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Aloefiber reinforced corn starch films: influence of alkali hydrolysis, bleaching and acid hydrolysis on microsrostructure, mechanical property of biocomposite

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Abstract: Biocomposite films made from corn starch and aloe fibers (Agave Americana) were prepared using solutioncasting method. Aloe fibers were treated with NaOH, bleached with sodium chlorite and acetic acid buffer solution, and subsequently acid hydrolysed to obtain cellulose nanocrystals. Biocomposites in the form of films were prepared by mixing starch, glycerol, sorbitol with various fiber compositions (0 -10%).Scanning electron microscopic analysis showed that impurities from raw fiber has been removed during alkali hydrolysis, part of cellulose, hemicellulose and lignin were removed during bleaching process and complete removal of lignin and complete fibrilation occurred during acid hydrolysis. Proper reinforcement was not observedin case of raw and alkali hydrolysed fiber. The effect of bleached and acid hydrolysed treatment and filler contents of biocomposites were evaluated through mechanical tests. Results showed that the tensile strength increased after bleaching and acid hydrolysis treatments and the optimum filler content was 6% .The maximum tensile strength at 6% loading of the biocomposite was 7.2MPa. Maximum tensile modulus at 6% loading of cellulose nanocrystals was 272.4MPa

Keywords: Biocomposites, bleaching, acid hydrolysis, tensile strength, reinforcement.

Introduction

Natural source based composites are considered to be promising substitutes or complements to their non-biodegradable petrochemical-based counterparts[1]Although many types of new polymers are being industrially produced (PLA, PHA, PCL, PEA and others), polymers from agricultural sources are the most studied by researchers, especially polysaccharides. Among the films made from polysaccharides, those obtained from starch are the most important because it is one of the most commonly used agricultural raw materials, since it is a renewable source, inexpensive and widely available[2]. Beyond this, it has good film-forming properties. The best known materials for making these green materials are starch and cellulose[3]. Films developed from starch are described as isotropic, odorless, tasteless, colorless, non-toxic and biodegradable. Unfortunately, there are some strong limitations for developing starch based products, since they present poor tensile properties and high water vapor permeability when compared to conventional films derived from crude oil[2] on account of their hydrophilic nature and their sensitivity to moisture content, a factor that is difficult to control[4]. Previous studies demonstrated that tailoring starch with cellulose helps to minimize this problem and bring about an improvement in thermal stability.[5]

Starch is a natural polymer consisting of amylose and amylopectin. Among the major sources of starch are maize, cassava, sweet potato, yam, corn, rice, oats, and peas[5]. In nature, starch can be solubilized in the presence of water and/or a plasticizer followed by heating and mixing, which produces a substance known as thermoplastic starch (TPS)[6]. When a starch suspension is heated, semicrystalline TPS granules start to swell and absorb water, which is accompanied by the destruction of hydrogen bonds between the macromolecules[7]. In recent years, starch has found use in the food industry, and its modified forms have been employed in industrial packaging materials, disposable cups, and also in pharmaceuticals.

Cellulose, which is one of the main components in most natural fibers, is composed of repeating d-glucopyranose units. It is a semicrystalline natural polymer that exhibits both amorphous and crystalline phases reported. The diameter of celluloses fibril is between 5 and 10 nm while the length is dependent on the source of the cellulose[8]. Nowadays, it is common practice among researchers to use this linear semicrystalline polysaccharide as a nano-reinforcer in composites. This is not just because of the good mechanicals properties imparted by the nano-sized cellulose but also due to its high aspect ratio (L/D) and its ability to form continuous networks [9].The nano-sized cellulose has many advantages owning to its high stiffness and high specific area.

Aloe or Agave Americna is a natural tropical plant that is grown commercially in many places around the world and is among the crops that are rich in cellulose. Physically, Aloe stem consist of two types of fibers, the core (internal fiber) and the bark (outer fiber). The pith of Aloe fibers can be equated with the fibers found in hard wood[10]. It was reported that the lignin content in Aloe fiber ranges between 5.9 and 19% while that of hemicellulose is between 15 and 23%. Cellulose constitutes the major content and ranges between 44 and 63.5% [11].

The objective of this study was to show the effect of alkali hydrolysis, bleaching and acid hydrolysis of Aloe fibers in increasing their reinforcing capacity in thermoplastic corn starch – aloe fiber biocomposites. The reinforcing effect effect was studied in terms of mechanical properties (tensile strength, tensile modulus) of the biocomposite. In order to present comparable results, the variation of filler loading for each treatment was used to study the properties of the composites.

Materials

Aloe fiber (Agave Americana) was provided by Chandra prakash & Co. (Rajasthan) and native corn starch (CS) was supplied by Rassigum factory (Chennai) .Sulfuric acid (98%), sodium hydroxide (99%), sodium chlorite (80%), and glacial acetic acid (99.5%) were purchased from SISCON (Chennai). All of the chemicals were used without purification. Laboratory grade sorbitol (98%, Sigma–Aldrich) and glycerol (99.5%, SYSTERM-chemAR) were used as plasticizers for preparing the bio-composites.

Methodology

Preparation of cellulose nanocrystals from Aloe fibers

Aloe fibers were cut into small pieces (approximately 5mm) and treated with a 4 wt% NaOH solution at 80^{O}C for 4 hours under mechanical stirring. This alkali treatment was conducted three times, and after each treatment, the fibers were filtered and washed with distilled water to remove the alkali-soluble components. A subsequent bleaching treatment was conducted to remove the residual lignin. The solution used in this treatment consisted of equal parts of acetate buffer (solution of 2.7 g NaOH and 7.5 mL of glacial acetic acid in 100 mL of distilled water), aqueous chlorite (1.7%w/v), and distilled water. The bleaching treatment was performed at 80^{O}C for 4 h under mechanical stirring and was repeated three times. The bleached fibers were subsequently filtered, washed with distilled water, and air dried. The fiber concentration was 5% (w/v) for all treatments[12].

Colloidal suspensions of cellulose nanocrystals were prepared from bleached Aloe fibers. Acid hydrolysis was conducted at 45^{o}C under mechanical stirring using 65 wt% H_2SO_4 (pre-heated) for 45 minutes. The suspension was kept in ice with cold distilled water to stop the reaction. The suspension was then centrifuged for 10 min at 10,000 rpm and 10^{o}C. This centrifugation step was repeated three times. The aqueous suspension was subsequently dialyzed against distilled water until a constant pH was attained. Ultrasonic treatment was then carried out to disperse the nanocrystals.The resulting suspension was subsequentlystored in the refrigerator[13].

Preperation of starch – fiber biocomposites

Fabrication of thermoplastic corn starch-raw aloe fiber, thermoplastic corn starch-alkali treated Aloe fiber, thermoplastic corn starch-bleached Aloe fiber, and thermoplastic corn starch-cellulose nanocrystals biocomposite films was based on solution casting[14]. An aqueous suspension of cellulose fibers prepared by mixing. Different percentages (2%,4%,6%,8%,10%) of raw, alkali hydrolyzed, bleached, acid hydrolyzed fibers were suspended in water (100ml) for 24 hours, in order to acilitate the incorporation of these fibers into the starch suspension. The suspension of fibers and water was stirred for 10 min at 14,000 rpm before adding starch and glycerol. Then 5% starch, 2g of sorbitol, 1g of glycerol were added Afterwards, under constant stirring (90 rpm), the recipient with the mixture was heated up to 71 ^{o}C in a hot water bath at a heating rate of 1 ^{o}C/min, and kept at this temperature for5 min. The mixtures without addition of fibers were preparedsimilarly[15].

Microscopic analysis.

The morphology of the fibers after each treatment was investigated using a Zeiss Supra 55VP field emission scanning electron microscopy (FESEM) at a magnification of 1000×. All the samples were mounted on aluminum stub by double-faced tape, coated with gold before observation to prevent charging with thickness around 0.01–0.1m (Sputter Coater model BioRAD, 2.2 kV, 2 min) and observed using an applied tension of 10 kV t.

Mechanical testing

The mechanical performance of the films was evaluated in terms of tensile strength and tear resistance strength using a universal testing machine (Instron model 5566, USA) at room temperature accord-ing to ASTM D882. A crosshead speed of 50 mm/min, initial grip distance of 40 mm, and load cell of 50 N were used for this test. The film thickness was determined at five points using a digital caliper (Mitutoyo, ±1m). The average thickness of the samples was 0.27 ± 0.02 mm. The samples were cut into a dumbbell shape and the average value of seven replicates for each sample was taken. The tensile test characteristics were calculated using Bluehill soft-ware 3.

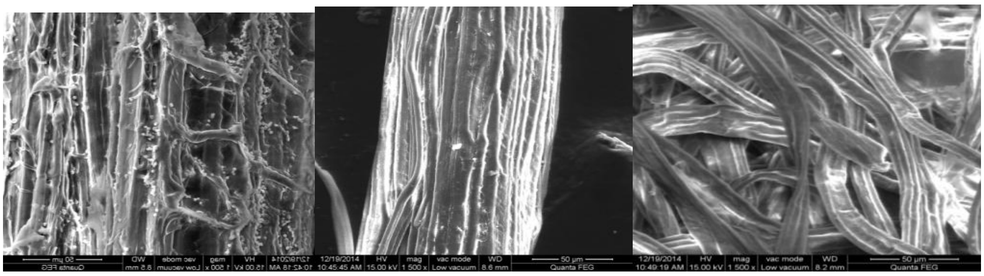
Results and discussion

Fiber morphology

A B C D

Figure 1Photographs of A.raw, B.alkali hydrolysed,C.Bleached, D.Cellulose nanocrystals of Aloe fibers

Figure 1 shows leaves of Aloe fibre at different stages of chemical treatment. The colour of the fiber changed from cream to light brown after alkali treatment and white after bleaching process



A **B** **C**

Figure 2.FESEM pictures of A.Raw fibers, B.Alkalihydrolysed fiber, C. Bleached fiber

Figure 2 presents Field Electron scanning electron microscope of Aloe fiber after different stages of treatment. A rough surface with impurities was clearly observed for Alkali treated fiber. However, after alkalization the rough surface of the raw fibers was destroyed. It was replaced by a smooth surface with relatively less impurities due to the removal of most of the hemicellulose, some lignin, and waxy materials that covered the peripheral surface of the fiber cell wall. In addition, the Aloe fiber bundle also started to separate into thinner fibers. The alkalization not only eliminated the highly branched hemicellulose and some of the lignin but also decreased the fiber dimension leading to produce finer fibrillar structures. During hot alkaline treatment, hemicellulose is hydrolyzed and part of the lignin undergoes depolymerization. For bleached fiber more significant changes of the fiber surface were observed. Further fibrilation of the fibers was seen due to the loss of lignin that was left in the fibers. The use of the bleaching agent NaClO2 and acetic buffer solution eliminated the lignin by oxidizing it, which led to its dissolution in alkaline medium and then fiber fibrilation[12].The cellulose nanocrystals dispersion produced after acid hydrolysis did not settle or flocculate because of the sulfate groups present on the surface during sulfuricacid treatment

Morphology of Starch Biocomposite film

A **B** **C**

Figure 3.Macroscopic visual images of starch biocomposites with 6% loading ofA. Alkali hydrolysed, B.Bleached and C. Cellulosenanocrystals.

Figure 3 shows macroscopic visual images of starch biocomposites with6% loading of raw, alkali hydrolysed, bleached and cellulose nanocrystals. Plain starch and cellulose nanocrystals reinforced starch displays smoother surface compared to the composites reinforced with raw, alkali hydrolysed and bleached fibers. The smooth surface observed indicates that cellulose nanocrystals with much smaller size are homogeneously dispersed with starch This fine dispersion of cellulose nanocrystalswithin the polymer matrix would results in an improvement in the mechanical properties of the nanocomposite compared to the plain starch and other composites. For plain starch reinforced with raw fiber, it is clear that the interfacial adhesion between the filler and matrix was poor. This can be readily seen from the absence of any physical contact between both components. The fibers are pulled out from the matrix and practically intact. Fracturing the sample did not lead to breaking the fiber. In addition, holes and spacing occur along the fiber, resulting in poor contact and inferior interfacial stress transfer.

Mechanical properties

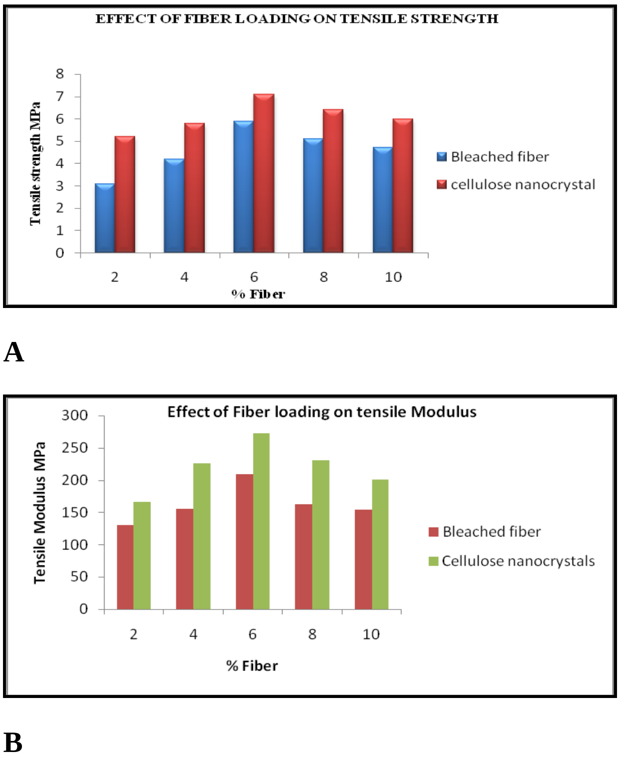


Figure 4. Effect of fiber treatment on A. Tensile strength and B. Tensile modulus

Tensile strength

The tensile strength of the films was determined and the results are plotted in Figure 4 .From the figure it is shown that the film reinforced with treated fibers had a higher tensile strength compared to the plain starch matrix film, which had the lowest tensile strength (2.4MPa). Alkali hydrolysed fiber had low tensile strength when compared to the plain starch matrix. The 6% cellulose nano crystals reinforced starch showed the highest tensile strength at 7.2MPa among the composites for all of the fiber compositions. Acid hydrolysis treatment resulted in increase of tensile strengthwhen compared to the control film. This significant improvement for starch cellulose nanocrystals was mainly due to the high specific area and high L/D ratio, which provided better reinforcement capability. This also reflected the strong interfacial interaction that occurred between starch and cellulose. The ability of the nanofibers to restrict the matrix mobility also contributed to this improvement. For alkali and bleached fiber biocomposites, no significant evolution upon filler loading was observed but the tensile strength value was systematically higher than for the neat matrix. This improvement was due to the strong interfacial interaction between starch and fibers, which brings about good stress transfer. On the other hand, the slight decrease for the composites at certain loadings was mainly due to entanglement of the fibers inside the matrix phase[12]. The decrease in tensile strength at 8% CNC loading was due to aggregation of nanocrystals in matrix phase

Tensile Modulus

Figure 4 B shows a plot of tensile modulus against fiber loading. The tensile modulus remains approximately same for biocomposites loaded with raw, alkali and bleached fibers but increased in case of alkali hydrolysed, bleached and acid hydrolysed fiber loading. The starch polymer matrix is reinforced by addition of fibers and this enhanced the stiffness of the biocomposite. Increase in tensile modulus may be related to increased stiffness. Biocomposites loaded with highly crystalline cellulose nanocrystals showed high stiffness with tensile modulus of 272.4MPa.Because of smaller size and high surface area displayed by cellulose nanocrystals increased the surface interaction between the filler and the matrix and led to mechanical improvement in term of its modulus.

Conclusion

Cellulose nanocrystals from *Agave Americana* were obtained by treating raw fibers with alkali, bleaching agent and acid .Field emission scanning electron microscopic analysis showed that hemicelluloses and lignin were completely removed at the end of acid hydrolysis and pure cellulose nanocrystals were obtained. Corn starch and Aloe fiber biocomposites were produced by solution casting technique using sorbitol and glycerol as plasticizer. Biocomposite films were cast using starch and different concentration of fiber (2%, 4%, 6%, 8%, 10%). The fiber loading enhanced mechanical properties of biocomposites, with biocomposites having 6% cellulose nanocrystals showing the highest tensile strength at 7.2 Mpa.This result indicates the existence of good stress transfer and interfacial interaction between matrix phase and the filler. This suggests that the cellulose nanocrystals produced are compatible with starch matrix and can act as good reinforcing agent.

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