



## Material Characterisation

## Characterisation of beta-chitin/poly(vinyl alcohol) blend films

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**Abstract**

Blend films of  $\beta$ -chitin (derived from squid pens) and poly(vinyl alcohol) (PVA) were prepared by a solution casting technique from corresponding solutions of  $\beta$ -chitin and PVA in concentrated formic acid. Upon evaporation of the solvent, films prepared from pure  $\beta$ -chitin and pure PVA were found to be transparent, while the film having 50/50 composition was found to be cloudy. Miscibility of the polymers in the amorphous phase of the films at various compositions was assessed using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM) techniques. The glass transition temperature of the blend films was found to increase slightly with an increase in the  $\beta$ -chitin content. The effect of blend compositions on apparent degree of crystallinity, mechanical properties, and swelling behavior of the as-prepared blend films was also investigated.

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*Keywords:*  $\beta$ -chitin; Poly(vinyl alcohol); Blend film

**1. Introduction**

Natural polymers as biotechnological or biomedical resources have been widely investigated because of their unique properties, which include, for example, nontoxicity, degradability, and biological compatibility. Chitin or poly(*N*-acetyl-D-glucosamine) is a polysaccharide which is abundantly available in nature as a component in cell walls of various fungi, as well as in shells of various insects and crustaceans. Chitin is predominantly present as a fibrillar crystalline material. Based on infrared spectroscopy and X-ray diffraction data, chitin can be found in one of the three crystalline forms [1]:  $\alpha$ -chitin,  $\beta$ -chitin and  $\gamma$ -chitin, respectively. The molecules in orthorhombic  $\alpha$ -chitin are arranged very tightly in an anti-parallel fashion.  $\alpha$ -Chitin is mainly present in shells of crabs, lobsters and shrimps.  $\beta$ -Chitin, obtained from

squid pens, takes the monoclinic form in which the chains are arranged in a parallel fashion, while  $\gamma$ -chitin is the form in which the molecules are arranged in both parallel and anti-parallel manner. As a result of the molecular packing, intermolecular interactions in  $\beta$ -chitin are weaker than those in  $\alpha$ -chitin, making  $\beta$ -chitin being more susceptible to dissolution in a number of solvents. This finally results in  $\beta$ -chitin being more reactive and versatile.

Studies related to film formation of chitin (i.e.,  $\alpha$ -chitin) have not been so popular as those of its deacetylated derivatives, i.e., chitosan. This is because chitin is insoluble in most common organic solvents, a direct result of the strong intra- and inter-molecular hydrogen bonding [2,3], while chitosan can even be dissolved in dilute organic acids. In certain applications, especially in the biomedical fields, chitin is more favorable than chitosan. This is due to the fact that the acetamide group present in chitin is similar to the amide linkage of protein in living tissues [4], making chitin more biocompatible than chitosan.

Blending is an especially important process for

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developing industrial applications of polymeric materials and compatibility among components has a marked influence on the resulting physical properties of polymer blends [5]. Through a suitable choice of polymer pairs, blends of polymers can often be tailor-made to exhibit specific and desirable properties. Blending a natural polymer with a synthetic one seems to be an alternative way of preparing polymeric alloys to meet specific applications. Studies related to blends of  $\alpha$ -chitin with a synthetic polymer, e.g., polycaprolactone [6,7], poly(3-hydroxybutyric acid) [8], and polyamide-6 [3], are available in the open literature.

Due to its good solubility,  $\beta$ -chitin can be solution-cast into films, but, because of its molecular rigidity and high overall apparent degree of crystallinity, the films obtained show rigid character. Blending  $\beta$ -chitin with another flexible, synthetic polymer seems to be an attractive way for improving properties of the films. Poly(vinyl alcohol) (PVA) is a nontoxic, water-soluble, synthetic polymer that is widely used in biomedical applications. With its excellent film-forming ability, PVA is a good candidate for use as membranes and hydrogels [9,10].

In this present contribution,  $\beta$ -chitin/PVA blend films were prepared by solution-casting from solutions of  $\beta$ -chitin and PVA in concentrated formic acid at various compositional ratios. The effect of blend compositions on physical properties, thermal properties, mechanical properties, morphology, and swelling behavior was studied and compared with those of pure components.

## 2. Experimental details

### 2.1. Materials

$\beta$ -Chitin was prepared from squid pens by acid and alkali treatment.  $\beta$ -Chitin was pulverized prior to use into powder, the size of which ranged from 71 to 75  $\mu\text{m}$ . PVA, purchased from Fluka, has the degree of polymerization of ca. 1600 and the degree of hydrolysis of ca. 99.5%. Formic acid (reagent grade, BDH Laboratory) and ethylene glycol (J. T. Baker) were used as-received.

### 2.2. Preparation of blend films

PVA was first dissolved thoroughly in concentrated formic acid (99%) to prepare 1% by weight (wt%) solution. Later, a known amount of  $\beta$ -chitin powder was suspended in concentrated formic acid (99%) at room temperature to prepare 1 wt% solution and the suspension was frozen overnight at 0  $^{\circ}\text{C}$ . After thawing at room temperature, the solution was filtered with a glass filter. A series of  $\beta$ -chitin/PVA blend films with different blend compositions were then prepared by solution-casting technique. The films obtained were allowed to dry at 60

$^{\circ}\text{C}$  for 12 h. The final thickness of the dried films was in the range of 30–50  $\mu\text{m}$ . All of the as-prepared films were kept under dry conditions before further use.

### 2.3. Measurements

Infrared spectra of the as-prepared films were recorded using a Bruker vector 3.0 FTIR spectrophotometer (FTIR). A Mettler DSC 822e/400 (DSC) was used to investigate thermal behavior of the films. To set the thermal history for all samples, each sample was first heated to 190  $^{\circ}\text{C}$  and then cooled to 0  $^{\circ}\text{C}$  at the scanning rate of 10  $^{\circ}\text{C}\times\text{min}^{-1}$ . The thermal properties of the films were measured in the second heating scan at the heating rate of 10  $^{\circ}\text{C}\times\text{min}^{-1}$ . The glass transition temperature ( $T_g$ ) and the melting temperature ( $T_m$ ) were determined as the inflection point of the specific heat increment and the onset of the endothermic melting peak of DSC traces, respectively. Thermal stability of the films was evaluated by a Perkin Elmer TGA7 (TGA) operated under nitrogen atmosphere and at a heating rate of 10  $^{\circ}\text{C}\times\text{min}^{-1}$  from 30 to 750  $^{\circ}\text{C}$ . A Rigaku D/MAX-2000 wide-angle X-ray diffractometer (WAXD) equipped with a  $\text{CuK}\alpha$  X-ray source operating at 40 kV and 30 mA was used to obtain diffractograms on the as-prepared films over the  $2\theta$  range of 5–40 $^{\circ}$  and the scanning speed of 5  $\text{degree}\times\text{min}^{-1}$ . Morphology of the etched surface of selected samples was observed on a JEOL 5200-2AE scanning electron microscope (SEM). A Lloyd tensile tester was used to assess the mechanical properties of the as-prepared films. The gauge length was 125 mm, and the crosshead speed used was 12.5  $\text{mm}\times\text{min}^{-1}$ .

The swelling behavior of the as-prepared films was carried out by measuring the weight of the films after immersion in distilled water and various salt solutions (i.e., 0.25 M solutions of NaCl,  $\text{CaCl}_2$ , and  $\text{FeCl}_3$ ) for 0–8 h in comparison with the dry weight of the films prior to the immersion. The degree of swelling was determined according to the following relationship:

$$\text{Degree of swelling (\%)} = [(W_s - W_d)/W_s] \times 100, \quad (1)$$

where  $W_s$  and  $W_d$  represent the weight of the films after and prior to immersion. It is important to note that all the experiments were carried at room temperature. Finally, the equilibrium degree of swelling of the as-prepared films was also determined after immersion in water or corresponding solutions for 4 days.

## 3. Results and discussion

Solutions of pure  $\beta$ -chitin, pure PVA, and their blends appeared to be homogeneous and transparent. The color of the solutions varied from colorless of pure PVA solution to yellowish with increasing  $\beta$ -chitin content. After

evaporation of the solvent, the as-prepared films of pure  $\beta$ -chitin and pure PVA were found to be transparent, while the 50/50  $\beta$ -chitin/PVA blend film was found to be cloudy. In addition, it was found that the blend films became more brittle with increasing  $\beta$ -chitin content.

### 3.1. Characteristics of $\beta$ -Chitin/PVA blend films

Since the molecules of both  $\beta$ -chitin and PVA are capable of forming hydrogen bonds, it is expected that some specific interactions could be formed between the molecules of different species. In this work, observation of the as-prepared blend films using FTIR did not indicate the presence of such intermolecular interactions (results not shown). However, Lee et al. [11] reported, based on their FTIR results, that intermolecular interactions between the molecules of  $\beta$ -chitin and PVA could in fact exist, because they found shifting of both hydroxyl and carbonyl stretching bands upon blending  $\beta$ -chitin with PVA. The difference between our results and their may be due to the difference in the molecular weight characteristics of the constituents studied.

Miscibility of  $\beta$ -chitin and PVA at various weight compositions was investigated by observing the  $T_g$  values of the as-prepared pure and blend films. Fig. 1 shows the second heating thermograms for pure  $\beta$ -chitin, pure PVA, and a series of  $\beta$ -chitin/PVA blend films. For pure PVA film, the  $T_g$  value was found to be ca. 35 °C, which was ca. 25 °C lower than that observed for the neat resin. This could be a result of the oxidative degradation upon dissolution in concentrated formic acid or the plasticizing effect due to the presence of residual solvent molecules in the as-prepared films or both. Based on DSC results, the  $T_g$  value for pure  $\beta$ -chitin film could not be observed in this work. However, Kim et al. [12] used a more sensitive DMTA technique to measure the  $T_g$  value for pure  $\beta$ -chitin and they reported it to be ca. 170 °C. For as-prepared blend films, single  $T_g$  shoulder peak was clearly observed for each blend composition.

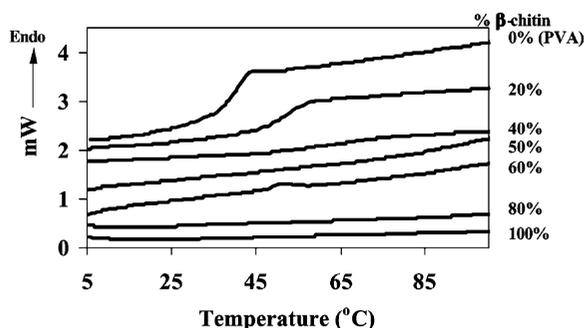


Fig. 1. The second heating thermograms for pure  $\beta$ -chitin, pure PVA, and a series of  $\beta$ -chitin/PVA blend films (recorded at 10 °C $\times$ min<sup>-1</sup>) in the temperature range where a glass transition should be observed.

The facts that only single  $T_g$  peak was observed for each blend composition and that the resulting  $T_g$  value was found to increase slightly with increasing  $\beta$ -chitin content indicated partial miscibility of  $\beta$ -chitin and PVA in the amorphous phase at the molecular level for any given compositional ratio.

The melting endotherms for pure  $\beta$ -chitin, pure PVA, and a series of  $\beta$ -chitin/PVA blend films are shown in Fig. 2. Clearly, the  $T_m$  value for pure PVA film was found to be ca. 180 °C, and the position of the melting endotherms for  $\beta$ -chitin/PVA blend films at various compositions tended to shift to a lower temperature with increasing  $\beta$ -chitin content. For pure  $\beta$ -chitin film, it is surprising to observe a broad endothermic peak, the onset of which was observed at ca. 120 °C. This could be a result of the relaxation of the acetamide groups attached to the C2 position in  $\beta$ -chitin chains [12]. It is worthy to note that the  $T_m$  value for pure  $\beta$ -chitin could not be observed, a direct result of the rigid-rod nature of the  $\beta$ -chitin molecular backbones making them being susceptible to degradation before melting. This phenomenon is, in fact, typical for many other polysaccharides.

Thermal stability of the as-prepared films can be observed by TGA technique. Fig. 3 shows the TGA curves for pure  $\beta$ -chitin, pure PVA, and 50/50  $\beta$ -chitin/PVA blend films. All of the samples tested showed initial weight loss at ca. 50 °C, likely a result of moisture evaporation upon heating. The amount of moisture content in all of the samples tested was almost similar. According to the derivative TGA curves, pure PVA film was found to degrade at ca. 270 °C (see Fig. 3; curve (a)), while pure  $\beta$ -chitin film showed two degradation peaks at ca. 262 and 349 °C, respectively (see Fig. 3; curve (c)). Apparently, the 50/50  $\beta$ -chitin/PVA blend film exhibited degradation behavior intermediate to those of the pure components, exhibiting two degradation peaks at ca. 269 and 342 °C, respectively (see Fig. 3; curve (b)). Table 1 lists the degradation peak values

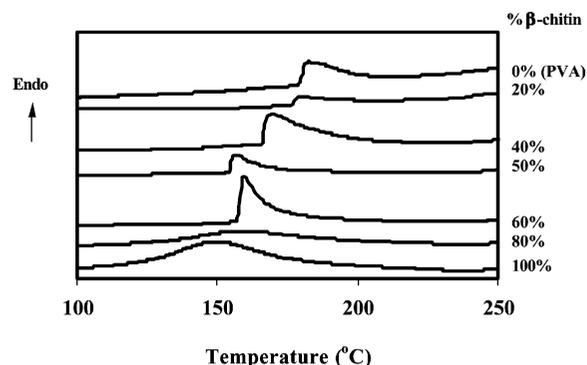


Fig. 2. The second heating thermograms for pure  $\beta$ -chitin, pure PVA, and a series of  $\beta$ -chitin/PVA blend films (recorded at 10 °C $\times$ min<sup>-1</sup>) in the temperature range where a melting endotherm should be observed.

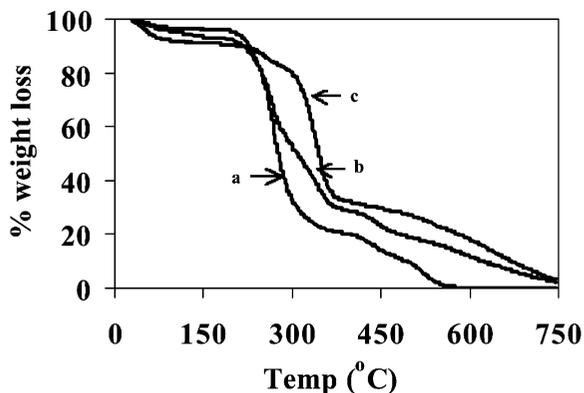


Fig. 3. TGA curves for pure  $\beta$ -chitin, pure PVA, and a series of  $\beta$ -chitin/PVA blend films (recorded at  $10\text{ }^{\circ}\text{C}\times\text{min}^{-1}$ ).

Table 1

Degradation temperature(s) of pure  $\beta$ -chitin, pure PVA, and a series of  $\beta$ -chitin/PVA blend films

Type of film	1st $T_d$ ( $^{\circ}\text{C}$ )	2nd $T_d$ ( $^{\circ}\text{C}$ )
$\beta$ -chitin	$262\pm 0$	$349\pm 1$
80/20 $\beta$ -chitin/PVA	$264\pm 2$	$348\pm 1$
60/40 $\beta$ -chitin/PVA	$265\pm 1$	$346\pm 2$
50/50 $\beta$ -chitin/PVA	$269\pm 1$	$342\pm 2$
40/60 $\beta$ -chitin/PVA	$271\pm 2$	$335\pm 2$
20/80 $\beta$ -chitin/PVA	$280\pm 2$	–
PVA	$270\pm 2$	–

(denoted  $T_d$ ) observed for all of the as-prepared films studied. For most blend compositions, the degradation behavior of the blend films was found to be intermediate to those of the pure components. Interestingly, only 20/80  $\beta$ -chitin/PVA blend film exhibited only single degradation peak, with the  $T_d$  value being much greater than those of the pure components. The reason for such peculiarity will be the matter for further investigation.

Fig. 4 illustrates WAXD patterns for pure  $\beta$ -chitin,

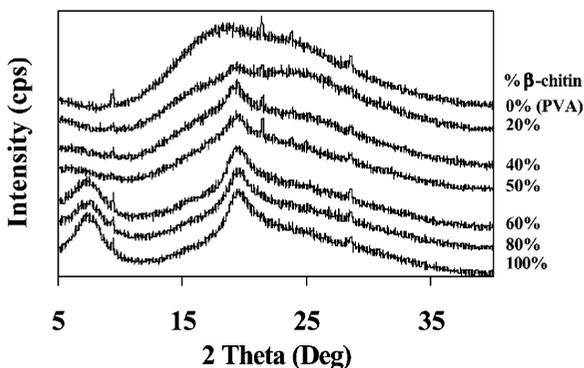


Fig. 4. WAXD patterns for pure  $\beta$ -chitin, pure PVA, and a series of  $\beta$ -chitin/PVA blend films.

pure PVA, and a series of  $\beta$ -chitin/PVA blend films. Obviously, the WAXD pattern for pure  $\beta$ -chitin film exhibited two crystalline peaks at the  $2\theta$  angles of ca.  $7.4$  and  $19.4^{\circ}$ , respectively. This observation is in general accordance with the finding by Ren and Tokura [13], who reported that the two characteristic crystalline peaks of  $\beta$ -chitin were found at  $8.50$  and  $19.98^{\circ}$ , corresponding to the (010) and (020) and ( $1\bar{1}0$ ) refraction planes, respectively. When PVA crystallized in a monoclinic unit cell (with the cell characteristics:  $a = 0.781$  nm,  $b = 0.252$  nm, and  $c = 0.511$  nm,  $\alpha = \beta = 90^{\circ}$ ,  $\gamma = 97.1^{\circ}$ ) [14], the main peaks in the WAXD pattern should appear at the  $2\theta$  angles of  $11.3$ ,  $19.7$ ,  $22.9$ ,  $28$ ,  $32.5$ , and  $40.9^{\circ}$  [15]. According to Fig. 4, the WAXD pattern for pure as-prepared PVA film only showed a broad crystalline peak at the  $2\theta$  angle of ca.  $18.7^{\circ}$ . For  $\beta$ -chitin/PVA blend films, the diffractograms appeared to be intermediate to those of the pure components. It is evident that, as  $\beta$ -chitin increased, not only did the intensity of  $\beta$ -chitin characteristic crystalline peaks become less pronounced, especially when  $\beta$ -chitin content was lower than 50 wt%, but the crystalline peaks became broader as well, suggesting a decrease in the size of  $\beta$ -chitin crystals as well as in the apparent degree of crystallinity. This might be a result of a dilution effect when PVA was blended with  $\beta$ -chitin.

Even though not shown in this paper, surface morphology of  $\beta$ -chitin/PVA blend films was also observed by scanning electron microscopy. After drying the films at room temperature for 48 h, the films with porous structure were obtained for all of the blend compositions. On the contrary, when the films were instead dried in an oven at  $60\text{ }^{\circ}\text{C}$  for 12 h, shrinkage in the films was observed. In order to observe the level of compatibility between  $\beta$ -chitin and PVA in as-prepared  $\beta$ -chitin/PVA blend films which were earlier dried at  $60\text{ }^{\circ}\text{C}$ , the films were etched in hot ethylene glycol which is a good solution to PVA and the resulting SEM micrographs are shown in Fig. 5. According to Fig. 5, certain level of phase separation in the micrometer scale is obvious in all of the blend compositions studied.

### 3.2. Tensile properties

The mechanical properties, in terms of tensile strength and percentage of elongation at break, were determined for pure  $\beta$ -chitin, pure PVA, and a series of  $\beta$ -chitin/PVA blend films and the results are reported as a function of  $\beta$ -chitin content in Figs. 6 and 7, respectively. For pure  $\beta$ -chitin film, the tensile strength and the percentage of elongation at break were found to be ca.  $5.1$  MPa and  $2.9\%$ , respectively. This agreed particularly well with the results obtained by Kim et al. [12], who reported that the tensile strength and the percentage of elongation at break for pure  $\beta$ -chitin film, which was solution-casted from its solution in formic acid, were ca.

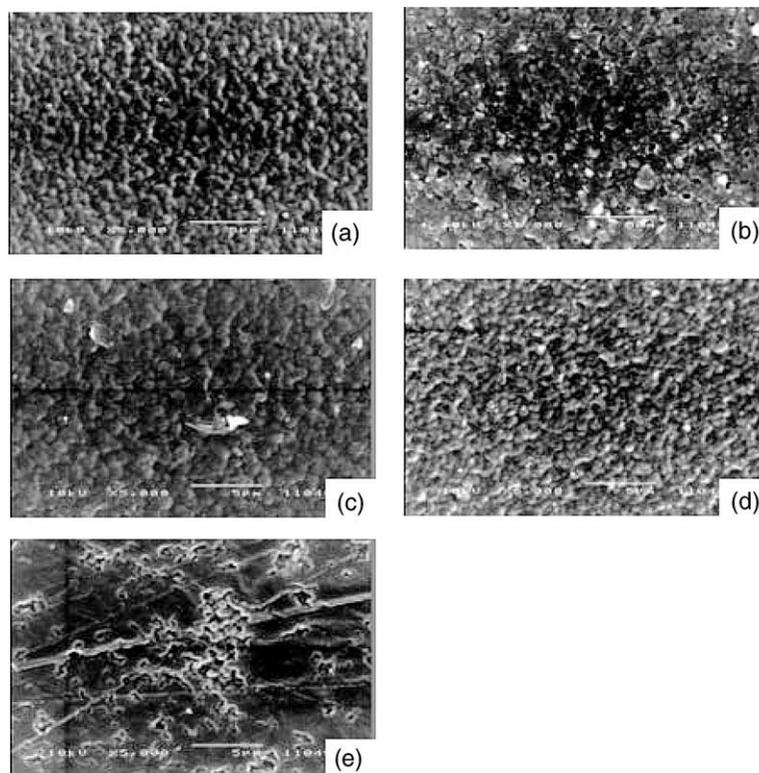


Fig. 5. Scanning electron micrographs of ethylene glycol-etched  $\beta$ -chitin/PVA blend films for (a) 80/20, (b) 60/40, (c) 50/50, (d) 40/60, and (e) 20/80 blend compositions, respectively.

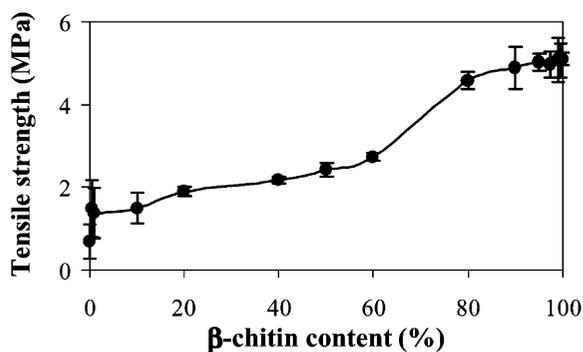


Fig. 6. Tensile strength for pure  $\beta$ -chitin, pure PVA, and a series of  $\beta$ -chitin/PVA blend films.

5.2 MPa and 5%, respectively. On the other hand, PVA exhibited a much softer character, with its tensile strength and the percentage of elongation at break being ca. 0.7 MPa and 165.2%, respectively. For  $\beta$ -chitin/PVA blend films, the tensile strength was found to increase, with increasing  $\beta$ -chitin content, from ca. 0.7 to 5.1 MPa, at the expense of the percentage of elongation at break, which was found to decrease from ca. 165.2 to 2.9%. Physically, the blend films appeared to be more brittle as  $\beta$ -chitin content increased.

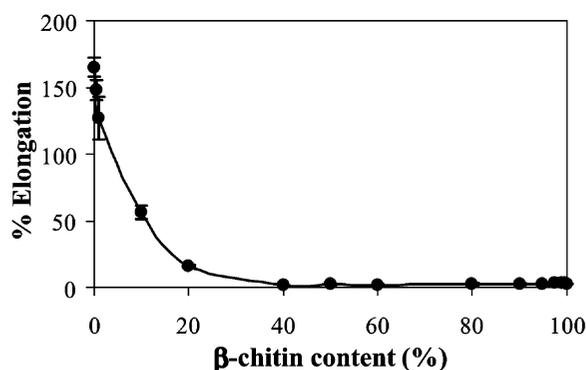


Fig. 7. Percentage of elongation at break for pure  $\beta$ -chitin, pure PVA, and a series of  $\beta$ -chitin/PVA blend films.

### 3.3. Swelling behavior

The degree of swelling of pure  $\beta$ -chitin, pure PVA, and a series of  $\beta$ -chitin/PVA blend films with different blend compositions is shown in Fig. 8 as a function of immersion time in distilled water. For a given blend composition, the degree of swelling increased with increasing immersion time. After 8 h of immersion time, it is interesting to note that the ultimate degree of swell-

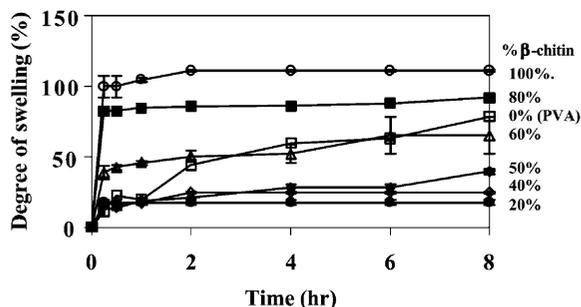


Fig. 8. Dynamic degree of swelling in distilled water for pure  $\beta$ -chitin, pure PVA, and a series of  $\beta$ -chitin/PVA blend films as a function of immersion time.

ing of pure  $\beta$ -chitin film was greater than that of pure PVA film (i.e., ca. 100% versus ca. 80%). With increasing  $\beta$ -chitin content, the ultimate degree of swelling after 8 hours of immersion time of  $\beta$ -chitin/PVA blend films was found to increase from ca. 15 to ca. 90%, when  $\beta$ -chitin content increased from 20 to 80 wt%. This behavior is in general agreement with results obtained for IPN hydrogel composed of  $\beta$ -chitin and PEG macromer [16].

The equilibrium degree of swelling (after 4 days of immersion time) for pure  $\beta$ -chitin, pure PVA, and a series of  $\beta$ -chitin/PVA blend films as a function of  $\beta$ -chitin content is shown in Fig. 9. Interestingly, the equilibrium degree of swelling of pure PVA film was now greater than that of pure  $\beta$ -chitin film (i.e., ca. 190% versus ca. 110%). Comparison of the results shown in Fig. 8 suggests that pure  $\beta$ -chitin film reached the equilibrium much faster than pure PVA film. For  $\beta$ -chitin/PVA blend films, the equilibrium degree of swelling was found to increase from ca. 30 to ca. 95%, when  $\beta$ -chitin content increased from 20 to 80 wt%. This is in accord with the ultimate degree of swelling after 8 h of immersion time observed earlier. It is rather surprising, however, that both the ultimate and equilibrium degrees of swelling of

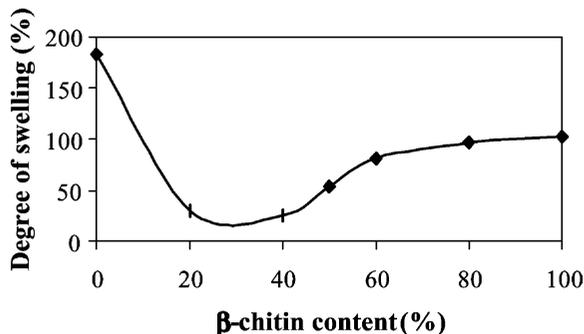


Fig. 9. Equilibrium degree of swelling in distilled water for pure  $\beta$ -chitin, pure PVA, and a series of  $\beta$ -chitin/PVA blend films.

the 20/80  $\beta$ -chitin/PVA blend film were found to be the lowest among the films studied, despite the high level of PVA content.

The equilibrium degree of swelling in various media (i.e., water, NaCl,  $\text{CaCl}_2$ , and  $\text{FeCl}_3$  solutions at the concentration of 0.25 M) of pure  $\beta$ -chitin, pure PVA, and a series of  $\beta$ -chitin/PVA blend films was investigated and the results are shown in Fig. 10. Evidently among of the media studied,  $\text{FeCl}_3$  solution was the best medium to swell the as-prepared films. According to a known fact that, when being present in water, ferric ion,  $\text{Fe}^{3+}$ , can exist in an hydrated form, e.g.,  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  [17], and the bulky size of the hydrated ferric ion can thus be responsible for the high degree of swelling of the as-prepared films studied. It could be further deduced from the results obtained that the blend films swell more substantially in trivalent ion solutions than in monovalent and bivalent ion solutions.

#### 4. Conclusions

In this contribution,  $\beta$ -chitin/PVA blend films were prepared by solution-casting from solutions of  $\beta$ -chitin and PVA in concentrated formic acid at various compositional ratios. The effect of blend compositions on physical properties, thermal properties, mechanical properties, morphology, and swelling behavior was investigated and the results were compared with those of pure components. DSC measurements showed that the glass transition temperatures of the blend films increased with increasing  $\beta$ -chitin content, while melting temperatures tended to shift to a lower temperature. Thermal stability of the blend films was found to be intermediate to those of the pure components. WAXD patterns indicated a reduction in the apparent degree of crystallinity of  $\beta$ -chitin with increasing PVA content. Surface morphology of ethylene glycol-etched  $\beta$ -chitin/PVA blend films suggested that a certain level of phase separation in a micrometer scale was found for blend films of all

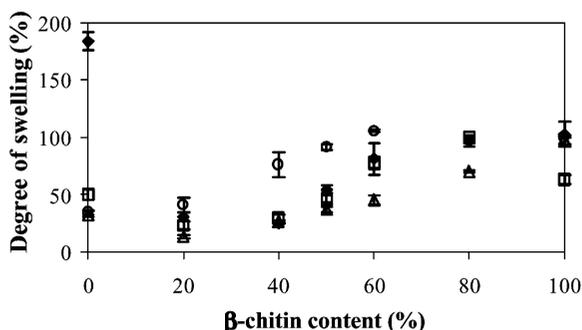


Fig. 10. Equilibrium degree of swelling in various media for pure  $\beta$ -chitin, pure PVA, and a series of  $\beta$ -chitin/PVA blend films. Keys: (◆) water, (□) NaCl, (△)  $\text{CaCl}_2$ , and (○)  $\text{FeCl}_3$ .

blend compositions. The tensile strength of the blend films was found to increase, with increasing  $\beta$ -chitin content, from ca. 0.7 to 5.1 MPa, at the expense of the percentage of elongation at break which was found to decrease from ca. 165.2 to 2.9%. The equilibrium degrees of swelling in distilled water of  $\beta$ -chitin/PVA blend films of all blend compositions were found to be lower than those of the pure constituents, with that of the 20/80  $\beta$ -chitin/PVA blend film being the lowest. Lastly, 0.25 M  $\text{FeCl}_3$  solution, among the various swelling media investigated, was the best to swell most of the films studied.

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