

Low *k* epoxy resin containing cycloaliphatic hydrocarbon with high crosslinking density

Lingqiang Kong, Yuanrong Cheng, Yunxia Jin, Tianke Qi, Fei Xiao

Department of Materials Science, Fudan University, Shanghai 200433, People's Republic of China

Correspondence to: F. Xiao (E-mail: feixiao@fudan.edu.cn)

ABSTRACT: High performance epoxy resins have attracted much research interest in the last decades. Herein, two novel epoxy monomers containing cycloaliphatic hydrocarbon, 1,4-bis(4-(*N,N*-diglycidylamino)phenoxy)cyclohexane (CyhEP) and 1,3-bis(4-(*N,N*-diglycidylamino)phenoxy)adamantane (AdaEP) were synthesized and characterized. They were cured with 4-methylhexahydrophthalic anhydride (MHHPA) to prepare the highly crosslinked thermosets. Both epoxy resins show good thermal stability ($T_{d5} > 300\text{ }^{\circ}\text{C}$), high glass transition temperature ($> 200\text{ }^{\circ}\text{C}$), and high storage modulus ($> 3.2\text{ GPa}$) due to their highly crosslinked structure. The AdaEP/MHHPA resin shows a low dielectric constant (3.4 at 1 MHz) because of the introduction of bulky rigid adamantane into the polymer. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43456.

KEYWORDS: crosslinking; dielectric properties; thermosets

Received 18 August 2015; accepted 17 January 2016

DOI: 10.1002/app.43456

INTRODUCTION

Epoxy resins have attracted much research interest as adhesives, coatings, composites, and insulants due to their good thermal and mechanical properties, excellent electrical properties, and good processability.^{1–8} With the development of the electronic industry, the epoxy resin with good heat resistance and low dielectric constant will play a more and more important role. Many researches focus on enhancing the thermal stability as well as decreasing the dielectric constant of the epoxy resins. Several methods have been developed to improve the thermal stability of the epoxy resin, such as introducing the rigid heat resistant groups like benzene, naphthalene, biphenyl, and imide^{8–10} into the epoxy resins; increasing the content of the epoxy group to improve the crosslinking density¹¹; preparing the liquid crystalline epoxy resin¹²; and modifying the epoxy resin with nanoparticles¹³ like nano-SiO₂^{14,15} and nano-montmorillonite.^{16–19} And various methods have been developed to achieve low *k* materials, such as introducing fluorinated groups,²⁰ bulky non-polar groups,²¹ and porous structure²² in a polymer. Unfortunately, these two parameters are in constant competition with one another. And the incorporation of cycloaliphatic hydrocarbon is one of the most common methods for this purpose.^{9,23,24} Adamantane is a rigid symmetric tricyclic hydrocarbon with three fused chair-form cyclohexane rings in a diamond lattice structure which has been introduced into many kinds of polymers, such as polyimides^{25–28} and poly(aryl ether ketone),^{29,30} to lower the dielectric constant. In our previous

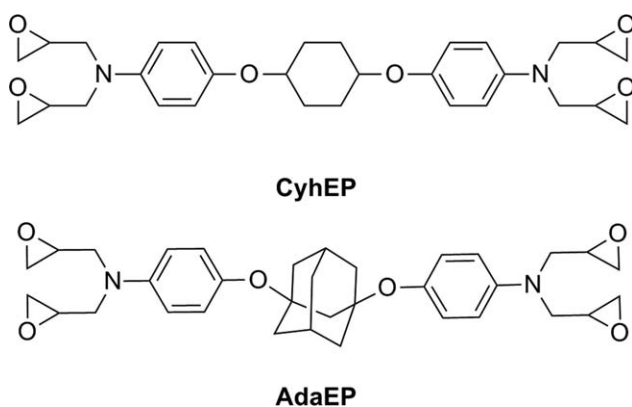
work,³¹ we introduced the adamantane into the benzocyclobutene siloxane to afford the heat resistant low *k* polymers.

In this article, we introduced the cycloaliphatic hydrocarbon, adamantane or cyclohexane, into the backbone of the epoxy resin to enhance the heat resistant and lower the dielectric constant. We attempted to develop thermal stable resins by increasing the crosslinking density with multiple epoxy groups. Moreover, the introduction of the non-polar cycloaliphatic hydrocarbon can reduce the polarizability of the polymer, thereby lowering the dielectric constant of the polymer. The molecular structures of the two novel multi-functional epoxy monomers containing adamantane or cyclohexane in the backbone are shown in Scheme 1. In addition, the curing behavior, dynamic mechanical property, thermal stability, and dielectric property of the resins were investigated.

EXPERIMENTAL

Materials

1,3-Adamantanediol (98%), 1,4-bis(4-nitrophenoxy)cyclohexane (99%), hydrazine hydrate (50%), 4-nitrophenol (98%), and *p*-fluoronitrobenzene (98%) were purchased from J&K Scientific. Epichlorohydrin (99%) was purchased from TCI. Sodium hydride (NaH, 60 wt %) was purchased from Aldrich. Extra dry tetrahydrofuran (THE, 99.9+%), *N,N*-dimethylformamide (DMF, 99.9+%) and triethylamine (TEA, 99%) were purchased from ACROS. 1-Cyanoethyl-2-ethyl-4-methylimidazole (2E4MZ-



Scheme 1. Molecular structure of CyhEP and AdaEP.

CN) and methylhexahydrophthalic anhydride (MHHPA) were supplied by Energy-Chemical.

Characterization

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ were measured using a Bruker DMX-400 spectrometer. Fourier transform infrared (FTIR) spectra were performed on a Nicolet Magna-IR 550 II FTIR spectrophotometer at a resolution of 4 cm^{-1} and using KBr pellets. Thermogravimetric analysis (TGA) was performed on a Shimadzu DTG-60H simultaneous DTA-TG apparatus at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen purge rate of $35\text{ mL}/\text{min}$. Differential scanning calorimetry (DSC) was measured on a TA Q200 calorimeter. Dynamic mechanical analysis (DMA) was carried out on a TA Q800 instrument by the three-point bending mode at a heating rate of $3^\circ\text{C}/\text{min}$ with the test frequency at 1 Hz . The dielectric constants of the polymers were measured by the capacitance method at various frequencies with an Agilent 4294A precision impedance analyzer at 25°C . The parallel plate capacitors were fabricated by depositing aluminum on both sides of the bulk epoxy resins in vacuum. The electrode areas were $13.00\text{ mm} \times 13.50\text{ mm}$. The thickness of CyhEP/MHHPA and AdaEP/MHHPA were 1.55 mm and 1.50 mm , respectively.

Synthesis of Monomers

1,4-Bis(4-aminophenoxy)cyclohexane. 1,4-Bis(4-nitrophenoxy)cyclohexane (25.0 g , 69.8 mmol), Pd/C (10% , 0.3 g), and ethanol (80 mL) were added to a 250-mL round-bottom flask under nitrogen protection. Then hydrazine hydrate (50% , 40 mL) was added to the mixture by syringe. The reaction was heated to reflux with stirring for 5 h . After the reaction was completed, the mixture was filtered with celite. The filtrate was extracted with dichloromethane ($100\text{ mL} \times 2$). The combined organic phase was washed with deionized water (100 mL), dried over Na_2SO_4 , filtered, and concentrated. The residue was recrystallized in ethanol to afford 1,4-bis(4-aminophenoxy)cyclohexane as a white solid (18.6 g , 89.4%). $^1\text{H-NMR}$ (400 MHz , CDCl_3 , ppm) δ : 6.77 (d, 4H, $J = 8.8\text{ Hz}$), 6.64 (d, 4H, $J = 8.8\text{ Hz}$), 4.17 (s, 2H), 3.43 (s, 4H), 2.10 – 1.59 (m, 8H). $^{13}\text{C-NMR}$ (100 MHz , CDCl_3 , ppm) δ : 150.6 , 140.4 , 118.2 , 116.4 , 75.5 , 28.1 .

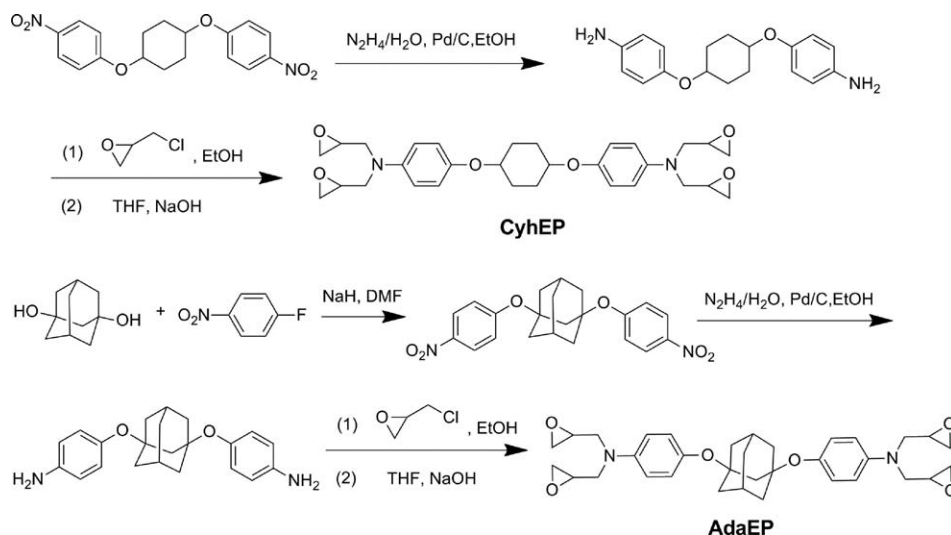
1,4-Bis[4-(*N,N*-diglycidylamino)phenoxy]cyclohexane. 1,4-Bis(4-amino-phenoxy)cyclohexane (3.8 g , 12.8 mmol), epichlorohydrin (9 mL), and ethanol (3 mL) were added into a 100-mL

round-bottom flask. The mixture was heated to 60°C with stirring overnight, and then it was concentrated to remove the excess epichlorohydrin. The residue was dissolved in 50 mL extra dry THF and NaOH (2.4 g , 60.0 mmol) was added. The mixture was heated to 60°C with stirring overnight. After the reaction was completed, 30 mL of deionized water was added. The mixture was extracted with ethyl acetate ($30\text{ mL} \times 3$). The combined organic phase was washed with deionized water ($30\text{ mL} \times 3$), dried over Na_2SO_4 , filtered, and concentrated to afford 1,4-bis(4-(*N,N*-diglycidylamino)phenoxy)cyclohexane (CyhEP) (6.0 g , 89.8%) as a pale yellow oil. $^1\text{H-NMR}$ (400 MHz , CDCl_3 , ppm) δ : 6.88 (m, 4H), 6.81 (d, 4H), 4.22 (s, 2H), 3.67 (m, 4H), 3.44 – 3.32 (m, 4H), 3.17 (m, 4H), 2.80 (m, 4H), 2.59 (m, 4H), 2.14 – 2.01 (m, 4H), 1.77 – 1.60 (m, 4H). $^{13}\text{C-NMR}$ (100 MHz , CDCl_3 , ppm) δ : 150.1 , 143.5 , 117.9 , 114.8 , 75.3 , 53.9 , 50.8 , 45.5 , 28.1 , 27.5 .

1,3-Bis(4-nitrophenoxy)adamantane. NaH (10.5 g , 262.5 mmol , $60\text{ wt } \%$) was added to a solution of 1,3-adamantanediol (20.0 g , 119.0 mmol) in extra dry DMF (150 mL) under nitrogen protection. The mixture was stirred at room temperature for about 30 min and then *p*-fluoronitrobenzene (35.2 g , 0.250 mol) was added. The mixture was heated to 130°C with stirring overnight. After the reaction was completed, the mixture was poured into 30 mL of deionized water. The precipitate was collected to afford 1,3-bis(4-nitrophenoxy)adamantane (40.0 g , 82.0%) as a yellow solid. $^1\text{H-NMR}$ (400 MHz , CDCl_3 , ppm) δ : 8.09 (d, 4H), 7.00 (d, 4H), 2.36 (s, 2H), 2.07 (s, 2H), 1.81 (m, 8H), 1.14 (s, 2H). $^{13}\text{C-NMR}$ (100 MHz , CDCl_3 , ppm) δ : 160.4 , 144.0 , 125.2 , 124.0 , 81.6 , 48.5 , 41.4 , 34.7 , 31.4 .

1,3-Bis(4-aminophenoxy)adamantane. 1,3-Bis(4-nitrophenoxy)adamantane (30.0 g , 73.2 mmol), Pd/C (10% , 0.2 g), and ethanol (130 mL) were added to a 250-mL round-bottom flask under nitrogen protection. Then hydrazine hydrate (50% , 30 mL) was added to the mixture by syringe. The reaction was heated to reflux with stirring for 5 h . After the reaction was completed, the mixture was filtered with celite. Then the filtrate was extracted with dichloromethane ($80\text{ mL} \times 2$). The combined organic phase was washed with deionized water (100 mL), dried over Na_2SO_4 , filtered, and concentrated. The residue was recrystallized in ethanol to afford 1,3-bis(4-aminophenoxy)adamantane as a white solid (22.0 g , 85.9%). $^1\text{H-NMR}$ (400 MHz , CDCl_3 , ppm) δ : 6.51 (d, 4H), 6.35 (d, 4H), 4.65 (s, 4H), 2.14 (s, 2H), 1.65 (s, 2H), 1.50 (t, 8H), 1.27 (s, 2H). $^{13}\text{C-NMR}$ (100 MHz , CDCl_3 , ppm) δ : 145.5 , 143.9 , 125.6 , 114.7 , 78.5 , 48.6 , 41.8 , 35.1 , 31.2 .

1,3-Bis[4-(*N,N*-diglycidylamino)phenoxy]adamantane. 1,3-Bis(4-aminophenoxy)adamantane (2.0 g , 5.7 mmol), epichlorohydrin (6 mL), and ethanol (3 mL) were added to a 100-mL round-bottom flask. The mixture was heated to 60°C with stirring overnight. Then it was concentrated to remove the excess epichlorohydrin. The residue was dissolved in 50 mL extra dry THF and 1.0 g NaOH was added. The mixture was heated to 50°C with stirring for 4 h . After the reaction was completed, 20 mL of deionized water was added. The mixture was extracted with ethyl acetate ($30\text{ mL} \times 3$). The combined organic phase was washed with deionized water ($30\text{ mL} \times 3$), dried over



Scheme 2. Synthetic routes of the epoxy monomers.

Na_2SO_4 , filtered, and concentrated to afford 1,3-bis[4-(*N,N*-diglycidylamino)phenoxy]adamantane (AdaEP) (2.7 g, 82.3%) as a pale yellow oil. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm) δ : 6.87 (d, 4H), 6.72 (d, 4H), 3.74–3.65 (m, 4H), 3.45–3.33 (m, 4H), 3.17 (m, 4H), 2.79 (m, 4H), 2.59 (m, 4H), 2.33 (s, 2H), 1.97 (s, 2H), 1.74 (s, 8H), 1.44 (s, 2H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , ppm) δ : 145.2, 144.8, 125.6, 112.9, 79.0, 53.6, 50.6, 48.0, 45.4, 41.4, 34.8, 31.1.

Preparation of the Polymers

For curing reactions, the molar ratio of epoxy ring to anhydride is 1/0.85. The liquid epoxy (AdaEP or CyhEP) was mixed with MHPA and 1 wt % of 2E4MZ-CN was added before curing as accelerator. Then the mixture was poured into the glass mold (40 mm \times 20 mm \times 1.50 mm). The mold with the resin was heated at 120 $^\circ\text{C}$ for 5 h and 160 $^\circ\text{C}$ for 2 h under nitrogen. After cooled down to room temperature, the thermosetting resins were polished as rectangular bars with a size of 20 mm \times 13 mm \times 1.50 mm for DMA test.

RESULTS AND DISCUSSION

Synthesis and Characterization of Epoxy Resins

The synthetic routes of the two epoxy monomers are shown in Scheme 2. 1,4-Bis(4-aminophenoxy)cyclohexane was obtained by reduction of 1,4-bis(4-nitrophenoxy)cyclohexane using hydrazine hydrate and 10% Pd/C in ethanol. Then it was reacted with epichlorohydrin in the presence of sodium hydroxide to give CyhEP. AdaEP was synthesized from 1,3-bis(4-nitrophenoxy)adamantane in a similar way. Both synthetic routes are simple and convenient. The epoxy monomers are pale yellow oils, which are convenient for further processing.

The $^1\text{H-NMR}$ of two epoxy monomers is shown in Figure 1. For AdaEP, the peaks at 6.87 and 6.72 ppm are attributed to the protons of benzene. The two multiple peaks at 3.74–3.65 ppm and 3.45–3.33 ppm are assigned to the methylene group attached to nitrogen. Likewise, the two quartet peaks at 2.79 and 2.59 ppm belong to the methylene of the epoxy group. The characteristic peak at 3.17 ppm is assigned to the proton

attached to the chiral carbon. The peaks at 2.33, 1.97, 1.74, and 1.44 ppm are attributed to the proton of adamantyl. The chemical shift of CyhEP is similar to AdaEP, instead of adamantyl, the protons of cyclohexyl appear at 2.14–1.60 and 4.22 ppm.

The $^{13}\text{C-NMR}$ of two epoxy resins is shown in Figure 2. For AdaEP, the peaks at 145.2, 144.8, 125.6, and 112.9 ppm are attributed to the benzene ring. The peaks at 53.6, 50.6, and 45.4 ppm are assigned to the glycidyl group. The peaks at 79.0, 48.0, 41.4, 34.8, and 31.1 ppm belong to the carbons of adamantyl group. For CyhEP, the carbons of benzene appear at 150.1, 143.5, 117.9, and 114.8 ppm, and the carbons of glycidyl group appear at the similar position with AdaEP. The peaks at 75.3 and 28.1 ppm are attributed to the cyclohexyl group. Both $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ are in good accordance with the chemical structure of AdaEP and CyhEP.

In the FTIR spectra (Figure 3), the characteristic absorption of the oxirane ring^{32,33} is observed at 908 cm^{-1} , which is

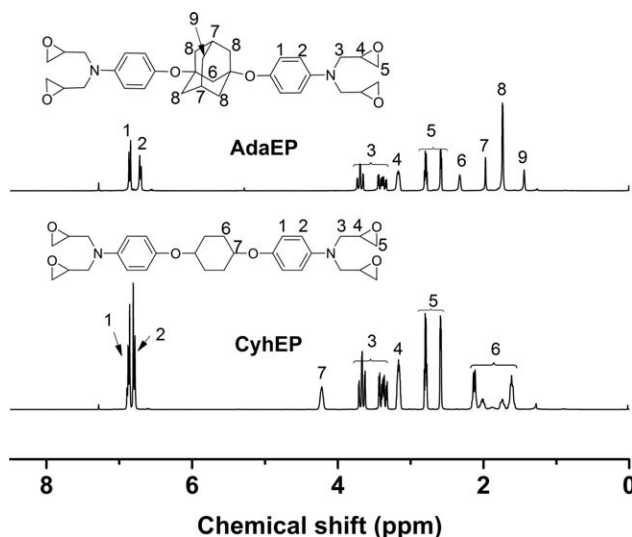


Figure 1. $^1\text{H-NMR}$ spectra of the epoxy monomers: AdaEP and CyhEP.

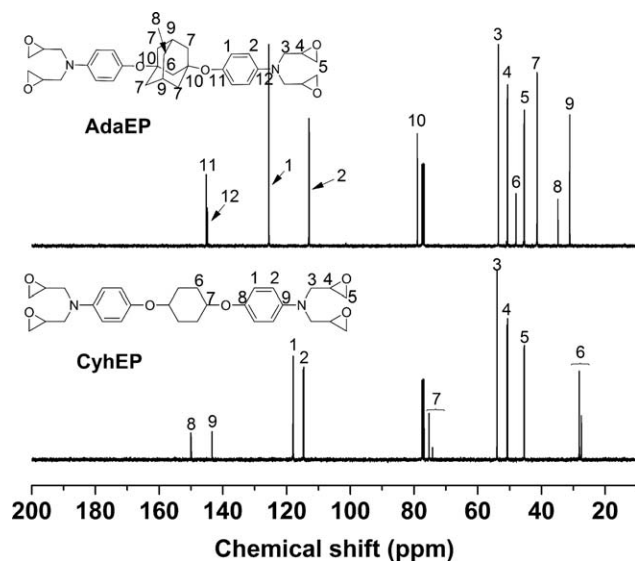


Figure 2. ^{13}C -NMR spectra of the epoxy monomers: AdaEP and CyhEP.

attributed to the C—O deformation vibration. The peaks at 2929 and 2858 cm^{-1} correspond to the C—H stretching vibration of adamantyl or cyclohexyl group. The peaks at 3049 and 3000 cm^{-1} are assigned to the C—H stretching vibration of benzene. The peak at 1453 cm^{-1} is attributed to the C—H bending vibration of methyl and methylene. The C=C stretching vibration of the benzene ring is observed at 1512 cm^{-1} . The characteristic peak of the =C—N stretching vibration appears at 1226 cm^{-1} .

Cure Behavior

The cure behavior of both epoxy resins were examined by DSC as shown in Figure 4. The DSC diagram of CyhEP/MHHPA shows an exothermic peak with onset at about 100 °C and maxi-

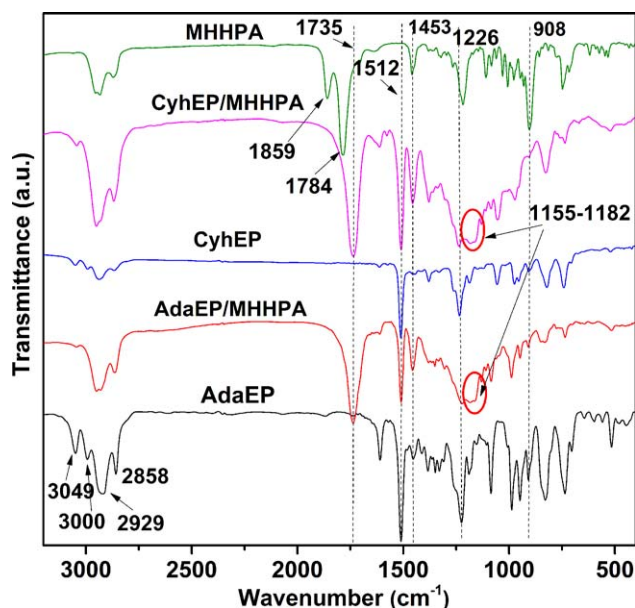


Figure 3. FTIR spectra of the monomers (AdaEP, CyhEP) and their polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

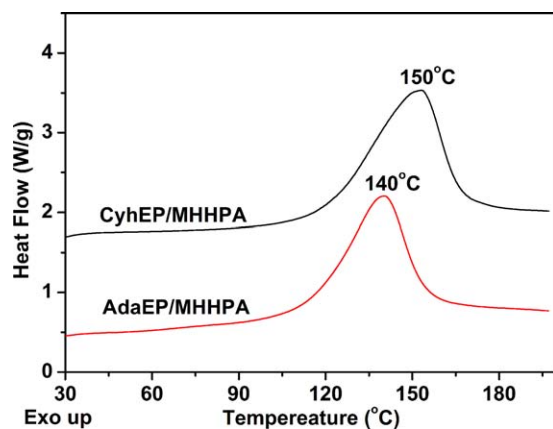


Figure 4. DSC thermograms of AdaEP/MHHPA and CyhEP/MHHPA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mum at 150 °C, and AdaEP/MHHPA shows an exothermic peak with onset at about 100 °C and maximum at 140 °C.

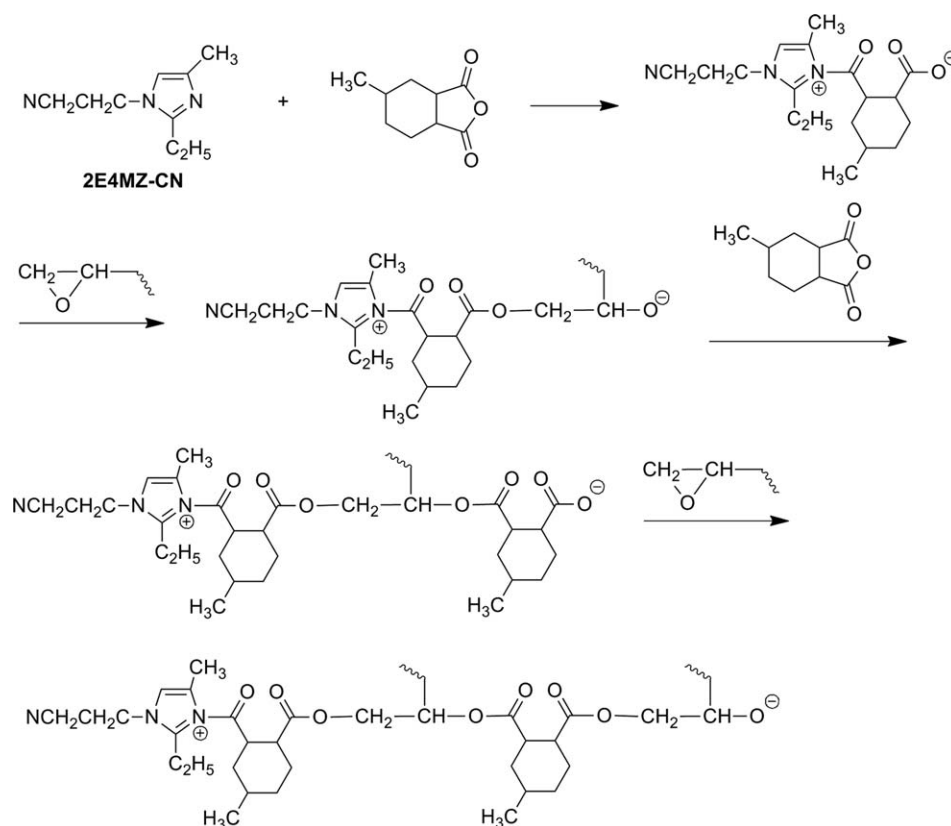
The curing reaction mechanism of the epoxy is shown in Scheme 3. The curing reaction is initiated by the attack of the accelerator 2E4MZ-CN on MHHPA to form the carboxylate anion. Then the oxirane ring is opened by the attack of the carboxylate anion, forming the ester bond and an alkoxy anion. The alkoxy anion attacks on another anhydride to form a new carboxylate anion. Thus, the curing reactions progress repeatedly to form the crosslinked structure.

The FTIR change after curing is shown in Figure 3. The peak at 1453 cm^{-1} is assigned to the asymmetric bending vibration of the methyl. The characteristic peaks of anhydride group of MHHPA at 1859 and 1754 cm^{-1} disappeared and the characteristic peak of oxirane at 908 cm^{-1} decreased significantly after curing. Moreover, the new peak at 1735 cm^{-1} and two wide peaks at 1155–1182 cm^{-1} are attributed to the stretching vibration of C=O and C—O of carboxylic ester of AdaEP/MHHPA and CyhEP/MHHPA, respectively, indicating that the anhydride reacted with oxirane group to form the ester in the curing reaction as shown in Scheme 3.

Thermal and Mechanical Properties

The thermal stability of the thermosets was examined by thermogravimetric analysis (TGA), as shown in Figure 5. For AdaEP/MHHPA, the temperature at 5% and 10% weight loss (T_{d5} and T_{d10}) are 302 °C and 330 °C, respectively. For CyhEP/MHHPA, the T_{d5} and T_{d10} are 308 °C and 314 °C, respectively. They had higher decomposition temperatures than the trifunctional cycloaliphatic epoxide (237 °C) without adamantane or cyclohexane in the backbone.³⁴

DMA was carried out to investigate the mechanical properties of the cured epoxy resins. Figure 6 shows the temperature dependence of the storage modulus and $\tan \delta$ for both epoxy resins. The storage modulus (E') of AdaEP/MHHPA and CyhEP/MHHPA is 3.8 GPa and 3.2 GPa at room temperature, respectively. The high E' suggests high stiffness of the resins. The E' of both epoxy resins remain constant up to 180 °C and then decreases sharply with the increase of temperature. The



Scheme 3. Curing mechanism of the epoxy.

glass transition temperature (T_g) of AdaEP/MHHPA and CyhEP/MHHPA is 206 °C and 224 °C, respectively, as determined by the peak temperature of $\tan \delta$. Both resins exhibit higher modulus and higher T_g than the diglycidyl ether of bisphenol A (DGEBA)/MHHPA polymer (146 °C).³⁵

The crosslinking density of the two epoxy resins can be calculated according to the equation [eq. (1)]^{36,37}

$$\rho = E' / 3RT \quad (1)$$

where ρ is the crosslinking density expressed in moles of elastically effective network chains per cubic meter of the sample, E'

is the storage modulus of the cured network at a temperature well above T_g , R is the universal constant (8.314 J/mol·K) and T is the absolute temperature at which the experimental modulus is determined. The E' ($T_g + 40$ °C) of AdaEP/MHHPA and CyhEP/MHHPA are 67.1 MPa and 115.3 MPa, respectively. The crosslinking density of AdaEP/MHHPA calculated by the eq (1) is 5.18×10^3 mol/m³, lower than that of CyhEP/MHHPA (8.61×10^3 mol/m³). That may be the reason why CyhEP/MHHPA shows a higher T_g than AdaEP/MHHPA. The lower crosslinking density of AdaEP/MHHPA is probably due to the rigid adamantyl structure, which increases the steric hindrance between the

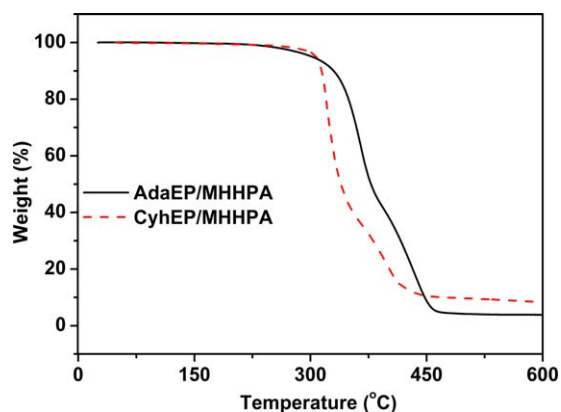


Figure 5. TGA of the cured epoxy resins under nitrogen. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

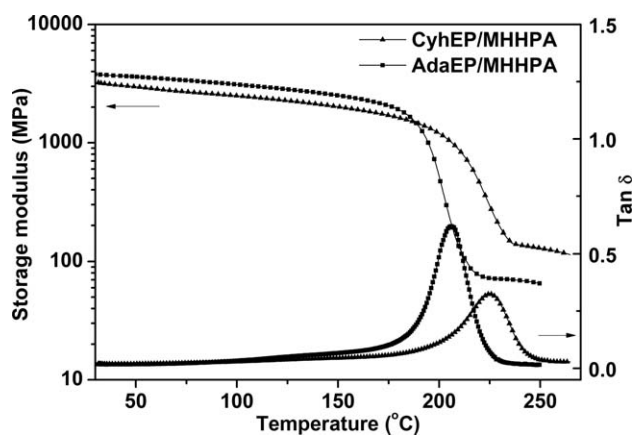


Figure 6. Storage modulus and $\tan \delta$ of the cured epoxy resins.

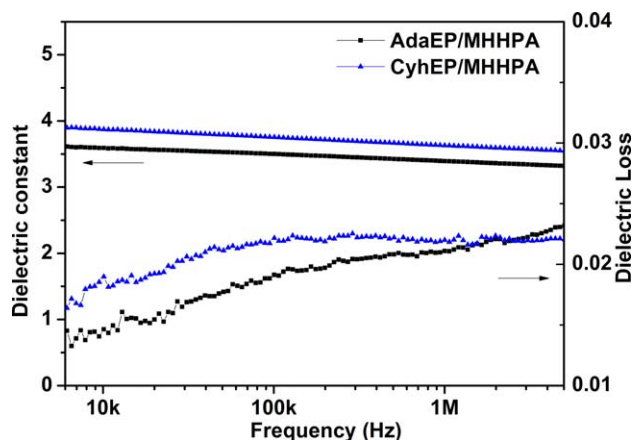


Figure 7. Frequency dependency of dielectric constant and dielectric loss of the epoxy resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chains, thus hinders the crosslinking and increases the free volume of the polymer.

Dielectric Properties

Dielectric constant (k) and dielectric loss are important parameters for materials applied in the electronic packaging industry. Figure 7 reveals the frequency dependence of the dielectric constant and dielectric loss ranging from 6 kHz to 5 MHz at room temperature. The k values of AdaEP/MHHPA and CyhEP/MHHPA were 3.39 and 3.63 at 1 MHz, respectively, and the dielectric losses were 0.021 and 0.022 at 1 MHz, respectively. Moreover, k value of both resins showed less frequency dependence in the measuring range. The adamantyl group exhibited better effect than cyclohexyl group to decrease the k value of the polymers.

CONCLUSIONS

We synthesized and characterized two novel multifunctional epoxy resins. Both epoxy resins exhibited high glass transition temperature ($T_g > 200^\circ\text{C}$, $\tan \delta$), high thermal stability and high storage modulus due to their highly crosslinked structure. Because of the introduction of the rigid adamantyl group into the polymer, the AdaEP/MHHPA shows a low dielectric constant of 3.39 at the frequency within 1–5 MHz which is lower than the most of the epoxy resins in the markets. The good dielectric, thermal and mechanical performance of the epoxy resins shows potential application in the microelectronic packaging.

ACKNOWLEDGMENTS

This research was supported by National Science and Technology Major Project with the contract No. 2013ZX02505.

REFERENCES

1. Semenovich, H. M.; Fainleib, O. M.; Slinchenko, O. A.; Brovko, O. O.; Sergeeva, L. M.; Dubkova, V. I. *React. Funct. Polym.* **1999**, *40*, 281.

2. Wang, C.; Liao, Z. *Polym. Bull.* **1991**, *25*, 559.
3. Shin, Y.; Kawae, A.; Okamura, H.; Shirai, M. *React. Funct. Polym.* **2004**, *61*, 293.
4. van de Grampel, R. D.; Ming, W.; van Gennip, W. J. H.; van der Velden, E.; Laven, J.; Niemantsverdriet, J. W.; van der Linde, R. *Polymer* **2005**, *46*, 10531.
5. Gordon, K. L.; Thompson, C. M.; Lyon, R. E. *High Perform. Polym.* **2010**, *22*, 945.
6. Hwang, H.; Hsu, S.; Chung, C.; Wang, C. *React. Funct. Polym.* **2008**, *68*, 1185.
7. Shang, C. Y.; Zhao, X. J.; Yang, X.; Zhang, Y.; Huang, W. *High Perform. Polym.* **2012**, *24*, 683.
8. Pan, G.; Du, Z.; Zhang, C.; Li, C.; Yang, X.; Li, H. *Polymer* **2007**, *48*, 3686.
9. Xu, K.; Chen, M.; Zhang, K.; Hu, J. *Polymer* **2004**, *45*, 1133.
10. Kaji, M.; Endo, T. *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37*, 3063.
11. Rane, U. G.; Sabnis, A. A.; Shertukde, V. V. *Int. J. Polym. Sci.* **2014**, *2014*, 1.
12. Wang, C.; Lee, M. *J. Appl. Polym. Sci.* **1999**, *73*, 1611.
13. Li, Y.; Badrinarayanan, P.; Kessler, M. R. *Polymer* **2013**, *54*, 3017.
14. Sprenger, S. *J. Appl. Polym. Sci.* **2013**, *130*, 1421.
15. Zheng, Y.; Chonung, K.; Wang, G.; Wei, P.; Jiang, P. *J. Appl. Polym. Sci.* **2009**, *111*, 917.
16. Hussain, F. *J. Compos. Mater.* **2006**, *40*, 1511.
17. Brown, J. M.; Curliss, D.; Vaia, R. A. *Chem. Mater.* **2000**, *12*, 3376.
18. Maniar, K. K. *Polym. Plast. Technol.* **2004**, *43*, 427.
19. Kaynak, C.; Nakas, G. I.; Isitman, N. A. *Appl. Clay Sci.* **2009**, *46*, 319.
20. Yuan, C.; Jin, K.; Li, K.; Diao, S.; Tong, J.; Fang, Q. *Adv. Mater.* **2013**, *25*, 4875.
21. Long, T. M.; Swager, T. M. *J. Am. Chem. Soc.* **2003**, *125*, 14113.
22. Volksen, W.; Miller, R. D.; Dubois, G. *Chem. Rev.* **2009**, *110*, 56.
23. Wang, L.; Wong, C. P. *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37*, 2991.
24. Wang, L.; Li, H.; Wong, C. P. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 3771.
25. Watanabe, Y.; Shibasaki, Y.; Ando, S.; Ueda, M. *Polym. J.* **2005**, *37*, 270.
26. Chern, Y.; Shiue, H. *Macromol. Chem. Phys.* **1998**, *199*, 963.
27. Chern, Y.; Shiue, H. *Macromolecules* **1997**, *30*, 4646.
28. Mathews, A. S.; Kim, I.; Ha, C. *J. Appl. Polym. Sci.* **2006**, *102*, 3316.
29. Wang, G.; Geng, Z.; Zhu, X.; Zhang, S.; Liu, X. *High Perform. Polym.* **2010**, *7*, 779.
30. Geng, Z.; Lu, Y.; Zhang, S.; Jiang, X.; Huo, P.; Luan, J.; Wang, G. *Polym. Int.* **2014**, *63*, 333.

31. Kong, L.; Cheng, Y.; Jin, Y.; Ren, Z.; Li, Y.; Xiao, F. *J. Mater. Chem. C* **2015**, *1*, 3364.
32. Horák, D.; Rittich, B.; Španová, A. *J. Magn. Magn. Mater.* **2007**, *311*, 249.
33. Patterson, W. A. *Anal. Chem.* **1954**, *5*, 823.
34. Chen, Z.; Zhao, L.; Wang, Z. *Polymer* **2013**, *54*, 5182.
35. Xiao, F.; Sun, Y.; Xiu, Y.; Wong, C. P. *J. Appl. Polym. Sci.* **2007**, *104*, 2113.
36. Urbaczewski-Espuche, E.; Galy, J.; Gerard, J.; Pascault, J.; Sautereau, H. *Polym. Eng. Sci.* **1991**, *31*, 1572.
37. Levita, G. D.; Petris, S.; Marchetti, A.; Lazzeri, A. *J. Mater. Sci.* **1991**, *26*, 2348.