

Polymeric Resin from Renewable Resources: Studies on Polymerization of the Phenolic Component of Coconut Shell Tar

Today there is much discussion on the utilization of renewable resources for polymer applications. This is partly due to the recognition that the supply of petroleum and coal is limited and that the cost of petrochemicals is on the increase. Thus, biomass which consists mostly of polymers and monomers of natural origin offers itself as a suitable renewable resource. A good number of reviews and research papers have already come up indicating their importance.¹⁻⁵

Materials based on the coconut tree form a major renewable resource of the tropical regions of the world.⁶ Of these materials, the coconut shells are available to the tune of about 4.2 million tons per year.⁶ The shells on destructive distillation give (see Fig. 1) coconut shell char, which is used as a filler in plastics and for the development of activated carbon. Coconut shell tar (CST) is a byproduct obtained during the distillation process and was considered as a waste so far. The CST is a tarry oil, dark brown in color with a characteristic unpleasant empyreumatic odor. Except for some identification of the components, not much work has been done on it. It is reported to contain many monomers, the major one being phenolic in nature.⁷ This paper deals with the enrichment and polymerization of the phenolic components of CST.

EXPERIMENTAL

Materials and Methods

CST was obtained from M/s. Carbo Chemicals Industries Ltd., Calicut, and the same was used without further purification. Phenol (GR) and formaldehyde (AR) were obtained from Glaxo Laboratories. Acetone (GR), oxalic acid (GR), sodium hydroxide (GR), and hexamethylene tetramine were obtained from Sarabhai M. Chemicals.

Isolation and Separation of Phenolic Components of CST

CST (100 mL) was distilled at atmospheric pressure, and fractions coming out at 100°C, at 103–105°C, and at 118–120°C were collected. The first fraction was water (22%), the second fraction was crotonaldehyde (3%), and the third fraction was acetic acid (11%). The residue was refluxed with 3% sodium hydroxide for 2 h and neutralized with glacial acetic acid. It was dissolved in acetone and filtered to remove free carbon. The filtrate, after the removal of acetone, was used for polymerization.

Polymerization

A two-stage Novolak resin (P:F mol ratio = 1:0.8) was prepared from CST. A 500-mL resin kettle was fitted with a reflux condenser, stirrer, and thermometer. To the reaction vessel

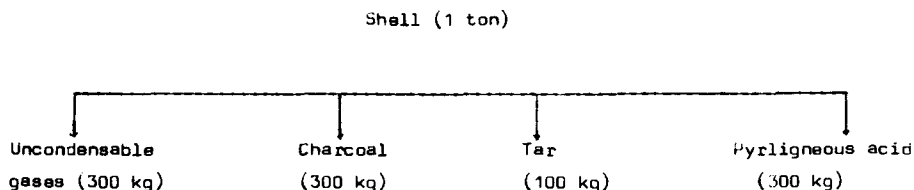


Fig. 1. Coconut shell distillation products.

was added 33.8 g (0.16 mol) of CST, 10.38 mL of 37% aqueous (0.128 mol) formaldehyde, and 1 g of oxalic acid. The reaction mixture was stirred and heated in a water bath at 100°C for 5 h. Vacuum was then applied to remove water of condensation. The yield was found to be 97%. The resin thus obtained was soluble in acetone and alkali. It was cured by mixing with hexamine (0.8%) and then hot pressing at the pressure of 1000–2000 lbf/in.² at 130°C for 1.5 h. Viscosity measurements of the polymer were carried out using a Ubbelohde viscometer at 30°C.

Mechanical Testing—Lap Shear Test

Lap Shear test of the Novolak resin was carried out according to ASTM standard D 1002.⁸ A solution of the resin and hexamine in acetone was applied between two plywood pieces each of length 3.5 in. and thickness 0.06 in. (area of overlap was 1 in.²) cured at 130°C (curing time 1.5 h) and shear strength was measured using an Instron Testing Machine at a crosshead speed of 20 mm/min.

Scanning electron micrographs were taken using a Jeol 35 C Microscope.

RESULTS AND DISCUSSION

Results of the preliminary examination of CST, the phenol enriched CST and the Novolak resin is given in Table I. The total phenol content after distillation was raised from 36% to 45% and after the removal of free carbon to 51.5%. Figure 2 gives the data on the process of enriching the phenol in CST. The intrinsic viscosity of the Novolak obtained was 0.025 dL/g whereas the corresponding value for phenol formaldehyde resin prepared under the same condition was 0.035 dL/g. Figures 3(a) and (b) show the SEM of the surface of the uncured resin of CST and phenol, respectively, and appear to be similar in nature.

The Novolak obtained from CST on curing with hexamine at 130°C gave a hard product. When the resin was placed between two wood pieces and pressed, good adhesion was indicated. Pending the development of the final formulation, only open tack time and lap shear were measured in this case. Shear strength obtained through lap shear experiment (according to ASTM D 1002) using the Instron Testing Machine gave a comparatively good idea about the strength property of the CST resin. The shear strength of CST resin was measured at solid contents of 13.8% and 27.7% with varying open tack time (Fig. 4). At 13.8%, CST resin showed a maximum open tack time of 45 s and shear strength of 94.55 N/cm². At 27.7% corresponding values were 60 s and 71.30 N/cm². These results are compared with that of a P-F resin under similar condition (Table II).

The SEM photographs of the fractured surface of CST and phenol resin (lap shear test samples) indicate that both the samples have gotten fractured in a similar pattern, though the shear strength of the latter is about double that of the former [Figs. 5(a) and (b)].

It is apparent from these results that the strength of the CST resin is only just half of that of P-F resin. It has been indicated early that CST contains a large number of components and only the nonpolymerizable and major components like water and acetic acid are removed. The system therefore contains other ingredients in small amount, which may give rise to bond weakening effects or which may form weak boundary layers weakening the adhesive bond.

TABLE I
Chemical and Physical Analytical Data

	CST	Phenol-enriched CST	CST Novolak resin
Acid value	63.59	15.503	20.62
Total phenol content (%)	35	45	—
Free carbon (%)	1.57	6.5	—
Density (g/cc)	1.178	—	1.2995
Intrinsic viscosity (dL/g)	—	—	0.025

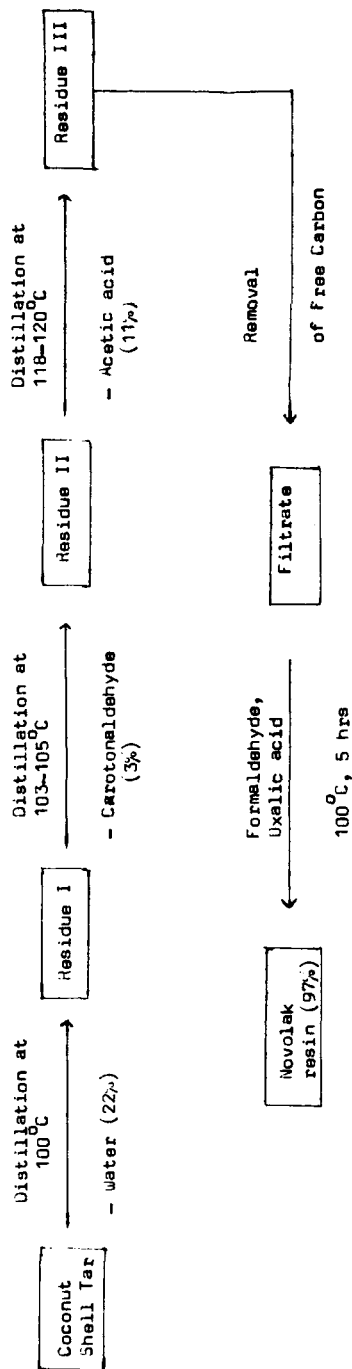


Fig. 2. Flow sheet for the enrichment of the phenolic component of coconut shell tar.

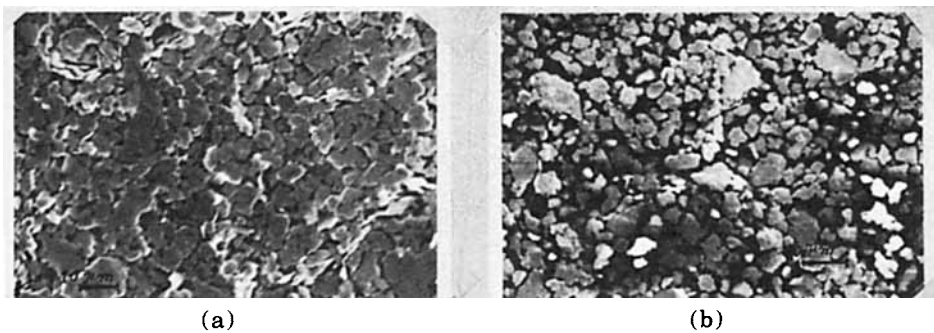


Fig. 3. SEM Photographs of the surface of the uncured polymer obtained from (a) CST and (b) phenol-formaldehyde.

The system therefore needs further purification of phenol content of CST to remove the bond weakening substances. The present work, however, indicates the possibility of utilization of CST and similar materials as a source of phenol.

Thanks are due to Mr. K. Sukumaran and Mr. K. K. Ravikumar for measurements of the mechanical properties and to Mr. Peter Koshy and Mr. Adinarayanaswami for SEM measurements. Thanks are also to Dr. C. Pavithran for helpful discussions and to Dr. K. G. Satyanarayana and Dr. A. G. Mathew for encouragement and support.

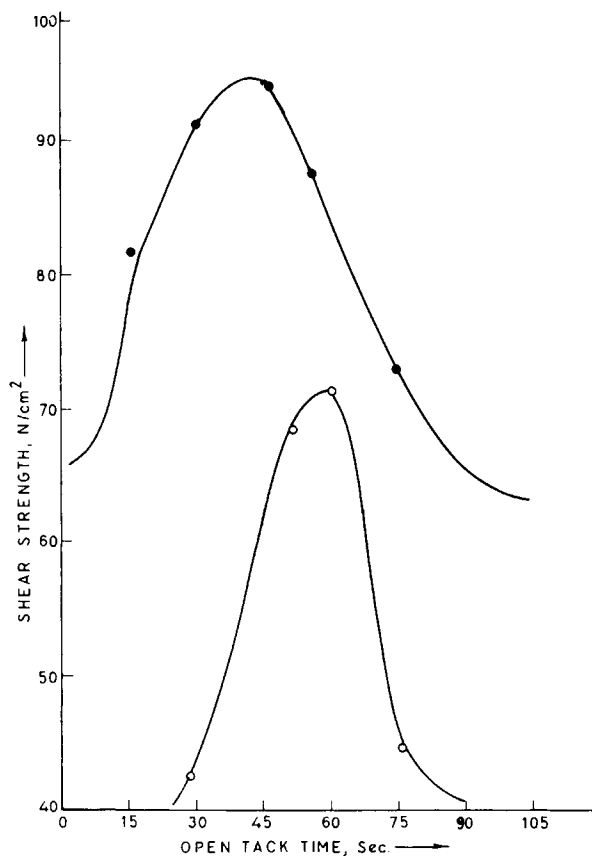


Fig. 4. Plot of shear strength against open tack time: (●) solid content 13.8%; (○) solid content 27.7%.

TABLE II
Comparison of the Shear Strength Values of Coconut Shell Tar Resin with That of Phenol Formaldehyde Resin

	Solid content (%)	Open tack time (s)	Shear strength (N/cm ²)
CST resin	13.8	45	94.55
	27.7	60	71.30
PF resin	13.8	60	232.50
	27.7	60	167.40

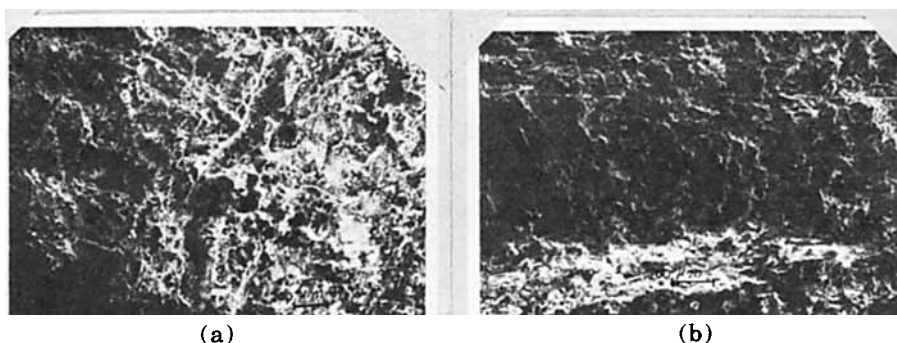


Fig. 5. SEM Photographs of the fractured surface obtained after the lap shear test of (a) CST resin and (b) phenol-formaldehyde resin.

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Received April 24, 1984
Accepted September 11, 1984