RESEARCH ARTICLE

Investigation into hemp fiber- and whisker-reinforced soy protein composites

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Whiskers, designated as W, were prepared from hemp fibers. Both fibers and whiskers were characterized by Fourier transform infrared spectroscopy, thermogravimetric analysis. Scanning electron microscopy and transmission electron microscopy were used to evaluate the dimensions of the fibers and whiskers, respectively. By incorporating different weight fraction of the fibers and whiskers into soy protein isolate, we prepared two different composites designated as SC and SC-W, respectively. Thiodiglycol was used as a plasticizer for the preparation of composites. The SC and SC-W composites were characterized and compared in terms of mechanical properties, volume fraction of porosity, and water uptake. The results indicated that there was not much significant difference in the properties of the composites. In fact, mechanical properties of fiber-reinforced composites were higher than whisker-reinforced composites at optimum weight fractions. This study can give us the idea about the judicious use of fibers or whiskers as reinforcement materials.

1 Introduction

There are often considerable problems with respect to the reuse of classical fiber-reinforced composites, mainly because of the very high stability of fibers and matrices. Simple landfill disposable systems are becoming scarce because of increasing environmental sensitivity. Therefore, environmentally compatible alternatives are explored and examined, for example, the recovery of raw materials or biodegradation of materials in certain circumstances. The general criteria for the choice of suitable reinforcing fibers are elongation at failure, thermal stability, adhesion of fibers and matrix, and longtime behavior. Several papers have reported the usage of natural fibers in preparing soy protein isolate (SPI)-based composites [1–5]. However, with the introduction of whiskers [6–9] derived from natural fibers, research focus has shifted from fibers to whiskers as reinforcement materials. Whiskers have become one of the most promising means of dramatically increasing the physical properties of composites. Hence it is important to compare the properties of the composites reinforced by fibers and whiskers.

We have shown, in our earlier work [10], the successful use of thiodiglycol (TDG) as a new and efficient plasticizer for the fabrication of soy protein films. TDG is the hydrolysis product of distilled mustard (HD) [$(ClC_2H_4)_2S$] [11,12] and is relatively nontoxic with stability below 170°C. Nontoxic implies slightly irritant to the eyes. The TDG plasticized SPI films showed high compatibility and comparable mechanical properties to that of the glycerol plasticized one. More importantly, the water resistance of TDG-plasticized SPI films was higher. In recent years, hemp fibers have been examined as the reinforcement agents in biocomposites [13–15]. Hemp fibers are obtained from the bast of the annual shrub, *Cannabis sativa L* and are widely cultivated plant of industrial importance. Hemp fibers are widely used in the modern production of durable fabrics and specialty papers. The fiber bundle strength, as reported by Sankari [16], varies between 650 and 1050 MPa. In this paper, the use of hemp fibers and whiskers for the preparation of biocomposites has been reported. Fiber- and whisker-reinforced composites with SPI and TDG as matrix and plasticizer, respectively, were fabricated. The mechanical properties, thermal behavior, volume fraction of porosity, and water resistance were compared. This work may contribute to the development of composites with new plasticizers and can give us the idea of the justified use of fibers and whiskers as reinforcement materials.

2 Materials and methods

2.1 Materials

SPI with a protein content of about 91% (dry basis) was purchased from Hubei Yunmeng Protein Technology Co. (Yunmeng, Hubei, China). Acetone, benzene and carbon tetrachloride, sulfuric acid and sodium hydroxide were acquired from Shanghai Chemical Co., Shanghai, China. TDG (bp = 164–166°C, mol. wt. = 122.19 g/mol and density = 1.182 g/mL) was received from Sigma. Hemp fibers were donated by Kunming Qincheng Commercial and Trading Co., Ltd., China.

2.2   Separation and modification of fibers

Bundle of hemp fibers was fully dipped in acetone for 24 h and then dried at 60°C for 24 h. Modification of the hemp fibers was carried out by immersing the bundle of fibers in 10% NaOH solution for 6 h at 25±1°C, followed by washing with distilled water till neutral and then dried in an oven at 60°C for 24 h. Alkali modified and unmodified fibers were designated as AH and H, respectively. For the preparation of short-fiber random composites, alkali modified fibers were cut to different lengths ranging from 5 to 25 mm with an increment of 5 mm in each step.

The denier of the hemp fibers was determined by weighing accurately 20 fibers of 5 cm length according to the method mentioned in Identification of Textile Materials [17]. Three such measurements were performed, and the average weight of 100-cm-long fibers (5×20 cm) was obtained. The denier, which is the weight of 9000 m of fibers, has been reported. The diameter of the raw and alkali-treated fibers was determined using a scanning electron microscope (SEM). Readings at 15 different points were taken, and an average of 15 readings was reported.

2.3   Preparation of whiskers by acid hydrolysis

Hemp fiber whiskers were prepared according to the method in Ref. [9] for the preparation of nano starch crystals. In a typical process, 12 g of hemp fibers, cut to very small length, was mixed in 400 mL of 3.2 mol/L H_2SO_4 for 5 days at 40°C with mechanical stirring. It was observed that after 2–3 days, apparent reduction in the length of the fibers happened. To determine the insoluble portion of the hemp fiber whiskers, exact amount of hemp fibers suspension was taken after different time intervals. The suspension was washed with distilled water and dried to determine the insoluble weight. After 4 days, the weight of the insoluble fibers almost remained the same. Therefore the reaction was stopped after 5 days. Whiskers prepared by acid hydrolysis are represented as W.

2.4   Preparation of soy protein composites

Short fiber-reinforced composites were prepared in two stages. In the first stage, 30% of TDG SPI was mixed with room temperature SPI for about 1 h in 0.025 mol/L and 0.1 mol/L NaOH solution, separately. The pH was between 9.5–10 and 12.5–13.0, respectively. The effect of the fiber length (5 to 25 mm) and weight fraction (5% to 25%) on the properties of composites were evaluated. Different lengths of the fibers at constant weight fraction (10%) were added to the SPI-TDG mixture. The fibers and the matrix were mixed in

order to coat the fibers uniformly. The resulting mixtures were then poured on glass plate for the preparation of the films by solution casting method. The films were peeled off after drying in an oven at 60°C for 24 h. In the second stage, the peeled off films were subjected to hot press at 140°C for 20 mins under pressure of 15 MPa. The composites thus obtained with 0, 5, 10, 15, 20, and 25 mm of fibers were designated as 0SC, 5SC, 10SC, 15SC, 20SC, and 25SC, respectively. By controlling the weight fraction of the fibers at optimum length in soy protein as 0, 5, 10, 15, 20, and 25 wt %, the composites were coded as SC0, SC5, SC10, SC15, SC20, and SC25, respectively. For comparison, composites designated as SC-U were also prepared with unmodified fibers (U) at optimum length and %.wt (percentage weight fraction). To see the effect of long fibers, the composites were prepared by taking 70-mm length of the treated and untreated fibers at optimum %.wt.

Whiskers reinforced soy protein composites were also prepared in the same way as in preparing the short-fiber random oriented composites with 0.025 mol/L NaOH. The composites thus prepared were designated as SC-W; here, W represents whiskers. By controlling the %.wt of whiskers in soy protein as 0, 5, 10, 15, 20, 25, and 30, the composites were coded as SC0-W, SC5-W, SC10-W, SC15-W, SC20-W, SC25-W, and SC30-W, respectively.

2.5   Characterization techniques

Transmission electron microscope (TEM) image of dilute suspension of whiskers was performed on a TEM-100CX, JEOL electron microscope at an accelerating voltage of 100 kV. SEM images of H, AH, SC0, SC20, and SC20-W were taken on a FESEM (Sirion, USA) electron microscope at an accelerating voltage of 30 kV. For structural characterization, Fourier transformed infrared spectra (FTIR) spectra of H, AH, and W (as KBr pellets) were recorded on a Nicolet 5700 FTIR spectrometer (Thermo Electron Co., USA) in the range of 4000 to 400 cm^{-1} using the KBr-disk method. Wide angle X-ray diffraction (WXRD) patterns of the H, AH, and W powder were recorded on a WXRD instrument (XRD-6000, Shimadzu, Japan) with Cu K_α, radiation ($\lambda = 0.154$ nm). X-ray diffraction data were collected from $2\theta = 4$–40° at a scanning rate of 2°·min^{-1}. Thermogravimetric analysis (TGA) of approximately 5 mg dried H, AH, W, SC0, and SC20-W were carried out at a heating rate of 10°C·min^{-1}, between room temperature and 700°C in nitrogen atmospheres on a Pyris TGA linked to a Pyris diamond TA lab system (Perkin-Elmer Co., USA). The optical transmittance (T_r) of the SC-W films was measured with a UV-Vis spectrophotometer (Shimadzu UV-160A, Japan) from a wavelength of 400 to 1000 nm. The tensile strength, elongation at break, and

Young's modulus of the composites were measured on a universal testing machine (CMT6503, Shenzhen SANS Test Machine Co. Ltd., Shenzhen, China) with a tensile rate of $5 \, \text{mm} \cdot \text{min}^{-1}$ according to ISO527-3: 1995 (E). The samples were preconditioned at 57% RH for 3 days at room temperature before performing the experiment. An average value of five replicates of each sample was taken.

The sample crystallinity (X_{cr}) was determined by two methods. The first one is by taking the amorphous and crystalline contribution to the diffracted intensity. In the second method, the sample crystallinity was determined by means of the equation given below using the height of the 200 peak ($I_{200} = 22.7°$) and the minimum between the 200 and 110 peaks ($I_{AM} = 18°$). I_{200} represents both the crystalline and amorphous material, whereas I_{AM} represents the amorphous material only.

$$X_{cr} = \frac{I_{200} - I_{AM}}{I_{AM}}. \tag{1}$$

The expression requires that the amorphous material diffracts with the same intensity at 18° and 22.7° and that the crystalline cellulose does not contribute to the intensity at 18° [18].

2.6 Water uptake

Water uptake of the samples was evaluated according to ASTM D570-81. The composites and the fibers were preconditioned separately at 50°C for 24 h, cooled in desiccators, and weighed (W_o). The preconditioned specimens were immersed in distilled water at room temperature for 26 h. After the samples removed from water, the containers were placed in an oven at 50°C in order to evaporate the water. The residuals were the water-soluble contents (W_r). The sum of the weight gain of the samples (W_t) and the weight of the water-soluble residuals was counted as the total absorbed water. An average value of three readings has been reported. The water uptake of the samples being immersed in water was calculated as follows:

$$\text{Water uptake}(\%) = \frac{(W_t + W_r) - W_o}{W_o} \times 100. \tag{2}$$

2.7 Density

Density of fibers and composites was determined using a density gradient column prepared using benzene and CCl_4 with densities of 0.865 and 1.59 g/cm^3 at 25°C, respectively. Small tightly placed bundle of fibers and a small piece of SC0 film were dropped in the column. The samples were left overnight for equilibration; then the height was marked. The

densities were then determined from the calibration plot. The densities were measured in triplicate to obtain an average value.

2.8 Volume fraction of porosity

Volume fraction of porosity in the composites was determined by the method given by Thygesen *et al.* [19]. The composite volumes V_c was calculated based on the average values of the thickness t_c measured at 15 points, the length l_c measured at 3 points, and the width b_c measured at 3 points, where the subscript c denotes composites.

$$V_c = t_c \times l_c \times b_c. \tag{3}$$

The fibers and the matrix weight in the composites w_f and w_m were calculated theoretically. The volume fractions of the matrix (V_m) and fibers (V_f) were calculated based on the densities of the fibers and the matrix.

$$V_m = \frac{w_m}{\rho_m \times v_c}; \quad V_f = \frac{w_f}{\rho_f \times v_c}. \tag{4}$$

Assuming that, on a macroscopic scale, a composite material can be divided into three components, fibers, matrix, and porosity, the volume fraction of porosity V_p (p denotes porosity) can be calculated as

$$V_p = 1 - V_m - V_f. \tag{5}$$

3 Results

3.1 Structural characterization of fibers and whiskers

Table 1 shows the physical properties of the fibers and whiskers. The density of the hemp fibers (1.45 g/cm^3) was found to be lower than some of the other natural fibers such as ramie (1.55 g/cm^3) and cotton (1.55 g/cm^3) [17]. Treatment of fibers with 10% NaOH resulted in a marginal increase in the density (1.46 g/cm^3), which may be due to the depletion of lignin present in the fibers. Denier of the fibers decreased from 281±5 to 232±3.5 upon alkali treatment, which can be correlated with (13±2)% weight loss. Additionally, the water uptake of the alkali-treated fibers was 20% higher than untreated ones. WXRD patterns for H, AH, and W are shown in Figure 1. Crystallites of cellulose present in fibers are very small, resulting in considerable peak broadening and overlap [20]. In the X-ray diffraction pattern of fibers, a main diffraction peak at $2\theta \sim 22.7°$ associated with the diffraction plane of (002) of cellulose I was observed. A broad unresolved peak in the range of 13°–18° (2θ) corresponds to (101) and (101) crystallographic planes of cellulose. The intensity of both the peaks (22.7° and 13°–18°) increased after

treatment with alkali. The crystallinity index (X_{cr}) of fibers and whiskers are presented in Table 1.

Table 1 Crystallinity index, density, and water uptake of alkali-treated (AH), untreated hemp fibers (H), and whiskers (W)

samples	crystallinity index[a] (%)	crystallinity index[b] (%)	density (g/cm³)	water uptake (%)
H	53	70	1.45	26.4
AH	57	72	1.46	31.5
W	71	80	-*	-*

* Density and water uptake of W cannot be determined because of the powdery nature of the sample.
a Crystallinity index determined by the amorphous method.
b Crystallinity index determined by the Segal method.
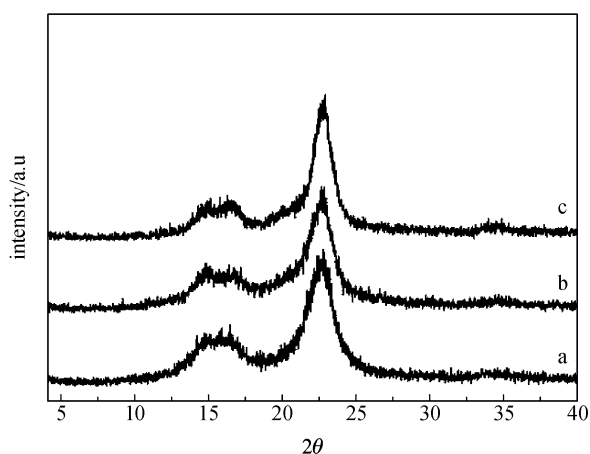
**Figure 1** WXRD patterns of (a) alkali-treated hemp fibers; (b) untreated fibers; (c) and whiskers.

Figure 2 (a) and (b) shows the SEM micrographs of untreated and alkali-treated fibers. The fibers presented a clean and a smooth surface, whereas unevenness of the surface was observed after alkali treatment. Roughness, shrinkage, and entanglement in the alkali-treated fibers increased because of the rupture of alkali-sensitive bond. The average diameter of the fibers decreased from 12 μm (6 μm) to 9.1 μm (4.5 μm) upon treatment with alkali. The data in the bracket represented the minimum value for the diameter of the fibers. Figure 2(c) shows the TEM image of the whiskers. The insoluble residues obtained after 5 days of acid hydrolysis were observed in the form of aggregates having the length of 175 to 350 nm. However, the average length and diameter calculated by taking 20 whiskers into consideration was 340 and 60 nm, respectively. It can be observed that there was considerable decrease in the diameter of the fibers upon hydrolyzing with acid.

The structural characterization of fibers before and after alkali treatment was performed using FTIR and is presented in Figure 3. The absorbance peaks at 3425, 2917, and 1641 cm^{-1} were attributed to –OH, C–H, and C＝O stretching and vibration, respectively. Absorbance peaks in the range of 1000–1550 cm^{-1} represented the lignin and hemicellulose. Absorbance peak at 1245 cm^{-1} was indicative of C–O stretching of acetyl groups in lignin. Treatment with alkali resulted in the loss of lignin from the fibers. The intensity of peak at 1510 cm^{-1} attributed to C＝C stretching of aromatic ring decreased for AH. Other absorbance peaks did not show any significant changes in the intensity. Figure 4 shows the TG/DTG traces of H, AH, and W samples recorded in nitrogen atmosphere at a heating rate of 10°C/min. The traces were characterized by noting down the initial decomposition temperature (T_i), final decomposition temperature (T_f), and associated mass loss (%). The temperature of maximum rate of mass loss was determined from derivative thermogravimetric (DTG) traces. Weight losses of 5% below 150°C in all the fibers were due to loss of the absorbed moisture. Raw fibers and the alkali-treated fibers showed very sharp one-step mass loss with T_{max} at 343°C and 347°C, respectively. Whiskers showed broad peak below 250°C with reduced T_{max} values. The decrease in T_{max} values from 347°C to 200°C is
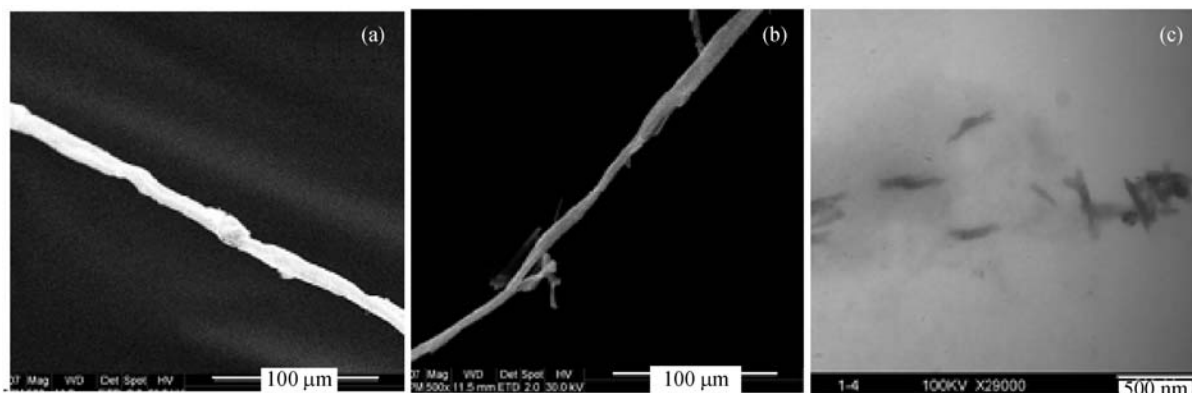
Figure 2 SEM (left and middle) images of (a) the raw fiber; (b) 10% alkali-treated fiber; (c) TEM (right) image of whiskers.
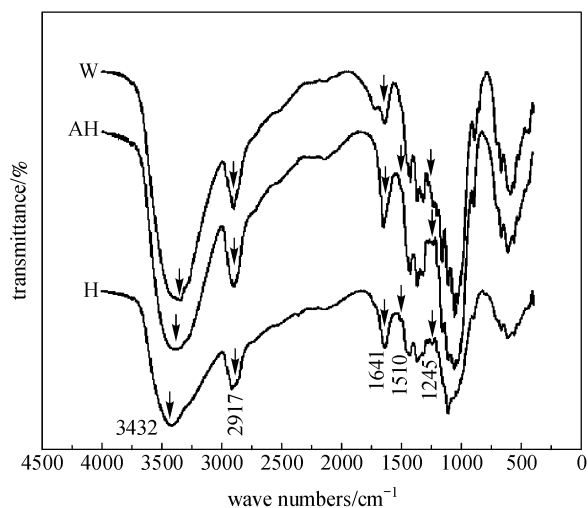
Figure 3 FTIR scans of fibers (H), alkali-treated fibers (AH), and whiskers (W).
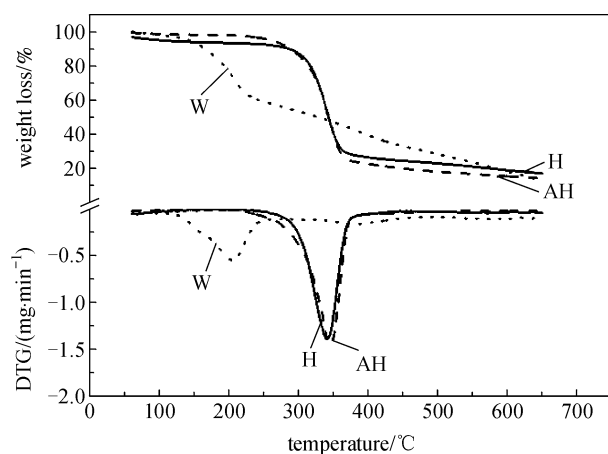
**Figure 4** TGA (top) and DTG (bottom) curves of fibers (H), alkali-treated fibers (AH), and whiskers (W).

ascribed to the presence of sulfate groups on the surface of the nanoparticles resulting from the sulfuric acid treatment.

## 3.2 Structure of fiber- and whisker-reinforced composites

The dispersion of hemp fibers in the matrix is shown in Figure 5. Because the surface of the fibers became rough and the diameter of the fibers decreased after alkali treatment, the dispersion of alkali-treated fibers in soy protein was found to be better. The surface morphology of short fiber- and whisker-reinforced soy protein composites was homogeneous (not shown). Fractured surface of the SC0 was smooth (Figure 5(a)), but the fractured surface of the SC20 showed few fibers which were short in length and protruding out, suggesting a brittle failure (Figure 5(b)). Some white domains corresponding to the whiskers, as particle, in the perpendicular plane of the SC20-W composite films appeared (Figure 5(c)). The fractured surface displayed homogeneous surface, suggesting uniform distribution of whiskers in the soy protein. In addition, fractured surface of whisker-reinforced soy protein composites showed agglomeration of whiskers. The values of transmittance (400–1000 nm) for the whisker-reinforced composites are shown in Figure 6. Transmittance of about 66% was observed in the SC0 sample. With the increase in %.wt of the fibers in the composites, transparency decreased from 51% to 21%. This is due to the opaque appearance of whiskers.

3.3 Properties of the composites

Table 2 shows the mechanical properties of the composites prepared by fibers or whiskers. The incorporation of fibers of any length (from 5 to 25 mm) in soy protein at 5%.wt resulted in the increase in tensile strength and modulus and a decrease in the % elongation at break and water uptake compared with the native films. With the increase in the length of the fibers from 5 to 25 mm, tensile strength and modulus decreased from 16.93 to 7.36 MPa and 882.8 to 277.1 MPa, respectively, which may be due to delamination of the fibers. This observation shows that there is the formation of strong
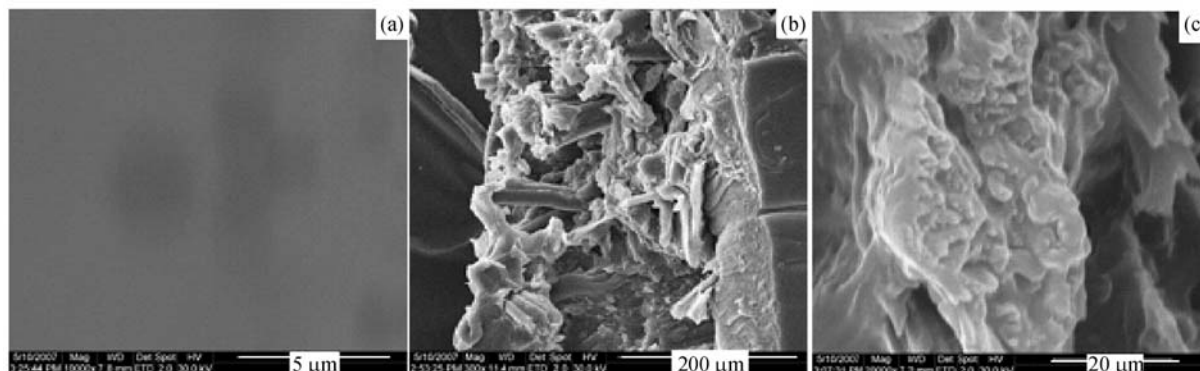
Figure 5 SEM images taken for cross sections of soy protein film and composites: (a) SC0, (b) SC20, and (c) SC20-W.
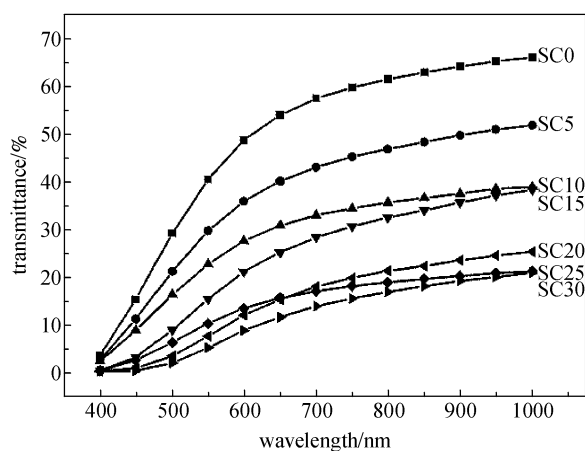
Figure 6 Transmittance of whisker-reinforced composites at different weight fraction (%).

linkages between functional groups of the cellulose (present in the fibers) and the soy protein. Thus, 5 mm has been found to be the critical length of the fibers that can be used for the reinforcement in SPI. High mechanical properties with high water uptake were observed for SC5 composite prepared with

0.1 mol/L NaOH than with 0.025 mol/L NaOH. This may be due to the availability of a large number of exposed functional groups of proteins because of the unfolding, which ultimately led to high water absorption. Hence, for comparable mechanical properties and low water absorption, concentration of 0.025 mol/L NaOH in soy protein dispersion was used for the preparation of composites.

Similarly, there was the increase in the tensile strength and modulus and the decrease in the percentage of elongation at break and the water uptake with the increase in weight fraction (5%–25%) of the fibers. At higher %.wt of the fibers, more fibers are available per unit cross-section area of the composites. Hence, tensile strength and modulus increased whereas the percentage elongation at break decreased. Tensile strength (13.40 MPa) and modulus (299.1 MPa) of the unmodified fiber-reinforced composite, coded as SC25-U, were lower than SC25. There was an increase in the fiber's reinforcement effectiveness, after alkali treatment, which resulted in increased mechanical properties of the composites. Roughness in the alkali-treated fibers increased as confirmed by SEM (Figure 2(a), (b)), which may lead to better interaction between fibers and matrix. The direction of the

**Table 2** Mechanical properties and water uptake of the composites

samples	properties			
	tensile strength (MPa)	modulus (MPa)	% elongation at break	water uptake (%)
(a) composites with different length of fibers in 0.1 mol/L NaOH				
0SC	3.25	19.2	133.34	670
5SC	16.93	882.8	10.11	316
10SC	8.87	417.4	4.41	394
15SC	8.25	425.2	7.15	354
20SC	7.20	282.5	18.77	388
25SC	7.36	277.1	14.42	352
(b) composites with different weight fraction of fibers in 0.025 mol/L NaOH				
SC0	4.84	48.2	130.10	150
SC5	8.34	284.1	7.81	111
SC10	8.79	310.8	9.79	87
SC15	15.18	458.9	9.40	85
SC20	14.56	495.4	9.14	77
SC25	15.45	592.6	7.68	62
(c) composites with different weight fraction of whiskers in 0.025 mol/L NaOH				
SC0-W	4.84 (3.85)	48.2 (34.5)	130.10 (160.5)	150 (269)
SC5-W	7.52 (7.17)	199.0 (54.7)	63.98 (86.25)	114 (304)
SC10-W	8.28 (7.10)	252.0 (232.9)	62.52 (70.21)	102 (271)
SC15-W	7.96 (7.10)	356.4 (325.9)	14.95 (39.5)	89 (152)
SC20-W	9.91 (9.52)	464.8 (443.3)	12.31 (13.97)	58 (154)
SC25-W	9.11 (9.14)	382.8 (474.8)	18.33 (10.63)	79 (151)
SC30-W	8.34 (11.17)	446.2 (540.2)	5.44 (7.56)	69 (143)

Data in parentheses represent whiskers reinforced composites prepared only by solution casting method.
Readings are the average of five measurements.

measurement of mechanical properties for long fiber-reinforced composites was along the fiber's orientation direction. Tensile strength and modulus for SC25 with long fibers were 26.50 MPa and 802.1 MPa, whereas those for SC25-U were 21.57 MPa and 733.3 MPa. This shows significant reinforcement effect of long fibers because of less flaws or low stress bearing points. However, water uptake of the prepared SC25 composites with long fibers was $(70\pm5)\%$, which was almost the same as that of composites prepared at optimum length and %.wt.

Optimum %.wt of the whiskers was found to be 30 and 20 for the composites prepared by solution casted and hot press methods, respectively. Tensile strength and modulus of SC20-W were 9.52 and 443.3 MPa for solution-casted sample, whereas those prepared by hot press were 9.91 and 464.8 MPa. There were not much difference in the mechanical properties of the SC20-W composites prepared by different methods, but there was significant difference in the water uptake values. The water uptake for SC20-W prepared by the solution casting and hot pressing was 154% and 58%, respectively. This may be attributed to less compact structure of composites prepared by solution casting method.

Figure 7 shows the TGA and DTG curves of the SC0 and SC20-W composites. Three T_{max} values designated as $T_{max}1$, $T_{max}2$, and $T_{max}3$ corresponding to temperature range of room temperature (RT) to 200°C, 200–300°C, and 300–400°C, respectively, were observed for the samples. The first step mass in SC20-W, attributed to the loss of adsorbed moisture, was lower than SC0. This is due to the increased crystallinity of the whiskers, as confirmed by WXRD data (Table 1). The second step mass loss from 200–300°C was attributed to the loss of TDG as plasticizer. The $T_{max}2$ for SC20-W increased from 247°C to 255°C, but the mass loss in this temperature
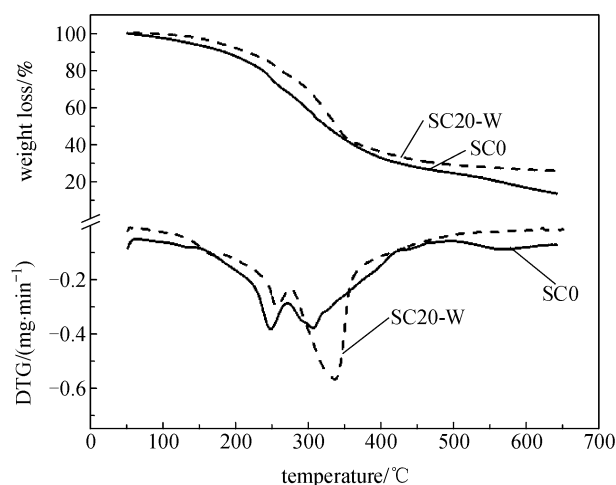
Figure 7 TGA (top) and DTG (bottom) curves of soy protein film and whisker-reinforced composite.

range was lower than that of SC0. Third mass loss was attributed to the degradation of soy protein. $T_{max}3$ values also increased from 308 to 337°C for SC20-W sample. The char yield of the SC0 at 650°C was lower than that of SC20-W. based on all these results, it can be concluded that there is an increase in the thermal stability of the composites because of strong interactions between cellulose and soy protein.

The density and volume fraction of the composites are listed in Table 3. The density of the SC-W was slightly higher than SC. V_p was less than 10% in all the composites, which indicated good interaction between fibers and the matrix. V_p was negligible for SC5, which may be due to the low amount of the fibers in the composites. There was a decrease in V_p with an increase in %.wt of the fibers, and at optimum %.wt, the value of V_p was negligible for composites.

Table 3 Density and volume fraction of the porosity of the composites

samples	density (g/cm³)	V_p	samples	density (g/cm³)	V_p
SC0	1.32	-	SC0-W	1.32	-
SC5	1.33	0	SC5-W	1.33	0.064±0.01
SC10	1.34	0.098±0.01	SC10-W	1.33	0.050±0.01
SC15	1.34	0.082±0.01	SC15-W	1.35	0.061±0.01
SC20	1.35	0	SC20-W	1.37	0.002±0.001
SC25	1.38	0.009±0.005	SC25-W	1.39	0.063±0.01
			SC30-W	1.41	0.097±0.015

V_p represents volume fraction of the porosity.

4 Discussion

There is depletion of lignin in the alkali-treated fibers which accounts for the changes in the structure as proved by WXRD, FTIR, and SEM. It has been observed that the removal of lignin by alkali treatment caused the fiber bundles to separate and shrink. The X_{cr}, as calculated by [18], was compared with the amorphous method, and this fact was highlighted by Thygesen et al. [20] for the different cellulosic fibers. The morphology of whiskers, prepared from fibers, was similar to that reported for starch nanocrystals [21].

Whisker-reinforced protein composites showed a decrease in transmittance values with an increase in %.wt of the whiskers in the same way as reported by Wang et al. [7] for cellulosic whisker-reinforced soy protein composites. This may be attributed to the opaque suspension of cellulosic whiskers in the sulphuric acid. However, increase in transmittance of blend membranes from cellulose and SPI, with increasing cellulose content, has been reported by Chen et al. [22]. The increase is due to the transparent nature of the cellulose prepared in precooled aqueous alkaline solution. Lodha et al. [1] and Liu et al. [5] have prepared ramie and

Indian grass fiber-reinforced soy protein composites. They have reported high tensile strength (15–30 MPa) and Young's modulus (1500–2000 MPa) at optimum length and %.wt. of the fibers. On the other hand, at optimum %.wt, low tensile strength (9–10 MPa) and modulus (130–150 MPa) have been reported for cellulose [7] and chitin [6] whisker-reinforced soy protein composites. Hemp fibers and whisker-reinforced soy protein composites, reported herre, also gave same range of mechanical properties at optimum weight fractions as reported elsewhere. We think agglomeration of whiskers may be responsible for low reinforcement effects in protein-based composites. It is interesting to note that, at optimum %.wt, V_p was zero or almost negligible for both fiber- and whisker-reinforced composites, indicating that the composites prepared by either of the reinforcement materials were without pores.

5 Conclusions

The composites prepared by reinforcing with fibers at optimum weight fractions, showed high mechanical properties compared to whisker-reinforced ones. However, water uptake of both types of composites was same. Agglomeration behavior of the whiskers could have contributed to the decrease in whiskers reinforcement effect. Hence, whiskers obviously provide much higher properties as any nanoparticle, but the critical point is the effective dispersion of these nanoparticles.

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References

1. Lodha, P.; Netravali, A. N., *J. Mat. Sci.* **2002**, *37*, 3657
2. Mohanty, A. K.; Khan, M. A.; Sahoo, S., *J. Mat. Sci.* **2000**, *35*, 2589
3. Otaigbe, J. U.; Goel, H.; Babcock, T.; Jane, J., *J. Elast. Plast.* **1999**, *31*, 56
4. Paetau, I.; Chen, C. Z.; Jane, J. L., *Ind. Eng. Chem. Res.* **1994**, *33*, 1821
5. Liu, W.; Mohanty, A. K.; Askeland, P; Drzal L T.; Misra, M., *Polymer* **2004**, *45*, 7589
6. Lu, Y.; Weng, L.; Zhang, L., *Biomacromolecules* **2004**, *5*, 1046
7. Wang, Y.; Cao, X.; Zhang, L., *Macromol. Biosci.* **2006**, *6*, 524
8. Tjong, S. C.; Meng, Y. Z., *J. Appl. Polym. Sci.* **1999**, *72*, 501
9. Angellier, H.; Boisseau, S. M.; Dole, P.; Dufresne, A., *Biomacromolecules* **2006**, *7*, 531
10. Kumar, R.; Wang, L.; Zhang, L., *J. Appl. Polym. Sci.* **2009**, *111*, 970
11. Lachance, R.; Paschkewitz, J.; Dinaro, J.; Tester, J. W., *J. Supercrit. Fluids* **1999**, *16*, 133
12. Singh, B.; Prasad, G. K.; Suryanarayana, M. V. S.; Banerjee, S., *Carbon* **2001**, *39*, 2131
13. Madsen, B.; Lilholt, H., *Compos. Sci. Technol.* **2003**, *63*, 1265
14. Mwaikambo, L. Y.; Ansell, M. P., *Compos. Sci. Technol.* **2003**, *63*, 1297
15. Khoathane, M. C.; Vorster, O. C.; Sadiku, E. R., *J. Reinf. Plast. Compos.* **2008**, DOI: 10.1177/0731684407086325
16. Sankari, H., *Ind. Crops Prod.* **2000**, *11*, 73
17. The Textile Institute (1985) Identification of Textile Materials, 7th Edition, Manchester
18. Segal, L.; Creely, J. J.; Martin, A. E.; Cornad, C. M., *Text. Res. J.* **1959**, *29*, 786
19. Thygesen, A.; Thomsen, A. B.; Danie, G.; Lilholt, H., *Ind. Crops Prod.* **2007**, *25*, 147
20. Thygesen, A.; Oddershede, J.; Lilholt, H.; Thomsen, A. B.; Stahl, K., *Cellulose* **2005**, *12*, 563
21. Angellier, H.; Choisnard, L.; Boisseau, S. M.; Ozil, P.; Dufresne, A., *Biomacromolecules* **2004**, *5*, 1545
22. Chen, Y.; Zhang, L., *J. Appl. Polym. Sci.* **2004**, *94*, 748