Tailored Thermal and Mechanical Properties of Epoxy Resins Prepared Using Multiply Hydrogen-Bonding Reactive Modifiers

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ABSTRACT: In this study, we synthesized a phosphorus-containing triply functionalized reactive modifier, DOPO-tris(azetidine-2,4-dione), and a phosphorus-free doubly functionalized reactive modifier, bis(azetidine-2,4-dione), and embedded them into epoxy resin systems. We characterized these synthesized reactive modifiers using Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, elemental analysis, and mass spectrometry. During the thermosetting processes, we reacted the epoxy curing agents 4,4-diaminodiphenylmethane and tris(4-aminophenyl)amine with the multiply hydrogen-bonding reactive modifiers and epoxy monomers. The introduction of the DOPO segment, strongly hydrogen bonding malonamide linkages, and hard aromatic groups into the backbones of the synthesized reactive modifiers resulted in epoxy networks exhibiting tailorable crosslinking densities, flexibilities, glass transition temperatures, thermal decomposition temperatures, and flame retardancies. Furthermore, dynamic mechanical analyses indicated that intermolecular hydrogen bonding of these reactive modifiers enhanced the thermal and physical properties of their epoxy resins through the formation of unique pseudocrosslinked polymer networks. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2411–2420, 2011

Key words: crosslinking; epoxy; reactive modifier; polymer networks; hydrogen bond

INTRODUCTION

Thermosetting epoxy resins exhibiting toughness, low shrinkage, excellent adhesion, and corrosion resistance are widely used in, for example, adhesives, surface coatings, laminates, potting materials, fiber-reinforced composites, semiconductor encapsulation, and electrical insulation.[1] Nevertheless, much like organic polymer materials in general, the low impact strength and flammability of epoxy materials limit their application. As a result, several approaches have been developed to enhance the flexibility, thermal properties, mechanical properties, and flame resistance of epoxy materials.[2–5]

The most feasible approach of improving the properties of epoxy resins is incorporating general additive or reactive-type compounds within them. Three approaches have been adopted in previous studies to eliminate the brittleness of epoxy resins while ensuring high impact strengths and elongations after curing: (1) adding or *in situ* formation of rubber or thermoplastic particles into the epoxy matrix (these materials act merely as additives),[6–8] (2) introducing long-chain molecules into the epoxy resins during the curing process,[9,10] and (3) increasing the crosslinking density or enhancing the strength and number of intermolecular forces.[5,11–13] The major problem encountered with the first two methods are incompatibility between the modifiers and epoxy resins which leading to the decrease of glass transition temperatures (T_g) and phase separation. The reactive modifiers are of interest because they can sustain the polymer's performance for a longer time, while reducing the influence of the physical, mechanical, and artifactitious properties provided by introducing strongly hydrogen bonding urea, urethane,[9] amide,[12] or ester[13] functional groups into the epoxy resins. Moreover, increasing the number and strength of the intermolecular interactions not only improves an epoxy resin's adhesion but also increases the polymer network intensity. Because a high crosslinking density usually leads to high degrees of shrinkage and brittle properties, a curing agent that provides a toughening effect must be used to afford tailoring of the flexibility for practical applications.

Multifunctional 9,10-dihydro-9-oxa-10-phosphaphe-nanthrene 10-oxide (DOPO) derivatives, such as DOPO-containing epoxies, amines, itaconic acids, maleimides, and phenols, have been developed for use as reactive additives for flame-retardant materials.[14] In prior studies, Lin et al. developed DOPO-containing triamine and triol curing agents that enabled epoxy resins to exhibit high values of T_g ($\sim 190°C$) and high crosslinking densities.[15,16] Wang and Lee synthesized a series of DOPO-containing curing agents and multifunctional epoxy monomers; they obtained a high value of T_g (235°C) when using a tetrafunctional naphthalene-containing epoxy resin.[17] Phosphorus-containing compositions featuring high phosphorus contents usually exhibit poor processability and deteriorated material properties, in particular with respect to the values of T_g, due to the presence of soft —P—O— linkages.[12,18] Higher crosslinking densities, using multifunctional reactive curing agents, have been adopted to avoid any negative effects on the values of T_g of the epoxy materials. DOPO derivatives possessing phosphorus contents of 1–3% appear to have limited influence on physical properties relative to other phosphorus-containing epoxy resins because of their inherently aromatic-rich, cyclic structures.

Recently, we developed a family of phosphorus-containing poly(oxyalkylene)amine curing agents and bismaleimides for use in the preparation of thermosetting epoxy resins[3,5] that exhibited well-tuned flexibility and flame-retardant properties. In addition, using the building block 4-isocyanato-4′-(3,3-dimethyl-2,4-dioxo-acetidino)diphenylmethane (IDD), which exhibits selective reactivity, we synthesized a series of polyurea/malonamide dendritic structures.[19] We suspect that the presence of strong noncovalent interactions, particularly hydrogen bonds, in the novel side-chain and end-capped dendritic polyurethanes significantly improved their mechanical properties, especially with respect to the shape memory effect.[20,21]

In this study, we synthesized a doubly functionalized reactive epoxy modifier, bis(azetidine-2,4-dione), and a triply functionalized phosphorus-containing reactive epoxy modifier, DOPO-tris(azetidine-2,4-dione), and subsequently incorporated them into systems of diglycidyl ether of bisphenol-A (DGEBA) cured with 4,4′-diaminodiphenylmethane (DDM) or tris(4-aminophenyl)amine (TPA). The ring-opening addition reactions of the azetidine-2,4-dione units in the presence of the primary amines enabled the modifiers to act as reactive epoxy curing agents.[19] The flexibility of the epoxy polymers and the strength of their hydrogen bonding interactions could be tailored through varying the content of strongly hydrogen bonding malonamide linkages. Dynamic mechanical analysis (DMA) confirmed that various degrees of molecular interaction were pres-

ent, associated with multiple hydrogen bonds between the reactive modifier units and the epoxy, resulting in tougher thermosetting resins. It is believed that phosphorus-containing compounds can quench flammable radicals like H or OH and reduce the energy of the flame in the gas phase, forming a heat and oxygen-resistant protective carbonaceous layer in the solid phase at higher temperatures.[12] Therefore, we also investigated the thermal properties, flame retardancy, and degradation behavior of these modified epoxy polymers.

EXPERIMENTAL

Materials

Methylenedi-p-phenyl diisocynate (MDI), isobutyryl chloride, tris(4-nitrophenyl)amine, and DDM were purchased from Arcos or Aldrich and used as received. Triethylamine (TEA) and hydrazine monohydrate was purchased from TEDIA. The liquid epoxy resin, DGEBA, with an epoxide equivalent weight of 188 (trade name: BE188), was purchased from Chang Chun Co., Taiwan. Xylene, N,N-dimethylformamide (DMF), dioxane, EtOH, and cyclohexane were distilled under reduced pressure over CaH_2 and stored over 4 Å molecular sieves. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-yl-tris(4-aminophenyl) methane (DOPO-triamine) and IDD were prepared according to reported synthetic routes.[15,17]

Instrumental analysis and measurements

Infrared spectra were recorded using a PerkinElmer Paragon 500 FTIR spectrophotometer. ^{1}H-NMR spectra were recorded using a Varian Gemini-300 FT-NMR spectrometer. Elemental analysis was performed using an F002 Heraeus CHN-O rapid elemental analyzer using acetanilide as a standard. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed using a Seiko SII Model SSC/5200 operated at a heating rate of 10°C/min under N_2 atmosphere. The thermal degradation temperature (T_d) was defined as the temperature at which 5% weight loss occurred. DMA was performed using a PerkinElmer SII DMA 7e instrument. The storage moduli (E') and values of tan δ were determined for samples (length, 15 mm; width, 10 mm; thickness, ~ 1.5 mm) that had been subjected to the temperature scan mode at a programmed heating rate of 5°C/min from ambient temperature to 250°C at a frequency of 1 Hz and an amplitude of 6 μm. The test method was performed using a three-point bending mode with a tension ratio at 110%. The limited oxygen index (LOI) was measured using a Stanton Redcraft Flame Meter. A flame was applied from the top of the chimney for

TABLE I
Curing Compositions of Epoxy Resin Samples

Sample	Composition	Functional group molar ratio	Weight ratio (wt %)	Nitrogen content (wt %)	Phosphorus content (wt %)
A1	TPA/BE188/Bis(azetidine-2,4-dione)	1.1/1/0.1	22/71/7	4.75	0
A2	TPA/BE188/Bis(azetidine-2,4-dione)	1.3/1/0.3	24/58/18	5.92	0
A3	TPA/BE188/Bis(azetidine-2,4-dione)	1.5/1/0.5	25/49/26	6.69	0
B0	TPA/BE188/DOPO-tris(azetidine-2,4-dione)	1.0/1/0	21/79/0	4.05	0
B1	TPA/BE188/DOPO-tris(azetidine-2,4-dione)	1.1/1/0.1	20/64/16	5.23	0.35
B2	TPA/BE188/DOPO-tris(azetidine-2,4-dione)	1.3/1/0.3	19/45/36	6.76	0.75
B3	TPA/BE188/DOPO-tris(azetidine-2,4-dione)	1.5/1/0.5	18/36/46	7.43	0.97
C0	DDM/BE188/Bis(azetidine-2,4-dione)	1.0/1/0	21/79/0	2.97	0
C1	DDM/BE188/Bis(azetidine-2,4-dione)	1.1/1/0.1	22/70/8	3.68	0
C2	DDM/BE188/Bis(azetidine-2,4-dione)	1.3/1/0.3	24/58/18	4.68	0
C3	DDM/BE188/Bis(azetidine-2,4-dione)	1.5/1/0.5	26/49/25	5.47	0
D1	DDM/BE188/DOPO-tris(azetidine-2,4-dione)	1.1/1/0.1	20/63/17	4.29	0.35
D2	DDM/BE188/DOPO-tris(azetidine-2,4-dione)	1.3/1/0.3	19/46/35	5.70	0.75
D3	DDM/BE188/DOPO-tris(azetidine-2,4-dione)	1.5/1/0.5	19/35/46	6.83	0.97

10 s and then the percentage of oxygen in the O_2 and N_2 mixture that was just sufficient to sustain the flame was defined to be the LOI. Mechanical properties were measured at room temperature using an EZ test machine (Shimadzu, Japan) operated at a crosshead speed of 1 mm/min.

Synthesis of bis(azetidine-2,4-dione)

A solution of TEA (101 g, 1.00 mol) in xylene (100 mL) was added to a solution of MDI (100 g, 0.4 mol) and isobutyryl chloride (95.63 g, 0.88 mol) in xylene (300 mL). The mixture was heated under reflux for 7 h and then cooled to room temperature. The resulting solution was filtered to remove the salt and concentrated to a volume of 50 mL. The product was then crystallized from cyclohexane to yield a white powder (67%). FTIR (KBr, cm^{-1}): 1858 (C=O), 1734 (C=O). ^{1}H-NMR [DMSO-d_6, δ (ppm)]: 1.38 (12H, CH$_3$), 3.98 (2H, ArCH$_2$Ar), 7.29–7.33 (4H, ArH), 7.59–7.63 (4H, ArH).

Synthesis of DOPO-tris(azetidine-2,4-dione)

DOPO-triamine (0.5 g, 1 mmol) was added to a solution of IDD (1.37 g, 4.3 mmol) in DMF (100 mL). The solution was stirred at room temperature under a N_2 atmosphere for 12 h and then poured slowly into a mixture of water and MeOH (1 : 1). The precipitate was filtered off and dried under vacuum at 60°C to yield the product (74%). FTIR (KBr, cm^{-1}): 1740 (C=O), 1856 (C=O), 1190 (P=O), 3348 (NH). ^{1}H-NMR [DMSO-d_6, δ (ppm)]: 1.38 (18H, CH$_3$), 3.87 (6H, CH$_2$), 7.10–7.58 (44H, ArH), 8.54 (6H, NH). MS: m/z = 1463 [M$^+$]. Anal. Calcd. for $C_{88}H_{74}N_9O_{11}P$: C, 72.17%; H, 5.09%; N, 8.61%; O, 12.02. Found: C, 71.95%; H, 5.33%; N, 8.06%; O, 11.84%.

Synthesis of TPA[22]

Tris(4-nitrophenyl)amine (15.2 g, 0.4 mmol) and Pd/C (10 wt %, 1.0 g) were added to dioxane/EtOH (2 : 1, 720 mL) in a 1-L four-necked flask and then stirred at 80°C under a N_2 atmosphere. Hydrazine monohydrate (80 mL) was then added dropwise over 5 h; when the addition was complete, the reaction mixture was heated under reflux for a further 20 h. The cooled reaction mixture was filtered and the filtrate poured into water (4 L). The precipitate was filtered off and dried under vacuum (10.2 g, 89%). The crude product was recrystallized (EtOH) to give TPA as gray crystals (m.p. 246°C). ^{1}H-NMR [DMSO-d_6, δ (ppm)]: 6.58 (6H, ArH), 6.43 (6H, ArH), 4.72 (6H, NH$_2$).

Preparation of cured epoxy resins

The reactive-type modifiers DOPO-tris(azetidine-2,4-dione) and bis(azetidine-2,4-dione) were blended with the amine curing agents DDM and TPA, respectively, at 120°C in a homogeneous state for 10 min and then BE188 was poured into the mixture. The reactants were mixed homogeneously at various equivalent ratio formulations. For all systems, curing was performed at 140°C for 2 h and then at 180°C for 2 h, with postcuring at 220°C for 2 h. The cured epoxy polymers are listed in Table I.

RESULTS AND DISCUSSION

Synthesis and characterization of reactive modifiers

The epoxy modifiers were synthesized through coupling of the isocyanate-containing IDD with the primary aromatic amine DOPO-triamine and the diamine DDM to form urea linkages and terminal
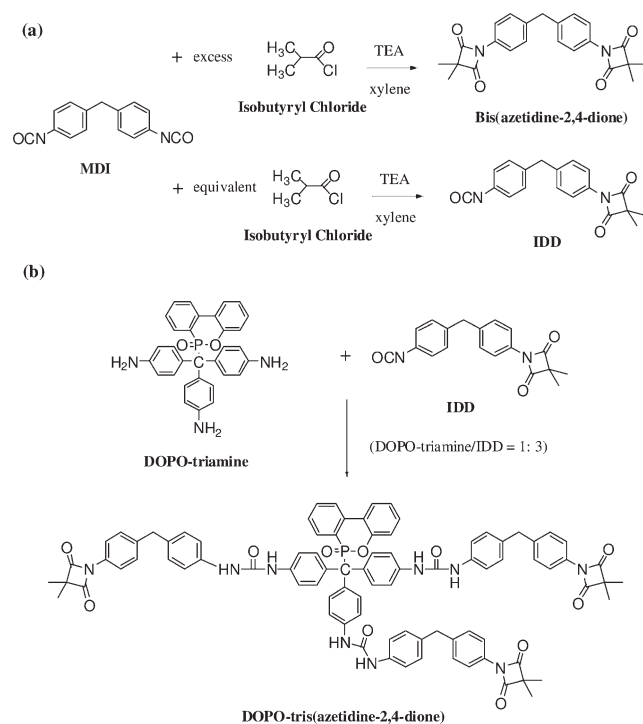
Scheme 1 Synthesis of reactive modifiers.

reactive azetidine-2,4-dione functional groups (Scheme 1). The FTIR spectra of bis(azetidine-2,4-dione) and DOPO-tris(azetidine-2,4-dione) reveal (Fig. 1) the same characteristic absorptions at 1740 and 1878 cm^{-1}, due to the presence of the end-capped azetidine-2,4-dione groups. The strong absorption of the isocyanate group of IDD at 2260 cm^{-1} disappeared completely after its reactions with DDM and DOPO-triamine. The FTIR spectrum of DOPO-tris(azetidine-2,4-dione) exhibited additional absorptions at 1652 (C=O stretching), 1190 (phosphine oxides), and 3348 (NH stretching) cm^{-1}. We also used ^{1}H-NMR spectroscopy to confirm the chemical structures of the reactive modifiers (Fig. 2). The aromatic protons appear as signals between 7.10 and 7.63 ppm. The spectra of both compounds revealed signals at 1.38 and 3.87 ppm, which we assign to the protons of their CH$_3$ and CH$_2$ groups, respectively. For DOPO-tris (azetidine-2,4-dione), the signal for the protons of the NH units in the urea linkages appears at 8.54 ppm. The integral intensities of all of the signals are consistent with the values calculated for the proposed structures. Taken together, our spectroscopic evidence supports the successful synthesis of the doubly functionalized bis(azetidine-2,4-dione) and the triply functionalized DOPO-tris(azetidine-2,4-dione).

Reactivity and curing process

Figure 3 presents DSC thermograms of bis(azetidine-2,4-dione) and DOPO-tris(azetidine-2,4-dione) recorded

during their curing with amine curing agents. The reactivities of the ring-opening reactions were directly observed from the starting temperatures of the exothermic peaks. For an equivalent functional group molar ratio in a blend of DDM and bis(azetidine-2,4-dione), we detected an endothermic peak for the melting of bis (azetidine-2,4-dione) at 84°C and then a significant, broad exothermic peak, ranging from 110 to 145°C, that represented the ring-opening reaction between the azetidine-2,4-dione groups and the primary amine, forming malonamide linkages. Likewise, DOPO-tris(azetidine-2,4-dione) cured with TPA at an equivalent molar ratio also exhibited a broad melting transition from 60 to 110°C. Notably, the reactivity of DOPO-tris(azetidine-2,4-dione) toward amine curing agents appears to be greater and more complicated than that of bis(azetidine-2,4-dione), according to our observation of a sharp exothermic peak ranging from 110 to 130°C and a second exothermic peak ranging from 130 to 180°C. The complicated reactivity of DOPO-tris(azetidine-2,4-dione) toward TPA possibly results from its higher molecular weight and an electronic effect contributed by its electron-withdrawing phosphine oxide groups.[18] From these observations, we conclude that the curing reaction of BE188 with TPA and the polymerization of the reactive modifiers occurred within a similar processing window. Figure 3(c,d) display the second heating scans for the cured resins. We observe a clear glass transition at 115°C for the cured DDM/bis(azetidine-2,4-dione) under the same heating conditions, but no such transition for the cured TPA/DOPO-tris(azetidine-2,4-dione) sample, implying the existence of a densely intercrosslinked and interpenetrated polymer network for the latter. Table I lists the compositions, molar ratios, weight ratios, and nitrogen and phosphorus contents of the cured epoxy polymers.
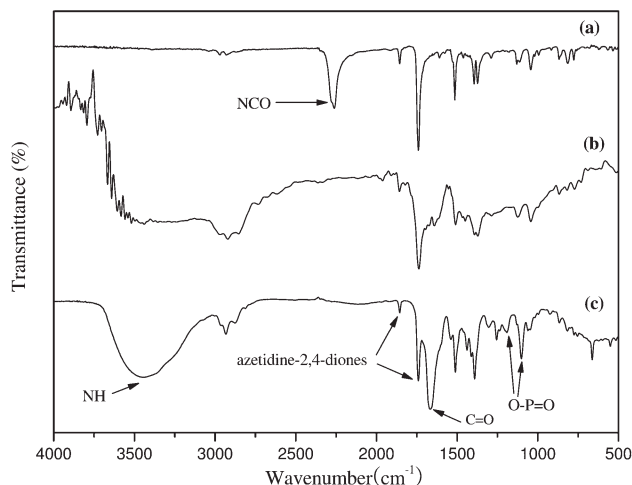

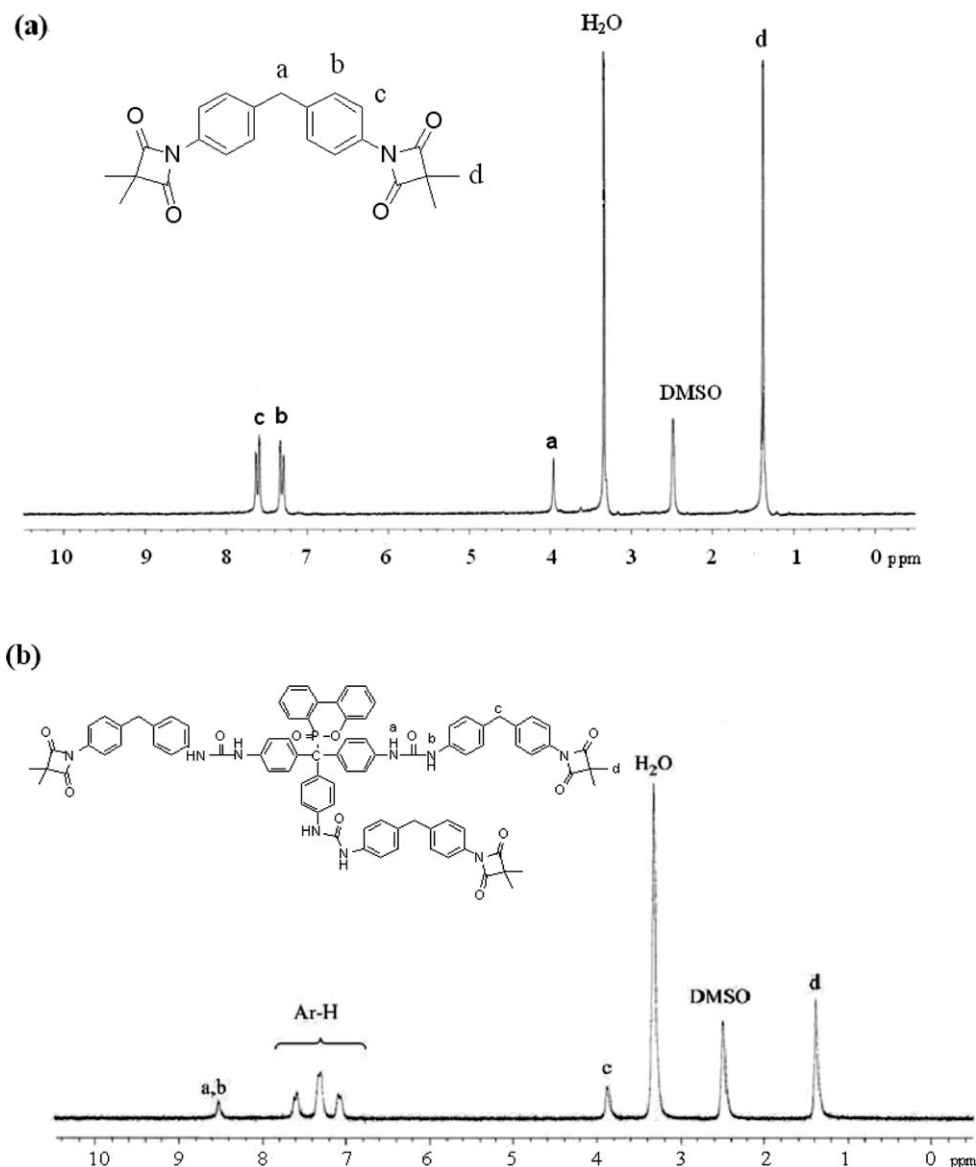**Figure 1** FTIR spectra of (a) IDD, (b) bis(azetidine-2,4-dione), and (c) DOPO-tris(azetidine-2,4-dione).

Figure 2 ^{1}H-NMR spectra of (a) bis(azetidine-2,4-dione) and (b) DOPO-tris(azetidine-2,4-dione).

Thermal and flame retardancy properties of the cured epoxy resins

Table II lists the thermal properties of the cured epoxy polymers, as measured using DSC, TGA, and DMA. Because DSC did not reveal the glass transitions of all of the resulting epoxy resins, due to instrument sensitivity or highly crosslinked structures, we performed DMA analyses to obtain further information regarding molecular mobility. To compare the thermal properties, we divided the cured epoxy polymers into four series (A–D in Tables I and II). We investigated the effects of various molar ratios of the curing amine, BE188, and modifiers on the cured epoxy thermosets. The content of the curing amine was held approximately constant (18–26 wt %) while that of BE188 was decreased from 79 to 35 wt %. The additional reactive modifiers, present at molar ratios of 0.1, 0.3, and 0.5,

were predictably consumed by the equivalent-ratio amines. By incorporating the modifiers into the epoxy formulations, the crosslinking density varied as a result of the reactions between the modifiers and the amine curing agents. The amine-cured epoxy materials B0 and C0, formed in the absence of reactive modifiers, exhibited values of T_g of 135 and 153°C, respectively. We attribute the unexpectedly low temperature for the glass transition of the triamine TPA-cured C0 sample to its nitrogen atom-centered core with three twistable p-toluidine groups, which increased the polymer's conformational flexibility or free volume and, consequently, lowered the value of T_g.[23,24] Figure 4 reveals that the values of T_g for the sets of epoxy resins followed the general trend B > C = D > A. Typically, adding reactive modifiers to the epoxy increased the values of T_g of the four systems, relative to those of the
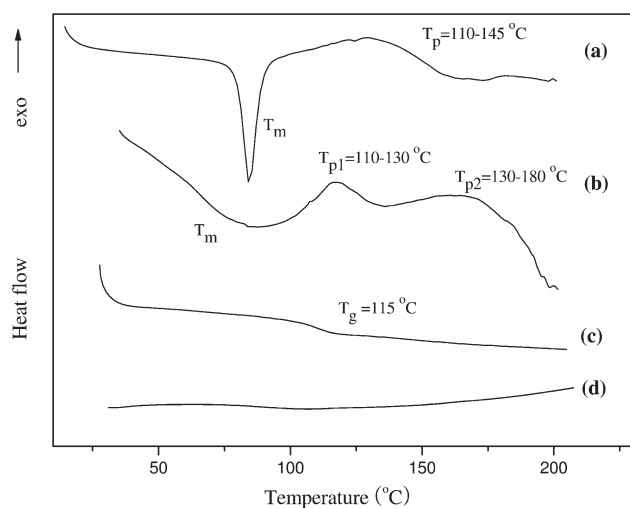
Figure 3 DSC thermograms of (a,b) the first heating processing of (a) DDM/bis(azetidine-2,4-dione) (equal molar ratio) and (b) TPA/DOPO-tris(azetidine-2,4-dione) (equal molar ratio) and (c,d) the second heating processing of (c) DDM/bis(azetidine-2,4-dione) (equal molar ratio) and (d) TPA/DOPO-tris(azetidine-2,4-dione) (equal molar ratio).

neat epoxies. When the modifier content was less than 17 wt % (molar ratio = 0.1) in all systems, the highest values of T_g in systems A–D were 140°C for A1, 187°C for B1, 163°C for C1, and 159°C for D1, respectively. The values of T_g decreased upon increasing the reactive modifier's content, but still remained higher than

TABLE II
Thermal and Mechanical Properties of the Cured Epoxy Resin Samples

	Thermal property				Mechanical property[a]	
Sample	T_g (°C)[a]	T_d (°C)[b]	Char yield[c]	LOI[d]	Storage modulus at 100°C (GPa)	Loss modulus (GPa)
A1	140	337	29	30	2.18	1.64
A2	129	317	20	32	2.56	2.29
A3	137	310	24	33	2.51	2.08
B0	135	327	26	21	0.67	0.73
B1	187	318	32	31	1.64	1.56
B2	175	301	32	35	1.81	1.60
B3	164	306	33	38	2.13	1.67
C0	153	363	15	20	1.76	1.16
C1	163	327	17	29	1.53	2.23
C2	156	353	19	30	2.28	3.27
C3	141	347	26	31	1.37	1.74
D1	159	331	23	30	1.20	1.53
D2	142	319	19	30	3.14	3.43
D3	127	318	25	31	0.98	1.40

[a] Measured through DMA at a heating rate of 5°C/min under N_2.
[b] The 5% weight loss decomposition temperature determined through TGA at a heating rate of 10°C/min under N_2.
[c] Measured through TGA at 800°C at a heating rate of 10°C/min under N_2.
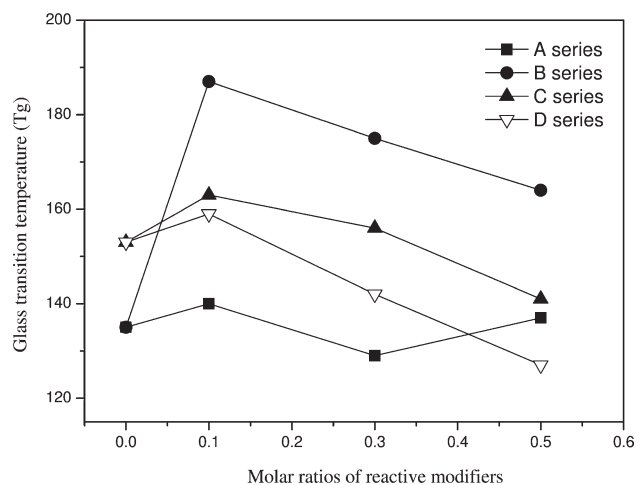[d] LOI, limited oxygen index.

Figure 4 Distribution of the values of T_g of the epoxy resins incorporating different molar ratios of the reactive modifiers.

those of the systems prepared without reactive modifiers, except for the D series, due to overloading of DOPO-tris(azetidine-2,4-dione) (0.5M ratio, 46 wt %) or the lower crosslinking density. Among our epoxy resins, the B system, which was cured using TPA and DOPO-tris(azetidine-2,4-dione), provided the highest crosslinking density, even though it incorporated some soft phosphorus-containing units. We observed relatively lower values of T_g for series C and D, due to their lower crosslinking densities resulting from the relatively long molecular chain lengths that were generated by chain-extension between DDM and the reactive modifiers, even for triply functionalized DOPO-tris(azetidine-2,4-dione). An equivalent molecular ratio of the doubly functionalized curing amine DDM and the reactive modifiers also resulted in chain-extension reactions in the matrix, exerting a smaller effect toward improving the crosslinking density. In the TPA/BE188/bis(azetidine-2,4-dione) systems (A series), the chain-extension effects and twistable structure of the amine TPA were overwhelming factors affecting their large crosslinking densities. For the same molar ratio increase (from 0.1 to 0.3), the TPA-cured epoxy resins (A series) exhibited relatively lower values of T_g than did the DDM-cured systems (C and D series), as revealed in Figure 4. Moreover, increasing the phosphorus contents in the epoxy polymers from 0.35 to 0.97 wt % (B and D series) resulted in large decreases in their values of T_g and T_d, especially in the lesser-crosslinked D system, as indicated in Figure 5. We attribute the enhancements in glass transition temperatures to the presence of covalently linked polymer networks and noncovalently linked multiply hydrogen-bonded modifier units that restricted the relaxation of the epoxy molecular chains.

Table II reveals that the 5% decomposition temperatures (T_d) of all of the epoxy resins in series A-D
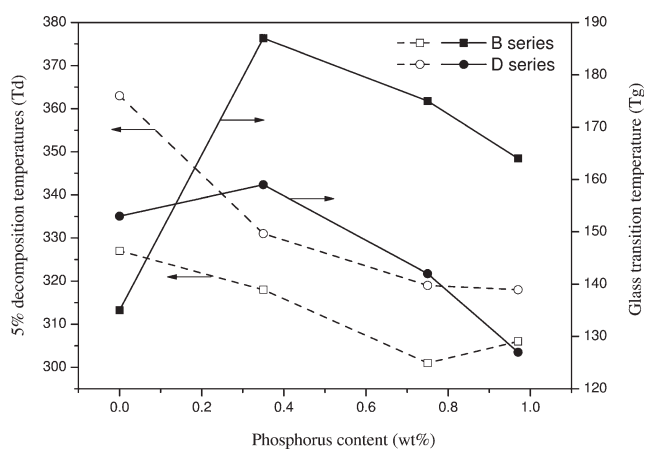
Figure 5 Thermal properties of cured epoxy resins incorporating various phosphorus contents.

ranged from 301 to 363°C, with char yields in the range 15–33 wt %. The degradation temperatures of the series of phosphorus-containing epoxy resins B and D were lower than those of their phosphorus-free counterparts, with the values of T_d decreasing upon increasing the DOPO content, but still remaining above 300°C. This phenomenon is similar to that observed for previously reported DOPO-containing cured epoxy systems.[25,26] For the epoxy resins incorporating the phosphorus-free reactive modifiers, the C series were more thermally stable than the A series, suggesting again that the thermal stability depends on their different crosslinking densities. Moreover, as revealed in Table II, all of the epoxy resins containing reactive modifiers had relatively higher char yields than did the neat polymers. The char yields of the cured epoxy resins generally followed the order B > A > C = D. Indeed, the char residue levels of the B series of samples benefited from their nitrogen atom-containing, multiple phenyl and DOPO units, providing superior thermal stability in the range 450–800°C. We conclude that the introduction of suitable reactive modifiers could increase both the char yield and the thermal stability.

We examined the flame retardancy of the cured epoxy resins by measuring their LOIs (Table II). The incorporation of reactive modifiers significantly raised the LOIs from 21 to 28–38 for the phosphorus-containing systems in series B and D and from 20 to 28–32 for the phosphorus-free systems in series A and C. The LOIs increased steadily upon increasing the quantities of DOPO-tris(azetidine-2,4-dione) or bis(azetidine-2,4-dione) introduced into the epoxy resins systems. The increased flame retardation was realized in the epoxy systems incorporating the reactive modifiers because they possessed phosphorus- and nitrogen-containing units and high aromatic contents, as listed in Table I. Phosphorus-containing fire-retardants are particularly effective in epoxy

resins because the phosphate esters or phosphoric acids formed during the thermal decomposition of phosphorus-containing products tend to react with OH groups and involve the epoxy resin structure in the charring.[3,12,16] We conclude that our two studied reactive modifiers—but especially DOPO-tris(azetidine-2,4-dione)—are capable of serving as multifunctional additives that simultaneously improve epoxy resin's glass transition temperature, thermal stability, and flame retardancy.

Thermodynamic properties of the cured epoxy resins

We used DMA to measure the storage modulus (E'), loss modulus (E''), and tan δ of cured epoxy resins as shown in Table II. For the triamine TPA and diamine DDM-cured epoxy resins B0 and C0, we observed elastic plateau at temperatures above 125°C (B1) and 160°C (C1), which greatly increased (to above 175°C) when the DOPO-tris(azetidine-2,4-dione) was introduced [Fig. 6(a)]. The observed increases in the transitions for the A and B series
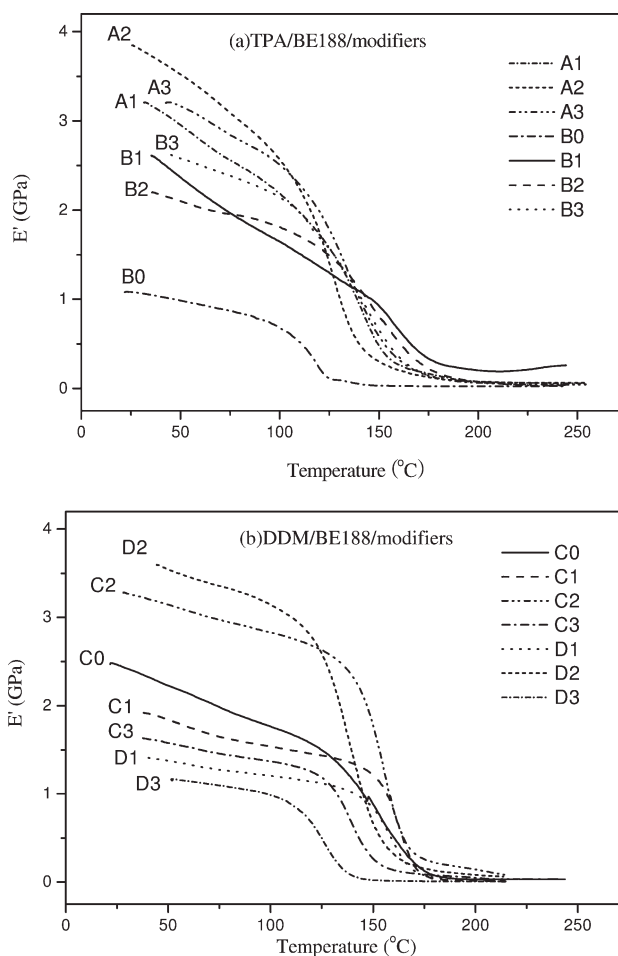

Figure 6 Storage moduli (E') of the cured epoxy resins formed from (a) TPA/BE188/modifiers and (b) DDM/BE188/modifiers.

[TPA-cured, Fig. 6(a)] appeared to be more regular than those of series C and D [DDM-cured, Fig. 6(b)]. In general, the elastic behavior at temperatures below the glass transition temperature is independent of the crosslinking density.[27,28] As revealed in Table II and Figure 6(a), the addition of DOPO-tris(azetidine-2,4-dione) into the B series of epoxy resins increased the storage modulus (E') at 100°C by $\sim$ 145% for B1, 170% for B2, and 218% for B3, relative to that for the neat epoxy resin B0. We observed similar results for the loss moduli (E'') in the B series. In addition, the introduction of bis(azetidine-2,4-dione) increased the values of E' by 225–282% and the values of E'' by 125–214%. These results suggest that incorporation of malonamide and epoxy linkages as hydrogen bonding sites effectively enhanced the mechanical properties of the polymers.[21] It appears that the introduction of triamine TPA as a curing agent in systems A and B provided more hydrogen bonding sites than did the introduction of diamine DDM in systems C and D; hence, we observed significant improvements in the values of E' and E'' relative to those of the reactive modifier-free systems. A similar comparison of systems C and D revealed [Table II, Fig. 6(b)] positive enhancements only at a 0.3M ratio for C2 (E' increase of $\sim$ 18%; E'' increase of $\sim$ 182%) and D2 (E' increase of $\sim$ 78%; E'' increase of $\sim$ 196%). In the diamine DDM-cured epoxy systems, the addition of DOPO-tris(azetidine-2,4-dione) in the D series enhanced the values of E' and E'' to significantly greater degrees than did the addition of bis(azetidine-2,4-dione) in the C series. This result is reasonable because DOPO-tris(azetidine-2,4-dione) possesses more azetidine-2,4-dione end groups than bis(azetidine-2,4-dione) does and, hence, it introduced more malonamide functional groups after ring-opening reactions, thereby strengthening the effect of hydrogen bonding. In addition, a 0.5M ratio for C3 and D3 provided obviously negative results for the values of E' and E'', due to overloading (46 wt %) of the reactive modifiers, leading to incompatibility[13] and lower crosslinking densities as a result of the relatively long molecular chains generated through chain-extension between the doubly functionalized DDM and the reactive modifiers.

Figure 7 presents the tan δ relaxation peaks, corresponding to the glass transitions of the epoxy resins, as measured using DMA. The traces of the TPA-cured epoxy resins A1, A2, B2, and B3 exhibited two relaxations at high temperature [Fig. 7(a)]. The first relaxations at lower temperatures pertain to their glass transitions; the later ones, observed at higher temperatures, increased upon increasing the content of the reactive modifier (from A1 to A2 and from B1 to B3). This finding indicates that higher contents of reactive modifier moieties increased the complexity
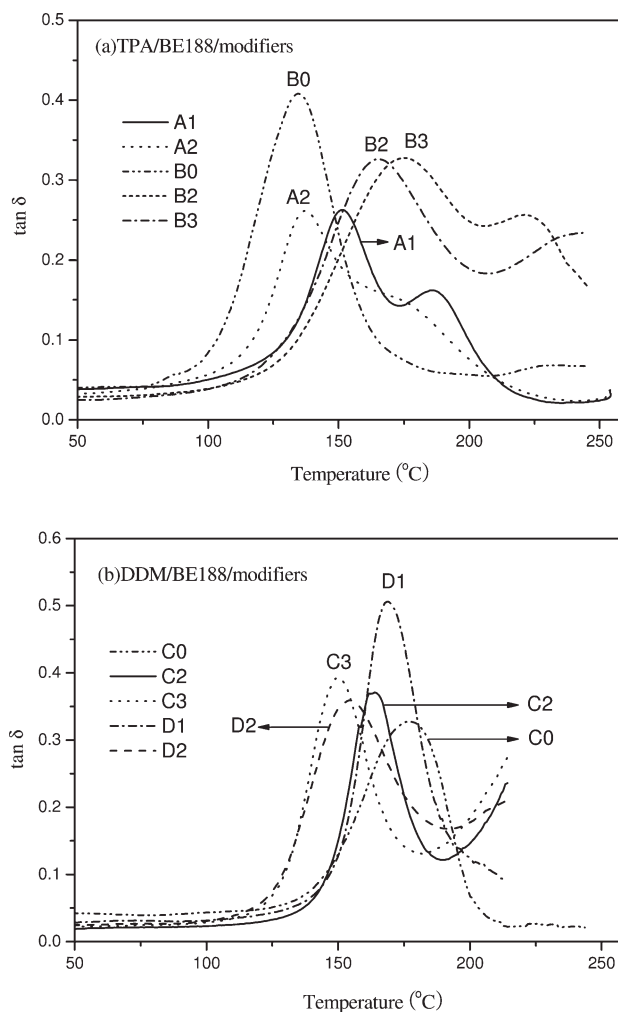

Figure 7 Values of tan δ of the cured epoxy resins formed from (a) TPA/BE188/modifiers and (b) DDM/BE188/modifiers.

of the interpenetrating networks. The diamine DDM-cured C and D series possessed relatively lower degrees of interpenetration and, therefore, did not display such phenomena: only one transition peak appears in Figure 7(b).

In previous investigations,[20,21] we have used analogous systems featuring malonamide and urea groups to prepare supermolecules stabilized through hydrogen bonding. The malonamide linkages generated from the ring-opening reactions of the azetidine-2,4-diones with the NH or OH groups of DDM, TPA, and BE188 are strongly hydrogen-bonding sites that determine the extent of physical crosslinking within the epoxy resins. DMA studies revealed that the mechanical strength, measured in terms of the storage modulus (E'), increased in the networks as the content of reactive modifiers increased, especially in the more highly crosslinked TPA-cured networks. Scheme 2 provides a conceptual illustration of the cured epoxy systems, in which embedded multiply hydrogen-
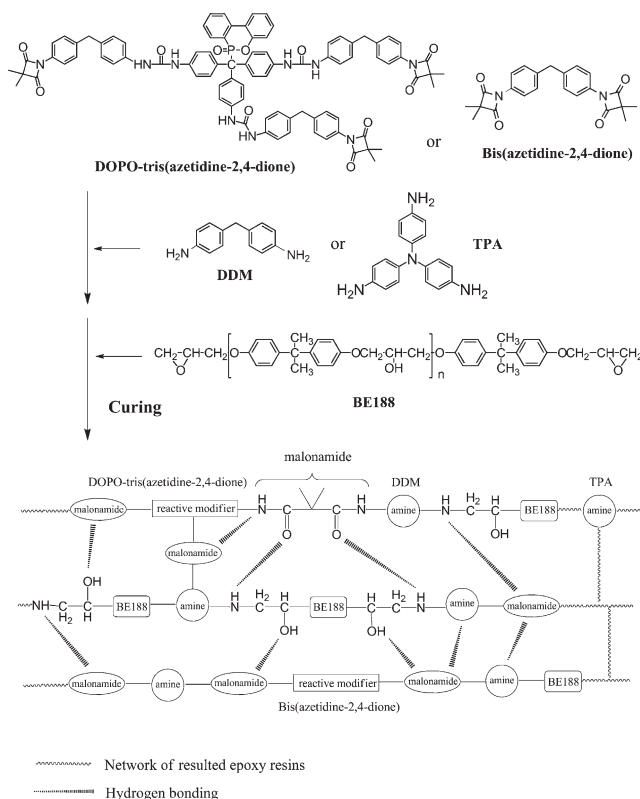
Scheme 2 Representation of the cured epoxy resins featuring multiply-hydrogen-bonded units derived from reactive modifiers.

bonding reactive modifiers promoted intermolecular interactions and tailored the mechanical flexibility through unique pseudocrosslinked polymer networks.

Tensile properties

Figure 8 presents stress–strain curves of the cured epoxy resins. The neat epoxy resins prepared without a reactive modifier exhibited relative low tensile strengths (fracture strengths) of 25–27 MPa and elongations at break of 2–3%. Most of the polymer films exhibited low elongation, indicating that they may be considered as hard and strong materials. The presence of the reactive modifier had a profound effect on the tensile properties, presumably because of the high crosslinking density and strong intermolecular forces. In Figure 8, sample D2, which had the highest crosslinking density because of its triply functionalized modifier, exhibited the highest fracture stress (146 MPa) and a relatively low elongation at break (1%) relative to those of the other epoxy formulations. These results are consistent with those from the DMA studies (D2 exhibited the highest values of E' and E'' of 3.14 of 3.43 GPa, respectively, in Table II). In contrast, incorporating the doubly func-

tionalized bis(azetidine-2,4-dione), instead of DOPO-tris(azetidine-2,4-dione), caused the elongation at break of the C1 sample to increase slightly, confirming that chain-extension effects facilitated more-flexible networks. In the TPA-cured systems, the elongations at break remained invariant for B1 and B2, but the tensile strength underwent a slight increasing from 27 to 43 and 38 MPa, respectively. These trends are also consistent with the results of their DMA studies (values of E' increasing from 0.67 GPa for the unmodified epoxy to 1.64–1.81 GPa and values of E'' increasing from 0.73 to 1.56–1.60 GPa in Table II). In addition, measurement of the area under the stress–strain curve revealed that the fracture energy[29] underwent a considerable improvement, equal to that of the impact strength, upon incorporating a modifier. The relative integral areas of the modified epoxies B1 and B2 were slightly larger than that of the neat epoxy, due to their higher degrees of crosslinking; for C1 and D2, they were approximately double those of the neat epoxy. Thus, the reactive modifiers had reinforcement effects on the epoxy materials through the formation of unique pseudocrosslinked polymer networks.

CONCLUSIONS

We have prepared and characterized two novel reactive modifiers: a doubly functionalized bis(azetidine-2,4-dione) and a triply functionalized DOPO-tris(azetidine-2,4-dione). The use of multiply hydrogen-bonding reactive epoxy modifiers effectively provided the sites for formation of polymer networks with improved thermal and physical properties of cured epoxy resins. DSC analysis revealed that the reactivity of the DOPO-tris(azetidine-2,4-dione) modifier toward amino group-containing curing agents was more complicated than that of
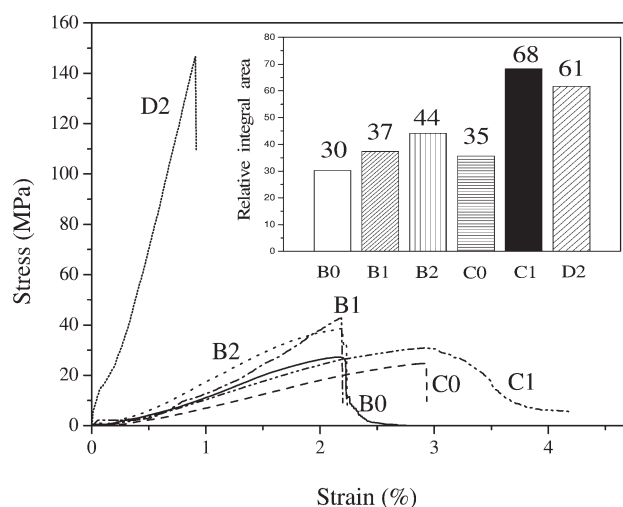

Figure 8 Stress–strain curves for the cured epoxy resins.

bis(azetidine-2,4-dione). The combination of malonamide linkages, phosphorus-containing DOPO groups, multiple phenyl groups, and strong hydrogen bonding sites in the modifiers, curing agents, and epoxy resin resulted in epoxy polymers exhibiting tunable application properties. Thermal analyses revealed that the values of T_g of the polymer networks were dependent on the crosslinking density and the content of the multiply hydrogen-bonding reactive modifiers. High char yields (>30%) and large LOIs (up to 38) indicated that the phosphorus-containing resultant epoxies exhibited pronouncedly improved flame-retardancies, but with slightly reduced thermal stabilities during the early periods of the degradation process. On the basis of DSC, DMA, TGA, and LOI analyses, we conclude that the mechanical properties and flame-resistance of the epoxy thermosets were greatly enhanced when the reactive modifiers were embedded within the matrix. In particular, the TPA/BE188/DOPO-tris(azetidine-2,4-dione) system, which exhibited a high crosslinking density, possessed excellent and desirable physical properties, suggesting that it might have practical application. Further investigation about the effect of multiply hydrogen-bonded species on epoxy resins and their practical applications is needed.

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