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Preparation and characterization of α-chitin whisker-reinforced chitosan nanocomposite films with or without heat treatment

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Abstract

α-Chitin whisker-reinforced chitosan nanocomposite films were prepared by solution-casting technique. The α-chitin whiskers were prepared by acid hydrolysis of α-chitin from shrimp shells. The length of the as-prepared whiskers ranged between 150 and 800 nm, while the width ranged between 5 and 70 nm, with the average values being about 417 and 33 nm, respectively. The addition of α-chitin whiskers did not affect much the thermal stability and the apparent degree of crystallinity of the chitosan matrix. The tensile strength of α-chitin whisker-reinforced chitosan films increased from that of the pure chitosan film with initial increase in the whisker content to reach a maximum at the whisker content of 2.96 wt% and decreased gradually with further increase in the whisker content, while the percentage of elongation at break decreased from that of the pure chitosan with initial increase in the whisker content and leveled off when the whisker content was greater than or equal to 2.96 wt%. Both the addition of α-chitin whiskers and heat treatment helped improve water resistance, leading to decreased percentage of weight loss and percentage degree of swelling, of the nanocomposite films.

Keywords: Nanocomposite; α-chitin whisker; Chitosan; Mechanical properties; Swelling behavior

1. Introduction

Nanocomposites are a relatively new class of composites with at least one phase having a dimension in the vicinity of 1–1000 nm. As most of the present-day nanofillers used to prepare nanocomposites with synthetic polymeric materials are inorganic (Schmidt & Malwitz, 2003), their processability, biocompatibility, and biodegradability are much more limited than those of naturally organic ones. In nature, a large number of animals and plants synthesize extracellular high-performance skeletal biocomposites that consist of a matrix reinforced by fibrous biopolymers (Neville, 1993; Preston, 1967). Cellulose is a classical example where the reinforcing elements exist as whisker-like microfibrils that are biosynthesized and deposited in a continuous manner (Itoh, O'Neil, & Brown, 1983; Itoh & Brown, 1984). Favier, Chanzy, and Cavaillè (1995) was the first to prepare cellulose whiskers from tunic of tunicate *Microcosmus fulcatus* by acid hydrolysis (i.e. tunicin whiskers) and use them as reinforcing nanofillers in a terpolymer of styrene and butyl acrylate (i.e. poly(S-*co*-BuA) latex). Since then, tunicin whiskers have been used as reinforcing nanofillers in poly(β-hydroxyoctanoate) (PHO) (Dubief, Samain, & Dufresne, 1999), poly(hydroxyalkanoate) (PHA) (Defresne, Kellerhals, & Witholt, 1999), plasticized maize starch (Neus Angles, & Dufresne, 2000a,b), and poly(oxyethylene) (Samir, Alloin, Sanchez, & Dufresne, 2004). Cellulose whiskers from wheat straw can also be prepared and have been used as reinforcing nanofillers in poly(S-*co*-BuA) latex (Dufresne, Cavaillè & Helbert, 1997; Helbert, Cavaillè & Dufresne, 1996).

Whiskers from other polysaccharides, such as starch (Dufresne, Cavaillè, & Helbert, 1996; Dufresne & Cavaillè, 1998) and chitin (Marchessault, Morehead, & Walter, 1959; Revol & Marchessault, 1993), can also be prepared. Unlike tunicin whiskers which can only be prepared by hydrolysis in strong sulfuric acid (H_2SO_4) solutions (Favier et al., 1995; Dubief et al., 1999; Defresne et al., 1999; Neus Angles, & Dufresne, 2000a,b; Samir et al., 2004; Helbert et al., 1996; Dufresne et al., 1997; Marchessault et al., 1959;

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Revol & Marchessault, 1993), both starch and chitin whiskers can be prepared by hydrolysis in hydrochloric acid (HCl) solutions (Dufresne et al., 1996; Marchessault et al., 1959). Chitin is a high molecular weight biopolymer found predominantly in exoskeleton shells of arthropods as well as the internal flexible backbone of cephalopods. Chemically, chitin molecules consist of *N*-acetyl-D-glucosamine units. Chitin is known to be non-toxic, odorless, biocompatible with living tissues, and biodegradable (Kumar, 2000). Chitin whiskers have been successfully prepared from crab shells (Marchessault et al., 1959; Revol & Marchessault, 1993; Nair & Dufresne, 2003a,b,c; Lu, Wend & Zhang, 2004), squid pens (Paillet & Dufresne, 2001), and tubes of *Riftia pachyptila* tubeworms (Morin & Dufresne, 2002). Regardless of the chitin sources, the commonly-used hydrolytic condition for obtaining chitin whiskers is 3 N HCl at the boil for 90 min under vigorous stirring (Marchessault et al., 1959; Revol & Marchessault, 1993; Nair & Dufresne, 2003a,b,c; Lu et al., 2004; Paillet & Dufresne, 2001; Morin & Dufresne, 2002).

Since there have not been prior reports on the preparation of chitin whiskers from shrimp shells, α-chitin whiskers were then prepared by acid hydrolysis of α-chitin from shells of *Penaeus merguiensis* shrimps in the present contribution. Nanocomposite films using the obtained α-chitin whiskers as nanofillers were prepared by solution-casting from mixtures of chitosan solution and α-chitin whisker suspensions. The effect of α-chitin whiskers on thermal, crystal structure, mechanical, weight loss, and swelling behavior of α-chitin whisker-reinforced chitosan nanocomposite films was investigated and reported for the first time.

2. Experimental

2.1. Materials

Shells of *P. merguiensis* shrimps were donated from Surapon Foods Public Co., Ltd (Thailand). An aqueous solution of sodium hydroxide (NaOH) (50% w/w) was donated from KPT Corporation Co., Ltd (Thailand). Anhydrous NaOH pellets, sodium borohydride ($NaBH_4$), glacial acetic acid (99.8% w/w), and hydrochloric acid (HCl) (37% w/w) were of analytical grade and purchased from Carlo Erba (Italy). Sodium azide was purchased from J.T. Baker (USA). All of the materials were used without further purification.

2.2. Preparation of chitosan

Chitosan was obtained from deacetylation of β-chitin from pens of *Loligo pealei* squid by refluxing β-chitin flakes in 50% w/w NaOH solution containing 0.5% w/w $NaBH_4$ to prevent extensive depolymerization. The ratio of β-chitin flakes to NaOH solution was 1 g of the flakes to 10 ml of the NaOH solution. The deacetylation was performed by heating the mixture in an oil bath at 100° C for 2 h. The obtained chitosan flakes were dried in an oven at 60° C for another 24 h. The process was repeated about three times to obtain chitosan with high enough degree of deacetylation (DD). The DD of the as-prepared chitosan was determined based on an infrared spectroscopic method (Sabnis & Block, 1997) to be about 94.6%, while the viscosity-average was determined based on the Mark-Houwink equation ($[\eta]=K\bar{M}_v^a$, where $[\eta]$ is the intrinsic viscosity, $\bar{M}_v$is viscosity-average molecular weight, and K and a are constants specific to a polymer–solvent pair which, for chitin, they were determined to be 6.59×10^{-3} ml g^{-1} and 0.88 (Wang, Bo, Li, & Qin, 1991), respectively) to be about 1.53×10^6 Da.

2.3. Preparation of α-chitin whiskers

Decalcification and deproteinization of shrimp shells to obtain α-chitin were carried out according to the procedure described in reference (Shimahara & Takigushi, 1988). The DD of the obtained α-chitin was determined based on another infrared spectroscopic method (Sannan, Kurita, Ogura, & Iwakura, 1978) to be about 17.7%, while the viscosity-average molecular weight was determined based on the Mark-Houwink equation with K and a parameters being 8.93×10^{-2} ml g^{-1} and 0.71 (Wang et al., 1991), respectively, to be about 2.42×10^6 Da.

Chitin whiskers from the obtained α-chitin of shrimp shells were prepared based on the method of Nair and Dufresne (2003a,b,c); Lu et al. (2004); Paillet and Dufresne (2001); Morin and Dufresne (2002). The whisker suspension were prepared by hydrolyzing α-chitin samples with 3 N HCl at its boiling point (i.e. 104° C) for 90 min under vigorous stirring. The ratio of 3 N HCl to α-chitin was 30 cm^3 g^{-1}. After acid hydrolysis, the suspensions were diluted with distilled water, followed by centrifugation at 10,000 rpm for 5 min. This process was repeated three times. The suspension were then transferred to a dialysis bag and dialyzed in running water for 2 h and later in distilled water overnight. The pH level of the suspensions was later adjusted to 2.5. Dispersion of whiskers was completed by 5-min ultra-sonification treatment for every 40-cm^3 aliquot. Sodium azide was added to the suspensions to prevent bacterial growth and later refrigerated prior to further use. The solid content of the as-prepared whisker suspensions was about 1.48 wt%.

2.4. Preparation of α-chitin whisker-reinforced chitosan films

The chitosan solution was first prepared by dissolving 1 g of chitosan flakes in 49 g of 2% v/v aqueous solution of acetic acid with stirring at room temperature for 12 h. The as-prepared α-chitin whisker suspensions in varying amount were then added to the chitosan solution (with appropriate addition of 2% v/v aqueous solution of acetic acid to obtained 100 g of the mixed suspension) to achieve the whisker content in the range of 0–29.6 wt%. The chitosan/α-chitin whisker suspension was further stirred mechanically for 2 days before being poured onto a plastic mold. After the solvent was evaporated at 40° C for 2 days in a convection oven, α-chitin whisker-reinforced chitosan nanocomposite films with thicknesses varying between 30 and 50 μm were obtained.

2.5. Heat treatment

To decrease the solubility in water, both pure chitosan and α-chitin whisker-reinforced chitosan film samples were heat-treated by saturated steam in an autoclave at 110° C. After heat treatment for 5 min, the samples were removed from the autoclave and stored in a desiccator chamber at ambient temperature for at least 24 h prior to further characterization.

2.6. Characterization

Morphological appearance and sizes of the as-prepared α-chitin whiskers was observed using a JEOL JEM-200CX transmission electron microscope (TEM). Samples of α-chitin whiskers were prepared from a drop of a dilute α-chitin whisker suspension, which was deposited and let dry on a formvar grid.

Pure chitosan and α-chitin whisker-reinforced chitosan films without heat treatment were characterized for their thermal stability, crystalline structure and qualitative apparent degree of crystallinity, and tensile properties. A TGA 2950 DuPont thermogravimetric analyzer (TGA) was used to investigate the thermal stability of pure chitosan, as-prepared α-chitin whiskers, and α-chitin whisker-reinforced chitosan films. A sample of about 3–5 mg was placed in a platinum pan. The scanning range was 30–700° C using a heating rate of 10° C min^{-1} in nitrogen atmosphere. A Rint2000 Rigaku wide-angle X-ray diffractometer (WAXD) was used to determine the crystalline structure and the qualitative apparent degree of crystallinity of pure chitosan, as-prepared α-chitin whiskers, and α-chitin whisker-reinforced chitosan films. Cu Kα radiation was generated using a DC potential of 40 kV and a filament current of 30 mA. The scanning 2θ range was 5 to 40° at a scanning speed of 5°/min and a step scan of 0.02°. A Lloyd LRX universal tester was used to determine the tensile strength and the percentage of elongation at break of pure chitosan and α-chitin whisker-reinforced chitosan films, according to ASTM D882 standard test method. The dimension of the films was $15\times150\ \text{mm}^2$, with the thickness ranging from 30 to 50 μm. The gauge length and the crosshead speed were 50 mm and 50 mm min^{-1}, respectively. The reported values were averages from five measurements.

Heat-treated pure chitosan and α-chitin whisker-reinforced chitosan films were characterized for their weight loss and swelling behavior when being submerged in distilled water. The weight loss determination was tested on samples cut into a disc shape with diameter being 17 mm and thickness ranging between 25 and 35 μm. The samples were submerged in distilled water at 37° C for 24 h. The percentage of weight loss was determined gravitationally (i.e. weight loss (%) $=(W_0-W_1)/W_1\times100$, where W_0 and W_1 represent the dry weight of the samples before and after submersion in distilled water, respectively). In the swelling behavior determination, film samples after heat treatment for 5 min were also cut into a disc shape with the dimensions being similar to the specimens used for the weight loss determination. After submersion for a specified period (between 0 and 120 min), the percentage degree of swelling of the samples was determined gravitationally (i.e. degree of swelling (%) $=(W_2-W_0)/W_0\times100$, where W_0 and W_2 represent the dry, original weight of the samples and the weight of the samples after submersion in distilled water for a specified period, respectively).

3. Results and discussion

3.1. Morphological appearance and sizes of α-chitin whiskers

Fig. 1 shows a TEM image of a dilute suspension of α-chitin whiskers from acid hydrolysis of *P. merguiensis* shrimp shells. Such a suspension exhibited a colloidal behavior. This is due to the presence of the positive charges (NH_3^+) on the whisker surface, which results from the protonation of the amino groups of chitin in acidic conditions (Marchessault et al., 1959; Revol & Marchessault, 1993). The suspension contained chitin fragments consisting of both individual microcrystals and aggregated microcrystals. The chitin fragments consisted of slender rods with sharp points that had broad distribution in size as illustrated in Fig. 2. The length of the chitin fragments

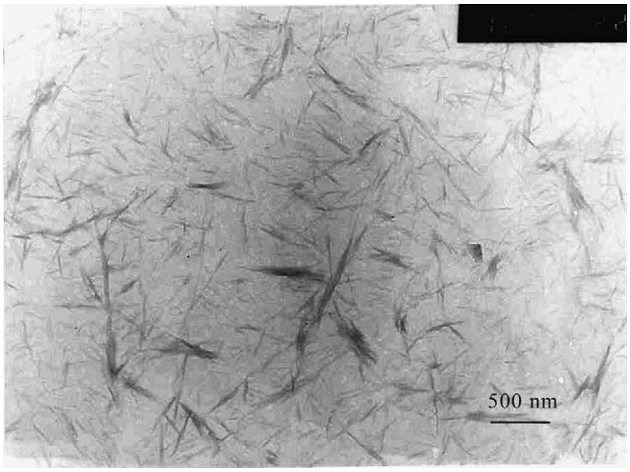

Fig. 1. Transmission electron micrograph of a dilute suspension of α-chitin whiskers from *Penaeus merguiensis* shrimp shells.

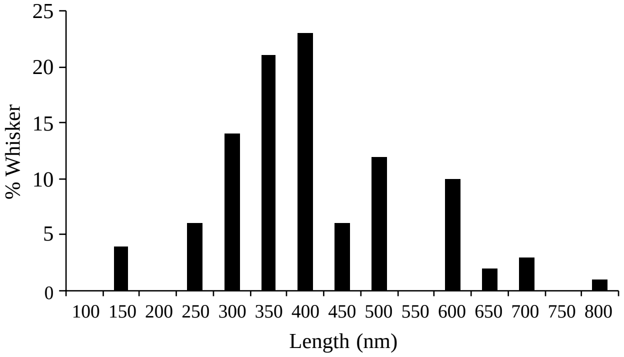

Fig. 2. Histogram showing the length distribution of as-prepared α-chitin whiskers.

ranged from 150 to 800 nm, while the width ranged from 5 to 70 nm. More than 75% of the whiskers however had a length below 420 nm. Statistic evaluation of the results shown in Fig. 2 suggests that the average length and width of these whiskers were about 417 and 33 nm, respectively, with the average length to width ratio (*L*/*d*) of these whiskers being about 17. These dimensions are in line with the reported values for chitin whiskers obtained from crab shells ($L=50$–300 nm and $d=6$–8 nm (Marchessault et al., 1959; Revol & Marchessault, 1993); $L=100$–600 nm and $d=4$–40 nm (Nair & Dufresne, 2003a–c); and $L=100$–650 nm and $d=10$–80 nm (Lu et al., 2004)) and squid pens ($L=50$–300 nm and $d=\sim 10$ nm (Paillet & Dufresne, 2001)), but are much shorter in length when comparing with the chitin whiskers from Riftia tubes ($L=500$ nm to 10 μm and $d=\sim 18$ nm (Morin & Dufresne, 2002)).

3.2. Characterization of α-chitin whisker-reinforced chitosan films without heat treatment

The α-chitin whisker-reinforced chitosan nanocomposite films were prepared by solution casting. The whisker content in the films ranged between 0 and 29.6 wt% and the thickness of the films ranged between 30 and 50 μm.

3.2.1. Thermal stability

Fig. 3 shows TGA thermograms of pure chitosan, as-prepared α-chitin whiskers, and resulting α-chitin whisker-reinforced chitosan films having the whisker content of 14.8 and 29.6 wt%, respectively. All of the samples investigated showed initial weight loss in the temperature range of about 60–80° C, likely a result of the loss of moisture upon heating. The moisture content of pure chitosan and α-chitin whisker-reinforced chitosan films was identical (i.e. about 12%), while that of the as-prepared α-chitin whiskers was about 8%. After the loss of moisture, pure chitosan and chitosan nanocomposite films showed an almost identical two-step weight loss behavior, with the main difference being observed in the temperature range of 300–400° C, within which a slight decrease in the percentage of weight loss was observed with increasing whisker content (see Fig. 3; curves (a)–(c)). According to the derivative TGA curves, pure chitosan and chitosan nanocomposite films exhibited two degradation peaks at about 200 and 300° C. Though not completely relevant, β-chitin also exhibited two degradation peaks at about 260 and 350° C (Peesan, Rujiravanit, & Supaphol, 2003). On the contrary, the as-prepared α-chitin whiskers only showed one weight loss after the loss of moisture, with the peak of the derivative curve being observed at about 347° C (see Fig. 3; curve (d)). The results suggest that the presence of α-chitin whiskers did not affect much the thermal stability of the α-chitin whisker-reinforced chitosan films.

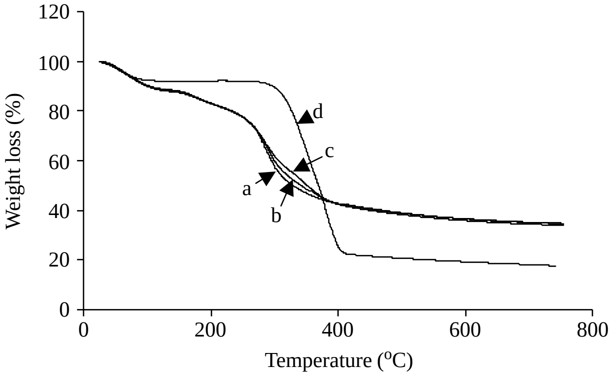

Fig. 3. Thermogravimetric analyses of (a) pure chitosan, α-chitin whisker-reinforced chitosan films having different whisker contents of (b) 14.8 and (c) 29.6 wt%, respectively, and (d) as-prepared chitin whiskers.

3.2.2. Crystalline structure and qualitative apparent degree of crystallinity

Fig. 4 illustrates WAXD patterns of pure chitosan, as-prepared α-chitin whiskers, and resulting α-chitin whisker-reinforced chitosan films having the whisker content ranging between 2.96 and 29.6 wt%. WAXD pattern of pure chitosan film (i.e. pattern (a)) showed two weak scattering peaks at 2*θ* angles of about 11 and 18°, which is in general accordance with the results reported by Jaworska,

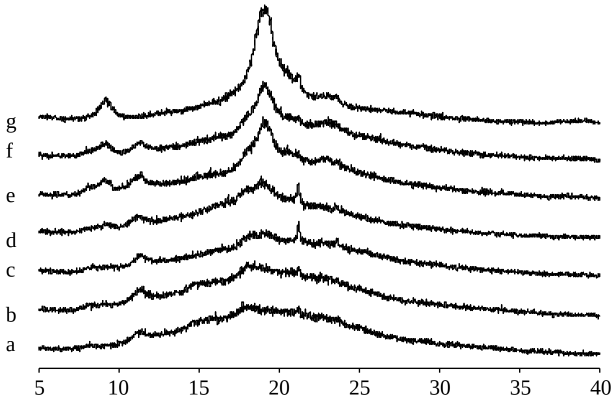

Fig. 4. Wide-angle X-ray diffraction patterns of (a) pure chitosan and α-chitin whisker-reinforced chitosan films having different whisker contents of (b) 2.96, (c) 7.40, (d) 14.8, (e) 22.2, and (f) 29.6 wt%, respectively, and (g) as-prepared chitin whiskers.

Sakurai, Gaudon, and Guibal (2003). The result suggests very low qualitative apparent degree of crystallinity of the pure chitosan film. For as-prepared α-chitin whiskers, their WAXD pattern (i.e. pattern (g)) exhibited two major scattering peaks at 2θ angles of about 9 and 19°, respectively. Cho, Jang, Park, and Ko (2000) reported that α-chitin with a DD value of 8.6% shows two strong scattering peaks at 2θ angles of about 9 and 19°, including three weak scattering peaks at about 20, 23, and 26° and when the DD value increased to 24.7%, only the strong peaks at 9 and 19° were evident. They concluded that the degree of order (DO) of α-chitin decreased with increasing DD and at high DD value (i.e. 49%) the crystal even resembled that of β-chitin (Cho et al., 2000). Based on their results (Cho et al., 2000), it is postulated that the observed two scattering peaks at 9 and 19° for as-prepared α-chitin whiskers could attribute to the relatively high DD value of the original α-chitin (i.e. 17.7%) and the decreased DO of α-chitin due to hydrolytic treatment.

For the resulting α-chitin whisker-reinforced chitosan films, the WAXD patterns showed all of the scattering peaks belonging to those of the pure components (see patterns (b)–(f) in Fig. 4), with the strong scattering peaks of α-chitin whiskers being more pronounced with increasing whisker content. However, with increasing whisker content, the relative intensity and width of the scattering peaks belonging to the chitosan matrix did not change. These results indicate that the presence of α-chitin whiskers did not affect the apparent degree of the crystallinity of the matrix.

3.2.3. Tensile properties

Fig. 5 shows tensile strength and percentage of elongation at break of pure chitosan and α-chitin whisker-reinforced chitosan films having the whisker content in the range of 0.74–29.6 wt%. The tensile strength of the nanocomposite films initially increased from that of the pure chitosan film (i.e. 64.9 ± 0.7 MPa) with increasing whisker content to reach a maximum value (i.e. 83.8 ± 2.9 MPa) at the whisker content of about 2.96 wt% and gradually decreased with further increase in the whisker content. Bahrami, Kordestani, Mirzadeh, Mansoori, and Iranian (2003) reported a tensile strength value of 57.2 ± 0.7 MPa for chitosan (DD = 85.6%) which was cast from a solution of chitosan in 1% v/v aqueous acetic acid solution. The discrepancy between the tensile strength values could be a result of the difference between the DD values and the molecular weights of the chitosan samples used. On the contrary to the tensile strength, the percentage of elongation at break of the nanocomposite films decreased steadily from that of the pure chitosan film (i.e. 11.7 ± 0.6%) with increasing whisker content and leveled off when the whisker content was greater than or equal to 2.96 wt%. Interestingly, the observed percentage of elongation at break value of 11.7% for the pure chitosan film is in general agreement with the value of 9.0% reported by Bahrami et al. (2003).

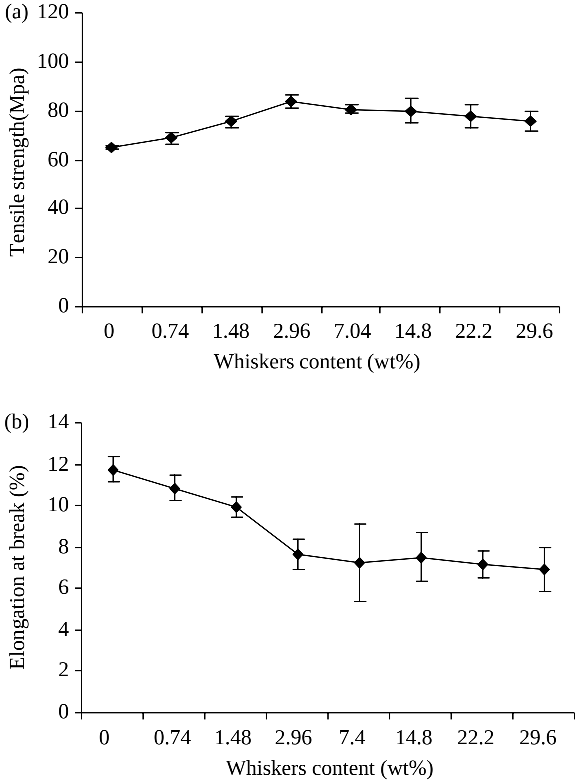

Fig. 5. (a) Tensile strength and (b) percentage of elongation at break of pure chitosan and α-chitin whisker-reinforced chitosan films as a function of whisker content.

The increase in the tensile strength of the nanocomposite films with increasing α-chitin whisker content could be due to the interaction between chitosan molecules and α-chitin whiskers via hydrogen bonding. Such interaction, however, caused the nanocomposite films to be more rigid as the whisker content increased and, as a result, the percentage of elongation at break decreased. It is worth noting that a similar behavior to what has been observed here was also observed for soy protein isolate films reinforced with α-chitin whiskers from crab shells, in which the tensile strength of the films initially increased with increasing whisker content and leveled off when the whisker contents was about 20 wt% or greater, while the percentage of elongation at break decreased steadily with increasing whisker content (Lu et al., 2004).

3.3. Characterization of heat-treated α-chitin whisker-reinforced chitosan films

Chitosan has often been used in a film form in a variety of applications, ranging from tissue engineering, wound dressing, controlled release, and food packaging (Aksungur, Sungur, Unai, Iskit, Squier and Senel, 2004; Chen et al., 2004; Dong, Cheng, Tan, Zheng, & Jiang, 2004; Kucharska, Niekraszewicz, & Struszczyk, 2002). Due to its solubility in water and some other aqueous solutions, actual utilization of chitosan films is limited. In order to increase its water resistance, dry or moist heat treatment has been applied to render insolubility to chitosan derivative films, which was attributed to either the crosslinking of chitosan molecules and/or the increase in the crystallinity (Lim & Wan, 1995; Ritthidej, Phaechamud, & Koizumi, 2002). In this work, pure chitosan and α-chitin whisker-reinforced chitosan films were heat-treated by saturated steam in an autoclave at 110° C for either 5 or 10 min. The color of the films changed from transparent before heat treatment to pale yellow after being treated for 5 min and to yellowish brown after being treated for 10 min.

3.3.1. Weight loss in distilled water

Prior to discussing the weight loss of heat-treated pure chitosan and α-chitin whisker-reinforced chitosan films in distilled water, the weight loss of the untreated films in distilled water is worth mentioning. For determination of weight loss, the films have to be able to retain their shape for more than 24 h. Due to the high solubility of chitosan in water, pure chitosan and α-chitin whisker-reinforced chitosan films could not retain their shape for the specified time. Specifically, pure chitosan and chitosan films having the whisker content of less than or equal to 7.4 wt% could retain their shape in the first 4 h of submersion in water, while chitosan films with the whisker content of more than or equal to 14.8 wt% could retain its shape within the first 6 to 18 h. The results obtained suggest that the presence of α-chitin whiskers in chitosan matrix increased its stability in water.

The percentage of weight loss of heat-treated pure chitosan and as-prepared α-chitin whisker-reinforced chitosan films after submersion in distilled water for 24 h is summarized in Table 1. For pure chitosan and chitosan nanocomposite films at a given α-chitin whisker content, heat treatment was responsible for a much reduction in the percentage of weight loss and the percentage of weight loss decreased with increasing the treatment time. For a given heat treatment condition, the percentage of weight loss of the nanocomposite films decreased monotonically from that of the pure chitosan film (i.e. 15.4 or 11.3% for 5 or 10 min of heat treatment) with increasing whisker content.

Table 1
Percentage of weight loss in water of pure chitosan and α-chitin whisker-reinforced chitosan films with and without heat treatment

Whisker content (wt%)	Weight loss (%)	
	Autoclave 5 min	Autoclave 10 min
0	15.4±0.5	11.3±2.4
0.74	13.4±1.1	10.3±0.7
1.48	12.3±0.1	10.1±0.1
2.96	12.1±2.4	10.0±0.2
7.40	12.2±3.0	9.3±0.6
14.8	12.6±2.7	9.6±0.9
22.2	10.1±1.6	9.0±0.3
29.6	10.6±0.6	9.6±2.5

The studies on the weight loss in distilled water of pure chitosan and as-prepared α-chitin whisker-reinforced chitosan films with or without heat treatment reveal that both the presence of α-chitin whiskers and the heat treatment helped improve the stability of the films in water and the increase in the whisker content and/or the heat treatment time resulted in a decrease in the percentage of weight loss of the films.

3.3.2. Swelling behavior in distilled water

The degree of swelling of pure chitosan and chitosan films reinforced with either 7.4 or 29.6 wt% α-chitin whiskers after heat treatment for 5 min is plotted as a function of the submersion time in Fig. 6. For a given film type, the percentage degree of swelling increased very abruptly with initial increase in the submersion time up to about 5 min, after which the percentage degree of swelling increased gradually to reach an equilibrium value at long submersion times. Bahrami et al. (2003) reported that the percentage of degree of swelling of pure chitosan film in phosphate buffer saline solution (pH≈7.2–7.4) for 1 h was about 225±20%, which is quite comparable to the value of 244±7% observed in this work. Comparatively among the film types investigated, the equilibrium percentage degree of swelling (at the submersion time of 120 min) of pure chitosan film was the highest (i.e. about 250%), followed by chitosan films reinforced with 7.4 (i.e. about 200%) and 29.6 wt% α-chitin whiskers (i.e. about 140%), respectively. Since the heat treatment for all of the films investigated was the same, the decrease in the degree of swelling of the films with addition and increasing α-chitin whiskers must be responsible for such behavior. In soy protein isolate films reinforced with α-chitin whiskers from crab shells (Lu et al., 2004), the equilibrium percentage degree of swelling also decreased with increasing whisker content. The reduction in the degree of swelling could be a result of the strong

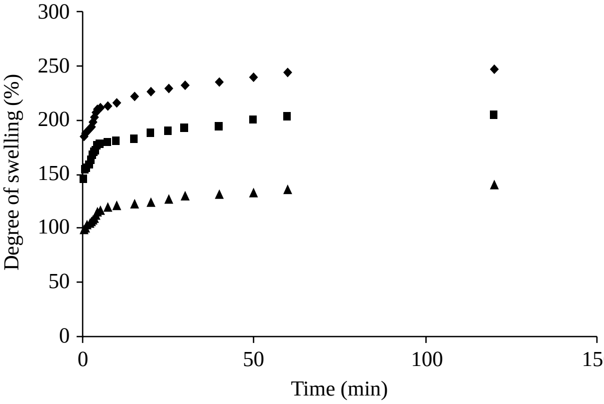

Fig. 6. Degree of swelling of (◆) pure chitosan and α-chitin whisker-reinforced chitosan films having different whisker contents of (■) 7.4 and (▲) 29.6 wt%, respectively, after heat treatment in an autoclave for 5 min as a function of immersion time.

hydrogen bonding between chitosan molecules and the whiskers (Neus Angles & Dufresne, 2000a,b,c; Lu et al., 2004).

4. Conclusions

Chitin whisker-reinforced nanocomposites films were prepared by blending suspensions of α-chitin whiskers from *P. merguiensis* shrimp shells with a solution of chitosan in an aqueous acetic acid solution. The as-prepared α-chitin whiskers consisted of slender parallel rods with a broad distribution in both length and width. The average length and width of these whiskers were about 417 and 33 nm, respectively, with the average aspect ratio between the length and the width being about 17. The presence of the whiskers did not affect much the thermal stability and the apparent degree of crystallinity of the chitosan matrix. The tensile strength of α-chitin whisker-reinforced chitosan films increased from that of the pure chitosan film with initial increase in the whisker content to reach a maximum at the whisker content of 2.96 wt% and decreased gradually with further increase in the whisker content, while the percentage of elongation at break decreased from that of the pure chitosan with initial increase in the whisker content and leveled off when the whisker content was greater than or equal to 2.96 wt%. Both the presence of α-chitin whiskers and heat treatment decreased the affinity to water of the chitosan/α-chitin whiskers nanocomposite films, as reflected by the observed decreased in both of the percentage of weight loss and the percentage degree of swelling of the films with either increase in the whisker content or the heat treatment time. The reduction in the affinity to water causes the chitosan/α-chitin whiskers nanocomposite films to be more stable when being used in an aqueous environment.

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