

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Preparation and Characterization of Nanocomposite Films from Chitin Whisker and Waterborne Poly(ester-urethane) With or Without Ultra-Sonification Treatment

Ming Zeng<sup>ab</sup>, Huina Gao<sup>a</sup>, Yaoqing Wu<sup>a</sup>, Liren Fan<sup>a</sup>, Aiping Li<sup>a</sup>

<sup>a</sup> Engineering Research Center of Nano-Geomaterials of Ministry of Education, China University of Geosciences, Wuhan, P. R. China <sup>b</sup> State Key Laboratory of Geological Process and Mineral Resources, China University of Geosciences, Wuhan, P. R. China

Online publication date: 05 July 2010

**To cite this Article** Zeng, Ming , Gao, Huina , Wu, Yaoqing , Fan, Liren and Li, Aiping(2010) 'Preparation and Characterization of Nanocomposite Films from Chitin Whisker and Waterborne Poly(ester-urethane) With or Without Ultra-Sonification Treatment', *Journal of Macromolecular Science, Part A*, 47: 8, 867 – 876

**To link to this Article:** DOI: 10.1080/10601325.2010.492277

**URL:** <http://dx.doi.org/10.1080/10601325.2010.492277>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Preparation and Characterization of Nanocomposite Films from Chitin Whisker and Waterborne Poly(ester-urethane) With or Without Ultra-Sonification Treatment

MING ZENG<sup>1,2,\*</sup>, HUINA GAO<sup>1</sup>, YAOQING WU<sup>1</sup>, LIREN FAN<sup>1</sup> and AIPING LI<sup>1</sup>

<sup>1</sup>Engineering Research Center of Nano-Geomaterials of Ministry of Education, China University of Geosciences, Wuhan, P. R. China

<sup>2</sup>State Key Laboratory of Geological Process and Mineral Resources, China University of Geosciences, Wuhan, P. R. China

Received January 2010, Accepted March 2010

Two series of nanocomposite films were prepared from waterborne poly(ester-urethane) and chitin whisker with and without ultrasound treatment coded as CW/WPU and CHW/WPU, respectively. The effects of ultra-sonification method and chitin whisker content on the chemical compositions, crystallization behavior and miscibility were studied by attenuated total reflection Fourier transform infrared (ATR-FTIR), wide-angle X-ray diffraction (WXR), dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM). Thermal stability and mechanical properties of the films were measured by thermogravimetric analysis (TGA) and tensile test, respectively. The results revealed that both nanocomposite films exhibited a certain degree of miscibility when chitin whisker content was lower than 30 wt%, resulting in higher thermal stability and tensile strength than the pure waterborne poly(ester-urethane) film. Interestingly, the composite films CW/WPU with ultrasound treatment possessed better miscibility, storage modulus, thermal stability and tensile strength than those without ultrasound treatment over the entire composition range studied here. The difference can be attributed to the relatively higher dispersion level of whisker within poly(ester-urethane) matrix resulting in relatively stronger entanglement and interaction between both components. The ultrasound treatment can effectively improve the miscibility and mechanical properties of the casting nanocomposite films with nano-meter size chitin whisker added. This indicated that the structure, miscibility and mechanical properties of the nanocomposite films depended significantly on the preparation method.

**Keywords:** Nanocomposite, waterborne polyurethane, chitin whisker, ultra-sonification

## 1 Introduction

Nanocomposites are relatively a new class of composites with at least one phase having a dimension in the vicinity of 1–1000 nm. They occupy some unique outstanding properties compared with the conventional microcomposite counterparts. The development and application of nanocomposites has attracted both academic and industrial interest in the last decades. It is especially important that nanocomposite material provides a novel way for modification and exploitation of natural polymers (1–3). Much effort has been devoted to the use of nano-meter size fillers from cellulose, starch and chitin as reinforcing agents in polymeric matrix. The advantages of natural nanofillers are

their low density, availability, biocompatibility, biodegradability and resulting lower cost relative to synthetic nanofillers.

Chitin, a (1→4)-linked polysaccharide composed of 2-acetamido-2-deoxy-β-D-glucopyranose residues, is widely distributed in nature (4,5). Materials made of chitin or modified chitin have the attractive advantages of being non-toxic, biodegradable, antibacterial and biocompatibility, which possess potentials for industrial, agricultural and medical applications (6,7). Chitin whiskers (CW) have been prepared from crab shells, squid pens, shrimp shells and tubes of *riftia pachypitila* tubeworms, and used as a new kind of nanofillers to reinforce synthetic polymeric matrix and natural ones (8–15). Chitin whiskers and chemical modified whiskers have been reported as the reinforcing elements in matrixes such as styrene and butyl acrylate copolymers, poly(caprolactone), chitosan, starch and natural rubber (9–17). However, chitin whisker has a low level of dispersion within the matrixes, so the development of chitin whisker based nanocomposites is restricted due to the present processing technique.

\*Address correspondence to: Ming Zeng, Engineering Research Center of Nano-Geomaterials of Ministry of Education, China University of Geosciences, Wuhan 430074, P. R. China. Tel: 0086-15623351996; E-mail: mingzeng@cug.edu.cn or zengming318@163.com

Waterborne polyurethanes with good flexibility, as a non-toxic, nonflammable and environment-friendly material, allow a broad range of application areas. These products present many features related to conventional solvent-borne polyurethanes with the advantages of presenting low viscosity at high molecular weight and good applicability (18–20). Waterborne poly(ester-urethane)s (WPU) with polyester as soft domain are a versatile class of man-made polymer products in the medical, automotive and industrial fields, and have been found to be susceptible to biodegradation by microorganisms (21,22). It is worth noting that the WPU based nanocomposites combines the elastic behavior of WPU with the strength and stiffness of the reinforcing phase (23,24).

In recent work, we studied the influence factors of casting method such as casting substrate, crosslinker and temperature for the natural polymer based composites (6,7,19,20,25). It is noted that the processing technique plays a major role in the mechanical properties of resulting composite films. Therefore, more research should focus on the effect of preparation method on the resultant morphology and mechanical properties. Ultra-sonification as a green preparation method is applied in the fields of chemistry and material science. However, the effects of ultra-sonification treatment on the structure, morphology and mechanical properties of nanocomposites have been scarcely reported. In this study, ultra-sonification method is expected to favor a high level of whisker dispersion within the polymer matrix, leading to satisfied interfacial interaction between chitin whiskers and polymeric matrix. A basic understanding of the behavior for casting films with or without ultra-sonification may be essential for a successful research and development of new material. We attempted to prepare and characterize novel nanocomposite films using waterborne poly(ester-urethane) as the semicrystalline matrix and chitin whisker as the reinforcing phase. The effects of ultra-sonification method and chitin whisker content on the chemical compositions, crystallization behavior, miscibility and mechanical properties of nanocomposites were investigated.

## 2 Experimental

### 2.1 Synthesis of WPU

Anionic WPU was prepared through a two-stage polymerization process. The WPU dispersion was prepared through our modified action process with NCO/OH=1.6. Commercial 2,4-toluene diisocyanate (TDI; Shanghai Chemical Co., China) was vacuum-dried at 80°C for 2 h, and used as hard segment. Poly(ethylene glycol adipate) (PEG;  $M_n = 1982$ ; Tiangou Polyurethane Factory, Jiangsu, China) was vacuum-dried at 120°C for 5 h, and used as soft segment. Dimethylol propionic acid (DMPA, Chengdu Polyurethane Co., China) was also vacuum-dried at 110°C for 2 h, and

used as chain extender and anionic center. Triethylamine (TEA; Jiangbei Chemical Co., China) and ketone as neutralized reagent and solvent, respectively, were immersed in 3-Å molecular sieves for more than a week to dehydrate before use.

The dry PEG was introduced in a three-necked flask, and heated to 80°C with mechanical stirring, and then TDI in one portion was added with stirring to be continued at 80°C for 1 h. Then, an equivalent amount of dried DMPA was added in one portion to the mixture. The reaction was carried out for 2–3 h until the NCO-group content reached a given value, as determined by dibutylamine back titration (18). Ketone was added to reduce the viscosity of the prepolymer. Finally, the product was cooled to 45°C, and neutralized with TEA. The WPU was formed by dispersing in deionized water for a period of 30 min to get the solid content of the WPU to be 20 wt%.

### 2.2 Preparation of CW

Chitin was supported by Zhejiang Jinke Sea Biochemical Co. (China), and its viscosity average molecular weight ( $M_\eta$ ) and degree of acetylation are  $1.31 \times 10^6$  and 92.5%, respectively. It was used without further treatment. The CW was prepared based on the methods reported [8–10,13,16,17]. The ultrasound generator (JY88—II type bio-cell disrupter) was manufactured by Shanghai Xin Zhi Biology Research Institute, and Ningbo Xin Zhi Science and Equipment Institute, China.

The CW suspension was prepared by hydrolyzing the chitin sample with 3N HCl at the boiling point under stirring for 1.5 h. The ratio of 3N HCl to chitin was 30 ml/g. After acid hydrolysis, the suspensions were diluted with distilled water followed by centrifugation (5000 tr/min for 5 min) and decanting the supernatant, then the residue was treated two times according to the above process. Next, the suspension were transferred to a dialysis bag and dialyzed in the running water for 6 h, and then in the distilled water for 24 h until the pH=4 was reached. The dispersion of whisker (3.3 wt%) was completed by three successive 2-min ultrasonic treatments under the ultrasound power of 500 W for every 40 ml aliquot. The obtaining whisker was subsequently filtered to remove residual aggregates, and then the CW suspension was obtained. Finally, the CW suspension was refrigerated prior to further use after adding sodium azide to prevent bacterial growth.

### 2.3 Fabrication of Nanocomposite Films

Desired quantities of the suspensions of CW and WPU mentioned above were mixed together, and then stirred at room temperature for 3 h to obtain a mixture suspension. The different weight ratio of CW in solid content of the mixture dispersion (i.e., 5, 10, 20, and 30 wt%) with and without ultrasound treatment were coded as 5%CW/WPU,

10%CW/WPU, 20%CW/WPU, and 30%CW/WPU, and 5%CHW/WPU, 10%CHW/WPU, 20%CHW/WPU, and 30%CHW/WPU, respectively. There are many influence factors of ultrasound treatment affecting the ultimate mechanical properties of nanocomposite films. The ultrasound treatment conditions were optimized in terms of ultrasound power, treatment time and treating quantity. The CW/WPU series mixtures were treated by two successive half-minute ultrasonic treatments under the ultrasound power of 500 W for every 40 ml aliquot. Then all mixtures were cast on a glass plate mold and dried at 50°C for 24 h to obtain casting films. Pure film of WPU and dried CW powder were coded as WPU and CW, respectively.

## 2.4 Characterization

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was carried out on a Thermo Nicolet 670 spectrometer. Spectra in the optical range of 4000–500  $\text{cm}^{-1}$  were collected over 64 scans with a resolution of 4  $\text{cm}^{-1}$ . The measurements were made at room temperature, on a diamond using a variable-angle ATR unit at a nominal incident angle of 45°. Optical alignment of the unit was set to achieve maximum throughput of the infrared beam to the detector. Samples were taken at random from the flat films.

Wide-angle X-ray diffraction (WAXD) were recorded on an X-ray diffraction (D/MAX3B, Rigaku Denki, Japan), by using Cu K $\alpha$  radiation ( $\lambda = 15.405$ ) at 40 kV and 30 mA with a scan rate of 4°/min. The diffraction angle ranged from 10 to 50°.

Dynamic mechanical analysis (DMA) was carried out with a dynamic mechanical thermal analyzer (DMTA-V, Rheometric Scientific Co., USA) at 1 Hz and a heating rate of 5°C/min in the temperature range from 0 to 120°C. The specimens with a typical size of 10 mm  $\times$  10 mm (length width) were used here.

The images of chitin whisker were observed by environmental scanning electron microscopy (ESEM, JSM-35CF, NEC, Japan). Scanning electron microscopy (SEM) images of the films were taken with a microscope (X-650, Hitachi, Japan). The films were frozen in liquid nitrogen and snapped immediately, and then vacuum-dried. The surface and cross section of the films were sputtered with gold, and then observed and photographed.

Thermogravimetric analysis's (TGA) of the specimens with 1 mm length and 1 mm width were carried out with a thermobalance (STA409, Netzsch, Germany) under air atmosphere from 25 to 600°C, at a heating rate of 10°C/min.

Tensile strength and elongation at break of the films were measured on a versatile tester (CMT-6503, Shenzhen SANS Test Machine Co. Ltd., China) according to the ISO6239-1986 standard with a tensile rate of 5 mm/min. The size of the films was 70 mm length, 10 mm width, with 50 mm

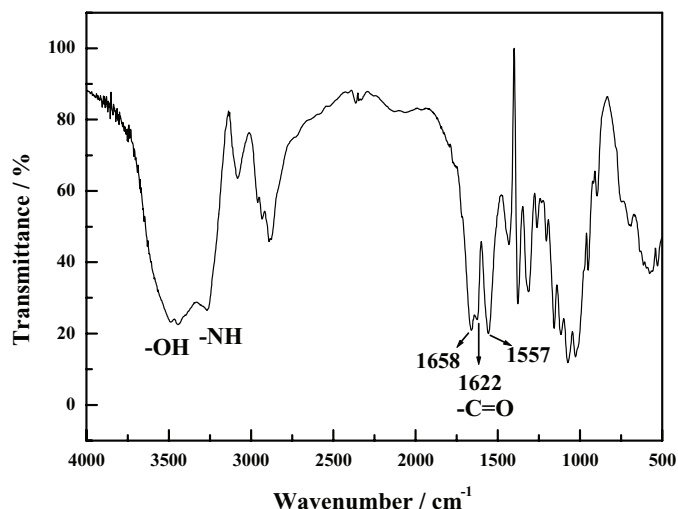


Fig. 1. Fourier transform infrared spectrum of chitin whisker obtained from the evaporation of the chitin whisker suspension.

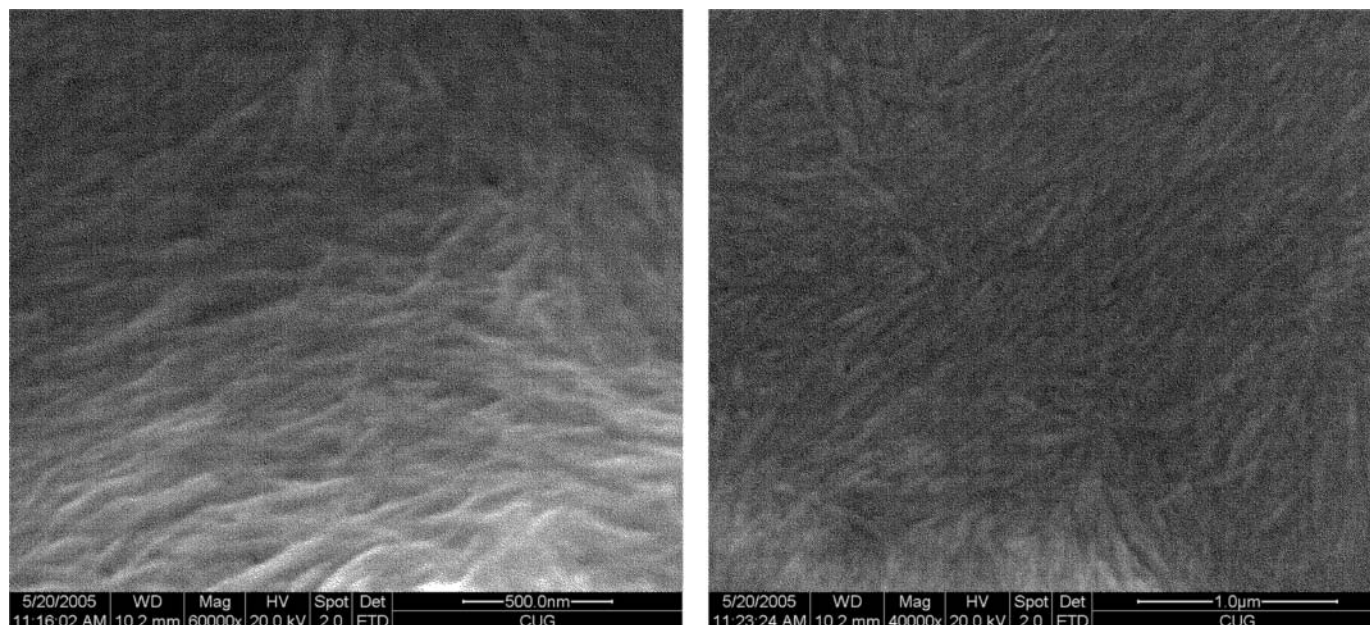
distance between two clamps. Five parallel measurements were carried out for every sample.

## 3 Results and Discussion

### 3.1 Structure and Morphology of Chitin Whisker

A Fourier transform infrared spectrum (Fig. 1) of chitin whisker was obtained from the evaporation of chitin whisker suspension in order to display the absence of residual proteins on the fragments. In the carbonyl region, the spectrum represents three strong absorption peaks at 1658, 1622 and 1557  $\text{cm}^{-1}$  corresponding to characteristic peaks of chitin whisker obtained from crab shells (10,16). The absence of the peak at 1540  $\text{cm}^{-1}$  corresponding to the proteins proves that the successive treatments were strong to eliminate all the proteins and obtain the pure chitin whiskers.

Figure 2 shows environmental scanning electron microscopy images with different scales of chitin whisker obtained from the evaporation of whisker suspension on the surface of mica. Such a suspension exhibited a colloidal behavior due to the presence of the positive charges ( $\text{NH}_3^+$ ) on the chitin whisker surface, which resulted from the protonation of the amide group of chitin in acidic conditions. The suspension contained chitin fragments consisting of both individual microcrystals and aggregated microcrystals. The microcrystals seem to be entangled based on the images, but individual chitin whiskers are not very difficult to observe. These fragments have a broad distribution in length (L) ranging from 100 to 650 nm and diameter ranging from 10 to 70 nm. There is no major morphological change associated with the reported values for chitin whiskers obtained from crab shells (10,16).



**Fig. 2.** Environmental scanning electron microscopy images of chitin whisker obtained from the evaporation of chitin whisker suspension on the surface of mica (left: high magnification; right: low magnification).

### 3.2 Crystallization Behavior and Miscibility of Nanocomposites

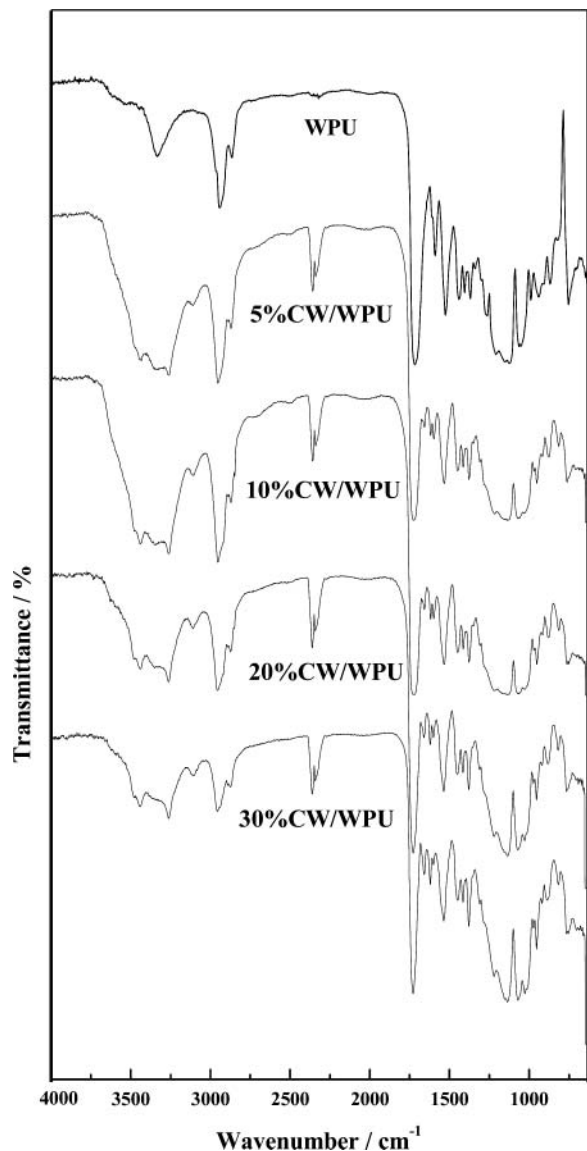
Polyurethanes are capable of forming several kinds of hydrogen bonds that have been the subjects of numerous investigations using infrared spectroscopy (25–27). Almost all of the infrared research on WPU has been focused on two principal vibration regions: the NH stretching vibration and the C=O stretching vibration. The NH group in the urethane linkage is the donated proton, while the acceptor groups may include urethane C=O as well as C=O of the ester linkage when polyester is present. Changes in the frequency and intensity of CO and NH absorption bands are correlated to structural alteration. In this investigation, the presence of functional NCO groups of WPU is expected to allow favorable interactions with hydroxyl and acetamide groups of chitin.

Figure 3 shows the infrared spectra ( $4000\text{--}500\text{ cm}^{-1}$ ) of the films WPU and CW/WPU. The intensities of hydrogen-bonded  $\text{--NH}$  and hydroxyl group centered at  $3358$  and  $3485\text{ cm}^{-1}$ , respectively, increased as the introduction of chitin whisker for the films CW/WPU with the ultrasound treatment. Meanwhile, a shoulder peak centered around  $3440\text{ cm}^{-1}$  for the films CW/WPU became obviously strong, implying that original inter- and intra-molecular hydrogen bonds in the WPU networks were destroyed resulting from the dispersion of chitin whisker within WPU matrix. Furthermore, the band at  $2980\text{--}2850\text{ cm}^{-1}$  of films CW/WPU assigned to the stretching of methylene groups of the polyester soft segment became weaker than that of pure film WPU (28–30). The intensity of the peaks decreased with an increase of CW, and the extent of decrease

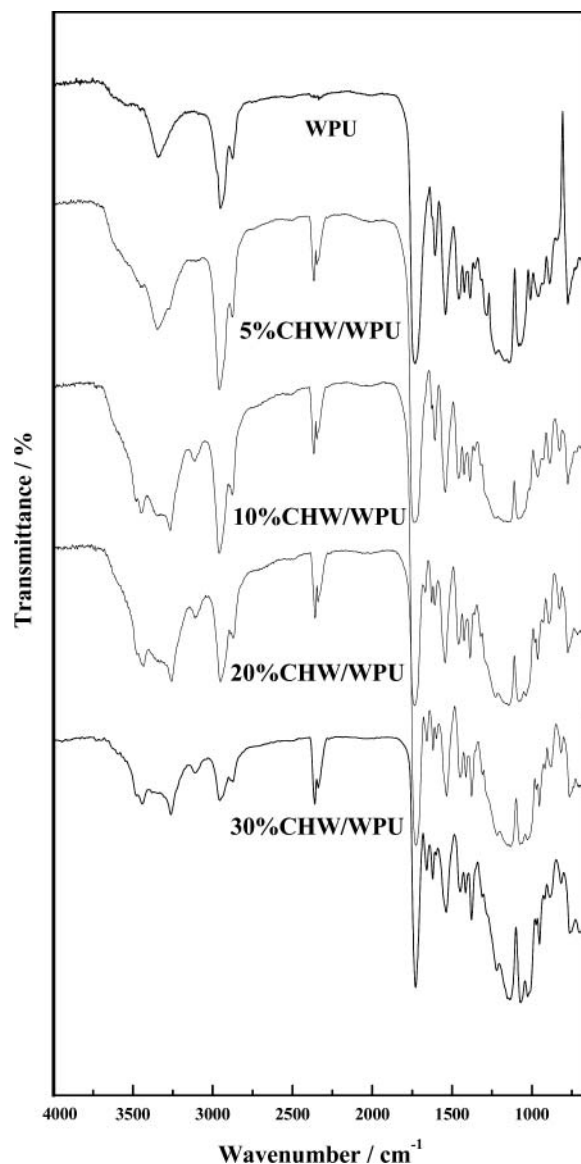
is related to the blending ratio, also implying that abundant hydroxyl and acetamide groups in chitin whisker facilitate the formation of hydrogen bonding with NCO group in the hard segment of WPU. Moreover, the band at  $1640\text{ cm}^{-1}$  was attributed to the hydrogen-bonded C=O formed from the polyester soft segment. The intensities of the peaks were lower for the films CW/WPU than that of the film WPU, which suggest that there exists intermolecular interaction between WPU and CW. In addition, as the content of chitin whisker was increased from 5 to 30 wt%, the chitin whisker characteristic peaks for the films CW/WPU appeared apparently.

Figure 4 shows the infrared spectra ( $4000\text{--}500\text{ cm}^{-1}$ ) of the films WPU and CHW/WPU without the ultrasound treatments. The similar tendency is observed from the CO and NH regions from Figure 4, which suggest that interfacial interaction occurred between both components. Therefore, it confirmed that there are intermolecular interactions between WPU and CW for the nanocomposite films with or without ultrasound treatment.

WAXD measurements were carried out to evaluate the crystalline state of the films. Figures 5 and 6 illustrate WAXD patterns of WPU, CW, and 10 wt% chitin whisker reinforcing WPU without and with ultra-sonification treatments. Two major scattering peaks centered at  $12^\circ$  and  $19^\circ$  for CW powder, suggesting the relatively low DD value of original chitin whisker according to the conclusion obtained by Cho. et al. (16). For polyurethanes containing crystalline soft segments with amorphous hard segments, the X-ray scattering peak comes mainly from the crystalline soft segments. However, a broad reflection centered at  $21^\circ$  for WPU film indicating the amorphous nature, resulting



**Fig. 3.** FTIR spectra of WPU and CW/WPU nanocomposite films with ultrasonic treatment.



**Fig. 4.** FTIR spectra of WPU and CHW/WPU nanocomposite films without ultrasonic treatment.

from the relatively low reaction temperature and cure temperature of the preparation [21]. In Figure 5, the WAXD pattern of film 10%CHW/WPU exhibits the presence of four major peaks at  $2\theta = 19, 21, 22$  and  $24^\circ$ . These four peaks in the wide-angle region show the sharp shape and low intensity, which correspond to the order arrangement of polyester soft segment, indicating the weak intermolecular interactions between WPU and CW resulting in the crystalline domain formation. In Figure 6, the diffraction peak for the film 10%CW/WPU became slightly higher and narrower than the pure WPU film. Moreover, the amorphous peak centered at  $2\theta$  angles of  $19^\circ$  similar with CW main scattering peak, resulting from chitin whisker network formed within WPU matrix. The suppression of WPU crystallization found in the CW/WPU nanocomposite might

be due to at least two factors. One is the formation of the intermolecular hydrogen bond between CW and polyester based WPU. Another is the rigid environment that arises from inflexible polysaccharide molecules network formation of nano-meter size chitin whisker.

The storage modulus  $E'$  and mechanical loss factor ( $\tan \delta$ ) as functions of temperature for the films are shown in Figures 7 and 8, respectively. The storage moduli of CW could not be obtained because it is too brittle to form the film. In Figure 7, the  $E'$  value of the film 10%CHW/WPU was lower than that of the WPU film when the temperature increased to  $50^\circ\text{C}$ . On the contrary, the film CW/WPU shows higher storage moduli than that of the pure WPU film in the same temperature range. The  $E'$  values of the film WPU decreased dramatically with an increase of

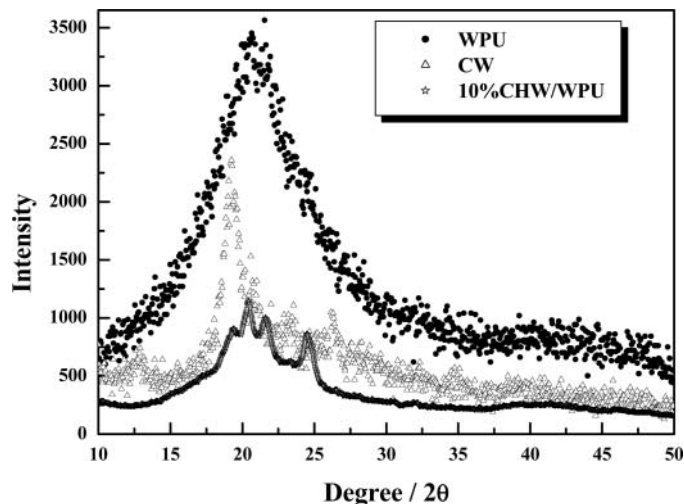


Fig. 5. WAXD spectra of WPU, CW and 10%CHW/WPU.

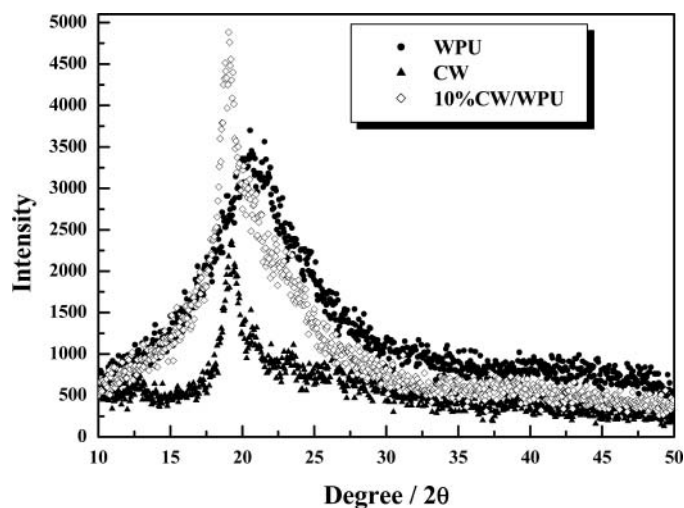


Fig. 6. WAXD spectra of WPU, CW and 10%CW/WPU.

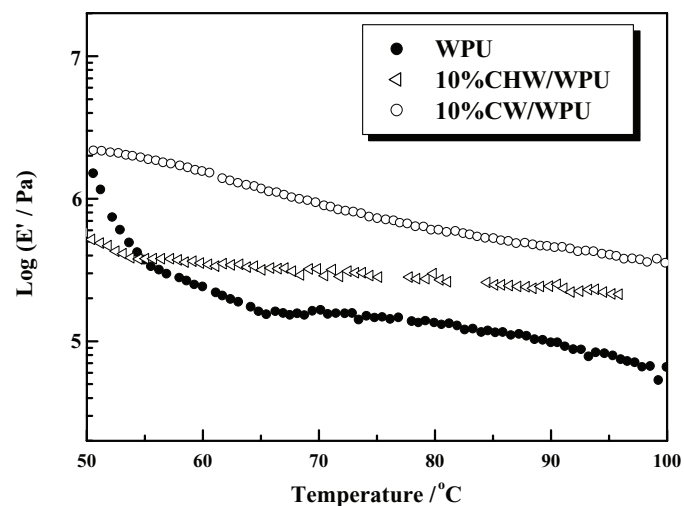


Fig. 7. Storage modulus as a function of temperature for the films WPU, 10%CHW/WPU, and 10%CW/WPU.

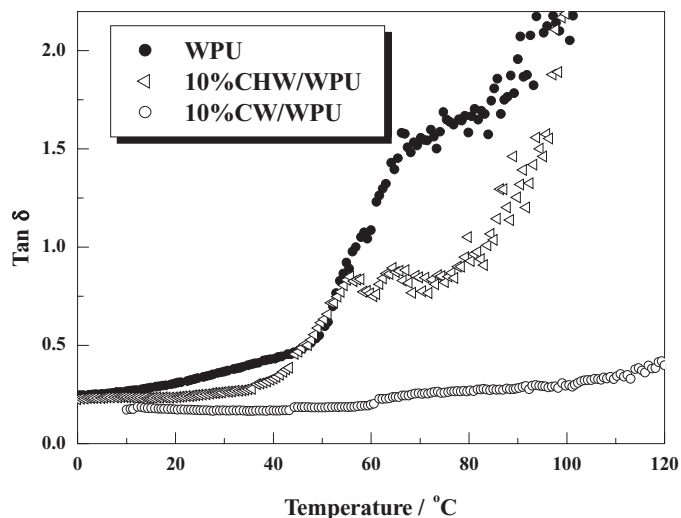
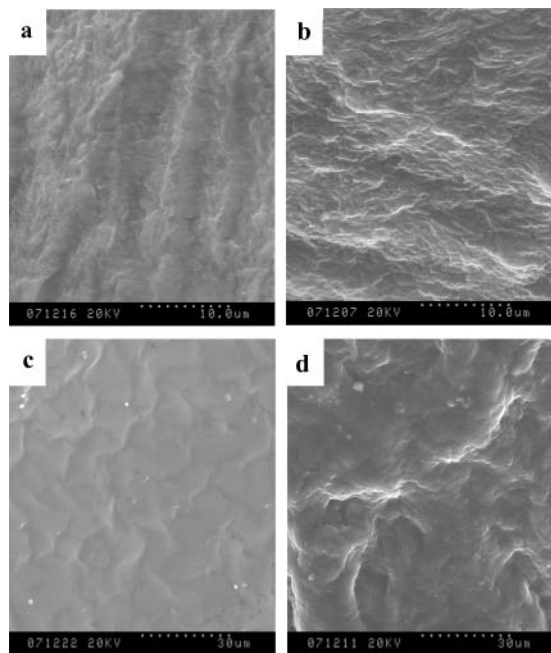


Fig. 8. Tan  $\delta$  as a function of temperature for the films WPU, 10%CHW/WPU, and 10%CW/WPU.

temperature from 50 to 70°C, accompanying the transition from plastic state to rubbery state. However, the films CHW/WPU and CW/WPU had relatively higher storage modulus even when the temperature was above 100°C. The improvement of modulus for the film with nano-meter size chitin whisker added was attributed to the formation of a rigid chitin whisker network within the WPU matrix. Moreover, the film CW/WPU had a higher moduli than that of CHW/WPU film even when the temperature above 100°C, resulting from more effective reinforcement for the film CW/WPU than that of the CHW/WPU film without the ultrasound treatment.

The temperature dependence of tan  $\delta$  from DMA is given in Figure 8. Usually, the  $\alpha$ -relaxation, tan  $\delta$  peak, reflects the glass transition, and may be analyzed to provide information about the motion of molecules (31). If the two starting materials had phase separation and prevented interaction, there are two  $T_g$  peaks corresponding to two components for the blends. There is only one peak of  $T_g$  corresponding to WPU in the DMA thermogram for the nanocomposite films, indicating a certain degree of miscibility between CW and WPU. Furthermore, the height and width of the  $\alpha$ -relaxation peak can be used to analyze the trend of molecular motion of cross-linking polymers (31). The height of the tan  $\delta$  peaks for the films CHW/WPU and CW/WPU decreased compared with that of the pure film WPU. Because tan  $\delta$  is the ratio of viscous to elastic moduli, it can be surmised that the decreasing height is associated with a lower segmental mobility and thus is indicative of a higher degree of crosslinking density with chitin whisker added.

In addition, the lower magnitude of tan  $\delta$  peak of the CW/WPU film suggesting that the stronger intermolecular interaction occurred between WPU and CW using the ultrasound treatment.



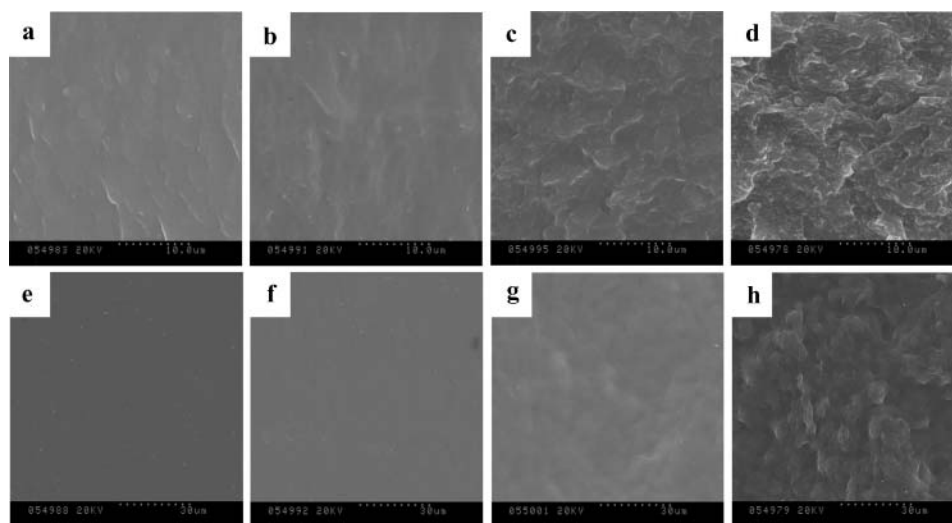
**Fig. 9.** Cross sections of the films 10%CHW/WPU (a) and 30%CHW/WPU (b); and free surfaces of the films 10%CHW/WPU (c) and 30%CHW/WPU (d).

SEM observation can give information of the morphological change and miscibility (32). Figures 9 and 10 show the SEM photographs of the cross-sections (top) and free surfaces (bottom) of the films CHW/WPU and CW/WPU, respectively. The cross-section and surface morphologies of CW/WPU films are completely different from that of CHW/WPU films. In Figure 9, the CHW/WPU films display rather rough surfaces, indicating the heterogeneous nature of the reaction mixture leads to a two-phase mor-

phology. Meanwhile, the films also display a rather rough cross-sections, the reaction mixture gives rise to a bimodal distribution of chitin whisker in WPU matrix because of chitin whisker with the poor dispersion within WPU matrix. However, different morphology was observed in the SEM photographs of the films CW/WPU in Figure 10. No clear two-phase morphologies appeared in the free surfaces and cross-sections for the CW/WPU films when the chitin whisker content increased from 5 to 10 wt%, compared with the micro-domain structure of CHW/WPU films, indicating a strong interaction between CW and WPU. When the chitin whisker content was increased from 20 to 30 wt% in the CW/WPU films, the cross-section morphologies seem to form the rigid chitin network in the WPU matrix and become more dense structure, suggesting the effectiveness of the intermolecular penetration. In view of the SEM analysis of CW/WPU films with ultrasound treatment, the relatively strong intermolecular interaction between WPU and CW occurred to interrupt the crystal domain of WPU and form compact chitin network with higher dispersion level, resulting in a good miscibility between both components.

### 3.3 Thermal and Mechanical Properties of Nanocomposites

Thermal degradation patterns of the films are shown in Figures 11 and 12. A small weight loss at 25–200°C was assigned to the release of moisture and TEA from the samples. The weight losses at 300–500°C were believed to be caused by oxidation and degradation. Almost complete decomposition was observed at 600°C. Generally, the thermal degradation of the blend films in dynamic conditions and in the presence of oxygen shows three decomposition stages (33). The degradation onset temperature of the nanocomposite films is around 250°C (start for the first



**Fig. 10.** Cross sections of the films 5%CW/WPU (a), 10%CW/WPU (b), 20%CW/WPU (c) and 30%CW/WPU (d); and free surfaces of the films 5%CW/WPU (e), 10%CW/WPU (f), 20%CW/WPU (g) and 30%CW/WPU (h).



**Table 1.** Thermogravimetric analyses data of the samples: temperatures (°C) according to the weight loss (%)

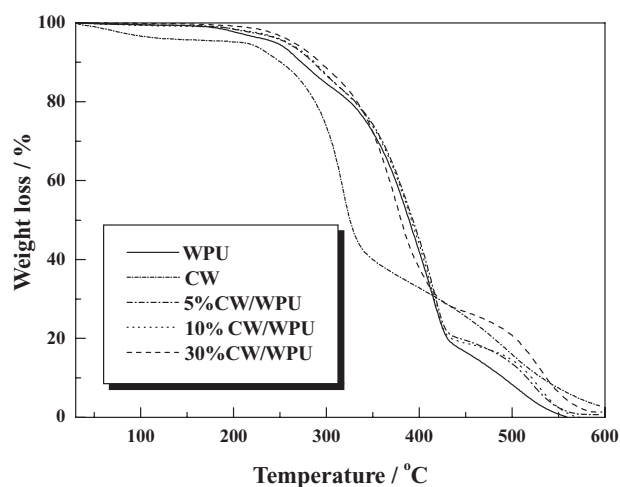
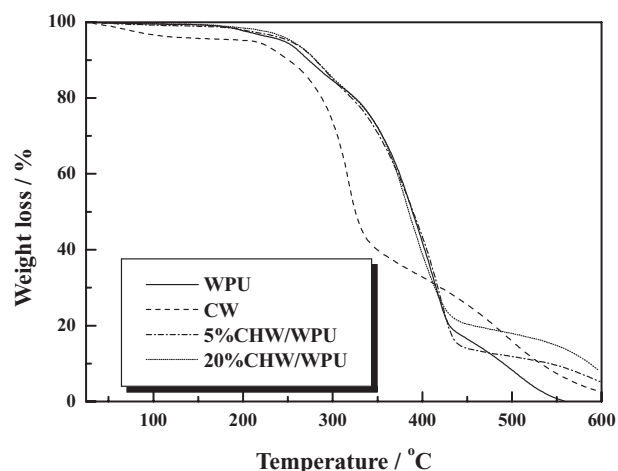
| Weight loss/% | WPU | CW  | 5% CW/WPU | 5% CHW/WPU | 10% CW/WPU | 20% CHW/WPU | 30% CW/WPU |
|---------------|-----|-----|-----------|------------|------------|-------------|------------|
| 5             | 245 | 208 | 256       | 252        | 257        | 256         | 264        |
| 10            | 273 | 249 | 284       | 280        | 286        | 277         | 293        |
| 20            | 325 | 286 | 330       | 321        | 329        | 322         | 333        |
| 30            | 355 | 304 | 359       | 351        | 358        | 353         | 353        |
| 50            | 388 | 324 | 392       | 390        | 391        | 385         | 380        |
| 80            | 430 | 479 | 442       | 429        | 434        | 429         | 503        |

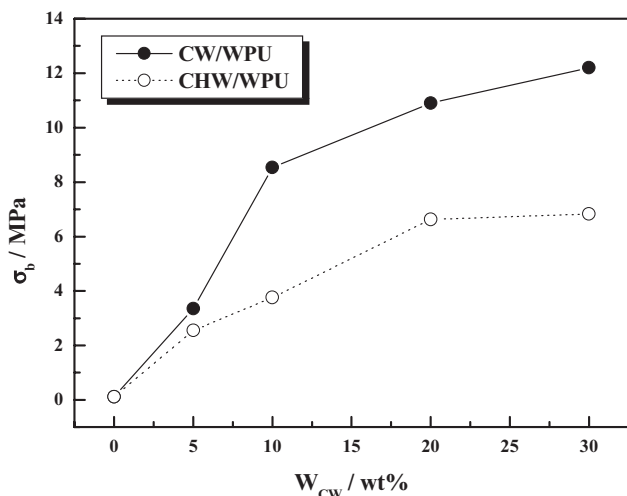
stage), and an increasing decomposition rate is observed between 250 and 380°C (the second stage) when the weight losses reached about 50 wt%. The third stage of decomposition for temperatures are higher than 400°C corresponding to the advanced fragmentation of the chain formed in the first and second stages of decomposition, as well as to the secondary reactions of dehydrogenation and gasification processes. Data related to the temperature corresponding to the weight losses of the initial weights are summarized in Table 1. Chitin whiskers exhibited two degradation peaks at about 260 and 350°C. The CW/WPU and CHW/WPU films exhibited much higher thermal stability than that of the pure WPU film and chitin whisker. The hydrogen-bonded chitin whisker network induced a thermal stabilization of the composite up to 250°C, which is higher than the temperature of 200°C at which chitin whisker starts to decompose, indicating the reinforcing effect of nano-meter size chitin whiskers in the WPU matrix. These findings supported the conclusions obtained by DMA and SEM. In addition, there is no clear increase of the thermal stability for the nanocomposite films CW/WPU and CHW/WPU when the chitin whisker content was increased from 5 wt% to 10 wt% and from 5 wt% to 20 wt%, respectively. However, it is interesting that when the chitin whisker content increased to 30 wt% for the CW/WPU film, there existed a distinct increase compared with other films. Both whisker-

matrix interaction and chitin whisker network are responsible reasons for the higher thermal stability with increase of chitin whisker content.

Furthermore, both 5%CW/WPU and 5%CHW/WPU films showed an almost identical two-step weight loss behavior, with the main difference being observed when the temperature is higher than 300°C. The film 5%CW/WPU appeared as having the higher thermal stability among the wide temperature range, compared with the film 5%CHW/WPU without the ultrasound treatment. The results suggesting that more effective reinforcement and stronger interactions between WPU and CW occurred with the ultrasound treatment.

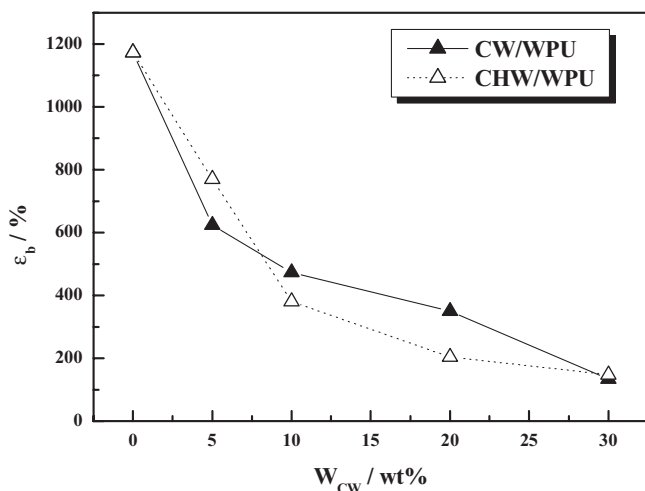
The CW content  $W_{CW}$  (wt%) dependence of the tensile strength and elongation at break for the films CW/WPU and CHW/WPU are shown in Figures 13 and 14, respectively. The  $\sigma_b$  values for the CHW/WPU films increased from 2.55 to 6.83 MPa with an increase of CW content from 5 to 30 wt%. Similarly, the tensile strength of the CW/WPU films increased with increasing CW content from 3.35 to 12.2 MPa. Therefore, the tensile strength of the nanocomposite films is significantly higher than that of the pure WPU film. The improvement in the tensile strength could be resulted from an enhancement in interpenetration and the interaction between WPU and CW molecules. On the contrary, the elongation at break values for the

**Fig. 11.** Thermogravimetric analyses of WPU, CW, 5%CW/WPU, 10%CW/WPU and 30%CW/WPU.**Fig. 12.** Thermogravimetric analyses of WPU, CW, 5%CHW/WPU and 20%CHW/WPU.



**Fig. 13.** CW content ( $W_{cw}$ ) dependence of the tensile strength ( $\sigma_b$ ) for the films CW/WPU and CHW/WPU.

nanocomposite films decreased with an increase of chitin whisker content accordingly shown in Figure 14. However, all nanocomposite films contain the relatively high strain values ( $> 100\%$ ) even when the chitin whisker content reached at 30 wt%, resulting from the relatively high density with chitin whisker added in WPU matrix. It is worth noting that the presence of chitin network in the WPU matrix results in a significant increase of strength, without much lowering the elongation at break. In addition, compared with the films CHW/WPU, the films CW/WPU possessed better tensile strength and similar elongation at break values. This result implies that the film CW/WPU containing CW content have both more complete chitin whisker cross-linking networks than that of the CHW/WPU films without ultrasound treatment, and stronger interaction between CW and WPU than others.



**Fig. 14.** CW content ( $W_{cw}$ ) dependence of elongation at break ( $\epsilon_b$ ) for the films CW/WPU and CHW/WPU.

## 4 Conclusions

Two series of nanocomposite films, CW/WPU and CHW/WPU, were successfully prepared from waterborne poly(ester-urethane) and chitin whisker with and without ultrasound treatment, respectively. The results revealed that both nanocomposite films had higher thermal stability and tensile strength than the pure WPU film when CW content was lower than 30 wt%, suggesting a certain degree of miscibility and nano-meter size whisker reinforcing effect. It was worth noting that the CW/WPU films exhibited better miscibility, storage modulus, thermal stability and tensile strength than those of the CHW/WPU films over the entire composition range studied here. This difference can be attributed to a higher level of whisker dispersion within WPU matrix resulting in stronger entanglement and interaction between WPU and CW in the CW/WPU films with ultrasound treatment. Therefore, the structure, miscibility and mechanical properties of the nanocomposite films depended significantly on the preparation method, and using the ultrasound treatment can effectively improve the miscibility and mechanical properties of the casting nanocomposite films with nano-meter size chitin whisker added.

## Acknowledgments

This work was supported by national high-tech R&D program (863 program) for the 11th five-year plan, Ministry of Science and Technology, P. R. China (2006AA100215), SRF for ROCS, State Education Ministry, P. R. China, the Special Fund for Basic Scientific Research of Central Colleges, China University of Geosciences (Wuhan) (contract grant number: CUGL090223), and the major grant of the State Key Laboratory of Geological Process and Mineral Resources (contract grant number: GPMR200918).

## References

1. Azizi Samir, M.A.S., Alloin, F. and Defresne, A. (2005) *Biomacromolecules*, 6, 612–626.
2. Azizi Samir, M.A.S., Montero Mateos, A., Alloin, F., Sanchez, J.Y. and Dufresne, A. (2004) *Electrochem. Acta.*, 49, 4667–4677.
3. Dufresne, A., Kellerhals, M.B. and Witholt, B. (1999) *Macromolecules*, 32, 7396–7401.
4. Muzzarelli, R.A.A. Chitin, Pergamon Press: New York, p. 1, 1977.
5. Rinaudo, M. (2006) *Prog. Polym. Sci.*, 31, 603–632.
6. Zeng, M., Zhang, L., Wang, N. and Zhu, Z. (2003) *J. Appl. Polym. Sci.*, 90, 1233–1241.
7. Zeng, M., Zhang, L. and Zhou, Y. (2004) *Polymer*, 45, 3535–3545.
8. Marchessault, R.H., Morehead, F.F. and Walter, N.M. (1959) *Nature*, 184, 632–633.
9. Revol, J.F., Godbout, L. and Dong, X.M. (1994) *Liq. Cryst.*, 16, 127–134.
10. Gopalan Nair, K. and Dufresne, A. (2003) *Biomacromolecules*, 4, 657–665.

11. Gopalan Nair, K. and Dufresne, A. (2003) *Biomacromolecules*, 4, 666–674.
12. Gopalan Nair, K. and Dufresne, A. (2003) *Biomacromolecules*, 4, 1835–1842.
13. Lu, Y., Weng, L. and Zhang, L. (2004) *Biomacromolecules*, 5, 1046–1051.
14. Paillet, M. and Dufresne, A. (2001) *Macromolecules*, 34, 6527–6530.
15. Morin, A. and Dufresne, A. (2002) *Macromolecules*, 35, 2190–2199.
16. Sriupayo, J., Supaphol, P. and Blackwell, J. (2005) *Carbohydr. Polym.*, 62, 130–136.
17. Sriupayo, J., Supaphol, P. and Blackwell, J. (2005) *Polymer*, 46, 5637–5644.
18. Hepburn, C. *Polyurethane Elastomers*, Applied Science Publishers: New York, pp. 101 to 13, 1982.
19. Zeng, M. and Zhang, L. (2006) *Macromolecular Materials and Engineering*, 291, 148–154.
20. Zeng, M. and Zhang, L. (2006) *J. Appl. Polym. Sci.*, 100, 708–714.
21. Chen, K.S., Yu, T.L. and Chen, Y.S. (2001) *J. Polym. Res.*, 8, 99–109.
22. Howard, G.T. (2002) *International Biodeterioration & Biodegradation*, 49, 245–252.
23. Brinkman, E. and Vandevoorde, P. (1998) *Progress in Organic Coatings*, 34, 21–25.
24. Duecoffre, V., Diener, W., Flosbach, C. and Schubert, W. (1998) *Progress in Organic Coatings*, 34, 200–205.
25. Zeng, M., Zhang, L. and Kennedy, J.F. (2005) *Carbohydr. Polym.*, 60, 399–409.
26. Luo, N., Wang, D.N. and Ying, S.K. (1996) *Polymer*, 37, 3577–3583.
27. McKiernan, R.L., Heintz, A.M., Hsu, S.L. and Atkins, E.D.T. (2002) *Macromolecules*, 35, 6970–6974.
28. Queiroz, D.P., de Pinho, M.N. and Dias, C. (2003) *Macromolecules*, 36, 4195–4200.
29. Yen, F.S., Lin, L.L. and Hong, J.L. (1999) *Macromolecules*, 32, 3068–3079.
30. Yen, F.S. and Hong, J.L. (1997) *Macromolecules*, 30, 7927–7938.
31. Ishida, H. and Allen, D.J. (1998) *Polymer*, 39, 4487–4495.
32. Kuo, S.W., Chan, S.C. and Chang, F.C. (2003) *Macromolecules*, 36, 6653–6661.
33. Filip, D., Simionescu, C.I. and Macocinschi, D. (2002) *Thermochimica Acta*, 395, 217–223.