

Effect of Molecular Weight and Content of PDMS on Morphology and Properties of Silicone-Modified Epoxy Resin

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ABSTRACT: To achieve a stable blend of a bisphenol A type epoxy resin and poly(dimethylsiloxane) (PDMS), reaction between hydroxyl (OH) groups of the epoxy and silanol groups of hydroxyl-terminated (HT) PDMS has been investigated. The chemical structures of the HTPDMS-modified epoxies were characterized by Fourier transform infrared (FTIR) and ^1H - and ^{13}C -NMR spectroscopy. To allow further understanding of the influence of viscosity and content of HTPDMS on the blend morphology, four different viscosities of HTPDMS were used in three content levels. The morphologies of modified epoxy resins were observed with optical microscopy. The modified epoxies were cured with a cycloaliphatic polyamine. The morphologies of modified epoxies were investigated by using scanning electron microscopy (SEM)/energy dispersive X-ray (EDX) technique.

The cured films showed droplet in matrix morphology with different mean droplets size which was influenced by the viscosity and the content of the incorporated HTPDMS. To illustrate the effect of the morphologies of the cured samples on mechanical properties, tensile strength tests were performed. The introduction of HTPDMS into the epoxy altered the tensile behavior according to its viscosity and content. Surface properties of the cured films were evaluated by sessile drop method. The results clearly indicate that the hydrophilic surface of the epoxy turns to a hydrophobic one due to the modification with HTPDMS. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 162–178, 2012

Key words: epoxy; poly(dimethylsiloxane); mechanical properties; morphology; coatings

INTRODUCTION

Epoxy resins are considered as one of the most important thermosetting polymers with many desirable properties such as good heat and solvent resistance, remarkable adhesive strength, ease of cure, and processing. They are widely used as binders for coatings and in adhesive applications^{1,2}; however, they have drawbacks such as inferior weathering resistance,³ low fracture energy,⁴ comparatively low hydrophobicity,⁵ and low impact resistance⁶ that limit their wide range of applications in high performance coatings. Numerous attempts have been made to overcome these limitations including incorporating inorganic fillers,⁷ liquid rubbers,^{8–10} and nanofillers¹¹ into epoxy resins. The use of poly(dimethylsiloxane) (PDMS) as a modifier for the cured epoxy matrix may present some advantages such as enhancement of the mechanical and hydrophobic properties^{12–14} flame retardancy,¹⁵ of epoxy resins. However, it has to be considered that PDMS is not compatible with epoxy resin and phase separation

and bleeding of the PDMS component may happen. To prevent macro-phase separation in epoxy and PDMS blends, different methods have been proposed, such as (a) using silane-based compatibilizer,^{5,6,16–21} (b) copolymerizing dimethyl siloxane with diphenyl siloxane,^{22–27} (c) introducing reactive groups into PDMS chains to bond with epoxy resins,^{3,13,28–43} and (d) a combination of the last two methods.⁴⁴

PDMS-epoxy blend is initially immiscible at room temperature; however, chemically bonding of epoxy to the PDMS chain by the reaction between their reactive groups such as hydroxyl (OH)^{12,21–27,29}, oxirane,^{19,30,31} and amine^{32–37,45} leads to partial compatibilization. The resulted modified epoxy resins are heterogeneous with PDMS-rich domains irregularly dispersed in the epoxy-rich matrix.

According to Wu,³⁹ in immiscible polymers the size, shape, and distribution of one phase in the other depends on the matrix viscosity, mixing shear rate, interfacial tension of two polymers, and viscosity ratio of dispersed phase to continuous phase. The molecular weights and blend composition of two incompatible polymers have a great influence on phase behavior of the polymer blend.

In the present research, PDMS with different molecular weights and contents was incorporated into a

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solid epoxy resin. All these PDMSs have OH end groups which can react directly with OH groups of the epoxy resin in the presence of tetraisopropyltitanate (TPT) as a catalyst in a fusion process. A stable dispersion of hydroxyl-terminated PDMS (HTPDMS) particles in epoxy matrix was achieved via the reaction between the OH groups of the epoxy and the silanol groups of HTPDMS. The chemical structures of the PDMS-modified epoxy resins were confirmed by Fourier transform infrared (FTIR) and ^1H - and ^{13}C -NMR spectroscopy, and their morphologies were observed with optical microscopy. Later, the resulted resins were cured with a cycloaliphatic amine as a curing agent in a stoichiometric ratio relative to the measured epoxy equivalent weight (EEW) of the modified epoxy resins. The morphologies of the cured films were investigated by using scanning electron microscopy (SEM)/energy dispersion X-ray (EDX) technique. To illustrate the influences of the molecular weight and content of PDMS on the mechanical properties of the cured epoxy resin, tensile strength tests was performed on the products films. Hydrophobicity of the cured films was evaluated by measuring of their contact angles with different media (water and diiodomethane) in a sessile drop method.

EXPERIMENTAL

Materials

An epoxy resin based on diglycidyl ether of bisphenol A having epoxide equivalent weight of 420 g/eq was used in this study which was obtained from KZPC (Iran). Four HTPDMS with different molecular weights were purchased from Aldrich (United States). Some data of HTPDMS, which was declared by the producer, are listed in Table I. TPT was obtained from Aldrich and was used as catalyst. Xylene was purchased from Merck (Germany) and used as received. A cycloaliphatic amine was used as curing agent, known as Epikure F205 obtained from Hexion (United States). Hydrogen equivalent weight in the Epikure F205 was 102–104 g/mol, viscosity = 500–700 mPas.

Synthesis of HTPDMS-modified epoxy

A 250 CC three neck round-bottom reactor, equipped with mechanical stirrer (a four blade shaft

TABLE I
Properties of the Hydroxyl-Terminated Poly(dimethylsiloxane)s

Sample	Type	Functionality	Viscosity (cSt)	M_n (g/mol)
25	Dimethyl	Hydroxyl	25	550
65	Dimethyl	Hydroxyl	65	—
90	Dimethyl	Hydroxyl	90–150	—
1800	Dimethyl	Hydroxyl	1800–2200	—

TABLE II
Composition of Epoxy Resin and HTPDMS

Sample	Epoxy resin (g)	HTPDMS (g)
Epoxy	100	0
25-5	95	5
25-10	90	10
25-15	85	15
65-5	95	5
65-10	90	10
65-15	85	15
90-5	95	5
90-10	90	10
90-15	85	15
1800-5	95	5
1800-10	90	10
1800-15	85	15

with a constant mixing rate of 400 rpm), thermometer, and a nitrogen inlet was used for sample preparation.

The reactor was charged with the various amount of epoxy according to Table II and heated to 70°C until the epoxy resin melted. Then three different amounts of HTPDMS and 0.02 wt % (of the total reactant) TPT were added. The mixture was stirred vigorously and heated up to 130°C for 5h.

Curing process

The unmodified and the HTPDMS-modified epoxy resins were dissolved in xylene in 3/1 ratio (by weight) and mixed with a stoichiometric amount of curing agent. The stoichiometric amount of curing agent (W_{CA}) was calculated as follows:

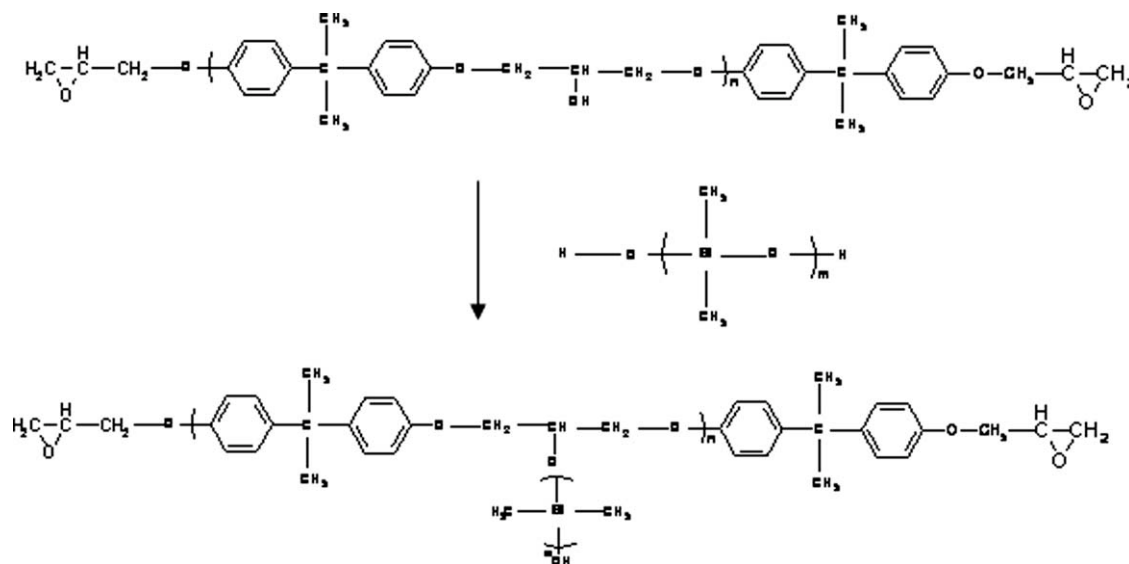
$$W_{CA} = (W_{\text{Epoxy}} * A) / \text{EEW} \quad (1)$$

where W_{EPOXY} is the amount of the unmodified and modified epoxy resins, A is the hydrogen equivalent weight of the curing agent (104 g/eq), and EEW is epoxy equivalent weight of the epoxy resins. The mixtures were stirred for 15 min and casted on Teflon coated plates. Curing reaction was accomplished in ambient temperature after 1 week.

Measurements

Infrared spectra of both epoxy and HTPDMS-modified epoxy resins were determined by a Perkin–Elmer infrared spectrometer (Perkin–Elmer, spectrum one) using KBr pellets. It covered wavelength range of 4500–450 cm^{-1} , at 4 cm^{-1} resolution.

^1H -NMR and ^{13}C -NMR spectra were recorded on Bruker Avance (400 MHz) using acetone as the solvent. EEW of the samples was measured according to ASTM D1652. The samples of 0.5 g were dissolved in acetic acid and titrated with hydrogen bromide with the aid of crystal violet as indicator. The



Scheme 1 the reaction of the epoxy and HTPDMS.

average of EEW value is obtained from 3 measurements. A BEL photonics transition optical microscope was used to determine the morphology of the uncured samples.

The morphology of fractured surface of the cured film of HTPDMS-modified epoxy resins was studied using SEM LEO1455VP. The specimens were obtained from the hand breaking of the frozen samples. The EDX was used to determine the location and also the relative composition of Si and C elements on the fractured surface.

Contact angle measurement of the cured samples was performed by contact angle measuring G100. The used liquids were water (72.8 dyn/cm) and diiodomethane (50.8 dyn/cm). The free surface energy was determined through the solution of the Wu equation.³⁹

A gel permeation chromatography (GPC) Agilent 1100 RI (refractometer index) PLgel column 10 μ m, equipped with three columns of 300 \times 7.5 mm (500 A, 10³ A, 10⁴ A in series) was used for GPC analysis. Tetrahydrofuran (THF) with a flow rate of 1 mL/min was used as the mobile phase. A series of seven polystyrene standards were used to establish a calibration curve of log (molecular weight) versus retention time. The molecular weight was calculated based on the PS standards.

Stress-strain measurements were performed according to ASTM D2370-98 at 25°C by using Santam ST5 with a crosshead speed of 10mm/min. Reported data is the average of three measurements.

RESULTS AND DISCUSSION

The HTPDMS-modified epoxy resins were prepared by the condensation reaction between the OH

groups of epoxy resin and the silanol groups of HTPDMS. HTPDMS in four different viscosities was used to modify the bisphenol A-based epoxy resin. TPT which is known as a condensation catalyst was used to aid the reaction between the OH groups of resins. Scheme 1 shows the proposed reaction.

The proposed structure is confirmed by spectral analysis (FTIR, ¹H-NMR, and ¹³C-NMR). FTIR spectrum of the unmodified and modified epoxy resins (sample 25-10) are shown in Figures 1 and 2, respectively. The important characteristic peaks are listed in Table III.

Emerging the absorption peak for Si-O-C at 1085cm⁻¹ confirms the condensation reaction between the OH groups of epoxy and HTPDMS. Since the oxirane peak at 914 cm⁻¹ did not diminish or disappear, it could be concluded that the backbone of the modified molecule did not change. The absorption peak of Si-CH₃ at 804 cm⁻¹ and Si-O-Si at 1011 cm⁻¹ indicates that HTPDMS was incorporated into the epoxy structure. The existence of OH absorption band at 3434 cm⁻¹ in the sample 25-10 indicates that not all the OH groups were consumed during the modification reaction.

The formation of HTPDMS-epoxy copolymer was evaluated by ¹H- and ¹³C-NMR with respect to diminishing or appearance of the vital groups. The corresponding ¹H-NMR spectra of the unmodified and modified epoxy resins (sample 25-10) are illustrated in Figures 3 and 4, respectively. The peak assignments are summarized in Table IV.

The proton at 2.64 ppm which is assigned for the OH group has weakened due to the OH group consumption during the reaction. The chemical shift at 0.13 ppm which is assigned to the proton in the

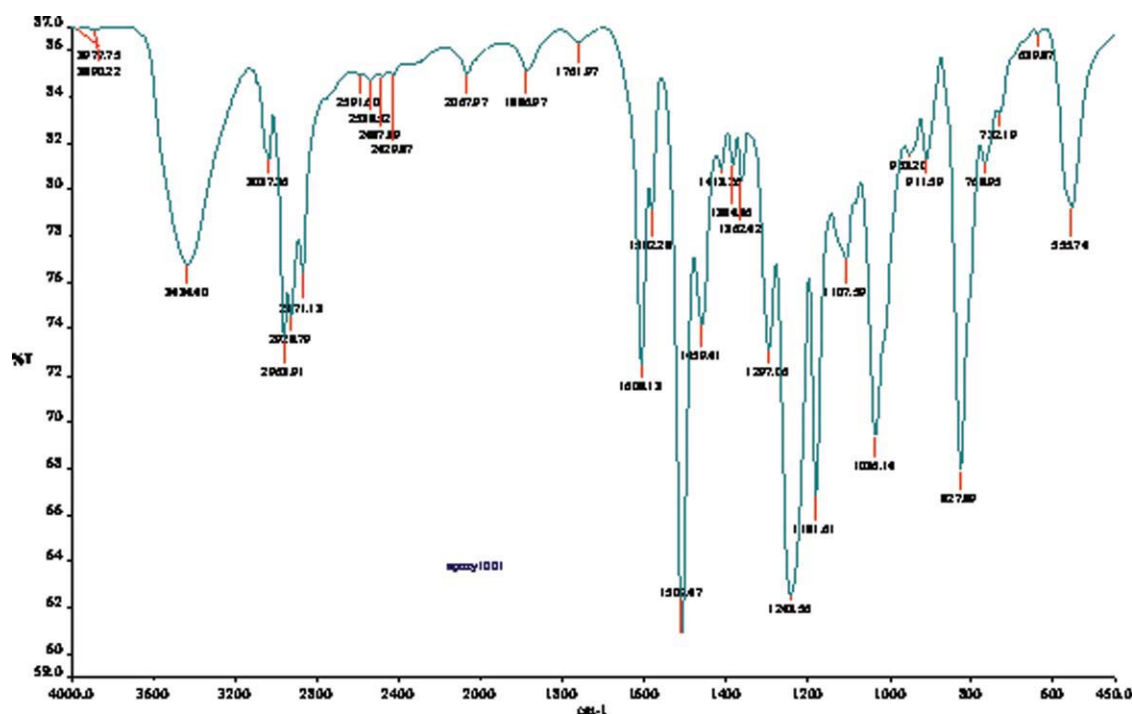


Figure 1 FTIR spectra of the unmodified epoxy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Si-CH₃ group (H¹¹) demonstrates that siloxane chain is connected to the epoxy backbone.^{22–26}

The corresponding ¹³C-NMR spectra of the unmodified and modified epoxy resins (sample 25-10) are illustrated in Figures 5 and 6, respectively. The peak assignments are listed in Table V. The appearance of the chemical shifts at 1.1 ppm of car-

bon in the Si-CH₃ group demonstrates the connection of the siloxane chain to the epoxy backbone.^{20–24}

EEW measurement

The measured and also calculated EEW of the HTPDMS-modified and unmodified epoxy resins are

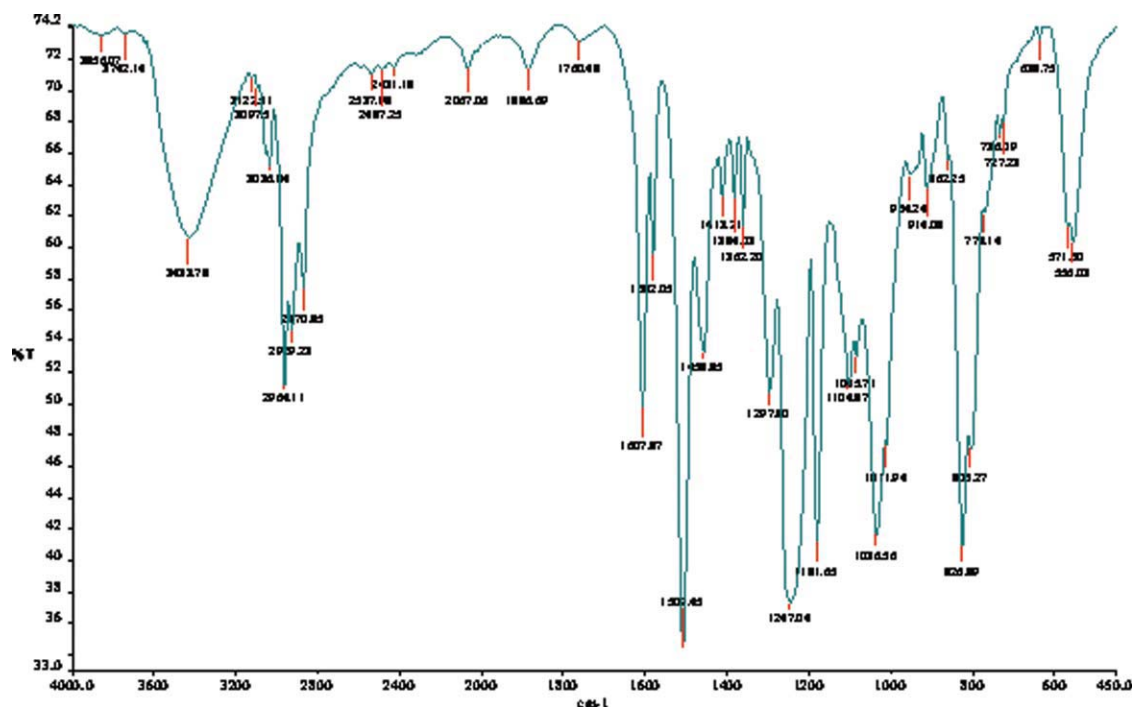


Figure 2 FTIR spectra of the silicone-modified epoxy (sample 25-10). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
FTIR Peak Assignment of the Unmodified Epoxy and Sample 25-10

Unmodified epoxy		Modified epoxy (25-10)	
Peak value	Peak assignment	Peak value	Peak assignment
3434	OH group	3433	OH group
3037,2963,2928	CH ₃ group	3037, 2964, 2929	CH ₃ group
2928,2871,1459	CH ₂ group	2929, 2870, 1458	CH ₂ group
1362	(CH ₃) ₂ C	1362	(CH ₃) ₂ C
1608, 1582, 1509, 1036, 1107, 827	Substituted aromatic group	1607, 1582, 1509, 1036, 1107, 826	Substituted aromatic group
1297	C-O-C group	1297	C-O-C group
911	Epoxy (oxirane) group	914	Epoxy (oxirane) group
		1085	CHO-Si group
		805	Si-CH ₃ group
		1011	Si-O-Si

listed in Table VI. EEW calculation was made based on the proposed reaction which does not involve the ring opening of the epoxy. Beside FTIR and ¹H- and

¹³C-NMR analysis, the relatively good agreement between the experimental and calculated data confirms the proposed reaction.

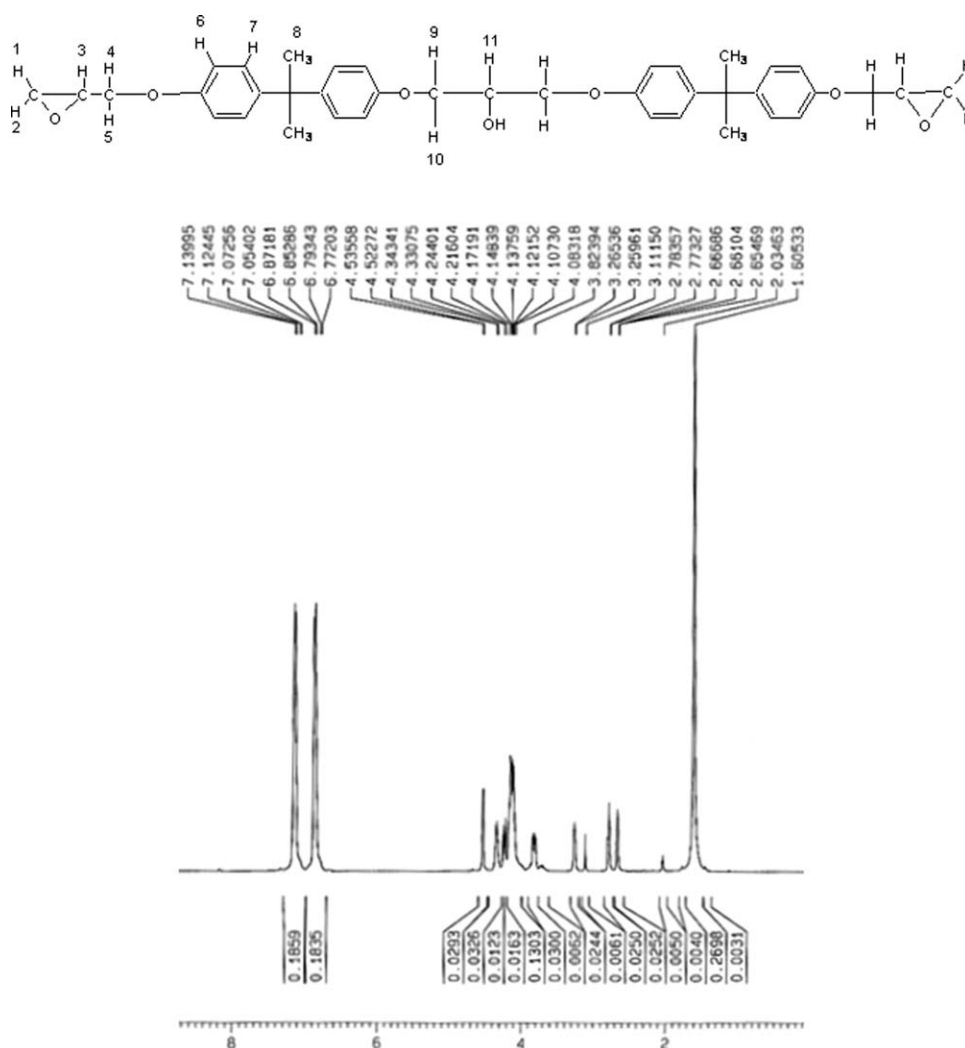


Figure 3 ¹H-NMR spectra of the unmodified epoxy resin.

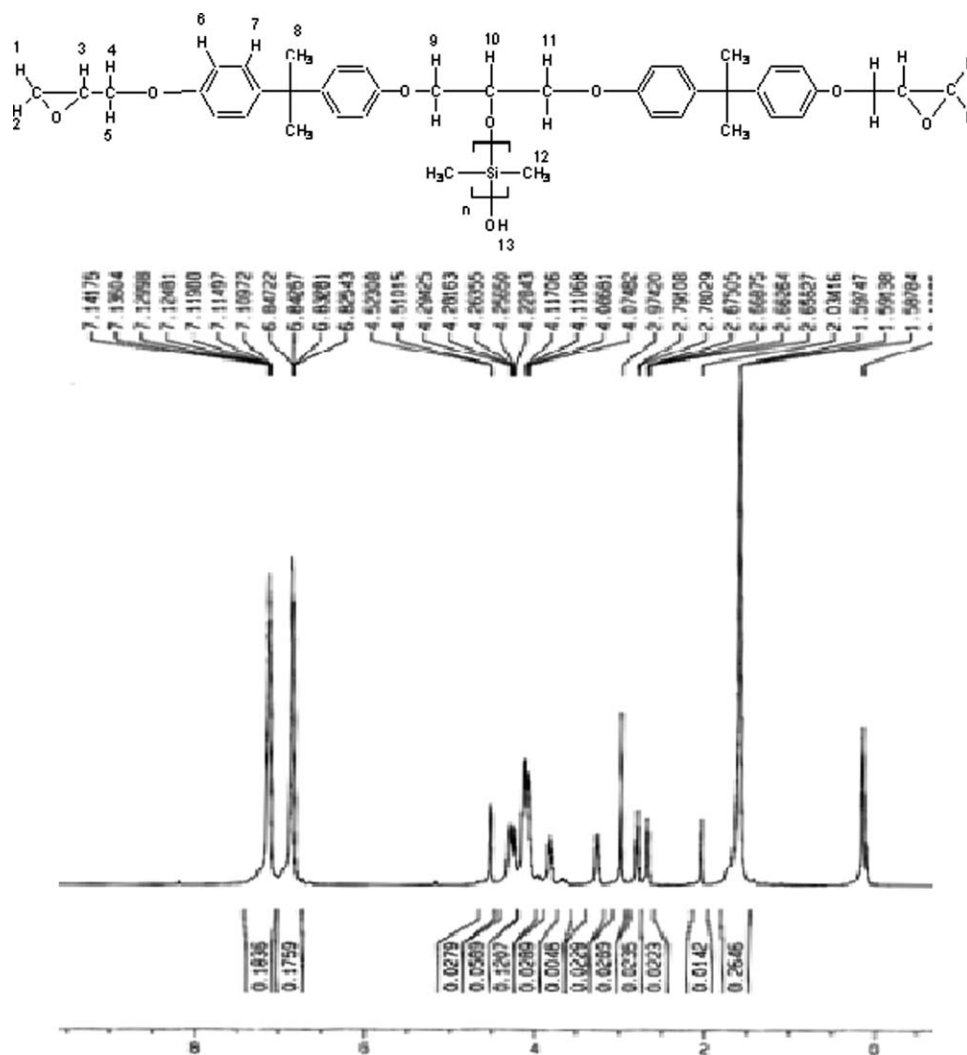


Figure 4 ¹H-NMR spectra of the modified epoxy resin (sample 25-10).

Morphology of samples before curing reaction

To observe the morphology of the modified samples, optical microscopy was used. Figure 7 shows the optical micrographs of the specimens containing 10

TABLE IV
¹H-NMR Peak Assignments of Unmodified Epoxy and Sample 25-10

H(epoxy)	Assignment	H(25-10)	Assignment
H ¹	2.79	H ¹	2.66
H ^{1'}	2.77	H ^{1'}	2.97
H ²	3.26	H ²	3.26
H ³	3.93	H ³	3.96
H ^{3'}	4.33	H ^{3'}	3.93
H ⁴ =H ⁷	6.85	H ⁴ =H ⁷	6.84
H ⁵ =H ⁸	7.13	H ⁵ =H ⁸	7.11
H ⁶	1.6	H ⁶	1.59
H ⁹	4.08	H ⁹	4.25
H ^{9'}	4.13	H ^{9'}	4.51
H ¹⁰	4.13	H ¹⁰	4.29
H ¹¹	2.66	H ¹¹	0.13

wt % HTPDMS with different viscosities. They indicate that there are two distinct phases including HTPDMS droplets and the epoxy continuous phase.

At the beginning of the reaction the blends of HTPDMS and epoxy resin show a bi-continues behavior in which the droplets of HTPDMS dispersed in the epoxy resin as continues phase. So it is reasonable to assume that the reaction occurs in the interphase of the immiscible blend of HTPDMS and epoxy resin (see Fig. 8).

The HTPDMS-modified epoxy resin forms at the interphase and can dissolve in both phases and acts as compatibilizer agent resulting in interfacial energy agreement and improved compatibility. The dispersed phase size can be considered as a criterion for partial compatibility in the samples. The mean HTPDMS droplet size in the samples was determined by Bell View Analyzer and illustrated in Figure 9.

The microscopic observations indicate that the increase in the viscosity of HTPDMS leads to an

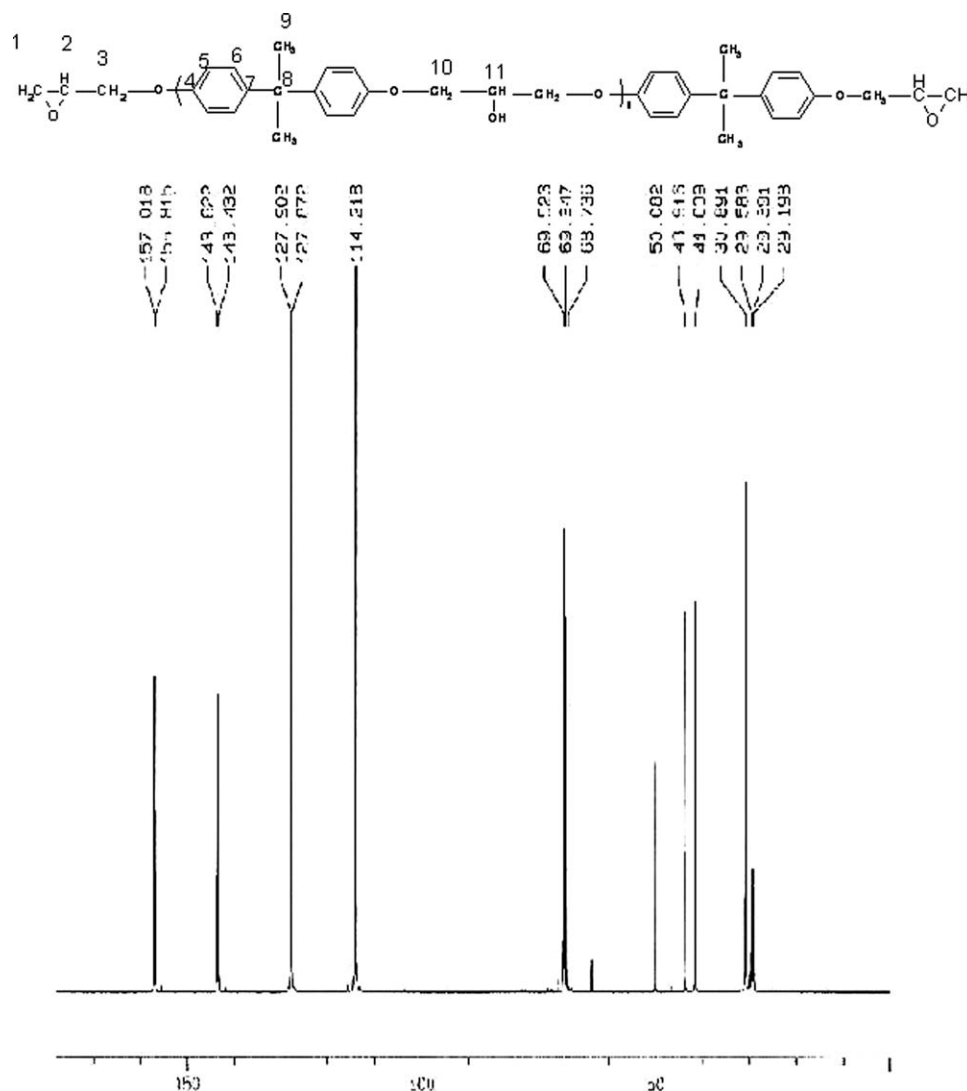


Figure 5 ^{13}C -NMR spectra of the unmodified epoxy.

increase in the dispersed phase size with the exception of the samples containing HTPDMS with the highest viscosity (i.e., HTPDMS 1800). Samples of HTPDMS 1800 have the smallest dispersed phase size among the other viscosities. Wu³⁹ theory can be used to describe this behavior. Wu found a correlation between the size of the dispersed phase and the viscosity ratio, qualitatively similar to the Taylor's prediction:

$$r = (2\Gamma p^{\pm 0.84}) / \eta_m \gamma \quad (2)$$

where γ is the shear rate, r is the number-averaged particle size, Γ is the interfacial tension between the two components forming the dispersion, and p ($p = \eta_d / \eta_m$) is the viscosity ratio, in which η_d and η_m are the viscosities of the dispersed phase and the matrix, respectively.

The exponent sign is positive when $P > 1$ and negative when $P < 1$. The equation predicts that the

finest morphology is achieved in a blend of equiviscous components ($P = 1$).

To study the effect of HTPDMS viscosity, all material parameters which could affect the equation were kept constant. The matrix viscosity and also the shear rate were totally the same for all the samples. The effective parameters are the interfacial tension and the relative viscosity which are the function of the HTPDMS viscosity.

Since the viscosity ratio of HTPDMS 1800 to the epoxy resin at 130°C can approach unit, it may be concluded that the dispersed phase size in the samples of 1800-5, 1800-10, and 1800-15 should be the smallest. The viscosity ratios of HTPDMS 25, 65, and 90 to the epoxy resin at 130°C can be considered the same, so P is not a significant factor in other samples. The interfacial tension between HTPDMS and the melted epoxy may be a governing factor to determine the size of HTPDMS droplets in these samples.

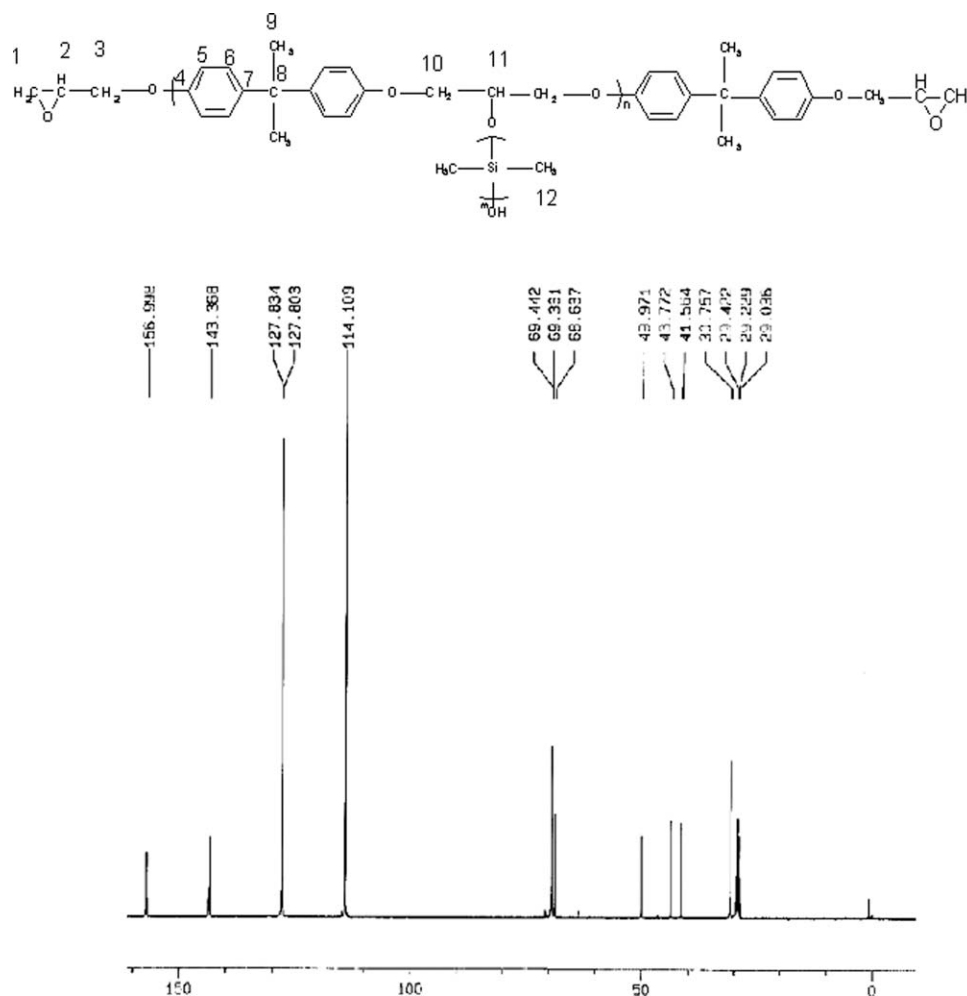


Figure 6 ^{13}C -NMR spectra of the modified epoxy resin (sample 25-10).

The microscopic observation indicates that increasing the dispersed phase concentration from 5% to 15% leads to an increase in the particle size in all samples except those samples containing HTPDMS 1800. The HTPDMS droplet size increases when the concentration of the dispersed phase increases from 5% to 10% and decreases when the concentration of HTPDMS is 15%.

TABLE V
 ^{13}C -NMR Peak Assignments of Unmodified Epoxy and Sample 25-10

C(epoxy)	Assignment	C(25-10)	Assignment
C ¹	43.91	C ¹	43.77
C ²	50.08	C ²	49.97
C ³	156.8	C ³	69.44
C ⁴	114.2	C ⁴	156.99
C ⁵	128.9	C ⁵	114.1
C ⁶	143.4	C ⁶	127.8
C ⁷	29.58	C ⁷	143.36
C ⁸	69.5	C ⁸	41.56
C ⁹	41.63	C ⁹	30.75
C ¹⁰	68.73	C ¹⁰	68.63
C ¹¹	69.34	C ¹¹	69.33
		C ¹²	1.1

Stability study

To study the HTPDMS-modified epoxy samples stability and ascertain that no macro-phase separation occurs during storage, stability test was performed. The samples were diluted with 25 wt % xylene and were observed in the stability column at 25°C for a period of two months. No appreciable changes were

TABLE VI
The Experimental and Calculated EEW

Code	Experimental	Calculated
Epoxy	420	—
25-5	502	442
65-5	505	442
90-5	516	442
1800-5	514	442
25-10	509	466
65-10	506	466
90-10	519	466
1800-10	537	466
25-15	549	494
65-15	549	494
90-15	536	494
1800-15	571	494

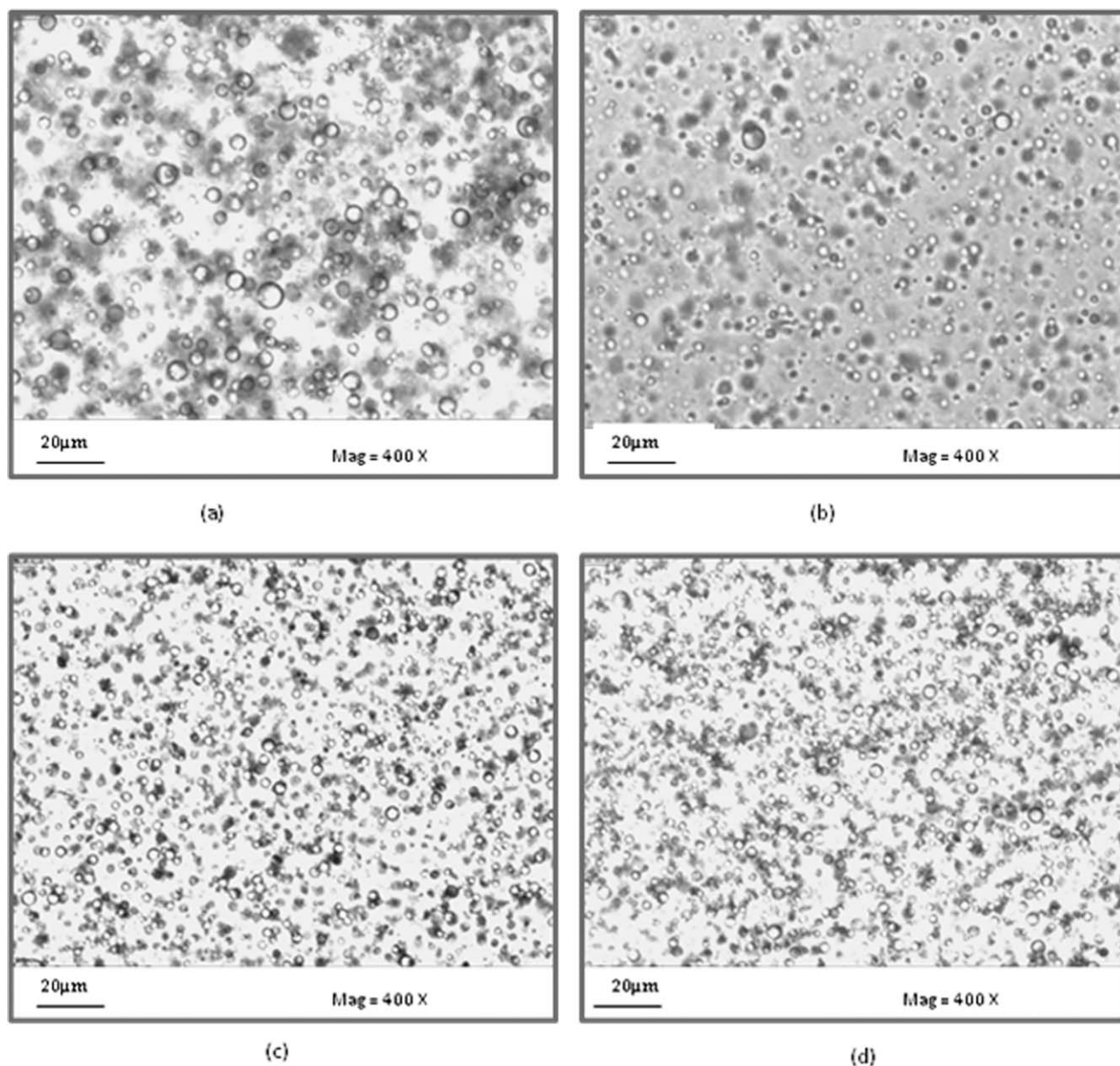


Figure 7 Optical micrographs of silicone-modified epoxy: (a) 25-10, (b) 65-10, (c) 90-10, and (d) 1800-10 (400 \times).

observed in the samples after 2 months which confirms the stability of the HTPDMS-modified epoxy resins.

Self-polymerization of HTPDMS

To study the possibility of self-polymerization reaction in HTPDMS, TPT was separately introduced to the four different HTPDMS resins in the same condition of the main reaction. Table VII shows the molecular properties of HTPDMS resins before and after the reaction.

TPT is a well known catalyst in etherification reactions and is also introduced as a coupling agent. Since HTPDMS has OH groups, self-polymerization is not unlikely. As it was expected, weight average

molecular weight of HTPDMS resins increased after the reaction. As the HTPDMS molecular weight increases, M_w enhances which leads to an increase in the polydispersity index (PDI) of HTPDMS resins (see Fig. 10). This possibility should be considered that the catalyst might have acted as a coupling agent and encouraged a branching or crosslinking reaction in the linear HTPDMS resins.

The HTPDMS resins with the viscosities of 25, 65, and 90 cSt are still in the liquid state after the reaction, but HTPDMS with viscosity of 1800 cSt has converted to gel state. It could be concluded that the state of the HTPDMS residue is solid in the domain centers of samples of 1800-5, 1800-10, and 1800-15, whereas it can be liquid in the other samples.

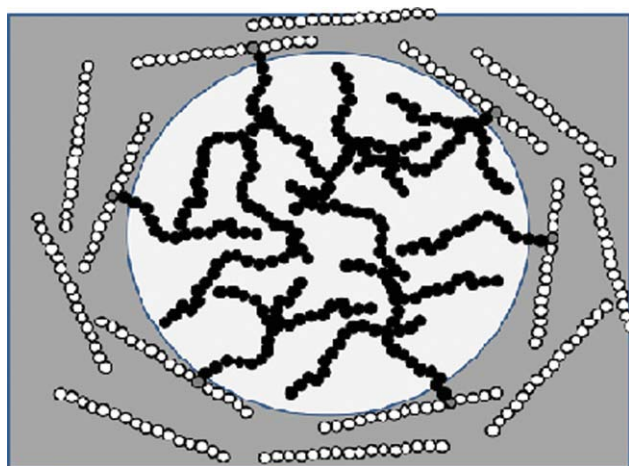


Figure 8 The proposed model for the reaction in the interphase. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Morphology of samples after curing reaction

The unmodified and modified epoxy resins were dissolved in Xylene by weight ratio of 3/1, and cured using a cycloaliphatic amine in the ambient temperature for a long enough time to achieve fully cured samples. Figure 11 shows the FTIR spectra of the cured sample 25-10 and indicates that all oxirane groups have been consumed during the curing reaction.

SEM was used to study the morphology of the fractured surface of the cured HTPDMS-modified epoxy specimens. As shown in Figure 12, the HTPDMS domains are dispersed in the continuous epoxy matrix. The mean dispersed phase size of the samples containing 15% of HTPDMS with the various viscosities is shown in Figure 13. Similar to the uncured samples, the increase in the viscosity of HTPDMS led to an increase in the dispersed phase size in the cured films of samples with the exception of samples containing HTPDMS 1800.

To study the dispersed phase more accurately, EDX was applied. Figure 14 shows the map of elemental

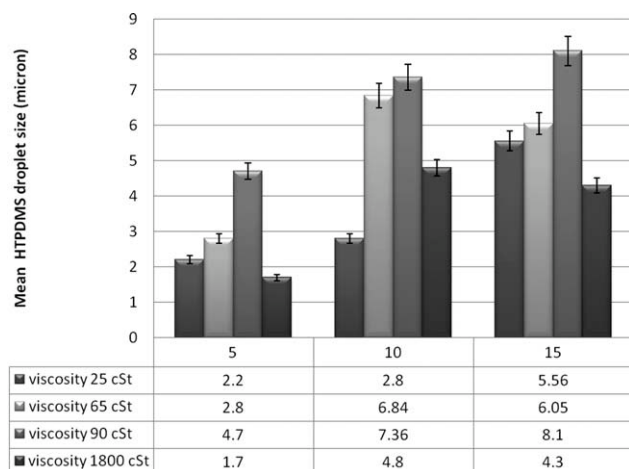


Figure 9 Mean droplet size of HTPDMS in the samples before curing reaction.

TABLE VII
Molecular Properties of HTPDMS Before and After the Reaction

HTPDMS viscosity (cSt)	Before reaction			After reaction		
	M_n (g/mol)	M_w (g/mol)	PDI	M_n (g/mol)	M_w (g/mol)	PDI
25	658	758	1.15	1349	1619	1.24
65	4166	8061	1.93	3903	8673	2.22
90	5034	9420	1.87	5004	12,487	2.49
1800	23,978	53,564	2.23	Gel	Gel	Inf

analysis of the fractured surface of cured film of the sample 1800-10. Green regions show the existence of carbon representing epoxy, and the red ones indicate the presence of Si (HTPDMS). According to the map of elemental analysis, one of the HTPDMS domains with a radius of 2.25 μm was selected for further investigation (see Fig. 15). The relative compositional gradient across the boundaries was studied along a line that crossed the HTPDMS domain. Although the absolute amounts of the components are not accessible from EDX analysis, we can totally trust the relative amounts. The two critical areas including the domain center and the matrix which we expected to differ a lot in relative composition were selected. Two other spots between the later ones in 0.75 and 1.5 μm from the center were also selected. The spots are shown in Figure 15, and the EDX result is reported in Table VIII. Since Si amount is the highest in the domain center and is zero in the matrix, and as this decreases gradually, it could be concluded that there is a gradient layer of siloxane in the domain.

Mechanical properties

Effect of HTPDMS viscosity on mechanical properties

The introduction of HTPDMS into the epoxy resin altered the tensile behavior according to its viscosity.

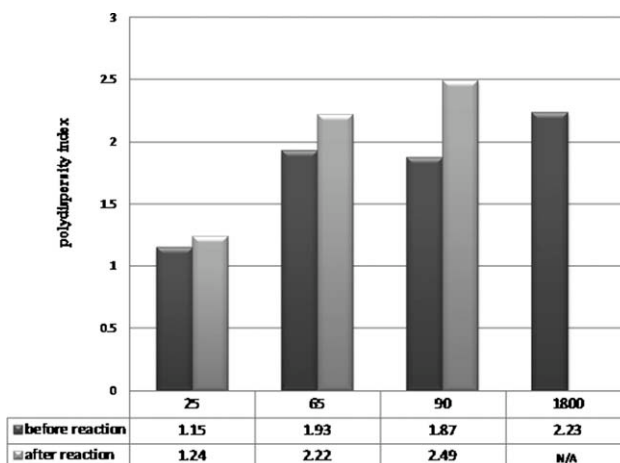


Figure 10 Polydispersity index of HTPDMS before and after the reaction.

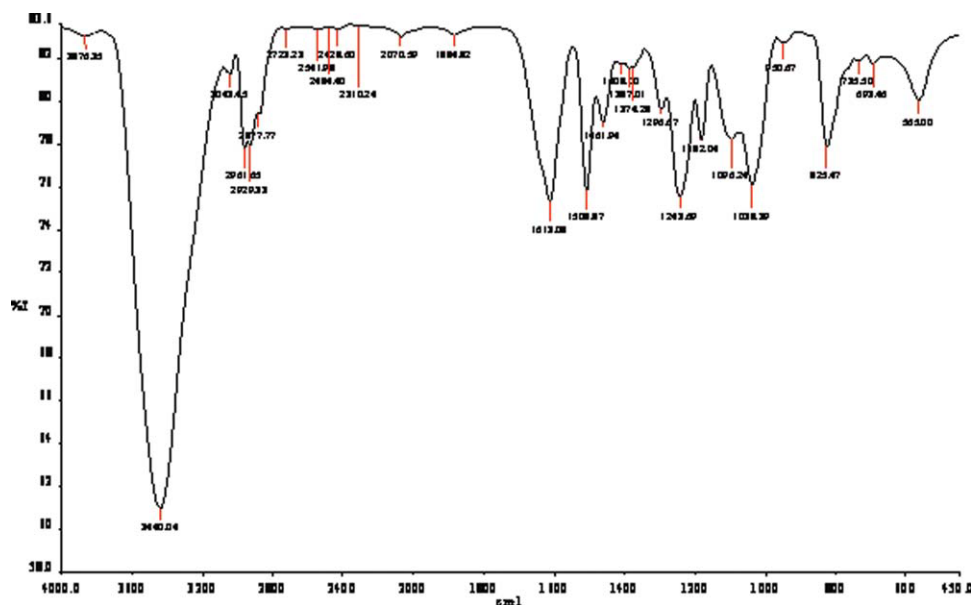
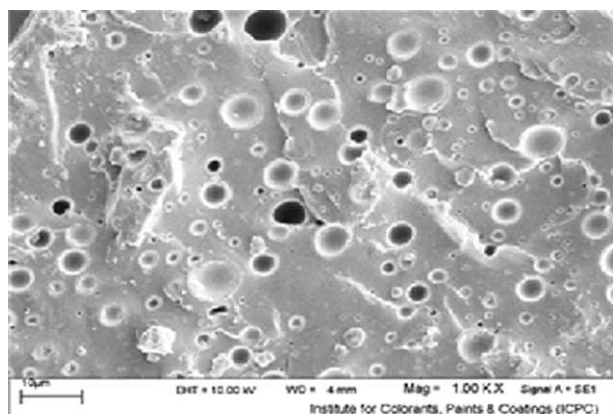


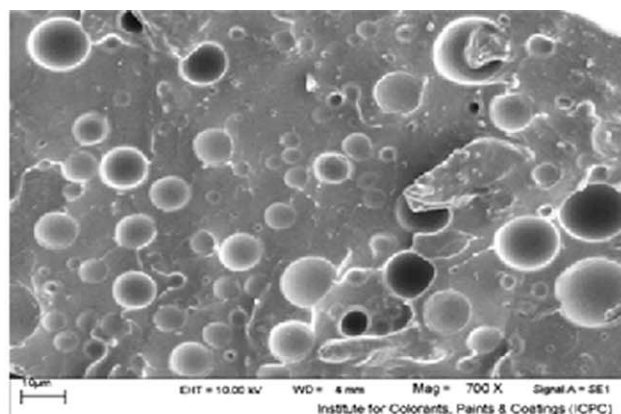
Figure 11 FTIR spectra of sample 25-10 after curing reaction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Stress-strain curves of the cured films of the unmodified and modified epoxy resins with 15% HTPDMS (different viscosities 5, 65, 90, and 1800 cSt) are shown in Figure 16.

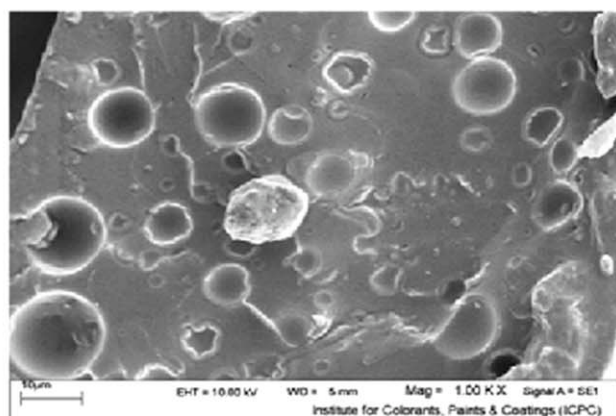
Figure 17 shows the Young modulus of the cured films of pure epoxy and also HTPDMS-modified epoxy resins. It can be seen that the Young modulus of all cured samples decreases in comparison with the



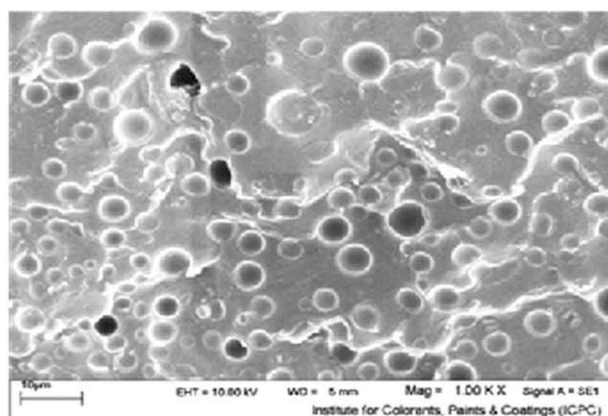
(a)



(b)



(c)



(d)

Figure 12 SEM micrograph of silicone-modified epoxy: (a) 25-15, (b) 65-15, (c) 90-10, and (d) 1800-15.

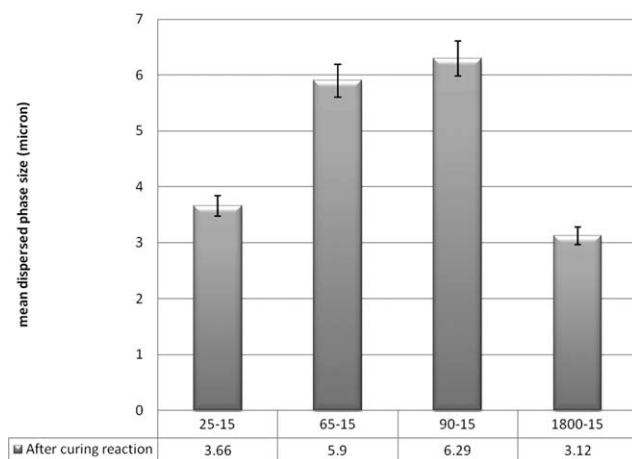


Figure 13 Mean dispersed phase size of silicone-modified samples containing 15% of the various HTPDMS.

pure epoxy film. As the viscosity of HTPDMS increases, the cured samples demonstrate a decrease in the Young modulus. The effect of HTPDMS viscosity on elongation at break is illustrated in Figure 18. As can be seen incorporating 15% PDMS into epoxy resin amplify the elongation at break from 10% in 25-15 to 43% in 1800-15 compared to the neat epoxy film. The enhancement of elongation is 13% in 65-15, whereas is 22% in 90-15. The modulus of toughness is the energy needed to fracture materials and is calculated based on integrating the stress-strain curves. Actually materials absorb this amount of energy before fracture. As it is illustrated in Figure 19, incorporating HTPDMS into epoxy resin enhances the toughness because of the high-energy absorption of HTPDMS chains. Although the toughness of epoxy is completely improved in 1800-15, its change is nonsignificant in the other samples.

As it is illustrated in Figure 13, there is no significant difference between the HTPDMS domain size in the cured films of samples 25-15 and 1800-15, but

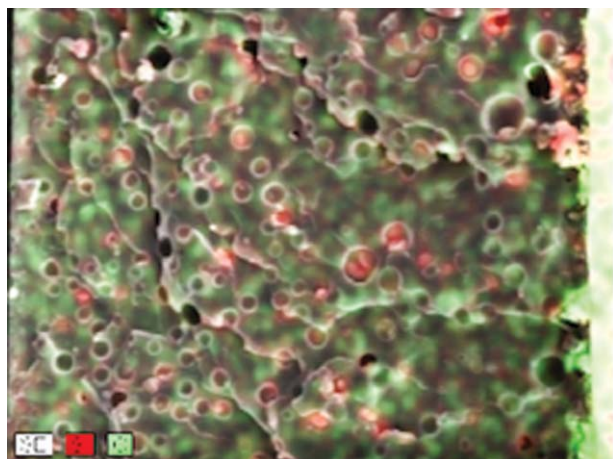


Figure 14 SEM/EDX image of sample 1800-10. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

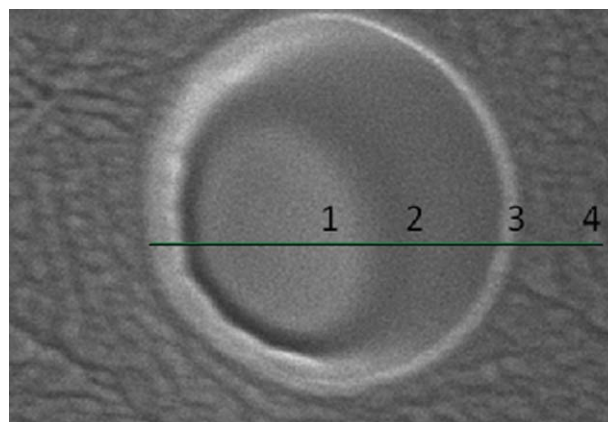


Figure 15 One of the HTPDMS domains in sample 1800-10. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a large difference between the modulus of these two specimens is observed which may be due to the state of HTPDMS domains. HTPDMS residue in the domains of cured 1800-15 may be solid, whereas it is liquid in the samples 25-15. These two samples did not show noticeable difference in the mean particle size and just have different HTPDMS domain state. So it could be concluded that the nature of the domains in the samples can play a vital role in the mechanical properties of HTPDMS-modified epoxy resins. The strong effect of HTPDMS residue state on the elongation at break and the fracture energy of cured films of the samples 25-15 and 1800-15 are evidences for this conclusion. But it seems that the mechanical properties of samples 25-15, 65-15, and 90-15 have been influenced by the mean particle size of HTPDMS domains, and the viscosity of HTPDMS in these samples has no significant effect.

Effect of HTPDMS content on mechanical properties

The introduction of HTPDMS into the epoxy resin altered the tensile behavior according to its content. Stress-strain curves of the cured films of the unmodified and modified epoxy resins with the different amounts of HTPDMS 1800 (5%, 10%, and 15%) are shown in Figure 20. It revealed that the samples containing 5% and 10% HTPDMS undergo plastic deformation. As they exhibit a very high plastic deformation, they can be considered as ductile materials.

TABLE VIII
Relative Composition of Si and C Atoms Across the Domain in Figure 12

Point	1 (domain center)	2	3 (interphase)	4 (matrix)
%Carbon	8.02	7.43	12.76	16.65
%Silicon	19.32	13.31	6.43	0

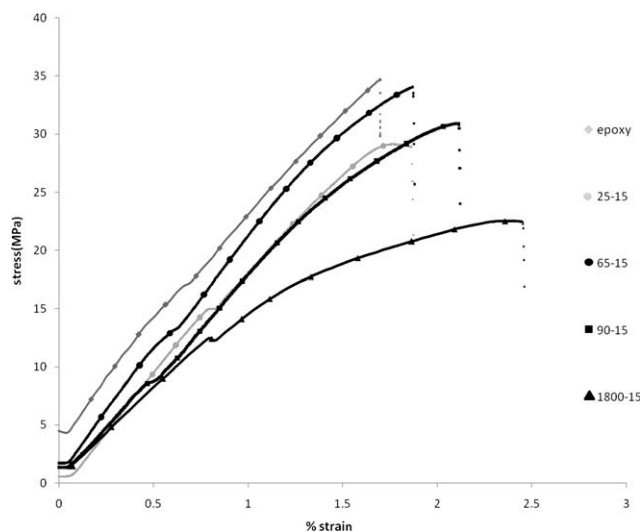


Figure 16 Stress–strain curves of silicone-modified samples containing 15% of the various HTPDMS.

Young modulus of the unmodified and HTPDMS-modified epoxy containing different amounts of HTPDMS 1800 is illustrated in Figure 21. It can be seen that Young modulus follows a decrease trend as HTPDMS content increases. It means that the higher amounts of HTPDMS provide more toughness in the epoxy.

As is illustrated in Figure 22, the introduction of 5 and 10 wt % HTPDMS into the epoxy resin causes an abrupt increase in elongation at break about 100%. It was shown that the elongation at break of specimen 1800-15 is the maximum among the other samples. The enhancement in elongation at break of 1800-15 is 43% compared to the neat epoxy film which is totally insignificant in comparison with 100% and 107% of the cured films of 1800-5 and 1800-10, respectively.

According to Figure 23, incorporating HTPDMS 1800 into the epoxy resin, increases the fracture energy with reference to the cured neat epoxy. As the amount of HTPDMS increases, the cured sam-

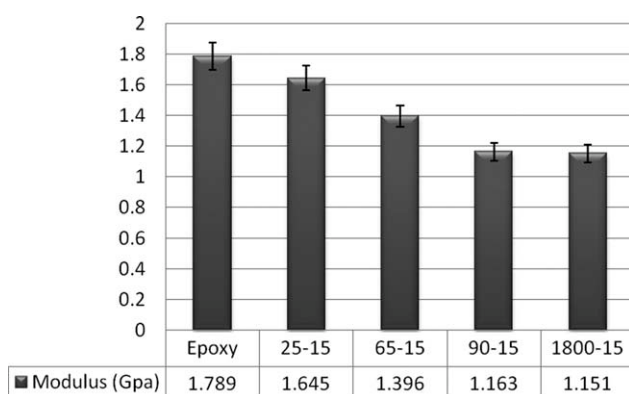


Figure 17 Young modulus of silicone-modified samples containing 15% of the various HTPDMS.

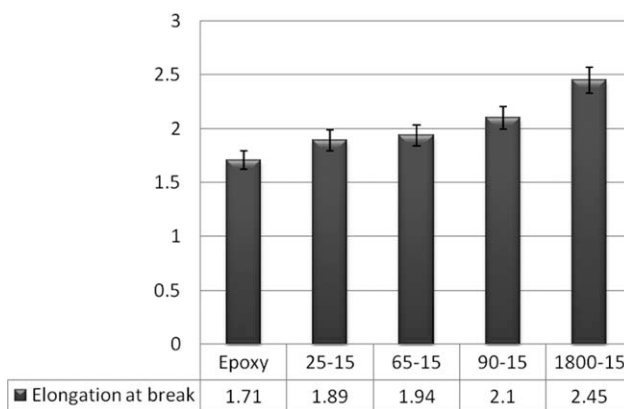


Figure 18 Elongation at break of silicone-modified samples containing 15% of the various HTPDMS.

ples demonstrate a decrease in the fracture energy. The cured film of sample 1800-5 which goes plastic deformation improved the fracture energy about 130% compared to the neat epoxy film. As was mentioned before, this specimen can be considered as a ductile material.

Surface properties

Effect of HTPDMS viscosity on surface properties

The static contact angle was measured on the cured films of the unmodified and modified epoxy resins containing 15% HTPDMS (with different viscosities of 5, 65, 90, and 1800 cSt). The surface properties of the samples are listed in Table VIII. As is shown in Figure 24, incorporating HTPDMS with various viscosities into the epoxy resin demonstrated a strong effect on the water contact angle. The lowest water contact angle for the modified sample (sample 65-15) was 98.5° which is 9° greater than for the unmodified epoxy cured film. These results clearly indicate that the hydrophilic surface of the epoxy resin turns to a hydrophobic one due to the modification with HTPDMS. The greatest water contact angle is

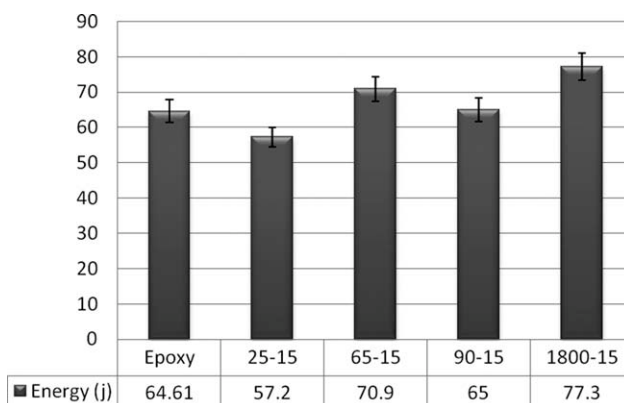


Figure 19 Fracture energy of silicone-modified samples containing 15% of the various HTPDMS.

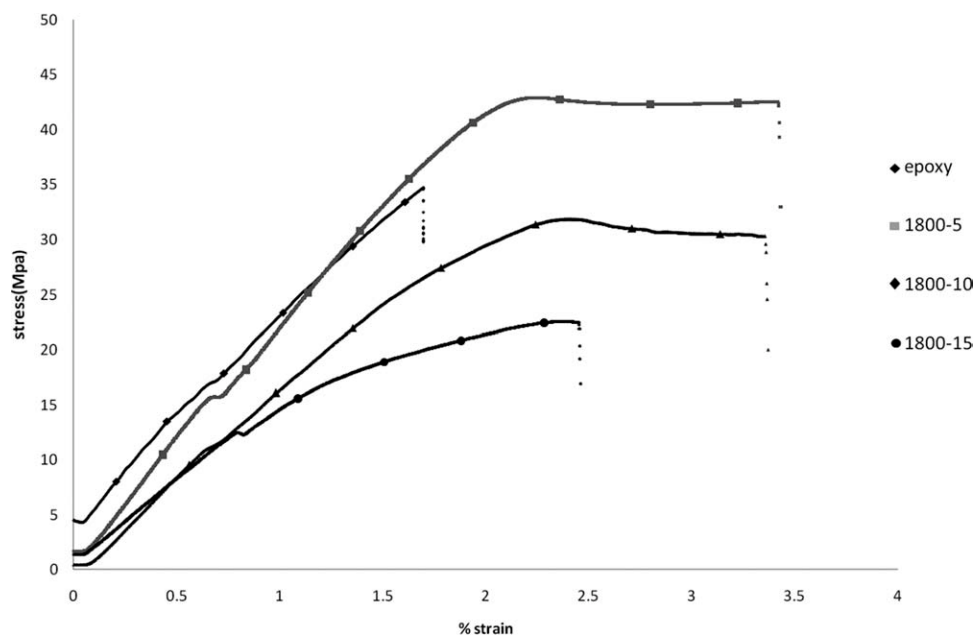


Figure 20 Stress–strain curve of silicon-modified epoxy containing different amount of HTPDMS 1800.

observed on the cured film of the sample 90-15 with the largest mean HTPDMS domain size before the curing reaction ($8.1 \mu\text{m}$). So it is normally expected that the largest HTPDMS domains formed on the surface of this sample. Although the smallest mean HTPDMS domain size has been reported for the sample 1800-15 ($4.3 \mu\text{m}$), the high water contact angle of the film of this sample may be attributed to the higher molecular weight of HTPDMS 1800. Higher molecular weight of HTPDMS experience greater entropic penalty for residing near the interphase. Due to this reason, the orientation tendency toward the surface increases as HTPDMS molecular weight increases. If HTPDMS chain locates at the film surface, motivated by the later phenomena, the layer thickness depends on the root-mean-square (rms) radius of Gyration.⁴⁶ The mean square root of HTPDMS increases by increasing the degree of

polymerization.^{47,48} It could be concluded that as HTPDMS molecular weight increases, its layer gets thicker at the surface. The greater water contact angle of the cured film of the sample 25-15 than of the film of the sample 65-15 may be related to higher possibility of HTPDMS 25 migration to the surface due to its lower molecular weight compared to HTPDMS 65.

The surface free energies of the cured samples were determined through the solution of the Wu equation. The HTPDMS molecular weight had a significant influence on surface energy. As it is shown in Figure 25, the surface energy of the modified epoxy diminishes 32% by incorporating HTPDMS 1800 comparing to the surface energy of cured neat epoxy resin. The highest surface energy among the HTPDMS-modified samples belongs to the film of sample 65-15. Since surface energy of HTPDMS is

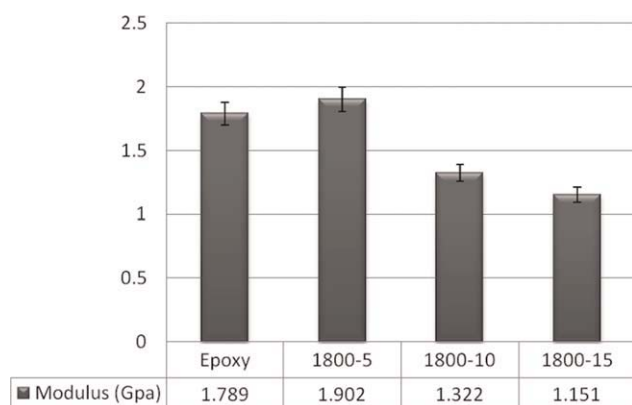


Figure 21 Young modulus of silicon-modified epoxy containing different amount of HTPDMS 1800.

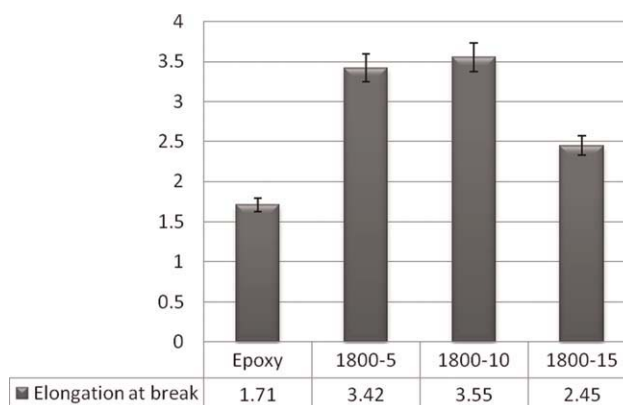


Figure 22 Elongation at break of silicon-modified epoxy containing different amount of HTPDMS 1800.

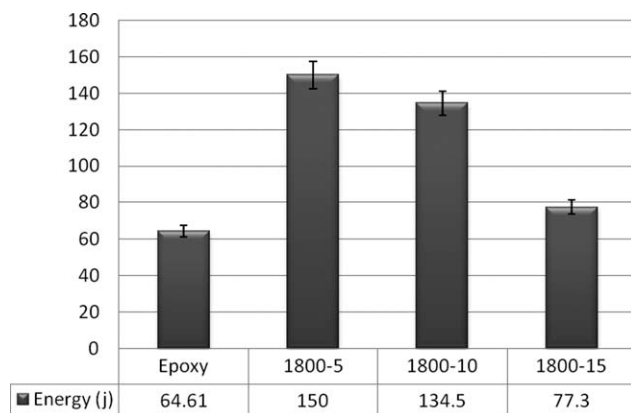


Figure 23 Fracture energy of silicon-modified epoxy containing different amount of HTPDMS 1800.

much lower than that of the epoxy, and HTPDMS is grafted into the epoxy chain, it can be concluded that HTPDMS chain orient toward the surface to decrease the interfacial tension between the film and the environment. The HTPDMS chain length has a significant influence on contact angle and surface energy. The longer ones lead to a higher contact angle and lower surface energy. As mentioned above, the lower surface energy of the cured film of the sample 25-15 compared to the film of sample 65-15 may be attributed to higher possibility of HTPDMS 25 migration to the surface to minimize the interfacial tension between the surface and the environment compared to the HTPDMS 65.

Effect of HTPDMS content on surface properties

The static contact angle was measured on the cured films of the unmodified and modified epoxy resins with the different amounts of HTPDMS 1800 (5%, 10%, and 15%). The surface properties of the samples are listed in Table IX.

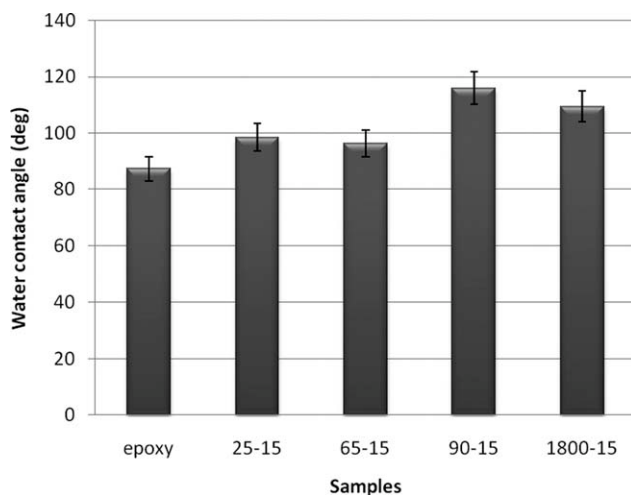


Figure 24 Water contact angle of silicon-modified samples containing 15% of the various HTPDMS.

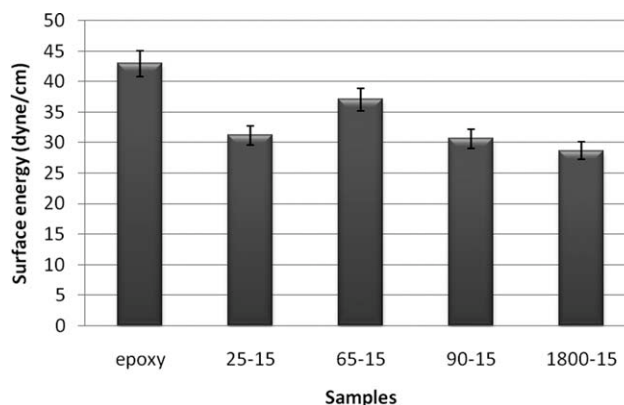


Figure 25 Surface energy of silicone-modified samples containing 15% of the various HTPDMS.

Figures 26 and 27 show the effect of HTPDMS content on contact angle and surface energy of the modified samples, respectively. Higher amount of HTPDMS resulted in an increase in the contact angle and a decrease in the surface energy of the cured samples. In the highest amount of HTPDMS, the contact angle increases about 25° and the surface energy decreases 33% in comparison with the cured film of the unmodified epoxy. Higher amounts of HTPDMS may form a thicker layer on the film surface and so increase the water contact angle.

CONCLUSIONS

HTPDMS in four different viscosities was incorporated into a bisphenol A type epoxy resin through etherification reaction between silanol groups of PDMS and hydroxyl groups of the epoxy resin. FTIR, ^{13}C -NMR, and ^1H -NMR were used to characterize the structure of the synthesized HTPDMS-modified epoxy. The morphology of uncured HTPDMS-modified epoxy was observed by optical microscopy. It was found that HTPDMS droplets are dispersed in the epoxy matrix, and the droplet size increases with increasing HTPDMS viscosity and content with the exception of the samples containing HTPDMS 1800. It has been found out that the state of the HTPDMS residue is solid in the domain

TABLE IX
Surface Energy Measurement of Silicone-Modified Samples Containing 15% of the Various HTPDMS

Surface energy (dyn/cm)	Contact angle(deg)		Code
	CH_2I_2	Water	
42.93	46	87.3	Epoxy
31.21	65.8	98.5	25-15
37.05	53	96.3	65-15
30.62	53.9	116	90-15
28.66	63.1	109.4	1800-15

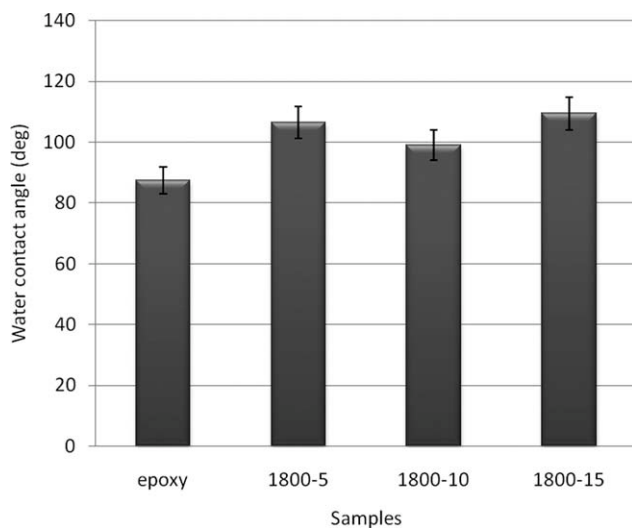


Figure 26 Water contact angle of silicon-modified epoxy containing different amount of HTPDMS 1800.

centers of samples containing HTPDMS 1800, whereas it can be liquid in the other samples.

The amine-cured samples were studied by SEM/EDX analysis. It was revealed that the reaction is occurred through the interphase of the epoxy and HTPDMS blend. Tensile properties of the cured samples of silicone-modified epoxy indicate that incorporation of HTPDMS into the epoxy decreases the Young modulus and increases the elongation at break in comparison with the neat according to HTPDMS viscosity. The cured sample, containing 15% HTPDMS 1800, shows the highest enhancing elongation at break and also the highest fracture energy among all samples. The Young modulus decreased with increasing the content of HTPDMS 1800 in the cured samples. The cured sample containing 10% HTPDMS 1800 showed the highest value of elongation at break (i.e., 3.55) and the high-

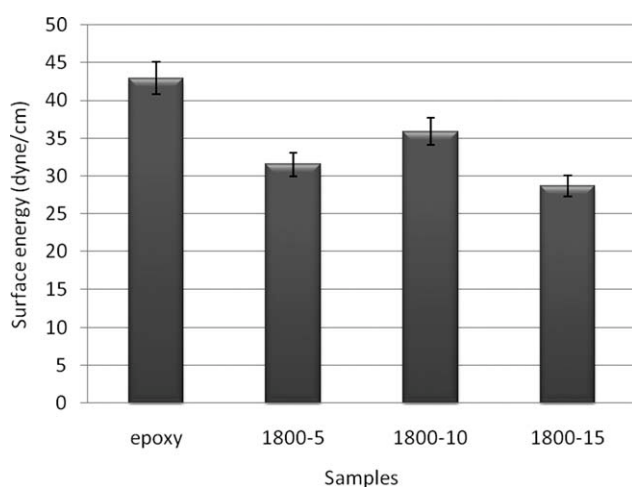


Figure 27 Surface energy of silicon-modified epoxy containing different amount of HTPDMS 1800.

TABLE X
Surface Energy Measurement of Silicon-Modified Epoxy Containing Different Amount of HTPDMS 1800

Code	Contact angle(deg)		Surface energy (dyne/cm)
	Water	CH ₂ I ₂	
Epoxy	87.5	46.6	42.93
1800-5	106.5	58.2	31.54
1800-10	99	53.5	35.89
1800-15	109.4	63.1	28.66

est fracture energy belonged to the sample containing 5% HTPDMS 1800 (i.e., 150 J).

The results of contact angle measurement indicate that the hydrophilic surface of the epoxy resin turns to a hydrophobic one due to the modification with HTPDMS. The viscosity of HTPDMS has a strong effect on water contact angle and surface energy of the cured samples. The cured sample containing 15% HTPDMS 90 exhibits the highest water contact angle (i.e., 116°), whereas the sample with 15% HTPDMS 1800 has the lowest surface energy (i.e., 28.66 dyn/cm).

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