

# Amino-Capped Aniline Trimer/Epoxy Resin Intercrosslinked Networks

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Received 4 January 2005; accepted 29 July 2005

DOI 10.1002/app.23607

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** An amino-capped aniline trimer (ACAT) in emeraldine base form was reacted with an epoxy resin to produce intercrosslinked networks. The quinoid structure of the ACAT was able to crosslink on curing and, thus, led to a very high glass-transition temperature of the cured resin. The epoxy resin cured with the ACAT showed superior thermal properties over the resins cured with *p*-phenylenediamine and 4,4'-diaminodiphenylamine. These findings

were based on differential scanning calorimetry, IR, dynamic mechanical analysis, and thermogravimetric analysis data. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 222–226, 2006

**Key words:** crosslinking; glass transition; networks; resins; thermal properties

## INTRODUCTION

Polyanilines (PANIs) and oligoanilines have been widely investigated as organic semiconductors, battery electrodes, and corrosion inhibitors.<sup>1–12</sup> The oligomers are superior to high-molecular-weight PANIs in many aspects; for example, they have better solubility and fewer structural defects. Moreover, the electroactivity of the oligomers is comparable with that of the polymer. It is particularly surprising that the effective conjugation length in PANI rarely exceeds three aniline units.<sup>13</sup>

Aniline trimers have been useful models for PANI.<sup>11,13</sup> They are useful materials in their own right for such PANI-esque applications as corrosion inhibition,<sup>14,15</sup> sensing materials,<sup>16</sup> and catalysts in oxidation reactions.<sup>17</sup> It has been demonstrated that the aniline trimer is even more effective in corrosion inhibition than PANI,<sup>9,10</sup> and blends of aniline trimers and epoxy resins have also been shown effective in corrosion inhibition. Experimental and computational methods have been performed to investigate the electronic structure and thermodynamic properties of aniline trimers in the use of corrosion inhibition.

The terminal amino group of the aniline trimer is reactive toward epoxy resins. However, little attention has been paid to the behavior of the aniline trimer in the curing of epoxy resins. This study was devoted to

the intercrosslinked network of amino-capped aniline trimer (ACAT)/epoxy resin. The microstructure and thermal properties were investigated, and *p*-phenylenediamine (PDA)/epoxy resin and 4,4'-diaminodiphenylamine (DADPA)/epoxy resin systems were studied for comparison.

## EXPERIMENTAL

### Materials

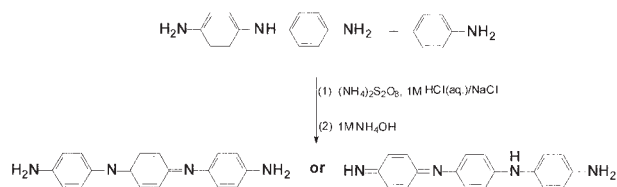
Aniline was purchased from Beijing Wushi Fine Chemicals Co. and was distilled under reduced pressure before use. PDA (Beijing Jinglong Chemical Reagent Co.) was recrystallized from ethanol. 4,4'-Diaminodiphenylamine sulfate was purchased from Fluka Co.; it was converted to DADPA by treatment with ammonium hydroxide. Analytical-reagent-grade ammonium persulfate (Beijing Yili Fine Chemicals Co.) was used as the oxidant. Analytical-reagent-grade *N*-methyl-2-pyrrolidone and hydrochloric acid were from Beijing Yili Fine Chemicals and were used as received.

The epoxy resin used in this study was diglycidyl ether of bisphenol A (DGEBA; Epon-828, Shell Co.).

### Synthesis of the ACAT

The ACAT in emeraldine base (EB) form was synthesized according to the method of Wei et al.<sup>18</sup> The process is illustrated in Scheme 1. In the typical procedure for the synthesis, 7.40 g (0.796 mol) of freshly distilled aniline and 23.65 g (0.796 mol) of 4,4'-diami-

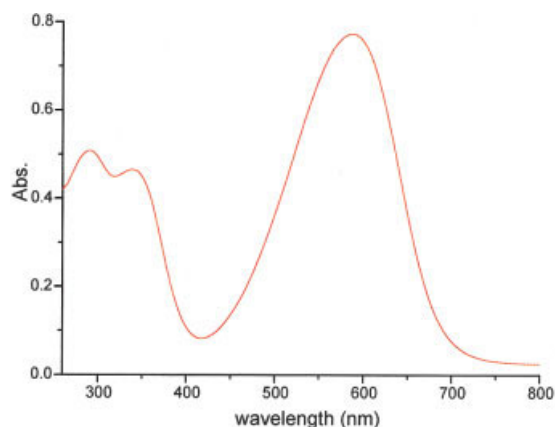
Correspondence to: T. Zhao (tzhao@infoc3.icas.ac.cn).



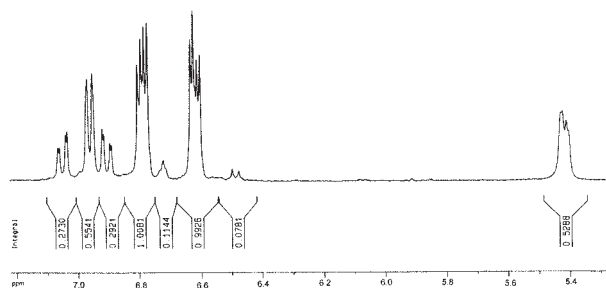
**Scheme 1** Synthesis of the ACAT in EB form.

nodiphenylamine sulfate were dissolved in 800 mL of 1M aqueous HCl containing 75 g of NaCl, and the solution was cooled to below  $-5^\circ\text{C}$ . A solution of 18 g (0.789 mol) ammonium persulfate in 200 mL of 1M aqueous HCl precooled to  $-5^\circ\text{C}$  was added dropwise into the previous solution. The reaction was maintained at  $-5^\circ\text{C}$  for 1 h. The purple precipitate was collected by filtration under reduced pressure and washed with 400 mL of 1M aqueous HCl precooled to below  $0^\circ\text{C}$ . The product was then treated with 100 mL of 10% aqueous ammonia at room temperature for 3 h and thoroughly washed with distilled water. When the product was filtered and dried under dynamic vacuum at  $50^\circ\text{C}$  overnight, a purple powder of the ACAT was obtained (overall yield 22%). The electronic spectrum (Fig. 1) and the NMR spectrum (Fig. 2) were consistent with that given in the literature.<sup>18</sup>

In the  $^1\text{H-NMR}$  spectrum of the ACAT in  $\text{DMSO-}d_6$  with a tetramethylsilane standard, the signals for the ring protons appeared in the range 6.5–7.1 ppm, which were superposed to the signal of the B—NH—B proton. The signal for the terminal B—NH<sub>2</sub> protons appeared at 5.4 ppm. The ratio of the integrate signal of the terminal —NH<sub>2</sub> protons to the ring protons indicated that the ACAT was a mixture of the tau-tomers:



**Figure 1** Ultraviolet-visible spectrum for the ACAT in EB form. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 2**  $^1\text{H-NMR}$  spectrum of the ACAT in EB form.

### Preparation of the cured resins

The ACAT was mixed with Epon-828 at a weight ratio of 0.38:1 (the molar ratio of terminal amino groups to epoxy groups was 1:2) at a temperature between 60 and  $80^\circ\text{C}$ . Then the mixture was poured into a mold and deaerated under dynamic vacuum at  $60\text{--}80^\circ\text{C}$ . The curing schedule was  $80^\circ\text{C}$  for 2 h,  $120^\circ\text{C}$  for 2 h,  $160^\circ\text{C}$  for 2 h, and  $180^\circ\text{C}$  for 4 h.

Epoxy thermosets with PDA and DADPA as curing agents were prepared with the same procedure. For the preparation of the cured resins, the molar ratios of amino groups to epoxy groups were exactly controlled (Table I).

### Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Bluke Tensor 27 FTIR spectrophotometer. Electronic spectra were recorded on a Shimadzu 1601 PC UV spectrophotometer. Thermogravimetric analysis (TGA) was carried out with a Netzsch STA 409 PC integrated thermal analyzer at a heating rate of  $10^\circ\text{C}/\text{min}$ . A differential scanning calorimeter (Mettler-Toledo DSC822e) was used to obtain the thermograms. Dynamic mechanical analysis (DMA) was performed on a Netzsch DMA 242 C dynamic mechanical analyzer. The programmed heating rate was  $5^\circ\text{C}/\text{min}$ .

## RESULTS AND DISCUSSION

### Glass transition of the epoxy resins cured with amino-capped aniline oligomers

Amine-capped aniline oligomers can be seen as aromatic diamines. It is known that the reaction of an epoxy resin with a diamine gives an intercrosslinked network, as illustrated in Scheme 2.

The glass-transition temperature ( $T_g$ ) of the cured epoxy resin is dependent on the network structure: a curing agent with stiffer and shorter skeleton will give rise to a higher  $T_g$ . DMA diagrams of the epoxy resins cured with amino-capped aniline oligomers are shown in Figure 3. PDA is the smallest member of amino-capped aniline oligomers. Therefore, the resin

**TABLE I**  
 $T_g$  of the Cured Epoxy Resins<sup>a</sup>

Curing resin	Curing agent	Structure	N—H functionality	$T_g$ (°C) <sup>b</sup>
1	PDA		4 <sup>c</sup>	172
2	DADPA		4 <sup>c</sup>	158
3	DADPA		5 <sup>c</sup>	122
4	ACAT		4 <sup>c</sup>	207
5	ACAT		4 <sup>d</sup>	200

<sup>a</sup>Curing schedule: 80°C for 2 h, 120°C for 2 h, 160°C for 2 h, and 180°C for 4 h.

<sup>b</sup>The peak temperature of  $\tan \delta$  in the DMA diagram.

<sup>c</sup>Molar ratio of functional groups, epoxy group: N—H = 1:1.

<sup>d</sup>Molar ratio of functional groups, epoxy group: N—H = 1:0.8.

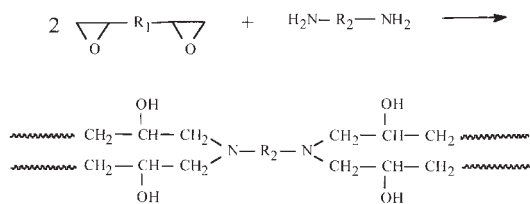
cured with PDA should have had the highest  $T_g$  value. It is understandable that cured resin 1 in Table I showed a higher  $T_g$  than that cured with the dimer (no. 2). The B—NH—B amino group of DADPA did not take part in the reaction with epoxy groups on curing. Accordingly, cured resin 3, in which this group was counted in the stoichiometric calculation, showed a  $T_g$  much lower than that of the cured resin 2.

It was to our surprise that the ACAT constructed intercrosslinked networks with the epoxy resin, which showed a  $T_g$  higher than the resin cured with PDA for about 30°, even if the proportion departed from the stoichiometric ratio. It is likely that the quinoid structure in the trimer played a great part in the network structure.

### ACAT/epoxy resin intercrosslinked network

Thermally induced crosslinking of PANI in EB form is known, and the mechanism for the quinoid crosslinking (Scheme 3) was illustrated recently by means of FTIR and solid-state NMR studies.<sup>19</sup>

The ACAT was similar to EB PANI in thermal crosslinking behavior, as shown by the differential scanning calorimetry (DSC) thermogram (Fig. 4), in which the endothermic peak at 81°C was attributed to the melting of the crystalline powder and the exother-

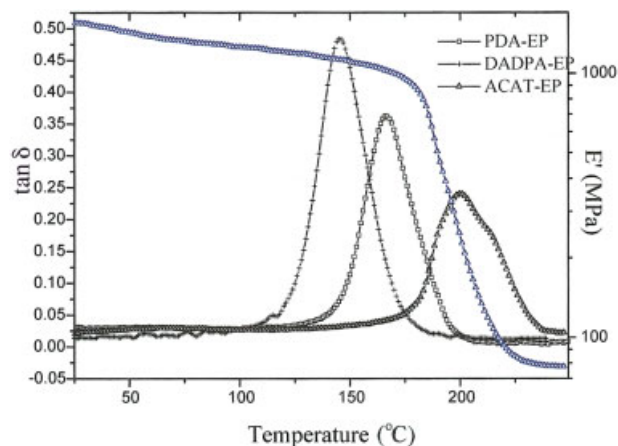


**Scheme 2** Crosslinking of the epoxy resin with diamine.

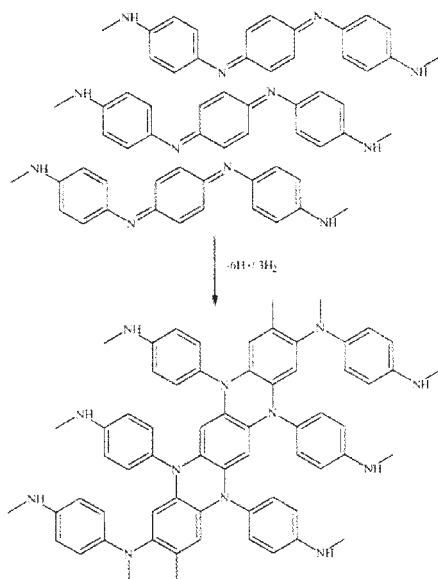
mic peak at 187°C was attributed to the quinoid crosslinking reactions (enthalpy = 43.7 kJ/mol).

The occurrence of quinoid crosslinking in the ACAT/epoxy resin intercrosslinked networks was confirmed by the reaction enthalpy. The enthalpy for the reaction of 1 mol of DGEBA with 0.5 mol of PDA was 158 kJ, whereas the enthalpy was 205 kJ for the reaction of 1 mol of DGEBA with 0.5 mol of ACAT (the corresponding DSC curves are illustrated in Fig. 4). The difference of 47 kJ was far beyond the experimental error. It was likely that, in the latter case, the enthalpy of the addition reaction of N—H groups to epoxy groups was superposed by that of the quinoid crosslinking.

Quinoid crosslinking in the ACAT/epoxy resin intercrosslinked networks was further supported by IR spectra. In the spectrum for ACAT [Fig. 5(a)], the band



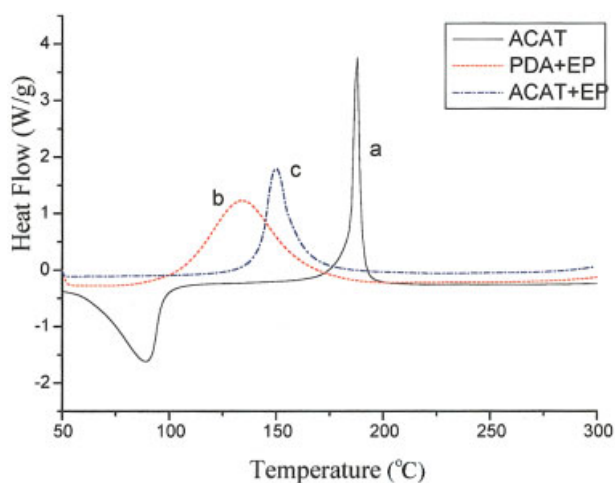
**Figure 3** DMA diagrams for the epoxy resins cured by PDA, DADPA, and ACAT in EB form. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



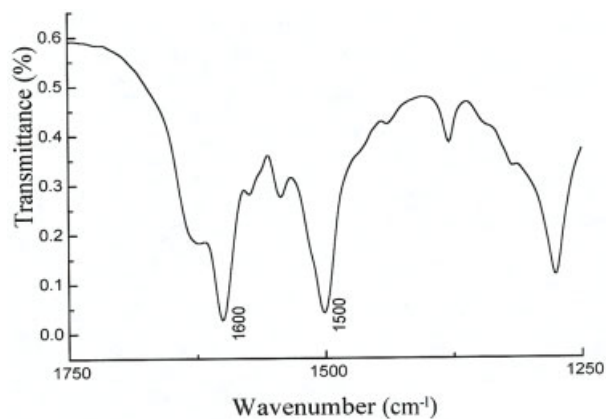
**Scheme 3** Mechanism of quinoid crosslinking.

at  $1500\text{ cm}^{-1}$  for benzenoid ring stretching and the band at  $1600\text{ cm}^{-1}$  for quinoid ring stretching were of similar intensity. In Figure 5(b), spectrum 1 is for the mixture of the ACAT and epoxy resin, and spectrum 2 is for the ACAT-cured epoxy resin. When these two spectra were compared, a significant reduction in the quinoid band on curing was observed. It is reasonable to suppose that the quinoid structure of ACAT was converted to a benzenoid structure according to Scheme 3 on curing of the epoxy resin.

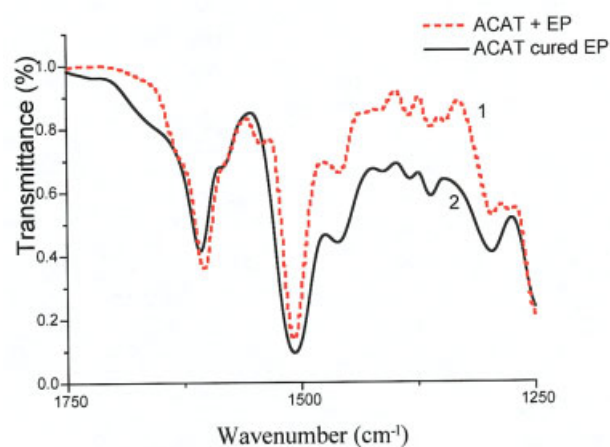
Therefore, we concluded that the interchain linkages in the ACAT/epoxy resin intercrosslinked network were due not only to the amino-to-epoxy addition but also to the quinoid crosslinking.



**Figure 4** DSC curves for (a) ACAT, (b) PDA plus EP, and (c) ACAT plus EP. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



(a)



(b)

**Figure 5** IR spectra for (a) ACAT and (b) (1) the mixture of ACAT and the epoxy resin and (2) the ACAT-cured epoxy resin. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

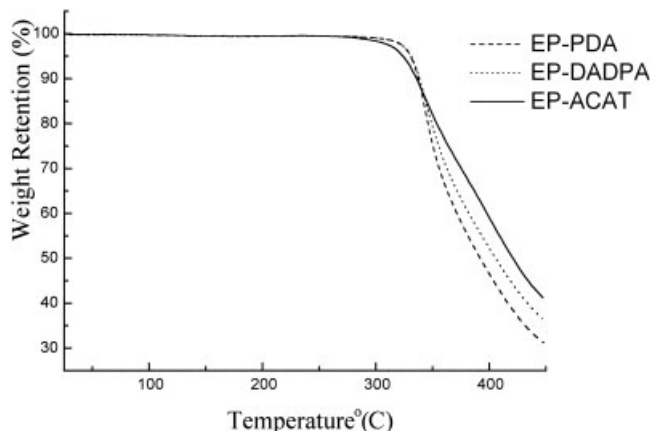
### Properties of the epoxy resin cured with the ACAT

Because of the contribution of quinoid crosslinking, the ACAT/epoxy resin intercrosslinked network showed superior thermal properties.  $T_g$  of the ACAT-cured epoxy resins was about  $30^\circ$  above that of the resin cured with PDA and DADPA. The storage modulus above  $T_g$  was high as well (see Fig. 3). The ACAT-cured epoxy resin showed improved weight retention at high temperatures, as demonstrated by the TGA diagram (Fig. 6).

The ACAT-cured epoxy resin had fair mechanical properties. The measured values of flexural strength (76 MPa) and flexural modulus (1.9 GPa) were quite normal for an epoxy resin cured with aromatic polyamines.

### CONCLUSIONS

The reaction of the ACAT and epoxy resin gave an intercrosslinked network with a very high crosslink-



**Figure 6** TGA diagrams for epoxy resins cured with (a) PDA, (b) DADPA, and (c) ACAT.

ing density. The interchain linkages were due not only to the amino-to-epoxy addition but also to the quinoid crosslinking. The epoxy resins cured with the ACAT were superior, with a high  $T_g$ , high modulus above  $T_g$ , and better weight retention at high temperatures.

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