

Structural Effect of Phenalkamines on Adhesive Viscoelastic and Thermal Properties of Epoxy Networks

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ABSTRACT: Phenalkamine, the Mannich reaction products from cardanol, formaldehyde, and polyamines were prepared using ethylene diamine, diethylene triamine and triethylene tetraamine. These products were characterized by high-pressure liquid chromatography (HPLC), infrared spectroscopy, and nuclear magnetic resonance spectroscopy (^1H NMR). Clearly resolved peaks due to presence of triene, diene, monoene, and saturated side chain containing species of cardanol were observed in HPLC. The presence of characteristic methylene linkages of Mannich bases at δ 3.5–4.0 ppm was observed by ^1H NMR. These curing agents were reacted with diglycidyl ether of bisphenol-A at room temperature and the curing times were optimized. The cured resins showed good adhesion with

different metal surfaces particularly higher values were observed with copper due to its high surface energy. The viscoelastic properties of the cured samples were determined by dynamic mechanical thermal analysis. The storage modulus (E') was found to be in the order of 10^9 Pa and $\tan \delta$ values are around 90°C . A reduction in storage modulus (E') and an increase in $\tan \delta$ values on postcuring were observed. Thermogravimetry analysis showed two-stage degradation above 250°C for the cured samples. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4741–4748, 2006

Key words: phenalkamine; epoxy; adhesive; dynamic mechanical thermal analysis; thermal properties

INTRODUCTION

Epoxy polymers have been extensively exploited among thermosetting resins due to their chemical resistance, outstanding adhesive properties, and good mechanical and physical properties.^{1,2} Their applications range from laminated circuit boards, carbon fiber composites, electronic encapsulants, and adhesives. Curing can result in a three-dimensional network whose properties dependent on the extent and density of crosslinking. While there are many types of curing agents for the epoxy coating industry, the Mannich bases have been popularly used due to the structural versatility. The condensation product of phenols, formaldehyde, and amine, namely the Mannich bases are particularly useful as low temperature curatives for epoxies.^{3–6} It is known that the phenol containing compounds enhances the rate of nucleophilic ring opening of epoxies by amines.^{7,8} Another advantage of Mannich bases is, its high molecular weight (M_w , 400–1000 g/mol) that can improve the physical properties of cured material.⁹ But these classical Mannich

bases also have short pot life, lack of flexibility, unsatisfactory water resistance.

Attempts have been made in the literature to alleviate the drawbacks of Mannich bases by using alkyl substituted phenols. Cardanol, the main product obtained by thermal treatment of cashew nut shell liquid (CNSL), is a phenol derivative having a C15 unsaturated hydrocarbon chain as meta substitute.¹⁰ The phenalkamine obtained from cardanol were aimed to satisfy all requirements for the industrial and high performance coating industries, as a curing agent.¹¹ The main characteristics are extraordinary combination of long pot life and rapid cure even at low temperature. This combination of desirable properties is a necessity for the formulation of paints for industrial maintenance and marine application. In addition to this, moisture tolerance of phenalkamine curing agent allows application under wet or humid condition even on wet or damp surface.

Their unique structure can explain the fact that they have an unusual combination of desirable properties, which can be identified in the resulting cure resins. The aromatic backbone is responsible for the high chemical resistance. The side aliphatic chain is hydrophobic and can make these resins water resistant. The Phenolic-OH group makes phenalkamine very active even at low temperature. The amine side chain is responsible for the high crosslinked density. In addition to low temperature curing (with workable

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pot life), the ability to resist moisture while curing, make them ideal for temperature insensitive cure.

Synthesis of Mannich bases from cardanol has been reported in patent literature. Commercial resins believed to be the condensation products of aliphatic amines with cardanol and formaldehyde is available as phenalkamine. However, information on the composition, characterization, and cured resin properties are not available in the open literature.

The objective of this present work is to develop phenalkamine-curing agents from cardanol for room temperature curing of epoxy resins using different diamine. This article provides the details of synthesis and characterization and curing behavior of phenalkamine with epoxy resin. Adhesive, viscoelastic, and thermal properties of the cured products will be discussed.

EXPERIMENTAL

Materials

Ethylene diamine, para formaldehyde from S.D. Fine-Chem, India, diethylene triamine was received from Aldrich Chemicals (Milwaukee, USA), and triethylene tetraamine was purchased from Sisco, India. Diglycidyl ether of bisphenol-A (Lapox, B-11, EEW = 187) was obtained from Atul Products, India. Cardanol was procured from M/s Rishab Resins and Chemicals, Hyderabad.

Preparation of phenalkamine curing agent

Phenalkamine from cardanol was prepared by Mannich condensation reaction using formaldehyde and amines such as ethylenediamine, diethylene triamine, and triethylene tetraamine.¹² The reaction scheme and the structure of phenalkamine are shown in Figure 1.

A three-necked flask fitted with a water segregator and a thermometer was charged with 100 g (0.33 mol) cardanol and 30 g (0.5 mol) ethylene diamine. The contents were mixed with magnetic stirrer and heated up to 80°C. Then 16 g (0.53 mol) para formaldehyde was added in 5–6 portions to the above reaction mixture. After the addition of above contents the temperature of the mixture was raised to 100–120°C and the reaction was carried out for about 1 h. From the above reaction product, water was distilled off by applying vacuum.

Composition of epoxy/phenalkamine network for room temperature cure

Phenalkamine was used to establish room temperature curing of epoxy resin. The equivalent weight of the phenalkamine was decided by its amine value. Phenalkamine are known to react with epoxy nonsto-

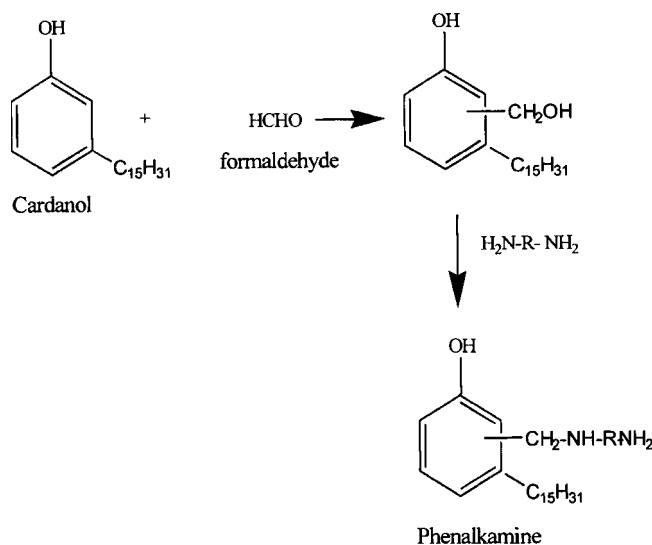


Figure 1 Structure of phenalkamine synthesized from cardanol.

chiometrically. To arrive at a best composition of the network, we have mixed epoxy and phenalkamine curatives in the equivalent ratios of 1 : 1, 1 : 2, and 1 : 3 respectively, at room temperature and observed the physical properties.

The epoxy phenalkamine compositions were named as EA-I, EA-II, EA-III, EB-I, EB-II, EB-III, EC-I, EC-II, and EC-III, where E is abbreviate of epoxy, letters A, B, and C indicates ethylene diamine (A), diethylene triamine (B), and triethylene tetraamine (C) and numbers I, II, and III represent composition 1 : 1, 1 : 2, and 1 : 3 respectively. The cure schedule for these samples is 24 h at room temperature followed by postcure for 1 h at 150°C.

Instrumentation

¹H NMR spectra were recorded with a Bruker M54-300 (300 Hz) NMR Spectrometer with CDCl₃ as solvent. Phenomenex HPLC with phenogel columns was used to record the chromatograms. THF was used as the solvent and the flow rate is 0.8 mL/min. FTIR testing was performed with Thermo Nicolet Nexus 670 Spectrometer using KBr pellets. Brookfield viscometer (LVT Model) was used to determine viscosities of phenalkamine samples.

Viscoelastic properties and glass transition temperatures of cured samples were studied using Rheometric Scientific Dynamic Mechanical Thermal Analyzer (DMTA IV model). Viscoelastic studies of cured sam-

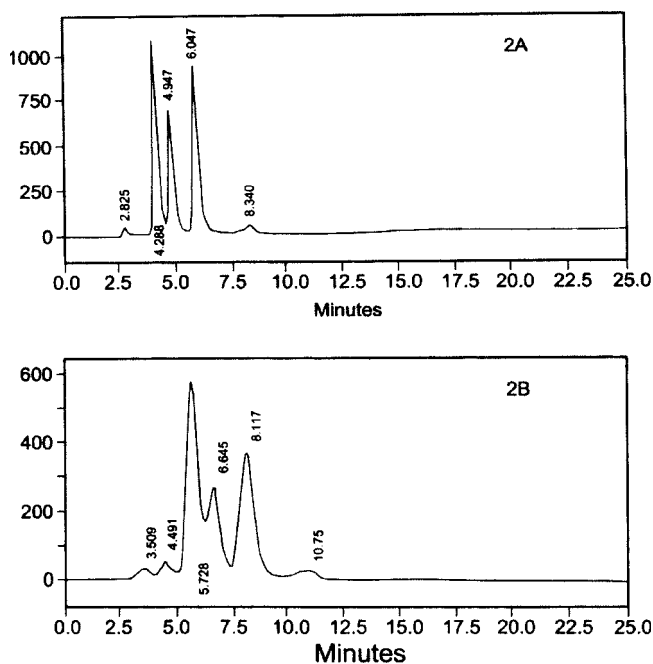


Figure 2 HPLC of phenalkamine (A) and cardanol (B).

ples were done on rectangular bars with specimen dimension of $20 \times 10 \times 1.2 \text{ mm}^3$ in tensile mode at 1 Hz frequency with a heating rate of $3^\circ\text{C}/\text{min}$. Evolution of storage modulus (E') and energy dissipation ($\tan \delta$) with temperature were measured.

Thermo gravimetric Analyzer (851 Mettler Toledo TGA instrument) was used to study the thermal decomposition of the blends. Cured samples were weighed in the sample pan and then heated in a TGA furnace at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. DTG was also recorded simultaneously. Microtech tensile testing machine was used to characterize tensile properties of the resin system.

RESULTS AND DISCUSSION

Characterization of phenolkamine curatives

The Mannich condensation products are identified with HPLC. The chromatogram of cardanol along with phenalkamine curative was given in Figure 2. The chromatograms of pure cardanol [Fig. 2(B)] gave four different peaks at retention times of 5.73, 6.65, 8.12, and 10.73 min respectively. These are due to presence of triene (39.6%), diene (20.2%), monoene (31.4%), and saturated (2.7%) side chain components that present in cardanol. According to the published reports the cardanol is a mixture of 41% triene, 21% diene, 34% monoene, and about 3% of saturated aliphatic side chain.^{13,14} The same sequences of peaks were also observed with Mannich bases although at a lower retention times compared to cardanol. The peaks in the chromatogram for phenalkamine [Fig. 2(A)]

appeared at 4.29, 4.95, 6.05, and 8.34 min respectively, due to triene (37.3%), diene (21.9%), monoene (32.8%), and saturated side chain (1.05%) components of cardanol.

The infrared (IR) spectrum of phenalkamine is given in Figure 3, which is similar to the spectra reported in literature.¹⁵ The adduct indicated characteristic absorption at $3200\text{--}3400 \text{ cm}^{-1}$ (N—H stretch), $2850\text{--}3000 \text{ cm}^{-1}$ (alkyl group), $1620\text{--}1500$ (aromatic C=C stretch), and 1276 cm^{-1} (aliphatic C—N stretch). In the ^1H NMR spectra (Fig. 4) of cardanol phenalkamine the peak at $6.5\text{--}6.9 \delta$ is due to aryl protons of benzene nuclei, the peak around the region 6.45δ is owing to the phenolic-hydroxyl, the peak at $5\text{--}5.4 \delta$ is due to unsaturated (C=CH) protons of a long alkyl side chain originally present in the cardanol. The small peak at 0.9δ is due to the terminal methyl group of the side chain. The peak at $1.2\text{--}2.5 \delta$ is due to the protons of long aliphatic side chain, methylene protons of amine.¹⁶ The observed peak $3.5\text{--}4.0 \delta$ is the characteristic chemical shift for the methylene linkages (ph-CH₂N) in the Mannich structures.^{9,17,18} All these peaks in the spectra indicate that the Mannich reaction has taken place. The ratio of integration for peaks (aromatic/ph-CH₂N/methylene protons of amine) is in good agreement with the theoretical structure of phenalkamine A at 3/3/6.

The amine functionalities are main crosslinking sites and their reactivity is indicated by its amine value. Amine value and molecular weight were determined by standard procedure and have been presented in Table I. Curing agent with higher amine value might show higher activity towards the curing reaction. Phenalkamine synthesized with triethyl tetraamine would show highest activity and will take less time to cure comparatively.

Viscosity is an important property for coating system. The lower the viscosity the better is the substrate adhesion, spread out, and ease of coating. The viscosities of phenalkamines ranged from 1250 to 1600 mPa s

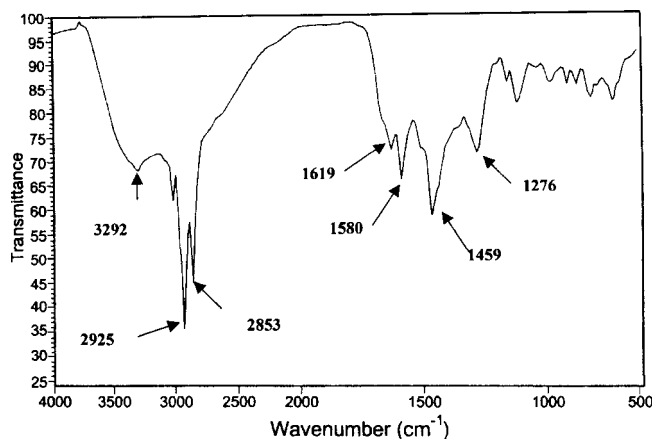


Figure 3 IR spectra of phenalkamine (B) curing agent.

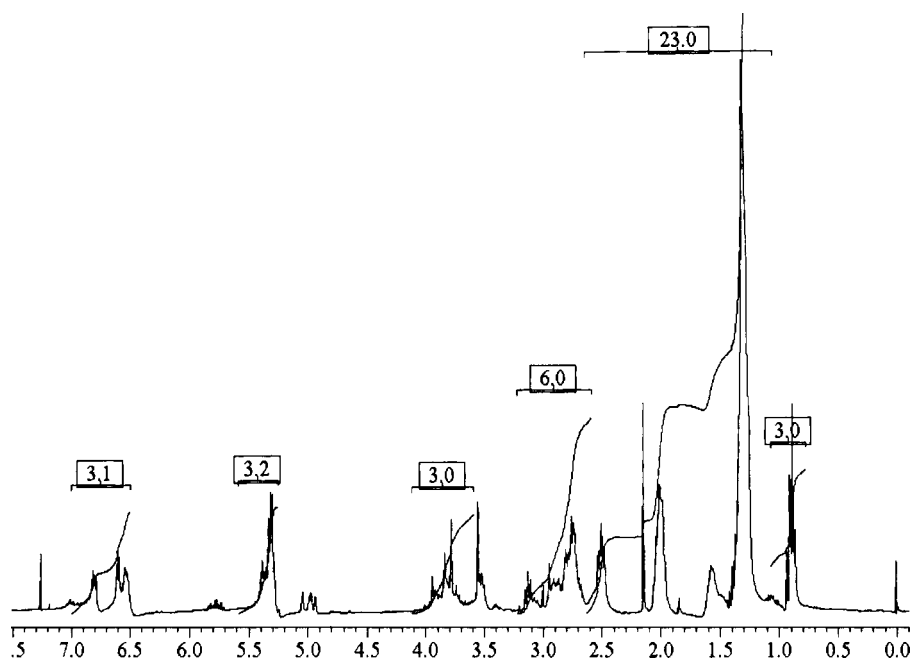


Figure 4 NMR spectra of phenalkamine (A) curative sample.

depending on the amine used and may provide better class of coating. In this series of phenalkamine the viscosities seems to be reducing with increasing chain flexibility. Higher viscosity was observed with phenalkamine made with ethylene diamine, where as triethylene tetraamine a higher homologue with longer alkyl chain gave a lower viscosity product. This is in line with the observation made by some researchers earlier that the viscosities of Mannich bases reduced with decrease of aromatic content in their systems.^{9,15} Phenalkamine compatibility with epoxy was measured by analyzing the clarity of the cured thin film containing of epoxy resin and phenalkamine. It is observed that the clarity of the films are very good indicating good compatibility with the epoxy resin which is an important factor for an appearance for the cured system.⁶

Room temperature curing and FTIR analysis

Phenalkamine was used to establish room temperature curing of epoxy resin. The equivalent weight of the phenalkamine was decided by its amine value. The crosslinking of epoxy resin takes place through the amine groups or the hydroxyl groups generating further active hydrogen group. Diethylene triamine and triethylene tetraamines with 5 and 6 active hydrogen atoms are highly active aliphatic amines compared to ethylene diamine.

In general the primary and secondary amines act as reactive hardeners, while the tertiary amines are catalytic. Although Mannich reaction decrease the functionality of amine, the presence of Phenolic-hydroxyl functionality on the aromatic ring produces a substantial accelerating effect on the epoxy curing reaction as

phenoxide is a stronger nucleophile than amine group. Above curatives can gives room temperature curing due to its high exothermic temperature.

Infrared measurement were used to observe the extent of reaction at room temperature as well as after postcuring. Epoxy resin was mixed with curing agent and kept for 24 h at room temperature. FTIR spectrum of the epoxy resin with and without curing agent are given in the Figure 5. The —OH band at 3410 cm^{-1} has become broader after room temperature curing and further after postcuring (thermal curing), which could be due to the formation of OH groups by epoxide ring opening. Simultaneously the peak at $913\text{--}916\text{ cm}^{-1}$ shows significant reduction in epoxide group absorbance with room temperature curing agent. These results show that the curing is mostly complete in 24 h at room temperature. The rest of the epoxide is cured thermally at 150°C .

Adhesive properties

Phenalkamine are known to react with epoxy non-stoichiometrically. To arrive at a best composition of the network, we have mixed epoxy and phenalk-

TABLE I
Amine Values and Viscosity of Phenalkamine Curatives

Sample	Amine value (mg KOH/g)	Viscosity (mPa s)	Clarity
Phenalkamine A	946.8	1600	Clear
Pyhenalkamine B	1001	1400	Clear
Phenalkamine C	1033.9	1250	Clear

amine curatives in the equivalent ratios of 1 : 1, 1 : 2, and 1 : 3 respectively, at room temperature for 24 h. For phenalkamine system, the curing time was optimized by visual/physical method, which are presented in Table II.

The higher the primary amine concentration in the mixture the faster it cures. In case of EA system, it was observed that 1 : 3 compositions with high amine concentration were found to be brittle, whereas 1 : 1 composition with low amine concentration took a long time and also the curing was incomplete. We have

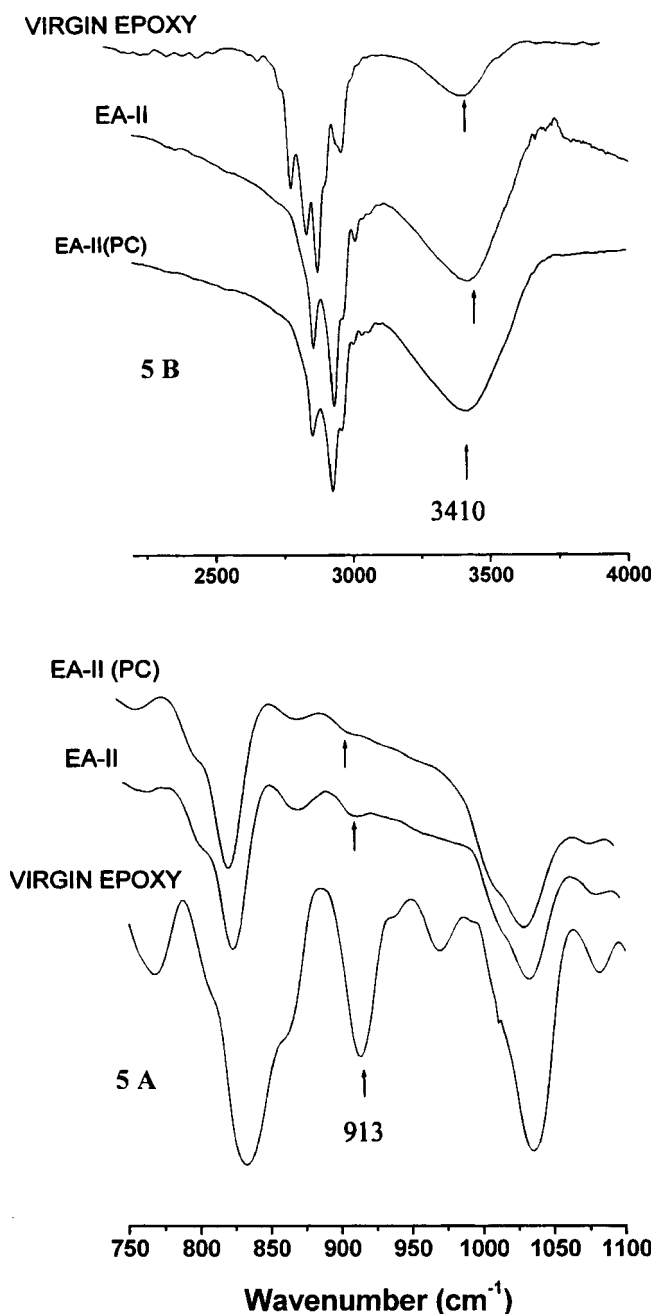


Figure 5 Comparative IR spectra of virgin epoxy resin with room temperature cured and postcured EA-II sample: (A) 1100–750 cm^{-1} and (B) 4000–2200 cm^{-1} .

TABLE II
Optimization of Epoxy Curing with Phenalkamine at Room Temperature

Curing agent	Sample	Curing time	Physical appearance/tensiometer [$\times 10^6 \text{ N/m}^2$] ^a	
			24 hr	48 hr
Phenalkamine A	EA-I	3 days	Tacky	Tacky
	EA-II	24 hr	12.3	12.3
	EA-III	18 hr	Brittle	Brittle
Phenalkamine B	EB-I	18 hr	10.5	10.6
	EB-II	12 hr	Brittle	Brittle
	EB-III	12 hr	Brittle	Brittle
Phenalkamine C	EC-I	15 hr	7.6	7.9
	EC-II	10-12 hr	Brittle	Brittle
	EC-III	10-12 hr	Brittle	Brittle

^a Amendment #2 with copper adherend.

selected the composition (1 : 2) on the basis of its curing time and properties. The sample is denoted as EA-II. Systems EB, EC showed brittle behavior with 1 : 2 and 1 : 3 compositions and the curing was found to faster because of high amine concentration. So we have picked up EB-I and EC-I for adhesive property evaluation.

Samples EA-II, EB-I, and EC-I were applied on different metal cylinder (Cu, Al, brass) and after 24 h the samples were tested for tensile strengths. Prior to application of adhesive mixture the surface of the metal were cleaned with acetone. The results are presented in Table III.

It can be seen that phenalkamine cured epoxy resin have a very good adhesion on different metal surface. It was found that Cu has highest adhesion strength than Al and brass. Adhesive strength is affected by various factors related to interface of metal and material, along with mode of film application and surface treatment of metal surface. Above all surface energy is the major director for adhesion strength, because it is directly proportional to physical bond (Van der Waals force). The reason for high value of tensile strength of copper is due to its high surface energy than Al and brass, which is an alloy of Zn and Cu. As Zn has very low surface energy with respect to Cu, bringing down overall surface energy of the brass alloy.

TABLE III
Adhesive Properties of Various Samples by Tensiometer

Sample	Adhesive strength ($\times 10^6 \text{ N/m}^2$) Metal		
	Cu	Al	Brass
EA-II	12.3 (9.1)	11.9 (7.9)	8.1 (6.2)
EB-I	10.4 (8.4)	8.9 (6.8)	7.6 (5.9)
EC-I	7.6 (6.8)	6.8 (5.3)	5.3 (3.8)

Amendment #2 values represented in parentheses are for postcured samples at 150°C for 1 hr.

TABLE IV
Tan δ and Storage Modulus Values of Various Sample Analyzed by DMTA

Sample	E' at room temperature (Pa) $\times 10^9$	Tan δ peak (T_g) $^{\circ}\text{C}$	Tan δ peak height	Width at half height of Tan δ
EA-II	3.77 (1.483)	87.49 (116.48)	0.7864 (0.6342)	21 (25)
EB-I	7.018 (1.503)	86.81 (130.63)	0.9867 (0.8169)	20 (24)
EC-I	7.97 (1.39)	93.08 (127.84)	0.9372 (0.8266)	20 (24)

Amendment #2 values represented in parenthesis are for postcured samples at 150°C for 1 hr.

Postcured samples showed reduced value of adhesion (tensile mode) strength, which can be explained by increased crosslinking density of resin, results as a cohesive failure. Crosslinking density reduces elongation, which always results as a reduction in tensile strength.

Phenalkamine–epoxy cured resin viscoelastic properties

Rectangular bars of cured and postcured specimens were subjected to DMTA for viscoelastic properties. DMTA provides a direct link between materials chemical make up and its mechanical behavior. The scan was recorded as a function of temperature from 50 to 250°C covering three areas, the glassy state, the transition state, and the rubbery plateau of each sample. E' , the storage modulus, dissipation energy (tan δ) are the important parameters that can be drawn from the spectra. The storage modulus of a solid sample at room temperature provides a measure of material's stiffness under shear deformation whereas tan δ (E''/E') peak gives the ultimate T_g of the system. The numerical values are summarized in the Table IV. The comparative analysis of storage modulus curves has been figured in Figure 6.

Storage modulus of room temperature cured sample and postcured (thermally cured) samples are in the range of 10^9 Pa. In all cases the storage modulus of postcured samples are reduced, as compared to the room temperature cured samples and reached approximately same level for all the samples.

The peak of the tan δ is associated with the Glassy transition can be analyzed to provide qualitative insight of the sample structure. The tan δ values found to be similar for samples EA-II and EB-I but a slight increase was observed for EC-I. It suggests that all three samples might be cured to same extent. Rests of it were cured at 150°C , where difference in tan δ could be observed due to difference in number of amine active sights. Presence of more amine active sites are able to create more crosslinks,⁹ consequently high T_g could be achieved. Moving towards diamine system (A-II) to triamine (B-I) and tetraamine (C-I) crosslinking has decreased as indicated

by increase in tan δ height. There is no clear difference in case of sample EB-I and EC-I, which is cured with curing agent with tri and tetraamine system (B,C). The reason may be that more active sites might cause extremely fast curing and as a result no further

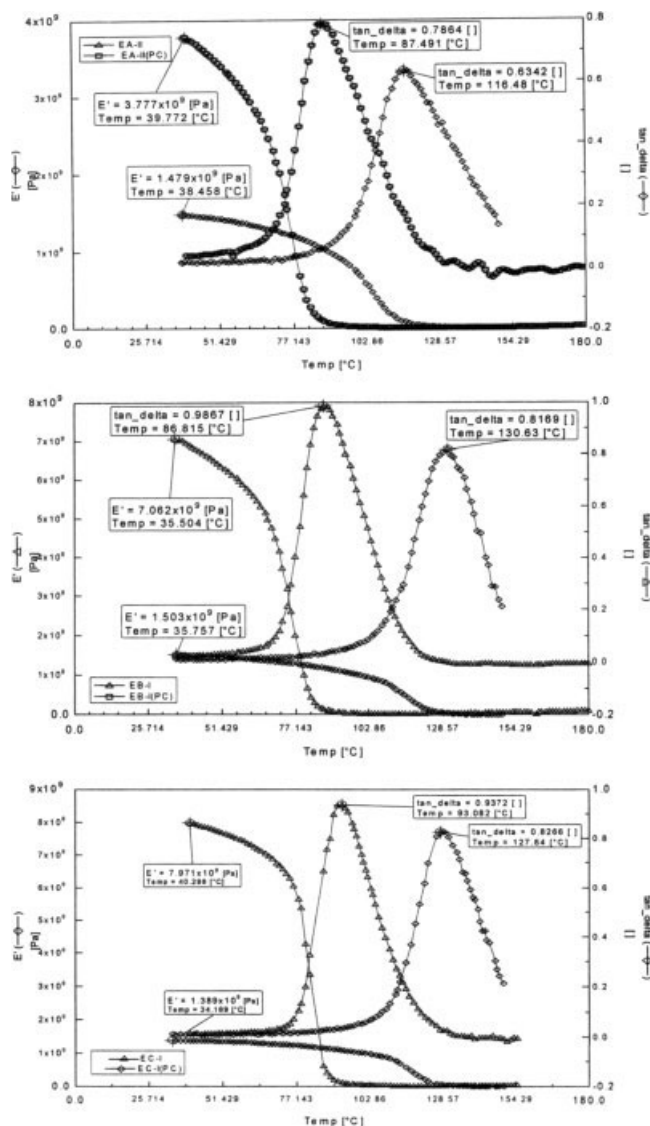


Figure 6 DMTA of phenalkamine epoxy samples cured and postcured: (a) Sample EA-II, (b) sample EB-I, and (c) sample EC-I.

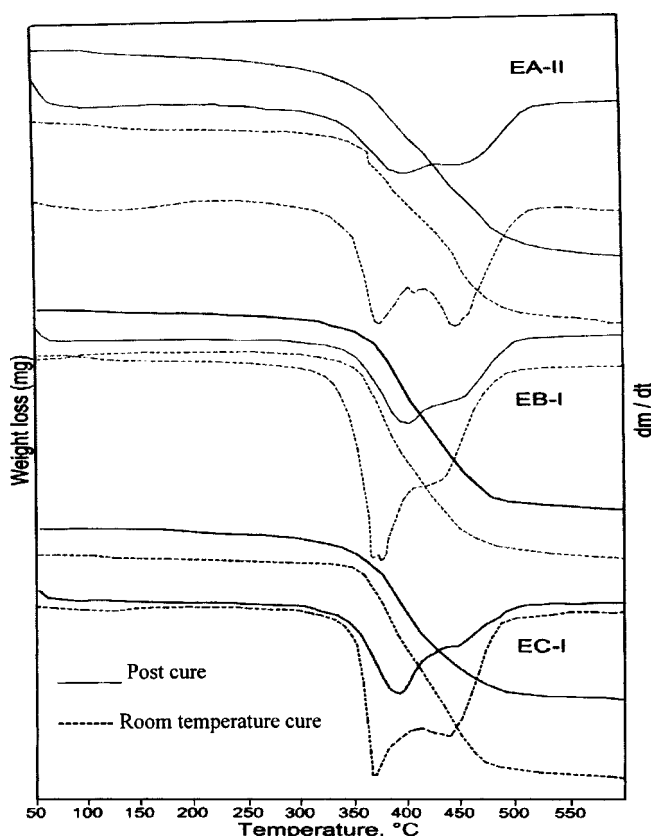


Figure 7 Comparative thermal study of room temperature and postcured samples with corresponding derivative thermograms.

improvement in crosslinking density was observed. The height of $\tan \delta$ peak which is associated with toughness, decreased after postcuring, indicating increase in crosslinking density.¹⁹

Thermogravimetric analysis

Thermo gravimetric analysis of the cured samples was conducted in nitrogen atmosphere and the thermo grams of the three different phenalkamine curatives with epoxy were given in Figure 7. The thermal stability was compared by initial decomposition temperature, maximum decomposition temperature (Dmax), IPDT (integral procedural decomposition tempera-

ture), and by char yields at 600°C, with the values presented in Table V.

As seen from the plots and values given in Table V, the room temperature cured epoxy phenalkamine samples showed two stage decomposition. The first stage of weight loss occurred between 250 and 300°C with a maximum decomposition at 360°C. The second stage decomposition started around 400–410°C with a maximum loss at 440°C. Postcured samples also showed two stage decomposition with a slightly higher decomposition temperatures but the derivative decomposition peaks appear to be closer without any clear separation as in the case of room temperature curing. The first and second stage degradation may be assumed due to aliphatic chain of Mannich base and Mannich base cured epoxy polymer degradation respectively.

Their integral procedural decomposition temperature proposed by Doyal²⁰ has been used for assessing the relative thermal stability of the polymers.

$$\text{IPDT} = A^*(T_f - T_i) + T_i$$

where A^* is the ratio of the area under the experimental curve divided by the area under total TGA thermo gram. T_i and T_f is the initial and final experimental temperature respectively. IPDT value represents the relative thermal stability of the sample investigated. IPDT data revealed that thermal stability is increased in case of postcured sample but it is not very far from room temperature cured sample. Char residue is also showed a slight increase in case of postcured sample.

CONCLUSIONS

Cardanol, the main product obtained by thermal treatment of CNSL, has been reacted with formaldehyde and aliphatic amines such as: ethylene diamine, diethylene triamine, and triethylene tetraamine to prepare a line of three Mannich bases for low temperature cure of epoxy resins.

Phenalkamine cured epoxy resin have a very good adhesion on different metal surface and it was also

TABLE V
TGA Analysis of Cured Epoxy Phenalkamine Samples

Sample	IDT ₁ (°C)	Dmax ₁ (°C)	IDT ₂ (°C)	Dmax ₂ (°C)	A ^a	Char yield at 600°C	IPDT (°C)
EA-II	250	360	410	440	0.7465	10.00	360.6
EA-II (PC)	280	385	420	450	0.7569	11.50	366.3
EB-I	300	360	400	440	0.7672	15.86	372.0
EB-I (PC)	320	390	430	450	0.7776	19.15	377.7
EC-I	270	360	400	440	0.7878	9.00	383.4
EC-I (PC)	320	380	430	450	0.7984	12.27	389.1

^a Amendment #2 Subscripts 1 and 2 represent first and second peak observed in thermogram. T_i , T_f are 50°C and 600°C for IPDT calculation.

found that Cu has highest adhesion strength than Al and brass due to its high surface energy. On postcuring adhesion strength decreased owing to increased crosslinking density of resin resulting in cohesive failure. Storage modulus (E') of room temperature cured sample and postcured samples are in the range of 10^9 Pa. Remarkable change in $\tan \delta$ values were observed on postcuring as a result of participation of more amine active sites.

Epoxy phenalkamine samples showed two stage degradation. The first stage being the decomposition of aliphatic chain of Mannich base and the second stage due to cured epoxy polymer degradation. A slight increase in IPDT and char residue was observed in case of postcured sample.

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