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Dynamic mechanical and thermal properties of copolymer from *o*-allylphenol and 4,4′-diaminodiphenyl methane-based benzoxazine and bisphenol-A type novolac epoxy resin

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Abstract Benzoxazine/epoxy copolymers were prepared by solution blending bis(4-(8-allyl-2*H*-benzo[e][1,3]oxazin-3(4*H*)-yl)phenyl)methane (*o*AP-ddm) with bisphenol-A type novolac epoxy resin (bis-ANER), followed by thermally polymerization of the blend. The copolymerization behavior of *o*AP-ddm/bis-ANER was investigated by Fourier transform infrared spectroscopy and differential scanning calorimetry (DSC). With the increasing of bis-ANER fraction, the exothermic peak in DSC curve changes from one to two overlapped peaks, and the second peak shifts to higher temperatures. Dynamic mechanical analysis results show that a single peak appears in each tan δ curve of the *o*AP-ddm/bis-ANER copolymers. With the bis-ANER content increasing, the storage modulus and the peak temperature of tan δ peak increase, whereas the tan δ peak height decreases. Thermogravimetric analysis results indicate that the onset temperatures of mass loss and the char yields at 800 °C of the *o*AP-ddm/bis-ANER copolymers decrease with the increase of bis-ANER content.

Keywords Benzoxazine · Epoxy resin · Copolymer · Differential scanning calorimetry · Dynamic mechanical properties

Introduction

Benzoxazines are a new class of thermosetting resins that can be polymerized into polybenzoxazines via thermally activated ring-opening reaction [1–3]. Due to low melt viscosities of benzoxazines and excellent physical properties of the corresponding polybenzoxazines, benzoxazines have been used as high performance matrices for advanced composite materials in aerospace, automobile, and electronics industries [4–7].

Recently, an allyl-containing bifunctional benzoxazine (*o*AP-ddm) based on *o*-allylphenol and 4,4′-diaminodiphenyl methane was synthesized [8], and a relatively low glass transition temperature (T_g) and a high flexibility are shown for the corresponding polybenzoxazine [Poly(*o*AP-ddm)] due to the presence of allylic C=C bonds. To enhance the properties of Poly(*o*AP-ddm), it is considered to copolymerize *o*AP-ddm with epoxy resins.

Benzoxazine/epoxy copolymers were first studied by Ishida and Allen [9], and it was revealed that the glass transition temperature, flexural stress, and flexural strain at break gain a significant increase over those of the polybenzoxazine homopolymer due to a significant increase in crosslinking density of the copolymers. Thereafter, various benzoxazine/epoxy systems were studied and their copolymers show synergistic behavior in mechanical properties [10–17]. Thus, the ability of benzoxazines to form alloys with epoxy resins can provide benzoxazines with a broader range of applications.

Bisphenol-A type novolac epoxy resin (bis-ANER) is a multi-functional epoxy resin that has been employed as a matrix for high performance fiber-reinforced composites in aerospace industry and as an encapsulant for electronic components [18–20]. According to the chemistry of benzoxazine and epoxy, bis-ANER can be employed to copolymerize with *o*AP-ddm, and the phenolic hydroxyl groups formed from the oxazine ring-opening can react with the oxirane rings in bis-ANER and give ether links and new hydroxyl groups.

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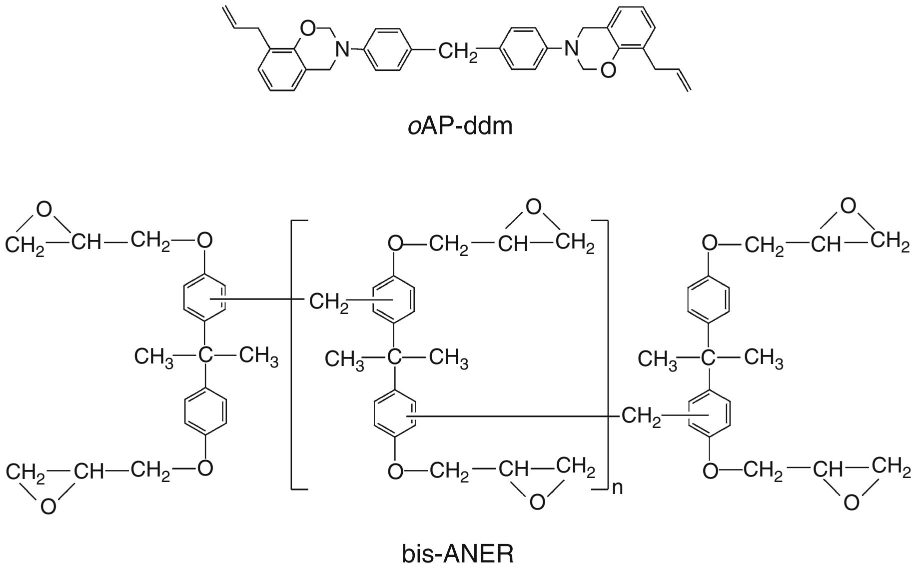
Scheme 1 Chemical structures of *o*AP-ddm and bis-ANER



In this study, *o*AP-ddm/bis-ANER blends were prepared by a solution method. The copolymerization behavior of *o*AP-ddm/bis-ANER was investigated by Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC), and the mechanical properties and thermal stabilities of *o*AP-ddm/bis-ANER copolymers were studied with dynamic mechanical analysis and thermogravimetry, respectively.

Experimental

Materials

o-Allylphenol was supplied by Shandong Laizhou Hualu Accumulator Co., Ltd., China. Bisphenol-A and 4,4′-diaminodiphenyl methane (DDM) were purchased from Shanghai Jingchun Chemical Reagent Co., Ltd., China. Formaldehyde (37 % aqueous), toluene, chloroform, and epichlorohydrin were obtained from Tianjin Chemical Reagent Co., Ltd., China. All chemicals were used as received.

*o*AP-ddm was synthesized from *o*-allylphenol, DDM, and formaldehyde via a solution method [8], and bis-ANER was synthesized from bisphenol-A, formaldehyde, and epichlorohydrin [21]. The epoxy equivalent weight of bis-ANER is 213 g equiv^{-1}, which was determined by the hydrochloric acid–acetone method. The structures of *o*AP-ddm and bis-ANER are shown in Scheme 1.

Preparation of *o*AP-ddm/bis-ANER copolymers

*o*AP-ddm was mixed with bis-ANER by dissolving in chloroform with mechanical stir and ultrasonic method in various mass ratios of 90/10, 80/20, 70/30, 60/40, and 50/50. Then, the *o*AP-ddm/bis-ANER solution was poured into a preheated steel mold, and the mold was kept in a vacuum oven conditioned at 70 °C for a period of time to remove the chloroform. Subsequently, the vacuum oven was step-heated to 100, 120, 140, 160, and 180 °C and hold at each temperature for 1 h, thereafter, hold at 200 °C for 6 h. Finally, the sample was cooled freely to room temperature.

Measurements

A Nicolet 380 FTIR spectrometer was used to study the structure changes in the copolymerization of *o*AP-ddm/bis-ANER at a resolution of 4 cm^{-1}. *o*AP-ddm/bis-ANER blend was dissolved in chloroform, and the solution was coated on a KBr disk to form a thin uniform film. When the solvent was completely evaporated at about 50 °C in a vacuum oven, the disk was scanned by the FTIR spectrometer. Thereafter, the disk was placed in an air-circulating oven with a fixed temperature. During the polymerization reaction, the disk was removed periodically for measurement.

The copolymerization behaviors of *o*AP-ddm/bis-ANER blends were monitored by a PerkinElmer Diamond differential scanning calorimeter operating in nitrogen. The *o*AP-ddm/bis-ANER samples of approximately 6.5 mg were scanned at a heating rate of 10 °C min^{-1}.

A Perkin-Elmer DMA-8000 dynamic mechanical analyzer was used to determine the dynamic storage modulus (E') and loss factor (tan δ) of the *o*AP-ddm/bis-ANER copolymers using the single cantilever bending mode. Measurement was performed on rectangular specimens with dimensions of 10.0 × 5.8× 2.3 mm by heating from

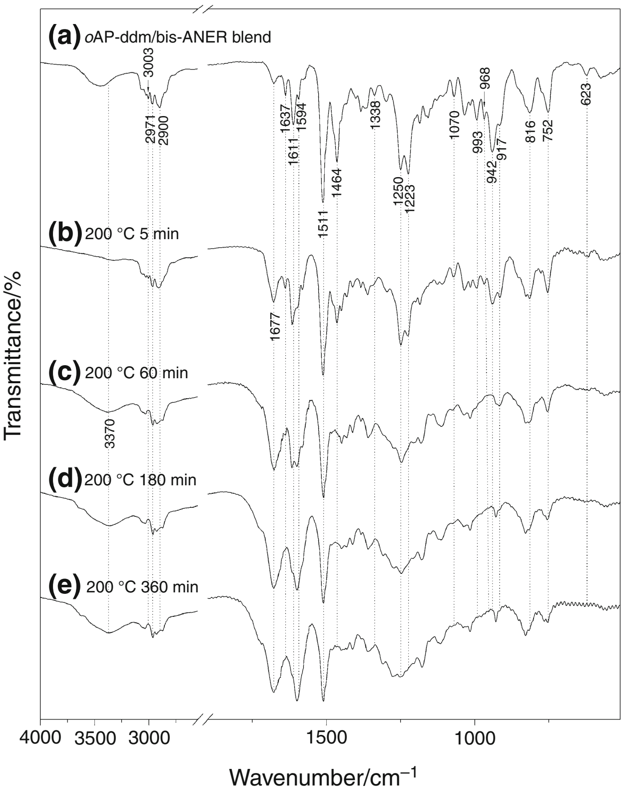


Fig. 1 FTIR spectra of *o*AP-ddm/bis-ANER (70/30) polymerized at 200 °C in air for various times

25 to 250 °C, with a heating rate of 2 °C min^{-1} and a frequency of 1 Hz.

Thermogravimetric analysis was performed on a Shimadzu TGA-40 thermogravimeter, and fine powder samples of approximately 3.5 mg of *o*AP-ddm/bis-ANER copolymers were heated to 800 °C at a heating rate of 10 °C min^{-1} in a nitrogen flow of 50 mL min^{-1}.

Results and discussion

Structure changes in the copolymerization of *o*AP-ddm/bis-ANER

Figure 1 shows the FTIR spectra of *o*AP-ddm/bis-ANER blend with a mass ratio of 70/30 and the corresponding copolymerized products obtained at 200 °C for various times in air. The absorption peaks at 968 and 942 cm^{-1} are the characteristic modes of the benzene ring with an oxazine ring attached, and the absorptions at 1,223 and 1,070 cm^{-1} are due to the asymmetric and symmetric stretching vibrations of C–O–C of the oxazine ring, respectively [22]. The peak at 1,637 cm^{-1} belongs to the olefinic C=C stretching vibration, and the absorption at 993 cm^{-1} is attributed to the olefinic C–H out-of-plane bending vibration, whereas the peak at 917 cm^{-1} is due to the olefinic C–H out-of-plane bending vibration and the characteristic absorption of epoxy group. The absorptions at 1,611, 1,594, and 1,511 cm^{-1} are associated with the aromatic C=C stretching vibrations. The aromatic C–H out-of-plane bending vibrations of the aromatic ring are observed at 816, 752, and 623 cm^{-1}. The peaks located at 3,062, 3,026, and 3,003 cm^{-1} correspond to the aromatic and allylic =C–H stretching vibrations. The C–H asymmetric stretching vibration of CH_2 is at 2,971 cm^{-1}, and the C–H stretching vibration of CH is at 2,900 cm^{-1}, whereas the C–H symmetric stretching vibration of CH_2 is at 2,847 cm^{-1}. The absorption peak at 1,464 cm^{-1} corresponds to the CH_2 bending vibration of the oxazine ring, and the absorptions at 1,338 and 1,250 cm^{-1} are due to the CH_2 wagging and twisting vibrations, respectively.

In the isothermal copolymerization of *o*AP-ddm/bis-ANER blend, the structure changes can be perceived from the variations of intensities of the characteristic absorption peaks in the FTIR spectra shown in Fig. 1. As can be seen, the intensities of the absorption peaks at 1,464, 1,250, 1,223, 968, and 942 cm^{-1} decrease gradually with the copolymerization proceeding, resulted from the oxazine ring-opening reaction. At the same time, the intensities of the peaks decrease obviously at 3,026, 3,003, 1,637, 993, and 917 cm^{-1}, due to the radical polymerization of the allyl groups and the oxirane ring-opening reaction. In addition, a new appeared peak at approximately 3,370 cm^{-1} is due to the hydroxyl groups formed from the oxirane ring-opening reaction, and the intensity of the peak at 1,677 cm^{-1} increases with increasing time is due to the carbonyl groups formed from the oxidation of allylic double bonds.

Copolymerization behavior of *o*AP-ddm/bis-ANER

The non-isothermal DSC curves of *o*AP-ddm/bis-ANER blends are shown in Fig. 2. The interesting feature of the copolymerization reaction is that the shape of the exothermic peak for *o*AP-ddm/bis-ANER blends varies with composition. For *o*AP-ddm, only one exothermic peak can be seen in the DSC curve, corresponding to the oxazine ring-opening polymerization and the radical polymerization of allyls of *o*AP-ddm [8]. For *o*AP-ddm/bis-ANER blends, when bis-ANER content is relatively low, a single exothermic peak is observed and the peak temperature is almost independent of the amount of bis-ANER; whereas two highly overlapped exothermic peaks can be observed when bis-ANER content is relatively high, and the second exothermic peak shows a significant shift to a higher temperature with an increasing content of bis-ANER in the blends. In principle, the copolymerization of *o*AP-ddm/bis-ANER blends not only involves the

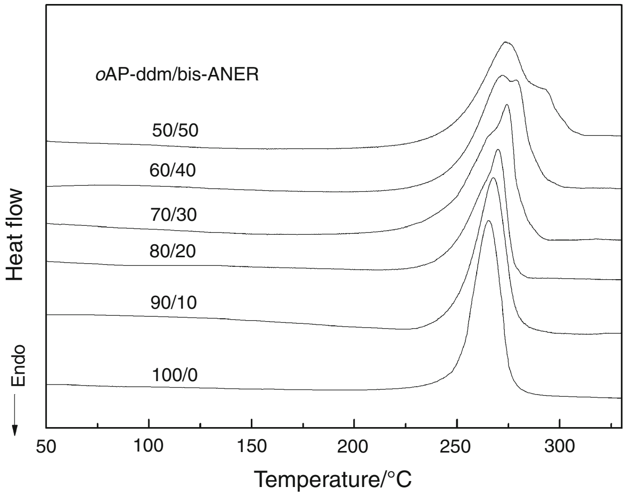


Fig. 2 Non-isothermal DSC curves of *o*AP-ddm/bis-ANER blends

oxazine ring-opening polymerization and the radical polymerization of allyls of *o*AP-ddm but also the etherification between oxirane rings and phenolic hydroxyl groups formed from the oxazine ring-opening, whereas the reaction between oxirane rings and phenolic hydroxyl groups is expected to proceed after phenolic hydroxyl groups formed from the oxazine ring-opening of *o*AP-ddm. Thus, the first exothermic peak at lower temperature corresponds to the oxazine ring-opening reaction and the radical polymerization of allyls, and the second exothermic peak at higher temperature is belong to the ring-opening reaction of oxirane ring.

The shift degree of the second peak to a higher temperature compared to the first one depends on the composition of the binary blend, because the reaction between *o*AP-ddm and bis-ANER is catalyzed by phenolic hydroxyl groups formed from the oxazine ring-opening reaction. For the *o*AP-ddm/bis-ANER blends with a lower bis-ANER fraction, such as 10 and 20 %, relatively more phenolic hydroxyl groups formed from the oxazine ring-opening reaction result in the oxirane ring-opening reaction proceeding more quickly, and the peak associated with the ring-opening reaction of oxirane ring cannot be discerned in the DSC curve. For the *o*AP-ddm/bis-ANER blend with 30 % bis-ANER, the phenolic hydroxyl groups formed from the oxazine ring-opening reaction are enough to catalyze the oxirane ring-opening reaction at a relatively low temperature, and the second peak is more prominent than the first one in the DSC curve due to a relatively high bis-ANER content. Whereas for blends with 40 and 50 % bis-ANER, the lower *o*AP-ddm, relatively less phenolic hydroxyl groups formed from the oxazine ring-opening reaction result in the ring-opening reaction of oxirane ring proceeding slowly, and the second peak shifts to a higher temperature position in the DSC curves.

In addition, the reaction enthalpies (ΔH) of the copolymerizations of *o*AP-ddm/bis-ANER blends with composition of 90/10, 80/20, 70/30, 60/40, and 50/50 are 268, 270, 274, 272, and 273 J g^{-1}, respectively, and the ΔH values of *o*AP-ddm/bis-ANER blends maintain almost constant with a rising of the bis-ANER content and are higher than that of *o*AP-ddm (241 J g^{-1}) [8]. Based on the reaction mechanism, the ΔH of the copolymerization of *o*AP-ddm/bis-ANER blend is the enthalpy change that occurs in the oxazine ring opening polymerization, the radical polymerization of allyls, and the etherification between oxirane rings and phenolic hydroxyl groups formed from the oxazine ring-opening. Because more reactions are involved in the copolymerization of *o*AP-ddm/bis-ANER blend than in the polymerization of *o*AP-ddm, the network structures of *o*AP-ddm/bis-ANER copolymers are more complex than that of Poly(*o*AP-ddm), and a difference in ΔH occurs between the copolymerization of *o*AP-ddm/bis-ANER blend and the polymerization of *o*AP-ddm.

Dynamic mechanical properties of *o*AP-ddm/bis-ANER copolymers

Figure 3 shows the curves of the storage modulus (E') and loss factor (tan δ) versus temperature for *o*AP-ddm/bis-ANER copolymers, and Table 1 lists the E', glass transition temperature (T_g), and height and width at half height of the tan δ peaks. As can be seen from Fig. 3 and Table 1, the E' values of *o*AP-ddm/bis-ANER copolymers at 25 °C initially increase with an increasing amount of bis-ANER over Poly(*o*AP-ddm), and maintains almost constant for copolymers with bis-ANER content range of 20–50 %. With the temperature rising, the E' values of *o*AP-ddm/bis-ANER copolymers decrease slowly in the glassy state, and then decrease rapidly at different temperatures for various compositions. Moreover, the E' values of *o*AP-ddm/bis-ANER copolymers in the rubbery plateau increase with an increasing amount of bis-ANER. The higher rubbery plateau modulus of the copolymers, which has higher amount of bis-ANER, is possibly attributed to a higher crosslinking density in the copolymers. According to rubber elasticity theory, it is acceptable that the crosslinking density of a polymer can be estimated from the equilibrium value of the relaxation modulus in the rubbery state [23], and an empirical Eq. (1) was proposed by Nielsen and Landel to describe the approximate relationship [24], which is reported to better describe the elastic properties of dense networks [25–27].

$$\log\left(\frac{E'_e}{3}\right) = 7.0 + 293(\rho_x) \qquad (1)$$

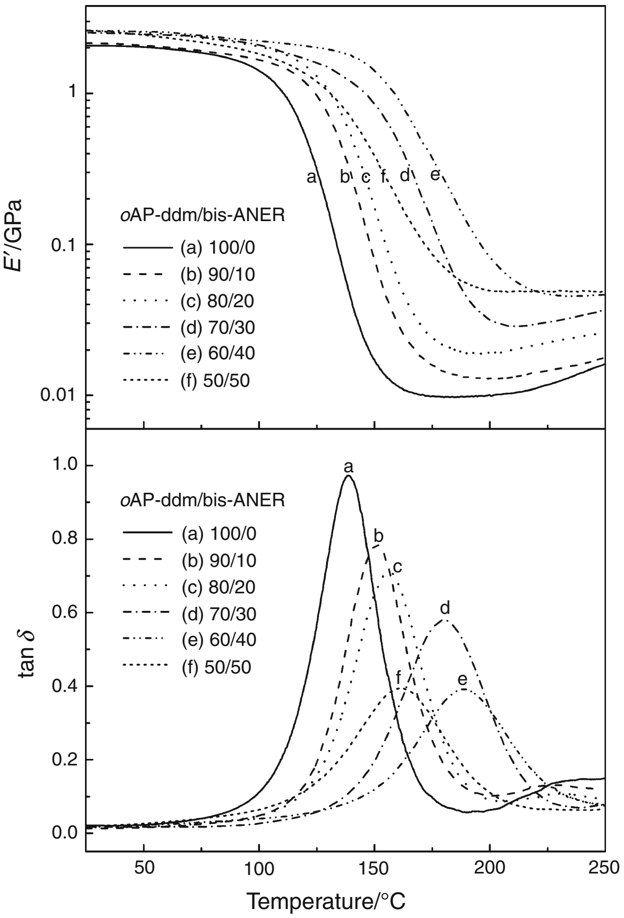


Fig. 3 Curves of storage modulus and loss factor versus temperature for *o*AP-ddm/bis-ANER copolymers

where E'_e (dyne cm^{-2}) is an equilibrium elastic modulus in rubbery plateau and ρ_x (mol cm^{-3}) is the crosslinking density which is the mole number of network chains per unit volume of the polymers. Based on Eq. (1), the crosslinking densities of the copolymers can be calculated from the plateau of the storage shear modulus in the rubbery state (G'_e), which equals $E'_e/3$, and E'_e in the rubbery region is determined by taking the value at the inflection point of the plateau. The calculated results are summarized in Table 1. It is evident that the crosslinking density of the copolymers increases with the bis-ANER content rising.

Corresponding to the variation of E' with temperature, a single dissipation energy peak is shown on each tan δ curve associated with the glass transition, indicating no detectable phase separation in the copolymers. T_g is defined as the temperature corresponding to the maximum of tan δ peak. Initially, the incorporation of bis-ANER in *o*AP-ddm has the effect of increasing the T_g of the copolymer over Poly(*o*AP-ddm). The highest T_g, 189 °C, is demonstrated by the copolymer with 40 % bis-ANER and is 50° higher than that of Poly(*o*AP-ddm). However, the copolymer with 50 % bis-ANER experiences a decrease in T_g and exhibits a T_g of 162 °C, due to the fact that the phenolic hydroxyl groups formed from the oxazine ring-opening reaction not only serve to catalyze the copolymerization, but also participate as reactants and therefore are consumed by the reaction. Thus, as the mass ratio of *o*AP-ddm to bis-ANER is lower than the stoichiometric ratio of components in the sense of the number of reaction groups for copolymerization, unreacted bis-ANER molecules may remain and interfere with network formation or act as a plasticizer.

Table 1 Analysis of the DMA curves of *o*AP-ddm/bis-ANER copolymers

*o*AP-ddm/bis-ANER	E'/GPa (25 °C)	T_g/°C	Height of tan δ peaks (arbitrary units)	Width of tan δ peaks/°C (half ht.)	ρ_x ($\times 10^{-3}$)
100/0	2.07	139	1.42	30.4	1.81
90/10	2.15	152	1.08	35.7	2.19
80/20	2.59	157	0.98	35.2	2.72
70/30	2.52	180	0.82	43.5	3.35
60/40	2.60	189	0.51	45.8	4.05
50/50	2.59	162	0.51	46.4	4.15

It was reported that the height of the tan δ peak decreases with increase of crosslinking density [9]. For *o*AP-ddm/bis-ANER copolymers, the height of the tan δ peak decreases as bis-ANER content in the copolymers is increased, resulting in a lower segmental mobility and fewer relaxing species, and thus is indicative of a higher degree of crosslinking for bis-ANER rich copolymers. The peak width at half height, however, broadens as the addition of bis-ANER increases the number of modes of branching and results in a wider distribution of structures. Consequently, the range of temperatures at which the different network segments gain mobility has increased.

Thermal stability of *o*AP-ddm/bis-ANER copolymers

Figure 4 shows the TG curves of *o*AP-ddm/bis-ANER copolymers in nitrogen. The 5 % mass loss temperatures are 324, 313, 310, 305, 302, and 300 °C for copolymers with bis-ANER content of 0, 10, 20, 30, 40, and 50 %, respectively, indicating that the thermal stability of *o*AP-ddm/bis-ANER copolymers decrease with the increase of bis-ANER content. Moreover, the char yields at 800 °C of the *o*AP-ddm/bis-ANER copolymers with 0, 10, 20, 30, 40, and 50 % bis-ANER are 37.7, 36.7, 35.6, 34.1, 30.6, and 28.9 %, and they also decrease with the increase of bis-ANER content. Therefore, the thermal stability of bis-ANER moiety is lower than that of *o*AP-ddm moiety in *o*AP-ddm/bis-ANER copolymer networks.

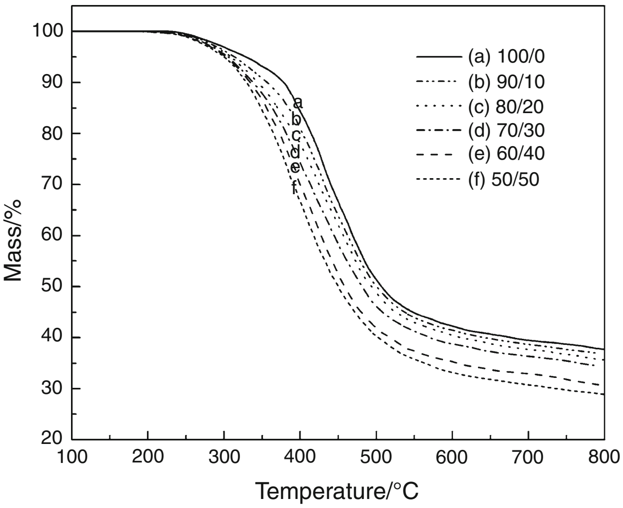


Fig. 4 TG curves of *o*AP-ddm/bis-ANER copolymers

Conclusions

The *o*AP-ddm/bis-ANER copolymers were prepared. With the increasing of bis-ANER fraction, the exothermic peak in DSC curve changes from one to two overlapped peaks, and the second peak shifts to higher temperatures. A single peak is shown in each tan δ curve of the *o*AP-ddm/bis-ANER copolymers. With the bis-ANER content increasing, the storage modulus and the peak temperature of tan δ peak increase, whereas the tan δ peak height decreases. The onset temperatures of mass loss and the char yields at 800 °C of the *o*AP-ddm/bis-ANER copolymers decrease with the increase of bis-ANER content.

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