



Green nanocomposites based on thermoplastic starch and steam exploded cellulose nanofibrils from wheat straw

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ABSTRACT

The objective was to characterize the properties of cellulose nanofibril/TPS based nanocomposites. The cellulose nanofibrils were extracted from wheat straw using steam explosion, acidic treatment and high shear mechanical treatment. These nanofibrils were dispersed in thermo plastic starch (TPS) using a Fluko high shear mixer in varying proportions and films were casted out of these nanocomposites. The cellulose nanofibrils were characterized using AFM, TEM, SEM, TGA, FTIR and WAXRD and the nanocomposite films were analyzed in terms of SEM, WAXRD, TGA, DSC, mechanical and barrier properties. XRD and TGA results confirmed the crystalline nature of nanofibrils. AFM and TEM images revealed fiber diameter in the range 30–70 nm. TGA depicted an increasing in residue left with increase in cellulose nanofibrils content. Mechanical properties increased with nanofiber concentration. Barrier properties also improved with addition of nanofillers up to 10% but further addition deteriorated properties due to possible fiber agglomeration.

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1. Introduction

Growing environmental concerns have created an urgent need to develop biodegradable materials that have comparable properties to polymeric materials at an equivalent cost. Natural biopolymers have an advantage over synthetic biodegradable polymers as they are renewable raw materials.

Starch based biodegradable polymers have great commercial potential for bio-plastic, but some of the properties like brittleness, low heat distortion temperature, high gas permeability, low melt viscosity for further processing, etc. restrict their use in a wide-range of applications. Therefore, modification of the biodegradable polymers through innovative technology is a challenge for materials scientists. Adding nano-reinforcement to pristine polymers to preparing nanocomposite has already proven to be an effective way to improve these properties concurrently (Sinha Ray & Okamoto, 2003). Thus, *green nanocomposites* are being considered as the next generation materials. With the aim of improving thermo-mechanical properties, decreasing water sensitivity of polymers and to preserve the biodegradability, natural fibers are being used as biodegradable fillers. It has been observed that mixing natural fibers with polysaccharides (such as thermoplastic starch) improve

their mechanical properties (Curvelo, de Carvalho, & Agnelli, 2001; Dufresne & Vignon, 1998; Dufresne, Cavallé, & Vignon, 1998).

Cellulose, the building material of long fibrous cells, is a strong natural polymer. Cellulose nanofibers are inherently low cost and are easily available. They are also eco-friendly as they are easy to recycle by combustion, besides consuming less energy during manufacturing. Thus, cellulose nanofiber based composites are an attractive class of nanomaterials on account of low cost, lightweight and high-strength (Helbert, Cavallé, & Dufresne, 2004; Podsiadlo et al., 2005). Cellulose nanofibers have tremendous attraction due to their unique characteristics such as very large surface to volume ratio, high surface area, good mechanical properties including a high Young's modulus, high tensile strength (Hitoshi & Akira, 2007), low coefficient of thermal expansion (Nishino, Matsuda & Hirao, 2004) and formation of highly porous mesh as compared to other commercial fibers. The supramolecular structure of cellulose determines many of its chemical and physical properties. In the fully extended molecule, adjacent chain units are orientated by their mean planes at an angle of 180° to each other. Thus, the repeating unit in cellulose is the anhydro-cellulobiose unit and number of repeating units per molecule is half the DP. This may be as high as 14,000 in native cellulose, but purification procedures usually reduce it to the order of 2500 (Nevell & Zeronian, 1985).

Various types of cellulosic reinforcements have been used and tested in natural polymers such as potato pulp-based microfibrils (Alain, Danièle, & Michel, 2000; Dufresne & Vignon, 1998) bleached

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leafwood fibers (Funke, Bergthaller, & Lindhauer, 1998), bleached eucalyptus pulp fibers (Curvelo et al., 2001), flax fibers and ramie fibers or crystallites (Soykeabkaew, Pitt Supaphol, & Rujiravanit, 2004), tunicin whiskers (Anglès & Dufresne, 2000, 2001), etc. A high compatibility occurs between starch matrix and cellulose nanofibrils with enhanced performance (e.g., mechanical properties and water sensitivity) due to 3D hydrogen bonds network formed between different components.

In the present study, steam treatment with subsequent explosive defibrillation to extract cellulose nanofibrils from wheat straw was performed. The steps include alkaline steam treatment, bleaching and acidic treatment phases followed by mechanical treatment in a high shear homogenizer. Hydrochloric acid has been used for hydrolysis instead of sulfuric acid which is a common choice as it assists with dispersion and separation of nanofibrils due to sulfate ester groups are introduced randomly on the surface resulting in nonflocculating suspensions. For composite applications, the sulfate groups are problematic due to the decreased thermal stability after drying, precluding typical polymer melt processing. Battista and Smith (1962) discovered that formation of stable suspensions can also be achieved by hydrolysis of cellulose using hydrochloric acid followed by mechanical disintegration. The cellulose nanofibrils extracted by above treatment were characterized using TEM, AFM, SEM, FTIR, WAXRD and TGA. These nanofibrils were then reinforced into thermoplastic starch to obtain completely biodegradable nanocomposites by solvent casting in aqueous phase. The nanocomposites so prepared were characterized using SEM, WAXRD, TGA, DSC, Mechanical and their barrier properties studied.

2. Experimental

2.1.1. Materials

Wheat straws were obtained from neighboring fields. They were thoroughly washed to remove any extraneous impurities and dried before use. This is an extremely low cost material which is used for cattle feed. For preparation of thermoplastic starch (TPS), regular maize starch (10% moisture content) of Labochem India Pvt. Ltd. was used along with plasticizer (glycerol) supplied by Swan Scientific, Chandigarh (India). Other chemicals used in the experiment, i.e. sodium hydroxide (NaOH), hydrochloric acid (HCl), hydrogen peroxide (H₂O₂) were supplied by MERCK India Pvt. Ltd.

2.1.2. Extraction of cellulose nanofibrils from wheat straw

2.1.2.1. Alkaline treatment

It was given in two steps. In the first step wheat straw fibers of length around 2–5 cm were soaked in 2% sol. of NaOH overnight and then treated in 10–12% NaOH solution (fiber to liquor ratio around 1:10) in an autoclave at pressure around 15 lb for 4 h. Pressure was then suddenly released resulting in explosive defibrillation of fiber. The first treatment removed excessive impurities from the surface of the fibers and made fibers swollen that made further treatment easy. The second treatment removed excessive amount of lignin from the fibers. The obtained wheat straw pulp was then washed several times in distilled water to get rid of alkali.

2.1.2.2. Bleaching treatment

Alkaline treated pulp was then soaked in 8% solution of H₂O₂ (v/v) overnight. This bleached pulp was then rinsed with abundant distilled water.

2.1.2.3. Acidic treatment

Bleached pulp was treated with 10% HCl (1N) solution and mixed using Branson 2510 E-DTH ultrasonicator at temperature around

60 ± 1 °C for 5 h. Finally the fibers were taken out and washed several times with distilled water in order to neutralize the final pH and then dried.

2.1.2.4. Mechanical treatment

Fibers were suspended in water and continuously stirred with a Fluko FA25 high shear homogenizer for 15 min. High shearing action breaks down the fiber agglomerates and result in nanofibrils.

2.1.3. Preparation of TPS/cellulose nanofibril nanocomposite films

Thermoplastic starch nanocomposites reinforced with cellulose nanofibers (CNFs) extracted from wheat straw were prepared using simple method. Cellulose nanofibers were dispersed in distilled water and sonicated for almost 3 h. Maize starch was added with 30% glycerol and shear mixed for 10 min by using Fluko FA25 homogenizer (10,000 rpm). Dispersion of cellulose nanofibers was added to the starch, glycerol mixer and further shear mixed for 20 min. Starch + glycerol + CNFs mixture was continuously stirred (at 80–100 rpm) using a mechanical stirrer and heated at 75 ± 3 °C. After the solution became viscous, it was poured on to leveled Borosil glass petridishes and kept at around 37 °C for 2 days until it was completely dry. Solution cast films of TPS cellulose nanocomposites were made with 5, 10 and 15% nanofibers (as per dry weight of nanocomposites). The film thickness was controlled by pouring calculated amount of mixture on the petridish. The films of thickness approximately 80 μm were obtained and conditioned at 43% RH using saturated solution of K₂CO₃·2H₂O at 25 °C for 15 days before testing was done.

2.1.4. Characterization of cellulose nanofibrils and nanocomposites

Chemical composition of fibers was estimated according to the following ASTM procedure: α-cellulose (ASTM D1103-55T), lignin (ASTM D1106-56) and holocellulose (ASTM D1104-56). The standard deviations were calculated by conducting several replicate measurements for each sample. The α-cellulose, hemicelluloses and lignin content were calculated by Eqs. (1)–(3) as follows:

$$\alpha\text{-Cellulose percentage (A)} = \frac{\text{weight of oven dry } \alpha\text{-cellulose residue}}{W \times P} \times 100 \quad (1)$$

$$\text{Hemicellulose percentage} = \frac{\text{weight of oven dry holocellulose residue}}{W \times P} \times 100 - A \quad (2)$$

$$\text{Lignin percentage} = \frac{\text{weight of oven dry lignin residue}}{W \times P} \times 100 \quad (3)$$

where *W* is the weight of the original oven dry fiber sample and *P* is the proportion of moisture-free content.

Scanning electron microscope model JSM JEOL-6490 was used for microstructural analysis of cellulose microfibrils obtained after steam explosion. Nanocomposite films were frozen in liquid nitrogen and broken into small pieces. Samples were mounted on a metal stub and platinum coated by using sputter coating technique for 20 s to make them conducting. Images of fibers were taken at 20 kV accelerating voltage.

AFM imaging was used to characterize the dimensions and homogeneity of cellulose nanofibrils obtained after chemical and mechanical treatment. The images were scanned in tapping mode in air using silicon cantilevers (Bioscope II AFM, VEECO). Drive frequency of the cantilever was about 200–300 kHz with scan rate of

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