

# Amine Functional Chloroaniline Acetaldehyde Condensate-Modified Epoxy Networks

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**ABSTRACT:** An investigation was carried out to modify the fracture toughness of cured diglycidyl ether of bisphenol-A (DGEBA) resin networks with amine functional chloroaniline acetaldehyde condensate (AFCAC) as toughening agent. The resulting networks displayed significantly improved fracture toughness. The AFCAC was synthesized by the condensation reaction of chloroaniline and acetaldehyde in the acid medium (pH-4) and characterized by FTIR and NMR spectroscopy, elemental analysis, viscosity measurements, and mole of primary and secondary amine analysis. The DGEBA and AFCAC were molecularly miscible but developed a two-phase micro-

structure upon network formation. Epoxy/AFCAC compositions were systematically varied to study the effect of concentration on the impact, adhesive, tensile, and flexural properties of modified networks. The dynamic mechanical analysis and scanning electron microscopy studies showed two-phase morphology in the cured networks where AFCAC particles were dispersed. The AFCAC-modified epoxy network was thermally stable up to around 338°C. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3717–3726, 2008

**Key words:** fracture; toughness; modification

## INTRODUCTION

Epoxy resins are one of the most important classes of thermosetting polymers. These networks have many desirable properties, which include high tensile strength, excellent chemical and corrosion resistance, and good dimensional stability according to May et al.,<sup>1</sup> Potter,<sup>2</sup> Bauer<sup>3</sup> etc. Consequently, these materials are widely used for many important applications such as coating, structural adhesives, reinforced plastics, and matrix resins for advanced composite materials.<sup>4–7</sup> Unfortunately, these highly crosslinked networks are inherently brittle and consequently have limited utility in applications requiring high impact fracture strength, or even thermal cycle resistance.

Incorporation of elastomeric modifiers has served as a successful means of enhancing the fracture strength of brittle materials. According to Chen et al.,<sup>8</sup> Ratna et al.,<sup>9–13</sup> Murli et al.,<sup>14</sup> Kar et al.,<sup>15</sup> Robinette,<sup>16</sup> Chikhi et al.,<sup>17</sup> and Ozturk et al.,<sup>18</sup> the elastomeric modifiers such as amine terminated butadiene-co-acrylonitrile (ATBN), carboxyl terminated butadiene-co-acrylonitrile (CTBN), and acrylate elastomer had

been widely used for this purpose. In the field of thermoplastics, a new concept has been proposed for toughening by inclusion of rigid polymer particles in the ductile polymer matrix. Several works had been done using rigid polymer like poly(ether sulfone) (PES) and poly(ether imide) PEI.<sup>19–26</sup> The result showed an improvement in fracture toughness. The basic approach used in modifying the epoxy resin with rigid polymer or oligomers has some similarity to the ATBN, CTBN modifiers. In this system, the polymers are miscible with the epoxy in the initial stages of curing reaction but undergo phase separation during the later stages.

The present article discusses the synthesis and characterization of the rigid oligomers amine functional chloroaniline acetaldehyde condensate (AFCAC) and its role as modifiers for epoxy resin using an ambient temperature curing agent triethylene tetramine.

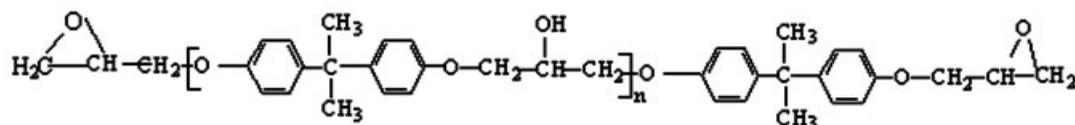
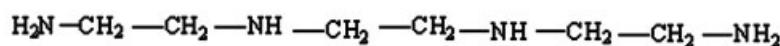
## EXPERIMENTAL

### Materials

The chloroaniline and acetaldehyde used in this work were obtained from Merck Fine Chemicals. The epoxy resin was diglycidyl ether of bisphenol-A (DGEBA) type (Ciba Geigy, Araldite LY 556) with an equivalent weight per epoxide group of  $195 \pm 5$ . An ambient temperature hardener, triethylene tetramine (Ciba Geigy, HY 951), was used as a curing

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**Epoxy resin (DGEBA):****Hardener (HY 951)**

Scheme 1 Chemical structures of epoxy resin and hardener.

agent. The chemical structures of epoxy resin and hardener are given in Scheme 1. Isopropanol, ethylene glycol, and salicylaldehyde used for potentiometric titration were obtained from Merck Fine Chemicals.

**Synthesis of AFCAC**

AFCAC was synthesized by the reaction of chloroaniline with acetaldehyde. Chloroaniline (2.197 mol) was first of all mixed with sufficient amount of HCl to reach pH 4 of the medium. Then the pale yellow colored solution was taken into a three-necked flask fitted with a stirrer and was stirred without heating. Now the required amount of acetaldehyde (2.197 mol) was added to it at a fixed interval of 10 min over a period of 1 h and the stirring was continued for 10 h. Then the stirring was stopped and the product was washed with 2% NaOH first and then with water till the mixture became neutral. Finally, the red colored liquid product was dried in an oven at 90°C. The yield of the product was 90%.

**Characterization of AFCAC**

The elemental analysis for carbon, hydrogen, and nitrogen estimations were done with a 2400 series-II C, H, N analyzer, Perkin-Elmer.

FTIR spectrum of the neat AFCAC sample between KBr discs was obtained with a Thermo-Nicolet Nexus-870-FTIR spectrometer.

<sup>1</sup>HNMR spectrum was recorded on a Bruker AC 200 spectrometer. Sample was dissolved in deuterated chloroform, and tetramethylsilane (TMS) was used as the internal standard.

Viscosity measurements were carried out with TA instruments (model AR1000, Newcastle, DE) in a parallel plate configuration (0.04-m diameter, 0.001-m gap) at various shear rates at 25°C.

Mole of primary and secondary amine per kilogram of AFCAC was determined by potentiometric titration according to Siggia method.<sup>27</sup> In this method, little amount (0.0005 kg) of AFCAC was taken into a 100-mL beaker and dissolved in 1 : 1

ethylene glycol-isopropanol mixture (0.000025 m<sup>3</sup>). Then the resulting solution was titrated with 1N hydrochloric acid prepared in the 1 : 1 ethylene glycol-isopropanol mixture. The neutralization point was determined by plotting the apparent pH against milliliters of acid. The total mole of amine/kg was calculated from the following method:

$$\text{Mole total amine/kg} = (\text{m}^3 \text{ of HCl} \times N \times 1000) / (\text{kilograms sample})$$

To determine the secondary amine mole only, same method was done after addition of salicylaldehyde (0.0000025 m<sup>3</sup>) in the sample solution and the mole was calculated by the above method as:

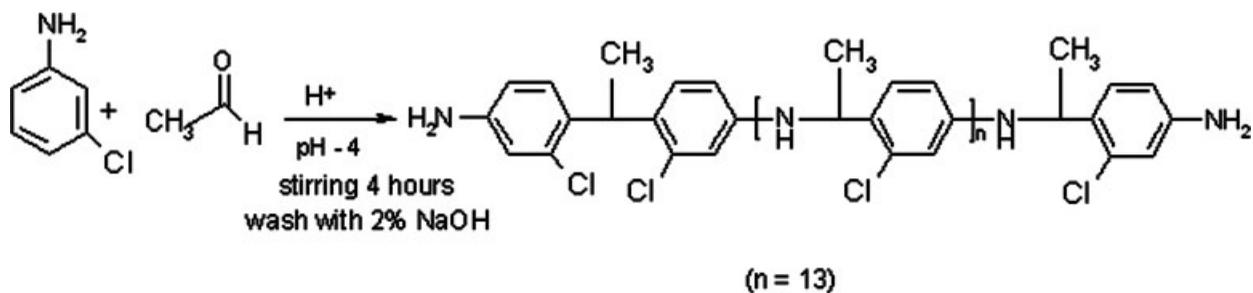
$$\text{Mole secondary amine/kg} = (\text{m}^3 \text{ of HCl} \times N \times 1000) / (\text{kilograms sample})$$

Now the primary amine mole was calculated by subtracting the secondary amine mole from total amine mole.

Modification of epoxy resin by AFCAC was done by two processes. In one step process, liquid AFCAC was mixed with epoxy resin by stirring at room temperature. The required amount (13 phr) of hardener triethylene tetramine (HY 951) was subsequently added, mixed thoroughly, and poured into aluminum mold. The samples were cured at room temperature for 24 h and postcured for 2 h at 150°C. In the two-step process, first the liquid rigid oligomer AFCAC was mixed with epoxy resin by stirring at room temperature. This formulation was heated at 80°C for 1 h and then cooled slowly to room temperature. After this required amounts (13 phr) of hardener, triethylene tetramine (HY 951) was subsequently added, mixed thoroughly, and poured into aluminum mold. The samples were cured at room temperature for 24 h and postcured for 2 h at 150°C.

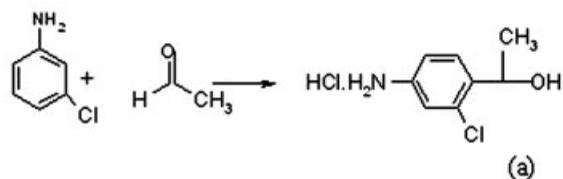
**Testing and analyses**

The Izod unnotched impact test was carried out according to ASTM D 4812-93 specifications using

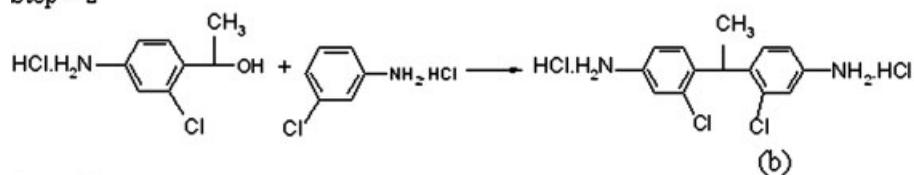


Scheme 2 Reaction details of AFCAC formation.

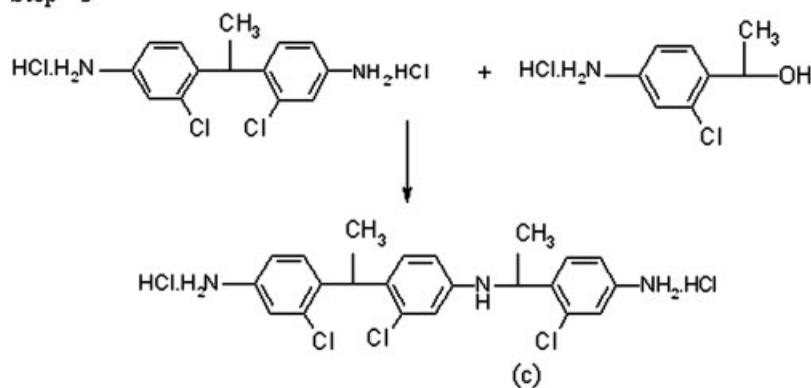
Step - 1



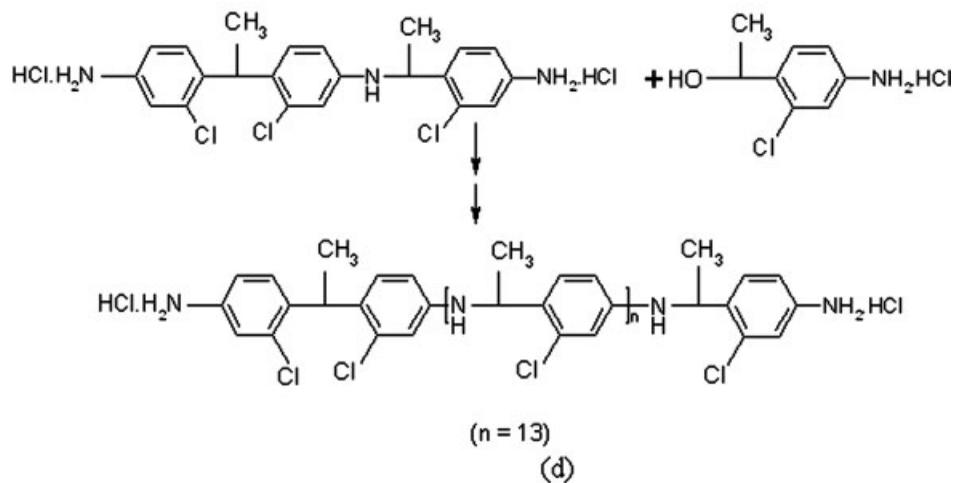
Step - 2



Step - 3



Step - 4



Scheme 3 Reaction mechanism of AFCAC formation.

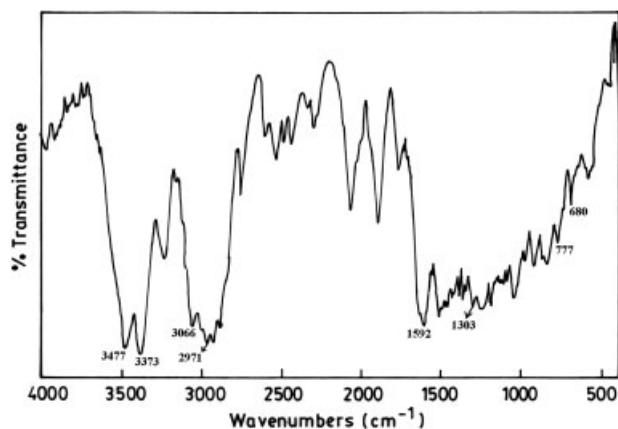


Figure 1 FTIR of AFCAC.

an impact tester with a striking velocity of  $3.35 \text{ ms}^{-1}$ . Impact test specimens in all cases were  $0.125 \text{ m} \times 0.01 \text{ m} \times 0.01 \text{ m}$ . The impact test was carried out at room temperature and impact energy was reported in  $\text{Jm}^{-2}$ . Five test samples were used for each formulation.

Single lap shear strength was determined for aluminum–aluminum (B 51 SWP) bonds according to ASTM D-1002-01 standard using aluminum sheets of size  $0.0889 \times 0.0254 \text{ m}^2$  with an overlap of  $0.0254 \text{ m}$ . The thickness of the sheets was  $0.0016 \text{ m}$ . The adhesive formulation was applied uniformly on both the surfaces to be mated and these were mated using contact pressure and cured. The adhesive was  $0.00003 \text{ m}$  thick and the coating length was  $0.0127 \text{ m}$  longer than the adhering length. The joint strength was measured in a universal testing machine (Zwick 4308) after 7 days of bonding. The crosshead speed of  $0.02 \text{ m/min}$  was used for lap shear strength measurements at  $25^\circ\text{C}$ . Three replicates were used per adhesive formulation. The procedure for the surface treatment of aluminum adherend included four steps.

1. The aluminum adherend was washed with acetone thoroughly; then it was placed in an air-forced oven in a vertical position and dried at  $60^\circ\text{C}$  for 2 h.

2. The acetone cleaned aluminum adherend was dipped in freshly distilled chloroform for 24 h; then it was dried in an air-forced oven in a vertical position at  $60^\circ\text{C}$  for 30 min. Any contact with the surface of the adherend to be bonded was avoided.
3. The chloroform cleaned aluminum adherend was dipped in a  $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$  solution at  $69^\circ\text{C}$  for 30 min. The composition of the solution was  $\text{K}_2\text{Cr}_2\text{O}_7 : \text{H}_2\text{SO}_4 : \text{H}_2\text{O} = 1 : 10 : 30$  by weight. After dipping, the aluminum adherend was washed with cold distilled water for 3–5 min. A well-treated aluminum adherend should have a continuous uniform water film on the surface, indicating absence of any organic contamination. Otherwise, the treatment was repeated again until a satisfactory result was obtained.
4. The water washed aluminum adherend was finally dried in an air-forced oven in a vertical position at  $60^\circ\text{C}$  for 1 h. The portion of the adherend, which would be adhered, was in the upper top when placed vertically. The adherend thus treated was used within 6 h.

The flexural strength was examined on a universal-testing machine Instron 4303 at a  $0.0015\text{-m/min}$  crosshead speed. Rectangular samples according to ASTM D-790 were used for the flexural strength determination.

The tensile strength was determined in an Instron universal-testing machine 4303 at a  $0.005\text{-m/min}$  crosshead speed. Dumb-bell shaped type IV samples according to ASTM D-638 were used for the tensile strength determination.

A scanning electron microscope (SEM) (Hitachi, S 415 A) was used to analyze the fracture surfaces of the toughened epoxy networks. A thin section of the fracture surface was mounted on aluminum stub ( $0.030 \text{ m}$ ) using conductive (silver) paint and was sputter coated with gold before fractographic examination. The SEM micrographs were obtained under conventional secondary electron imaging conditions with an acceleration voltage of  $25 \text{ kV}$ .

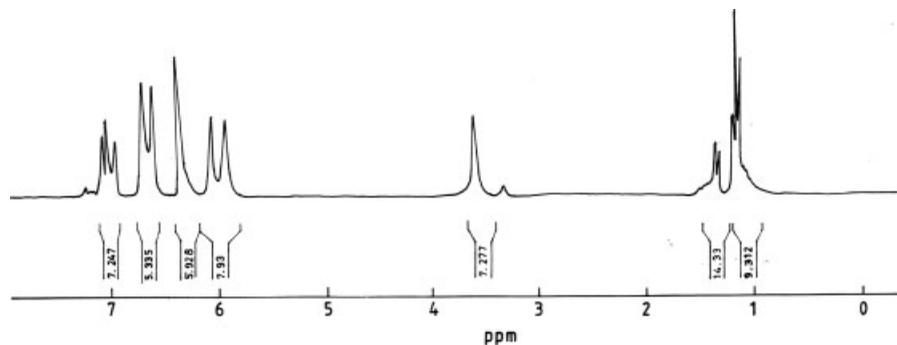


Figure 2  $^1\text{H}$  NMR of AFCAC.

**TABLE I**  
Results of Elemental Analysis of AFCAC

Elements	Theoretical value (%)	Experimental value (%)
C	62.24	61.89
H	5.18	4.93
N	9.21	9.53

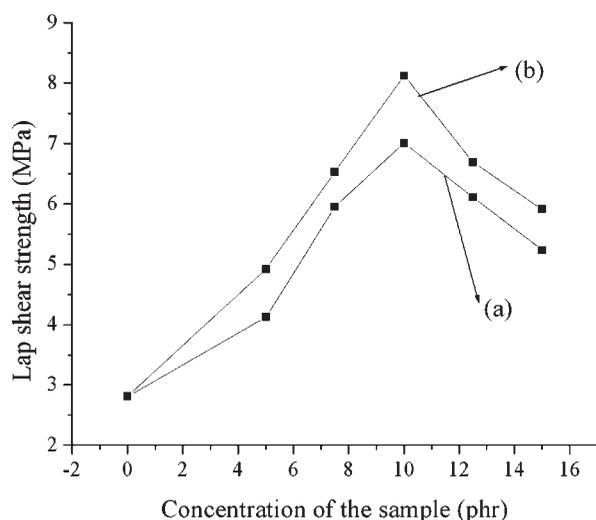
Dynamic mechanical analysis (DMA) was carried out by DMA2980 of TA instruments at the frequency of 1 Hz using single cantilever clamp at the heating rate of 5°C/min. Sample size was 0.0175 m × 0.01 m × 0.002 m. Samples were analyzed from -100 to 150°C.

Thermal analysis was carried out by using Perkin-Elmer Instrument (Pyris Diamond DTA/TG), under nitrogen atmosphere, at a heating rate of 10°C per minute.

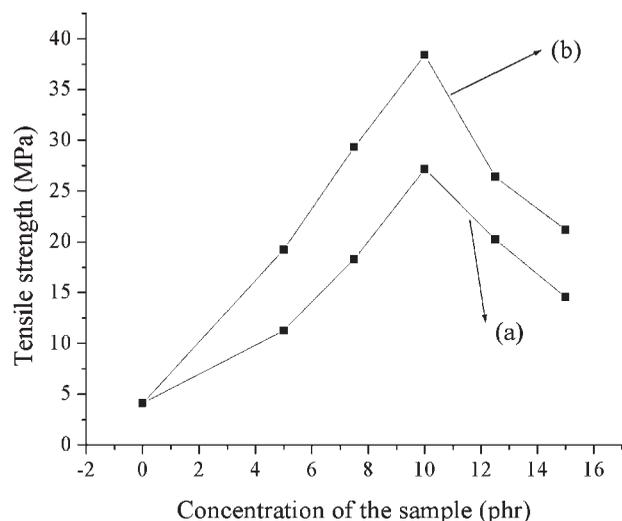
## RESULTS AND DISCUSSION

### Mechanistic explanation of AFCAC formation

The formation of AFCAC can be explained by the following mechanism (Schemes 2 and 3). In the first step of Scheme 3, first drop of acetaldehyde reacts with chloroaniline hydrochloride to give the intermediate (a). As acetaldehyde was added drop-wisely and chloroaniline and acetaldehyde were taken in equimolar ratio, so after step-1, chloroaniline would be excess in reaction medium. This excess chloroaniline reacts with (a) to give (b) in step-2. As the reaction was going on, the formation of product (b) would be much more and amount of chloroaniline would be lower in reaction medium. At that moment, the intermediate (a) would see the product



**Figure 3** Lap shear strength of modified epoxy in (a) one-step and (b) two-step process.



**Figure 4** Tensile strength of modified epoxy in (a) one- and (b) two-step process.

(b) in huge amount in the medium and reacts with it to give product (c) (step-3), (In this step, there is a possibility of reaction of acetaldehyde with product b, but it does not occur which is supported by elemental analysis latter on) which on further reaction with (a) repeatedly (step-4) gives the expected product AFCAC (d). The formation of the AFCAC was justified from FTIR spectroscopy, elemental analysis, and mole of primary and secondary amine determination by potentiometric titration. The formation of AFCAC was further justified from <sup>1</sup>H NMR spectroscopic study by observing characteristic peaks and by comparing the peak area ratio of aliphatic and aromatic protons with that of number ratio of aliphatic and aromatic protons. All these supporting documents have been discussed latter in details.

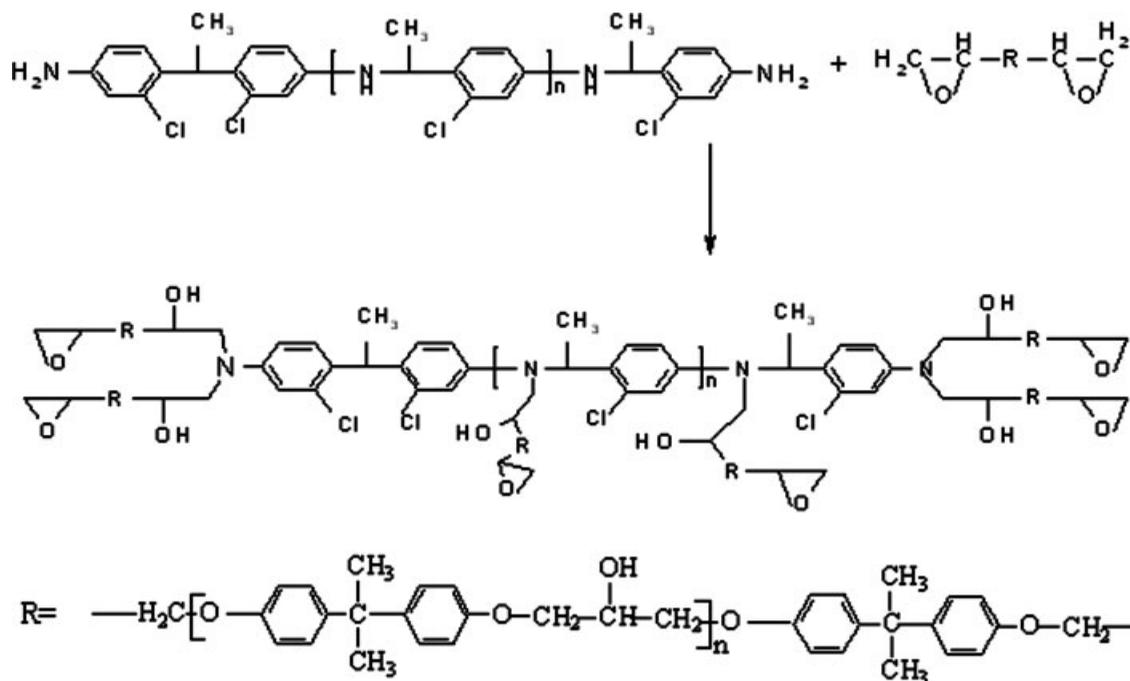
### Characterization of AFCAC

To characterize the structure of AFCAC, the sample was subjected to FTIR and <sup>1</sup>H NMR spectroscopic analyses. The spectra are presented in Figures 1 and 2 respectively, and prominent peaks are identified.

In FTIR spectrum (Fig. 1), the characteristic peaks at 3373–3477 cm<sup>-1</sup> and 1473 cm<sup>-1</sup> are responsible for N–H stretching and N–H bending, respectively.

**TABLE II**  
Viscosity Results of AFCAC

Shear rate (s <sup>-1</sup> )	Viscosity (cP)	Average viscosity (cP)
19.90	1973	1967.4
49.98	1965	
79.22	1963	
120.11	1972	
199.00	1964	



Scheme 4 Reaction between AFCAC and DGEBA resin.

The aromatic and aliphatic C—H stretching at  $3066\text{ cm}^{-1}$  and  $2971\text{ cm}^{-1}$ , respectively, confirms the presence of aromatic and aliphatic moieties in the probable structure. It can be further supported by the peaks at  $1303\text{ cm}^{-1}$  and  $1592\text{ cm}^{-1}$  which are due to C—N aromatic stretching and C=C aromatic ring stretching, respectively, and by C—Cl stretching frequencies at  $680$  and  $777\text{ cm}^{-1}$ .

In  $^1\text{H}$  NMR spectrum (Fig. 2), the aromatic protons come at the region from  $6.1\text{ ppm}$  to  $6.8\text{ ppm}$ . There is also a triplet at  $7\text{ ppm}$  for secondary amine proton, which couples with aliphatic  $-\text{CH}_2$  proton. Doublet at  $1.3\text{ ppm}$  and quartet at  $1.2\text{ ppm}$  are due to methyl and methylene protons, respectively. The singlet signal at  $3.7\text{ ppm}$  is due to primary  $\text{NH}_2$  proton. All these confirm the structure of AFCAC. The formation of AFCAC was also justified from NMR by matching the peak area ratio of aliphatic and aromatic protons with that of number ratio of aliphatic and aromatic protons. The peak area ratio of ali-

phatic and aromatic protons ( $23.64/19.1$  i.e.  $1.24 : 1$ ) was almost same with that of aliphatic and aromatic protons number ratio ( $64/51$  i.e.  $1.25 : 1$ ).

The observed results of elemental analysis are given in Table I along with theoretical values. The experimental values are in good agreement with the theoretical values. As the elemental analysis does not show the presence of oxygen atom so it can be concluded that the final AFCAC does not contain oxygen but if in step-3 (Scheme 3) acetaldehyde reacts with product (b) then the final product should contain  $-\text{OH}$  group at either of the ends. To confirm the presence of amine group in AFCAC, total mole of amine, mole of primary amine, and mole of secondary amine per kilogram of AFCAC have been calculated from the results of potentiometric titration (Aniline was used as internal standard), and their corresponding values per kilogram of AFCAC are  $6.17$ ,  $0.77$ , and  $5.4$ , respectively. These results confirm the presence of both primary and secondary

TABLE III  
Compositions, Impact, and Flexural Strengths of Unmodified and AFCAC-Modified Epoxy Networks

Sample	Composition			Impact strength ( $\text{J/m}^{-2}$ )		Flexural strength (MPa)	
	LY 556	HY951	AFCAC	One step	Two step	One step	Two step
T-0	100 parts	13 phr	0 phr	110	110	58.48	58.48
T-1	100 parts	13 phr	5 phr	200	320	94.32	124.36
T-2	100 parts	13 phr	7.5 phr	340	435	132.17	174.15
T-3	100 parts	13 phr	10 phr	500	610	180.35	228.87
T-4	100 parts	13 phr	12.5 phr	370	480	144.82	192.57
T-5	100 parts	13 phr	15 phr	230	350	110.50	156.11

**TABLE IV**  
**Viscosity of DGEBA and the Product between the Reaction of DGEBA and Liquid AFCAC at Room Temperature and 80°C Separately**

Sample	Shear rate (s <sup>-1</sup> )	Viscosity (cP)	Average viscosity (cP)
DGEBA	5.588	3425	3439.75
	22.24	3434	
	33.33	3445	
	49.99	3455	
DGEBA + AFCAC at room temperature for 1 h (S-1)	5.588	4692	4666
	22.24	4665	
	33.33	4652	
	49.99	4655	
DGEBA + AFCAC at 80°C temperature for 1 h (S-2)	5.588	6750	6745.50
	22.24	6733	
	33.33	6754	
	49.99	6746	

amine in AFCAC. From the mole of primary amine per kilogram of AFCAC (0.77), molecular weight of AFCAC has been also calculated and this calculated molecular weight (2597) is further supported by elemental analysis as given in Table I.

The viscosity results of AFCAC are summarized in Table II. From the Table, it is evident that with increase in shear rate the difference in viscosity is not significant, which indicates that it is low molecular weight Newtonian fluid.

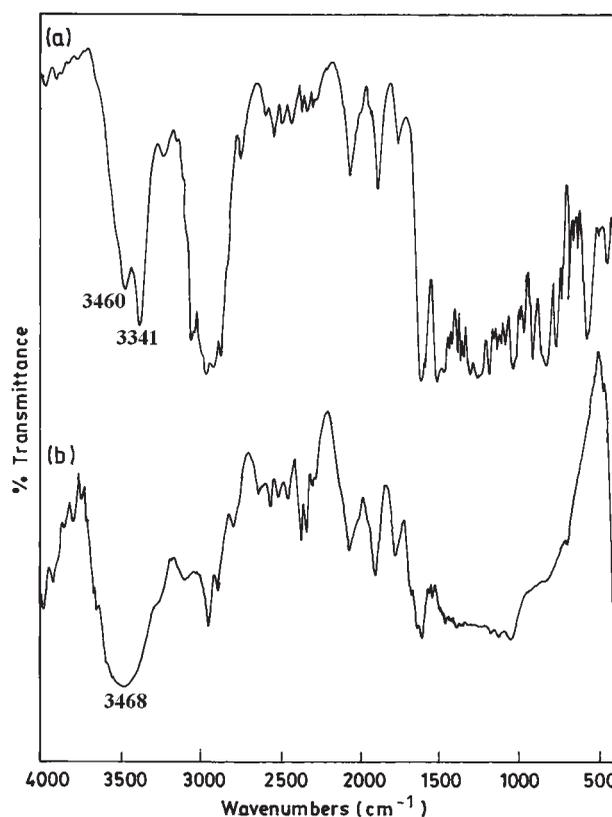
#### Chemical mechanistic of the modified epoxy resin by incorporation of AFCAC

For effective toughening, the AFCAC is required to be chemically bonded to the epoxy matrix. For this reason, before curing, desired amount of AFCAC was mixed with epoxy resin by stirring and reacted at 80°C for 1 h. The reaction mixture was allowed to cool to ambient temperature. The epoxide group of DGEBA is expected to react with both the primary and secondary amine groups of the AFCAC and form chemical bonds between the epoxy and the AFCAC. The reaction mechanism is shown in Scheme 4. The product was epoxy end capped chloroaniline acetaldehyde condensate—epoxy copolymer that is capable of reacting with the hardener triethylene tetramine in the same way as epoxy.

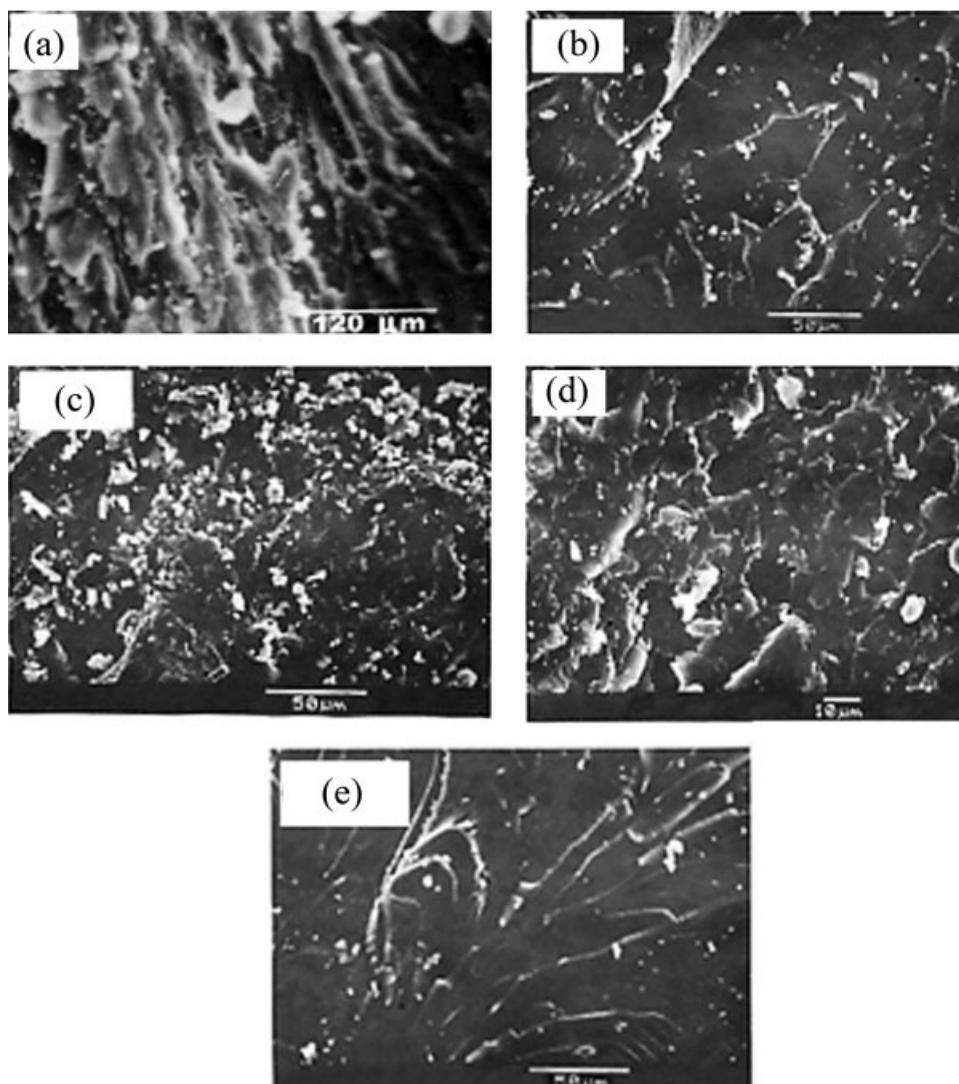
#### Impact, adhesive, tensile, and flexural properties of modified networks

Modification of mechanical properties like impact, adhesive, tensile, and flexural occurred by incorporation of AFCAC into epoxy resin. Using different concentration of AFCAC various formulations were made. All the formulations along with impact and flexural strengths are given in Table III. The effect of incorporation of AFCAC on adhesive and tensile strengths of modified networks is shown in Figures

3 and 4, respectively. The results show that impact, adhesive, tensile, and flexural strengths are vastly improved than unmodified one. The increase depends on the concentration of the AFCAC. The maximum increase is obtained at 10 phr (parts per hundred parts of epoxy resin) of AFCAC and after that the strength decreases with increase in concentration. This is because after an optimum concentration, the AFCAC acts more as a flexibilizer rather than a toughening agent. The amine groups of AFCAC are expected to participate in the curing



**Figure 5** FTIR spectra of S-1 (a) and S-2 (b).

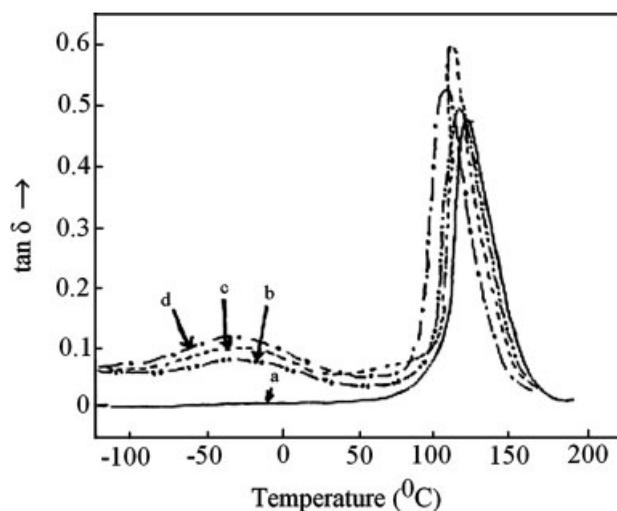


**Figure 6** SEM micrographs of (a) unmodified epoxy, (b) modified epoxy, (AFCAC 5-phr), (c) modified epoxy (AFCAC 10-phr), (d) modified epoxy (AFCAC 12.5-phr), and (e) modified epoxy (AFCAC 10-phr in one-step).

reaction of epoxy. In the initial stage, the liquid AFCAC is miscible with the epoxy resin and produces a clear homogeneous solution. This good mixing promotes the chemical reaction and network formation. During the curing process, as the molecular weight increases, the component separates with in the reaction medium to form a second dispersed phase (confirmed from DMA and SEM). This two-phase microstructure consisting of small rigid oligomer particles dispersed and bonded to the epoxy matrix results in higher toughness according to Hedric et al.<sup>20</sup> When the concentration becomes higher than 10 phr, the compatibility of AFCAC with the matrix is too great to form separate oligomer phase, that is, the system becomes homogeneous, and toughness decreases.

It is also clear from the result that mechanical strengths in two-step process are more than the one

step process. This was because in two-step process, the reaction between AFCAC and epoxy was maximum, that is, almost completing due to high temperature rather than one step process. This fact was confirmed by the viscosity results given in Table IV. From the viscosity results, it was clear that the product obtained by the reaction of AFCAC and DGEBA at room temperature (S-1) was less viscous than by the reaction at high temperature (S-2). This was also supported by the FTIR spectra shown in Figure 5. In this figure, the product (S-1) shows peak at  $3341\text{ cm}^{-1}$  and  $3460\text{ cm}^{-1}$  due to primary  $\text{-NH}$  stretching and  $\text{-OH}$  stretching, respectively, indicating the presence of unreacted amine group, but the product (S-2) shows only peak at  $3468\text{ cm}^{-1}$  due to  $\text{O-H}$  stretching indicating that there was no unreacted amine group in it, and the reaction became completed.



**Figure 7** DMTA of unmodified (a), 5 phr AFCAC modified (b), 10 phr AFCAC modified (c), and 15 phr AFCAC modified (d) epoxy networks.

### Scanning electron microscopy of fracture surfaces

To correlate the molecular and morphological parameters with the fracture properties of the toughened networks, the microstructure of the fracture surfaces for AFCAC-modified networks were analyzed by SEM. The SEM photographs for the toughened networks in two-step process containing different concentration of AFCAC and in one step process containing 10-phr concentration of AFCAC are shown in Figure 6. Beyond 10 phr, there is no improvement in impact, adhesive, tensile, and flexural strengths rather a drop is observed. This may be explained considering the changes in morphology of the fractured surfaces of the cured epoxy resin by the addition of liquid oligomers. The fracture surface of unmodified cured epoxy is homogeneous without any dispersed particles [Fig. 6(a)]. For the AFCAC-modified formulations up to certain concentration (10 phr) of AFCAC, the morphology is a two-phase microstructure [Fig. 6(b,c)]. At 10 phr, the morphology consists of relatively small polymer particles uniformly dispersed in the epoxy matrix [Fig. 6(c)]. This two-phase microstructure is believed to increasing the breaking strength by a crack terminating mechanism, and the fractured surface appears cavitated. On increasing the concentration of AFCAC above 10 phr, the second phase becomes indistinguishable from the matrix due to aggregation [Fig. 6(d)]. The polymer that does not phase-separate can lead to flexibilization of cured epoxy resin and hence can decrease the rigidity according to Ochi et al.<sup>28</sup>

In the SEM micrograph [Fig. 6(e)] of modified (10-phr of AFCAC) epoxy networks in one step process shows larger particle than the micrograph [Fig. 6(c)] in two-step process as a result of aggregation. So the

phase separation in one-step process is not so much as in case of two-step process. This explains the cause of lowering of mechanical strength in one-step process.

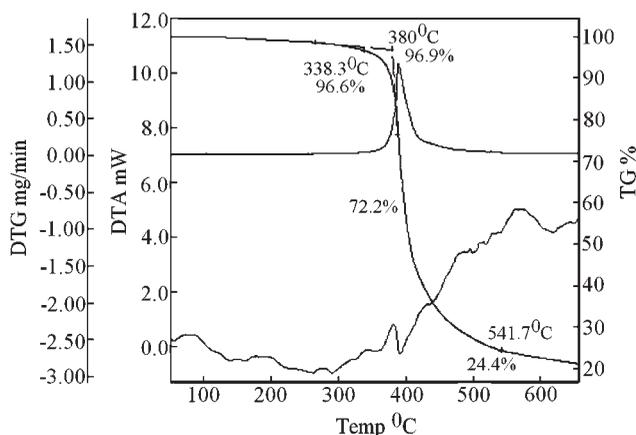
### Thermomechanical analysis of AFCAC-modified epoxy networks

The unmodified epoxy and AFCAC-modified epoxy networks in the two-step process were subjected to DMA analysis. Figure 7 presents the loss factor ( $\tan \delta$ ) against temperature plot for the unmodified epoxy, and 5 phr, 10 phr, and 15 phr AFCAC-modified epoxy networks. From the figure, it is clear that all the modified networks show two relaxation peaks, one at low temperature and the other at high temperature. The former peak is attributed to the  $\alpha$ -relaxation of AFCAC and the latter peak is due to the  $\alpha$ -relaxation of epoxy networks according to Angola et al.<sup>21</sup> The values of  $\tan \delta$  peak temperature (indicative of  $T_g$ ) and  $\alpha$ -relaxation temperature of AFCAC are summarized in Table V. From the Table, it is evident that for the modified network up to a certain concentration (10 phr) of AFCAC there is a little change in the  $T_g$  value when compared with the unmodified epoxy network, but a depression of the  $T_g$  for the modified network was observed at higher concentration of AFCAC. This can be attributed to the fact that in case of modified networks with higher concentration of AFCAC, the AFCAC oligomer dissolves, that is, tendency of its phase-separation decreases. However, all the blends exhibit a higher  $\tan \delta$  height in comparison to the pure epoxy indicating better dissipation of mechanical energy and hence higher impact, tensile, and flexural strengths.

The thermogravimetric (TG), differential thermogravimetric (DTG), and differential thermal analysis (DTA) diagram of AFCAC-modified (10 phr) epoxy resin are given in Figure 8. From TG experiment, it was found that, 3.4% loss of modified product at a temperature (70–338°C) was presumably due to the absorbed water. Between temperatures 338–542°C, the loss was 72.2%, which was due to degradation of cured modified epoxy network. From DTG curve, it was clear that maximum rate of weight loss occurred at 380°C temperature. The DTA curve

**TABLE V**  
DMTA Analysis of Modified Epoxy

Sample	$T_g$ (°C)	Temperature for $\alpha$ relaxation of AFCAC (°C)
T-0	125	–
T-1	122	–35
T-3	117	–40
T-5	109	–30



**Figure 8** Thermogravimetric curve of AFCAC-modified (10 phr) epoxy network under nitrogen atmosphere at a constant heating rate (10°C/min).

showed chemical changes in the modified epoxy networks with increase in its temperature.

### CONCLUSIONS

Epoxy resin (DGEBA) was modified with the liquid AFCAC and cured with ambient temperature curing agent triethylene tetramine. The liquid AFCAC was miscible with the epoxy precursor and upon network formation a two-phase structure developed in which the AFCAC formed discrete particles evenly dispersed in the epoxy matrix. The resulting networks showed significantly enhancement of fracture toughness with respect to the impact, adhesive, tensile, and flexural strengths. The improvement of results depends upon the concentration of the modifiers. The optimum result was obtained at 10-phr concentration of AFCAC. The AFCAC-modified epoxy network was thermally stable up to around 338°C.

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