

The Effects of Polyamic Acid on Curing Behavior, Thermal Stability, and Mechanical Properties of Epoxy/DDS System

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ABSTRACT: A thermoplastic modification method was studied for the purpose of improving the toughness and heat resistance and decreasing the curing temperature of the cured epoxy/4, 4'-diaminodiphenyl sulfone resin system. A polyimide precursor-polyamic acid (PAA) was used as the modifier which can react with epoxy. The effects of PAA on curing temperature, thermal stability and mechanical properties were investigated. The initial curing temperature (T_i) of the resin with 5 wt % PAA decreased about 50°C. The onset temperature of thermal decomposition and 10 wt %-weight-loss temperature for the resin system containing 2 wt % PAA increased about 60°C and 15°C respectively. Besides, the value of impact toughness and plain strain fracture toughness for the modified epoxy resin increased ~ 190% and 55%, respectively. Those changes were attributed to the outstanding thermal and mechanical properties of polyimide, and more importantly to formation of semi-interpenetrating polymer networks composed by the epoxy network and linear PAA. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: polyamic acid; curing behavior; thermal stability; flexural properties; impact toughness; plane-strain fracture toughness; semi-interpenetrating polymer network structure

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INTRODUCTION

Epoxy resins have been widely used in diverse applications due to their excellent thermal and mechanical properties, including construction, electronics, adhesives, and coating.¹ When the applications of epoxy resins spread to advanced technical field such as aerospace industry, high performance resins were demanded. The applications of epoxy resin were often limited for its poor heat resistance inherent brittleness resulted from their cross-linked structure. Although epoxy resin could be toughened by introducing reactive liquid elastomers such as carboxyl-terminated butadiene acrylonitrile rubber (CTBN) or cross-linked elastomers,^{2,3} these routes generally lead to the loss of modulus and heat resistance, which will limit a number of high-performance applications of these resin systems.⁴ Therefore, exploitation of approaches for toughening the epoxy resins without sacrificing modulus and heat-resistance would enlarge of their applications.⁵

4,4'-diaminodiphenyl sulfone (DDS) is extensively used as curing agent for epoxy due to its low cost and the DDS-cured epoxies have higher decomposition temperature than epoxies cured by other curing agent such as dicyandiamide.⁶ However,

the curing temperature of epoxy/DDS system is also very high, which leads to higher requirements of the processing equipment and bring excess cost of manufacture. Furthermore, it would increase the interior stress of the product which would result in premature damage.

Polyimides are widely used for applications where high thermal stability, excellent mechanical properties and chemical resistance are required. Many researches using polyimides as modifier for epoxy resin systems have been carried out, which mainly to improve the thermal stability and toughness. Most of the studies mentioned above are based on physical blending of unreactive linear polyimides.⁷ In this study, we used polyamic acid as a modifier which is the precursor of polyimide with reactive group including amine and carboxyl group. The PAA was introduced into the resin system by stirring with epoxy and following prereaction with epoxy before the curing agent (DDS) was added. This method of using PAA has the advantages that the PAA and epoxy could be mixed to form a homogeneous solution by stirring and the semi-IPN structure could be formed by the entanglement of PAA chains and epoxy during the prereaction and curing reaction. The IPN or semi-IPN technique is

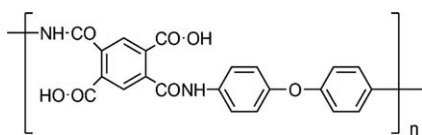


Figure 1. Chemical structure of polyamic acid.

one of the effective modifications for the epoxy resins with low fractions of thermoplastic.⁸ The existence of PAA exhibited excellent mechanical properties and noticeable thermal stability in the cured resin and was favorable to the curing rate of epoxy system due to the hydroxyl group which generated during the pre-reaction between PAA and epoxy.

Epoxy resins cured with PAA have been reported as the application of adhesion⁹ or with high percent of PAA solely to improve the heat-resistance¹⁰ which would lead to high cost. However, seldom studies investigated the effects of PAA on the properties of epoxy including curing behavior, thermal stability, and mechanical properties all together and made all the properties mentioned above reach an optimal point. In this study, it was noteworthy that the preparation of a new low-cost resin system would lower the curing temperature while the thermal stability was not affected, and improved the toughness while the modulus and other mechanical properties could be maintained or improved simultaneously; moreover, we studied the comprehensive effects of PAA on the epoxy resin. At last, we proposed the mechanism of lowering the curing temperature and toughening mechanism from a unique angle based on the predecessor's research.

EXPERIMENTAL

Materials

The epoxy resins used in this study were mixed by a liquid bisphenol-A diglycidyl ether (E-51) supplied by Shanghai Resin, and a solid bisphenol-A diglycidyl ether (CYD-011) supplied by BaLing petrochemical. The curing agent was 4, 4'-diaminodiphenyl sulphone (DDS) obtained from Sinopharm Chemical Reagent. Polyamic acid (PAA) which used as modifier in this study was provided by YueZi chemical and its chemical structure was as shown in Figure 1. All the reagents were utilized as supplied without further purification.

Sample Preparation

The E-51 and the polyamic acid were mixed together in various weight ratios, followed by stirring at room temperature for 1–2 h until a clear homogeneous solution was formed. Then the CYD-011 was added. The weight ratio of E-51 and CYD-011 was designed as 1 : 1. In each experiment, the E-51 and CYD-011 we added were 120 g altogether. The amount of DDS was 26.28 g and the amount of PAA were 0.6, 1.2, 1.8, 2.4, 3, and 6 g for different PAA content of 0.5, 1, 1.5, 2, 2.5, 5 wt %, respectively. The mixture of epoxy and PAA was stirred at 90°C in water bath for 2 h until a dark yellow solution was obtained. Then the curing agent was added into the mixture stirring until the DDS dissolved. The solution was poured into a PTFE mould and degassed in a vacuum oven at -0.1 Mpa. The obtained epoxy resin was cured as the curing schedule of 140°C/2 h+160°C/2 h+180°C/2 h+220°C/2 h.

Characterization

Fourier transform infrared spectroscopy (FTIR) spectra were performed with Nicolet 5700 with a resolution of 0.09 cm^{-1} . Differential scanning calorimetry (DSC) was conducted on a Perkin–Elmer Pyris 1 DSC under nitrogen circumstance. Thermal gravimetric analysis (TGA) was performed in nitrogen environment at a heating rate of $10^\circ\text{C}/\text{min}$. Flexural test was carried out at a crosshead speed of $2\text{ mm}/\text{min}$ according to ISO-178.¹¹ Impact property was determined by Charpy impact instrument according to ISO-179.¹² The plane-strain fracture toughness of the cured epoxy resin was evaluated through the K_{IC} (the critical-stress-intensity factor for the initiation of crack growth), which is indicative of the resistance of a material to fracture, determined from 3-point bend specimens according to ASTM D5045.¹³ The dynamic mechanical analysis was performed on a Netzsch DMA 242 in the bending mode with a frequency of 1 Hz and at a heating rate of $5^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Pre-reaction of PAA and Epoxy

To prepare a series of epoxy resins modified by PAA, the epoxy and PAA were mixed in water bath under 90°C for 2 h. The PAA has reactive functional groups including primary amino, secondary amide, and carbonyl which could trigger the ring-open reaction of epoxy. The potential reaction mechanism at low temperature has been proposed for the PAA/Epoxy system as shown in Figure 2.¹⁴ In the low temperature regime, it has the possibility that the epoxy ring-open reaction occurred via

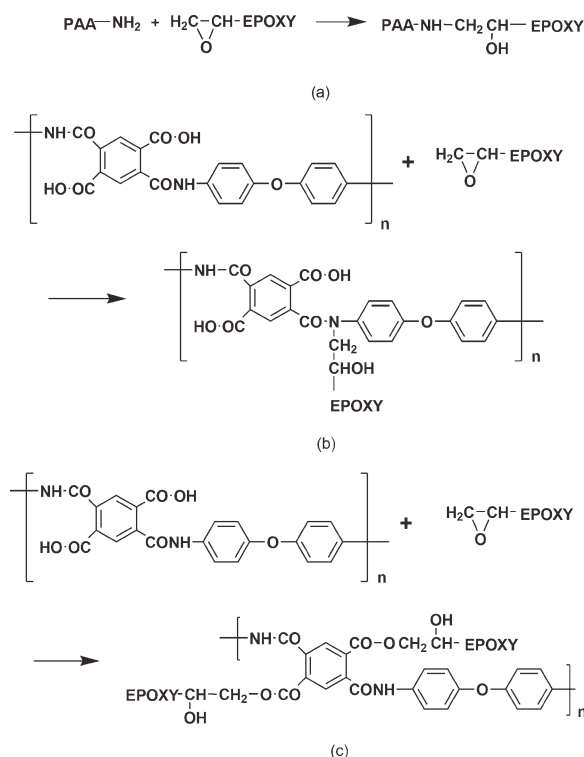


Figure 2. Potential reaction mechanisms: (a) primary amino group-epoxy reaction, (b) secondary amide group-epoxy reaction, (c) Carboxyl group-epoxy reaction.

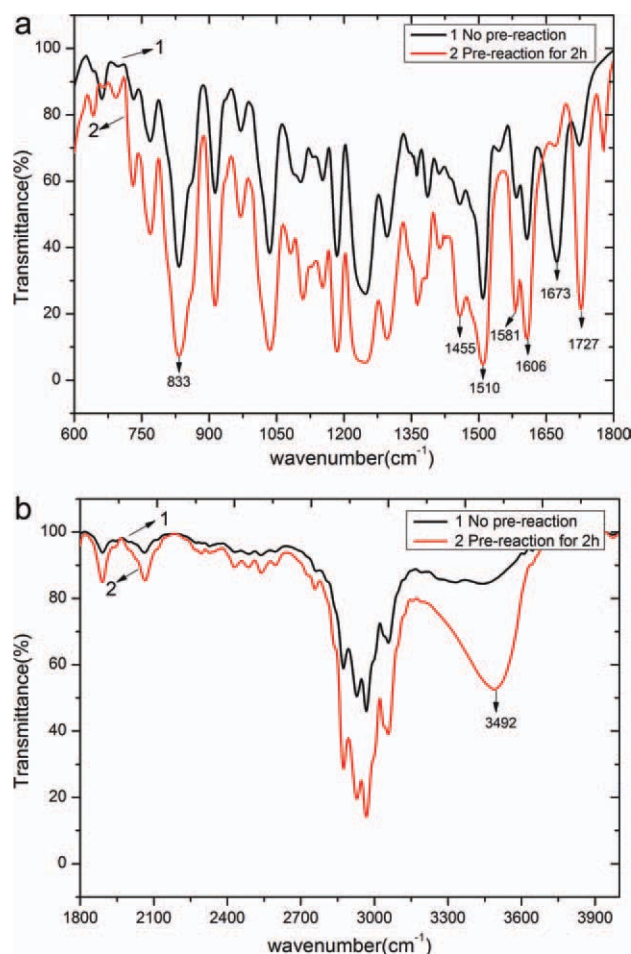


Figure 3. The FTIR spectrum of PAA/Epoxy system before and after pre-reaction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the reaction between epoxy group and primary, secondary amides, or carboxylic groups of polyamic acid.

The reaction mechanism proposed above can be verified by FTIR spectrum as shown in Figure 3 which show the FTIR spectra of Epoxy/PAA mixture before and after pre-reaction for 2 h. The absorption of 1455 cm^{-1} , 1581 cm^{-1} , and 1606 cm^{-1} are attributed to the stretching vibration of benzene skeleton. In this study, the absorption at 1606 cm^{-1} was taken as the reference band when comparing with the variation of other chemical groups for the good stability of benzene group during the pre-reaction. After pre-reaction both of the values of absorbance at 833 cm^{-1} (characteristic absorption for antisymmetric stretching vibration of epoxy ring skeleton) dividing the absorbance at 1606 cm^{-1} ($A_{833\text{cm}^{-1}}/A_{1606\text{cm}^{-1}}$) and 1510 cm^{-1} (absorption for bending vibration of secondary amine group $-\text{NH}$) dividing the absorbance at 1606 cm^{-1} ($A_{1510\text{cm}^{-1}}/A_{1606\text{cm}^{-1}}$) after pre-reaction all decrease indicating the consumption of secondary amine group and epoxy group. The consumption of carboxyl group can be proved by the almost disappearance of the absorption at 1673 cm^{-1} (absorption for stretching vibration of $\text{C}=\text{O}$ in carboxyl group) and the show up of the absorption at 1727 cm^{-1}

(absorption for stretching vibration of $\text{C}=\text{O}$ in ester group). In Figure 3(b), it can be observed that the characteristic band corresponding to hydroxyl group (3492 cm^{-1}). Its broad range is an evidence of the existence of a great variety of chemical compounds that favor the formation of hydrogen bonds.¹⁵ (a) FTIR spectrum in the $600\text{--}1800\text{ cm}^{-1}$; (b) FTIR spectrum in the $1800\text{--}4000\text{ cm}^{-1}$.

Curing Behavior of Epoxy/DDS System

Information obtained from DSC measurements can be related to the curing behavior of resin system. The curing reaction of the epoxy/DDS resin systems containing different PAA weight ratio was investigated by DSC at the heating rate of $10^\circ\text{C}/\text{min}$ as shown in Figure 4.

Normally, the epoxy resin system with the curing temperature up to 130°C can be classified as high temperature curing system which would increase the interior stress of the sample and even lead to premature damage if that could be done, although high curing temperature could bring higher heat-resistance to the products.⁶ Therefore, many attempts had been made to decrease the curing temperature of epoxy/DDS system while the heat-resistance is not affected.

In this article, the PAA was added into epoxy resin and followed by the procedure of pre-reaction. Then the DDS was added as curing agent. Figure 4 shows the DSC thermograms of PAA/E51/CYD011/DDS samples with different weight ratios of PAA while the initial curing temperature T_b , peak curing temperature T_p and the final curing temperature T_f of all the samples are summarized in Table I.

As shown in Figure 4, the curing temperature of epoxy/DDS system decrease remarkably with an increase in the PAA content. A remarkable drop of the onset curing temperature from 194.5°C to 124.5°C is achieved by adding 10 wt % PAA. This behavior can be related to the presence of the hydroxyl in the epoxy resin generated during the pre-reaction which can be seen in Figures 2 and 3. According to autocatalytic model for the curing of epoxy,¹⁶ the hydroxyl group generated by the ring-open reaction between epoxy group and primary and

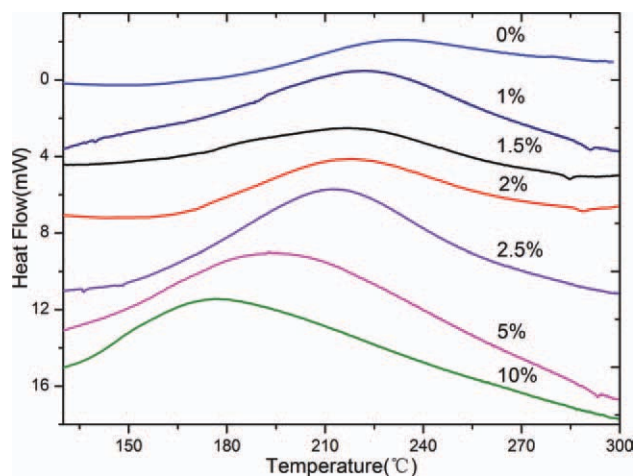


Figure 4. DSC curves for PAA/E51/CYD011/DDS system with different weight ratios of PAA at $10^\circ\text{C}/\text{min}$.

Table I. Effects of PAA on T_b , T_p , T_f and ΔH for Samples with Different Weight Ratio of PAA

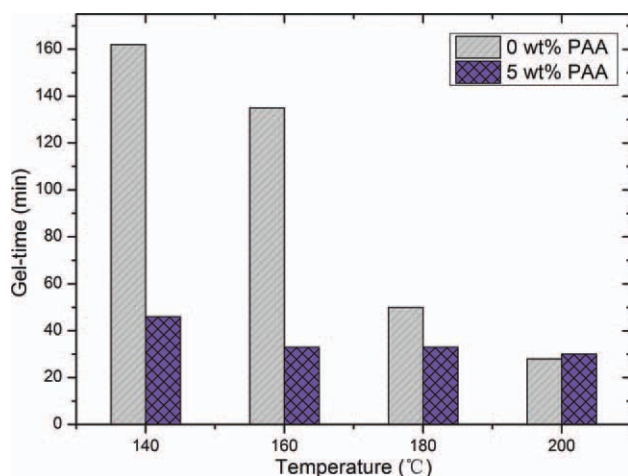
PAA content (%)	$T_b/^\circ\text{C}$	$T_p/^\circ\text{C}$	$T_f/^\circ\text{C}$	ΔH (J/g)
0	194.5	231.2	284.4	-115.8
1	183.1	222.8	283.9	-121.3
1.5	167.1	217.8	283.2	-118.6
2	154.9	217.7	259.8	-126.5
2.5	146.5	214.1	261.4	-203.5
5	138.8	199.3	255.9	-201.2
10	124.5	182.4	255.6	-193.3

secondary amine group can be taken as a kind of catalyst to the resin system. Thus, in this study, the formed hydroxyl groups well accelerated the following curing reaction occurring between epoxy and DDS leading to the decrease of the curing temperature.

As we can see from Table I, the T_b , T_p , T_f all decreased with the increase of PAA content owing to the increase of the hydroxyl groups which depend on the concentration of PAA. The heat of exotherm for the curing process which is the value of the area integrated from T_i to T_f increase with the raise of the PAA content. The increase of the heat of exotherm can be attributed to the decrease of the T_i and the increase of the curing degree which result from the favorable effects of PAA on epoxy resin.

Beside of the descent of curing temperature with the increase of PAA content, the gel-time of the resin systems drop abruptly at the same time, as shown in Figure 5, especially before 180°C , which indicate the favorable effect of PAA on the curing rate to epoxy resin. However, it's disadvantageous to the operability of the resin if the gel-time was too short which would impose more restrictions on the application of the resin system. Consequently, the content of PAA would better be less than 5%.

The value of activation energy of the thermal reaction associated with the rates of chemical reaction, which was studied by DSC

**Figure 5.** Effect of PAA on the gel-time of epoxy/DDS resin system. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]**Table II.** E_a of Epoxy Resin Systems Containing PAA Obtained by Kissinger's Analysis

PAA content (wt %)	$d[\ln(\beta/T_p^2)]/d(1/T_p)$	E_a (KJ/mol)
0	-7.55368	62.8013
1	-7.30608	60.7428
2.5	-5.67862	47.2121
5	-5.55421	46.1777

at different heating rates (5, 10, 15, and $20^\circ\text{C}/\text{min}$) between 50 and 300°C . The dynamic analysis of DSC is based on the Kissinger¹⁷

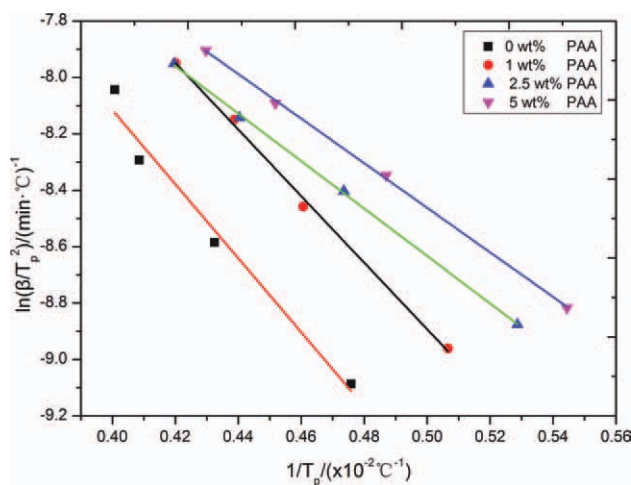
$$E_a\beta(RT_p^2) = Ae^{-E_a/RT_p} \quad (1)$$

where E_a is the activation energy, β is the heating rate, R is the gas constant, T_p is the peak curing temperature and A is the pre-exponential factor. By taking the logarithm of eq. (1), we obtain the Kissinger equation:

$$-\ln(\beta/T_p^2) = -\ln(AR/E_a) + (1/T_p)(E_a/R) \quad (2)$$

From eq. (2), the activation energy E_a can be obtained from multiplying R by the value of $d[\ln(\beta/T_p^2)]/d(1/T_p)$ which can be deduced from the plot of $d[\ln(\beta/T_p^2)]/d(1/T_p)$ versus $1/T_p$. All the values of E_a for the epoxy resin with different PAA content are listed in Table II. From Table II, it can be seen that the E_a value of epoxy resin systems decrease with the increase of PAA content indicating the accelerating effects of PAA to epoxy resin/DDS system. The plots of $\ln(\beta/T_p^2)$ against $1/T_p$ for resin systems with different PAA content show in Figure 6.

The structure of modified epoxy resin after cured is proposed in Figure 7. During the pre-reaction, the epoxy linked to PAA chains by chemical reaction which can be seen in Figure 7(a) and the schematic diagram of pre-reaction is demonstrated in Figure 7(b). After the addition of DDS, the curing reaction

**Figure 6.** Plots of $\ln(\beta/T_p^2)$ versus $1/T_p$ for resin systems with different PAA content. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

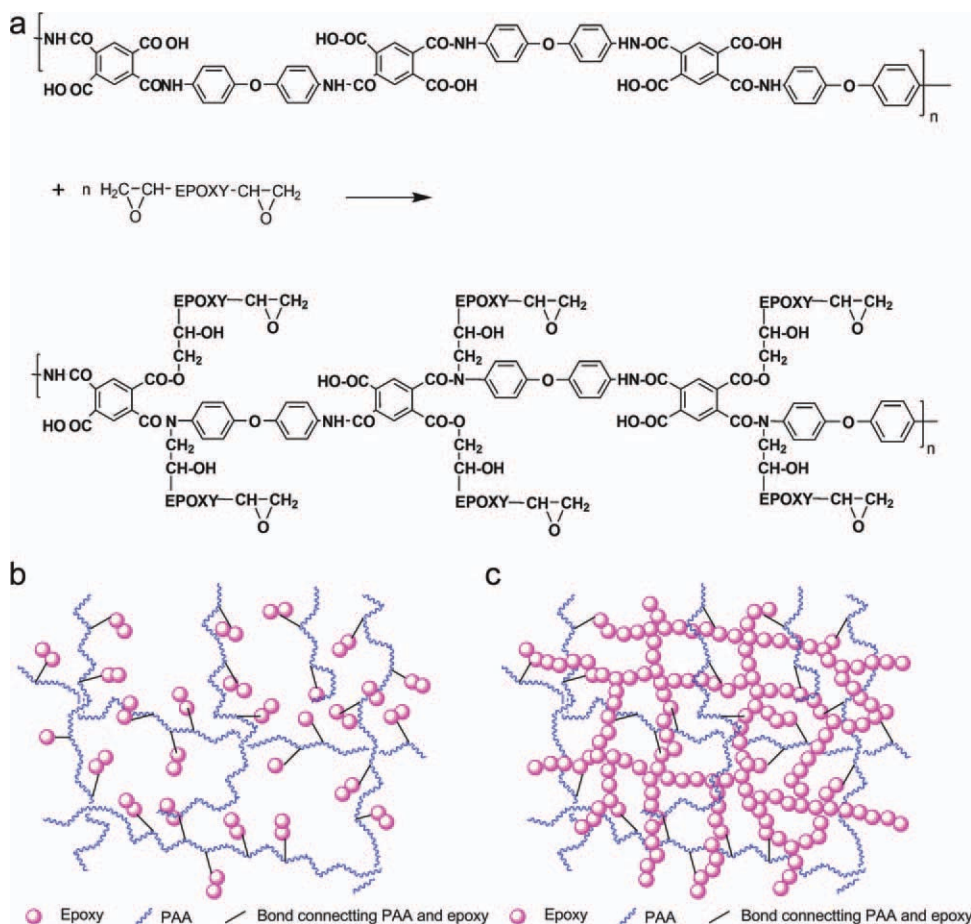


Figure 7. The reaction mechanism of forming semi-IPN structure in epoxy resins modified by PAA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

between the epoxy group and DDS occurs and the formation of a three dimensions cross-linking network structure forms as seen in Figure 7(c). (a) Reaction between epoxy and PAA; (b)

The structure after pre-reaction; (c) The structure after fully cured.

Thermal Stability Analysis

Thermal stability of the resin systems with different weight ratios of PAA after cured is investigated by TGA. As shown in Figure 8, the epoxy resin without adding PAA decompose in two distinct steps starting tardily at about 280°C for the first step and 500–540°C for the second step. The 10% weight loss of neat epoxy resin is 359.6°C and the residual percentage after thermal analysis to 600°C is only 6.2% (in Table III). The degradation profiles of resin systems containing different weight ratios of PAA all also show two steps. However, the onset of the first stage of weight loss is approximately at 350°C increasing

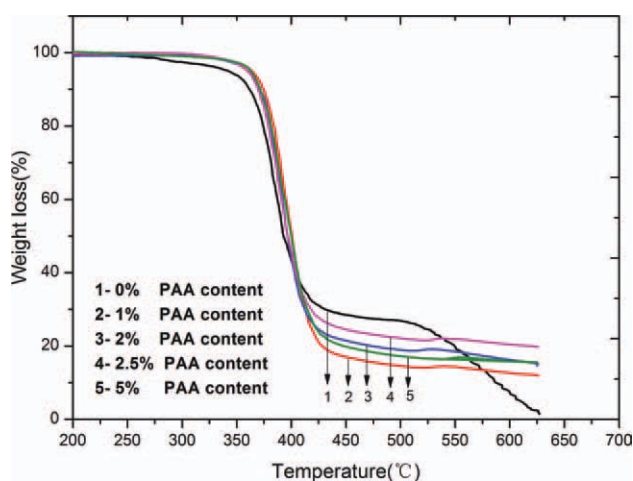


Figure 8. TGA curves of neat epoxy and epoxy resin modified by PAA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. TGA Analysis of Resin Systems Modified by Different Amount of PAA

PAA content (%)	0	1	2	2.5	5
Onset temperature (°C)	280.4	352.6	343.2	338.7	352.9
10% weight loss temperature (°C)	359.6	375.8	374.5	370.0	373.1
residue percentage of 600°C (%)	6.2	13.5	18.1	20.9	15.8

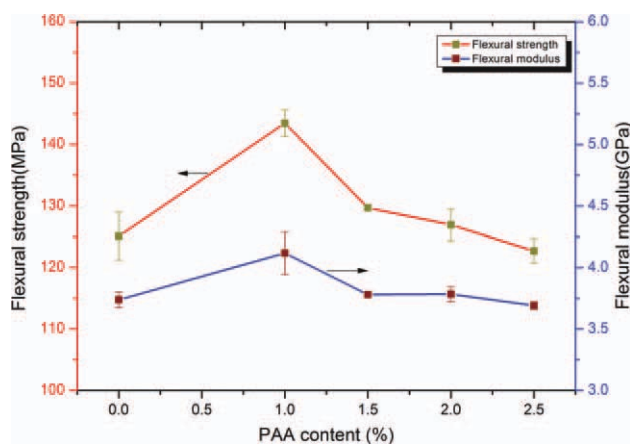


Figure 9. Effects of PAA on the Flexural strength and flexural modulus. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nearly 70°C compared with neat epoxy resin, and particularly the second stage of weight loss is severely restrained only showing a slight slope after 525°C. The 10%-weight-loss of resin systems scatter between 370–375°C which increases about 10°C and the residual percentage after thermal analysis to 600°C increases to 13.5%–20.9%.

The mechanism of the improvement of thermal stability can be ascribed to the formation of semi-IPN structure in the cured resin system which would be discussed in section 3.5. Furthermore, the introduction of PAA containing high density of benzene ring which would contribute to the heat resistance of material is another reason for the enhancement of the thermal stability.

Effect of PAA on Mechanical Properties

The most common approach to toughen brittle epoxy resin is introducing a toughening agent into the epoxy network, such as epoxidized natural rubber,¹⁸ polyetherimide,¹⁹ Poly(ether ether ketone)²⁰ etc., which have been reported to improve the tough-

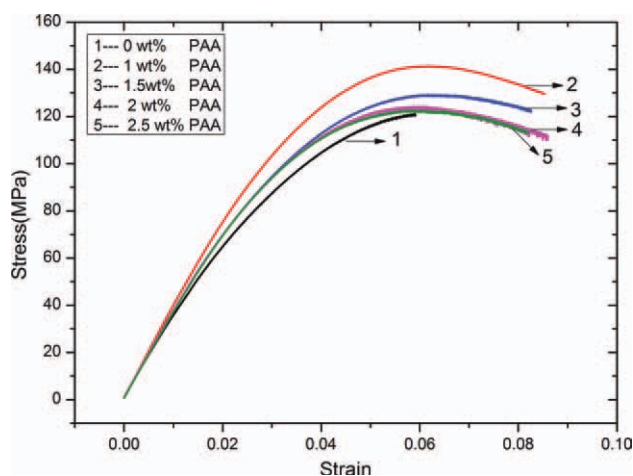


Figure 10. Flexural stress–strain relationship of resin casting body for different weight ratios of PAA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

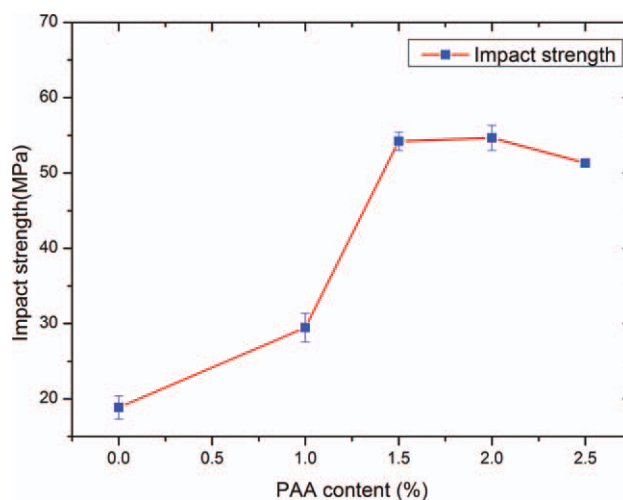


Figure 11. Effect of PAA on impact strength. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ness of epoxy resin. Modification to the epoxy structure is also an effective method to improve the mechanical properties including chemical modification from a given rigid epoxy backbone to a more flexible backbone structure, increase of epoxy monomer molecular weight or decrease of the crosslink density of a cured resin.^{21–23} However, the above-mentioned toughening methods might also lead to significant reduction of modulus and tensile strength, which were undesirable for engineering applications.

In this study, the flexural properties of resin casting body were examined and the results can be seen in Figure 9. It can be seen that the flexural strength and modulus increase around 14.7% and 10.1%, respectively when the addition of PAA is 1 wt %.

Although the increase of flexural strength and modulus are not so prominent, the flexural strain of the casting body modified by PAA are remarkably enhanced when compared with the neat epoxy resin, which can be seen in Figure 10.

The appearance of yield stress of the resin systems after adding PAA indicates the enhancement of toughness for the material. During the test, the rupture is not observed in one or two samples after yield point while the crosshead rate is same with the neat epoxy specimens (2 mm/min). Those unfractured samples exhibit elasticity to a certain extent which is especially significant to brittle material indicating the excellent flexural property of the resin after modified.

The impact strength test can provide information on the impact toughness of cured resin. Figure 11 shows the results of impact measurement of the cured resins containing different weight ratios of PAA.

The impact strength of resin systems containing PAA substantially increases by around 190% due to the presence of PAA in the epoxy network after cured which could reduce the crosslink density as a result of the dilution effect of the uncross-linked thermal plastic chains²⁴ and maintain the strength by forming semi-IPN structure which would be discussed in section 3.5.

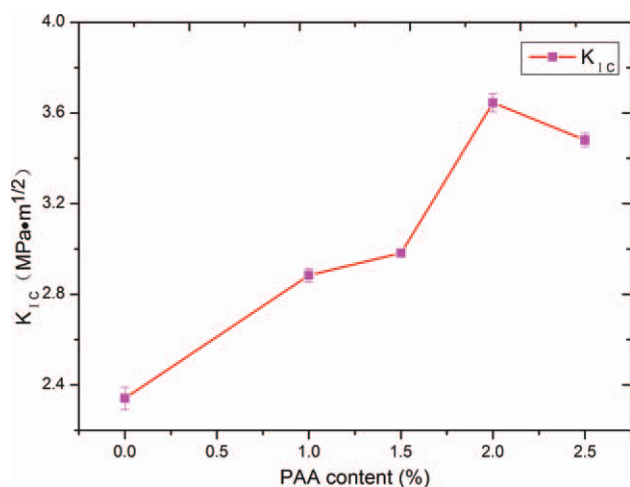


Figure 12. Effect of PAA on plane-strain fracture toughness. [Color figure can be viewed in the online issue, which is available at www.onlinelibrary.com.]

The plane-strain fracture toughness of cured resins modified with PAA is shown in Figure 12. The value of K_{IC} which represents the fracture toughness gradually increases with the PAA content up to 2 wt % and slightly decreases when PAA content is 2.5 wt %. The fracture toughness of the cured resin containing 2 wt % PAA increases about 55.7% compared with the unmodified resin, which shows the same trend with impact toughness.

The fractured surface for the cured epoxy resins containing 0, 1.5, 2 wt % PAA after impact toughness testing were observed with a SEM. The specimens were etched by THF for 10 h. The results are shown in Figure 13. It can be seen that the fractured surface of the resin unmodified is smooth and the crack is rare and unidirectional, which exhibits the characteristic of brittle fracture. Differently, the crack density on the fracture surface of epoxy resin containing 1.5 wt % PAA is much greater than that of unmodified resin and the cracks-branching is also observed which can absorb energy during the impact damage. For the resin containing 2 wt % PAA its fracture surface is rough and ridgy. This morphology originates from the crack blunting based on plastic shear deformation of matrix. (a) The sample with 0 wt % PAA; (b) The sample with 1.5 wt % content; (c) The sample with 2% content.

From the $\tan \delta$ -peak change of dynamic mechanical analysis in Figure 14, it can be seen that the glass transition temperature (T_g) of the cured resin with the PAA content of 1 and 2 wt % decreases slightly when compared with the neat epoxy resin, which probably results from the dilution effect of the PAA chains into the epoxy networks and coincides with the changes of mechanical properties. Moreover, because only one $\tan \delta$ -peak appears for the resins containing 1 wt % and 2 wt % vPAA, the miscibility between the epoxy and PAA domains can be confirmed.

Toughening Mechanism of PAA-Modified Epoxy

The formation of a semi-IPN structure (Figure 7) is assumed to be the principle mechanism of the PAA-modification for the improved toughness of the cured resins containing PAA.

Most of the former studies about the toughening mechanism of epoxy modified by thermoplastic concentrated on physical blending and phase-separation.^{7,24,25} On the basis of the pre-reaction and the special chemical groups and the high molecular weight of PAA, the mechanism in this study we put forward is as follows which is not only the semi-IPN structure but also containing chemical bond connecting the PAA and epoxy network.

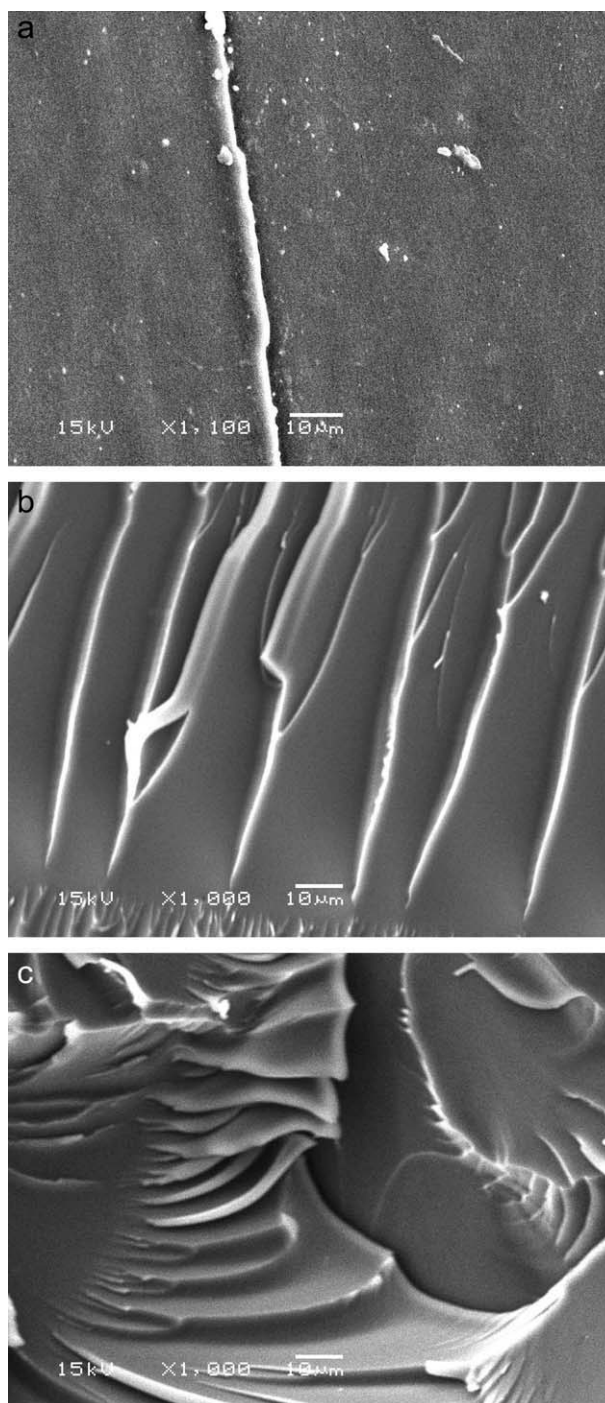


Figure 13. Scanning electron micrographs of the fractured surfaces for the cured epoxy resins with different PAA contents.

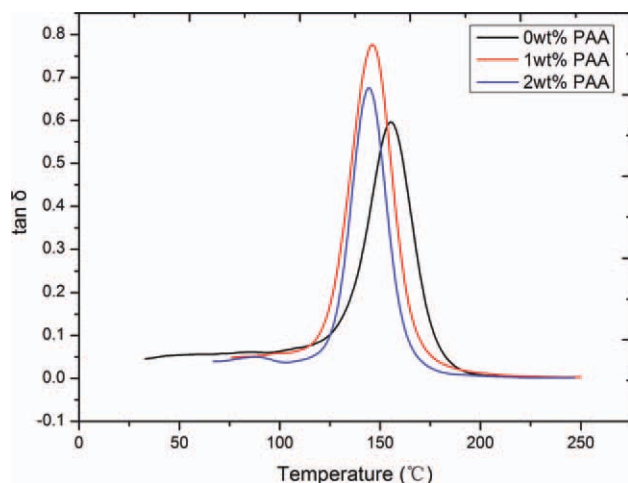


Figure 14. The $\tan \delta$ change of resins containing 1 and 2 wt % PAA. [Color figure can be viewed in the online issue, which is available at www.onlinelibrary.com.]

Because of the high molecular weight of the PAA we used, the molecular chains of PAA could entangle with the epoxy during the stirring until a homogeneous mixture formed. Then the reactions between amine, carboxyl groups in PAA and epoxy groups would take place when the mixtures was bathed in 90°C water to form the structure as shown in Figure 7(b), which can be proved by the FTIR (Figure 2). After the DDS is added, the reaction between the epoxy groups in structure (b) and the amine groups in DDS occurs to form a three-dimensions network structure as shown in Figure 7(c). Finally, in the cured resins modified by PAA, there is a complicated network consisting of the cured epoxy network and the tangled PAA/epoxy chains which form a semi-IPN structure as diagrammatized in Figure 7. The impact and fracture toughness are improved due to the reduction of the density of cross-linking which can decrease the brittleness for one thing, furthermore the formation of semi-IPN structure which could absorb impact energy to prevent the occurrence of damage.

CONCLUSIONS

In the epoxy resin modified with PAA, the generating of hydroxyl group during the prereaction between epoxy and PAA has effects on the curing temperature of the modified resin. Meanwhile, the formation of semi-IPN structure for the presence of PAA chains in the cured epoxy resins improves the heat resistance and mechanical properties.

For the epoxy resin with PAA as a modifier, the curing temperature and the gel-time decrease with the increase of PAA attributed to the favorable effect of hydroxyl group which generated in the prereaction. The improvement of heat resistance is ascribed to the introduction of PAA chains whose benzene ring density is higher than epoxy and partly to the presence of PAA chains in the cured epoxy which can constrain the second decomposition. The flexural properties analysis shows that the bending-resistance capacity of the resin modified by PAA increased. Impact performance test and plain-strain fracture

toughness test show that incorporation of PAA enhances the impact toughness substantially and the resistance to fracture. The toughness improvement and the good compatibility between epoxy and PAA can be proved by the SEM and DMA, respectively.

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