

Effect of Nanofillers as Reinforcement Agents for Lignin Composite Fibers

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ABSTRACT: *Biobased nanocomposites* and composite fibers were prepared from organosolv lignin/organoclay mixtures by mechanical mixing and subsequent melt intercalation. Two organically-modified montmorillonite (MMT) clays with different ammonium cations were used. The effect of organoclay varying from 1 to 10 wt % on the mechanical and thermal properties of the nanocomposites was studied. Thermal analysis revealed an increased in T_g for the nanocomposites as compared with the original organosolv lignin. For both organoclays, lignin intercala-

tion into the silicate layers was observed using X-ray diffraction (XRD). The intercalated hybrids exhibited a substantial increase in tensile strength and melt processability. In the case of organoclay Cloisite 30B, X-ray analysis indicates the possibility of complete exfoliation at 1 wt % organoclay loading. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2877–2881, 2010

Key words: biomaterials; lignin; nanocomposites; organoclay; lignin fibers; mechanical properties

INTRODUCTION

Lignin is arguably the second most abundant macromolecule on earth. It is a principle component in wood providing structural integrity, resistance to biodegradation, and facilitating water transport within the plant. Commercially, lignin plays a vital role in pulp and paper manufacturing as part of chemical recovery process. Lignin is primarily burnt as a fuel for energy, however, as a part of the biorefinery concept, value-added utilization of lignin is critical.¹

Traditionally, a small amount of lignin, less than 2% of that produced, has been used as low cost filler or dispersants, adhesives, and surfactants.² Recently, thermoplastics with high lignin content have been produced by alkylating kraft lignin³ or blending kraft lignin with synthetic polymers.^{4–7} These new lignin-based materials possess mechanical properties comparable to polystyrene. Although 100% kraft lignin and alkylated kraft lignin films and fibers are quite brittle, they can be effectively plasticized by blending with suitable polyesters^{5,7} and polyethers.⁴

Lignin structure and properties vary depending on the wood species, industrial process utilized to isolate it, etc. Of the various technical lignins, organosolv lignins, such as those produced as part of bioethanol production,⁸ differ significantly from

other technical lignins. Structurally, organosolv lignins have a higher relative amount of phenolic hydroxyl groups, a more oxidized structure, possess low T_g 's and are easy to thermally process.⁹ As a result, organosolv lignins have advantages over other industrial lignins for composite-material applications. Feldman et al.¹⁰ reported that Alcell/poly(vinyl chloride) composites possess superior mechanical properties over comparable kraft and sodium-lignosulfonate-based materials. Likewise, Kadla et al.¹¹ have shown that Alcell lignin (organosolv lignin isolated by acidic ethanolysis of hardwood) is readily transformed into filament form suitable for carbon fibers without any chemical modification.

It has been shown that organic–inorganic hybrids/composites exhibit unexpected properties synergistically derived from the two components.^{12–14} The most notable case is that developed by Toyota where nanoreinforced nylon has been used to replace steel in engine components.¹⁵ Such polymer-layered nanocomposites (PLC) can be prepared using conventional polymer-processing techniques.^{15–18} Incorporation of only a few percent of nanofiller, such as organoclay,^{19–21} greatly improves mechanical, thermal, and barrier properties of the PLC as compared to that of the pristine polymer.²² The performance improvement of PLC depends greatly on the distribution, arrangement, and interfacial bonding between the silicate layers and the polymer matrix.²³ In this article, we report on the incorporation of organoclays into lignin, and its impact on the resulting lignin fiber properties.

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TABLE I
Structural Information of the Two Clays Utilized
in this Study

| Clay | Ammonium cation | XRD peak | Basal |
|--------------|--|------------------------|---------------|
| | | position (2 θ) | spacing (001) |
| | | degree | nm |
| Cloisite 20A | (CH ₃) ₂ (HT) ₂ N ⁺ Cl ⁻ | 3.90 | 2.42 |
| Cloisite 30B | (CH ₃)(T)(CH ₂ CH ₂ OH) ₂ N ⁺ Cl ⁻ | 4.73 | 1.88 |

T = tallow (~65% C18, ~30% C16, ~5% C14), HT = hydrogenated tallow.

EXPERIMENTAL

Materials

Two types of organically-modified montmorillonite (MMT) organoclays, Cloisite 30B and Cloisite 20A were purchased from Southern Clay Co. (Austin TX, USA). The structures of the respective counter ions of the organoclays and the related structural/physical information is listed in Table I.

Alcell lignin was obtained from Repap Enterprises INC. and used as received. The chemical and physical properties of the Alcell lignin are in Table II.

Lignin/clay composites preparation

The Alcell lignin was mechanically mixed with varying amounts of organoclay in a Retsch PM 200 ball-mill at 300 or 600 rpm for 10 or 30 min. The organoclay content was varied from 1 to 10 wt %. The various mechanically mixed Alcell/organoclays were then thermally extruded using a Dynisco Laboratory Mixing Extruder (Atlas Electric Devices Co.) equipped with ca. 0.8 mm spinneret.¹¹ The motor speed was 270 rpm (residence time ~30 s), and extrusion temperatures were varied between 130 and 150°C depending on the hybrid composition.

Characterization of Alcell/organoclay composites

X-ray diffraction (XRD) studies were performed using a Bruker D8 Discover X-ray diffractometer with an area array detector. Scans were collected from lignin/organoclay composites in the form of

extruded “sticks” at 40 kV and 20 mA in the 2 θ range from 0 to 10 degrees using Cu K α radiation.

Glass transition temperatures, T_g , of the Alcell lignin and Alcell/organoclay mixture powders and composite fibers were determined on TA Instruments Q 1000 DSC at a scan rate of 10°C/min over a temperature range of 0–150°C. All measurements were made using 2–3 mg samples in aluminum hermetic pans under a nitrogen atmosphere. The glass transition temperature was recorded at the midpoint temperature of the heat capacity transition of the second heating run. The result for each sample was reported as the average of 5 runs with standard deviations ~1°C. Prior to determining the T_g , thermogravimetric analysis (TGA) was performed to estimate the decomposition temperature of all samples.

Fourier transform Infrared (FTIR) analysis of the lignins was performed using the diffuse reflectance Fourier transform infrared (DRIFTIR) method. The lignin powder (10 mg) was dispersed in KBr (200 mg) and DRIFTIR measurements were recorded on PerkinElmer Spectrum One FTIR Spectrometer; 32 scans were collected with a spectral resolution of 4.0 cm⁻¹.

Molecular mass distributions were determined by gel permeation chromatography (GPC) using an Agilent 1100 series HPLC system equipped with two μ -Styragel columns (HR-4 and 5E) at 40°C and tetrahydrofuran (THF) (0.1 mol) as the eluting solvent. The GPC system was calibrated using standard polystyrene samples with molecular weights ranging between 580 and 1800 K. The injection volume was 100 μ L, and the lignin concentration was 1 mg mL⁻¹ THF (0.1 mol).

The mechanical strength of the composite fibers were measured with an Instron model 5565 using a 1 kN load cell and a gauge length of 25 mm. All reported values are the average of more than 20 fibers per sample. Fiber diameters were determined using a calibrated optical microscope and were recorded as the average of three measurements taken along the fiber.

RESULTS AND DISCUSSION

Impact of mechanical and thermal treatments on Alcell lignin structure

To enhance the dispersion of the organoclay within the lignin matrix, we utilized mechanical mixing of

TABLE II
Chemical Properties of Alcell lignin⁶

| | Functional groups (mmol/g) | | | | Molecular mass | |
|---------------|----------------------------|----------|----------|-----|----------------|-----|
| | Hydroxyl | | Methoxyl | S/G | MW | PDI |
| | Aliphatic | Aromatic | | | | |
| Alcell lignin | 3.6 | 4.3 | 5.6 | 2.3 | 2200 | 1.7 |

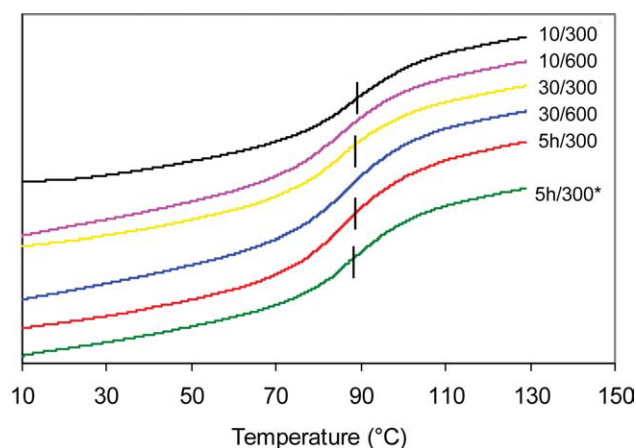


Figure 1 Effect of ball-milling on the T_g of Alcell lignin; time (min)/rpm; * no cooling period. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the components before thermal extrusion. However, as it is known that ball-milling can affect the chemical structure of native lignin during its isolation,²⁴ we needed to assess the effect of ball-milling on Alcell lignin to ensure, we were not manipulating the chemical and macromolecular properties. To do this, we utilized differential scanning calorimetry (DSC) and DRIFTIR spectroscopy. Figure 1 shows the DSC results obtained for lignin ball-milled for 10 and 30 min at 300 rpm and 600 rpm, as well as for 5 h at 300 rpm with and without a 10 min cooling interval after each 30 min of ball-milling. It can be seen that the glass transition temperature, T_g for all of the lignin preparations was $86 \pm 1^\circ\text{C}$, indicating no changes occurred in the macromolecular structure of the lignin as result of the various mechanical treatments.

DRIFTIR analysis (Fig. 2) and GPC analysis (Fig. 3) of the Alcell lignin before and after mechanical mixing (30 min at 600 rpm) and subsequent thermal extrusion also show no noticeable difference

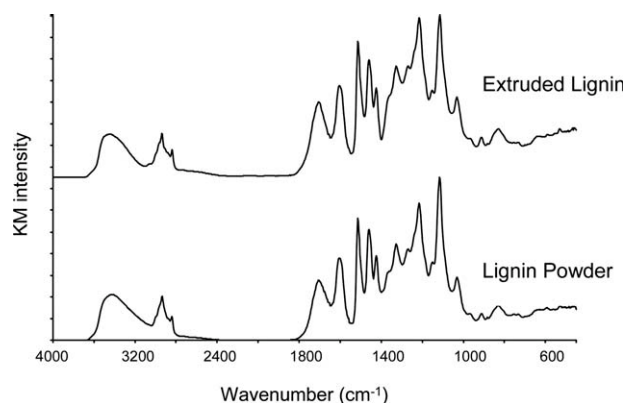


Figure 2 DRIFTIR spectra of Alcell lignin powder and fiber after mechanical mixing and thermal extrusion.

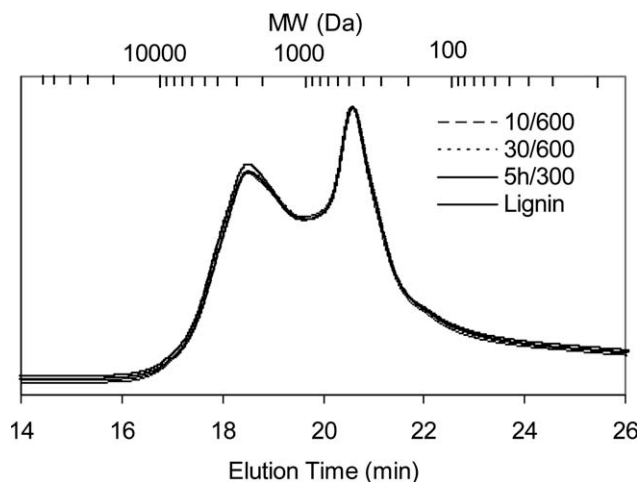


Figure 3 Effect of ball-milling on the GPC profile of Alcell lignin; time (min)/rpm.

between the samples. These results are quite surprising, considering the known effects of ball-milling on native lignin structure. However, this may be due to the fact that this is a severely degraded technical lignin and the milling conditions are quite mild as compared to those required to separate lignin from wood.

Alcell/organoclay composite fibers

Two organoclays, Cloisite 20A and 30B were evaluated as reinforcing agents in Alcell lignin. These two organoclays were chosen based on the differences in ammonium counterion; Cloisite 20A being more hydrophobic, containing an ammonium group with two methyl and two hydrogenated tallow groups, versus Cloisite 30B which contains an ammonium group with a single methyl and tallow group, and two hydroxy ethyl groups (Table I). Based on these chemical differences, it is anticipated that the two organoclays would disperse differently within the Alcell lignin, and hence produce different reinforcement and resulting composite properties.

The effect of mechanical action on the blending of organically-modified clays with Alcell lignin was evaluated using DSC. As per the milling study described above, the two organoclays and the Alcell lignin were mechanically mixed in a Retsch PM 200 ball-mill for 10 and 30 min at 300 and 600 rpm. To maximize the interaction with the lignin, a high organoclay content (10 wt %) was used. Table III shows the T_g 's of the original lignin and the various lignin/organoclay mixtures.

The observed T_g of the Alcell lignin increased upon addition of organoclay, with the highest T_g for the Alcell/organoclay mixtures occurring under the most severe conditions tested; ball-milling for 30 min at 600 rpm. As these conditions did not affect

TABLE III
Effect of Mechanical Mixing Time and Speed on the Glass Transition Temperature (T_g) of the Alcell Lignin and Alcell/Organoclay Mixtures (Organoclay Content - 10 wt %)

| | Mechanical mixing | | T_g ($^{\circ}\text{C}$, $\pm 1^{\circ}\text{C}$) |
|--------------|-------------------|-------------|--|
| | Time (min) | Speed (rpm) | |
| Lignin | 0 | 0 | 90 |
| Cloisite 20A | 10 | 300 | 107 |
| | 10 | 600 | 111 |
| | 30 | 300 | 107 |
| | 30 | 600 | 110 |
| Cloisite 30B | 10 | 300 | 106 |
| | 10 | 600 | 107 |
| | 30 | 300 | 106 |
| | 30 | 600 | 111 |

the chemical or macromolecular structure of the lignin (Figs. 1 and 2), and facilitate the best mixing of components, these conditions were chosen for the preparation of the lignin/organoclay composite fibers.

In addition to affecting the T_g of the lignin powders, the addition of organoclay to Alcell lignin also improved its thermal processibility; the organoclay reinforced Alcell lignin more readily formed continuous fibers, and the fibers were less brittle as compared to those from the pure lignin. Organoclay addition also decreased the temperature required to melt spin the lignin fibers, with increasing organoclay content further lowering the required melt spinning temperature. As expected, the effect on melt spinning was different between the two organoclays. The Alcell/Cloisite 20A melt spinning temperatures were slightly higher than those of the corresponding Alcell/Cloisite 30B mixtures. Likewise, differences were observed in the thermal and mechanical properties of the melt spun fibers.

Table IV lists the glass transition temperatures of unextruded (powder) and extruded (fiber) Alcell/organoclay (5 wt %) hybrids. In general, thermal extrusion of the lignin/organoclay mixtures led to a slight increase in T_g , both before and after thermal extrusion. Interestingly, the increase in T_g is comparable to that observed for the thermal extrusion of lignin alone, and may be the result of lignin condensation reactions rather than increased interaction with the organoclay.²⁵ Compared to the Cloisite 30B composites, the Alcell/Cloisite 20A composites exhibit a similar, within error, T_g .

A substantial increase in tensile strength was observed upon addition of Cloisite 20A and Cloisite 30B into the Alcell lignin. Incorporating just 5 wt % of Cloisite 20A lead to a 54% increase in tensile strength, while the same amount of Cloisite 30B enhanced the tensile strength by more than 70%. These results support previous systems, wherein

TABLE IV
Tensile Strength and Glass Transition Temperatures of Alcell Lignin and Alcell Lignin/Cloisite Organoclay Composite Fibers (Organoclay Content - 5 wt %)

| | Alcell | Alcell/ Cloisite 20A | Alcell/ Cloisite 30B |
|---|------------------|-------------------------|-------------------------|
| Spinning temperature ($^{\circ}\text{C}$) | 160–170 | 150–165 | 150–165 |
| Glass transition ($^{\circ}\text{C}$) | | | |
| Powder | 90 (± 3) | 96 (± 3) | 93 (± 3) |
| Fiber | 103 (± 3) | 107 (± 3) | 103 (± 3) |
| Tensile strength (MPa) | 15.8 (± 1) | 24.4 (± 1) | 26.8 (± 1) |

organoclay addition enhances mechanical properties through modified phase morphology and improved interfacial properties.²⁶ Both of the organoclays possess hydrophobic Tallow groups, which can interact with lignin through nonbonding hydrophobic interactions. However, Cloisite 30B contains hydrophilic hydroxy ethyl groups on the ammonium cation, which may interact with Alcell lignin through hydrogen bonding interactions.⁴ Such interactions may not substantially affect the observed T_g , but may enhance dispersion of the organoclay within the polymer matrix.

The most common technique used to characterize the structure of polymer-silicate hybrids and study the kinetics of polymer-melt intercalation is XRD. By monitoring the position, shape, and intensity of the basal reflection from the silicate layers, the hybrid structure (intercalated, where extended polymer chains occupy the interlayer space between silicate layers or exfoliated, where the silicate layers are dispersed in a continuous polymer matrix) may be identified.²⁷ Briefly, for exfoliated hybrids, the extensive layer separation associated with delamination of

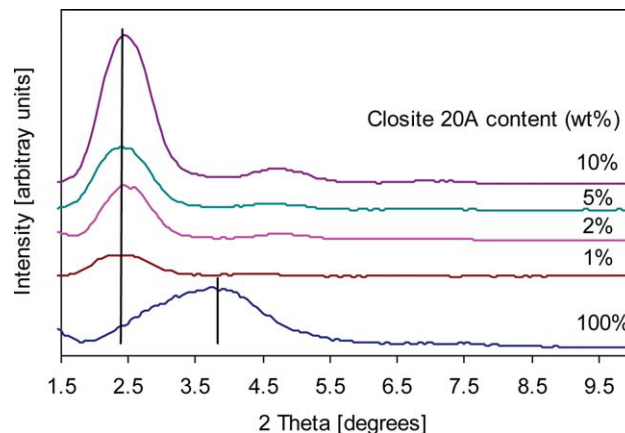


Figure 4 XRD patterns of Cloisite 20A and Alcell/Cloisite 20A hybrids with clay contents of 1, 2, 5, and 10 wt %. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

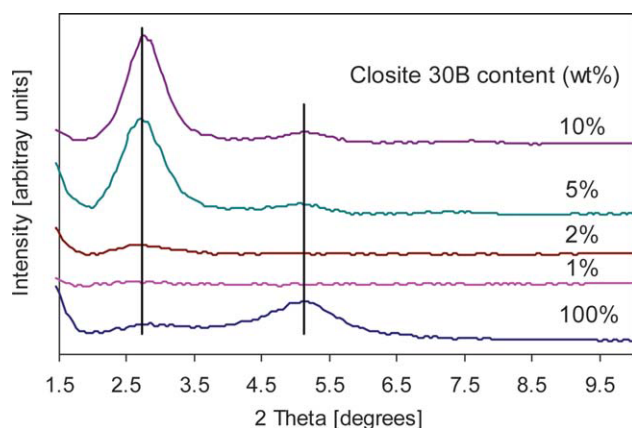


Figure 5 XRD patterns of Cloisite 30B and Alcell/Cloisite 30B hybrids with clay contents of 1, 2, 5, and 10 wt %. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the original silicate structure in the polymer matrix results in the eventual disappearance of any coherent X-ray scattering from the layers. On the other hand, for intercalated hybrids, the finite layer expansion associated with polymer intercalation results in the appearance of a new basal reflection corresponding to the larger gallery height. Finally, in systems in which the registry of the clay nanolayers is retained (conventional composites), the characteristics (position, height, and width) of the silicate basal reflection remain unchanged. Figures 4 and 5 show the XRD patterns of Alcell lignin hybrids reinforced with Cloisite 20A and Cloisite 30B at clay contents varying from 1 to 10 wt %.

As expected lignin doesn't show any XRD pattern, due to its amorphous state. Cloisite 20A and Cloisite 30B, however exhibit a single peak at $2\theta = 3.9^\circ$ and $2\theta = 5.0^\circ$, respectively. For all of the Cloisite 20A hybrids (Fig. 4) a new peak appears at $2\theta = 2.4^\circ$ indicating intercalation of Alcell into the galleries of the silicate layers of the Cloisite 20A. This corresponds to an increase in the d -spacing from ~ 2.4 to ~ 3.7 nm. Similarly, the Cloisite 30B hybrids also see a change in the XRD pattern (Fig. 5), with the original peak at $2\theta = 5.0^\circ$ disappearing and a new peak at the lower 2θ forming, again indicating significant intercalation of Alcell into the clay galleries. Likewise, there is an increase in the d -spacing of the clay platelets from ~ 1.9 to ~ 3.2 nm. However, in the case of the Cloisite 30B hybrids, at low organoclay loading, ~ 1 wt %, the XRD pattern does not show any peaks, consistent with exfoliation of the filler.

CONCLUSIONS

Novel lignin-organoclay hybrids were prepared through a melt intercalation method using two commercially available organoclays, Cloisite 30B and

20A. Both organoclays produced lignin intercalation compounds irrespective of the different hydrophobicities of the organo component (ammonium cations) in these clays. The T_g 's for both systems were increased as compared to the pristine lignin suggesting favorable interaction between the lignin macromolecules and the organoclays. The addition of the organoclays to the Alcell lignin decreased the extrusion temperatures and improved the extrusion properties enhancing the spinnability of lignin/organoclay composite fibers, which exhibit an obvious increase in tensile strength with regards to the original organosolv lignin.

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