## Effect of Composition on Adhesive Blends Consisting of Neoprene and Phenol-Cardanol-Formaldehyde Copolymer

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# Effect of Composition on Adhesive Blends Consisting of Neoprene and Phenol-Cardanol-Formaldehyde Copolymer

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*This study is concerned with the adhesive properties of blends consisting of a copolymer phenolic resin and neoprene rubber. The phenolic resin is the condensation product of formaldehyde and a mixture of phenol and cardanol, a substituted phenol. Cardanol is the main ingredient of cashew nut shell liquid, a renewable resource and a cheap agro-by-product. The specific objective of the study is to arrive at optimum stoichiometric ratios between total phenol and formaldehyde (P/F ratio) so that the best peel and shear properties are obtained for aluminum-aluminum (Al–Al), styrene butadiene rubber-styrene butadiene rubber (SBR–SBR), and Al–SBR specimens. In general, the composition of the resin (represented by the P/F ratio) has only limited influence over the shear properties. Peel strength, on the other hand, is influenced by the P/F ratio. It is found to be a maximum for a P/F ratio of 1:1.5–1:1.7 for all cases. The results also prove that cardanol, a cheap renewable resource, can be a useful starting material for adhesive formulations.*

## INTRODUCTION

Elastomeric adhesives containing polychloroprene rubber and phenolic resin are a versatile class of bonding materials [1]. The rapid development of bond strength combined with tack or auto-adhesion as well as resistance of the cured bondline to heat, oxidation, water,

solvents, oils, acids, and alkalis have led to the extensive use of neoprene in adhesives [2]. Phenolic resins are employed in a wide range of applications from commodity construction materials to high technology applications in electronics and aerospace. The ultimate performance of a fully cured phenol formaldehyde (PF) resin largely depends on its synthesis parameters including the phenol/formaldehyde (P/F) molar ratio, sodium hydroxide/phenol (NaOH/P) molar ratio, reactivity, and so on [3]. The F/P ratio and NaOH/P molar ratios affect the cure shrinkage [4] and surface tension of PF resol resins [5]. Both ratios also affect the rigidity of the cured resins, showing that high F/P and NaOH/P ratios give high relative rigidity. Among phenolic resins, substituted phenolic resins provide improved compatibility with rubbers.

Cardanol, the main ingredient of cashew nut shell liquid (CNSL), is a meta-substituted phenol. It has a side chain with 15 carbon atoms at the meta position of the benzene ring [6–7]. The structure of cardanol is given in Figure 1. The authors have employed phenolic resins based on the co-condensation of a mixture of phenol and cardanol for rubber-to-rubber bonding, metal-to-metal bonding, and rubber-to-metal bonding [8]. Peel and shear properties of (a) aluminum to aluminum
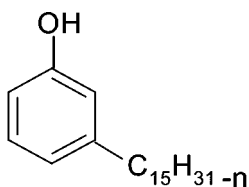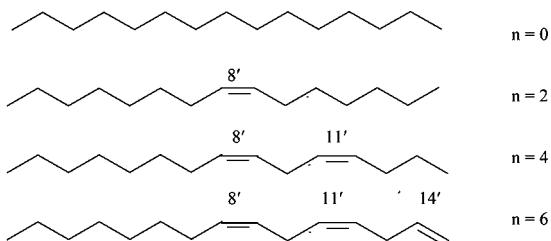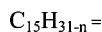


FIGURE 1 Structure of cardanol.

(Al–Al), (b) SBR to SBR (SBR–SBR), and (c) aluminum to SBR (Al–SBR) bonds are evaluated under varying conditions of total phenol/formaldehyde (P/F) ratios. Further, the total resin content for each phenol/cardanol ratio that gives optimum results is also established. Although Al-Al and SBR-SBR specimens were bonded with a single component adhesive formulation, a primer/adhesive combination was employed for Al-SBR bonds. The adhesive formulation developed for metal-to-metal bonding has been used as the primer and the one for rubber-to-rubber bonding as the adhesive for rubber-metal bonding. The primer, by design, contains more resin with the result that on curing the modulus of the cured film will be closer to that of the metal. The adhesive, on the other hand, will have a lower modulus because of lower resin content. Hence the primer-adhesive combination establishes a steady reduction in tensile modulus from that of the metal to that of the rubber. An earlier study [8] identified an optimum resin content of 80 phr of the phenolic copolymer resin in the primer as yielding the best peel and shear values for Al-SBR bonds. Hence the resin content of primer formulations in this case has been kept constant at 80 phr.

## EXPERIMENTAL

### Materials

Phenol, formalin (40% formaldehyde), and solvents (toluene and methyl ethyl ketone) were obtained from Merck India Ltd. All chemicals were of analytical grade. The polychloroprene (neoprene) rubbers (AD and W grades) were obtained from DuPont, Akron, Ohio and had a Mooney viscosity [ML(1 + 4) at 100°C] of 45. Styrene butadiene rubber (SBR 1502) used was manufactured by Japan Synthetic Rubber Co. Ltd., Tokyo and had a Mooney viscosity [ML(1 + 4) at 100°C] of 45. CNSL, obtained from Vijayalakshmi Cashew Exports, Kollam, India, was as per Indian Standard, IS 840. It had the following specifications: specific gravity 0.95–0.97, viscosity at 30°C—550 cp (max), ash—1% by wt (max), iodine value by Wijs method—250. Carbon black was supplied by Phillips Carbon Black Ltd., Cochin, India. It had DBP absorption $102 \pm 5$ cc/100 g and the iodine number is 82. Precipitated silica (Grade GSL-150) was procured from Sameera Chemicals, Kottayam, India. 3-aminopropyltriethoxysilane was supplied by Sigma Aldrich, Bangalore, India. Sulphur was supplied by Standard Chemical Company (Pvt) Ltd., Mumbai and had the following specifications: acidity 0.01% max, ash 0.01% max and solubility in $CS_2$ 98% max. ZnO was supplied by M/s. Meta Zinc Ltd., Mumbai. It

had the following specifications: ZnO content—98%, acidity—0.4% max, heat loss (2 h at 100°C)—0.5% max. Zinc phosphate was supplied by Research Lab, Mumbai, India. Aluminium substrates used was of type 1100 of 99% purity.

## Substrate Preparation

The mixing and homogenization of SBR and other compounding ingredients for the substrates were done on a laboratory size (150 mm × 30 mm) two-roll mill as per ASTM D3186 prior to compression molding in a hydraulic press. The compound was molded into 150 mm × 150 mm × 2 mm sheets employing a pressure of 200 kg/cm$^2$ and a temperature of 150°C. The time of cure was in accordance with the results of cure studies initially done on a Rubber Process Analyser (RPA 2000 supplied by Alpha Technologies, USA). The molding was cut into strips of 100 mm × 25 mm × 2 mm size to serve as substrates. Aluminum strips of size 100 mm × 25 mm were machined from 0.8 mm thick metal sheets to serve as substrates for peel studies on metal-to-metal bonds. Aluminum strips of 100 mm × 25 mm × 1.6 mm were used for testing shear strength of Al-Al bonds as well as peel and shear strengths of Al-SBR bonds.

Mechanical cleaning (surface roughening) was done manually on both metal and rubber substrates with a No. 100 emery paper. This lasted 1–2 min for metal and 3–4 min for rubber substrates. It resulted in a weight loss of about 0.4% for rubber and 0.25% for Al substrate. For metal strips, solvent degreasing with trichloroethylene followed the mechanical cleaning. A single adhesive layer (approximately 0.1 mm thick) was applied onto each substrate on an area of 25 mm × 25 mm.

## Resin Preparation

A resole type resin synthesized by condensing an excess of formaldehyde with phenol under alkaline conditions was preferred as it is heat reactive. Cardanol was separated from commercial CNSL by distillation under reduced pressure (1 mm Hg). The pale yellow fraction collected at 206–208°C is cardanol [9]. Phenol-cardanol-formaldehyde (PCF) resin was synthesized by reacting a mixture of phenol and cardanol with an aqueous solution of formaldehyde (formalin) at 90°C for about 1 h [10–11].

Different copolymers with varying stoichiometric ratios between total phenols and formaldehyde (1:1.5, 1:1.7, 1:2, 1:2.3, and 1:2.5) were prepared. For each stoichiometric ratio two different phenolic resins

with varying phenol/cardanol ratio (wt%), viz. 60/40 (PCF-I), and 80/20 (PCF-II), were synthesized. The resins thus obtained were neutralized, dried, and subjected to tests to determine the gel time as per DIN EN 6043. This involves keeping a specified amount of the resole resin in a test tube at 100°C and stirring until gelling takes place. The gel time is an indication of the cure time as well as its crosslinkability.

## Thermal Studies

Thermogravimetric analysis of the synthesized resins was carried out using TA Instruments Model TQ 50 TGA, at a heating rate of 20°C in nitrogen atmosphere. The sample purge flow rate of the nitrogen was kept at 60 ml/min.

## Adhesive Formulation and Application

The PCF resin was added to neoprene solution in toluene containing other ingredients (Table 1) depending on the nature of the substrate. The neoprene consisted of blends of Grades AD and W at a ratio of 90/10 wt%. Such blends were found to give better performance compared to pure grades [12]. The adhesive was applied onto the substrates using a brush and 30 min were allowed for drying the film at 30°C. The substrates viz. Al–Al, SBR–SBR and Al–SBR, were subsequently joined and curing completed under heat and pressure. A pressure of 50 kg/cm$^2$ and a temperature of 150°C were maintained in the press for 30 min. These values were found to be optimal from an earlier study [8]. From the same investigation the two adhesive

**TABLE 1** Adhesive Formulations

| Ingredient | Al-to-Al bonding | SBR-to-SBR bonding |
|---|---|---|
| Neoprene AD | 90 phr | 90 phr |
| Neoprene W | 10 phr | 10 phr |
| Silica | 4 phr | — |
| Acetylene black | — | 6 phr |
| Sulfur | 1 phr | 0.5 phr |
| Zinc phosphate | 1.5 phr | — |
| Silane | 2 phr | — |
| Phenolic resin | 20–100 phr | 10–50 phr |
| Toluene | 604 g | 426 g |
| Methyl ethyl ketone | 615–1010 g | 438–588 g |
| Total solid content (%) | 15–17 | 20–22 |

formulations given in Table 1 were identified for SBR-to-SBR bonding and Al-to-Al bonding.

## Al–Al Bonding

The neoprene rubber was masticated on a two-roll mill at a friction ratio of 1:1.25 to reduce crystallinity and improve solubility. Other ingredients were incorporated in the following order during mastication: silica, sulphur, and zinc phosphate. The temperature of the rolls was maintained at $70 \pm 5^{\circ}C$ during mastication, which lasted for about 10 min. The compounded rubber was dissolved in toluene so as to obtain a 15 wt% solution. The PCF resin was dissolved in methyl ethyl ketone separately and subsequently blended with the rubber solution. The resin concentration was varied from 20 to 100 phr for each resin prepared with a different total phenol/formaldehyde ratio. T-peel test was performed as per ASTM D 1876 and shear strength test as per ASTM D 1002 with a grip separation rate of 50 mm/min at $30^{\circ}C$. The Al specimens selected for peel test were only 0.8 mm thick. This made them flexible permitting T-peel test to be done. The Al specimens for shear test were thicker, 1.6 mm.

## SBR–SBR Bonding

The neoprene rubber was masticated on a two-roll mill and acetylene black and sulphur was added one by one for 10 min. The friction ratio was kept at 1:1.25 and the temperature of the rolls maintained at $70 \pm 5^{\circ}C$ during mastication. It was then dissolved in toluene over a period of 12 h at room temperature to obtain a 20 wt% solution. The resin concentration was varied from 10 to 50 phr in this case. The resulting adhesive formulations were tested for T-peel and shear strengths.

## SBR–Al Bonding

SBR-to-Al bonding studies were carried out using an adhesive-primer combination. Different phenolic resins (1:1.5, 1:1.7, 1:2, 1:2.3, and 1:2.5) were employed for formulating the adhesive as well as the primer. For this study, the resin content was fixed in the primer at 80 phr [8] the resin content and was varied in the adhesive from 20 to 50 phr in steps of 10 phr. The primer was applied only on the metal surface by brush. The adhesive coating was applied on the dried primer coating as well as on the rubber surface. $180^{\circ}$ peel test was

performed as per ASTM D 903 and shear strength as per ASTM D 1002 with a grip separation rate of 50 mm/min at 30°C.

## RESULTS AND DISCUSSION

Gel time studies on the synthesized phenolic resins indicate that shorter gel times are achieved as more and more formaldehyde is employed for the synthesis. This is because of higher methylol content and a greater possibility of condensation between methylol groups. A high formaldehyde resin, in general, leads to a short gel time and often a short shelf life. From comparison of the two curves in Figure 2 the presence of cardanol is found to marginally increase the gel time, although at high formaldehyde ratios the difference is not very noticeable.

Table 2 presents data from thermogravimetric studies conducted on resins synthesized with different compositions. The peak degradation temperature shows a decreasing tendency as the formaldehyde content goes up. This is because at higher formaldehyde ratios there are fewer benzene rings per molecule of the condensate and oxidation/degradation becomes easier. As the cardanol content in the mixture increases in relation to phenol, there is a reduction in the residue weight. This is explained by the presence of the long aliphatic side chain of the cardanol molecule. This side chain is prone to degradation comparatively earlier. The residue weight is seen to maximize at a stoichiometric ratio of 1:1.7. As may be seen from subsequent results the overall performance of the adhesive reaches an optimum at this stoichiometric ratio. This can be attributed to an optimal molecular weight attained by the resin under these conditions.
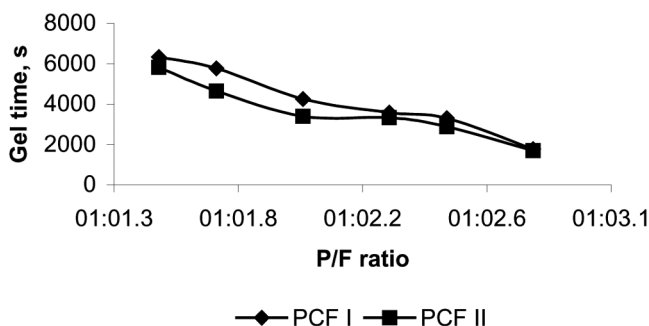
**FIGURE 2** Gel time of the synthesized resins.

**TABLE 2** Thermogravimetric Data of Phenol-Cardanol-Formaldehyde Copolymer

| P/C | P:F | Onset temperature °C | Peak degradation temperature °C | Char residue wt% |
|-----|-----|----------------------|--------------------------------|------------------|
| 60/40 | 1:1.5 | 333 | 459 | 13.64 |
|  | 1:1.7 | 341 | 413 | 30.06 |
|  | 1:2.0 | 357 | 443 | 28.46 |
|  | 1:2.3 | 351 | 437 | 25.20 |
| 80/20 | 1:1.5 | 348 | 461 | 14.24 |
|  | 1:1.7 | 352 | 440 | 33.96 |
|  | 1:2.0 | 352 | 443 | 32.89 |
|  | 1:2.3 | 344 | 450 | 25.35 |
|  | 1:2.5 | 344 | 447 | 23.12 |

Figure 3 is a plot of peel strength obtained for Al–Al bonds employing phenolic resins of varying P/F ratios. A P/F ratio of 1/1.7 is found to give the best peel strength. Optimum resin content for this case is about 80 phr although peel strength is not very sensitive to P/F ratio in the range of 40–100 phr. Lower amounts of formaldehyde signify higher monomer molecular weights and a lower extent of crosslinking. The difference in performance between resins with varying P:F ratios is not significant at lower resin contents, say 20–40 phr. As the formaldehyde content goes up beyond 80 phr peel strength falls drastically due to the high desity of crosslinking.

Referring to Figure 4, shear strength of Al–Al bonds are also maximum for a P:F ratio of 1:1.7. A high methylol content facilitated by high formaldehyde ratios is not conducive to shear strengths of
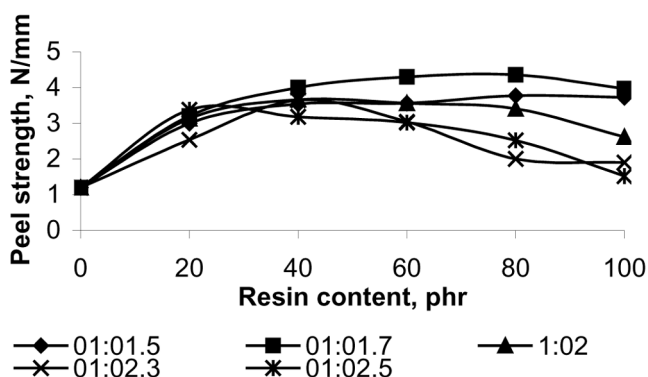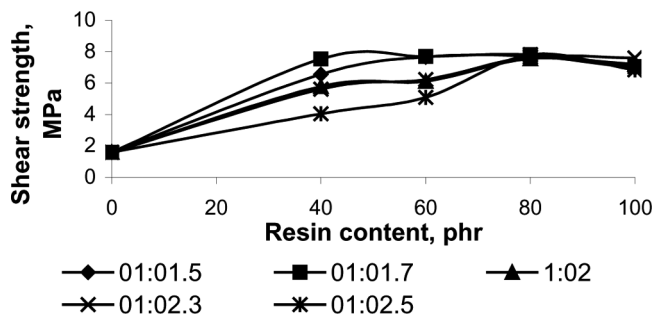


**FIGURE 3** Al–Al peel strength.

**FIGURE 4** Al–Al shear strength.

Al–Al bonds, especially at resin contents less than 80 phr. At a high resin concentration of 80 phr all the resins are almost equivalent in performance. A probable explanation is the lowered tack at high formaldehyde contents and consequent higher degrees of crosslinking. At such high formaldehyde contents more resin is needed to make up for reduced tackiness.

Figure 5 shows the peel strength of SBR–SBR specimens. The resin with P:F ratio of 1:1.7 yields high peel strength irrespective of the resin content. But surprisingly, the best peel strength is shown by the resin with a P:F ratio of 1:2.3 at a low concentration of 10 phr. As the relative amounts of formaldehyde goes up, the peel strength tends to fall at high resin contents. The performance of the resin with 1:2.3 stoichiometry points to the complex relationship between phenolic resin chemistry and performance of the final adhesive formulation.
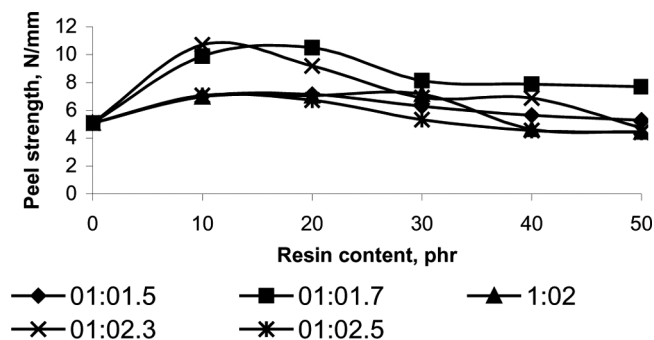
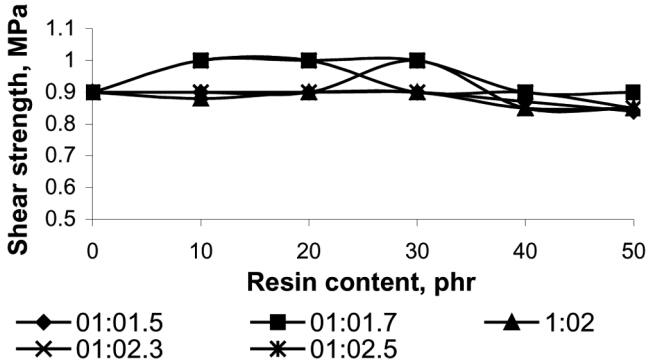

**FIGURE 5** SBR–SBR peel strength.

**FIGURE 6** SBR–SBR shear strength.

Figure 6, wherein the shear strength of SBR–SBR specimens are plotted indicates that all the P:F ratios studied lead to comparably high values. All the tests end in fracture of the substrates. The resin with P:F ratio of 1:1.7 retains its superiority especially at lower resin contents. For a resin with a particular P:F ratio, the dependence of shear strength on resin content is marginal.

Figure 7 shows the variation of peel strength of Al–SBR bonds with P:F ratio. The resin with a P:F ratio of 1:1.5 shows a clear superiority. In general, the bonds perform better at lower resin contents, say 20 phr, in the adhesive. A resin with low formaldehyde and hence lower degree of crosslinking is beneficial for SBR–Al bonding.

Figure 8 shows that a low formaldehyde content (1:1.5) leads to high shear strength in Al–SBR bonds. The maximum shear strength is obtained at 30–40 phr. The resin content and P:F ratio has only
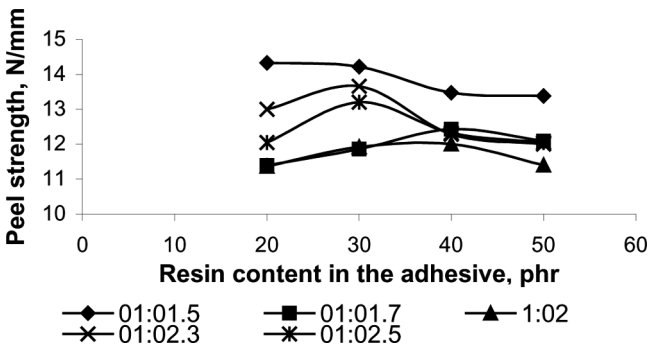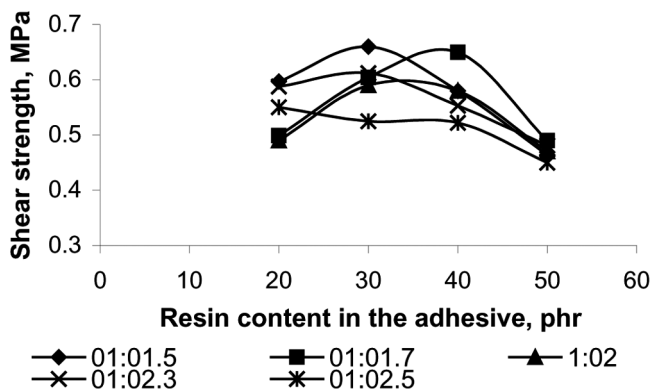


**FIGURE 7** SBR–Al peel strength.

**FIGURE 8** SBR–Al shear strength.

marginal significance in improving the shear strength. The extent of crosslinking and methylol content (indicated by P/F ratio) and the comparative stiffening of the adhesive film by the presence of the thermoset resin do not influence the shear strength to any significant extent.

Table 3 shows the visually observed failure patterns during testing of various samples. It can be seen that Al–Al specimens undergo cohesive failure of the adhesive film when tested for T peel test. The necessary amounts of the resin for peak performance are found to be less as the relative proportion of formaldehyde goes up. Higher formaldehyde content leads to a higher degree of crosslinking and a higher $T_g$. The latter two properties curtail molecular flexibility and reduce the peel strength. Hence the cohesive failure pattern. In the case of lap shear strength a high degree of crosslinking leads to higher strengths. The high lap shear strength surpasses the structural strength of the substrate and leads to substrate fracture. The higher degree of crosslinking resulting from additional formaldehyde content has no substantial impact on the performance as even a low formaldehyde content (1:1.5) is enough to give sufficient crosslinking and cause substrate fracture.

For SBR–SBR specimens, peel strength performance is generally good. The fracture mode is not uniform. Similar to Al–Al specimens, lap shear failure of SBR–SBR joints results from substrate fracture. Only comparatively low percentages of the resin are required. Because SBR has a lower strength, peel strength values are at times high enough to cause substrate fracture. As in the case of Al–Al specimens, formaldehyde content of the resin has no effect either on the fracture mode or the requisite resin content.

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**TABLE 3** Failure Pattern of Adhesive Bonds

| Phenol/ Cardanol | P:F ratio | Substrate bonded | Test performed | Type of failure | Resin content of the best formulation, phr |
|---|---|---|---|---|---|
| 60/40 | 1:1.5 | Al–Al | T peel strength | Cohesive failure of adhesive film | 80 |
| | 1:1.7 | ″ | ″ | ″ | 80 |
| | 1:2.0 | ″ | ″ | ″ | 40 |
| | 1:2.3 | ″ | ″ | ″ | 40 |
| | 1:2.5 | ″ | ″ | ″ | 20 |
| 80/20 | 1:1.5 | Al–Al | Lap shear strength | Substrate failure | 80 |
| | 1:1.7 | ″ | ″ | ″ | 80 |
| | 1:2.0 | ″ | ″ | ″ | 80 |
| | 1:2.3 | ″ | ″ | ″ | 80 |
| | 1:2.5 | ″ | ″ | ″ | 80 |
| 60/40 | 1:1.5 | SBR–SBR | T peel strength | Cohesive failure of adhesive film | 20 |
| | 1:1.7 | ″ | ″ | ″ | 20 |
| | 1:2.0 | ″ | ″ | ″ | 30 |
| | 1:2.3 | ″ | ″ | ″ | 10 |
| | 1:2.5 | ″ | ″ | ″ | 10 |
| 80/20 | 1:1.5 | SBR–SBR | Lap shear strength | Substrate failure | 10 |
| | 1:1.7 | ″ | ″ | ″ | 10 |
| | 1:2.0 | ″ | ″ | ″ | 10 |
| | 1:2.3 | ″ | ″ | ″ | 10 |
| | 1:2.5 | ″ | ″ | ″ | 10 |
| 60/40 | 1:1.5 | SBR–Al | 180° peel strength | Cohesive failure of the rubber substrate | 20 |
| | 1:1.7 | ″ | ″ | ″ | 40 |
| | 1:2.0 | ″ | ″ | ″ | 40 |
| | 1:2.3 | ″ | ″ | ″ | 30 |
| | 1:2.5 | ″ | ″ | ″ | 30 |
| 60/40 | 1:1.5 | SBR–Al | Lap shear strength | Cohesive failure of the rubber substrate | 30 |
| | 1:1.7 | ″ | ″ | ″ | 40 |
| | 1:2.0 | ″ | ″ | ″ | 30 |
| | 1:2.3 | ″ | ″ | ″ | 30 |
| | 1:2.5 | ″ | ″ | ″ | 20 |

SBR–Al specimens fail by cohesive failure of the rubber substrate for all conditions. There is no dependence on the formaldehyde content. The adhesive–primer combination has surpassed the rubber strength in both peel and shear modes. In general, only peel properties are affected to any extent by variations in P:F ratio. This only

underlines the fact that the peel properties are more sensitive to the degree of crosslinking of the resin. It is also evident that the adhesive bond in all cases is sound and strong, leading to cohesive failure of either the adhesive or substrate fracture.

## CONCLUSION

The study reveals that cardanol, a cheap renewable resource, can be an effective starting material for adhesive formulations. It is found that the gel time of the phenolic copolymer synthesized from cardanol and phenol decreases as the proportion of formaldehyde in relation to total phenol goes up. The presence of cardanol only marginally affects the thermal stability of the copolymer. A strong adhesive bond is formed in all cases of Al–Al, Al–SBR, and SBR–SBR specimens studied. The method of preparation of the resin reflected by the P:F ratio is seen to influence only the peel properties. Whereas Al–Al bonding requires higher levels of resin addition of the order of 80 phr, SBR–SBR specimens require the least amount of resin (10–30 phr). Al–SBR specimens perform best when the resin content of the adhesive is in the range of 20–40 phr.

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