

# Study on the Graft Copolymerization of Lignosulfonate and Acrylic Monomers

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## Synopsis

Graftings of acrylonitrile and methyl methacrylate onto lignosulfonate were studied, respectively, with and without the lignosulfonate ozonized. Copolymerization was redox-initiated by peroxide-ferrous ions. Monomer conversion and grafting efficiency depended essentially on reaction medium and the amount of peroxide charged. Among the media employed, the magnitude of the medium effect on conversion was found to be in the following order: water, dioxane, and methanol. The conversions in water of acrylonitrile and methyl methacrylate were 55 and 90%, respectively, when using 3% hydrogen peroxide. Beyond this 3% charge, both the grafting efficiency and the degree of lignosulfonate grafted approached certain limits. Ozonization appeared to be capable of stimulating the active centers in lignin macromolecules, whereon acrylic monomers could be grafted. Better grafting efficiency was obtained with the ozonized lignosulfonate.

## INTRODUCTION

Lignin had been considered as a nonvalue (or small-value) by-product by pulp industries for a long time until it was recognized to be a potential resource for chemicals and materials, as manifested very clearly in two recent conferences.<sup>1,2</sup> Because of that recognition, the research of the utilization of lignin regains its momentum.

During the last decade or so, a number of works have been reported on the modification of lignin, leading the way to obtain products having new and unique properties. Lignin has been successfully used, taking advantage of its phenolic structure, in producing thermosetting materials. Adhesives for particle boards and panel products can be made by polycondensing lignin derivatives—in black liquor or spent sulfite liquor—with urea formaldehyde<sup>3</sup> or phenol formaldehyde<sup>4</sup> resin. Polyol intermediates in the production of polyurethanes have been prepared by reacting lignin with either a carboxylic acid or anhydride, or followed by a reaction with an oxyalkylating medium such as propylene oxide.<sup>5,6</sup>

In addition to the phenolic structure, free radicals of lignin are known to be formed during the synthesis of lignin and also during the chemical pulping of wood.<sup>7,8</sup> These free radicals are not related to impurities or unstable species trapped in the lignin polymer but form an integral part of the lignin macromolecules. Further oxidation could increase the content of free radicals, enhancing the participation of lignin in radical reactions. Results have been published on the graft copolymerization of lignin and styrene<sup>9-13</sup> or acrylic monomers<sup>14-16</sup>, initiated by the use of peroxides or induced by gamma or UV radiation.

Ozonization has usually been used by wood chemists as an effective method to obtain lignin of lower molecular weight and other carbonyl chemicals, involving

the cleavage of double bonds or the aromatic nuclei of lignin. Nevertheless, ozonization was considered capable of generating lignin macroradicals, either via the "insertion reaction" with double bonds (ozonide) or via the cleavage of atomic hydrogen.<sup>17</sup> The ozonized lignin was found to be capable of being grafted with styrene.<sup>9,18</sup>

The present work is a continuation of that reported recently.<sup>9</sup> The main objective was to utilize lignin available commercially, instead of using lignin specifically prepared in the laboratory, to derive lignin-plastic copolymers. Calcium lignosulfonate was used as the backbone polymer and grafted with acrylonitrile and methyl methacrylate. The capability of ozonization in stimulating lignin free radicals, thus improving grafting efficiency, was also studied.

## EXPERIMENTALS

### Materials

A commercial calcium salt of lignosulfonate (CaLS) (Toranil-B, St. Regis Paper Co.), purified through ultrafiltering a 2% water solution (by means of a millipore immersible molecular separator) and vacuum drying the filtrate, was utilized throughout this work. Acrylonitrile (AN), methyl methacrylate (MMA), and styrene (ST) were distilled under vacuum to remove stabilizers; the central cut of each distillation was collected in a dark bottle and stored in a refrigerator. Methanol was also purified by distillation. The other chemicals were of reagent grade and used without further purification.

### Copolymerization and Ozonization

Graft copolymerization was redox initiated using hydrogen peroxide and ferrous chloride and was conducted under nitrogen atmosphere. In a series of experiments, lignosulfonate was ozonized before reacting with monomer. The detailed experimental procedures for copolymerization and for ozonization have been described previously.<sup>9</sup> After copolymerization, appropriate organic solvents and water were used, respectively, to extract the homopolymers formed and the unreacted lignosulfonate in the reaction product. Wherever no specification is given, the reaction conditions used in this work were fixed as follows: CaLS = 1 g; monomer = 5 ml measured at 25°C (AN = 4.00 g,  $7.85 \times 10^{-2}$  mol; MMA = 4.70 g,  $4.50 \times 10^{-2}$  mol; ST = 4.52 g,  $4.34 \times 10^{-2}$  mol.); ferrous chloride = 15 mg; hydrogen peroxide = 30 mg; reaction medium = 20 ml. When using water as a reaction medium, a small quantity of emulsifier (1 g/100 ml, Tween 20) was employed. The organic solvents used to extract the homopolymers were dimethyl formamide for AN, acetone for MMA, and methylethyl ketone for ST.

### Isolation of Grafted Polyacrylic Chains

The grafted polyacrylic chains were isolated from copolymers by a mild acidolysis with sodium chlorite and acetic acid; the procedure used was similar to that described in ref. 14. One part of copolymer was suspended in 200 parts of water; then the mixture was heated to 70°C before adding 4 parts of sodium chlorite and 8 parts of acetic acid. After 1 hr of acidolysis, the insoluble acrylic

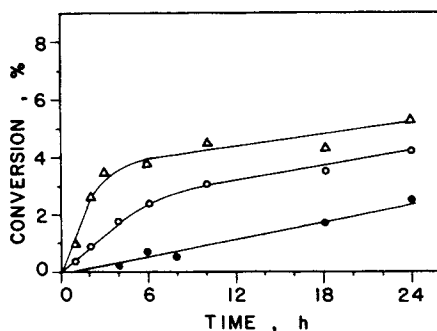


Fig. 1. Variation of the total conversion with reaction time, in methanol at 50°C, for the systems of MMA-CaLS (▲), AN-CaLS (○), and ST-CaLS (●).

polymer was recovered by filtration. The recovered polymer was subjected several times to acidolysis and filtration to ensure complete delignification. Through this method, polymer chains encountered no risk of degradation.

### Interpretation of Results

The terms used to interpret copolymerization results were defined as follows:

$$\text{Total monomer conversion, \%} = \frac{[(\text{TS} - \text{WL})/\text{M}] \times 100}{1}$$

$$\text{Grafting efficiency, \%} = \frac{[(\text{TS} - \text{WL} - \text{SE})/(\text{TS} - \text{WL})] \times 100}{1}$$

$$\text{Degree of lignosulfonate grafted, \%} = \frac{[(\text{WL} - \text{WE})/\text{WL}] \times 100}{1}$$

TABLE I  
Effect of Reaction Medium on the Copolymerization of Methyl Methacrylate and Lignosulfonate<sup>a</sup>

Reaction medium	Monomer conversion, %	Grafting efficiency, %	Degree of lignosulfonate grafted, %
Water	90.2	30.1	60.5
Water-dioxane (1:1)	79.5	18.5	62.8
Water-methanol (1:1)	30.7	11.7	46.3
Methanol	2.8	7.6	5.3

<sup>a</sup> At 50°C, 120 min of reaction.

TABLE II  
Effect of Reaction Medium on the Copolymerization of Acrylonitrile and Lignosulfonate<sup>a</sup>

Reaction medium	Monomer conversion, %	Grafting efficiency, %	Degree of lignosulfonate grafted, %
Water	55.0	54.2	50.2
Water-dioxane (1:1)	54.2	45.1	52.6
Dioxane	48.3	27.6	56.4
Water-methanol (1:1)	28.5	21.3	32.7
Methanol	1.2	—	—

<sup>a</sup> At 50°C, 120 min of reaction.

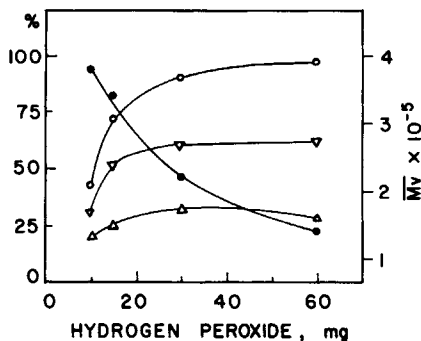


Fig. 2. Effect of peroxide charge on the copolymerization of methyl methacrylate and lignosulfonate in water medium; at 50°C, 120 min of reaction. (O) conversion; (Δ) grafting efficiency; (∇) degree of Ca-LS grafted; (●) molecular weight of MMA homopolymer.

where WL, stands for the lignosulfonate used in the reaction; M, the monomer; TS, the total solid obtained after reaction; SE, the solvent-extractable fractions, and WE, the water-extractable fraction. All these symbols have the same weight unit.

## RESULTS AND DISCUSSION

It was reported recently<sup>9</sup> that graft copolymerization of lignosulfonate (LS) and styrene proceeded well when using methanol as a reaction medium. Therefore, in this work, methanol was chosen as the first reaction medium to study the copolymerization of LS and acrylic monomers (AN or MMA). Figure 1 illustrates the relationship between monomer conversion and reaction time, for three systems of copolymerization conducted in this medium. As seen, under similar reaction conditions, the initial conversion rate of MMA was about 3 and 12 times higher in comparison to those of AN and ST, respectively. MMA appeared to be the most reactive monomer among the three studied; taking into account the quantity of monomer used in each reaction, the initial mole concentration of MMA was approximately equal to that of ST but about one-half of that of AN. Also as seen, lignosulfonate seemed to have no inhibiting effect on the copolymerization in both systems of MMA-CaLS and AN-CaLS, as it

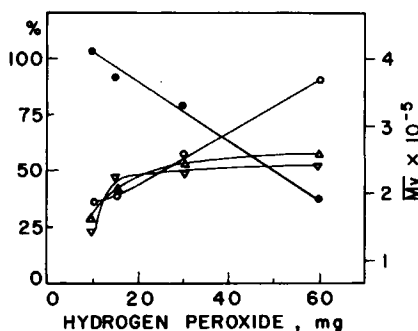


Fig. 3. Effect of peroxide charge on the copolymerization of acrylonitrile and lignosulfonate in water medium; at 50°C, 120 min of reaction. (O) conversion; (Δ) grafting efficiency; (∇) degree of CaLS grafted; (●) molecular weight of AN homopolymer.

did in the ST-CaLS system. Theoretically, the same effect could also be imposed on the two former systems owing to the quinonoid structure of lignosulfonate; however, the induction period might be too short to be measured.

In the previous work, after 24 hr of reaction, no copolymerization was found for the ST-CaLS system when water was used as the reaction medium, though at a higher temperature (75 or 90°C) some homopolymerization of styrene was traced. On the contrary, extremely better copolymerization was attained in water medium than in methanol for the MMA-CaLS system. Table I summarizes the results for the copolymerization of MMA and CaLS in different reaction mediums, including water, water-dioxane mixture (1:1 v/v), water-methanol mixture (1:1 v/v), and methanol. After 2 hr of reaction, the conversion of MMA was about 3% in methanol and as high as about 90% in water. Both the grafting efficiency and the degree of lignosulfonate grafted were also higher in water than in methanol medium. It can be noted that the medium effect of dioxane on copolymerization was between those of water and methanol. The data showing the effect of medium for the AN-CaLS system are presented in Table II. From these two tables a common conclusion can be drawn, i.e., the effect of medium on copolymerization appeared in the following order: water, dioxane, methanol. The inverse order in medium preference observed between the ST-CaLS and the two acrylic-CaLS systems might be explained through the polarity of these three monomers: styrene has electropositive (i.e., electron-releasing) substituent, while acrylic monomers have electronegative (i.e., electron-attracting) substituents.

TABLE III  
Effect of Peroxide Charge on the Copolymerization of Methyl Methacrylate and Lignosulfonate in Water Medium<sup>a</sup>

Hydrogen peroxide, mg	Monomer conversion, %	Grafting efficiency, %	Degree of lignosulfonate grafted, %	$\overline{M}_v \times 10^{-5}$ <sup>b</sup> of PMMA	
				Homopolymer	Grafted chains
10	42.6	20.2	30.1	3.82	3.55
15	72.3	23.7	52.4	3.40	3.11
30	90.2	30.1	60.5	2.18	2.33
60	96.4	28.4	61.0	1.42	1.50

<sup>a</sup> At 50°C, 120 min of Reaction.

<sup>b</sup> Average molecular weight obtained viscometrically in methylethyl ketone at 25°C.

TABLE IV  
Effect of Peroxide Charge on the Copolymerization of Acrylonitrile and Lignosulfonate in Water Medium<sup>a</sup>

Hydrogen peroxide, mg	Monomer conversion, %	Grafting efficiency, %	Degree of lignosulfonate grafted, %	$\overline{M}_v \times 10^{-5}$ <sup>b</sup> of PAN	
				Homopolymer	Grafted chains
10	37.2	28.3	31.2	4.12	3.94
15	39.7	41.6	46.4	3.70	3.77
30	55.0	54.2	50.2	3.27	3.08
60	89.4	56.4	52.1	1.93	1.76

<sup>a</sup> At 50°C, 120 min of reaction.

<sup>b</sup> Average molecular weight obtained viscometrically in dimethyl formamide at 25°C.

When initiated by redox (hydrogen peroxide and ferrous chloride), graft copolymerization was believed to occur essentially through the reaction of lignosulfonate with the peroxide radical. Thus the amount of peroxide used played an important role in the control of copolymerization. Figures 2 and 3 demonstrate the influences of peroxide charge on the copolymerization for the systems of MMA-CaLS and AN-CaLS, respectively; the corresponding data are given in Tables III and IV.

As shown in Figure 2, in the range of peroxide charge studied, there was no distinguishable variation in the grafting efficiency—the values observed were situated between 20 and 30%. The conversion of MMA monomer and the degree of LS grafted initially increased with the amount of peroxide charge. When the charge of peroxide increased from 10 to 30 mg, the conversion of MMA rose from 43 to 90%, and the degree of LS grafted from 30 to 60%; both increased about two times. Beyond 30 mg, further increase in peroxide charge achieved only a small gain in the conversion and no further augmentation in the degree of LS grafted. This suggested that a limited amount of peroxide radicals reacted directly with the lignin macromolecules, resulting in the formation of the active sites whereon polymer chains were grafted. Beyond that limit (the so-called saturation point<sup>9</sup>), it was speculated that the excess of peroxide radicals worked essentially with acrylic monomers which turned out to be homopolymers. This suggestion could be supported further by the variations of the molecular weights of both the homopolyacrylics obtained in the grafting reactions and the grafted polyacrylic chains—both molecular weights decreased with increasing peroxide charge in all the range studied, as shown in Table III.

The grafting efficiency and the degree of LS grafted for the AN-CaLS system (Fig. 3) leveled off at a lower peroxide charge, i.e., 15 mg compared to 30 mg for the MMA-CaLS system. Both approached a plateau around 55%, while the monomer conversion of AN tended to increase with the peroxide charge. The molecular weight of the AN homopolymers and the grafted polymer chains was inversely proportional to the peroxide charge. As a consequence, the same speculation concerning the saturation point of the peroxide charge was believed to be applicable to this system as well.

With the comparison of Figures 2 and 3 (or Tables III and IV), it appeared that AN was more capable than MMA of being grafted onto lignin macromolecules.

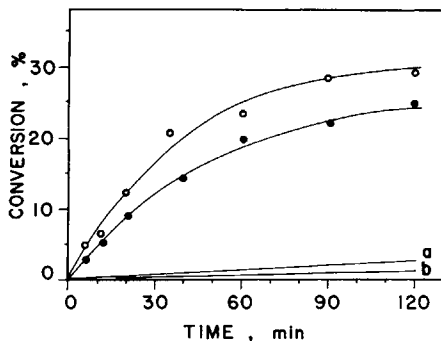


Fig. 4. Graft copolymerization of lignosulfonate with MMA (a, O) and with AN (b, ●) in methanol at 50°C; ozone charge = 100 mg. Lignosulfonate ozonized (O, ●), and lignosulfonate not ozonized (a, b).

TABLE V  
Effect of Ozone Charge on the Copolymerization of Acrylics and Lignosulfonate<sup>a</sup>

Mono- mer	Reaction medium	Ozone, mg	Monomer conversion, %	Grafting efficiency, %	Degree of ligno- sulfonate grafted, %	$M_v \times 10^{-5}$ of polymer	
						Homo- polymer	Grafted chains
Methyl methac- rylate	Methanol	0	2.8	7.6	5.3	6.10	—
		50	17.2	14.5	12.6	5.85	5.62
		100	29.8	21.2	20.8	6.23	6.01
	Water	180	40.5	25.1	38.4	5.79	5.33
		0	90.2	30.1	60.5	2.18	2.33
		50	88.6	33.7	65.3	—	—
		100	94.8	34.6	73.9	2.01	2.38
160	92.8	41.1	84.3	2.34	2.16		
Acrylo- nitrile	Methanol	0	1.1	—	—	—	—
		100	24.8	28.6	32.5	7.02	7.41
	Water	210	43.2	35.4	57.0	7.22	7.17
		0	55.0	54.2	50.2	3.27	3.08
		100	76.0	62.5	59.4	3.08	2.98

<sup>a</sup> At 50°C, 120 min of reaction.

In other words, under the same reaction conditions, AN had a higher grafting efficiency than MMA, although the conversion of the former was lower than that of the latter.

The effect of the ozone charge on the copolymerization is shown in Figure 4 for the two acrylic-CaLS systems. A considerable increase in monomer conversion as well as in the initial conversion rate can be observed when a comparison is made between the upper curves (with LS ozonized) and the lower ones (with LS not ozonized). With the use of the ozonized LS, the initial conversion rates of monomers were increased about 40 and 50 times, respectively, for the systems of AN-CaLS and MMA-CaLS in methanol medium. The data showing the effect of ozone charge on the other grafting parameters are listed in Table V, wherein the results obtained from using water as the medium are also included.

It can be seen from Table V that for all the cases studied, ozonization exhibited a positive influence on both the grafting efficiency and the degree of LS grafted; i.e., the higher the ozone charge, the better the performance of copolymerization. As noted, the monomer conversion for the MMA-CaLS system increased with increasing ozone charge in methanol medium, but it did not vary significantly in the water medium. In the case of AN-CaLS system, the change of monomer conversion with ozone charge was also more moderate in water than in methanol medium. Thus, a conclusion was drawn that the effect of ozone charge on monomer conversion was more pronounced when the copolymerization was carried out in methanol rather than in the water medium. This suggested that either a reactivity difference or a stability difference of the ozonized lignin radicals existed in these two mediums. In other words, these radicals were more

reactive in methanol than in water, or these radicals were more stable in methanol, i.e., a part of these radicals probably vanished when distributed in water. Consequently, ozone charge exhibited less influence on monomer conversion in water than in methanol.

It is interesting to note, also from Table V, that there was no significant change in the molecular weight of polyacrylics when the charge of ozone was varied in each medium, notwithstanding the remarkable change from one medium to the other. Recalling how the molecular weights of polyacrylics decreased with increasing peroxide charge (see Tables III and IV), it appeared that ozonization might increase the number of active centers in the lignin macromolecules and these centers substantially favored the graft of polymer chains onto the lignin, rather than the formation of homopolymers.

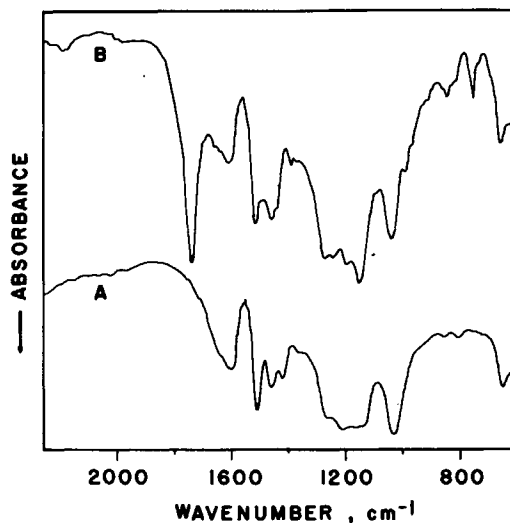


Fig. 5. Infrared spectra of original and grafted lignosulfonate samples. (A) = CaLS; (B) = CaLS-PMMA.

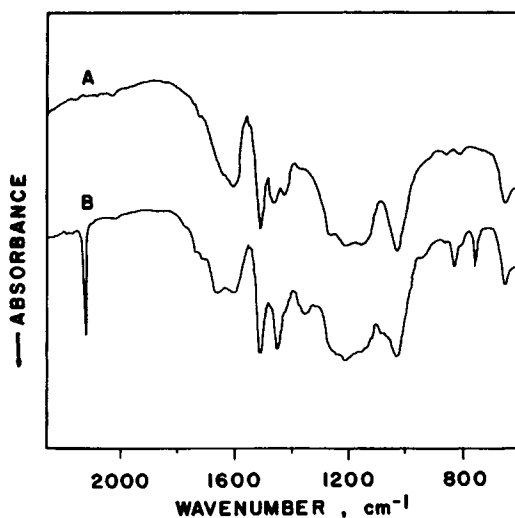


Fig. 6. Infrared spectra of original and grafted lignosulfonate samples. (A) = CaLS; (B) = CaLS-PAN.



So far as the temperature effect on monomer conversion was concerned, a conversion of as high as 90% could be achieved in the MMA-CaLS system in water medium at 50°C; thus, no attempt was made to conduct copolymerization at higher temperatures to obtain higher conversion. On the other hand, a few copolymerizations were carried out at 65°C for the system of AN-CaLS, in view of the rather low conversion (about 55%) attained at 50°C for this system. The initial conversion rate observed at 65°C was about twice that observed at 50°C, but the gain in monomer conversion (after 2 hr of reaction) from the temperature increase was only about 10% (62.8% at 65°C with respect to 56.4% at 50°C). Furthermore, no distinguishable difference was found in the grafting efficiency and in the degree of LS grafted. Therefore, a reaction temperature of 50°C was selected for the two acrylic-CaLS systems studied.

When comparing the homopolymerization of AN and the copolymerization of AN-CaLS (both were conducted under the same reaction conditions), it was interesting to find that the presence of CaLS accelerated considerably the initial conversion of AN. Using as examples the reactions at 50°C, in water medium, the initial conversion rate of AN in the copolymerization was about four times higher than that in the homopolymerization. However, the monomer conversion rate slowed down after 20 min of reaction, in the case of copolymerization; while the rate in the case of homopolymerization remained steady until about 60 min of reaction. Eventually, the conversion after 2 hr of reaction was higher in the second case (70%) than in the first (56%). Similar results were also observed when comparing the homopolymerization of MMA and the copolymerization of MMA-CaLS. This indicated that lignosulfonate had a positive influence on the initial conversion rate of acrylic monomers, implying that there was participation of lignin macroradicals in the beginning of the copolymerization.

The copolymers obtained were brownish amorphous solids and insoluble in most organic solvents at room temperature, but the lignin backbone could be degraded by acid or alkali at elevated temperature. For this reason, no information on the molecular weights of the products is provided. Nevertheless, some infrared spectra are shown in Figures 5 and 6 for the copolymers of MMA-CaLS and AN-CaLS, respectively; the spectra of a purified CaLS sample is also shown in each figure for comparison. It can be seen that each copolymer possesses the characteristic absorption bands of lignosulfonate; namely, the covalent sulfonate bonds in the range of 1220–1145  $\text{cm}^{-1}$  and the aromatic ethers stretching at 1265  $\text{cm}^{-1}$ . Furthermore, in Figure 5, there are strong bands at 1730  $\text{cm}^{-1}$  (attributed to the methacrylate carbonyl stretching vibration) and at 1155  $\text{cm}^{-1}$  (owing to the phenolic ester), and in Figure 6, the characteristic nitrile absorptions at 2250 and 1660  $\text{cm}^{-1}$ .

## CONCLUSION

Commercially available calcium lignosulfonate can be effectively grafted with methyl methacrylate and with acrylonitrile, using redox initiation involving ferrous chloride and hydrogen peroxide. Better copolymerization results were obtained in water than in the methanol medium. Increase in peroxide charge increased the monomer conversion and decreased the molecular weights of the acrylic homopolymers while the grafting efficiency and the degree of lignosulfonate grafted approached certain limits. Ozonization positively affected the

performance of copolymerization and showed no influence on the molecular weights of the homopolymers or of the grafted polyacrylic chains.

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