Industrial Crops and Products 71 (2015) 173–184

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Sisal nanofibril reinforced polypropylene/polystyrene blends: Morphology, mechanical, dynamic mechanical and water transmission studies

Asha Krishnan K[a,*], Cintil Jose[c], Rohith K. R[a], K.E. George[b]

[a] Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi, Kerala 682022, India
[b] Albertian Institute of Science and Technology, Archbishop, Angel Mary Nagar, Kochi, Kerala 682022, India
[c] Department of Chemistry, Newman College, Thodupuzha, Kerala 685585, India

ARTICLE INFO

Article history:
Received 3 November 2014
Received in revised form 14 March 2015
Accepted 24 March 2015

Keywords:
Sisal
Cellulose nanofiber
Polypropylene
Polystyrene
Mechanical property
Morphology

ABSTRACT

In this work, cellulose nano fibers were extracted from sisal leaves using steam explosion technique. The chemical composition, morphology and thermal properties of the nano fibers and their intermediate products were characterized. The progressive removal of noncellulosic constituents is confirmed by FTIR studies. X-ray diffraction reveals that crystallinity increased with successive chemical treatments. Characterization of the fibers by SEM and TEM gives evidence for the formation of cellulose nano fibers. TGA results show that the cellulose nano fibers exhibit enhanced thermal properties over the untreated fibers. The effect of cellulose nanofibers on the mechanical and morphological properties of polypropylene/polystyrene blend has been studied. Water transmission data shows that the addition of 0.5 wt% CNF decreased the transmission rate in the composite. Mechanical properties improve with the incorporation of cellulose nano fiber.

1. Introduction

Significant research effort has been poured into the manufacturing of sustainable materials due to public's growing demand for more environmentally friendly products, depletion of petroleum resources, and heavy environmental legalization. Cellulose, world's most abundant natural, renewable, biodegradable polymer, is a classic example of reinforcing element, which occurs as whisker like microfibrils that are biosynthesized and deposited in a continuous fashion. This quite "primitive" polymer can be used to create high performance nanocomposites presenting outstanding properties. This reinforcing capability results from the intrinsic chemical nature of cellulose and from its hierarchical structure. High strength and stiffness, the surface reactivity (with numerous hydroxyl groups), the specific organization as well as the small dimensions of nanocellulose may well impart useful properties for the reinforcement of composite materials.

Cellulose nano fibers based on plants have attracted significant interest in the last few decades due to sustainability, availability and characteristics such as high surface area-to-volume ratio, high Young's modulus and tensile strength, low coefficient of thermal expansion, better electrical and thermal properties as compared with other commercial fibers. The term "nano-fibers" are the elementary assemblies of distinct polymer units (based on glucopyranose in the case of cellulose nanofibrils) that have diameters in the order of tens of nanometers (Frone et al., 2011). Cellulose is the main component of several natural fibers such as cotton, flax, sisal etc. It is the world's most abundant natural, renewable, biodegradable polymer. Cellulose is a polydispersed linear polymer of β(1,4)-D-glucose with a syndiotactic configuration. In cell walls, cellulose nano fibers are embedded in matrix substances such as hemicellulose and lignin and the removal of the matrix substances has been performed before the fibrillation process. Different raw materials used for production of cellulose nano fibers are banana (pseudo stem), jute (stem), pineapple (leaf) (Abraham et al., 2011), kenaf bast fibers (Kargarzadeh et al., 2012), coconut husk fibers (Rosa et al., 2010), oil palm empty-fruit-bunch (Fahma et al., 2010), and hemp fibers (Dai et al., 2013).

Several methods are used to extract cellulose nano fibers from the plant cell wall, based on chemical and mechanical treatments (Silverio et al., 2013; Pasquini et al., 2010). Chen et al. (2011) isolated nano fibers from four different sources (wood, bamboo, wheat straw and flax fibers) by a chemical-ultrasonic treatment. Panthapulakkal and Sain (2012) reported the isolation of

* Corresponding author. Tel.: +91 9446447851.
E-mail address: principal@aisat.ac.in (A. Krishnan K).

http://dx.doi.org/10.1016/j.indcrop.2015.03.076
0926-6690/

cellulose nano fibers from wood pulp fibers by mechanical defibrillation. Paakko et al. (2007) prepared nanoscale cellulose fibrils by enzymatic pre-treatment methods. Fahma et al. (2010) isolated cellulose nano fibers from oil palm empty-fruit-bunch using sulfuric acid hydrolysis. The steam explosion technique includes steam treatment at elevated pressure and temperature followed by sudden release of pressure, during which the flash evaporation of water exerts a thermo mechanical force causing the material to rupture. The steam explosion process was first introduced by Mason in 1927. He used the technique to defibrate wood into fiber for board production (Mason, 1927). Cherian et al. (2008) reported that steam explosion process lead to the hydrolysis of glycosidic bonds in hemicellulose and cleavage of hemicellulose—lignin bonds. It also resulted in an increased solubilization of hemicellulose in water and increased the solubility of lignin in alkaline or organic solvents.

In this work, cellulose was extracted from sisal fibers, which is an abundant natural source. Sisal fibers are composed of cellulose (50–74%), lignin (8–11%), hemicellulose (10–14%), pectin (1%) and wax (2%) (Bledzki and Gassan, 1999; Hon, 1996; Han and Rowell, 1996). Because of its high cellulose content, cellulose extraction from these fibers could lead to high quantity of nanofibers. It has been one of the most traded sources due to its characteristics such as the low cost, low density, specific resistance, biological degradability, CO_2 neutrality, renewability, good mechanical properties, non-toxicity and furthermore can be easily modified by a chemical agent improving their mechanical and thermal properties. The most important advantages of sisal fibers are their low cost (0.16 US$/pound vs. 1.48US$/pound for glass fibers), light weight (1.5 g/cm3 vs. 2.5 g/cm3 for glass fibers), and one of the highest tensile strengths of all natural fibers (511–635 MPa) (Li et al., 2000; Eichhorn and Young, 2001).

Improved mechanical properties and reinforcing capability of nanocellulose at lower loadings make it a potential material for the processing of polymer nanocomposites. Chand et al. (2012) prepared the nano fibers from sisal by using acid hydrolysis and studied the reinforcing effect of nano fibers in different polymers such as LDPE, LLDPE and PP. The studies showed that mechanical properties of composites exhibit the improved strength up to 2 phr of nano fiber loading in to LDPE and LLDPE composites, while PP composites show a reduction in strength (Chand et al., 2012). In another study Siqueira et al. (2011) extracted the cellulosic nanoparticles from sisal fibers using different processing routes, viz. a combination of mechanical shearing, acid and enzymatic hydrolysis. The reinforcing ability of cellulosic nanoparticles was studied by using natural rubber as the matrix (Siqueira et al., 2011). Polymer blends have attracted great attention both industrially and academically because of their flexibility and versatility to create new materials with desired properties from existing virgin polymers. Polypropylene (PP) and polystyrene (PS) are two of the widely used plastics and their blends have also received considerable attention. This blend has been selected for this study because of the recent interest in these materials for automotive applications. Blending an amorphous polymer and a semi crystalline polymer will offer a balance of impact strength/ stiffness. However, PP and PS are widely regarded as immiscible due to lack of interfacial adhesion between the components. In recent years, a new concept of compatibilization by using nanoparticles such as nanoclay, nanotube etc. has been introduced (Suprakas et al., 2004; Kyung et al., 2007). In this study cellulose nanofibers are proposed to be used as modifier. Shamsabadi et al. (2014) extracted cellulose nano fibers (CNF) from wheat straws using a chemo-mechanical method and investigate its effect in polyethylene/starch blend. The enhancement in tensile properties was obtained at 8 wt% of CNF.

The aims of this work were to produce cellulose from sisal fibers through acid correlated steam treatment and incorporation of these nanofibers to study its effect on the properties of polypropylene/polystyrene blend (PP/PS blend). It was shown that the use of high aspect ratio cellulose whiskers induces a mechanical percolation phenomenon leading to outstanding and unusual mechanical properties through the formation of a rigid filler network.

2. Methodology

2.1. Materials

Polypropylene homopolymer (REPOL H200MA: Mn: 2.9×10^4, PDI: 4.2) with a melt flow index of 25 g/10 min (230 °C/2.16 kg) was purchased from Reliance Industries limited, Mumbai, India. General purpose Polystyrene (Mn: 2.8×10^4, PDI: 1.2, MFI (200 °C/5 kg) is 12 g/10 min) was obtained from Supreme Petrochem Ltd., India.

2.2. Isolation of cellulose nano fibers (CNF)

Sisal leaves were peeled and chopped into short length of about 0.5–1 cm and treated with 2 wt% NaOH in an autoclave and kept under 137 Pa pressure for one hour. Then the pressure was released immediately and subsequently washed with water. The fibers were then dried in an air oven at 50 °C for 2 h. Then fibers were bleached using a mixture of sodium hydroxide, acetic acid and a mixture of 1:3 sodium hypochlorite solution. Each bleaching took 1 h and the process was repeated for six times. After bleaching, the fibers were washed in distilled water until the smell of the bleaching agent was removed and then dried. The steam exploded bleached fibers were treated with 10% oxalic acid in an autoclave under pressure of 25 psi in an autoclave for 15 min. The pressure was released immediately and the process was repeated eight times. The fiber was suspended in water and subjected to continuous stirring with a mechanical stirrer of type RQ-1.27 A and 9000 R.P.M for 4 h. The suspension was kept in an oven at 90 °C till it was fully dried.

2.3. Preparation of nanocomposite

PP/PS (80/20) and the cellulose nanofibers (CNF) in varying amounts (0.25–5 wt%) were prepared by melt mixing using an internal mixer (Haake Rheomix 600 with a volumetric capacity of 69 cm^3 fitted with roller rotors) at 180 °C with a rotor speed of 50 rpm, and the mixing time is 8 min for each sample. After mixing the melt was pressed in a hydraulic press, cut into pieces and injection molded in a DSM Micro 10cc Injection Molding Machine, with a barrel temperature of 190 °C.

2.4. Characterization techniques

2.4.1. Characterization of cellulose nano fibers

The chemical composition of the sisal fibers at each stage of treatment was determined according to the ASTM standards [α-cellulose (ASTM D 1103-55T), hemicellulose (ASTM D 1104-56), lignin (ASTM D 1106-56), and moisture content (ASTM D 4442-92)].

FTIR spectra recorded on a Thermo Nicolet FTIR Spectrometer Model Avatar 370. Untreated, alkali-treated, bleached and acid-treated sisal fiber samples were analyzed. Prior to the experiment, fibers were dried in an air oven at 60 °C for 12 h. The FT-IR spectrum of each sample was obtained in the range of 500–4000 cm^{-1}.

Surface morphology of sisal fibers was observed using Scanning electron microscopy [JEOL Model JSM 6390LV scanning electron microscope (SEM)]. The fibers were subjected to gold sputtering prior to electron microscopy to give the necessary conductivity.

Transmission electron microscopy was used to find out the dimensions of the cellulose nanofibers and nanocomposite obtained from the sisal fibers. Transmission electronic microscopy