

The Use of Lignosulfonic Acid in the Synthesis of Water-Dispersible Polyaniline

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ABSTRACT: Polyaniline was synthesized in the presence of lignosulfonic acid to yield a product (LIGNO-PANI) that is water-dispersible. Several samples ranging from 0 to 70% lignosulfonate (LS) were prepared. These samples were then evaluated for differences in dispersibility and conductivity. As the percent of LS in the samples was increased, the water-dispersibility of the LIGNO-PANI also increased. The particle size of the samples as well as the conductivity of the samples decreased with increasing percentages of LS in the samples.

After extensive washings, however, the conductivity remained fairly constant (~ 0.4 S/cm) regardless of the amount of LS in the samples. Additionally, elemental analysis, TGA, and IR data were used to demonstrate that the LS is grafted to polyaniline during the synthesis of LIGNO-PANI. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1496–1500, 2008

Key words: conducting polymers; FTIR; graft copolymers; renewable resources; water-soluble polymers

INTRODUCTION

Polyaniline is an intrinsically conductive polymer (ICP) that has the potential for use in a number of applications such as light emitting diodes,¹ rechargeable batteries,² electromagnetic interference shielding,³ and smart windows.⁴ One very promising application is in the area of corrosion prevention. It has been found that ICPs, such as polyaniline, can inhibit corrosion when applied to a metal surface.^{5,6} Lignosulfonic acid-doped polyaniline (LIGNO-PANI) has also proven to exhibit excellent corrosion prevention characteristic.⁷

Conventional polyaniline, however, is limited by its processability.⁸ Emeraldine base, the nonprotonated, nonconducting form of polyaniline, for example, has only limited solubility in organic solvents such as *N*-methyl-2-pyrrolidone, *N,N*-dimethylacetamide, and *N,N*-dimethylformamide. Polyaniline doped with most acids is insoluble in common organic solvents.

Several methods have been developed to help improve the processability of polyaniline. One involves using acids which generate soluble counter-

ions when the base form of the polymer is doped. A variety of sulfonic acids have been used as dopants because of the solubility of the sulfonate counterion.⁹ In addition to monosulfonic acids, polysulfonic acids have also been used as dopants.¹⁰ Tanninsulfonic acid is a polysulfonic acid that has previously been shown to improve solubility when aniline was synthesized in its presence. This result was shown in an article recently submitted for publication to this same journal.¹¹ Lignosulfonic acid is another polysulfonic acid that can be used in the synthesis of polyaniline to form a water-dispersible product, LIGNO-PANI. It is highly dispersible in polar aprotic solvents such as dimethyl sulfoxide and tetrahydrofuran in its conducting state. This is because of the high solubility of the lignosulfonate (LS) incorporated as a dopant.^{12,13} To the authors knowledge, LIGNO-PANI is the only ICP to be mass produced in the United States and sold under the name Teslart[®] (Polyone, Lemont, IL).

Lignin is the component of plants and trees that gives them rigidity. Lignin also helps keep water from penetrating the plant and helps the plant to resist microbial decay. As one of the major noncellulosic component of wood, it is a renewable resource and byproduct of the paper industry. Lignin is composed of functionalized phenylpropane units connected through alkyl and aryl ether linkages. Sulfonation or sulfomethylation of these lignins (structure shown in Fig. 1) results in a highly water-soluble product.¹⁴

Several graft copolymers have previously been prepared to improve solubility or to modify proper-

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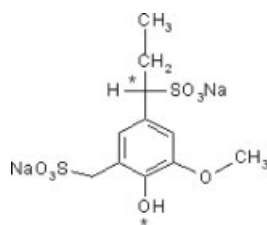


Figure 1 A typical sulfonated/sulfomethylated lignin monomer unit. The asterisks denote possible aniline-binding sites.

ties of different conducting polymers. Meister et al. have shown that when lignin is reacted with 2-propanamide and 2,2-dimethyl-3-amino-4-oxohex-5-ene-1-sulfonic acid it forms a graft terpolymer that is water soluble.¹⁵ Meister et al. has also shown that lignin can be synthesized with 2-propenamide as well as 1-phenylethylene to form graft copolymers with lignin.^{16–20} Jo and coworkers have shown that aniline can be reacted with poly(styrenesulfonic acid-*co*-aminostyrene) also resulting in a copolymer with improved solubility.²¹ Phillips et al. have published the reactions and properties of pulp and paper-based graft copolymers.²² Chitosan, which has amino groups on the polymer side chain, has also been modified using ethylene oxide to form water-soluble products.²³ Possible sites of grafting polyaniline to the lignosulfonic acid are indicated by an asterisk in Figure 1.

This article presents evidence in the form of elemental analysis, thermogravimetric analysis (TGA), and IR data that suggests lignosulfonic acid not only acts as a dopant, but also grafts to the polyaniline during the synthesis of LIGNO-PANI.

EXPERIMENTAL

Materials

Sodium persulfate (98%), aniline (99%), iron (II) sulfate heptahydrate (ACS reagent), sulfuric acid (95–98%), hydrochloric acid (37%), sodium hydroxide pellets, and potassium bromide (FTIR grade) were purchased from Sigma-Aldrich Chemical (St. Louis, MO). The BF16 lignosulfonate was provided by Westvaco (Charleston Heights, SC), Petrochemicals Department, as REAX 825E. All reagents were used without further purification, except aniline, which was distilled once prior to use.

Synthesis of emeraldine base polyaniline

A 4.00 mL sample of distilled aniline was added to 134 mL of deionized (DI) water and adjusted to a pH of 4.00 using concentrated hydrochloric acid. After the addition of aniline, the solution was again adjusted to a pH of 4.00 using hydrochloric acid.

The solution was then oxidatively polymerized at 0°C using sodium persulfate as the oxidant in a 1 : 1.1M ratio of aniline to sodium persulfate. All samples to be sent off for elemental analysis were subjected to a series of washings to ensure that the samples were as pure as possible. Therefore, after the samples had reacted for 4 h, a 50% sodium hydroxide solution was added to the reaction mixture to adjust the pH to 11. The dedoped PANI was then washed successively with 400 mL of (3%) sodium hydroxide solution, 200 mL of DI water, 200 mL of 1.2M hydrochloric acid or sulfuric acid, 200 mL water, and 200 mL sodium hydroxide. The filtered solid was then redispersed in 400 mL sodium hydroxide solution using a high-speed homogenizer (18,000 rpm) for 5 min. The washing sequence described earlier was then repeated an additional six times, followed by redispersion in the sodium hydroxide solution. After the seventh washing, the product was washed with 2000 mL of DI water. The precipitate was collected and vacuum dried. The dried product was pulverized and sent to a laboratory for elemental analysis.

Synthesis of LIGNO-PANI

LIGNO-PANI was prepared by dissolving sodium lignosulfonate (between 0.454 g for 10% and 9.539 g for 70%) in 134 mL of DI water. The sodium salt was then protonated by titration with a strong acid, such as hydrochloric acid, to bring the pH of the solution to 4.00. To this aqueous solution of lignosulfonic acid was added 4.00 mL of distilled aniline. The solution was then oxidatively polymerized at 0°C by adding 11.48 g of sodium persulfate as the oxidant (1 : 1.1M ratio between aniline and the persulfate). After 4 h, the product was collected by vacuum filtration and washed with DI water.

Although the majority of polyaniline syntheses are performed in environments with a starting pH of less than 1, LIGNO-PANI has been synthesized at an initial pH of 4 to reduce the competition between the hydrochloric acid and the lignosulfonic acid as the dopant. Preparing the solutions at a pH of 4 helps ensure that a greater probability of the lignosulfonic acid is initially available for doping. Additionally, a consequence of the decomposition of persulfate is that additional acid is introduced into the system resulting in a pH less than 1 during polymerization.

Samples with various ratios of LS to aniline were prepared. The percentage of LS in the starting reaction mixture for these samples ranged from 10 to 70% by weight based on total dry weight of LS and aniline. After the LIGNO-PANI reaction had progressed for 4 h, the pH of the reaction mixture was brought to 11.00 using sodium hydroxide and the

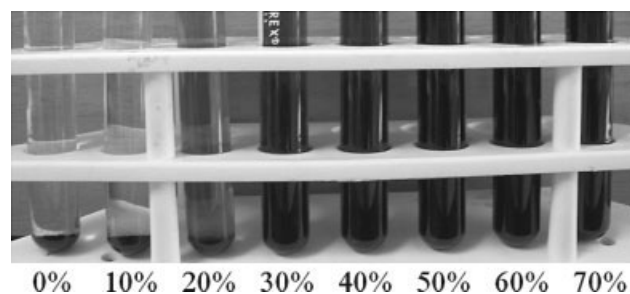


Figure 2 Dispersibility of LIGNO-PANI samples after being allowed to stand for over a week in test tubes.

same series of washings were completed as described in the "Synthesis of emeraldine base polyaniline" section.

Synthesis of *ex situ* doped LIGNO-PANI

Freshly prepared liginosulfonic acid was added to a wet cake of emeraldine base and allowed to stir overnight. The amount of LS was equivalent to that added to the 20% LIGNO-PANI (meaning 20% LS to 80% aniline before synthesis). Liginosulfonic acid was prepared by passing a solution of LS through a column containing Dowex cation exchange resin. After filtration, the mixture was adjusted to a pH of 11 using a 50% sodium hydroxide solution and then filtered. The sample was then taken through the series of seven washes as described in the "Synthesis of emeraldine base polyaniline" section.

FTIR analysis

FTIR was performed on KBr pellets containing the dedoped samples which had been washed seven times, using a Nicolet Magna 550 FTIR.

Conductivity studies

Conductivities of pressed pellets were measured using an Alessi 4-point probe in conjunction with a Keithly voltmeter and programmable current source.

Thermogravimetric analysis

TGA was performed on the samples using a Mettler-Toledo TG50 controlled by a PC. Approximately 30 mg of sample in a crucible was placed in the oven. The samples were heated from 40 to 1000°C at 10°/min in air.

Elemental analysis

C, H, N, and S elemental analysis was performed by Galbraith Laboratories (Knoxville, Tennessee).

Nuclear magnetic resonance

Proton NMR spectra were obtained using a Bruker AC-F 200 MHz Superconducting Multinuclear Nuclear Magnetic Resonance (NMR) Spectrometer. Solutions were prepared by dissolving 0.100 g of sample in 1.00 mL of deuterated dimethylsulfoxide (DMSO- d_6) containing a 1% (v/v) TMS. After thoroughly mixing, the solution was then filtered through glass wool and collected in an NMR tube.

RESULTS AND DISCUSSION

Characterization of doped LIGNO-PANI samples

Each synthesized sample was evaluated for differences in dispersibility and conductivity. Dispersibility was visually observed to improve with increasing amounts of LS. This was demonstrated qualitatively by dissolving approximately equal amounts of wet LIGNO-PANI sample containing between 0 and 70% LS. There was a noticeable difference between samples containing 20 and 30% LS in the LIGNO-PANI preparation as shown in Figure 2. Although the PANI and 10% samples dispersed readily in the water, they completely precipitated after a few days leaving the supernatant completely clear. After 2 weeks, the 20% LIGNO-PANI sample resulted in a great deal of precipitate, yet the supernatant solution still maintained a green appearance. The 30–70% samples, however, resulted in only a small amount of precipitate, if any, and their supernatant maintained a rich green color after 2 weeks sitting undisturbed.

Conductivities were also determined for each of the samples and are shown in Figure 3 (dashed line). With the exception of an initial increase of the 10% LIGNO-PANI sample over the PANI sample,

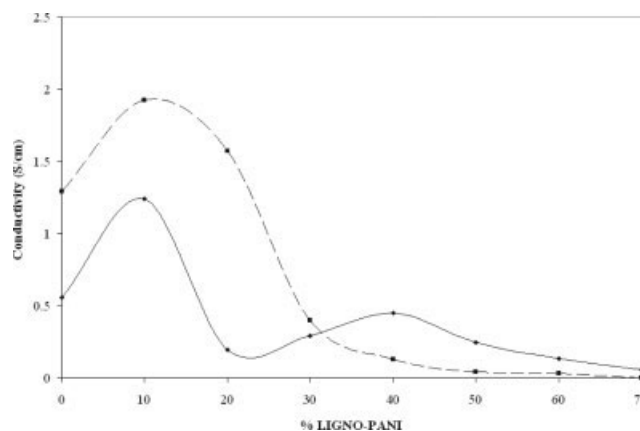


Figure 3 Conductivities of various percent LIGNO-PANI samples. Dashed line represents conductivities of samples washed only with water, whereas solid line represents samples washed seven times as explained in the Experimental section.

conductivities generally decreased with increasing amounts of LS. The samples that were washed seven times (solid line in Fig. 3) are discussed in the next section.

Evidence for grafting

Although experimental observations indicate that the incorporation of LS results in a more dispersible PANI, further experiments were performed to determine if the LS was permanently incorporated into the polymeric species. Elemental analysis was performed on each sample to identify the amount of LS that was grafted to the polyaniline. The samples were prepared in the same way as the other samples, but then washed thoroughly as described in the Experimental section using acid, base, and water to ensure that all impurities and dopants were removed. These dried dedoped samples were then sent for elemental analysis and the results are shown in Table I. The only sources of sulfur are the oxidant and the LS, whereas the only source of nitrogen is the polyaniline. To account for the amount of sulfur present from the oxidant, elemental analysis was performed on a PANI sample prepared containing no LS. A plot of the sulfur to nitrogen ratio (S/N) shows an excellent correlation which increases with increasing amounts of LS, up to 60%, as shown in Figure 4. The 60 and 70% ratio, however, remains fairly constant, showing that a maximum amount of LS has been incorporated.

It is possible that some LS remaining in the samples after washing is a result of physical interactions and not grafting. To determine the magnitude of this interaction, a control sample in which the LS acted only as a dopant was prepared (comparison in Table I). This sample was synthesized by adding freshly prepared lignosulfonic acid to dedoped HCl-PANI. This solution was allowed to stir overnight to ensure maximum doping. The amount of lignosulfonic acid added was equivalent to the amount of LS present in the synthesis of 20% LIGNO-PANI. Elemental analysis confirms that all the LS are removed by washings. When compared, the sulfur to nitrogen ra-

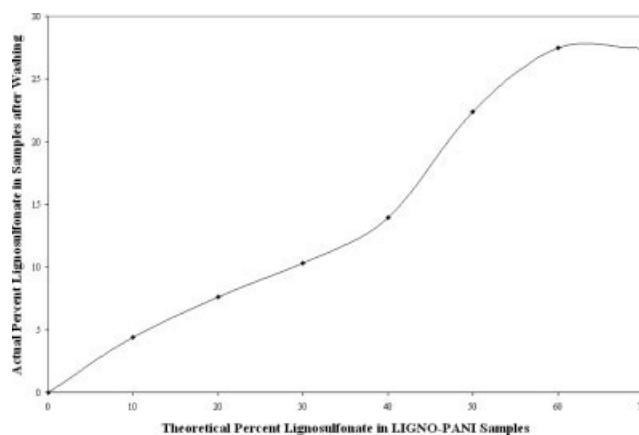


Figure 4 The percent lignosulfonate remaining in the washed samples as calculated from the elemental analysis results versus the percent lignosulfonate added in the synthesis.

tio of this product is slightly lower (0.0156) than pure PANI (0.0159) but considerably lower than the 10% LIGNO-PANI sample (0.0447). This indicates that none of the lignosulfonic acid stays bound throughout all the washings when it is acting as a dopant. The amount of LS remaining in the LIGNO-PANI samples after seven washes, therefore, must be due to something more than the LS acting as a dopant.

Elemental analysis also indicates that there is a maximum amount of LS that can be grafted onto PANI. This maximum is reached when greater than 60% LS is used in the reaction mixture. The presence of this maximum precludes occlusion from being the cause of the persistent presence of LS in the washed samples.

The conductivities of the HCl redoped samples are shown in Figure 3. Samples that were only washed once with DI water demonstrated a fairly predictable trend of decreasing conductivities (Fig. 3, dashed line) with increasing amounts of LS. When the samples were washed seven times *vide supra*, however, this trend is disrupted and the conductivities remain fairly constant (Fig. 3, solid line) with increasing amounts of LS. The decrease in conductivities for the samples washed only with water is likely due to excess LS present in the sample. LS is an insulator and should, therefore, decrease the conductivity. After repeated washings, however, all the excess LS should have been removed. This, in turn, should allow the conductivities to remain fairly constant with increasing amounts of LS. The overall low conductivities of the washed samples is most likely a result of inefficient redoping.

Figure 5 shows additional evidence of grafting in the infrared spectrum of the dedoped samples that have been washed seven times as described earlier. The peak at 1030 cm^{-1} is attributed to a sulfur-oxy-

TABLE I
Elemental Analysis Results of the LIGNO-PANI

Percent LIGNO-PANI	Percent Sulfur	Percent Carbon	Percent Hydrogen	Percent Nitrogen
0	0.23	74.95	4.94	14.48
10	0.62	73.41	4.93	13.88
20	0.84	69.74	4.64	12.74
30	1.04	69.66	4.87	12.43
40	1.29	69.14	4.97	11.97
50	1.8	67.92	4.72	11.02
60	1.99	65.37	4.61	10.11
70	1.79	61.15	4.48	9.12
Control	0.22	73.85	4.66	14.13

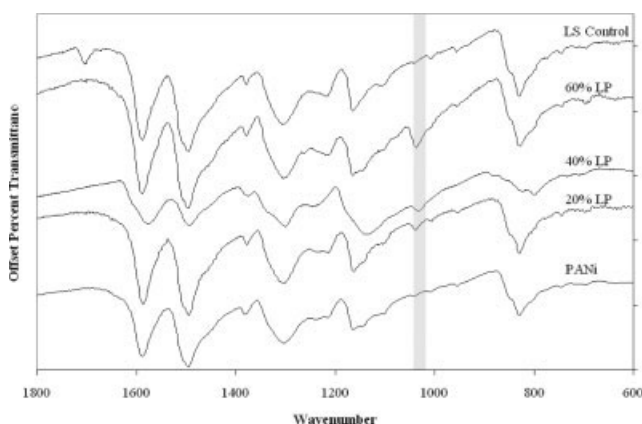


Figure 5 Normalized and offset IR spectra of (from bottom to top): (a) PANI; (b) 20% LIGNO-PANI; (c) 40% LIGNO-PANI; (d) 60% LIGNO-PANI; and (e) LS PANI (control). The 1030 cm^{-1} peak, which corresponds to the S—O stretch of ionic sulfonates, is highlighted showing increasing amounts of lignin from the 20 to 60% LIGNO-PANI.

gen stretch which is present in LS. A very small peak is seen at 1030 cm^{-1} for the PANI sample presumably because of the oxidant [Fig. 5(a)]. The remaining samples show a definite increase in absorbance (a decrease in percent transmittance) at 1030 cm^{-1} for the 20, 40, and 60% LIGNO-PANI samples [Fig. 5(b–d)]. The spectrum for the comparison sample in which LS was only a dopant is also shown [Fig. 5(e)]. The very small amount remaining is evidenced by the small 1030 cm^{-1} peak. The peak is smaller than the PANI sample synthesized with no LS. This, in addition to the elemental analysis results, would indicate that the lignosulfonic acid is not acting only as a dopant, but actually is grafting to the PANI.

TGA of the samples were also performed. The results showed an onset of weight loss around 400°C . For LIGNO-PANI samples containing 10 to 40% LS, the greatest weight loss was observed at 500°C (for the 10% LS), 496°C (for the 20% LS), 484°C (for the 30%), and 477°C (for the 40% LS). In HCl doped PANI, the onset of degradation was also around 400°C with the greatest weight loss occurring at 492°C .

Proton NMR data were also obtained for various samples. Unfortunately, however, LS is virtually transparent, even though it has a large number of hydrogens. Small peaks are observed at 1.2, 7.0, and 8.4 ppm. These peaks, however, are also observed with the PANI sample as well.

CONCLUSIONS

The incorporation of LS during the synthesis of PANI results in a water-dispersible conducting poly-

aniline. Dispersibility of this polymer was found to increase as the amount of LS in the reaction mixture was increased from 0 to 60%.

Conductivities, on the other hand, are observed to decrease for the unwashed polymer with increasing amounts of LS as a result of its inherent insulating properties. When the polymers were washed repeatedly with acid and base to remove any unreacted LS, however, the samples demonstrated consistent conductivities after redoping.

Finally, through FTIR and elemental analysis of the thoroughly washed samples, it was shown that the LS is not only acting as a dopant. There is a significant permanent incorporation of the LS presumably through a grafting mechanism. Results indicate that a maximum of $\sim 60\%$ LS can be incorporated.

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