Cardanol-Based Novolac Resins as Curing Agents of Epoxy Resins

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ABSTRACT: Two different novolac resins, named Nov-I and Nov-II, containing an amount of unreacted cardanol of 35 wt % and 20 wt %, respectively, were synthesized by the condensation reaction of cardanol and paraformaldehyde using oxalic acid as catalyst. Cardanol is the main constituent of cashew nut shell liquid, a renewable natural resource. The cardanol-based novolacs were tested as curing agents of the diglycidyl ether of bisphenol A epoxy resin employing 2-ethyl-4-methyl-imidazole as catalyst and differential scanning calorimeter and thermogravimetric studies were performed to identify the final thermal properties of the cured resins. In addition, tensile tests were carried out to evaluate the mechanical properties of the epoxy resin cured with the novolacs, which showed to deserve consideration as effective epoxy curing agents. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3585–3591, 2009

Key words: CNSL; cardanol; novolacs; epoxy resins; curing agents

INTRODUCTION

The need to reduce the use of fossil fuel derived monomers in the manufacture of polymers is evident as a result of the spiralling cost and the high rate of depletion of the petrochemical-derived stocks. This requires the investigation and use of natural and renewable sources which can serve as alternative feedstocks of monomers for the polymer industry.

Cashew nut shell liquid (CNSL) is a renewable natural resource obtained from the cashew (*Anacardium occidentale* L.) nut as a by-product during the process of removing the cashew kernel from the nut and its total production approaches one million tons annually.[1–3] In its natural form, the crude CNSL is essentially a mixture of different unsaturated long-chain phenols and represents a good natural alternative to petrochemically derived phenols.[4] CNSL constitutes nearly 25% of the total weight of the nut and is composed of anacardic acid (3-*n*-pentadecylsalicylic acid) and smaller amounts of cardanol (3-*n*-pentadecylphenol), cardol (5-*n*-pentadecylresorcinol), and methylcardol (2-methyl-5-*n*-pentadecylresorcinol), the long aliphatic side-chain being saturated, mono-olefinic (8), di-olefinic (8, 11), and tri-olefinic (8, 11, 14) with an average value of two double bonds per molecule.[5,6] The thermal treatment of cashew nuts and CNSL induces the partial decarboxylation of anacardic acid, which is completed by the subsequent purifying distillation. The result is an industrial grade cardanol, in the form of a yellow oil containing cardanol (about 90%), with a smaller percentage of cardol and methylcardol.[3]

The interesting molecular structure of cardanol gives some attractive properties such as quick drying after baking, high electrical insulation, and good thermal stability. In addition, cardanol can react with formaldehyde by condensation polymerization to give polymers similar to phenol–formaldehyde resins.[7–9] Cardanol–formaldehyde resins are special phenolic materials having key properties such as high-temperature resistance, modulus retention at elevated temperatures, resistance to chemicals and detergents, high surface hardness, and low cost. Acid catalyzed condensations with an excess of cardanol produce novolac type resins, which are thermoplastic resins, whereas base catalyzed conditions with an excess of formaldehyde result in the formation of resol resins.[10]

Although cardanol and its derivatives can be converted to polymers with better processability, hydrocarbon solubility and resistance to acids and alkalis than conventional phenol-based systems, little has been published on the development of polymeric materials from CNSL and, in particular, from novolac-type phenolic resins prepared from cardanol. This kind of resins have been studied and proposed only recently for applications in the fields of surface coatings,[11] rubber

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reinforcement,[12,13] brake linings,[14] composites,[15,16] photoresist for microlithography,[17,18] polyurethanes,[19,20] and few others.[21–23] In the last years, cardanol-based novolac resins have been also studied as modifiers of commercial epoxy resins to improve the mechanical properties and toughness of these.[24,25]

In this study, we investigated for the first time the use of cardanol-based novolac resins as curing agents of commercial epoxy resins. The novolacs were prepared by the condensation reaction of cardanol and paraformaldehyde using oxalic acid as catalyst and tested as curing agents of epoxy resins. The final thermal properties of the cured resins were evaluated by differential scanning calorimeter (DSC) and thermogravimetric studies. Moreover, tensile tests were carried out to assess the mechanical properties of the epoxy resin cured with the novolacs.

EXPERIMENTAL

Materials

Cardanol (with a purity of about 86%) was kindly supplied by Oltremare Spa (Bologna, Italy). The commercial grade diglycidyl ether of bisphenol A (DGEBA) epoxy resin EC01 was obtained from Camattini Spa (Collecchio, Italy). The epoxy equivalent weight (EEW) of EC01 ranged from 184 to 190 g/eq. Paraformaldehyde (≥95%), anhydrous oxalic acid (≥97.0%) and HPLC grade tetrahydrofurane (THF) were purchased from Fluka (Steinheim, Germany). Deuterated chloroform ($CDCl_3$, 99.8 atom% D), 2-ethyl-4-methylimidazole (2,4-EMI) (95%), and analytical grade chloroform and diethyl ether were obtained from Sigma-Aldrich (Steinheim, Germany). Silica Gel 60 (230-400 Mesh) was supplied by Merck (Darmstadt, Germany). All materials were used as received without further purification.

Preparation of cardanol-based novolacs

Two different novolacs, named Nov-I and Nov-II, were synthesized by the condensation reaction of cardanol and paraformaldehyde using an oxalic acid/cardanol weight ratio of 1/100 and 3/100, respectively. Both novolacs were obtained using the following procedure: cardanol (200 g, 0.66 mol) and oxalic acid were mixed in a 500 mL three-necked round bottom flask equipped with a mechanical stirrer, a thermometer, and a Dean-Stark apparatus connected to a condenser; the system was preheated at 70°C and then paraformaldehyde (12.03 g, 0.40 mol) was added. The temperature was then raised to 100°C, keeping the system under vigorous stirring for about 6 h. The traces of water and acid catalyst were removed by raising the temperature to 115°C. The unreacted cardanol in the novolacs prepared was determined by silica gel column chromatography using chloroform as eluant.

Measurements

Fourier transform infrared spectroscopic analysis

Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrophotometer by KBr pellet method in the spectral range from 4000 cm^{-1} to 400 cm^{-1}.

Nuclear magnetic resonance spectroscopic analysis

Proton nuclear magnetic resonance (^1H-NMR) spectra were recorded on a Bruker Advance 400 NMR spectrometer operating at 400 MHz with $CDCl_3$ as solvent and TMS as internal standard. Sample temperature was stabilized at 25°C.

The novolacs used for ^1H-NMR analyses were purified by silica gel column chromatography using chloroform as eluant, to remove the unreacted cardanol.

The average number of cardanol units in the novolacs was calculated from the integration of the methylene and aromatic regions of the ^1H-NMR spectrum using the following equation:

$$[\mathrm{Ar}]/[\mathrm{CH_2}] = (2n+6)/(2n+2)$$

where $[\mathrm{Ar}]/[\mathrm{CH_2}]$ is the ratio of the aromatic protons to the methylene protons and n is the number of cardanol units.

Gel permeation chromatographic analysis

Gel permeation chromatography (GPC) was performed by using a Knauer Smartline high-pressure liquid chromatography (HPLC) system equipped with a Knauer Smartline UV detector 2500 set at 254 nm. A set of three consecutive Varian styrene-divinylbenzene copolymer gel columns was employed at 38°C; they were one MesoPore and two PLgel (300 × 7.5 mm, 3 μm), whose molecular weight range detection is up to 25,000 and up to 4000, respectively. THF was used as mobile phase at a flow rate of 1.0 mL/min and the sample injection volume was 20 μL. For analyses, the samples were dissolved in THF at a concentration of 0.2% (w/w). The calibration was performed with narrow polydispersity polystyrene standards, which had molecular weight in the range of 162–371,100 Daltons.

Rheological measurements

Viscosity measurements were carried out by using an Ares cone and plate rheometer. The viscosity of the novolacs was determined before and after their purification by silica gel column chromatography using chloroform as eluant. The novolacs were purified to remove the unreacted cardanol.

DSC analysis

DSC analyses were carried out by using a Mettler Toledo DSC 823^e under nitrogen atmosphere. All samples (3–5 mg) were prepared in sealed aluminum pans and the nonisothermal scans were performed at 10°C/min over a temperature range of 25–300°C. The glass transition temperature (T_g) was obtained by rerunning the experiment twice. The temperature at half extrapolated tangents of the step transition midpoint was used as the glass transition.

Mechanical testing

The tensile properties of the cured resins in the form of standard dumbbell-shaped test specimens were investigated according to ASTM D 638-99, using a dynamometer LLOYD LR30K equipped with a 5 kN capacity load cell at a testing speed of 5 mm/min. An Epsilon Technology Corp. extensometer was used to record the elongation of the specimens. The resins were cured at 150°C for 2 h. The mechanical data reported are the average of five trials.

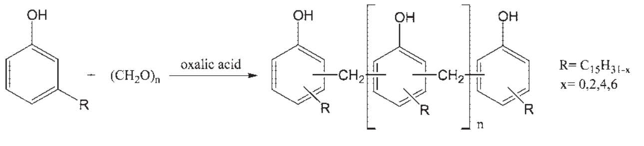
Thermogravimetric analysis

Thermogravimetric investigations were performed on a Mettler Toledo TGA/STDA 851^e. The samples (15–20 mg) were heated from 25 to 850°C at a heating rate of 20°C/min under nitrogen atmosphere (balance purge, 140 mL/min; sample purge, 50 mL/min).

RESULTS AND DISCUSSION

Characterization of cardanol-based novolacs

The cardanol-based novolacs were prepared by the condensation reaction of cardanol and paraformaldehyde using oxalic acid as catalyst, as shown in Scheme 1. The unreacted cardanol in the novolacs prepared, which was determined by silica gel column chromatography, amounted to 35 wt % and 20 wt % in Nov-I and Nov-II, respectively. The novolacs were characterized by GPC and FTIR and ^{1}H-NMR spectroscopy. Figure 1 shows the FTIR spectra of cardanol and the cardanol-based novolacs in the spectral region from 1900 cm^{-1} to 600 cm^{-1}. The presence of the methylene group (—CH$_2$—) linking two benzene rings was revealed by the appearance of the peak at about 1435 cm^{-1} in the spectrum of both the novolacs. The appearance of the peaks at about 966, 812, 1105, and 1189 cm^{-1} in the novolac spectra are due to the ortho substitution in benzene nuclei confirmed also by the bands appeared at 1637 and 1727 cm^{-1}. These results are in accordance with spectral data previously reported.[20,26,27]



Scheme 1 Synthesis of the cardanol-based novolacs.

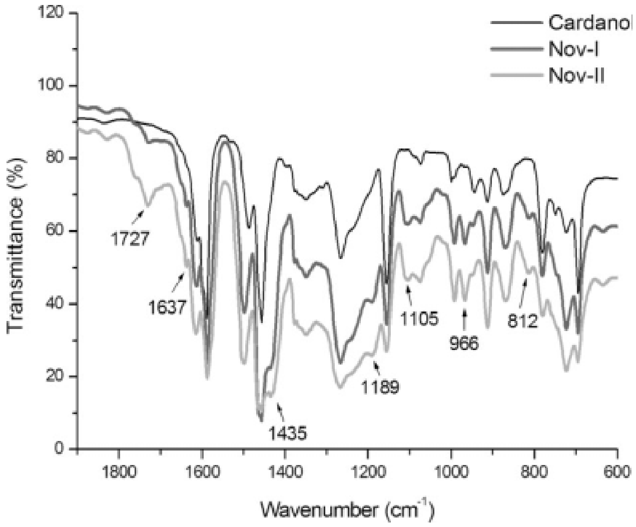


Figure 1 FTIR spectra of cardanol and the cardanol-based novolacs.

The GPC chromatograms of the cardanol-based novolacs are shown in Figure 2. The peaks of cardanol and trimer at 22.98 and 21.10 min, respectively, can be easily identified in the chromatograms. The

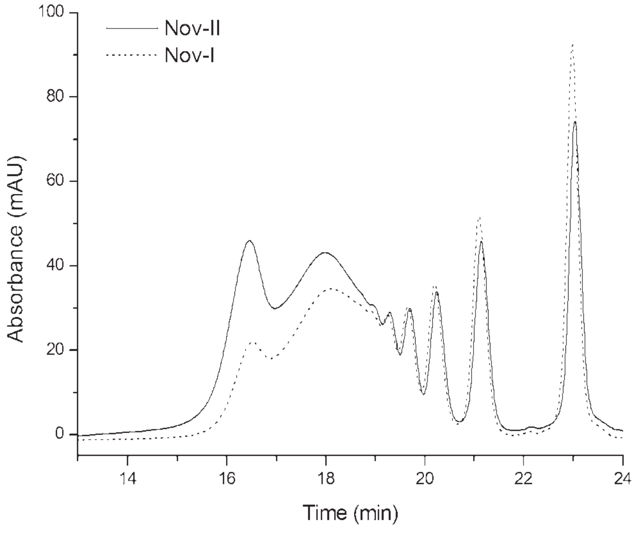


Figure 2 GPC chromatograms of the cardanol-based novolacs.

TABLE I
Viscosity of the Cardanol-Based Novolacs before and after Purification by Silica Gel Chromatography

	Viscosity at 25°C (cPs)	
	Before purification	After purification
Nov-I	7000	38,000
Nov-II	34,000	53,000

other peaks at 20.22 and 19.67 min can be attributed to tetramer and pentamer, respectively. At higher molecular weights, the GPC analysis is rather convoluted because of the dramatic increase in the number of possible isomers as the number of cardanol units increases,[28] resulting in a difficult assignment of other peaks. Since polystyrene standards were used for GPC calibration, the data obtained can be considered qualitatively only.[28] Consequently, ^{1}H-NMR studies were performed to determine the average number of cardanol units in Nov-I and Nov-II, which were found to be 3.8 and 5.2, respectively. This indicated that Nov-I is formed on average by hexamer, whereas Nov-II contains on average heptamer.

The viscovity of the novolacs was also determined before and after their purification by silica gel column chromatography and the results obtained are reported in Table I. As can be seen, before purification, Nov-II has a higher viscosity. After purification, the viscosity of Nov-II kept higher than that of Nov-I, confirming the higher average molecular weight of Nov-II, as showed by ^{1}H-NMR results.

Characterization of the epoxy resin cured with cardanol-based novolacs

DSC analysis

The cardanol-based novolacs, prepared as described earlier, were used as curing agents of the DGEBA epoxy resin employing 2,4-EMI as catalyst. DSC studies were performed to investigate the polymerization mechanisms and the final thermal properties of the cured resins.

Preliminary DCS analyses were carried out using Nov-I as curing agent of the epoxy resin to study the occurring polymerization processes. The Nov-I/epoxy resin weight ratio was varied from 60/40 to 20/80 keeping constant the DGEBA/2,4-EMI molar ratio at a value of 10/1. The samples were prepared first by heating the 2,4-EMI at 45°C under nitrogen atmosphere and then by adding the Nov-I/epoxy resin mixture to the catalyst under stirring at room temperature for 10 min. The DSC data and thermograms of the epoxy resin cured with Nov-I are reported in Table II and Figure 3, respectively.

TABLE II
DSC Data of the Epoxy Resin Cured Using a DGEBA/2,4-EMI Molar Ratio of 10/1 and Varying the Nov-I/Epoxy Resin Weight Ratio from 60/40 to 20/80

Nov-I/Epoxy resin	ΔH (J/g)	Peak temperature (°C)	T_g (°C)
60/40	164	151	30
50/50	187	155	35
40/60	256	147	61
30/70	313	141	83
20/80	333	137	110

As shown in Figure 3, a single DSC peak was recorded using a Nov-I/epoxy resin weight ratio of 60/40 that corresponded approximately to the stoichiometric ratio of phenolic hydroxyl groups to epoxide groups. As the novolac resin content decreased and, thus, an excess of epoxide groups to phenolic hydroxyl groups occurred, a further DSC peak appeared. This indicated a complex polymerization mechanism, as previously proposed for the curing of epoxy resins with bisphenol A using 2,4-EMI as catalyst.[29–31] According to these studies, we supposed that the epoxide groups reacted only with the phenolic hydroxyl groups of the novolac when the higher novolac amount was used, giving rise to a single DSC peak. In this case, a linear polymer containing secondary hydroxyl groups could be formed. As the novolac content decreased, a second sharper peak in the DSC thermograms appeared. This could signify that the epoxide groups not involved in the polymerization with the phenolic hydroxyl groups reacted with the secondary hydroxyl groups to form aliphatic ethers.[29–31] Therefore, Nov-I/epoxy resin weight ratios lower than 60/40 could lead to the crosslinking of the resin.

In addition, lower peak temperatures and higher reaction enthalpies were progressively observed as the epoxy resin content increased (Table II). This

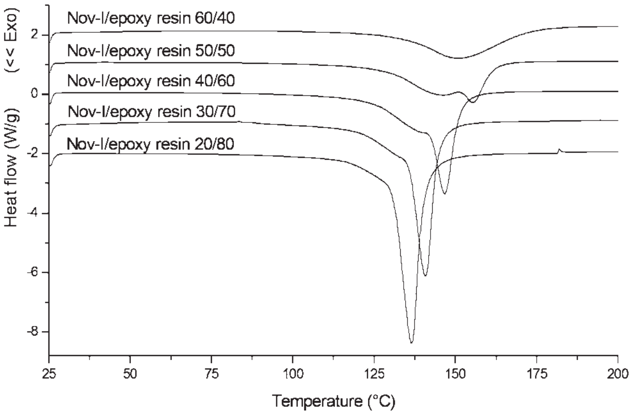


Figure 3 DSC thermograms at 10°C/min under nitrogen atmosphere of the epoxy resin cured using a DGEBA/2,4-EMI molar ratio of 10/1 and varying the Nov-I/epoxy resin weight ratio from 60/40 to 20/80.

TABLE III
DSC Data of the Epoxy Resin Cured Using a DGEBA/2,4-EMI Molar Ratio of 10/1 and the Nov-II/Epoxy Resin Weight Ratios of 30/70 and 20/80

Nov-II/Epoxy resin	ΔH (J/g)	Peak temperature (°C)	T_g (°C)
30/70	311	141	96
20/80	341	138	116

behavior can be explained considering that the catalyst concentration within the reaction mixture increased as the amount of the epoxy resin augmented. Moreover, progressively, higher T_g values were found as the epoxy resin content increased (Table II), indicating that the higher the amount of epoxy resin was used, the higher cross-linking density of the final polymer was obtained.

To evaluate the changes of the thermal data when the epoxy resin was cured using Nov-II instead of Nov-I, DSC analyses were also carried out for the epoxy resin cured with Nov-II. In particular, the thermal tests were performed only for the polymers characterized by the novolac/epoxy resin weight ratios of 30/70 and 20/80, which showed the highest T_g values when Nov-I was used as curing agent (Table II). Also in this case, a constant DGEBA/2,4-EMI molar ratio of 10/1 was utilized. DSC data and thermograms of the epoxy resin cured with Nov-II are reported in Table III and Figure 4, respectively.

As deduced from the comparison of the DSC data reported in Tables II and III, the use of Nov-II instead of Nov-I as curing agent increased the T_g values. This could be explained by both the higher average molecular weight and the lower content of unreacted cardanol of Nov-II. In fact, since cardanol has only one hydroxyl group, it could act as polymer chain terminator, resulting in an increasing average molecular weight of the polymer as the cardanol amount decreases.

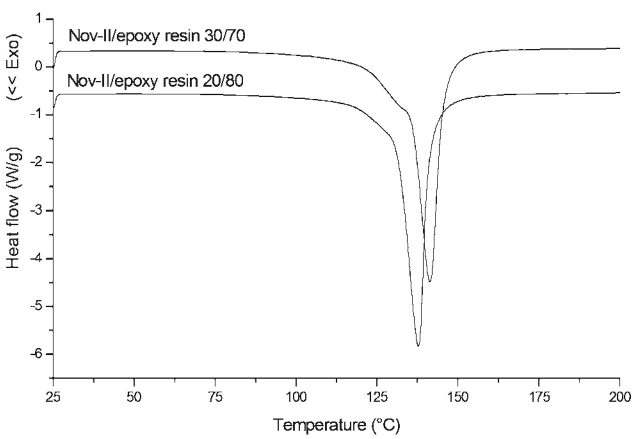


Figure 4 DSC thermograms at 10°C/min under nitrogen atmosphere of the epoxy resin cured using a DGEBA/2,4-EMI molar ratio of 10/1 and the Nov-II/epoxy resin weight ratios of 30/70 and 20/80.

TABLE IV
Tensile Properties of the Epoxy Resin Cured Using a DGEBA/2,4-EMI Molar Ratio of 10/1 and the Novolac/Epoxy Resin Weight Ratios of 30/70 and 20/80

	Nov-I/Epoxy resin		Nov-II/Epoxy resin	
	30/70	20/80	30/70	20/80
Young modulus (MPa)	1700 ± 136	2200 ± 200	1995 ± 155	2487 ± 86
Tensile strength (MPa)	35 ± 3	42 ± 6	36 ± 4	49 ± 2
Elongation at break (%)	2.4 ± 1.4	2.8 ± 0.8	4.0 ± 0.8	3.2 ± 0.4

Mechanical testing

Tensile tests were performed on the samples obtained using the novolac/epoxy resin weight ratios of 30/70 and 20/80 at a constant DGEBA/2,4-EMI molar ratio of 10/1. The data obtained are reported in Table IV. It can be observed an improvement of the mechanical properties with the increase of the epoxy resin amount for the polymers prepared using both the novolacs. This behavior confirmed an increasing cross-linking density of the final polymer as the amount of the epoxy resin increased, as suggested by the DSC results described earlier.

In addition, we observed that, using a novolac/epoxy resin weight ratio of 30/70, the resin cured with Nov-II showed better mechanical properties compared with that cured with Nov-I, because of both the higher average molecular weight and the lower content of unreacted cardanol of Nov-II. The same results were observed comparing the resins cured with both the novolacs using a novolac/epoxy resin weight ratio of 20/80.

Thermogravimetric analysis

The thermogravimetric analysis (TGA) curves of the samples obtained using the Nov-I/epoxy resin weight ratios of 30/70 and 20/80 at a constant DGEBA/2,4-EMI molar ratio of 10/1 (Fig. 5) showed that the thermal resistance of the cured resins in nitrogen atmosphere did not change significantly with the increase of the novolac amount. The same was observed for the resins cured with Nov-II (Fig. 6). In any case, the TGA curves showed only one-step mass loss corresponding to a single thermal degradation process, which occurred at temperatures

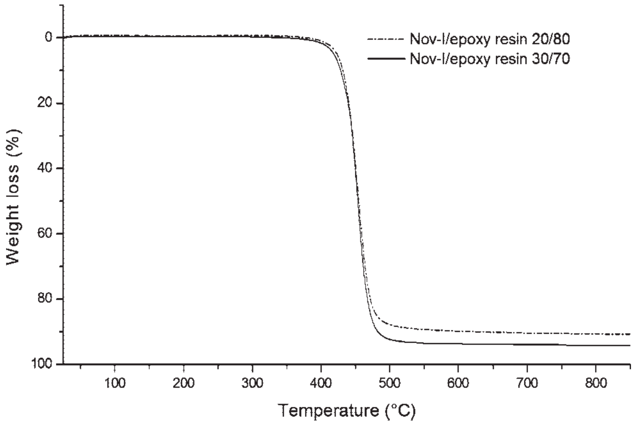


Figure 5 TGA curves of the epoxy resin cured using a DGEBA/2,4-EMI molar ratio of 10/1 and the Nov-I/epoxy resin weight ratios of 30/70 and 20/80.

higher than 400°C, as indicated by the thermogravimetric data reported in Table V. These results could be explained considering the high cross-linking density of the cured resins due to the use of 2,4-EMI as catalyst and, moreover, to the high amount of aromatic rings within the cured resins.

In addition, the employ of Nov-II instead of Nov-I as curing agent did not result in any appreciable change of the thermal resistance of the cured resins, indicating that the amount of unreacted cardanol in the novolacs prepared did not affect significantly the thermal degradation temperature of the final resin.

TABLE V
Decomposition Temperatures for 10% and 50% Weight Loss (T_{10} and T_{50}, Respectively) and Weight Loss at 850°C of the Epoxy Resin Cured Using a DGEBA/2,4-EMI Molar Ratio of 10/1 and the Novolac/Epoxy Resin Weight Ratios of 30/70 and 20/80

	Nov-I/Epoxy resin		Nov-II/Epoxy resin	
	30/70	20/80	30/70	20/80
T_{10} (°C)	428	431	428	431
T_{50} (°C)	453	455	452	455
Weight loss (%)	94.4	91.1	91.0	91.3

CONCLUSIONS

In this study, the use of two different cardanol-based novolac resins, named Nov-I and Nov-II, as curing agents of commercial epoxy resins was investigated. DSC studies showed that novolac/epoxy resin weight ratios lower than 60/40 led to the crosslinking of the resin as result of an increasing number of secondary hydroxyl groups available for cross-linking reactions. An improvement of the mechanical properties with the increase of the epoxy resin amount was also observed. On the other hand, the thermal resistance of the cured resin in nitrogen atmosphere did not change significantly varying the novolac amount and only one-step mass loss corresponding to a single thermal degradation process, occurring at temperatures higher than 400°C, was observed.

In addition, it was found that the use of Nov-II instead of Nov-I as curing agent did not affect significantly the thermal degradation temperature of the final resin, but increased the T_g values and improved the mechanical properties of the cured resin because of both the higher molecular weight and the lower content of unreacted cardanol of Nov-II.

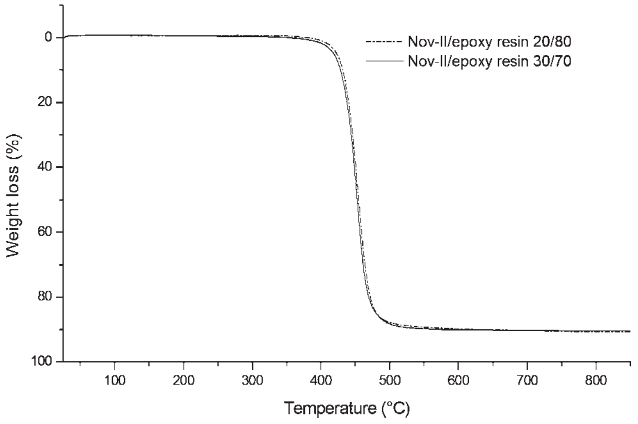


Figure 6 TGA curves of the epoxy resin cured using a DGEBA/2,4-EMI molar ratio of 10/1 and the Nov-II/epoxy resin weight ratios of 30/70 and 20/80.

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