

Novel Phenolic Resins with Improved Mechanical and Toughness Properties

Francisco Cardona,¹ Alan Lau Kin-Tak,¹ Jessica Fedrigo²

¹Centre of Excellence in Engineered Fibre Composites, Faculty of Engineering and Surveying, University of Southern Queensland, Queensland 4350, Australia

²Politech Montpellier University, Montpellier, Materials Department, Place Eugene Bataillon – 34095, Montpellier Cedex 5, France

Received 7 December 2010; accepted 19 April 2011

DOI 10.1002/app.34719

Published online 23 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Novel phenolic type of thermoset resins were synthesized, and their mechanical and toughness properties were evaluated. Phenol Formaldehyde (PF) phenolic resins were modified to broaden their applications for modern composite structures. A first modification consisted of copolymerization of Phenol with Cardanol during the synthesis of resole phenolic (CPF) resins. The modified phenolic resins (CPF) were prepared at various molar ratios of total Phenol to Formaldehyde (F : P ratio) and with different weight ratios of Phenol to Cardanol. CPF resins with a maximum content of 40 wt % of Cardanol were synthesized and used. The CPF resins were applied as a plasticizer and toughening agent to the base PF resins. Both resins (CPF/PF) were mixed in different proportions, and their thermal and mechanical properties were then

established. A full miscibility of the two resins was observed with the formation of a single-phase system. An increase in the content of Cardanol resulted in a proportional increase of the flexural strength and fracture toughness together with a decrease of the flexural modulus of the cured CPF/PF resins. Further increased plasticizing and toughening effect was also observed by the blending of the CPF resins with propylene glycol. The higher toughness and flexibility effect of the CPF resins was obtained with a F : P molar ratio equal to 1.25 and with a Cardanol content of 40% (w/w). © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2131–2139, 2012

Key words: thermosets; CPF resins; toughness; strength; crosslink density

INTRODUCTION

Phenolic resins are known as the oldest thermosetting polymers, and they have been used in many industrial applications in sectors such as automotive, computing, aerospace, and building.¹ In aerospace applications, the most important use of phenolic resins is in the manufacturing of high-performance composites.² Reviews of the phenolic resins are available in the literature.^{1–3} Phenolic resins are thermosetting resins produced by the condensation of Phenol with aldehyde wherein water is produced as a by-product.

As mentioned, phenolic resins are thermosetting in nature and have properties of high-temperature resistance, infusibility, and flame retardance. Their structures are widely variable, and the following conditions are known to affect the properties of the phenolic resin, they are (i) the mole ratio of Phenol to Formaldehyde, (ii) reaction time, (iii) temperature, (iv) water content, and (v) residual Phenol and Form-

aldehyde content. Substituted Phenols and higher aldehydes have been used to produce phenolic resins with specific properties such as reactivity and flexibility. The variety of phenolic resins available is quite large as the ratio of Phenol to aldehyde, the reaction temperature, and the catalyst selected can be varied.⁴ The reaction of Formaldehyde with Phenol can lead to either a resole (P : F > 1.0) or a novolak type (P : F < 1.0) of phenolic resin. It depends on the type of catalyst used and the P : F ratio. The catalyst can be an acid, base, or neutral material. In this work, we are interested only in phenolic resins prepared under basic conditions (resole type), which require a P : F ratio > 1.0 (this means an excess of Formaldehyde in relation to the molar amount of Phenol).

The synthesized liquid resole resin is cured by heating it to elevated temperature (150°C) or to lower temperature (80°C) with the aid of an acid catalyst. The cure proceeds through polycondensation reaction of the different substituted Phenols, giving place to the formation of a cured phenolic resin.^{5–8} The chemical structure of the reactive components (Phenol, Cardanol, and Formaldehyde) and of the cured cardanol phenol formaldehyde (CPF) resin, are presented in Figure 1. A proposed chemical mechanism of synthesis and structure of

Correspondence to: F. Cardona (cardona@usq.edu.au).

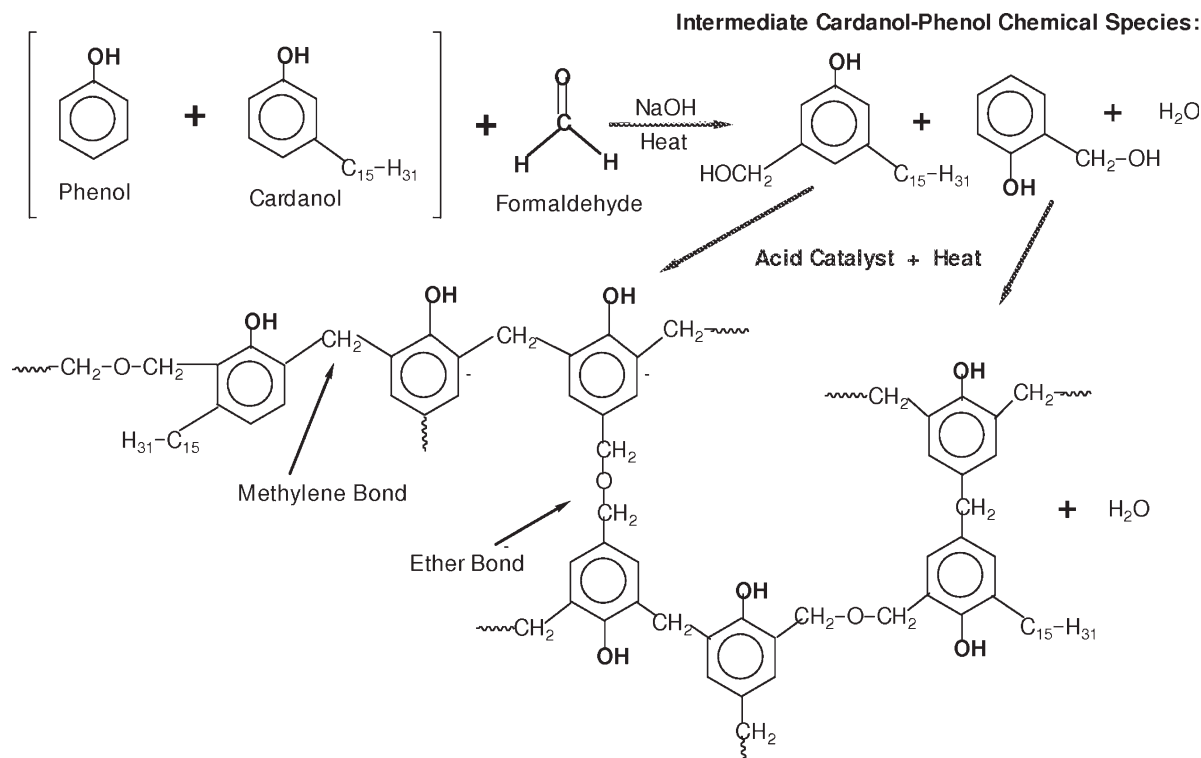


Figure 1 Chemical structures and proposed chemical mechanism of the synthesis and curing of the CPF resins.

the crosslinked CPF resin are also presented in Figure 1. There are two possible modes for the condensation reactions in Phenol Formaldehyde (PF) resins,⁵ they are the methylene bridges ($-CH_2-$) form at a low pH and high temperature ($150^\circ C$) when two hydroxymethyl-phenol molecules react with each other and the formation of the ether bridges ($-CH_2-O-CH_2-$) results from the interaction of two hydroxymethyl-phenol molecules at low temperatures and near neutral pH. Both these types of chemical linkage are included in Figure 1.

Although a significant number of publications on PF resins has been done specifically in the fields of kinetics and reaction modeling,^{9–11} flammability and thermal analysis^{12–16} and mechanical performance^{17,18} investigations of the modifications of these resins with natural renewable components from synthesis to final performance have been limited. In this study, blends of a phenolic resin (PF) with modified phenolic resins by the partial substitution of Phenol with Cardanol in the synthesis with Formaldehyde (CPF resins) were prepared and investigated. Also the effect of propylene glycol (PG) on the mechanical properties of the CPF/PF resin blends was investigated. The purpose of blending the two types of resin resins and adding PG was to prepare a more flexible resin; one even exhibiting higher toughness than the standard PF resins. Ultimately, this work can be used to develop a more fundamental understanding of the structure–prop-

erty relationships and the different toughening mechanisms of the phenolic resins for applications in civil engineering structures.

Cashew nut shell liquid (CNSL) is a natural product and specifically a by-product of the cashew nut processing industry, which is mostly located in countries of Asia, Africa, and South America. CNSL is a naturally occurring phenolic material that has the advantages of low cost and renewable supply and with a need to conserve petrochemicals, increased application of CNSL gains added importance. It contains a variety of phenolic compounds with side chains of varying degrees of unsaturation at the meta-position. The main constituents of commercial grade CNSL (obtained after the roasting of the raw cashew nut shells) are Cardanol, Cardol, 2-methyl cardol, and small amounts of Anacardic acid. By the distillation of CNSL, these chemical species mostly convert to Cardanol. In this study, the CPF resins were synthesized using Cardanol obtained from Satya Cashew Chemicals (Chennai, India) (<http://www.sccpl.com/>). The chemical structure of Cardanol is shown in Figure 1.

Because of the Phenolic nature and unsaturation in the side chain, Cardanol offers reaction sites on the aromatic ring and also on the side chain, which makes it a suitable raw material for variety of reactions.^{19–25} One of the best known applications of CNSL and Cardanol resins is in the manufacturing of asbestos-free break-pads for the automobile

industry,²⁶ due to their high thermal stability and oxidation resistance at elevated temperature. Cardanol reacts with active methylenes like Formaldehyde or hexamethylene tetramine via the hydroxyl group and can undergo addition polymerization through unsaturation present in the side chain. Therefore, different type of resins can be synthesized from Cardanol and also from chemically modified CNSL.^{27–32} The use of compatible additives able to form a single phase when mixed with resole phenolic resins, such as PG, was also investigated in this work. PG is compatible with phenolic resins due to the presence in PG of the hydroxy groups (OH), similarly to the PF resin chemical structure. The effect of different amounts of added PG on the mechanical properties of the CPF/PF blended resins was evaluated after the postcuring of the resins. The purpose of these modifications was to prepare a more flexible and tougher phenolic resin, suitable for application in laminates and composites in civil engineering structures.

EXPERIMENTAL

Resin synthesis

The CPF resins were prepared with different mixtures of Cardanol and Phenol reacting with Formaldehyde in the presence of an alkaline catalyst. Phenol was replaced with Cardanol up to 40% by weight in the synthesis. The reactions were carried out in a glass reactor equipped with a stirrer, a condenser, and an internal heating unit. The required amounts of Phenol (88 wt % in water from Huntsman, Australia), Cardanol and *para*-formaldehyde were mixed by keeping the molar ratio of total Phenol (Phenol + Cardanol) to Formaldehyde at 1 : 1.25 for the first set of resins (CPF resin I), then 1 : 1.50 for the second set (CPF resin II), and 1 : 2.0 for the last set (CPF resin III). An aqueous solution of NaOH-46% (4%, w/w, on the basis of total Phenol) was employed as the catalyst. The temperature was maintained at 60°C for 1 h, then rise to 80°C for 1 h, and finally reduced to 60°C for 1 h. The chosen acidic catalyst for curing of the CPF and CPF/PF resin blends was a mix of xylene-sulfonic and phosphoric acids with water (Phencat10 catalyst from Momentive Specialty Chemicals, Columbus, OH), which cures the phenolic resins relatively slowly and therefore enable better control and properties to be achieved. An amount of 3–4 wt % of the catalyst was normally used, and the gel-times of the CPF/PF resins are shown in Figure 2. Clearly, the presence of the CPF resins increased the gel-time of the blended resins. After curing the test specimens at room temperature for 8 h, the samples were post-cured at 80°C inside of an oven for 4 h. Dynamic

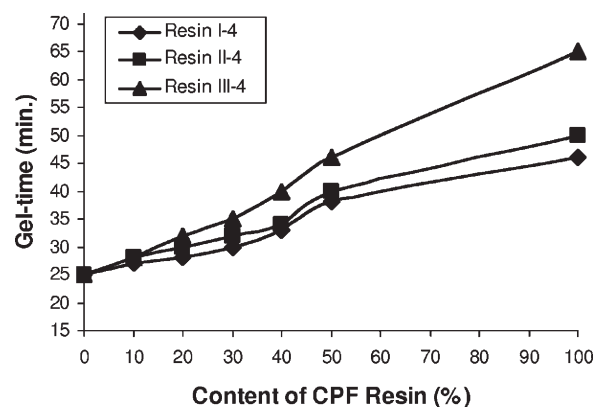


Figure 2 Plot of the Gel-times (min) vs CPF/PF blended resins (CPF resins with 40 wt% of Cardanol content).

mechanical analysis (DMA), mechanical tests (flexural), and fracture toughness tests were carried out.

Infrared spectroscopy analysis

The infrared (IR) spectra of the synthesized CPF resin II-4 of the neat Cardanol and of the phenolic resin are shown in Figure 3. The peak associated with the OH— group attached to the phenyl ring in the resins is observed in the region 3290–3370 cm^{-1} . The peak found at 1200 cm^{-1} in the IR spectrum of the CPF resin II-4 is associated with the presence of ether linkages. The peaks at 2926 cm^{-1} and 2854 cm^{-1} in the IR signal of the Cardanol resin are associated with the methylene groups present in the aliphatic side chain of the molecule. Similar methylene chemical groups in the CPF resin II-4 are identified in the IR spectrum of the resin by the peaks at 2922 cm^{-1} and 2851 cm^{-1} , which are also associated with to etherification reactions during the synthesis of the CPF resins. The peaks for mono-substitution at 752 cm^{-1} and 690 cm^{-1} in the phenyl ring are significantly decreased in the synthesized CPF resin II-4. This confirms that the synthesis of the CPF resin has taken place through the *ortho*- and/or *para*- positions of the phenyl ring. Significantly, the vibrations at 911 cm^{-1} , 880 cm^{-1} , and 694 cm^{-1} in the IR signal of the Cardanol resin are due to the side chain double bonds. These IR peaks have reduced in size in the spectrum of the CPF resin II-4, indicating that some degree of polycondensation has also taken place through the double bonds present in the aliphatic side chain of the Cardanol. This explains the increase in viscosity of the synthesized CPF resins that was observed with increasing Cardanol content in the resins.

Analysis and results

After postcuring (4 h at 80°C), the samples were cut and tested for flexural modulus (MPa), elongation at

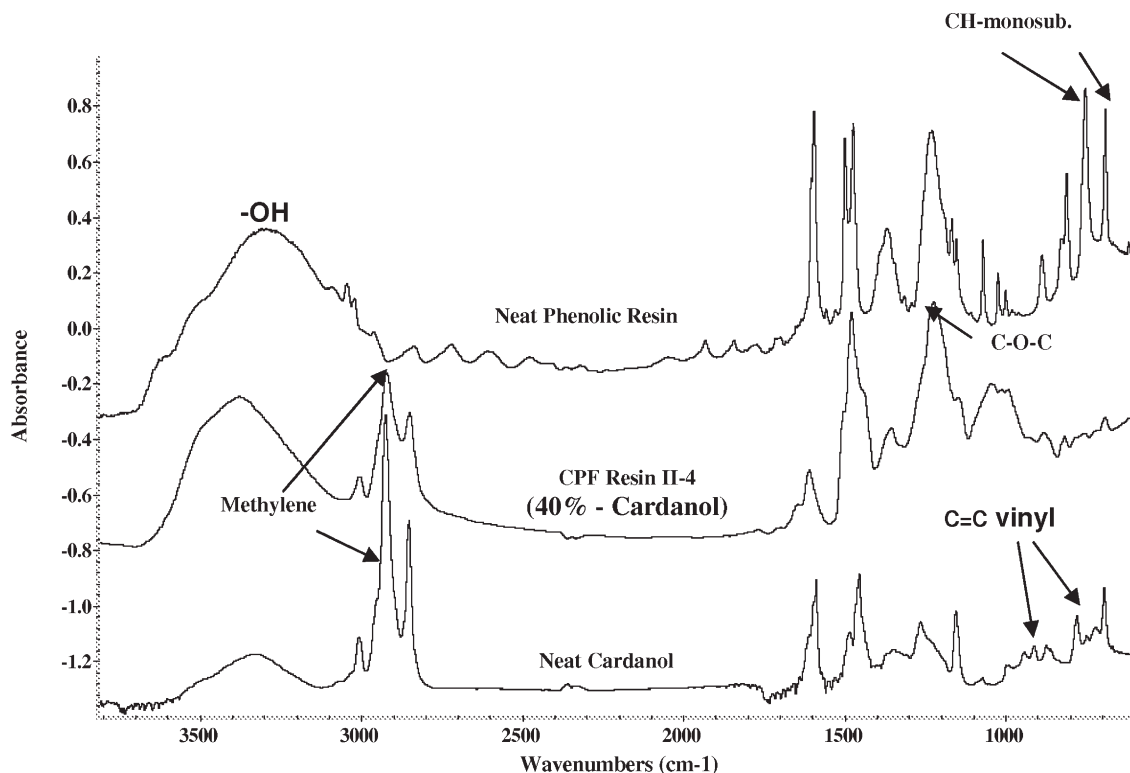


Figure 3 Infrared spectra of the neat Cardanol (bottom), neat phenolic (top) and of the synthesized CPF resin-II-4 (middle).

break (%), and stress at break (MPa), taking the average values of three specimens for each sample. This mechanical test was carried out using a MTS machine (10 kN). Fracture toughness tests were performed using the same test machine (MTS 10kN). The critical stress intensity factor, K_{Ic} , was calculated using the following equation³³:

$$K_{Ic} = (PQ/BW^{1/2}) \cdot f(a/W), \quad (1)$$

where PQ is the load corresponding to a defined increment of crack length, B is the specimen thickness, W the width, and the function $f(a/W)$ is a geometry dependent factor that relates the compliance of the specimen to the ratio of crack length and width.

Dynamic mechanical thermal analysis

DMA has been a well established method in thermal analysis for many years. The DMA measurement consists of the observation of the time-dependent deformation behavior $x(t)$ of a sample under periodic and sinusoidal deformation force with very small amplitudes $F(t)$. This method make it possible to calculate the Young's modulus E' (storage modulus) and E'' (loss modulus) as well as the mechanical loss factor $\tan \delta$ (damping) of the sample in dependence on temperature and deformation frequency. Glass transition temperature values (T_g) of the resins can

be obtained from the top of the $\tan \delta$ peak, as previously reported.^{34,35} In this study, the dynamic mechanical properties of the CPF/PF resin blends have been investigated to analyze the relationship between the $\tan \delta$ and the glass transition temperature (T_g) in one side and the P : F molar ratio and the Cardanol content in the CPF resins on the other side. The plots in Figure 4 reveal that the substitution of Phenol with Cardanol in the resins shifts the glass transition temperature (T_g) of the cured resins to lower temperatures. Additionally, the DMA analysis revealed that a decrease in the Formaldehyde :

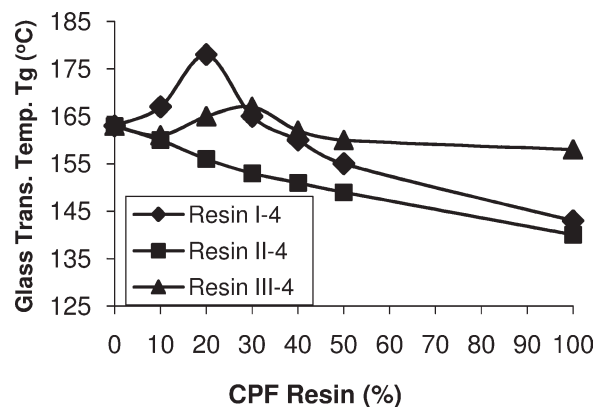


Figure 4 Glass Transition temperatures (T_g) of the CPF/PF resin blends (CPF resins with 40 % w/w of Cardanol content).

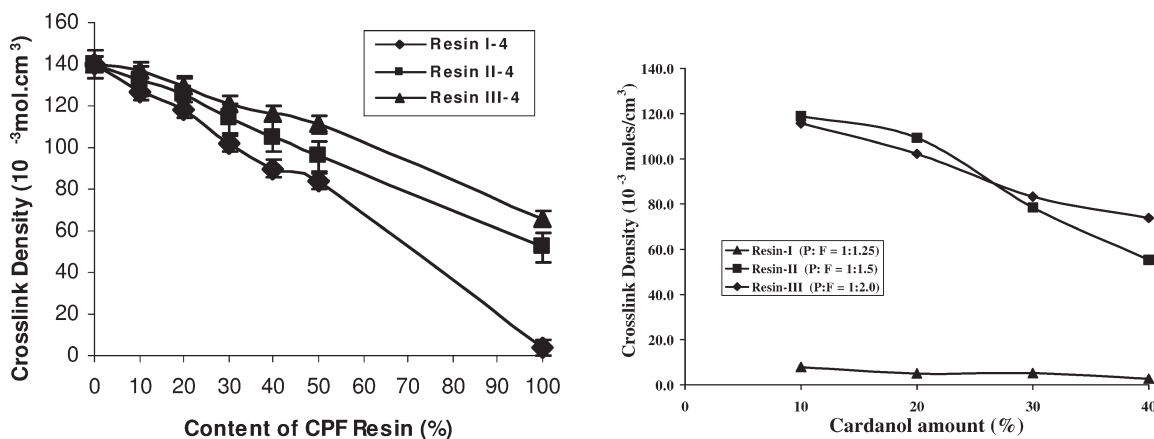


Figure 5 Crosslink density of the CPF/PF blends (with 40 % of Cardanol content). For comparison, presented are the plots of the crosslink density of the three sets of CPF resins vs. Cardanol content (w%).

Phenol (F : P) molar ratio resulted in a decrease in the T_g value of the cured CPF and blended resins, as shown in Figure 4. Significantly, this observation is more pronounced for the CPF resin I-4 (F : P = 1.25 : 1.0 and with 40% of Cardanol content), with the T_g equal to 137°C. The decrease in the F : P molar ratio of the CPF resins also resulted in longer gel-times of the blended resins (see Fig. 2).

Crosslink density

The crosslink density can be defined as the fraction of monomer units that are crosslinked.³⁶ The crosslink density can be calculated from the rubber elasticity theory³⁷:

$$\nu = E/3RT, \quad (2)$$

where ν represents the crosslink density (number of moles of chains per cm³), R is the gas constant (8.314 J/K mol), T is the temperature in Kelvin, and E is the elastic modulus taken from the storage modulus of the DMA analysis at 50°C above the T_g value of each sample.

It has been reported that the standard PF resole resins, synthesized with NaOH as a catalyst, is highly crosslinked with a very brittle matrix.³⁸ The postcuring of this resin induces the formation of the dimethyl phenol and trimethyl phenol bonds. When the material cools back to room temperature, residual thermal stresses accumulate in the cured matrix. When a crack is initiated and propagated through the highly crosslinked matrix, the resin cannot deform or distribute the stress due to the high concentration of thermal stresses. The inability of the resin to accommodate the stresses at the crack tip makes the material brittle and is ultimately responsible for the low fracture energy and toughness of the PF phenolic resin. To reduce this brittleness a phenolic resin with lower crosslink density has to be

synthesized. The crosslink density curves of the CPF resins and of the CPF/PF resin blends are presented in Figure 5. As expected, the crosslink density values of the CPF resins showed a decrease with increasing Cardanol content. In particular, the crosslink values of the CPF resins I are much lower (from a value of 8×10^{-3} mol/cm³ for 10% Cardanol content to a value of 2×10^{-3} mol/cm³ for a resin with 40% of Cardanol content) than those of the other resins and stay relatively constant with increasing Cardanol content. This indicates that the ultimate properties of CPF resins are quite sensitive to the F : P molar ratio, with the crosslink density decreasing with the value of this molar ratio. Moreover, the crosslink density values of the synthesized CPF resins are significantly lower than the value for the PF resin (140×10^{-3} mol/cm⁻³). Clearly, the presence of Cardanol decreases the crosslink density making the resole phenolic resins less brittle. This confirms that the characteristic brittleness of phenolic resins is due to the high crosslink density (about 100 times higher than that of epoxy resins). The partial substitution of Phenol with Cardanol in the synthesis of the resins significantly reduces the crosslink density, producing a phenolic resin with lower brittleness and increased toughness.

Mechanical properties

Table I presents the results of the flexural tests of the blended CPF/PF resins with different weight ratios of the two blended resins (0–100%). The results are from the synthesized CPF resin I (P : F ratio 1 : 1.25) with Cardanol content from 10% to 40% by weight. The CPF-I resin showed the larger change in its ultimate mechanical properties in comparison with the other two synthesized CPF resin formulations (II and III) in this work. This is due to its lower P : F molar ratio. The values presented in

TABLE I
Results of the Flexural Tests of the Synthesized CPF-I Resin with Different Cardanol Content (From 10% to 40%) and Blended with Different Amount of Phenol Formaldehyde (PF) Resin (CPF/PF Blends)

Synthesized cardanol-phenol formaldehyde resin (CPF)	Maximum flexural strain (%)						
	CPF/PF blended resins (wt %)						
	CPF/PF 0/100	CPF/PF 10/90	CPF/PF 20/80	CPF/PF 30/70	CPF/PF 40/60	CPF/PF 50/500	CPF/PF 100/0
CPF-I with 10% Cardanol	1.15	1.28	1.38	1.52	1.67	1.80	1.92
CPF-I with 20% Cardanol	1.15	1.40	1.88	2.10	2.34	2.52	2.86
CPF-I with 30% Cardanol	1.15	1.84	2.46	2.95	3.32	3.78	4.20
CPF-I with 40% Cardanol	1.15	2.24	3.00	3.62	3.90	4.30	4.75
	<i>Maximum flexural strength (MPa)</i>						
CPF-I with 10% Cardanol	32.2	33.4	35.8	37.0	38.2	39.3	41.4
CPF-I with 20% Cardanol	32.2	34.6	36.7	39.5	40.2	42.0	43.6
CPF-I with 30% Cardanol	32.2	35.8	38.8	42.2	44.4	46.5	48.8
CPF-I with 40% Cardanol	32.2	37.4	42.2	45.7	48.0	51.8	54.5
	<i>Flexural modulus (MPa)</i>						
CPF-I with 10% Cardanol	2530	2460	2320	2240	2180	2120	1960
CPF-I with 20% Cardanol	2530	2430	2370	2220	2040	1960	1910
CPF-I with 30% Cardanol	2530	2410	2320	2160	1860	1770	1680
CPF-I with 40% Cardanol	2530	2360	2120	1930	1750	1680	1540

Previous to the tests the blended resins were cured for 24 h at room temperature followed by a postcuring of 4 h at 80°C.

Table I clearly indicate that the flexural modulus (MPa) for the blended CPF/PF resins decreased with the CPF-I resin content, whereas the max. stress (MPa) and the strain values (%) increased with the amount of CPF-I resin. The results confirm that the decrease in brittleness and the changes in the mechanical properties of the CPF/PF blends are enhanced with the amount of Cardanol present in the CPF-I resins. Therefore, the less brittle and more flexible of the cured CPF/PF resin blends was observed for the blends with the resin CPF-I-4 (with 40% of Cardanol content). Further confirmation of the high flexibility of the CPF resin I-4 is given by the fact that this CPF resin formulation showed the lower crosslink density value, as previously mentioned (see Fig. 5).

The critical stress intensity factor K_{Ic} ($\text{Mpa m}^{1/2}$) is indicative of the toughness of the cured resins. The fracture toughness of the samples prepared with the CPF resin I ($P : F = 1.25$) is higher than that of the neat PF phenolic resin ($0.9 \text{ Mpa m}^{-1/2}$) for all levels of Cardanol content (up to 40%), as shown in Figure 6(a). Significantly, at 40% content of Cardanol, the fracture toughness factor (K_{Ic}) value is similar for the resins I and II. This indicates that at 40% content of Cardanol the difference of the $P : F$ molar ratio between resin I (1.25) and resin II (1.50) does not affect significantly the fracture toughness of the synthesized CPF resins. However, the fracture toughness factors of the samples with resin III ($P : F$ ratio equal to 1.0 : 2.0) were lower than the value for the neat PF phenolic resin, which is due to the higher brittleness

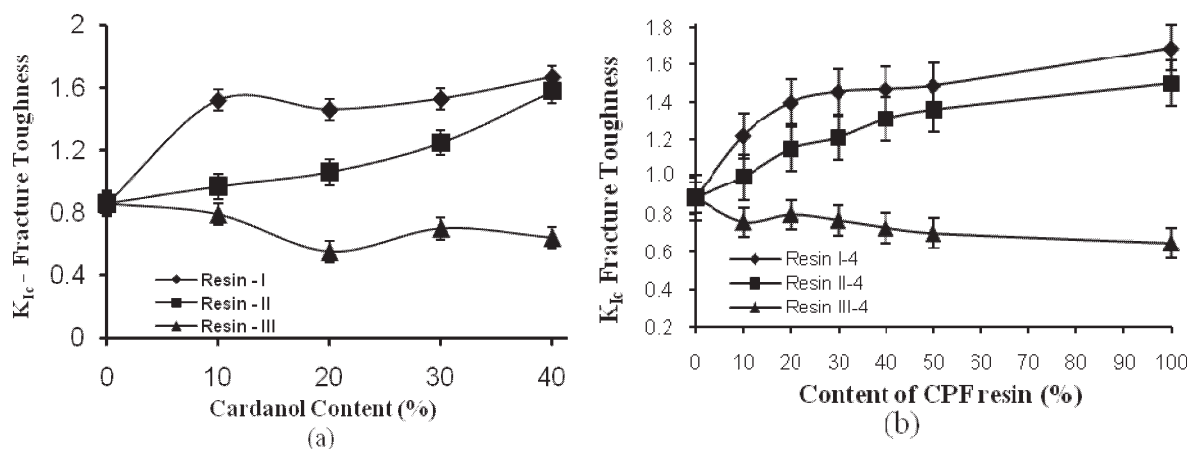


Figure 6 Fracture toughness factor K_{Ic} (MPa) of the Cardanol modified resins (I, II and III) vs. Cardanol content (%) (a) and vs the CPF amount blended with PF resin (b).

TABLE II
Best Results of the Different Tests Carried Out on the CPF Resins and on the Blended CPF/PF Resins

Test	PF resin	CPF resin I (P : F = 1.25)	CPF resin II (P : F = 1.5)	CPF resin III (P : F = 2.0)
Crosslink density ($\times 10^{-3}$ mol/cm ³)	140	3 : 40% Cardanol	45 : 40% Cardanol	58 : 40% Cardanol
Flexural stress (MPa)	31	61 MPa Resin I-3 (100%)	64 MPa Resin II-4 (100%)	53 MPa Resin III-2 (50%)
Flexural modulus (MPa)	2508	1495 MPa Resin I-4 (100%)	1520 MPa Resin II-4 (100%)	1725 MPa Resin III-4 (100%)
Flexural max. strain (%)	1.23	4.10% Resin I-4 (100%)	4.80% Resin II-4 (100%)	2.35% Resin III-2 (50%)
Fracture toughness K_{Ic} (MPa/m ²)	0.89	1.66 Resin I-4 (100%)	1.58 Resin II-4 (100%)	1.18 Resin III-3 (50%)

of the samples from resin III in comparison with the other two types of CPF resins. This is further confirmed by the higher crosslink density and T_g values of the samples from resin III in comparison with the respective values of samples from resins I and II (see Figs. 4 and 5). A similar trend can be observed for the fracture toughness factor of the samples prepared from blends of CPF and PF resins [see Fig. 6(b)], where the samples prepared using the CPF resin III showed lower values than the blends prepared with the CPF resins I and II. In a similar fashion as with the previous tests in this study, the fracture toughness values confirmed the high sensitivity of the results with the P : F molar ratio used during the synthesis of the CPF resins. The higher values of the fracture toughness of the resins investigated in this work, were obtained for the resin with the lower P : F ratio (resin I) and the values increased with the increasing Cardanol content in the resin. The enhanced fracture toughness of the resins with the increasing amount of Cardanol is attributed to a greater level of flexibility and ability for spatial rearrangement introduced into the thermoset network by the aliphatic side chain of the Cardanol molecule. Finally, the best results obtained in this study of the mechanical tests and the crosslink density values of the CPF and of the blended CPF/PF resins, in comparison with the neat PF resin, are presented in Table II. Most of the best results corresponded to the synthesized CPF resins with 40% content of Cardanol and without PF resin (100% of CPF resin).

Effect of PG

The addition of 20% (w/w) of PG has an effect on the mechanical flexural properties of the resins. A comparative plots of the modulus (MPa), the max. stress (MPa) and the max. strain (%) of the CPF resin-I versus Cardanol content in the CPF resins, are shown in Figure 7. The obtained results evidenced a significant decrease in the flexural modulus and flexural max. stress of the CPF resins mixed with PG, in comparison with the equivalent CPF samples without PG. However, the max. strain (%) comparatively increased for the CPF resins with PG. This mechanical behavior between the CPF samples with and without PG was observed at all the different levels of Cardanol content investigated in this work (up to 40% w/w), as shown in Figure 7.

The observed decrease in the flexural modulus and max. stress, together with the increase in the max. strain of the resins with PG, is due to the plasticizing and toughening effect of the added PG inside of the cured phenolic network. These results from the mechanical test point to a relatively less brittle resin as a result of the presence of PG, and this is further confirmed by a consistent decrease in the glass transition temperature (T_g) and the crosslink density values of the CPF resins with PG in comparison with the equivalent values for the resins without PG, as shown in Figure 8. The addition of PG reduced the crosslink density of the resole phenolic resins with Cardanol, which also resulted in an

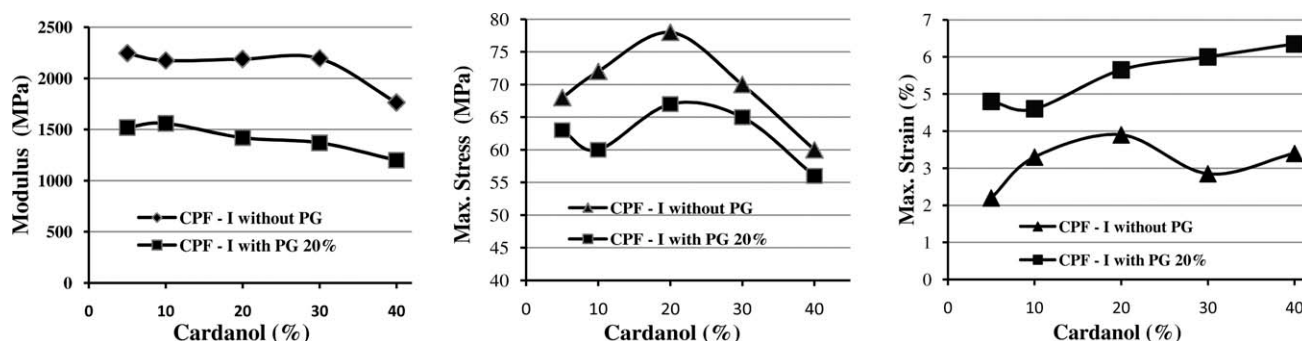


Figure 7 Results of the flexural tests of the CPF resins (Resin - I) with and without Propylene Glycol (20 % w/w) vs Cardanol content in the CPF resins. In preparation for the tests the samples were cured for 24 h at RT followed by a post-curing of 4 h at 80°C.

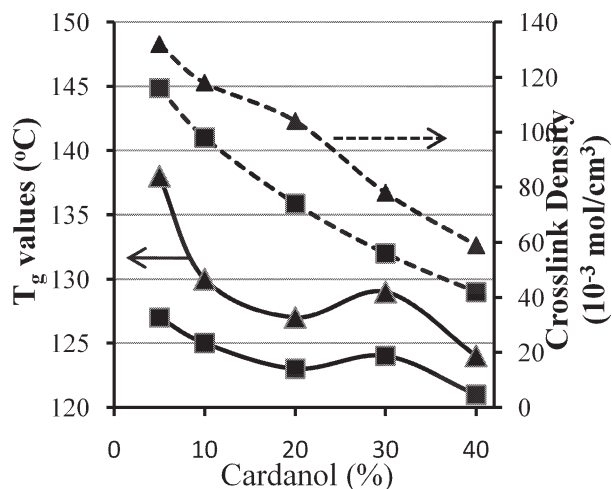


Figure 8 Glass Transition Temperature (solid lines) and Crosslink Density (dash lines) of the CPF-II resins with (■) and without Propylene Glycol (20 % w/w) (▲) vs Cardanol content in the resins. In preparation for the tests the samples were cured for 24 h at RT followed by a post-curing of 4 h at 80°C.

equivalent decrease in the value of the glass transition temperature (T_g) of the resins. These results of the mechanical and thermal properties of the modified CPF resins with the addition of PG indicated that the PG acts as a toughening and plasticizing agent to the CPF resins, and its use allows for the controlled modification of the mechanical and thermal properties of the resole phenolic resins.

CONCLUSIONS

The physical and mechanical properties of cured samples obtained from the blends of CPF and PF phenolic resins are strongly affected by the amount of Cardanol present and also by the experimental conditions during the synthesis of the CPF resin, in particular by the total Phenol (Cardanol + Phenol)/Formaldehyde molar ratio.

The results obtained by the DMA analyses of the postcured resin CPF/PF blends revealed the decrease of the crosslink density and T_g values with increasing Cardanol content and also with the decreasing total Phenol/Formaldehyde molar ratio. This effect was due to the flexibility enhancement that the introduction of Cardanol generates inside of the phenolic molecular network. However, the samples prepared with the synthesized CPF resin III presented a higher variability in their results, which clearly is associated with the high P : F molar ratio used in the synthesis of this CPF resin (1.0 : 2.0). Further research work is required to fully investigate this particular aspect of the effect of high concentration of Formaldehyde during the synthesis process in the ultimate properties of the Cardanol based resole phenolic resins (CPF).

The flexural strength and fracture toughness tests further confirmed the plasticizing effect of the partial replacement of Phenol with Cardanol in the synthesized CPF resins. This effect was also evident in the blends of the synthesized resins with the PF phenolic resin, which showed an improvement in the flexural strain, the stress and the fracture toughness values with increasing Cardanol content. This indicates a decrease in the characteristic brittleness of the neat PF phenolic resin, which is also associated with a proportional decrease in the flexural modulus of the cured CPF resins with increasing Cardanol content. The best results in this study were obtained with the formulation of total Phenol/Formaldehyde molar ratio equal to 1.25 and with 40 wt %-Cardanol substitution of Phenol. Therefore, Cardanol can serve as an effective substitute of Phenol in the synthesis of phenolic resin and is able to improve the toughness of the cured resins and also is an economically and environmentally friendly alternative in the synthesis of the resole phenolic resins. The addition of PG to the CPF resins had a proportional effect on the mechanical and thermal properties of the cured resins, which allows its use as a plasticizing and toughening agent to the phenolic resins.

References

- Gardziella, A.; Pilato, L. A.; Knop, A. *Phenolic Resins: Chemistry, Applications, Standardization, Safety and Ecology*, 2nd ed; Springer Verlag: Berlin, 2000; p 12.
- Burkhart, T. The chemistry and application of phenolic resins or phenoplasts. In *Waterborne & Solvent Based Surface Coating Resins and Their Applications*; Thomas, P., Ed.; Wiley: Chichester, 1998; Vol. 5, p 1.
- Reghunadhan Nair, C. P. Adv in addition-cure phenolic resins. *Prog Polym Sci* 2004, 29, 401.
- Waitkus, P. A.; Morrison, T. N. Polymer composition for curing novolac resins. US Patent 6,569,918, assigned to Plastics Engineering Company (Sheboygan, WI); 2003.
- Shafizadeh, J. E.; Guionnet, S.; Tillam, M. S.; Seferis, J. C. *J Appl Polym Sci* 1999, 73, 505.
- Knop, A.; Pilato, L. A. *Phenolic Resins-Chemistry, Applications and Performance*; Springer-Verlag: Berlin, Germany, 1985; Vol. 12.
- Kornblum, N.; Smiley, R. A.; Blackwood, R. K.; Iffland, D. C. *J Am Chem Soc* 1955, 77, 269.
- Yeddanapalli, L. M.; Francis, D. J. *J Makromol Chem* 1968, 119, 17.
- Sebnik, A.; Vizovisek, I.; Lapanje, S. *Eur Polym Sci* 1973, 10, 273.
- Pal, P. K.; Kumar, A.; Gupta, S. K. *Polymer* 1981, 22, 1699.
- Grenier-Loustalot, M.; Laroque, S.; Grenier, P.; Leca, J.; Bedel, D. *Polymer* 1994, 35, 33.
- Nyden, M. R.; Brown, J. E.; Lomakin, S. M. *Polym Mater Sci Eng* 1994, 71, 301.
- Kourtides, D. A. *Polym Compos* 1984, 5, 143.
- Kourtides, D. A.; Parker, J. A.; Gilwee, W. G., Jr.; Lerner, N. A. *J Fire Flammability* 1976, 7, 401.
- Follensbee, R. A.; Koutsky, J. A.; Christiansen, A. W.; Myers, G. E.; Geimer, R. L. *J Appl Polym Sci* 1993, 47, 1481.
- Pizzi, A.; Garcia, R.; Wang, S. *J Appl Polym Sci* 1997, 66, 255.
- Redjel, B. *Plast Rubber Compos Process Appl* 1995, 24, 221.

18. Charalambides, M. N.; Williams, J. G. *Polym Compos* 1995, 16, 17.
19. Mahanwar, P. A.; Kale, D. D. *J Appl Polym Sci* 1996, 61, 2107.
20. Harvey, M. T. US Patent (to Harvel Corp.); 1939, 2,157,126.
21. Aggarwal, S. N.; Sivasamban, M. A.; Aggarwal, J. J. *Paint Mfr* 1966, 36, 29.
22. Wasserman, D.; Dawson, C. R. *Ind Eng Chem* 1945, 37, 396.
23. Carraher, C. E.; Sperling, L. H. *Polymer Applications of Renewable Resource Materials*; Plenum Press: New York, 1981.
24. Roy, S. S.; Kundu, A. K.; Maili, S. *J Appl Polym Sci* 1988, 36, 1283.
25. Manjula, S.; Sudha, J. D.; Bera, S. C.; Pillai, C. K. S. *J Appl Polym Sci* 1985, 30, 1767.
26. Bijwe, J. *Polym Comp* 1997, 18, 378.
27. Mary Lubic, Eby Thomas Thachil. *Int J Polym Mater* 2003, 52, 793.
28. Yamada, Y. Jpn. Patent No. 8099 (to Cashew Co. Ltd.); 1965.
29. Dhamney, C. P. *Paintindia* 1979, 29, 3 and 1983, 33, 7.
30. Vernekar, S. P. *Indian J Technol* 1980, 18, 170.
31. Murthy, B. G. K.; Menon, M. C.; Aggarwal, J. S.; Zaheer, S. H. *Paint Mfr*. 1961, 31, 47.
32. Tyman, J. H.; Wilczynski, P.; Kashani, M. A. *J Am Oil Chem SOC* 1978, 55, 663.
33. Unnikrishnan, K. P.; Thachil, E. T. *Int J Polym Mater* 2006, 55, 385.
34. Nielsen, L. E.; Landel, R. F. *Mechanical Properties of Polymers and Composites*, 2nd ed.; Marcel Dekker: New York, 1994; p 35.
35. Khot, S. N.; Lascala, J. J.; Can, E.; Morye, S. S.; Williams, G. I.; Palmese, G. R.; Kusefoglu, S. H.; Wool, R. P. *J Appl Polym Sci* 2001, 82, 703.
36. Galia, M.; Svec, F.; Frechet, J. M. *J Polym Sci A Polym Chem Ed* 1994, 32, 2169.
37. Fay, J. J.; Murphy, C. J.; Thomas, D. A.; Sperling, L. H. *Polym Eng Sci* 2004, 31, 1731.
38. Shafizadeh, J. E.; Guionnet, S.; Tillman, M. S.; Seferis, J. C. *J Appl Polym Sci* 1999, 73, 505.