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Preparation and characteristics of β-chitin and poly(vinyl alcohol) blend

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Mechanical properties of blend films of β-chitin and poly(vinyl alcohol) (PVA) in dry and wet states were improved compared to those of homopolymers. Fourier transformed infra-red (*FT* i.r.) spectra of the blend showed the transition of hydroxyl and carbonyl stretching bands upon blending. The subtraction infra-red spectra of blend 70/30 indicated that the blend showed an intermolecular interaction and the reduction of crystallinity compared with those of pure β-chitin. Wide angle X-ray diffraction (WAXD) patterns of the blend also exhibited the loss of crystallinity of β-chitin and PVA upon blending. The blends, however, showed a mixed-crystal structure. Dielectric analysis of the blend showed the transition of α- and β-relaxation peaks of β-chitin upon blending, appeared at 182°C and 97°C, respectively. For blends, the temperature of the maximum loss (T_{max}) of β-chitin appeared at around 182°C shifted to a lower temperature region. Differential scanning calorimetric analysis of the blend also showed the transition of melting endotherms of the blend. Transmission electron microscope (TEM) studies of blends using ruthenium tetraoxide as a staining agent were examined to reveal the micro-structure and miscibility of the blends. The TEM micrograph of blend 70/30 shows some microseparations, but it is still believed to be miscible in the blends. Copyright © 1996 Elsevier Science Ltd.

(Keywords: β-chitin; PVA; blend; α-relaxation; β-relaxation)

INTRODUCTION

Three polymorphic crystal structures of chitin[1] are known, α-, β- and γ-structure. Crystal structures of three chitins have been extensively studied. α-Chitin is the tightly compacted, most crystalline orthorhombic form where the chains are arranged in an anti-parallel fashion. It can be obtained from the shell of crabs, lobsters and shrimps. β-Chitin, obtained from the pen of loligo and squid has the monoclinic form where the chains are parallel[1]. While α-chitin is not usually soluble in most organic solvents, β-chitin is even swollen in water and dissolved easily in formic acid. γ-Chitin is a mixture of α- and β-chitin.

Generally, insolubility of chitin in many organic solvents limits the use of chitin compared with cellulose in many applications. There have been many attempts to overcome the solubility problem of chitin including chemical modification of chitin[2–4], finding new solvents[5,6] etc. Blending is an especially important process for developing industrial applications of polymeric materials. Compatibility among components has a marked influence on the mechanical properties of polymer blends[7]. Intermolecular interactions regulate the compatibility among the component polymer molecules[7].

Blending natural polymer with synthetic polymer seems to be an interesting way of preparing polymeric composites. Cellulose/poly(vinyl alcohol) (PVA) blend has been extensively studied by Nishio and coworkers[8,9] and Shibayama *et al.*[10] who concluded that cellulose was partially soluble in common organic solvents such as *N*,*N*-dimethylacetamide-lithium chloride (DMAc-LiCl), dimethylsulfoxide–tetraethyl ammonium chloride (DMSO-TEAC). Interestingly, Kondo *et al.* revealed the regioselective hydrogen bonding between cellulose and PVA[11]. Moreover, cellulose was blended with poly(vinyl pyrrolidone)[12], poly(methyl methacrylate)[13] and poly(2-hydroxy ethyl methacrylate)[14]. PVA can be blended with poly(*N*-vinyl pyrrolidone)[15] and hydroxypropyl methyl cellulose[16]. Here, hydrogen bonding interaction is an important aspect of miscibility. Chitosan/PVA blend was studied by Miya and coworkers[17,18] and the present authors[19] and their application to Vitamin-B_{12} permeation by Nakatsuka and Andrady[20]. Their blood compatibility and permeability properties were investigated by Chandy and Sharma[21]. However, no study has been reported on the chitin/PVA blend system.

Chitin is known as a potentially useful biopolymer produced in huge amounts in nature[22]. There have been many studies of chitin as a biocompatible material, such as for artificial skin[23,24], suture[25], coating materials[26], as a drug carrier[27–29] and so on. Most chitin studies are, however, based on readily accessible α-chitin whose main chains arrange in an anti-parallel fashion with strong intermolecular hydrogen bonding. α-Chitin is thus characterized by poor solubility and reactivity and its physical properties are that it is very rigid and brittle.

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In contrast, β-chitin has much weaker intermolecular hydrogen bonding ascribable to the parallel arrangement of the main chains. We have reported thermal and mechanical properties of β-chitin in our previous report[30]. Moreover, it shows higher solubility and swelling than α-chitin[31,32]. Nevertheless, β-chitin still has some extent of rigidity and brittleness. For these reasons, it is expected that mechanical properties of β-chitin can be improved through blending with PVA which is highly elastic in spite of its crystalline feature and is also known as a biocompatible material. Accordingly, the blend of β-chitin and PVA is a good candidate for new biomaterial with enhanced mechanical properties.

In this paper, we report on a solution blend of two polymers containing hydrogen bonding group, PVA and β-chitin. Acetamide, ether oxygen and hydroxyl groups allow for inter- and intramolecular interactions between the two chains. The objective of the present study is to prepare and characterize the β-chitin and PVA blend. We will report on the miscibility of the two polymers in the solid state due to intermolecular interactions by means of Fourier transform infra-red spectroscopy (*FT* i.r.), wide angle X-ray diffraction (WAXD), differential scanning calorimetry (d.s.c.), dielectric analysis (d.e.a.) and transmission electron miscroscopy (TEM).

EXPERIMENTAL

Materials

β-Chitin was extracted from squid pen by modified Hackmann method[1], dried at 60°C vacuum oven and used as a 60-mesh powder. PVA (DP = 2500, degree of deacetylation = 99%) was supplied by Shinetsu Co. The formic acid as a solvent was 99% reagent grade purchased from Janssen Chimica and used without further treatment. The ruthenium (IV) oxide hydrate as a staining agent for TEM study was also purchased from Janssen Chimica.

Preparation of blend

A known amount of β-chitin was dissolved in formic acid (99%) to prepare 2 wt% solution at room temperature and filtered by 2G1 glassfilter manufactured by Schott. Later 2 wt% PVA–formic acid solution was added at room temperature. The composition of the β-chitin:PVA was 90/10, 80/20, 70/30, 60/40 and 50/50 in wt% and designated as CP91, CP82, CP73, CP64 and CP55, respectively. The blend films were prepared by casting the mixed solutions on a glass plate and drying in a drying oven at 40°C for 24 h. The obtained films were evacuated in vacuum oven for 24 h over 100°C to remove the residual solvent inside the films. The resulting films were transparent but somewhat brittle. The brittleness of the films, however, was reduced as the PVA content increased.

Characterization

Structure of blends was confirmed by *FT* i.r. analysis which was performed by means of a Nicolet Magna i.r. spectrometer. Samples were thin films spread on KBr discs from 1 wt% formic acid solutions, dried under vacuum at 100°C overnight. An X-ray diffractometer (Rigaku Denki RAD-C) was used to characterize the crystal structure of the blend. WAXD patterns were also recorded with a flat film camera using nickel-filtered Cu-Kα radiation in $2\theta = 5$–30°. D.s.c (TA Instruments Model 910) characterized the thermal property of the blend with 5°C min^{-1} heating rate and 50 ml min^{-1} N_2 flow rate.

Dielectric measurements were conducted to observe the glass transition temperature (T_g) and relaxation behaviours of samples. Measurements of dielectric constant, ε', and dielectric loss factor, ε'', were carried out using the d.e.a. (TA Instruments DEA 2970). The dielectric spectra were recorded at frequency of 10 Hz over the temperature ranging from 45 to 250°C, the heating rate being 1°C min^{-1}, in an atmosphere of 50 ml min^{-1} nitrogen. Experiments were carried out on cast films with dimensions of 30 × 30 × 0.1 mm using ceramic parallel plate sensor.

A universal testing machine (Instron Model 4201) measured the tensile strength and elongation of each blend sample in dry and wet states with an extension rate of 10 mm min^{-1} at room temperature. Test films for dry state were prepared by drying them over 100°C for 24 h to remove the residual solvent. For the wet state measurement, the films were immersed into the water until equilibrium water content (EWC) was achieved. Reported values are the mean of the five samples and the deviation from the mean is within ±5%.

TEMs were taken with a JEOL 2000 EX2 electron microscope at an accelerating voltage of 100 kV. To prepare samples for TEM, clean glass slides were dipped in 1 wt% polymer solutions. Solvent-cast thin films of β-chitin, PVA and blends were prepared by evaporation of the solvent under vacuum at 40°C for 24 h. A concentration of 1 wt% of polymer in formic acid yielded films between 3000 and 7000 Å thick. The films were removed from the glass plate by immersing the slide glass into deionized water. Sections (2 mm × 2 mm) of the films were lifted from the water surface onto copper microscope grids. A 0.5 wt% RuO_4 solution in deionized water was used for staining. Film-covered grids were vapour stained in a glass-covered dish for 3 h at room temperature and kept in dry and cold states until electron micrographs were taken.

RESULTS AND DISCUSSION

In the course of studying β-chitin/PVA blends, we have found that β-chitin forms optically clear homogeneous blends with PVA and that the tensile strength of the blend is greater than the homopolymers. Enhancement of mechanical properties appears both in the dry and wet states as shown in *Table 1*, although the tensile strength values in the wet state are, in general, much smaller than those in dry state. β-Chitin showed a tensile strength of 5.0 MPa and elongation at break of 5.8% in dry state. Upon mixing with PVA, the tensile strength generally decreased and elongation at break increased with PVA contents. Notice that CP73 shows 5.17 MPa and 26.1% elongation value. CP73 is a composition at which the tensile strength shows a maximum, but it differs somewhat in wet samples. The appearance of the maximum at the ratio of 70/30 in dry state suggests the existence of specific intermolecular interaction between β-chitin and PVA.

FT i.r. spectroscopy is one of the most powerful techniques for investigation of multi-component systems, because it provides information on the blend

Table 1 Mechanical properties of β-chitin, blends and PVA dry and wet states

	Dry state		Wet state (EWC)	
Sample	Tensile strength (MPa)	Elongation at break (%)	Tensile strength (MPa)	Elongation at break (%)
β-chitin	5.0 ± 0.12	5.8 ± 0.15	0.4 ± 0.01	20 ± 0.65
CP91	4.46 ± 0.08	13.1 ± 0.31	0.9 ± 0.02	15.6 ± 0.42
CP82	3.04 ± 0.09	13.6 ± 0.42	0.35 ± 0.01	21.3 ± 0.11
CP73	5.17 ± 0.16	26.1 ± 0.94	0.38 ± 0.01	29.2 ± 0.12
CP64	4.09 ± 0.09	41.1 ± 0.62	0.37 ± 0.01	45.4 ± 1.24
CP55	3.18 ± 0.05	87.5 ± 1.97	0.25 ± 0.01	47.2 ± 1.35
CP46	2.53 ± 0.02	77.4 ± 2.05	0.12 ± 0.00[a]	44.3 ± 1.02
CP37	1.75 ± 0.04	129.4 ± 5.97	0.24 ± 0.01	77.1 ± 2.34
PVA	2.17 ± 0.04	487 ± 11.50	3.1 ± 0.01	423 ± 15.64

[a] 0.003

composition as well as on the polymer–polymer interaction. Our discussion will mainly concentrate on the hydroxyl and carbonyl stretching vibration bands in *Figure 1*, as they are expected to be affected by hydrogen bonding interactions.

Figure 1 shows the *FT* i.r. spectra for β-chitin, blends and PVA samples. Stretching vibration of hydroxyl groups in chitin, blends and PVA appears at around 3450 cm^{-1}. The –OH stretching vibration at 3459 cm^{-1} peak in the pure β-chitin does not appear in the blend samples and not only the characteristic shape of the spectrum of β-chitin change in the blend, but also the peak shifts to a lower frequency range, indicating that there should occur a stronger hydrogen bonding interaction between –OH of PVA and –OH or $-NHCOCH_3$ of β-chitin in the blend. Stretching vibration spectra of acetamide group of β-chitin appear at 1663 and 1564 cm^{-1} while that of blends appears at 1639–1645 cm^{-1} and 1560–1562 cm^{-1}, respectively.

Figure 2 exhibits the subtraction i.r. spectra of the blend 70/30 (CP73). Intermolecular interactions in the polymer blends may be elucidated by comparing the spectrum of the pure β-chitin with the subtraction spectrum that should represent the spectrum of β-chitin resulting from intermolecular interactions with PVA in the blend. Spectrum (b) of pure PVA was subtracted from the spectrum of blend (a) to give the spectrum of β-chitin in the blend. It is known that 854 cm^{-1} band of PVA is the only absorption band without any superposition of those due to chitin[18,33]. In the subtraction spectrum, the 854 cm^{-1} band was smoothly cancelled out (see *Figure 2c*). The spectrum of blend (a) is generally very similar to that of pure PVA (b), and the subtraction spectrum (c) shows the characteristic β-chitin spectrum, as in (d). The detailed characteristic feature in the 1800–800 cm^{-1} region of β-chitin in spectrum (d) is generally well reproduced in the subtraction spectrum (c). The difference between the subtraction spectrum (c) and spectrum (d) should arise from intermolecular interactions between β-chitin and PVA in the blend. There are five differences between the subtraction spectra of CP73 (c) and the spectra of pure β-chitin (d). The first is the feature in the –OH stretching vibration region as we mentioned above. The 3459 cm^{-1} peak in the pure β-chitin disappeared in the blend and the shape of this peak is changed and shifted to a lower frequency at 3416 cm^{-1}. Moreover, the peak intensity of the blend is stronger than that of pure β-chitin relative to amide band appeared at around 1660 cm^{-1}. Secondly, the strong band at 2884 cm^{-1} in the pure β-chitin is not shown as a separate band in the blend but only as a shoulder. Thirdly, the sharp band at 1041 cm^{-1} in the pure β-chitin becomes an unseparated shoulder. Fourth, the amide bands of pure β-chitin at 1663 and 1564 cm^{-1} are shifted to a lower frequency region at 1638 and 1562 cm^{-1}. Besides, their intensity was reduced because most of the acetamide group in the β-chitin takes part in hydrogen bonding. Finally, the weak band at 613 cm^{-1} in the pure β-chitin has almost disappeared in the blend.

Disappearance of the 3459, 1041 and 613 cm^{-1} bands which were reported to be related to the crystallization of chitin indicated that intermolecular interaction between β-chitin and PVA[17,18] disturbed crystallization of β-chitin in the blend state. It should be noticed that the crystallization-sensitive band of PVA at 1153 cm^{-1} is observed for PVA and blend samples with a similar intensity without any significant change in frequency. This means that PVA in the blends could have the same crystalline structure as in the pure PVA. This agrees well with the result that the X-ray diffraction pattern of the blend is essentially the same as the pure PVA, as discussed later.

These facts suggest that the enhancement of mechanical properties of the blends are due to intermolecular interaction by hydrogen bonding which prevents β-chitin from crystallization, but does not sufficiently destroy the crystalline structure of PVA. The intermolecular interactions seem to play an important role in the formation of the amorphous region inside the blend.

WAXD patterns of chitin, CP73 and PVA are shown in *Figure 3*. The WAXD pattern of pure PVA is composed of several diffraction rings which could be indexed by using the lattice parameters[8] $a = 7.81$, $b = 2.52$, $c = 5.51$ Å and $\beta = 91.7°$. PVA shows a typical monoclinic crystal structure where crystalline peaks appeared at $2\theta = 11.3°$ (100), 19.7° (101) (10$\bar{1}$), 22.9° (200), 28° (20$\bar{1}$) (201), 32.5° (002) and 40.9° (111) (11$\bar{1}$)[8]. β-Chitin also shows a monoclinic structure where crystalline peaks appeared at $2\theta = 9.8°$ (101) and 19.5° (020) (110)[33]. The lattice parameters of β-chitin are: $a = 4.85$, $b = 9.26$, $c = 10.38$ Å and $\beta = 97.5°$[33]. For the blends, their reflection patterns are almost the same as those of PVA with small reduction in their intensity.

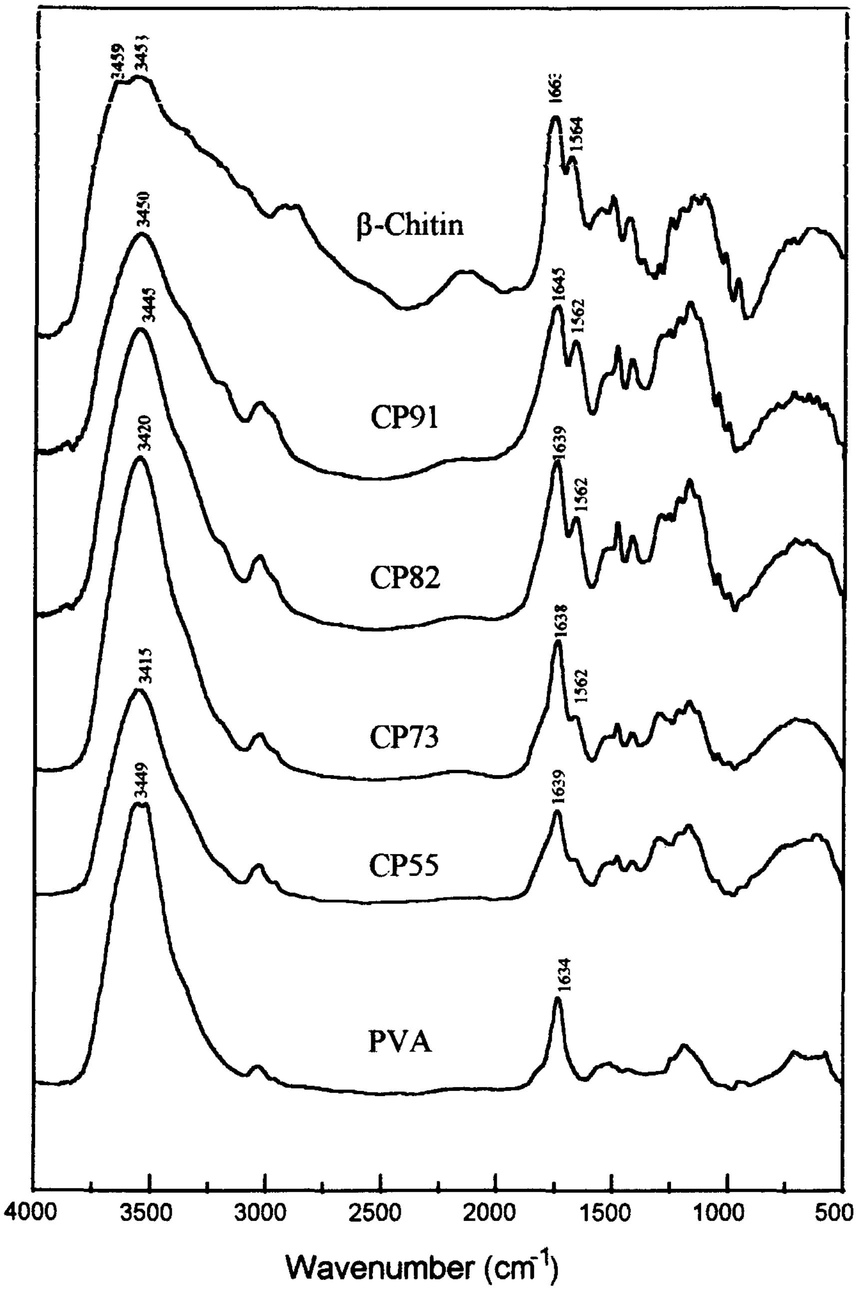

Figure 1 *FT* i.r. spectra of β-chitin, CP91, CP82, CP73, CP55 and PVA

The pictures of X-ray diffraction by Laue camera also show their reflection patterns (*Figure 4*). The reflection patterns of blends are somewhat diffused compared to those of each β-chitin and PVA, but there is no definitive evidence of the formation of a so-called mixed-crystal structure. We admitted, however, that the crystallinity of each polymer was strongly affected by the presence of the other component. The diffraction intensities of the individual polymers decreased with increasing content of the other component. Here it should be noted that every reflection pattern of the blends has characteristic diffraction patterns of PVA. This means that in the blends the crystalline structure of PVA is essentially sustained, whereas it is not in the case of β-chitin. That is to say, the crystalline structure of β-chitin is mainly destroyed upon blending.

Figures 5 and *6* exhibit the d.s.c. melting and thermograms for chitin, blends and PVA samples, respectively. β-Chitin is very rigid and we cannot detect any noticeable transition temperature in the d.s.c. thermograms. On the other hand, the pure PVA shows a relatively large and sharp melting endothermic peak at 218°C and crystallization peaks at 191°C, respectively. As PVA is blended with β-chitin up to 50/50 (CP55), the intensity of the peak is reduced rapidly, with a lower shift of crystalline melting peaks appearing at 210°C and a crystallization peak appearing at 160°C, respectively. In the blends containing 30 wt% or less PVA, it becomes difficult to detect the peaks clearly in the d.s.c. curve. This result implies that an increase of β-chitin content in the blend causes a rapid decrease of crystallinity of the PVA. However, it could also be thought that a rigid β-chitin chain prevents detection of peaks by d.s.c. A more sensitive

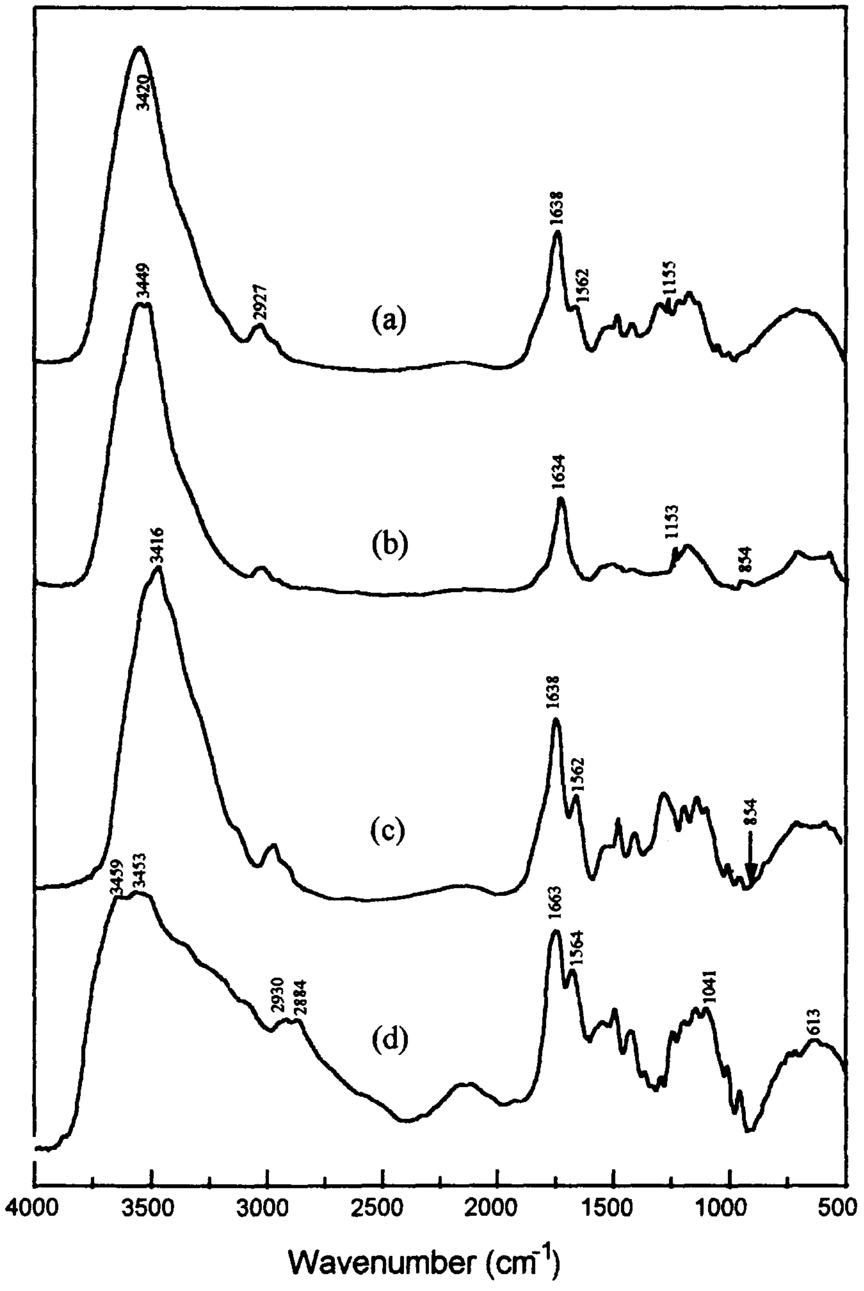

Figure 2 *FT*i.r. spectra of (a) CP73; (b) PVA; (c) subtraction; (d) β-chitin

d.e.a. of the blends was conducted for clarifying this possibility.

To examine the viscoelastic properties, dielectric analysis was performed. D.e.a. was found to be a very sensitive technique for investigating molecular relaxation behaviour. It is especially useful for detecting the glass transition temperature (T_g) of a sample that cannot be observed by normal calorimetric measurements. For example, T_g of polymers having crosslinked structure or of natural polysaccharides consisting of a rigid-rod polymer backbone that start to degrade before the second order transition could really be seen. We have reported on the thermal relaxation behaviours of α-chitin and β-chitin using d.e.a. and dynamic mechanical thermal analysis (d.m.t.a.)[30,34]. The dependence of the dissipation factor, tan δ, obtained from ε' (the dielectric constant) and ε'' (the loss factor) on temperature at 10 Hz are represented in *Figure 7* for β-chitin, blends and PVA. The transition peaks were sharp, characteristic of a one-phase system. Two relaxation peaks appeared at 97 and 182°C in β-chitin. On the upper temperature region at around 182°C for β-chitin, the temperature of the maximum loss, T_{max}, is a consequence of a decrease in the steric effect hindering the micro-Brownian motion of the chain segment, which is responsible for the α-relaxation of β-chitin. The lower one at around 97°C is assigned to β-relaxation due to side chain effect. Our recent study on thermal analysis of β-chitin by d.e.a.[30] reported that two relaxation peaks were also observed between 123 and 155°C and between 185 and 203°C. The variation of transition temperature is due to frequency adopted in measurement. As the frequency increases, the

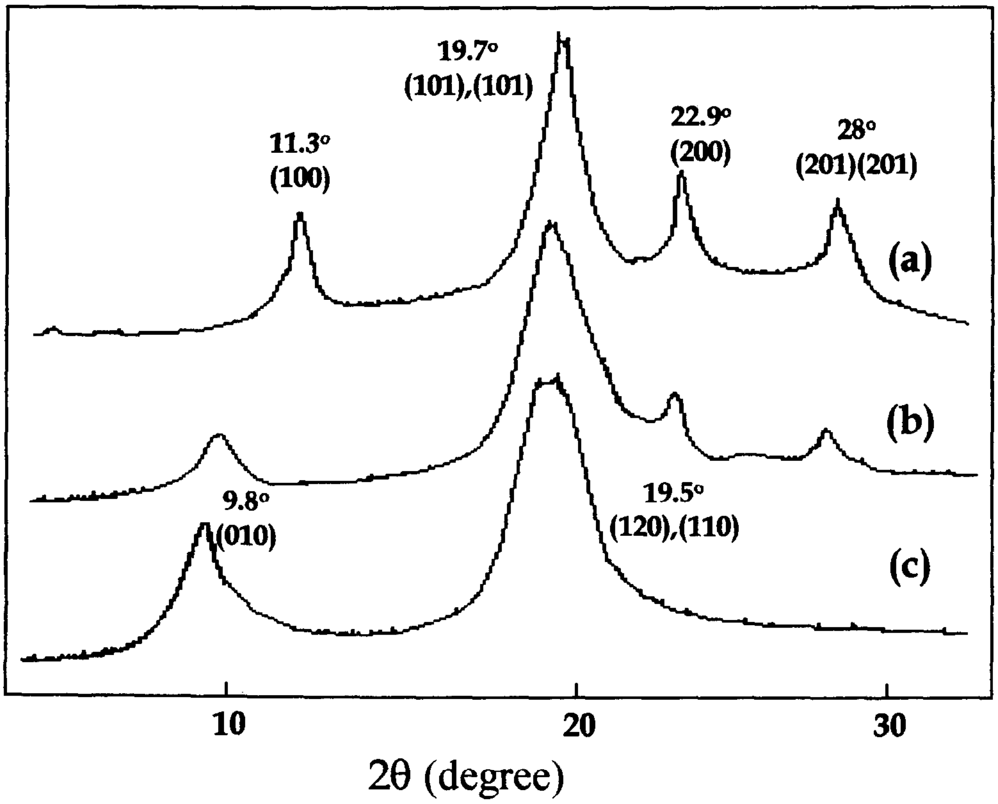

Figure 3 WAXD patterns of (a) PVA; (b) CP73 and (c) β-chitin

relaxation temperatures of tan δ maximum loss increase. This is a general consequence attributed to decrease in the steric effects hindering the micro-Brownian motion. The transition at 182°C is assigned to be a relaxation in polymer main chain, T_g of β-chitin. The other tan δ maximum value that appeared at 97°C may be caused by the acetamide group attached to C2 position in β-chitin. In the case of PVA, two significant T_{max} values were shown at 69 and 209°C, respectively, which may be the T_g and melting temperature (T_m) of PVA. A value of 88°C has been reported for the T_g of PVA in previous report for PVA 98% hydrolysed and determined by d.m.t.a. technique at 1 Hz and a heating rate of 5°C min^{-1}[35]. The difference of two values is due to differences in the rate of heating and instrument employed.

The d.e.a. thermograms for the blends have three relaxation peaks at around 80, 150 and 200°C. The highest relaxation temperature at around 200°C may be assigned to the T_m of PVA. Two α-relaxations, close to the T_g of β-chitin and PVA, were observed for the blends. The intensity of each peak changed with the composition of the corresponding component in the blend. *Table 2* shows the variation of the T_g of each phase with blend composition. As the PVA content increased, all the glass transition peaks moved into the middle of the original two T_gs of pure β-chitin and PVA, meaning that the two materials have some intermolecular interaction due to hydrogen bonding upon blending. The transition breadth of the peaks decreased significantly for the middle composition, namely, these phenomena are considered that two materials are inclined to be as one which has one T_g since they are miscible.

We have tried to take electron micrographs by TEM to investigate the microstructure and the miscibility between β-chitin and PVA inside the blends. *Figure 8* shows the morphology of CP73. Although TEM has many advantages to obtaining information on heterogeneous polymer systems, a number of difficulties arise when polymer thin films are examined[36]. For example, uncontrollable structural change, film damage and uncertain morphological contrast can occur. Therefore, we have operated the microscope at low intensities of 100 kV and carefully kept the specimen cool before examination to avoid any deterioration of the specimen. Moreover, the specimen was vapour-stained by RuO_4 to obtain the picture with adequate contrast. In the case of homopolymers, PVA film was darker than β-chitin, suggesting that PVA was more easily reacted and stained by RuO_4 than β-chitin. Hence, the darker region in *Figure 8* was thought to be PVA, whose dimensions are approximately 500 nm. This fact suggested that there would be a microphase-separation between the two polymers to some degree.

Although the microseparation occurred in the blend as was seen in the TEM, β-chitin and PVA could not be thought that they were immiscible with each other. The boundary between two phases was very ambiguous and the size of separation was too small to explain they are separated definitely. Besides, we have discussed sufficient evidence to prove the miscibility between β-chitin and PVA, such as the reduction of crystallinity as was seen in the *FT*i.r., WAXD and d.s.c. and the trace of hydrogen bonding according to *FT*i.r., d.e.a. and d.s.c. analysis. All the results in this study generally illustrate the miscibility between β-chitin and PVA. The blend of 70/30

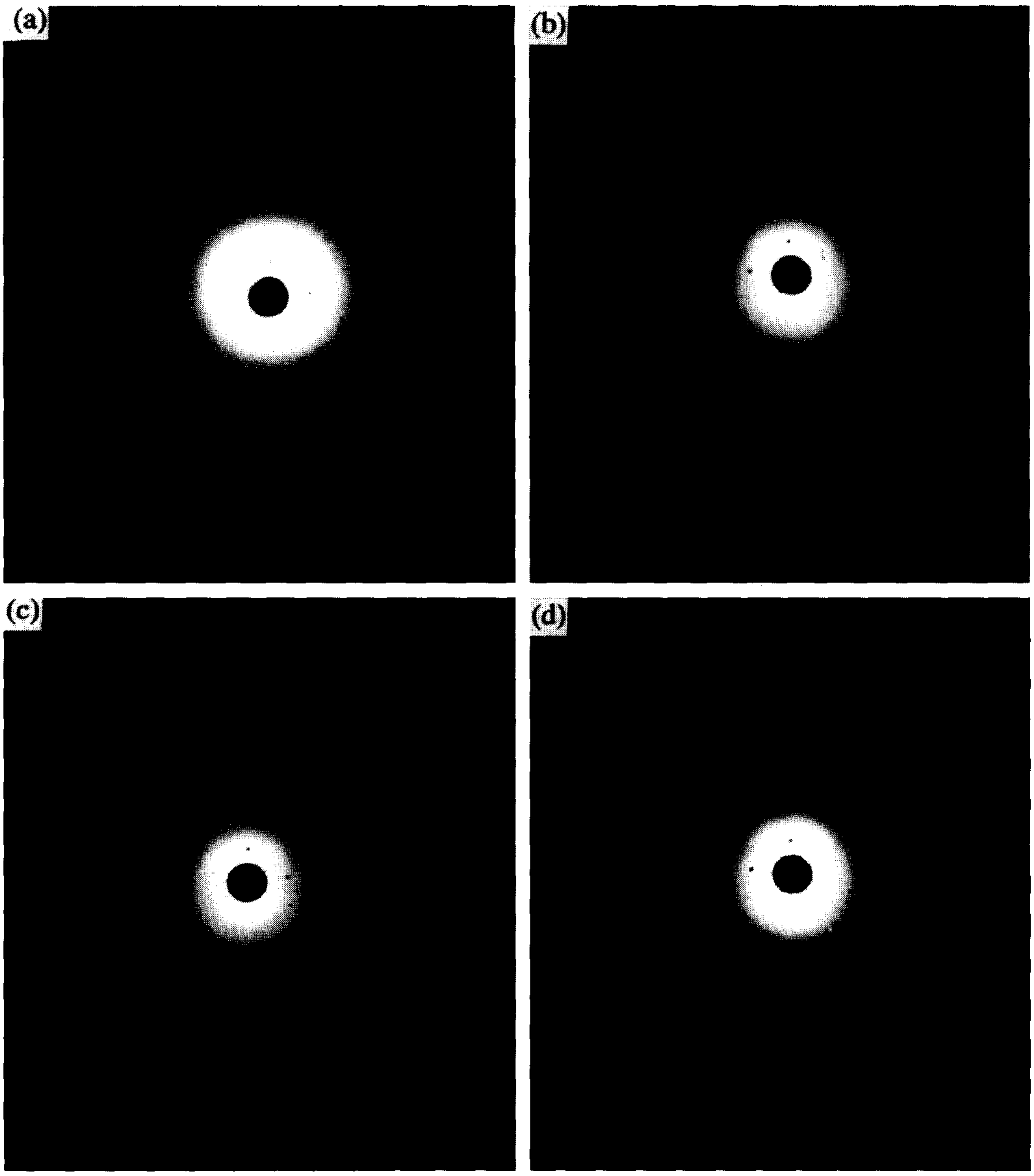

Figure 4 WAXD patterns by Laue camera: (a) PVA; (b) CP73; (c) CP55; (d) β-chitin

exhibits the maximum tensile strength, which is better than that of pure β-chitin, with reasonable elongation at break value.

CONCLUSION

Blend films of β-chitin and PVA could be easily obtained over the whole composition range from solutions in formic acid by solution blending and casting onto the glass plate. By visual inspection, there was no evidence of phase separation in any of the blend compositions. Mechanical properties of blends were enhanced relative to those of β-chitin and PVA. The tensile strength and elongation at break of CP73 in a dry state were 5.17 MPa and 26.1%, respectively, while pure β-chitin has 5.0 MPa tensile strength and 5.8% elongation value. This enhancement is caused by the existence of specific intermolecular interactions between β-chitin and PVA in the blend. *FT*i.r. analysis revealed this interaction from the shift and change of intensity of –OH and $-NHCOCH_3$ bands. In addition, the disappearance of the 3450, 1041 and 690 cm^{-1} bands in the blends confirmed that the crystallization of β-chitin was disturbed by interactions with PVA upon blending. The crystallinity of PVA, however, still remained, showing that the crystalline structure of PVA was not destroyed completely in the blend. WAXD patterns also showed reduction of crystallinity of β-chitin as diffused rings in the blend, but hold the rings of PVA. The melting point depression of the PVA component observed in the d.s.c. measurements supported the presence of such an interaction. Judging from the result of d.e.a. analysis, it is presumed that the two materials have intermolecular hydrogen bonds in the blend state. As was seen in the TEMs, we could identify a darker region as large as 0.5 μm, which was considered to be PVA stained by RuO_4. The boundary of the two phases was, however, so vague, and the dimension of microseparation was small

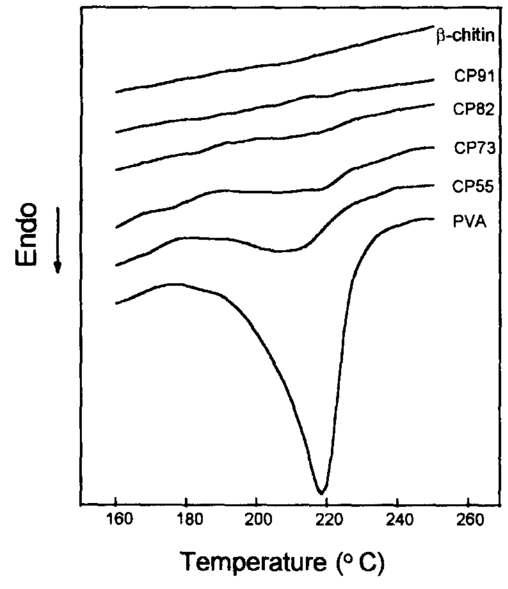

Figure 5 D.s.c. melting thermograms of PVA, blends and β-chitin

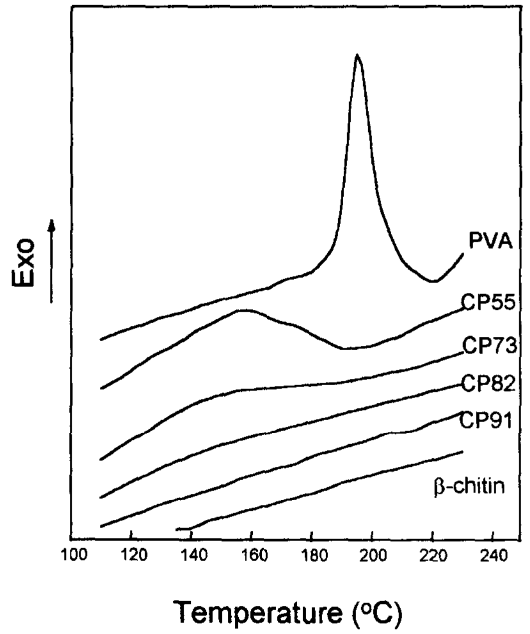

Figure 6 D.s.c. thermograms for crystallization of PVA, blends and β-chitin

enough, to allow explanation that they are generally miscible with each other. Consequently, it seems reasonable to conclude that the blends between β-chitin and PVA exhibit some level of miscibility on the whole.

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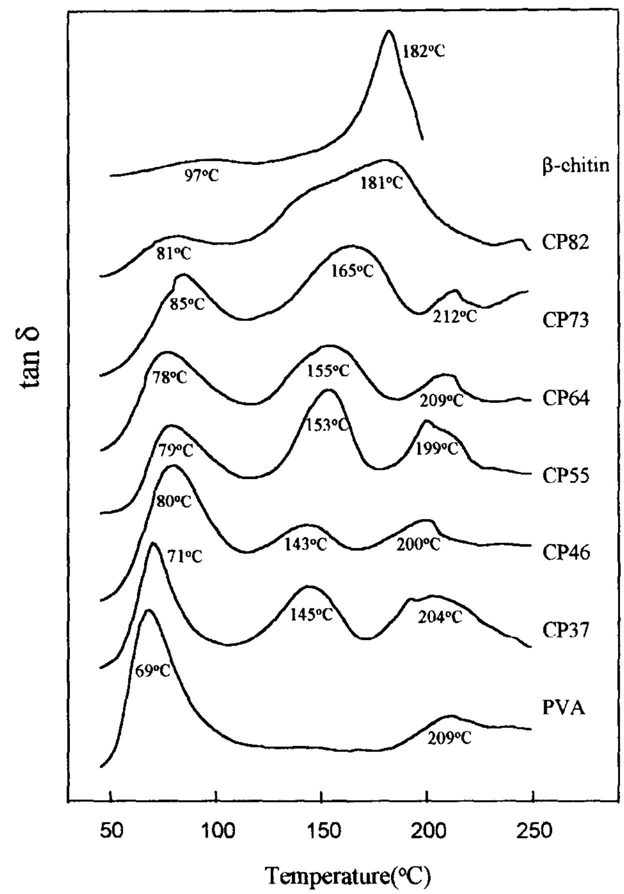

Figure 7 D.e.a. thermograms of PVA, blends and β-chitin at the frequency of 10 Hz

Figure 8 TEM of CP73 stained with RuO_4 vapor. PVA is the darker phase (× 10 000, —500 nm)

Table 2 Variation of T_g values of β-chitin, blends and PVA from d.e.a. experiments and the difference of the two values in each blend sample

Samples	$T_{g(PVA)}$ (°C)	$T_{g(\beta\text{-chitin})}$ (°C)	$T_{g(\beta\text{-chitin})} - T_{g(PVA)}$
β-chitin	–	182	–
CP82	81	181	100
CP73	85	165	80
CP64	78	155	77
CP55	79	153	74
CP46	80	143	63
CP37	71	145	74
PVA	69	–	–

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