Novel Adamantane-Containing Epoxy Resin

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ABSTRACT: A novel adamantane-containing epoxy resin diglycidyl ether of bisphenol-adamantane (DGEBAda) was successfully synthesized from 1,3-bis(4-hydroxyphenyl)adamantane by a one-step method. The proposed structure of the epoxy resin was confirmed with Fourier transform infrared, ^{1}H-NMR, gel permeation chromatography, and epoxy equivalent weight titration. The synthesized adamantane-containing epoxy resin was cured with 4,4'-diaminodiphenyl sulfone (DDS) and dicyandiamide (DICY). The thermal properties of the DDS-cured epoxy were investigated with differential scanning calorimetry and thermogravimetric analysis (TGA). The dielectric properties of the DICY-cured epoxy were determined from its dielectric spectrum. The obtained results were compared with those of commercially available diglycidyl ether of bisphenol A (DGEBA), a tetramethyl biphenol (TMBP)/epoxy system, and some other associated epoxy resins. According to the measured values, the glass-transition temperature of the DGEBAda/DDS system (223°C) was higher than that of the DGEBA/DDS system and close to that of the TMBP/DDS system. TGA results showed that the DGEBAda/DDS system had a higher char yield (25.02%) and integral procedure decomposition temperature (850.7°C); however, the 5 wt % degradation temperature was lower than that of DDS-cured DGEBA and TMBP. Moreover, DGEBAda/DDS had reduced moisture absorption and lower dielectric properties. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 737–742, 2007

Key words: dielectric properties; synthesis; thermal properties

INTRODUCTION

Epoxy resins have been widely applied industrially for surface-coating and painting materials, matrices of composites, adhesives, insulated materials, encapsulating materials for microelectronic devices, and so forth because of their combined excellent properties, including good processability, thermal and chemical resistance, moisture resistance, superior electrical and mechanical properties, and good adhesion to many substrates. The properties of a cured epoxy polymer largely depend on the chemical structure of the initial resins. Therefore, by the incorporation of some special moieties into the backbone of an epoxy resin, the properties of the cured epoxy polymer can be tailored and improved to suit some particular application. In particular, with the increasing use of epoxy resins as encapsulating materials in the integrated-circuit industry, intensive research has been conducted to develop novel epoxy resins characterized by improved thermal and dielectric properties, lower moisture absorption, and better dimensional stability. Moieties employed for such purposes include naphthalene, stilbene, aromatic ester, biphenyl, fluorene, fluorine, and cycloaliphatics.[1–7]

Adamantane is a very symmetric tricyclic hydrocarbon with three fused chair-form cyclohexane rings in a diamond lattice structure. This compound is thermodynamically very stable, and it has unusual effects on polymer behavior. The incorporation of adamantane as a pendant group or in the backbone of polymers, such as polyimides,[8] polyamides,[9] polysulfones,[10] polyesters,[11] and poly(ether ether ketone),[12] usually leads to an enhanced glass-transition temperature (T_g) and thermal stability, better hydrophobicity, and improved dielectric properties.[13–15] Wei et al.[16] synthesized a new adamantane-based curing agent and reported that an epoxy polymer cured with this novel curing agent also exhibited superior thermal properties and good dielectric performance at high frequencies. Significantly, Wei et al.'s research enlightened the perspective of adamantane in epoxy applications. However, the multiple steps for the synthesis of TAPA and its poor processability may restrict its further application as a curing agent. However, easy-processing adamantane-containing epoxy can be obtained much more easily without the other properties of the cured epoxy polymer being sacrificed. Therefore, we were motivated to incorporate adamantane moieties into

the backbone of an epoxy resin rather than curing agents of epoxy resins to achieve a novel cured epoxy having better processability, increased thermal stability, lower moisture absorption, and lower dielectric constants, which are highly desired characteristics for encapsulating materials.

This work concentrates primarily on the synthesis of an adamantane-containing epoxy resin (DGEBAda) derived from 1,3-bis(4-hydroxyphenyl)adamantane. Then, the thermal properties, moisture absorption, and dielectric properties of the cured epoxy polymers were investigated in detail.

EXPERIMENTAL

Materials

All reagents and solvents were reagent-grade. 1,3-Dibromoadamantane, 4,4′-diaminodiphenyl sulfone (DDS), dicyandiamide (DICY), 2-methylimidazole (2-MI), and iron(III) chloride were used without purification. Epichlorohydrin, phenol, and acetone were distilled before use; in particular, potassium permanganate was used for acetone purification to eliminate reductive residues. Diglycidyl ether of bisphenol A (DGEBA, DER 331) with an epoxy equivalent weight of 185.5 g/equiv was obtained from Dow Chemical Co.

Synthesis of 1,3-bis(4-hydroxyphenyl)adamantane

A 150-mL, round-bottom flask was charged with 1,3-dibromoadamantane (6.00 g, 20.4 mmol), phenol (60.0 g, 0.638 mmol), and iron(III) chloride (1.10 g, 6.78 mmol). The flask was fitted with a reflux condenser and an outlet leading to a beaker with a NaOH solution to trap the HBr that evolved in the reaction. The reaction was stirred at 80°C for 16 h. The excess phenol was removed through the stirring of the product in 500-mL portions of hot water three times. The product was dried in vacuo, and the crude product first was extracted in a Soxhlet extractor with methanol and then recrystallized from methanol to afford 2.94 g (45.0 wt % yield) of colorless crystals.
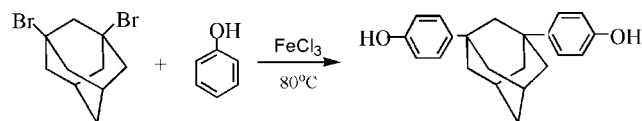
Scheme 1 Schematic diagram for the synthesis of 1,3-bis(4-hydroxyphenyl)adamantine.

mp: 199–201°C. IR (KBr, cm^{-1}): 3355 (Ar—OH), 2918, 2850 (C—H), 1613, 1514 (aromatic C—C).
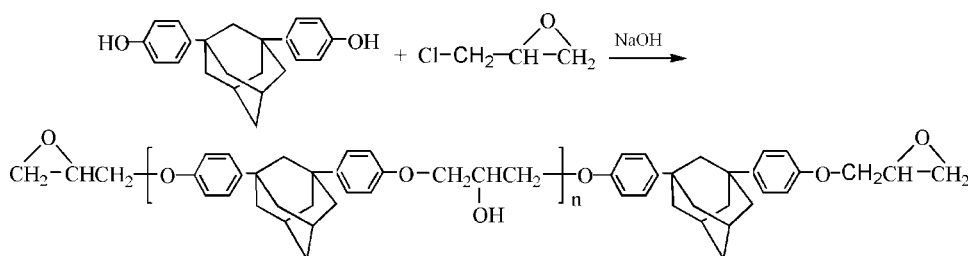
Synthesis of DGEBAda

To a four-necked, round-bottom flask equipped with a nitrogen inlet, heating mantle, stirrer, thermocouple, and temperature controller, 1.0 g (3.125 mol) of 1,3-bis(4-hydroxyphenyl)adamantane, 2.97 mL of isopropyl alcohol, and 4.34 g of epichlorohydrin were added. The reaction temperature was controlled at 80°C, and 0.625 g of 40 wt % aqueous NaOH was added dropwise within 1 h; then, the mixture was reacted at that temperature for 6 h. After the reaction was completed, the salt was filtered, and then the filtrate was washed with water three times. After the separation of the organic phase from the mixture, excess epichlorohydrin and the solvent were distilled from the organic phase by a rotary instrument to give a yellow, ropy, liquid product.

Epoxy equivalent weight: 266 g/equiv. Number-average molecular weight: 567. Weight-average molecular weight/number-average molecular weight: 1.12. IR (KBr, cm^{-1}): 1615, 1512 (aromatic C—C), 1246 (alkyl–aryl C—C), 911 (oxirane ring).

The reaction equation is shown later in Scheme 2.

Curing procedure

DGEBAda was cured with DDS or DICY in a stoichiometric ratio. For the DDS-cured system, the mixture was dissolved homogeneously in acetone as a solvent, which evaporated later at 40°C in vacuo. The samples were kept in a refrigerator before the differential scanning calorimetry (DSC) experiment was performed. The cured samples were prepared at 150°C for 2 h, at 180°C for 3 h, and at 200°C for 3 h. After that, the samples were allowed to cool slowly

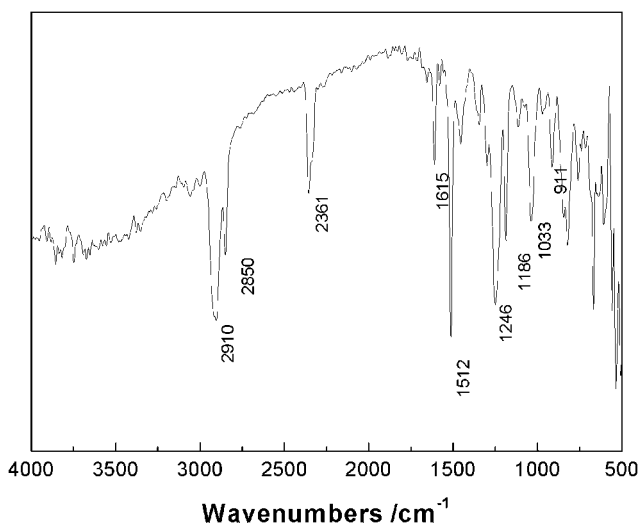**Scheme 2** Schematic diagram for the synthesis of DGEBAda.

Figure 1 FTIR spectrum of DGEBAda.

to the ambient temperature to prevent cracking. For the DICY-cured system, epoxy and DICY were also dissolved in acetone, and 0.5 wt % 2-MI was used as a curing accelerator. After the removal of the solvent with the same method, the formulation was cured at 200°C for 4 h and then also slowly cooled to the ambient temperature.

Characterization

A PerkinElmer Fourier transform infrared (FTIR) spectrophotometer (Japan) was used to record IR spectra (KBr pellets). [1]H spectra were recorded on Inova 400 NMR spectrometers with CDCl$_3$ as the solvent and tetramethylsilane as the internal standard. Gel permeation chromatography (GPC) was performed on a WAT044207 HT3 gel permeation chromatograph in the solvent tetrahydrofuran (THF).

The curing reaction kinetics of the DGEBAda/DDS system were investigated with DSC scans in a nitrogen atmosphere at heating rates of 5, 10, 15, and 20°C/min separately with a Universal differential scanning calorimeter (Netzsch, Germany). Thermogravimetric analysis (TGA) was carried out with a Universal thermogravimetric analyzer at a heating rate of 10°C/min under nitrogen from the ambient temperature to 800°C. The integral procedure decomposition temperature (IPDT) of the cured epoxy polymer was calculated according to the method described in Park and Cho's work.[17] The epoxy equivalent weight of the adamantane-containing epoxy resin was measured by the HCl/acetone titration procedure. Samples with a diameter of 10 mm and a thickness of 1 mm were dried *in vacuo* at 120°C until the moisture had been expelled. After cooling to room temperature, the sample was weighed, placed in 100°C water for 72 h, and weighed again. The moisture absorption was calculated as follows: Weight gain (%) = $(W/W_0 - 1) \times 100$, where W is the weight of

the sample after its placement in 100°C water for a certain period and W_0 is the weight of the sample before its placement in water. The dielectric constant and dielectric loss were determined with a Novocontrol GmbH (Germany) dielectric spectrometer at 25°C from 10^{-1} to 10^6 Hz.

RESULTS AND DISCUSSION

Characterization of DGEBAda

1,3-Bis(4-hydroxyphenyl)adamantane, the precursor of DGEBAda, was synthesized with the Friedel–Crafts reaction reported by Chern and Shiue[18] (Scheme 1). The melting point of the monomer was in the range of 199–201°C, the same as that reported by Chern and Shiue; this suggested that the purity of 1,3-bis(4-hydroxyphenyl)adamantane was very high because of its small melting range. IR spectroscopy also confirmed the formation of 1,3-bis(4-hydroxyphenyl)adamantane.

A novel adamantane-containing epoxy resin (DGE-BAda) was synthesized by a conventional one-step procedure starting with 1,3-bis(4-hydroxyphenyl) adamantane and epichlorohydrin, as shown in Scheme 2. The FTIR spectrum of DGEBAda exhibited the characteristic oxirane absorption at 911 cm^{-1} (Fig. 1). The chemical structure of DGEBAda could be further confirmed by the other absorption peaks at 2906 and 2848 cm^{-1} for C—H, at 1615 and 1512 cm^{-1} for aromatic C—C, and at 1246 cm^{-1} for alkyl–aryl C—C. Figure 2 shows the ^{1}H-NMR spectrum of DGEBAda. In the ^{1}H-NMR spectrum, one can see the characteristic chemical shift at δ = 7.2 ppm (s, 4H, aromatic). The peak at 2.7–4.2 is the characteristic peak of oxirane. The peaks for adamantane were displayed as follows: δ 1.7 (br s, 2H, H-6), δ 1.9 (m, 10H, H-2, H-4, H-8, H-9, H-10), and δ 2.3 (br s, 2H,
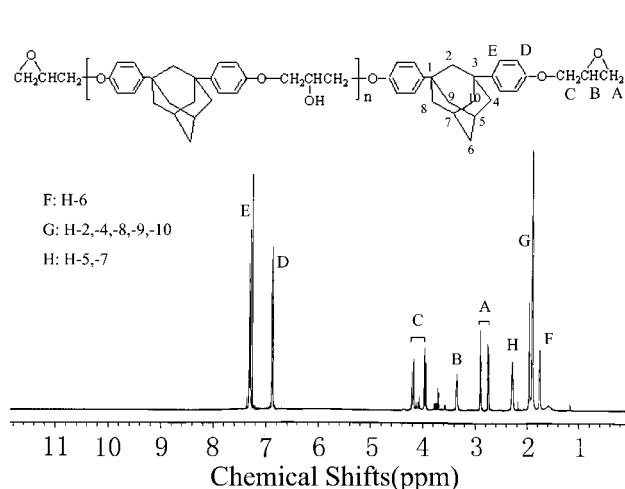

Figure 2 ^{1}H-NMR spectrum of DGEBAda.

TABLE I
Solubility Behavior of the DGEBAda Epoxy Resin

Solvent	Solubility[a]	Solvent	Solubility[a]	Solvent	Solubility[a]
DMSO	++	Acetone	++	Trichloromethane	+
DMF	++	Methyl benzene	+	Isopropyl alcohol	−
NMP	++	Benzene	+	n-Hexane	−
THF	++	Methanol	−	Ether	−
Ethyl acetate	++	Alcohol	−		

[a] ++ = easily dissolved; + = soluble; − = partially soluble (tested at the ambient temperature).

H-5, H-7). They coincide with the ^{1}H-NMR spectrum of the adamantane moiety reported by Chern[8] quite well. Generally, an epoxy is a syngeneic mixture of compounds, and some hydroxyl hydrogen should be confirmed by ^{1}H-NMR because of the existence of repeat units in which hydroxyl hydrogen is contained. However, for DGEBAda, no peak in ^{1}H-NMR for hydroxyl hydrogen (δ 5) was observed, and this means that the number of repeat units was quite small and that a low-molecular-weight epoxy resin was obtained by the one-step method.

The solubility of DGEBAda was tested in various solvents. Table I summarizes these results. Because of the incorporation of adamantane into the backbone of the epoxy resin, DGEBAda exhibited excellent solubility toward these test solvents. It was highly soluble in strongly polar solvents, such as dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), and N-methyl-2-pyrrolidone (NMP). Acetone and ethyl acetate also had a good capacity for dissolving DGEBAda. A test of the solubility suggests that DGEBAda has perfect solubility in common solvents, and this makes DGEBAda an easy-processing epoxy resin.

Curing behavior of the DGEBAda/DDS system

The curing reaction of DGEBAda/DDS was investigated intensively with DSC. Table II shows the results of the dynamic runs obtained by DSC for the DGEBAda/DDS curing reaction at heating rates of 5, 10, 15, and 20°C/min. The onset and peak temperatures shifted to higher temperatures with the increase in the heating rate, whereas the final temperature of the system was not sensitive to the change in the heating rate. The peak temperature had a good linear correlation with different heating rates (the linear relation coefficient was 0.98), and when it was extrapolated to a zero heating rate, the peak temperature was 196.4°C, which can be considered a suitable curing temperature for the DGEBAda/DDS system. The DSC exothermic peak of DGEBAda/DDS was higher than that of the DGEBA/DDS system[19] and quite close to that of the tetramethyl biphenol (TMBP)/DDS system;[20] this means that the DGEBAda/DDS system might be directly applied in industry.

To evaluate the kinetic parameters of the DGEBAda/DDS system, the widely applied Kissinger and Ozawa methods were adopted to calculate the apparent activation energy (E_a).

The Kissinger expression gives

$$-\ln\left(\frac{\beta}{T_p{}^2}\right) = \frac{E_a}{RT_p} - \ln\frac{AR}{E_a} \quad (1)$$

where T_p is the peak temperature at which the maximum conversion rate occurs in the DSC exotherm, β is the heating rate, A is the Arrhenius constant, and R is the ideal gas constant. Another theoretical treatment, Ozawa's equation, can be expressed as follows:

$$\ln\beta = -1.052\frac{E_a}{RT_p} + \ln\frac{AE_a}{R} - \ln F(\alpha) - 5.331 \quad (2)$$

where $F(\alpha)$ is a conversion-dependent term. The E_a values, obtained from the slopes of the $-\ln(\beta/T_p{}^2)$ versus $1/T_p$ plot and the $-\ln\beta$ versus $1/T_p$ plot for the DGEBAda/DDS system, are 56.8 and 61.9 kJ/mol, respectively, which parallel those of other common aromatic diamine–epoxy systems, such as the DGEBA/DDS system (ca. 62–69 kJ/mol) and TMBP/DDS system (57.03 kJ/mol). This result indicates that DGEBAda has an activity for the curing reaction similar to that of commercial DGEBA and TMBP epoxy resins.

Properties of the cured DGEBAda

Thermal properties of the DGEBAda/DDS system

T_g of the DDS-cured DGEBAda was determined with DSC, whereas the thermal stability and thermal

TABLE II
Curing Behavior of DGEBAda/DDS

Heating rate (°C/min)	Onset temperature (°C)	Peak temperature (°C)	Final temperature (°C)
5	100.6	209.6	304.5
10	147.5	229.1	311.2
15	186.7	243.0	307.2
20	187.5	253.5	310.2

TABLE III
Thermal Properties of the Various Epoxy Systems

Sample	T_g by DSC (°C)	5% loss in N_2 by TGA (°C)	Char yield at 800°C (%) in N_2	IPDT (°C)
DGEBAda/DDS	223	364	25.02	850.7
DGEBA/DDS[a]	193	377	11.50	587
TMBP/DDS[b]	239	404	14.17	

[a] The data were taken from ref. 21.
[b] The data were taken from ref. 22.

degradation behavior of the system were investigated with TGA. Table III summarizes these results.

T_g of the DGEBAda/DDS system was markedly higher than that of the DGEBA/DDS system and comparable to that of the TMBP/DDS system. The fact that T_g was higher than that of the DGEBA/DDS system was attributed to the fact that the rigid and bulky adamantyl element increased the rigidity of the cured polymer chain, which, in turn, appeared to require much more energy to develop the segmental mobility needed to reach T_g. The temperature of the DGEBAda/DDS system at a 5% weight loss was 364°C in an N_2 atmosphere, which was lower than that of the DDS-cured DGEBA and TMBP systems. However, the char yield and IPDT of the DGEBAda/DDS system (25.02% and 850.7°C, respectively) were much higher than those of the DDS-cured DGEBA and TMBP systems. A higher char yield indicated that the introduction of the adamantane moiety favored the formation of char residue because of the higher C/H weight ratio of adamantane,[21] whereas a higher IPDT value suggested that the adamantane moiety could improve the inherent thermal stability of the thermoset substantially.
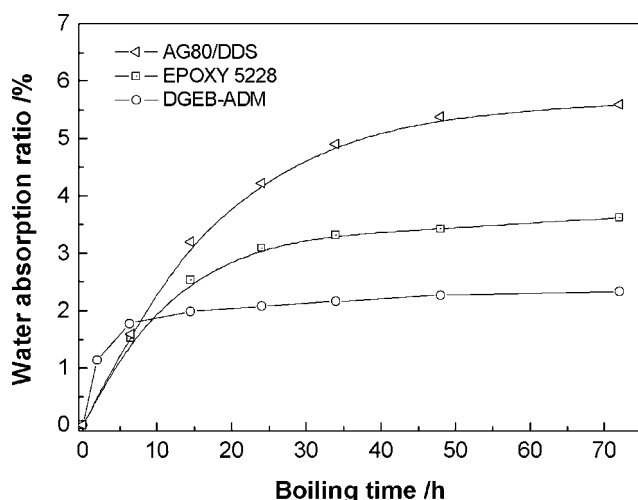
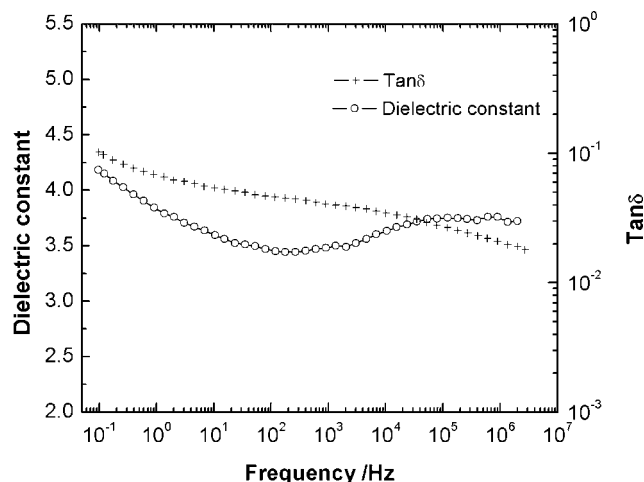**Figure 3** Moisture absorption behavior of various epoxy systems.

Figure 4 Dielectric constant versus the frequency for the DGEBAda/DICY system.

Moisture absorption

Moisture absorption will reduce T_g of encapsulating materials and may cause popcorn effects during the fabrication process. Moisture absorption will also ionize the ionic impurities (e.g., Cl$^-$) and thus corrode the integrated circuits. Furthermore, moisture absorption will increase an encapsulating material's dielectric constant.[23] Therefore, lower moisture absorption is favorable for encapsulating materials.

Graphs of the water uptake are shown in Figure 3. Obviously, compared with the tetraglycidyl-4, 4'-diaminophenymethane (TGDDM) and epoxy 5228 systems, the DGEBAda/DDS system had lower water uptake (%). A fluorene-based epoxy resin also has excellent moisture resistance[5] (3.0%, 48 h), but under the same conditions, the water uptake of the DGEBAda/DDS system was only 2.26%. It is possible to conclude that the waterproofing effect of the adamantane moiety improved the moisture resistance of the cured DGEBAda.

Dielectric properties

The dielectric properties of the DGEBAda/DDS systems were determined by the measurement of the dielectric constant and dielectric loss at different frequencies (10^{-1}–10^6 Hz). Figure 4 shows the variation of the dielectric constant as a function of the frequency. The dielectric constant and dielectric loss were 3.43–4.18 and 0.018–0.101, respectively. Table IV presents the dielectric constant of the DGEBAda/DICY system and those of its counterparts detected at 1 MHz at 25°C. The lower dielectric constant of DGEBAda/DDS was probably due to the fact that adamantane, a fully aliphatic hydrocarbon, led to lower hydrophobicity and polarity for the cured epoxy polymer. On the other hand, the steric hindrance

TABLE IV
Dielectric Parameters of the Various Epoxy Systems at 1 MHz and 25°C

Sample	DGEBAda/ DICY	DGEBA/ DICY	ENL/ DICY[a]	ENL/ PN[a]
Dielectric constant	3.74	4.73	3.8	4.1

[a] The data were taken from ref. 25.
ENL and PN represent an epoxy resin and a bisphenol A-formaldehyde novolac, respectively.

of adamantane lowered the activity of the main chain and side chain, and this went against the orientation polarization of polar groups in the cured epoxy polymer. Therefore, the DGEBAda/DDS system had a lower dielectric constant. These kinds of positive effects of adamantane are also consistent with results reported in studies of adamantane-based polyimides.[15,18,24]

CONCLUSIONS

A novel epoxy resin (DGEBAda) containing adamantane was successfully synthesized in one step from 1,3-bis(4-hydroxyphenyl)adamantane. The structure of DGEBAda was confirmed through epoxy equivalent weight, IR, ^{1}H-NMR, and GPC characterization. When cured with DDS, DGEBAda exhibited curing activity similar to that of commercially available DGEBA and TMBP epoxy resins. The DSC results demonstrated that the DGEBAda/DDS system had a much higher T_g than the DGEBA/DDS system, and its T_g nearly approached that of the TMBP/DDS system. According to TGA, the DGEBAda/DDS system had a higher char yield (25.02%) and IPDT (850.7°C) because of the thermal stability of the adamantane moiety. However, the 5 wt % degradation temperature was lower than that of cured DGEBA and TMBP. Moreover, DGEBAda/DDS had reduced moisture absorption and lower dielectric constants because of the hydrophobic property of adamantane. The combination of a high T_g, outstanding resistance to moisture absorption, improved dielectric properties, and curing behavior similar to that of DGEBA and TMBP makes DGEBAda a possible candidate for encapsulating materials.

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