



# Comparison of the reinforcing effects for cellulose nanocrystals obtained by sulfuric and hydrochloric acid hydrolysis on the mechanical and thermal properties of bacterial polyester



Hou-Yong Yu <sup>a,b</sup>, Zong-Yi Qin <sup>b</sup>, Lin Liu <sup>a</sup>, Xiao-Gang Yang <sup>a</sup>, Ying Zhou <sup>a</sup>, Ju-Ming Yao <sup>a,\*</sup>

<sup>a</sup>The Key Laboratory of Advanced Textile Materials and Manufacturing Technology of Ministry of Education, College of Materials and Textile, Zhejiang Sci-Tech University, Hangzhou 310018, China

<sup>b</sup>State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

## ARTICLE INFO

### Article history:

Received 15 May 2013

Received in revised form 26 June 2013

Accepted 20 July 2013

Available online 6 August 2013

### Keywords:

- A. Nanoparticles
- A. Particle-reinforced composites
- B. Mechanical properties
- B. Thermal properties
- E. Processing

## ABSTRACT

Two kinds of cellulose nanocrystals (CNCs) obtained by sulfuric acid hydrolysis (CNC-S) and hydrochloric acid hydrolysis under hydrothermal condition (CNC-H) were used as organic nanoreinforcement to enhance the mechanical property and thermal stability of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). Comparison of the reinforcing effects for different CNCs on the properties of PHBV was carried out. Compared to CNC-S, CNC-H exhibited the larger aspect ratio, higher crystallinity, and especially no residual acid groups. Moreover, better dispersion of CNC-H with larger loading contents could be introduced into PHBV matrix, which was beneficial to form more intermolecular hydrogen bonding interactions, leading to the formation of refined crystalline structure of PHBV although the crystallization rate was promoted due to stronger reinforcing effects of CNC-H. Therefore, at the same contents, the reinforcing effect of CNC-H was stronger than CNC-S. More importantly, compared to the neat PHBV, the tensile strength and Young's modulus of the nanocomposite with 12 wt.% CNC-H were enhanced by 175% and 300%, respectively, meanwhile the initial decomposition temperature ( $T_0$ ) and maximum decomposition temperature ( $T_{max}$ ) were increased by 58.1 and 52.1 °C, respectively.

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## 1. Introduction

Cellulose nanocrystals (CNCs) from abundantly renewable resources have recently attracted considerable interest in their role as reinforcing agents in nanocomposites because of their unique characteristics, such as the nanoscale dimensions, high surface reactivity, light weight, non-toxic, biodegradable, and especially remarkable mechanical properties (138 GPa of Young's modulus and 1.7 GPa of tensile strength). By adding a small amount of low-density CNCs as an organic nanoreinforcement, the mechanical properties have been greatly enhanced for various biodegradable polymers [1–5]. The reinforcing effect of the CNCs depends on not only the interaction between the CNCs and polymer chain, but also their surface groups on the CNC, adding content and state of dispersion within the matrix [6–8]. It has been demonstrated that strong hydrogen bonding interactions occurred between carbonyl groups of PHBV and hydroxyl groups in CNCs [8–11].

In previous work, the CNCs are prepared through sulfuric acid hydrolysis of cellulose raw materials in aqueous solution, and then freeze-dried. Generally, sulfate groups could be attached on the

surface of CNCs, which would induce a considerable decrease in degradation temperatures [12–14]. On the other hand, although small amounts of sulfate groups of CNC surfaces would cause electrostatic repulsion between CNCs, ensuring their excellent stability of the aqueous suspensions, it did not mean that they also exhibited good dispersion in organic solvent. Generally, it is very difficult to avoid the aggregation of the CNCs during nanocomposite preparation when the as-produced CNCs are directly dispersed into organic polymer solution again. As a result, no obvious enhancement on the thermal stability of the PHBV nanocomposites can be observed [9,10]. Recently, the efficient dispersion of CNCs in organic solution of PHBV can be achieved by a solvent exchange approach, as a result, simultaneous enhancement on the mechanical property and thermal stability of PHBV can be observed [8]. However, it should be pointed out that sulfated CNCs with low contents cannot improve the crystallization behavior and thermal stability of PHBV because such CNCs showed weak heterogeneous nucleation effect and would release sulfuric acid during thermal degradation process [8,13,14]. Most recently, an approach for fabricating thermally stable cellulose nanocrystals with high yield of 93% through hydrochloric acid hydrolysis under hydrothermal condition combined with ammonia neutralization treatment was presented by our group [12]. More interestingly, good stability of

\* Corresponding author. Tel.: +86 571 86843618; fax: +86 571 86843619.

E-mail address: [yaojm@zstu.edu.cn](mailto:yaojm@zstu.edu.cn) (J.-M. Yao).

aqueous CNC suspensions can be obtained due to the existence of ammonium groups, which can easily be totally removed by simple heat treatment. Therefore, no residual acid groups and ammonium groups were generated on the CNC surfaces, which might be beneficial to improve thermal property of the resulting nanocomposites. In this work, solvent exchange approach was employed to disperse CNCs obtained by sulfuric acid hydrolysis and hydrochloric acid hydrolysis under hydrothermal condition into the polymer matrix, and then the reinforcing effects for two kinds of CNCs on the mechanical and thermal properties of PHBV were compared.

## 2. Experimental section

### 2.1. Materials

PHBV ( $M_n = 5.90 \times 10^4$ ,  $M_w = 1.58 \times 10^5$ , and the molar ratio of HV is 2.57%) was obtained from Tiannan Biological Material Co., Ltd. (Ningbo, China) and purified by reprecipitation in methanol from chloroform solutions. Commercial microcrystalline cellulose (MCC, particle size: about 20  $\mu\text{m}$ ), sulfuric acid (98%), hydrochloric acid, ammonia, acetone, chloroform and  $\text{CaCl}_2$  were purchased from the Shanghai Guoyao Group Chemical Reagent Co., Ltd. (Shanghai, China). Chloroform was distilled over  $\text{CaCl}_2$  before using and other reagents were used as received without further purification.

### 2.2. Preparation of the CNC/PHBV nanocomposites

The details for preparing the CNC-S and CNC-S/PHBV nanocomposite films have been given in elsewhere [8]. Two kinds of CNCs were prepared by sulfuric acid hydrolysis and hydrochloric acid hydrolysis under hydrothermal condition, which were denoted as CNC-S and CNC-H, respectively. The CNC-S aqueous suspension was produced by sulfuric acid hydrolysis of the MCCs at 50 °C for 1 h under strongly mechanical stirring, following by water washing and centrifugation (12,000 rpm at 10 °C for 20 min) [8]. The CNC-H aqueous suspension was prepared by hydrochloric acid hydrolysis of the MCCs in the hydrothermal kettle at 110 °C for 3 h, following by ammonia neutralization, and then heated at 100 °C for 1 h to remove the residual ammonium groups [12].

All the as-prepared CNC suspensions were subsequently solvent-exchanged from water to acetone, then from acetone to chloroform by several successive centrifugation steps (12,000 rpm at 10 °C for 45 min), then CNC suspension in chloroform was stored at 4 °C before using. The CNC/PHBV nanocomposites (1–20 wt.% CNCs) were prepared by gradually adding the CNC suspensions into chloroform solution of PHBV. The CNC/PHBV nanocomposite films with the thickness of approximately 50  $\mu\text{m}$  were obtained on a glass slide through the solution casting technique. After being visibly dried, the films were further dried under vacuum at 40 °C until no obvious absorption of chloroform ( $754 \text{ cm}^{-1}$ ) appeared in the IR spectrum.

### 2.3. Characterization

The morphologies of CNC-S, CNC-H and the fractured morphologies of the nanocomposite films were observed on a field emission scanning electron microscopy (FE-SEM, HITACHI S-4800) at 5.0 kV. The films were frozen in liquid nitrogen and fractured.

The chemical structures were characterized on a Nicolet 8700 Fourier transform infrared spectrometer. Each spectrum was collected with 64 scans and  $2 \text{ cm}^{-1}$  resolution. The crystal structures were determined on a RIGAKU D/Max-2550 PC diffractometer with an area detector operating under  $\text{Cu K}\alpha$  ( $1.5418 \text{ \AA}$ ) radiation (40 kV, 40 mA). All the samples stood for 2 weeks at room temper-

ature to reach equilibrium crystallization before using. The degree of crystallinity was taken as the ratio of the sum of areas under the crystalline diffraction peaks to the total area under the curve between  $2\theta = 10^\circ$  and  $60^\circ$ . The crystallite sizes of 200 lattice planes were estimated by using the well-known Scherrer equation [11,15]:

$$D_{hkl} = \frac{0.9\lambda}{B_{hkl} \cos \theta} \quad (1)$$

where  $D_{hkl}$  is the crystallite size in the direction normal to the  $hkl$  family of lattice planes,  $\lambda$  is the radiation wavelength ( $1.54 \text{ \AA}$ ), and  $B_{hkl}$  is the full width at half-maximum in radians of the reflection of that family of lattice planes.

The non-isothermal crystallization and melting behavior were characterized on a differential scanning calorimetry (MDSC TA-2910). The sample was firstly heated from room temperature to 200 °C at a rate of 20 °C/min, and kept at 200 °C for 5 min to eliminate the previous heat history. Then the sample was cooled to 0 °C at a rate of 10 °C/min, and heated again to 200 °C at a rate of 10 °C/min. Main thermal parameters were obtained from DSC curves, such as non-isothermal crystallization temperature ( $T_c$ ), cold crystallization temperature ( $T_{cc}$ ), onset temperature of crystallization ( $T_{c(\text{onset})}$ ) and width at half-height of crystallization peak ( $\Delta W$ ).

Tensile properties of neat PHBV and the nanocomposite films were measured on a Kexin WDW3020 electronic universal testing machine. Tensile specimens with 10 mm in width, 50  $\mu\text{m}$  in thickness, and 50 mm in gauge length were loaded at a constant tensile rate of 1 mm/min, and ten replicates were tested for each sample.

The TGA was conducted on a NETZSCH TG 209 F1 thermogravimetric analyzer from 30 to 600 °C under a dynamic nitrogen atmosphere with the flow rate of 30 mL/min and the heating rates of 10 °C/min, respectively. Main thermal parameters were obtained from TGA curves, such as initial decomposition temperature ( $T_0$ ) and maximum decomposition temperature ( $T_{\text{max}}$ ).

## 3. Results and discussions

### 3.1. Fractured morphology

The dimension of the CNCs is relative to the preparation method, which will directly influence the reinforcing effect on the properties of polymers. As shown by the FE-SEM images in Fig. 1(a) and (d), the CNCs prepared through different routes exhibited similar rod-shaped morphology, but compared with that for CNC-S, the aspect ratio for CNC-H increased from 14.4 to 16.4 [12], which was also supported by the AFM observations in Fig. S1. The state of the dispersion of CNCs in the PHBV matrix can be estimated by observing the fractured morphologies of the PHBV/CNC nanocomposites. It has been demonstrated that the solvent-exchange approach can prevent the aggregation of the CNCs in polymeric matrix [8]. It is found that similar striated and smooth fractured surface can be observed for both the nanocomposites as the CNC contents increased to 10 wt.% as shown in Fig. 1(b) and (e), but the CNC-H can be well dispersed into PHBV matrix, even with larger adding contents of 12 wt.% in Fig. S2. Once the CNC with higher contents of 20 wt.% were added into polymeric matrix, the CNC-S can be in various levels of aggregation making them tens of nanometers wide or more as shown in Fig. 1(c), whereas the relatively slight aggregation of CNC-H was observed in Fig. 1(f). It implied that the well-dispersed CNC-H with larger contents could be added into PHBV matrix, and stronger hydrogen bonding interactions between two components might be formed in the nanocomposites.

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