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Wet Pulverization of Waste Jute Fibers as Reinforcement for Biodegradable Nanocomposite Films

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Abstract

In the present study, waste jute fibers formed in textile industries, were wet pulverized to nanoscale using high energy planetary ball milling. The rate of refinement of uncleaned jute fibers having non-cellulosic contents was found slower than the cleaned jute fibers. This behavior is attributed to the strong holding of fiber bundles by non-cellulosic contents which offered resistance to the defibrillation during wet milling. In addition, the pulverization of fibers in the presence of water prevents the increase in temperature of mill which subsequently avoided sticking of material on the milling container. After three hours milling, the diameter of nanofibers was observed around 50 nm. In the further stage, obtained nanofibers were incorporated under 1 wt%, 5 wt% and 10 wt% loading into poly lactic acid composite films. The potentials of jute nanofibers were investigated for improvement in mechanical and barrier properties of films. The maximum improvement in mechanical properties was observed in case of 5 wt% composite film where Young's modulus was increased to 3.3 GPa from 1.0 GPa as compared with neat PLA film.

Keywords: Textile fibrous waste; Wet milling; Jute nanofibers; Biodegradable composite films

Introduction

The demand for textiles has increased significantly in the last decade due to rise in living standards of people. However, increased demands of textiles also brought the challenges to dispose significant amount of wastes, generated during the processing and end of life textile materials [1-2]. In recent years, research on recycling and reuse of textile wastes, instead of landfilling or incineration, has gained a lot of importance due to the increased awareness of environmental concerns. Traditionally, textile wastes have been converted to individual fiber stage through cutting, shredding, carding, and other mechanical processes. The fibers are then rearranged into products for applications in garment linings, household items, furniture upholstery, automotive carpeting, automobile sound absorption materials, carpet underlays, building materials for insulation and roofing felt, and low-end blankets [1-2]. However, recent increased competition and reduced profit margins of such industries have forced the researchers to find alternative more profitable applications of textile wastes. One such interesting way is to separate the nanofibrils or nanocrystals from the textile wastes and subsequently incorporate them into high performance functional products.

The lists of previous literature articles have reported the remarkable mechanical properties of cellulose nanofibers in the range of 130-160 GPa resulted from parallel arrangement of molecular chains without folding [3-5]. As a result cellulose nanofibers have been used in value added applications such as reinforced biodegradable nanocomposites, foams, aerogels, optically transparent functional materials and oxygen-barrier layers [6-8].

The non-cellulosic substances in waste jute fibers (i.e. lignin, hemicelluloses, and waxy materials) hinder the reaction between hydroxyl groups of fibers and polymer matrices and consequently deteriorate the mechanical properties of composites [9-11]. In order to have better bonding between fibers and matrix, the non-cellulosic contents must be removed from the waste jute fibers. In the present study, pre-treatment of waste jute fibers with sequential action of alkali and bleaching was carried out, due to its inexpensive nature [12-13], for removal of lignin and hemicelluloses. In the subsequent stage, cleaned waste jute fibers were subjected to wet pulverization in high energy planetary ball milling process to separate jute nanofibers. During the process of ball milling, fibers tend to defibrillate under the shearing action of frictional force of balls and subsequently refine to nanosegments due to the impact force [7-8]. In fact, ball milling technique has been found to be simple, economical and ecofriendly, over commonly preferred strong acid hydrolysis used for separation of cellulose nanocrystals.

The present paper deals with wet pulverization of waste jute fibers to nanoscale using high energy planetary ball milling process. The prepared nanofibers were then incorporated into polylactic acid to improve their mechanical, thermal and barrier properties. The biodegradable nanocomposite films can be expected to serve in food packaging films, agriculture mulch cover etc.

Experimental

Materials

Short waste jute fibers were obtained from India. The fibers were measured to have a density of 1.58 g/cm^3, modulus of 20 GPa, tensile strength of 440 MPa and elongation of 2%. Polylactic acid (PLA) was purchased from NatureWorks LLC, USA through local supplier Resinex, Czech Republic. The PLA had a density of 1.25 g/cm^3 and the average molecular weight (Mw) of 200,000. Chloroform which was used as solvent, purchased from Thermofisher, Czech Republic.

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Pulverization of jute fibers to nanofibers

In the beginning chemical pre-treatment of jute fibers was carried out sequentially with 4 wt% Sodium Hydroxide (NaOH) at 80°C for 1 hour and with 7 g/l Sodium Hypochlorite (NaOCl) at room temperature for 2 hours under pH 10-11. Subsequently the fibers were antichlor treated with 0.1% Sodium Sulphite (Na_2SO_3) at 50°C for 20 min [7].

High energy planetary ball milling (Fritsch pulverisette 7, Germany) was used for wet pulverization of waste jute Fibers in distilled water. The sintered corundum container of 80 ml capacity and zirconium balls of 3 mm diameter were chosen for 3 hours of wet milling. The ball to material ratio (BMR) was kept at 10:1 and the speed was kept at 850 rpm with reverse rotation of containers. At the end of wet milling, jute particles were separated from water by centrifugation at 4000 rpm and simultaneously transferred to isopropanol to avoid hornification during drying [7].

Particle size distribution of wet milled jute particles was studied after each hour of milling on a dynamic light scattering instrument (Malvern zetasizer nano series). Deionized water was used as dispersion medium and it was ultrasonicated for 5 min with bandelin ultrasonic probe before particle size measurement. Refractive index of 1.52 for water was used to calculate particle size of wet milled jute fibers.

In addition, morphologies of wet milled jute particles were observed on Scanning Electron Microscope (SEM) of TS5130-Tescan at 30 KV accelerated voltage and on field emission Scanning Electron Microscope (FESEM) of Zeiss at 5 kV accelerated voltage. The amount of 0.01 g of jute particles was dispersed in 100 ml acetone and then a drop of the dispersed solution was placed on aluminum foil and gold coated after drying.

Preparation of Nanocomposite thick films

PLA/jute nanofiber composite films with 1, 5 and 10 wt% filler content were prepared by mixing the calculated amount of jute nanofibers with 5% PLA in chloroform using a magnetic stirrer. The stirring was performed at room temperature for 3 hours. The composite mixture was further ultrasonicated for 10 min on Bandelin Ultrasonic probe mixer with 50-horn power. The final mixtures were then cast on a Teflon sheet in order to prevent sticking of the nanocomposite film. The films were kept at room temperature for 2 days until they were completely dried and then removed from the Teflon sheet. Neat PLA film was also prepared as a reference control sample for comparison purpose.

Characterization

Differential scanning calorimetry (DSC): The melting and crystallization behavior of the neat and composite films were investigated on DSC 6 Perkin Elmer instrument using pyris software under nitrogen atmosphere with sample weight of 7 mg. The sample was heated from 25°C to 200°C at a rate of 5°C/min. The crystallinity (%) of the PLA was estimated from the following Equation (1)

$$\%Crystallinity = \left(\Delta H_f / w \times \Delta H_0\right) \times 100\% \quad (1)$$

Where ΔH_f is heat of melting of sample, ΔH_0 is heat of melting of 100% crystalline PLA 93 j/g [8] and is mass fraction of PLA in nanocomposite.

Mechanical properties: Tensile testing was carried out using a miniature material tester Rheometric Scientific Mini Mat 2000 with a 1000 N load cell at a crosshead speed of 10 mm/min. The samples were prepared by cutting strips from the films with a width of 10 mm. The length between the grips was kept 100 mm. Ten samples were measured for each sample. Further the morphology of nanocomposite films was investigated using scanning electron microscope TS5130-Tescan SEM at 20 KV accelerated voltage. 2.4.3 Oxygen Barrier Properties

Oxygen barrier property (ml/m^2.24 h.0.1 MPa) of 10 cm circular sample was measured by manometric method using permeameter Lyssy L100-5000 on Systech Instrument, USA at 23°C and 0% RH respectively

Water vapour barrier: Water vapour barrier property (g/m^2.d) of 6.5 cm circular sample was measured using gravimetric method ZM-23 at 38°C and 85% RH respectively.

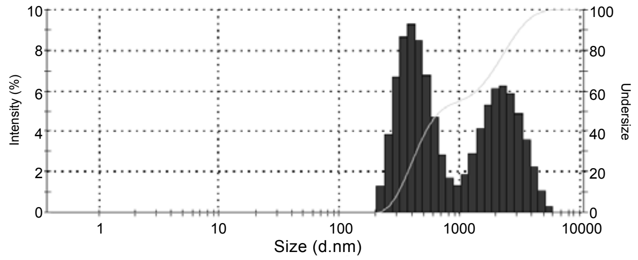
Results and Discussions

Effect of milling condition on particle size reduction of jute fibers

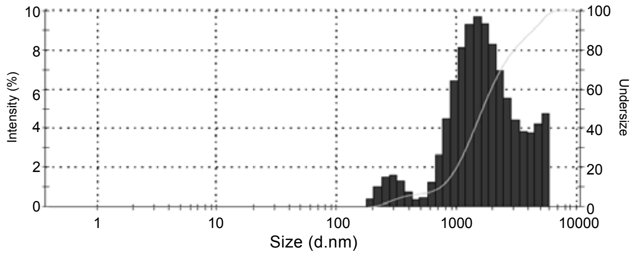
Under one hour of dry milling, jute fibers were pulverized to micro particles with average size of 1480 nm in wider particle size distribution as shown in Figure 1a and Figure 2a. The multimodal distribution of particles is attributed to increase in temperature within the mill because of continuous impact of balls [7]. The increase in temperature of mill resulted into the deposition of jute particles on the surface of milling container and balls. In case of wet milling, the increase in temperature was slowed down by deionised water which consequently resulted in narrow particle size distribution with average particle size to ~640 nm after one hour of wet milling as shown in Figure 1b and Figure 2b. In other words, uniformity in impact action of balls on every individual particle can be guaranteed during milling in wet condition [7].

Effect of wet milling time on particle size reduction of jute fibers

When waste jute fibers were subjected to extended duration of wet milling, the average particle size reached to 443 nm after 3 hours of wet milling and the particle size distribution changes slowly from multimodal nature to unimodal nature as shown in Figure 3a. This

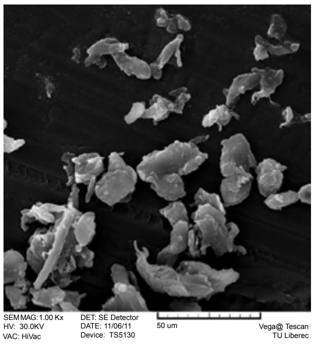


(a) One hour dry milling

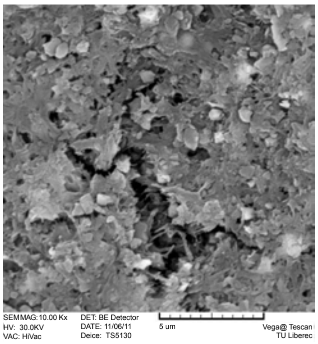


(b) One hour wet milling

Figure 1: Particle size distribution of jute particles after ball milling.



(a) One hour dry milling



(b) One hour wet milling

Figure 2: SEM image of jute particles.

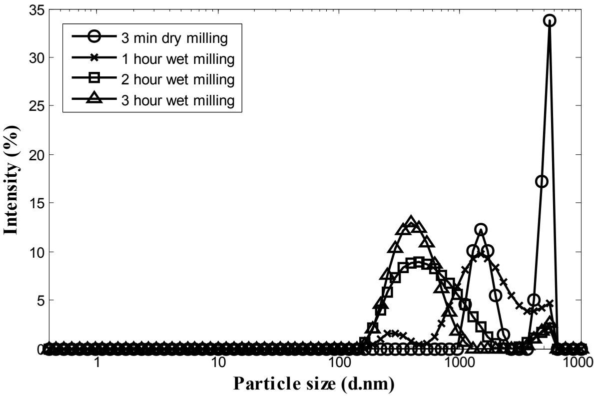


Figure 3a: Effect of extended wet milling time on pulverization.

showed the consistency and homogeneity in milling action on every individual particle as milling continued for longer time. However, the surface of milling balls which are of expensive materials, also started to get deteriorated with increase in the wet milling time [7].

The shape of jute particles was observed in the form of nanofibers having diameter around 50 nm as shown in Figure 3b. It was also possible to see few particles without aspect ratio which might be considered as agglomerates of hundreds of individual jute nanofibers.

Thermal behavior of nanocomposite films

Table 1 show that T_g and T_m values of PLA increased with the increased loading of jute nanofibers. The maximum improvement was observed in case of 10 wt% of jute nanofibers where T_g was increased from 42°C to 49°C and T_m was increased from 147°C to 153°C as compared to the neat PLA film. The higher values of T_g are attributed to the delay in polymer relaxation due to restriction in chain mobility caused by presence of nanofibers. On the other hand, the increased value of T_m can be attributed to the formation of bigger crystals. The wider peak of crystallization temperature for nanocomposite films shown in Figure 4 indicated enhanced crystallization rate of PLA molecules in presence of jute nanofibers due to their nucleating ability. The increase in crystallinity of PLA after addition of jute nanofibers was confirmed from the increase in heat of melting values given in Table 1.

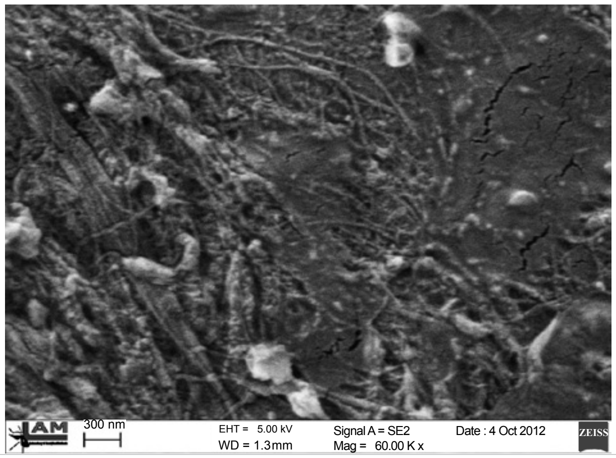


Figure 3b: FESEM image of particle size after 3 hour wet milling.

Sample	T_g (°C)	T_c (°C)	T_m (°C)	ΔH (J/g)	Crystallinity%
Neat PLA	42.35	98.85	147.49	17.33	18.63
1% JNF+PLA	42.84	97.90	153.15	20.52	22.28
5% JNF+PLA	46.01	97.70	153.14	24.74	26.84
10% JNF+PLA	49.00	96.43	153.97	26.38	30.21

Table 1: DSC values of neat PLA and PLA/JNF composite films.

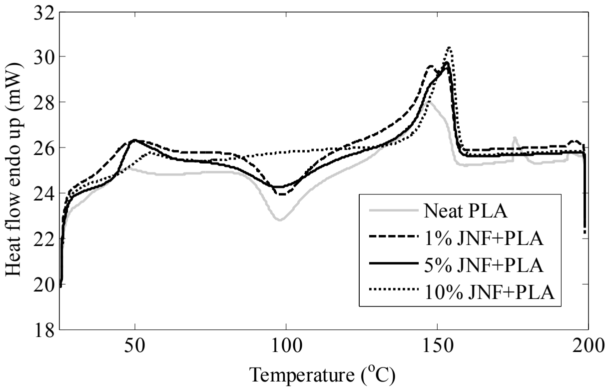


Figure 4: DSC of neat PLA and PLA/JNF composite films.

Mechanical properties of nanocomposite films

Figure 5 shows that the modulus of the PLA films increased significantly from 1.04 GPa to 3.3 GPa with the addition of 5 wt% jute nanofibers. The improved interaction between nanofibers and matrix, together with higher crystallinity of PLA in composites, can be attributed to the increase in modulus of the composites as compared to neat PLA. In order to understand the interaction between PLA and jute nanofibers, the morphology of fractured surfaces were studied

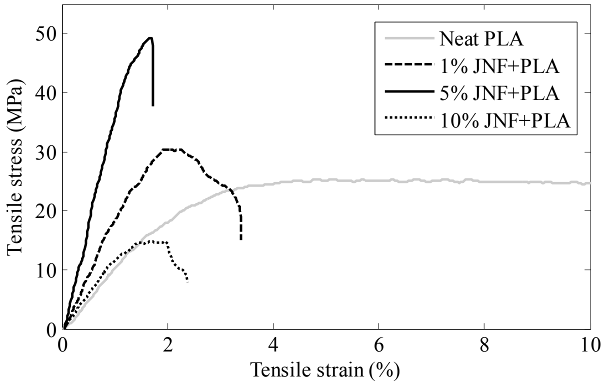


Figure 5: Stress-strain curve of neat PLA and PLA/JNF composite films.

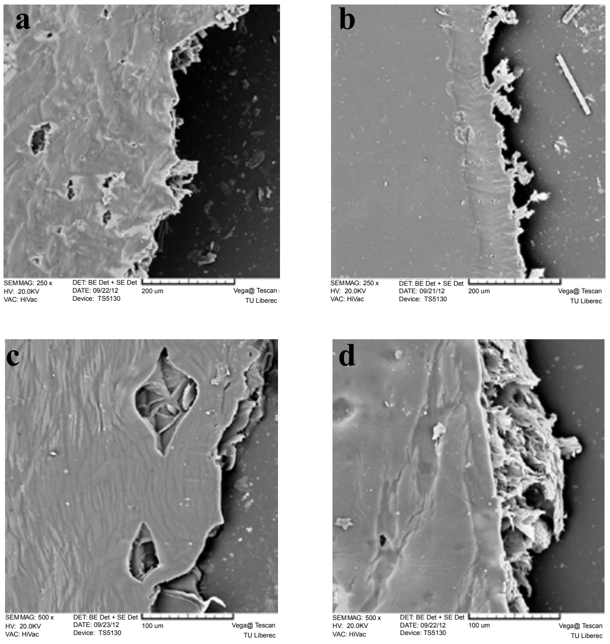


Figure 6: Fractured surfaces of films a: Neat PLA film b: 1% JNF/PLA film c: 5% JNF/PLA film d: 10% JNF/PLA film.

under the SEM as shown in Figure 6. The fractured surface of 5 wt% nanocomposites (Figure 6c) shows presence of wrinkles in contrast to smooth surface of 1 wt% nanocomposite (Figure 6b). The wrinkles and roughness on the surface indicated greater stress transfer from matrix to jute nanofibers and consequent improvement in modulus of 5 wt% nanocomposite. Similarly less number of voids around filler and matrix explained very good interfacial adhesion between them. With further increase in loading of jute nanofibers to 10 wt%, the modulus of composite films dropped significantly to 1.0 GPa. This could be explained by the clustering of nanofibers at higher loading, which results into formation of voids at the interface of filler-matrix as shown in Figure 6d.

Barrier properties of PLA/JNF composite film

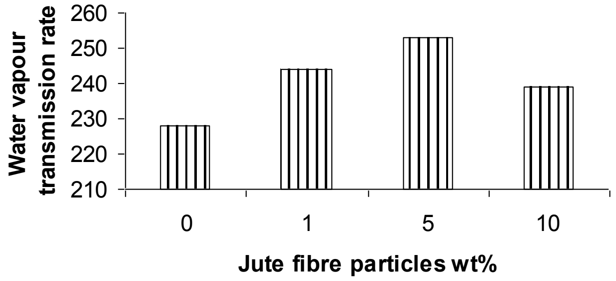


Figure 7: Moisture barrier of PLA/JNF film.

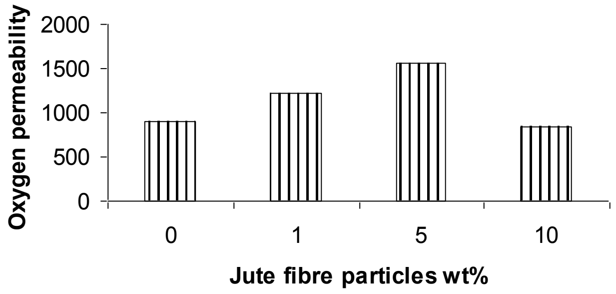


Figure 8: Oxygen barrier of PLA/JNF film.

Previous studies reported that improvement in barrier properties is directly related to tortuosities created by nanoparticles. The tortuous nature of path depends on shape and aspect ratio of the filler, degree of exfoliation or dispersion, filler loading and orientation, adhesion to the matrix, moisture activity, filler-induced crystallinity, polymer chain immobilization, filler-induce solvent retention, degree of purity, porosity and size of the permeate [9,11].

PLA films after addition of jute nanofibers showed poor performance in water vapor and gas barrier behavior at lower loading. Permeation rate of water vapor found to increase in composite PLA films loaded with 1 wt% and 5 wt% jute nanofibers and maximum permeation was observed in 5 wt% loading as shown in Figure 7. Similarly the permeation rate of oxygen was also observed higher in 1 wt% and 5 wt% composite films than neat PLA films from Figure 8. The main reasons behind poor barrier properties at lower loading can be related to least improvement in crystallinity of matrix. In this way, the improvement in barrier performance at higher filler loading (i.e. 10 wt%) is attributed to maximum improvement in crystallinity of matrix.

Conclusion

The pulverization of jute fibers by high energy wet milling process is simple, economical and environment friendly approach for separation of nanofibers. The diameter of nanofibers reached to 50 nm after 3 hours of wet milling. This technique has a very good scope on industrial scale for refinement of large amount of waste fibers generated in the textile industry.

When jute nanofibers were incorporated into PLA matrix for preparation of biodegradable nanocomposite films, the maximum improvements in mechanical properties were observed at 5 wt% loading of nanofibers. The improvements in properties are attributed to the increased interaction of nanofibers along with increased crystallinity of PLA. However, the deterioration in properties at 10 wt% loading of jute nanofibers is attributed to the nonhomogeneous stress transfer from matrix to fillers due to poor dispersion and agglomerations of nanofibers at higher filler loading. Further, the poor barrier performance of PLA films at lower loading of nanofibers is related with least improvement of crystallinity of matrix.

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