Focus on Gradientwise Control of the Surface Acetylation of Cellulose Nanocrystals to Optimize Mechanical Reinforcement for Hydrophobic Polyester-Based Nanocomposites

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ABSTRACT: Surface acetylation of cellulose nanocrystals (CNCs) imposes an important effect on CNC-related mechanical enhancement of hydrophobic polyester-based composites, of which interfacial properties still need optimization. In the present work, the surface acetylation of CNCs was adjusted as a gradient of above ca. 10%. Then, we found that the surface energy of acetylated CNCs (ACNs) decreased and thus their hydrophobicity increased as the surface acetylation degree increased. Hence, the ACNs with varied degrees of acetyl substitution (DSsurface) values were attempted to reinforce a kind of hydrophobic polyester, poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (PHB). The results indicated that a smaller discrepancy in the surface energy between the CNC surface and the PHB matrix was obtained, as the surface acetylation degree increased, and then, the affinity and interaction between the two components increased, which improved the homogeneous distribution of ACNs in the PHB matrix. Besides, in comparison to the nanocomposites filled with 15 wt % unmodified CNCs, the tensile strength of those with ACNs of 62.9% DSsurface was 43.3% higher. This study was the first attempt to adjust the surface substitution degrees with a gradient profile for the surface modification of CNCs and prove that acetylation gradient control is an effective and facile strategy to optimize the mechanical properties.

INTRODUCTION

Bio-based materials and innovative process technologies that could reduce the dependence on fossil fuel and enable development on a sustainable material basis have aroused growing interest. Among biologically inspired nanocomposites, cellulose is probably among the most promising sources for producing nanoparticles. Particularly, because of the rodlike morphology and impressive mechanical properties, such as high specific modulus, low density, nontoxicity, biocompatibility, liquid crystalline order, and high surface area-to-volume ratio, cellulose nanocrystals (CNCs) have obtained much attention in many applications, especially as a novel kind of renewable nanoreinforcer in nanocomposites. Their mechanical properties could be significantly enhanced by introducing a relatively low loading level of CNCs. Furthermore, the active hydroxyl groups on the surface of CNCs could contribute as sites forming interactions with the polymer matrix, like the hydrogen bond between hydroxyl groups of poly(ethylene glycol) and CNCs. Besides, it has been reported that the tensile strength and modulus of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) increased by 35.5 and 77%, respectively, with 5 wt % CNCs due to the strong interfacial bonding between the nanoparticles and the polymer. It has also been reported that due to the increase in crystallinity of the matrix and the strong filler–filler interactions via hydrogen bonding, the tensile strength of polyhydroxybutyrate valerate nanocomposites increased from 12.7 to 17.1 MPa by loading 10 wt % CNCs. However, the abundant hydroxyl groups (−OH) on the CNC surface and their high hydrophilic property resulted in poor interfacial compatibility and weak interaction between the CNCs and the hydrophobic polymer matrix, leading to a significant deterioration in the mechanical properties of nanocomposites, which greatly restricted the use of CNCs.
Thus, physical and chemical modifications were considered as ideal approaches for controlling the surface chemical structure and hydrophilic/hydrophobic properties of CNCs by adjusting the parameters of functional groups, such as their category and mass percentage. Moreover, the introduced groups may exhibit similar hydrophobicity with the polymer matrix and even provide sites to interact with the polymer matrix. As a result, considerable improvement in miscibility between the functionalized CNCs and the polymer matrix together with a better dispersability of nanofilms could be obtained and thus improved the load transfer at the filler/matrix interface and stress equilibrium in the whole nanocomposite system, which eventually led to achieving high mechanical performances.

Thus, over the last decade, many researchers have been focusing on improving the interfacial compatibility or interaction between the CNCs and the polymer matrix and achieving the homogeneous dispersion of CNCs in the hydrophobic polymer matrix through chemical functionalization, and it has been reported that the tensile strength, Young’s modulus, and elongation at break of the poly(3-hydroxybutyrate-co-3-hydroxyvalerate)-based nanocomposites with 20 wt % poly(3-hydroxybutyrate-co-3-hydroxyvalerate)-modified CNCs were 113, 95, and 17% higher than those of the neat one, respectively. In those studies, the improvements were mainly ascribed to the better dispersion of fillers and strong interfacial adhesion between the fillers and the matrix due to the chain entanglement.

Although it has been confirmed that the surface functionalization of CNCs enabled to enhance mechanical properties, further optimization of mechanical properties by adjusting the surface functionalization degree of CNCs was seldom explored due to the challenge on controlling the degree of substitution or grafting of the micromolecules, which limited further studies on the effect of CNC surface modification on the relationship between the structure and properties of composites together with the interface interaction between the CNCs and the polymer matrix. In this work, to control the surface substitution of CNCs, we optimized the modifying method of CNCs and investigated the effect of preparing parameters on the surface acetylation degree of CNCs. Besides, the effect of CNC surface functionalization on mechanical reinforcement was investigated by using poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (PHB), a typical hydrophobic polymer, as the matrix. First, the gradient degrees of CNC surface acetylation were measured by adjusting the molar ratio of –OH on the CNC surface and acetic anhydride (AA) through the esterification reaction between –OH and AA. Then, the dependence of mechanical properties of nanocomposites upon the surface acetylation gradient of CNCs was discussed by studying the interfacial compatibility of nanocomposites upon the surface acetylation gradient of CNCs using the baseline constructed by extrapolating two lines toward the CNC surface could be controlled by adjusting the paired reactive groups might become a facile approach to control the surface acetylation degree of CNCs and the limit of efficient regulation was 40:1 of AA versus OH$_{\text{CNC-surface}}$ in moles.

Because the FTIR results showed that the acetylation of AA toward the CNC surface could be controlled by adjusting the molar ratio of the paired reactive groups, the accurate values of surface acetyl substitution might be further confirmed by tests of element analysis. On the basis of the change in weight fraction of the C element by the acetylation for CNCs, the degree of acetyl substitution on the ACN surface (DS$_{\text{surface-acetyl}}$) was calculated by eq 1. Table 1 summarizes the weight fractions of C, H, and S (obtained from the acid hydrolysis with sulfuric acid) elements in the ACNs as well as the calculated DS$_{\text{surface-acetyl}}$ values of the ACNs. With an increase from 5:1 to 40:1 in the molar ratios of AA versus OH$_{\text{CNC-surface}}$, the DS$_{\text{surface-acetyl}}$ values increased from 11.1 to 62.9%. Especially, for the as-prepared ACNs in this work, the DS$_{\text{surface-acetyl}}$ values showed a discrepancy of at least ca. 10%. In addition, when the molar ratios of AA versus OH$_{\text{CNC-surface}}$ increased from 40:1 to 80:1, the DS$_{\text{surface-acetyl}}$ Value varied a little. It was well consistent

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**RESULTS AND DISCUSSION**

**Surface Acetylation Control of CNCs.** First, the introduction of the acetyl group to CNCs was identified by the Fourier transform infrared (FTIR) spectra of unmodified and ACNs in Figure 1. We found that after reaction with AA, the peaks located at 1745 and 1242 cm$^{-1}$ (the stretching vibrations of $-\text{C}=$O stretching and $-\text{C}–\text{O}–\text{C}$ in the acetyl groups introduced on the CNC surface) of CNCs emerged. Moreover, the C–O stretching vibration located at ca. 1060 cm$^{-1}$, which was assigned to the glucopyranose ring of cellulose, was selected as a comparison for normalizing the variation of the intensity of the peak located at 1745 cm$^{-1}$. In this case, the peak heights located at 1745 and 1060 cm$^{-1}$, that is, $I_{1745}$ and $I_{1060}$ were determined from the spectra of all ACNs using the baseline constructed by extrapolating two lines between the valleys at 1790 and 1700 cm$^{-1}$ and between the valleys at 1500 and 860 cm$^{-1}$, and hence were used to calculate the $I_{1745}/I_{1060}$ values as the normalized peak intensity of $-\text{C}=$O stretching vibration. As depicted in Table 1, it was worthy to note that the variation of the $I_{1745}/I_{1060}$ values was positive to the increase in the feeding molar ratios of AA versus hydroxyl groups on the CNC surface (OH$_{\text{CNC-surface}}$) and reached a constant plateau that changing the feeding molar ratio of AA versus OH$_{\text{CNC-surface}}$ was higher than 40:1. These results indicated that changing the feeding molar ratio between the paired reactive groups might become a facile approach to control the surface acetylation degree of CNCs and the limit of efficient regulation was 40:1 of AA versus OH$_{\text{CNC-surface}}$ in moles.

Because the FTIR results showed that the acetylation of AA toward the CNC surface could be controlled by adjusting the molar ratio of the paired reactive groups, the accurate values of surface acetyl substitution might be further confirmed by tests of element analysis. On the basis of the change in weight fraction of the C element by the acetylation for CNCs, the degree of acetyl substitution on the ACN surface (DS$_{\text{surface-acetyl}}$) was calculated by eq 1. Table 1 summarizes the weight fractions of C, H, and S (obtained from the acid hydrolysis with sulfuric acid) elements in the ACNs as well as the calculated DS$_{\text{surface-acetyl}}$ values of the ACNs. With an increase from 5:1 to 40:1 in the molar ratios of AA versus OH$_{\text{CNC-surface}}$, the DS$_{\text{surface-acetyl}}$ values increased from 11.1 to 62.9%. Especially, for the as-prepared ACNs in this work, the DS$_{\text{surface-acetyl}}$ values showed a discrepancy of at least ca. 10%. In addition, when the molar ratios of AA versus OH$_{\text{CNC-surface}}$ increased from 40:1 to 80:1, the DS$_{\text{surface-acetyl}}$ Value varied a little. It was well consistent...
with the dependence of the $I_{1745}/I_{1060}$ values upon the molar ratios of AA versus OH$_{\text{CNC-surface}}$ from the FTIR test and suggested that the highest critical point of the molar ratio of AA versus OH$_{\text{CNC-surface}}$ for adjusting the surface acetylation of AA toward CNCs should be 40:1.

Morphological and Crystalline Characters of ACNs. As well known, the high aspect ratio and crystalline rigidity of CNCs contribute to a percolation approach and high stress endurance, respectively, and thus are essential to mechanical reinforcement for polymeric materials.11 As a result, surface chemical modification needs to maintain the rodlike morphology and crystalline structure of CNCs as far as possible. Fortunately, as shown in the transmission electron microscopy (TEM) images of Figure 2, all ACNs inherited the rodlike morphology of the pristine CNCs. Meanwhile, Table 2 also depicts that the statistics such as mean length and diameter almost remained unchanged with a slight decrease (AA initiated a slight acid hydrolysis of CNCs) after surface acetylation and gave the aspect ratios of ACNs equivalent to that of pristine CNCs. It demonstrated that the surface acetylation of AA toward CNCs was moderate enough to avoid obviously dismantling the original morphologic structure of CNCs.

Moreover, the preservation of a rigid crystalline structure in ACNs after surface acetylation was expected and the XRD patterns of both ACNs and CNCs are shown in Figure 3. The predominant diffraction peaks at 2$\theta$ values of 14.7, 16.4, 22.7, and 34.5° were attributed to the diffraction planes 101, 101, 002, and 040 in the crystal type of cellulose I, respectively.24 In comparison with pristine CNCs, all of the crystalline characteristic peaks were clearly presented in the ACN samples. It suggested that the ACNs preserved the initial crystal form of cellulose in CNCs (although the crystalline index decreased slightly due to the low crystallinity of acetylated celluloses, whose repeating units in polymer chains and thus lattice

| sample no. | dimensions (nm) | L/D | $\nu_{\text{Rc}}$ (wt. %) | crystalline dimensions (nm) | $I_c$ (%) |
|------------|----------------|-----|--------------------------|-----------------------------|----------|
| CNC        | 163 ± 55       | 18 ± 5 | 9.06                     | 8.2                         | 85.4     |
| ACN(I)     | 163 ± 34       | 17 ± 5 | 9.59                     | 8.3                         | 82.1     |
| ACN(II)    | 159 ± 37       | 16 ± 4 | 9.93                     | 8.2                         | 81.6     |
| ACN(III)   | 151 ± 37       | 15 ± 4 | 10.1                     | 8.1                         | 80.2     |
| ACN(IV)    | 147 ± 35       | 16 ± 3 | 9.19                     | 8.2                         | 80.8     |
| ACN(V)     | 145 ± 36       | 15 ± 3 | 9.67                     | 8.1                         | 77.7     |

$\nu_{\text{Rc}} = 0.7/(L/D)$.  

Table 1. Contents of C, H, and S Elements and the Calculated Surface Hydroxyl Groups Content ($n_{\text{surface-OH}}$) and Degree of Acetyl Substitution ($\text{DS}_{\text{surface-acetyl}}$) as Well as the Normalized Peak Intensities of $-\text{C}=\text{O}$ Stretching Vibration ($I_{1745}/I_{1060}$) for the CNCs and ACNs Prepared from the Varied Feeding Ratios of AA vs OH$_{\text{CNC-surface}}$

| samples | C (%) | H (%) | S (%) | $n_{\text{surface-OH}}$ (mmol/g) | DS$_{\text{surface-acetyl}}$ (%) | $I_{1745}/I_{1060}$ |
|---------|-------|-------|-------|---------------------------------|---------------------------------|---------------------|
| CNC     | 42.55 | 6.52  | 0.27  | 1.20                            | 11.1                            | 0.25 |
| ACN(I)  | 42.87 | 6.45  | 0.14  | 27.4                            | 37.2                            | 0.66 |
| ACN(II) | 43.34 | 6.32  | 0.00  | 37.4                            | 62.9                            | 0.78 |
| ACN(III)| 43.62 | 6.26  | 0.01  | 37.4                            | 63.2                            | 0.77 |
| ACN(IV) | 44.36 | 6.33  | 0.08  | 62.9                            | 63.2                            | 0.77 |
| ACN(V)  | 44.37 | 6.29  | 0.00  | 62.9                            | 63.2                            | 0.77 |

Figure 2. TEM images of the pristine CNCs and the ACNs derived from the feeding molar ratio of AA vs OH$_{\text{CNC-surface}}$.
parameters in crystals are different from those of CNCs). Subsequently, a profound research on the changes of the crystalline extent and crystal dimensions was carried out. Table 2 summarizes the values of the crystallinity index \( I_c \) calculated by eq 2 as well as the dimensions of crystal planes \( (B_{002}, B_{101}, \text{and } B_{110}) \) calculated by eq 3. Obviously, the well-consistent crystalline dimensions of CNCs and ACNs further strongly supported the fact that no transformation of the crystal structure of cellulose occurred in the process of surface acetylation. At the same time, the crystalline index only showed a slight decrease, suggesting that moderate surface acetylation of AA retained the initial crystallinity of CNCs to the maximum extent.

**Effects of Surface Acetylation Degree on the Hydrophobicity of CNCs.** Because the surface acetylation could increase the hydrophobicity of CNCs, the equilibrium contact angles of CNCs, ACNs, and hydrophobic PHB toward water and ethylene glycol as well as the corresponding \( \gamma_s^+, \gamma_s^p, \text{and } \gamma_s^d \) values were measured (as shown in Table 3). The result showed that the increase of the acetylation degree exercised a positive influence on hydrophobicity and resulted in a gradual approach to the equilibrium contact angle and surface energy (including \( \gamma_s^+, \gamma_s^p, \text{and } \gamma_s^d \)) values of neat PHB. Such exciting results indicated that higher DSSurface-acetyl of ACNs might exhibit stronger compatibilization with PHB in the subsequent preparation for nanocomposites. Especially, when the feeding molar ratio of AA versus OH\(_{\text{CNC-surface}}\) was higher than 40:1, the \( \gamma_s^+, \gamma_s^p, \text{and } \gamma_s^d \) values of ACNs tended to be at a constant level of 18.8, 23.9, and 42.7 mJ/m\(^2\), respectively, which were very close to those of PHB at 15.6 (\( \gamma_s^+ \)), 21.1 (\( \gamma_s^p \)), and 36.7 (\( \gamma_s^d \)) mJ/m\(^2\).

**Effects of Surface Acetylation of Cellulose Nanoparticles on Disperity with the PHB matrix.** In view of the fact that the increase of DSSurface-acetyl resulted in the approach of surface energy to the PHB matrix for the ACNs, the enhanced miscibility between the ACN surface and the PHB matrix was expected and could be confirmed if the dispersity of ACNs increased in the PHB-based nanocomposite films. Thus, Raman mapping spectra of the cellulose component in PHB were used to characterize the distribution of unmodified and ACNs in the PHB matrix. As shown in Figure 4, the black portions were assigned to cellulose component-dominant regions from CNCs or ACNs, whereas the red portions represented the PHB-dominant regions. Meanwhile, the other visible colors, such as yellow, green, and blue, might represent the regions of the mixtures, which consisted of varied compositions of the cellulose component versus PHB. When the loading level of CNCs or ACNs was 6 wt %, the morphologies of nanocomposites in Figure 4A, D, G depicts the fact that the black isolated “islands” of cellulose component-dominant regions dispersed into the red continuous “ocean” of the PHB-dominant matrix. Obviously, in comparison to the unmodified CNC-filled nanocomposites in Figure 4A, the ACN-filled nanocomposites in Figure 4D, G shows smaller size of black cellulose component-dominant regions, suggesting that the surface acetylation improved the uniformity of distribution for CNCs in the PHB matrix. With an increase in the loading level of CNCs from 6 to 30 wt %, Figure 4B, C depicts that the black CNC-dominant region gradually expanded as a relatively isolated broad phase, whereas the whole nanocomposite system showed a heterogeneous morphology on the scale of the laser sampling volume. Correspondingly, the size of the ACN-dominant region almost did not increase with an increase in the loading level of ACNs, which was replaced with more mixed regions marked by yellow, green, and blue colors. These results indicated that the surface acetylation toward CNCs improved the interpenetrability between ACNs and PHB and hence gave a relatively homogenous morphology for the ACN-filled nanocomposites, as shown in Figure 4E, F, H, I. On the other hand, the increase in the DSSurface-acetyl of ACNs also facilitated the uniformity in compositions of nanocomposites. Especially, as shown in Figure 4E, H for the ACN-filled nanocomposites containing a moderate loading level of 15 wt %, the distribution of ACNs first displayed as a small island similar to the morphologies of nanocomposites with low CNC and ACN loading level and then presented an increasing homogeneity, with a continuous increase in the DSSurface-acetyl of ACN. The analogous effect of ACN DSSurface-acetyl on the dispersity of fillers in the matrix could be observed in Figure 4F, I, when the nanocomposites contained 30 wt % of ACNs. However, the excess loading level inhibited the uniformity of the nanocomposite morphologies. These results demonstrated that the interfacial miscibility between ACN and PHB significantly increased as the DSSurface-acetyl increased and the compatibility between ACN and PHB could be improved via surface acetylation. As a result, the maximum tensile strength should be obtained in a higher CNC loading level when the

![Figure 3. XRD patterns of pristine CNCs and ACNs derived from the feeding molar ratio of AA vs OH\(_{\text{CNC-surface}}\).](image)

Table 3. Contact Angle (\( \theta \)) Values toward Water and Ethylene Glycol as Well as Nonpolar Component (\( \gamma_s^+ \)), Polar Component (\( \gamma_s^p \)), and Total (\( \gamma_s \)) Surface Energy Values for the Unmodified CNCs and ACNs Prepared from the Feeding Molar Ratio of AA vs OH\(_{\text{CNC-surface}}\)

| samples | contact angle, \( \theta \) (deg) | water | ethylene glycol | \( \gamma_s^+ \) (mJ/m\(^2\)) | \( \gamma_s^p \) (mJ/m\(^2\)) | \( \gamma_s \) (mJ/m\(^2\)) |
|---------|--------------------------------|-------|----------------|----------------------------|----------------|----------------|
| CNC     | 29.6                           | 18.1  | 4.3            | 66.7                      | 71.0            |
| ACN(I)  | 36.5                           | 21.3  | 6.1            | 57.3                      | 63.4            |
| ACN(II) | 45.8                           | 25.2  | 10.0           | 43.4                      | 53.4            |
| ACN(III)| 51.9                           | 26.5  | 14.2           | 33.4                      | 47.6            |
| ACN(IV) | 58.9                           | 30.4  | 18.8           | 23.9                      | 42.7            |
| ACN(V)  | 59.2                           | 31.2  | 18.6           | 23.9                      | 42.5            |
| PHB     | 65.9                           | 43.9  | 15.6           | 21.1                      | 36.7            |
Effects of Surface Acetylation Degree of the CNC on the Fracture Morphologies of PHB-Based Nanocomposites. As depicted in the laser micro-Raman mapping images of the nanocomposites filled with CNCs and ACNs, adjusting the loading level and DS_{surface-acetyl} of nano-fillers in the matrix resulted in phase transformation of the CNC/PHB composites. Thus, to further study the phase interfaces between CNCs and PHB, scanning electron microscopy (SEM) was employed. As shown in Figure 5, when the loading level of nanoparticles was 6 wt %, there were no obvious interfaces among the fracture morphologies of nanocomposites (Figure 5 A,D,G), which suggested that the size of the particles and their aggregates of CNCs or ACNs were still on nanoscale at this loading level. When the addition of the nanoparticle content was higher, e.g., 15 wt % (Figure 5B,E,H) and 30 wt % (Figure 5C,F,I), the smoothness of the fracture morphology of PHB-based nanocomposites increased with DS_{surface-acetyl} suggesting that the interface compatibility between ACN and the PHB matrix increased with the DS_{surface-acetyl}. The microstructure observation of SEM images for the nanocomposites further demonstrated that the ACN with higher DS_{surface-acetyl} could be dispersed in the PHB matrix more uniformly, which was consistent with the analysis and results, as mentioned above. Moreover, the fracture morphology of the nanocomposites with 15 wt % cellulose nanoparticles was further investigated by field emission-SEM (FE-SEM), as shown in Figure 6. Many white dots on the fractured surface and coarse film surface were found in PHB/CNC-15 nanocomposites (Figure 6A), indicating their high heterogeneity. For PHB/ACN(II)-15 nanocomposites (Figure 6B), the fractured surface was smoother and rod-shaped nanoparticles were observed in the nanocomposites, which referred to slight aggregates of ACN(II). It was worth noting that smooth fractured surfaces were observed for PHB/ACN(IV)-15 nanocomposites and few rodlike ACNs(IV) were found in the nanocomposite, which indicated that ACN(IV) nanoparticles were well embedded into the PHB matrix, suggesting a uniform dispersion of ACN(IV) within the PHB matrix and strong interfacial interaction between the two components.

Optimizing Mechanical Reinforcement via Regulating Surface Acetylation Degree of CNCs. Besides improving compatibility of CNCs and PHB, the aim of surface acetylation toward CNCs was to achieve high mechanical performances via the strategy of improving the miscibility between CNC and the PHB matrix as well. Figure 7 depicts the dependence of tensile strength ($\sigma_b$), Young’s modulus ($E$), and elongation at break...
(εb) of PHB-based nanocomposites upon the loading level of CNCs and ACNs as well as the surface acetylation degree of ACNs. Obviously, the incorporation of both unmodified and ACNs resulted in mechanical reinforcement, namely, the enhancement of Young’s modulus and tensile strength, with an increase in the loading level of CNCs and ACNs. Meanwhile, the increase in the surface acetylation degree of CNCs resulted in higher Young’s modulus and tensile strength and less expense of elongation at break. Furthermore, especially for tensile strength, the increase in the DS_{surface-acetyl} of ACNs might offset the negative effect of the high loading level of ACNs. The nanocomposites containing the ACNs with high DS_{surface-acetyl} as 62.9% showed the highest tensile strength (43.6% higher than that of PHB/CNC-15 nanocomposite), and their elongation at break was 12.6% and higher than that of the PHB filled with 15 wt % unmodified CNCs.

To reveal the mechanism of variation on mechanical properties of PHB-based nanocomposites, the mechanical properties of PHB-based nanocomposites reinforced with either CNCs or ACNs were further investigated by dynamic mechanical analysis (DMA). Figure 8 shows the trends of the storage modulus (E’) and the loss tangent (tan δ) as a function of the temperature for neat PHB and PHB-based nanocomposites, respectively. The obtained data for glass transition temperature (T_g) extracted from the tan δ peak are summarized in Table 4. By loading unmodified CNCs with low content (6 wt %), the storage modulus E’ of the PHB-based nanocomposite increased, which could be ascribed to the reinforcing effect of the CNC, but when the content increased, E’ decreased, which probably resulted from the poor dispersability of the highly hydrophilic CNCs within the hydrophobic matrix, and led to the aggregation of CNCs, but when the surface of CNC was acetylated, the modulus of the composites was found to continuously increase upon filler addition (Figure 8A–C). In addition, a higher maximum reinforcement could be obtained as the DS_{surface-acetyl} increased. This result could be ascribed to the stronger adhesion between the PHB matrix and ACNs with higher DS_{surface-acetyl}, which led to a more efficient stress transfer at the interface.

Figure 5. SEM images of the fracture morphologies of nanocomposites: (A) PHB/CNC-6, (B) PHB/CNC-15, (C) PHB/CNC-30, (D) PHB/ACN(II)-6 (E) PHB/ACN(II)-15, (F) PHB/ACN(II)-30, (G) PHB/ACN(IV)-6, (H) PHB/ACN(IV)-15, and (I) PHB/ACN(IV)-30.

Figure 6. FE-SEM images for the fracture morphologies of (A) PHB/CNC-15, (B) PHB/ACN(II)-15, and (C) PHB/ACN(IV)-15 nanocomposites.
In the glass transition, the drop in the storage modulus and the decrease in the damping intensity (tan $\delta$) were gradually reduced as loading levels of the filler increased, regardless of the type of cellulose nanoparticles. This suggested that the presence of the cellulose nanoparticles promoted the segmental restrictions of PHB chains. In addition, the reinforced nanocomposites exhibited higher $T_g$ than that of the neat PHB (Table 4) due to the strong interaction between the filler and the matrix in reinforced nanocomposites. It was noteworthy that higher $T_g$ could be obtained as the DS$_{\text{surface-acetyl}}$ of CNCs and ACNs increased, which could be attributed to the improved interaction between the PHB matrix and ACNs. These results suggested that the matrix–filler interaction and compatibility could be improved by controlling the acetylation degree of CNCs and the filler content.

On the other hand, the DSC curves of neat PHB and nanocomposites are shown in Figure 9 and the data of melting ranges are shown in Table 4, which were assigned to the PHB component in the nanocomposite films. The results indicate that the loading level and DS$_{\text{surface-acetyl}}$ of CNCs and ACNs had almost no influence on the onset and end temperature of melting transition as well as the crystallinity degree ($\chi_{c,\text{PHB}}$) for the PHB matrix. So, the crystalline structure and degree of the PHB matrix were not the dominant mechanical reinforcing factors of the nanocomposites. Thus, the further mechanically reinforcing effects via surface acetylation of CNCs would be concluded as follows: (i) the hydrophobicity of the surface on CNCs was adjusted to be close to that of PHB via gradient acetylation control, which increased the dispersity, compatibility, and interaction between CNCs and PHB; (ii) as confirmed above, the surface acetylation toward CNCs did not impair the rigid crystalline structure and rodlike morphology (i.e., high aspect ratio) of CNCs, which played a key role in reinforcing fillers.

Effects of Surface Acetylation Degree on the Rheological Properties of CNC/PHB Composites. In view of the fact that surface groups on the CNCs should have significant influence on the rheological behavior of the nanocomposites, a melt rheological analysis was performed to study the effect of surface acetylation on the rheological properties of the samples. Figure 10 shows the viscosity ($\eta^*$), storage modulus ($G'$), and loss modulus ($G''$) of the PHB-based nanocomposites filled with varied loading levels of CNCs and ACNs. We found that the $G'$, $G''$, and $\eta^*$ of PHB-based
nanocomposites were slightly higher than those of neat PHB at 6 wt % loading of the rigid CNC. Besides, as the DS_{surface-acyetyl} of CNCs increased, the dispersity of cellulose nanoparticles in PHB increased and then the size of rigid cellulose nanoparticles and their aggregation in the melt PHB matrix decreased, which resulted in the $G'$, $G''$, and $\eta^*$ of the PHB-based nanocomposites to decrease with the increase of the DS_{surface-acyetyl} of CNCs at the loading level of 6 wt %. However, when the loading level reached 15 wt %, the $G'$, $G''$, and $\eta^*$ of the PHB-based nanocomposites were much higher than those of the neat PHB. Meanwhile, the neat CNC would heavily aggregate in the PHB matrix at this loading level due to their low compatibility, leading to the PHB chains moving harder in the PHB matrix. Then, when the loading level was much higher than the $\nu_{RC}$ and increased to 30 wt %, the density of cross-linking of CNCs or ACNs in the PHB matrix increased significantly, leading to $G'$, $G''$, and $\eta^*$ of the PHB/CNC-30 and PHB/ACN(II)-30 increasing and approaching those of PHB/CNC-30 (as shown in Figure 10C–C'). These results indicated that the rheological properties of CNC/PHB composites could also be adjusted by controlling the DS_{surface-acyetyl} of ACNs, which was meaningful to the processing of CNC/PHB composites.

**CONCLUSIONS**

In the present work, the surface acetylation degree of CNCs via reaction with AA could be effectively adjusted as a gradient of above ca. 10% by adjusting the feeding molar ratio of CNC surface hydroxyl versus AA, as demonstrated by FTIR spectroscopy and elemental analysis. To improve the compatibility between CNCs and PHB, the surface properties of CNCs were adjusted to a similar value as those of PHB via...
surface acetylation and characterized by contact angle measurement. As a result, the dispersity of CNCs in the PHB matrix increased substantially with increase in DS_{surface-acetyl} of ACNs, which was confirmed by Raman mapping spectra. Meanwhile, mechanical properties of PHB-based composites significantly increased via surface acetylation. Specifically, the tensile strength and elongation at break increased by 43.3 and 12.6% when DS_{surface-acetyl} increased from 0 to 62.9%. To reveal the reinforcing mechanism of surface acetylation, the crystallinity, interfacial properties, and microstructure of PHB/CNC and PHB/ACNs nanocomposites were characterized by XRD, DMA, and SEM, respectively, and we found that the rodlike morphology and crystallinity of CNCs varied little when the hydroxyl groups (−OHs) on the surface of CNCs were substituted by acetyl groups, but the interfacial interaction between PHB and CNCs significantly increased as DS_{surface-acetyl} increased. Considering the fact that the dispersity of CNCs in PHB also increased with the DS_{surface-acetyl} it can be concluded that the adjustment of the surface properties of CNCs and improvement of the compatibility between PHB and CNCs from the modification were the dominant factors of the reinforcing effect on the surface acetylation.

### MATERIALS AND METHODS

**Materials.** PHB was purchased from Tianjin Green Bio-science Co., Ltd. (Tianjin, China), with a melt flow index of 3.6 g/10 min (170 °C, 2.16 kg) and a relative density of 1.2 g/cm³. Cotton linter was supplied by Hubei Chemical Fiber Group Co., Ltd. (Xiangyang, China). AA, sulfuric acid (H₂SO₄), acetonitrile, chloroform (CHCl₃), pyridine, sodium hydroxide (NaOH), and other analytical-grade reagents were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Pyridine was dried and purified according to standard procedures before use, and the other reagents were used as received.

**Extraction of CNCs.** CNCs were prepared by acid hydrolysis of native cotton linter according to the previous work with a minor modification. The cotton linter was first treated by 2 wt % aqueous NaOH and then stirred constantly for 12 h at ambient temperature to remove lignin and hemicellulose. The purified cotton linter was first washed with distilled water followed by filtration and evaporation and then was dispersed in 65 wt % aqueous H₂SO₄. Thereafter, it was mechanically stirred for 50 min at 45 °C to hydrolyze the amorphous or paracrystalline parts of cellulose. Subsequently, the resultant suspension was diluted with iced water and centrifuged with distilled water five times. Finally, the treated suspension was dialyzed with distilled water for 5 days and then freeze-dried to produce the CNCs in a powder form. The puriﬁcation of CNCs was carried out with a constant stir under nitrogen atmosphere in a three-necked round-bottomed flask equipped with a condenser. First, the CNC powder was dispersed in anhydrous pyridine via ultrasonication for 15 min to obtain a homogeneous suspension. Then, a solution of AA in anhydrous pyridine was added and reacted with a condenser for 50 min at room temperature to acetylate the surface of CNCs (DS_{surface-acetyl} 0−62.9%).

**Surface Acetylation of CNCs.** Surface acetylation of CNCs was carried out with a constant stir under nitrogen atmosphere in a three-necked round-bottomed flask equipped with a condenser. First, the CNC powder was dispersed in anhydrous pyridine via ultrasonication for 15 min to obtain a homogeneous suspension. Then, a solution of AA in anhydrous pyridine was added and reacted with a condenser for 50 min at room temperature to acetylate the surface of CNCs (DS_{surface-acetyl} 0−62.9%).

### Table 4

| samples       | T_g (°C) | T_m range (°C) | ΔH_m (J/g) | X_c,PHB (%) |
|---------------|----------|----------------|-------------|-------------|
| PHB/CNC-6     | 6.4      | 113.4−178.6    | 30.6        | 22.0        |
| PHB/CNC-15    | 6.8      | 110.4−177.5    | 27.5        | 21.0        |
| PHB/CNC-30    | 6.6      | 110.1−175.1    | 30.0        | 25.4        |
| PHB/ACN(II)-6 | 7.2      | 108.5−174.1    | 29.5        | 22.5        |
| PHB/ACN(II)-15| 8.3      | 110.1−176.9    | 28.4        | 24.0        |
| PHB/ACN(II)-30| 9.3      | 109.4−173.3    | 24.8        | 25.4        |
| PHB/ACN(IV)-6 | 7.1      | 108.8−174.4    | 31.5        | 24.1        |
| PHB/ACN(IV)-15| 8.6      | 109.6−173.6    | 27.0        | 22.8        |
| PHB/ACN(IV)-30| 9.7      | 109.4−173.3    | 24.3        | 25.0        |

 ΔCH_m is the melting enthalpy of 100% crystalline polyester and w_f is the weight fraction of polyester in the blends. ΔH_m of PHB is 139.3 J/g. From DMA Experiments, and Melting Temperature (T_m), Heat Enthalpy (ΔH_m) of the PHB-Based Nanocomposites and the Crystallinity Degree of the PHB Component (X_c,PHB) from Differential Scanning Calorimetry (DSC) Thermograms.

**Figure 9.** DSC curves of PHB-based nanocomposites with varied content of (A) CNC, (B) ACN(II), and (C) ACN (IV).
pyridine was added dropwise into the CNC suspension. Subsequently, the reaction mixture was kept at 80 °C with constant stirring under nitrogen atmosphere. After 5 h, the product was isolated by precipitation with 1.0 L distilled water and purified by washing with distilled water three times and subsequently with acetone/water solution to eliminate the unreacted chemicals. Finally, ACN powders were obtained by freeze-drying. In this case, the feeding molar ratios between AA and hydroxyl groups on the CNC surface (OHCNC-surface) were set as 5:1, 10:1, 20:1, 40:1, and 80:1 to obtain the corresponding samples coded as ACN(I), ACN(II), ACN(III), ACN(IV), and ACN(V), respectively.

Preparation of Hydrophobic Polyester-Based Nanocomposites. A kind of hydrophobic polyester, PHB, was reinforced with unmodified and ACNs by the process of solution blending and subsequent casting molding. First, a desired amount of CNCs (or ACNs) was dispersed into chloroform under a sonication treatment for 5 min and then mixed with PHB. Subsequently, the mixture was mechanically stirred until the PHB was completely dissolved. Finally, the homogeneous suspension containing PHB together with CNCs (or ACNs) was casted into a Teflon mold and evaporated overnight at ambient temperature to produce the nanocomposite films with a thickness of about 0.2 mm. According to the loading level of CNCs or ACNs, the resultant nanocomposite films were coded as PHB/CNC-x or PHB/ACN-x, respectively. According to the contents of CNCs or ACNs in the nanocomposites as 0, 3, 6, 9, 15, 20, 25, and 30 wt %, the symbol of “x” in the sample codes might be replaced by the corresponding numbers. Meanwhile, the “ACN” in the sample codes might be replaced by ACN(I), ACN(II), ACN(III), and ACN(IV), respectively, according to the used ACN sources with varied surface acetylation degrees.

Characterization by FTIR Spectroscopy. The FTIR spectra of CNCs and all ACNs were recorded on a Nicolet 6700 FTIR spectrometer (Nicolet Instruments) in the range of 4000–400 cm⁻¹ using the method of KBr platelet.

Elemental Analysis. The contents (%) of carbon (C), hydrogen (H), and sulfur (S) were measured from elemental analysis (Elemental Vario EL Cube, Germany). Moreover, the degree of acetyl substitution (DSurface-acetyl) for ACNs was calculated according to the following equation.
\[ DS_{\text{surface-acetyl}} = \frac{n_{\text{surface-acetyl}}}{n_{\text{surface-OH}}} = \frac{\Delta C/12}{2} \cdot \frac{n_{\text{surface-OH}}}{n_{\text{surface-OH}}} \]  

where \( n_{\text{surface-acetyl}} \) is the amount of surface acetyl groups on ACN, \( n_{\text{surface-OH}} \) is the amount of surface hydroxyl groups on CNCs, and \( \Delta C \) is the increment of carbon content after surface acetylation (\( \Delta C = C_{\text{ACN}} - C_{\text{CNC}} \)).

**TEM.** The TEM observations were carried out on an H-7000FA transmission electron microscope (Hitachi, Tokyo, Japan), with an acceleration voltage of 75 kV. A small amount of CNC and ACN powders were dispersed in distilled water to give a suspension with a concentration of 0.1 wt %, respectively, and then negatively stained with a 2% (w/v) ethanol solution of uranyl acetate.

**XRD Measurement.** The XRD patterns of dry CNC and ACN powders were recorded on a D/Max-IIIA X-ray diffractometer (Rigaku Denki Co., Ltd., Tokyo, Japan) with Cu Kα1 radiation (\( \lambda = 0.154 \text{ nm} \)) at 40 kV and 60 mA in a 2θ range of 5°–70°. Moreover, the crystallinity indices (\( I_c \)) of CNCs and ACNs were calculated according to the Segal equation27 as follows

\[ I_c = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \]  

where \( I_{002} \) is the intensity of the peak located at 22.7° of 2θ that is associated with the (002) diffraction plane of cellulose crystal and \( I_{am} \) represents the intensity of the baseline at 18.0° of 2θ. Additionally, the crystalline dimensions associated with every diffraction plane in the CNCs and ACNs were calculated by the Scherrer equation27,28 as follows

\[ B_{hkl} = \frac{0.9\lambda}{\beta_{1/2} \cos \theta} \]  

where \( B_{hkl} \) is the average crystalline width of a specific plane, \( \lambda \) represents the wavelength of incident X-rays and is equal to 0.154 nm in this study, \( \beta \) is the diffraction angle located at the center of the peak, and \( \beta_{1/2} \) (in radius) represents the full width at half-maximum of the reflection peak.

**Contact Angle Measurement.** The contact angle measurements of the CNCs and ACNs were performed at ambient temperature using a dynamic drop tensiometer (DSA10; KRÜSS GmbH, Germany). The powdered CNCs and ACNs were compacted under a pressure of 20 MPa to obtain the tested plate with smooth surfaces. The Owens–Wendt approach29 was used to relate the dispersive and polar contributions of the surface energy of the tested specimens to the contributions of the surface tension of liquids, which were calculated according to the following equation

\[ \gamma_L(1 + \cos \theta) = 2\sqrt{\gamma_L^d + 2\sqrt{\gamma_L^p + \gamma_S}} \]  

where the variables \( \gamma_L, \gamma_p, \) and \( \gamma_S \) represent the total, dispersive, and polar surface energies, respectively; the subscripts of “L” and “S” refer to the liquid drop and the solid surface, respectively; and \( \theta \) denotes the contact angle between the solid substrate and the liquid drop. The liquids with varied dispersive and polar surface tensions, such as water and ethylene glycol in this case, were used to determine the surface energy of CNCs and ACNs, and the \( \gamma_L, \gamma_p, \gamma_S \) values of water28 and ethylene glycol30 are 72.8, 21.8, and 51.0 mJ/m², and 48.0, 29.0, and 19.0 mJ/m², respectively.

**Laser Raman Spectroscopy.** The Raman images for PHB nanocomposites were taken on an inVia Laser Micro-Raman spectrometer (Renishaw, Britain). The excitation wavelength of the laser source was 785 nm, which was powered at 50 mW.

**Rheological Measurement.** The rheological behaviors of PHB-based nanocomposites were investigated by a discovery hybrid rotational rheometer (TA Instruments) with two parallel plates (\( \phi = 25 \text{ mm} \)). Considering the susceptibility of thermal degradation of cellulose nanoparticles and the melting temperature of PHB, the testing temperature was set at 160 °C. The sample was loaded onto the bottom plate to be preheated for 3 min at 160 °C. The dynamic frequency sweep test was performed to determine the dynamic properties of the nanocomposite systems, and the strain and frequency ranges used during testing were 1% and 0.1–500 rad/s, respectively.

**Tensile Test.** The tensile strength (\( \sigma_t \)), elongation at break (\( \varepsilon_b \)), and Young’s modulus (\( E \)) of the nanocomposite films filled with CNCs or ACNs were measured on a CMT6503 universal testing machine (SANS, Shenzhen, China), with a crosshead rate of 5 mm/min. The \( \sigma_t, \varepsilon_b \), and \( E \) recorded in this article were the average of five tests.

**SEM.** The SEM observation was carried out on an X-650 scanning electron microscope (Hitachi, Tokyo, Japan) to observe the fractured surface of the nanocomposite sheets. In addition, a FE-SEM observation was carried out on a Zeiss Ultra Plus scanning electron microscope (Zeiss, Germany). All samples were frozen in liquid nitrogen and then immediately snapped. And the fractured surfaces were gold-plated and then observed and photographed.

**DMA.** DMA experiments of PHB nanocomposites were carried out on a Universal v4.5A TA Instrument (DE) in a temperature range of −60 to 100 °C at a 3 °C/min heating rate and 3 Hz constant frequency in the tensile configuration.

**DSC.** The nonisothermal crystallization and melting behavior were observed by using a NETZSCH DSC 214 instrument (NETZSCH Co., Germany) under a nitrogen atmosphere in the range of −70 to 200 °C at a heating rate of 20 °C/min after pretreatment for eliminating thermal history (specifically, heating from room temperature to 110 °C and then cooling to −70 °C).

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The article was written through contributions of all authors. All authors have given approval to the final version of the article.

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**Notes**

The authors declare no competing financial interest.

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**ABBREVIATIONS**

CNC, cellulose nanocrystal; PHB, poly(3-hydroxybutyrate-co-4-hydroxybutyrate); PCL, poly(ε-caprolactone); AA, acetic anhydride; ACN, acetylated cellulose nanocrystal; FTIR, Fourier transform infrared; DMA, dynamic mechanical analysis; DSC, differential scanning calorimetry; SEM, scanning electron microscopy; XRD, X-ray diffraction; TEM, transmission electron microscopy

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