

# Modification of epoxy–novolac resins with polysiloxane containing nitrile functional groups: synthesis and characterization

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## Abstract

Synthesis of the statistical epoxidized polycyanopropylmethylsiloxane-co-polydimethylsiloxanes (PCPMS-co-PDMS) has been demonstrated. The modified polysiloxanes were prepared via a two-step method; (1) the ring-opening polymerization of octamethylcyclotetrasiloxane ( $D_4$ ) and tetramethylcyclotetrasiloxane ( $D_4H$ ), (2) hydrosilylation reaction of the polysiloxane prepolymers with allyl cyanide and allyl glycidyl ether. Molar ratios of  $D_4H$  and  $D_4$  were varied to produce the modified polysiloxanes with differences in polarity.  $^1H$ -NMR,  $^{29}Si$ -NMR,  $^{13}C$ -NMR and FTIR were used to monitor the formation of the modified polysiloxanes and DSC was used to study their thermal behaviors ( $T_g$ ,  $-118$  to  $-68$  °C). The use of the modified polysiloxanes as an elastomeric component in epoxy–novolac networks was also investigated. TEM and their transition temperatures suggested that the epoxy–novolac networks with high content of PDMS modifiers exhibited microphase separation. The fracture toughness properties of the networks with the polysiloxane modifiers were improved over the controls without polysiloxanes.

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## 1. Introduction

Novolac resins have been widely used in many applications such as adhesives, coatings, construction, and composite matrices in the aerospace and electronic industries. This is due to their high strength, excellent flame retardant, low cost, good chemical and corrosion resistance and good dimensional stability [1–3]. Hexamethylenetetraamine (HMTA) is normally used as a curing agent to produce high crosslink density networks

[4,5]. However, this reaction can generate volatile by-products such as ammonia which lead to voids in the networks. For this reason, HMTA cured Novolac networks are generally brittle in nature and have low fracture energies and impact strengths, probably due to the voids combined with the high crosslink densities. Curing novolac resins with epoxy resins can produce networks without volatile by-products. These can be reinforced with glass or carbon fibers to yield tough, void-free composites, which also retain much of the flame-retardant properties of phenolics [6].

Elastomeric and thermoplastic modifiers have been successfully incorporated into epoxy networks to improve their fracture energies and impact strengths [7,8].

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Functionalized polysiloxanes have been investigated as elastomers for this purpose [9–13]. Polysiloxanes, widely known as silicone, are of particular interest due to their extremely low glass transition temperatures and flexibility, their hydrophobic surface properties, good thermal stability and excellent flame retardant [14–17].

In this research, phenol-formaldehyde novolac resins will be cured with bisphenol-A epoxy resins (Epon 828®) using polysiloxanes as elastomeric modifiers. Our objective has focused on improving fracture toughness of the networks. One approach has been to investigate effects of polysiloxane modifiers with different chemical compositions. A series of polysiloxanes with dimethylsiloxy and cyanopropylmethylsiloxy units have been prepared. Dimethylsiloxane has non-polar characteristics, while cyanopropylmethylsiloxane has polar characteristics due to the nitrile pendant groups. The more polar compositions in the polysiloxane provide better miscibility with novolac resins while the more nonpolar compositions provide better phase separation in the networks. As a result, the various molar ratios of dimethylsiloxane (nonpolar) to cyanopropylmethylsiloxane (polar) were synthesized as a means to improve fracture toughness of the networks.

In the present paper, the synthesis of the epoxidized polysiloxane is described. Structure characterizations of the polymers were performed using  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ ,  $^{29}\text{Si-NMR}$  and FTIR. Glass transition temperatures of the polysiloxane modifiers with different polar compositions were determined from DSC. Thermal properties and fracture toughness of epoxy–novolac networks containing polysiloxane elastomeric modifiers were also discussed.

## 2. Experimental

### 2.1. Materials

Octamethylcyclotetrasiloxane ( $\text{D}_4$ ) and tetramethylcyclotetrasiloxane ( $\text{D}_4\text{H}$ ) (Dow Corning) were dried over  $\text{CaH}_2$  under a nitrogen atmosphere overnight, then fractionally distilled under vacuum. 1,1,3,3-Tetramethyldisiloxane (Aldrich), hydrogen hexachloroplatinate(IV) hydrate (Aldrich), and trifluoromethane sulfonic acid (Aldrich) were used as-received. Allyl cyanide and allyl glycidyl ether (Aldrich) were dried over activated molecular sieves for at least 2 days, then fractionally distilled. Acetone, diethyl ether, and silica gel (Aldrich) were used as-received.

### 2.2. Synthesis

#### 2.2.1. Synthesis of the polysiloxane prepolymers

Polydimethylsiloxane prepolymers (PDMS) with controlled molecular weights of  $\approx 1000$  g/mol were pre-

pared by equilibrium acid-catalyzed ring-opening polymerization of octamethylcyclotetrasiloxane ( $\text{D}_4$ ).  $\text{D}_4$  (100.0 ml, 0.322 mol) and 1,1,3,3-tetramethyldisiloxane (16.9 ml, 0.096 mol) used as the endcapper, were added into a 250 ml flame dried flask capped with a septum under nitrogen. The temperature was increased to 65 °C and trifluoromethane sulfonic acid catalyst (triflic acid) (0.36 ml, 0.65 wt.% based on siloxane monomers) was slowly added via a syringe. The reaction was equilibrated at 65 °C for 48 h. The acidic mixture was cooled to room temperature, dissolved in diethyl ether, then neutralized by repeatedly extracting with water. The mixture was dried over sufficient anhydrous magnesium sulfate with continuously stirring for 30 min, and subsequently filtered through a filter paper. Diethyl ether was evaporated using a rotary evaporator for 30 min. The cyclic monomers remaining upon the equilibrium were removed by vacuum stripping at 120 °C for at least 4 h.

Polymethylhydrosiloxane prepolymers can be synthesized in the same procedure as described in the synthesis of PDMS but using tetramethylcyclotetrasiloxane ( $\text{D}_4\text{H}$ ) instead of  $\text{D}_4$ . The copolymers containing different moieties of dimethylsiloxane and methylhydrosiloxane (25:75, 50:50 and 75:25, respectively) were achieved by introducing  $\text{D}_4\text{H}$  and  $\text{D}_4$  in feed corresponding to the targeted molar ratios of each component in the copolymers.

#### 2.2.2. Synthesis of the epoxidized polydimethylsiloxane (epoxidized PDMS)

Allyl glycidyl ether (4.8 ml) (one and a half times excess over Si–H bonds in the prepolymers) and hydrogen hexachloroplatinate(IV) hydrate (0.03 g) catalyst were introduced into a 250 ml 4-neck flask equipped with a dropping funnel, magnetic stir bar, thermocouple and nitrogen inlet. A PDMS prepolymer terminated with Si–H groups (20.0 g, 0.014 mol) was charged to a dropping funnel. After the temperature was raised to 55 °C, a few drops of the PDMS prepolymer were added. The temperature increased a few degrees due to the exothermic reaction. The remaining PDMS prepolymer was added in approximately 2 ml increments over about a 2 h period. The reaction of each increment was monitored by FTIR, observing the disappearance of the Si–H peak at  $2156\text{ cm}^{-1}$ . After the reaction was complete, the temperature was increased to 180 °C for 2 h to decompose the catalyst. The mixture was cooled to room temperature, and then filtered through silica gel using acetone as a solvent. The excess of allyl glycidyl ether as well as acetone was removed by distillation at 120 °C for at least 4 h.

#### 2.2.3. Synthesis of the epoxidized polycyanopropylmethylsiloxane (epoxidized PCPMS)

A polymethylhydrosiloxane prepolymer (20.0 g, 0.017 mol) and allyl cyanide (two times molar excess

over Si–H bonds, 61.8 ml) were added to a 250 ml 4-neck flask equipped with a dropping funnel, mechanical stirrer, thermocouple and nitrogen inlet. Allyl glycidyl ether (three moles per mole of polymer, 5.9 ml) and hydrogen hexachloroplatinate(IV) hydrate (0.037 g) were charged to the dropping funnel. The temperature was increased to 55 °C, then the allyl glycidyl ether with the Pt catalyst was slowly added dropwise over about a 2 h period. The temperature increased 2–3 °C after each addition due to the exothermic reaction. After all of the reactants were added, the reaction was allowed to proceed for 48 h. The temperature was then increased to 180 °C for 2 h to decompose the catalyst. The mixture was cooled to room temperature, and then filtered through silica gel using acetone as a solvent. The unreacted allyl cyanide and acetone were vacuum stripped at 120 °C for at least 4 h.

#### 2.2.4. Synthesis of the epoxidized polycyanopropylmethylsiloxane–polydimethylsiloxane (epoxidized PCPMS-co-PDMS)

The epoxidized poly(PCPMS-co-PDMS) was prepared in the same fashion as described in the synthesis of the epoxidized PCPMS but using poly(dimethylsiloxane-co-methylhydrosiloxane) copolymer as a prepolymer. Briefly, three moles of allyl glycidyl ether per mole of the polymer were used in all cases. An excess of allyl cyanide based on the number of moles of Si–H bonds in the copolymers were also applied for every composition.

#### 2.3. Preparation of modified-epoxy–novolac networks

Two series of epoxy–novolac networks containing 65 and 50 wt.% of the novolac component modified with the polysiloxane oligomers were investigated. Each series was prepared with systematically varied amounts of the polysiloxane modifiers ranging from 10 to 30 wt.%. The epoxy resin, novolac resin and polysiloxane modifier were melt blended at 170 °C for 30 min to achieve workable viscosities. Vacuum was applied to remove air bubbles in the reaction mixtures. The mixtures were then poured into a preheated mold to obtain sample bars with thickness  $\approx 3.10$  mm, width  $\approx 6.20$  mm and length  $\approx 35$  mm. The sample bars were cured at 140 °C for 4 h and then 220 °C for 3 h.

#### 2.4. Characterization

FTIR was performed using a Perkin-Elmer Model 1600 Series FTIR Spectrophotometer. The neat samples were cast directly onto sodium chloride plates. The spectra were acquired by collecting 32 scans with a resolution of  $8\text{ cm}^{-1}$ .  $^1\text{H-NMR}$ ,  $^{29}\text{Si-NMR}$  and  $^{13}\text{C-NMR}$  were performed on a 400 MHz Bruker NMR spectrometer using  $\text{CDCl}_3$  as a solvent.  $^1\text{H-NMR}$  was obtained using 5 mm o.d. sample tubes while  $^{29}\text{Si-NMR}$  and  $^{13}\text{C-NMR}$  were obtained using

10 mm o.d. tubes.  $\text{Cr}(\text{acac})_3$  was added to the solutions for  $^{29}\text{Si-NMR}$  measurements to decrease the relaxation times. GPC was conducted on a water instrument (Waters 2690) equipped with microstyragel columns (HR1 + 3 + 4) and a refractive index detector. Chloroform was used as solvent with flow rate of 1 ml/min at 30 °C. Thermal analyses of the epoxidized polysiloxanes were conducted on a Perkin-Elmer Pyris-1 DSC. The samples were heated from –130 to 200 °C with a heating rate 10 °C/min. The  $T_g$  values taken from the midpoints of the curves were determined from the second scans.

Transmission electron microscopy (TEM) was utilized to study microphase separation of the networks. The images were obtained on a Philips 420T TEM at 100 kV. The networks were microtomed at room temperature using a Reichert-Jung Ultracut-E ultramicrotome.

The glass transition temperatures ( $T_g$ ) of the networks were measured on a Perkin-Elmer dynamic mechanical analyzer, model DMA-7. The  $T_g$ 's were obtained from the Tan delta peaks. The three-point bend mode using rectangular specimens was used throughout the testing with a scan rate of 5 °C/min.

Fracture toughness measurements were performed using an Instron model 4204 instrument. The single-edge notch-bending mode (SENB) according to ASTM D5045-95 standard test method was used throughout the testing. In the first step, the center of the specimen bar was notched using a saw. Pre-crack was then initiated by putting a cold razor blade immersed in liquid nitrogen prior to use and tapping with a rubber hammer. The crack length was about 40–60% of the specimen width ( $W$ ). The measurements were performed with 1 mm per minute crosshead speed at ambient temperature. The  $K_{1c}$  values were calculated using the following equation:

$$K_{1c} = P \times 1000^{3/2} \times 25.4 \times [2.9(a/W)^{1/2} - 4.6(a/W)^{3/2} + 21.8(a/W)^{5/2} - 37.6(a/W)^{7/2} + 38.7(a/W)^{9/2}] / B \times W^{3/2}$$

where

$P$  is the maximum force (N),

$a$  is the crack length (mm),

$W$  is the specimen width (mm)  $\approx 6.20$  mm,

$B$  is the specimen thickness (mm)  $\approx 3.10$  mm.

At least five different specimens were tested for each samples.

### 3. Results and discussion

The siloxane copolymers of poly(cyanopropyl)methylsiloxane and polydimethylsiloxane were prepared

following a two-step synthesis (Fig. 1): (1) preparation of siloxane prepolymers through acid-catalyzed ring-opening polymerization of  $D_4/D_4H$ , and (2) epoxidation of the siloxane prepolymers via hydrosilylation reactions. In the first step, the siloxane prepolymers with targeted molecular weight of 1000 g/mol were synthesized through the equilibrium ring opening equilibrium polymerization of  $D_4$  and/or  $D_4H$  using 1,1,3,3-tetra-methyldisiloxane as the endcapping reagent to control molecular weight and to obtain Si–H terminals. Incorporation of  $D_4H$  in feed led to the polymers containing methylhydrosiloxane units. Hence, the amount of  $D_4H$  relative to  $D_4$  monomers in feed reflected the moiety of the methylhydrosiloxy units in the copolymers. According to GPC results, the ratio of linear to cyclic species at equilibrium was approximately 85 wt.% linear chains and 15 wt.% small cyclics. The cyclics remaining upon the reaction equilibrium were removed by evaporation under reduced pressure.

$^{29}\text{Si}$ -NMR was used to quantify the molecular weights and to confirm the molar ratios of dimethylsiloxy to methylhydrosiloxy units in the prepolymer (Fig. 2). The observed molecular weights were somewhat higher than the targeted molecular weights. This is likely attributable to the loss of low molecular weight linear species during vacuum stripping off the equilibrium cyclics. The signals at  $\approx -4$  ppm in  $^{29}\text{Si}$ -NMR spectrum correspond to the silicons at the chain terminals and were used for the molecular weight determinations. As the figure depicts, the chemical shifts of these peaks are quite sensitive to the chemical structure of the penultimate units. Two other regions of the  $^{29}\text{Si}$ -NMR spectra corresponding to the dimethylsiloxy units (peak b at  $\approx -20$  ppm) and to the methylhydrosiloxy units (peak c at  $\approx -34$  ppm) are presented. As with the endgroup signals, silicons adjacent to methylhydrosiloxy units are shifted downfield relative to those between dimethylsiloxy units. Interestingly, the molar ratios of methylhydrosiloxy to dimethylsiloxy units of the copolymers determined from the ratio of the integral of the corresponding signals are comparable to the expected values (Table 1).

Pendent and terminal silicon hydrides on the prepolymers were hydrosilylated with mixtures of allyl glycidyl ether and allyl cyanide to produce a systematic series of epoxy functional compositions. Three moles of allyl glycidyl ether per mole of the prepolymer were introduced to provide sufficient functionality for epoxy–novolac network formation, while allowing for enough distance between crosslinks for phase separation of the polysiloxane soft segment in the materials. The hydrosilylation reaction of allyl glycidyl ether was significantly faster than for allyl cyanide. Thus, it was possible to utilize the calculated molar ratio of epoxide groups (since these reacted quantitatively) in hydrosilylation mixtures with an excess of the allyl cyanide. The purpose of incor-

porating allyl cyanide into the chains was to increase the polarity of the polysiloxane modifiers to tailor phase mixing with the epoxy and novolac resins.

The hydrosilylation reactions were monitored by FTIR to observe the disappearance of the strong Si–H stretching peak at  $2156\text{ cm}^{-1}$  (peak c, Fig. 3). It should be noted that this peak did not completely disappear even after 48 h of reaction. This may be a result of steric hindrance from bulky substituents hydrosilylated into these prepolymers. In addition to the Si–H peak decreasing in intensity, peak a at  $2246\text{ cm}^{-1}$  corresponding to the  $-\text{C}\equiv\text{N}$  groups in allyl cyanide also decreased while peak b at  $2222\text{ cm}^{-1}$  corresponding to the  $-\text{C}\equiv\text{N}$  groups in the polymer chains increased.

The extents of reaction of the hydrosilylations were obtained via  $^1\text{H}$ -NMR (Fig. 4). Percent conversion of hydrosilylations was determined based on the integration ratio of the signal at 4.7 ppm (peak m) corresponding to Si–H (hydrogens directly attached to Si) to the signal at 0 ppm corresponding to Si– $\text{CH}_3$  (methyl protons on Si). Increasing PCPMS contents in the copolymers tended to decrease the reaction conversions. It is rationalized that more steric hindrance occurred when higher numbers of cyanopropyl methylsiloxy units presented in the copolymers. It should also be noted that approximately 10–15% of the hydrosilylation reaction of allyl cyanide took place via reverse addition (Makovnikov addition) yielding a cyano isopropyl structure (peak  $c_1$ ,  $c_2$  and  $c_3$ ), whereas the major product of this reaction was cyano *n*-propyl structure (anti-Makovnikov addition) (peak b, e and f).

Molecular weights of the copolymers and the average number of epoxies per chain were elucidated by  $^{13}\text{C}$ -NMR. The methylene carbons attached to the terminal silicons (peak k at 14 ppm) (Fig. 5) were used in conjunction with methyl peaks in the repeating units (peaks l, m, n, and o) to calculate their molecular weights. Epoxy functional units were distinguished from nitrile units using carbons on the functional groups. The epoxy functionalities calculated from peak e are  $\geq 2$  per chain as expected (Table 2).

The thermal behavior of the polymers was investigated using DSC. The  $T_g$ 's of the polysiloxane were between  $-118$  and  $-68\text{ }^\circ\text{C}$  depending on the copolymer composition (Fig. 6). Compositions with higher molar ratios of PDMS had lower glass transitions. This can be attributed to increased mobility of dimethylsiloxy groups relative to bulky cyanopropylmethylsiloxy groups.

The networks in the present investigation were obtained from the curing reaction of the epoxidized PDMS-co-PCPMS or the corresponding homopolysiloxane with a bisphenol-A diglycidyl ether based epoxy resin (Epon828) and novolac resin. The purpose of adding epoxy resin was to increase the functionality of epoxy groups in the reaction as well as to decrease the viscosity of the mixture. The difference in the solubility parameters

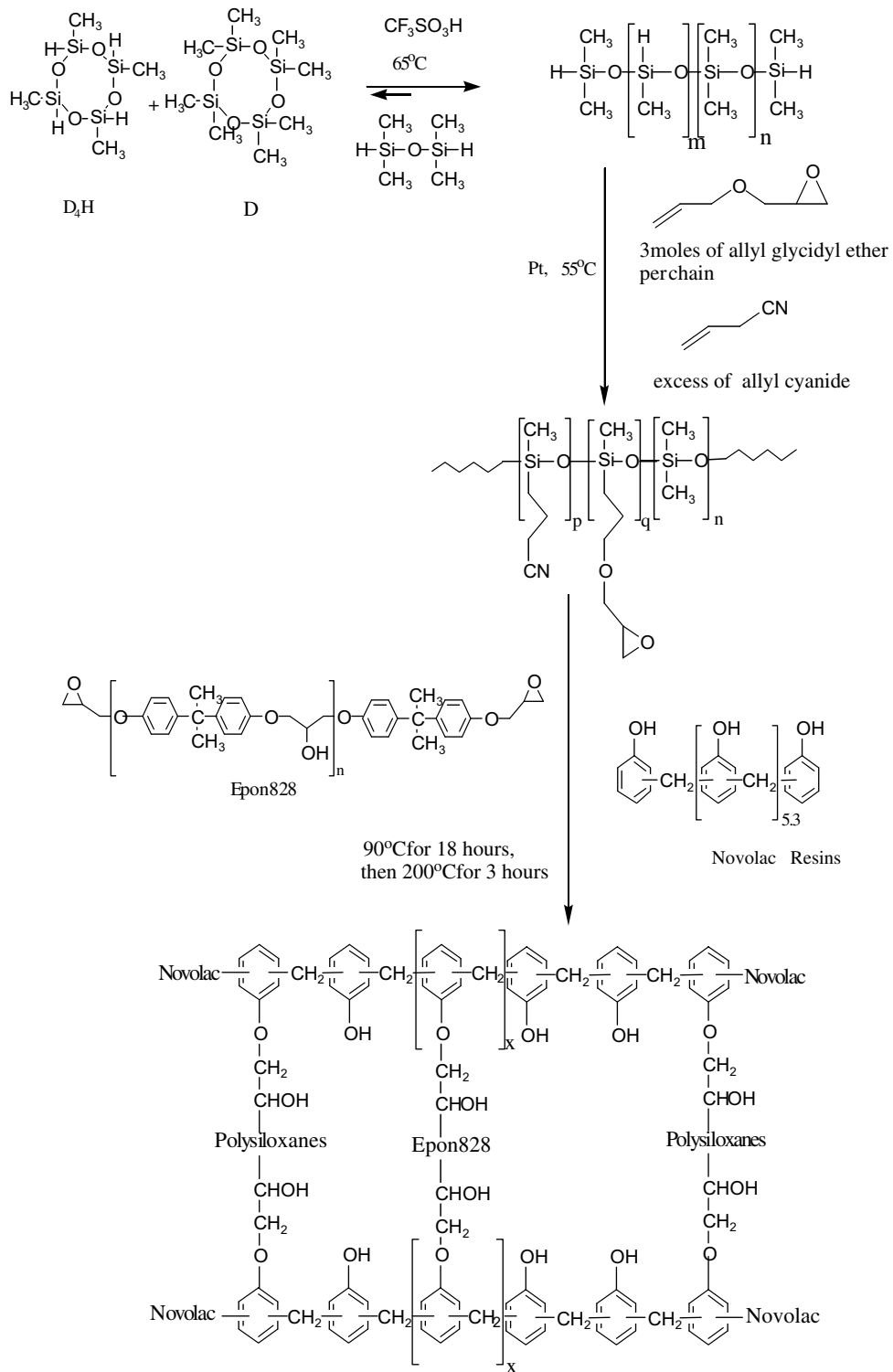


Fig. 1. The synthetic scheme of the polysiloxane-modified epoxy-novolac networks.

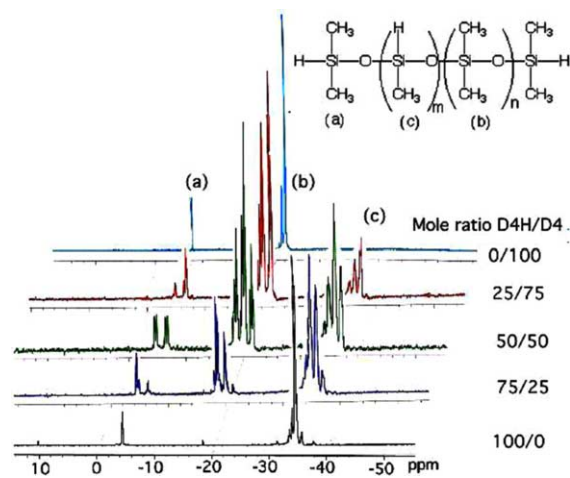


Fig. 2.  $^{29}\text{Si}$ -NMR spectra of the siloxane prepolymers with different compositions.

of the novolac resin, epoxy resin and siloxane elastomer is a key parameter to control the degree of phase separation of the network. Hence, the objective of the present work is to control the solubility parameter of the siloxane oligomer in such a way that it is miscible with the novolac and epoxy resins at the initial stage and exhibits micro-phase separation during the curing reaction. To achieve this goal, polycyanopropylmethylsiloxane (PCPMS) were incorporated into the siloxane oligomers to increase polarity. Therefore, the polarity of the siloxane elastomer can be tailored by adjusting molar ratio of PCPMS to PDMS.

Two series of epoxy–novolac networks containing 65 and 50 wt.% of the novolac component modified with the siloxane oligomers ranging from 10–30 wt.% were studied. It should be noted that the series with 65 wt.% novolac had higher equivalent ratios of phenol to epoxy, resulting in lower network densities or higher molecular weights between crosslink ( $M_c$ ). Therefore, the series with 65 wt.% novolac are expected to be tougher than the other series. However, a disadvantage of the series

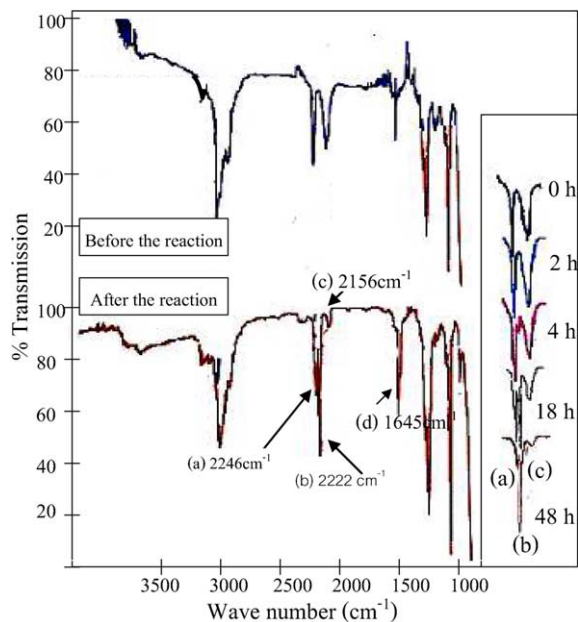


Fig. 3. FTIR monitoring the epoxidation of the siloxane prepolymers. The inset demonstrates the time evolution of the  $\approx 2000\text{ cm}^{-1}$  region.

with the higher novolac content was that the materials were difficult to process due to the high viscosity of the novolac resin.

The blends containing polycyanopropylmethylsiloxane (e.g., 100/0 molar ratio of PCPMS/PDMS) and high compositions of PCPMS (e.g., 75/25 molar ratio of PCPMS/PDMS) were transparent whereas those containing more dimethylsiloxane units (50/50, 25/75 and 0/100 molar ratio of PCPMS/PDMS) were phase separated and appeared as opaque samples. It is hypothesized that hydrogen bonding between the phenolic hydroxyls and nitrile groups on the modifier may contribute to phase mixing. However, no shift in the nitrile FTIR peak at  $2222\text{ cm}^{-1}$  was observed upon mixing the modifier with the novolac resin. The mixtures containing

Table 1

Compositions of the siloxane prepolymers and their average molecular weights

D <sub>4</sub> H/D <sub>4</sub> molar ratio in feed	Expected $M_n$ (g/mol)	Molar ratio of methylhydro/dimethyl siloxy units <sup>a</sup>	$M_n^a$ (g/mol)	Polydispersity index <sup>b</sup>
0/100	1000	0/100	1410	1.25
25/75	1000	24/76	1670	1.24
50/50	1000	47/53	1620	1.32
75/25	1000	74/26	1620	1.30
100/0	1000	100/0	1500	1.24

<sup>a</sup> Based on  $^{29}\text{Si}$ -NMR spectra.

<sup>b</sup> Based on GPC.

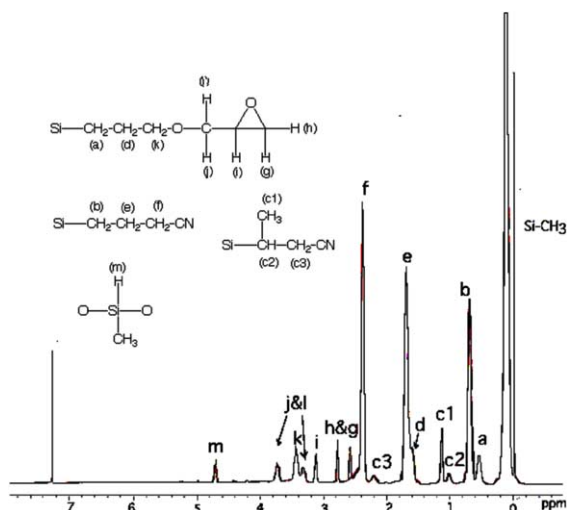


Fig. 4.  $^1\text{H-NMR}$  of the epoxidized polysiloxanes in  $\text{CDCl}_3$ .

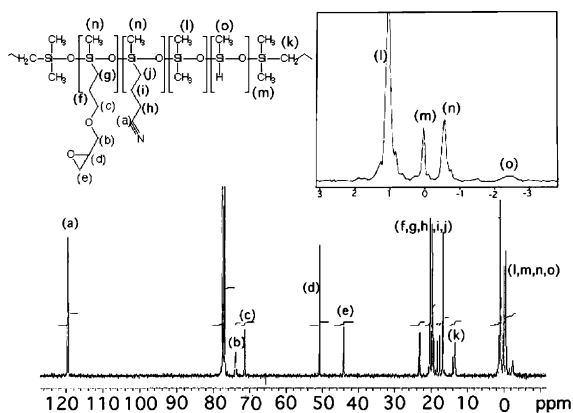


Fig. 5.  $^{13}\text{C-NMR}$  of the epoxidized polysiloxanes in  $\text{CDCl}_3$ .

more than 20 wt.% polydimethylsiloxane modifiers were macrophase separated and could not be blended successfully. In cases where the resins were microphase separated,

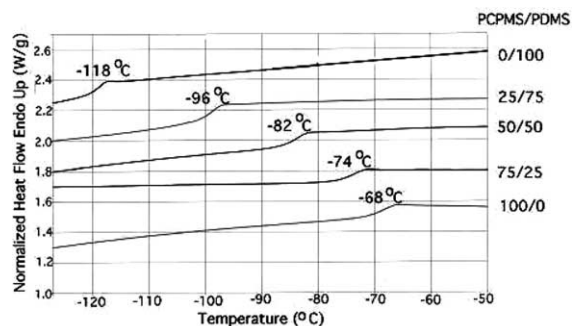


Fig. 6. The second scan DSC of the epoxidized polysiloxanes obtained at  $10\text{ }^\circ\text{C/min}$  from  $-130$  to  $200\text{ }^\circ\text{C}$ .

the networks also showed phase separation and were opaque (Table 3). In general, as the percentage of dimethylsiloxane units in the modifier was increased, the modifier phase size also increased in the networks.

Fig. 7 shows representative surface morphology for the network at 65 wt.% of the novolac resin, 25 wt.% epoxy resin and 10 wt.% of the polysiloxane modifiers with varied molar ratios of PCPMS/PDMS. TEM images of the networks containing PCPMS/PDMS molar ratios of 100/0 and 75/25 were featureless, indicating phase homogeneity. On the other hand, the polarity of the polysiloxane modifiers was decreased with lower PCPMS/PDMS ratios (50/50, 25/75 and 0/100 molar ratios), and the TEM images showed that microphase separation had occurred. With 50/50 and 25/75 PCPMS:PDMS, the occluded modifier phases were approximately 1–4  $\mu\text{m}$  in diameter (Fig. 7b and c). Particle size increased significantly ( $\approx 4\text{--}6\text{ }\mu\text{m}$ ) without the presence of small elastomeric domains observed for the network containing only PDMS modifier (without PCPMS) (Fig. 7d). This phenomenon is attributed to the difference in polarity of polar novolac resin and epoxy resin to non-polar PDMS component. Hence, it can be surmised that the morphology of the networks depends on the siloxane

Table 2

Compositions of the epoxidized polysiloxanes and their glass transition temperatures

Molar ratio of PCPMS/PDMS	Expected $M_n$ (g/mol) <sup>a</sup>	%Conversion <sup>b</sup>	Epoxy/chain <sup>b</sup>	$M_n$ (g/mol) <sup>c</sup>	$T_g$ ( $^\circ\text{C}$ ) <sup>d</sup>	Polydispersity index <sup>e</sup>
0/100	1410	100	2.0	1600	-118	1.32
25/75	2190	92	2.2	2200	-96	1.45
50/50	2550	88	2.8	2500	-82	1.50
75/25	3020	90	2.0	3000	-74	1.42
100/0	3320	79	2.7	3300	-68	1.30

<sup>a</sup> Based on the experimental molecular weights of the prepolymers.

<sup>b</sup> Based on  $^1\text{H-NMR}$  spectra.

<sup>c</sup> Based on  $^{13}\text{C-NMR}$  spectra.

<sup>d</sup> Based on DSC thermographs.

<sup>e</sup> Based on GPC.

Table 3  
Appearance of the polysiloxane containing epoxy–novolac networks

Novolac/Bis-A epoxy/siloxanes (wt.%)	Phenol/epoxy (eq/eq)	PCPMS/PDMS copolymer (molar ratio)					
		0/100	25/75	50/50	75/25	100/0	
65/35/0	3.4/1	–	–	–	–	–	Clear
65/25/10	4.3/1	Opaque	Opaque	Opaque	Clear	Clear	–
65/15/20	6.2/1	<i>a</i>	Opaque	Opaque	Clear	Clear	–
50/50/0	1.8/1	–	–	–	–	–	Clear
50/40/10	2.1/1	Opaque	Opaque	Opaque	Clear	Clear	–
50/30/20	2.6/1	<i>a</i>	Opaque	Opaque	Clear	Clear	–
50/20/30	3.4/1	<i>a</i>	<i>a</i>	Opaque	Clear	Clear	–

*a* = the mixtures were immiscible.

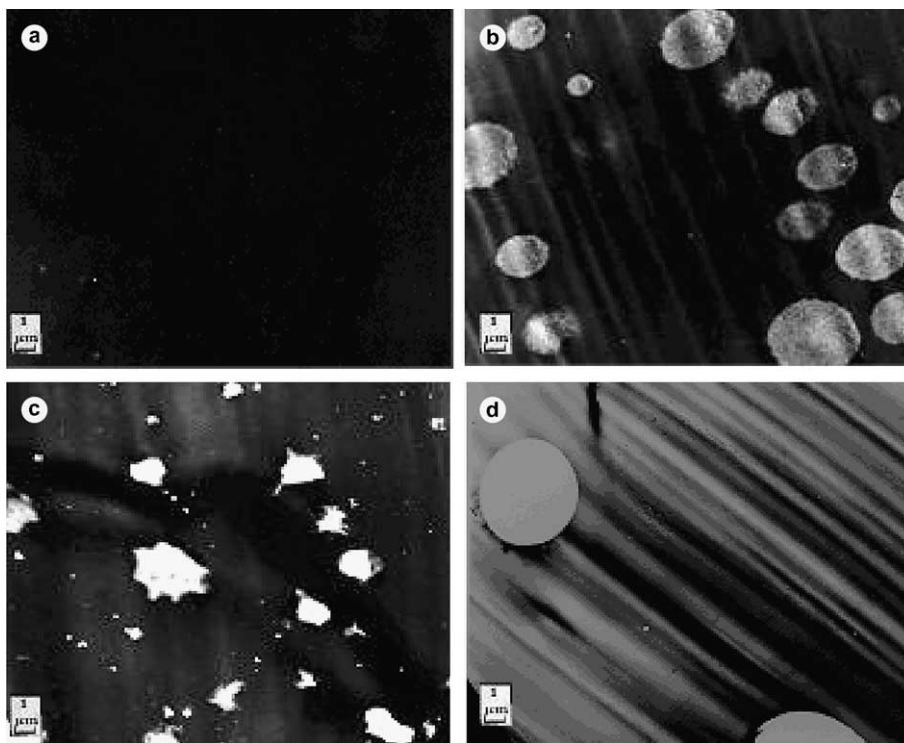


Fig. 7. TEM micrographs showing microphase separation of the networks (65 wt.% novolac, 25 wt.% epoxy and 10 wt.% polysiloxanes with various mole ratios of PCPMS/PDMS: (a) 100/0 and 75/25, (b) 50/50, (c) 25/75 and (d) 0/100.

elastomeric composition, resulting in the compatibility between the elastomeric phase and epoxy–novolac matrix.

The glass transition temperatures ( $T_g$ ) of the networks prepared from 65 wt.% of the novolac resin, 25 wt.% of the epoxy resin, and 10 wt.% of the polysiloxane modifiers at various molar ratios of PCPMS/PDMS were also studied (Fig. 8). Two relaxations were observed in most cases. The higher transition temperatures correspond to the continuous epoxy–novolac matrix. These  $T_g$ 's gradually decreased as the PDMS content

in the polysiloxane copolymer increased. In addition, higher weight percent of the polysiloxanes in the networks also decreased the major glass transition further. This depression in the  $T_g$  of the networks indicates partial miscibility between epoxy–novolac matrix and the elastomeric component. In the other word, the continuous network phase contains some of the siloxane modifier. However, as a result of partial miscibility of these two phases, the strength of the networks was sacrificed as indicated by the depression of the moduli.



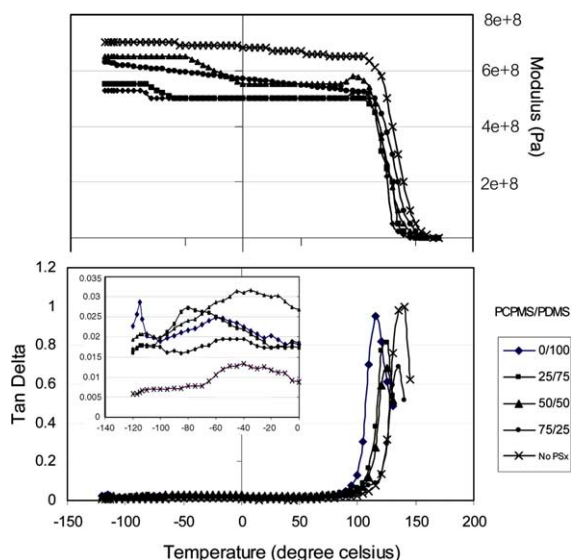


Fig. 8. DMA thermogram of 65 wt.% novolac, 25 wt.% epoxy and 10 wt.% polysiloxanes with various compositions obtained at 5 °C/min. The inset is an expansion of temperatures ranging from –120 to 0 °C region.

The novolac–epoxy network control material without polysiloxane modifier exhibits a broad transition centered around –40 °C (the inset in Fig. 8). This has been previously attributed to motion of the hydroxy ether groups of bisphenol-A epoxy resins [9]. Low temperature transitions corresponding to the polysiloxane phases were clearly observed for molar ratios of 25/75 and 0/100 PCPMS/PDMS modifiers (Fig. 8). As the PCPMS content in the modifier was increased, it became difficult to distinguish whether a transition existed corresponding to a soft phase because of the

possible overlap with the poly(hydroxy ether) backbone.

The fracture toughness of the networks was investigated by measuring the critical-stress-intensity factors,  $K_{Ic}$ , under plane-strain conditions. The higher values of  $K_{Ic}$  indicate higher resistance to crack propagation, and also indicate increased toughness. Two control networks containing 65 and 50 wt.% of the novolac component (without polysiloxane) were compared. The 65 wt.% novolac:35 wt.% epoxy sample possessed a higher average molecular weight between crosslinks ( $M_c$ ) due to higher values of phenol/epoxy equivalent ratio, and hence, showed a higher  $K_{Ic}$  toughness as expected (Table 4). Network compositions containing 10 wt.% polysiloxane at any PCPMS/PDMS molar ratios were all significantly tougher than the controls (the network without polysiloxane modifier) (Fig. 9B). However, increasing polysiloxane content up to 20% or 30% did not improve their toughness any further but lowered as compared to the networks containing only 10% polysiloxane. The toughness values of two series of the networks (50 wt.% and 65 wt.% novolac resins) show similar trend in dependence of siloxane composition on their toughness relative to the control. Namely, the copolymers with the 50/50 molar ratio of PCPMS/PDMS showed the maximum  $K_{Ic}$  values in both systems (Fig. 9A). In combination with the fact that these materials contain elastomeric domains in the matrix (Fig. 7b), it is believed that these elastomeric domains can absorb the energy generated during fracture, resulting in high  $K_{Ic}$  values. On the other hand, the elastomeric domains in the networks containing 0/100 molar ratio of PCPMS/PDMS (Fig. 7d) show extremely large particles, which are thought to be composites of both epoxy–novolac and elastomer. Instead of

Table 4  
Fracture toughness properties of the polysiloxane containing epoxy–novolac networks

Novolac/Epon828/PSx (wt.%)	Phenol/epoxy (eq/eq)	PCPMS/PDMS (molar ratio)	$K_{Ic}$ (MPa $m^{1/2}$ )
65/35/0	3.4/1	–	0.75 ± 0.05
65/25/10	4.3/1	75/25	1.09 ± 0.05
		50/50	1.23 ± 0.05
		25/75	0.87 ± 0.07
		0/100	0.80 ± 0.03
65/15/20	6.2/1	25/75	0.48 ± 0.02
50/50/0	1.8/1	–	0.57 ± 0.01
50/40/10	2.1/1	75/25	1.09 ± 0.05
		50/50	1.11 ± 0.01
		25/75	1.00 ± 0.02
		0/100	0.79 ± 0.03
50/30/20	2.6/1	75/25	1.05 ± 0.04
		50/50	0.93 ± 0.13
		25/75	1.12 ± 0.06
50/20/30	3.4/1	50/50	0.71 ± 0.04

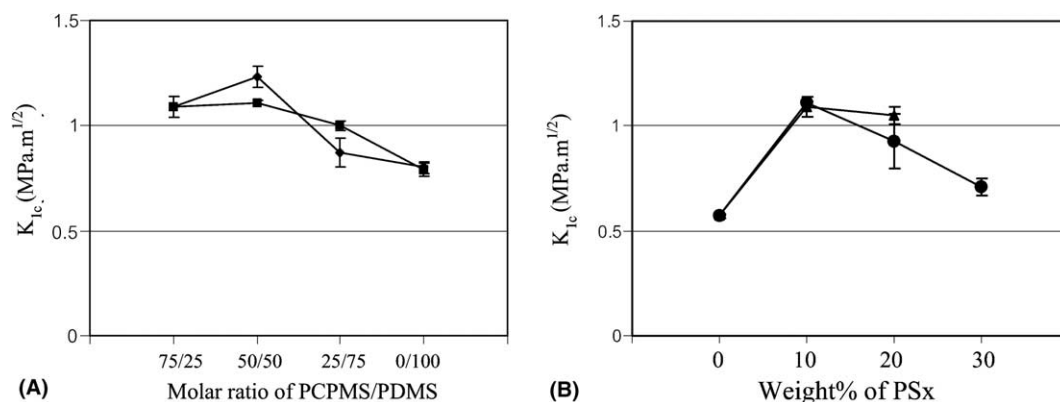


Fig. 9. The plots illustrating the dependence of toughness on network composition, (A) effect of polysiloxane composition on toughness, (◆) representing the mixture of 65% novolac resin, 25% epoxy resin and 10% polysiloxane, (■) representing the mixture of 50% novolac resin, 40% epoxy resin and 10% polysiloxane, (B) effect of polysiloxane content on toughness, (●) representing the mixture of 50% novolac resin, 0–30 wt.% of 50/50 molar ratio of PCPMS/PDMS copolymer, and the corresponding amount of epoxy resin, (▲) representing the mixture of 50% novolac resin, 0–20 wt.% of 75/25 molar ratio of PCPMS/PDMS copolymer, and the corresponding amount of epoxy resin.

absorbing the energy upon cracking, these elastomeric particles tear easily, resulting in low  $K_{1c}$  values.

#### 4. Conclusions

Novolac–epoxy networks can be modified with reactive epoxy functional polysiloxane oligomers containing various levels of polar nitrile pendent groups. At 10 wt.% polysiloxane, as the molar ratio of PCPMS/PDMS increases, the phase miscibility increases. At a 50/50 PCPMS/PDMS modifier composition, networks with 65 wt.% novolac, 25 wt.% epoxy and 10% polysiloxane exhibit a phase structure with micron size included rubber phases ( $\approx 1\text{--}4\ \mu\text{m}$  in diameter). These networks have significantly improved toughness over the control (the network without polysiloxane modifier). Further characterization of such networks is warranted and will be discussed in a future paper.

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