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# Synthesis and characterization of poly(*o*-methoxyaniline)–lignosulfonate composites

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## ABSTRACT

Poly(*o*-methoxyaniline)–lignosulfonate (POMA–LGS) composites were synthesized through oxidative chemical polymerization of *o*-methoxyaniline by ammonium persulfate (APS) in the presence of sodium lignosulfonate (NaLGS). The structure of the composites was investigated using FTIR, UV–vis spectroscopies and SEM. The AC conductivity and free radical scavenging of the composites were also tested. The LGS content was found to have a strong influence on the structure and properties of the composites. A higher LGS content led to composites with a higher AC conductivity, a higher specific surface area, as well as a greater radical scavenging capacity. A new composite formation mechanism was proposed, with the sulfate group dissociated from the oxidant of APS as the main dopant, POMA particles as adsorbate and LGS as the adsorbent.

## 1. Introduction

Polyaniline (PANI) is an intrinsically conducting polymer (ICP) that has become an appealing target of research because of its facile synthesis, having a low cost monomer and good environmental stability [1]. The main disadvantage that restricts the industrial scale application of PANI is its lack of processability, which is associated with its insolubility and infusibility, especially in its conducting form [2]. Ring substituted PANI derivatives are, in this context, of potential interest because they would be expected to induce improved processability due to the decreased rigidity of the polymer chains that result from the introduction of substituent groups [3]. Poly(alkoxyanilines) are among the most frequently studied ring-substituted PANI derivatives, and the preparation of the simplest poly(alkoxyaniline), i.e. poly(methoxyaniline) has been explored by electrochemical polymerization [4], chemical oxidative polymerization [5], and less-common methods such as solid-state polymerization [6] and high-temperature polymerization [7].

Another approach toward improved processability is the incorporation of dopant counter-ions associated with the conducting polymer backbone. Most studies into conducting polymer dopants focus on sulfonic acids as counter-ions, such as camphor sulfonic acid [8], dodecylbenzenesulfonic acid [9], and para-toluene sulfonic acid [10]. However, these dopants are not cost-effective and are environmentally disadvantageous in terms of renewability of the materials [11]. Lignin is one of the most abundant biopolymers in nature, second only to cellulose [12]. Lignosulfonate (LGS) is an inexpensive byproduct from the pulp processing industry [13]. It is a highly water-soluble polysulfonic product composed of functionalized phenylpropane units connected through alkyl and aryl ether linkages [14]. It contains both hydrophilic groups, e.g. sulfonic, phenolic, hydroxyl, and hydrophobic groups, e.g. aryl and aromatic carbons [15], as shown in Scheme 1. LGS has gained more and more attention and has been used to synthesize PANI–LGS composites by several research groups. One of these products, LIGNO-PANI$^{TM}$, was reported to be water dispersible [16,17]. It is also of significant industrial importance as it was reported to be the first commercially mass produced water-borne conducting polymer in the US [18]. Further, given that lignosulfonate has been reported as a radical scavenger [16], we are exploring in this study the prospect that POMA–LGS composites may be even more useful in free radical scavenging. However, to the best of our knowledge, there has been no report about the synthesis and characterization of poly(*o*-methoxyaniline)–lignosulfonate (POMA–LGS) composites. In addition, the formation mechanism of the conducting polymer–LGS composites as well as the role of LGS in the reaction system has not yet been well elucidated. In this

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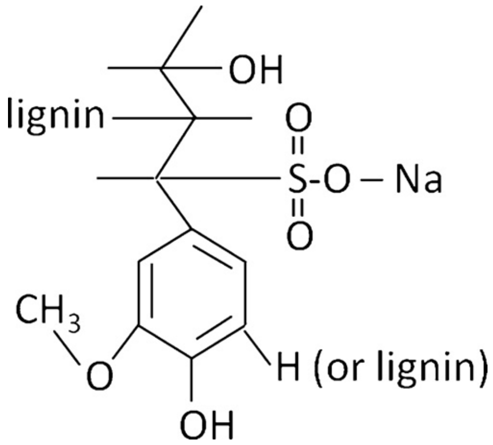

**Scheme 1.** Molecular structure of lignosulfonic acid sodium salt (NaLGS).

study, we report for the first time the synthesis and characterization of POMA–LGS composites, its formation mechanism, and the effect of LGS content on the structure and properties of the composite products.

## 2. Experimental

### 2.1. Materials

*o*-Methoxyaniline (OMA, 99%), ammonium persulfate (APS, 98%) and sodium lignosulfonate, or lignosulfonic acid sodium salt (NaLGS, $M_n \sim 7000$, $M_w \sim 52{,}000$) were all purchased from Sigma–Aldrich and used as received.

### 2.2. Synthesis of POMA–LGS

Due to the structural complexity of NaLGS molecules, the quantitative determination of molar ratios of sulfonic acid groups to OMA monomers was not possible [13]; therefore POMA–LGS composites with different empirical weight ratios of NaLGS to monomer were prepared by oxidative chemical polymerization. This was undertaken using APS, at a molar ratio of OMA to APS of 1:1.25 in a NaLGS aqueous solution. In a typical preparation, different amounts of NaLGS (1.29 g, 2.58 g, 6.45 g, and 12.93 g, respectively) were dissolved in 300 mL of deionized water to make the NaLGS solution to be used as the reaction medium. 0.105 mol of OMA (12.93 g) was dispersed in 225 mL of the NaLGS solution, followed by the dropwise addition of 0.13 mol of APS dissolved in the remaining 75 mL NaLGS solution. The reaction was allowed to continue at room temperature for 5 h under constant magnetic stirring. The resulting POMA–LGS precipitate was washed with excess deionized water repeatedly until the filtrate was colorless in order to remove the remaining free NaLGS and water-soluble oligomeric by-products [19]. The products were then dried in a vacuum oven at 40 °C for 48 h. The final composites were denoted as LGS-0.1, LGS-0.2, LGS-0.5, and LGS-1.0 for POMA–LGS with NaLGS/OMA weight ratios of 0.1, 0.2, 0.5, and 1, respectively.

### 2.3. Characterization

Elemental analysis was performed by the Campbell Microanalytical Laboratory at the University of Otago, Dunedin, New Zealand.

The polymer structure was investigated by Fourier transform infrared spectroscopy (FTIR) using a germanium attenuated total reflection (ATR) accessory in conjunction with a Thermo Electron Nicolet 8700 FTIR spectrometer, taking 64 scans at 4 $\text{cm}^{-1}$ resolution.

The UV–vis absorption spectra of the polymers dissolved in dimethylformamide (DMF) were recorded from 200 to 820 nm using a Schimadzu UV-2101PC UV–vis spectrophotometer.

AC conductivity of the samples in the frequency range 1–10,000 Hz was measured with a VersaSTAT 3 instrument after pressing the samples into pellets.

Composite powder morphologies were investigated using a Philips XLGS-0.50S field emission scanning electron microscope (SEM) with an accelerating voltage of 10 kV. The samples were 10 mm in diameter, mounted on aluminum studs using adhesive graphite tape and sputter coated with palladium using a Polaron SC7640 Sputter Coater at 5–10 mA and 1.1 kV for 5 min.

$N_2$ physisorption isotherms were determined at liquid nitrogen temperature (−195 °C) using a Micromeritics Tristar 3000 instrument. Specific surfaces areas were calculated from the $N_2$ adsorption data according to the Brunauer–Emmett–Teller (BET) method using $P/P_0$ values in the range of 0.05–0.2. Cumulative pore volumes and pore diameters were calculated from the adsorption isotherms by the Barrett–Joyner–Halenda (BJH) method. Samples were degassed at 60 °C under vacuum for 2 h prior to the $N_2$ adsorption measurements.

The antioxidant activity of the POMA–LGS samples were assessed via reaction with 1,1-diphenyl-2-picrylhydrazyl (DPPH) free radicals. Each test sample (1.0 mg) was added to 20 mL of a 250 μM DPPH solution in methanol and kept in the dark at room temperature. An aliquot of the DPPH solution was transferred to a cuvette with a 1 cm path length and the absorbance at 516 nm was measured using a Schimadzu UV-2101PC UV–vis spectrophotometer. The absorbance of the control DPPH solution was also measured and subtracted as the background. The antioxidant activity was evaluated as the percentage of the initial amount (in micromoles) of DPPH scavenged per mg of POMA–LGS composite.

## 3. Results and discussion

### 3.1. Composite analysis

Elemental analysis results are listed in Table 1. The oxygen content was determined by difference. It is clear that the sulfur content increased, and the nitrogen content decreased, as the NaLGS/OMA ratio was increased from 0.1 to 1.0. Some of the sulfur present came from sulfate dopant ions formed from the APS oxidant [20], and therefore the sulfur percentage does not accurately reflect LGS percentage. Based on the nitrogen percentage, the weight percentage of LGS in the final composites, labeled LGS-0.1, LGS-0.2, LGS-0.5 and LGS-1.0, were calculated to be 2.6%, 5.3%, 16% and 29%, respectively; compared with the starting percentages of NaLGS used in the reaction of 9.1%, 17%, 33% and 50%. Another noteworthy point is that with the relatively small amount of LGS content in the composites (compared with the reaction content), the actual sulfur provided by LGS for samples of LGS-0.1, LGS-0.2, LGS-0.5 and LGS-1.0 were calculated to be 0.16%, 0.32%, 0.98% and 1.77%, while sulfur provided by APS dissociation was 1.97%, 2.21%, 1.85% and 1.96%. Therefore, most of the sulfur in the final composites was determined

**Table 1**
Elemental analysis results for POMA–LGS with different NaLGS/OMA weight ratios.

| Sample | C (%) | H (%) | N (%) | S (%) | O (%) | LGS (wt%) |
|---|---|---|---|---|---|---|
| POMA | 50 | 5.3 | 8.4 | 2.9 | 33 | NA |
| LGS-0.1 | 60 | 5.2 | 8.2 | 2.1 | 24 | 2.6 |
| LGS-0.2 | 60 | 5.4 | 8.0 | 2.5 | 24 | 5.3 |
| LGS-0.5 | 60 | 5.4 | 7.1 | 2.8 | 24 | 16 |
| LGS-1.0 | 58 | 5.6 | 6.1 | 3.7 | 27 | 29 |
| NaLGS | 40 | 5.0 | 0.36 | 6.1 | 42 | 94[a] |

[a] Based on the difference of sodium percentage (6.00%) obtained by the same technique.