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Characterization of the effects of lignin and lignin complex particles as filler on a polystyrene film

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ABSTRACT

The work in this research outlines the use of lignin precipitated from lignocellulosic substrate as fillers after modified with transition metal cations, Fe(III), Ni(II) and Co(II), in the production of a polystyrene based composite for polymer packaging applications. Virgin polystyrene was compared with lignin and lignin complex filled composites with loading of 5% by weight prepared using twin screw extrusion. The lignin complexes were first characterized by the UV spectra to identify the new absorption bands occurred due to the complex formation. Moreover, lignin model, namely vanillin, was used to notify the geometric structure of the resulting complexes applying the GC mass spectra. Scanning electron microscopy was used to indicate the change in the morphological structure of the filler particles. On the other hand, the mechanical and thermal analysis for the resulting polymer composites was studied and it was noticed that the type of lignin or lignin complex plays a roll in the results. The inclusion of the Co(II)–lignin complex was observed to increase the tensile strength of the resulting polymer composite and a decrease of the glass transition temperature. Furthermore, light wave lengths and UV fluorescent microscope were used to identify the change of color for the resulting polymer film.

1. Introduction

Recently, both the polymer industry and the academia began to focus on developing polymer blends and composites with novel and valuable properties, in order to enlarge the spectrum of available materials [1]. Various polymeric materials are known for specific or unique characteristics and melt blending of polymers with fillers during extrusion is a useful method of combining the desired properties of different materials [1]. On the other hand, wood and agricultural residues are mainly composed of carbohydrates, lignin, and extractives. In the recent decade, a great attention of the world agricultural research was focused on non-wood materials with perspective for environmental industrial utilization. The process, by which raw materials are pulped, produces large amounts of highly polluting waste water [2,3]. The black liquor resulting from the pulp industry consists mainly of lignin. Lignin is a natural polymer, which is biologically produced through random polymerization processes with a great structural heterogeneity. Lignin is a complex of three-dimensional amorphous polymer embedded in extracellular matrix of plants that provides the plant with a variety of functions.

It is well known that lignin is one of the major components of biomass and a potential source for aromatic chemicals. It is an aromatic polymer of phenylpropane units with a complex structural heterogeneity that makes up its particular resistance to microbial degradation [4]. This polyphenolic material, however, could potentially serve as a renewable chemical feedstock if suitable conversion chemistry is developed [5]. Currently, many lignins are known with properties and compositions that vary according to the origin of the lignin and the treatment it has been subjected to. The black liquor of the wood and non wood-based pulp industry is the main source of the lignins being used. One of the potential uses of lignin is as a heavy metal adsorbent in industrial effluents.

The work described herein investigates the use of lignin precipitated from the resulting black liquor as filler in the production of composites by melt blending polystyrene with the lignin particles. The work was carried out in order to produce polymer composites that had unique color change properties for special application by modifying the properties of the lignin using transition metal ions.

The presence of transition metal ions in lignin rich pulp fibers has negative consequences on pulp brightness and brightness stability [6]. Metal ions can cause the formation of colored compounds on the pulp fibers. Lignin model compounds can be used to study the effect of various functional groups within the lignin polymer on light absorption when complexed with different metal ions. The implication of lignins in the holding back of metals and the transformation of organic matter are only partially known [7,8]. The

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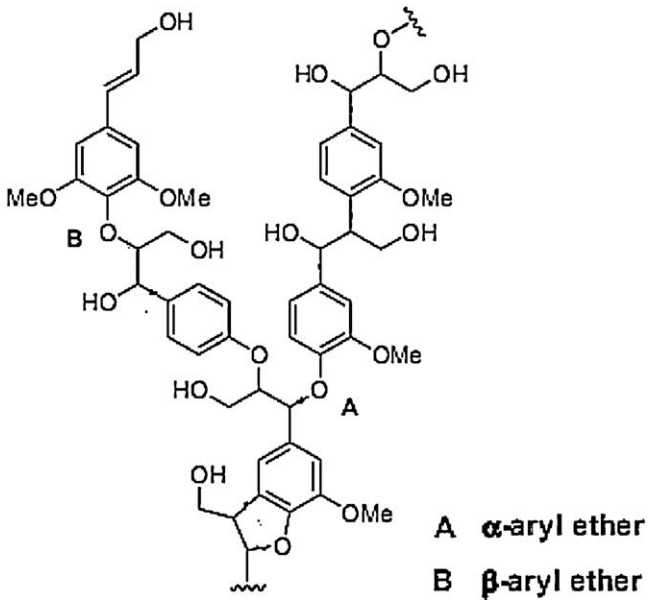

Structure 1. Chemical structure for lignin.

reactions can occur in solution or at the solid–solution interface since a fraction of lignin is soluble in aqueous solution.

The light absorptive characteristics of complexes involving lignin-like compounds are less well known. This is important in terms of the relative abundance of different combinations of functional groups in lignin, where the difficulty of the study of lignins comes from their complex structure, which cannot be known [9]. Lignin is a cross-linked, phenolic polymer built from three basic phenyl propane monomers (*p*-hydroxycinnamyl, coniferyl, and sinapyl alcohols), Structure 1. Chemical modification of technical lignins is a well-established field of research that spans organic chemistry, wood chemistry, and polymeric materials chemistry [10,11]. The heterogeneous polymeric structure of lignins is rich with alcohol and phenol functional groups; therefore, by manipulating lignin's reactive functional groups, it is possible to adjust the physical and chemical properties of the material and thus a majority of modification strategies can be carried out [11–22].

Consequently, some model molecules, precursors of lignin, which have similar active sites of complexation (phenolic and methoxy groups), have been chosen to understand the reactivity of lignin with an iron (III) cation [8,23]. Moreover, to our knowledge, this work is the first study of cobalt (II) complexation on both lignin models and lignin precipitated from black liquor. For this reason, vanillin, which is a phenolic compound that has both hydroxyl and methoxyl groups, was chosen as the lignin model compound (LMC) to be studied as well as lignin precipitated from the black liquor resulting from alkaline pulping of rice straw. Their spectral properties, in terms of their reaction and complexation products with cobalt (II), nickel (II) and iron (III) were determined. Furthermore, application with polystyrene polymer to produce Co(II)–lignin–polystyrene composite was investigated.

2. Experimental

2.1. Materials

Vanillin was purchased from Aldrich with purity of 99%. Potassium nitrate (KNO_3) and metallic salts Co(II) chloride ($CoCl_2{\cdot}6H_2O$); Ni(II) sulfate ($NiSO_4$) and Fe(III) chloride ($FeCl_3$), were also purchased from Aldrich.

2.2. Isolation of solubilized lignin

The lignin samples were obtained from the black liquor of alkaline pulping of rice straw as follows:

The black liquor resulting from the alkaline pulping of rice straw was acidified to pH 1.5 by a dropwise addition of concentrated sulfuric acid (H_2SO_4). The acidified mixtures were then heated in a water bath at 100 °C for 1 h with continuous stirring. The precipitated lignin fraction was cooled to room temperature, filtered in a Buchner funnel, and then washed with hot water till neutrality. The final product was air-dried at ambient conditions.

The isolated lignin was re-dissolved in 17.5 (w/w) NaOH, and precipitated with concentrated H_2SO_4 (pH 1.5) using the procedure described earlier. The precipitated lignin was filtered and then washed with hot water until the filtrate was clean and then air-dried at ambient laboratory conditions.

2.3. Sample preparation

Metal surface complexes were prepared by sorption of metal cations onto lignin and lignin model. One gram of vanillin (V) sample was suspended in a 30 mL of 0.1 M KNO_3 overnight at room temperature with continuous stirring. Metal solutions for iron (Fe^{3+}), nickel (Ni^{2+}) and cobalt (Co^{2+}) were introduced at concentration of 2.0×10^{-4} mol L^{-1}. The mixture was stirred first at room temperature for 1 h, then at 60 °C for 2½ h. After which, precipitation was carried out with sodium bicarbonate and the precipitate was filtered, washed then air-dried.

The same experiments were achieved with the alkali lignin (AL) precipitated from the black liquor.

2.4. Characterization of the lignin fractions

2.4.1. UV spectra

UV spectra were recorded on a CALLED UNICAM 500, THERMOSPECTRONIC UV visible Recording Spectrophotometer. Lignin sample and model, as well as modified samples with metal ions (5 mg) were dissolved in dimethyl sulfoxide (DMSO) (10 mL). A 1 mL aliquot was diluted to 10 mL with DMSO, and the absorbencies between 200 and 400 nm were measured.

2.4.2. Mass spectrometry

A Finnigan SSQ 7000 instrument was used for the characterization of the molecular ion fragments of the produced LMC–metal ion complexes, as well as AL–metal ion complex.

2.4.3. Scanning electron microscopy

Scanning electron microscopy (SEM) was used to investigate the morphology of different types of materials, i.e. AL, AL–Co^{2+}, vanillin and Co(II)–vanillin, as well as $CoCl_2{\cdot}6H_2O$ by using a scanning electron microscopy (QUANTA 200 – FEI). The specimens were coated with gold/palladium and observed using an applied tension of 10–12.5 kV.

2.4.4. Composites preparation

The samples of powdered AL, V and their complexes, in a 5%, were extruded with the polymeric matrix, polystyrene (PS), at 75 rpm with a Micro 15-cc Twin Screw Compounder system (DSM Research, Geleen, The Netherlands) at 130 °C for 10 min. The PS was first mixed with the powdered lignin, vanillin and their cobalt(II) complexes then added to the mixer until the thermoplastic matrix was melted and the mixing maintained for additional 10 min. The resulting composites were molded into films of 0.5 mm thick.