SYNTHESIS OF ELASTOMERIC PHENOLIC RESINS WITH IMPROVED TOUGHNESS AND FLEXIBILITY

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Abstract

Novel phenolic resins (PF) with improved fracture toughness and flexibility properties were synthesised and evaluated. A first modification consisted in the copolymerization of Phenol with a natural renewable component (Cardanol) during the synthesis of PF resins (CPF). An increases in the content of Cardanol resulted in a proportional increases in the flexural strength and in the fracture toughness together with a decreases in the flexural modulus of the cured CPF/PF blended resins. Further increased plasticizing and toughening effect was observed by the blending of the CPF/PF resins with propylene glycol (PG).

Introduction

Phenolic resins have become a common product of the synthetic polymer industry over the past 80 years [1]. These resins have been used extensively in the production of moulded plastics, wood products, and aerospace components. In constructing aerospace components, the most important use of phenolic resins is in the manufacturing of high-performance composites [2]. Structures are widely variable, and the following conditions are known to affect the properties of the phenolic resin: the mole ratio of phenol to formaldehyde, reaction time, temperature, water content, and residual phenol content. Phenolic resins are prepared by the reaction of formaldehyde (F) with phenol (P) and depending of the F:P molar ratio and the type of catalyst the reaction can lead to either a resol or a novolak type of phenolic resin. Our research work is focused on the modification of phenolic resins, which are prepared under alkaline conditions (resole type), which require a F:P ratio > 1.0 (this means an excess of Formaldehyde in relation to the molar amount of Phenol) [3, 4]. Most of the published research work on resol resins have been focused specifically in the fields of kinetics and reaction modelling [5-7], flammability and thermal analysis [8-12], and mechanical performance [13, 14], however the investigations of the modifications of these phenolic resole resins with natural renewable components from synthesis to final performance have been limited. The resin properties can be modified by reacting phenol with other aldehydes, by etherification of phenol, and by

using substituted phenols. This study is focused on the modification of a resol PF resin by the partial substitution of phenol with Cardanol in the synthesis with formaldehyde (named as CPF resin). The purpose of these modifications was to prepare a resin with improved toughness and flexibility, even exhibiting rubber-like elasticity, if such an effect is possible in this type of polymeric system.
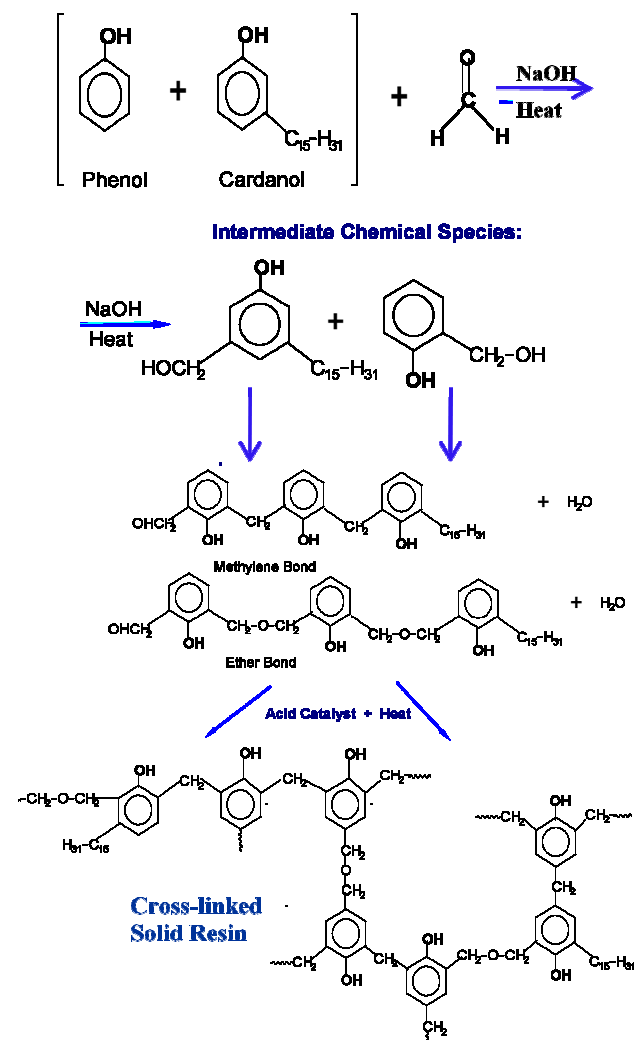

Figure 1. Chemical reaction mechanism for the synthesis and curing of the CPF resins.

Cardanol is obtained by the distillation of Cashew nut shell liquid (CNSL), which is a natural product obtained from the shells of the cashew nut. In this study modified resole resins were synthesized using Cardanol obtained

from Satya Cashew Chemicals Pty Ltd (India) and the proposed synthesis mechanism of the CPF resin, including the intermediate species and the final cross-linked structure are presented in Fig 1. The poly condensation with formaldehyde or formaldehyde containing reactives is the most commons technique of preparing a thermoset resin from CNSL [15]. 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 a variety of reactions [16-18]. Cardanol reacts with formaldehyde or hexamethylene tetramine via the hydroxyl group to produce Cardanol-Formaldehyde (CF) resins [19, 20]. The aliphatic side chains of Cardanol usually carry one, two, or three double bonds, making cardanol a mixture of four components varying in the degree of side-chain unsaturation [21, 22], which allows the Cardanol to undergo addition polymerization through these double bonds. Therefore, different types of resins can be synthesized from Cardanol, and also from the chemically modified CNSL [23-27].

One of the best known applications of CNSL and Cardanol resins is in the manufacturing of asbestos-free break pads for the automobile industry [28], which is due to their high thermal stability and oxidation resistance at elevated temperature. In general, PF phenolic resins have high thermal and chemical resistance but also high rigidity [29, 30], which limits their applications in FRP laminates and composites for civil engineering structures. While CF resins have a similar chemical profile to PF resins, they have a much higher flexibility and a lower cost [31], which makes them more suitable for modern civil engineering applications. Therefore, liquid phenolic resins prepared by the combination of Cardanol and Phenol (CPF) should have some specific properties and overcome some disadvantages of neat PF resins. However, these types of resins prepared by the combination of Cardanol/Phenol, have not been fully investigated. In this study we report the results of the physical and mechanical characterization of CPF resins.

Materials and Synthesis of CPF Resins

The CPF resins were prepared with different mixtures of Cardanol and Phenol which reacted with Formaldehyde in the presence of an alkaline type of catalyst (see Figure 1). Phenol was replaced with Cardanol by up to 40% by weight in the synthesis of different resins. 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 w % in Water), Cardanol and para-formaldehyde were mixed by keeping the mole ratio of total phenol (phenol + cardanol) to formaldehyde at 1:1.25 for the first set of resins (resin-I), then 1:1.50 for the second set (resin-II) and 1:2.0 for the last set (resin-III). An aqueous solution of NaOH 46% (4 %, w/w, on the basis of total phenol plus cardanol) was employed as the catalyst. The temperature was maintained at 60°C for 1h, then raised to 80°C for 1h and finally reduced to

60°C for 1h. The CPF resins were neutralised to a pH ~ 7.0 using an acid solution of PTSA- 75%. The chosen acidic catalyst for the curing of the CPF resins was a phosphoric acid (Hexion Phencat10 from Burdon Pty Ltd), which cures the PF phenolic resins relatively slowly (gel-time equal to 45~60 min.) and therefore enabled better final mechanical properties to be achieved. After adding the catalyst (3.0 pph) to the liquid CPF resins, the test specimens were initially cured at room temperature for 8-hours, followed by post curing inside of an oven at 80°C for 4-hours. Infrared spectroscopy analysis, DMA analysis, mechanical tests and fracture toughness of the post-cured CPF samples were carried out. For comparison, samples of neat PF resin were also cured and characterized in this study. The used neat PF resin was a low-viscosity commercial phenolic resin from Hexion Specialty Chemicals Australia Pty Ltd (Cellobond J2027L).
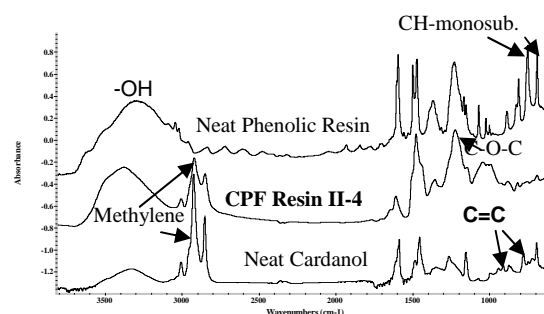

Figure 2. Infrared spectra of the neat Cardanol (bottom), neat phenolic resin (top) and of the synthesised CPF resin-II-4 with 40 % of Cardanol (middle).

The infrared spectra of the synthesized CPF resin-II-4, the neat Cardanol and the neat PF resin are shown in Fig 2. The peak associated with the OH- group attached to the phenyl ring in the resins is observed in the region 3290 cm^{-1} to 3370 cm^{-1}. The peak found at 1200 cm^{-1} in the infrared spectrum of resin-II-4 is associated with the presence of ether linkages. The peaks associated with the methylene groups 2926 cm^{-1}, 2854 cm^{-1} in the neat cardanol and 2922 cm^{-1} and 2851 cm^{-1} in resin-II-4 are due to the Cardanol side chain and also to etherification reactions. 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 polymerisation has taken place through the ortho- and/or para- positions. However, the vibrations at 911cm^{-1}, 880cm^{-1} and 694cm^{-1} in the IR signal of the Cardanol are due to the side chain double bonds. These infrared peaks have reduced in size in the spectrum of the resin-II-4 indicating that the poly-condensation has also taken place through some of the double bonds in the aliphatic side chain.

Results

Dynamic Mechanical Analysis

Dynamic–mechanical 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 behaviour $x(t)$ 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 δ (damping) of the sample in dependence on temperature and deformation frequency. Glass Transition Temperature values (Tg) of the resins is obtained in this work from the top of the tan δ peak, as previously reported.
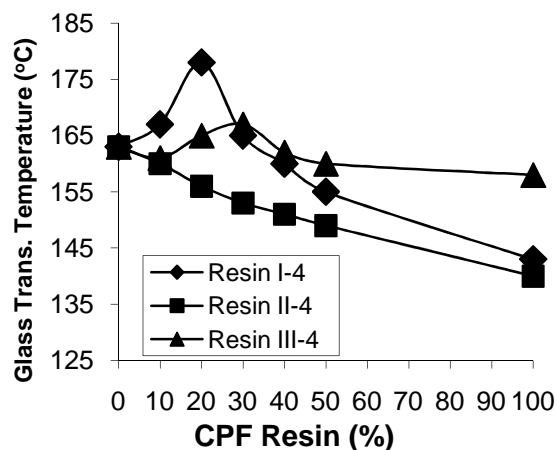

Figure 3. Glass Transition temperatures (T_g) of the CPF/PF resin blends (40 % w/w content of Cardanol in the CPF resins).

In this study the dynamic mechanical properties of the CPF/PF resin blends have been investigated to establish the relationship between the glass transition temperature (Tg) of the CPF resins and the synthetic parameters of the resins such as the P:F molar ratio and the Cardanol content in the CPF resins. The plots in Fig 3 reveal that the substitution of Phenol with Cardanol in the resins shifts the Glass Transition Temperature (Tg) of the cured resins to lower temperatures. Additionally, the DMA analysis revealed that a decrease in the Formaldehyde: Phenol (F:P) molar ratio resulted in a decreases in the Tg value of the cured CPF and of the blended resins. 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 Tg equal to 137 $^{\circ}$C.

Crosslink Density

The crosslink density can be defined as the fraction of monomer units that are cross-linked [32]. The crosslink density can be calculated from the rubber elasticity theory [33]:

$$\nu = E/3RT \qquad (1)$$

where ν represents the crosslink density (number of moles of chains per cm^3), R is the gas constant (8.314 J/K-mole), T is the temperature in Kelvin, and E is the elastic modulus taken from the Storage Modulus of the DMA analysis at 50 $^{\circ}$C above the Tg value of each

sample. In order to reduce the characteristic brittleness of a phenolic resin a modified PF resin, such as CPF with Cardanol, , has to be synthesized. The crosslink density curves of the CPF resins and of the CPF/PF resin blends are presented in Fig. 4. 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 is much lower 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} moles/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.
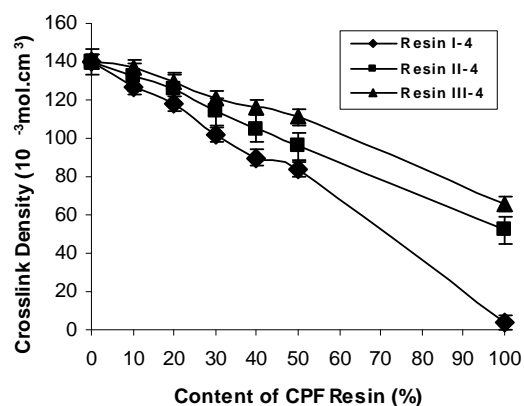

Figure 4. Crosslink density values of the blended CPF/PF resins vs CPF resins content.

Mechanical Properties

The result of the Flexural stress of the blended CPF/PF resins are presented in Fig 5. The results correspond to the CPF resin-I (P:F ratio 1:1.25), which showed the larger change in its ultimate mechanical properties in comparison with the other CPF resin formulations (II and III). This is due to its lower F:P molar ratio. As shown in Fig 5 the max. stress (MPa) increased with the amount of the CPF-I resin in the blends and the content of Cardanol in the CPF-I resins. The decrease in brittleness and the changes in the mechanical properties of the CPF/PF resin blends are enhanced with the amount of Cardanol present in the CPF resins and with the decrease of the F:P molar ratio.

The fracture toughness or critical stress intensity factor K_{Ic} (MPa.m$^{1/2}$) for the CPF resin I with 40 % of Cardanol is about 85 % higher than that for the neat PF resin (0.9 MPa.m$^{1/2}$), as shown in Fig 6. From the three sets of CPF resins with different F:P molar ratio

investigated in this work, the CPF resin-I showed the larger increase in the values of the fracture toughness factor K_{Ic} with increasing Cardanol content.
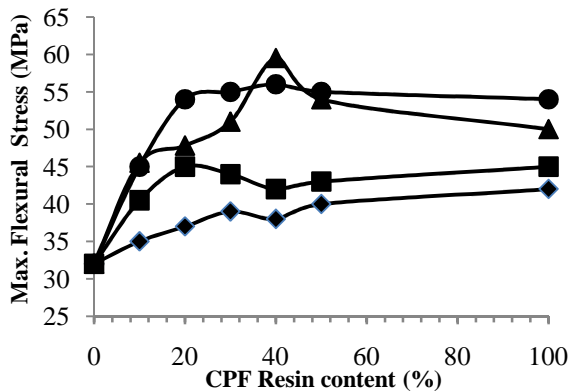

Figure 5. Plots of the Flexural stress (MPa) vs. CPF-I resin content. The CPF resin with 10% (♦), 20% (■), 30% (▲) and 40% (●) of Cardanol content.
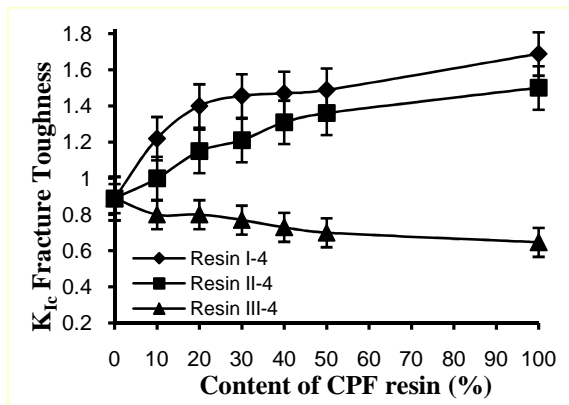

Figure 6. Fracture toughness factor K_{Ic} (MPa $.m^{-1/2}$) of the CPF/PF blended resins . In preparation for the tests the samples were cured for 24 h at RT followed by post-curing of 4 h at 80 ^{o}C.

The enhanced fracture toughness of the CPF resins I may be attributed to a greater level of flexibility and ability for spatial rearrangement inside of the thermoset network, induced by the relatively low crosslink density of the resins. In contrast, the values of the fracture toughness factor K_{Ic} for the CPF resin III remained relatively constant with increasing Cardanol content, and with values lower than the K_{Ic} value of the neat PF resin, as shown in Fig 9. 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 polymeric network by the aliphatic side chain of the Cardanol molecule.

Effect of Propylene Glycol

The addition of 20% (w/w) of Propylene-Glycol (PG) has an effect on the mechanical flexural properties of the resins. Comparative plots of the max. Stress (MPa), Modulus (MPa) and the Strain (%) of the CPF resin – I vs. Cardanol content (%) in the CPF resins, are shown in Fig 7.
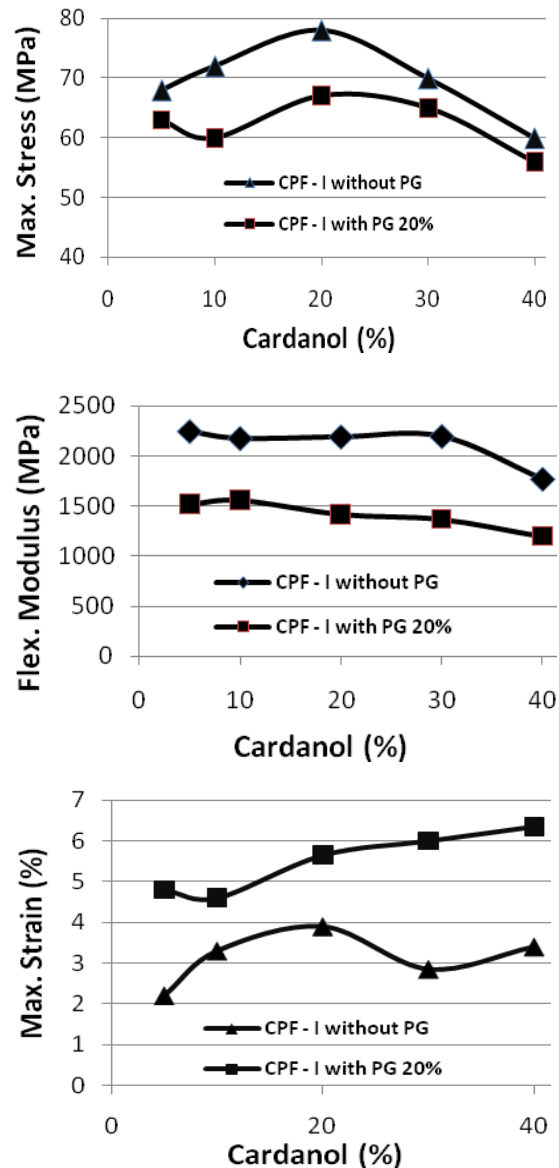

Figure 7. Flexural properties of the CPF resins (Resin – I) with and without Propylene Glycol (20 % w/w) vs Cardanol content in the CPF resins.

The obtained results evidenced a significant decrease in the flexural max. Stress and in the Modulus of the CPF resins mixed with PG, in comparison with the equivalent CPF samples without PG. However, as shown in Fig 7, the Strain of the CPF samples with PG was higher than the equivalent samples without the PG. This mechanical behaviour 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 Fig 7. The observed decrease in the mechanical flexural properties of the resins with PG is due to the plasticizing and toughening effect of the added propylene glycol inside of the cured phenolic network.

Conclusions

CPF resins were synthesized with different amounts of Cardanol content. The physical and mechanical properties of the cured samples obtained from the blends of CPF and PF phenolic resins were established. The properties 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 flexural 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 CPF 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. The addition of Propylene glycol to the CPF resins had a proportional effect on the mechanical of the cured resins, which allows its use as a plasticizing and toughening agent to the resole phenolic resins with and without the presence of Cardanol in the chemical structure.

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