

Preparation of synthetic wood composites using ionic liquids

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Abstract Synthetic wood composite films containing cellulose, hemicelluloses, and lignin, the three major components of natural wood, were prepared in a room temperature ionic liquid solvent, 1-ethyl-3-methylimidazolium acetate, [EMIM][Ac]. Various synthetic wood composites were obtained by dissolution of individual wood components together with additives, including polyethylene glycol (PEG), chitosan, and multi-wall carbon nanotubes (MWNTs) in [EMIM][Ac]. The addition of water affords a gel that was dried in either a low humidity environment or under vacuum. Synthetic wood films showed smoother surface textures, higher water resistance, and higher tensile strengths than cellulose films formed by the same

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methods. Tailor-made synthetic wood composites were also prepared having a variety of desirable properties, including antimicrobial activities, controlled hydrophobicity/philicity, high relative dielectric constant, and a high degree of cohesiveness.

Introduction

Composites are engineered materials made from two or more constituents with different physical or chemical properties (Šimkovic 2008). Biopolymer-based composites recently have garnered considerable interest, as they can decrease dependency on fossil fuel and are often biocompatible, biodegradable and possess a high degree of functionality. Biopolymers are naturally obtainable macromolecules including polysaccharides, polyphenols, polyesters, polyamides, and proteins (Lee et al. 2010). The inherent biodegradability of these materials makes biopolymers particularly promising for developing environmentally friendly materials. While films of cellulose and cellulose blends have been solvent cast (Davé and Glasser 1997; Chanzy et al. 2003), the preparation of such biopolymer-based materials remains a challenge because of the low solubility of many biopolymers in conventional solvents. Therefore, there is a strong interest in devising new, non-aqueous solvents for the dissolution of biopolymers to prepare biopolymer-based composite materials (Novoselov et al. 2007).

Lignocellulosic biomass, such as agricultural residues, forestry wastes, waste paper, and energy crops, has long been recognized for their potential value as sustainable sources of biopolymer composites (Himmel et al. 2007; Li et al. 2008). Lignocellulose consists of three major biopolymers—cellulose, hemicelluloses, and lignin—all of which have distinct chemical, physical, and structural properties (El Seoud et al. 2007). Cellulose, a linear polysaccharide of D-glucose residues linked by β -(1 \rightarrow 4)-glycosidic bonds (Fig. 1a), is the most abundant renewable biopolymer on earth (Brown 2004). It has excellent thermal and mechanical properties. Hemicelluloses are heterogeneous, branched polymers of pentoses, hexoses, and acetylated sugars, with xylans (Fig. 1b) being the most plentiful of the hemicelluloses (Saha 2003). Lignin is an aromatic network polymer composed of phenylpropanoid units (Fig. 1c) and helps to bind together cellulose and hemicelluloses (Chandra et al. 2007).

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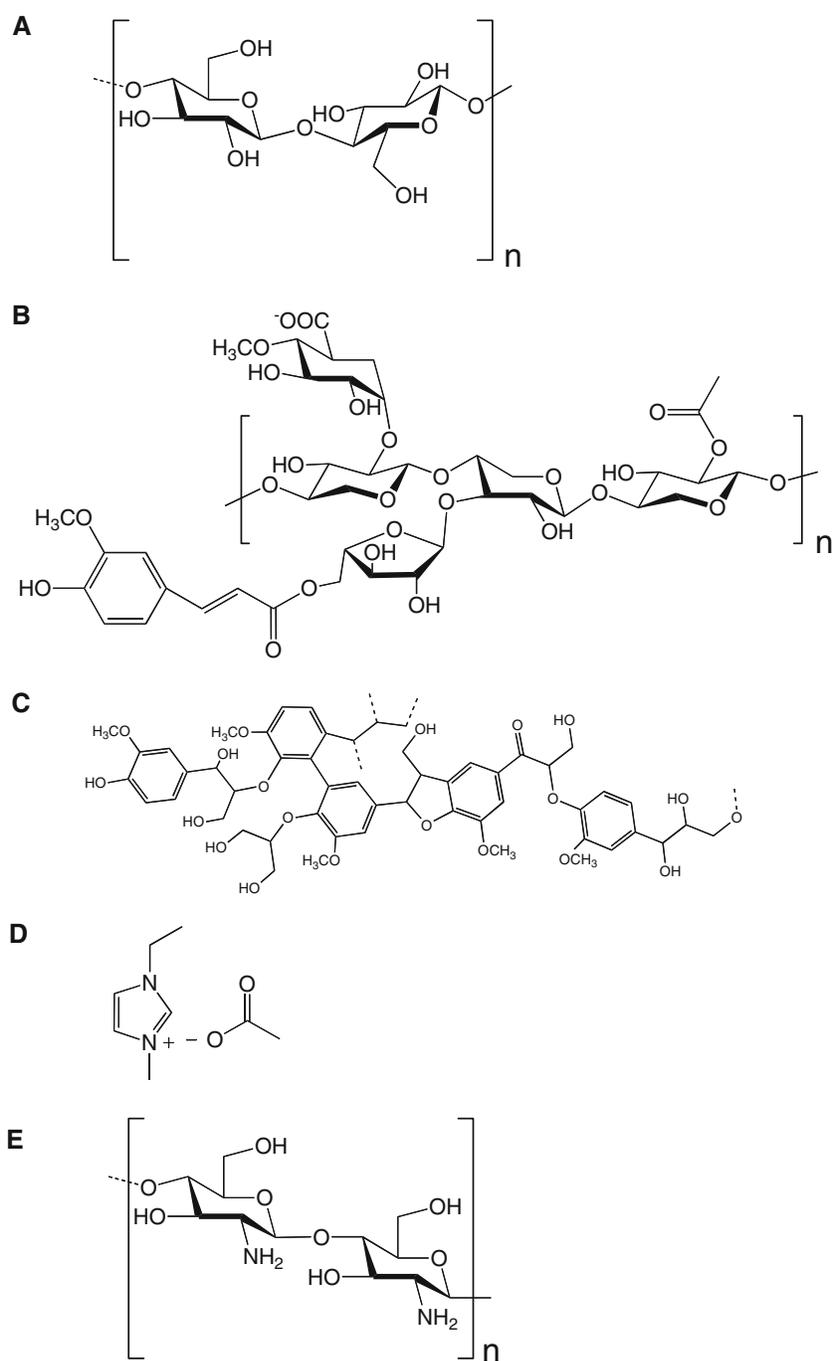


Fig. 1 Structure of **a** cellulose, **b** xylan, **c** lignin, **d** [EMIM][Ac], and **e** chitosan with varying levels of deacetylation

The use of 1-alkyl-3-methylimidazolium salts as solvents for cellulose was first reported by the Rogers group (Swatloski et al. 2002). They tested the ability of ILs containing the 1-butyl-3-methylimidazolium ([Bmim]) cation with various anions to dissolve cellulose, and the most effective anion was found to be the chloride. Cellulose could be dissolved at 25 wt% in [Bmim][Cl] assisted by microwave irradiation, and the dissolved cellulose can be reconstituted by the addition of an anti-solvent such as water, ethanol, or acetone. These results have opened up new paths for commercially relevant routes to homogeneous cellulose chemistry for the preparation of various unmodified cellulose composites. Recently, acetate, formate, methyl phosphate, and dicyanamide counter anions of 1-alkyl-3-methylimidazolium salts were reported as good ILs for cellulose dissolution (Fukaya et al. 2006; Zhao et al. 2008, 2009a; Kosan et al. 2008). Among the room temperature, ILs with low viscosity and toxicity suitable for cellulose dissolution are 1-ethyl-3-methylimidazolium acetate ([EMIM][Ac]) (Fig. 1d) and formates of allylimidazolium-based ILs. Recently, the solubilities of kraft lignin in various ILs were investigated in the laboratory (Lee et al. 2009). The highest lignin solubility was obtained using [Mmim][MeSO₄] and [Bmim][CF₃SO₃]. ILs containing the [Cl] anion also showed high solubility (>100 g/kg).

Several groups have reported the full dissolution of woods in ILs (Fort et al. 2007; Kilpeläinen et al. 2007; Sun et al. 2009). By dissolving wood in ILs, solutions were obtained that could be used to analyze the biopolymer composition of woods. Furthermore, these wood components could be functionalized with acetyl, benzoyl, and carbonyl groups (Chiappe and Pieraccini 2005; Sheldon et al. 2002; Welton 1999). To date, however, the reconstitution of wood, having selected and defined ratios of cellulose, hemicelluloses, and lignin, together with additives inducing special properties from fully dissolved solutions in ILs, has not been reported. In this study, the authors hypothesized that wood components, cellulose, hemicelluloses, and lignin could each be prepared in IL solution and mixed in varying amounts to fabricate wood films and wood coating composites with specialized properties (Wu et al. 2009).

Experimental

Materials

Cellulose solution in [EMIM][Ac] (CellionicTM, degree of polymerization ~ 680), xylan from birch wood (xylose residues > 90% by high performance anion exchange (HPAE) chromatography), [EMIM][Ac], PEG (MW 400), and chitosan from crab shells (MW 150,000, deacetylated 75–85%) was obtained from Sigma–Aldrich (St. Louis, MO). Indulin AT, a purified softwood kraft lignin from pine, was generously provided by MeadWestvaco (Charleston, SC). High-purity multi-wall carbon nanotubes were obtained from Swan Chemical Inc. (ElicarbMW, ~95% pure).

Preparation of synthetic wood solutions in [EMIM][Ac]

Xylan (0.3 g) and lignin (0.2 g) were mixed with Cellionic™ (10 g containing 0.5 g cellulose) in a 100-mL round bottom flask. The flask was heated with stirring at 90°C for 3 h. The resulting dissolved synthetic wood solution [5% cellulose, 3% xylan, and 2% lignin all (wt%)] was used alone or in combination with additives (5% (w/w) PEG or 0.5% (w/w) chitosan) at 90°C with stirring for 2 h to prepare synthetic wood/polymer composites. Synthetic wood/MWNT composites were prepared by first using a mortar and pestle to grind 10 mg MWNTs for 20 min in 1 g [EMIM][Ac] to disperse the MWNTs. The MWNTs remained dispersed for over 1 month in [EMIM][Ac]. The dispersed MWNTs were next mixed with synthetic wood solution (cellulose/xylan/lignin, 5/3/2, wt%).

Preparation of synthetic wood composites film and coating

Synthetic wood solutions (with and without additives) were spin-coated on glass slides. The speed of the spin-coater was increased in steps from 500 to 2,500 rpm over 3 min, after which the wood solutions gelled. Coated synthetic wood solution was maintained at room temperature for 10 min and then gently washed with water for 10 min to remove [EMIM][Ac]. The synthetic wood hydrogel obtained was dried in a desiccator to remove residual water. After drying for 3 h, a flexible synthetic wood film was obtained that could be easily peeled off from the glass slide. After longer drying periods of 1 day or more, the synthetic wood film tightly attached to the glass slide and could not be easily removed. Thus, all free films tested in the current study were dried for 3 h.

Scanning electron microscopy (SEM) measurements

Scanning electron microscopy was conducted on a JEOL 6335 JSM with an accelerating voltage of 10 kV. The synthetic wood films were sputter-coated with a thin gold layer before measurements.

Contact angle measurements

Contact angle measurements used to qualitatively assess the hydrophobicity of the composite films were performed with 100-00 NRL C.A. Goniometer from Ramé-Hart Instrument Co. (Netcong, NJ) using deionized water at room temperature.

Analysis of optical

Films of the same thickness (0.1 mm) were cast as described above. Optical properties of a synthetic wood film (5% cellulose 3% xylan and 2% lignin) were compared with a control cellulose film with a UV–Vis–NIR spectrophotometer.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed using a TA Instruments TGA Q50 connected to a computer. Temperature was ramped at 1°C per minute, from room temperature up to 500°C, with the furnace open to allow airflow along with nitrogen purge gas.

Tensile strength test

The tensile strength properties were determined from cast films peeled off and dried for an additional 24 h under vacuum at room temperature to remove residual water. Mechanical test specimens were cut from larger samples of synthetic wood using a scalpel. Rectangular test samples (20 mm long, 10 mm wide, 0.1 mm thick) were obtained in the principal fiber direction (assessed by inspection) of the synthetic wood. Specimens were then mounted in an INSTRON Materials Testing Machine (Model 5543) equipped with a 10-N static load cell (Serial # 43311), using hydraulic grips (Instron 2712-001), and loaded to failure using a constant rate (0.25 mm/min) elongation protocol. Specimens were tested with a 5-mm gauge length, and load, time, and grip-to-grip displacement were measured. Tensile strength was calculated by dividing the peak load by the initial cross-sectional area of the specimen.

Electrical measurements

A True RMS MultiMeter (Model Number 22-816) obtained from Extech Instruments (Waltham, MA) was used to test the resistance of the MWNT-synthetic wood composite. The two electrodes were inserted at different positions into the composite, and resistance was measured, all of which show very high ($M\Omega$) sheet (in-plane) resistance. Measurements of relative dielectric constant values for both standard and MWNT-modified samples were performed with an Agilent Precision 4284A LCR meter over a range of 10 Hz–1 MHz.

Antimicrobial activity

Staphylococcus aureus was grown in culture media and re-suspended in phosphate buffer at a concentration of 10^4 CFU/ml. Five microliters of cell suspension was incubated with cellulose, synthetic wood, and synthetic wood/chitosan-coated slide glasses (coated surface is 2 cm \times 2 cm) for 1 h. Then, 0.05 ml of cell suspension was spread on a LB agar plate and incubated for 24 h at 37°C. Each slide glass was also stamped on a LB plate and incubated for 24 h. The antibacterial efficacy of synthetic wood film composites was compared with that of the cellulose control by counting colonies under UVA illumination.

Results and discussion

Preparation of synthetic wood film

A synthetic wood solution, consisting of 5% (w/w or w/v) cellulose fiber, 3% (w/w) hemicelluloses (xylan from birchwood), and 2% (w/w) kraft lignin, was prepared in [EMIM][Ac] to mimic a real wood sample. [EMIM][Ac] was selected as an excellent solvent for wood components because of the solubility of each wood component in this IL. Cellulose and lignin are soluble in [EMIM][Ac] at 90°C at concentrations >200 and >300 g/kg, respectively (Lee et al. 2009). After 3 h of incubation at 90°C, all three wood components dissolved in [EMIM][Ac], affording a completely clear solution. Following warm-up, and after washing with water to remove [EMIM][Ac], a synthetic wood hydrogel was formed (Fig. 2a), which upon drying for 3 h, afforded a transparent and flexible synthetic wood film that could be easily recovered by peeling it from the glass slide (Fig. 2b) (Aaltonen and Jauhiainen 2009). When the synthetic wood film was dried for 1 day in the desiccator, it bonded tightly to the glass slide forming a synthetic wood coating. Potential applications of films for biodegradable packaging materials require high water resistance and good tensile strength. For these reasons, synthetic wood solutions containing cellulose, xylan, and lignin (5:3:2) in [EMIM][Ac] were used to obtain films and coating with more optimal properties (Fig. 3d). Synthetic wood solutions in [EMIM][Ac] gave improved film forming properties when compared with cellulose or cellulose/lignin solutions in [EMIM][Ac] (Fig. 3a–c). Synthetic wood films showed stronger hydrophobic character than control cellulose films. Contact angle measurements of de-ionized water on cellulose films gave an average value of 45°, while 1–1 blended films of cellulose and lignin had average contact angle values of 54°. This can be attributed to both the effect of lignin making the surface smoother and also to the reduction of the number of cellulose hydroxyl groups available on the surface (since this film has only 50% cellulose by weight). This effect was further confirmed on synthetic wood films with cellulose, xylan, and lignin (5:3:2), which had the highest average contact angle values at 72°. This is attributed to the increased smoothness of the film, with a similar number of exposed hydrophilic cellulose hydroxyl groups on the surface as in the cellulose–lignin mixed film. The idea that the surface roughness contributes significantly is supported by the fact that this film has less hydrophobic lignin, yet has the highest contact angle of all the films studied. The tensile strength of synthetic wood film

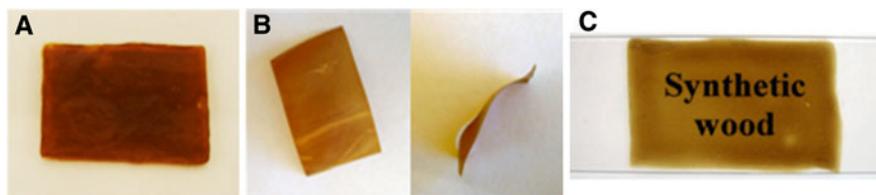


Fig. 2 Synthetic wood. **a** Wet hydrogel, **b** freestanding film (*top* and *side* views), and **c** coating on glass

was 61.7 ± 5.6 MPa, substantially higher than the 1 MPa reported for xylan films (Goksu et al. 2007) and also higher than the 15–60 MPa values reported for functionalized cellulose films (Tharanathan 2003). The high tensile strength of the synthetic wood film appears to result from the presence of lignin, despite the absence of any covalent chemical bonding between the cellulose and the lignin. Strong hydrogen bonding between cellulose, xylan, and lignin is a likely source of this improved tensile strength, as some hydroxyl groups of lignin are quite acidic and therefore prone to hydrogen-bonding interactions. An additional consideration is that lignin can act as a rigid structural component, which behaves as a cross-linker among linear-structured cellulose and xylan. Therefore, the composite films formed by this method showed significantly enhanced mechanical strength compared with similar cellulose or xylan films (Fig. 3).

2-D AFM images show that the outer surface of cellulose film (Fig. 4a) has a much rougher surface than the cellulose/xylan/lignin film (Fig. 4c). Cellulose/lignin film (Fig. 4b) afforded a surface that was not uniform. This surface heterogeneity may explain why the cellulose/lignin films become brittle with increasing lignin content.

The 1-D AFM line scans from the 2-D maps shown in Fig. 4 allow for an empirical comparison of the surface roughness of the studied films (Fig. 5). It can be seen that the films become smoother with the addition of lignin and are smoothest with the addition of both xylan and lignin. Each 2-D map shows the location of three representative 1-D line scans, and these are color-coded and begin at the white/blue box, which corresponds to the blue box shown at the start of the 1-D line scan graphs. The surface roughness can be observed by simply comparing the vertical scales. The approximate magnitudes of surface features for the cellulose, cellulose–lignin, and cellulose–xylan–lignin films are 300, 100, and 50 nm, respectively.

SEM was also used to image cellulose, a cellulose/lignin, and a cellulose/xylan/lignin film (Fig. 6). The brittleness of the cellulose only film was readily apparent from its fragmented surface. The cellulose/lignin film gave a surface made of scales while the cellulose/xylan/lignin film had a relatively smooth surface.

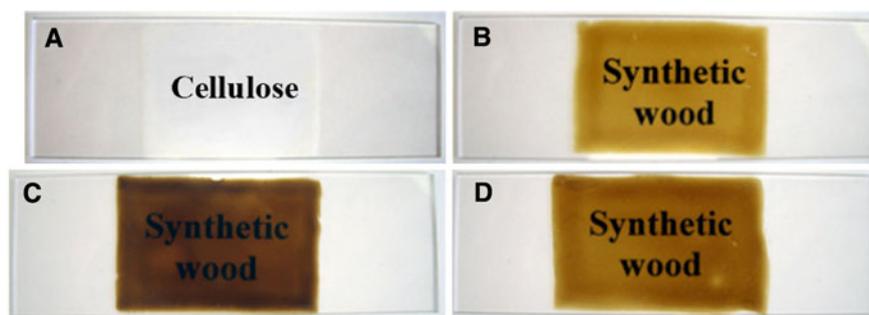


Fig. 3 Synthetic wood films and a cellulose film placed on paper with the printed words “synthetic wood” to illustrate color intensity and transparency. **a** Cellulose only for comparison, **b** cellulose/lignin (5/2, wt% in [EMIM][Ac]), **c** cellulose/lignin (5/5, wt% in [EMIM][Ac]), and **d** cellulose/xylan/lignin (5/3/2 wt% in [EMIM][Ac])

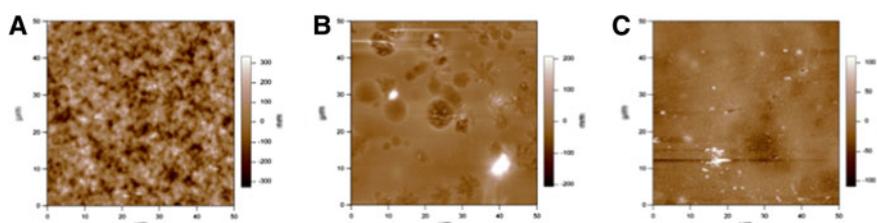


Fig. 4 AFM images of the surface of the synthetic wood films. **a** Cellulose only, **b** cellulose/lignin (5/5, wt% in [EMIM][Ac]), and **c** cellulose/xylan/lignin (5/3/2, wt% in [EMIM][Ac])

Thermal stability of the synthetic wood films was evaluated by using a representative sample (5% cellulose, 3% xylan, and 2% lignin). The sample was placed into the weighing pan, and the furnace temperature was raised until thermal breakdown was observed as a drop in weight, which is caused by sample material vaporizing in the presence of air. Thermal breakdown of a control cellulose film began to occur at $\sim 200^{\circ}\text{C}$, and the synthetic wood sample began at $\sim 230^{\circ}\text{C}$, which represents a moderate improvement in thermal stability. This improvement in thermal stability can be partially explained by the fact that at temperatures of around 600°C , cellulose loses more than 95% mass due to thermal degradation. Meanwhile, at the same temperature, lignin mass loss does not exceed 60% (Bartkowiak and Zakrzewski 2004). Additionally, there are cross-linking and hydrogen-bonding interactions between the lignin and the cellulose and xylan that also improve the thermal stability of these films.

Optical properties of a synthetic wood film (5% cellulose, 3% xylan, and 2% lignin) were compared with a control cellulose film with a UV–Vis–NIR spectrophotometer (Fig. 7). While both films were optically transparent in the visible spectrum, the synthetic wood film showed strong absorption in the blue to violet region of the visible spectrum, which is consistent with the characteristic brown color of the film. The synthetic wood showed improved absorbance of infrared over cellulose, which suggests it would perform better as an insulating film. Synthetic wood also significantly outperformed the cellulose control film in UV absorption. The cellulose did not perform well for longer wavelength UVA light, and this is important to note as sunlight consists of more UVA than UVB. Both films effectively blocked UVB radiation, but the synthetic wood clearly outperforms the cellulose control in absorption of electromagnetic radiation. This can have important implications in applications such as UV-blocking coatings (e.g., sunglasses and medicine bottles), thermal insulation (e.g., food packaging), and preventing damage such as photo-bleaching from visible light (e.g., windows and protective cases).

Synthetic wood composite films

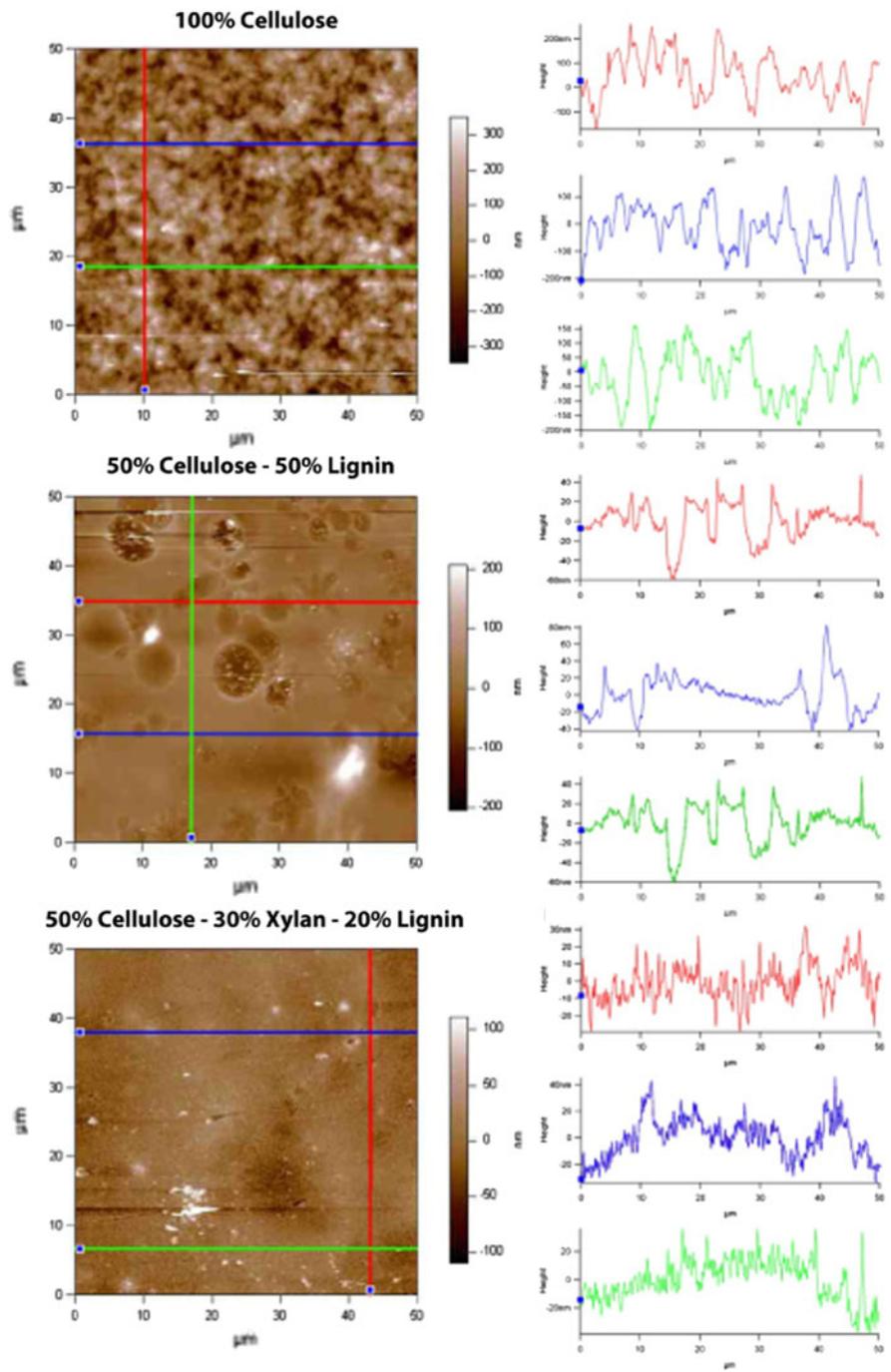
The major reason for using ILs to prepare biopolymer composites is the excellent solvating power of ILs, which can be exploited in the generation of hybrid composites containing both natural and unnatural components. To that end, various

Fig. 5 1-D AFM line scans from the 2-D AFM maps shown in Fig. 4. These line scans give cross-sectional data that show the relative surface roughness of the films. Each map shows 3 line scans to the right (corresponding to the cross section by color). The cellulose film has the highest roughness with approximately 300-nm surface features. The cellulose–lignin film has approximately 100-nm surface features. The cellulose–xylan–lignin synthetic wood film was the smoothest with approximately 50-nm surface features

synthetic wood/polymer or nanoparticle composites were prepared by dissolving wood components and polymers in [EMIM][Ac] followed by reconstitution with water. Synthetic wood (cellulose/xylan/lignin, 5/3/2, wt%)/polymer (5% PEG (MW 400) and 0.5% chitosan (Fig. 1e)) composites were prepared (Fig. 8). After mixing for 3 h at 90°C, all of the components fully dissolved to afford a clear viscous solution that was spin-coated onto a glass slide. A transparent and thin film of synthetic wood/polymer composite was obtained after washing with water to form a hydrogel, and then subsequent drying removes water and solidifies this film (Gabrielii and Gatenholm 1998). The surface of the synthetic wood/PEG composite film (Fig. 8a) was stickier and more hydrophilic than the synthetic wood film, with an average contact angle of 32°, which is less than all other tested samples, due to the humectant properties of PEG.

The surface of the synthetic wood (Fig. 8a) and synthetic wood/chitosan composite films (Fig. 8b) showed an antibacterial effect when exposed to *Staphylococcus aureus*, affording 46 and 96% bacterial resistance, respectively, which represents a significant improvement compared to a cellulose control which shows negligible activity. The kraft lignin has been reported to be an antibacterial reagent for phytopathogenic bacteria (Dizhbite et al. 2004). Also, chitosan is a well-known antibacterial compound (Möller et al. 2004). It is generally agreed that positive charges on chitosan molecules interface with the negatively charged residues of the macromolecules on bacterial cell surfaces, and this leads to bacterial cell death (Lee et al. 2009, 2010). Therefore, synthetic wood/chitosan films likely have excellent antibacterial properties by the combined effects of both kraft lignin and chitosan.

Synthetic wood/multi-wall carbon nanotube (MWNT) composites were next prepared by using a mixture of synthetic wood solution and dispersed MWNTs. The mixture of MWNT and synthetic wood in [EMIM][Ac] (cellulose/xylan/lignin/MWNTs, 5/3/2/0.025 or 0.1 wt%) was film cast on the glass slide. The resulting synthetic wood/MWNT film was dark and transparent indicating that the MWNTs were well dispersed (Fig. 8c). The synthetic wood material prepared with MWNTs maintained a very high resistance (megaohms), even at high loading, suggesting that it would make a suitable candidate for a flexible high dielectric insulator composite. High relative dielectric constant (ϵ_r) polymer composites are gaining increasing interest in the field of materials science. Polymer composites containing MWNTs can have quite high relative dielectric constant values (Yang et al. 2009; Zhao et al. 2009b). When the MWNT network approaches the percolation threshold for conduction but does not reach it, the values of the relative dielectric constant are substantially improved. This opens up the possibility of controlled formation of high and low dielectric materials. An example of such an application is in the functional components of batteries and supercapacitors (Pushparaj et al. 2007).



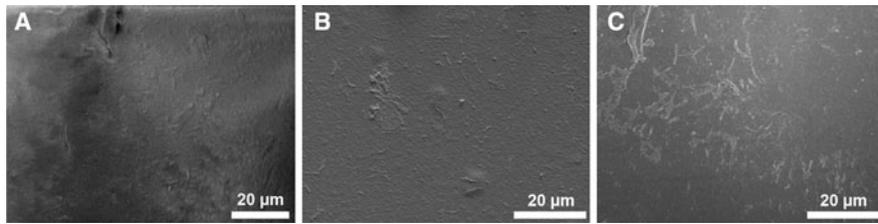


Fig. 6 SEM analysis of synthetic woods prepared from [EMIM][Ac] solutions containing **a** 5% cellulose, 0% xylan, and 0% lignin; **b** 5% cellulose, 0% xylan, and 5% lignin; and **c** 5% cellulose, 3% xylan, and 2% lignin

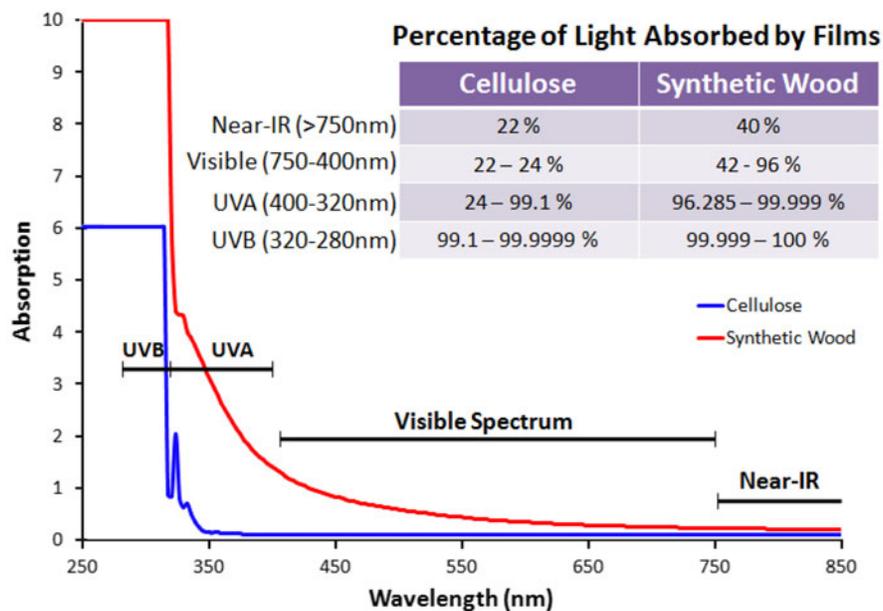


Fig. 7 UV–Vis–NIR study of two composite films. The cellulose control shows lower absorption over all wavelengths, with the synthetic wood sample absorbing nearly 100% of both UVA and UVB

To confirm the improvement of the dielectric properties of the synthetic wood composite by the addition of MWNTs, the relative dielectric constant of a 0.1 wt% MWNT loaded sample (Fig. 8d) was measured along with a standard synthetic wood control sample (Fig. 3d). The MWNT loaded sample had a significantly improved value of $\epsilon_r \approx 57$, compared to the value of the control $\epsilon_r \approx 13$, when measured at 1 MHz.

Conclusion

In this work, synthetic wood composite films were prepared consisting of cellulose, xylan, and lignin, the three major components of lignocellulosic biomass. These

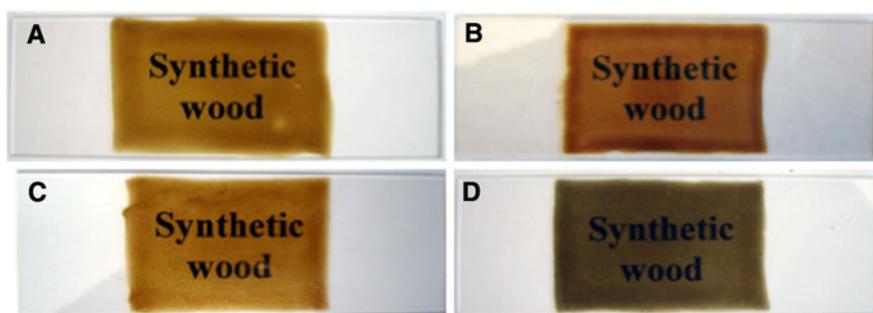


Fig. 8 Synthetic wood composite coatings with property altering additives. **a** cellulose/xylan/lignin/PEG (5/3/2/5, wt% in [EMIM][Ac]), **b** cellulose/xylan/lignin/chitosan (5/3/2/0.5, wt% in [EMIM][Ac]), **c** cellulose/xylan/lignin/MWNTs (5/3/2/0.025, wt% in [EMIM][Ac]), and **d** cellulose/xylan/lignin/MWNTs (5/3/2/0.1, wt% in [EMIM][Ac])

films were spin-coated from [EMIM][Ac] and reconstituted with water and dried. Synthetic wood films had improved physicochemical properties compared with cellulose, xylan, and lignin films. The advantages of synthetic wood composites include low production cost by using renewable biomaterials, reduced biodegradability compared with cellulose composites because of the presence of lignin, greater water resistance, and potential for modification and functionalization. Tailor-made synthetic wood films can be obtained simply by changing component ratios of synthetic wood solution in [EMIM][Ac]. By including additives in synthetic wood composites, a wide variety of materials can be prepared having special properties, such as high tensile strength, conductivity, and antimicrobial properties. Film color might also represent an important property if the films were to be used for the packaging of light-sensitive materials. The role of lignin in the 3-D network of the material and the possible influence this may have on the observed tensile strength will require further characterization of the crystallinity of the materials and will be the focus of future studies.

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