

Functionalization of lignin: Fundamental studies on aqueous graft copolymerization with vinyl acetate

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ABSTRACT

The second most abundant natural polymer, lignin, an under-valued co-product from the pulp and paper, and biofuel industry has a great potential to be utilized to engineer value-added, green products. Graft copolymerization of vinyl acetate (VAc) on lignin was performed using potassium persulfate as an initiator and ammonium iron (II) sulfate as a catalyst. Aqueous reaction medium is used for the preparation of graft copolymer as a cost effective and greener route. The effects of reaction conditions were studied to obtain optimal grafting percentage with very low homopolymer formation. The effects of various factors like temperature, initiator concentration, amount of monomers, and volume of catalyst found to have considerable effects on grafting efficiency. Highest grafting of 60% was observed for 1:1.5 ratio of lignin and vinyl acetate at 70 °C in presence of 9.24×10^{-2} mol/L initiator and 5.1×10^{-4} mol/L of catalyst concentration. Graft copolymerization was identified from the new absorption peaks at wavelengths around 1720 cm^{-1} and 1210 cm^{-1} (Fourier transform infrared spectroscopy), and the new degradation peak observed at 339 °C (thermogravimetric analysis). Reinforcing or blending of VAc-g-lignin with desirable polymers can yield value-added greener products.

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1. Introduction

Lignin is one of the most abundant renewable resources with the annual production of more than 50 million tonnes from the biofuel, pulp and paper industries (Thielemans et al., 2002). The biofuel, pulp and paper industries generate lignin as a by-product of their processes and burn it to recover energy or dump it in landfills (Stewart, 2008). At the current rate at which fossil fuels are being consumed and the negative effect they have on the environment an alternative resource necessary to be utilized to replace fossil fuels. Currently scientists are trying to develop value added materials using lignin to substitute fossil fuel based products because of the abundant availability of lignin from renewable resources.

The biological role of lignin is to fill the space between the cell wall of plants as well as to help the water movement in plants (Kuroda et al., 2007). Lignin can be extracted from plants by various processes. The extraction methods and source of lignin vary the properties of lignin. The kraft extraction process uses black liquor to extract lignin and hemicellulose from cellulose in wood fibres

(Chakar and Ragauskas, 2004; Guerra et al., 2006; Lawoko et al., 2005).

Lignin is a highly complex material with a large variety of functional groups, which include: hydroxyl, aromatic and methyl functional groups (Mohamad Ibrahim et al., 2010). Although the structure of lignin is complex, there are only three monomeric units (p-coumaryl, coniferyl and synapyl alcohol) that create the lignin molecule (Fig. 1). From these three units the phenylpropanoid units, guaiacyl (G), syringyl (S) and p-hydroxyphenyl propane (p-H), are made (Brunow et al., 1999). The structure and properties of lignin varies with the method of extraction and origin. Softwood lignin (spruce and pine) mainly derived from the G unit but the hardwood lignin derived from the various ratios of S/G (Ralph et al., 1998). Along with slight variations in physical properties, the structure of lignin is also known to vary a great deal. The three different monomeric units of lignin can bond in different ways, which creates a very complex lignin structure (Ämmälähti et al., 1998). This complex quinonic structure makes lignin difficult to functionalize (Thielemans et al., 2002).

The functionalization of lignin can generate greater economic uses for lignin rather than burning as an energy recovery source. Functionalization with desirable monomers can generate lignin-based biocomposites that have a wide array of applications ranging from the automotive industry to industrial uses (Lora and Glasser, 2002).

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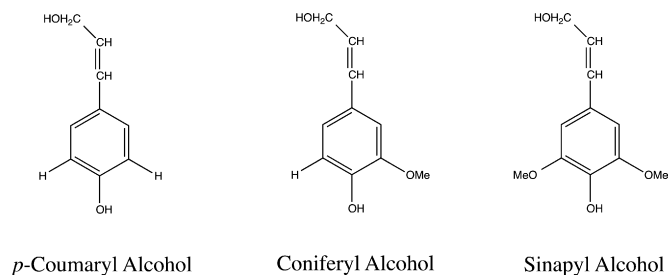


Fig. 1. Monomeric units for lignin formation.

By chemical modification of lignin, properties such as elasticity, ion-exchange capabilities and thermal resistance can be increased (Mai et al., 2000). Free-radical polymerization provides a simple method to functionalize lignin with vinyl monomers. Being a cost effective and simple method, graft copolymerization can generate desirable properties by simply varying the reaction conditions. Desired physical and chemical properties can be attained by modifying the variables such as concentration of reactants, initiator, catalyst and temperature. Selection of initiator and catalyst systems for graft copolymerization reactions is critical to achieve good degree of grafting. Potassium persulfate can act as an initiator that help to control the graft co-polymerization (Detrembleur et al., 2002).

Free radicals can be generated via chemical methods (Mohamad Ibrahim et al., 2010), chemo-enzymes (Mai et al., 2000) or by irradiation (Phillips et al., 1973). The graft co-polymerized materials are used in a number of applications in various fields ranging from adhesives, paint, coating materials, and emulsifiers to moulding materials and biomedical instrumentation. Poly(vinyl acetate), is a very ductile material, (Sánchez-Cabezudo et al., 2010) that can synthesize via free-radical polymerization. Recent work on poly(vinyl acetate) have blended it with poly(pyrrole) (Ppy) to improve the electrical conductance of Ppy over 90 days (Hosseini and Entezami, 2003) as well as enhance mechanical properties of less ductile materials (Jin et al., 2000). By grafting vinyl acetate onto lignin, the mechanical, and thermal properties of lignin can be enhanced and help to make better material with more desirable properties.

In this study, vinyl acetate was selected as monomer for grafting on lignin in presence of the initiator potassium persulfate (KPS) and the catalyst ammonium iron (II) sulfate. The influence of a various factors like reaction temperature, monomer concentration, initiator concentration and catalyst concentration on the graft copolymer formation were investigated to optimize the reaction conditions. The properties such as thermal stability, and hydrophobic character also reported.

2. Experimental

2.1. Materials

Lignin in powder form was received from FP Innovations, Canada. It was dried in an convection oven set to 100 °C for 48 h to remove the moisture. Vinyl acetate of purity greater than 99% was purchased from Sigma–Aldrich, Canada. The hydroquinone inhibitor was removed by washing with 2% sodium hydroxide solution. Ammonium iron (II) sulfate hexahydrate and potassium persulfate were purchased from Sigma–Aldrich, Canada and were used as is.

2.2. Graft copolymerization

Desired amount of lignin was placed in a 250 mL three-necked round bottom flask equipped with condenser tube. Vinyl acetate

Table 1
Reaction conditions used for the experiments.

Lignin (g)	Vinyl acetate (mL)	Catalyst $\times 10^{-4}$ (mol/L) ^a	Initiator $\times 10^{-2}$ (mol/L) ^b	Temperature (°C)
4	4	1.275	9.24	80
4	6	1.275	9.24	80
4	8	1.275	9.24	80
4	6	1.275	9.24	80
4	6	2.550	9.24	80
4	6	5.1	9.24	80
4	6	12.75	9.24	80
4	6	5.1	4.62	80
4	6	5.1	9.24	80
4	6	5.1	13.86	80
4	6	5.1	9.24	60
4	6	5.1	9.24	70
4	6	5.1	9.24	80

^a Catalyst – ammonium iron (II) sulfate.

^b Initiator – potassium persulfate.

was added slowly on to the lignin inside the flask. The mixture was kept for 15 min to adsorb VAC on to lignin and 40 mL water was added to the mixture with stirring. To this mixture, the initiator potassium persulfate and the catalyst ammonium iron (II) sulfate hexahydrate were added with constant stirring and continued the stirring till the completion of reaction at the desired temperature (Table 1). After the completion of the reaction, the reaction mixture was washed with distilled water till the pH of the filtrate become neutral. It was then dried at 100 °C using a convection oven for 24 h. The homopolymer, poly(vinyl acetate), was removed by extracting with toluene using a Soxhlet extractor for 24 h. The sample was then dried at 100 °C in a vacuum oven for 6 h.

The percentage of grafting and homopolymer formation was calculated using the following equations.

$$P_G = \frac{W_2 - W_1}{W_2} \times 100 \quad (1)$$

$$P_H = \frac{W_3 - W_2}{W_1} \times 100 \quad (2)$$

where W_1 is the initial weight of the lignin, W_2 is the weight of sample obtained after the Soxhlet extraction, W_3 is the weight of the sample before the extraction. P_G and P_H represent the grafting percentage and homopolymer percentage respectively.

In order to understand the changes suffered by lignin as a result of the chemical reaction, and the loss of material during the filtration and extraction process, a blank sample was prepared. Such blank was treated exactly under the same experimental conditions without monomer. Poly(vinyl acetate) was also prepared under the same experimental conditions.

2.3. Fourier transform infrared spectroscopy

The infrared spectroscopy of the samples was done using NICOLET 6700 ATR-FTIR instrument. Each spectrum was recorded with 36 scans in the frequency range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} . Analysis was done using the OMNIC spectra software supplied with the machine.

2.4. Differential scanning calorimetry

Glass transition temperature (T_g) of the samples was measured using differential scanning calorimeter (DSC) model TA Q200 from TA instruments. Analysis was conducted under the nitrogen atmosphere with 5–7 mg of sample in aluminium pan. The samples were heated from 30 to 200 °C at a heating rate of 10 °C/min.

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