



Synthesis and characterization of polyvinyl alcohol/nanospherical cellulose particle films

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ABSTRACT

A procedure for synthesizing cellulose nanospheres with size of 5.9 and 10.9 nm for cotton linter and linen, respectively, was developed. A series of polyvinyl alcohol (PVA)/nano-cellulose films were cast. Mechanical, biodegradation and scanning electron micrograph (SEM) of nano-cellulose-filled PVA films were studied. With the addition of 20% nano-cellulose from linen there was an increase in the tensile strength and percentage elongation at break. The SEM indicates the change in the morphological structure of the PVA films in the presence of different percent of nano-cellulose.

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1. Introduction

Naturally renewable biopolymers, such as polysaccharides, proteins and lipids, can form into either coatings or stand-alone films (Kester & Fennema, 1986). Biopolymer films have been the focus of worldwide attention for the past few decades because they offer favorable environmental advantages in terms of recyclability and reutilization compared to conventional synthetic polymeric films. Many research studies on biopolymer coatings and films for food packaging applications have been reported (Gennadios, 2002; Gennadios & Weller, 1990; Kester & Fennema, 1986; Miller & Krochta, 1997). However, biopolymer films are limited in their ability to obtain wide commercial application due to disadvantages in mechanical properties and brittleness. Although plasticizers are generally added into film-forming solutions to prevent film brittleness or cracking caused by intermolecular forces (Lieberman & Gilbert, 1973; Sothornvit & Krochta, 2001), the weakness of biopolymer films in mechanical properties may not be easily overcome.

Polyvinyl alcohol (PVA) is a material with technological potential as a water-processable polymer. It has wide commercial application due to its unique chemical and physical properties (Masuhiro, Giuliano, & John, 1994). PVA is a nontoxic, highly crystalline, and water-soluble polymer and has good film-forming and high hydrophilic properties. However, PVA as a soluble polymer

cannot be used in the treatment of waste waters. Thus, it has to be converted to a completely insoluble material with high mechanical properties.

Development of ecofriendly packaging materials is a continuing area of challenge for packaging technologists. The excellent chemical resistance, optical and physical properties of PVA resins, has resulted in its broad industrial uses. PVA is often modified by combination with other polymers or fillers to enhance its performance and barrier properties. Incorporation of naturally occurring polymers or fillers like cellulose and/or starch into other polymeric materials enhances the ecofriendliness.

Over the past decades, interest in sustainability and green chemistry has lead to a renewed interest in novel cellulosic materials (Ragauskas et al., 2006) and composites (degree Well et al., 2004) derived from a variety of celluloses (Samir, Alloin, & Dufresne, 2005). Cellulose, which is a natural polysaccharide, is one of the most abundant materials in the natural world, and its biosynthesis, chemistry, and ultra structure remains as active field of study (Klem, Heublein, Fink, & Bohn, 2005; Klemm, Schmauder, & Heinze, 2002). It is a linear (1–4)- β -glucopyranan having three hydroxyl groups at the C2, C3, and C6 positions per anhydro glucose unit. In addition, the cellulose molecule has only one hemiacetal at the reducing end and one secondary hydroxyl group at the C-4 position of the non-reducing end. The hemiacetal hydroxyl group, different from the others, can be substituted with some nucleophiles by nucleophilic substitution, i.e., glycosidation. A functional group can be, therefore, introduced only into the

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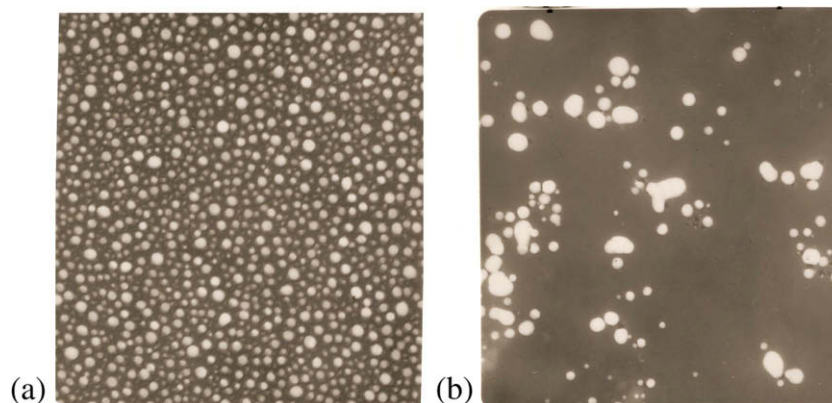


Fig. 1. TEM images of cellulose nano-particles with an average size of (a) 5.9 nm for cotton linter, and (b) 10.9 nm for linen ($\times 40,000$).

hemiacetal carbon at the reducing end with high regioselectivity (Kamitakahara & Nakatsubo, 2005).

PVA, cellulose and starch are polar polymers; thus a composite of PVA and cellulose or starch is likely to produce a material having excellent mechanical properties. Incorporation of starch and cellulose into the PVA matrix changes the physicochemical properties of the material and thus modifies the polymer structure at both the molecular and the morphological levels (Siddaramaiah, Nagarahalli, Ravi, Kumar, & Jagadeesh, 1999). This study reports on the effect of nano-cellulose content, resulted from cotton linter and linen, on the properties of PVA films, such as mechanical, and microstructural parameters. These studies were carried out to assess their potential uses as packaging films.

2. Experimental

2.1. Materials

Cellulose fibers from cotton linter and bleached linen were used for the production of nano-cellulose. PVA [degree of polymerization: 17,000–18,000; and hydrolyzed between 99.0% and 99.8% from poly(vinyl acetate) used in this study] was obtained from M/s. Loba Chem (India) and corn starch was obtained from M/s. Riddhi Siddhi Chemicals Ltd. (India).

2.2. Pretreatment

Cellulose fibers, from cotton linter and bleached linen, were treated in a method described by Zhang, Elder, Pu, and Ragauskas (2007), where 30.0 g of the cellulose fibers was transferred into 5.0 M sodium hydroxide (NaOH) solution (250.0 mL) warmed to 80 °C for 3 h. The slurry was then filtered and thoroughly washed with distilled water until the wash water was neutral. The resulting cellulosic fibers were air-dried, and then added to 250.0 mL dimethylsulfoxide (DMSO) in a 80 °C water bath for 3 h. The fibers were then filtered and washed with distilled water (3×250 mL).

2.3. Synthesis and purification of nano-cellulose

The pretreated fibers were transferred into an acidic aqueous solution consisting of 1000 mL mixed acid (made of 600 mL distilled water, 100 mL of 10.0 N HCl and 300 mL of 36.0 N H₂SO₄) and this suspension was heated in a water bath at 80 °C with a continuous stirring until the fiber slurry turned into milky colloid suspension. The mixture was then transferred into centrifuge bottles and centrifuged. The fractions were continuously washed by addition of distilled water and centrifuged. After washing, the products

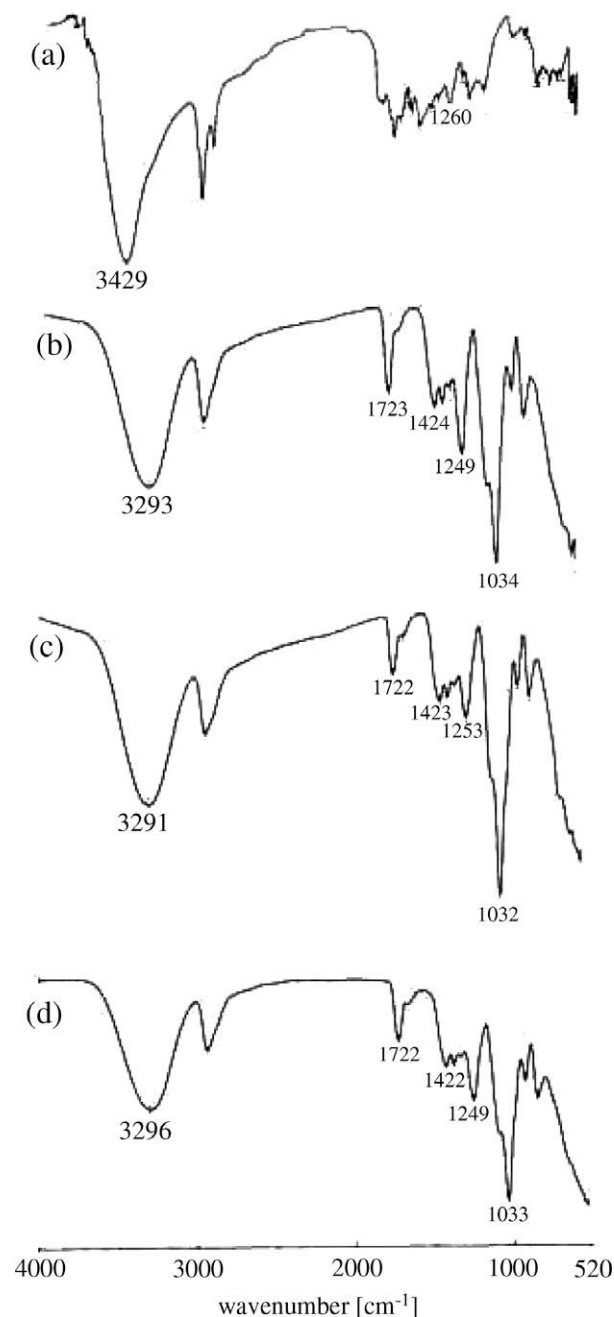


Fig. 2. FT-IR and ATR for (a) PVA, (b) PVA/20% CL, (c) PVA/40% CL and (d) PVA/60% CL.

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