Studies on the mechanical, thermal, morphological and barrier properties of nanocomposites based on poly(vinyl alcohol) and nanocellulose from sugarcane bagasse

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A B S T R A C T

Nanocomposites from poly(vinyl alcohol) [PVA] in linear and crosslinked state were synthesized using varying proportions of bagasse extracted nanocellulose. These were characterized by tensile, thermal, X-ray diffraction (XRD), moisture vapor transmission rate (MVTR), and morphological studies. Crosslinked PVA and linear PVA nanocomposite exhibited highest tensile strength at 5 wt.% and 7.5 wt.% of nanocellulose respectively. Thermogravimetric analysis (TGA) studies showed higher thermal stability of nanocomposite made of crosslinked PVA and nanocellulose with respect to linear PVA and nanocellulose. TEM and AFM studies confirm the formation of nanocomposites while the SEM images show the dispersion of nanocellulose particles in them.

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1. Introduction

Polymer nanocomposites are made up of nanometric particles (nanofillers) dispersed in a polymer matrix. The incorporation of a small amount of nanometer-sized filler can yield composites with enhanced properties earnestly required for many industrial and technological applications [1]. The conventional polymer–inorganic filler nanocomposites can have improved stiffness, strength, hardness and high temperature creep resistance compared to the unfilled polymers [2–6]. These nanocomposites have recently become an issue of great concern from environmental, economic and performance point of view. This can be alleviated by the replacement of inorganic fillers with natural ones [7].

Cellulose, synthesized mainly in biomass by photosynthesis, is the most abundant natural biopolymer in the world. Natural cellulosic fibers, particles, fibrils (micro and nano scale), and crystals/whiskers are used as reinforcement while making environmental friendly products. These cellulosic materials have many advantages including, renewability, low cost, low density, low energy consumption, high specific strength, modulus, biodegradability and biocompatibility with less susceptibility to fracture during processing due to their high aspect ratios in composites [8,9]. In addition, the waste disposal becomes easier by

combustion for lignocellulosic filled composites (that can be completely converted into water and CO_2) [10]. That is why, the possibility of using lignocellulosic fillers in the plastic industry have received considerable attention. Automotive applications display strong promise for natural fiber reinforcements as well [11–14]. Potential applications of lignocellulosic fiber based composites in railways, aircraft, irrigation systems, furniture industries, and sports and leisure items are currently being researched [15].

Cellulose fibers modified at nanometer size induce much higher mechanical properties to polymer matrices as regards to common cellulose fibers because of their higher crystallinity and mechanical properties combined with higher surface area and active interfaces [16]. Crystalline cellulose nanofibers often referred to as nanowhiskers display an elastic modulus of 120–150 GPa [17]. Due to their strongly interacting surface hydroxyl groups [18], cellulose nanowhiskers have a significant tendency for self-association, which is advantageous for the formation of load-bearing percolating architectures within the host polymer matrix [19]. The spectacular reinforcement of polymers observed for this class of materials is attributed to the formation of rigid nanowhisker networks in which stress transfer is facilitated by hydrogen-bonding between the nanowhiskers [20]; Van der Waals interactions also have been shown to play a significant role [18]. However, these same nanowhisker–nanowhisker interactions can also lead to aggregation during the nanocomposite fabrication [21], which significantly reduces the mechanical properties of the resulting

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materials compared to predicted values [20]. The traditional approach to solve this problem is surface functionalization, which mediates particle–particle and particle–polymer interactions and significantly influences nanoparticle dispersion [22–25].

A drawback of the nanocellulosic filler is their high moisture absorption and the consequent swelling leading to decrease in mechanical properties. Moisture absorption and corresponding dimensional changes can be largely prevented by removing the reactivity of the surface hydroxyl groups of the nanocellulose by way of either intramolecular interactions or by intermolecular interactions with another hydrophilic biocompatible polymer.

Polyvinyl alcohol (PVA) has excellent film forming and emulsifying properties. It has also high tensile strength and flexibility. Roohani et al. [26] have accounted for this excellent film forming ability of PVA due to the hydrogen bonding in PVA-cellulose whiskers or nanofibers. PVA is also a biodegradable polymer [27] making it suitable in combination with cellulosic materials to produce green nanocomposites.

In this paper, we have made an attempt to modify the properties of PVA [28] by way of incorporating highly reactive nanocellulose isolated from waste sugarcane bagasse, the synthesis of which is described in detail in our previous work [29]. The objective of the present work thus is to evaluate the effect of incorporation of nanocellulose on the thermomechanical properties of linear and crosslinked PVA, in relation to their morphologies accrued from the system of blending used. In this context, the applicability of such film in packaging fields has been adjudged with respect to their moisture vapor transmission rate (MVTR) performance.

2. Experimental

2.1. Materials

Polyvinyl alcohol [degree of polymerization: 1700–1800; M.W.: 75,000–80,000; and degree of hydrolysis between 98% and 99% from poly(vinyl acetate)] and glyoxal ($\sim$40% content in water) were supplied by Loba Chemie Pvt. Ltd., India. Other reagents used were: sodium hydroxide (Merck, India), sulfuric acid (Merck, India) and hydrochloric acid (Merck, India). All chemical reagents were used without any further purification processes. Nanocellulose used was synthesized from waste sugarcane bagasse in our laboratory.

2.2. Methods

2.2.1. Isolation of nanocellulose

The nanocellulose suspensions were obtained by acid hydrolysis of cellulose isolated from sugarcane bagasse according to a method described in our previous work [29]. Briefly, the delignified and hemicellulose free cellulose was hydrolyzed with 60 wt.% sulfuric acid at 50 °C for 5 h under strong agitation. The resulting suspension was cooled to room temperature and washed with distilled water by successive centrifugations until pH 7 was achieved. Finally, the suspension was sonicated (UP-500 Ultrasonic Processor with Probe) for 5 min in an ice bath to avoid overheating. The suspension was kept refrigerated until use. The concentration of nanocelluloses in the final dispersion was determined gravimetrically. TEM studies on the resulting particles revealed that the majority of them have the dimensions 170 nm × 35 nm which were further confirmed by AFM studies [29].

2.2.2. Preparation of PVA nanocomposite films reinforced with nanocellulose

The PVA solution was first prepared by dissolving free-flowing granules of PVA in distilled water to a concentration of 5 wt.%, and stirred at 80 °C for 3 h in a round bottom flask equipped with a condenser. Varying proportions of nanocellulose suspension with known solid content of 1 wt.% were added to the prepared PVA solution to adjust the nanocellulose concentration to 2.5, 5, 7.5 and 10 wt.% (of the weight of the solid PVA content) respectively. The mixtures were further mechanically stirred for another 2 h and sonicated for 2 min. The final suspensions were then cast in a polypropylene petridish and dried at the ambient temperature for 2 days. The resulting composite films were then placed in a vacuum oven at 60 °C to ensure complete removal of water. The films thus obtained were kept in the desiccator to remove any remaining water and also to equilibrate for 24 h before characterization.

2.2.3. Preparation of crosslinked PVA composite films containing nanocellulose

In order to obtain crosslinked PVA films reinforced with nanocellulose, a 5 wt.% aqueous solution of PVA was first prepared and crosslinked with glyoxal (10 wt.% of solid PVA) in the following process. To a 30 ml reaction vial containing magnetic stirrer, a known amount of glyoxal solution was combined with 10 ml of distilled water, followed by PVA solution as prepared above. The pH of the solution was adjusted to 4 with 1 M HCl solution. The reaction mixture was stirred at 80 °C for an hour and allowed to cool down to room temperature. The product mixture was then neutralized to pH = 7.0 with 1 M NaOH solution [30]. The nanocellulose suspension as prepared earlier was added to the crosslinked PVA solution at 2.5, 5, 7.5 and 10 wt.% (of the weight of the solid PVA content) loadings. The crosslinked PVA–nanocellulose suspension was further mechanically stirred, sonicated and then cast on a polypropylene petridish. The nanocomposite films were obtained by the evaporation of water followed by the drying method.

3. Characterization methods

3.1. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the various films were recorded with a spectrophotometer (Jasco FTIR 6300, UK) equipped with an attenuated total reflectance (ATR) device using a tri-glycene sulfate (TGS) detector. The spectrum for each sample was recorded in the region of 500–4500 cm^{-1} at a resolution of 4 cm^{-1}. The resulting FTIR spectra were compared to evaluate the effects of nanocellulose filling in the PVA films, based on the intensity and shift of vibrational bands.

3.2. Mechanical properties

The mechanical behavior [tensile strength (TS), % elongation at break (% Eb), yield force (YF)] and pictorial representation of stress–strain behavior of specimen undergoing tensile deformation of the various PVA composite films with varying proportions of nanocellulose was determined using an Instron H50KT (Tinius Olsen Ltd., UK), tensile testing equipment. The maximum force of the cell used in the tensile tests on Instron Machine is 100 N. Tensile deformation was determined at a crosshead speed of 50 mm/min. The tests were carried out at room temperature, 25 °C. The dimensions of the test samples according to the standard test method ASTM D638 were as follows: length 50 mm, width 25.4 mm and thickness 0.05 mm. TS, % Eb, YF were calculated on the basis of initial sample dimensions, and the results were presented as the average of five measurements.

3.3. Thermal properties

3.3.1. Thermogravimetric analysis (TGA)

TGA of the films was carried out using a Netzsch TG 209 F1 instrument. Approximately 6 mg of each sample was heated from