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Effect of pretreatment of bagasse fibers on the properties of chitosan/microfibrillated cellulose nanocomposites

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Abstract Bleached bagasse pulp was pretreated with dilute alkali and xylanase enzymes before isolation of microfibrillated cellulose using ultra-high friction grinding and high-pressure homogenization. The isolated nanofibers were used with chitosan polymer to prepare chitosan nanocomposites by solution casting at nanofiber loading from 2.5 to 20%. The effect of nanofibers loading on moisture sorption, dry and wet tensile strength, crystallinity, thermal stability, and dynamic mechanical thermal properties was studied using tensile testing, X-ray diffraction (XRD), thermogravimetric analysis (TGA), and dynamic mechanical thermal analysis (DMTA). Nanocomposites with good transparency were obtained at the different nanofibers loadings. Chitosan nanocomposites made using nanofibers isolated from bagasse fibers treated with xylanase or alkali showed higher dry and wet tensile strength than those made using nanofibers isolated from untreated bagasse pulp. DMTA results showed higher storage modulus and indicated higher glass transition temperature for the chitosan nanocomposites than that of neat chitosan. XRD patterns showed that, at low nanofibers loading, addition of bagasse nanofibers to chitosan matrix increased ordering of chitosan chains upon drying the nanocomposites films.

Introduction

Microfibrillated cellulose (or so called cellulose nanofibers) isolated from different lignocellulosic materials represents a distinctive natural nanomaterial with high reinforcing effect coupled with availability of raw materials, biodegradability, and biocompatibility [1]. For these reasons, an increasing number of publications emerged during the last few years concerning the isolation of microfibrillated cellulose from different lignocellulosic sources and their use in advanced nanocomposites with different natural and synthetic polymer matrices for different applications [2]. Agricultural residues are an important source for cellulose fibers in different areas of the world. Bagasse is among the most widely used lignocellulosic materials for paper and composite manufacture in countries that have no forests. In a previous work, cellulose nanofibers were isolated from bagasse and rice straw using ultrafine grinding followed by high-pressure homogenization [3].

Many studies have been published on pretreatment of cellulose fibers prior to isolation of nanofibers to facilitate their isolation and/or improve the properties of isolated nanofibers using chemical methods [4–11] or using enzymes [12–14]. The use of enzyme technology is preferred to chemical methods due to the high selectivity of the enzymes and it is environmentally cleaner.

Chitosan is a naturally occurring polysaccharide polymer composed of glucosamine and *N*-acetyl glucosamine with properties that depend largely on the degree of acetylation, molecular conformation, molecular weight, and its distribution [15]. It finds many applications mainly in

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biomedical area due to its high resistance toward microbial attack [16]. In such applications, chitosan is used with other organic or inorganic materials to improve its mechanical and dimensional stability in wet conditions [17–19]. Considerable work was focused on mixing chitosan with different polymers such as polyethylene glycol [20], polyvinyl alcohol and alginate [21], hyaluronic acid [22], and starch [23] to prepare composite materials with improved properties. Chitosan has very similar chemical structure to cellulose. The compatibility between these two abundant polymers has been utilized in different studies to prepare composites for different applications [24–27]. However, the transparency of chitosan film containing cellulose fibers or derivatives is greatly reduced.

In the area of nanocomposites using chitosan as a matrix and cellulose nanofibers as a reinforcing materials, few studies have been published so far. In those studies, microfibrillated celluloses isolated from wood pulp and tunicin cellulose were used as reinforcing elements and also to enhance wet strength properties of chitosan [28–32].

The aim of this work is to study the use of nanofibers isolated from untreated bagasse pulp, bagasse pulp pretreated with xylanase enzymes, or bagasse pulp treated with dilute alkali in preparation of biodegradable nanocomposites with improved tensile properties and possible applications in the area of tissue engineering.

Experimental

Materials

Bleached kraft bagasse pulp was kindly supplied by Qena Company for Pulp and Paper, Qena, Egypt. Chemical composition of bagasse was: α-cellulose 70.6%, pentosans 26.8%, ash 0.82%, and degree of polymerization (DP) of 1174.

Chitosan powder (high molecular weight grade, degree of deacetylation: 84.7%; viscosity: 200 mPa in 1% acetic acid; relative molar mass: M_r 400,000) was obtained from Sigma-Aldrich. Sodium chloride, potassium chloride, sodium phosphate dibasic, potassium phosphate monobasic, and glacial acetic acid were reagent grade chemicals and used as received.

Pretreatment of bagasse pulp

For alkali pretreatment, bagasse pulp was treated with 5% sodium hydroxide for 45 min at 50 °C. After treatment, the pulp was washed thoroughly with water, dilute acetic acid (2% solution), and finally with water until neutral pH. For xylanase treatment, *Trichoderma reesei* NRRL 6156 fungus was used for production of crude xylanase enzymes using a PMY liquid medium supplemented with 5% corn cobs as an inducer carbon source for xylanase [33]. Xylanase activity was determined as described earlier [34]. Enzymatic treatment of bagasse pulp with xylanase enzymes was carried out as follows: 20 g of bleached bagasse pulp were treated with crude xylanase enzymes in citrate buffer (PH 5.3) in 500 mL conical flask at 10% consistency. The concentration of xylanase enzymes was 60 IU g^{-1}. The hydrolysis reaction mixture was kept under shaking condition (200 rpm) at 50 °C for 4 h. At the end of reaction period, the pulp was filtered and washed thoroughly with distilled water.

Isolation and characterization of nanofibers from untreated and treated bagasse pulps

The pulps were first disintegrated by high-shear mixer using pulp suspensions of 2% consistency. The fibers were then refined using high-shear ultrafine friction grinder, or so called supermasscolloider (MKCA6-2, Masuko Sanguo, Japan) and passed through the instrument up to 30 times. The gap between the discs was adjusted to 9 µm. The refined fibers were homogenized using a two-chamber high-pressure homogenizer (APV-2000, Denmark) after being diluted with water to 1% consistency and passed through the instrument for one time. The pressure was kept at 40 bar in one chamber and 400 bar in the other chamber. Transmission electron microscopy (TEM) was carried out using a JEOL 1230 transmission electron microscope (Japan) with acceleration voltage 100 kV. A drop of fibers suspension was used on a copper grid with carbon film. Chemical composition and degree of polymerization (DP) of the different isolated nanofibers were determined by viscosity measurement of the samples dissolved in copper-ethylyene diamine solution [35].

Preparation of chitosan nanocomposites

Chitosan was dissolved in 2% (wt/wt) acetic acid solution. The concentration of chitosan in the solution was 2% (wt/v). Mixtures of cellulose nanofibers and chitosan solution were prepared by thoroughly stirring the nanofibers with chitosan overnight. Nanofiber loadings from 2.5 to 20%, based on weight of chitosan, were used. The films were obtained by casting in 15-cm diameter Petri dishes and dried in an oven with circulating air at 35 °C for 24 h. The films were removed from the dishes and kept in a relative humidity of about 50% at 25 °C for 48 h before testing.

Characterization of chitosan nanocomposites

Tensile properties of the obtained films were measured using a Lloyd universal testing machine (Lloyd, England) at crosshead speed of 2 mm/min using a load cell of 1 kN. The width of the films was about 1 cm and the gauge length was 4 cm. Wet tensile strength testing was carried out using a Lloyd universal testing machine at crosshead speed of 2 mm/min using a load cell of 100 N. The samples were immersed in phosphate saline buffer (137 mM NaCl, 2.7 mM KCl, 10 mM sodium phosphate dibasic, 2 mM potassium phosphate monobasic) at pH 7.4 for 24 h before testing [18]. At least five strips from each sample were tested and the results averaged. Moisture sorption at 75% relative humidity was determined by keeping preweighed nanocomposites films (three samples of about 5-cm diameter) in opened bottles inside a closed desiccators containing saturated solution of sodium chloride at 25 °C. After different intervals, the samples were taken out, weighed, and the increase in weight due to moisture sorption was calculated. Diffraction patterns were obtained using a Phillips X-ray diffractometer using Cu-Ka radiation at 40 kV and 25 mA. Crystallinity index of cellulose nanofibers was calculated from the X-ray diffraction patterns according to the following equation [36]:

$$\mathrm{CrI} = (I_{002} - I_{\mathrm{am}})/I_{002}$$

where I_{002} and I_{am} are the intensities of the peaks at 2θ of about 22 and 18, respectively.

A Perkin-Elmer Thermogravimetric analyzer was used to study the thermal stability. The heating rate was set at 10 °C/min over a temperature range of 50–600 °C. Measurements were carried out in nitrogen atmosphere, with a rate of flow of 50 cm^3/min. Dynamic mechanical properties were measured using Anton Paar Rheometer, (Anton Paar, Austria) in tensile mode at a frequency of 1 Hz, strain of 0.1%, and at the heating rate of 3 °C/min over the temperature range of −100 to 200 °C.

Results and discussion

Chitosan nanocomposites were prepared using nanofibers isolated from untreated bagasse, alkali-treated bagasse, and xylanase-treated bagasse by ultrafine grinding followed by high-pressure homogenization. Microfibrils and microfibrillar bands were obtained by the action of grinding and homogenization but the presence of microfibrillar bands decreased as a result of the homogenization [3, 14]. Figure 1 shows TEM image of the isolated nanofibers and Table 1 shows chemical composition, crystallinity, and diameter of the isolated nanofibers. Nanofibers isolated from alkali-treated pulp had the highest α-cellulose content and DP followed by those isolated from xylanase-treated pulp while those isolated from untreated pulp had the lowest α-cellulose content and DP. In addition, nanofibers isolated from alkali-treated pulp had lower hemicelluloses than those isolated from untreated and xylanase-treated pulps. Although microfibrils isolated from different pulps had close diamters the isolated nanofibers from the untreated pulp had microfibrillar bands with higher diameter were observed in case of using untreated pulp. The percentage of nanofibers used in the chitosan nanocomposites was from 2.5 to 20 wt%. All the prepared nanocomposite films showed good transparency even at the high fiber loading (Fig. 2).

Crystallinity of chitosan nanocomposites

Both cellulose and chitosan are semi-crystalline polymers. When chitosan is dissolved in dilute acetic acid and cast into film, the formed film is highly amorphous. In the previous published work on using cellulose nanofibers in chitosan nanocomposites [28–32], the effect of addition of the nanofibers on crystallinity of chitosan was rarely studied. Susana et al. [31] reported that the incorporation of microfibrillated cellulose seemed not to affect the crystalinity of the chitosan matrices since no relevant changes on diffraction profiles of the nanocomposites were observed.

In the current work, the effect of addition of cellulose nanofibers isolated from untreated, alkali-treated, or xylanase-treated bagasse on the crystallinity of chitosan matrix was studied by XRD. Figure 3 shows the XRD patterns of bagasse nanofibers isolated from untreated pulp, chitosan, and chitosan nanocomposites with different nanofibers

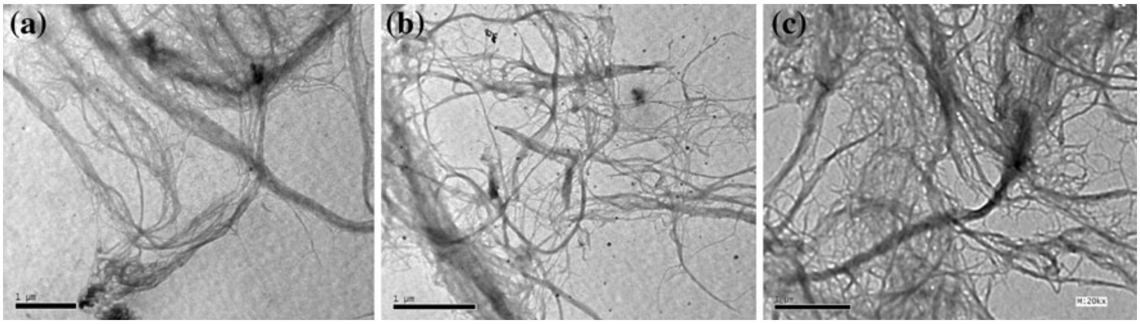

Fig. 1 TEM of nanofibers isolated from untreated bagasse (**a**), alkali-treated bagasse (**b**), and xylanase-treated bagasse (**c**)

Table 1 Properties of nanofibers isolated from untreated, alkali-treated, and xlanase-treated bagasse pulp

	Nanofibers isolated from		
	Untreated pulp	Alkali-treated pulp	Xylanase-treated pulp
Diameter range[a]			
Microfibrils	7–24 nm	11–30	9–25
Microfibrillar bands	Up to 140 nm	Up to 75 nm	Up to 90 nm
α-Cellulose	71.7	78.9	73.5
Pentosans	29.7	20.7	23.3
Degree of polymerization	1135	1647	1248
Crystallinity[b]	74.2	76.1	73.9

[a] Range of diameter observed in the TEM images

[b] Calculated from XRD patterns

Fig. 2 Neat chitosan and chitosan nanocomposite films with 20% bagasse nanofibers

loadings. Bagasse nanofibers showed the known XRD pattern of cellulose I, namely, peaks at 2θ angles at about 16 and 23, due to reflections from 11′0 & 110 and 020 lattice planes, respectively [37]. The other nanofibers isolated from dilute alkali- and xylanase-treated pulps also showed cellulose I diffraction pattern (not shown). On the other hand, the "as casted" chitosan exhibited diffraction pattern with very broad peak centered at 2θ of about 22 indicating the high amorphous nature of chitosan film. In case of chitosan nanocomposites, addition of bagasse nanofibers to chitosan matrix resulted in diffraction patterns showing two peaks at about 2θ angles of 20 and 23, which belongs to both of cellulose and chitosan. In addition, another peak appeared at about 2θ angle of about 12. The 2θ peak at 12 was higher in intensity at lower nanofibers loading. The appearance of this peak, which is usually seen in case of acetic acid-dissolved chitosan neutralized by alkali [38, 39], indicates that presence of the nanofibers increases the ordering of chitosan chains upon drying. This trend is in contrary to the expected since presence of cellulose nanofibers between the chitosan chains is expected to result in decrease in packing of chitosan chains, i.e., the lower crystallinity of chitosan. The peaks in the region from 2θ angle from 22 to 16, which include the peaks of chitosan and cellulose, were overlapped with each others and made it difficult to estimate the crystallinity index of chitosan as a result of adding the nanofibers. Regarding the effect of kind of nanofibers used on the crystallinity of chitosan, using of nanofibers isolated from alkali- or xylanase-treated pulps resulted in notable increase in the intensity of the peaks at 2θ angles of 12 and 20, especially in the case of nanofibers isolated from alkali-treated (Fig. 4). These results indicate better interaction between chitosan and nanofibers isolated from alkali-treated and xylanase-treated pulp than that between chitosan and nanofibers isolated from untreated pulp.

Moisture sorption of chitosan/cellulose nanofibers nanocomposites

Moisture sorption by hydrophilic polymers noticeably affects their mechanical properties and thus may limit their use in humid conditions. The effect of loading of chitosan with cellulose nanofibers on moisture sorption was studied at 75% relative humidity at 25 °C. Figures 5 and 6 show moisture sorption of the nanocomposites made using the different nanofibers for 1 month. As shown in Fig. 5, addition of nanofibers isolated from untreated pulp to chitosan resulted in an increase in moisture sorption at the beginning of the test and up to 1 week. After that, nanocomposites containing high nanofibers loading ($\geq$10%) had lower moisture sorption than neat chitosan. Moisture sorption decreased on increasing the nanofibers loading, especially at longer exposure to moisture.

The effect of the kind of nanofibers on moisture sorption of nanocomposites was studied at 20% loading of nanofibers isolated from untreated, alkali-treated, and xylanase-treated bagasse (Fig. 6). There was no significance difference in moisture sorption of the different nanocomposites up to 7 days of the test. At longer exposure to moisture, nanocomposites containing nanofibers isolated from alkali- or xylanase-treated pulps had slightly lower moisture sorption than that containing nanofiber isolated from untreated bagasse. This could be attributed to the lower hemicelluloses and slightly higher crystallinity of nanofibers isolated from xylanase- and alkali-treated pulp.

Tensile properties of chitosan nanocomposites

Figures 7 and 8 show the tensile properties of the prepared nanocomposites. Adding the nanofibers to chitosan resulted

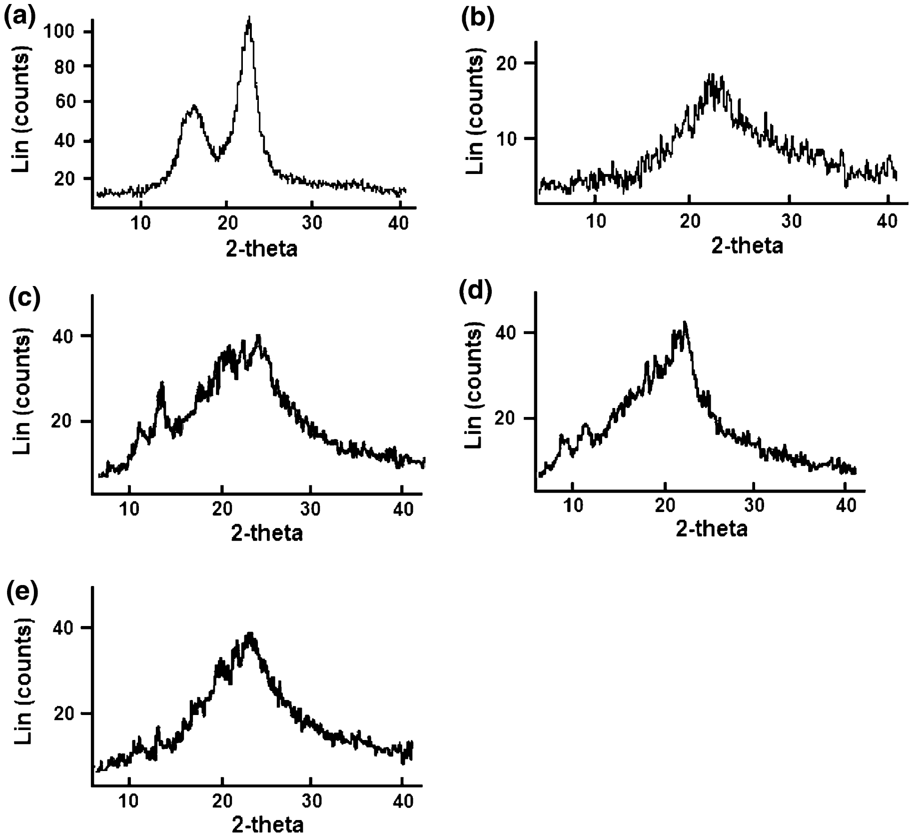

Fig. 3 XRD patterns of cellulose nanofibers isolated from untreated bagasse (**a**), chitosan (**b**), chitosan nanocomposites containing nanofibers isolated from untreated bagasse 5% (**c**), 10% (**d**), and 20% (**e**)

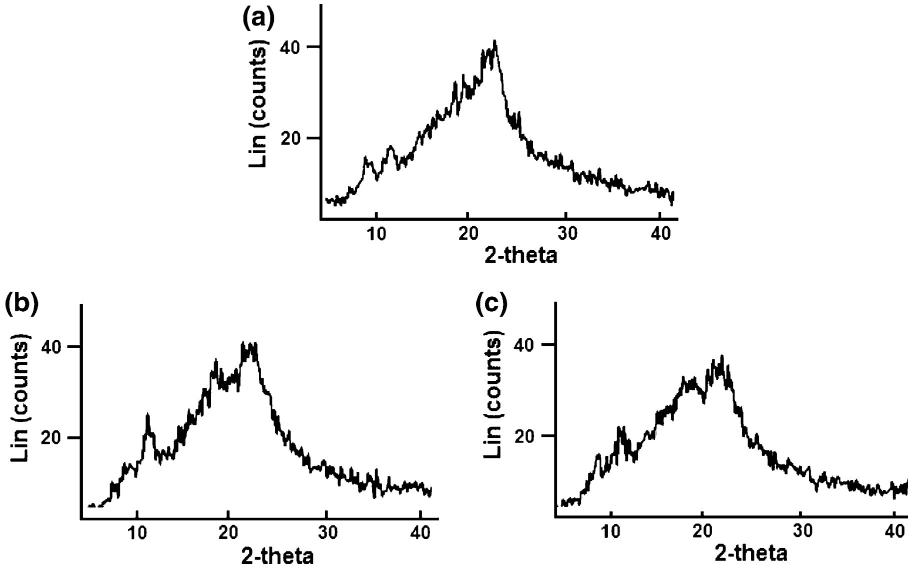

Fig. 4 XRD patterns of chitosan nanocomposites containing 10% nanofibers isolated from untreated bagasse (**a**), 10% nanofibers isolated from alkali-treated bagasse pulp (**b**), and 10% nanofibers isolated from xylanase-treated bagasse pulp (**c**)

in improvement of the tensile strength, which increased with increasing the nanofibers loading. The improvement in tensile strength was significant even at 2.5% nanofibers loading and could be attributed to formation of percolated/interconnected network of the nanofibers within the chitosan matrix [28]. The increase in tensile strength values at 20% nanofibers loading were about 192, 220, and 211% for chitosan nanocomposites containing nanofibers isolated from untreated bagasse, xylanase-treated bagasse, and alkali-treated bagasse, respectively. It is interesting to see that the tensile strength values for nanocomposites made using 20% of the different nanofibers were close to the tensile strength of nanopaper sheets made from the nanofibers only. But it should be taken into consideration

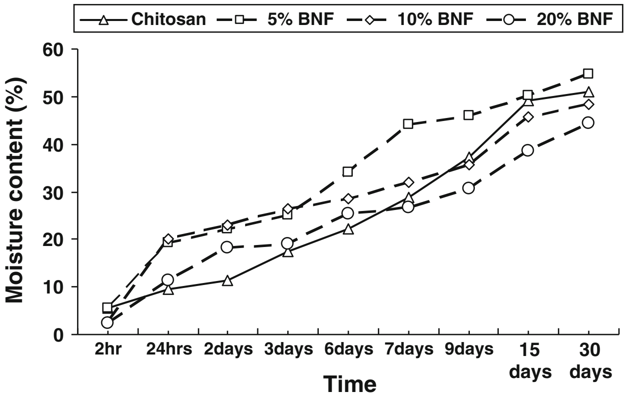

Fig. 5 Moisture sorption of chitosan nanocomposites prepared using different ratios nanofibers isolated from untreated bagasse pulp (BNF) at 75% relative humidity

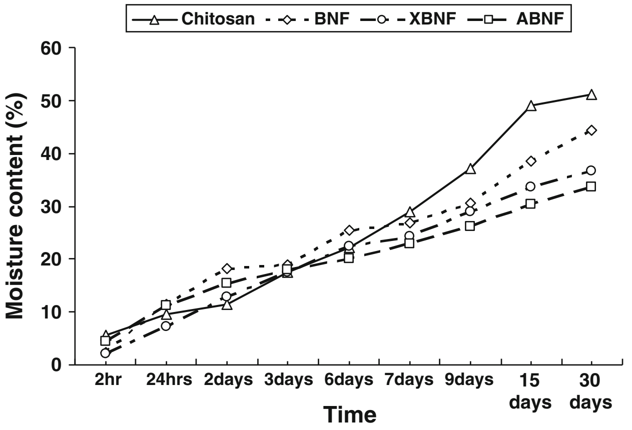

Fig. 6 Moisture sorption of chitosan nanocomposites prepared using 20% of nanofibers isolated from untreated pulp (BNF), xylanase-treated pulp (XBNF), and alkali-treated bagasse pulp (ABNF) at 75% relative humidity

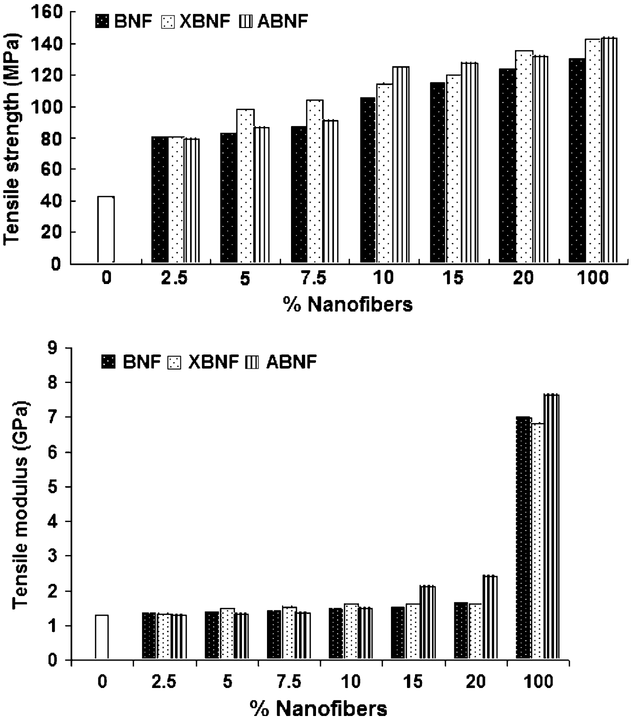

Fig. 7 Tensile strength and modulus of chitosan nanocomposites prepared using nanofibers isolated from untreated pulp (BNF), xylanase-treated pulp (XBNF), and alkali-treated bagasse pulp (ABNF)

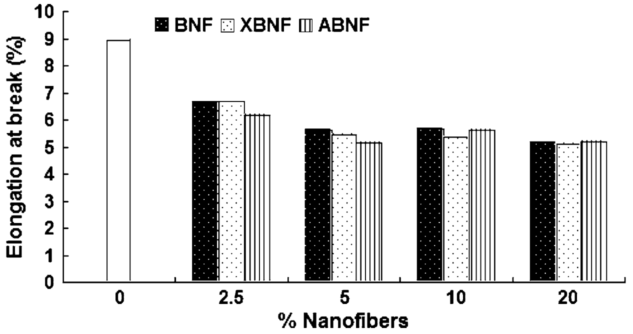

Fig. 8 Elongation at break of chitosan nanocomposites prepared using nanofibers isolated from untreated pulp (BNF), xylanase-treated pulp (XBNF), and alkali-treated bagasse pulp (ABNF)

that the nanopaper sheets were prepared by hot-pressing wet nanofibers at 100 °C for 2 h then at 60 °C for 8 h while chitosan nanocomposites were prepared by solution casting and drying at 35 °C overnight [14].

Regarding the effect of the kind of the nanofibers on tensile strength of the nanocomposites, no significant difference in tensile strength was noticed on using the nanofibers isolated from the different pulps when using low nanofibers loading (2.5%). But at higher concentration, there was generally a slightly higher tensile strength for nanocomposites made using nanofibers isolated from the alkali-treated and xylanase-treated pulp than those made using nanofibers isolated from untreated bagasse pulp. This could be the higher α-cellulose, degree of polymerization (DP), smaller diameter of microfibrillar bands (higher surface area), and crystallinity of the nanofibers isolated from the alkali and xylanase pretreated pulps as previously mentioned in Table 1. In addition, the better order of chitosan chains which was deduced from the XRD patterns mentioned above may result in increasing the tensile strength.

Regarding the tensile moduli of the nanocomposites, the values were close to each others and to that of neat chitosan up to 10% of nanofibers loading. At higher nanofibers loading, chitosan nanocomposites prepared using nanofibers isolated from alkali-treated pulp were remarkably higher than the other nanocomposites. This could be due to the higher α-cellulose, DP, and crystallinity of nanofibers isolated from the alkali-treated pulp than those isolated from the other pulps. Tensile modulus of all chitosan nanocomposites samples was remarkably less than that of nanopaper sheets made from 100% nanofibers.

Addition of nanofibers to chitosan generally resulted in a decrease in elongation at break as shown in Fig. 8; the decrease was significant at low nanofiber loading (2–5%) and no further decrease occurred at higher nanofiber loading. This could be due to the formation of percolated/interconnected network of the nanofibers within the chitosan matrix as mentioned above. No significant difference was found regarding the effect of the kind of nanofibers used on the elongation at break.

Wet tensile strength of chitosan nanocomposites

The effect of bagasse nanofibers on wet tensile strength of chitosan was studied and the results are presented in Fig. 9. It was noticed that films made from neat chitosan suffered from large increase in width due to swelling in the buffer solution before the test. In case of chitosan nanocomposites, the increase in width was very small even at 2.5% loading. This is an important requirement for materials used in tissue engineering where dimensional stability is important in wet conditions. The wet tensile strength of the chitosan nanocomposites was significantly improved even at the low nanofibers loading. The significant improvement of wet tensile strength and decrease of swelling of chitosan due to addition of cellulose microfibrils was reported before and was attributed to the formation of percolated/interconnected network of the nanofibers [28] and crosslinking between chitosan and the trace amount of carbonyl groups that exist in cellulose [31]. Nanocomposites made using the nanofibers isolated from xylanase and alkali-treated pulps had higher wet tensile strength than that made using nanofibers isolated form the untreated pulp. The reasons for that could be partially due to lower hemicelluloses, higher crytallinity, and higher DP of nanofibers isolated from xylanase- and alkali-treated pulps. The mechanism of how alkali and xylanase treatment of bagasse could increase the crosslinking between chitosan, which is in form of acetic acid-protonated chitosan, and isolated nanofibers is not clear but the results indicate better interaction between chitosan and nanofibers isolated from alkali- and xylanase-treated pulp.

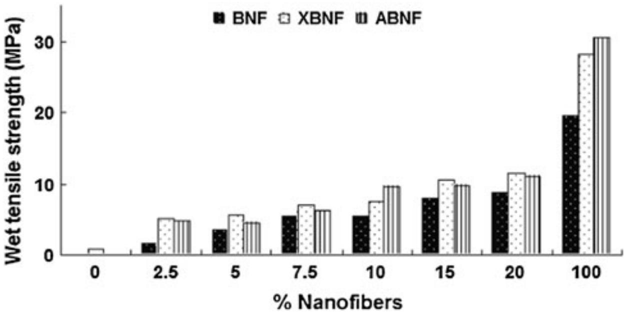

Fig. 9 Wet tensile strength of chitosan nanocomposites prepared using nanofibers isolated from untreated pulp (BNF), xylanase-treated pulp (XBNF), and alkali-treated bagasse pulp (ABNF)

The maximum wet tensile strength of the different nanocomposites was much lower than nanopaper sheets made from the nanofibers only.

DMTA of chitosan nanocomposites

The DMTA curves of the “as cast” chitosan and chitosan loaded with the nanofibers isolated from untreated bagasse, xylanase-treated bagasse, and alkali-treated bagasse are shown in Fig. 10. Neat chitosan shows significant decrease in storage modulus due to relaxation processes with peaks at about 10 and 155 °C. The first decrease in storage modulus, which started at about −60 °C and reached its peak at about 10 °C, could be recognized as β relaxation associated with local motion of side groups in chitosan [40]. At temperature higher than freezing temperature of water, structural reorganization of packing of chitosan molecules due to an increase of residual water mobility, volume expansion, and change in hydrogen bond strength took place. Thus, an increase in storage modulus was observed and reached its maximum value at about 45 °C [40]. Tan δ curves of neat chitosan showed peaks in accordance with the change in the storage modulus but the first peak which started at −50 °C was very broad. The most pronounced relaxation process (α relaxation) with maximum decrease in storage modulus and the highest tan δ peak was at about 155 °C, i.e., at glass transition temperature of chitosan [41].

Presence of nanofibers in chitosan matrix resulted in an increase in the storage modulus and shift of the tan δ peak at 152 °C to about 164 °C at the different nanofibers loading. The increase in nanofibers loading resulted in an increase of the storage modulus of the nanocomposites but the position of tan δ peak at 164 °C, which corresponds to glass transition temperature, did not affect by increasing the nanofibers loading. In addition, the area under the tan δ peak that corresponds to T_g of chitosan remarkably reduced in case of addition of nanofibers. This reflects much less damping of tensile modulus, i.e., lower tensile loss modulus, at T_g of chitosan in case of presence of the nanofibers than in case of neat chitosan. It also clearly shows the reinforcing effect of the nanofibers on chitosan above its T_g and the interaction between the nanofibers and chitosan chains, which are in the form of positively charged quaternary acetic acid salt. On the other hand, the decrease of the storage modulus of the β relaxation process at 10 °C in case of the different nanocomposites was higher than that occurred in case of neat chitosan. Therefore, the area under

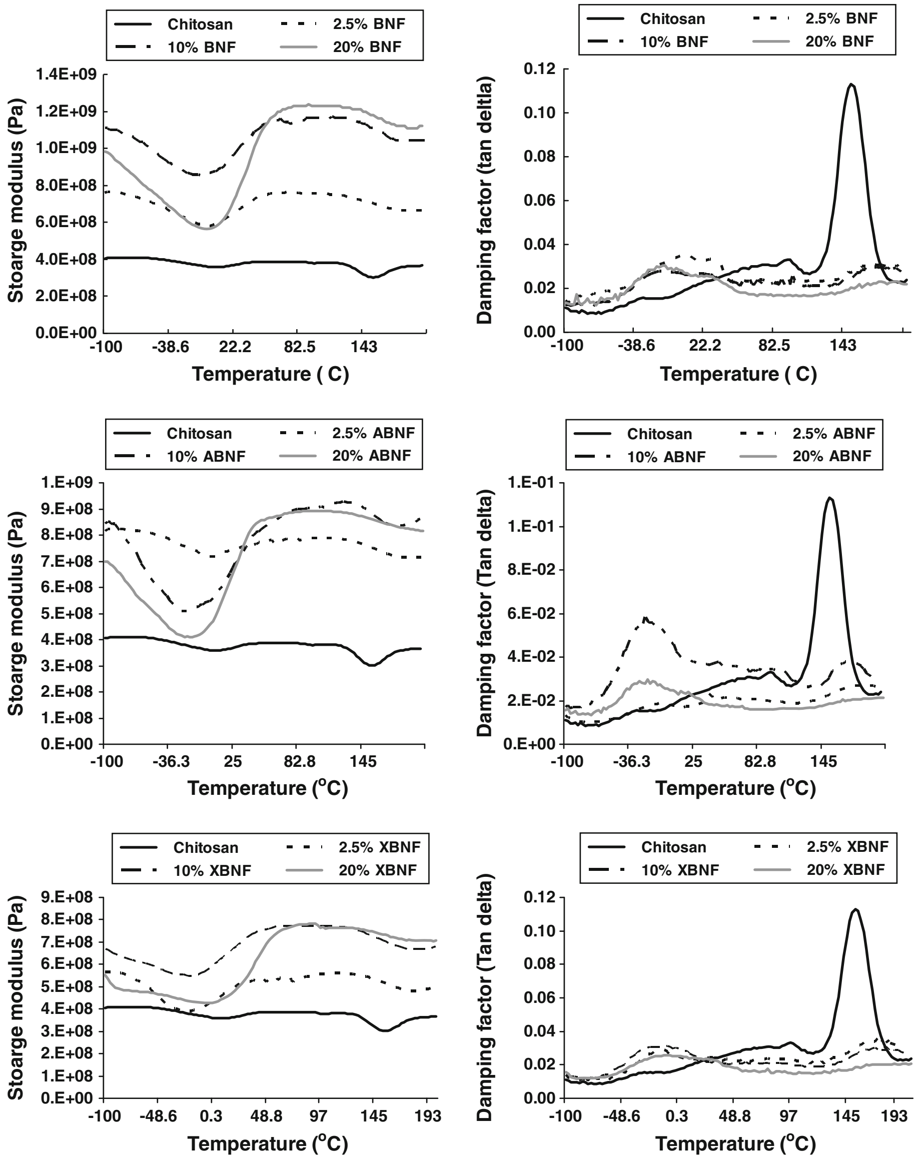

Fig. 10 DMTA of chitosan and chitosan nanocomposites prepared using nanofibers isolated from untreated bagasse pulp (BNF), alkali-treated bagasse pulp (ABNF), and xylanase-treated bagasse pulp (XBNF)

the tan δ peak at 10 °C was bigger than that of neat chitosan. This means that the motion of the side chains of chitosan was easier in the presence of the nanofibers.

Regarding the effect of the kind of nanofibers, no difference in the position or the intensity of tan δ peak at T_g of chitosan was found in case of using nanofibers isolated from untreated, alkali-treated, or xylanase-treated bagasse pulps in the nanocomposites.

Thermal stability of chitosan nanocomposites

Thermal stability of chitosan nanocomposites prepared using the different isolated nanofibers was studied using thermogravimetric analysis (TGA). Figure 11 shows TG curves cellulose nanofibers, chitosan, and the different nanocomposites. Chitosan, cellulose, and chitosan nanocomposites showed initial loss of water up to about 140 °C followed by weight loss due to degradation of the polymers. Thermal degradation of the neat chitosan film started at lower temperature than bagasse nanofibers probably due to the detachment of the acetyl groups of chitosan and the residual acetic acid in chitosan film which can accelerate thermal degradation. However, the rate of thermal degradation of nanofibers is much faster than chitosan as it clear from the TG curve and the residual weight at 500 °C, which is much higher in case of chitosan. Addition of the nanofibers to chitosan did not affect the onset degradation temperature of chitosan but the residual char at 500 °C was lower with increasing the nanofibers loading. Regarding the effect of kind of nanofibers on thermal stability of nanocomposites, using nanofibers isolated from alkali-treated pulp resulting in slightly higher

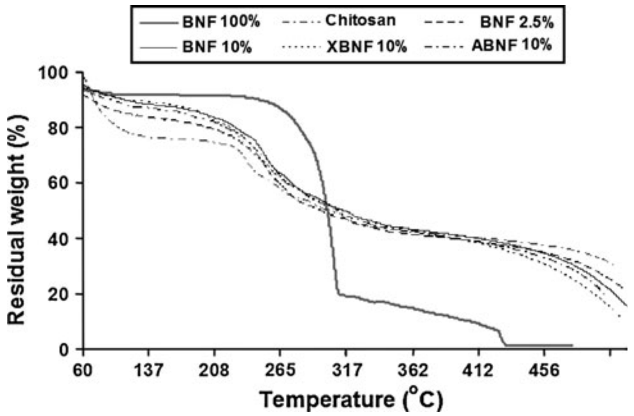

Fig. 11 TGA curves of chitosan (C), bagasse nanofibers (BNF 100%), chitosan nanocomposites containing 10% nanofibers isolated from untreated pulp (BNF 10%), xylanase-treated pulp (XBNF 10%), and alkali-treated pulp (ABNF 10%)

onset degradation temperature and maximum weight loss temperature for the first stage. This could be due to the lower hemicelluloses content, which are less thermally stable than cellulose, in case of using nanofibers isolated from alkali-treated pulp. In addition, the residual char at 500 °C was higher in case of using the nanofibers isolated from the alkali-treated pulp than in case of using nanofibers isolated from the other kinds of pulps.

Conclusions

Cellulose nanofibers isolated from bagasse can significantly improve wet and dry tensile strength of chitosan and increase its glass transition temperature. Low loadings of cellulose nanofibers can increase the ordering of chitosan chains during drying of chitosan solution. Nanofibers isolated from bagasse pulp pretreated with xylanase enzymes or dilute alkali improve wet and dry tensile strength properties of chitosan nanocomposites more than the nanofibers isolated from untreated pulp.

References

1. Borges AC, Bourban P-E, Pioletti DP, Månson J-A (2010) Compos Sci Technol. doi:10.1016/j.compscitech.2010.07.018
2. Siró I, Plackett D (2010) Cellulose 17(3):459
3. Hassan ML, Mathew AP, Hassan EA, El-Wakil NA, Oksman K (2010) Wood Sci Technol. doi:10.1007/s00226-010-0373-z
4. Dufresne A, Dupeyre D, Vignon MR (2000) J Appl Polym Sci 76(14):2080
5. Malainine ME, Dufresne A, Dupeyre D, Mahrouz M, Vuong R, Vignon MR (2003) Carbohydr Polym 51(1):77
6. Habibi Y, Heux L, Mahrouz M, Vignon MR (2008) Carbohydr Polym 72(1):102
7. Rondeau-Mouro C, Bouchet B, Pontoire B, Robert P, Mazoyer J, Buléon A (2003) Carbohydr Polym 53(3):241
8. Wang B, Sain M (2007) Compos Sci Technol 67(11–12):2517
9. Morán JI, Alvarez VA, Cyras VP, Vázquez A (2008) Cellulose 15(1):149
10. Zuluaga R, Putaux JL, Cruz J, Vélez J, Mondragon I, Gañán P (2009) Carbohydr Polym 76(1):51
11. Saito T, Nishiyama T, Putaux JL, Vignon M, Isogai A (2006) Biomacromolecules 7(4):1687
12. Henriksson M, Henriksson G, Berglund LA, Lindström T (2007) Eur Polym J 43(8):3434
13. Pääkkö M, Ankerfors M, Kosonen H, Nykänen A, Ahola S, Österberg M, Ruokolainen J, Laine J, Larsson PT, Ikkala O, Lindström T (2007) Biomacromolecules 8(6):1934
14. Hassan ML, Mathew AP, Hassan EA, Oksman K (2010) Wood Fiber Sci 42(3):1
15. Pillai CKS, Paul W, Sharma CP (2009) Prog Polym Sci 34(7):641
16. Rabea EI, E-T Badawy M, Stevens CV, Smagghe G, Steurbaut W (2003) Biomacromolecules 4(6):1457
17. Li Z, Ramay HR, Hauch DK, Xiao D, Zhang M (2005) Biomaterials 26(18):3919
18. Lee E-G, Shin D-S, Kim H-E, Kim H-W, Koh Y-H, Jang J-H (2009) Biomaterials 30(5):743
19. Silva SS, Ferreira RAS, Fu L, Carlos LD, Mano JF, Reis RL (2005) J Mater Chem 15:3952
20. Kiuchi H, Kai W, Inoue Y (2008) J Appl Polym Sci 107(6):3823
21. Pei HN, Chen XG, Li Y, Zhou HY (2008) J Biomed Mater Res A 85A:566
22. Xu H, Ma L, Shi H, Gao C, Han C (2007) Polym Adv Technol 18(11):869
23. Bourtoom T, Chinnan MS (2008) LWT—Food Sci Technol 41(9):1633
24. Shih C-M, Shieh Y-T, Twu Y-K (2009) Carbohydr Polym 78(1):169
25. Veerapur RS, Gudasi KB, Aminabhavi TM (2007) J Memb Sci 304(1–2):102
26. Lima IS, Lazarin AM, Airoldi C (2005) Int J Biol Macromol 36(1–2):79
27. Twu YK, Huang HI, Chang SY, Wang SL (2003) Carbohydr Polym 54(4):425
28. Nordqvist D, Idermark J, Hedenqvist MS (2007) Biomacromolecules 8(8):2398
29. Gällstedt M, Hedenqvist MS (2006) Carbohydr Polym 63(1):46
30. Taniguchi T, Okamura K (1998) Polym Int 47(3):291
31. Hosokawa J, Nishiyama M, Yoshihara K, Kubo T, Terabe A (1991) Ind Eng Chem Res 30(4):788
32. Susana CM, Fernandes SC, Freire CSR, Silvestre AJD, Neto CP, Gandini A, Berglund LA, Salmén L (2010) Carbohydr Polym 81(2):394
33. Medeiros RG, Silva FG, Salles BC, Estelles RS, Filho E (2002) J Ind Microbiol Biotechnol 28:204
34. Bastawde KB (1992) World J Microbiol Biotechnol 8:45
35. Browning BL (1967) Methods of wood chemistry, vol 2. Interscience, New York, p 387
36. Segal L, Creely JJ, Martin AE, Conrad CM (1945) Text Res J 29(10):786
37. Wada M, Heux L, Sugiyama J (2004) Biomacromolecules 5(4):1385
38. Chesnutt BM, Viano AM, Yuan Y, Yang Y, Guda T, Appleford MR, Ong JL, Haggard WO, Bumgardner JD (2008) J Biomed Mater Res A 88(2):491
39. Tripathi S, Mehrotra GK, Dutta PK (2010) Carbohydr Polym 79(3):711
40. Mucha M, Pawlak A (2005) Thermochim Acta 427(1–2):69
41. Neto CG, Giacometi JA, Job AE, Ferrira FC, Fonseca JL, Pereira MR (2005) Carbohydr Polym 62(2):97