Montmorillonite–levan nanocomposites with improved thermal and mechanical properties

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ABSTRACT

This work reports on the structure and properties of novel nanocomposites composed of exfoliated montmorillonite clay blended with levan, a polysaccharide produced by *Bacillus* sp. Dry levan is very brittle, making it difficult to obtain stand-alone films. MMT–levan composites were prepared by solution blending in water, coating on plastic surfaces, partial drying at 50 °C, and conditioning in air at 50–60% relative humidity. This process results in freestanding, transparent, and flexible films of pure levan and MMT–levan composites plasticized by 10–15 wt% water. XRD patterns from levan–MMT composites indicate an MMT interlayer spacing 0.62 nm greater than that of the starting MMT, suggesting re-stacking of MMT platelets coated by adsorbed, uncoiled levan molecules. FTIR results suggest that levan adheres to MMT via water-mediated hydrogen bonding between the levan's hydroxyl groups and MMT surface oxygens. MMT–levan composites have improved thermal stability and a well-defined glass transition temperature that increases with MMT loading. The tensile moduli of levan–MMT composites increase by as much as 480% relative to pure levan. The XRD and mechanical property results suggest that MMT reinforces levan through a filler network structure composed of MMT platelets bridged by adsorbed levan molecules, enhanced when the MMT loading becomes high enough (5–10 wt% MMT) to induce an isotropic–nematic transition in MMT platelet orientation.

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1. Introduction

Polysaccharides offer considerable promise as sustainable, biodegradable materials for packaging and other applications (Johansson et al., 2012; Majeed et al., 2013; Tang, Kumar, Alavi, & Sandeep, 2012). Polysaccharides extracted from plants, such as cellulose, hemicellulose, starch, pectin, and chitin, have received much attention (Chivrac, Pollet, & Averous, 2009; Rhim & Ng, 2007; Sinha Ray & Bousmina, 2005; Sorrentino, Gorrasi, & Vittoria, 2007; Yu, Dean, & Li, 2006), perhaps because their source materials are widely available in mass quantities and at low cost. Exopolysaccharides secreted by microbes often have well-defined structure and high molecular weight (French, 1989), but they have received less attention because they have not been readily available in large quantities and high purity. Advances in microbial fermentation have resulted in increasing availability of high purity, well characterized biopolymers, especially polyhydroxyalkanoates (Johansson et al., 2012; Sinha Ray & Bousmina, 2005; Sorrentino et al., 2007; Tang et al., 2012; Yu et al., 2006). Among the exopolysaccharides, levan has been produced by large-scale

fermentation (Bodie, Schwartz, & Catena, 1985; Han & Watson, 1992; Keith et al., 1991; Kim et al., 2005; Küçülaşik et al., 2011; Liu et al., 2010; Poli et al., 2009; van Dyk, Kee, Frost, & Pletschke, 2012).

Levan and inulin are fructans, fructose-based polysaccharides produced by many plants and microorganisms (French, 1989). Levan consists of D-fructofuranosyl monomers joined by $\beta(2 \rightarrow 6)$ linkages and branched via $\beta(2 \rightarrow 1)$ linkages (Supporting information, Fig. S1). Plant fructans have relatively low degrees of polymerization (<100 fructofuranose monomers, or residues) with molecular weights on the order of 10^4 Da. Microbial levans, on the other hand, typically have higher degrees of polymerization (~10,000 residues) and molecular weights (~10^5–10^7 Da). Chemical analyses in conjunction with ^{13}C NMR indicate that branching occurs on up to 30% of the residues in levan (Seymour, Knapp, & Jeanes, 1979; Simms, Boyko, & Edwards, 1990). Electron microscopy images (Ingelman & Siegbahn, 1944; Newbrun, Lacy, & Christie, 1971), data from light scattering and sedimentation (Bahary, Stivala, Newbrun, & Ehrlich, 1975; Stivala, Bahary, Long, Ehrlich, & Newbrun, 1975), small-angle X-ray scattering (Khorramian & Stivala, 1982; Stivala & Khorramian, 1982), and viscometry (Arvidson, Rinehart, & Gadala-Maria, 2006; Kasapis, Morris, Gross, & Rudolph, 1994) all agree that levan molecules in aqueous solutions do not undergo gelation with increasing solution

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concentration and have a compact, globular structure (spheroidal or ellipsoidal).

Levan's high molecular weight and water solubility make it attractive for various industrial applications, including cosmetics, pharmaceutical coatings, and adhesives (Combie, 2006; Kim et al., 2005; Kang et al., 2009) There have been only a few studies aimed at developing levan as a bio-based plastic for packaging applications. Barone and Medynets (2007) used compression molding and melt extrusion to prepare cohesive, pliable levan films plasticized by glycerol. Levan films containing less than 10 wt% glycerol were too brittle to be characterized by tensile testing. Films containing 10–35% glycerol had tensile moduli less than 0.1 GPa and glass transition temperatures (T_g) ranging from 60 °C (10 wt%) down to 0 °C (30 wt%). These property values are too low to permit the use of levan/glycerol films in packaging or structural applications. Manadhar, Vidhate, and D'Souza (2009) prepared levan fibers by electrospinning from concentrated solutions (60 wt%), but fiber mechanical properties were not reported. The poor mechanical properties of pure levan films are probably related to its molecular structure: despite its high molecular weight, levan's highly branched, compact globular structure does not permit significant intermolecular entanglement. This leads to brittleness in neat levan, and low tensile modulus in glycerol-plasticized levan.

Recent reviews (Chivrac et al., 2009; Johansson et al., 2012; Majeed et al., 2013; Rhim & Ng, 2007; Sinha Ray & Bousmina, 2005; Sorrentino et al., 2007; Tang et al., 2012; Yu et al., 2006) demonstrate that, in many cases, biopolymer nanocomposites have properties superior to those of the corresponding pure biopolymer. Examples of recent work in this vein are studies of xylan (Unlu, Gunister, & Atici, 2009; Viota, Lopez-Viota, Saake, Stana-Kleinschek, & Delgado, 2010) or xyloglucan (Kochumalayil et al., 2013) reinforced with MMT. The present work explores the possibility of improved thermal and mechanical properties for nanocomposites of exfoliated montmorillonite (MMT) dispersed in levan. Improved properties may extend levan's range of applications to include barrier packaging with unique features, such as edible packaging or accelerated biodegradability.

2. Experimental procedures

2.1. Materials

Levan powder derived from *Bacillus* sp. was obtained from Montana Polysaccharides (Winnsboro, SC). The as-received levan was dissolved in deionized water (~18 MΩ resistivity, Barnstead Nanopure) with prolonged stirring to produce a 10.0 wt% solution. The solution was centrifuged at 2000 rpm for 100 min at 20 °C (Eppendorf model 5403, Brinkmann) and the clear supernatant solution was retained. Samples of this solution were diluted and used for light scattering characterization. A concentrated stock solution of purified levan was prepared from the supernatant by removing water using a rotary evaporator. Dry weight analysis indicated that the solid content of the final levan stock solution was 27.5 wt%. In order to inhibit bacterial growth, 0.5 wt% sodium azide was added to the concentrated levan stock solution.

Sodium montmorillonite (MMT) clay (Cloisite® Na⁺, Southern Clay Products) was dispersed in water using a procedure (Ploehn & Liu, 2006) known to produce suspensions containing >95% exfoliated MMT platelets. As-received MMT powder was added to deionized water to produce a 1.0 wt% suspension. The suspension was stirred continuously at room temperature for at least 24 h, ultrasonicated (model FS28, Fisher Scientific) for 30 min, and then centrifuged at 4000 rpm for 60 min to remove mineral contaminants and unexfoliated MMT. The supernatant MMT suspension was retained; dry weight analysis indicated a MMT concentration of 0.7 wt%. AFM characterization of suspensions prepared in this way (Ploehn & Liu, 2006) indicated nearly complete exfoliation of MMT into individual platelets with an average thickness of 0.97 nm. The MMT platelets have a log-normal distribution of aspect ratio with a mean of 166 ± 86 and a median of 147 (Ploehn & Liu, 2006).

2.2. Film preparation

MMT–levan nanocomposite films were prepared by solution blending of the stock levan solution (27.5 wt%) and the stock MMT suspension (0.7 wt%). Appropriate quantities of the levan solution and MMT suspension were blended so that the final solid films contained 0, 1.0, 5.0, or 10.0 wt% MMT. The aqueous levan–MMT blends were stirred for 60 min, ultrasonicated for 30 min, and then concentrated using a rotary evaporator, producing viscous coating suspensions containing approximately 5 wt% total solids (levan + MMT). The coating suspensions were coated onto Mylar® sheets using the drawdown coating method to prepare levan–MMT nanocomposite films. The wet films were dried in an air-circulated oven at 50 °C for approximately 2–4 h, determined through trial-and-error as optimal for removing most, but not all of the moisture. Insufficient drying produces tacky films that are difficult to peel, while complete drying produces brittle films that tend to crack when peeled from the Mylar®. After peeling, the films were conditioned in ambient air, at room temperature (~23 °C) and 50–60% relative humidity, to equilibrate the water content. The final film thickness varied from 80 to 280 μm, depending on the MMT content, coating suspension viscosity, and drawdown coating procedure.

2.3. Characterization methods

2.3.1. Solution characterization

We used UV–vis spectrophotometry (UV–vis) and static and dynamic light scattering (SLS, DLS) and to characterize levan's molecular structure and solution properties. Solution optical absorbance was characterized by UV-vis measurements (Shimadzu model UV-2101PC). Light scattering experiments employed a Brookhaven BI-200 goniometer, BI-9000AT correlator (Brookhaven Instruments) and Ar-ion laser (Lexel model 95; λ = 514.5 nm). For DLS, samples of stock levan solution were diluted with DI water and pH adjusted by titrating with 1.0 M NaOH or 37% HCl. Intensity autocorrelation data were analyzed using quadratic cumulants or CONTIN methods via the Brookhaven system software.

Prior to SLS, we measured the refractive index (n) of levan solutions of varying concentrations (Abbé Mark II refractometer) to determine the specific refractive index increment (dn/dc). For concentrations up to 50 mg/mL (~0.5 wt%), n varies linearly with c, yielding dn/dc = 0.1427 ± 0.0010 mL/g, in excellent agreement with the value of Stivala et al. (1975). For SLS measurements, DI water was filtered three times using 0.2 μm cellulose acetate filters. The levan stock solution was either used unfiltered or filtered once with a 0.45 μm cellulose acetate filter, with subsequent dilution using filtered DI water. Scattered intensity, measured as a function of scattering angle θ and c, were analyzed via Zimm and Berry plots (Brookhaven software). We calibrated these measurements with solutions of a polystyrene standard (2.0×10^6 Da) in toluene (Fig. S2). The Berry plot yielded better agreement of the MW value. Thus Berry plots were used to determine radius of gyration (R_g), molecular weight (MW), and second virial coefficient (A_2) values.

2.3.2. Solid film characterization

Solid film samples were ground using a Wiley mill, and the powder was sieved with a #60 mesh screen. Wide-angle X-ray diffraction (WAXD) employed a powder diffractometer (Rigaku MiniFlex II) using Cu Kα radiation (λ = 1.5419 Å). Scattered intensity data were recorded from 3° to 40° (2θ) at a rate of 0.5° per min