Multifunctionalization of Novolac Epoxy Resin and Its Influence on Dielectric, Thermal Properties, Viscoelastic, and Aging Behavior

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ABSTRACT: In this article, novolac epoxy was functionalized using p-hydroxybenzoic acid as pendent groups, which offered weak acidic environment and were cured with methyl etherified amino resin (HMMM). Its chemical structure was characterized by Fourier transform infrared (FT-IR), ^{1}H nuclear magnetic resonance (^{1}H NMR) and differential scanning calorimeter (DSC). To comprehensively investigate its performance, HMMM was used as a curing agent. The modified epoxy exhibited higher storage modulus, lower thermal expansion coefficient, better moisture resistance, better resistance to degradation and lower dielectric constant. Furthermore, the aging behavior was investigated using dynamic mechanical analysis and scanning electron microscopy, which showed that the activation energy of glass transition increased after aging and cured MDEN was more difficult to age. Moreover, the relation between storage modulus and curing rate was established; the low curing rate of MDEN decreased the growth rate of storage modulus and reduced the internal stress, which was beneficial for processing. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40157.

INTRODUCTION

Epoxy resins have been widely applied in many areas, such as aerospace and electronics industries in the form of surface coating, structural adhesives, advanced composites, and packaging materials due to their well-balanced properties. For example, epoxy resins have excellent thermal stability, moisture resistance, chemical stability, superior electrical, and mechanical properties and good adhesion to many substrates.[1–3] However, when epoxy resins were used as packaging materials in integrated circuit, many problems have been appeared especially after the soldering reflow process, such as packaging cracking, delamination and poor performance in humidity testing. Therefore, epoxy resins with lower coefficient of thermal expansion (CTE), higher toughness, better heat and moisture resistance are significantly required. For these reasons, modifications of epoxy resins in both backbone and pendent groups have been continuously attempted to stimulate their complex performances.[4,5]

Many approaches have been developed to improve the overall performances of epoxy resins by introducing rigid structure into the main chain of the resin or designing multifunctional epoxy monomer to increase the cross-linking density. Pan et al.[6] have synthesized novel epoxy resin via condensation of bisphenol A and 1-naphthaldehyde, and the cured resins exhibited higher glass transition temperature, enhanced thermal stability and

better moisture resistance. Besides, compared to that of the common cycloaliphatic epoxy resin ERL-4221 from Shell, a novel tri-functional cycloaliphatic epoxy resin starting from dicyclopentadiene showed better thermal stability and similar thermal expansion coefficient.[7] Moreover, a series of tri-functional epoxy resins were prepared by the condensation of 2, 6-dimethylol-4-methylphenol with phenol, cresol, 2, 6-dimethylphenol or 2-naphthol, respectively and followed by epoxidation with halohydrin. Among them, the naphthalene-containing epoxy resin had the highest elastic modulus, highest glass transition temperature, highest thermal stability, and the lowest CTE and moisture absorption properties.[8] Zhang et al.[9] have modified bisphenol type epoxy resin by p-aminobenzoic acid, which led to the formation of a product with both hydrophilic and lipophilic properties. As much as we know, much interesting work was focused on the main chains of functionalized epoxy resins.[10–13] However, there are few studies on modifying multifunctional epoxy resin with grafting pendent groups to develop promising epoxy resins.

Herein, novolac epoxy resin as a multifunctionalized epoxy resin was investigated by chemical modification method, due to the amounts of oxirane as pendent groups in the main chain. The p-hydroxybenzoic acid (PHBA) was introduced into the side chain of novolac epoxy resin via a ring opening reaction of the epoxide
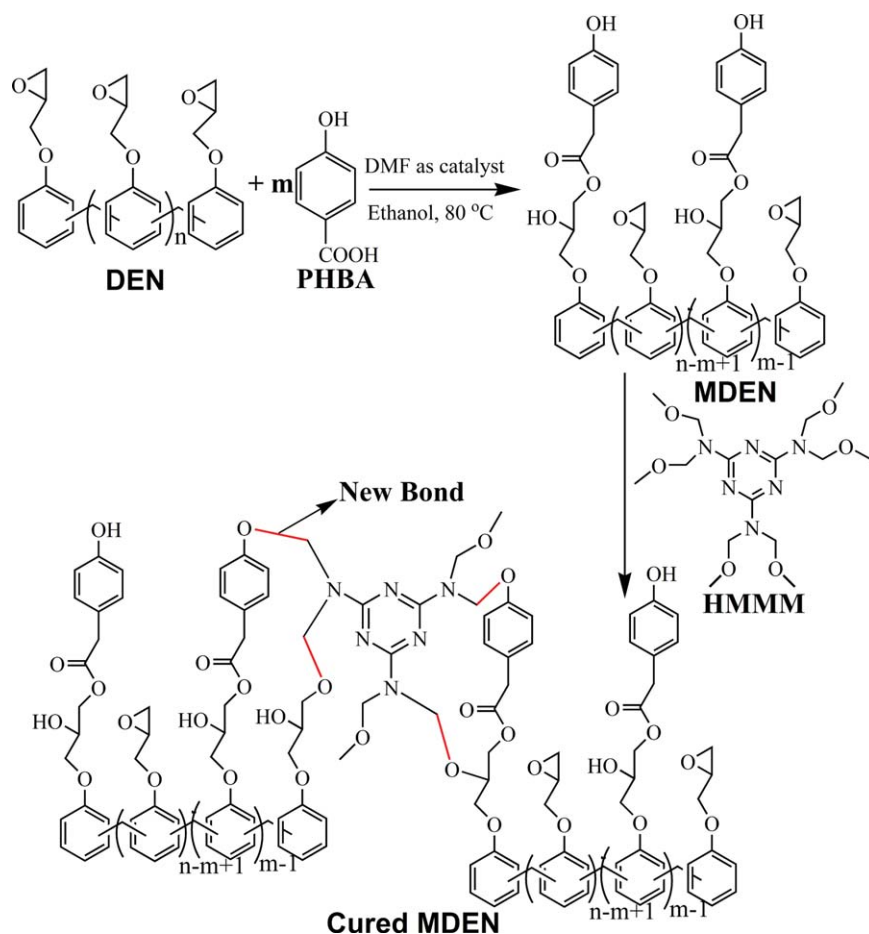
Scheme 1. Schematic representation of modification of DEN and its curing reaction.

ring. Moreover, the methyl etherified amino resin, with rigid triazine moieties, was used as a curing agent to cross-link modified novolac epoxy resins. The thermal resistance, dielectric, rheological, and mechanical properties of the resulting cured system were investigated. Meanwhile, the aging behavior of these cured epoxy resins was investigated through calculating activation energy of glass transition from dynamic loss (tan δ). Furthermore, the relation between the storage modulus and curing rate was established, which was used to instruct the processing.

EXPERIMENTAL

Materials

Novolac epoxy resin of DEN 431 (Epoxy equivalent weight of 177–200 g/mol) was obtained from Dow Chemical Company. Methyl etherified amino resin of Cymel 303 (HMMM) was supplied by Cytec Industry and used as a curing agent, these chemical structures were shown in Scheme 1. 2-ethyl-4-methyllimidazole (EMI-2, 4) (Analytical grade, Shanghai Chemical Reagent Factory, China) was used as an accelerator in the curing reaction without further purifications. PHBA (analytical grade, Aladdin reagent Co., Ltd) was used as received. All solvents and other chemicals were of reagent grade and used as received.

Modification of Novolac Epoxy Resin

The reaction was performed in a 150 mL glass reactor equipped with a reflux condenser and a magnetic stirrer. DEN resin (2.6

g) and ethanol (6 mL) were poured into a reactor, and then the mixture was stirred at 50°C for 0.5 h to dissolve the resin. The resultant solution was stirred and heated for 12 h at 80°C after 1.0 g of PHBA and 0.05 mL of dimethylformamide (DMF) were added into the solution and the calculated molar equivalent of PHBA to phenolic functionality was ca. 0.53. Subsequently, the reaction was stopped and cooled down to room temperature to obtain the modified DEN (MDEN), and the MDEN was filtrated and washed with ethanol/water (1/5;v/v) to remove the unreacted PHBA. The obtained solid was dried at 50°C under vacuum.

Preparation of Cured Polymer

The MDEN resin and amino resin in a mass ratio of 1.8:1 were dissolved in acetone to be mixed evenly at room temperature. Then, the solvent was evaporated under vacuum before performing the differential scanning calorimeter (DSC) experiment. For thermo-mechanical analysis (TMA), the required specimens were obtained through a hot press molding; for dielectric analysis and dynamic-mechanical analysis, K Control Coater (R K Print-Coat Instruments Ltd) was used to form a film on a copper foil. The curing reaction between DEN and amino resins was accelerated by EMI-2, 4 because of the low activity of DEN with HMMM.[14] The prepregs were cured in an air circulated oven at a programmed curing progress, which was set as follows: 40– 110°C,
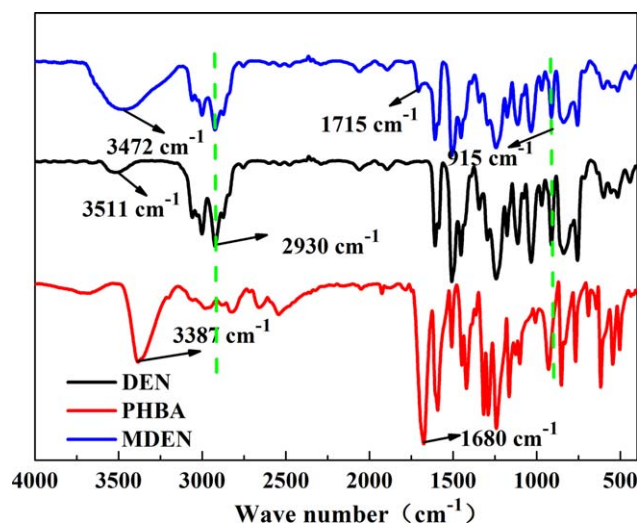
Figure 1. FTIR spectra of DEN, PHBA and MDEN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

110°C/2 h, 110–150°C, 150°C/2 h, 150–200°C, 200°C/3 h, 200–40°C, and the corresponding ramp rate was 5°C/min.

Characterization

The Fourier transform-infrared (FT-IR) spectra were recorded on a Bruker Vertex 70 spectrometer in the range of 4000–400 cm^{-1}.

^{1}H nuclear magnetic resonance (^{1}H NMR) characterizations were carried out by a Bruker 500 NMR spectrometer using chloroform d (CDCl$_3$) as the solvent and tetramethylsilane as the internal standard.

DSC measurements were conducted on a TA Q20–1173 DSC thermal system at a heating rate of 10°C/min from −50 to 100°C to confirm the glass transform temperature (T_g).

Thermo-gravimetric analysis (TGA) was performed on a TA SDTQ600 thermo-gravimetric analyzer; the samples were scanned from 30 to 710°C under a nitrogen atmosphere at a heating rate of 10°C/min.

Surface morphology of fractured surface was performed using a scanning electron microscope (Nova Nano SEM).

Dynamic thermo-mechanical analysis (DMA) was carried out with a TA Q800–1751 using 30 × 5 × 0.1 mm^3 rectangular films. The sample was subjected to tension-film deformation mode at a heating rate of 3°C/min and a frequency of 1 Hz under air atmosphere.

TMA was performed on Netzsch TMA 402F1 under nitrogen atmosphere at a heating rate of 3°C/min. The specimen was scanned twice, the first scan was aimed to eliminate the moisture and erase the thermal history.

The rheological behavior was measured using an Anton Paar MCR302 rheometer with a heating rate of 2.5°C/min and ranging from 40 to 280°C

The dielectric properties were measured using Agilent 4294A impedance analyzer in the frequency range of 100–10^7 Hz at the room temperature.

Moisture absorption was determined as follows: the samples were dried under vacuum at 80°C for 12 h, and then cooled down to room temperature. The samples were weighted and placed in 100°C water, and weighted every 3 h to obtain the gain with immersion time.

RESULTS AND DISCUSSION

Modification and Characterization of DEN

The strategy of modification of DEN was schematically illustrated in Scheme 1. It can be seen that the carboxyl opened the epoxy ring via an esterification in the presence of DMF as catalyst and the esterification was at random. To verify that the DEN was successfully modified by PHBA, the FT-IR spectra were shown in Figure 1. It can be found that the peak at 1680 cm^{-1} was the characteristic peak of C═O of PHBA, while the characteristic peak at 3387 cm^{-1} was assigned to the stretching vibrations of ─OH (carboxyl and phenol hydroxyl group). The absorption peak at 915 cm^{-1} was due to the epoxy group, and the characteristic peak of ─CH$_2$─ was found at 2930 cm^{-1}. After modification, the peak of C═O shifted from the 1680 to 1715 cm^{-1}, due to the formation of an ester, while the peak of ─OH shifted to 3472 cm^{-1}, because of the disappearance of carboxyl group and the appearance of a secondary hydroxyl group. Besides, to the FTIR of DEN and MDEN, the specific peak at 2930 cm^{-1} attributed to the stretching vibration of saturated C─H remained unchanged throughout the modification and could be considered as an internal standard. The relative intensity of peak at 915 cm^{-1} ascribing to epoxide ring decreased by 25% after DEN was modified.[14–17] These implied that the PHBA has reacted and opened the epoxy rings and grafted to the side chain of novolac epoxy resin.

The chemical structure of the MDEN was confirmed further by the ^{1}H NMR spectra as shown in Figure 2. The chemical shifts of the phenol hydroxyl protons and the protons in the benzene ring nearest the carboxyl were observed at 7.80–8.05 ppm, the protons on ─COOH were not observed at 12.40 ppm [Figure 2(a)].[18] These implied that there was no free PHBA, and the PHBA was successfully grafted/bonded to DEN. Simultaneously, the protons of methylene and methine in the oxirane ring of the DEN were observed at 2.59–2.90 ppm and 3.15–3.38 ppm [Figure 2(b)], while some of these protons shifted to 4.20–4.55 ppm after opening the epoxy ring of the resin [Figure 2(a)]. Moreover, the chemical shift at 2.20 ppm was assigned to the ─OH generated from opening of epoxy as shown in Figure 2(a).[6–8] Besides, it was calculated that 24.1% of epoxy groups were substituted with PHBA from the integration of these NMR data, which was consistent with the results of FTIR.

The glass transition temperature is an intrinsic property of an amorphous polymer and reflects the motion transition of polymer chains. The DSC curves of MDEN and DEN were shown in Figure 3. It can be found that the T_g of MDEN was improved from −12.42°C (DEN) up to 65.75°C (MDEN) by ∼78°C. This observation was consistent with the results of Zhang.[19] This improvement may be resulted from the following reasons: 1) The polarity of hydroxyl in MDEN could enhance the attractive force between polymer chains and hinder the internal rotation of chains; 2) comparing with DEN, the higher molecular weight
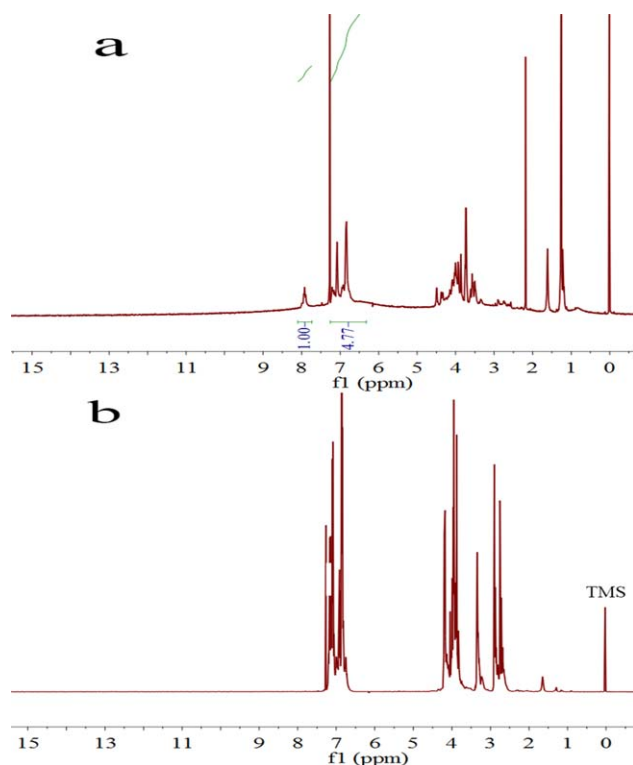
Figure 2. ^{1}H NMR spectra of MDEN (a) and DEN (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of MDEN was beneficial to the improvement of T_g; 3) the introducing of rigid structure of benzene rings could also hinder the internal rotation of main chain, resulting a higher T_g.[19]

The aforementioned results of FT-IR spectra, ^{1}H NMR spectra and DSC well demonstrated that the DEN was successfully modified by PHBA. To further evaluate the superiority of MDEN, the DEN and MDEN were cured with amino resins, respectively, and then their mechanical, thermal, dielectric and rheological properties were investigated.
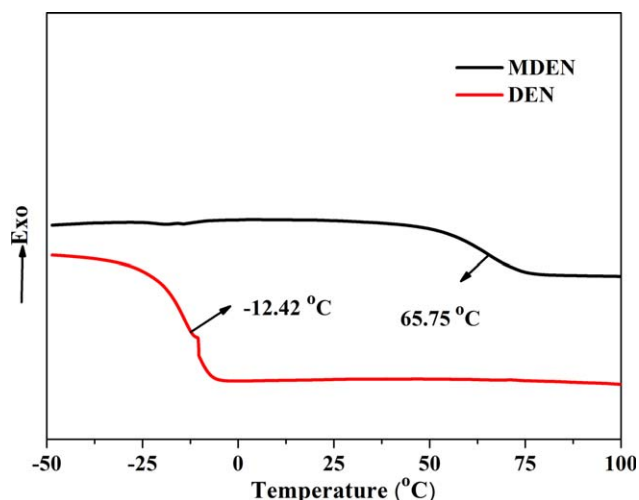

Figure 3. DSC curves of MDEN and DEN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Mechanical Properties

DMA was employed to track the viscoelastic responses of polymer under deformation, and to understand the occurrence of molecular mobility transitions such as main transition associated with glass transition and other relaxations.[5,20,21] Figure 4(a) showed the temperature dependence of storage modulus (E) and tan δ of cured MDEN and DEN. It can be found that the storage modulus of cured MDEN was higher than that of cured DEN both in the glassy and rubbery regions, which were characterized by the temperature of the maximum peak of tan δ [Figure 4(b)]. Their storage modulus were 3.56 and 2.67 GPa for cured MDEN and DEN, respectively, which were much higher than the previous studies. Wang synthesized a naphthalene-containing tri-functional epoxy resin for electronic application with storage modulus less than 2.2 GPa;[22] Xu synthesized a novel epoxy resin bearing naphthyl and limonene moieties with storage modulus less than 3.2 GPa.[3] These superiorities indicated that grafting with pendent groups could comparable with design of main chain and was more convenient.
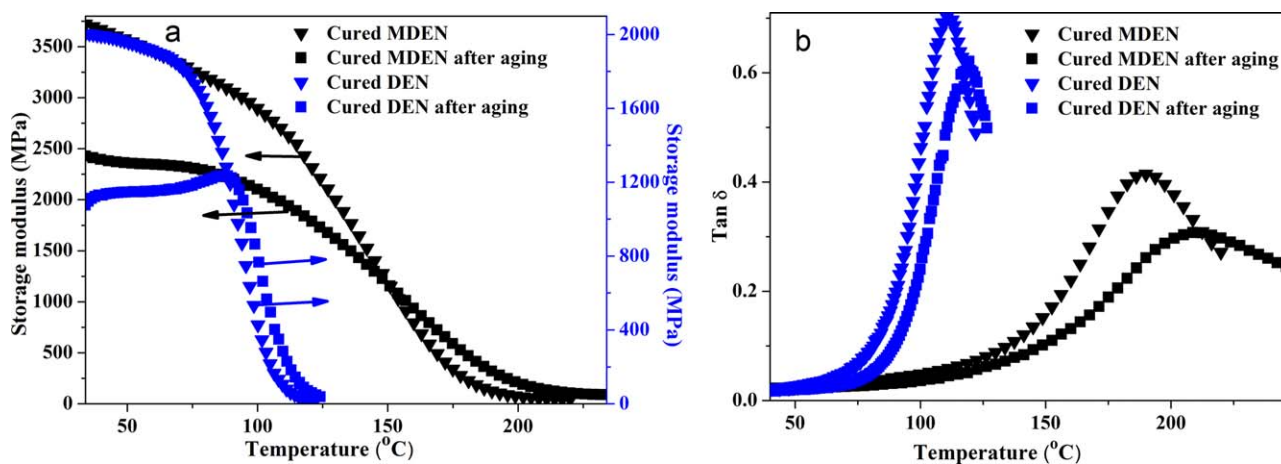
Figure 4. Temperature dependences of storage modulus (a) and tan δ (b) for cured DEN, MDEN, and their corresponding samples after aging. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
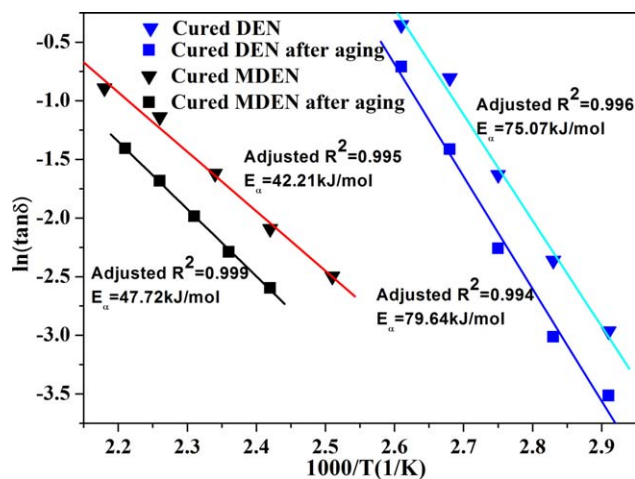
Figure 5. Linear plot of ln (tan δ) versus $1/T$ based on Eyring theory. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

According to some literature data, higher retention value of E for cured MDEN at higher temperature indicated higher cross-linking density. The cured MDEN exhibited much higher T_g (189.14°C) than that of the cured DEN by 80°C. These results were beyond the cured BGTF/HMPA (175°C) and BGTF/DDM (170°C) by Tao,[21] and cured novel cycloaliphatic epoxy (178°C) by Xie.[5] In general, the T_g of cured polymer depended strongly on the molecular structure and cross-linking density. Therefore, these results may confirm that the T_g value can be improved drastically by introducing some rigid groups into epoxy or the hardener. One possibility may result from the higher rigidity of benzene ring and triazine ring, which could hinder the thermal movements and the rotation of polymer chains. Another possible explanation could be the higher cross-linking density in cured MDEN networks and these observations were agreement with that of Xu and Pan.[3,6]

Aging Behavior and Thermal Properties
Besides, DMA was applied to study the aging behaviors of polymers.[23,24] After aging, E values of cured MDEN and DEN

decreased in the glassy region. While at temperature above T_g, the situation was reversed. Based on aging theories, polymers experienced density change, degradation and cross-linking simultaneously during thermal process.[25,26] Degradation resulted in the fracture of backbone chains, decrease of molecular weight and destruction of properties; while cross-linking caused formation of chemical bond between chains and hardened polymers. When the cured samples experienced one thermal circle from 40 to 250°C at the ramp rate of 5°C/min, the cured MDEN could keep the retention of modulus at 65% in glassy region, while the cured DEN only kept the retention at 58%. However, these observations in storage modulus were not consistent with P.O. Bussiere' results, which was due to different aging evolution using different aging method.[23] The following reasons could explain the differences: 1) The rigid structure prevented the air from reaching the center of networks, which caused less effect on cured MDEN. 2) At the same thermal process, the higher T_g made cured MDEN keep shorter time at rubbery region. Reversely, the air and moisture could penetrate into the cured DEN more easily and the aging was more serious. Another phenomenon was that aging increased the width and the peak temperature of tan δ. Increase of width resulted from degradation, which caused the uniformity of polymers to get worse. After aging, the T_g of cured MDEN and DEN shifted to 204.21 and 119.03°C, respectively. Vodovotz got the similar results using DMA to investigate the effect of aging on thermomechanical properties of white bread and found that tan δ increased in temperature, decreased in amplitude, and increased in breadth with aging.[24] These could be explained through activation energy of glass transition. According to Eyring absolute reaction speed theory, the following equation was applied;[27]

$$\ln\,(\tan\delta)\,=\,C-E_a/RT$$

The values of activation energy of glass transition (E_a) can be determined from the slope of the plot of ln (tan δ) versus $1/T$, as shown in Figure 5. The obtained values of the activation energy were 42.21 and 75.07 kJ/mol for the cured MDEN and DEN, respectively; after aging, these values increased to 47.72 and 79.64 kJ/mol, respectively. These contrasts may result from
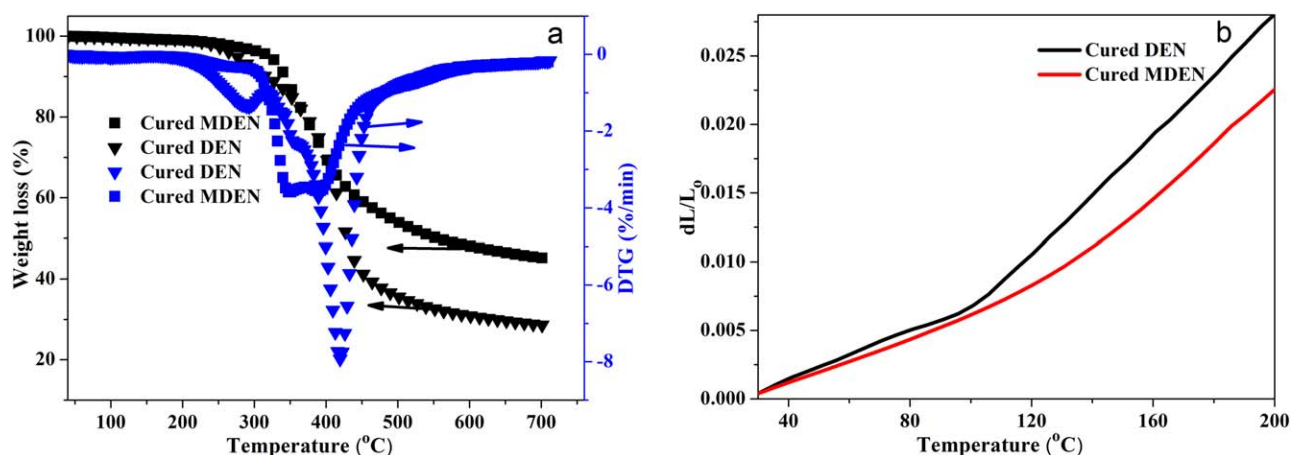
Figure 6. TGA (a) and TMA (b) traces of cured MDEN and cured DEN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 1. Thermal Properties and TMA Analysis of the Cured Polymers

Samples	T_5[a] (°C)	T_{10}[b] (°C)	T_{max}[c] (°C)	Char yield at 600°C (%)	Char yield at 700°C (%)	CTE ($\times 10^{-6}$/°C) Glassy region Rubbery region	$T_{g,TMA}$ (°C)
Cured MDEN	321.22	343.10	350.65	48.13	45.18	80.27	118.87
						183.99	
Cured DEN	275.03	315.50	420.17	31.18	28.61	93.30	99.72
						217.83	

[a] T_5, temperature of 5% weight loss.
[b] T_{10}, temperature of 10% weight loss.
[c] T_{max}, temperature of maximum of weight loss under nitrogen atmosphere.

the following reasons: 1) Thermal process to polymers caused voids and made the interfacial effect more obvious. 2) Thermal process led to cross-linking of chains and made structures condensed, which had a stronger inhibition against the partial movements of structural units of polymer chains. These inhibitions promoted the activation energy and made the tan δ shift to higher temperature. These observations were consistent with results of Song.[27] Therefore, a method was proposed to assess the aging extent based on the value change of E_a.

Thermal stability and thermal degradation behaviors were assessed by TGA under nitrogen atmosphere, which are shown in Figure 6(a). The temperature corresponding 10% weight loss was taken as an index of thermal stability. The corresponding temperatures for the cured MDEN and DEN were 343.10 and 315.50°C, respectively. From the DTG curves of cured MDEN and DEN, it can be seen that the temperatures of maximum rate of weight loss were 350.65 and 420.17°C, respectively. In results of Xu, the temperature corresponding 10% weight loss and maximum rate of weight loss were 343°C and 385°C for best cured epoxy, respectively.[3] Finally, cured MDEN and DEN reserved 48.13 and 31.18% char yield at 600°C, respectively. These results indicated that the cured MDEN exhibited higher char yield with higher degradation temperature compared to that of the cured DEN. Similar to the above properties, the thermal stability and thermal degradation behavior were also controlled by introducing of benzene ring and increase of cross-linking density.[28,29]

The inflection point of the thermal expansion plot was defined as $T_{g,TMA}$.[30] The TMA curves of cured MDEN and DEN were shown in Figure 6(b). The cured MDEN possessed a much higher $T_{g,TMA}$ (118.87°C) than that of cured DEN (99.72°C), reflecting a higher cross-linking density. All the results of TGA and TMA were also summarized in Table 1. Obviously, the cured MDEN had smaller CTE (80.27 $\times 10^{-6}$, 183.99 $\times 10^{-6}$/°C) than that of cured DEN (93.30 $\times 10^{-6}$/°C, 217.83 $\times 10^{-6}$/°C) in the glassy and rubbery regions, respectively. The network thermal motion was believed to involve the vibration of side groups and the motion of crosslink segment, the introducing of benzene ring may restrict these mobility and improve the dimensional stability of the cured polymers. These improved properties were consistent with the results of Xie and Zhang, and resulted from introducing rigid structure to epoxy.[5,7]

Viscoelastic Behavior

Rheological measurements were employed to monitor the viscoelastic behavior of the resins during the chemical reaction. It was possible to observe the temperature at which storage modulus started to grow, which meant that the 3D cross-linking stage had begun and to check how fast this stage took place. The storage modulus and curing rate as function of temperature was plotted in Figure 7. It should be noted that the level of scatter in storage modulus profiles was due to the fact that the torque values produced by the resin flow were below the sensibility of the transducer. The storage modulus of these epoxy resin systems changed little with the balance between temperatures increasing and crosslinking occurs. However, as the temperature increased higher than a definite degree, the modulus increased dramatically because of the gelation occurred during this stage. For DEN, its storage modulus increased rapidly at 125°C, while the corresponding value for MDEN was 200°C. These observations were agreement with the results of Tao.[21] The delay effect was attributed to low curing rate (da/dt), which was a differential equation of conversion (a) on time. And the differences in curing rate were attributed to the differences in the activation energy and curing mechanism, which had been discussed in our previous paper.[14] Besides, the low curing rate could reduce the internal stress during curing and MDEN had higher storage modulus after curing completely.
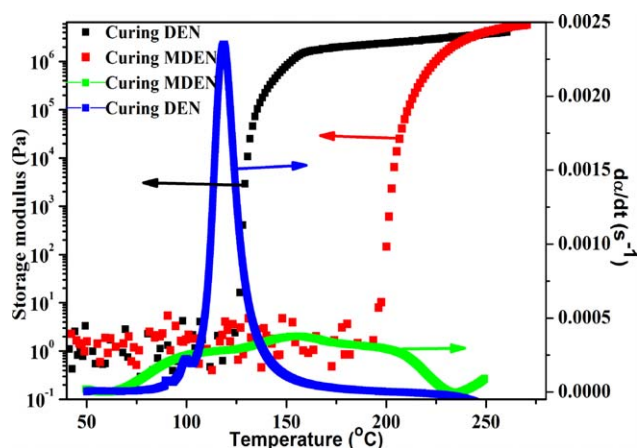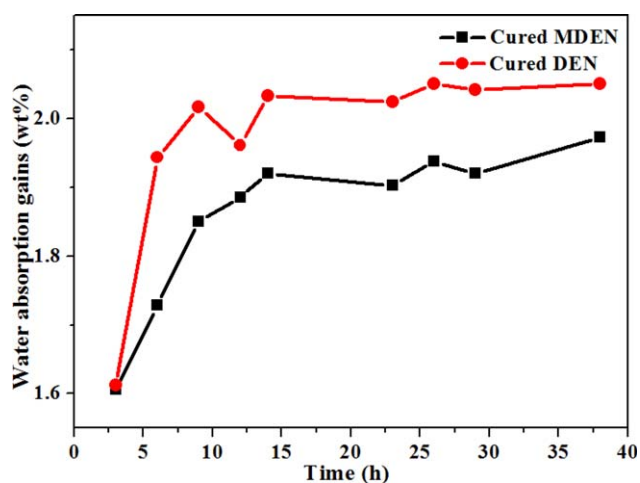

Figure 7. Variation of storage modulus and curing rate on temperature at the heating rate of 2.5°C/min for curing DEN and curing MDEN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
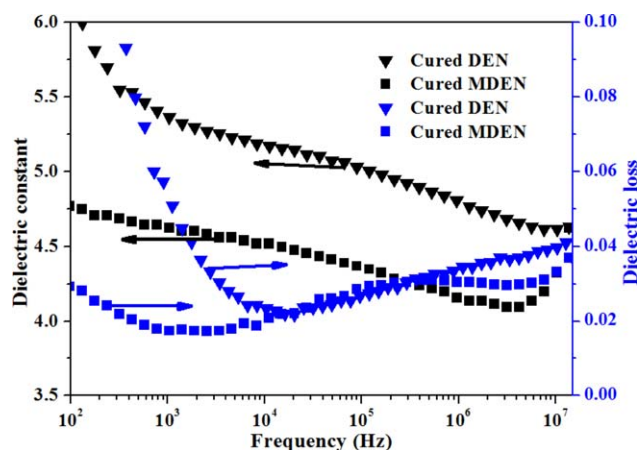
Figure 8. Frequency dependence of dielectric constant and loss (tan δ) for cured MDEN and DEN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 9. Time dependence of water absorption gains for cured MDEN and DEN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Dielectric Properties

Figure 8 represented the frequency dependence of dielectric constant and loss (tan δ) for cured MDEN and DEN. It can be seen that the dielectric constant and loss of cured MDEN were about 4.14 and 0.0305, respectively; while these values of cured DEN are about 4.80 and 0.0339, respectively, at 1 MHz and room temperature. It was worth noting that there were many

researches on dielectric properties of epoxy cured with different hardeners. Wu used phenol-novolac to cure o-cresol novolac epoxy resin and observed that the dielectric constant was 6.47, which was much higher than our results.[31] Moreover, Singh V studied the dielectric properties of aluminum-epoxy and obtained the dielectric constant of 6.22 for neat epoxy.[32] These
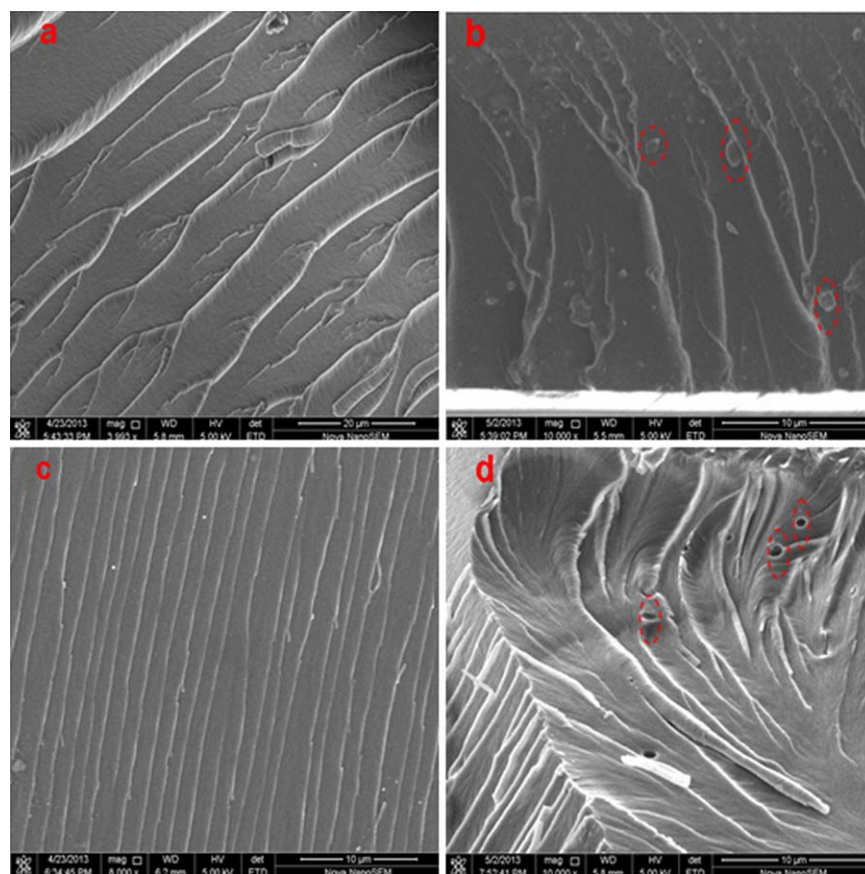
Figure 10. SEM images of cured DEN (a), cured DEN after aging (b), cured MDEN (c) and cured MDEN after aging (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

results and studies indicated that the modification and HMMM as hardener can improve dielectric properties. As we know, the dielectric constant was closely related to the polarity of compounds. The following reasons may explain these changes: 1) the HMMM hardener had the similar structures as bismaleimide–triazine with triazine ring, which had lower dielectric constant.[33] 2) Introducing of phenol hydroxyl is in favor of the curing reaction. The existence of phenol hydroxyl can offer a weak acidic environment, which was benefit to reaction between ─OCH$_3$ of amino resins and ─OH of MDEN. This reaction was difficult to occur in DEN curing system.[34,35] The consumption of ─OH could decrease the polarity of cured MDEN. 3) Because of steric hindrance of DEN and amino resin, the ─OCH$_3$ got difficult to react with ─OH, which was generated via etherification of ─OCH$_3$ with epoxide ring, leading to the opening of epoxide ring. Existence of amounts of hydroxyl increased the polarity of cured DEN.[36] The corresponding curing mechanism has been discussed in our other paper.[14]

Moisture Absorption

In the practical usage, absorbed moisture was found to plasticize the epoxy resin, causing a lowering of the T_g and in turn affecting the mechanical properties.[6,37] Figure 9 represented the time dependence of water absorption gains for cured MDEN and DEN. It could be found that the water absorption of these epoxy resins reached a plateau with the time prolongation to 13 h. Moreover, cured MDEN had better moisture resistance (1.95%) than that of cured DEN system (2.04%). The result was lower than the Pan' result (above 2.2%), and our modification of grafting pendent groups was more convenient than his introducing rigid structure into the main chain.[6] Obviously, the hydrophobic benzene moieties were responsible for the lower absorption gains. Moreover, during the curing process, ─OH groups were generated via ring opening of epoxy groups, and existence of amounts of hydroxyl increased the hydroscopicity of cured DEN.

Microscopy Investigation

SEM was used to investigate the morphology of cured DEN, cured MDEN and their corresponding samples after aging. From Figure 10(a,c), it could be found that fractured surfaces of the cured DEN was smooth, glassy and homogeneous without any plastic deformation, while the fractured texture was denser and the corresponding surface was rougher in cured MDEN, which enabled cured MDEN to absorb more energy and to have higher modulus. These observation also confirmed that the cured MDEN had higher storage modulus below T_g. However, in Figure 10(b,d), it can be observed that there were some gaps occurring and the fracture texture became blurring because of oxidation. These observations verified the influence of oxidation on properties and were consistent with the results of Dinakaran and Kumar.[38,39]

CONCLUSIONS

As discussed from the results of FTIR, ^{1}H NMR spectra and DSC, the PHBA has been successfully grafted/bonded to DEN via opening the epoxide rings of the resins. With the introducing of PHBA in the skeleton, the resulting polymers cured with amino resins exhibited much higher storage modulus (3.56 GPa

at 50°C), higher glass transition temperature (189.14°C by DMA), lower thermal expansion coefficient (80.27 × 10^{-6}/°C in glass region), lower water absorption (1.95%), better resistance to thermally oxidative degradation (∼343.10°C at 10% mass loss) and lower dielectric constant (4.14 at 1 MHz) as compared to that of cured DEN (4.8 at 1 MHz). Besides, activation energies of glass transition were obtained from mechanical dissipation, and these values shifted to 47.72 and 79.64 kJ/mol, the corresponding T_g increased after aging for the cured MDEN and DEN, respectively. Moreover, the relation between storage modulus and curing rate was established to instruct the material process. These excellent properties make it an attractive candidate for electronic packaging and composite materials.

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