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

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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 ($T_d$) 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 carboxyl 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...
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 µm), sulfuric acid (98%), hydrochloric acid, ammonia, acetone, chloroform and CaCl$_2$ were purchased from the Shanghai Guoyao Group Chemical Reagent Co., Ltd. (Shanghai, China). Chloroform was distilled over 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 µm 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 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 cm$^{-1}$ resolution. The crystal structures were determined on a RIGAKU D/Max-2550 PC diffractometer with an area detector operating under Cu K$_\alpha$ (1.5418 Å) radiation (40 kV, 40 mA). All the samples stood for 2 weeks at room temperature 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 2θ = 10° and 60°. The crystallite sizes of 200 lattice planes were estimated by using the well-known Scherrer equation [11,15]:

$$D_{hlk} = \frac{0.9\lambda}{B_{hlk}\cos \theta}$$

where $D_{hlk}$ is the crystallite size in the direction normal to the hkl family of lattice planes, $\lambda$ is the radiation wavelength (1.54 Å), and $B_{hlk}$ 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 ($T_{c(onset)}$), and width at half-height of crystallization peak (ΔW).

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 µm 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 ($T_d$) and maximum decomposition temperature ($T_{max}$).

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 as-prepared CNC-H can be well dispersed into PHBV matrix, even with larger contents of 12 wt.% in Fig. S2. Once the CNC with higher contents increases 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 contents of 12 wt.% in Fig. S2. Once the CNC with higher contents of 20 wt.% were added into polymetric 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.
3.2. Intermolecular hydrogen bonding interaction

Fig. 2(a) illustrates FT-IR spectra for two kinds of CNCs and the nanocomposites with various CNC contents. All the characteristic bands of PHBV and CNCs appeared in the FT-IR spectra of the nanocomposites. It is also worth noting that a new peak at 1205 cm\(^{-1}\) assigned to S=O stretching from sulfate groups appears in the CNC-S, which indicated that hydrolyzing cellulose with sulfuric acid involved esterification of the hydroxyl groups during acid hydrolysis [12,14]. On the contrast, no obvious band corresponding to acid groups or ammonium ions could be found for the CNC-H, which indicated the existing ammonium groups in the CNCs could easily be removed by simple heat treatment [12]. Moreover, two typical O-H stretching bands (3342 and 3436 cm\(^{-1}\)) from intra- and intermolecular hydrogen bonds appeared at two side of a broad band (3410 cm\(^{-1}\)) for CNCs, which can be ascribed to the stretching vibrations of the hydrogen bonded and free O-H groups, respectively [2,8,16–18]. With the increase of the CNC contents, the intensity for low-frequency band increased, whereas that for the high-frequency band slightly reduced (in Fig. S3(a) and (c)). It shows that no new chemical bonds appeared, but the strong hydrogen bonding interaction did occur in the nanocomposites.

As shown in Fig. S3(b) and (d), the band situated at around 1728 cm\(^{-1}\) could be assigned to the hydrogen bonded C=O groups, and 1746 cm\(^{-1}\) to free C=O groups [4,8,16,18,19]. The hydrogen bond fraction (\(F_{\text{H-A}}\)) can be determined by the curve-fitting of

![Fig. 1. FE-SEM images for (fractured) morphologies of the CNC-S (a), 10% CNC-S/PHBV (b), 20% CNC-S/PHBV (c), CNC-H (d), 10% CNC-H/PHBV (e) and 20% CNC-H/PHBV (f).](image)

![Fig. 2. FT-IR spectra (a) and the hydrogen bond fraction (\(F_{\text{H-CO}}\)) (b) for two kinds of CNCs and the nanocomposites with various CNC contents.](image)
the carbonyl band with Gauss/Lorentz spectral function. With the increase of the CNC contents, the band position for hydrogen-bonded component gradually shifted from 1723 cm\(^{-1}\) for neat PHBV to 1728 cm\(^{-1}\) for the nanocomposites with 20 wt.% CNC-S. But for CNC-H based nanocomposites, the hydrogen-bonded band of all the nanocomposites were located at 1728 cm\(^{-1}\), and the total area of the carbonyl bands becomes larger as the CNC contents increased, whereas that for free component was almost unchanged. These results hinted the formation of hydrogen bonding interaction for CNC-H based nanocomposites might be stronger than that of CNC-S based nanocomposites. Because no absorption band of the CNCs appeared in this region, any change here should be directly attributed to changes in the carbonyl group environments of PHBV, such as formation of hydrogen bonds. The \(F_{\text{H-CO}}\) values can be calculated to further estimate the amount of formed hydrogen bonding interaction in the nanocomposites, and determined by the following equation [7,8,17]:

\[
F_{\text{H-CO}} = \frac{A_H}{(r_{\text{H}/A_H} + A_A)} = \frac{A_H}{(A_H + r_{\text{H}/A_A})}
\]

where \(A_H\) and \(A_A\) are the peak areas of free and hydrogen bonded component, respectively, and \(r_{\text{H}/A_H}\) is the specific absorption ratio of the above two bands. Herein a minimal error would be obtained by using 1.32 of \(r_{\text{H}/A_H}\), as being close to 1.40 applied for PHBV/bisphenol A composites [8,16]. Fig. 2(b) gives the \(F_{\text{H-CO}}\) of the nanocomposites as a function of the CNC contents, and \(F_{\text{H-CO}}\) values listed in Table 1. It is observed that at the same CNC contents, the \(F_{\text{H-CO}}\) of CNC-H based nanocomposite was larger than that of CNC-S based nanocomposite. It indicates the formation of more intermolecular interaction occurred in the CNC-H based nanocomposites due to relatively good dispersion of CNC-H within nanocomposites (in Fig. 1). With the increase of the CNC contents, \(F_{\text{H-CO}}\) firstly increased from 0.25 for the nanocomposite with 1 wt.% CNC-H to a maximum value of 0.44 for 12 wt.%, and then slightly decreased to 0.42 for 20 wt.%. From above, it is clearly seen that among all the nanocomposites, the strongest intermolecular hydrogen bonding interaction appeared in the nanocomposite with 12 wt.% CNC-H.

### 3.3. Crystal structure and crystallinity

The physical properties of the nanocomposites depend not only on the strength of the intermolecular forces, but also the change in the crystallinity of PHBV. Therefore, the crystal structures of neat PHBV, CNC-S, CNC-H and the nanocomposites were studied. The WAXD patterns, crystallinities (\(X_c\)) and \(D_{200}\) of the samples are shown in Fig. 3. The CNC-S and CNC-H exhibited typical pattern of cellulose I diffractogram. With the addition of CNC-S, the additional PHBV diffraction peaks occurred, indicating that the CNC-S did not cause new crystalline symmetries of PHBV. With the increase of the CNC-S contents, the positions of the (021), (101) and (111) diffractions shifted to higher angles (Fig. S4(a)), which illustrated the structure change of PHBV crystalline occurred because of the formation of defective PHBV crystals in the presence of CNC-S. It has reported that the CNCs prepared by sulfuric acid hydrolysis would hinder chain diffusion and folding during PHBV spherulitic growth [8,11]. Surprisingly, a new diffraction peak at 33.2\(^o\) between the (004) diffractions of CNC-H and (002) diffractions of PHBV appeared in the CNC-H based nanocomposites when the CNC-H contents was more than 5 wt.%. Moreover, the width at half-height of (110), (021), (101) and (111) diffractions were larger than those of CNC-S based nanocomposites (Fig. S4(b)).

This can be ascribed to the preferential growth of PHBV crystals along the direction of the longitudinal direction of cellulose axis, but restrictions in its vertical direction due to the existence of CNC-H.

Fig. 3(b) shows the crystallinities (\(X_c\)) and \(D_{200}\) for neat PHBV, CNC-S, CNC-H and the nanocomposites with various CNC contents, and corresponding data are summarized in Table 1. It is found that the \(X_c\) of the CNC-H was higher than that of CNC-S. Compared to neat PHBV, the \(X_c\) of the CNC-S based nanocomposites increased a maximum value of 64.1% for 1 wt.% CNC-S, and decreased gradually to 52.7% for 20 wt.% CNC-S. On the contrary, the \(X_c\) reduced to 51.9% for 12 wt.% CNC-H, and then increased to 54.8% for 20 wt.% CNC-H. It is well known that CNCs are the most efficient nucleation agent to promote the crystallization rate, but not the crystallinity, and the CNCs can influence the crystallization of PHBV in two opposite ways [8,10]. On one hand, the CNCs can act as a nucleating agent to increase the nucleation and overall crystallization rate, leading to more perfect PHBV crystals. On the other hand, owing to the strong interactions between the CNCs and PHBV, the motion of the PHBV chains is restricted and subsequently the crystallinity decreases. From above, the intermolecular interaction in the CNC-H based nanocomposites was stronger than that of the CNC-S based nanocomposites (in Fig. 2(b)). Therefore, the crystallinity of the CNC-H based nanocomposites decreased greatly with the increase of CNC contents (below 12 wt.%). The slightly increase in the crystallinity of the nanocomposites with high CNC contents was due to the agglomeration of CNC-H with the higher crystallinity (in Table 1), which was consistent with FE-SEM results in Fig. 1. In addition, the \(D_{200}\) of both kinds of nanocomposite were smaller than that of neat PHBV, and decreased dramatically with the increase of CNC contents, indicating that two kinds of CNCs hindered the diffusion and folding of PHBV chains due to the confinement effects of the CNCs. Furthermore, at the same CNC contents, compared to the CNC-S based nanocomposites, the CNC-H based nanocomposite showed the smaller \(D_{200}\) implying that stronger confinement effects in this kind of nanocomposites. Especially, the nanocomposites with 12 wt.% CNC-H exhibited the smallest \(D_{200}\) among all the nanocomposites, hinting that the strongest confinement effects occurred in the nanocomposites due to homogeneous dispersion of CNC-H within PHBV (the formation of more hydrogen bonding interactions) as revealed by FE-SEM observations (Fig. 1 and Fig. S2) and mechanical property assessments.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>(F_{\text{H-CO}})</th>
<th>(X_c) (%)</th>
<th>(D_{200}) (nm)</th>
<th>(T_c) (°C)</th>
<th>(\Delta T) (°C)</th>
<th>(\Delta T_m) (°C)</th>
<th>(D_{200}) (°C)</th>
<th>(T_m) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHBV</td>
<td>0.25</td>
<td>58.1</td>
<td>30.9</td>
<td>24.3</td>
<td>16.4</td>
<td>229.4</td>
<td>245.8</td>
<td></td>
</tr>
<tr>
<td>CNC-S</td>
<td>0.39</td>
<td>84.3</td>
<td>5.9</td>
<td>22.8</td>
<td>228.2</td>
<td>322.5</td>
<td>363.9</td>
<td></td>
</tr>
<tr>
<td>CNC-H</td>
<td>0.30</td>
<td>86.6</td>
<td>6.0</td>
<td>23.1</td>
<td>228.2</td>
<td>322.5</td>
<td>363.9</td>
<td></td>
</tr>
<tr>
<td>10% CNC-S /PHBV</td>
<td>0.37</td>
<td>53.9</td>
<td>12.1</td>
<td>92.3</td>
<td>6.9</td>
<td>280.8</td>
<td>292.9</td>
<td></td>
</tr>
<tr>
<td>10% CNC-H /PHBV</td>
<td>0.41</td>
<td>52.5</td>
<td>10.8</td>
<td>100.4</td>
<td>6.8</td>
<td>284.6</td>
<td>293.3</td>
<td></td>
</tr>
<tr>
<td>12% CNC-H /PHBV</td>
<td>0.44</td>
<td>51.9</td>
<td>10.1</td>
<td>109.6</td>
<td>6.5</td>
<td>287.5</td>
<td>297.9</td>
<td></td>
</tr>
</tbody>
</table>

\(F_{\text{H-CO}}\) was obtained from the results of deconvoluted FT-IR spectra.

\(X_c\) was calculated from the WAXD patterns, \(D_{200}\) was calculated by using the well-known Scherrer equation.

\(\Delta T\) and \(\Delta T_m\) were obtained from the TGA curves at the heating rate of 10 °C/min.
and decreased gradually when the CNC contents increased to 12 wt.%. The crystallization temperature of the CNC-H based nanocomposites was higher than that for the neat PHBV and the CNC-S based nanocomposites, whereas the cold crystallization peak at 41.2 °C can be observed in the second heating scans. By introducing two kinds of CNCs, no cold crystallization peak appeared in both the nanocomposites, and the Tc increased gradually to 92.3 °C for 10 wt.% CNC-S, 100.4 °C for 10 wt.% CNC-H. With the increase of CNC-H contents, the Tc increased to 109.6 °C for 12 wt.% CNC-H (in Table 1). These results implied the easier crystallization of the PHBV occurred in the presence of the CNC-H due to the lower activation energy barrier in the high-temperature region [20], and its heterogeneous nucleation effect was stronger than CNC-S. In addition, as shown in Fig. 4(a), a double melting peak appeared during melting-recrystallization-melting process became stronger for both kinds of nanocomposite compared to neat PHBV. With the increase of the CNC contents, the melting temperature shifted to higher temperature (in Fig. S5(b) and (d)), indicating that the PHBV crystals with the higher perfection and thicker lamellar layers can be achieved by homogeneous incorporation of CNCs in polymeric matrix [8–10].

Fig. 4(b) presents the Tc and Tc(onset) − Tc for neat PHBV and the nanocomposites with various CNC contents. It can be seen that the Tc of the nanocomposites continuously increased as the CNC contents increased to 10 wt.% for CNC-S, 12 wt.% for CNC-H. Then the Tc decreased gradually when the CNC contents increased to 20 wt.% (in Fig. S5(a) and (c)). It should be noted that with addition of 1 wt.% CNC-S, a weak cold crystallization peak at 38.8 °C appeared in the nanocomposites, which was denoted by the black arrow in Fig. 4(b). However, no cold crystallization peak was observed in the CNC-H based nanocomposites even with 1 wt.% CNC-H (as shown in Fig. S5). For example, with addition of 1 wt.% CNC-H, Tc was about 62.6 °C. When the CNC content was around 12 wt.%, the highest Tc of 109.6 °C can be obtained. In the previous reports, the cold crystallization peak can be still observed for the nanocomposite with 5 wt.% CNCs prepared by sulfuric acid hydrolysis, and the Tc decreased by about 10 °C as compared to PHBV (51.2 °C) [8–10]. It is well known that the cold crystallization can be remarkably suppressed in the second heating scan once the nanocomposites did undergo enough crystallization in the first cooling process. This result implied that the crystallization of PHBV became easier in our system. Moreover, at the same CNC contents, the Tc of the CNC-H based nanocomposites was higher than that for the CNC-S based nanocomposites, but its Tc(onset) − Tc value was lower compared to neat PHBV and the CNC-S based nanocomposites. The parameter Tc(onset) − Tc is generally used herein to be a measure of the overall rate of crystallization, and the smaller the Tc(onset) − Tc is, the greater the rate of crystallization is [8,19,21].

Moreover, the ΔW of the CNC-H based nanocomposites was smaller than that of the CNC-S based nanocomposites. This is because the stronger confinement on the growth of PHBV crystals were induced by CNC-H (in Fig. 3(b)), resulting in the smaller crystals with narrow size distribution. From above, these results revealed that the incorporation of CNCs could increase not only the nucleation rate of the nanocomposites, but also the crystallization rate, leading to a narrow distribution in the PHBV crystallite size. Owing to the better dispersion of CNC-H within the PHBV matrix, the nucleation effect of CNC-H was stronger than CNC-S, and thus the higher Tc and the smaller Tc(onset) − Tc can be achieved in the CNC-H/PHBV nanocomposites.
3.5. Mechanical properties

It is well known that good dispersion of the CNCs in the polymer matrix was beneficial to form more hydrogen bonding interactions between them, which is a prerequisite for achieving an excellent mechanical properties of the CNC/polymer nanocomposites [2,6,8]. Fig. 5 gives the tensile strength, Young's modulus and elongation to break as a function of the CNC contents for neat PHBV and the nanocomposites with CNC-S and CNC-H. It is clear that two kinds of CNCs incorporated into the PHBV matrix can induce an enhancement in the mechanical properties of both the nanocomposites. It is found that compared to neat PHBV, by loading 10 wt.% CNC-S, the maximum tensile strength and Young's modulus were improved by 149% and 250%, respectively. With addition of 10 wt.% CNC-H, the tensile strength and Young's modulus increased greatly by 166% and 282%, respectively. These improvements could be attributed to the restrained chain movement during the deformation, and the refined crystalline structure of the PHBV after the addition of CNCS [8–10]. The greater enhancements in the mechanical properties of the CNC-H based nanocomposites can be ascribed to two aspects: on one hand, compared to the CNC-S, CNC-H shows the larger aspect ratio, higher degree of crystallinity and stronger nucleation effect on the PHBV crystallization under relatively good dispersion of CNC-H in the PHBV matrix. On the other hand, instead of some sulfate groups in CNC-S surfaces, only larger amount of hydroxyl groups in CNC-H surfaces, which were beneficial to form more hydrogen bonding interactions in the nanocomposites. Moreover, once the CNC content exceeds 10 wt.% CNC-S or 12 wt.% CNC-H, slight decreases in the tensile strength, Young's modulus and the elongation to break occurred. More importantly, when the CNC-H contents increased to 12 wt.%, the maximum tensile strength and Young's modulus can be increased remarkably by 175% and 300%, while the elongation to break reduced to 6.8%. On the contrary, by introducing 5 wt.% freeze-dried CNCs prepared by sulfuric acid hydrolysis, the film showed 77% improvement in Young’s modulus, and 35.5% increase in tensile strength [10]. Because the CNCs applied in these works were similar in size, it is believed that the aggregation of the CNC-S and CNC-H was efficiently reduced in the nanocomposite preparation via the solvent-exchange approach. Especially, hydrochloric acid hydrolysis under hydrothermal condition can avoid the generation of acid groups in the CNC-H surfaces.

3.6. Thermal stability

Fig. 6 shows TGA, initial decomposition temperature ($T_d$) and maximum decomposition temperature ($T_{max}$) as a function of the CNC contents for neat PHBV and the nanocomposites with CNC-S and CNC-H at the heating rate of 10 °C/min, and main thermal parameters are summarized in Table 1. It is found that the $T_d$ and $T_{max}$ of the CNC-H were about 322.5 and 363.9 °C, respectively, which were higher than 228.2 and 245.4 °C for CNC-S due to its surface sulfated groups that would significantly lower the degradation temperature [12,22,23]. As shown in Fig. 6(a) and Table 1, compared to neat PHBV, a great increase in the $T_d$ and $T_{max}$ of both the nanocomposites occurred, indicating the thermal stability of the nanocomposites was higher than neat PHBV. In Fig. 6(b), it can be seen that with the increase of the CNC contents, the $T_d$ and $T_{max}$ were substantially increased for 10 wt.% CNC-S, and then decreased slightly for 20 wt.% CNC-S (as shown in Fig. S6(a)). Besides, it is worth noting that the $T_d$ and $T_{max}$ of the nanocomposites with 1 wt.% CNC-S decreased by 3.9 and 1.5 °C compared with those of neat PHBV. This can be explained that the elimination of sulfuric acid in residual sulfated anhydroglucose units in CNC-S required less energy, and thus they could be released at much lower temperatures during the thermal degradation process [12]. Finally, the released sulfuric acid would further accelerate the decomposition of PHBV, as a result, poor thermal stability of the nanocomposites occurred. Reversely, at the same CNC contents, the $T_d$ and $T_{max}$ for the CNC-H based nanocomposites was higher than those of...
CNC-S based nanocomposites, illustrating the higher thermal stability of CNC-H based nanocomposites can be achieved. For example, with addition of 1 wt.% CNC-H, the $T_0$ and $T_{\text{max}}$ increased by 21.4 and 17.6°C compared to neat PHBV. As the CNC contents increased, $T_{\text{max}}$ gradually increased to the maximum of 297.9°C for the nanocomposite with 12 wt.% CNC-H, and then reduced slightly to 294.3°C for 20 wt.% CNC-H (as shown in Fig. S6(b)). Compared with those for neat PHBV, the $T_0$ and $T_{\text{max}}$ of the nanocomposites with the best thermal stability were increase by about 58.1 and 52.1°C, respectively. On the contrary, a slight increase or even decrease in the thermal stability has been reported in previous works [3,6,9,10,24–29]. For example, a decrease from 295°C for neat PHBV to 290°C for the nanocomposite with 5 wt.% CNCs occurred although the dispersion of CNCs in PHBV matrix could be improved by using PEG as a compatibilizer [10]. These results indicated the reinforcing effect depended on not only the CNCs reinforcement in the polymeric matrix, but also the number of formed intermolecular hydrogen bonding interactions between CNCs and PHBV. The higher thermal stability of the nanocomposites can be achieved by introducing CNC-H, which was attributed to the formation of much more intermolecular hydrogen bonding interactions, and no residual acid groups on CNC-H surfaces and its good dispersion within polymer matrix that would restrict the formation of six-membered ring ester during the degradation process of PHBV [8].

4. Conclusions

The green nanocomposites were successfully prepared by homogeneously incorporating two kinds of CNCs (CNC-S and CNC-H) with various contents into PHBV matrix. Simultaneous enhancements on the mechanical property and thermal stability of the nanocomposites were achieved by introducing both CNCs, although the reinforcing effect of CNC-H with the same contents was stronger than CNC-S. This can be attributed to higher stress endurance of CNC-H with larger aspect ratio and higher crystallinity, no residual acid groups, and stronger heterogeneous nucleation effect and the formation of more intermolecular hydrogen bonding interactions through achieving the uniform dispersion of CNC-H within PHBV matrix. As a result, when 12 wt.% CNC-H was introduced, compared to the neat PHBV, the tensile strength and Young’s modulus of the nanocomposite were enhanced by 175% and 300%, respectively, meanwhile the $T_0$ and $T_{\text{max}}$ increased by 58.1 and 52.1°C, respectively. The result of this study will have an important impact on broadening the practical use of such nanocomposites to optimize the processing conditions and their final properties.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.compscitech.2013.07.024.

References