Effect of Silane Treatment on Physicochemical Properties of Lignocellulosic *C. indica* Fiber

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ABSTRACT: Present work deals with the mercerization of *Cannabis indica* fibers and their subsequent surface modification by aminopropyl triethoxysilane. The reaction parameters like time and concentration of the sodium hydroxide for mercerization were optimized. *C. indica* fibers treated with different silane concentration solutions were subjected to evaluation of some of their properties like swelling behavior in different solvents, moisture absorbance under different humidity levels, and resistance toward chemicals such as sodium hydroxide and hydrochloric acid. *C. indica fibers* treated with 2% aminopropyl triethoxysilane solution have been found more resistant toward moisture, water, and chemicals when compared with that of untreated fibers. Morphological, structural changes, thermal stability, and crystallinity of both silane treated and mercerized fibers have been studied by SEM, FTIR, TGA, and XRD techniques. Silane treatment has been found to cause decrease in crystallinity but increase in the thermal stability of the fibers. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 2473–2484, 2012

Key words: surface modification; crystallinity; thermal stability; scanning electron micrograph

INTRODUCTION

Natural fibers reinforced polymer composites is an important branch in the field of the composites materials which have been studied by many workers for decades.[1–8] These materials are renewable, cheap, completely or partially recyclable, and bio degradable. Natural fibers have different origins such as wood, pulp, cotton bark, nut shells, bagasse, corncobs, bamboo, cereal straw, and vegetable (e.g., flax, jute, hemp, sisal, and ramie).[9–11] The availability, renewability, low density, price, and satisfactory mechanical properties make the natural fibers an attractive ecological alternative to glass, carbon, and other man-made fibers used for the manufacturing of the composites.[12,13] The constituents of natural fibers are cellulose, hemicelluloses, lignin, and pectins with a small quantity of the extractives and these constituents vary depending on the origination of the fiber. The presence of the hydroxyl group in the lignocelluloses makes natural fiber hydrophilic and moisture sensitive in nature. Therefore these polar fibers have inherently low compatibility with nonpolar matrix. Hydrogen bonds formed between the hydrophilic fibers tend to agglomerate fibers into bundles and get unevenly distributed within the nonpolar matrix during the compounding process, thereby resulting in poor interfacial adhesion.[14,15] However, for efficient transfer of the stress from matrix to the fibers, a number of investigations have been made which help to improve the interfacial adhesion.[13,16–18] These treatments include pretreatment of the natural fibers surface by coupling agent and/or the modification of the matrix by grafting with the reactive moieties such as acrylic acid, maleic anhydride, etc. Chemical treatment of the natural fibers not only reduces their moisture sorption process but also increases surface roughness, which helps in enhancing the interfacial adhesion between the fiber and matrix, resulting in improved mechanical performance of fiber-reinforced composites.

Among the different coupling agent, silanes are recognized as efficient coupling agents extensively used in composites and adhesive formulations.[19] Silane coupling agents have three main advantages: (i) they are commercially available in large scale, (ii) at one end, they bear alkoxysilane group capable of reacting with OH– rich surface and (iii) at the other end they have a large number of functional groups which can be tailored as a function of the matrix to be used. The last feature ensures good compatibility between the reinforcing element and the polymer matrix. Silane coupling agents have been also applied in inorganic filler reinforced polymer composites successfully.[20] The reaction of the silane coupling agents with lignocelluloses fibers has been found to be quite different from that of reaction

with glass surface. This difference in reactivity is due to the fact that cellulose surface reacts only with the prehydrolyzed silanes.[21] A number of authors have attempted to understand the silane–cellulose system.[22–24] The interaction of the silane coupling agents with the lignocellulosic fibers and the effect of some parameters such as silane structures, hydrolysis process of silanes, pH, the initial amount of silanes with respect to cellulose, and the adsorption contact time on their anchoring capability onto the fiber surface have been ascertained. The interaction of silane coupling agents with natural fibers mainly proceeds through four steps: (i) hydrolysis, (ii) self-condensation, (iii) adsorption, and (iv) grafting.[25,26] These reactions are generally carried out in acid-catalyzed condition as this condition helps to increase the rate of hydrolysis of silanes into silanols when compared with the condensation process. The competing reactions of hydrolysis and condensation in an ethanol/water (80/20, w/w) solution at different pH values were ascertained *in situ* using ^{1}H, ^{13}C, and ^{29}Si-NMR spectroscopy. Different authors have applied different methods for silane treatment and have studied the effect of silane treatment on surface morphological and hygroscopic character of the natural fibers.[18,27,28]

Cannabis indica fibers collected from higher reaches of the Himalayan Region have been found to contain approximately 68% cellulose. Traditionally, this fibrous material belonging to Himalayan region has been used by local people for making low-cost articles like ropes, bags, socks, boots, mats. *C. indica* is a short plant, usually less than 6 ft in height but rarely over 8ft and found in India, Pakistan, Afghanistan, and other surrounding areas. All of these countries fall in South Asia and have extremely variable weather conditions. Literature survey has revealed that not much work has been done on utilization of this fiber for the preparations of natural fiber reinforced polymer composites.[29,30]

The present study investigates the effect of mercerization and silane treatment on the moisture resistance, thermal stability, surface morphology, chemical resistance behavior, and crystallinity properties of *C. indica* fibers, so that these fibers could be used for various industrial applications including synthesis of bio-composites.

EXPERIMENTAL

C. indica fibers were collected from higher reaches of Himalayan region in Himachal Pradesh. The fibers were at first washed thoroughly with 2% detergent solution and then dried in an hot air oven at 70°C for 24 h. The dried fibers were designated as untreated fibers. Then these fibers were subjected to soxhlet extraction with acetone for 72 h followed by

washing with double distilled water and air drying to remove waxes and other water soluble impurities prior to various chemical treatments.

Surface modification of fiber

The surface modification of *C. indica* fibers was carried through the following chemical treatments:

Mercerization

C. indica fibers were immersed in 2% NaOH for the different time intervals at room temperature to optimize the mercerization time. The fibers were then washed several times with distilled water to remove any traces of NaOH sticking to the fiber surface, neutralized with dilute acetic acid, and finally washed again with distilled water. The fibers were then dried at room temperature for 48 h followed by oven drying at 70°C to a constant weight. After the optimization of the time, the mercerization of *C. indica* fiber was also carried out in 2, 4, 6, 8, 10, 12, and 14% NaOH solutions to study the effect of different concentrations of NaOH on the mercerization of the fibers.

Silane treatment

The pretreated fibers (mercerized) were dipped for 1 h in alcohol–water mixtures (60 : 40 v/v) containing different concentrations of the aminopropyl triethoxysilane coupling agent. The pH of the solution was maintained between 3.5 and 4 by using acetic acid and pH indicators strips. The treated fibers were then washed with double distilled water and subsequently dried in hot air oven at 70°C to a constant weight. Swelling, moisture sorption, and chemical resistance behavior of the silane-treated *C. indica* fiber were then studied to optimize the silane concentration.

EVALUATION OF PHYSICAL AND CHEMICAL PROPERTIES

Chemical resistance

The chemical resistance of the silane-treated fiber was studied as a function of percent weight loss of fiber when treated with different chemicals. A known amount (W_i) of the silane-treated fiber was treated with a definite volume of hydrochloric acid and sodium hydroxide of different strengths for a time interval 24 h. The fibers were then washed 2–3 times with distilled water and finally dried in oven at 70°C to a constant weight to get the final weight (W_f). The percent weight loss was determined using the following formula[31]:

$$\%\text{Wt.loss} = \frac{W_i - W_f}{W_i} \times 100$$

Swelling behavior

The swelling behavior of the raw and surface-modified samples of *C. indica* fiber was studied in different polar and nonpolar solvents such as water, butanol, dimethyl formamide, and carbon tetra chloride. Dry samples of silane treated as well as raw fibers (1.0 g) were suspended in 100 mL of the solvents kept at 35°C for 24 h. The solvent that adhered on the surface of the samples was removed by softly pressing the fibers between the folds of the filter paper. The samples were weighed again to obtain the final weight. The percent swelling was calculated by using the following relationship[31]:

$$\%Swelling = \frac{W_f - W_i}{W_i} \times 100$$

where W_i = initial weight of the dried fiber and W_f = final weight after the swelling.

Moisture absorption study

The moisture absorption study of the silane treated as well as raw fiber was performed at different humidity levels ranging from 20 to 80% for a fixed time interval of 24 h. The percent moisture absorption was studied as a function of weight gain and was calculated using the following formula[31]:

$$\%Moisture\ absorbance\ (Mabs) = \frac{W_f - W_i}{W_i} \times 100$$

where W_f is the final weight of the sample taken out from the humidity chamber and W_i = is the weight of the dried samples.

CHARACTERIZATION OF RAW AND SURFACE-MODIFIED *C. INDICA* FIBER

Infra red spectroscopy (IR)

IR spectra of the mercerized, silane treated, and raw fiber were recorded with KBr pellets on PERKIN ELMER RXI spectrophotometer.

Scanning electron microscopy

Scanning electron microscopic (SEM) studies of raw/surface-modified *C. indica* fibers were carried out on a LEO 435 VP electron microscope. To conduct the SEM all the samples were gold plated to make them conducting. Scanning was synchronized with microscopic beam for the maintenance of small size over large distance relative to the specimen. All of images were taken at a resolution of 1000×.

Thermal analysis

Thermogravimetric analysis (TGA), differential thermal analysis (DTA), and derivative thermogravimetric (DTG) of the raw and surface-modified *C. indica* fiber were conducted on a Perkin–Elmer thermal analyzer (Pyris Diamond make) at a heating rate of 10°C/min. Thermogram were recorded over a temperature range of 25–800°C in the presence of air with the flow rate of 200 mL/min.

X-ray diffraction studies

X-ray diffraction studies were performed on X-ray diffractometer (Brucker D8 Advance), using Cu Kα (1.5418 Å) radiation, a Ni-Filter, and a scintillation counter as a detector at 40 KV and 40 mA on rotation from 5° to 80° at 2θ scale.

Each sample was finely powdered onto small particle size and homogeneously mixed before subjected them for X-ray exposure. The finely powdered sample was distributed in the cavity of the sample holder with the help of glass slide. The randomly oriented powdered sample with uniform surface was exposed to X-rays from all possible planes. The angle of scattering of diffracted beam was measured with respect to incident beam of X-rays to find out the relative intensity.

Crystallinity index (C.I) was determined by using the wide-angle X-ray diffraction counts at 2θ angle close to 22° and 15°. The counter reading of peak intensity close to 22° and 15° is said to represent the crystalline material and amorphous material in cellulose, respectively. Percent crystallinity and crystallinity index (C.I) were calculated using the following equation:[32]

$$\%C_r = \frac{I_C}{I_C + I_A} \times 100$$

$$C.I = \frac{I_C - I_A}{I_C}$$

where I_C and I_A are the crystalline and amorphous intensities at 2è scale close to 22° and 15° angles.

RESULTS AND DISCUSSION

Reaction parameters for mercerized and silane-treated *C. indica* fibers

The number of active sites, lignin contents, waxy material, and other impurities present on the polymer backbone of the natural fibers affects the extent of surface modifications. The most important reaction parameters that affect mercerization were reaction time and NaOH concentration. Extensive studies were made to optimize these parameters. The optimized mercerized *C. indica* fibers were then
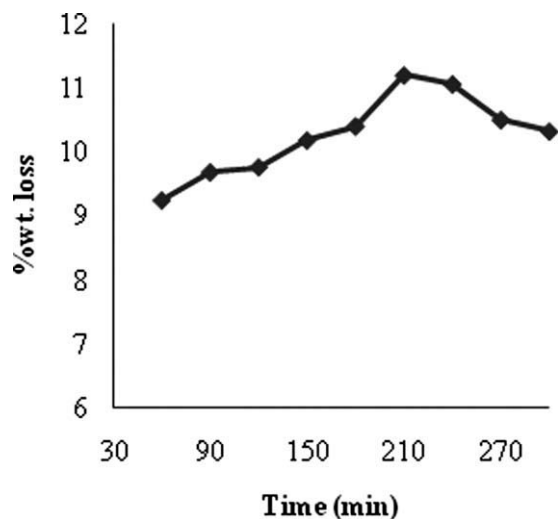
Figure 1 Effect of time on mercerization of *Cannabis indica* fiber at 2% alkali treatment.

given silane treatment with different silane concentrations, so as to cause maximum coupling between the fiber and the silating agent.

Effect of time

Reaction time has a significant effect on the surface modification. The effect of reaction time on surface modification of fiber was studied in terms of weight loss of polymer backbone, which may be probably due to removal of cementing material such as lignin, pectin, and hemicelluloses and also due to dissolution of short-chain cellulose. In case of mercerization of the *C. indica* fiber, maximum mercerization was observed at 210 min as shown in Figure 1. The decrease in the weight loss beyond optimum reaction time may be due to trapping of sodium ions in
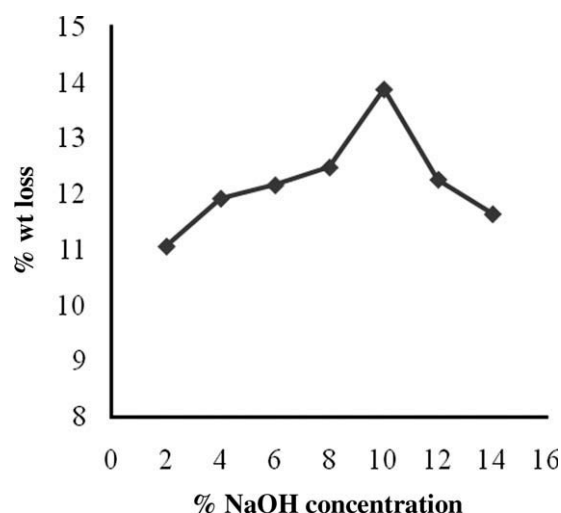

Figure 2 Effect of alkali concentration on mercerization of *Cannabis indica* fiber.

the layers of the lignocellulosic fibers and other side reactions, which may not favor further weight loss.

Effect of alkali concentration

The effect of alkali concentration on percent weight loss of polymer backbone is shown in Figure 2. Initially the weight loss increases with the increase in alkali concentration and shows maximum weight loss at 10% alkali concentration. This happens due to the removal of lignin, hemicelluloses, pectin, and other surface impurities with NaOH. However, beyond 10% alkali concentration decrease in weight loss has been observed. This probably could be due to trapping of sodium ion in the layers of the lignocellulosic fibers or may due to formation of the Na–cellulose complexes. Sobue et al. have classified the existence of various sodium-cellulose complexes as a function of sodium hydroxide concentration and temperature.[33] However, the exact mechanism is still to be investigated.

Effect of silane treatment

By proper surface and/or bulking treatment with silanes, normally hygroscopic natural fibers can be converted into a hydrophobic reinforcement for non-polar polymer matrices. Surface coating of the natural fibers cause partial decrease in water sorption rate but it cannot completely reduce the amount of water to be absorbed.

Alkoxy silanes are able to form bonds with hydroxyl groups of cellulose. Silanes initially undergo hydrolysis to form silanols which then undergoes condensation and then the bond formation with the fibers. Silanols can form polysiloxane structures by reaction with hydroxyl group of the fibers. Silanol forms stable covalent bond with the fiber by reacting with the hydroxyl group of the fiber. The possible reactions are shown in Schemes 1 and 2.

The uptake of the silane is very much dependent on number of factors like hydrolysis time, organic moiety of silane, temperature, and pH as these factors affect increase in silane solubility, improvement in the thickness of the surface film, and development of a uniform cover on the surface.
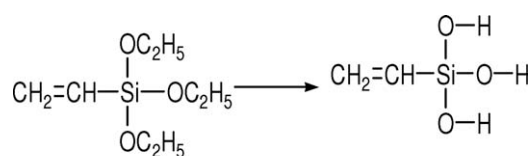
Hydrolysis of Silane

Scheme 1 Hydrolysis of silane.
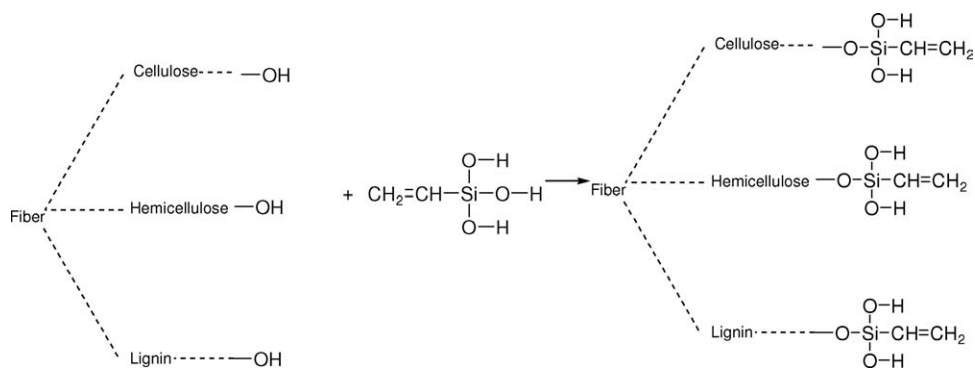
Scheme 2 Hypothetical reaction of fiber and silane.[34]

Physical and chemical properties

Swelling behavior

Figure 3 shows the percent swelling of the raw and silane-treated fiber in different solvents. The raw fiber possesses hydrophilic groups at C_2, C_3, and C_6 of glucose unit, which have strong affinity with water. Therefore the raw *C. indica* fiber shows maximum swelling with polar solvents like water and *n*-butanol and least swelling with the nonpolar solvents like CCl_4. From the figure, it is clear that with increase in silane concentration there is decrease in the swelling with the polar solvent whereas swelling increases with the nonpolar solvents. Further 2% silane-treated *C. indica* fiber showed maximum hydrophobic character which could be due to maximum penetration of the silane molecules into fiber pores and resulting in mechanical interlocked coating on the fiber surface. With further increase in silane concentration beyond 2% a decrease in the hydrophobic character has been observed. This decrease could be attributed to two reasons. First one is the formation of the cage 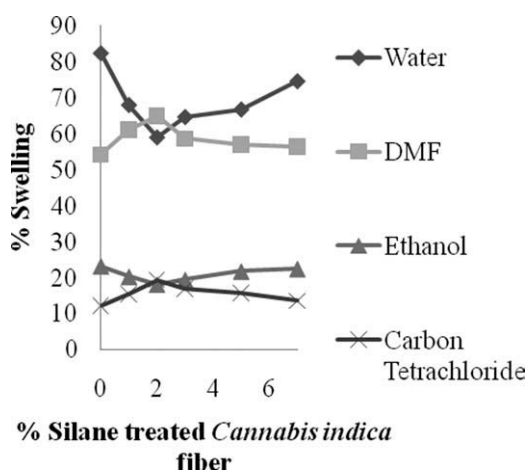like three-dimensional network structure of the polysi-loxane in the solution due to self-condensation of the silanol which may reduce number of silanol groups adsorbed to fibers[25] and second one is due to increase in the viscosity of the solvents. Both of these factors cause hindrance in the penetration of the silane molecules into the fiber pores.

Chemical resistance

The chemical resistance has been studied in terms of a weight loss of the fiber with dilute solutions of strong acids and bases. The effect of acid (HCl) and the base (NaOH) was studied by keeping the raw and silane-treated fibers in acid or base for a period of 24 h and the result obtained showed the same trend. It is clear from Figures 4 and 5 that with the increase in silane concentration weight loss of the fiber decreases and the minimum weight loss was found at 2% silane concentration. This probably could be due to the fact that with the increase in the silane concentration the active sites which are prone to attack on the fiber backbone got blocked and hence showed maximum resistance. The enhancement of silane concentration beyond 2% showed
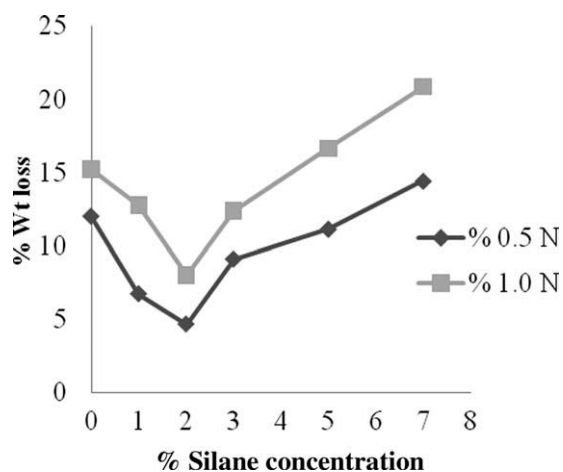

Figure 3 Effect of silane treatment on swelling behavior in different solvent.

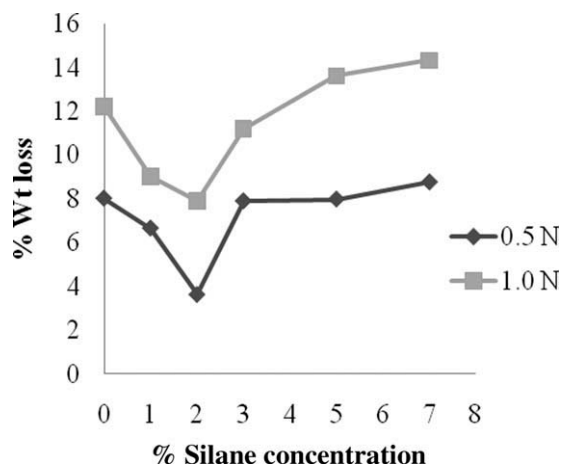**Figure 4** Effect of silane treatment on resistance to acid.

Figure 5 Effect of silane treatment on resistance to base.

least chemical resistance behavior. This may be due to increase in self-condensation of the silanol with increase in silane concentration which results in the formation of linear and a cage-like three-dimensional structure of the polysiloxane during the silane treatment which ultimately reduces the number of silanol group to be adsorbed onto the fibers[25] (Fig. 6). The silanol condensation will also restrict the penetration of silane into cell wall due to its increased molecular size.

Moisture absorption study

Raw *C. indica* fiber has been found to show 2.35, 3.12, 3.89, and 4.42% moisture absorption at 20, 40, 60, and 80% humidity levels, respectively (Fig. 7). From the figure, it is clear that 2% silane-treated fiber showed lower moisture absorption as compared to raw and 1, 3, 5, and 7% silane-treated fibers (Fig. 7). These results can also be explained on the same basis as discussed above in section "Swelling behavior".
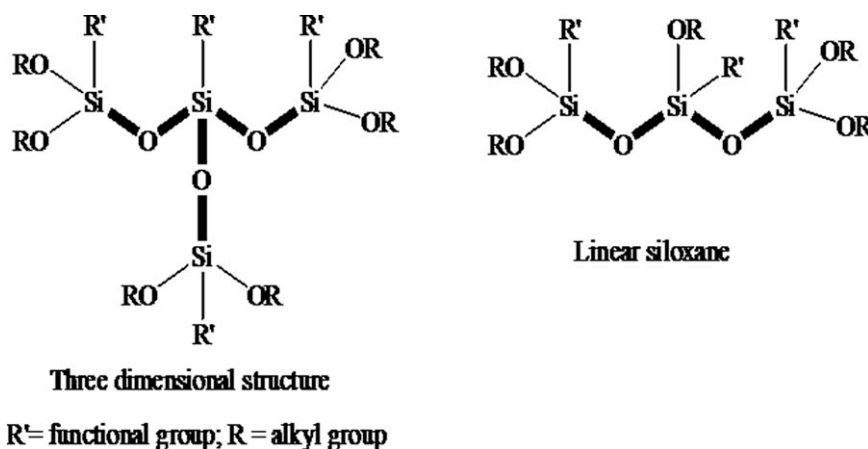
FTIR analysis

The FTIR spectra of raw *C. indica* fiber showed characteristic absorptions of its constituents namely cellulose, hemicellulose, lignin, and moisture. The IR absorptions peaks and its relation to various functional groups in the constituents of the fiber are shown in Table I. For untreated and treated *C. indica* fibers, an intense and broad peak ranging from 3024 to 3691 cm^{-1} was obtained which could be due to the hydrogen bonded –OH vibration of the cellulose structure fiber. It could be clearly identified that strong band around 1733 and 1252 cm^{-1} disappears when *C. indica* fiber is treated with dilute NaOH solution [Fig. 8(A,B)]. This behavior has been associated to the mercerization of the lignocellulosic fibers. Mercerization removes the waxy epidermal tissue, adhesive pectins, and hemicelluloses that bind fiber bundles to each other and to the pectins and hemicelluloses-rich sheet of core. The peak at 1733 cm^{-1} is assigned to the carbonyl group of the pectins.

The mercerized silane-treated *C. indica* (MSCF) fiber spectra which is used to confirm the silane coupling with cellulose on the *C. indica* fiber is shown in Figure 8(C). Well-defined absorption band at 1202 cm^{-1} in the spectra is associated to the Si–O–C and adsorption band at 699.5 cm^{-1} and a shoulder at 735, are assigned to Si–O–C bonds.

Morphological studies

Surface morphology of both treated and untreated *C. indica* fiber was studied through scanning electron microscopy and the results are shown in Figures 9 and 10. From these figures, it has been observed that untreated fibers were of aggregated micro fibril. The untreated fiber surface clearly shows the presence of the oils and waxy substances. Treatment of the fibers with alkali brings about the process of swelling and dissolution. The fiber surface shows more fibrillation
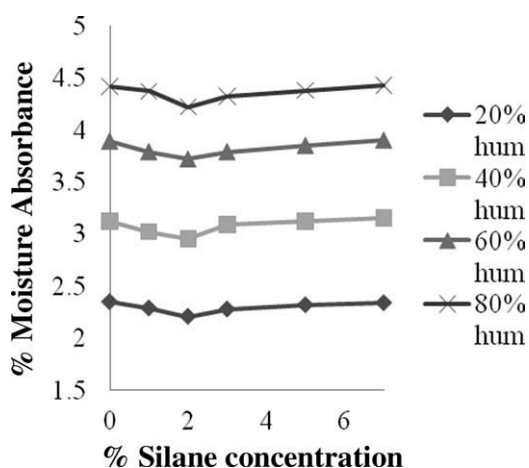

Three dimensional structure

R'= functional group; R = alkyl group

Figure 6 Schematic presentation of linear siloxane and three-dimensional polysiloxane cage structures.

Figure 7 Effect of silane treatment on moisture absorbance behavior at different humidity levels.

because of the removal of lignin, waxes, and hemicelluloses as shown in the SEM micrographs [Fig. 9(B–D)]. The maximum fibrillation was achieved with 10% NaOH treatment. Further increase in alkali concentration led to decrease in fibrillation due to trapping of the sodium ions in the layers of the fibers or formation of cellulose–Na complex as discussed earlier. It has also been observed that the fiber surface becomes rough on alkali treatment. However, on silane treatment surface features of the fibers are not clearly visible due to surface coating of aminopropyl triethoxysilane onto fiber surface (Fig. 10). Further, the surface smoothness has been found to increase with the increase in the silane concentration [Fig. 10(A–C)]. These SEM images further support the FTIR spectra regarding mercerization and grafting of silane molecules.

TGA analysis of the *C. indica* fiber

Thermal behavior of raw, mercerized, and silane-treated fibers was studied as a function of % weight

TABLE I
Peak Position and Assignment of Chemical Groups in the Untreated, Alkali Treated, and Silane-Treated *Cannabis indica* Fiber

Wave number (cm^{-1})	Functional group
3395.9	OH stretching
2922.3	C—H$_n$ symmetric and asymmetric stretching vibrations
1733.1	Carbonyl group of pectins
1635	C=O stretching mainly ketones and esters
1429.3	C=C stretching
1063, 1169, and 1252	CH bending
1000–1500	C—O—C stretching aromatic region related to lignin
1202	Si—O—C stretching
699.5, 735	Si–O–Si bond

loss with increase in temperature (Figs. 11, 12, and 13). In the case of raw fibers, a weight loss of around 8.5% before 100°C took place due to moisture loss. On further heating thermal decomposition of the fiber was found to take place in two successive stages. A weight loss of around 50% was observed in the first stage (200–350°C) of the decomposition due to depolymerization, dehydration, and glucosan formation that was followed immediately by the second stage (350–490°C) decomposition. The second-stage decomposition following the first stage started around 350°C which continued till 490°C with a weight loss amounting to around 37.5%. The first-stage decomposition observed after the moisture loss could be attributed to complex reactions other than hemicelluloses decomposition, which is reported to take place in the temperature range 220–320°C.[35,36] The second-stage decomposition may be due to cellulose decomposition and char combustion.[35,37,38] Some of the results of TGA and DTA analysis for raw, mercerized, and silane treated are summarized in Table II. For the raw fibers, the initial decomposition temperature (IDT) has been found to be 287°C (24.6% weight loss) and final decomposition temperature (FDT) to be 490°C (95.31% weight loss). In case of mercerized fibers, there is negligible change in the IDT values but FDT values increase considerably. However, the IDT and FDT values of silane-treated fibers have been found to be higher than mercerized and raw fiber. If we consider 30% weight loss as standard for comparison for the alkali-treated *C. indica* fiber samples, then it has been found that 8 and 10% mercerized fiber showed better thermal stability, i.e., higher decomposition temperature (DT) as comparison to 12% mercerized fiber. Similarly if we consider 60% weight loss for the mercerized samples
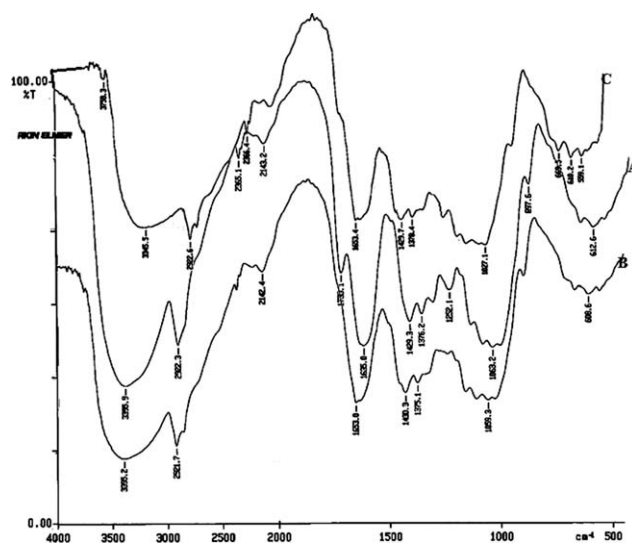

Figure 8 FTIR spectrum of (A) untreated (B) alkali treated, and (C) silane-treated *Cannabis indica* fiber.
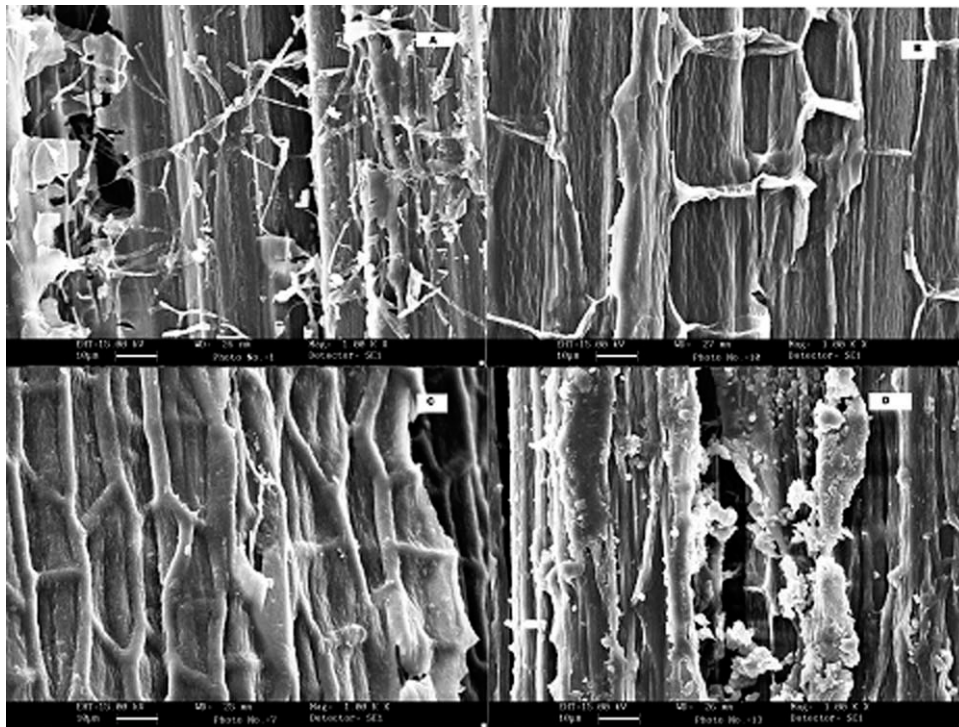
Figure 9 Surface morphology of untreated and mercerized *Cannabis indica* fibers. (A) Untreated, (B) 8% alkali treated, (C) 10% alkali treated, (D) 12% alkali-treated fibers.

it turns out that 12% mercerized *C. indica* fiber is more stable than 10 and 8% mercerized *C. indica* fiber. The residual char left at 500°C increased considerably from 3.6 to 25% in the case of alkali-treated fiber. A similar observation has been also reported by Saha et al.[39] They explained that
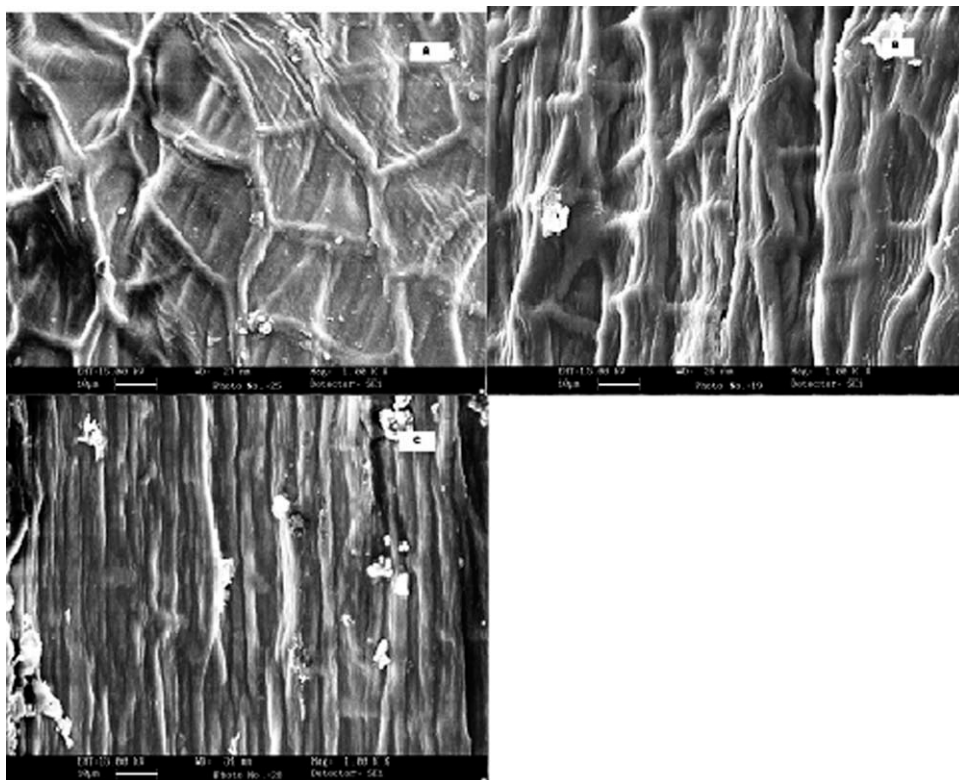

Figure 10 Surface morphology of the aminopropyl triethoxysilane-treated *Cannabis indica* fiber. (A) 1% Silane treated, (B) 2% Silane treated, (C) 3% Silane treated.

Figure 11 TGA thermogram of the untreated *Cannabis indica* fiber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mercerization reduces the hemicelluloses to a considerable extent, giving rise to lignin–cellulose complex, thereby making the product more stable than the raw sample and this was reflected in the increased amount of the residual char. And if we make a comparison for 30 and 60% weight loss of the raw, mercerized, and

Figure 12 TGA thermograms of the alkali-treated *Cannabis indica* fiber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
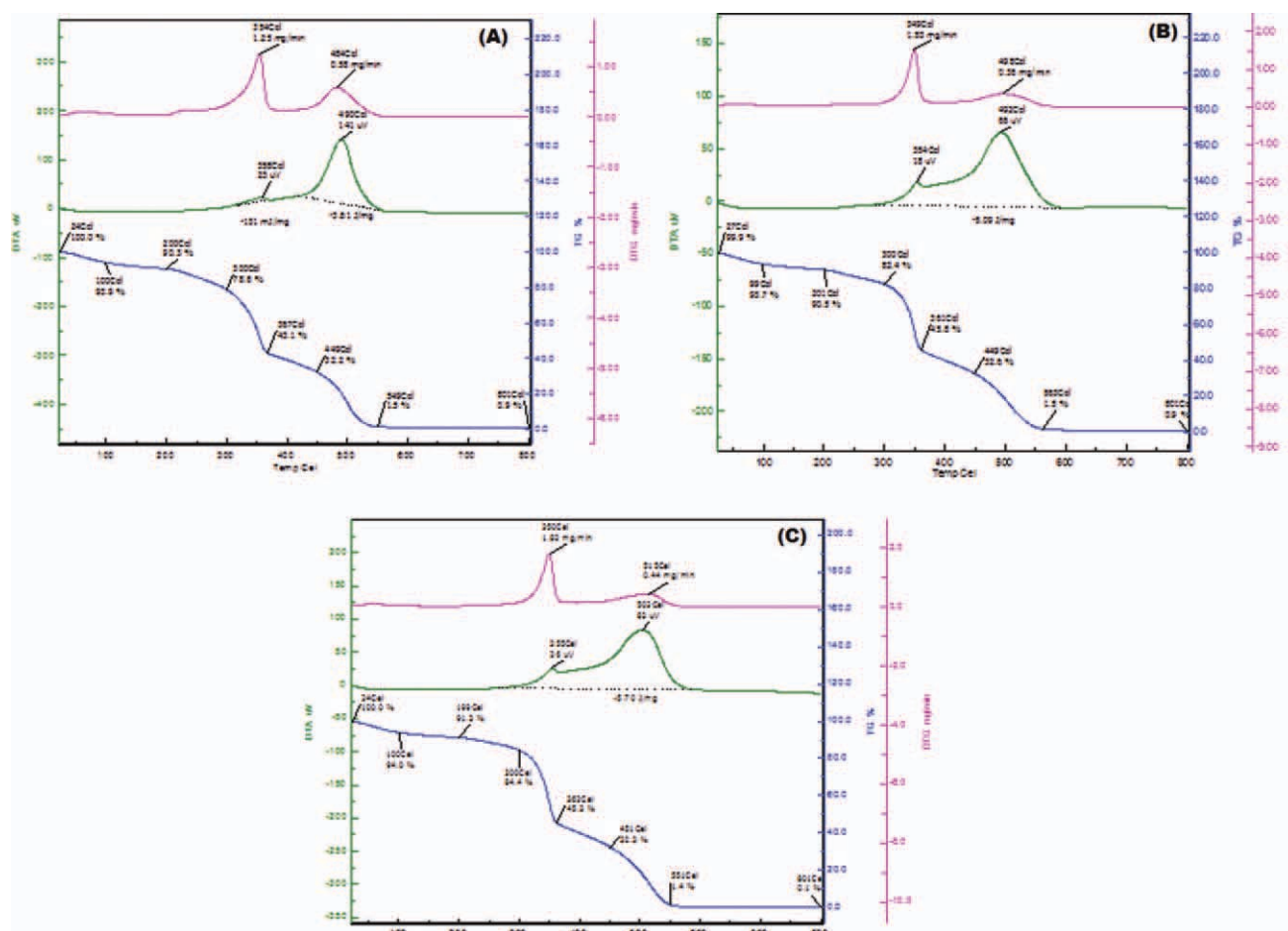
Figure 13 TGA thermograms of silane-treated *Cannabis indica* fiber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

silane-treated fiber for the thermal stability then it is clear from Table II that silane-treated *C. indica* fiber showed the highest thermal stability. And among 1, 2, and 3% silane-treated fiber, 2 and 3% silane-treated fiber have almost the same thermal stability but was higher than the 1% silane-treated fiber.

Further TGA studies of the raw, mercerized, and silane-treated *C. indica* fibers have been supported by DTA evaluation as shown in Table II. It is clear

from the table that DTA of raw fiber showed exothermic peaks at 328.0°C (15 µV) and 492.0°C (167 µV), and there was continuous exothermic combustion of the raw sample at the furnance temperature in the presence of atmospheric oxygen, which indicate the complete breakdown of C—C and C—O bonds. In case of the treated *C. indica* fibers, a continuous exothermic rise in temperature has been observed.

TABLE II
Thermogravimetric Analysis of the Raw and Mercerized and Silane-Treated *Cannabis indica* Fiber

Sr. No	Treatment	IDT (°C)/wt % loss	FDT (°C)/wt % loss	DT (°C) 30 wt % loss	DT (°C) 60 wt % loss	DT (°C) 90 wt % loss	DT (°C) (98.3–99.5) wt % loss	Exothermic peak at temperature (µV)
1	Raw	287/24.6	490/95.31	302	356	476	675	336 (22); 472 (231)
2	8% alkali treated	290/23.2	501/97.30	308	355	489	802	337 (18); 483 (185)
3	10% alkali treated	285/22.5	507/91.4	306	359	502	802	328.0 (15); 492 (167)
4	12% alkali treated	263/20.1	525/81.4	295	369	746	>800	329 (16); 519 (155); 746 (131)
5	10% alkali treated + 1% silane treated	322/27.5	528/96.5	328	391	769	769	358 (23); 490 (141)
6	10% alkali treated + 2% silane treated	330/24.9	540/95.7	339	400	541	541	355 (26); 503 (83)
7	10% alkali treated + 3% silane treated	325/23.2	549/98.4	338	399	574	574	354 (18); 492 (66)

Sr. No	Sample	At 2θ scale		Crystallinity (%)	C.I
		I_{22}	I_{15}		
1	Raw	709	348	67.07	0.5091
2	8% alkali treated	859	380	69.33	0.5576
3	10% alkali treated	882	375	70.16	0.5748
4	12% alkali treated	800	320	71.42	0.5875
5	10% alkali treated + 1% silane treated	490	270	64.70	0.4489
6	10% alkali treated + 2% silane treated	530	298	64.00	0.4377
7	10% alkali treated + 3% silane treated	890	410	68.46	0.5393

X-ray diffraction study

X-ray diffraction studies of the raw, mercerized, and silane-treated *C. indica* fiber have been shown in Table III. Since cellulosic fibers generally contain both crystalline and amorphous region, it is evident that X-ray diffraction patterns of such materials will show both region in the form of sharp peak and diffused pattern.

It is clearly observed that C.I of the *C. indica* fiber increased with increase in alkali concentration. The increase in the percentage of crystallinity index of alkali-treated fibers occurs because of the removal of the cementing materials and hemicelluloses, which leads to the interfibrillar regions to be less dense and less rigid and better packing of the cellulose chains.[40] As the alkali concentration is increased, the C.I increases because more and more amorphous and cementing materials are removed from the fiber surface. Also at 8, 10, 12% alkali concentration, hydroxide ions could be fully hydrated and they may not be able to penetrate and disrupt the cellulose lattice due to size restriction.[41,42]

However, on silane treatment a considerable decrease in C.I of the fiber has been observed. It is generally accepted that when silane coupling agent reacts with hydroxyl group of cellulosic fiber, alkoxy silanes undergoes hydrolysis, condensation, and subsequently bond formation. In addition to above, formation of polysiloxane structures also takes place. Such a large coupling molecules will destroy packing of the cellulose chains to a certain extent and causes disorder in the crystalline pattern of the main polymeric backbone. At 3% silane concentration, there is an increase in the percent crystallinity. This probably could be due to the formation of cage-like three-dimensional structures which inhibits the penetration of the silane molecules onto fiber surface.

CONCLUSIONS

Mercerized and silane treatments result in modification of the *C. indica* fiber. This has been confirmed by FTIR, SEM, XRD, and TGA analysis. XRD study showed that crystallinity of the raw fibers increased after the mercerization but decreased considerably after the silane treatment. Thermal stability of the silane-treated fibers has been found to be higher than that of mercerized fiber. It has also been observed that there is an enhancement in the chemical resistance and hydrophobic behavior of silane-treated *C. indica* fiber. Looking into environmental concerns, these properties of modified cellulosic fibers could be important in the preparation of natural fiber reinforced polymer composites which in turn would find extensive application in various fields.

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