylsiloxane (Tego® HSi 2311, OH value = 44.9 mg KOH/g)	Degussa, Germany
ICPTES Aradur® 250	Isocyanatopropyltriethoxysilane Polyamidoamine type curing agent, amine value = 425–455 mg KOH/g	Shinetsu, Tokyo, Japan Huntsman, Germany
DGEBA	Diglycidyl ether of bisphenol A epoxy resin, epoxide equivalent weight: \sim 500 g/equiv	Wuxi Resin Plant, Wuxi, China
DBTDL	Dibutyltin dilaurate, 95%	Aldrich, St. Louis, MO

surface properties, and the effects of curing temperature, are reported and compared by conventional methods including scanning electron microscope (SEM) and contact angle.

EXPERIMENTAL

Materials

The raw materials used in this study are presented in Table I. All other organic solvents were used as received. 50% (wt %) toluene solution of DGEBA was obtained before usage. Silyl-terminated PCL-PDMS oligomer (PCS-2Si) was synthesized by reacting PCL/HPDMS (5/1, wt/wt) with ICPTES in the presence of catalyst DBTDL according to previously reported procedure,⁴ as shown in Scheme 1. A homogeneous 70% (wt %) of PCS-2Si in dried xylene/toluene (5/4, v/v) was obtained.

Preparation and curing of modified epoxy resin composite films

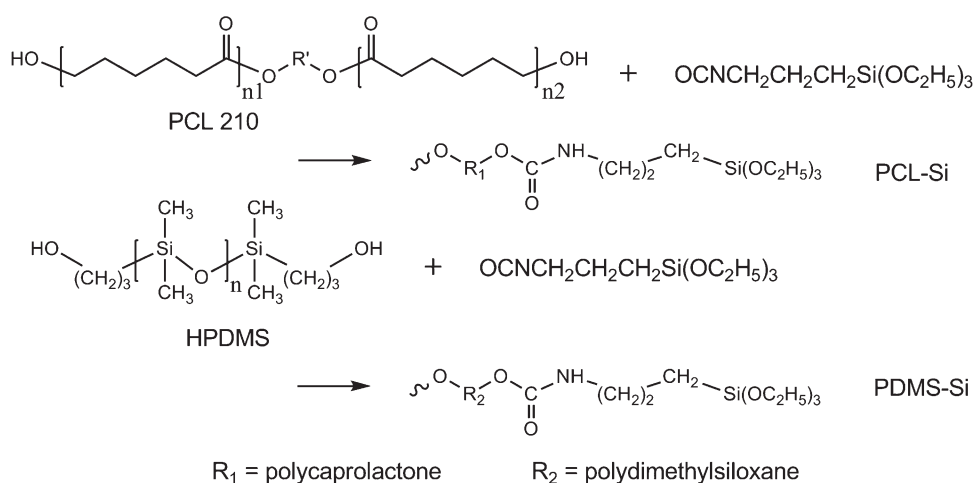
To prepare the films, the calculated amounts of DGEBA and PCS-2Si were weighed into a beaker and kept at ambient temperature for a week with a

continuous magnetic stirring. To the DGEBA/PCS-2Si system, varying ratios of Aradur 250 were added according to their stoichiometric equivalents. The compositions are given in Table II. After continuous stirring, the mixture was poured into a Teflon mold, and solvent was completely evaporated to obtain a series of polymer films containing DGEBA and PCS-2Si. The formed film was cured in the following conditions: (1) at ambient temperature for 2 weeks, and (2) in an oven at 50°C for 1 week. They were named System I and System II, respectively. The mold was cooled to get a cured sheet with a thickness of 1–1.5 mm and cut into suitable dimensions for testing.

Characterizations

Morphology of the fractured surface of the sample was carried out with a JSM 5600LV SEM. The samples were cooled in liquid nitrogen and fractured with a sharp blow, and the fractured sections were first sputtered with gold before examination.

Surface tension determination was obtained through contact angle measurements with a series of solvents having different surface tension by applying the Owens and Wendt method⁸ on contact angle values. Here, contact angles were measured with an



Scheme 1 Preparation of PCS-2 Si.

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

Sample no.	PCS-2Si (g)	DGEBA (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

OCA 20 Contact Angle System (Dataphysics Instruments GmbH, Germany) at room temperature, and the probe liquids were water and formamide (HCONH_2). The results were the mean value of five replicates.

Solvent swelling degree was determined by taking a definite weight (m_d , about 0.5 g) of the dry sample and introduced into CaCl_2 -dried toluene for 7 days at 25°C . The excess solvent was removed by gentle cleanse with a laboratory tissue. The swelled sample was weighed m_s , which included the mass of the solvent absorbed. The swelling degree (Δm) of each sample was expressed as the amount of absorbed solvent per 100 g of dry sample, calculated as:

$$\Delta m (\%) = \frac{(m_s - m_d)}{m_d} \times 100$$

Chemical resistance of cured specimens was performed in distilled water, acid (10 wt % H_2SO_4), alkali (10 wt % NaOH), and salt (10 wt % NaCl) solutions. Samples with a size of $30 \times 30 \text{ mm}^2$ were weighed (m_i) and immersed in aforementioned solution of 250 mL in sealed bottles at 50°C . After 7 days, all of the samples were taken out of the solutions, cleaned with water stream, and continually soaked in water for 1 week to remove all of the salt in the sample. Then samples were dried under dynamic vacuum for 24 h at ambient temperature and weighed again (m_s). Weight change (Δm) used to indicate the chemical resistance of all samples was determined by using the following equation:

$$\Delta m (\%) = \frac{(m_s - m_i)}{m_i} \times 100$$

RESULTS AND DISCUSSION

Morphologies of the composites

The microstructure of composite was dependent on the interactions between the continuous phase and the dispersion phase. It had been reported⁴ that

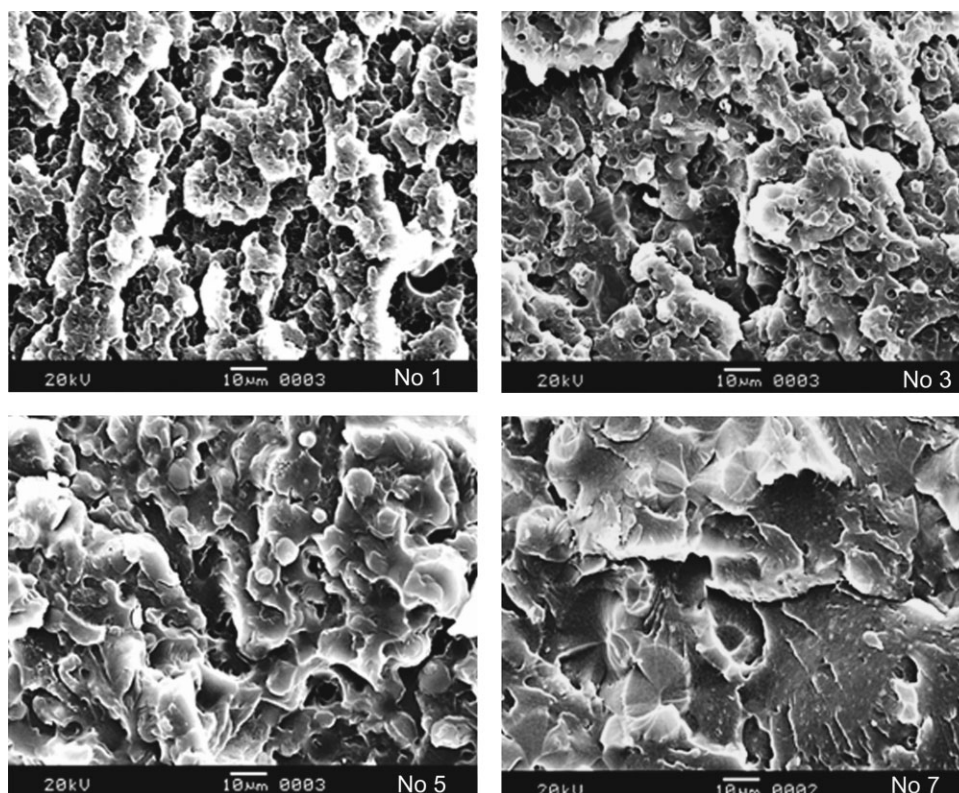


Figure 1 SEM micrographs of PCS-2Si modified epoxy resin with various PCS-2Si contents cured at room temperature: (A1) 10%, (A3) 30%, (A5) 50%, and (A7) 70%.

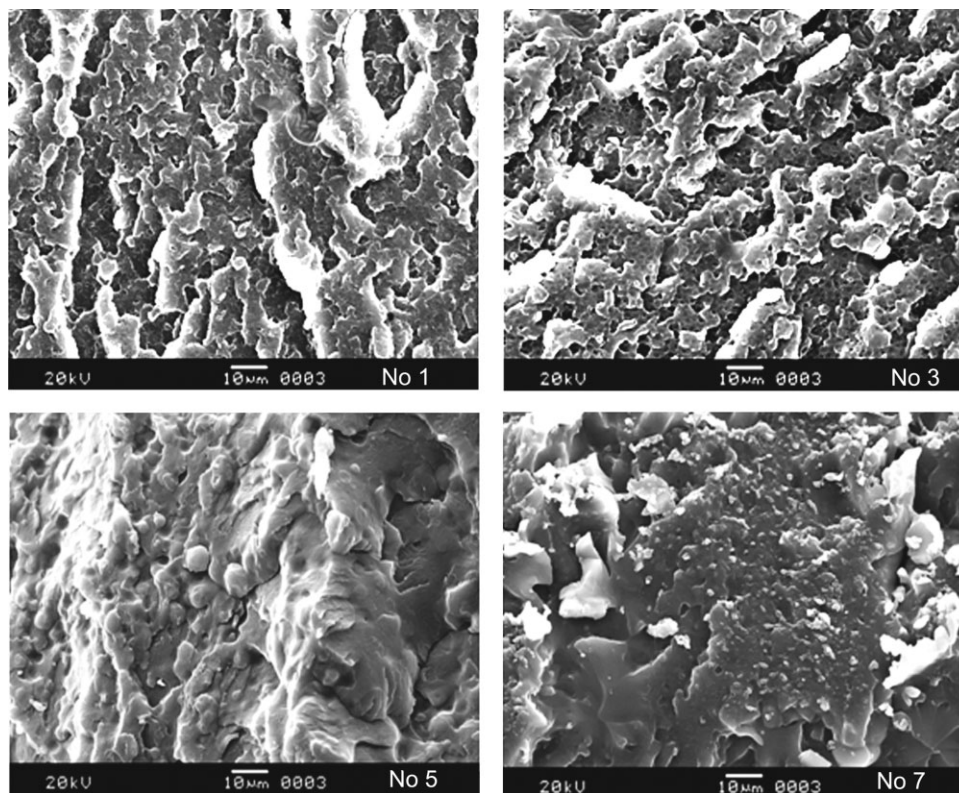


Figure 2 SEM micrographs of PCS-2Si modified epoxy resin with various PCS-2Si contents cured at 50°C: (A1) 10%, (A3) 30%, (A5) 50%, and (A7) 70%.

there was a distinct two-phase structure in PCS-2Si modified epoxy resin composites, due to the difference of polarity among the blends and their interactions, and that content of PCS-2Si in modified epoxy composites had greater effect on the morphological properties of the composites. Figures 1 and 2 selectively showed the morphologies of Samples 1, 3, 5, and 7 of Systems I and II, respectively. Distinctly, like the morphologies, Samples 1 and 3 of System I and Samples 1 and 3 of System II also had ductile fracture signs, where cured PCS-2Si-rich emerged as dispersion phase with irregular cavities and round-shaped distributions.⁴ However, the dispersion domain size of Samples 1 and 3 of System II was significantly smaller than that of Samples 1 and 3 of System I, indicating an improved dispersion of cured PCS-2Si-rich phase in cured epoxy continuous phase. Similarly, when the content of PCS-2Si increased to 50%, where phase inversion began,⁴ epoxy-rich dispersions in Samples 5 and 7 of Figure 2 were more combined with PCS-2Si-rich phase than that in Figure 1, leading to less ductile-fracture signs. These data showed that the curing temperature also had a great effect on the morphologies of the composites. This could be explained as follows. It had been reported in our early reports^{2,4} that there existed the following processes in silyl-terminated polycaprolactone modified epoxy resins

and PCS-2Si modified epoxy with lower content of PCS-2Si: epoxy curing, rubber modifiers aggregating induced by sol-gel process, and aggregated and grown rubber phase undergoing phase separation from cured epoxy resin due to the miscibility difference. Clearly, curing temperature would have great effects on these processes. It had been shown^{9,10} that a relatively homogeneous morphology could be obtained at a higher temperature due to the increased curing rate of epoxy resin. But, on the other side, higher temperature also led to easier diffusion of all components and simultaneously accelerated the sol-gel process, making PCS-2Si undergo phase separation much more easily. Therefore, the size of dispersion phase would be determined by the synergetic competition between the rate of the curing and rate of modifier diffusion and aggregation during the process of phase transformation.^{11,12} When curing rate of epoxy resin was the dominant factor, the dispersion domain size would be smaller, because the cured epoxy resin networks formed at a higher rate not only limited the diffusion of PCS-2Si, but also limited the diffusion and then aggregation of PCS-2Si phase formed in small size effectively. So, Samples 1 and 3 of System II had significantly smaller dispersion domain size than those of System I in Figure 1. Similarly, the Samples 5 and 7 of System II had more homogeneous

morphologies because the curing rate of epoxy resin controlled predominantly the phase transformation. Of course, the improved miscibility for System II might benefit partly from the fact that there existed possibly more chemical interaction between epoxy resin and PCS-2Si chain, such as epoxy group reacting urethane of PCS-2Si.

Solvent swelling properties

As one method used to determine the crosslink densities of crosslinked thermoset materials, a swelling test was always performed to qualitatively evaluate the crosslinked density.^{13,14} Generally, highly crosslinked structures took up less solvent than lightly crosslinked ones,^{15,16} as more limited space and pathways were available for solvent molecules to diffuse within the former structure.¹⁷ Figure 3 showed the dependence of the swelling value Δm versus the PCS-2Si content of the different systems, respectively. Clearly, Δm value of the two systems increased with increase of the PCS-2Si content, indicating that increasing PCS-2Si contents significantly increased the coefficient of solvent expansion and decreased the crosslinked network density of the cured modified epoxy resins. These were because there were much more of soft $-C-O-$ and $-Si(CH_3)_2-O-Si-$ chain when higher content of PCS-2Si was introduced, as soft chains, especially $-Si(CH_3)_2-O-Si-$, much favored the solvents diffusing and absorbing within the network due to decreased crosslinked density.³ When the curing temperatures were compared, Δm value of System I was significantly larger than that of System II, especially for higher content of PCS-2Si, implying

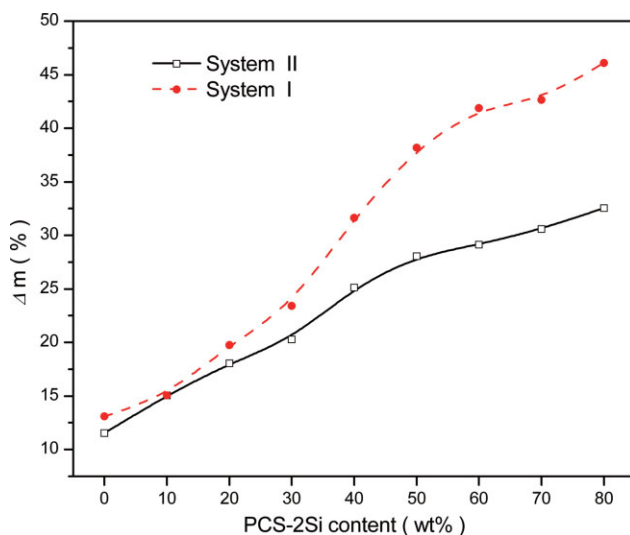


Figure 3 Solvent swelling data of the composites cured at different curing temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

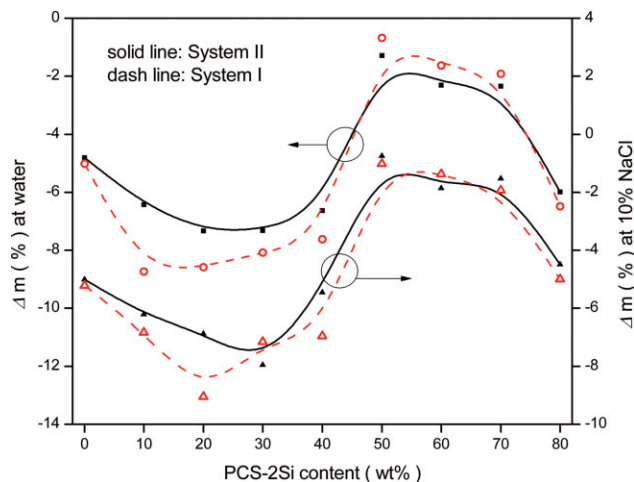


Figure 4 Chemical resistances data of the composites cured at different curing temperature after immersed in water and 10% NaCl for 7 days at 50°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

that System I had less crosslinked density than System II at same content of PCS-2Si. These data might come from the following factors: (1) aggregated PCS-2Si particles in System II were more diffused than that in System I (shown as Figs. 1 and 2), reducing the amount of solvent absorbed within aggregated PCS-2Si; (2) higher temperature favored the formation of denser networks through much chemical interactions, such as epoxy reacting with urethane of PCS-2Si chain and epoxy resin with curing agent. The latter interaction could be verified from the fact that Δm of neat epoxy resin in System II was smaller than that in System I. Especially when the content of PCS-2Si increased above 50%, Δm of System II became much smaller than that of System I, it was possibly come from the more chemical interaction between epoxy and urethane of PCS-2Si aside from strengthened epoxy-curing agent networks.

Chemical resistances

The chemical resistance of the samples was studied in H_2O , 10% NaCl, 10% H_2SO_4 , and 10% NaOH. It was experimentally shown the change in their weight could be neglected after all samples were immersed at room temperature for 7 days, even 14 days, indicating that all of these composites had good chemical resistance at room temperature. But the weight of all samples was reduced after they were soaked in chemicals at 50°C, as shown in Figures 4 and 5. Considering the composition of the modified systems, the reduction of weight could be thought to mainly come from the hydrolysis of ester of polycaprolactone and amide of curing agent.

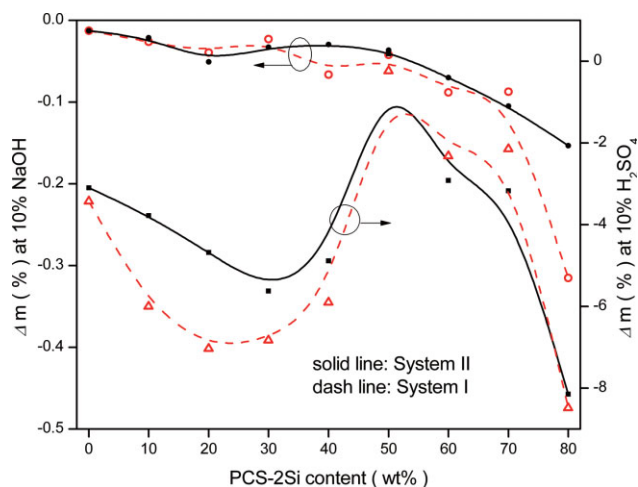


Figure 5 Chemical resistances data of the composites cured at different curing temperature after immersed in 10% H₂SO₄ and 10% NaOH for 7 days at 50°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Now considering the data for immersion in H₂O, 10% NaCl, and 10% H₂SO₄ in Figures 4 and 5, it could be found that all neat epoxy resins had a larger value of Δm , indicating that crosslinked networks were easily dissociated by H₂O, NaCl, and H₂SO₄ via hydrolysis of amide. And also, all Δm curves had horizontal "S" shapes with the change of PCS-2Si content, indicating the chemical resistance of the modified system first decreased, then increased, and last decreased after incorporating PCS-2Si. Solvent swelling had shown that incorporating PCS-2Si greatly reduced the formation of more highly crosslinked networks in modified system, making chemicals easy to penetrate and diffuse; then, hydrolysis easily takes place. Also, the increased content of PCS-2Si increased the content of polycaprolactone, ester of which was labile to hydrolysis, so these two factors resulted in bad chemical resistance. But, on the other side, the increased content of PCS-2Si made the surface of samples become more hydrophobic due to siloxane units migrating to the surface of sample (discussed below). Because the chemicals had less penetration and diffusion in the more hydrophobic surfaces, the dissociation of epoxy networks and hydrolysis of esters could be limited, and accordingly, an improved chemical resistance could be obtained. Therefore, the chemical resistance of the modified system would be determined by the competition among the crosslinked network density, hydrophobicity, and hydrolysis during immersion. When hydrolysis was the dominant factor, chemical resistance of the modified system would decrease; on the contrary, the modified systems had increased chemical resistance when the other two factors predominated. Based on the competition, it was easily understood why 50% PCL-2Si

modified epoxy resin had the highest chemical resistance, as hydrophobicity predominated over network density and hydrolysis during immersion. When curing temperature was compared, it was found that System II generally had better chemical resistance than System I had, because the former had more highly crosslinked networks than the latter, although System I was more hydrophobic (as mentioned below).

However, different from the data shown after immersion in H₂O, 10% NaCl, and 10% H₂SO₄, samples immersed in 10% NaOH had less change in weight. This might be because crosslinked epoxy resin networks were more resistant to hydrolysis in aqueous NaOH solution, indicated by Δm of neat epoxy resin after being immersed in H₂O, 10% NaCl, 10% H₂SO₄, and 10% NaOH. So the hydrolysis of esters and amide was greatly limited by the stable epoxy network associated with increased network density and higher hydrophobicity.

Surface properties

In order to have a preliminary surface characterization of the composites, contact angles were determined by using water and formamide as probe liquids, as shown in Figure 6. The results showed that the contact angles of modified epoxy resins were much larger than that of neat epoxy. The surface of the modified system was hydrophobic and had lower surface polarity, whereas the surface of neat epoxy was hydrophilic. In order to understand more clearly the effect of PCS-2Si content and curing temperature on the surface properties of the composites, surface tension values of the prepared films

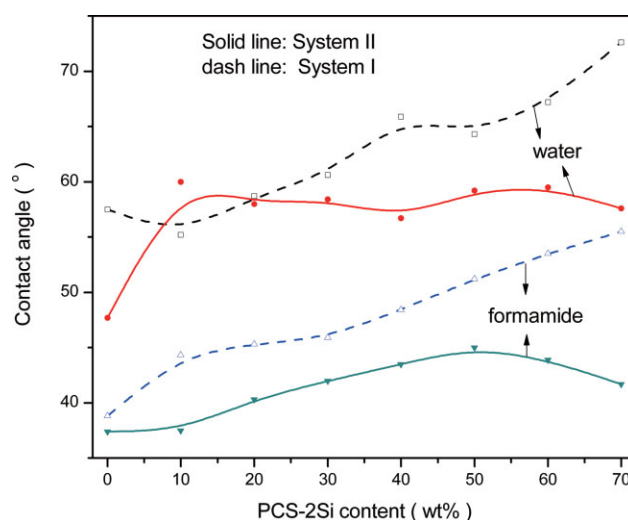


Figure 6 Contact angles of the composites cured at different curing temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

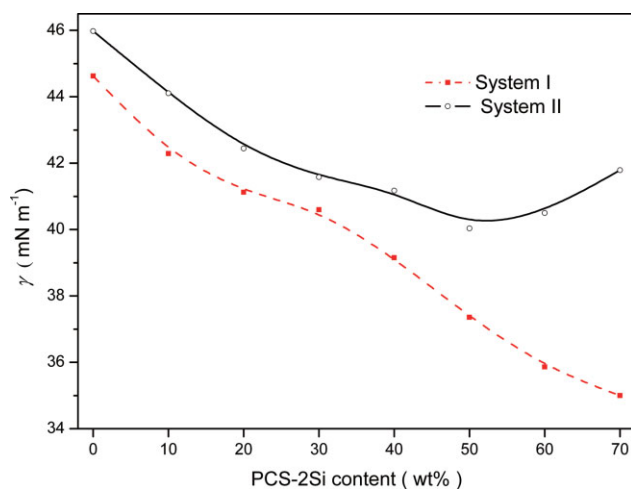


Figure 7 Surface tensions of the composites cured at different curing temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

were determined by applying the Owen–Wendt method to the static contact angle values, and reported in Figure 7. Significantly, at the same curing temperature, the modified system with higher content of PCS-2Si had a lower surface tension, because there were more siloxane units migrating to the surface of the films during the formation of film when higher content of PCS-2Si was added. These results had been explained through different measuring techniques,^{4,18,19} such as XPS.⁴ However, at the same content of PCS-2Si, System I had a lower surface tension than System II. It had been pointed out in the Morphology section that curing rate of epoxy resin was the dominant factor during the phase transformation, so the cured epoxy resin networks formed at a higher rate limited the diffusion of PCS-2Si, accordingly, reducing the quantity of siloxane units migrated to surface of the films during the formation of films. In addition, another factor might come from the fact that System II had denser networks mentioned as solvent swelling above, which limited the migration of siloxane after film formation, so System II was more hydrophilic.

CONCLUSIONS

A series of epoxy resin composites containing different contents of alkoxy silane functionalized PCS-2Si were prepared after curing with polyamidoamine curing agent at different temperatures. The composites were well characterized by SEM, solvent swelling, chemical resistance, and surface properties as a function of PCS-2Si content. Based on the results presented above, the following conclusions were obtained:

1. The composites with different PCS-2Si content had different miscibility between continuous and dispersion phase, especially higher curing temperature favored the miscibility.
2. Increasing PCS-2Si content reduced the density of networks of the composites, but higher curing temperature led to the formation of more highly crosslinked networks.
3. Chemical resistance of the composites with different PCS-2Si content had different resistance to water, 10% NaCl, 10% H₂SO₄, and 10% NaOH; all composites had good resistance to 10% NaOH, but the composites containing 50% of PCS-2Si had highest chemical resistance to water, 10% NaCl, and 10% H₂SO₄; higher curing temperature improved chemical resistance.
4. The composites with higher content of PCS-2Si had lower surface tension, but the surface tension was increased when higher curing temperature was used.

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