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SUGAR CANE BAGASSE LIGNIN IN RESOL-TYPE RESIN: ALTERNATIVE APPLICATION FOR LIGNIN-PHENOL-FORMALDEHYDE RESINS

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Key Words: Sugar cane bagasse; Lignin; Resol; Thermal analysis; Phenolic resins; Lignin-phenol-formaldehyde resins; Molded resins

ABSTRACT

Lignin can be recovered from sugar cane bagasse, which is widely available in Brazil as a residue from sugar mills. Many reports can be found in the literature on the partial replacement of phenol by lignin in phenolic-type resins, but normally only their application as an adhesive is considered. This work is part of a study intended to look for other uses for lignin-phenol resins; for instance, in molded materials. Resols were prepared with the partial replacement of phenol by organosoluble sugar cane bagasse lignin (10, 20, 40, 100% w/w), and the pre-polymers were characterized by TGA and DSC. The cure reaction was performed in a mold in a process monitored by infrared spectroscopy. The resins obtained were characterized by TGA, DSC, and DMTA. TGA and DSC results revealed that endothermic and exothermic steps are probably involved in the cure reaction. From infrared results it can be inferred that lignin is really incorporated to the phenol polymer chain, where it acts as a chain extender. DMTA analyses showed that lignin-phenol-formaldehyde resins retain their modulus at elevated temperatures. The overall

properties show that the partial substitution of phenol by lignin in phenolic molded-type resins is feasible.

INTRODUCTION

There are some factors which indicate a future large volume application for lignin besides its use for the generation of energy. Among them are

- The trend to use renewable resources as raw materials
- The large production of lignin as a by-product in mills

Up to the present, its potential for use as a component in polymeric materials has not been investigated to a great extent [1].

Lignin can be recovered from sugar cane bagasse, which is largely available in Brazil as a residue from sugar mills.

The presence of phenolic rings in its complex structure makes the use of lignin as a phenol replacement feasible, for example, in thermosetting resins.

The largest volume application of phenolic resins is in plywood adhesives. Probably as a consequence of this market, most reports found in the literature focusing on the partial replacement of phenol by lignin are in this area [2-6].

Applications for phenolic resins which require the presence of substantial amounts of solvents, e.g., adhesives, may decrease because of restrictions due to their volatile organic content. On the other hand, other applications for phenolic resins have enhanced their marketplace, e.g., in molding compounds and in foams [7-9].

The present work is part of a more general study which searches for alternative uses of lignin-phenol-formaldehyde resins, e.g., as molded resins. Organosolv lignin was chosen because of its higher solubility in the reaction medium compared with those obtained by conventional pulping techniques [10].

EXPERIMENTAL

Purification of Raw Material

Sugar cane bagasse was first preextracted with water (70°C) in order to remove the residual saccharose, water-soluble ashes, and low molecular weight polysaccharides. The first step was followed by screening in a 16-mesh sieve in order to separate the fiber of the pitch. The fibers were then submitted to ethanol/cyclohexane (1:1; v/v) extraction in a Soxhlet to remove the waxy material. The fibers were dried at room temperature.

Extraction of Lignin

The lignin was extracted from the sugar cane bagasse by the acetosolv process (93% acetic acid, 0.2% HCl, 6.8% H₂O w/w; temperature 109°C; pulping time 3 hours) [11]. The black liquor was concentrated under reduced pressure, and then the lignin was precipitated in water at 70°C.

The isolated lignin was purified by dissolution in acetone. In this solvent the impurities—mainly the polyoses—remain insoluble. After filtration the lignin was precipitated as described previously. The purified lignin was used in all pre-polymers preparation.

Lignin Characterization

The methoxyl content was determined by the TAPPI T 2M-60 method; the phenolic hydroxyl content was determined by conductivimetry. The number-average molecular weight, M_n , was determined by vapor pressure osmometry (Knauer equipment, standard: benzil; solvent: DMF; temperature: 90°C). Elemental analysis was performed in a Perkin-Elmer Elemental Analyser 2400 CHN. Thermogravimetric analysis was developed in a 951-DuPont system with a heating rate of 10°C/min in a N₂ atmosphere.

Pre-Polymers: Synthesis and Characterization

Phenol was partially substituted by lignin (0, 10, 20, 40, 100% w/w) with a 1/1 phenol/formaldehyde molar ratio and 4% (in relation to total weight) of the catalyzer NaOH.

Formaldehyde (37%) was added to the NaOH lignin solution with mechanical stirring. After 30 minutes under reflux (97°C), the solution was cooled to room temperature. In this way the methylol group (—CH₂OH) was introduced to the phenolic rings of lignin. Formaldehyde and phenol were then added to the methylolated lignin while keeping the temperature at 97°C for 40 minutes. Then HCl was added at room temperature until the solution was neutralized. The water was eliminated under reduced pressure. The same procedure was used for the preparation of the pre-polymer without lignin.

The pre-polymers were characterized by TGA and DSC with the same equipment and conditions described for lignin analysis.

Cure Reaction

The cure reaction was performed in a mold which was initially submitted to 100 kg_f/cm² at 50°C for 20 minutes. The pressure was then released and the temperature was raised to 120°C for 60 minutes, followed by 150°C for 40 minutes. During the cure process, samples were removed at intervals of 20 and 30 minutes for infrared spectroscopy monitoring. The 1010 cm⁻¹ absorption was monitored (methylol group stretching) in a 1320 Perkin-Elmer spectrometer. The 1600 cm⁻¹ absorption (C=C aromatic ring stretching) was used as an internal reference, and the CDS13-PE computer program was used to calculate the ratio between the two absorption areas. The same procedure was used for lignin without the addition of phenol/formaldehyde [12].

In order to verify the residual lignin content, the resins were submitted to THF extraction in a Soxhlet system. The extractives were analyzed by high pressure size exclusion chromatography (HPSEC-Waters UV detector at 254 nm; three PL gel columns were used in series: 10³, 500, 100; 1 mL/min; solvent: THF; standards: polystyrene/divinylbenzene, 25°C).

Under the conditions used in the present work it was not possible to obtain a molded resin when phenol was absent from the formulation (100% lignin).

The resins obtained were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under the same conditions described above. Dynamic mechanical thermal analysis (DMTA, bending mode) was performed by using samples made in a mold with the dimension 12 mm × 48 mm × 2 mm as required by PL Polymer Laboratories equipment. The conditions of measurement were 1 Hz, 25 to 225 °C, and 20 °C/min.

RESULTS AND DISCUSSION

Characterization of Lignin

The average content values of the methoxyl and phenolic hydroxyl groups were 13.1 and 7.0%, respectively, with respect to the total weight of lignin. The number-average molecular weight, M_n , was 830 g/mol, and the elemental analysis values were 62.3% C, 5.5% H, and 32.2% O. These results lead to $C_{9.0}H_{7.2}O_{2.2}(OCH_3)_{0.80}(OHphen.)_{0.77}$ as the structural formula of the phenol propane unit. TGA analysis for lignin showed that the maximum weight loss occurs around 385 °C (thermogram not shown). In previous work an attempt was made to determine the T_g of acetosolv lignin by DSC [12]. The experiment led to a glass transition of 170 °C. This value is inside the range mentioned by Sarkanen (125–195 °C) for lignins extracted from different biomaterials [13]. Rials found T_g values around 95 °C [14] for organosolv lignins extracted from wood and having nearly the same number-average molecular weight (≈ 1000 g/mol) as the present lignin. Care must be taken when T_g is determined from DSC because normally it is not an easy task to determine exactly what the change in slope or position of the baseline is, and that is related to this transition. Yet, this value will not necessarily act for the T_g values found for lignin-phenol-formaldehyde resins discussed later because some rearrangements can occur with lignin due to the occurrence of nucleophilic reactions in the alkaline reaction medium [15]. These reactions mainly involve cleavage of carbon-to-oxygen linkages. In other words, the “macromonomer” incorporated in the structure of the resin probably does not have the same molecular weight as the lignin originally characterized.

Pre-Polymer Characterization

The TGA results for pre-polymers (Fig. 1) showed that a maximum weight loss occurs in the 100–170 °C range, and the DSC thermograms (Fig. 2) show a large endothermic peak (100–150 °C) and one exothermic peak around 210 °C. For a full interpretation of DSC results it is necessary to account that the onset of the cure process can occur for resins during thermogram scanning of the pre-polymer since only heat is necessary to start the crosslinking process.

Disagreement can be found in the literature in the data of thermal analysis of phenolic resins, including those with lignin in the formulation [2, 4, 14, 16]. Endothermic and exothermic peaks have been attributed to cure reactions. Considering only resol-type polymers, several parameters must be kept in mind in order to evaluate the described discrepancies. The pre-polymers have free positions and also

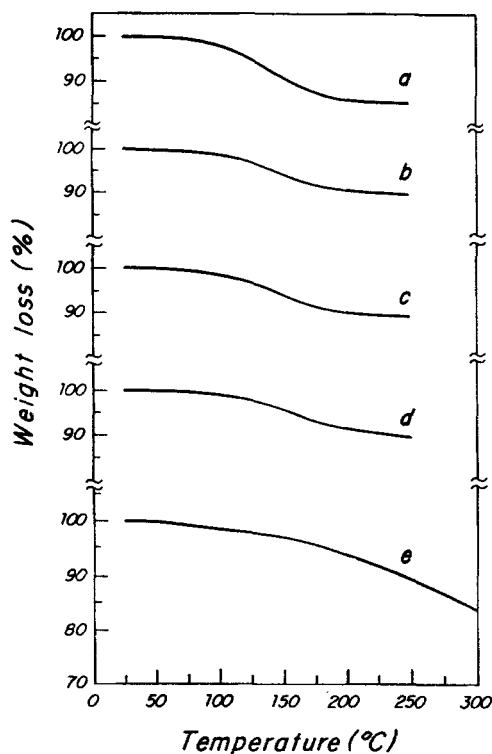


FIG. 1. TGA curves of phenol-formaldehyde (a) lignin-phenol-formaldehyde with 10, 20, 40% lignin (b, c, d, respectively), and lignin-formaldehyde (e) pre-polymers.

reactive groups (methylol groups) in the aromatic ring, which are both reactive sites in relation to the crosslinking process. Hence the cure step can be carried out by heating; novolac also need a cure agent [17]. Changes in formulation (as in the molar ratio of formaldehyde/phenol) in temperature, or in pressure can alter the proportion of ortho/para addition and also the relative quantity of methylenic/ether ring linkage. These alterations lead to a distinct process which results in different DSC thermograms [14, 16].

In the present work the large endothermic peak (100–170°C) can be related to a combination of cure step and the release of residual water [18]. Thermogravimetric analysis indicated a weight loss in the same temperature range (Fig. 1). Ysbrandy [16] reported that liquid or powder resoles need to reach only 150°C to attain thermosetting properties through an endothermic path. In Fig. 2 it is seen that for the pre-polymer prepared only with lignin, the endothermic peak has better resolution, which facilitates detection of water vaporization and the first cure step, which occurred at 100 and 140°C, respectively, in agreement with the above discussion.

The exothermic peak around 210°C can be attributed to a second residual cure stage [14]. In this step the reactions may occur by a distinct path in relation to the first one with the participation of other phenol ring positions and/or different bonds.

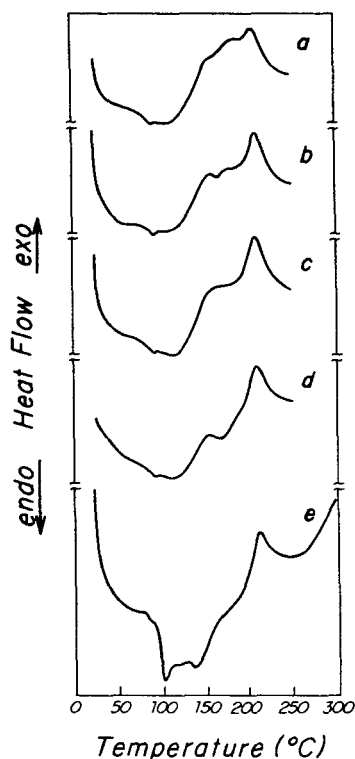


FIG. 2. DSC curves of phenol-formaldehyde (a), lignin-phenol-formaldehyde with 10, 20, 40% lignin (b, c, d, respectively), and lignin-formaldehyde (e) pre-polymers.

Cure Reaction

Cure Reaction Analyzed by Infrared Spectroscopy [12]

From Fig. 3 it may be inferred that for all resins the methylol absorption drops more intensively in the time interval where the mold is heated to 120°C (20–60 minutes). The same behavior is observed for the resin with 100% of lignin. This temperature is within the interval proposed as the first cure step.

HPGPC Results

Figure 4 represents the HPGPC chromatograms of the parts extracted from crosslinked polymers. For all samples the extractives correspond to less than 1% of the total weight. All nonreacted lignin could be extracted because THF is a good solvent for lignins. From Fig. 4 it can be seen that the extractives have a lower molecular weight than the added lignin. These results, coupled with those from infrared analysis, are evidence that lignin is really incorporated in the phenol polymer chain.

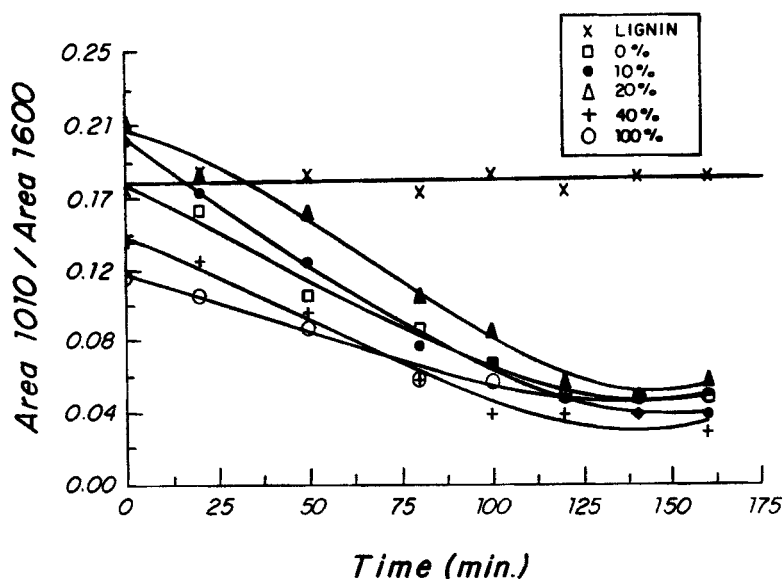


FIG. 3. Ratio of 1010 and 1600 cm^{-1} infrared peak area as a function of time during cure reaction.

Thermal Analysis of Resins

TGA Analysis

The principle feature of TGA thermograms (Fig. 5) is that thermal stability in the temperature range considered is nearly the same for all samples, that is, the introduction of lignin into the resin systems did not change the thermal stability. The total weight loss was around 5%.

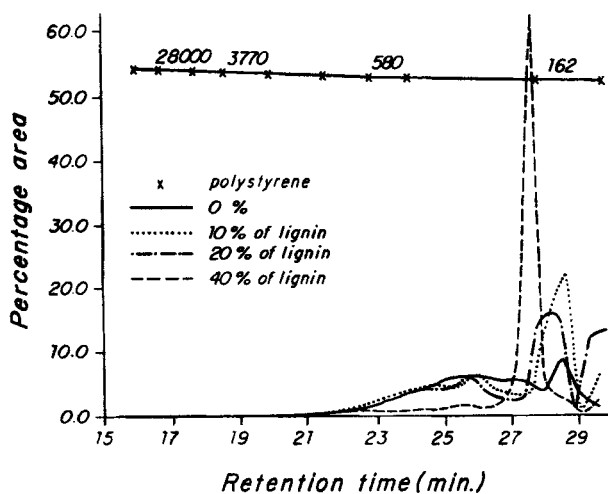


FIG. 4. Size exclusion chromatograms of the extractives obtained from THF Soxhlet extraction of phenol-formaldehyde and lignin-phenol-formaldehyde resins.

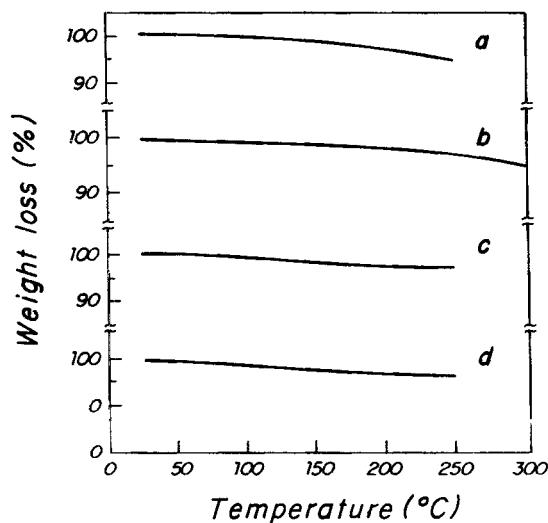


FIG. 5. TGA curves of phenol-formaldehyde (a) and lignin-phenol-formaldehyde with 10, 20, 40% lignin (b, c, d, respectively) resins.

DSC Analysis

The cure process was carried out in temperature cycles: 50°C (20 minutes), 120°C (60 minutes), and 150°C (40 minutes). The DSC results of the pre-polymers showed that the thermal crosslinking process can occur in this range, so it can be inferred that the temperature selected was a good choice. The pattern of resin thermograms (Fig. 6) is similar to that of pre-polymers. The endothermic peak is displaced around 25°C in relation to that of the pre-polymer. This peak can be related to the release of residual water and also to a continuation of the cure process. In spite of the well-selected cure temperature, the time interval considered was not enough to consume all the available reactive groups. The observed displacement may be due to the difficulty of motion of groups in a partially cured resin, which would require more thermal energy to react. Warfield [19] mentioned that to achieve complete thermal crosslinking, a resol was initially submitted to 38°C for 24 hours and then the temperature was successively risen in 15°C intervals until it reached 177°C, with the system held for 24 hours in each temperature stage. The samples had not been previously submitted to the exothermic temperature peak (210°C). If this temperature corresponds to a residual crosslink, as mentioned previously, the onset of the process could occur only during scanning.

DMTA Analysis

The dynamic modulus (E') is a mechanical property with great importance in any end-use application. From the dynamic-modulus-temperature curve (Fig. 7) it can be seen that the dynamic modulus starts to change around 100, 110, and 125°C for resins with 1, 10, and 20% of lignin, respectively. This behavior can be explained by the "macromonomer" characteristic of lignin, since its bulk can make the cooperative diffusional motion of chain segments more difficult. The resin with 40% lignin

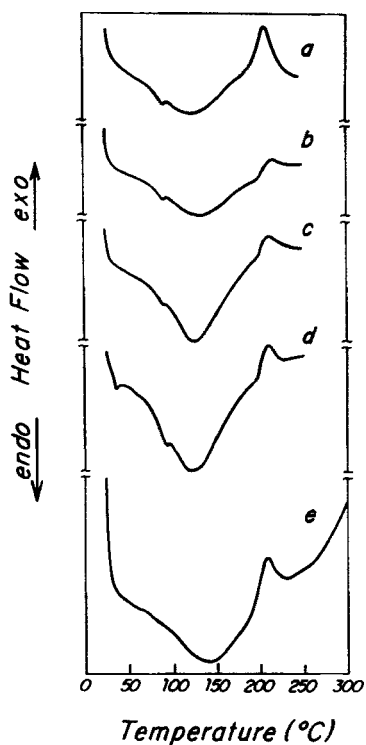


FIG. 6. DSC curves of phenol-formaldehyde (a), lignin-phenol-formaldehyde with 10, 20, 40% lignin (b, c, d, respectively), and lignin-formaldehyde (e) resins.

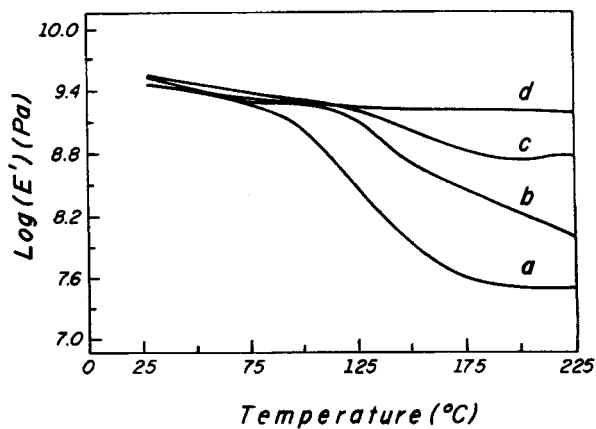


FIG. 7. Variation of storage modulus in a logarithmic scale ($\log E'$) with temperature for phenol-formaldehyde (a) and lignin-phenol-formaldehyde with 10, 20, 40% lignin (b, c, d, respectively) resins.

shows the behavior of a polymer which has very restricted rotational and diffusional motions, since the $\log E'$ value changes from 9.4 to 9.1 Pa in the 25 to 225°C interval.

The maximum heat dissipation by unit deformation occurs at a temperature where the loss modulus (E'') is maximum, and at 1 Hz this temperature is close to the T_g value determined by other methods [20].

Figure 8 shows the variation of $\log E''$ with temperature for the prepared resins. There is one maximum for the phenol-formaldehyde resin, with the glass transition around 100°C. On the other hand, two maxima can be seen for the phenol-lignin-formaldehyde resins.

If lignin was first methylolated and then reacted with phenol-formaldehyde, it is possible that sequences of lignin were formed in the first step. As a consequence, sequences of lignin and sequences of phenol rings would be present in the final product. Thus, the first peak can be related to motions of the phenolic segment. In this sense, the maximum observed around 125 and 140°C for 10 and 20% lignin, respectively, can be attributed to this transition. The displacement observed in these transitions compared to that of phenol-formaldehyde resin can be related to the presence of a more rigid lignin sequence in the neighborhood.

A maximum of 75°C is shown in relation to the resin with 40% lignin, and this can be attributed to rotational motions of the phenolic segments. For this percentage of lignin, it can be difficult for the methylolated phenol to interact with the bulkier sequences of lignin in the pre-polymer step. It is therefore proposed that the phenolic sequences can be linked as "branches." The local motion of these "branches" inserted into the network can be responsible for the transition observed at 75°C.

For resin with 10% lignin, the second transition appears as a shoulder around 185°C. On the other hand, for the resins with 20 and 40% lignin, the transitions are well defined by the peaks at 210 and 225°C.

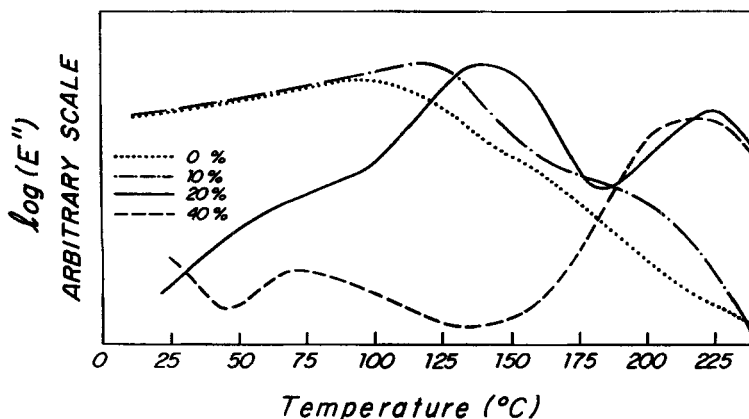


FIG. 8. Variation of \log loss modulus ($\log E''$) with temperature for phenol-formaldehyde and lignin-phenol-formaldehyde with 10, 20, 40% lignin resins.

CONCLUSIONS

From the results obtained it can be inferred that in the synthesis of resols described above, lignin reacts chemically with the phenol polymer chain, acting first as a chain extender rather than as a filler.

Molded resins with lignin in their formulations exhibit modulus retention at elevated temperatures, especially the resin prepared with 40% lignin. This is a promising result since the presence of lignin leads to improvement in the mechanical properties of the thermoset obtained.

It is necessary to introduce modifications in the formulation used in this work in order to replace phenol by lignin at a level higher than 40%, but the results indicate that replacement of phenol by sugar cane bagasse lignin in the preparation of phenolic molded resins is possible.

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