Conductive Epoxy/Amine System Containing Polyaniline Doped with Dodecylbenzenesulfonic Acid

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ABSTRACT: We developed a conductive epoxy/amine system containing polyaniline doped with dodecylbenzenesulfonic acid (PAni.DBSA). The curing behaviors of diglycidyl ether of bisphenol A with triethylenetetramine (TETA), PAni.DBSA, and both amine compounds at different concentrations were investigated by differential scanning calorimetry (DSC). Epoxy/TETA systems containing PAni.DBSA presented two distinct exothermic peaks at 90°C due to the cure by TETA as a hardener and at 236°C related to PAni.DBSA as the curing agent. The presence of PAni.DBSA in the systems constituted by epoxy/hardener in stoichiometric proportions resulted in a decrease in the glass-transition temperature of the epoxy matrix, as indicated by DSC and dielectric analyses. Electrical conductivity was determined in the epoxy/amine networks, with the TETA concentration kept constant and also in stoichiometric proportions of mixed hardener (TETA + PAni.DBSA) to epoxy resin. The last condition resulted in a higher electrical conductivity. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4059–4065, 2006

Key words: conducting polymers; curing of polymers; dielectric properties; resins

INTRODUCTION

Polyaniline (PAni) is considered one of the most promising electrically conducting polymers due to its easy synthesis, good environmental stability, moderate electrical conductivity, and low cost. In addition, it can be reversibly converted into a conductive insulating form through a simple protonation–deprotonation of the polymer.[1] Blending PAni with epoxy resin is a good method for developing conducting thermosetting composite materials with important properties such antistatic properties, electromagnetic shielding, and anticorrosive properties.[2,3] In addition, the lower density of PAni compared to other conducting fillers (e.g., carbon black and metal powder) makes these materials a good candidate for important applications in several fields, especially in the aeronautics industry. Despite the important applications, there are few reports in the literature related to epoxy/PAni systems.

Peltola et al.[4] reported on an antistatic, epoxy-based adhesive containing PAni doped with camphorsulfonic acid. They employed a Lewis acid as the curing agent. This curing agent was also used by Tsotra and Friedrich[5] in a composite containing polyaniline doped with dodecylbenzenesulfonic acid (PAni.DBSA) and epoxy resin. PAni.DBSA was also used by Jia et al.[6,7] in the development of conductive epoxy/anhydride systems. Other reports include blends of epoxy resin and PAni protonated with different acids.[8]

Epoxy resin can be cured by different systems, such as amines, anhydrides, mercaptans, and Lewis acids.[9,10] Among these hardeners, amine-type curing agents are the most popular, mainly for applications as coatings and adhesives, because of their relatively fast cure processes, which can be performed even at room temperature.[11,12] However, these basic curing agents also cause the deprotonation of PAni, thus decreasing its conductivity degree. Yang et al.[13] recently reported an alternative approach to the development of PAni/epoxy resin composites with oligomeric PAni in emeraldine base form followed by a doping process by the dipping of the cured film in an acetic acid solution of *p*-toluene sulfonic acid. Although this procedure resulted in films with high conductivity, this is not indicated for the development of coatings. Despite the dedoping process that normally occurs with amine-curing systems, this phenomenon could be

decreased with a specific amount of PAni and hardener.

In this study, we dealt with the effect of the concentration of PAni.DBSA on the curing parameters of an epoxy resin cured with an amine-based hardener. Because PAni can also act as the curing agent for epoxy resins,[14] we also determined the proportion of PAni and hardener necessary to maintain the stoichiometry ratio with the epoxy resin by differential scanning calorimetry (DSC) and studied the influence of different PAni/amine-type hardener ratios on the conductivity of the composites. The interaction between PAni and the epoxy components was also evaluated by dielectric analysis.

EXPERIMENTAL

Materials

Aniline (analytical grade, Merck, Darmstadt, Germany), ammonium peroxydisulfate (analytical grade, Vetec, São Paulo, Brazil), and dodecylbenzenesulfonic acid (DBSA; commercial grade, Proquimil LTDA, São Paulo, Brazil) were used as received without further purification.

The matrix polymer consisted of bisphenol A epoxy resin [diglycidyl ether of bisphenol A (DGEBA); DER 331] with an epoxide equivalent of 187 g/equiv, as determined by acid titration; the curing agent was based in triethylenetetramine (TETA; commercial grade, Dow Chemical, São Paulo, Brazil).

Synthesis of PAni.DBSA

PAni.DBSA was prepared by inverted emulsion polymerization according to the method described by Kinlen et al.[15] In a typical synthesis procedure of PAni.DBSA, 20 mL (0.22 mol) of aniline and 71.8 g (0.22 mol) of DBSA were dissolved in 1000 mL of toluene under constant stirring. The medium was kept at 0°C, and an aqueous solution containing 50.20 g (0.22 mol) of ammonium peroxydisulfate in 100 mL of water was slowly added to the reaction medium. After 6 h, the reaction medium was poured into methanol, filtered, washed several times with methanol, and dried in vacuo for 72 h.

Preparation of the PAni.DBSA/epoxy resin composite

Different amounts of PAni.DBSA were hand-dispersed with the epoxy resin in a mortar. Then, a preestablished amount of TETA was blended, and the mixture was poured into a silicon rubber disc mold (diameter = 3.8 cm; thickness = 2.0 cm) and cured at room temperature for 24 h, followed by an additional curing at 130°C for 2 h.
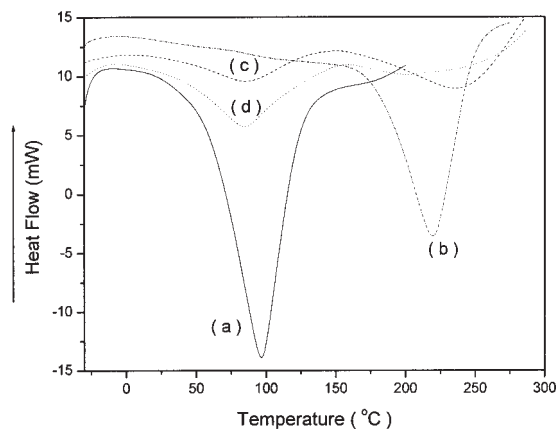
Figure 1 DSC thermograms showing the curing exotherm of DGEBA with (a) TETA, (b) PAni.DBSA, and TETA/PAni.DBSA mixed systems with (c) 5.0 and (d) 8.25 phr TETA.

Characterization

The electrical conductivity measurements were performed by the conventional four-point method, according to the literature,[16] on pressed pellets of composite particles prepared at room temperature. The equipment used for this measurement was composed of a Keithley 6517A electrometer (Cleveland, OH), a Minipa ET2907 multimeter (São Paulo, Brazil), and a homemade four-probe device with a medium distance between the probes of 0.171 ± 0.03 cm.

The DSC analyses were performed on a PerkinElmer model DSC 7 (Norwalk, CT) under a nitrogen purge. Samples of the epoxy/TETA system were heated from -30 to 200°C, whereas the blends with PAni.DBSA were heated from -30 to 300°C at a rate of 10°C/min. The heat of curing (ΔH) was determined from the first scan. The samples were cooled at room temperature and heated again at the same rate to obtain the glass-transition temperature (T_g) at the medium point of transition.

Dielectric relaxation measurements of the epoxy network and blends were made with a dielectric analyzer (TA Instruments model 2970; New Castle, DE) operating with parallel-plate electrodes. The electric modulus (M'') was obtained over a frequency range from 0.5 to 10^5 Hz and a temperature range from -130 to 200°C under dry nitrogen-gas purging.

RESULTS AND DISCUSSION

Effect of PAni.DBSA on the curing behavior of the epoxy resin/TETA system

Figure 1 compares the curing exotherms of the epoxy resin in the presence of TETA, PAni.DBSA, and the mixed TETA/PAni.DBSA system. A single exothermic peak was observed in both the epoxy/TETA [Fig. 1(a)] and the epoxy/PAni.DBSA systems [Fig. 1(b)]. The
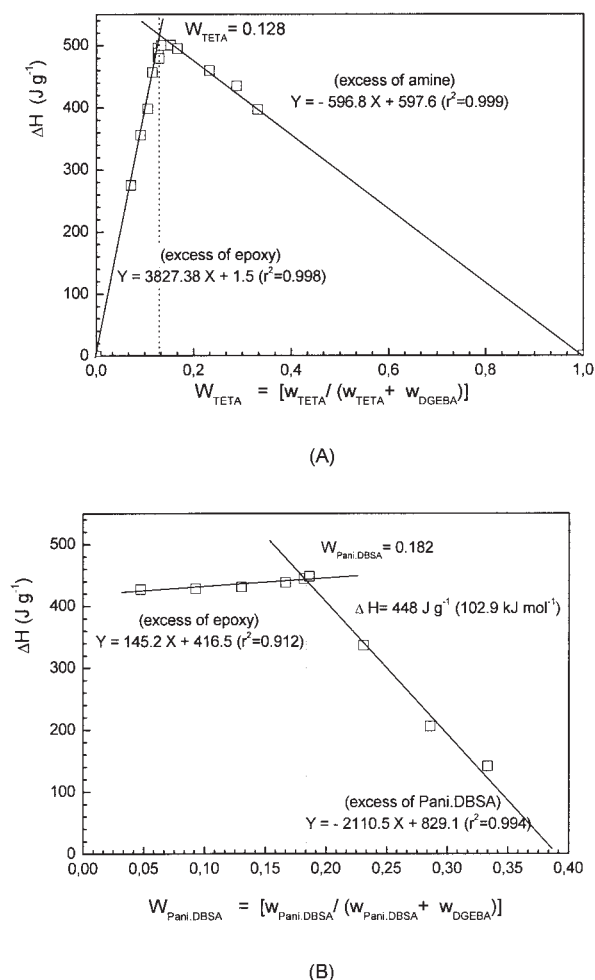
Figure 2 Dependence of ΔH of DGEBA on the (A) TETA and (B) PAni.DBSA concentrations (w_{DGEBA} = weight fraction of diglycidyl ether of bisphenol A).

reactivity of PAni.DBSA was low, as expected for an aromatic amine, and hence, curing occurred at higher temperatures. The presence of PAni.DBSA in the epoxy/TETA system resulted in a curing process characterized by two distinct exothermic peaks, indicating that even in the presence of a more reactive aliphatic amine, PAni.DBSA also participated in the curing process.

To investigate the stoichiometric proportions of the hardener related to the epoxy resin, ΔH and T_g of the resin were determined as a function of the hardener concentration with DSC analysis. According to the literature, at a stoichiometric epoxy/hardener ratio, the extent of cure is expected to be maximum, and consequently, the highest value of ΔH is observed.[17–19] Beyond the stoichiometric ratio, the ΔH value decreases due to dilution effect caused by the excess of hardener.

Figure 2 compares the experimental relationship of ΔH as a function of the hardener concentration for the epoxy/TETA and epoxy/PAni.DBSA single systems.

Systems constituted by TETA as the hardener presented the intersection of the experimental values at a weight fraction of triethylenetetramine (W_{TETA}) of 0.128 ± 0.01, which corresponded to a TETA concentration of 14.7 phr and an equivalent mass of 27.5 g/equiv. The ΔH value at maximum corresponded to 486 ± 10 J/g (106.6 kJ/equiv).

The intersection of the experimental values of ΔH for the epoxy/PAni.DBSA system was found at a weight fraction of polyaniline doped with dodecylbenzenesulfonic acid ($W_{PAni.DBSA}$) of 0.182 ± 0.01, which corresponded to a PAni.DBSA concentration of 23.8 phr and an equivalent mass of active groups of 44.5 g/equiv. The ΔH value at maximum corresponded to 448 ± 15 J/g (102.9 kJ/equiv).

The dependence of T_g on the epoxy resin/hardener equivalent mass ratio is illustrated in Figure 3. For the epoxy/PAni.DBSA system, it was impossible to perform measurements at a equivalent of active groups per equivalent of epoxy higher than 1.6 because it was
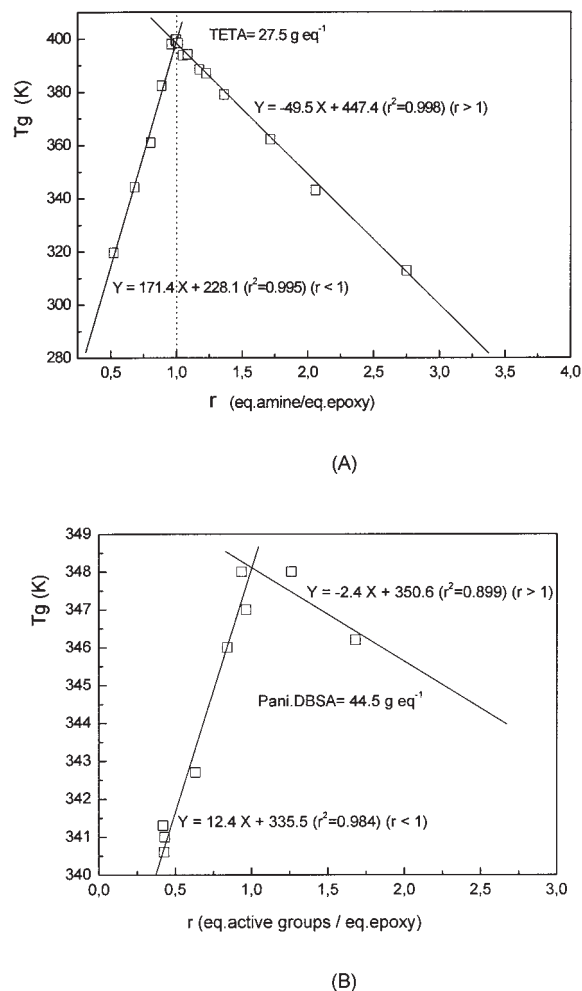
Figure 3 Dependence of T_g on the hardener/epoxy resin equivalent mass ratio (r); (A) TETA/DGEBA and (B) PAni.DBSA/DGEBA equivalent mass ratio.
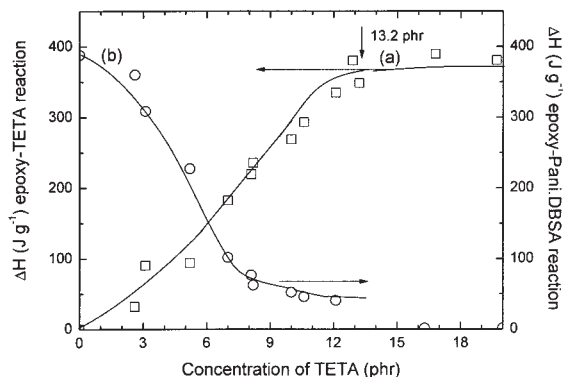
Figure 4 Effect of TETA concentration on ΔH of DGEBA containing 10 phr PAni.DBSA at (a) 90°C, related to TETA, and (b) at 230°C, related to PAni.DBSA.

very difficult to obtain a homogeneous dispersion of PAni.DBSA on the epoxy resin beyond this ratio. In both cases, the highest value of T_g was obtained at the stoichiometric proportion of the hardener–epoxy system. The T_g value for the epoxy/TETA system at the stoichiometric ratio was 124°C (397 K) and agreed with the value reported in literature for epoxy/aliphatic amine systems.[18–22] The highest T_g value for epoxy/PAni.DBSA system was 75°C (348 K) and corresponded to the stoichiometric proportion of the active groups in PAni.DBSA (44.5 g/equiv) and epoxy resin (187 g/equiv). This value was lower than those reported in the literature for aromatic amines[23,24] and was attributed to the presence of DBSA in the PAni conducting component, which could react with epoxy groups. The presence of DBSA partially inhibited the crosslinking reaction of epoxides with TETA groups, which caused the decrease in T_g. In addition, it could act as a plasticizer.

The curing parameters of the epoxy/PAni.DBSA/TETA mixing system was also evaluated. For this study, different amounts of TETA were added to a binary system constituted by DGEBA and 10 phr PAni.DBSA. This system presented two exothermic peaks, as illustrated in Figure 1. The effect of TETA concentration on ΔH related to the TETA hardener (at 90°C) and to the PAni.DBSA hardener (at 236°C) is illustrated in Figure 4. At low TETA concentrations, the reaction between PAni.DBSA took place to a great extent. As the TETA concentration in the system increased, ΔH related to the reaction between PAni.DBSA and the epoxy (236°C) decreased sharply. Beyond 12 phr TETA, the transition at 236°C was not detected.

We evaluated the stoichiometric proportion of hardener (TETA and PAni.DBSA) related to the epoxy resin by relating the total heat of curing (ΔH_{total}; at 90 and 236°C) with W_{TETA}. W_{TETA} was calculated according to the following equation:

$$W_{TETA} = \frac{w_{TETA}}{W_{TETA} + W_{composite}} \quad (1)$$

where $W_{composite}$ is the weight fraction of the mixture of diglycidyl ether of bisphenol A and polyaniline doped with dodecylbenzenesulfonic acid. Figure 5 shows the dependence of ΔH on different concentrations of TETA for the epoxy/PAni.DBSA system containing 10 phr PAni.DBSA. The highest ΔH value (obtained from the intersection of the experimental values) was observed at $W_{TETA} = 0.107 \pm 0.01$, which corresponded to a TETA concentration of 13.2 phr. The ΔH value at maximum corresponded to 410 ± 10 J/g[1] (104.4 kJ/equiv). Of course, the amount of TETA necessary to achieve the highest ΔH was lower in this system related to the epoxy/TETA system because of the participation of PAni.DBSA in the curing process.

The effect of PAni.DBSA on T_g of the epoxy resin was investigated with a stoichiometric ratio of a mixture of TETA and PAni.DBSA related to the epoxy resin. Different compositions were prepared, as summarized in Table I. The dependence of T_g on the PAni.DBSA content is illustrated in Figure 6. A continuous decrease of T_g was observed as the PAni.DBSA content in the system increased. Because the stoichiometric ratio was maintained in all composites, this behavior may have been due to the effect of DBSA.

Electrical conductivity of the composites

The electrical conductivity of the epoxy networks containing different amounts of PAni.DBSA was determined in systems with stoichiometric and nonstoichiometric ratios of hardener to epoxy resin. For systems without PAni.DBSA, the stoichiometric ratio was achieved with 14.7 phr TETA, which corresponded to 0.5347 equiv/100 g of epoxy resin. We prepared epoxy/PAni.DBSA networks in nonstoichiometric ratios by keeping the TETA concentration constant (14.7 phr, 0.5347 equiv) and increasing the amount of PAni.DBSA. For epoxy/PAni.DBSA networks at a stoichiometric ratio, the concentration of TETA hardener was
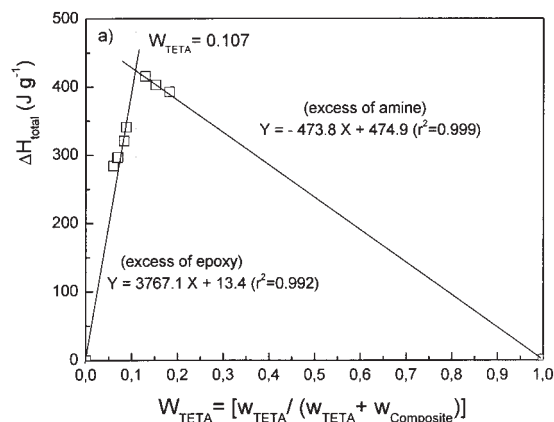
Figure 5 Dependence of ΔH_{total} of DGEBA containing 10 phr PAni.DBSA as a function of TETA concentration.

TABLE I
Compositions of the Epoxy Resins with Stoichiometric Amounts of the Mixed
Hardener (TETA/PAni.DBSA) Used for the Determination of T_g
and Electrical Conductivity

Concentration of PAni.DBSA (phr)	Concentration of PAni.DBSA (g/equiv)	Concentration of TETA (g/equiv)	Concentration of TETA (phr)
0	0	0.5347	14.70
1	0.0233	0.5114	14.06
2	0.0467	0.4880	13.42
4	0.0934	0.4413	12.13
5	0.1167	0.4180	11.49
7.5	0.1751	0.3596	9.89
10	0.2334	0.3013	8.28

decreased to compensate for the presence of PAni.D-BSA. Table II presents the results of electrical conductivity as a function of PAni.DBSA concentration. For nonstoichiometric ratios, the conductivity increased as the PAni.DBSA content in the network increased until a value around 3×10^{-8} S/cm was achieved with 10 phr PAni.DBSA. An increased amount of PAni.DBSA up to 30 phr did not exert any additional influence on the conductivity. The low conductivity of these composites, even with high amounts of PAni.DBSA, was due to the deprotonation process of PAni.DBSA caused by the aliphatic amine (TETA) as the curing agent. This phenomenon was also confirmed by the change of the color from dark green to dark blue, which is characteristic of the emeraldine base, just after the addition of TETA.

At the stoichiometric ratio, the TETA concentration decreased to compensate for the presence of PAni.D-BSA. The electrical conductivity values of the epoxy/PAni.DBSA networks were higher than those found for the nonstoichiometric ratio because the deprotonation occurred to a lower extent. For example, an elec-

trical conductivity three orders of magnitude higher was found in the system under stoichiometric conditions (with a low amount of TETA) because of the lower amount of TETA used to compensate for the presence of PAni.DBSA.

Dielectric properties of the epoxy/PAni.DBSA blends

The dielectric relaxation of the epoxy/TETA system is presented in terms of the imaginary component of M'' with temperature at different frequencies in Figure 7. M'' was calculated from the dielectric constant and dielectric loss (ε'') according to the following equation:

$$M'' = \frac{\varepsilon''}{(\varepsilon'')2 + (\varepsilon'')2} \tag{2}$$

Two distinct dielectric relaxations were observed, as shown in Figure 7. The first, between −75 and −50°C, was related to the β relaxation of the epoxy matrix,[25,26] and the second, between 100 and 150°C, corresponded to T_g of the epoxy network, which was similar to the values of T_g for epoxy/aliphatic amines-based systems.[18–22]

The influence of PAni.DBSA in the dielectric relaxations of epoxy/TETA is shown in Figure 8. As shown in Figure 8(a), with 10 phr PAni.DBSA, two dielectric relaxations were observed. At frequencies up to 50 Hz, the first relaxation occurred around 25°C and was attributed to the PAni component. The second relaxation corresponded to T_g of the epoxy network. The addition of PAni.DBSA caused a decrease in T_g, according to the DSC analyses. At frequencies higher than 50 Hz, only one relaxation corresponding to T_g was observed. In the same way, Figure 8(b) presents the dependence of M'' on the temperature for composition with 20 phr PAni.DBSA. In this case, the same behavior was observed. At frequencies up to 50 Hz, the first relaxation was observed around 10°C, and the second was observed at lower values than the epoxy
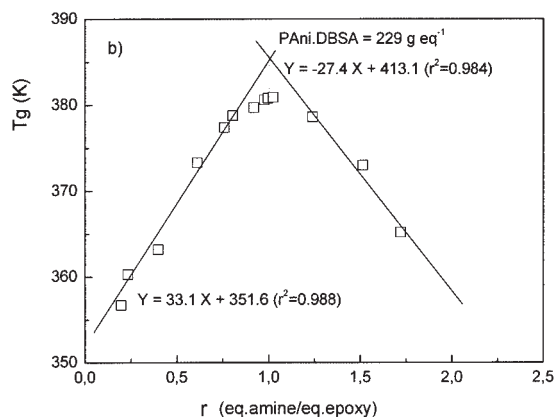

Figure 6 Dependence of T_g on the PAni.DBSA content in the DGEBA/TETA system with the stoichiometric ratio (r) of the hardener (TETA + PAni.DBSA) related to the epoxy resin.

TABLE II
Electrical Conductivity of the Epoxy/PAni.DBSA Networks

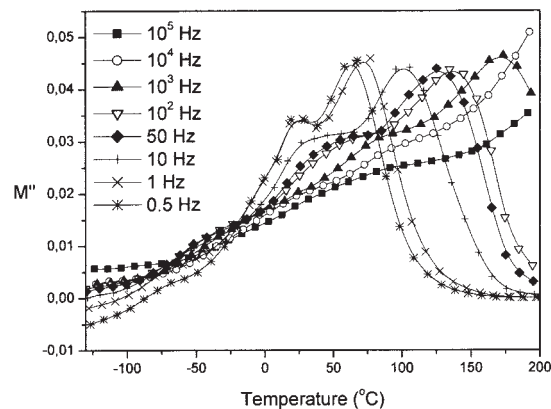| Blend composition (phr)			Concentration of active groups (g/equiv)			Electrical conductivity (S/cm)
DGEBA	TETA	PAni.DBSA	Epoxy	TETA	PAni.DBSA	
100	14.7	0	0.5347	0.5347	0	3.12×10^{-12}
100	14.7	5	0.5347	0.5347	0.1167	3.35×10^{-10}
100	14.7	10	0.5347	0.5347	0.2334	2.67×10^{-8}
100	14.7	15	0.5347	0.5347	0.3501	3.18×10^{-8}
100	14.7	20	0.5347	0.5347	0.4668	2.99×10^{-8}
100	14.7	30	0.5347	0.5347	0.7002	3.06×10^{-8}
100	14.06	1	0.5347	0.5114	0.0233	2.00×10^{-10}
100	13.42	2	0.5347	0.4880	0.0467	2.33×10^{-10}
100	12.13	4	0.5347	0.4413	0.0934	3.37×10^{-8}
100	11.49	5	0.5347	0.4180	0.1167	1.99×10^{-7}
100	9.89	7.5	0.5347	0.3596	0.1751	2.54×10^{-6}
100	8.28	10	0.5347	0.3013	0.2334	9.57×10^{-6}

network. Also, at frequencies higher than 50 Hz, only one relaxation of T_g was observed. The higher amount of PAni.DBSA caused a decrease in both relaxation temperatures.

The variation of M'' with temperature at a frequency of 10 Hz for the epoxy network and its blends with 10 and 20 phr PAni.DBSA is compared in Figure 9. We observed a strong decrease in T_g of the epoxy/TETA system as the concentration of PAni.DBSA increased.

CONCLUSIONS

DSC analyses revealed that PAni.DBSA reacted with the epoxy matrix, resulting in values of ΔH and T_g that were lower than system with TETA and aromatic polyamines. The presence of PAni.DBSA in the epoxy/TETA system resulted in a curing process characterized by two distinct exothermic peaks at 90°C due to the reaction of TETA as the hardener and at 236°C related to the reaction of PAni.DBSA with the epoxy matrix. This result indicates that even in the presence of a more reactive aliphatic amine, PAni.DBSA also participated in the curing process. We eval-
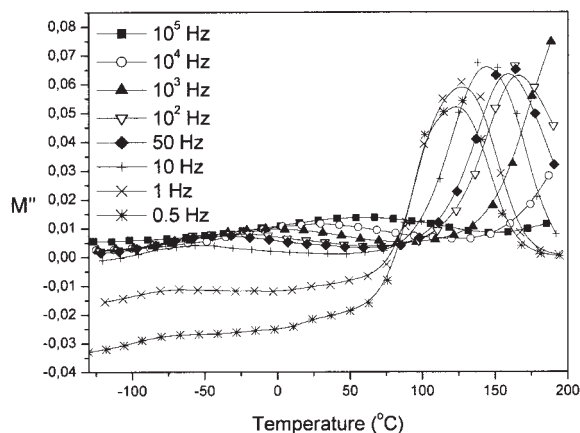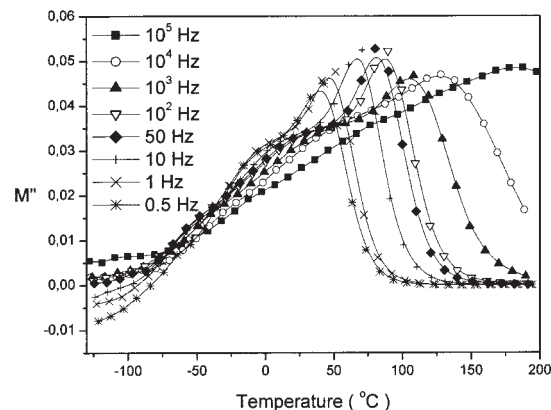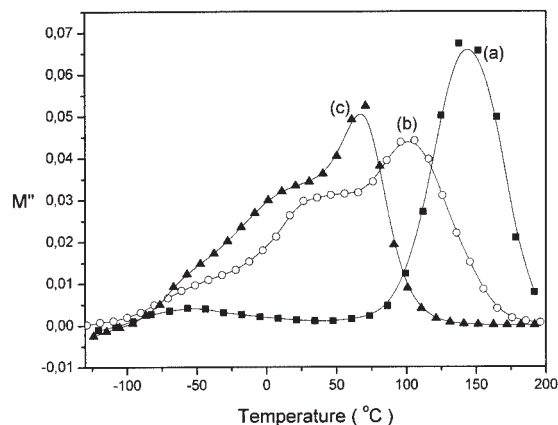
(A)

(B)

Figure 8 Dependence of the imaginary part of M'' on the temperature for (A) 100 : 10 and (B) 100 : 20 phr DGEBA/PAni.DBSA at different frequencies.

Figure 7 Dependence of the imaginary part of M'' on the temperature in the DGEBA/TETA system at difference frequencies.

Figure 9 Dependence of imaginary part of M'' on the temperature for (a) the DGEBA/TETA system and (b) 100:10 and (c) 100:20 phr DGEBA/PAni.DBSA at a frequency of 10 Hz.

uated the stoichiometric proportions of the epoxy/TETA and epoxy/PAni.DBSA systems by relating the corresponding ΔH with W_{TETA} and PAni.DBSA, respectively. These results were used to establish the amount of TETA in the epoxy/PAni.DBSA system with different proportions to keep the stoichiometric proportion of the mixed hardener (TETA + PAni.D-BSA) related to epoxy matrix. At these conditions, the increased amount of PAni.DBSA in the epoxy network resulted in a decrease in T_g, as observed by both DSC and dielectric analysis. This behavior was attributed to the presence of DBSA as the protonating agent of PAni, which could react with the epoxide groups.

To achieve the stoichiometric proportion of the epoxy/mixed hardener, the TETA concentration had to be decreased to compensate for the increased amount of PAni.DBSA. The electrical conductivities of these systems were higher than those corresponding to the epoxy/hardener systems with the same TETA concentrations. For example, with 5 phr PAni.DBSA, it was possible to achieve an electrical conductivity as high as 1.99×10^{-7}, whereas with a fixed amount of TETA, the conductivity was found to be 3.35×10^{-10}. TETA is an aliphatic amine, more basic than PAni, and can

deprotonate it and thus decrease the conductivity. With lower amounts of TETA, the deprotonation process was minimized.

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