

## The Preparation and Properties Study of Methoxy Functionalized Silicone-Modified Epoxy Resins

Qinyu Ren, Huawei Zou, Mei Liang

State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Sichuan University, Chengdu 610065, China

Correspondence to: H. Zou (E-mail: hwzou@163.com)

**ABSTRACT:** In this work, a series of siloxane epoxy resins (E3074) were synthesized through reaction of poly(methylphenylsiloxane) (DC-3074) with epoxy resin. The chemical structure of the resultant epoxy resin was determined by FTIR, GPC, and epoxy equivalent weight (EEW) tests. The mechanical measurements indicated that the tensile strength of E3074 was lower than that of neat epoxy resin after modification, while their elongations at break improved markedly when compared with that of epoxy resin. SEM revealed that the particle size of silicone had a significant effect on the mechanical properties of the modified epoxy resin. TGA results showed that the thermal stability of E3074 series was better than that of epoxy resin. The char residue of E3074 at 600°C increased with the incremental content of silicone. DMA tests displayed that the addition of silicone effectively enhanced the damping properties of epoxy resin. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40212.

**KEYWORDS:** flame retardance; glass transition; crosslinking; mechanical properties; morphology

Received 6 September 2013; accepted 19 November 2013

DOI: 10.1002/app.40212

### INTRODUCTION

Epoxy resin, which is one of the most important thermosetting polymers, demonstrates many excellent properties, such as high strength and modulus, good electrical insulation, etc. However, epoxy resin is generally brittle due to its highly cross-linked structure and how to improve the toughness of epoxy thermosets has been a hot spot for researchers both from academic and industry.<sup>1–10</sup>

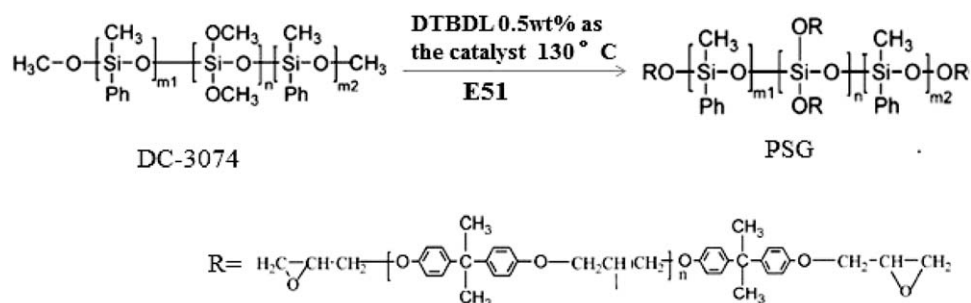
One of the most successful routines of toughness improvement is to incorporate polymeric modifiers into the thermosetting matrix to form fine morphological structures. Such polymeric modifiers can be thermotropic liquid crystal polymers (TLCP), which contain a large number of rigid mesogenic and a certain amount of the soft segment. TLCP modified epoxy retains good mechanical strength and heat resistance as well as markedly improved toughness.<sup>11–13</sup>

The addition of nanoparticles can also improve the toughness of epoxy resin matrix for its unique size effect, local field effect, and quantum effect.<sup>14</sup> However, this will simultaneously cause instable rheological properties, making it difficult to form. Liu et al.<sup>15</sup> used an amphiphilic poly(ethylene-alt-propylene)-*b*-poly(ethylene oxide) (PEP-PEO) block copolymer as a toughening agent to modify a bisphenol A-based epoxy. They found that the PEP-PEO could self-assemble into spherical micelles

within epoxy with an average diameter of 15 nm, giving rise to 180% improvement in fracture resistance.

Hyperbranched polymer can effectively regulate the structure and phase of cured epoxy resin by grafting different functional groups onto the molecule's outer layer.<sup>4,16,17</sup> The advantages of hyperbranched polymer modified epoxy include the following aspects: (1) the spherical three-dimensional structure can reduce shrinkage of the cured epoxy resin; (2) the end groups of hyperbranched polymer directly involve in the curing reaction to form three-dimensional cross-linked structure. In addition, a large number of terminal functional groups can also accelerate the curing speed; (3) the size and spherical structure of hyperbranched polymer can eliminate the filtering effect and play an inner toughening effect.

Interpenetrating network (IPN) system was introduced to modify the brittleness of epoxy resin since the late 1980s.<sup>18–20</sup> A variety of researchers have paid their attention on epoxy-polyurethane and epoxy-polyacrylate systems. Typical IPN system is a polymer run through another randomly, acting as forced inclusion and synergism effect. Hua<sup>20</sup> achieved a simultaneous interpenetrating polymer networks (SINs) consisting of epoxy resin and urethane acrylate resin (UAR). Results showed that the epoxy network could be toughened effectively by introducing the UAR network which was synthesized with poly(oxypropylene) polyol possessing low molecular weight; the impact



**Scheme 1.** Preparation of siloxane-modified epoxy resin.

strength increased appreciably and the tensile strength was close to that of pure epoxy network for the SIN material.

It is believed crucial to increase the compatibility and interfacial adhesion between epoxy matrix and thermoplastic modifier to improve the fracture resistance or toughness of epoxy. Polymers with flexible chains, such as polyetherimide,<sup>21,22</sup> polysiloxane<sup>23,24</sup> have been successfully utilized to blend with epoxy resins as disperse phases to effectively toughen epoxy resins. Polysiloxane possess excellent thermal ability, oxidation resistance, weatherability, low temperature resistance, low surface energy, and high dielectric strength, which can remedy the defect of epoxy resin at these aspects. Linear dimethylsiloxanes used as modifiers of epoxy resin can improve mechanical properties,<sup>25</sup> thermal stability, and fire retardancy<sup>26</sup> of the resulting epoxy blends.

In this work, an organic silicone intermediate (DC-3074) with high proportion of reactive functional groups was applied to modify epoxy resin, in hope of gaining great improvement of elongation at break within normal using conditions of epoxy. In order to improve the compatibility of polysiloxane and epoxy resin, DC-3074 was firstly reacted with a certain amount of epoxy, and then the curing process was carried out. In this article, effects of the addition of DC-3074 on the morphology and toughness of the silicone-modified epoxy resins were examined in detail. Furthermore, the char residue was calculated by means of thermal gravimetric analysis (TGA), and the fractured surfaces of the specimens were observed under the scanning electron microscope (SEM).

## EXPERIMENTAL

### Materials

Epoxy resin (E51), with the epoxide equivalent weight of 185–210, was supplied by Jiangsu Wuxi Resin Plant, China. Polypropylene oxide diglycidyl ether (DER732) was purchased from Dow Chemical Company. Methoxy-functionalized silicone resin (DC-3074) ( $M_w = 1400$ , methoxy content = 18 wt %) was supplied by Dow Corning Management, Shanghai. Dibutyltin diacetate (DTBDL), which was used as catalyst, was purchased from Chengdu Chemical Reagent Company, China. The curing agent, polypropylene oxide Jeffamine (EC-301) was bought from BASF Chemical Company (equivalent [H] weight: 57.5). All materials applied in this study were used as received.

### Preparation of Polyorganosiloxane-Bridged Epoxy Resins

A certain amount of E51 and DC-3074 were fed into a 250-mL three-neck round-bottomed flask, which was equipped with

reflux condenser, mechanical stirrer, and thermometer. Then, the blends were heated to 130 °C and 0.5 wt % DTBDL was added to the flask. The reaction was terminated after 4 h and the prereaction product was obtained. The reaction process was illustrated in Scheme 1 and the structure of the resultant was confirmed by Fourier Transform Infrared Spectroscopy (FTIR) and the molecule weight was determined by GPC.

### Curing of the Epoxy Resin

Epoxy resin, DER732 and the curing agent (EC-301) were mixed together in a beaker at room temperature. Then, bubbles in the mixture were removed by vacuum pumping. The reactant mixture was transferred into polytetrafluoroethylene (PTFE) molds to fabricate samples for mechanical tests. The curing reaction was conducted at 80 °C for 2 h then 125 °C for 3.5 h to access the complete conversion of the terminal groups for the macromers. The cured samples (E3074) were carefully removed from the mold and used for tensile and impact tests. The formulation of the epoxy system is listed in Table I.

### Characterization

FTIR spectrum was obtained with the help of a Fourier transform infrared spectrometer (Nicolet 570) using potassium bromide (KBr) pellets to investigate the structure of polyorganosiloxane-bridged epoxy resins (PSG). The spectra were recorded over the spectral range 400–4000  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ .

Polymer molecular weight ( $M_w$ ) was measured using a gel permeation chromatography (GPC), which consists of a HLC-8320 chromatograph (Tosoh, Japan) equipped with two columns (TSK gel super HM-H 6.0 × 150 mm) in serials. The samples were

**Table I.** Formulation of Epoxy Resin Modified with Silicone Intermediate (DC-3074)

Sample	DC-3074	E51	DER732	EC-301
EP	0	80	20	Equivalent
E3074-10	10	70	20	Equivalent
E3074-20	20	60	20	Equivalent
E3074-30	30	50	20	Equivalent
E3074-30	40	40	20	Equivalent

Except for the curing agent, the system was regarded as 100 parts. The amount of the EC-301 was calculated by the value of active hydrogen equivalent with epoxy values. DER732 was used to reduce the viscosity of the epoxy system.

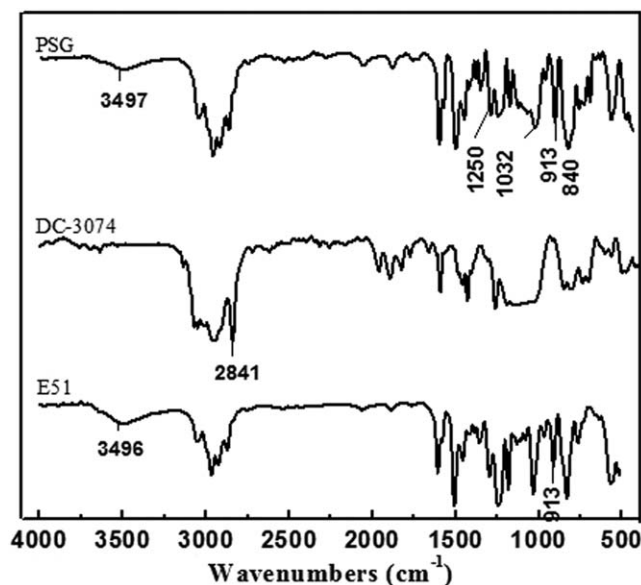


Figure 1. FTIR spectra of E51, DC-3074 and PSG.

analyzed at 40°C with THF as an eluent and the flow rate was set at 0.6 mL/min. Polystyrene (PS) was used as calibration standards.

Epoxide equivalent weight (EEW) of the PSG was determined according to the hydrochloric acid/acetone method. Weigh 0.5–1.0 g once to determine the EEW values. The analyses were performed in duplicate.

The tensile properties of the cured specimens were measured with an Instron (Instron 5567, Instron, USA) universal testing instrument at a rate of 10 mm/min according to ASTM D 638-96. The impact strength was tested with an Izod Impact Tester (MTS Co.) according to ASTM D-256 standard. The size of specimens was 4 mm × 10 mm × 80 mm. All mechanical values were taken from an average of five samples.

The morphology of the fracture surfaces was observed by using a scanning electron microscope (SEM: JSM-5900, JEOL, Japan) at an accelerating voltage of 10 KV. Prior to observation, the surfaces were coated with gold to enhance conductivity and prevent charging.

Thermogravimetric analysis (TGA) was conducted on a thermogravimetric analyzer (Q500, TA, USA) under dry nitrogen gas with a flow rate of 100 mL/min. Samples were heated at a rate of 10°C/min and the relative mass loss of the samples was recorded from 50°C to 600°C.

Dynamic mechanical analysis (DMA) was performed using an RSA III instrument (TA Instruments, USA) at a fixed frequency

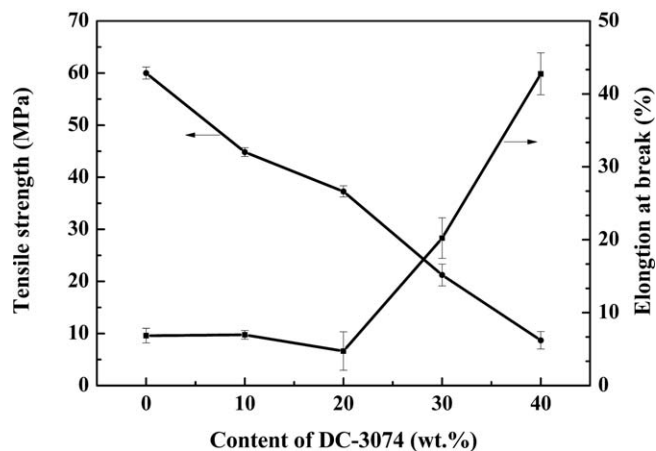


Figure 2. Tensile strength and elongation at break of E3074 systems vs. content of DC-3074.

of 1 Hz with a heating rate of 3°C/min. The test temperature was increased from 10 to 120°C.

## RESULTS AND DISCUSSION

### Characterization of PSG

The FTIR spectra of E51, DC-3074, and PSG are shown in Figure 1. The disappearance of characteristic peak for  $-\text{OCH}_3$  of DC-3074, which is located at 2841  $\text{cm}^{-1}$ , can be deduced from the spectra. In the meanwhile, the weakened signal for  $-\text{OH}$  groups at 3496  $\text{cm}^{-1}$  was noted and the stretching vibration of  $\text{Si}-\text{O}-\text{Si}$  bonds is detected at 1032  $\text{cm}^{-1}$  in the FTIR spectrum of PSG. The results indicate that E51 was successfully reacted with DC-3074. Moreover, the presence of epoxy group is confirmed by the absorption bands at 1250  $\text{cm}^{-1}$ , 913  $\text{cm}^{-1}$ , and 840  $\text{cm}^{-1}$ .

GPC tests show that the  $M_w$  value of DC-3074 is 1185 and the  $M_w$  of PSG-10 is 2048, which verify that the reaction between DC-3074 and E51 occurred.

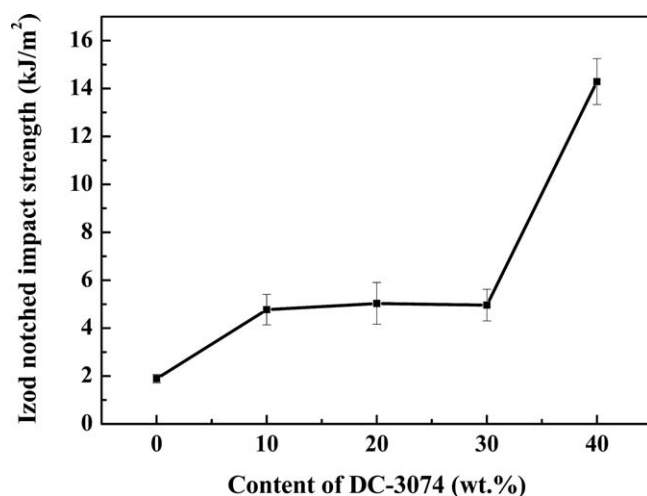
The EEW values of the synthesized PSG copolymer are listed in Table II. The calculated values which are based on the weight ratios and the experimental data of PSG copolymer agree quite well. The opening rate of epoxy ring remains almost unchanged. This further confirms the epoxy groups do not involve in the grafting reaction. The results are consistent with theoretical assumption and FTIR result.

### Mechanical Properties of Epoxy Resins

As shown in Figure 2, the tensile strength of copolymers E3074 (10-40) decreases significantly after chemical modification, but still meet the use requirement (>10 MPa). The observed experimental results may result from the presence of flexible siloxane

Table II. The EEW and Opening Rate of Epoxy Ring of PSG Systems

Sample code	E51	PSG-10	PSG-20	PSG-30	PSG-40
EEW (calculated value) (g/mol)	0.543	0.475	0.407	0.339	0.271
EEW (experimental value) (g/mol)	0.543	0.470	0.406	0.332	0.271
Opening rate of epoxy ring (%)	0	1.1	0.2	2.1	0



**Figure 3.** Impact strength of the E3074 systems vs. content of DC-3074.

linkage, free rotation of  $-\text{Si}-\text{O}-\text{Si}-$  bond as well as weak interface boundary between siloxane and epoxy matrix. According to Chen,<sup>27</sup> the addition of the second soft DC-3074 phase would reduce internal residual stress, leading to the increased tensile strength; however, the strength of E3074 phase is relatively low which brings about the decreased tensile strength. When the former effect dominates, the strength of the blend is enhanced through the addition of E3074. Otherwise, the strength would be decreased by the E3074 addition. From the subsequent tensile strength, it is obvious that the latter effect dominates in E3074 systems.

The elongation at break of E3074-40 reaches 43% at the E3074 content of 40 wt %, increasing 5-folds when compared with the unmodified resin. By contrast, when a small amount of silicone is added,  $-\text{Si}-\text{O}-\text{Si}-$  chains are not enough to change the high crosslinking network of epoxy resin; therefore, the elongation of E3074 systems remains unchanged. With further increasing DC-3074 to 40 wt %, the toughness of the resulting epoxy resin improves markedly which can be ascribed to the effect of flexible  $-\text{Si}-\text{O}-\text{Si}-$  skeleton, resilient behavior and constant stress dissipating capability.<sup>28</sup>

The impact strength values of the E3074 systems are plotted as a function of DC-3074 content in Figure 3. When the addition quantity of DC3074 is 30 wt % or less, a slight improvement of impact strength is observed. The reason may be due to the fact that the silicone particles in epoxy resin matrix are too small to generate plastic deformation. However, when the content of DC-3074 reaches 40 wt % in the system, the impact strength of E3074 reaches 14 KJ/m<sup>2</sup> and is 6-folds higher when compared with pure epoxy resin. The reason is that  $-\text{Si}-\text{O}-\text{Si}-$  skeletal bond has a length of 1.64 Å, which is significantly longer than that of the  $-\text{C}-\text{C}-$  bond (1.53 Å). Therefore, the steric interferences or intramolecular congestion is diminished. Moreover, the  $-\text{Si}-\text{O}-\text{Si}-$  bond angle 143° is much more open than the usual tetrahedral bond angle 110°. These structural features have a profound effect on the impact strength of a polymer and have enough mobility to absorb impact energy, thereby increasing the impact resistance of the polymer to a greater extent.<sup>29</sup>

### Morphology of Epoxy Resin

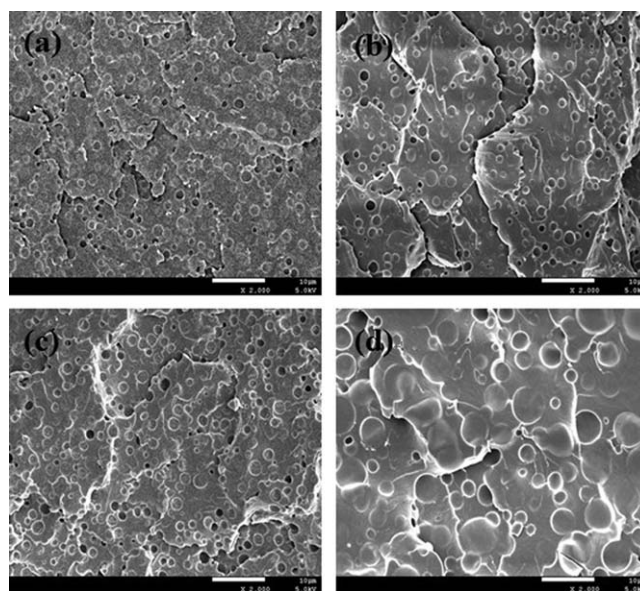
The morphology of the impact fracture surface of the modified epoxy is shown in Figure 4. As can be seen in Figure 4(a–c), it is obvious that all micrographs exhibit a phase-separated morphology and sea-island structure is formed. This morphological feature is conjectured to be responsible for the observed increase in the impact strength, and the modified system can be regarded as a particulate polymer composite which bases on epoxy matrix filled with second phase particles. It is reported that the rubber particles can be considered to bridge the crack as it propagates through materials.<sup>30</sup> Hence, the PSG particles are believed in this regard to act like rubber particles to block the propagation of the crack if occurred.

A simple Lange model is reported<sup>26</sup> to relate the fracture energy  $G_c$  to the line tension  $T$ :

$$G_c = G_m + T/D_s \quad (1)$$

$$D_s = 2d_p(1 - V_p)/3V_p \quad (2)$$

where  $G_m$  is the toughness of matrix;  $D_s$  which is defined by eq. (2) is interparticle spacing depending on particle diameter  $d_p$  and particle volume fraction  $V_p$ . It can be predicted that through eqs. (1) and (2) that the composite fracture energy increases with the decreasing particle size  $d_p$  of the second phase. Moreover,  $G_c$  would improve with the incremental  $V_p$  for a given  $d_p$ . Therefore, the fracture energy (i.e., impact strength) will initially increase with the increasing size of the second phase to a maximum value and after that fall with the further increasing of second phase. It can be deduced from Figure 4(a–c) that the average diameter of the disperse phase is nearly the same and this is exactly why the value of  $G_c$  remains almost unchanged. So is the fracture strength of the modified epoxy resin. In Figure 4(d), the  $d_p$  is much larger and this contribute to the higher impact strength of E3074-40. We strongly suggest that the increasing size of the disperse phase might be associated with the reagglomeration or coalescence of the disperse phase.<sup>31</sup>



**Figure 4.** SEM photos of fracture surfaces of E3074 system (a) E3074-10, (b) E3074-20, (c) E3074-30, and (d) E3074-40.



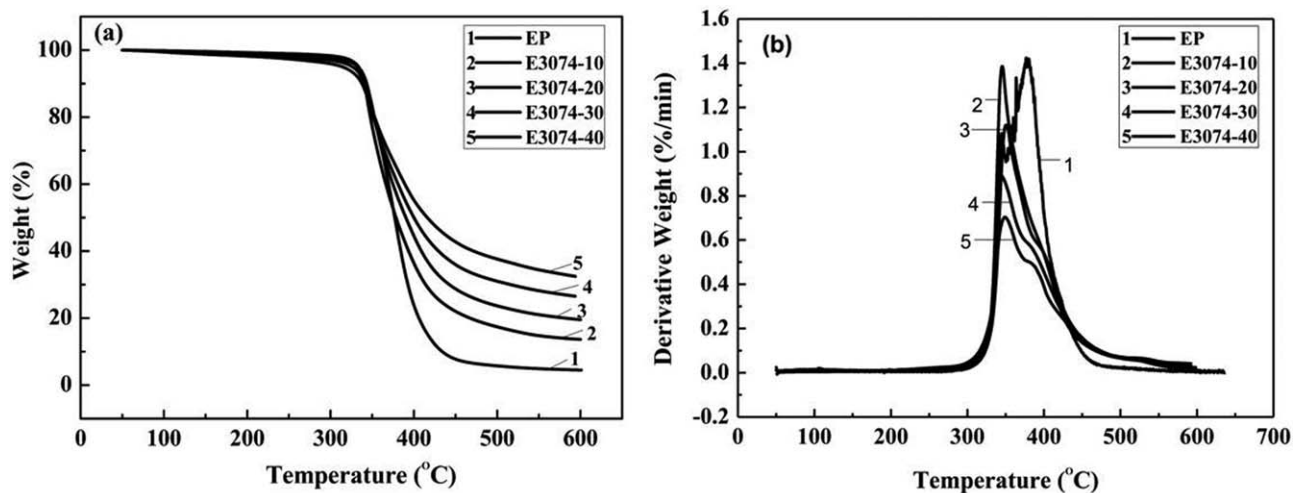


Figure 5. TGA (a) and DTG (b) curves for the samples.

Table III. Thermal Stability Factors of E-3074 Systems

Sample	$T_{-5\%}$ (°C)	$T_{max}$ (°C)	Solid residue at 600°C (%)	OI (%)
EP	332.1	347.0, 377.0	4.5	19
E3074-10	333.8	347.5	14.0	23
E3074-20	330.6	350.6	19.5	25
E3074-30	327.3	26.7	28	
E3074-40	324.9	348.6	32.3	30

### Thermal Stability of Epoxy Resins

The TGA curves of all the samples under nitrogen atmosphere are shown in Figure 5. The onset degradation temperature is the temperature at 5% weight loss ( $T_{5\%}$ ) and the solid residue at 600°C is obtained from the TG curve. The temperature of the maximum weight loss rate ( $T_{max}$ ) of samples is obtained from the DTG curve. In Figure 5 and Table III, it is observed

that the  $T_{5\%}$  of E3074-10 is higher than that of pure epoxy resin while the  $T_{5\%}$  for modified resins drops with the increasing content of DC-3074. The reason may be that when a small amount of DC-3074 is added, the thermoplastic poly (methylphenylsiloxane) (PMPS) segment can absorb thermal energy and dissipate thermal energy through its flexible siloxane structure. Because the  $T_{5\%}$  for silicone is much lower than that of epoxy resin,<sup>32</sup> the  $T_{5\%}$  for the modified resin will drop slowly with the increasing dosage of DC-3074. It is reported that the composition of siloxane at lower temperature can form a silicone-containing group. In the presence of silicone-containing group, a protective residue is formed which acts as a thermal insulation with excellent thermal stability.<sup>33</sup>

Figure 5 and Table III illustrate that there are two  $T_{max}$ s for neat epoxy while only one is detected for E3074 systems. This indicates that the degradation mechanism has been changed with the addition of DC-3074. Further study should be carried out to make the cleavage mechanism clear.

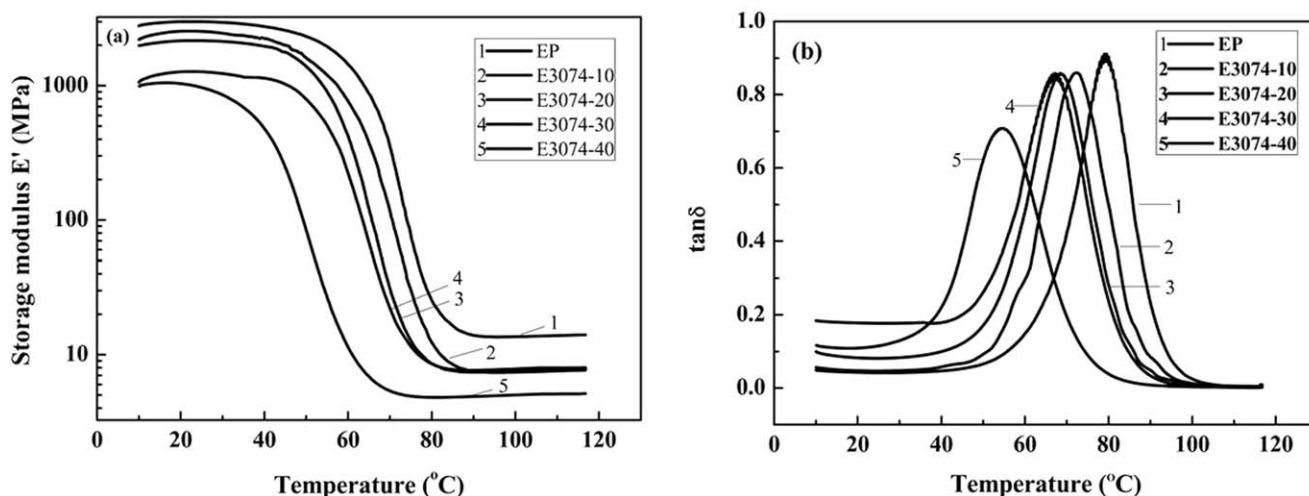


Figure 6. Storage modulus (a) and  $\tan \delta$  (b) of E3074 systems.

**Table IV.** DMA Characteristics of Cured E3074 Systems

Sample	$E'$ (MPa)	Half-band width (°C)	$\tan \delta_{\max}$	$T_g$ (°C)
EP	3005	15.6	0.91	79.0
E3074-10	2550	18.1	0.86	72.1
E3074-20	2167	18.4	0.86	68.4
E3074-30	1151	19.5	0.86	67.4
E3074-40	1052	23.6	0.71	54.2

It has been reported that the  $N_2$  residue (char) is a useful parameter for the study of flame retardancy of the composite materials since it can be easily correlated with the oxygen index (OI) through the empirical eq. (3) which is derived by van Krevelen.<sup>34</sup>

$$OI(\%) = 17.5 + 0.4(CR) \quad (3)$$

In this study, CR is defined as the char residue at 600°C. The limiting OI is defined as the minimum amount of oxygen needed in a nitrogen-oxygen (air) mixture to maintain combustion after ignition. In Table III, OI data for various prepared samples are exhibited. The char yield at 600°C increases from 4.5% (pure epoxy resin) to 32.3% (E3074-40), so the calculated OI rises from 19 to 30. This demonstrates that the introduction of PMPS produces a protective layer, thus improves the thermal degradation.

#### Viscoelastic Damping Characteristics of the Cured Epoxy Systems

The damping properties of neat epoxy and DC-3074 modified epoxy resin were investigated based on the  $\tan \delta$  curves and storage modulus curves which are obtained from DMA (see Figure 6). Storage modulus represents the capacity for materials to store the elastic deformation energy. Figure 6(a) and Table IV indicate that an increase in the DC-3074 content leads to a progressive decrease in elastic modulus of the modified epoxy resin from 3005 MPa to 1052 MPa. This is due to the fact that the DC-3074 is a soft phase which has much lower modulus than the epoxy matrix. Therefore, according to the modified rule of mixtures for particulate composites<sup>26</sup> which is applicable to the cases of polymer blends with second phase, the Young's modulus of the blends will then monotonically decrease with the increasing content of DC-3074.

The variation in  $T_g$  for the epoxy systems with respect to the DC-3074 content is given in Table IV. The  $T_g$ s of epoxy systems decrease from 79°C to 54°C which mainly depend primarily on the chain flexibility and the cross-linking density.<sup>35,36</sup> With the addition of DC-3074, —Si—O—Si— flexible chains are introduced into the systems, and cross-linking density is lower due to introduced PMPS particles in epoxy matrix. Therefore, the  $T_g$  of DC-3074 modified system is lower than that of neat epoxy resin. It should be pointed out that the lower  $T_g$  of PMPS cannot be measured within the range of experimental temperature employed. Nonetheless, it is noted that the value of the observed  $T_g$  is quite close to that of epoxy, indicating that the E3074 system is microphase-separated. The judgment is also confirmed by SEM observations.

## CONCLUSIONS

In this work, a series of PMPS modified E3074 were synthesized. FTIR and GPC results confirmed that reaction between E51 and DC-3074 occurred. The tensile and impact tests indicated that the introduction of —Si—O—Si— chains had much effect on the mechanical properties of curing epoxy resin. The SEM photos showed that the size of PMPS particles had much effect on the impact strength. It was found from the data of TG that E3074 copolymers exhibited excellent thermal stability. The DMA measurements indicated that silicone modified the damping characteristics of epoxy resin.

## ACKNOWLEDGMENTS

The authors would thank the National Natural Science Foundation of China (51273118) and the Science and Technology Pillar Program of Sichuan (2013FZ0006) for financial support, and the Analytical and Testing Center of Sichuan University for providing SEM observation.

## REFERENCES

1. Ueki, T.; Nishijima, S.; Izumi, Y. *Cryogenics* **2005**, *141*.
2. Thomas, R.; Durix, S.; Sinturel, C.; Omonov, T.; Goossens, S.; Groeninckx, G.; Moldenaers, P.; Thomas, S. *Polymers* **2007**, *48*, 1695.
3. Francis, B.; Rao, V. L.; Poel, G. V.; Posada, F.; Groeninckx, G.; Ramaswamy, R.; Thomas, S. *Polymers* **2006**, *47*, 5411.
4. Manjula, D. D.; Jaisankar, S. N.; Madhvesh, P. *Eur. Polym. J.* **2013**, *49*, 3561.
5. Lützen, H.; Bitomsky, P.; Rezwani, K.; Hartwig, A. *Eur. Polym. J.* **2013**, *49*, 167.
6. Thomas, R.; Ding, Y.; He, Y.; Yang, L.; Moldenaers, P.; Yang, W. *Polymers* **2008**, *49*, 278.
7. Pascault, J. P.; Williams, R. J. J.; Paul, D. R.; Bucknall, C. B. *Polym. Blends*. Vol. 1. **2000**, 379, 415.
8. Yang, G.; Zheng, B.; Yang, J. P.; Xu, G. S.; Fu, S. Y. *J. Polym. Sci.* **2008**, *46*, 612.
9. Xiaoqiang, H.; Dengsong, Z.; Hongrui, L. *Chin. Part* **2011**, *80*, 85.
10. Zheng, S.; Wang, H.; Dai, Q.; Luo, X.; Ma, D. *Macro. Chem. Phys.* **1995**, *196*, 269.
11. Zeng Fang H.; Song Ting T.; Xia Yu W. *Chin. Plas.* **2003**, *32*, 35.
12. Yu Mei J. *Polym. Mater. Sci. Eng.* **2009**, *150*, 153.
13. Zong Yong, G. J. *App. Polym. Sci.* **2007**, *105*, 1861.
14. Liang, Y. L.; Pearson, R. A. *Polymers* **2009**, *50*, 4895.
15. Liu J.; Sue, H. J.; Zachary, J. T. *Acta. Mater.* **2009**, *57*, 2691.
16. Zhu, C.; Lin, L. J.; Qi, B. *Chem. Adhe.* **2007**, *29*, 261.
17. Pawel, G. *Polymers* **2007**, *48*, 1857.
18. Bibbanand, A. *Eur. Polym. J.* **1994**, *30*, 1269.

19. Ying, L.; Sufen, M. *J. App. Polym. Sci.* **2000**, *41*, 2181.
20. Hua, F. J. *Eur. Polym. J.* **2000**, *36*, 27.
21. Bonnet, A.; Pascault, J. P.; Sautereau, H. *Macromolecules* **1999**, *32*, 8524.
22. Wang, M. H.; Yu, Y. F.; Wu, X. G.; Li, S. J. *Polymers* **2004**, *45*, 1253.
23. Gonzalez, M.; Kadlec, P.; Štěpánek, P.; Strachota, A.; Matejka, L. *Polymers* **2004**, *45*, 5533.
24. Piotr, M.; Hieronim, M.; Henryk, G. *Eur. Polym. J.* **2012**, *48*, 769.
25. Jin, F. L.; Park, S. J. *Polym. Deg. Stab.*, **2007**, *92*, 509.
26. Fu, S. Y.; Feng, X. Q.; Lauke, B.; Mai, Y. W. *Compos. Part B.* **2008**, 933.
27. Zhen, K. C. *Polymers* **2009**, *50*, 1316.
28. Wang, W. J.; Perng, L. H.; Hsiue, G. H.; Chang, F. C. *Polymers* **2000**, *41*, 6113.
29. Ananda Kumar, S. *Eur. Polym. J.* **2006**, *42*, 2419.
30. Lange, F.F. *Philos. Mag.* **1970**, *22*, 983.
31. Barton, J. M. *J. Macro. Sci. Chem. Part A.* **1974**, *8*, 25.
32. Lianli, D.; Minmin, S. *Chem. Res.* **2012**, *51*, 8178.
33. Wu, K.; Song, L.; Wang, Z. Z.; Hu, Y. *J. Polym. Res.* **2009**, *16*, 283.
34. Van Krevelen, D. W. *Polymers* **1975**, *16*, 615.
35. Elrehim, M. A.; Voit, B.; Bruchmann, B.; Eichhorn, K. J.; Grundke, K.; Bellmann, C. *J. Polym. Sci. Polym. Chem.* **2005**, *43*, 3376.
36. Lee, J. H.; Park, T. G.; Park, H. S.; Lee, D. S.; Lee, Y. K.; Yoon, S. C. *Biomaterials* **2003**, *24*, 2773.