Cure and Thermal Stability of Poly(amide-amidic acid)—cured Tetraglycidyl 4,4′-Diaminodiphenylmethane

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ABSTRACT: A novel curing agent, poly (amide-amidic acid) (PAA), was used to cure tetraglycidyl 4,4′-diaminodiphenylmethane (TGDDM). The initial cure and exothermic peak temperatures increased with increase in PAA content. The mechanism for the cure of TGDDM/PAA was proposed which involved, besides TGDDM cure, PAA imidization in the system. Examination of the morphology of the fractured surface using scanning electron microscopy showed that curing with PAA improved more the fracture toughness as compared to the conventional 4,4′-diaminodiphenylsulfone (DDS), and rendered TGDDM more fire resistant with higher char yield. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2854–2860, 2012

Key words: tetraglycidyl 4,4′-diaminodiphenylmethane; polyamide-imide; curing behavior; curing mechanism; thermal stability

INTRODUCTION

Owing to their excellent bonding, thermal, mechanical, dielectric, and aging characteristics, epoxy resins are widely used as high-performance protective coatings,[1,2] structural adhesives,[3] and matrix resins for composites.[4] Tetraglycidyl 4,4′-diaminodiphenylmethane (TGDDM) is an epoxy resin commonly used as polymeric matrix in high-performance coatings, especially in the aircraft industry. There have been ever increasing research interests on TGDDM since their discovery, especially on their cure behaviors using curing agents such as 4,4′-diaminodiphenylsulfone (DDS), 4,4′-diaminodiphenyl ether (DDE), and 4,4′-diaminodiphenyl methane (DDM) in the presence of various modifiers.[5–7]

Thermal and mechanical characteristics are key indicators during performance evaluation of TGDDM composites. This is essentially because the curing of such materials leads to a modification of their chemical structure,[5] an improvement of their flexural strength and inter-laminar fracture toughness,[8] as well as their thermal and mechanical properties.[9]

On heating, PAA is converted to poly(amide-imide) (PAI), a material of high thermal resistance and strength material. These properties are conferred by its high proportion of aromatic rings, double bonds, and heterocyclic imides along the polymer backbone.[10–12] Park et al.[13] investigated the effect of PAI addition (as a modifier) to the thermal, mechanical, and morphological properties of TGDDM/DDS blends.

In this study, TGDDM was cured using PAA (as curing agent) and the cure behavior and mechanisms were investigated by differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR), respectively. The mechanical strength and thermal stability were compared for TGDDM cured by PAA and the conventional DDS.

EXPERIMENTAL

Materials

The TGDDM base polymer and PAA curing agent were supplied by Olong Electrical Insulation Materials Co. Ltd (Changzhou, China) while the conventional curing agent (DDS) and dimethyl acetamide solvent (DMAc) were both supplied by Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). The chemical structures of the materials are shown in Table I.

PAA was synthesized through solution condensation of DDE (10.010 g, 0.05 mol) with benzene-1,2,4-trimellitic acyl chloride (TMAc, 10.530 g, 0.05 mol) in 100 mL of dimethyl acetone (DMAc) at room temperature. The reaction is shown in Scheme 1. The reaction occurred by the nucleophilic attack of the amino group and the carbonyl carbon of the anhydride and acyl chloride, then the anhydride ring opened, leading to the formation of PAA.

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TABLE I
Chemical Formulas of the Materials

Materials	Chemical formula
TGDDM	
PAA	
DDS	

Sample preparation

Samples for DSC analysis were obtained by mixing TGDDM with various PAA weight ratios. For this purpose, a two-stage process was adopted. A proper amount of PAA was first dissolved in a minimum amount of DMAc, and mixed with TGDDM at various weight ratios. The whole was then processed at 80°C in vacuo for 24 h to evaporate the solvent. The samples of TGDDM with various weight ratios of PAA of 0.23, 0.33, 0.44, 0.50, 0.56, 0.60, 0.64, and 0.67 have been designated as TP-1, TP-2, TP-3, TP-4, TP-5, TP-6, TP-7, and TP-8, respectively.

For FTIR analysis, TGDDM/PAA blends with a PAA weight ratio of 0.5 were pre-cured at 150°C for 1 h and then cured separately at 180 and 270°C for 3 h in an air-circulated oven. PAA was heated at 150°C for 1 h followed by 270°C for 3 h in an air-circulated oven.

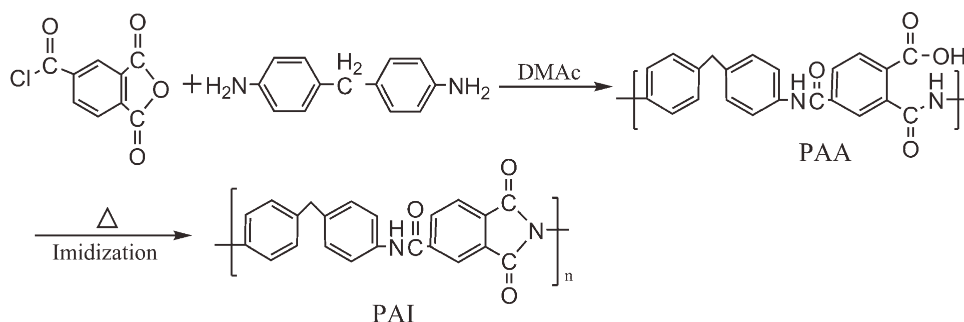
For fracture surface morphology, tensile strength and thermal stability tests, TGDDM/PAA blends with a PAA weight ratio of 0.5 were pre-cured at 150°C for 1 h and then cured at 180°C for 3 h in an air-circulated oven (named Sample CTP-4). TGDDM/DDS blends with a DDS 85% stoichiometric ratio were processed at 150°C for 6 h (named Sample TD) for comparative tests.[14]

DSC analysis

For curing studies, 4 ± 1 mg of freshly prepared samples were sealed in several alumina crucibles, and scanned in a DSC (DSC-60A, Shimadzu Co. Ltd., Kyoto, Japan) with an indium standard operating in dynamic mode. A stream of N_2 at a flow rate of 40 mL/min was used to protect the DSC cell. Non-isothermal scans were performed from 50°C to 300°C, at various heating rates (5, 10, 15, and 20 °C/min).

FTIR analysis

The analysis was conducted in a Fourier transform infrared spectroscopy spectrometer (FTIR, NEXUS-470, Thermo Nicolet, Waltham, Massachusetts, USA) using samples in KBr pellets.



Scheme 1 Chemical structure of PAI and the synthesis process of PAA and PAI.

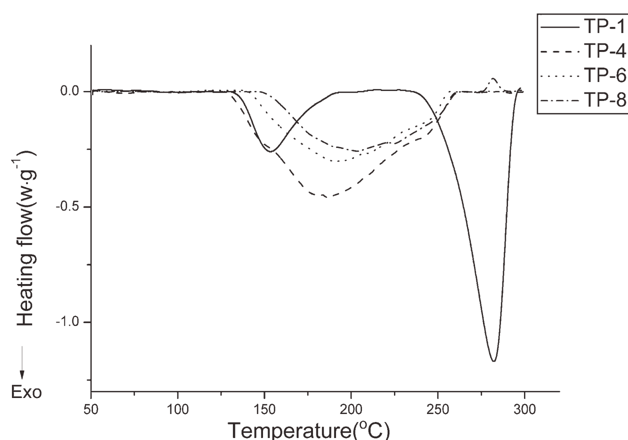


Figure 1 DSC scans of TGDDM in the presence of varying PAA weight ratios of 0.23(TP-1), 0.50(TP-4), 0.60(TP-6), and 0.67(TP-8).

Fracture surface morphology

The morphology of the fracture surface of the cured samples was examined with SEM (SEM-SUPERSCAN SSX-55, Shimadzu Co. Ltd., Kyoto, Japan). The cured samples were fractured in liquid nitrogen and coated with a layer of gold before observation.

Tensile strength

Tensile strength test was conducted with a universal testing machine (Instron 5842, Instron Engineering Co., Boston, Massachusetts, USA). The gauge length and crosshead speed were set as 20 mm and 5 mm/min, respectively.

Thermal stability

Thermal stability was investigated using thermo gravimetric analysis (TGA, Model 951, Perkin Elmer Co., Waltham, Massachusetts, USA) in nitrogen atmosphere (flow rate 40 mL/min). A heating rate of 20 °C/min and powdered samples of 3 ± 1 mg were used in each experiment.

RESULTS AND DISCUSSION

Cure behavior

DSC scans of PAA-cured TGDDM showed that the curing reaction depended on the PAA weight ratios (Fig. 1). As shown in Figure 2, the initial temperature where the curing starts (T_i), the temperature where the first detectable heat was released (T_{onset}), and the peak exotherm temperature (T_p) increased as the PAA content of the blends increased, indicating there by that the cure temperatures should be increased concomitantly with an increase in PAA content of the epoxy resins. Relatively higher temperatures are therefore necessary for the reaction to occur.

It is likely that an increase in PAA content blocks the TGDDM by decreasing the likelihood of reactions between TGDDM's epoxy functional groups and PAA's amide groups. In general, the heat of curing (ΔH) values increase with increase in conventional curing agents until a chemical equivalent ratio of active functional groups is reached. In this case, ΔH increased to a maximum that corresponded to a weight ratio of 0.5, and then decreased with further increase in PAA content. It could be assumed therefore that the excess PAA block the TGDDM, reducing thereby the extent of reactions that occur.

Two different exothermic peaks appeared in the samples TP-1 and TP-2. The one appeared at lower temperature corresponded to the curing of TGDDM, while the other corresponded to the intermolecular and intramolecular cyclization of TGDDM,[15] which was proved in the following FTIR analysis. Furthermore, the homopolymerization of TGDDM[15–17] that tends to occur at higher temperatures might also contribute to the DSC peak. There was one combined exothermic peak in samples TP-3, TP-4, TP-5, TP-6, TP-7, and TP-8, indicating that several different reactions took place in the system. Combined with the following FTIR results and analysis, besides the reaction of epoxy functional groups and secondary amide functional groups, some amount of the following reactions also took place in the system: PAA imidization,[10] TGDDM intermolecular and intramolecular cyclization, and some slight TGDDM homopolymerization. The reason of two exothermic peaks for TP-1 and TP-2 was that only a fraction of TGDDM could be cured by PAA (with a PAA weight ratios of 0.23, 0.33). The reaction of epoxy and imide functional groups has occurred before the temperature reached to 200°C, while the intermolecular and intramolecular cyclization of TGDDM could only occur at the temperature of more than 230°C. As a result, there were two totally separated exothermic peaks in the samples TP-1 and TP-2. When the PAA weight ratios increased, longer

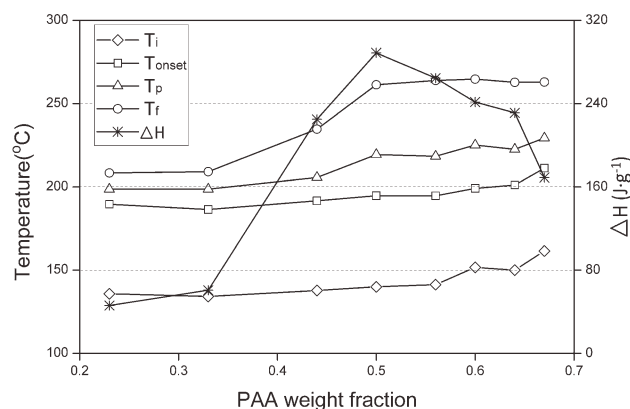


Figure 2 DSC scans of TGDDM cured with varying PAA weight ratios.

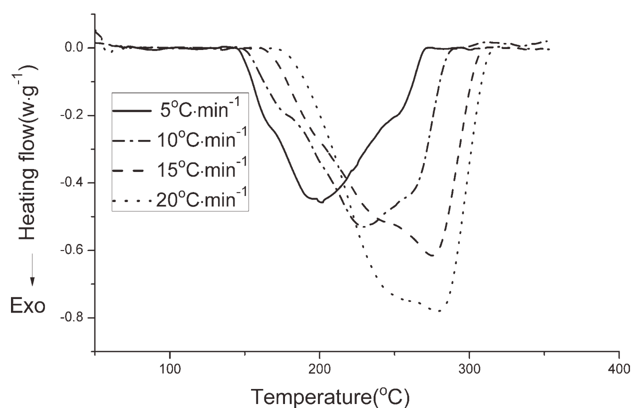


Figure 3 DSC scans of TGDDM in the presence of 0.5 weight ratio of PAA (TP-4) at different heating rates (β).

time will be taken to complete the reaction of epoxy and imide functional groups. The reaction could not be completed when the temperature reaches 230°C at which the intermolecular and intramolecular cyclization of TGDDM started to occur. In addition, PAA imidization took place as the PAA increased in a temperature range of 180–250°C. Consequently, one combined exothermic peak was observed in samples TP-3, TP-4, TP-5, TP-6, TP-7, and TP-8.

Several principles should be followed in the choice of the amount of curing agent: lower curing temperature, proper curing rate, and proper degree of crosslinking. In addition, considering the specificity of the PAA as a curing agent and based on our work, 0.5 is the most proper weight ratio of PAA.

The cure process was investigated using non-isothermal DSC (Fig. 3). A model free-estimation (Ozawa–Flynn–Wall method),[18] which allows to determine the activation energy (E) based on the variation of T with the heating rate, was applied to calculate E:

$$\ln\beta = \text{const} - 1.052E/RT$$

where β is the heating rate, R is the gas constant, and T is the temperature in kelvin. The PAA's activation energy (E) was estimated at 113.3 kJ/mol. This value is much higher than for most conventional curing agents (DDS, DDE, etc.), indicating thereby that as a curing agent, its reactivity is much slower than these agents.

Curing mechanism

From DSC analysis, it could be inferred that there were several different reactions in the blends. FTIR analysis was thus performed to confirm the successful cure of TGDDM by PAA and ascertain the proposed cure mechanism.

The band at 1535 cm^{-1} is attributed to the in-plane bending vibration of secondary amide N—H. Figure 4 shows three FTIR spectra: untreated PAA (a), PAA heated at 150°C for 1 h followed by 270°C for 3 h (b), and sample TP-4 pre-cured at 150°C for 1 h and cured at 270°C for 3 h. The intensity of the band that was obvious in spectrum (a), decreased in spectrum (b), and then disappeared in spectrum (c). The band of the in-plane bending vibration of N—H of secondary amide was both from positions (1) and (2) in untreated PAA. For the 270°C treated PAA, the secondary amide in position (2) took part in the thermal imidization reaction with the band originating from position (1). On heating the material (sample TP-4) at 270°C for 3 h, the band disappeared indicating thereby that the secondary amide in position (1) reacted with epoxy functional groups.

Figure 5 showed that FTIR spectra of (a)TGDDM, (b)PAA, and (c) TGDDM/PAA blends with a PAA weight ratio of 0.5 pre-cured at 150 for 1 h and then cured at 180°C for 3 h in an air-circulated oven (CTP-4). The band at about 915 cm^{-1} belongs to the characteristics transmission peak of epoxy group of TGDDM.[19,20] It can be found that this characteristics peak of epoxy group almost totally disappeared in spectrum(c) indicating that the epoxy group was all involved in the reaction (Scheme 2.). We can see that the band at 1535 cm^{-1} obviously present in spectrum (b) while totally disappeared in spectrum (c), indicating that almost all the secondary amide group of PAA participated in chemical reactions during the heating process. The band at 1780 cm^{-1} that could be assigned to the C=O asymmetric stretching vibration was absent in spectrum (b) but present in spectrum (c), implying thereby the reaction of imidization. The bands at 1290 cm^{-1} and 1260 cm^{-1} was

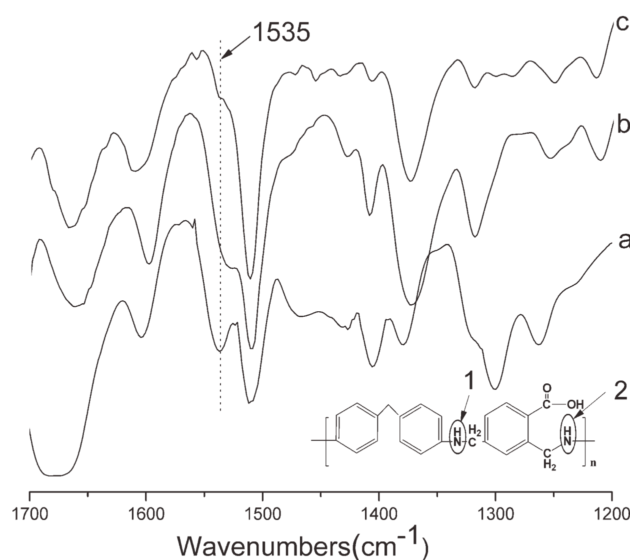


Figure 4 FTIR spectra of (a) untreated PAA, (b) PAA pre-cured at 150°C for 1 h and cured at 270°C for 3 h, and (c) TGDDM in the presence of 0.5 weight ratio of PAA (TP-4) pre-cured at 150°C for 1 h and cured at 270°C for 3 h.

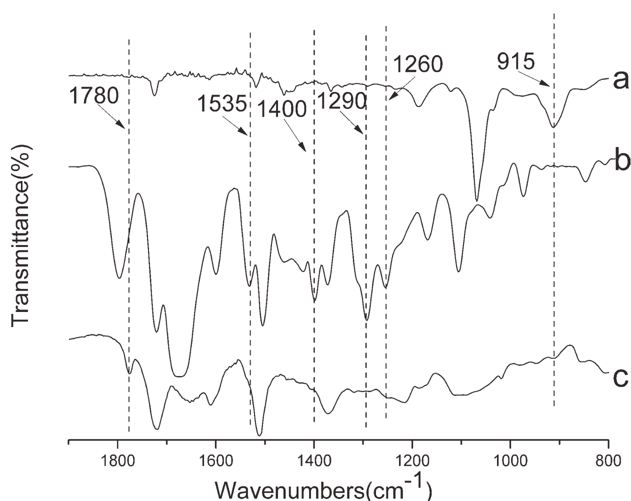


Figure 5 FTIR spectrums of (a)TGDDM, (b)PAA, and (c) TGDDM/PAA blends with a PAA weight ratio of 0.5 precured at 150 for 1 h and then cured at 180°C for 3 h in an air-circulated oven (CTP-4).

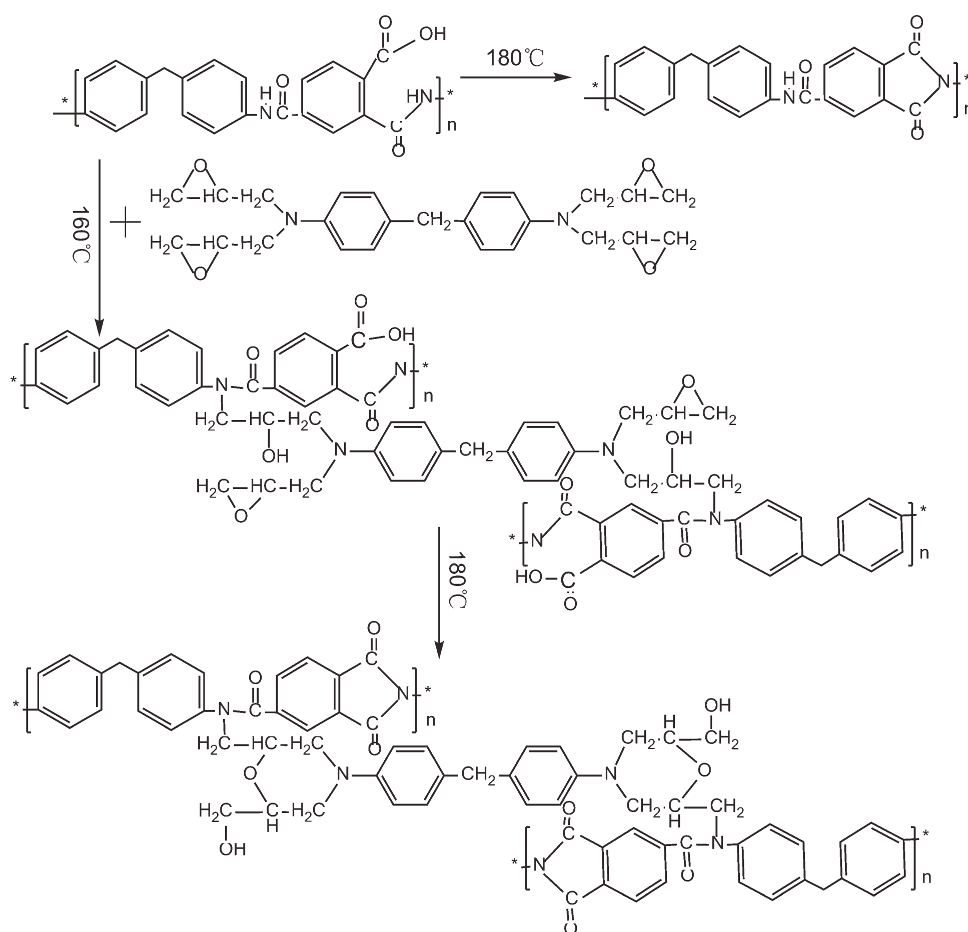
attributed to the carboxyl C—O stretching vibration while that at 1400 cm^{-1} was assigned to the carboxyl C—O—H in-plane bending vibration. These three bands were obvious in spectrum (b) but absent in spectrum (c), indicating PAA imidization during the heating process. The bands at 1120–1090 cm^{-1} was mostly attributed to the C—O bending vibration of five-membered epoxy ring. The bands could not be found in spectrum (a) and (b) but obviously present in spectrum (c), indicating the intermolecular and especially the intramolecular cyclization of TGDDM.

Based on our work and analysis above and the relevant literatures,[14–17] the reaction mechanism is shown in Scheme 2.

Fracture surface morphology and tensile strength

The fracture surface morphology of the sample CTP-4 and sample TD were examined with SEM and the results were shown in Figure 6. There were a mass of fragments in the fracture surface of the sample TD, in contrast to sample CTP-4. There was hardly any fragment in the fracture surface of the sample CTP-4. The result implied that TGDDM cured by 0.5 weight ratio of PAA possess better fracture strength than the one cured by DDS.

These assumptions were confirmed by tensile strength measurements, as the value obtained on CTP-4 (103 MPa) was much higher than on sample



Scheme 2 The dominant reactions of TGDDM in the presence of 0.5 weight ratio of PAA (TP-4) at different temperature.

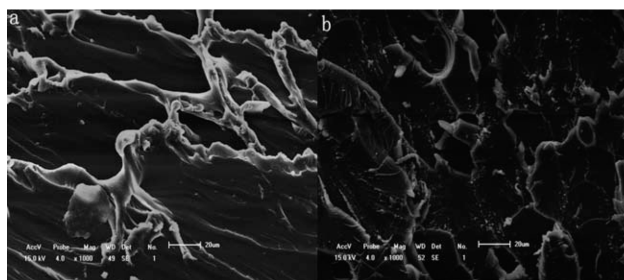


Figure 6 The fracture surface morphology of (a) TGDDM/PAA blends with a PAA weight ratio of 0.5 pre-cured at 150°C for 1 h and then cured at 180°C for 3 h in an air-circulated oven (CTP-4) and (b) TGDDM/DDS blends with a DDS 85% stoichiometric ratio processed at 150°C for 6 h (TD).

TD (22 MPa). The CTP-4 was much closer to pure PAA processed at 270°C for 3 h (110 MPa). It could be explained that the crosslinking density of CTP-4 was less than TD, which has been proved by DSC analysis. The elongation at break (7.8% for CTP-4, 1.2% for TD) also indicated that the crosslinking density of CTP-4 was less than TD. What's more, the polarity of the molecular chain of CTP-4 was higher than TD because of the existence of imide functional group in CTP-4. Thus the stronger intermolecular force, caused by the polarity of imide functional group, could absorb energy of tensile when macromolecular chains slipped. This could generate higher tensile strength. However, there was hardly any macromolecular chains slip for TD because of the high crosslinking density.

Thermal stability

Figure 7 shows TGA curves of samples CTP-4 and TD. The initial decomposition temperature (corresponding to 5% weight loss) was slightly higher for sample CTP-4 (347°C) than for sample TD (344°C). The temperature at which the rate of mass loss was maximum was lower for sample CTP-4 (397°C) than for sample TD (406°C). This could be explained by the fact that for the PAA-cured TGDDM, the degree of cure was lower and network structure less compact than DDS-cured TGDDM, owing to the lower reactivity of PAA. With increasing temperatures, the onset thermal decomposition of sample TD could be attributed to dehydration and the eventual formation of carbon–carbon double bonds.[5] On the other hand, the onset thermal decomposition of sample CTP-4 could be attributed partly to dehydration as well as to the decomposition of unreacted epoxy functional groups.

Thermal decomposition rate of sample CTP-4 was much slower than that of sample TD, probably due to the fact that predominant TGDDM reactions in the presence of DDS are between epoxy and amine groups (primary or secondary) and rarely of TGDDM intra-molecular and inter-molecular

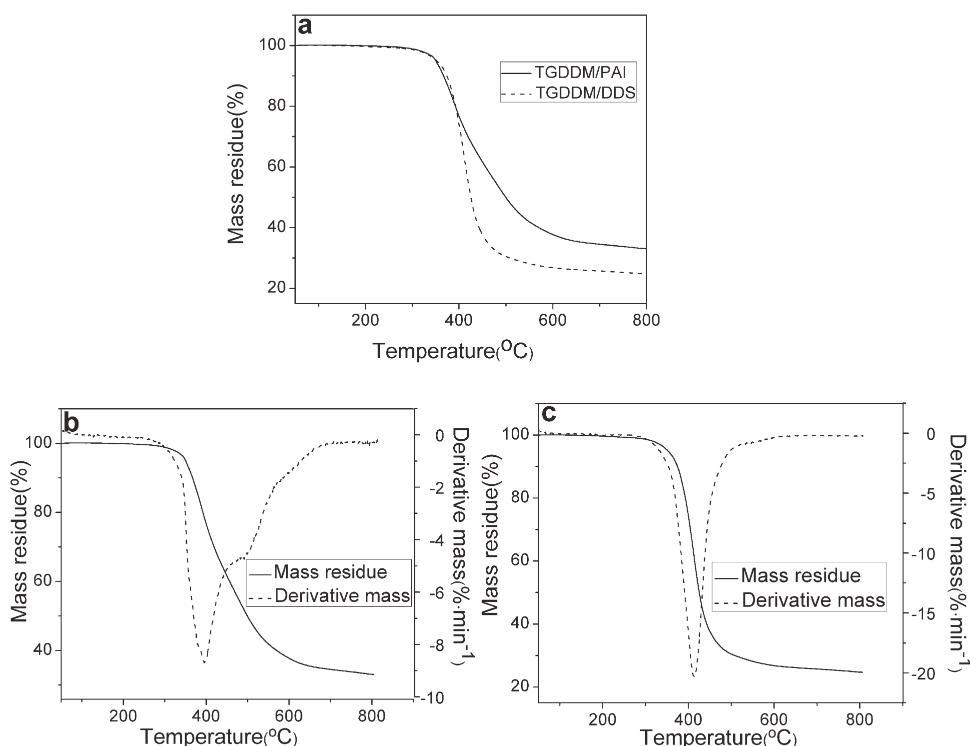


Figure 7 TGA traces of (a) TGDDM/PAA blends with a PAA weight ratio of 0.5 pre-cured at 150 for 1 h and then cured at 180°C for 3 h in an air-circulated oven (CTP-4), and TGDDM/DDS blends with a DDS 85% stoichiometric ratio processed at 150°C for 6 h (TD), (b) TGA and DTG traces of the sample CTP-4, (c) TGA and DTG traces of the sample TD.

cyclization.[10] In the TGDDM/PAA system, besides the reactions between epoxy and amines groups, TGDDM intra-molecular and inter-molecular cyclization as well of thermal imidization of polyamide-amidic acid were common. The cyclized and thermal imidization products were more thermally stable than the DDS cured TGDDM, and as such required more time to decompose.[20]

Figure 7(c) shows a single peak that could be attributed to the thermal decomposition of sample TD, while Figure 7(b) shows two different peaks. It could be explained that there are three dominating structures (homopolymerized TGDDM, imidization PAA, and cross-linked TGDDM/PAA). The peak at lower temperature (397°C) could be mainly attributed to the thermal decomposition of cross-linked TGDDM/PAA and homopolymerized TGDDM, the one at higher temperature (470°C) to thermal decomposition of PAA imidization.

The char yield (CR) (up to 800°C) of CTP-4 (33.1%) was higher than for sample TD (24.7%). The limiting oxygen index (LOI), calculated using the Van Krevelen and Hoftyzer method[21] ($LOI = 17.5 + 0.4\ CR$) showed that sample CTP-4 could be classified as a self-extinguishing resin ($LOI > 27.0\%$) and that a flame-resistant TGDDM resin can be obtained by using PAA as curing agent. With some reluctance, DDS-cured TGDDM can be classified as a self-extinguishing resin, thus its flame resistance is less than that of the TGDDM/PAA system.

CONCLUSIONS

In this study, PAA was used as a novel curing agent for TGDDM. The TGDDM/PAA mixture was characterized using DSC, SEM, tensile testing, FTIR, and TGA. DSC analysis showed that the curing behavior of PAA is different from that of the conventional curing agents. The value of the initial temperature where the curing starts (T_i) and the peak exotherm temperature (T_p) increased with increasing PAA content while the value of ΔH increased firstly and then decreased with increasing PAA content. DSC results indicated that several different reactions took place in the mixture, which was confirmed by FTIR analysis. The fracture toughness, tensile strength, char yield, and flame resistance of TGDDM were greatly improved on curing with PAA (at a 0.5 weight ratio) as compared to curing with DDS.

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