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Preparation and characterization of α-chitin whisker-reinforced poly(vinyl alcohol) nanocomposite films with or without heat treatment

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Abstract

α-Chitin whisker-reinforced poly(vinyl alcohol) (PVA) nanocomposite films were prepared by solution-casting technique. The α-chitin whiskers were prepared by acid hydrolysis of α-chitin from shrimp shells. The as-prepared whiskers exhibited the length in the range of 150–800 nm and the width in the range of 5–70 nm, with the average length and width being about 417 and 33 nm, respectively. Thermal stability of the as-cast nanocomposite films was improved from those of the pure PVA film with increasing whisker content. The presence of the whiskers did not have any effect on the crystallinity of the PVA matrix. The tensile strength of α-chitin whisker-reinforced PVA films increased, at the expense of the percentage of elongation at break, from that of the pure PVA film 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 degree of swelling, of the nanocomposite films.

Keywords: Nanocomposite; α-Chitin whisker; Poly(vinyl alcohol)

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 [1], 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 [2]. Cellulose is a classical example where the reinforcing elements exist as whisker-like microfibrils that are biosynthesized and deposited in a continuous manner [3]. Favier et al. [4] 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 copolymer 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) [5], poly(hydroxyalkanoate) (PHA) [6], plasticized maize starch [7], and poly(oxyethylene) [8]. Cellulose whiskers from wheat straw can also be prepared and have been used as reinforcing nanofillers in poly(S-*co*-BuA) latex [9].

Whiskers from other polysaccharides, such as starch [10] and chitin [11], can also be prepared. Unlike tunicin whiskers which can only be prepared by hydrolysis in strong sulfuric acid (H_2SO_4) solutions [4–9,11], both starch and chitin whiskers can be prepared by hydrolysis in hydrochloric acid (HCl) solutions [10,11]. 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 [12]. Chitin whiskers have been successfully prepared from crab shells [11,13,14], squid pens [15], and tubes of *Riftia pachyptila* tubeworms [16]. Regardless of the chitin sources, the commonly-used hydrolytic condition for obtaining chitin whiskers is 3 N

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HCl at the boil for 90 min under vigorous stirring [11,13–16].

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 poly(vinyl alcohol) (PVA) solution and α-chitin whisker suspensions. PVA was chosen as the matrix material, due to its excellent film-forming ability, chemical resistance, and good transparency. Due to such properties, PVA has found wide applications in membrane technologies [17]; however, its actual utilization is limited by its affinity to water, which leads to high degree of swelling and even complete solubilization of the resulting membranes. Consequently, the presence of α-chitin whiskers with or without heat treatment was expected to improve the resistance to water of the resulting nanocomposite films. Furthermore, thermal and mechanical properties of the nanocomposite films were also investigated.

2. Experimental

2.1. Materials

Shells of *Penaeus merguiensis* shrimps were donated from Surapon Foods Public Co., Ltd. (Thailand). Poly(vinyl alcohol) (PVA), having the weight-average molecular weight of about 72,000 Da and the degree of hydrolysis of about 97.5–99.5%, was purchased from Sigma-Aldrich (USA). 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 α-chitin whiskers

Decalcification and deproteinization of shrimp shells to obtain α-chitin were carried out according to the procedure described in reference [18]. The degree of deacetylation (DD) of the obtained α-chitin was determined [19] to be 17.7%, while the viscosity-average molecular weight 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 8.93×10^{-2} ml g^{-1} and 0.71 [20], respectively) to be 2.42×10^6 Da.

Chitin whiskers from the obtained α-chitin of shrimp shells were prepared based on the method of Dufresne et al. [13–16]. The whisker suspensions 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 suspensions 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 ultrasonification treatment for every 40-cm^3 aliquot. Sodium azide was added to the suspensions to prevent bacterial growth and the suspensions were refrigerated prior to further use. The solid content of the as-prepared whisker suspensions was about 1.48 wt%.

2.3. Preparation of α-chitin whisker-reinforced PVA films

The PVA solution was first prepared by dissolving 1 g of PVA powder in 49 g of distilled water at 90 °C with stirring for 3 h. The as-prepared α-chitin whisker suspensions in varying amount were then added to the PVA solution (with appropriate addition of distilled water to obtained 100 g of the final suspension) to achieve the whisker content in the range of 0–29.6 wt%. The PVA/α-chitin whisker suspension was further stirred mechanically for another 4 h before being cast onto a plastic mold. After the solvent was evaporated at 40 °C for 24 h in a convection oven, α-chitin whisker-reinforced nanocomposite films were obtained.

2.4. Heat treatment

To decrease their solubility in water, both pure PVA and α-chitin whisker-reinforced PVA 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.

2.5. Characterization

Morphological appearance and sizes of the as-prepared α-chitin whiskers were 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 PVA and α-chitin whisker-reinforced PVA films without heat treatment were characterized for their chemical functionalities, thermal stability, crystalline structure and qualitative apparent degree of crystallinity, tensile properties, and weight loss in distilled water. A TGA 2950 DuPont thermogravimetric analyzer (TGA) was used to investigate the thermal stability of pure PVA, as-prepared α-chitin whiskers, and α-chitin whisker-reinforced PVA films. A sample of about 3–10 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 PVA, as-prepared α-chitin whiskers, and α-chitin whisker-reinforced PVA 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 5–40° at a scanning speed of 5° min^{-1} and a step scan of 0.02°. A Thermo Nicolet Nexus 671 FT-IR was used to investigate the chemical functionalities and qualitative apparent degree of crystallinity of pure PVA, as-prepared α-chitin whiskers, and α-chitin whisker-reinforced PVA films. The measurements were conducted at 32 scans and a resolution of 4 cm^{-1}. A Lloyd LRX universal tester was used to determine the tensile strength and the percentage of elongation at break of pure PVA and α-chitin whisker-reinforced PVA films, according to ASTM D882 standard test method. The dimension of the films was 15×150 mm, with the thickness ranging from 30 to 50 μm. The gauge length and the crosshead speed were 50 and 50 mm min^{-1}, respectively. The reported values were averages from five measurements. 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 (%) $=(W_0-W_1)/W_0\times100$, where W_0 and W_1 represent the dry weight of the samples before and after submersion in distilled water, respectively).

Heat-treated pure PVA and α-chitin whisker-reinforced PVA films were characterized for their weight loss and swelling behavior when being submerged in distilled water. The weight loss determination was carried out using the same procedure previously described for samples without the heat treatment. 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 *Penaeus 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 resulted from the protonation of the amino groups of chitin in acidic conditions [11]. 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 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 suggested 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 [11]; $L=100$–600 nm and $d=4$–40 nm [13]; and $L=100$–650 nm and $d=10$–80 nm [14]) and squid pens ($L=50$–300 nm and $d=\sim10$ nm [15]), but are much shorter in length when compared with the chitin whiskers from Riftia tubes ($L=500$ nm to 10 μm and $d=\sim18$ nm [16]).

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

The α-chitin whisker-reinforced PVA 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. Chemical functionalities

Fig. 3 illustrates FT-IR spectra over the wave number range of 2000–400 cm^{-1} of pure PVA, as-prepared α-chitin whiskers, and resulting α-chitin whisker-reinforced PVA films having the whisker content ranging between 0.74 and 29.6 wt%. It should be noted that the hydroxyl stretching region of these spectra was not shown since the intensity was too strong to be critically analyzed. According to Fig. 3, the absorption peaks at 1440 cm^{-1} (CH_2 bending) and 858 cm^{-1} (CH_2 rocking) characteristic to PVA were obvious in the spectra of pure PVA and α-chitin whisker-reinforced PVA films [21], while the characteristic amide I peak at 1655 cm^{-1} (–CONH–) was evidenced in the spectra of as-prepared α-chitin whiskers and α-chitin whisker-reinforced PVA films [22]. It is obvious that the relative intensity of these characteristic peaks increased with increasing content of the corresponding component and that no additional peaks other than those characteristic to either PVA or α-chitin were observed in the spectra.

3.2.2. Thermal stability

Fig. 4 shows TGA thermograms of pure PVA, as-prepared α-chitin whiskers, and resulting α-chitin

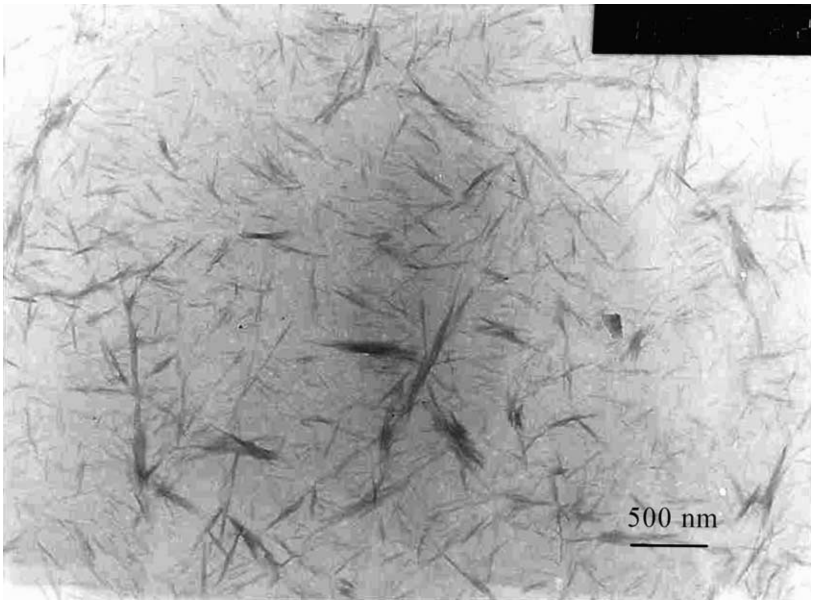

Fig. 1. Transmission electron micrograph of a dilute suspension of α-chitin whiskers from *Penaeus merguiensis* shrimp shells.

whisker-reinforced PVA films having the whisker content of 14.8 and 29.6 wt%, respectively. All of the samples investigated showed initial weight loss at about 60–80 °C, likely a result of the loss of moisture upon heating. The moisture content in these samples was almost similar (i.e. about 8%). According to the derivative TGA curves, pure PVA film exhibited a major degradation peak at 274 °C (Fig. 4; curve (a)), which is in excellent agreement with the value of 270 °C earlier reported [23], while as-prepared α-chitin whiskers showed a major degradation peak at 347 °C (Fig. 4; curve (d)). According to Fig. 4, the major degradation peaks for PVA films reinforced with 14.8 and 29.6 wt% α-chitin whiskers were immediate to those of the pure components, with the thermal stability of the nanocomposite films increased with increasing α-chitin whisker content.

3.2.3. Crystalline structure and qualitative apparent degree of crystallinity

Fig. 5 illustrates WAXD patterns of pure PVA, as-prepared α-chitin whiskers, and resulting α-chitin whisker-reinforced PVA films having the whisker content in the range of 2.96 to 29.6 wt%. WAXD pattern for pure PVA film (i.e. pattern (a)) shows a single scattering peak centering at 2θ angle of about 19°, which is in accord to an earlier result on PVA film cast from a solution of PVA in formic acid [23]. The result suggested that the as-cast PVA film was essentially amorphous. For as-prepared α-chitin whiskers, their WAXD pattern (i.e. pattern (g)) exhibits two major scattering peaks at 2θ angles of about 9 and 19°, respectively. Cho et al. [24] showed that α-chitin with a DD value of 8.6% exhibited 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 a high DD value (i.e. 49%) the crystal even changed to that of β-chitin [24]. Based on their results [24], 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.

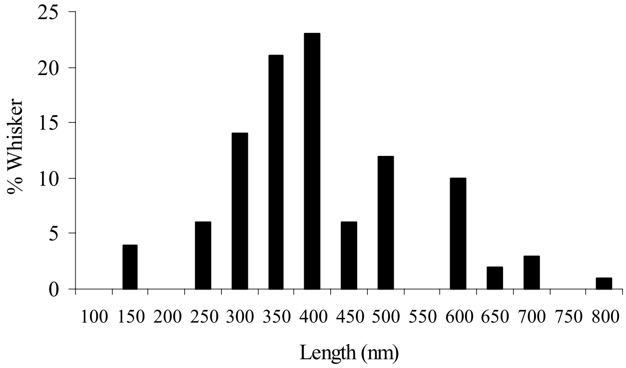

Fig. 2. Histogram showing the length distribution of as-prepared α-chitin whiskers.

For the resulting α-chitin whisker-reinforced PVA films, the WAXD patterns were immediate to those of the pure components (see patterns (b)–(f) in Fig. 5), with the strong scattering peaks of α-chitin whiskers (i.e. at about 9 and 19°) being more pronounced with increasing whisker content. To verify whether or not incorporation of α-chitin whiskers into PVA resulted in an increase in the crystallinity of the PVA matrix, FT-IR spectra, shown in Fig. 3, were reconsidered. It is well known that the absorption peak at 1144 cm^{-1} (C–O of doubly H-bonded OH in crystalline regions [21]) is useful for indication of the crystallinity of PVA. Apparently, the

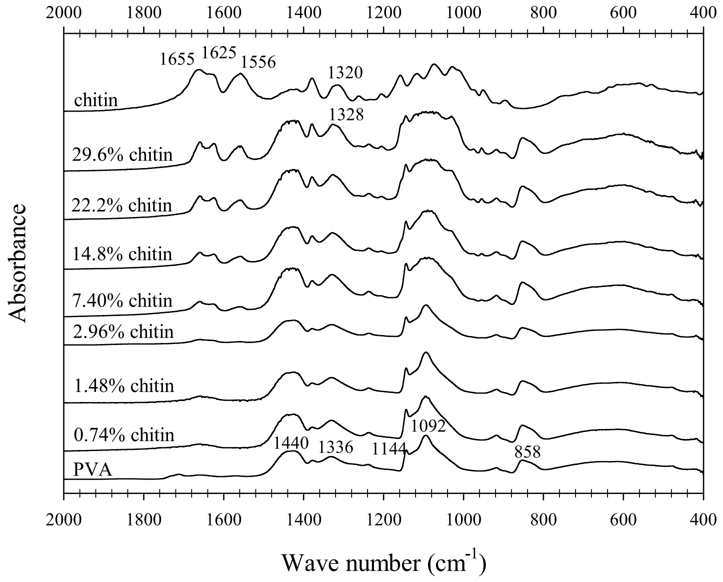

Fig. 3. FT-IR spectra of pure PVA, as-prepared α-chitin whiskers, and α-chitin whisker-reinforced PVA films having different whisker contents ranging from 0.74 to 29.6 wt%.

relative intensity of this peak was not found to increase with increasing whisker content, indicating that incorporation of α-chitin whiskers did not have an effect on the crystallinity of the PVA matrix.

3.2.4. Tensile properties

Fig. 6 shows tensile strength and percentage of elongation at break of pure PVA and α-chitin whisker-reinforced PVA films having the whisker content in the range of 0.74–29.6 wt%. It should be noted again that, based on the thermogravimetric analysis, the moisture content of these films was about 8%. The tensile strength of the nanocomposite films initially increased from that of the pure PVA film (i.e. 55.5 ± 3.1 MPa) with increasing whisker content up to the whisker content of about 2.96 wt% (i.e. 83.3 ± 2.1 MPa) and leveled off with further increase in the whisker content. The observed tensile strength value of 55.5 MPa for the pure PVA film was very comparable to the reported value of 53.3 MPa for dry PVA film which was cast from a solution of PVA in hot water [25]. The tensile strength value of PVA film is very sensitive to the moisture or water content in the film: a much lower tensile strength value could be obtained when the film is wet [25]. On the contrary to the tensile strength, the percentage of elongation at break of the nanocomposite films monotonically decrease from that of the pure PVA film (i.e. 14.7 ± 2.0%) with increasing whisker content (to the value of 5.3 ± 0.4% for the nanocomposite film having the whisker content of 29.6 wt%). Interestingly, the observed percentage of elongation at break value of 14.7% for the pure PVA film was in accord with the reported value of 16.2% [25]. It is worth noting that a similar behavior to what has been observed here was also observed for soy protein isolate films

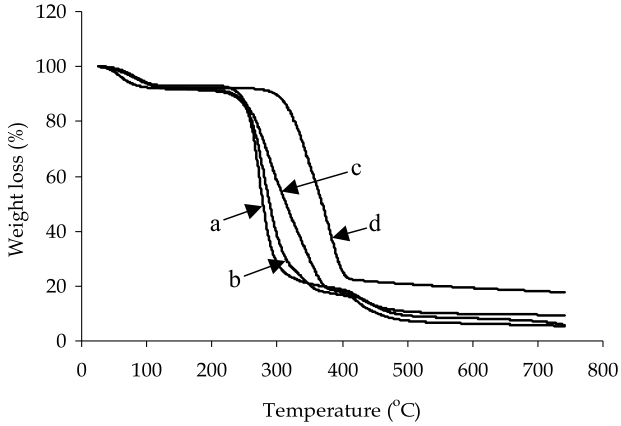

Fig. 4. Thermogravimetric analyses of (a) pure PVA, α-chitin whisker-reinforced PVA films having different whisker contents of (b) 14.8 and (c) 29.6 wt%, respectively, and (d) as-prepared chitin whiskers.

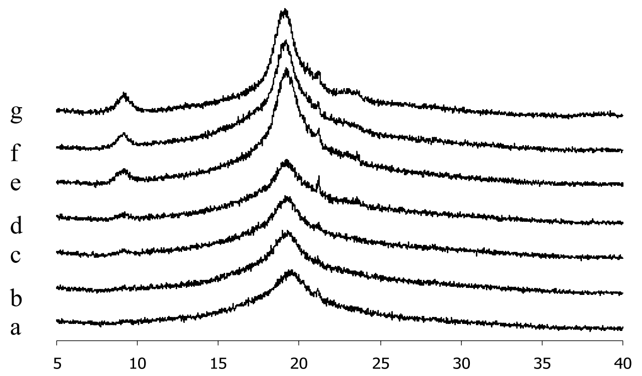

Fig. 5. Wide-angle X-ray diffraction patterns of (a) pure PVA and α-chitin whisker-reinforced PVA films having different whisker contents of (b) 2.96, (c) 7.40, (d) 14.8, (e) 22.2, and (f) 29.6 wt%, respectively, and (g) as-prepared chitin whiskers.

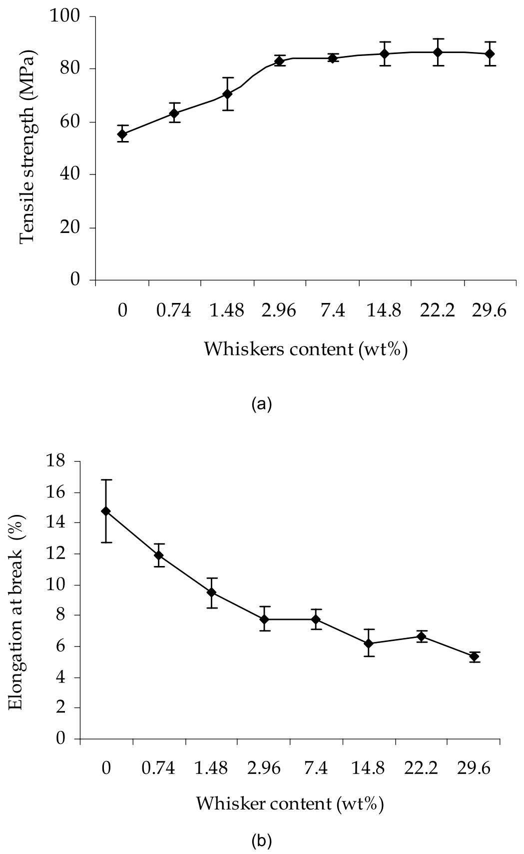

Fig. 6. (a) Tensile strength and (b) percentage of elongation at break of pure PVA and α-chitin whisker-reinforced PVA films as a function of whisker content.

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 only decreased with increasing whisker content [14].

The observed increase in the tensile strength of the nanocomposite films with increasing α-chitin whisker content could be due to the interaction between PVA molecules and α-chitin whiskers via hydrogen bonding. Such interaction, however, caused the nanocomposite films to be more rigid as the whisker content increased, resulting in the observed decrease in the percentage of elongation at breaks of these films. To verify whether or not interaction between PVA and α-chitin whiskers existed, FT-IR spectra, shown in Fig. 3, were reconsidered. Unfortunately, as previously mentioned, the hydroxyl stretching region of these observed spectra was too intense to be critically analyzed. However, it is interesting that the absorption peak at 1336 cm^{-1} (OH bending and CH wagging [21]) gradually shifted to 1328 cm^{-1} with increasing α-chitin whisker content, which could be an indication of the existance of some interactions between PVA molecules and α-chitin whiskers [26].

3.2.5. Weight loss in distilled water

The percentage of weight loss of pure PVA and as-prepared α-chitin whisker-reinforced PVA films after submersion in distilled water for 24 h was determined and the results are summarized in Table 1. Obviously, the percentage of weight loss of pure PVA film was about 90.8%. With only a small amount of α-chitin whiskers (i.e. about 0.74 wt%), the percentage of weight loss of the nanocomposite film reduced to about 86.9% and, with further increase in the whisker content to about 2.96 wt%, the percentage of weight loss of the films gradually decreased to about 82.3%. Abrupt decrease in the percentage of weight loss was observed (i.e. about 65.5%) when the whisker content increased to 7.4 wt%, while the percentage of weight loss of the nanocomposite films was observed to level off when the whisker content was greater than or equal to about 14.8 wt%. Interestingly, the presence of α-chitin whiskers in PVA films without any specific chemical alteration helps improve stability of the films in distilled water, especially when the whisker content was greater than or equal to 14.8 wt%. This finding may become very useful for improving the stability of PVA in aqueous media in actual biomedical applications where chemical alterations are minimally needed.

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

Heat treatment has been applied to PVA in order to reduce its affinity to water for applications where insolubility in water is required [27]. The heat treatment of PVA fibers also helps improve their mechanical properties and dimensional stability [27]. On of the principal effects of heat treatment on PVA at moderate temperatures (i.e. below 160 °C) is an increase in the crystalline fraction of the polymer; however, extensive heat treatment at higher temperatures induces some chemical changes, such as unsaturation, chain scission, and crosslinking [27]. In this work, both the pure PVA and α-chitin whisker-reinforced PVA films were heat-treated by saturated steam in an autoclave at 110 °C for either 5 or 10 min. No tanning was

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

Whisker content (wt%)	Weight loss (%)		
	Without heat treatment	Autoclave 5 min	Autoclave 10 min
0	90.8±3.1	36.8±0.9	13.6±1.7
0.74	86.9±6.9	28.7±3.2	12.0±0.2
1.48	84.3±8.8	18.6±1.5	10.2±1.8
2.96	82.3±5.4	19.3±1.2	9.5±0.7
7.40	65.5±9.0	18.0±0.2	8.9±1.0
14.8	60.4±1.5	18.7±1.9	7.8±1.5
22.2	60.3±5.6	17.8±2.6	7.0±2.2
29.6	60.3±1.8	17.1±2.4	7.2±0.6

observed for all of the heat-treated films, as they were all appeared to be transparent. The heat-treated films were tested for their weight loss and swelling behavior after submersion in distilled water.

3.3.1. Weight loss in distilled water

Table 1 summarizes the percentage of weight loss of heat-treated pure PVA and as-prepared α-chitin whisker-reinforced PVA films after submersion in distilled water for 24 h. For both pure and nanocomposite PVA films at a given α-chitin whisker content, heat treatment was responsible for a much reduction in the percentage of weight loss in comparison with that of the untreated films. For a given heat treatment condition, the percentage of weight loss of the nanocomposite films decreased monotonically from that of the pure PVA film (i.e. 36.8 or 13.4% for 5 or 10 min of heat treatment) with increasing whisker content. Interestingly, for films being heat-treated for 5 min, the percentage of weight loss seemed to level off (i.e. at about 17–19%) when the whisker content was greater or equal to 1.48 wt%, while, for films being heat-treated for 10 min, the percentage of weight loss seemed to level off (i.e. at about 7–10%) when the whisker content was greater or equal to 1.48 wt%. The studies on the weight loss in distilled water of pure PVA and as-prepared α-chitin whisker-reinforced PVA films with or without heat treatment revealed 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 duration 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 PVA and PVA 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. 7. 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 very gradually to reach an equilibrium value at long submersion times. Bahrami et al. [25] reported that the percentage of degree of swelling of pure PVA film in phosphate buffer saline solution (pH ≈7.2–7.4) for 1 h was about 360%. Comparatively among the film types investigated, the equilibrium percentage degree of swelling (at the submersion time of 120 min) of pure PVA film was the highest (i.e. about 540%), followed by PVA films reinforced with 7.4 (i.e. about 450%) and 29.6 wt% α-chitin whiskers (i.e. about 350%), 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 [14], 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 hydrogen bonding between PVA molecules and the whiskers [7,14].

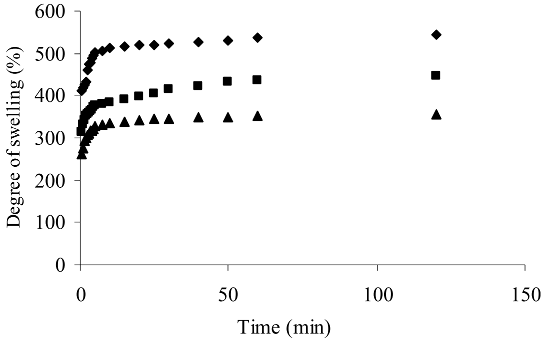

Fig. 7. Degree of swelling of (◆) pure PVA and α-chitin whisker-reinforced PVA films having different whisker contents of (■) 7.4 and (▲) 29.6 wt%, respectively, after heat treatment in an autoclave for 5 min as a function of immersion time.

4. Conclusions

Chitin whisker-reinforced nanocomposites films were prepared by blending suspensions of α-chitin whiskers from *Penaeus merguiensis* shrimp shells with solution of poly (vinyl alcohol) (PVA). 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. Incorporation of α-chitin whiskers helped improve the thermal stability of the resulting nanocomposite films, but it did not have any effect on the crystallinity of the PVA matrix. The tensile strength of the nanocomposite films initially increased with increasing whisker content and leveled off when the whisker content was greater than or equal to 2.96 wt%. On the contrary, the percentage of elongation at break only decreased monotonically with increasing whisker content. Both the presence of α-chitin whiskers and heat treatment decreased the affinity to water of the PVA/α-chitin whiskers nanocomposite films, as reflected by the observed decrease 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 duration. The reduction in the affinity to water causes the PVA/α-chitin whiskers nanocomposite films to be more stable when being used in an aqueous environment.

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