New waterborne polyurethane-based nanocomposites reinforced with low loading levels of chitin whisker

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Abstract. New waterborne polyurethane (WPU)-based nanocomposites were prepared by incorporating low loading levels of chitin whiskers (ChWs) as the nanophase. The resultant WPU/ChW nanocomposites exhibited prominent enhancement in both strength and Young's modulus, and maintained an elongation of greater than ca. 500%. The ChW loading level of 3 wt% showed the maximum tensile strength (28.8 MPa) and enhanced Young's modulus (6.5 MPa), ca.1.8- and 2.2-fold over those of neat WPU. The active surface and rigidity of ChW facilitated formation of the interface for stress transferring and contributed to higher stress-endurance. As the ChW loading level increased, self-aggregation of ChWs resulted in a decrease in strength; however, the rigidity of ChW still supported the increase in Young's modulus, and the nanocomposites containing 5 wt% ChWs had the highest Young's modulus (9.6 MPa). This work enriches the research into achieving high mechanical performance of waterborne polyurethane-based nanocomposites by introducing a natural nanofiller, and this high performance 'green' bionanocomposites will likely have promising prospects.

Keywords: nanocomposites, waterborne polyurethane, chitin whisker

1. Introduction

Public concern over the environment, the depletion of fossil fuels, and climate change has promoted the development of bionanocomposites in the past decade. Compared to polymeric resources from petroleum, natural polymers from renewable resources have the advantages of biodegradability, biocompatibility, non-toxicity, high reactivity, low cost, ease of availability, and so forth [1–3]. Natural nanofillers are the crystalline residues after acidic or alkaline hydrolysis of natural polysaccharides,

most notably the rod-like whiskers of cellulose [4] and chitin [5], and the platelet-like nanocrystal of starch [6, 7]. These nanofillers not only inherit all the advantages of the natural polymers, but also have a reinforcing function in composites, similar to traditional inorganic nanofillers [4, 5, 8–10], by virtue of their rigidity. Moreover, compared with inorganic nanofillers, the relatively active surface of natural nanofillers makes it easy to perform chemical derivation and grafting [11–13] or to form strong physical interactions.

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Chitin, a natural polymer, is an abundant renewable resource [14]. Structurally, chitin is very similar to cellulose, except that its basic monosaccharide is 2-acetamido-2-deoxy-D-glucose (*N*-acetyl-D-glucosamine). Chitin and its derivatives have excellent biocompatibility and physiological non-toxicity, such that it may be used for drug delivery, cell culture anticoagulant, sutures and coagulant, etc. [15–17]. Chitin whiskers (ChWs), obtained by removing protein and other impurities from chitin, also possess excellent rigidity and intensity and are often used as a reinforcing agent in nanocomposites [18]. They are being widely used in aerospace flight vehicle elements and components, as well as in the chemical industry, machinery, motorcars, biomedicine and other industrial applications. Nair and Dufresne [19] reported significant improvement in the mechanical properties of natural rubber reinforced by ChWs. Lu *et al.* [20] incorporated ChWs into soy protein to prepare thermoplastic composites, further confirming the reinforcing role ChW nanofillers play in composites.

Due to increasing concerns about human health and environmental-friendliness, organic, solvent-free polyurethane (i.e. waterborne polyurethane, WPU) with its low volatile organic compound (VOC) levels and non-toxicity has been rapidly developed and applied [21, 22]. Environmentally-friendly WPU can be applied to leather and textile finishing, floor coverings, adhesives, pressure sensitive adhesives, and so on [23–27]. Starch [28], soy protein [29], lignin [30], and chitin derivative [31] have been incorporated into WPU for the purposes of reducing cost, improving biodegradability, and enhancing mechanical performance. Additionally, cellulose whisker has also been filled into a WPU matrix as a reinforcing nanophase, resulting in a significant increase in strength and Young's modulus [32].

In this work, we incorporated very low loading levels of ChWs into WPU to prepare WPU/ChW nanocomposites. Subsequently, the structure and mechanical properties of the resultant nanocomposite materials were investigated by attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR), X-ray diffraction (XRD), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), scanning electron microscopy (SEM) and tensile tests.

2. Experimental part

2.1. Materials

Chitin (crab shell) was purchased from Yuhuan Ocean Biochemical Co. Ltd. (Zhejiang, China), and used as received. Polycaprolactone, with a number-average molecular weight (M_n) of 2000 (PCL₂₀₀₀), was purchased from Sigma–Aldrich Chemical Co. (Saint Louis, MO, USA). Diphenyl-methane-diisocyanate (MDI-100) was purchased from Yantai Wanhua Polyurethanes Co. Ltd. (Shandong, China). Dimethylol propionic acid (DMPA) was donated by Huzhou Changsheng Chemical Co. Ltd. (Zhejiang, China), and dehydrated under vacuum at 60°C for 12 h. Triethylamine (TEA) was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China), and redistilled before use. Analytical grade butanone solvent was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and dehydrated by adding CaH₂ and then distilling.

2.2. Preparation of chitin whiskers

According to the previous report [19], the procedure used for preparing a stable suspension of chitin whiskers is described as follows: Chitin was first boiled and mechanically stirred in a 5% KOH solution for 6 h to remove most of the proteins. It was then kept at room temperature overnight under constant stirring, followed by filtering and washing several times with distilled water. The resultant solid was bleached with 17 g of NaClO₂ in 1 l 0.3 M CH₃COONa for 6 h at 80°C, and the bleach solution changed every 2 h. After bleaching, the suspension was kept in a 5% KOH solution for 48 h to remove residual proteins and then centrifuged at 3600 rpm for 15 min. The purified chitin was hydrolyzed with boiling 3 N HCl for 90 min under mechanical stirring (30 ml HCl per 1 g chitin). Finally, the acid hydrolyzed suspension was diluted with distilled water, centrifuged (36 000 rpm for 15 min), and then dialyzed until the pH reached 4.0. The resultant chitin whiskers were completely dispersed using ultrasonic treatment or vigorous mechanical shearing, and stored at 6°C after adding sodium azide to inhibit bacterial growth.

2.3. Preparation of WPU/ChW nanocomposites

The synthesis of waterborne polyurethane (WPU) is depicted as follows: Both 4.98 g PCL₂₀₀₀ and 2.23 g

MDI were first dissolved in 10 g butanone and then placed into a three-necked round-bottomed flask equipped with a mechanical stirrer, a reflux condenser, and a dry nitrogen inlet. The reactant was then heated to ca. 70°C, and kept under a nitrogen atmosphere for 2 h with mechanical stirring. Thereafter, 0.46 g DMPA, a chain-extender, was dispersed in butanone and added to give a NCO/OH molar ratio of 1.6. The reaction temperature was elevated to 85°C and held here for 1 h. During this period butanone was occasionally added in order to lower the viscosity of the reactant. Afterward, the resultant product was cooled to less than 40°C, and then the –COOH of DMPA in the polyurethane chains was neutralized by adding 0.34 g TEA. Emulsification was subsequently carried out by adding icy water under severe shear to produce WPU latex with a solids content of 20 wt%. Finally, the desired amount of ChWs suspended in distilled water was added and the reaction was allowed to continue for another 0.5 h. The WPU latex was cast onto a Teflon mold after vacuum degassing, and allowed to solidify as a film at 60°C via water evaporation. By changing the ChWs content over a range of 0, 1, 2, 3, 4, and 5 wt%, a series of nanocomposite films were obtained, and coded as WPU, WPU/ChW-1, WPU/ChW-2, WPU/ChW-3, WPU/ChW-4 and WPU/ChW-5, respectively. The resultant films were stored at room temperature in a desiccator containing P₂O₅ with 0% relative humidity (RH) for 5 days.

2.4. Characterization

2.4.1. FTIR analysis

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra of all the films were recorded on a FTIR 5700 spectrometer (Nicolet, USA). The films were scanned in the range of 4000–700 cm^{−1} using Smart OMNT reflect accessories.

2.4.2. X-ray diffraction (XRD)

X-ray diffraction measurements were performed on a D/max-III A X-ray diffractometer (Rigaku Denki, Tokyo, Japan) using Cu K_α radiation ($\lambda = 0.154$ nm) at 40 kV and 60 mA with a scan rate of 12°·min^{−1}. The diffraction angle of 2 θ ranged from 2 to 60°.

2.4.3. Atomic force microscopy (AFM)

Atomic force microscopy was performed on a Digital 3100 IIIa microscope (USA). A droplet of a dilute whisker suspension was coated onto a flake of mica, and the water was evaporated at room temperature.

2.4.4. Scanning electron microscope (SEM)

Scanning electron microscope observation was carried out on an S-4800 scanning electron microscope (Hitachi, Japan) with an accelerating voltage of 10 kV. The films were frozen in liquid nitrogen and then snapped immediately. The fracture surfaces were sputtered with Pt, and then observed and photographed.

2.4.5. Differential scanning calorimetry (DSC)

Differential scanning calorimetry analysis was carried out on a DSC-204 instrument (Netzsch, Germany) under a nitrogen atmosphere at a heating or cooling rate of 20°C·min^{−1}. The specimen was scanned over the range of −150 to 100°C after a pre-treatment to eliminate thermal history and remove volatiles (heating from 20 to 100°C and then cooling to −150°C).

2.4.6. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis measurement was carried out on a DMA-242C dynamic mechanical analyzer (Netzsch, Germany) at a frequency of 1 Hz over the range of −150 to 100°C with a heating rate of 3°C·min^{−1}. A dual cantilever device was used and the specimen size was 40×10×ca. 0.5 mm³.

2.4.7. Tensile test

The tensile strength (σ_b), elongation at break (ϵ_b) and Young's modulus (E) were measured on a CMT6503 universal testing machine (SANS, Shenzhen, China) with a crosshead rate of 100 mm·min^{−1} according to method GB13022-91. The tested specimens were cut into quadrangle strips 10 mm wide and the distance between testing marks was 30 mm. The average value of five replicates of each sample was taken.

3. Results and discussion

3.1. Chitin whiskers

The AFM image of a dilute suspension of chitin whiskers (ChWs) is shown in Figure 1. The suspen-

Figure 1. AFM images of a dilute suspension of chitin whiskers (a) height image; b) phase image)

sion consisted of individual chitin fragments having a spindle shape. These fragments had a broad distribution in length (L), ranging from 100 to 350 nm, and diameter (D), ranging from 5 to 35 nm. Exact determination of the latter was difficult because of both the tapering of the chitin fragments and the presence of narrow microcrystals. The average of length and diameter were estimated to be 250 ± 50 and 20 ± 10 nm, respectively; therefore, the average aspect ratio, i.e. L/D , was 12.5 ± 5 , which is very close to the dimensions of squid pen ($L = 50 \sim 300$ nm, $D = 10$ nm, $L/D = 15$) [5] but much lower than chitin from Riftia tubers ($L = 0.5 \sim 10$ μ m, $D = 18$ nm, $L/D = 120$) [33]. For a three-dimensional network, the critical volume fraction (V_{Rc}) depends on the aspect ratio ($L/D = 12.5$) of the chitin whiskers since $V_{Rc} = 0.7 (L/D)$ [19]. Substitution of the L/D value of chitin whiskers into that equation yields a value of $V_{Rc} = 5.6$ vol%, or ca. 8.4 wt%. The highest ChWs content in this work was 5 wt%, which is lower than the critical weight fraction, so a three-dimensional network of chitin whiskers was absent in the as-prepared nanocomposites.

3.2. Mechanical properties of nanocomposites

Figure 2 shows the effects of the ChW loading level on the mechanical properties of the WPU/ChW

Figure 2. Effects of ChW loading level on tensile strength (σ_b), elongation at break (ϵ_b) and Young's modulus (E) of WPU/ChW nanocomposite films, with WPU film as reference

nanocomposites, including tensile strength (σ_b), Young's modulus (E) and elongation at break (ϵ_b). As expected, the rigidity of ChW enhanced the strength of WPU significantly. Compared with σ_b of 11.3 MPa and E of 3.0 MPa for neat WPU, the σ_b and E values of the WPU/ChW nanocomposites

were both enhanced. When the ChW loading level was 3 wt%, σ_b reached a maximum value of 20.8 MPa, approximately 1.8-fold over that of neat WPU. Thereafter, the continuous increase in the ChW loading level resulted in a slight decrease in σ_b , but the value of E continued to increase. When the ChW loading level reached 5 wt%, E increased to 9.6 MPa, ca. 3.2-fold over that of neat WPU. On the other hand, the change in ε_b as the ChWs content increased was just opposite of E , and all the ε_b values of the WPU/ChW nanocomposites were lower than that of neat WPU. In other words, enhancement of the strength and Young's modulus occurred at the expense of elongation; however, compared with the obvious enhancement of σ_b and E , a certain level of decline in ε_b is acceptable. From the above results, we found that neat ChWs had an evident reinforcing role, furthermore, with a ChW content of 3 wt%, σ_b reached the maximum value and E reached 6.5 MPa, which were ca. 1.8 and 2.2-fold over those of neat WPU, respectively. At this time, the ε_b value of the nanocomposites remained at 575.4%. Enhancement of the nanocomposite mechanical properties by ChWs may be attributed to the uniform dispersion of ChWs at the nanoscale as well as to the physical interaction between the ChW nanofiller and the WPU matrix [34] for the transfer of stress to the rigid ChW nanofiller. However, with an increase in the loading level of ChWs, self-aggregation of ChWs may break the original structure and interaction in the WPU matrix, resulting in a decrease in strength and elongation. The rigid nature of ChW and its aggregate, however, maintained the continuous increase in Young modulus.

3.3. Hydrogen bonding in nanocomposites

ATR-FTIR spectra of the WPU/ChW nanocomposites and the neat WPU are shown in Figure 3a. As is well known, the hydrogen bond is an essential physical interaction in waterborne polyurethane affecting the microphase separation structure and mechanical properties of materials [35]. In this case, the $-\text{NH}$ in the hard-segment was hydrogen-bonded with the $-\text{C}=\text{O}$ of the hard-segments, the ester $-\text{C}=\text{O}$ of the PCL₂₀₀₀ soft-segments and the $-\text{C}=\text{O}$ on the ChW surface. In addition, $-\text{OH}$ on the ChW surface also participated in hydrogen bonding with the $-\text{C}=\text{O}$ in the soft- and hard- segments. All

the nanocomposites showed the analogical $-\text{NH}$ bands with the main peak located at ca. 3314 cm^{-1} despite the absorption of $-\text{OH}$ in ChWs being embedded in them. As a result, absorptions in the range of $3450\sim 3250\text{ cm}^{-1}$ for all the WPU/ChW nanocomposites and WPU were divided into two peaks by curve-fitting (Figure 3b), i.e. Peak I located at $3391\text{--}3394\text{ cm}^{-1}$ and Peak II located at $3320\text{--}3339\text{ cm}^{-1}$. The former was the free $-\text{NH}$ absorption while the latter was the absorption of hydrogen-bonded $-\text{NH}$ for WPU, or included the additional $-\text{OH}$ absorption for the WPU/ChW nanocomposites. Table 1 summarizes the detailed locations and fractions of Peaks I and II for all the WPU/ChW nanocomposites and for WPU. The increasing Peak II fraction was not proportional to the increment contributed by $-\text{OH}$ absorption, indicating that the original hydrogen bonds associated with $-\text{NH}$ in the WPU matrix cleaved. When the ChW loading level was lower than 2 wt%, the relatively prominent increase in the fraction for Peak II was attributed to less inhibition to the original $-\text{NH}$ -based hydrogen bonding, and to the formation of hydrogen bonds associated with $-\text{OH}$, $-\text{NH}$ - and $-\text{C}=\text{O}$ on the ChW surface. The analogical $-\text{C}=\text{O}$ bands of the WPU/ChW nanocomposites and WPU were also divided into three peaks (Figure 3c), namely Peak III from the free $-\text{C}=\text{O}$ located at $1730\text{--}1732\text{ cm}^{-1}$, Peak IV from the hydrogen-bonded $-\text{C}=\text{O}$ in the amorphous region located at $1712\text{--}1713\text{ cm}^{-1}$ and Peak V from the hydrogen-bonded $-\text{C}=\text{O}$ in the ordered domain located at $1697\text{--}1698\text{ cm}^{-1}$ [36]. The location and fraction of these three peaks in the WPU/ChW nanocomposites and WPU are also summarized in Table 1. Adding ChWs appeared to slightly decrease the fraction of the free $-\text{C}=\text{O}$ peak (Peak III), indicating that the hydrogen bonding associated with $-\text{C}=\text{O}$ of hard-segments and PCL₂₀₀₀ soft-segments was improved. This was attributed to the newly formed hydrogen bonds between the $-\text{C}=\text{O}$ of the WPU component and the $-\text{OH}$ or $-\text{NH}$ - on the ChW surface. Although hydrogen bonding associated $-\text{C}=\text{O}$ was improved as a whole, the effect of adding ChW on the region of hydrogen bonding in the nanocomposites was distinctly different. With an increase in the ChW loading level, the increasing fraction of Peak IV suggested that the improvement of hydrogen bonding occurred mainly in the amor-

Figure 3. FTIR spectra of the WPU/ChW nanocomposite films and WPU film as reference ((a): full spectra; (b): the curve-fitting for the $-\text{NH}$ absorption of WPU/ChW nanocomposites as representative (—) experimental curve, (---) free $-\text{NH}$, ($\cdots$) hydrogen-bonded $-\text{NH}$; (c): the curve-fitting for the $-\text{C}=\text{O}$ absorption of WPU/ChW nanocomposites as representative (—) experimental curve, (---) free $-\text{C}=\text{O}$, ($\cdots$) hydrogen-bonded $-\text{C}=\text{O}$ in amorphous region, (- - -) hydrogen-bonded $-\text{C}=\text{O}$ in ordered domain)

Table 1. Location and Fraction of Curve-Fitting Peaks for the –NH and –C=O Bands in the FTIR Spectra of WPU/ChW Nanocomposites and WPU (Peak I: Free –NH; Peak II: Hydrogen-Bonded –NH; Peak III: Free –C=O; Peak IV: Hydrogen-Bonded –C=O in Amorphous Region; Peak V: Hydrogen-Bonded –C=O in Ordered Domain).

Sample code	–NH band				–C=O band					
	Peak I		Peak II		Peak III		Peak IV		Peak V	
	Location [cm ⁻¹]	Fraction [%]	Location [cm ⁻¹]	Fraction [%]	Location [cm ⁻¹]	Fraction [%]	Location [cm ⁻¹]	Fraction [%]	Location [cm ⁻¹]	Fraction [%]
WPU	3393.6	23.5	3320.8	76.5	1731.5	64.1	1712.4	27.2	1697.3	8.7
WPU/ChW-1	3393.1	19.6	3337.4	80.4	1730.2	62.8	1712.4	29.1	1697.5	8.1
WPU/ChW-2	3393.6	21.8	3337.4	78.2	1730.8	63.6	1712.9	29.8	1697.1	6.6
WPU/ChW-3	3393.6	21.1	3338.9	78.9	1731.7	62.1	1712.2	31.1	1697.1	6.8
WPU/ChW-4	3391.5	19.3	3338.9	80.7	1731.7	61.4	1712.4	30.8	1697.5	7.8
WPU/ChW-5	3393.1	18.9	3338.4	81.1	1730.8	60.4	1712.4	31.5	1697.3	8.1

phous region, while the slight decrease in the fraction of Peak V proved the cleavage of hydrogen bonding in the ordered domain. Usually, hydrogen bonding in the ordered domain was constructed by hard-segments in the WPU matrix, which suggested that adding ChW drew down the original ordered alignment among hard-segments.

3.4. Crystalline character of nanocomposites

Figure 4 shows the XRD patterns of the WPU/ChW nanocomposites with various ChW loading levels, as well as neat WPU and ChWs. When the ChWs loading level was lower than 2 wt%, the WPU/ChW nanocomposites inherited the amorphous nature of neat WPU, shown as a diffuse peak located at 20.06° of 2 θ , in spite of the fact that –C=O-based

hydrogen bonds constructed a small scale ordered domain in the WPU matrix, as mentioned above. Although the ChWs had a semi-crystalline character, at low loading levels and with relatively uniform dispersion, the well-defined diffraction peaks were absent in the nanocomposites. When the ChW loading level increased to 3 wt%, a weak diffraction peak appeared at 19.47° of 2 θ , which corresponded to the strongest diffraction of semi-crystalline ChWs located at 19.69° of 2 θ . When the ChW loading level increased to 4 wt%, a diffraction peak appeared at 9.04° of 2 θ . Furthermore, when the ChWs content reached 5 wt%, two other obvious diffraction peaks appeared at 21.18 and 23.44° of 2 θ , which corresponded to the diffraction of ChW located at 21.37 and 23.61° of 2 θ respectively. This proved that the ChWs existed in the nanocomposites and tended to self-aggregate with an increase in the ChW loading level.

Figure 4. XRD patterns of WPU/ChW nanocomposites as well as WPU and freeze-dried ChW powder

3.5. Thermal behaviour of nanocomposites

DSC and DMA were used to further understand the interaction between the ChW nanofiller and the WPU matrix, as well as the structural changes to the WPU matrix and the distribution of ChWs, by observing the variances in the domain-scale glass transition and the molecular-level α -relaxation assigned to the PCL₂₀₀₀ soft-segment, respectively. Table 2 summarizes the glass transition temperature at midpoint ($T_{g,mid}$), the heat-capacity increment (ΔC_p), the melting temperature (T_m) and the heat enthalpy (ΔH_m) of the WPU/ChW nanocomposites and the neat WPU. In the WPU/ChW nanocomposites, the temperatures of glass transition (T_g) and α -relaxation (T_α) of the PCL₂₀₀₀ soft-segment can be affected by ChWs in two opposite ways. First, the motion of the soft-segment may be suppressed by

Table 2. DSC data for WPU/ChW nanocomposites and WPU reference

Sample	$T_{g,mid}$ [°C]	ΔC_p [J/g·K]	$T_{m,PCL}$ [°C]	$\Delta H_{m,PCL}$ [J/g]
WPU	-47.5	0.19	45.2	2.34
WPU/ChW-1	-46.7	0.24	45.2	2.75
WPU/ChW-2	-45.9	0.24	46.4	4.15
WPU/ChW-3	-44.3	0.28	47.2	4.44
WPU/ChW-4	-45.4	0.32	48.9	6.24
WPU/ChW-5	-45.9	0.28	47.4	6.59

the steric hindrance of the rigid ChW nanophase and by hydrogen bonding onto the active ChW surface. This could result in a shift of T_g and T_a to a higher temperature. In the opposite way, incorporating ChWs may cleave the original interaction between the hard- and soft-segments and hence change the microphase structure in the WPU matrix. In other words, the soft-segment could escape from the binding of the hard-segment, leading to decreased T_g and T_a . The $T_{g,mids}$ of all the WPU/ChW nanocomposites were higher than that of neat WPU, suggesting that the restriction of ChWs to the mobility of soft-segments was dominant in spite of the inevitable cleavage of the original interaction between the hard- and soft-segments in the WPU matrix. When the ChW loading level was less than 2 wt%, the rigid ChWs homogeneously dispersed into the WPU matrix, and then

Figure 5. DSC thermograms of WPU/ChW nanocomposites and WPU as reference

inhibited the motion of the soft-segment, mediated by the newly formed interaction with the WPU component. At this time, the $T_{g,mids}$ increased with an increase in ChW loading level. When the ChW content reached 3 wt%, $T_{g,mid}$ of the nanocomposites showed the maximum value; however, increasing the ChW loading level caused the $T_{g,mids}$ to gradually decrease because the increasing loading level of ChW induced self-aggregation of the ChWs and hence weakened the restriction to motion of the soft-segment. This was proven by the obvious diffraction peaks that corresponded to the semi-crystalline character of ChW in the XRD pattern. On the other hand, compared with the ΔH_m value for the neat WPU of 2.34 J·g⁻¹, all the WPU/ChW nanocomposites showed dramatically higher ΔH_m values, suggesting that increasing the ChW loading level improved the crystallinity of the PCL component in the WPU matrix due to the nucleation effect of the ChW (Figure 5).

DMA is a powerful technique that reflects the mobility of the soft-segment through α -relaxation at the molecular-level, for which the specific heat increment of the domain-scale glass transition as measured by DSC is generally ill-defined. Figure 6 shows the logarithm of the storage modulus ($\log E'$) and the tangent of the loss angle ($\tan \delta$) as a function of temperature. The α -relaxation temperature at onset ($T_{\alpha onset}$) and the corresponding storage modulus ($\log E'$), α -relaxation temperature of loss peak ($T_{\alpha max}$), and the tangent of loss angle ($\tan \delta$) are summarized in Table 3. Obviously, the $T_{\alpha max}$ s of all the WPU/ChW nanocomposites were higher than that of neat WPU. Considering the improved hydrogen bonding associated with $-C=O$ in the amorphous region of the WPU matrix (seen in Table 1), the increase in $T_{\alpha max}$ s was attributed to the formation of interaction between the polar groups on the ChW surface and the WPU matrix. In this case, the suppression of ChWs to the mobility of soft-segments was proportional to the effective surface of ChWs. When the ChWs were homogeneously dispersed in the WPU matrix (the ChW loading level <2 wt%), the increasing interfacial area between the ChW nanofiller and the WPU matrix resulted in an increase in $T_{\alpha max}$ s and $T_{\alpha onset}$ s with an increase of the ChW loading level. This is in good agreement with the DSC results. Thereafter, with a continuous increase in the loading level of ChW, the ChWs

Figure 6. Logarithm of storage modulus ($\log E'$) and tangent of loss angle ($\tan \delta$) vs. temperature measured at 1 Hz for WPU/ChW nanocomposites with various ChW loading levels, and WPU as reference

Table 3. DMA data for WPU/ChW nanocomposites and WPU reference

Sample	$T_{\alpha \text{ onset}}$ [°C]	$\log E$ [MPa]	$T_{\alpha \text{ max}}$ [°C]	$\tan \delta$
WPU	-49.5	3.16	-30.4	0.22
WPU/ChW-1	-48.1	3.20	-30.0	0.26
WPU/ChW-2	-45.7	3.37	-29.8	0.20
WPU/ChW-3	-43.3	3.18	-24.5	0.28
WPU/ChW-4	-44.6	3.21	-28.9	0.24
WPU/ChW-5	-45.5	3.26	-29.5	0.21

gradually self-aggregated, resulting in the decrease of $T_{\alpha \text{ max}}$ s and $T_{\alpha \text{ onset}}$ s for the WPU/ChW nanocomposites. In the WPU/ChW nanocomposites, the rigidity was mainly contributed by the ChWs nanophase as filler [37] and the ordered hard-segment domain of WPU matrix. Although the ordered hard-segment domain of WPU matrix partly cleaved after adding ChW (seen in the discussion on the hydrogen bonding associated with C=O in ordered domain), the $\log E'$ of all the WPU/ChW nanocomposites were still higher than that of neat WPU due to the reinforcing function of rigid ChW. This was in positive correlation with the Young's modulus (E) of the nanocomposites.

3.6. Fracture morphologies of nanocomposites

Figure 7 shows the SEM images of fractured surfaces of the WPU/ChW nanocomposites and neat

WPU. When the ChW loading level was lower than 2 wt%, the WPU/ChW nanocomposites (Figure 7b and 7c) showed a fluctuant fractured surface similar to that of neat WPU (Figure 7a). This was attributed to the fact that at a lower loading level ChW uniformly dispersed in the WPU matrix and had almost no effect on the original structure and fractured behaviour of the WPU matrix. However, with an increase in the ChW loading level, the fracture morphologies gradually became smooth surfaces with regular and compact thin stripes. This brittle-fracture characteristic was in agreement with the decrease in strength and elongation at break, and was attributed to breakage of the original structure of the WPU matrix after adding higher levels of ChWs. In addition, with an increase in the loading level of ChW, the ChW nanophase in the WPU matrix could be observed, showing many white dots dispersed on the fracture surface. The SEM images seemed to verify the effects of increasing the ChW loading level on the increasing number and expanded size of the ChW nanophase in the nanocomposites.

4. Conclusions

New nanocomposite materials were prepared by casting and evaporating a mixture with waterborne

Figure 7. SEM images of fractured surfaces of WPU/ChW nanocomposites with various ChW loading levels and WPU as reference. ((a): WPU; (b): WPU/ChW-1; (c): WPU/ChW-2; (d): WPU/ChW-3; (e): WPU/ChW-4; (f): WPU/ChW-5)

polyurethane (WPU) as matrix and chitin whiskers (ChW) as nanofiller. The strength and Young's modulus of the nanocomposites were simultaneously enhanced and maintained ca. 500% elongation. Herein, the WPU/ChW-3 containing only 3 wt% ChWs had the maximum tensile strength (28.8 MPa) and enhanced Young's modulus

(6.5 MPa) that were ca. 1.8- and 2.2-fold over those of neat WPU, respectively. The WPU/ChW-5 containing 5 wt% ChWs had the highest Young's modulus (9.6 MPa), which was enhanced by ca. 220%. The prominent improvement of mechanical performance was attributed to the enduring stress of rigid ChW and stress transfer mediated by strong

interactions between the ChW nanofiller and the WPU matrix. This work rendered a strategy for achieving high mechanical performance of waterborne polyurethane-based nanocomposites by a simple method, and the novel bionanocomposites developed could have great potential applications.

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