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ORIGINAL RESEARCH

Characterization of natural cellulose fiber from corn stalk waste subjected to different surface treatments

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Abstract Crop stalk is a valuable source of cellulosic biomass and has attracted increasing attention as one kind of renewable resource. Cellulose fibers have potential as a reinforcement material to replace synthetic fibers used in biopolymer composites. This study addresses the modification and characterization of corn stem fibers extracted from corn stalk waste. The corn stem fibers were treated with alkali, silane and NaOH-silane solutions, and then, the chemical properties, surface morphology, mechanical behaviors and thermal stability of the corn stem fibers were characterized. The surface treatments improved the chemical and mechanical properties of the corn stem fibers. The fibers had rougher surfaces after the surface treatments. EDX and FTIR analysis confirmed that the surface treatments removed a certain amount of hemicelluloses, lignin and pectin from the natural fiber surface. XRD analysis results showed that the surface treatments had a positive impact on the crystallinity index of the natural fibers. The mechanical properties and thermal stability of the treated corn stem fibers were also found to be improved.

Keywords Corn stalk · Surface treatment · Fiber extraction · Cellulose fiber · Natural fiber · XRD

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Introduction

Environmental pollution, global warning, energy crisis and environment-friendly material needs have encouraged researchers to develop biocomposite materials for the aviation, automobile and marine industries (Rashid et al. 2016; Liu et al. 2019a, b; Singh et al. 2019). Natural fiber-reinforced composite materials have attractive properties in comparison to synthetic ones, such as light weight, abundance, biodegradability, nontoxicity, and low cost (Väisänen et al. 2017; Barari et al. 2016a, b). In recent years, natural fibers have attracted increasing attention as an eco-friendly and inexpensive substitute for synthetic

fibers in the reinforcement of composite materials (Barari et al. 2016a, b; Sepe et al. 2018). Natural fibers have many advantages and attractive features, such as abundance, light weight, biodegradability, renewability, low cost and high specific stiffness (Liu and Tisserat 2018; Indran et al. 2018; Sanjay et al. 2018). Natural fibers used to reinforce composite materials mainly include plant, animal and mineral fibers (Mittal et al. 2016). In recent years, plant fibers, such as stalk, base, leaf, seed, wood and grass, have become an important part of reinforcing materials and they are the most significant source of cellulosic fibers (Ramesh et al. 2017). Stalk fibers are mainly sourced from straws of different kinds of crops, including corn, barley, bagasse, wheat, sorghum, and rice (Ramesh et al. 2017).

Corn is an important worldwide agricultural crop, especially in northeast and northern China, such as in Jilin province. It is predicted that there are approximately 0.25 billion tons of corn stalks in China each year (Ma et al. 2018). However, less than half of the corn stalks are utilized, and most are thrown away or burned by local farmers, which is a waste of renewable biomass or biomass-derived resources and pollutes the water and air, such as haze (Wang et al. 2011). The pollution caused by corn stalks has become a global issue that needs to be addressed. In fact, numerous research studies in recent years have investigated the benefits of using annual corn stalk wastes in fiber reinforced biocomposite materials, low-cost housing, paper-making and packaging (Ma et al. 2018; Li et al. 2016). Research on the use of corn stalk waste could solve energy issues and environmental problems, and boost the agricultural economy (Bi et al. 2009).

It is well documented that a weakness of natural fiber is their poor compatibility with composite matrix due to their hydrophilic lignocellulosic molecules and low thermal stability (Zhou et al. 2016). Surface modification is a necessary step to prepare the reinforcing fibers used in biocomposite materials, and it is becoming a major area of research due to their large potential in industrial applications. In fact, alkali treatment or mercerization, silane treatment, use of maleated coupling agents, acetylation treatment, radiation and discharge treatments, benzoylation treatment and peroxide treatment have been widely reported so far (Venkata Krishna and Kanny 2016; Kumar et al. 2014; Liu et al. 2019a, b). Several studies (Yu et al. 2010; Asim et al. 2016; Orue et al. 2016) have reported that alkali and silane treatments are two of the most effective and most popular methods. These two surface treatments could improve the interfacial compatibility of the natural fiber and matrix, and change the microstructure of the natural fiber. Sangappa et al. (2014) evaluated the influence of NaOH solution treatment on the physical, chemical, and surface properties of Indian hemp fibers. The microstructural parameters of hemp fiber decreased with increasing treatment time. The surface of the natural fiber became rough and the fiber was suitable for reinforcement. Sang et al. (2017) investigated the surface modification of basalt fiber treated with a silane agent (KH-550). This work revealed that silane treatment could increase the tensile strength and modulus of basalt fiber, and improve the interface bonding strength between the poly(butylene succinate) matrix and the fiber in biocomposites. Moreover, the silane treatment of the natural fiber provided an effective way to prepare high-performance and biodegradable composite materials.

Although a large number of studies have been devoted to the application of corn stalk wastes and chemical surface treatment of natural fibers, the effects of different surface treatments on the chemical properties, surface morphology, mechanical behaviors and thermal stability of corn stem fibers have seldom been reported. In fact, different chemical treatment methods have a different impact on the natural fiber properties. Hence, an attempt is made in this paper to improve the chemical, morphological and mechanical properties and thermal stability of the raw corn stem fibers by various surface treatments. The present study demonstrated the influence of an alkali treatment, a silane treatment and a combined NaOH-silane treatment on the chemical properties, surface morphology, mechanical behaviors and thermal stability of such chemically treated corn stem fibers, and determined an effective treatment method to improve the natural fiber properties. The surface morphology of raw and treated corn stem fibers was observed using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The surfaces of untreated and treated corn stem fibers were evaluated using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy to investigate the structural and chemical changes in the fibers, respectively. The mechanical properties and thermal stability of the corn stem fiber were evaluated using a universal testing

machine and TGA analysis, respectively. The obtained morphology, chemical and structural information, as well as mechanical properties and thermal stability of the corn stem fibers, can help guide the surface treatment of natural fibers and the extraction of cellulose fibers applied in biopolymer composite applications.

Experimental materials and methods

Materials

Corn stalk has received extra attention due to its abundance and easy availability (Cai et al. 2016a, b). The corn stem has a compact layer of cell walls and a higher cellulose content in comparison to other parts of corn stalk, which can improve its mechanical strength (Luo et al. 2017). In this study, corn stalks were harvested on a farm in Jilin province, China. After air drying, the stems of the corn stalk were cleaned and dried, and the skins of the corn stems were obtained using a skin separator. Then, the corn stem fiber samples were prepared for the experiments. The silane coupling agent KH-550, γ-Aminopropyltriethoxysilane (APS, molecular mass of 221.37 g·mol^{-1}), used in this work was purchased from Jinan Jinhui Chemical Industry Co., Ltd. of China. In addition, all other chemical agents, such as NaOH and alcohol, were of analytical grade.

Fiber surface treatments

Corn stem fibers were treated with three types of chemical treatment methods, namely, an alkali treatment, a silane treatment and a combined NaOH-silane treatment. For the alkali treatment, corn stem fibers were soaked in 5 wt% sodium hydroxide solution for 30 min at room temperature and then rinsed with distilled water until the pH was equal to 7. After washing, the corn stem fibers were kept in a heat-treatment tank for 24 h at 90 °C. In the silane treatment, corn stem fibers were treated using a solution containing 5 wt% of silane coupling agent in a mixture of ethanol and water (80 vol%/20 vol% solution of ethanol/water) for 60 min under normal atmospheric pressure at room temperature, and then the fibers were rinsed with distilled water until the pH was equal to 7. Subsequently, the corn stem fibers were dried in a heat-treatment tank at 90 °C for 24 h. The temperature of silane treatment was chosen considering references in the literature (Sepe et al. 2018; Zhou et al. 2014). In the combined NaOH-silane treatment, part of the corn stem fibers were treated with NaOH solution as described in the NaOH-treatment step, and then they were treated with a silane solution as described in the silane-treatment step.

Morphology characterization

The lateral and transversal surfaces of untreated and treated corn stem fibers were evaluated by SEM (SU3500, Hitachi, Japan) at an operating voltage of 15 kV. All specimen surfaces were sputter coated with gold by using a SBC-12 sputter coater to improve the conductivity of the natural fibers prior to SEM observation.

EDX measurements

Energy dispersive X-ray spectroscopy (EDX) is a commonly used method to determine the quantity of elements (such as carbon, oxygen, and nitrogen) on a natural fiber surface. The elemental distributions on the raw and alkali-, silane- and NaOH-silane-treated corn stem fibers were determined by EDX (Oxford INCAx-sight, Oxford Instruments, UK), which was installed on the SEM. The data is expressed in atomic and weight percentages.

FTIR measurements

The untreated and treated corn stem fibers were evaluated using a FTIR spectroscopy (6800-50/NEXUS, ThermoNicolet, USA) to analyze the component changes of the natural fibers. FTIR spectra were recorded using an infrared spectrometer in the range of 675–4000 cm^{-1} with a resolution of 2 cm^{-1} at room temperature and in the dry environment. The corn stem fiber samples were dried using a special drying box.

XRD measurements

XRD patterns were obtained at an ambient temperature of 22 °C from radiation recorded by a 18 KW D/Max-2500PC diffractometer (Rigaku, Japan). The

tests were performed at 40 kV and 20 mA (5°–40°, 2°/min). The corn stem fiber samples are dry. The crystallinity index (CrI) was evaluated by the following equation based on the Segal empirical method (Segal et al. 1959):

$$CrI = \frac{I_{200} - I_{am}}{I_{200}} \times 100\%, \quad (1)$$

where I_{200} is the maximum intensity of the (200) lattice diffraction peak at a 2θ angle between 22° and 23°, and I_{am} is the minimum intensity of an amorphous area at a 2θ angle between 18° and 19° (Öztürk et al. 2010; Borchani et al. 2015; Seki et al. 2018).

Mechanical property measurements

Mechanical properties, including tensile strength, Young's modulus and elongation at break of the corn stem fibers, were measured at room temperature using an MTS Criterion40 universal testing machine (MTS Systems Corporation, USA) with a cross head speed of 1 mm/min and a fiber gauge length of 40 mm at 35 ± 3% relative humidity (RH). Twenty-five corn stem fibers were measured in each sample, and the test results were recorded as the average. The cross-sectional dimensions of the natural fiber samples were calculated accurately according to the failure surfaces of the fiber after each test. The tensile strength was evaluated by the following equation:

$$\sigma = F_b / S_0, \quad (2)$$

where σ is the tensile strength, F_b is the max force at fiber break, S_0 is the area of fracture, and the values of F_b can be obtained from the experimental data. Young's modulus was obtained from the slope of the stress–strain curves, and the elongation at break was also obtained from the experimental data.

TGA measurements

The thermal stability of the raw and silane-treated corn stem fibers was measured by thermogravimetric analysis (TGA) (SDT Q600, TA Instruments, USA) to evaluate the thermal degradation of the natural fibers. Approximately 10 mg of the natural fiber powder samples was analyzed, and the spectrum was recorded under an argon atmosphere from 40 to 650 °C at a heating rate of 10 °C/min and a flow rate of 30 mL/min.

Results and discussion

SEM analysis

The effect of different surface treatments on transversal and lateral surfaces was investigated using SEM. Figure 1a–1d show SEM micrographs of transversal surfaces of untreated and treated corn stem fibers. It can be observed in Fig. 1a that a vascular bundle and complete parenchyma cell were presented on the transversal surface of the fiber, and there was a large visible lumen in the center of the vascular bundle and parenchyma cell. Figure 1b–d show that the size of the lumen decreased, and the shape of lumen was irregular. The lumen of the corn stem fibers was invisible, and a large swelling of parenchyma cell walls could be observed in Fig. 1b and d. Meanwhile, the thickness of the cell wall of the fibers treated with alkali solution and silane solution increased, which is slightly larger than that of untreated fiber. However, the lumen completely collapsed in the process of NaOH-silane treatment, as shown in Fig. 1c. A similar result was reported by John and Anandjiwala (2008), who concluded that the natural crystalline structure of the cellulose was relaxed, which led to swelling of natural fibers during chemical treatment.

Figure 2a–d show SEM micrographs of lateral surfaces of the corn stem fibers. As shown in Fig. 2a, the surface of the natural fiber was smooth, unbroken and uniform. Generally, wax, pectin, lignin, hemicelluloses and cellulose are presented on a fiber surface (Nadlene et al. 2016); Except for cellulose, the other compositions could be removed by chemical treatment, which improved the mechanical properties and the poor compatibility of the natural fiber (Ramamoorthy et al. 2015). In comparison with the untreated corn stem fiber, the treated fibers had rough surfaces and appeared jagged in Fig. 2b and c. A possible explanation is that chemical treatments of the fibers lead to removal of hemicellulose, lignin and ash. Meanwhile, natural fibers with a rough surface would be the most desired (Ramamoorthy et al. 2015). According to the literature (Alvarez et al. 2003), alkali treatment of sisal fibers leads to rough fiber surfaces, and it also improves the mechanical properties of the natural fiber and the interface bonding strength between the fiber and composite matrix. Mohd Edeerozey et al. (2004) also evaluated the surface morphology of kenaf fibers treated with various NaOH concentrations. The

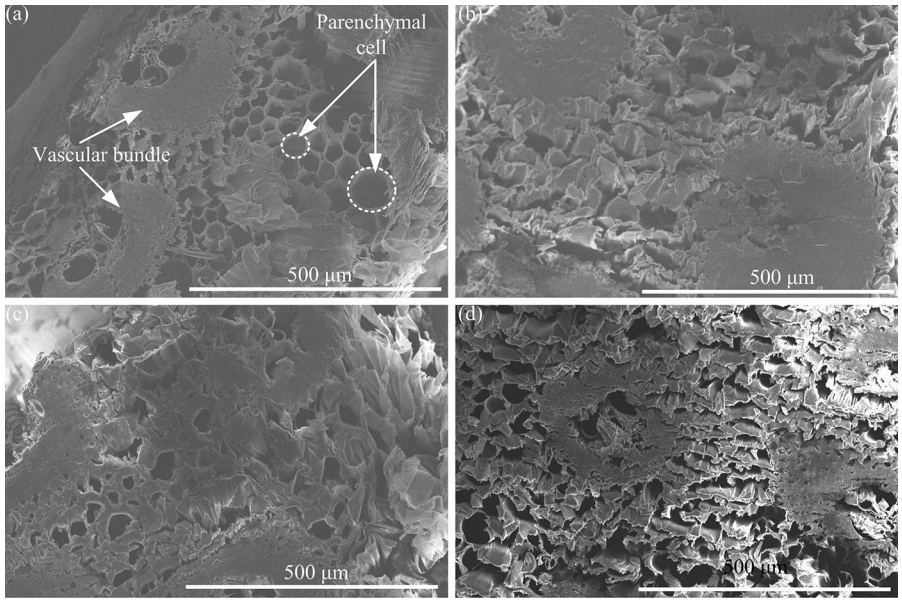

Fig. 1 SEM images of transversal surfaces of corn stem fibers. **a** Untreated fiber; **b** alkali-treated fiber; **c** NaOH-silane-treated fiber; **d** silane-treated fiber

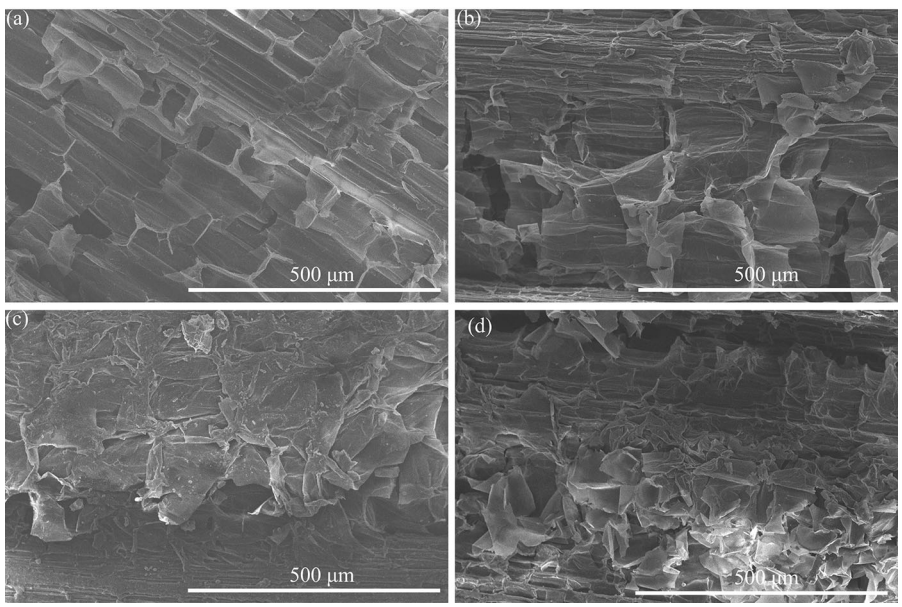

Fig. 2 SEM images of lateral surfaces of corn stem fibers. **a** Untreated fiber; **b** alkali-treated fiber; **c** NaOH-silane-treated fiber; **d** silane-treated fiber

experimental results concluded that the treated fibers had outstanding mechanical properties in comparison to the untreated fibers. The surface morphology of the silane-treated corn stem fiber in Fig. 2c and d presented a slightly regular and unadulterated surface free of residues in comparison to that of the other fibers. This difference is vital for the following reasons: (1) the ethanol/water mixture in the solution could remove part of pectin and hemicelluloses (Rachini et al. 2009) and (2) a siloxane layer formed on the surface of the fiber as the condensation of the silane groups [see Fig. 3 Liu et al. (2019a, b)]. The

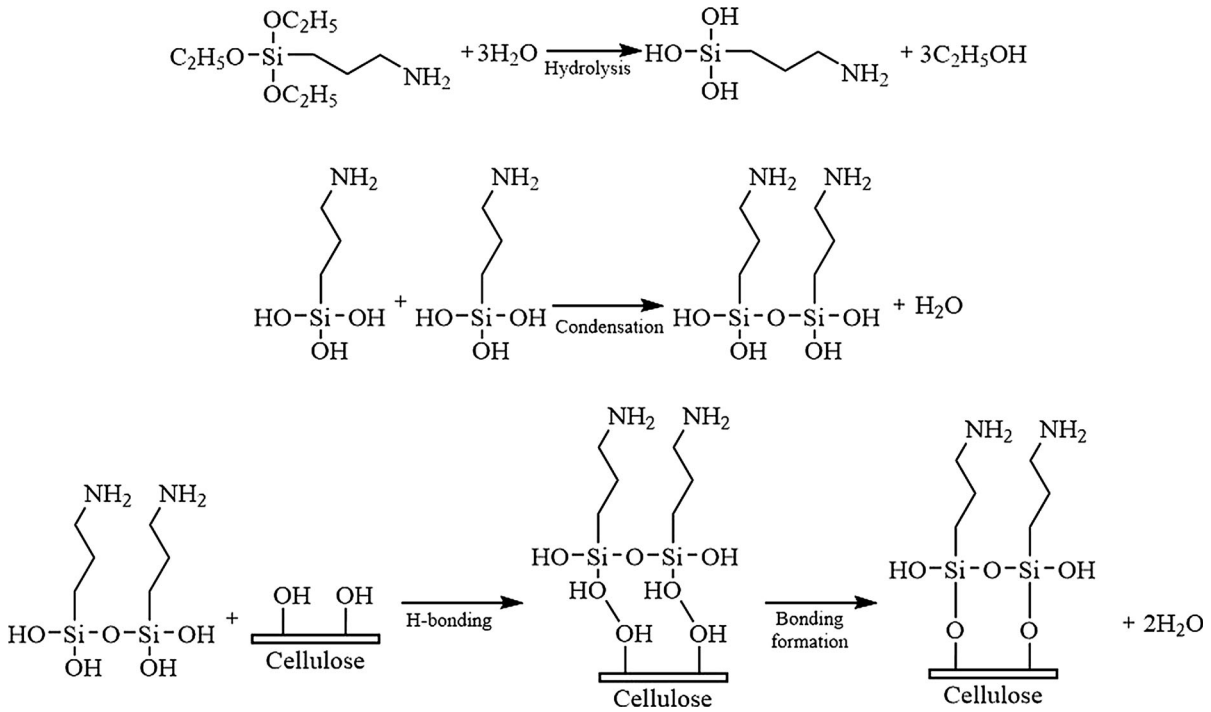

Fig. 3 Mechanism of interaction between the APS (KH-550) and cellulosic fibers

presence of APS could change the chemical composition of the surface of the corn stem fiber and, in turn, the surface morphology of the natural fibers.

EDX analysis

The data from the quantitative elemental corn stem fiber analysis before and after chemical modification in terms of weight and atomic weight are presented in Table 1. EDX analysis is one of the most popular techniques for quantitative and qualitative elemental analysis (Hassaini et al. 2017). A corn stem fiber is mainly composed of cellulose, lignin, hemicelluloses and waxes, and the chemical composition of the corn stem has been reported by Luo et al. (2017). The basic chemical elements in the corn stem fibers are carbon and oxygen. Inorganic elements, such as Al, Mg, Cl, K and Ca, can also be presented on the fiber surface, but in trace amounts (see Table 1). Table 1 shows that a certain amount of Na was presented in the outer layer of the natural fiber after NaOH treatment. This could be attributed to the type of bond formation and

Table 1 Weight and atomic percentage of untreated and treated corn stem fibers using EDX

Elements	Untreated (%)		NaOH (%)		NaOH-silane (%)		Silane (%)	
	Weight	Atomic	Weight	Atomic	Weight	Atomic	Weight	Atomic
C	55.95	63.06	35.87	44.17	48.47	56.48	44.03	52.35
O	43.11	36.47	53.11	49.10	47.01	41.12	52.08	45.34
Si	0.88	0.44	0.37	0.19	2.19	1.09	2.43	1.24
Na	–	–	9.01	5.80	1.82	1.11	–	–
Al	0.06	0.03	–	–	–	–	–	–
Mg	–	–	0.49	0.30	0.12	0.07	0.20	0.12
Cl	–	–	0.27	0.11	–	–	0.48	0.24
K	–	–	0.44	0.17	–	–	0.46	0.19
Ca	–	–	0.44	0.16	0.39	0.14	0.36	0.13

changes that take place on the surface of the corn stem fiber during the NaOH treatment. The reaction of NaOH and the corn stem fiber is as follows:

$$\text{Fiber} - \text{OH} + \text{NaOH} \rightarrow \text{Fiber} - \text{O}^{-}\text{Na}^{+} + \text{H}_2\text{O}. \quad (3)$$

The corn stem fiber treated with a silane solution led to incorporation of silicon. The results obtained are a good indication of Si in the silane-corn stem fiber structure, which could be explained by the fact that the silanization of cellulosic constituents of the corn stem fiber led to the formation of silanol functional groups (see Fig. 3). Table 1 also reveals a decrease in the percentage of carbon content and an increase in oxygen content after chemical treatments because the surface treatments may have removed part of the pectin and hemicelluloses from the surface of the treated fibers (Senthamaraikannan & Kathiresan, 2018). This result is consistent with the FTIR analysis results in "FTIR analysis" section.

FTIR analysis

Figure 4 shows the FTIR spectra of the corn stem fibers treated with different chemical solutions compared with that of the untreated fiber. The characteristic peaks at approximately 3349 cm^{-1}, 2917 cm^{-1}, 1723 cm^{-1}, 1513 cm^{-1}, 1243 cm^{-1}, and 898 cm^{-1} correspond to the O–H, C–H, C=O, C=C, C–O, C1–H bonds, respectively.

In the FTIR spectrum of the untreated corn stem fiber (black curve in Fig. 4), the characteristic peaks of cellulose, hemicellulose, pectin and lignin are visible, as mentioned in a previous publication (Sepe et al. 2018).

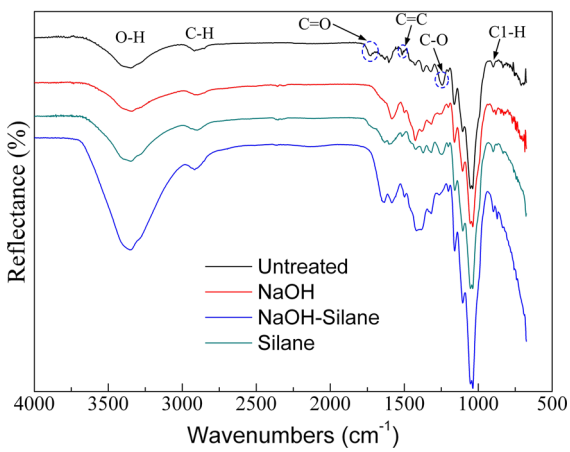

Fig. 4 FT-IR spectra of untreated and treated corn stem fibers

After alkali treatment, the peak at approximately 1723 cm^{-1} can be ascribed to the C=O bonds stretching from the hemicelluloses and pectin in the raw corn stem fibers, which was no longer visible in the treated corn stem fiber (Sepe et al. 2018). Meanwhile, a weak peak, at approximately 1513 cm^{-1}, could be ascribed to C=C group stretching vibration in the carbonyl of hemicellulose (Maache et al. 2017), and its absorbance was lower than that of the untreated fiber. A weak peak and lower absorbance in treated fibers were due to partial removal of lignin from the natural fiber surface. Moreover, the peak observed at approximately 1243 cm^{-1} (C–O bond stretching) was no longer observed in the corn stem fibers treated with alkali solution and NaOH-silane solution. This indicated that parts of lignin and hemicellulose in the treated fibers were removed (Shanmugasundaram et al. 2018).

It is well known that there should be Si–O–Si and Si–C stretching vibrations in the spectral curve of the silane-treated corn stem fibers (viridis and blue curves in Fig. 4). This agrees with the EDX analysis result, which confirmed the existence of silicon on the fiber surface after the silane treatments. However, the peak is not visible, as the concentration of the silane solution is relatively low and the signals are overlapped by organic component signals of the corn stem fibers (Sepe et al. 2018). Moreover, the peak at approximately 1243 cm^{-1} was lower than that of the untreated fiber, which indicated that part of the hemicellulose was removed during the silane treatment due to the effect of the ethanol/water mixture (Rachini et al. 2009).

XRD analysis

The X-ray diffraction patterns of untreated and treated corn stem fibers are shown in Fig. 5. As shown in Fig. 5, the X-ray diffraction pattern of the corn stem fiber presented major peaks at 2θ angles of approximately 15.54°, 16.28°, 22.12° and 34.54°, corresponding to lattice planes of peak 1 ((1–10)), peak 2 ((110)), peak 3 ((200)) and peak 4 ((004)) for cellulose I crystallites (French 2014; Dong et al. 2014; Jayaramudu et al. 2010). Peaks 1–3 are the characteristic peaks of cellulose I (French and Santiago 2013; Li et al. 2014; Borchani et al. 2015). Peaks 1 and 2 are

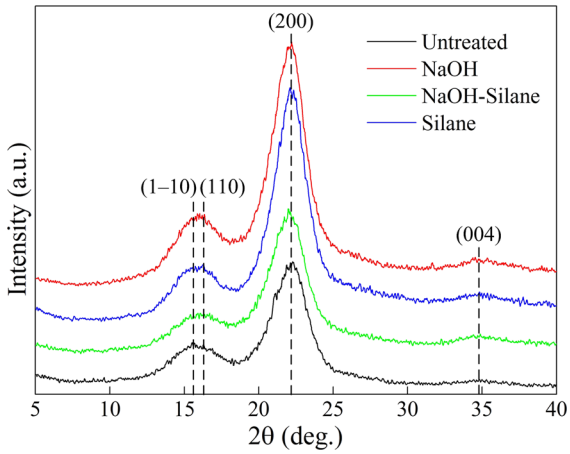

Fig. 5 XRD curves of untreated and treated corn stem fibers

most likely overlapping and appear as a single broad peak due to a large full-width at half-maximum (French and Santiago 2013; Ornaghi et al. 2014). XRD results also show that no structural transformation from the cellulose I to cellulose II polymorph occurred after the surface treatments.

The cellulose *CrI* calculated from the XRD patterns of each natural fiber is presented in Table 2. The *CrI* of the corn stem fibers that were untreated and treated with alkali solution, NaOH-silane solution and silane solution were approximately 58.2%, 65.7%, 64.4% and 69.7%, respectively. Interestingly, the degree of cellulose crystallinity increased after the chemical treatments, which is described as follows. The chemical treatments removed a part of noncrystalline materials, namely, hemicelluloses or lignin, in the natural fibers ("FTIR analysis" section), which could allow the cellulose fibers to adopt a more crystalline structure (Obi Reddy et al. 2013), and they also caused swelling of the parenchyma cell walls ("SEM analysis" section). Esteves (2009) concluded that cellulose crystallinity could increase after surface treatment due to the degradation of amorphous components in natural fibers and the rearrangement of cellulose molecules. The increase of *CrI* in the treated fibers could contribute towards its enhanced mechanical properties (Rong et al. 2001) and was also ideal for preparing biocomposite applications (Cai et al. 2016a, b).

Mechanical property analysis

Tensile tests were performed to investigate the mechanical properties of the corn stem fibers. Three important properties, including tensile strength, Young's modulus and elongation at break, were investigated in the tensile tests. In the present study, we learned that the mechanical properties were significantly affected by the chemical and morphological changes of the corn stem fibers.

Figure 6 shows typical tensile stress–strain curves of the raw and treated corn stem fibers. As shown in Fig. 6, the stress value in these curves suddenly dropped, which indicated that both raw and treated corn stem fibers are brittle in nature (Maache et al. 2017).

The mechanical properties of the corn stem fibers are presented in Table 2 and Fig. 7. From the results, it can be observed that the mechanical properties of the natural fiber changed dramatically with chemical treatments. The corn stem fiber treated with silane solution showed the highest tensile strength, 223.33 MPa, followed by the fiber treated with alkali solution, 152.90 MPa. The tensile strength of the fiber treated with NaOH-silane is 113.87 MPa, and the untreated fiber is 112.95 MPa. Overall, the decrease in tensile strength follows the order: silane > NaOH > NaOH-silane > untreated. The variations in the Young's modulus of untreated and treated natural fibers were similar to their tensile strengths. The

Table 2 Crystallinity characteristics and mechanical properties of untreated and treated corn stem fibers

	CrI (%)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
Utreated	58.2	112.95 ± 24.15	3.69 ± 0.96	3.64 ± 0.52
NaOH	65.7	152.90 ± 32.51	5.13 ± 1.18	3.67 ± 1.05
NaOH-silane	64.4	113.87 ± 19.36	4.63 ± 0.81	2.74 ± 0.36
Silane	69.7	223.33 ± 41.22	7.05 ± 1.07	4.02 ± 1.24

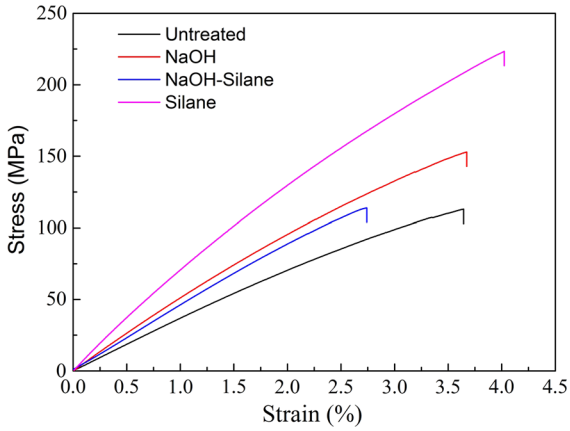

Fig. 6 Tensile stress–strain curves of untreated and treated corn stem fibers

Young's modulus of the treated corn stem fibers was higher than that of the untreated fiber. The Young's modulus of the fibers treated with silane and NaOH solutions increased by 91.06% and 39.02%, respectively, and by 25.47% in the fibers treated with NaOH-silane solution, with respect to the native fibers. Compared to the untreated natural fiber, the elongation at break improved 0.82% and 10.44% after silane and alkali treatments, respectively; however, it decreased by 24.73% in the fiber treated with NaOH-silane. The increases in the tensile strength and Young's modulus after chemical treatments can be attributed to the removal of hemicelluloses, pectin, and lignin from the corn stem fibers ("FTIR analysis" section) and the improved crystallinity of the natural fibers ("XRD analysis" section). As mentioned in the literature review (Onuaguluchi and Banthia 2016), the chemical composition of the natural fibers had a great effect on their mechanical properties; that is to say, their mechanical properties depended on the cellulose content in the natural fiber as well as the fiber surface treatment methods. Shanmugasundaram et al. (2018) also observed that appropriate removal of the noncellulose contents could improve the tensile strength and Young's modulus of the natural fibers. Moreover, Sang et al. (2017) mentioned that the surface modification of the fibers could improve the interfacial adhesion and the transmission of stress from the matrix to natural fibers to a certain degree. The slight increases in the tensile strength and Young's modulus and the decrease in the elongation at break occurred when the fiber was treated with NaOH-silane solution.

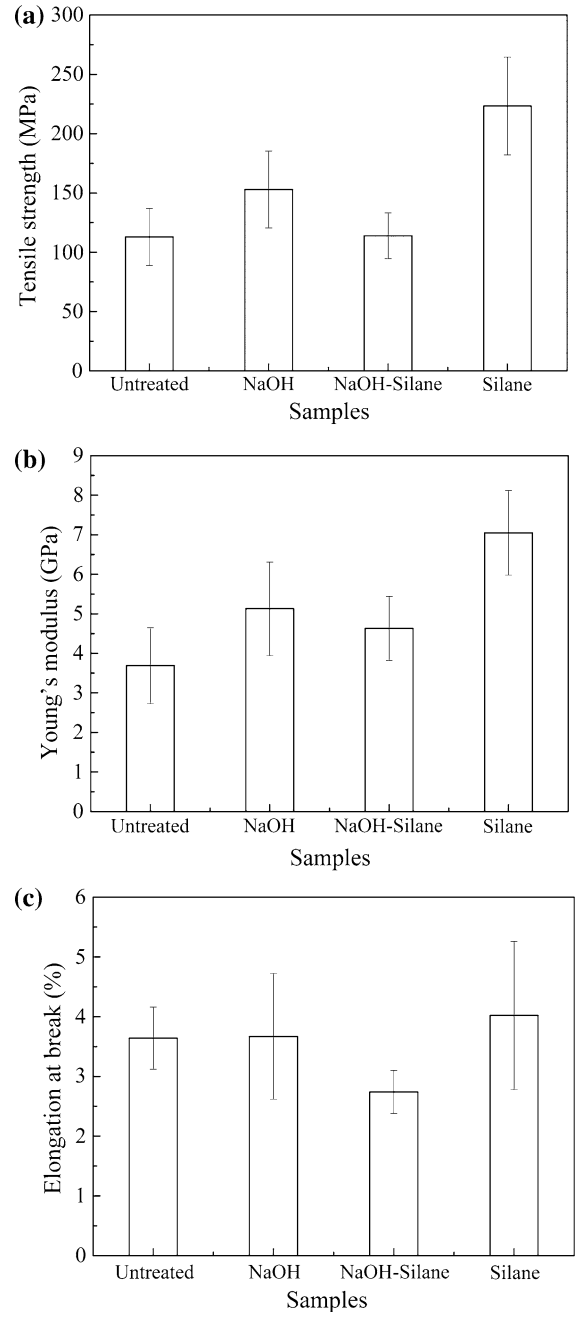

Fig. 7 Mechanical properties of untreated and treated corn stem fibers. **a** Tensile strength, **b** Young's modulus, **c** Elongation at break

Higher chemical concentration could remove more noncellulosic composition and impurities, but chemical degradation of the fiber and fiber breakdown decreased the tenacity and elongation at break (Ramamoorthy et al. 2015; Puglia et al. 2013). Fernandez

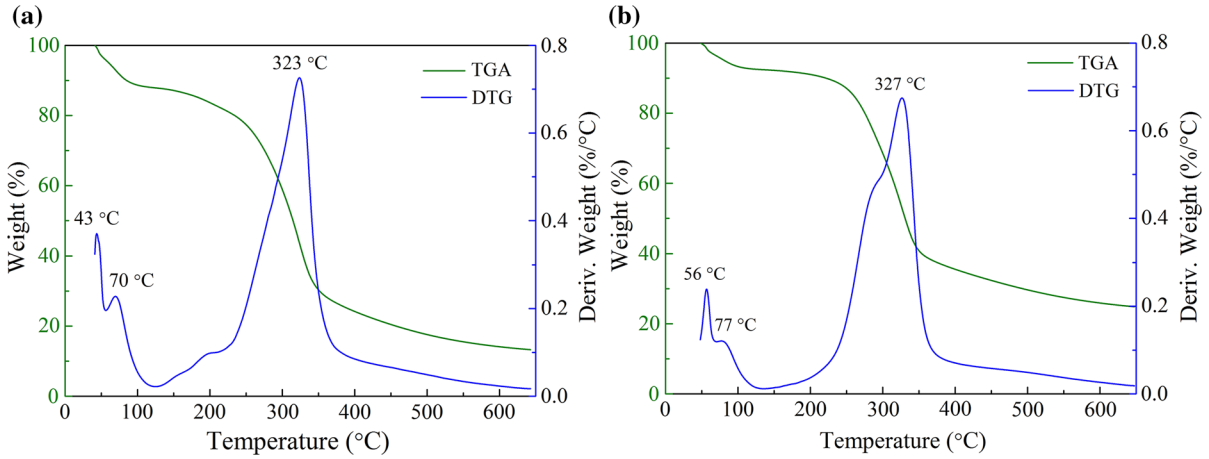

Fig. 8 TGA/DTG curves of **a** raw corn stem fiber and **b** silane treated corn stem fiber

et al. (2016) also concluded that a large removal of non-cellulosic composition induce the degradation of the natural fiber and then seriously impact the transverse tensile behaviors of the natural fiber reinforced composites. Moreover, it is need to develop the selective and non-degrading treatments which are better able to control the final performances of the bio-composite materials.

TGA analysis

Through the above analysis, silane-treated corn stem fiber showed excellent chemical and mechanical properties. In this section, we emphasize on the comparison and analysis of the thermal stability of the raw and silane-treated corn stem fibers. Thermal stability was investigated by TGA, and the TGA/DTG curves are presented in Fig. 8. The TGA/DTG curves clearly show that degradation of the raw and silane-treated corn stem fibers occurs in three different phases (Senthamaraikannan and Kathiresan 2018). In the first phase, 12.3% and 7.4% mass loss was presented for the raw and silane-treated corn stem fibers, respectively, at temperatures of 40–130 °C. The changes were attributed to the vaporization of moisture in the natural fibers (Mayandi et al. 2018; Rajan et al. 2018). In the second phase, thermal degradation occurred at approximately 180–300 °C with a mass-loss of 42.4% for the raw corn stem fiber and 36.3% for the silane-treated corn stem fiber due to the degradation of hemicellulose and the glycosidic linkages of cellulose (Indran et al. 2014). The final phase of mass loss occurred in the temperature range of 300–450 °C for the raw and silane-treated corn stem fibers. At this stage, a dramatic mass reduction of approximately 70% was observed at 323 °C for the raw corn stem fiber and 327 °C for the silane-treated corn stem fiber, which could be attributed to the thermal decomposition of α-cellulose (Belouadah et al. 2015). After saline solution treatment, the thermal stability and degradation temperature increased from 130 to 152 °C and from 323 to 327 °C, respectively. Similar degradation behavior could be found in previously published papers (Belouadah et al. 2015; Senthamaraikannan and Kathiresan 2018). From the DTG curves of the raw and treated natural fibers, it is indicated that both the thermal stability and degradation temperature of the treated fiber were increased, which could be attributed to the formation of a siloxane layer on the surface of the corn stem fiber (Seki et al. 2018). At 650 °C, the residual mass or char residue also increased from 16 to 22% after silane treatment. These residuals of cellulose degradation mainly included carbon residues and nondegraded fillers (Maache et al. 2017).

Conclusion

The influence of different surface chemical treatments on the chemical properties, surface morphology, mechanical behavior and thermal stability of the corn stem fibers were investigated, and the obtained results were discussed and reported in the present paper. SEM

images showed that the lumen of the corn stem fibers collapsed due to swelling of the cell wall, and the fiber lateral surface had a rough surface and appeared jagged due to the removal of noncellulosic contents after chemical treatments. EDX results are evidence of Si in the silane-corn stem fiber structure due to the formation of silanol functional groups on the fiber surface. The results obtained from the FTIR study confirm that noncellulosic materials are removed due to the influence of chemical treatments. XRD results proved that the crystallinity index of the corn stem fibers improved by following the chemical treatments. The chemical treatments led to improved mechanical properties of the corn stem fibers, which could contribute to different chemical structures and molecular rearrangements of the corn stem fibers. Moreover, appropriate removal of the noncellulose contents could improve the tensile strength and Young's modulus of the corn stem fibers. The thermal stability and degradation temperature of the treated fibers were also improved after surface treatments. The above comparison results confirm that the silane treatment was the optimum way to improve the comprehensive properties of the corn stem fibers. The improvements demonstrated in the present paper are critical to efficiently produce natural cellulosic fibers for fabrication of various biopolymer composite applications that could be applied in the aviation, automobile and marine industries. In the further work, we will further investigate the effect of silane solution with various concentrations on the morphological, chemical, physical and mechanical properties of the corn stem fibers.

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