

# Amine-Terminated Polysulfone as Modifier for Epoxy Resin

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**ABSTRACT:** The synthesis of carboxyl-terminated poly(ethylene glycol adipate) (CTPA) and amine-terminated poly(amide sulfone) (ATPS) based on the CTPA and 4,4'-diaminodiphenyl sulfone (DDS) is described. The products were characterized by IR and <sup>13</sup>C-NMR spectroscopic analysis, nonaqueous titration, viscosity measurement, and solubility characteristics. The developed ATPS was incorporated as a modifier into the epoxy matrix and its effect was studied by DSC and DMTA. It was found that ATPS forms a compatible blend with epoxy and imparts flexibility to the epoxy matrix. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 901–907, 1997

**Key words:** epoxy; polysulfone; dynamic mechanical; modifier; flexibilizer

## INTRODUCTION

Epoxy resins are a class of versatile polymer material which form networks on curing and are used extensively as matrix for fiber-reinforced plastics (FRP), surface coating, and structural adhesive. This is because of their high strength, low creep, very low cure shrinkage, good performance at elevated temperature, excellent resistance to corrosion, and good adhesion to many substrates. However, unmodified epoxies are relatively brittle with poor resistance to crack growth. Hence, modification of epoxy resin has been the subject of intense research interest.

Use of flexible long-chain hardeners and reactive diluents have been reported in the literature.<sup>1</sup> Following the work reported by McGarry and Wilner<sup>2</sup> that a carboxyl-terminated copolymer of butadiene and acrylonitrile (CTBN) is useful for the fracture toughness of epoxy resins, much work has been done in this field.<sup>3–5</sup> Other reactive liquid rubbers have also been examined, e.g., an amine-ended butadiene acrylonitrile oligomer,<sup>6</sup> carboxyl-ended polyisobutylene,<sup>7</sup> and functionalized siloxane and acrylates.<sup>8,9</sup> The modification

of epoxy resins with various types of ductile thermoplastics were studied as an alternative to reactive rubbers for improving the toughness of epoxy resin. Among thermoplastics, polyetherimides,<sup>10,11</sup> poly(aryl ether ketones),<sup>12,13</sup> poly(phenylene oxide),<sup>14</sup> and functionalized polysulfones<sup>15</sup> have been reported as effective modifiers. Polymers having a sulfone group are known to have good oxidative, thermal, and hydrolytic stability as well as good mechanical properties.<sup>16,17</sup> Hence, a modifier having a sulfone group will have an additional effect on the properties of a modified network along with its flexibilizing effect.

With this background, the present work was taken up to develop a low molecular weight liquid amine-terminated poly(ether amide sulfone) (ATPS) and to examine its effect as an impact modifier for epoxy. In this article, the synthesis and characterization of ATPS, its compatibility with epoxy, and the thermal analysis of modified epoxy network are discussed.

## EXPERIMENTAL

### Materials

Poly(ethylene glycol) PEG 400 (Glaxo Laboratories, Bombay, India), adipic acid (S.D. Fine

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Chem., India), 4,4'-diaminodiphenyl sulfone (DDS) (Suidhinath Laboratories, India), and *para*-toluene sulfonic acid (PTSA) (Sisco Laboratories, India) were used as received.

The epoxy resin was a liquid diglycidyl ether of bisphenol A 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 agent. The solvents, namely, toluene and methanol, were of analytical grade (BDH, India).

### Synthesis of Polymer

Polysulfone was synthesized by a two-step reaction: In the first step, carboxyl-terminated PEG adipate (CTPA) was prepared by reacting PEG with adipic acid in the ratio of 1 : 1.5 with 0.5% by weight of PTSA as the catalyst. A typical recipe was PEG (150 g; 0.375 mol), adipic acid (82.5 g; 0.565 mol), PTSA (1 g), and toluene (80 g). The reactions were carried out in a three-necked reaction flask fitted with a stirrer, nitrogen inlet, and Dean and Stark condenser. The water formed during the reaction was removed continuously from the reaction mixture using toluene as an azeotropic solvent. The reaction was monitored from the amount of water collected. After completion of the reaction (reaction time was about 4 h), the reaction mixture was subjected to distillation under reduced pressure at 70°C until no further loss in weight was observed.

CTPA thus obtained was further reacted with excess DDS at 165°C. CTPA (200 g; 0.16 mol) and DDS (60 g; 0.24 mol) were taken into the three-necked reaction flask fitted with stirrer, nitrogen inlet, and thermometer pocket and heated in a thermostated oil bath maintained at the requisite temperature. The water produced in the reaction was removed occasionally by applying a vacuum. The reaction was continued until the acid value was reduced to 20 or less. The time was about 14–16 h. The final product, ATPS, was then characterized.

### Characterization

Carboxyl contents were determined by titration with a methanolic solution of 0.10N KOH using phenolphthalein as an indicator. Viscosity measurements were carried out with a Haake rotoviscometer (Haake RV-3) at a shear rate range of 0–100 s<sup>-1</sup> at 27°C using an MV III head having

a clearance of 0.96 mm between the concentric cylinders of the viscometer.

IR spectra were taken in an FTIR spectrophotometer (Perkin-Elmer, Model 1650). <sup>13</sup>C-NMR spectra were recorded on a 500 MHz FTNMR instrument (Bruker AMX-500) using dimethylsulfoxide as a solvent and tetramethylsilane as an internal standard.

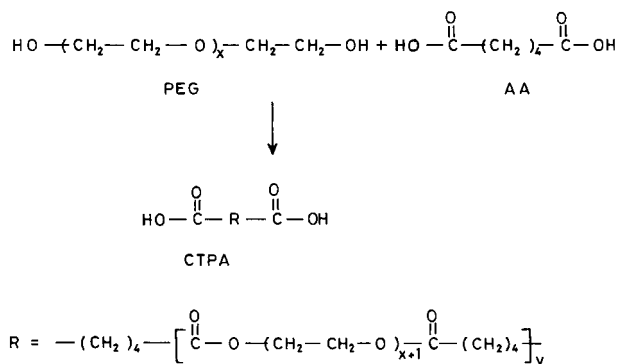
Solubility parameters were determined by the iteration method from the three-dimensional solubility parameters of the solvents in which the polymer is miscible.<sup>9,18,19</sup> The molecular weight of both CTPA and ATPS were determined by a Knauer vapor pressure osmometer (VPO) using tetrahydrofuran as a solvent and benzil as a standard.

Chemical coupling of ATPS with epoxy was studied in a differential scanning calorimeter (DSC) (DuPont 910). The glass transition temperatures (*T<sub>g</sub>*) of the cured epoxy and epoxy-ATPS blends were also determined from the same instrument. A heating rate of 10°C/min, sample weight of 20 mg, and a nitrogen flow of 60 mL/min were maintained for all the experiments.

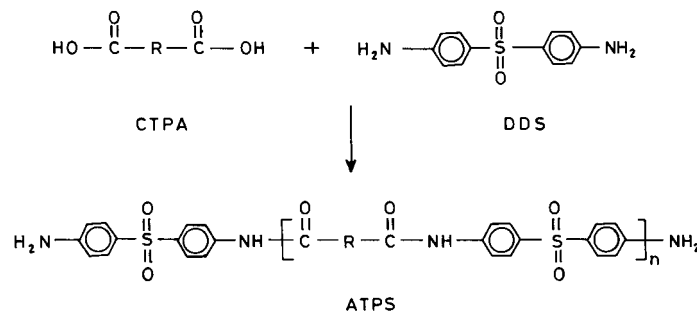
Dynamic mechanical analyses (DMA) were carried out for cured epoxy and epoxy/ATPS blends using a dynamic mechanical thermal analyzer (DMTA MK III, Rheometric Scientific) at a fixed frequency of 1 Hz and a heating rate of 3°C/min using liquid nitrogen for the subambient region. A dual cantilever mode was employed for sample of size of 14 × 10 × 2 mm.

### Curing Procedure

Liquid polysulfone was mixed with epoxy resin by stirring at room temperature. The required amount (13 pph) of hardener (HY 951) was subsequently added, mixed thoroughly, and poured into



**Reaction Scheme 1** Synthesis of CTPA.



**Reaction Scheme 2** Synthesis of ATPS.

a Teflon mold. Curing was done at room temperature for 24 h followed by 2 h at 150°C.

## RESULTS AND DISCUSSION

### Synthesis of CTPA and ATPS

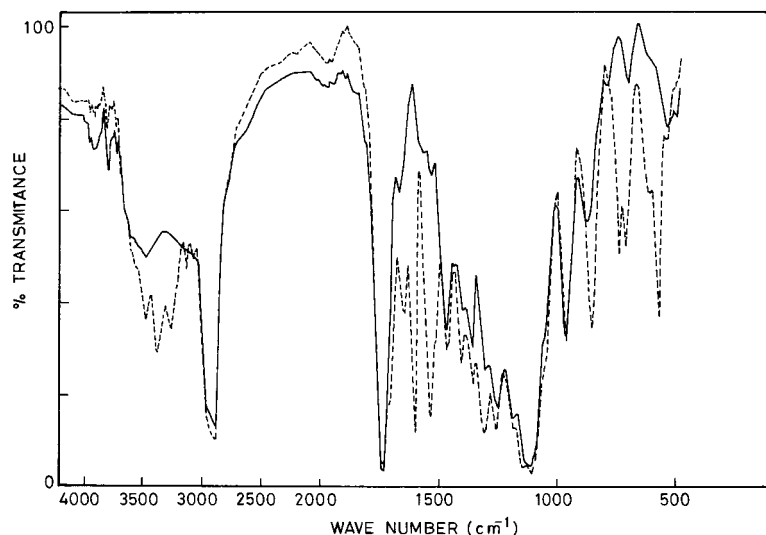
PEG 400 was reacted with adipic acid in the mol ratio of 1 : 1.5 to get CTPA. This is a carboxyl-hydroxy polycondensation reaction and the reaction is depicted in Scheme 1.

The terminal carboxylic acid groups of CTPA were utilized to obtain ATPS by the reaction of CTPA with DDS (1 : 1.5 mol ratio). The reaction details are shown in Scheme 2.

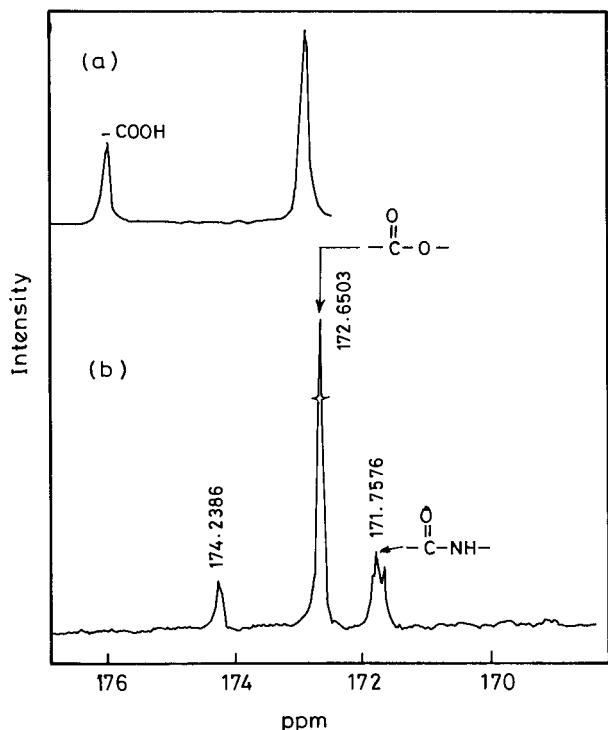
### Characterization of CTPA and ATPS

To characterize the structure of CTPA and ATPS, both samples were subjected to FTIR analysis. The spectra are presented in Figure 1 and promi-

nent peaks are identified. From the spectra, it is evident that, in addition to the peaks due to CTPA, ATPS shows peaks at 3354 and 3235  $\text{cm}^{-1}$  for N—H stretching. The peak at 3444.8  $\text{cm}^{-1}$ , a broad band (CTPA spectra), is due to O—H stretching of the carboxylic acid group. This peak in the case of ATPS is narrowed down and minimized. ATPS has also a peak at 3079.2  $\text{cm}^{-1}$  responsible for aromatic C—H stretching. This is further supported by the presence of peaks at 1592.6 and 1525.7  $\text{cm}^{-1}$ , which are the characteristic peaks for an aromatic ring. The amide linkage in the ATPS structure could be observed from the spectra of ATPS. Thus, the peaks at 1730 and 1634.9  $\text{cm}^{-1}$  are due to C=O stretching and N—H deformation, respectively, of the amide linkage. Furthermore, ATPS spectra has an additional small peak at 1349.9  $\text{cm}^{-1}$  responsible for C—N (aromatic) stretching. The peaks due to the sulfone group in the region of 1110–1180  $\text{cm}^{-1}$  become superimposed with those of C—O (ether) stretching and, hence, are not resolvable.



**Figure 1** IR spectra of (—) CTPA and (-----) ATPS.



**Figure 2**  $^{13}\text{C}$ -NMR spectra of (a) CTPA and (b) ATPS.

The structure of both CTPA and ATPS were also characterized by  $^{13}\text{C}$ -NMR analysis (Fig. 2). Two peaks at 174.2 and 172.6 ppm in the NMR spectrum of the adipate intermediate can be attributed to the existence of carboxylic and ester carbon. On subsequent formation of ATPS, the intensity of the peak at 174.2 ppm decreases sub-

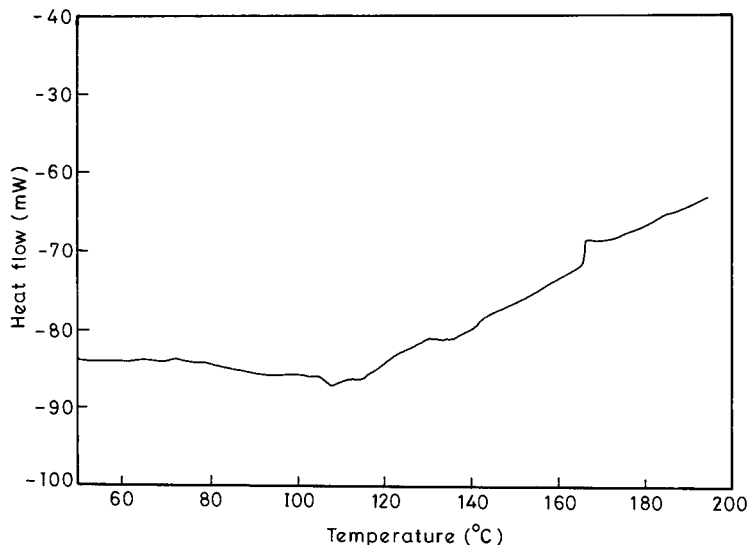
**Table I** Physicochemical Properties of ATPS

Resin	Acid Value	Viscosity <sup>a</sup> (Pa-s)	Solubility Parameter (cal/cc) <sup>0.5</sup>	Molecular Weight
CTPA	90	5.3	10.81	1125
ATPS	20	67.8	10.61	3345
LY556	—	7.4	10.32	425

<sup>a</sup> At 26°C.

stantially and an additional peak appears at 171.7 ppm. This indicates that reaction between amine and carboxylic acid has occurred, leading to the formation of amide linkage. The appearance of the amide carbon peak at lower ppm is natural as electronegativity of nitrogen is lower than that of oxygen and, thereby, —NH imparts a lower deshielding effect to —C=O carbon than to the —OH group.

The physicochemical properties of CTPA and ATPS are summarized in Table I. From the table, it is evident that the acid value decreases substantially as a result of the formation of ATPS. This low acid value indicates that it is essentially amine-terminated. This is further supported by the results of viscosity and molecular weight measurements. The viscosity of CTPA is 5.3 Pa-s, which increases substantially to 67.8 Pa-s due to the formation of ATPS by chain extension. Moreover, the VPO analysis results (Table I) show that ATPS has a higher molecular weight than that of CTPA. This viscous liquid ATPS seems to have a



**Figure 3** DSC scan of the mixture of epoxy and ATPS without any hardener.

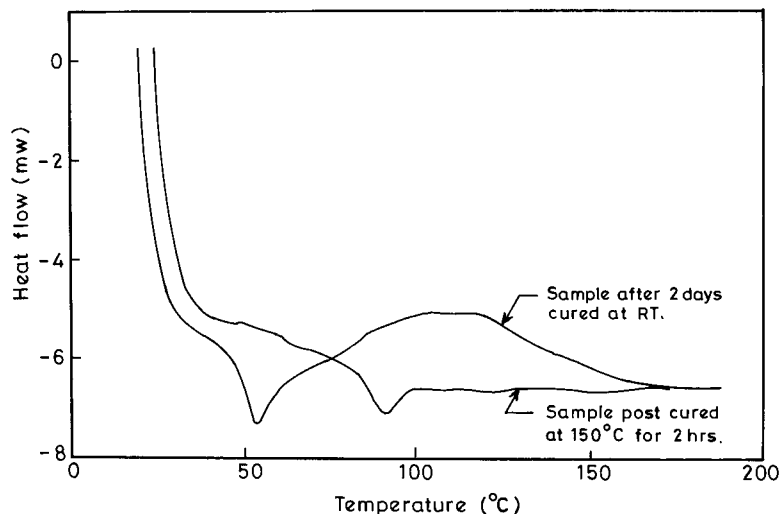


Figure 4 DSC scan of epoxy/ATPS blend before and after postcuring.

very good potential for its use as a flexibilizer for epoxy. To evaluate its compatibility with epoxy, its solubility parameter was determined by examining its miscibility in different solvents. The close proximity of solubility parameters ( $\Delta\delta_s = 0.4$ ) indicates high level of compatibility of ATPS with epoxy.

#### Thermal Analysis of Epoxy/ATPS Blend

The terminal amine groups and amide groups of ATPS are expected to participate in the curing reaction with epoxy. A DSC study was carried out to establish the reaction of ATPS and epoxy. The trace of epoxy and ATPS mixture without any hardener is shown in Figure 3. The exothermic nature of the plot at 100°C indicates the reaction of ATPS with epoxy only at elevated temperature, possibly due to the lower reactivity of the aromatic amine group.

A DSC scan of the epoxy-ATPS blend network cured for 2 days using a room-temperature hardener (HY 951) shows a residual exotherm (Fig. 4). The exotherm starts at a lower temperature

in the case of the blend due to the presence of the unreacted hardener which contains more reactive aliphatic amine groups. The same sample, when further cured for 2 h at 150°C, shows no residual exotherm and the glass transition region shifts to a higher temperature, which indicates further crosslinking at elevated temperature. Heat evolved during a curing reaction is often used to estimate the reaction rate and conversion.<sup>20,21</sup> Although the residual heat of reaction near the completion of curing cannot be measured by DSC,<sup>22</sup> the amount of heat evolved measured by DSC is still a valuable reference in the determination of curing characteristics. The absence of any residual exotherm in the postcured blend confirms the completion of curing of the epoxy with

Table II DSC Analysis of Epoxy/ATPS Blends

Composition of Blends (Epoxy/ATPS)	Glass Transition Temperature (°C)
100/0	115
100/10	103
100/20	95
100/30	82

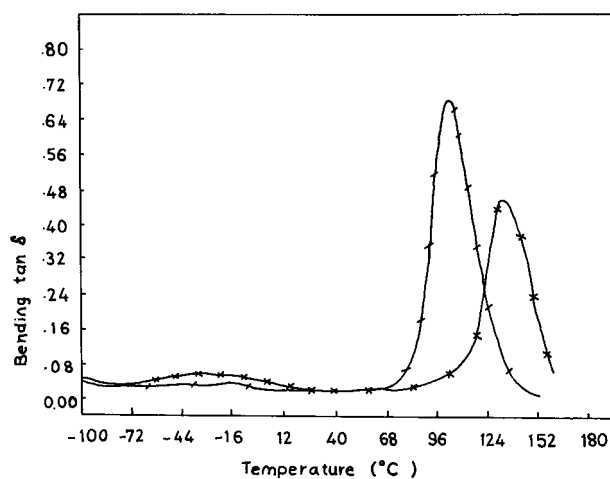


Figure 5  $\tan \delta$  vs. temperature plots for (--- $\Delta$ --- $\Delta$ ---) epoxy and (--- $\circ$ --- $\circ$ ---) epoxy/ATPS (100 : 30).

**Table III DMA Analysis of Epoxy/ATPS Blends**

Composition of Blends (LY 556/ATPS)	Storage Modulus <sup>a</sup> (GPa)	Tan $\delta$ Peak Temp ( $^{\circ}$ C)	Tan $\delta_{\max}$
100/0	2.63	139	0.60
100/10	2.08	126	0.71
100/20	1.50	117	0.66
100/30	1.27	106	0.74

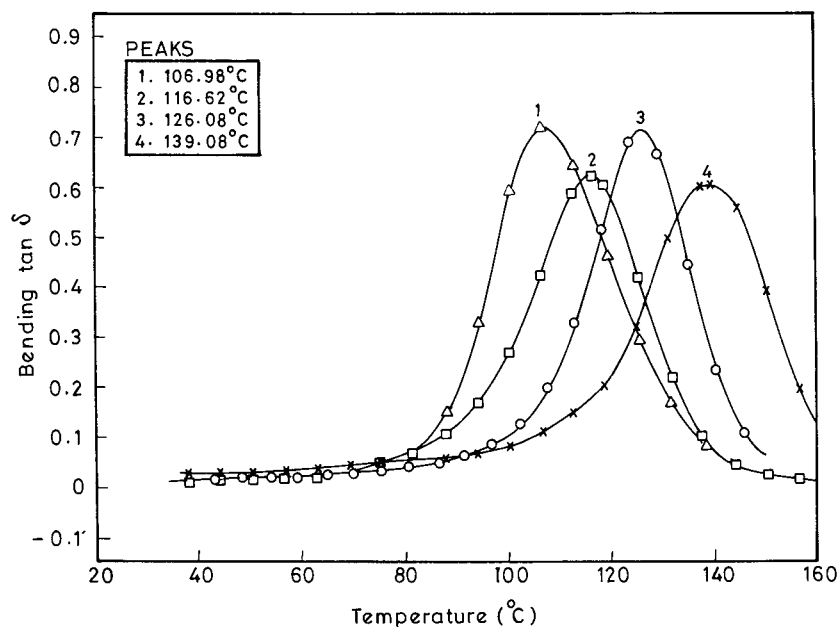
<sup>a</sup> At 35 $^{\circ}$ C.

the hardener as well as with ATPS on prolonged heating for 2 h at 150 $^{\circ}$ C.

All the blend networks exhibit a single glass transition temperature ( $T_g$ ) and the later gradually decreases with increase of ATPS concentration (Table II). This indicates that ATPS forms a compatible blend with epoxy and it imparts flexibility to the epoxy matrix. The flexibilizing effect of ATPS can be attributed to the presence of flexible ether and sulfone linkage. A similar observation was reported by Monternal et al.<sup>23</sup> where CTBN containing high acrylonitrile was used as a modifier.

The viscoelastic properties of epoxy and epoxy/ATPS blends were carried out by DMTA. To understand the morphology of the epoxy/ATPS blend, both pure epoxy and an epoxy/ATPS blend (100 : 30) sample were subjected to DMTA

analysis from -120 to 160 $^{\circ}$ C. The corresponding spectra are shown in Figure 5, where the loss factor (tan  $\delta$ ) measured at 1 Hz is plotted against temperature. From the figure, it is clear that both the epoxy and the epoxy/ATPS blend exhibit a single relaxation peak, which indicates that there is no phase separation. To study the effect of the incorporation of ATPS on the viscoelastic properties of a modified epoxy network, epoxy/ATPS blends of different compositions were analyzed by DMTA from room temperature (32 $^{\circ}$ C) to 160 $^{\circ}$ C. From the DMTA spectra, the values of storage moduli ( $E'$ ) at 35 $^{\circ}$ C, tan  $\delta_{\max}$ , and tan  $\delta$  peak temperature were obtained and are reported in Table III. The tan  $\delta$  vs. temperature plots are given in Figure 6. From the results, it is evident that the storage modulus ( $E'$ ) at 35 $^{\circ}$ C and the tan  $\delta$  peak temperature gradually decrease with increase of ATPS concentration. The decreasing trend of the tan  $\delta$  peak temperature (indicative of  $T_g$ ) supports the DSC results. However, all the blends exhibit a higher tan  $\delta$  in comparison to the pure epoxy due to the flexibilizing effect of ATPS. The difference between the exact temperature for the glass transition ( $T_g$ ) from DSC and from DMA is about 20 $^{\circ}$ C. It is expected due to the difference in the methods of measurement involved and different definition of transition temperature used.



**Figure 6** tan  $\delta$  vs. temperature plots for epoxy/ATPS blends: (--- $\times$ --- $\times$ ---) 100/0; (--- $\circ$ --- $\circ$ ---) 100/10; (--- $\square$ --- $\square$ ---) 100/20; (--- $\triangle$ --- $\triangle$ ---) 100/30.

## CONCLUSION

A low molecular weight amine-terminated polysulfone (ATPS) was developed which forms compatible blends with epoxy resin. The developed ATPS can be used as a flexibilizer for the cured epoxy matrix.

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