Facile Preparation of All Cellulose Self-reinforced Nanocomposites from Bamboo Shoot Fibers

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Research Article

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Abstract

Herein, a novel and facile fabrication method of self-reinforced all cellulose nanocomposite based on 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO) mediated oxidized bamboo shoot shell fibers was introduced. The composites were thoughtfully characterized. Cellulose nanowhiskers from the bamboo shoot fibers with the diameter of 60–90 nm and a large number of micropores were evenly distributed on the surface of the nanocomposite. Compared with the original fiber, the crystallinity of the composites increased, while the thermal stability decreased. The composite also showed good mechanical property and dimensional stability. It provides a promising and convenient route to obtain firm sheet-materials with micro- or nano- structures from nature cellulose fibers.

1 Introduction

Cellulose is considered to be the most abundant biopolymers in the world, which has remarkable characteristics such as low cost, renewability and biodegradability attracted the strong attention of the world (Tang, et al. 2021; Miao and Hamad, 2020). Cellulose can meet the growing demand for environmentally friendly and biocompatibility products, and it has been used for many different purposes, such as paper, medicine, packaging and decoration and so on (Megashah et al, 2020).

Cellulose nanofibers with outstanding characteristics such as high specific surface area and excellent tolerance, good mechanical properties, high resistance performance and low thermal expansion coefficient have aroused great interest in composite materials and all cellulose nanocomposites (ACC) (Li, Yan, Cai 2019; Abdul et al. 2014), which are often used in many applications, from aerospace industry to civil engineering and building applications (Zhang et al. 2019; Yu et al. 2018).

Nishino et al. (2004) proposed the definition of all cellulose composites (ACC). For natural cellulose fiber reinforced cellulose matrix, there is no interface problems and the composites are completely degradable due to the nature of cellulose materials of the two phases. As a kind of "green" composite, ACC has been an attractive choice (Adak and Mukhopadhyay, 2018; Xiong et al. 2014; Cao et al. 2020). ACC can be manufactured from many sources, such as natural fibers (kapok, hemp, pineapple leaves), pulp and microcrystalline cellulose (Shibata et al. 2013; Pullawan et al. 2014). Samouh et al. (2014) reported that the mechanical properties and dynamic mechanical properties of the composites are improved by adding sisal fiber into PLA. Vallejos et al. (2012) prepared all cellulose composite (ACC) fibers showed the typical widths in the nano- and micro-scale by electrospinning cellulose acetate (CA) and cellulose nanocrystals (CNC). Lu et al. (2020) prepared all cellulose composite (ACC) films with improved elongation at break and tensile strength through a blocked polyisocyanate (BPIC) induced cross-linking of hydroxyethyl cellulose (HEC) and cellulose nanocrystals (CNC).

Research on all-cellulose composites usually focused on the preparation with some new methods reported, such as partially dissolved cellulose self reinforced techniques (Gindl and Keckes 2007) and cellulose nanocomposites (Chen et al. 2019). The current work focuses on the influence of TEMPO

oxidation on features of the resultant ACCs. Herein, TEMPO oxidized bamboo shoot shell fibers was utilized as raw materials for the self reinforced ACC preparation by the means of partial dissolution. The ACCs obtained from bamboo shell cellulose fibers were characterized as morphology, FTIR, crystallinity index, thermostability, and mechanical strength.

2 Experimental

2.1 materials

Bamboo shoot shell were collected from the fiber plantation at Wuhan Textile University, China. Hydrogen peroxide solution (AR, 30 %), sulfuric acid (AR, 98 %), sodium hydroxide (NaOH), 2,2,6,6-tetramethylpiperidine-1-oxyl radio (TEMPO, 98%), dimethylsulfoxide (DMSO), sodium bromide (NaBr), 12 wt% sodium hypochlorite (NaClO) solution, ethanol and other chemicals were of laboratory grade (Shanghai Aladdin chemical Regent Inc., China) and used without further purification.

2.2 preparation of bamboo shoot shell fibers

The bamboo shoot shell is washed with warm water to remove the fluff and impurities on the surface, and then air dried. It was cut into small strips (longitudinal 30 mm, cross Sect. 2 × 2 mm)

a. Pickling: 2 ml/L H_2SO_4, pickling at 60℃ for 1 h, bath ratio 1:40.

b. Washing: washing at room temperature for 20 min.

c. Boiling-off: 24 g/L NaOH, 2 % Na_2SiO_3, 2 % Thiourea, 3 % Sodium polyphosphate, 35ml/L H_2O_2, 95 ℃ for 2.5 h, bath ratio 1:40.

d. Pickling: 1 mL/L H_2SO_4; pickling at room temperature for 5 min.

e. Washing: washing at room temperature for 5 min.

f. Drying: drying at 80 ℃. The dried mass was then dipped in DMSO (liquor ratio 1:15) followed by heating at 70 ℃ under water bath. Again after washing several times with distilled water, it was oven-dried at 70 ℃ for 24 h.

2.3 preparation of composite materials

The TEMPO oxidized bamboo shoot shell fiber was prepared according to our early report (Cao et al. 2013). The samples of bamboo shoot shell fiber (1 g) treated with DMSO were dispersed in the solution of distilled water (100 g), sodium bromide (0.20 g) and TEMPO (0.02 g). The reaction began with 12 wt% sodium hypochlorite solution (10ml) as the stirring was added. The pH was adjusted to about 10.5 with 2 wt% NaOH aqueous solution and monitored with pH meter. Add 5ml of ethanol without consuming NaOH, then stir for 20 minutes. The final product was washed with deionized water by successive centrifugations (5000 rpm for 10 min) until neutral. Oxidized cellulose slurry (1.0 g) was dispersed in 100 g of water and sonicated for 5 min at 10,000 rpm with an IKA T25 homogenizer (IKA Works, Shanghai,

China). Remove the supernatant, take the precipitate, pour it on the clean glass plate, use the self-made film scraper to scrape the film evenly and smoothly, keep the film thickness at 100 μm, and put it into the oven and dry at 80 ℃.

The scheme of the above processes for cellulose isolation and ACC realization was shown in Fig. 1.

2.4 Characterization

2.4.1 Scanning electron microscopy (SEM)

The microstructures of all samples were analyzed by tescan Vega 3 scanning electron microscope at 20 ℃.

2.4.2 Fourier transform infrared (FTIR) spectroscopy

The characteristic groups in bamboo shoot shell fiber and composite before and after treatment were determined by potassium bromide pressing method with vertex 70 Fourier transform infrared microspectrometer. The wavenumber test range was 400–4000 cm^{-1}.

2.4.3X-ray diffraction (XRD) measurement

The crystallinity of samples was determined by (D/max-2550pc, RIGAKU) X-ray diffractometer. The experimental conditions were as followed: Ka radiation of Cu target (X-ray wavelength 0.154 nm), tube voltage 40 kV, tube current 30 Ma for scanning, diffraction direction θ-2θ linkage scanning mode, scanning angle 5–45°, the scanning speed was 5 °/min.

2.4.4Thermal gravimetric analysis (TGA)

About 5.0 mg of bamboo shoot shell fiber and new self reinforced cellulose micro-nano composite samples were separately weighed and put into sdt2960 differential thermal gravimetric (DSC-TGA) analyzer (TA instruments company) sample pool for thermal performance measurement. The nitrogen flow rate was 50 ml/min, the heating rate was 10 ℃/min, and the temperature range was 30–600 ℃.

2.4.5 Tensile test

The tensile fracture properties of the new self reinforced cellulose micro-nano composites were tested by Instron 5565 universal material strength instrument. The clamping distance was 20 mm, and the average value was taken after 20 times of test.

3 Results And Discussions

3.1 Morphological Analysis.

Fig. 2 shows the surface and cross-section SEM images of the self reinforced all cellulose nanocomposite. As shown in Fig.1a, there are a large number of pores on the surface of the self reinforced cellulose nanocomposite, which are of great significance for the later application as filter and

adsorption material. In addition, a large number of cellulose whiskers with a diameter of about 60-90 nm separated from bamboo fibers can be seen evenly distributed on the surface of the nanocomposite, which is very helpful for improving the strength of the composite. As shown in Fig.1b, a large number of pores and nano fibers can also be seen from the cross-section structure of the composite, which is consistent with the results of the surface structure. The microstructure with pores and the coexistence of micro and nano fibers of the composite provides a basis for further application.

3.2 FTIR analysis

The investigation of chemical structure change in all samples was carried out through FT-IR absorption spectroscopy. **Fig. 3 shows the infrared spectra of (a) untreated bamboo shoot shell fiber, (b) alkali treated bamboo shoot shell fiber and (c) self reinforced cellulose nanocomposites.** Both the bamboo control sample and alkali treated bamboo cellulose have no absorption band from 1400 to 1700 cm^{-1}, but two strong absorption bands at 1639 and 1426 cm^{-1} derived from the carbonyl groups present in response to the TEMPO-mediated oxidation of cellulose whiksers presented in the nano-composite, indicating that hydroxyl groups at the C6 position of cellulose molecules are converted to sodium carboxylate (Ifuku et al. 2009). Meanwhile, all samples exhibits a broad band in the region of 3500-3200 cm^{-1} due to the free -OH stretching vibration of hydroxyl groups in cellulose molecules, again indicating not all -OH groups joining the reaction but a selective oxidation of the primary OH units. On the other hand, it can be seen that after TEMPO oxidation treatment, the self reinforced material still has the characteristics of cellulose fiber. However, the peaks at 3340 cm^{-1} and 1050 cm^{-1} were significantly enhanced, which was the characteristic peak of cellulose, indicating that more cellulose was released after TEMPO treatment. The peak at 1732 cm^{-1} of the self reinforced all cellulose nanocomposite was significantly weakened, indicating that hemicellulose was largely removed (Ibrahim et al. 2013).

3.3XRD Analysis

Fig. 4 showed the X-ray diffraction curves of (a) untreated bamboo shoot shell fiber (b) alkali treated bamboo shoot shell fiber and (c) self reinforced all cellulose nanocomposites. According to Fig. 3, it could be noted that the fibers show increasing orientation along a particular axis as the noncellulosic polysaccharides were removed and the amorphous zones are dissolved. The strong diffraction peaks of all samples appeared at 2θ=16° (the overlapped 1–10/110 peak) and 22°(200 crystalline peak) respectively (French, 2020), the results showed that the oxidation treatment of TEMPO does not change the crystal form of the samples (Franciele et al. 2013). The crystallinity of final composites (64.30 %) was significantly improved compared with that of untreated (30.80 %) and alkali treated bamboo shoot shell fiber (60.00 %). The slight increasing in the crystallinity after TEMPO oxidization, which was due to partial loss of the disordered regions during the washing process because of their increased water-solubility, was also observed by (Saito & Isogai, 2004). Because of the destruction of hydrogen bond and van der Waals force between cellulose macromolecules during the TEMPO oxidation, the crystallinity of composites was improved by the present of nanowhiskers who released single crystal. The high crystalline cellulose nanowhiskers could be more effective in providing better reinforcement for composite materials because

the high Young's modulus (138 GPa) of the crystal region along the longitudinal direction (Sakurada, Nukushina, and Ito 1962).

3.4 Thermal stability

Fig.5 shows the thermogravimetric analysis curves of (a) bamboo shoot shell, (b) bamboo shoot shell fiber and (c) self reinforced cellulose nanocomposites. It can be seen that the first weight loss stage is about 80 ℃, and the micro loss of bamboo shell and its fiber is about 5%, which is mainly due to the volatilization of water in the sample and the pyrolysis of micro molecules (Sa, Deshmukh, Pinjari 2019). From 220 to 270 ℃, the weight loss of bamboo shell and bamboo fiber is about 8%, which is mainly due to the cracking of hemicellulose. In the range of 270-370 ℃, the weight of bamboo shoot shell and bamboo shell fiber decreased sharply, which was caused by cellulose cracking (Lee et al. 2017). However, the weight of self reinforced cellulose nanocomposites began to decrease rapidly at 220 ℃, because tempo oxidized the primary hydroxyl group on the surface of cellulose to carboxyl group, which reduced the thermal decomposition point of self reinforced cellulose nanocomposites (Isogai, Saito, Fukuzumi 2011). When the temperature reaches 340 ℃, the weight of self reinforced cellulose nanocomposites decreases slightly, which is due to the cracking of hemicellulose. Due to the low content of nano cellulose in the self reinforced cellulose nanocomposites, its thermal stability is not obvious compared with bamboo shoot shell fiber. With the increase of temperature, the weight of self reinforced cellulose nanocomposites tends to be stable, and the thermal stability is relatively poor.

3.5 Tensile property

Fig. 6 shows the stress-strain curve of self-reinforced all cellulose nanocomposite. It can be seen that the characteristics of tensile fracture curve of the prepared composite are different from those of ordinary fibers. From the curve change, there is no obvious yield stage, it has high breakage strength of 45 MPa. It has the characteristics of low elongation, which is greatly related to its own molecular structure. The crystallinity of self reinforced cellulose nanocomposite is high, the macromolecules are arranged orderly, and the force between the molecules is large. In the process of stretching, the external force required to break the macromolecules is large (Chen et al. 2017). Due to the large binding force between macromolecules, the slip of the fiber is small when macromolecules are destroyed, which makes the low elongation at break (1.78 %). From the tensile fracture point of view, the self reinforced cellulose nanocomposite shows obvious brittle fracture characteristics. In all, the prepared nanocomposite has small elongation, small deformation and good dimensional stability under the action of large load.

4. Conclusions

In this study, bamboo shoot shell natural fiber was used as raw material to prepare self reinforced all cellulose nanocomposite by a simple method of TEMPO oxidation mediated cellulose. The results show that there are a large number of holes a large number of pores and cellulose whiskers with a diameter of about 60-90 nm separated from bamboo fibers on the surface of the nanocomposites, which are of great significance for the later application as filter and adsorption materials. The nanocomposite has good

dimensional stability indicating the possibility for replacing hard-wood resources and the great potential for utilizing agricultural wastes. This study presented a novel route that obtained micro-nano structural materials from cellulose. The prepared materials were potentially used in filtration, separation, reinforcement and so on. It is believed that the method described here could be easily extended to provide a strategy of fabricating all cellulose nanocomposites.

Declarations

Acknowledgement

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Declaration of interest statement

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of the manuscript entitled. This manuscript did not contain any animal studies or human participants involvement in the study, which also complies with ethical approval and ethical standards.

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Figures

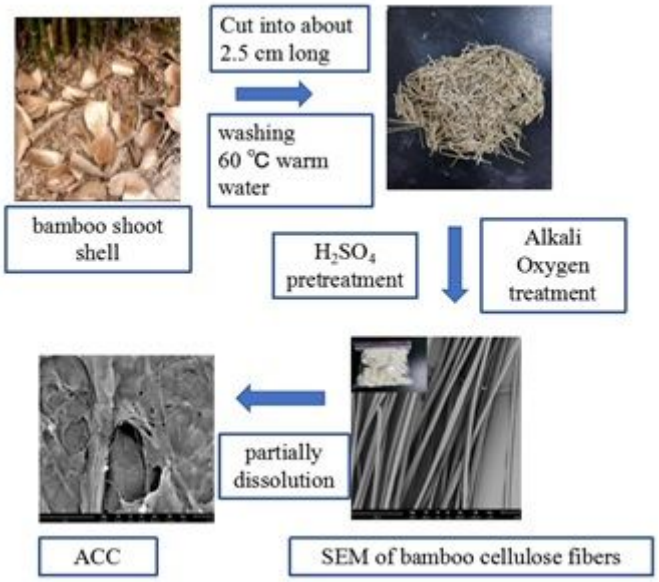

Figure 1

Schematic routes of cellulose isolation and ACC realization in this research.

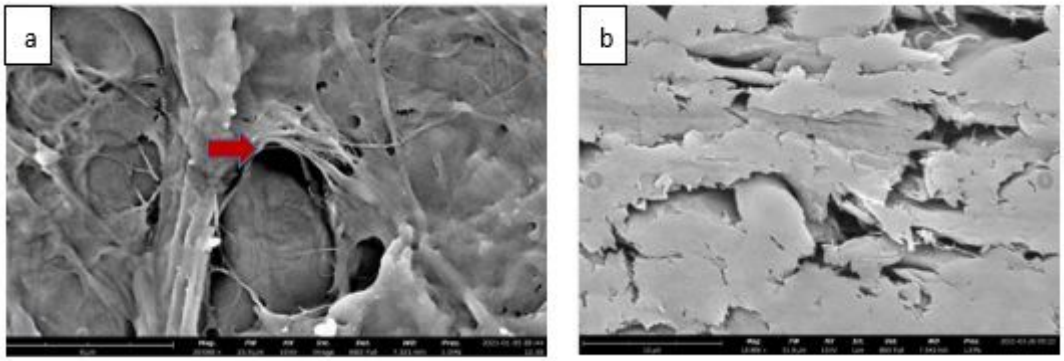

Figure 2

Thermal field SEM images of self reinforced all cellulose nanocomposite. (a) surface and (b) cross section.

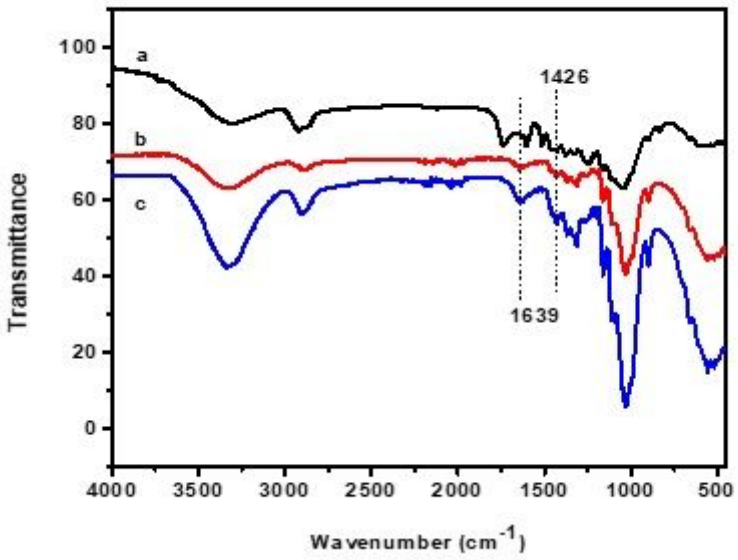

Figure 3

FTIR spectra of (a) untreated bamboo shoot shell, (b) alkali treated fiber, and (c) self reinforced all cellulose nanocomposite.

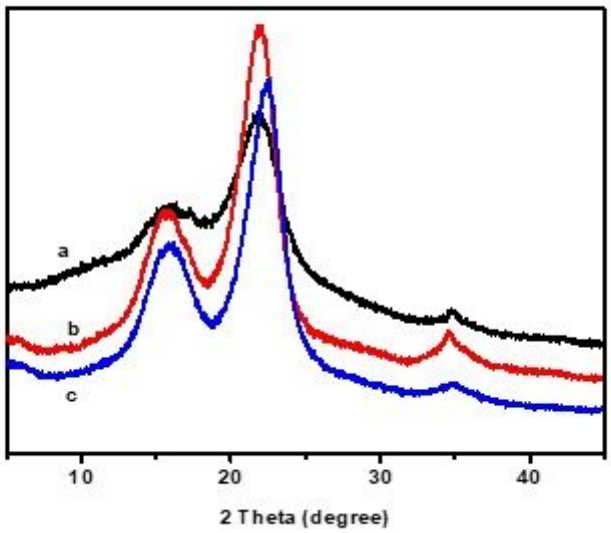

Figure 4

X-ray diffraction curves of (a) untreated fiber; (b) alkali treated bamboo shoot shell fiber and (c) self reinforced cellulose nanocomposite

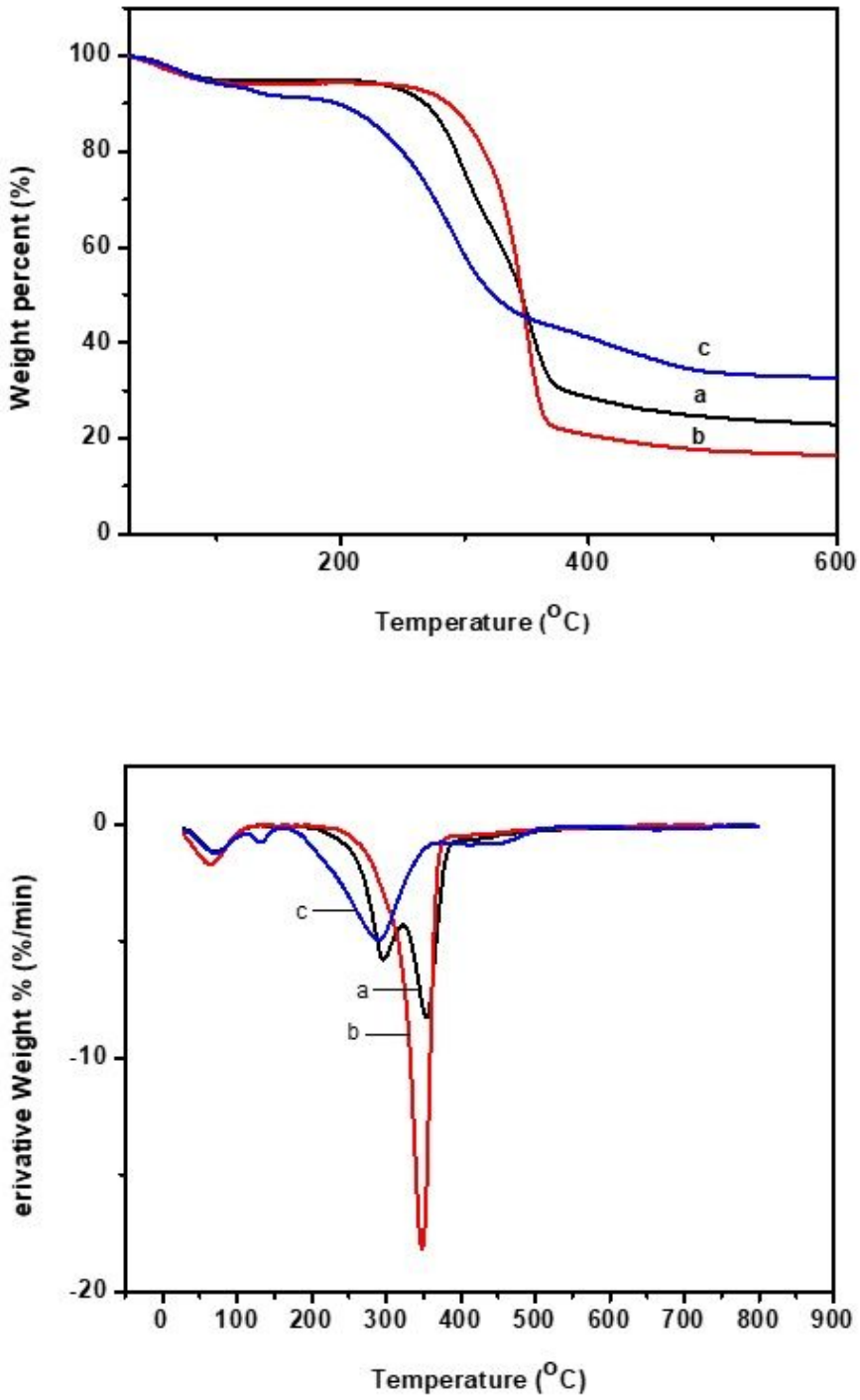

Figure 5

TGA curves of (a) bamboo shoot shell, (b) bamboo shoot shell fibers, and (c) self reinforced cellulose nanocomposites.

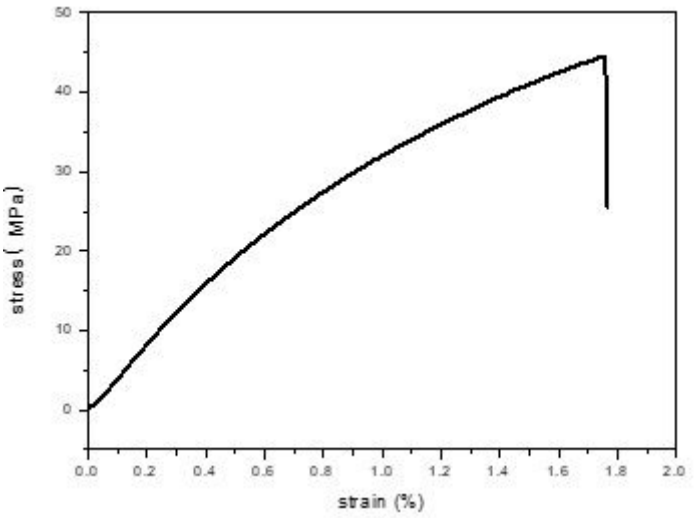

Figure 6

The stress-strain curve of self-reinforced all cellulose nanocomposite