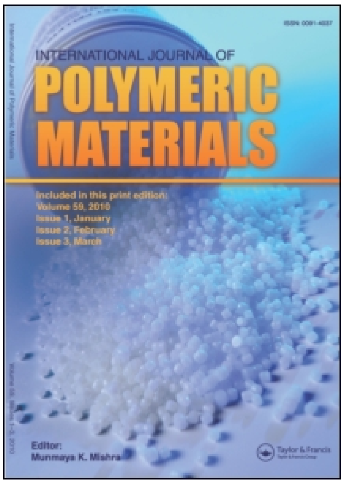

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Kamel, S.(2005) 'Preparation of Cation-Exchange Resin from Lignin', International Journal of Polymeric Materials, 55: 4, 283 — 291

To link to this Article: DOI: 10.1080/009140390945141

URL: http://dx.doi.org/10.1080/009140390945141

International Journal of Polymeric Materials, 55:283–291, 2006

ISSN: 0091-4037 print/1563-5333 online
DOI: 10.1080/009140390945141

Preparation of Cation-Exchange Resin from Lignin

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Lignin precipitated from black liquor of soda pulping of bagasse was used to prepare cation-exchange resin. The effects of sulfuric acid treatment and concentration of phenol and formaldehyde on the properties of the prepared cation-exchange resin were investigated. It was found that sulfonated resinified phenolized lignin gave a resin with an ion-exchange capacity higher than that of resin, which resulted from sulfonation of resinified lignin in the absence of phenol. Infrared spectroscopy of the prepared ion-exchange resin shows new bands at 1060, 1160, 1280, and 1330 cm^{-1}, *which indicate the presence of* SO_3.

Keywords: lignin, ion-exchange resin, sulfonation, IR

INTRODUCTION

In nature, lignin is the second most abundant organic material, after cellulose. Lignin is a phenolic polymer, so it has potential as an alternative raw material for phenolic resins, adhesives, etc. Although a large number of works on conversion of lignin to useful materials have used hydrocracking, pyrolysis, and derivativization, there are no lignin products produced commercially except for ligninsulfonate, which can be obtained from black liquor of sulfite pulping [1].

Waste black liquor, produced from soda or kraft pulping, is disposed of in water streams causing pollution, or used as a fuel for pulping chemical recovery in paper mills. Therefore, industrial usage of this waste black liquor is of great environmental and economical importance. Soda bagasse lignin has a high number of unsubstituted 3- and 5-positions on phenolic propanoid units [2]. As a result lignin can be used successfully in different applications.

Received 13 December 2004; in final form 17 January 2005.

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In the past 20 years, lignin showed potential for use as activated carbon [3], a binder as well as a coupling agent in particleboard [4–5] and as a reactive component during the polymerization of phenol/formaldehyde resin [6]. Also, the phenol was replaced by lignin in the preparation of novolac resins [7]. Glasser et al. [8], synthesized polymer from lignin and isocyanate whereas Feldman et al. [9] employed lignin in formation of polyurethane.

The most important polycondensates used to produce ion-exchange resins are derivatives of phenol and formaldehyde. Phenolic molecules that possess unsubstituted para and both ortho positions can react at three positions with formaldehyde and form a network with trifunctional junctions [10]. Yasuda and Asano [11] prepared strongly acidic cation-exchange resin from Klasion lignin of red pine by sulfonation of resinified sulfuric acid lignin. Also, ion-exchange resin was prepared from kraft lignin or hydroxymethylated kraft lignin of olive stone biomass by sulfonation of the polymerization product of kraft or hydroxymethylated kraft lignin with phenol and formaldehyde under acidic conditions [10].

In this study, cation-exchange resin was prepared from soda bagasse lignin. The effects of sulfuric acid treatment and concentration of phenol and formaldehyde on the properties of the prepared cation-exchange resin were investigated. Also, infrared spectroscopy of lignin and sulfonated resin were investigated.

EXPERIMENTAL

Materials

Lignin was separated from black liquor, which was obtained as a by-product from soda pulping of bagasse, by acidifying with HCl to pH 1.5, heating to 90°C, and then leaving it for 1 hour. The crude alkali lignin was filtered, washed with water, and dried in a vacuum oven [12]. Reagent grade formaldehyde of 37% concentration, phenol, chlorosulfonic acid, sulfuris acid, tetrachloroethane, and sodium hydroxide were used.

Methods

Preparation of Cation-Exchange Resin

Cation-exchange resin was prepared in three stages, namely, phenolation, resinification, and sulfonation stages.

Phenolation stage. A mixture of 1.0 g lignin and 6.3 g phenol in 15 ml of 72% sulfuric acid was stirred at 60°C for 5 h. After quenching by dilution with 560 ml water, the suspension was boiled for 3 h. The solids were filtered out and were thoroughly washed with warm water to give phenolized lignin [13].

Resinification stage. To a solution of 0.1 g lignin or phenolized lignin in 1 ml of 3 M NaOH, 0.5 ml of 37% formaldehyde was added. After heating at 60°C for 1 h and then at 180°C for another 1 h in a small autoclave heated in controlled electrical oven, this temperature is 10°C above the stated reaction temperature. The solid contents were filtered off washed with water, and then dried to give resinified phenolized lignin or resinified lignin [11].

Sulfonation stage. To a suspension of 0.1 g resinified phenolized lignin or resinified lignin in 2 ml tetrachloroethane there was added 0.25 g chlorosulfonic acid. After stirring at 50°C for 0.5 h and then at 100°C for another 1 h, the suspension was carefully made basic by the adding 20 ml 2M NaOH, then refluxed for 1 h. The contents were filtered off and washed with distilled water and then dried in a vacuum oven to give sulfonated resin (Na^+ form) [11].

Determination of Sulfur Content

The sulfur content of the prepared resins was determined quantitatively by using Vario E1-Elementar.

Determination of Ion-Exchange Capacity of Sulfonated Resin

To determine the ion-exchange capacity of the sulfonated resin, the H^+ form of sulfonated resinified phenolized lignin or sulfonated resinified lignin was regenerated by first washing the Na^+ form with 1M HCl and then with distilled water. The washed sample was oven dried. 0.1 g sulfonated resin (H^+ form) in 5 ml 0.05 M NaCl was allowed to stand for 2 h at room temperature with stirring at intervals. After filtering out the resin, the combined solution of the filtrate and the washings was titrated with 0.05 M NaOH using methyl orange as an indicator. By knowing the amount of alkali consumed, the ion-exchange capacity was calculated [14].

Characterization

Infrared (IR) spectra of lignin and sulfonated resins were recorded on a Perkin Elmer Spectrometer using KBr pellet, from 4000 to 400 cm^{-1}.

RESULTS AND DISCUSSION

Ion-exchange resin can be formed from lignin by sulfonation of resinified lignin or resinified phenolized lignin that formed from the

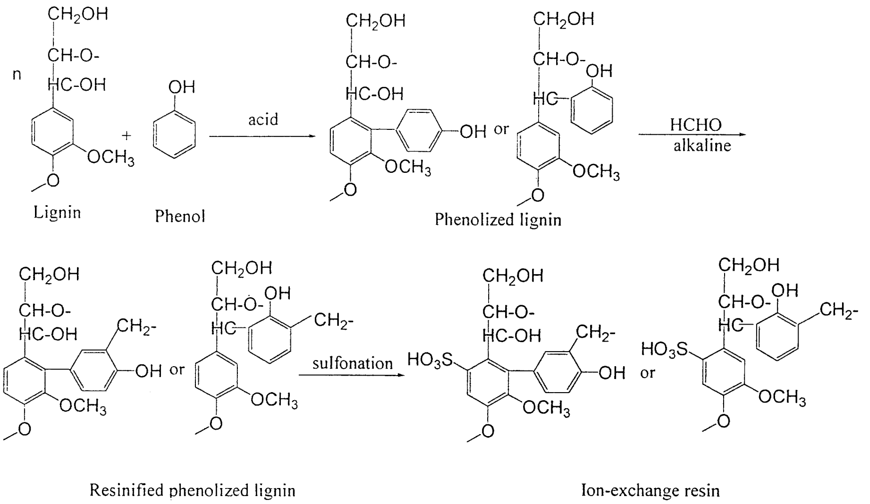

FIGURE 1 Preparation of ion-exchange resin from lignin.

reaction of formaldehyde with lignin or phenolized lignin (Figure 1). First this article studies the effect of treatment of lignin by 72% sulfuric acid before phenolation process on the ion-exchange capacity and the effect of phenol to lignin ratio as well as formaldehyde to phenolized lignin ratio on the properties of produced resin.

Treatment of Lignin with Sulfuric Acid

To study the effect of treatment of lignin by sulfuric acid, 0.1 g of soda lignin was treated with 72% sulfuric acid in the usual manner. The main reaction of lignin in 72% sulfuric acid treatment is intermolecular condensation between aromatic nuclei and side chain α-carbons of lignin [15]. Because condensed lignin easily exchanged its aromatic nuclei for those of simple phenolic compounds in the presence of sulfuric acid catalyst under mild condition [16], the main mode of phenolization of sulfuric acid lignin in the presence of sulfuric acid as a catalyst is shown in Figure 2.

From Table 1 it is shown that the sulfur content and ion-exchange capacity of untreated soda lignin were higher than that of soda lignin treated by sulfuric acid. This may be due to the steric hindrance of substituents, which were introduced during concentrated sulfuric acid treatment, which may lead to lowering the reactivity at the ortho position of the group.

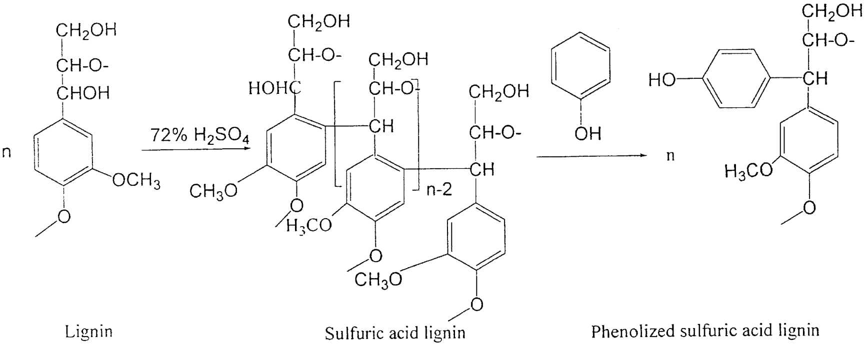

FIGURE 2 Phenolation of sulfuric acid lignin.

So, the more detailed research in this work would be done on untreated lignin.

Effect of Phenol to Lignin Ratio

The effect of phenol on lignin was studied, as shown in Table 2. The percent of formaldehyde used was 0.5 ml for each 0.1 g lignin or phenolized lignin. An increase of phenol percent increased the resin yield and accordingly increased the sulfonated yield. This may be due to the increase in the molecular weight of the obtained phenolized lignin, which attained about 300. On the assumption that the molecular weight of lignin is 186 [17] on the basis of the empirical formula $C_9H_{6.51}O_{1.62}(OH)_{1.01}(OCH)_{0.90}$, the reaction of one molecule of phenol results in a 50% weight gain of phenolized lignin because molecular weight of phenol is 94.

The sulfur content and ion-exchange capacity of sulfonated resinified phenolized lignin or sulfonated phenolized lignin was determined. An increase of phenol percent increased the sulfur content and accordingly increasd the ion-exchange capacity of resin. By further increasing the percent of phenol, a drastic reduction in yields, sulfur content, and

TABLE 1 Effect of Sulfuric Acid Treatment on Ion-Exchange Resin

Lignin treatment	Resin (S%)	Ion-exchange capacity (mEq/g)
Non-phenolized lignin	5.90	1.77
Non-phenolized sulfuric acid lignin	3.70	1.40
Phenolized lignin	10.17	3.18
Phenolized sulfuric acid lignin	5.53	1.79

TABLE 2 Effect of Phenol % on Ion-Exchange Resin

Phenol (gm)	Resin yield (%)	Sulfonated yield (%)	Resin (S%)	Ion-exchange capacity (mEq/g)
0.00	94.3	33.5	5.90	1.77
0.62	121.0	43.0	7.76	2.43
1.25	181.5	47.5	10.17	3.18
2.5	195.6	58.8	8.37	2.61
3.75	176.6	49.2	6.08	2.02
5.00	141.0	37.6	5.68	1.80

Resin yield based on lignin weight.
Sulfonated yield based on resin yield.
Weight of lignin 0.2 g.

ion-exchange capacity was noticed. This may be due to the obtained phenolized lignin consisting of phenyl propane units, which are condensed with up to four molecules of phenol [18] and this may lead to decrease the reactivity due to steric hindrance.

Effect of Formaldehyde to Phenolated Lignin Ratio

The phenolized lignin that was used to study the effect of formaldehyde on the properties of the obtained resin (Table 3) was prepared by reacting 1.3 g phenol and 0.2 g lignin in the presence of sulfuric acid.

As shown in Figure 1 formaldehyde reacts at the ortho-position of a phenolic hydroxyl group under the alkaline conditions. In Table 3, increasing formaldehyde ratio increases the number of the introduced groups, which led to increasing the resin and sulfonated yields. Also, increasing formaldehyde ratio increased the sulfur content and ion-exchange capacity of sulfonated resins.

TABLE 3 Effect of Formaldehyde % on Ion-Exchange Resin

Formaldehyde (ml)	Resin yield (%)	Sulfonated yield (%)	Resin (S%)	Ion-exchange capacity (mEq/g)
0.5	149.1	44.1	6.82	2.95
1.0	181.5	47.5	10.17	3.18
1.5	183.3	50.0	11.42	3.88
2.0	179.4	49.1	12.44	4.20

Resin yield based on lignin weight.
Sulfonated yield based on resin yield.

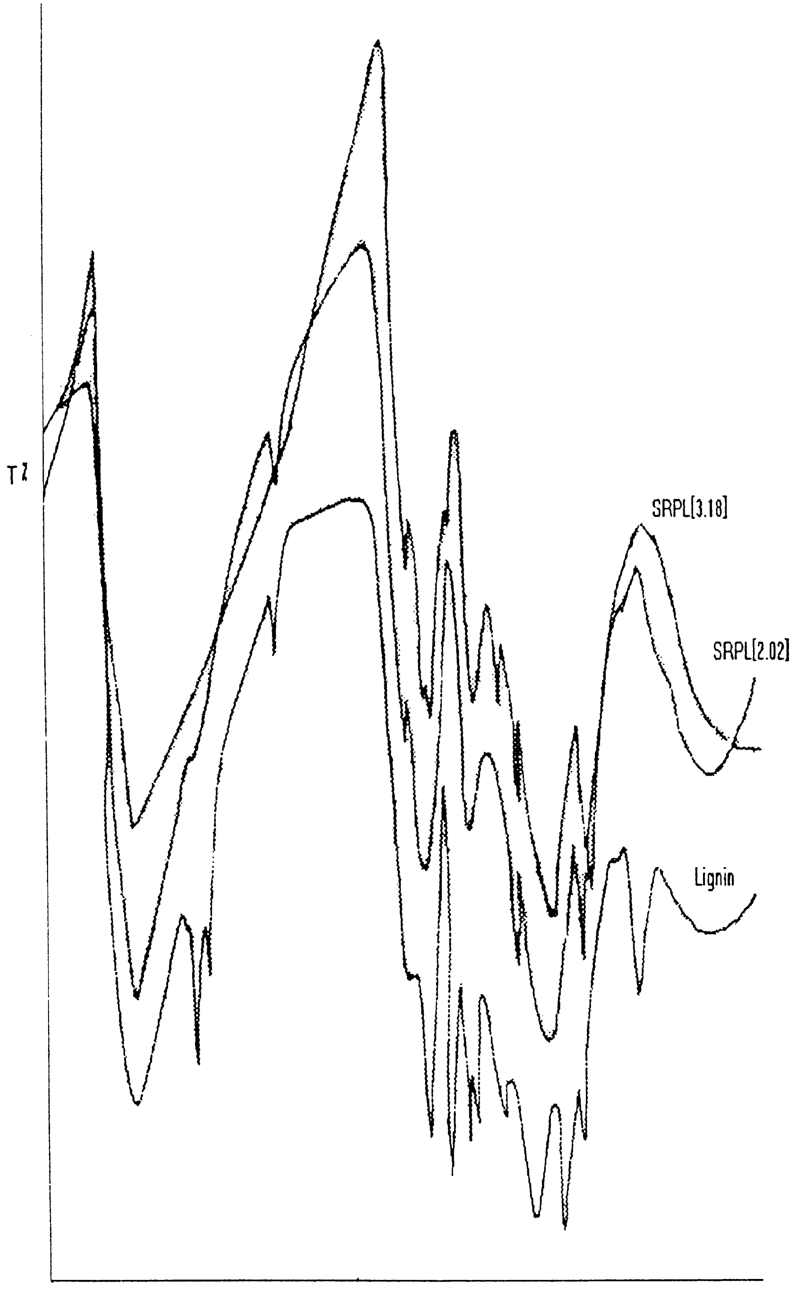

FIGURE 3 IR spectra of lignin and sulfonated resin (SRPL).

In general, the sulfonated resinified phenolized lignin or sulfonated phenolized lignin has an ion-exchange capacity higher than that of lignin itself (0.95 mEq/g). The ion exchange property of lignin results from the presence of carboxyl and phenolic hydroxyl groups in lignin, whereas the same property of sulfonated resinified phenolized lignin or sulfonated phenolized lignin results from carboxyl and phenolic hydroxyl groups beside the sulfonic groups originating from sulfonation. So, the ion-exchange capacity of lignin is less than that of sulfonated resinified phenolized lignin or sulfonated phenolized lignin.

Infrared Spectra

Figure 3 shows the IR spectra of alkali lignin isolated from soda black liquor produced from pulping of bagasse and sulfonated resins (ion-exchange capacity 3.18 and 2.02). The various bands of the IR spectra of these materials are summarized in Table 4. From this table, it is apparent that sulfonated resin (ion-exchange resin) does not show the bands at 1510, 1270, 1130, 1040, and 815 cm^{-1}, whereas lignin shows them. So, the sulfonated resin does not exhibit the syringyl vibrations and the guaiacyl band but lignin does. Additionally, sulfonated resin shows bands at 1330, 1280 (SO_2), 1160 (SO_2-O-), and 1060 (S=O) cm^{-1}, whereas lignin does not show them because it is not sulfonated.

On the other hand, from Figure 3 it is seen that the intensity of the band at 1710 cm^{-1} (COOH) increased by sulfonation. This indicates an oxidation of some side chains of lignin to carboxyl groups during sulfonation.

TABLE 4 IT Bands of Lignin and Sulfonated Resin

Band cm^{-1}	Group	Lignin	Sulfonated resin
3400–3200	OH	+	+
3024	C–H aromatic	+	+
1600, 1510	Aromatic ring	+	−
1710	COOH	+	−
1330, 1280	SO_2	−	+
1320, 1270, 1130	Syringyl vibrations	+	−
1160	$-SO_2-O-$	−	+
1060	S=O	−	+
1040	Guaiacyl band	+	−
815	2 neighboring H	+	−

CONCLUSIONS

Sulfonation of resinified lignin gave a resin with an ion-exchange capacity higher than that of sulfuric acid–treated lignin. Increasing the phenol percent in phenolation stage and formaldehyde percent in resinification stage increased the ion-exchange capacity of the resin and sulfonated yields. The ion-exchange capacity of the prepared resin is superior to that of the corresponding commercial phenol-type resin (2–3 mEq/g).

IR spectroscopy of the sulfonated resin shows a new band of SO_3.

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