Toughening of epoxy novolac resin using cardanol based flexibilizers

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ABSTRACT: In this work, two different cardanol based epoxies (Cardolite NC-514 and Cardanol NC-547) were employed as flexibilizers to toughen an epoxy novolac resin namely, poly[(phenylglycidyl ether)-*co*-formaldehyde] (PPGEF). 4,4′-Diamino-3,3′-dimethyl dicyclohexyl methane (BMCHA) was used as a curing agent. Differential scanning calorimetry and dynamic mechanical thermal analysis of the composites showed a gradual decrease in glass transition temperatures (T_g) with increase in cardolite content confirming the incorporation of flexible moieties into the brittle resin matrix. Improvement in toughening of PPGEF/Cardolite composites was manifested by increase in the izod impact strength of both the composites. The tensile strength increased marginally for composites with increasing amount of Cardolite NC-514 but decreased for the composites containing Cardolite NC-547. This was attributed to the lack of rotational motion in the chain due to close proximity of rigid phenyl rings in NC-547. SEM of the cryo-fractured surfaces of composites showed good compatibility between PPGEF and cardanol based flexibilizers. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43318.
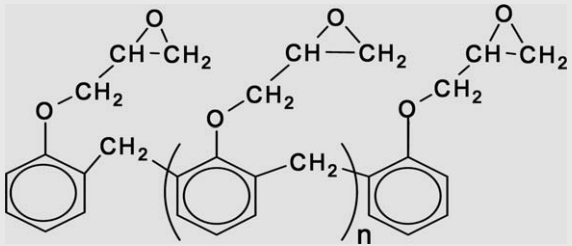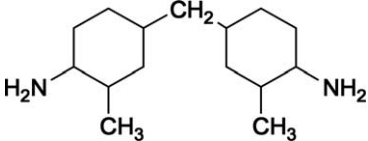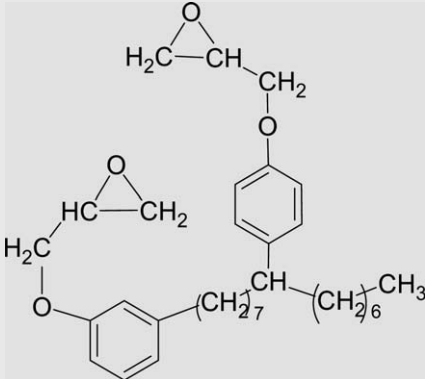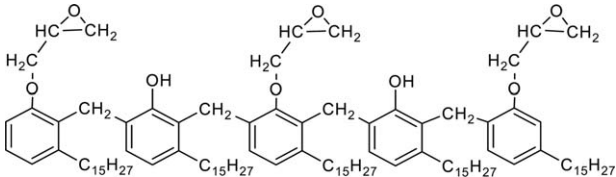
INTRODUCTION

Epoxy resins belong to the class of thermosetting polymers and have a wide range of applications in polymer composites, adhesives, high performance coatings, potting, encapsulations, and numerous other areas.[1–6] They have excellent mechanical and electrical properties, low cure shrinkage, very good adhesion to many substrates and good resistance to moisture.[7,8] However, conventional epoxy resins prepared from bisphenol-A and epichlorohydrin exhibit inherent brittleness and low elongation upon curing. In order to overcome these problems, rubbers such as CTBN, ATBN, ETBN, and HTPB have been incorporated into epoxy to toughen the epoxy matrix.[9–12] Liquid rubbers when incorporated in to epoxy resins, decrease the T_g, tensile strength and modulus of the overall composite which results as a specific drawback of such systems.[13–15] Another way of toughening epoxy resins is to incorporate phenolic moieties into the epoxy resin matrix.[16,17] In this context, epoxy novolac resins have become extremely important. Epoxy novolac resins are epoxidized novolac resins of higher functionality compared to the standard bisphenol-A based epoxy resins. These resins display very good properties of both thermal stability and chemical resistivity.[18] However, they lack sufficient elongation.[19] Therefore, the elongation property of epoxy novolac resins can be improved by incorporating some flexibilizers such as dibutyl phthalate,[20] tricresyl phosphate,[21] epoxy diluents,[22] hyper branched polymers,[23] liquid rubber, etc. Polysulfides flexibilizers have been used for toughening of novolac epoxy resins.[24,25]

In this work, an attempt has been made to toughen novolac epoxy resin namely, poly[(phenylglycidyl ether)-*co*-formaldehyde] (PPGEF) using two flexibilizers namely, Cardolite NC-514 and Cardolite NC-547. PPGEF is an epoxidized novolac resin, prepared by the reaction between novolac resin and epichlorohydrin in basic media. It has an average of 2.2 epoxide groups/molecule. The advantage of using cardolites as flexibilizers is that they are compatible with PPGEF and can be chemically linked to the base resin thus preventing the phase separation during the service. Further, both the flexibilizers are based on renewable resource materials and do not pose any environmental hazards. Cardolite NC-514 is di-functional glycidyl ether of an epoxy resin and Cardolite NC-547 is a polyglycidyl ether of an alkenyl phenol-formaldehyde novolac resin. Cardolite NC-514 is a branched and Cardolite NC-547 is a linear epoxy resin. We have undertaken a study of toughening of PPGEF with different contents of Cardolite NC-514 and Cardolite NC-547 as flexibilizers and using 4,4′-diamino-3,3′-dimethyldicyclohexyl methane (BMCHA) as a curing agent. The resin composites were characterized in terms of thermal and mechanical properties.

Table I. Structures of the Chemicals used for Composite Preparation

Chemicals	Structure
Poly[(phenylglycidyl ether)-*co*-formaldehyde] (PPGEF)	
4,4′-diamino-3,3′-dimethyldicyclohexyl methane (BMCHA)	
Di-functional glycidyl ether epoxy resin (Cardolite NC-514)	
Polyglycidyl ether of an alkenyl phenol formaldehyde novolac resin (Cardolite NC-547)	

EXPERIMENTAL

Materials

PPGEF, an epoxy novolac resin having an epoxy equivalent weight of 156 g eq^{-1} and a functionality of 2.2 was procured from Aldrich Chemicals, Bangalore and was used as received. 4,4′-diamino-3,3′-dimethyldicyclohexyl methane (BMCHA), a curing agent for epoxy novolac resin, was supplied by Hindustan Aeronautics Limited, Bangalore and was used as received. Di-functional glycidyl ether of an epoxy resin (Cardolite NC-514) and poly glycidyl ether of an alkenyl phenol-formaldehyde novolac resin (Cardolite NC-547) were procured from Cardolite Specialty Chemicals India, Mangalore and were used as received. The chemical structures and characteristics of all the raw materials used in this work are given in Tables I and II, respectively.

Preparation of Composites

Epoxy novolac composites were prepared by two step mixing process. Initially, PPGEF was mixed with Cardolite NC-514 in a

Table II. Characterization of the Chemicals used for Making Composites

Sr. No.	Properties	Epoxy novolac resin (PPGEF)	Amine (BMCHA)	Cardolite NC-514	Cardolite NC-547
1.	MW (g/mol)	345	236	980	2400
2.	Epoxy equivalent weight (EEW)	156.82	–	490	800
3.	Functionality	2.2	4	2	3
4.	Viscosity @ 25°C (mPas)	11,000–17,000	110	25,000	28,000
5.	Amine value (mg KOH/g)	–	470	–	V
6.	Solubility	Acetone	Acetone	Acetone	Acetone
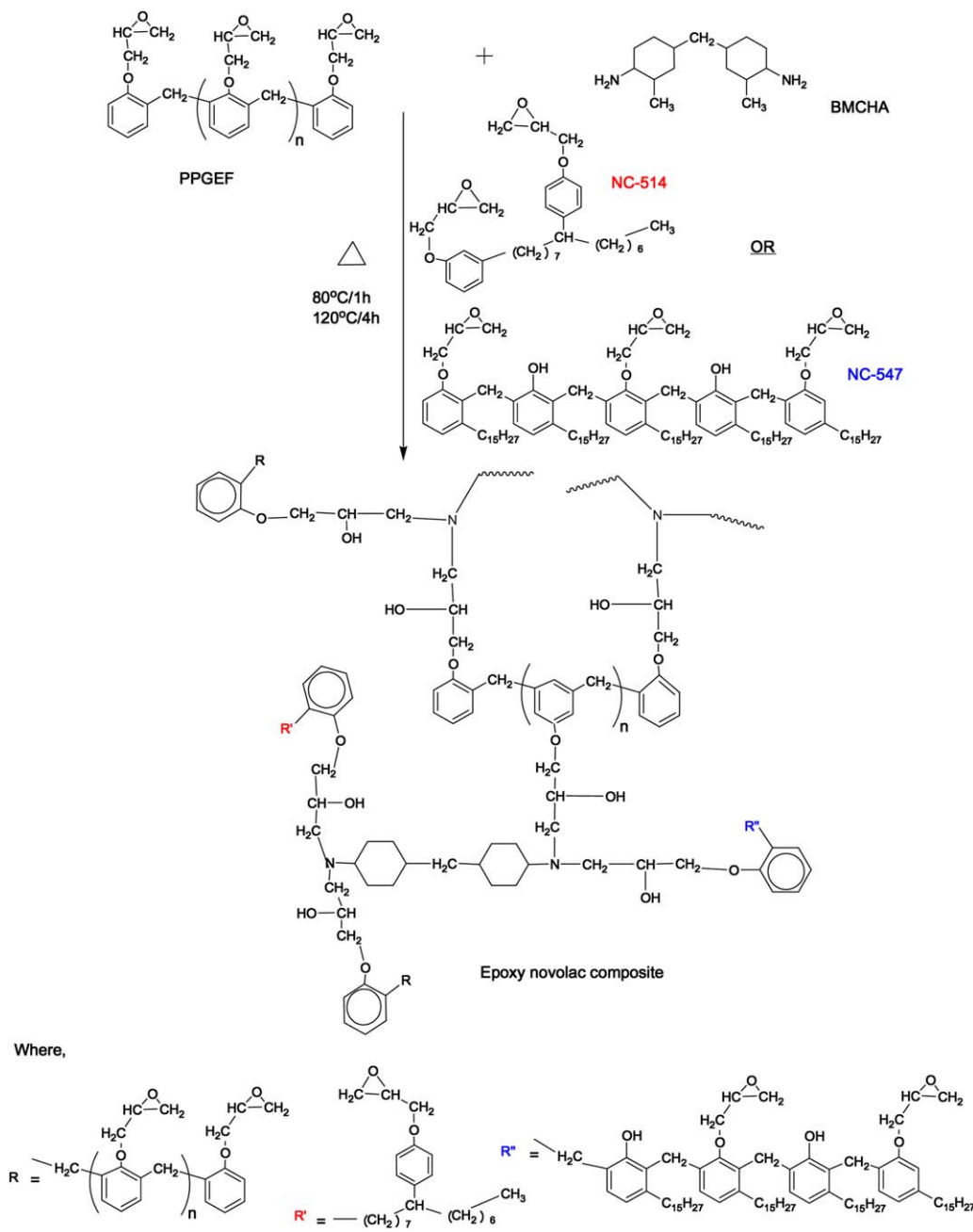
Scheme 1. Reaction between PPGEF, BMCHA, and Cardolite NC-514/Cardolite NC-547. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

beaker in different amounts ranging from 5 to 30% per hundred PPGEF varying by 5% in each composition. To this mixture, BMCHA was added in stoichiometric amount. The composite was thoroughly mixed at ambient temperature and vacuum was applied to remove any entrapped air bubbles. The homogeneous mixture was poured in greased PTFE molds and curing was done at 80°C/1 h and post curing at 120°C/4 h. The mold was cooled and the cured specimens were taken out for further characterization. Similarly, epoxy novolac composites with Cardolite NC-547 were prepared by varying its content upto 30% per hundred PPGEF. The sample code for example is denoted as follows: NC-514-00/NC-547-00 corresponds to the

neat epoxy novolac composite. NC-514-05/NC-547-05 corresponds to the composites containing 5% Cardolite etc.

CHARACTERIZATION

Fourier Transform Infrared Spectroscopic (FT-IR)
FT-IR spectra of the composite films were recorded on a Perkin Elmer Spectrum GX FT-IR spectrometer in the range of 4000–750 cm^{-1} with a resolution of 4 cm^{-1}. The measurements were performed in the ATR mode.

Differential Scanning Colorimetry (DSC)
DSC experiments were performed using DSC Q10 TA Thermal Analyzer using aluminum sample pans. The samples were
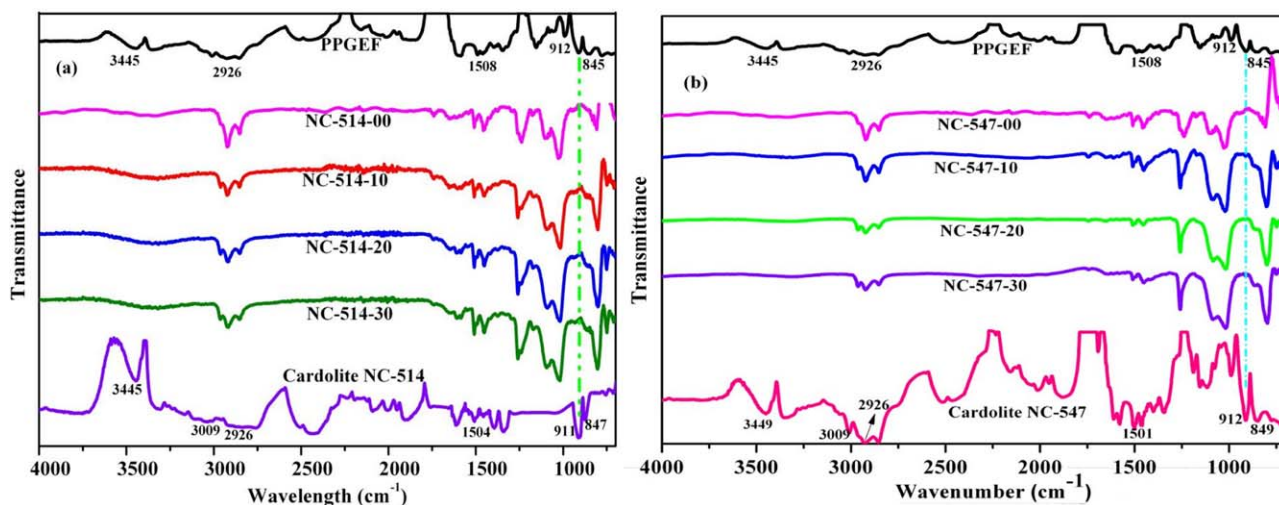
Figure 1. FTIR spectra for (a) PPGEF/Cardolite NC-514 and (b) PPGEF/Cardolite NC-547 composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

heated from 40 to 225°C with a heating rate of 10°C/min in the nitrogen atmosphere with a flow rate of 50 mL/min. Glass transition temperature (T_g), curing temperature and extent of curing were studied from the DSC thermograms.

Thermogravimetric Analysis (TGA)
TGA measurements were performed on a Perkin Elmer STA 6000 thermogravimetric analyzer. Around 10–15 mg sample was placed in a ceramic crucible and heated from 25 to 600°C at a heating rate of 10°C/min in an air atmosphere with a flow rate of 30 mL/min. The initial decomposition temperature at 5% weight loss ($T_{5\%}$), the temperature at which maximum degradation occurs ($T_{max\%}$), the temperature where 50% decomposition occurs ($T_{50\%}$) as well as char residue at 600°C were noted from TGA thermograms.

Dynamic Mechanical Thermal Analysis (DMTA)
DMTA studies were performed on a Rheometric Scientific DMTA dynamic mechanical analyzer to evaluate the viscoelastic

properties of the epoxy novolac composites. In the dynamic mode, the samples were heated from 40 to 150°C with a heating rate of 10°C/min. Three point bending method was used at a frequency of 1 Hz. Storage modulus (E') and loss tangent factor (tan δ) were recorded as a function of temperature. The dimensions of the samples were (25 × 10 × 1) mm.

Tensile Strength
Tensile strength and % elongation values were determined using an Instron Universal testing machine as per the standard ASTM D 638-V. A 10kN load cell was used for measuring the load and a constant cross head speed of 5 mm min^{-1} was maintained. At least five dog bone shaped specimens were prepared for each type of composite in mild steel mold and average value was considered.

Izod Impact Strength
The impact energies absorbed by the composites were measured on Ceast izod impactor. The specimens were prepared as per
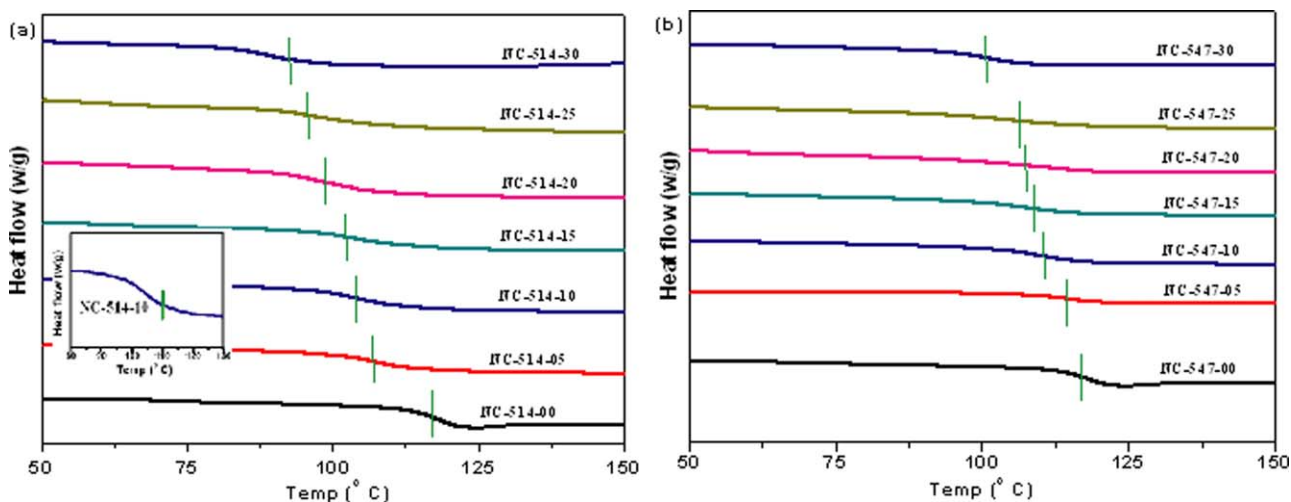

Figure 2. Differential Scanning Calorimetry curves for (a) PPGEF/NC-514 and (b) PPGEF/NC-547 composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. T_g from DSC and DMTA Analysis for PPGEF/NC-514 and PPGEF/NC-547 Composites

Sr. No.	Cardolite content (wt %)	T_g by DSC (°C)		T_g from tan δ peaks of DMTA (°C)	
		PPGEF/Cardolite NC-514 composites	PPGEF/Cardolite NC-547 composites	PPGEF/Cardolite NC-514 composites	PPGEF/Cardolite NC-547 composites
1.	00	120	120	128	128
2.	05	110	116	122	121
3.	10	108	112	120	119
4.	15	106	109	119	119
5.	20	102	108	116	118
6.	25	100	106	115	117
7.	30	90	100	112	116

the standard ASTM D 256-02. At least five specimens were prepared for each composition and an average value was considered.

Scanning Electron Microscopy (SEM)

The surface morphology analysis was performed on SEM Leica-440 scanning electron microscope at ambient temperature. The cryo fractured cured composite specimens were gold sputter coated prior to scanning.

RESULTS AND DISCUSSION

Epoxy Novolac Composites with Cardolite NC-514 and Cardolite NC-547

Epoxy novolac composites were prepared by the reaction between PPGEF and Cardolite NC-514 or Cardolite NC-547 in the presence of a curing agent BMCHA. The use of cardolites as flexibilizers in epoxy novolac composites has not been fully explored. Further, cardolites with similar epoxy structure can become more compatible with novolac epoxy resin. Although both the flexibilizers are based on epoxy, the chemical structures are different (see Table I). Cardolite NC-514 has a branched structure with flexible moiety in the main chain and Cardolite NC-547 has a linear structure with flexible $C_{15}H_{27}$ side chains.

This difference in the chemical structure can have an influence on the toughening characteristics of the resultant epoxy novolac composites. The composites with different contents of flexibilizers were prepared and examined for their structural, thermal, and mechanical properties. The reaction pathway between PPGEF and cardolite in presence of a curing agent, BMCHA can be seen in Scheme 1.

FT-IR Spectroscopy

The FT-IR spectra of neat PPGEF, Cardolite NC-514, Cardolite NC-547 along with cured epoxy novolac composites containing different amounts of cardolites are shown in Figure 1(a,b). The neat PPGEF resin showed characteristic peaks at 912 and 845 cm^{-1}, which correspond to the oxirane rings.[26] These oxirane ring peaks also appeared in neat Cardolite samples. The peak at 3445 cm^{-1} corresponds to the —OH groups of both neat PPGEF and cardolites.[27,28] The C-C stretching of aromatic groups in all the samples appeared at 1508 cm^{-1}.[29,30]

The reaction between PPGEF and Cardolite in presence of curing agent BMCHA resulted into disappearance of oxirane peaks at 912 and 845 cm^{-1} from the epoxy novolac composites. These observations confirmed the incorporation of cardolite flexibilizers in epoxy novolac composites.
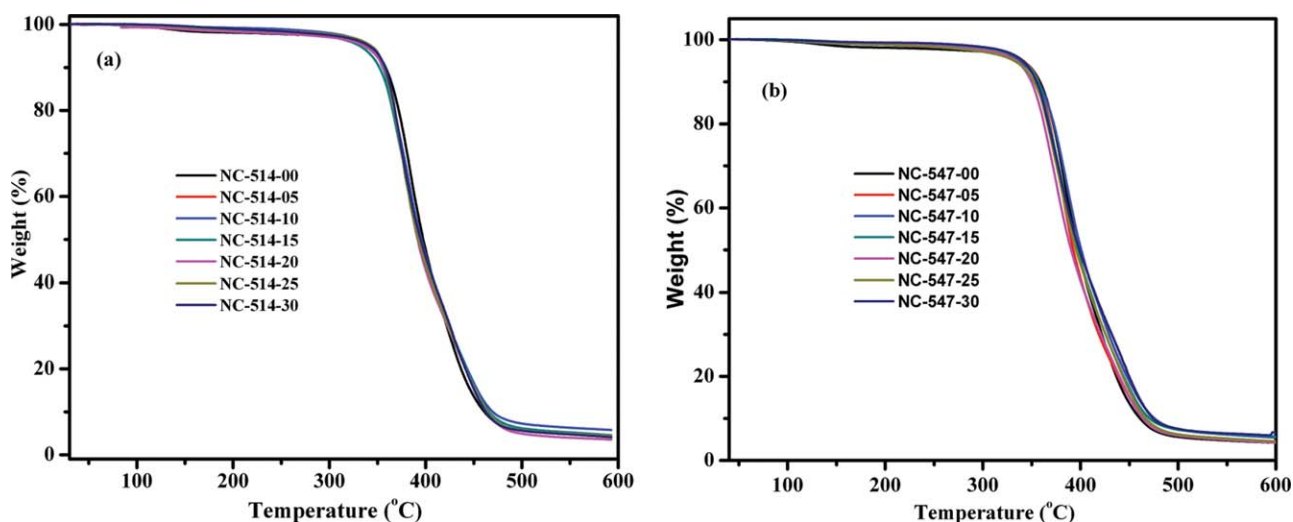

Figure 3. TGA curves for (a) NC-514 and (b) NC-547 composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Results of TGA in Air

Sr. No.	Sample code	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	$T_{max\%}$ (°C)	Char residue @ 600°C (%)
(a) PPGEF/Cardolite NC-514 composites					
1.	NC-514-00 (neat)	342	420	470	0
2.	NC-514-05	343	425	476	3.13
3.	NC-514-10	337	424	478	3.41
4.	NC-514-15	337	422	478	4.01
5.	NC-514-20	336	391	477	2.571
6.	NC-514-25	344	393	478	3.37
7.	NC-514-30	341	395	475	2.62
PPGEF/Cardolite NC-547 composites					
1.	NC-547-00 (neat)	342	420	470	0
2.	NC-547-05	341	393	476	3.62
3.	NC-547-10	336	401	482	4.35
4.	NC-547-15	340	396	476	4.63
5.	NC-547-20	334	390	474	3.00
6.	NC-547-25	331	395	475	3.03
7.	NC-547-30	341	399	482	2.29

Differential Scanning Calorimetry (DSC)

The DSC curves of epoxy novolac composites with different loadings of Cardolite NC-514 or Cardolite NC-547 along with the neat epoxy novolac (PPGEF) are shown in Figure 2(a,b). It can be readily seen that all the samples exhibited single T_g indicating no phase separation. The neat epoxy novolac resin (PPGEF) showed the T_g of 120°C. Upon incorporating cardolites, the decrease in T_g was observed with increasing amounts of cardolites. A similar trend was observed in the DMTA measurements also (see Table III). The decrease in T_g can be attributed to the flexibilizing effect of the cardolites.[31] Although the cardolites were chemically linked to the novolac epoxy by crosslinking, the value of T_g did not increase. It may be due to the

fact that the flexibility of the cardolite is more dominant as compared with the crosslinking of PPGEF.

It was also observed that in the case of Cardolite NC-514, the T_g decreased from 120°C (neat PPGEF) to 90°C (30 wt % Cardolite NC-514) upon incorporating cardolite NC-514 [**a magnified graph for NC-514-10 composite is shown in the** Figure 2(a)]. Whereas, the decrease in T_g with Cardolite NC-547 (30 wt % Cardolite NC-547) was only up to 100°C. The relatively more decrease in T_g with Cardolite NC-514 at the same loading can arise from more flexible nature of Cardolite NC-514 in which the flexible chain is situated in the backbone of the cardolite chemical structure. However, Cardolite NC-547 contains flexible groups in the side chain of the backbone and might induce less flexibility to the epoxy novolac composites. Further, Cardolite NC-547 with more number of epoxide groups can lead to more crosslinking during the curing reaction resulting in the overall decrease of flexibility of Cardolite NC-547 incorporated epoxy novolac composites. These observations were clearly seen in the DSC studies.

Thermogravimetric Analysis

Thermal degradation of neat PPGEF and epoxy novolac composites with cardolite flexibilizer was studied by TGA in the air atmosphere. The TGA curves of neat resin (PPGEF) and the epoxy novolac composites with different contents of Cardolite NC-514 and Cardolite NC-547 are shown in Figure 3(a,b) respectively.

It can be seen from the figure that all the composites have shown one-step degradation. Table IV show the results of TGA for PPGEF/Cardolite NC-514 and PPGEF/Cardolite NC-547 composites. The 5% weight loss temperature ($T_{5\%}$) that corresponds to the temperature when 5% of initial weight was lost, decreased with an increase in the cardolite content. However, the decrease was not significant. The major weight loss was found to occur in the temperature range of 300–500°C in all the epoxy novolac composites. About 50% degradation occurs at around 400°C, which is denoted as $T_{50\%}$. The maximum degradation was observed in the temperature range of 470–480°C due to the oxidative degradation in the presence of air.[32] It was also observed that the char residual at 600°C (char yield) was
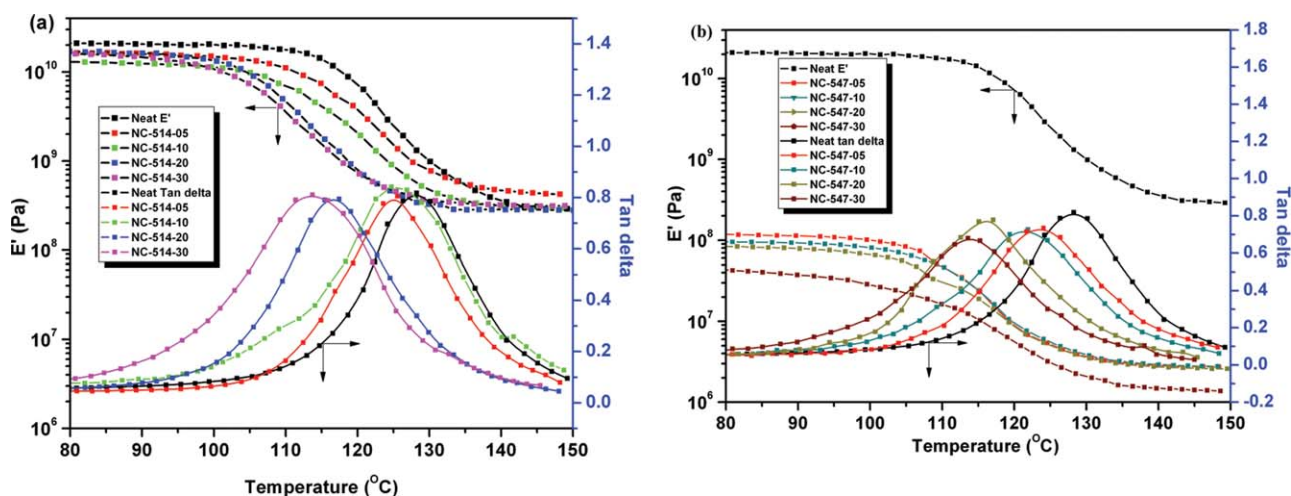

Figure 4. Storage modulus (E') and Tan δ plots of (a) PPGEF/Cardolite NC-514 and (b) PPGEF/Cardolite NC-547 composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. Mechanical Properties of PPGEF/Cardolite NC-514 and NC-547 Composites

Sr. No.	Samples	Tensile strength (MPa)	Elongation (%)	Impact strength (J/m)
	Neat PPGEF composite			
1.	Neat	71.5	2.46	24.5
	PPGEF/Cardolite NC-514			
2.	NC-514-10	72.4	2.93	33.3
3.	NC-514-20	74.3	3.02	42.4
4.	NC-514-30	76.2	2.72	68.6
	PPGEF/Cardolite NC-547			
5.	NC-547-10	68.9	2.60	36.9
6.	NC-547-20	64.1	2.88	40.8
7.	NC-547-30	63.7	2.15	53.3

slightly higher in the case of epoxy novolac with Cardolite NC-547, which may be due to more number of aromatic rings present in the Cardolite NC-547.

Dynamic Mechanical Thermal Analysis

The storage modulus (E') and the tan δ values of the cured neat epoxy novolac composite and epoxy novolac composites containing 5, 10, 20, 30 wt % of Cardolite NC-514 and Cardolite NC-547 as a function of temperature are shown in Figure 4(a,b). A single glass transition temperature (T_g) with a clear rubbery plateau region is observed. The storage modulus decreased gradually with the addition of cardolite revealing the increased flexibility of the epoxy novolac composites.[7] The storage modulus also dropped with increasing temperature and passed through T_g region before reaching the rubbery plateau, where the segmental motions of the network chain occur cooperatively.[5,33]

It can be clearly seen from the Figure 4 that, plots of loss tangent (tan δ) gave single peak which indicated that there was no phase separation in the cured epoxy novolac composition.[34] With respect to temperature, tan δ changed slightly below T_g, increasing to a peak of T_g (at T_{max}) and came back to near

zero. The decrease in T_g with an increase in cardolite content indicated the flexible nature of novolac epoxy composites which are otherwise brittle in nature.[35] The T_g values obtained **from the tan δ peaks** of DMTA are shown in Table III.

Mechanical Properties of Epoxy Novolac Composites

The incorporation of Cardolite NC-514 and Cardolite NC-547 flexibilizers in novolac epoxy resins affected the mechanical properties of the final cured epoxy novolac composites. The results are summarized in Table V. It can be found that in the case of composites with Cardolite NC-514, the tensile and impact strength increased with increase in cardolite content from 5 to 30 wt %. However, there was hardly any change in the % elongation w. r. t. increase in cardolite content. While the tensile strength increased by 5–6%, more effect of flexibilizer was seen in impact strength, which increased from 31.7 to 68.6 J/m with Cardolite NC-514 content from 5 to 30 wt %. The increase in impact strength could be attributed to the presence of flexible chains in the backbone of the Cardolite NC-514, which can absorb an appreciable amount of energy under the impact.[36] A moderate increase in the tensile strength of the
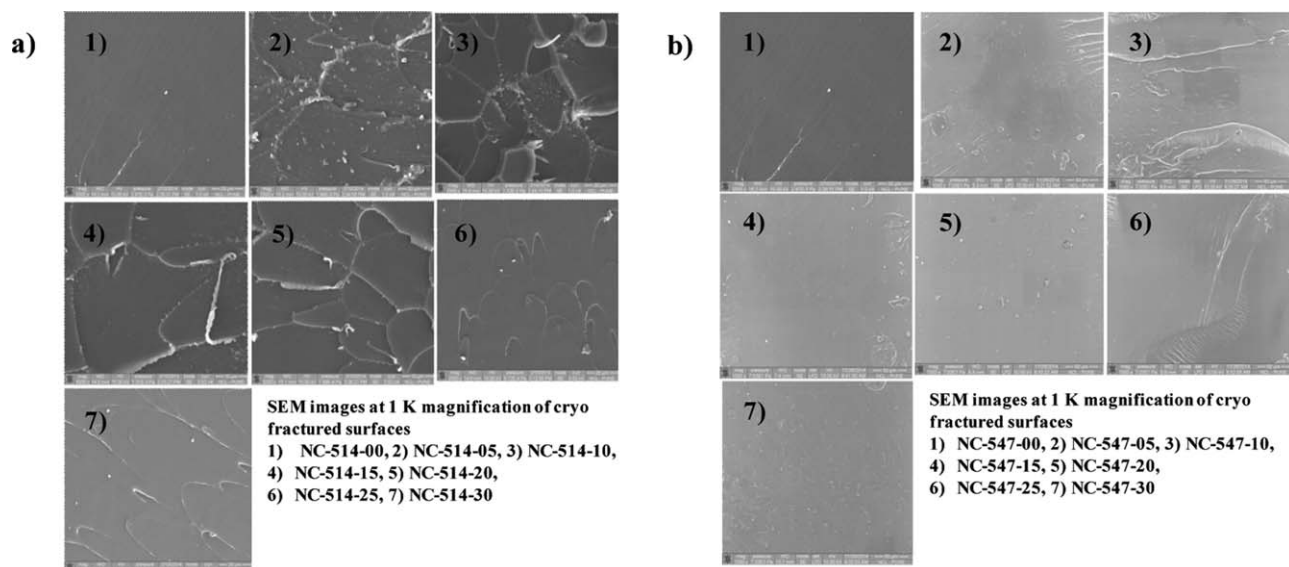

Figure 5. SEM images for (a) PPGEF/Cardolite NC-514 composites and (b) PPGEF/Cardolite NC-547 composites.

composites with Cardolite NC-514 may be due to the rotational motion around the flexible —CH_2 groups and shear yielding, which may result into strain hardening.[37,38] On the contrary, in the case of novolac epoxy composites with Cardolite NC-547, the tensile strength decreased from 71.5 MPa (neat epoxy composite) to 63.6 MPa (with 30 wt % Cardolite NC-547).

The decrease in tensile strength could be attributed to the hindered rotational motion in the chain as a result of the close proximity of rigid phenyl groups.[39–41] Further, the increase in impact strength was less as compared to the composites containing Cardolite NC-514. This could be due to the less flexible nature of Cardolite NC-547.

Scanning Electron Microscopy

The SEM images of the cryo fractured specimens for cured neat and cardolite incorporated epoxy novolac composites are shown in Figure 5. The specimens were scanned at a magnification of 1 K. The fractured surface of the neat composite [Figure 5(a.1,b.1)] shows a very smooth and plain morphology, which indicate that the fracture is brittle.[7] In all the scanned images, no phase separation was observed, which clearly indicates the compatibility of PPGEF and Cardolite NC-514/Cardolite NC-547. This can also be confirmed from the single T_g peaks obtained in DSC and DMA measurements. It can be seen from Figure 5(a.2–a.7), the fracture is ductile for the PPGEF/Cardolite NC-514 composites influenced by the incorporation of Cardolite NC-514. For PPGEF/Cardolite NC-547 composites [Figure 5(b.2–b.7)], the fractured surfaces indicate the homogeneity of PPGEF and Cardolite NC-547 upon curing.

CONCLUSIONS

In this study, two cardanol based flexibilizers (Cardolite NC-514 and Cardolite NC-547) with different chemical structures were used to toughen epoxy novolac resin namely, poly[(phenylglycidyl ether)-co-formaldehyde] (PPGEF). The DSC measurements on all the composites showed a single T_g indicating the compatibility of the flexibilizers with the epoxy novolac resin. The decrease in T_g with an increase in cardolite content indicated the toughening effect on the epoxy novolac resin. The decrease in storage modulus (E') of the composites also revealed the increase in overall flexibility. A significant increase in the toughening of the composites with increase in cardolite content was also manifested in the increase of impact strength. The SEM micrographs showed no phase separation indicating a better compatibility between the resin matrix and the flexibilizers.

ACKNOWLEDGMENTS

REFERENCES

1. Nigam, V.; Setua, D. K.; Mathur, G. N. *J. Appl. Polym. Sci.* **2003**, *87*, 861.

2. Robinette, E. J.; Ziaee, S.; Palmese, G. R. *Polymer* **2004**, *45*, 6143.

3. Tripathi, G.; Srivastava, D. *Mater. Sci. Eng.: A* **2007**, *443*, 262.

4. Thomas, R.; Ronkay, F.; Czigany, T.; Cvelbac, U.; Mozetic, M.; Thomas, S. *J. Adhes. Sci. Technol.* **2011**, *25*, 1747.

5. Jing, X.; Liu, Y.; Liu, Y.; Liu, Z.; Tan, H. *J. Appl. Polym. Sci.* **2014**, *131*, DOI: 10.1002/app.40853.

6. Wang, G.; Jiang, G.; Zhang, J. *Thermochim. Acta* **2014**, *589*, 197.

7. Luo, L.; Meng, Y.; Qiu, T.; Li, X. *J. Appl. Polym. Sci.* **2013**, *130*, 1064.

8. Unnikrishnan, K. P.; Thachil, E. T. *J. Elastomers Plast.* **2005**, *37*, 347.

9. Agrawal, J. P.; Agawane, N. T. *J. Propulsion Power* **2001**, *17*, 1035.

10. Lin, C. H.; Wang, Y. R.; Feng, Y. R.; Wang, M. W.; Juang, T. Y. *Polymer* **2013**, *54*, 1612.

11. Nigam, V.; Setua, D. K.; Mathur, G. N. *J. Therm. Anal. Calorimetry* **2001**, *64*, 521.

12. Gao, J.; Li, J.; Benicewicz, B. C.; Zhao, S.; Hillborg, H.; Schadler, L. S. *Polymer* **2012**, *4*, 187.

13. Kim, D. H.; Kim, S. C. *Polym. Eng. Sci.* **1991**, *31*, 289.

14. Verchere, D.; Pascault, J. P.; Sautereau, H.; Moschiar, S. M.; Riccardi, C. C.; Williams, R. J. J. *J. Appl. Polym. Sci.* **1991**, *43*, 293.

15. Unnikrishnan, K. P.; Thachil, E. T. *Polym.-Plast. Technol. Eng.* **2006**, *45*, 469.

16. Mathew, D.; Reghunadhan Nair, C. P.; Ninan, K. N. *J. Appl. Polym. Sci.* **1999**, *74*, 1675.

17. Makashir, P. S.; Agawane, N. T.; Mahajan, R. R.; Agrawal, J. P. *Indian J. Eng. Mater. Sci.* **2001**, *8*.

18. Clarke, J. A. In *Rubber-Modified Thermoset Resins*; Riew, C. K.; Gillham, J. K., Eds.; American Chemical Society: Washington, **1984**; Vol. *208*, Chapter 5, p 51.

19. Gouri, C. *J. Adhes. Sci. Technol.* **2002**, *16*, 1569.

20. Nikles, E.; Batzer, H.; Brugger, K.; Ernst, O. U.S. Pat. 3,203,920 (**1965**).

21. Harrington, J. A. U.S. Pat. 3,378,434 (**1968**).

22. Lassila, K. R.; Conner, M. D. U.S. Pat. 5,739,209-1 (**1998**).

23. Varley, R. J.; Tian, W. *Polym. Int.* **2004**, *53*,

24. Nigam, V.; Saraf, M. N.; Mathur, G. N. *J. Therm. Anal. Calorimetry* **1997**, *49*,

25. Nigam, V.; Dipak, K.; Setua, Mathur, G. N. *Polym. Eng. Sci.* **1999**, *39*,

26. Ge, H.; Li, S.; Liu, H.; Wang, D.; Chen, J. *J. Appl. Polym. Sci.* **2014**, *131*, DOI: 10.1002/app.39843.

27. Shukla, P.; Srivastava, D. *Int. J. Plast. Technol.* **2014**, *18*,

28. Ahmed, S.; Chakrabarty, D.; Bhowmik, S.; Mukherjee, S.; Rane, R. *J. Adhes. Sci. Technol.* **2015**, *29*, 1446.

29. Natarajan, M.; Murugavel, S. C. *High Perform. Polym.* **2013**, *25*, 685.

30. Li, J.; Zhang, G.; Deng, L.; Jiang, K.; Zhao, S.; Gao, Y.; Sun, R.; Wong, C. *J. Appl. Polym. Sci.* **2015**, *132*, DOI: 10.1002/app.42167.

31. Jaillet, F.; Nouailhas, H.; Auvergne, R.; Ratsimihety, A.; Boutevin, B.; Caillol, S. *Eur. J. Lipid Sci. Technol.* **2014**, *116*, 928.

32. Xia, L.; Xiong, J.; Shentu, B.; Weng, Z. *J. Appl. Polym. Sci.* **2014**, *131*, DOI: 10.1002/app.40825.

33. Tiimob, B. J.; Rangari, V. K.; Jeelani, S. *J. Appl. Polym. Sci.* **2014**, *131*, DOI: 10.1002/app.40867.

34. Thomas, R.; Durix, S.; Sinturel, C.; Omonov, T.; Goossens, S.; Groeninckx, G.; Moldenaers, P.; Thomas, S. *Polymer* **2007**, *48*, 1695.

35. Varley, R. J. *Polym. Int.* **2004**, *53*, 78.

36. Chonkaew, W.; Sombatsompop, N.; Brostow, W. *Eur. Polym. J.* **2013**, *49*, 1461.

37. Jiao, J.; Sun, X.; Pinnavaia, T. J. *Polymer* **2009**, *50*, 983.

38. Zhao, Y.; Chen, Z. K.; Liu, Y.; Xiao, H. M.; Feng, Q. P.; Fu, S. Y. *Compos. A* **2013**, *55*, 178.

39. Soyama, M.; Kiuchi, Y.; Iji, M.; Tanaka, S.; Toyama, K. *J. Appl. Polym. Sci.* **2014**, *131*, DOI: 10.1002/app.40366.

40. Seo, Y.; Hwang, S. S.; Kim, K. U.; Lee, J.; Hong, S. *Polymer* **1993**, *34*, 1667.

41. Anderson, K. S.; Schreck, K. M.; Hillmyer, M. A. *Polym. Rev.* **2008**, *48*, 85.