An Investigation of Cure and Thermal Stability of Poly(amide-amidic acid) Modified Tetraglycidyl 4,4′-Diaminodiphenylmethane/4,4′-Diaminodiphenylsulfone

Haiming Chen, Renguo Lv, Pei Liu, Hongyan Wang, Zhongyuan Huang, Ting Huang, Tongsheng Li

State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200433, People's Republic of China

Correspondence to: T. Li (E-mail: lits@fudan.edu.cn)

ABSTRACT: In this work, poly(amide-amidic acid) (PAA) was used to modify tetraglycidyl 4,4′-diaminodiphenylmethane (TGDDM)/4,4′-diaminodiphenylsulfone (DDS) system. Results of non-isothermal differential scanning calorimetry analysis indicated that PAA played a role of catalyst during the process of the curing reaction. The curing mechanism was studied by Fourier transform infrared spectroscopy, showing that the PAA acted as a co-curing agent in the system. The glass transition temperature decreased firstly and then increased with the increase of the PAA content. PAA equally rendered TGDDM more fire resistant with higher char yield. On examining the fracture surface morphology using scanning electron microscopy, it was observed that there was no obvious phase separation when the content of PAA was less than 20 phr (per hundred weight of TGDDM/DDS resin), however, phase separation was observed when the content of PAA was 25 and 30 phr. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Epoxy resins is a kind of the most widely used high-performance thermosetting materials, owing to their fascinating properties of high bonding strength, excellent thermal resistance, high mechanical strength, and outstanding dielectric and aging characteristics. They are widely used as high-performance protective coatings, structural adhesives, and matrix resins for composites in a number of fields ranging from aerospace industry, automobile industry to microelectronics industry.[1–3]
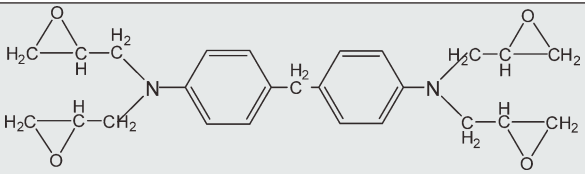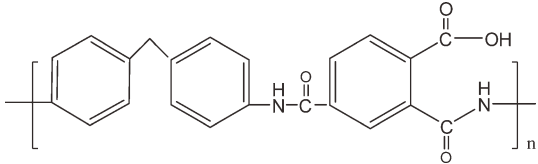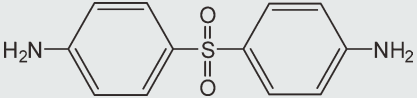
However, there are many shortages (poor toughness, poor weather fastness, poor impact strength, etc.) limiting the application of epoxy resins.[1–3] As a result, a variety of approaches have been developed to improve the performance of them. Generally speaking, the following methods have been applied to enhance the performance of epoxies: synthesis of new epoxies and curing agents,[4,5] incorporation of inorganic nanoparticles and elastomer toughening agents,[6–8] modified with thermoplastic resin.[9] Kaya et al.[4] synthesized a new schiff base epoxy oligomer resin and studied the thermal decomposition kinetics. Ma et al.[10] investigated the dispersion, mechanical and thermal properties of epoxy resin composites filled with the nanometer carbon black. Pearson et al.[11–15] studied the toughening effect and toughening mechanisms of elastomer-modified epoxies. Generally, much more time, work and some other resources will be cost for improving the performance of epoxy resin by the way of synthesis of new epoxies and curing agents. Although inorganic nanoparticles can improve the toughness and impact strength of the epoxy resin, some other properties are reduced. What is more, the costing of nanoparticles are also a little much. While elastomer can be very effective in increasing the fracture toughness, they suffer from drawbacks of reducing the modulus and the glass transition temperature.

As a result, researchers have focused a lot on thermoplastic toughening that has been widely applied in industry because it enhances toughness without compromising other desirable properties significantly. Li et al.[16–20] investigated the effects of the molecular structure, molecular weight, and content of various kinds of thermoplastic resin on the phase separation and mechanical properties in thermoplastic modified epoxy systems. Park et al.[21–23] investigated the thermal stabilities and mechanical behaviors of the epoxy resin modified by various kinds of thermoplastic plastics.

Table I. Chemical Formulas of the Materials

Materials	Chemical formula
TGDDM	
PAA	
DDS	

On heating, poly(amide-amidic acid) (PAA) converted to poly(-amide-imide) (PAI), a material of special engineering plastic with high thermal resistant and high strength due to its unique molecular structure consisting of a high proportion of aromatic rings, double bonds, and heterocyclic imide structures along the polymer backbone.[24–26] PAIs give a favorable balance between processability and performance. As a result, PAIs is widely applied in the field of coatings, adhesives, injection-molding, and extrusion products. What is more, there are secondary amine groups that give PAIs good miscibility with epoxies, because of which, PAA was used to cure TGDDM in our former work.[27] The characteristics of PAIs narrated above make it an excellent potential modifier to improve the performance of the epoxy resin. However, presently, there is hardly any research in which PAIs were used to reinforce epoxy resin directly. With this in mind, PAA was selected to modify tetraglycidyl 4,4'-diaminodiphenylmethane (TGDDM) with 4,4'-diaminodiphenylsulfone (DDS) acting as curing agent in this article. The curing behavior, curing mechanism, and modification mechanism were investigated. The glass transition temperature (T_g) was measured, and the phase morphology structure was observed to evaluate the effect of the modification.

EXPERIMENTAL

Materials
TGDDM and PAA used in this study were supplied by Changzhou Olong Electrical Insulation Materials (Changzhou, China). The curing agent (DDS) and dimethyl acetamide solvent (DMAc) were both supplied by Sinopharm Chemical Reagent

(Shanghai, China). The chemical structures of the materials were shown in Table I.

Sample Preparation
The samples used for differential scanning calorimetry (DSC) analysis were obtained by the following steps. First, 0, 5, 10, 15, 20, 25, and 30 g PAA were, respectively, added to TGDDM (70.26 g) diluted with 100 g DMAc. Second, 29.74 g DDS was added to the above solutions, followed by stirring at 60°C for 30 min to be fully dissolved. Finally, the resulting solutions were sprayed with 0.2 MPa high purity nitrogen gas using spray gun to a few pieces of 80°C heated clean aluminum foils. We have sprayed six times before we got a film with a thickness of 30–60 μm, and the aluminum foils were heated at 80°C to evaporate the DMAc in a blowing oven before each time we sprayed. Then, the sprayed aluminum foils were put in a vacuum oven at 80°C for 4 h to evaporate the remaining DMAc.

For Fourier transform infrared (FTIR) spectroscopy analysis, fracture surface morphology observation and thermal stability investigation, TGDDM/DDS/PAA blends were cured at 150°C for 2 h and followed by 200°C for 2 h in an air-oven. TGDDM/DDS blend with 85% stoichiometric ratio of DDS was processed at 150°C for 2 h followed by 200°C for 2 h for comparative test. The sample designation was shown in Table II.

DSC Analysis
4 ± 1 mg of freshly prepared samples were sealed in several alumina crucibles, and followed by scanning in a DSC (DSC-60A,

Table II. Sample Designation

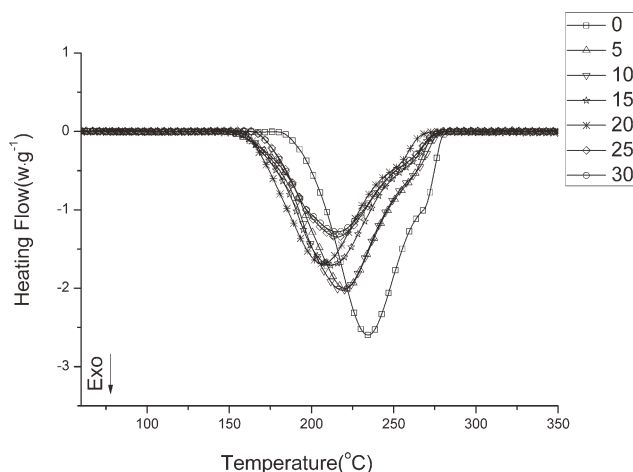| Component	Sample						
TGDDM (g)	70.26	70.26	70.26	70.26	70.26	70.26	70.26
DDS (g)	29.74	29.74	29.74	29.74	29.74	29.74	29.74
PAA (g)	0	5	10	15	20	25	30

Figure 1. DSC scans of TGDDM/DDS in the presence of various content of PAA ranging from 0 to 30 phr.

Shimadzu, Kyoto, Japan) with an indium standard operating in a dynamic mode. Non-isothermal scans were performed at heating rates of 10°C/min from 50°C to a maximum of 350°C, with a stream of N_2 at a flow rate of 40 mL/min protecting the DSC cell.

FTIR Analysis
The analysis was conducted in a FTIR spectrometer (FTIR, NEXUS-470, Thermo Nicolet, Madison, Wisconsin, USA) using samples in KBr pellets.

DMA Analysis
Dynamic mechanical tests were carried out by a dynamic mechanics analyzer (DMA 242C, NETZSCH, Bavaria, German) in the scanning temperature mode, in the range of 50–350°C, at a heating rate of 2.5°C/min, with an oscillating frequency of 1 Hz. The geometry of deformation was the tension mode. Samples with a size of $10.0 \times 3.5 \times 0.2$ mm³ were prepared for the experiment.

Thermal Stability
A thermogravimetric analysis (TGA, Model 951, Perkin Elmer, Waltham, Massachusetts, USA) was applied to investigate the thermal stability of the cured samples in nitrogen atmosphere (flow rate 40 mL/min). Powdered samples of 3 ± 1 mg and a heating rate of 20°C/min was used in every experiment.

Fracture Surface Morphology
A TS 5136MM scanning electron microscope (SEM, Tescan, Brno, Czech) was applied to observe the morphology of the fracture surface of the cured samples. The cured samples were fractured in liquid nitrogen and coated with a layer of gold before observation.

RESULTS AND DISCUSSION

Cure Behavior and Mechanism
DSC scans of PAA-modified TGDDM/DDS system indicated that PAA acted as a catalyst. As shown in Figures 1 and 2, the temperature where the first detectable heat is released (T_{onset}) decreased from 177.0°C (unmodified TGDDM/DDS) to 147.6°C (5 phr PAA modified TGDDM/DDS), and then increased with

PAA increasing. The peak exotherm temperature (T_m) decreased with the increase of PAA content. The decrease of T_{onset} and T_m indicated there by that the cure temperatures could be decreased when PAA was added. It can be explained that, firstly, PAA acted as a catalyst because of the carboxyl and secondary amine groups in PAA.[28] Hydrogen bonding formed between epoxy and carboxyl or secondary amine groups, promoting the ring opening of epoxy group. This resulted in the accelerating of epoxy curing reaction. The catalytic mechanism was shown in Scheme 1 (take carboxyl group for example). Secondly it was likely that an increase in PAA content blocks the TGDDM and DDS by decreasing the likelihood of reactions between TGDDM's epoxy functional groups and DDS's amide groups, which could explain that the value of T_{onset} increased with PAA increasing from 147.6°C (5 phr PAA modified TGDDM/DDS) to 159.4°C (30 phr PAA modified TGDDM/DDS). The value of the temperature of the end of curing exotherm (T_{end}) of PAA modified TGDDM/DDS was 4–7°C lower than that of unmodified TGDDM/DDS. However, there was no obvious variation among the T_{end}s of TGDDM/DDS modified by PAA from 5 to 30 phr. It could be explained that the thermal imidization of PAA taking place in a wide range of temperature, which was confirmed in the following FTIR analysis, kept the T_{end} at a relatively high temperature from 265.0 to 270.0°C, although the T_{onset} decreased by 20–30°C compared with unmodified TGDDM/DDS. The value of the heat of curing calculated by the measurement of area under the exothermic (ΔH) decreased with PAA increasing. It can be explained that, firstly, the heat released by the reaction of thermal imidization of per-unit mass of PAA was less than that released by the reaction of curing of per-unit mass of TGDDM/DDS. Additionally, it was likely that the adding of PAA decreased the crosslinking density of the cured TGDDM whether PAA acted as a modifier or co-curing agent.

The results of FTIR analysis were shown in Figure 3. The band at 915 cm^{-1} belongs to the characteristics transmission peak of epoxy group of TGDDM. Not any peak at this position was observed in spectra of all the samples, indicating that the epoxy group was all involved in the curing reaction. The band at 1535 cm^{-1} that could be assigned to in-plane bending vibration of secondary amide N—H, was absent in all of the spectra,
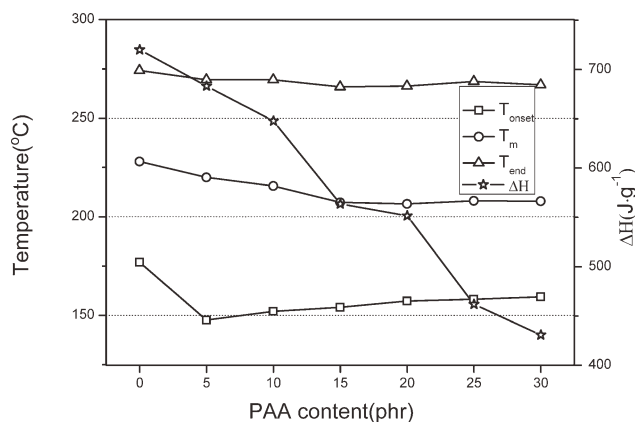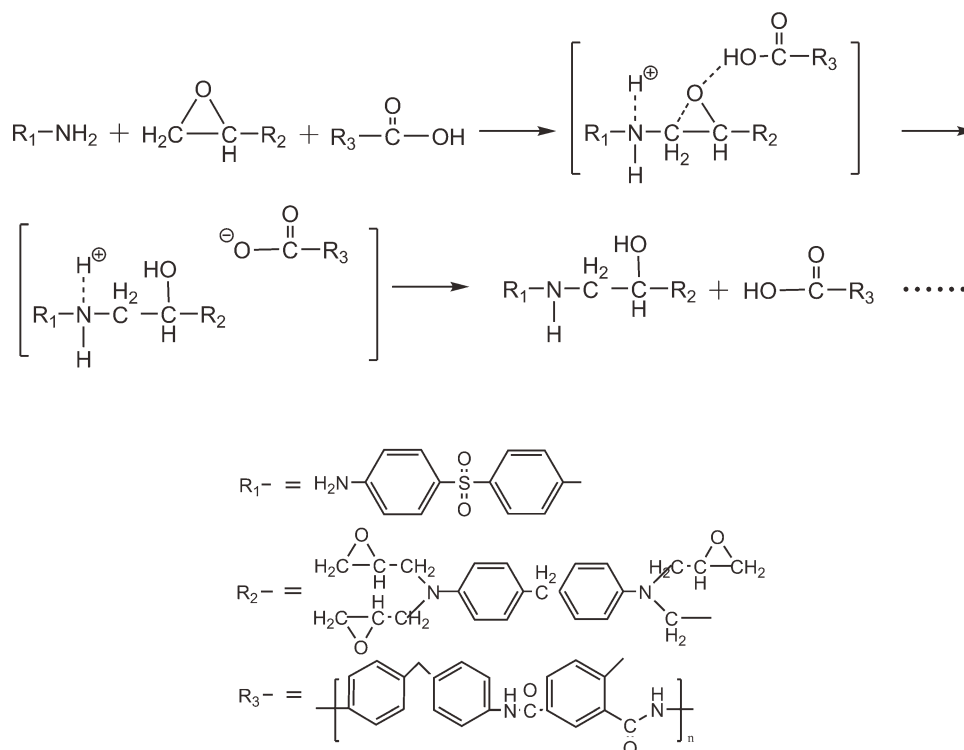

Figure 2. Results of DSC scans of TGDDM/DDS in the presence of varying content of PAA ranging from 0 to 30 phr.

Scheme 1. The catalytic mechanism (take carboxyl group, for example).

implying thereby that all of the secondary amide took part in the curing reaction in all range of the PAA content from 5 to 30 phr. The band at 1380 cm^{-1}, was attributed to the C—N stretching vibration of aromatic imides while that at 1778 cm^{-1} was assigned to the C—O asymmetric stretching of aromatic imides. These two bands were absent when the content of PAA was less than 15 phr but gradually increased as the increase of PAA content when the content of PAA was more than 20 phr.

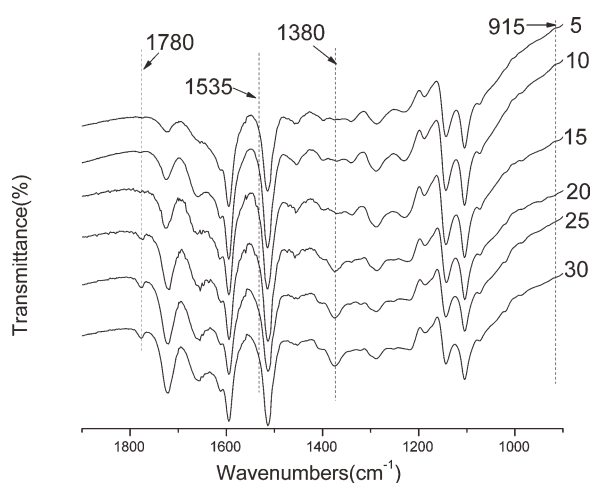Based on the FTIR analysis, the following conclusion could be drawn:

Figure 3. FTIR spectra of TGDDM/DDS in the presence of various content of PAA ranging from 5 to 30 phr.

Besides of primary and secondary amine of DDS, the secondary amide and maybe carboxylic acid functional groups of PAA took part in the reaction with TGDDM. In other words, PAA acted as a co-curing agent in the system, the curing mechanism was shown in Scheme 2.

Almost all of the PAA took part in the curing reaction acting as a co-curing agent when the PAA content was less than or equal to 15 phr. When the PAA content was more than or equal to 20 phr, part of the PAA acted as a co-curing agent. Thermal imidization of PAA took place in the remaining PAA. This also confirmed the explanation that why there was no obvious variation among the T_{end}s of TGDDM/DDS modified by PAA from 5 phr to 30 phr above in the DSC analysis.

Thermal Properties
Thermal properties were investigated from the points of viscoelasticity characteristic and thermal stability.

DMA is a technique that allows knowing, among other characteristics, the T_g of the materials, relating this to the maximum of the loss factor curve. The storage modulus (E') and tan δ as a function of temperature was shown in Figures 4 and 5. The E' of TGDDM/DDS modified with 5, 10, 15, and 20 phr PAA started to decrease at the beginning of the DMA test (the corresponding temperature was 50°C). However, the E' of TGDDM/DDS modified with 25 and 30 phr PAA stayed unchanging until the temperature reached to about 150°C. T_g decreased firstly and then increased as the increase of PAA content. It was less than 223°C (T_g of unmodified TGDDM/DDS) when the PAA content were 5, 10, and 15 phr, while it was more than 223°C when the PAA content were 20, 25, and 30 phr. It was likely
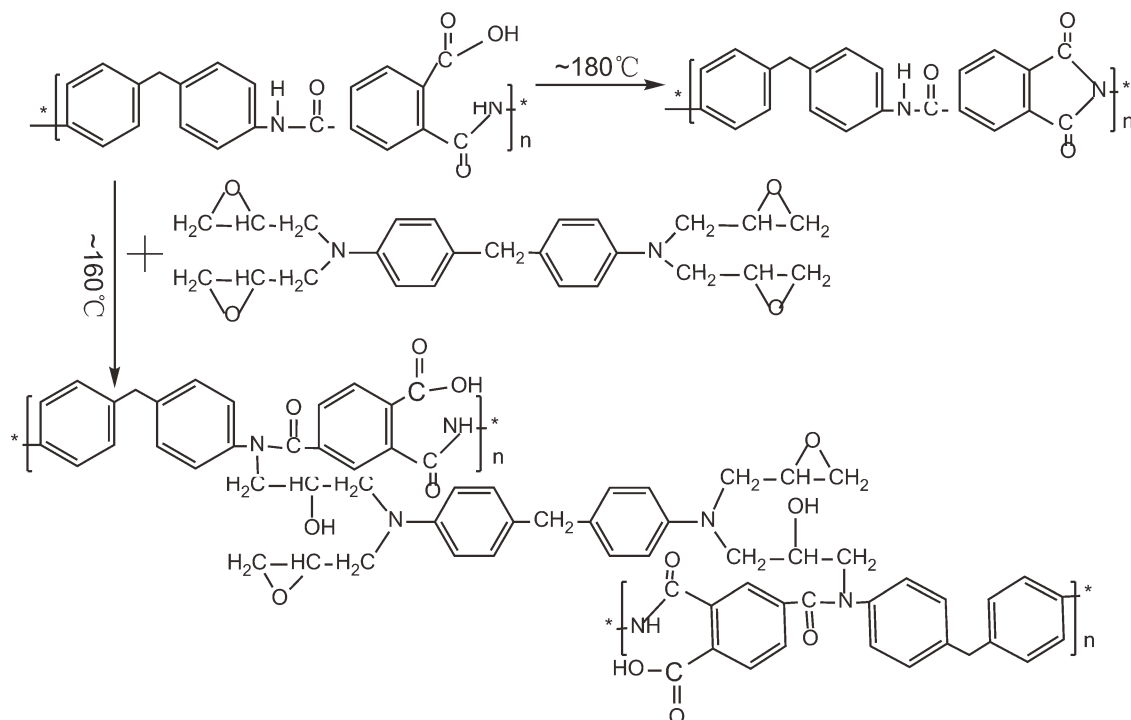
Scheme 2. The curing mechanism when PAA acted as a co-curing agent.

that the adding of PAA decreased the crosslinking density of the cured TGDDM whether PAA acted as a modifier or co-curing agent, leading to the decrease of T_g. However, when PAA acted both as a modifier and a co-curing agent (PAA content was more than 15 phr), a certain amount of PAI with a T_g of about 290°C came to exist. Additionally, the intermolecular Van der Waals force increased because of the formation of five-membered imide ring that is a functional group with strong polarity. As a result, higher T_g was generated. It was also noticed there were some small peaks corresponding to the secondary relaxation before the main peak. The corresponding temperature of the position of the secondary relaxation peak increased firstly and then decreased with PAA content increasing (Figure 5). The

highest secondary relaxation peak was obtained when the content of PAA was 25 phr. It was inferred that although the crosslinking density of the cured TGDDM decreased with the increase of PAA content, the small size motion units (such as side chain, relatively movable functional group, and chain segment) not increased because of the high molecular weight and reactivity (with TGDDM) of PAA before the content of PAA reached to 25 phr. However, the crosslinking density of the cured TGDDM significantly decreased when the content of PAA was 30 phr, leading to the existence of small size motion units, such as hydroxyl groups. This reduced the temperature of the secondary relaxation peak of the 30 phr PAA modified TGDDM.
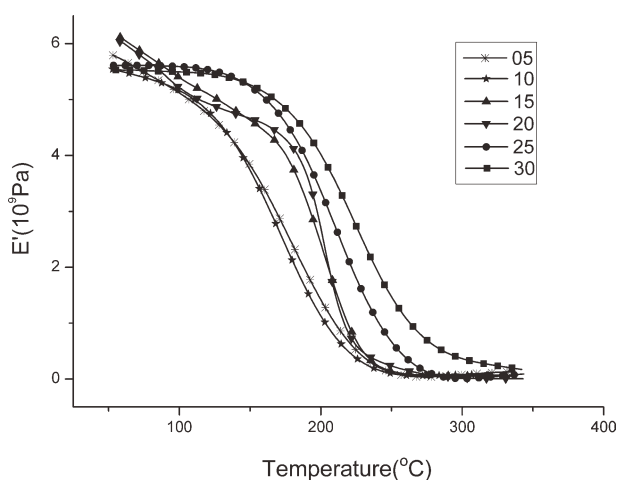

Figure 4. Dynamic mechanical spectra in terms of E′ for varying content of PAA modified TGDDM/DDS.
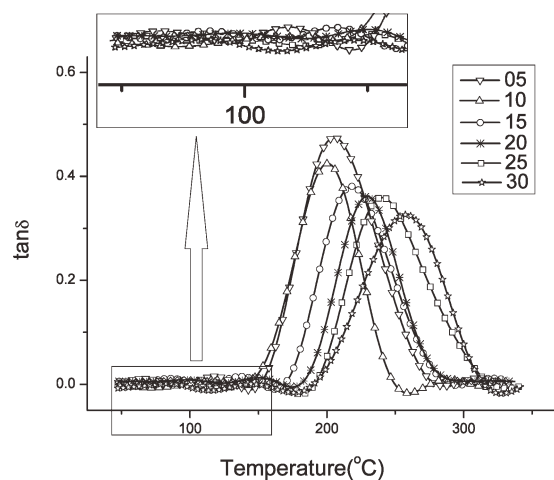

Figure 5. Dynamic mechanical spectra in terms of tan δ for varying content of PAA modified TGDDM/DDS.
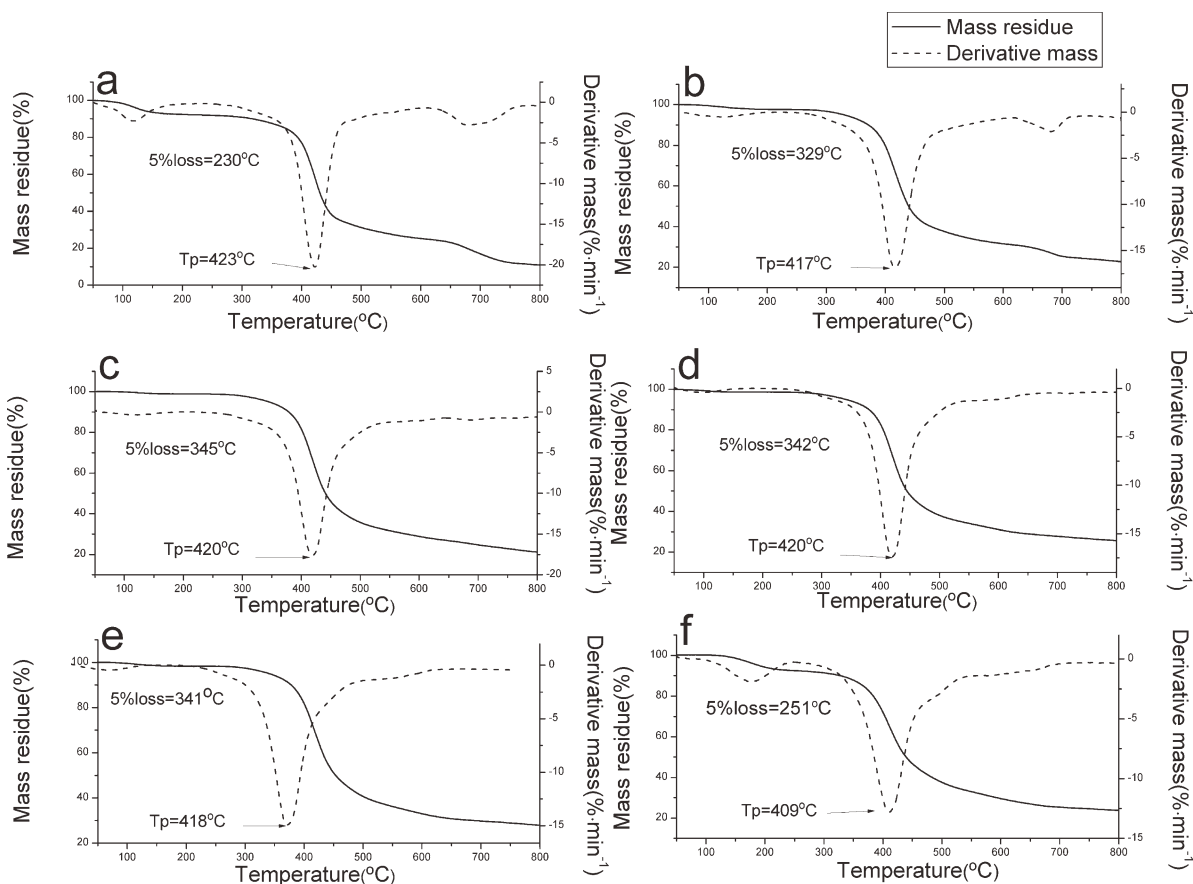
Figure 6. TGA/DTG traces of TGDDM/DDS in the presence of various content of PAI ranging from 5 to 30 phr. (a, b, c, d, e, and f correspond to 5, 10, 15, 20, 25, and 30 phr PAA modified TGDDM/DDS, respectively).

Figure 6 shows TGA/DTG traces of TGDDM with various content of PAI ranging from 5 to 30 phr. Results of the TGA analysis were shown in Table III. The initial decomposition temperature (corresponding to 5% weight loss, T_{onset}) of the PAA modified TGDDM/DDS composites were less than or equal to that of the unmodified TGDDM/DDS. The temperature at which the rate of mass loss is maximum (T_p) improved by about 15°C because of the adding of PAA. We also found that char yield (up to 800°C) was more than that of the unmodified TGDDM/DDS when the content of PAA were 20 and 25 phr. In contrast, the char yield decreased in the other PAA content. Together with the results of

FTIR analysis, it could be explained that the hydrone was produced and evaporated into the air as the formation of imide five-membered ring (Scheme 1). However, if all of the PAA acted as a co-curing agent, no hydrone was produced (Scheme 2). What is more, the char yield of PAI used in our experiment was 50.3%, much higher than that of unmodified TGDDM/DDS (24.7%). As a result, when TGA test was performed, less weight loss has been achieved because of the formation of imide five-membered ring. We also noticed that the T_{onset} and char yield of 30 phr PAA modified TGDDM/DDS were both decreased compared with unmodified TGDDM/DDS. It was likely that the crosslinking

Table III. The Char Yield and LOI of TGDDM/DDS in the Presence of Varying Content of PAA Ranging from 0 to 30 phr

PAA (phr)	T_{onset} (°C)	T_p (°C)	Char yield (%) at 800°C	LOI (%)	Fire resistant
0	344	406	24.7	27.1	E
5	230	423	20.0	21.4	F
10	329	417	22.7	26.1	C
15	345	420	20.9	25.4	C
20	342	420	25.5	27.3	E
25	341	418	27.7	28.1	E
30	251	409	23.7	26.5	C

F, C, and E stand for flammable, combustible, and self-extinguishing materials, respectively.
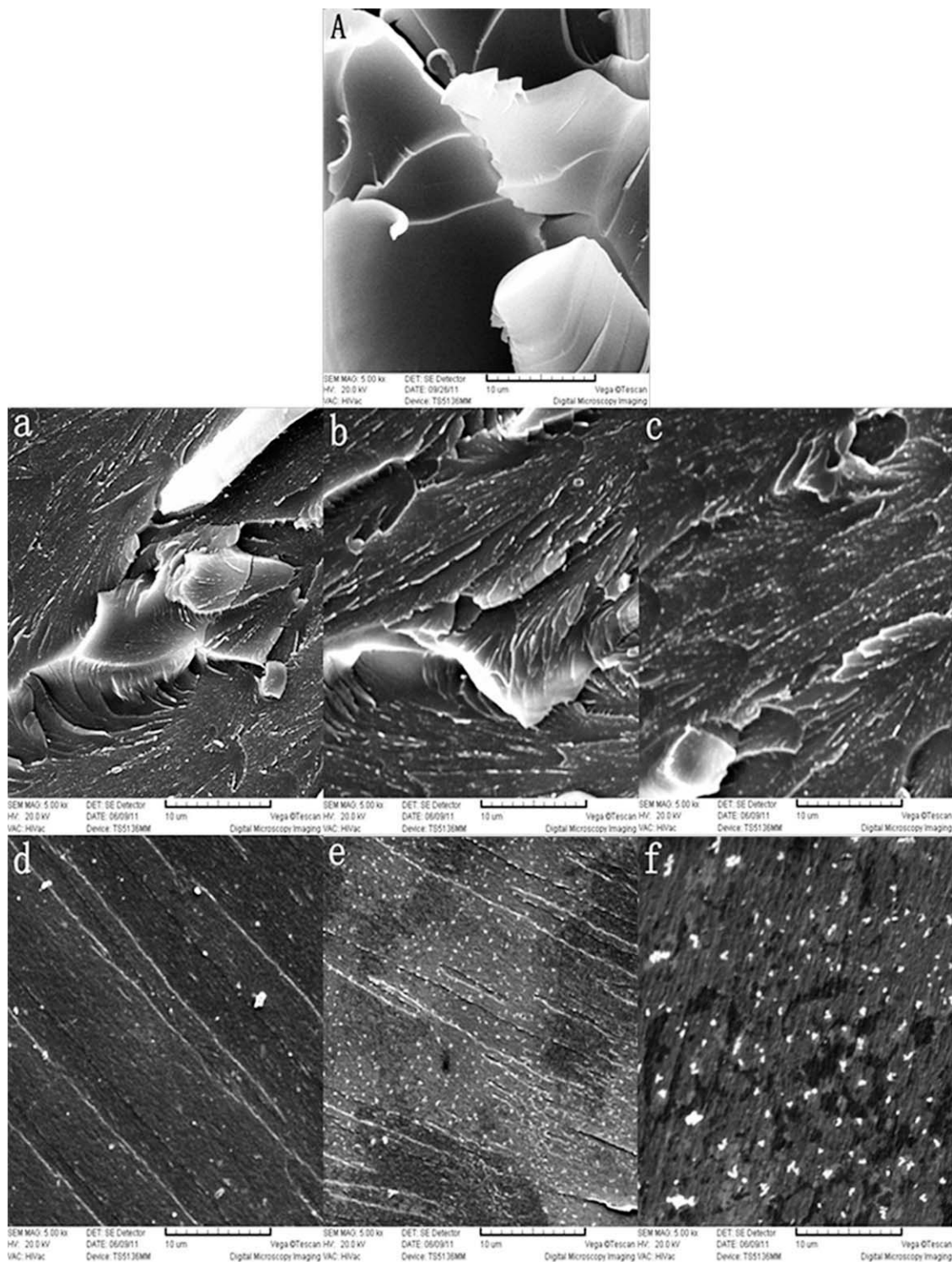
Figure 7. The fracture surfaces morphology of TGDDM with various content of PAA (A, a, b, c, d, e, and f correspond to 0, 5, 10, 15, 20, 25, and 30 phr PAA modified TGDDM/DDS, respectively).

density of the cured TGDDM decreased because of the adding of PAA, some groups that could be decomposed at relatively low temperature existed in the curing product. The following conclusions could be drawn. The char yield could be decreased if the

PAA acted only as a co-curing agent, and the formation of imide five-membered ring contributed to the increase of the char yield. As a result, only when the formation of five-membered imide ring can the thermal stability could be improved.

The limiting oxygen index (LOI) was calculated according to Van Krevelen and Hoftyzer method[29] [eq. (1)].

$$LOI = 17.5 + 0.4CR \qquad (1)$$

Here, CR stands for the char yield. The result was shown in Table III. On the basis of LOI values, the samples with PAA content of 20 and 25 phr can be classified as self-extinguishing materials (LOI > 27.0%). With some reluctance, unmodified TGDDM/DDS can be classified as a self-extinguishing resin, thus its flame resistance is less than that of the TGDDM/DDS modified with PAA of 25 phr.

Correlating the analysis of the DMA and TGA, it was likely that there were two different effects on structures of the cured TGDDM because of the adding of PAA, leading to the variation of thermal properties. Effect I: crosslinking density of the cured TGDDM decreased whether PAA acted as a modifier or co-curing agent. Effect II: chain segments from PAA with high ratio of benzene were introduced into the cured TGDDM whether PAA acted as a modifier or co-curing agent; additionally, a certain amount of PAI with a T_g of about 290°C came to exist in the crosslinking system when PAA acted both as a modifier and co-curing agent (PAA content was 20, 25, and 30 phr). Effect I will result in the decrease of T_g and thermal stability of the cured TGDDM. In contrast to Effect I, Effect II will improve T_g and thermal stability of the cured TGDDM. As a result, the viscoelasticity characteristic and thermal stability were determined by the combination of the two effects.

Fracture Surface Morphology

The properties of composites are related to the morphology of them. As a result, the fracture surfaces of the composites were examined by SEM to evaluate the phase morphologies of the blends. SEM images of PAA modified TGDDM/DDS composites were shown in Figure 7. There was only one continuous phase when the content of PAA was less than or equal to 20 phr. The PAI dispersed phase with no fixed shape came to exist when the PAA content were 25 and 30 phr. The size of the PAI dispersed phase when the PAA content was 30 phr was bigger than that of 25 phr. These could further certified that the reaction of thermal imidization of PAA. What is more, the roughness of the fracture surface reduced with the increasing PAA content. There were a mass of fragment-like structure in the fracture surface when the content of PAA was less than or equal to 15 phr, in contrast, There was hardly any fragment-like structure in the fracture surfaces when the content of PAA was more than or equal to 20 phr. The result implied that the toughness was improved with the increasing PAA content.

CONCLUSIONS

In this study, PAA was selected to modify TGDDM/DDS system, and the cure behavior and thermal property were investigated. The PAA modified TGDDM/DDS system was fully characterized using DSC, FTIR, DMA, TGA, and SEM.

1. PAA acted not only as a modifier but also as a catalyst and a co-curing agent during the process of the curing reaction. PAA acted as a catalyst because of the carboxyl and second-

ary amine groups in its molecular structure. When the content of PAA was less than or equal to 15 phr, almost all of the PAA took part in the curing reaction acting as a co-curing agent, when the PAA content was more than or equal to 20 phr, part of the PAA acted as a co-curing agent and the remaining PAA played a role of modifier.

2. T_g decreased firstly and then increased as the increase of PAA content. T_g was less than that of unmodified TGDDM/DDS (223°C) when PAA acted only as co-curing agents, while that was more than 223°C when PAA acted both as co-curing agents and modifier. The char yield would be decreased if the PAA acted only as a co-curing agent, and the formation of imide five-membered ring contributed to the increase of the char yield. As a result, only when the formation of imide five-membered ring can the thermal stability could be improved. Only one continuous phase was observed when the content of PAA was less than or equal to 20 phr. The PAI dispersed phase with no fixed shape came to exist when the PAA content were 25 and 30 phr. What is more, the toughness was improved with the increasing PAA content.

REFERENCES

1. Chen, P.; Wang, D. Z. Epoxy Resins and Its Application; Chemical Industrial Press: Beijing, **2004**; pp 220–424.

2. Potter, W. G. Epoxy resins; New York: Springer, **1970.**

3. MacQueen, R. C.; Granata, R. D. *Prog. Org. Coat.* **1996,** *28*, 97.

4. Kaya, I.; Dogan, F.; Gul, M. *J. Appl. Polym. Sci.* **2011,** *121*, 3211.

5. Wang, H. H.; Wang, H. W.; Zhou, G. Y. *Polym. Int.* **2011,** *60*, 557.

6. Lakshmi, A. S.; Narmadha, B.; Redd, B. *Polym. Degrad. Stab.* **2008,** *93*, 201.

7. Kornmann, X.; Thomann, R.; Mulhaupt, R.; Finter, J.; Berglund, L. A. *Polym. Eng. Sci.* **2002,** *42*, 1815.

8. Bagheri, R.; Pearson, R. A. *J. Mater. Sci.* **1996,** *31*, 3945.

9. Hwang, S.; Kim, M.; Kim, D.; Choe, Y.; Kim, W. *J. Chem. Eng. Jpn.* **2005,** *38*, 623.

10. Ma, A. J.; Chen, W. X.; Hou, Y. G.; Zhang, G. *Polym.-Plast. Technol.* **2010,** *49*, 916.

11. Bagheri, R.; Williams, M. A.; Pearson, R. A. *Polym. Eng. Sci.* **1997,** *37*, 245.

12. Bagheri, R.; Pearson, R. A. *Abstr. Pap. Am. Chem. Soc.* **1996,** *212*, 299.

13. Yee, A. F.; Peareon, R. A. *J. Mater. Sci.* **1986,** *21*, 2462.

14. Pearson, R. A.; Yee, A. F. *J. Mater. Sci.* **1986,** *21*, 2475.

15. Pearson, R. A.; Yee, A. F. *J. Mater. Sci.* **1989,** *24*, 2571.

16. Yu, Y. F.; Wang, M. H.; Gan, W. J.; Li, S. *J. Colloid Polym. Sci.* **2006,** *284*, 1185.

17. Gan, W. J.; Yu, Y. F.; Liu, X. Y.; Wang, M. H.; Li, S. *J. Colloid Polym. Sci.* **2009,** *287*, 23.

18. Gan, W. J.; Zhan, G. Z.; Wang, M. G.; Yu, Y. F.; Xu, Y. Z.; Li, S. *J. Colloid Polym. Sci.* **2007,** *285*, 1727.

19. Gan, W. J.; Xiong, W.; Yu, Y. F.; Li, S. J. *J. Appl. Polym. Sci.* **2009,** *114*, 3158.

20. Wu, X. G.; Cui, J.; Tang, X. L.; Yu, Y. F.; Li, S. *J. Chem. J. Chin. U* **2000,** *21*, 1305.

21. Jin, F. L.; Park, S. *J. Polym. Degrad. Stab.* **2007,** *92*, 509.

22. Jin, F. L.; Han, M.; Park, S. *J. Polym. Int.* **2006,** *55*, 1265.

23. Jin, F. L.; Park, S. J. *J. Polym. Sci. Polym. Phys.* **2006,** *44*, 3348.

24. Lee, S. H.; Choi, S. H.; Kim S. Y.; Youn, J. R. *J. Appl. Polym. Sci.* **2010,** *117*, 3170.

25. Yang, C. P.; Chen, R. S.; Wei, C. S. *Eur. Polym. J.* **2002,** *38*, 1721.

26. Yang, C. P.; Hsiao, S. H.; Hsiao, H. C. *J. Polym. Sci. Polym. Chem.* **1999,** *37*, 69.

27. Chen, H. M.; Lu R. G.; Liu, P.; Wang, H. Y.; Huang, T.; Huang, Z. Y.; Li, T. S. *J. Appl. Polym. Sci.* **2012,** *125*, 2854.

28. Hu, Y. M.; Wu, L. Y. Curing Agents; Chemical Industry Press: Beijing, **2004**. 2. 28.

29. Van-Krevelen, D. W.; Hoftyzer, P. J. Properties of Polymers; Elsevier: New York **1976**, p 529.