Reversible Thickening/Thinning Phenomena Observed for Polymer Blend Films in Water Media

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ABSTRACT: An interesting phenomenon, the thickening and thinning of polymer films in the water media, was investigated in this paper. The studied polymer films were cast from atactic poly(*R*,*S*-3-hydroxybutyrate)/poly(4-vinylphenol) (PVPh) and syndiotactic poly(*R*,*S*-3-hydroxybutyrate)/PVPh blends solution. The physical properties of the blend films were characterized by differential scanning calorimetry (DSC), and the hydrogen-bonding network in the blends was characterized with the employment of Fourier transform infrared spectroscopy (FT-IR). The thickening and thinning process of the polymer films in water media was monitored by the measurement of the thickness. The effects of temperature and surfactants on the process were evaluated, furthermore, and the essence of the thickening and thinning of the polymer films was discussed.

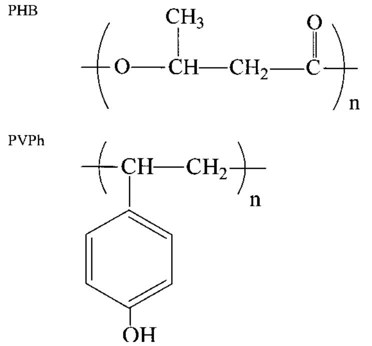
Introduction

In the past few years, much attention has been paid to poly(4-vinylphenol) (PVPh) blends, as the hydroxyl group of PVPh possesses the potential ability to form a strong intermolecular hydrogen bond with carbonyl, ether, or other functional groups of the second polymer.[1−3] A variety of binary blends containing PVPh have been studied, and almost all of these blends have been reported to be miscible in the amorphous state.[4−6]

Recently, we are studying the inter-associated hydrogen bonds in the binary blends of poly(*R*,*S*-3-hydroxybutyrate) (PHB) and PVPh (shown in Chart 1). Accidentally, a very interesting phenomenon is observed when we placed the blend films of PHB/PVPh in water media, that is, the shape of the blend films changes drastically upon exposure to water media but the weight and other properties of the film hardly change. Depending on the characteristics of the water media, the blend films either tend to sink in the water and the surface area of the films decreases obviously (the thickness increases), or they tend to float on the surface of water and the surface area of the test films increases evidently (the thickness decreases).

There is no investigation concerning about this phenomenon, i.e., deformation of polymer films in water media. It is well-known that there are many factors that would induce deformation. All these factors can be classified into two categories, one is the external factors and the other is the internal factors. The external factors are what the environment added to the samples, such as gravity field, surface tension, mechanical force, and so on. Usually, some factors like surface tension are mainly controlled by the condition of the environment like temperature, pressure, and humidity. They have no absolute relationship to what kinds of the samples are used. However, the internal factors, such as intermolecular interactions, the energy barrier between different crystalline forms, the flexibility, and the mobility of the polymer chains and some chemical reactions, are the characteristics of the samples. It is very difficult for us to judge what is the most important factor inducing deformation. In many cases, although deformation in some media usually originates from swelling and relaxation of the polymer films, it is not always the case.

Chart 1. Chemical Structures of PHB and PVPh



In the present work, the physical properties are characterized for binary blends of atactic poly(*R*,*S*-3-hydroxybutyrate) (a-PHB)/PVPh and syndiotactic poly(*R*,*S*-3-hydroxybutyrate) (s-PHB)/PVPh. At first, the miscibility of the blends is investigated by differential scanning calorimetry (DSC) and the hydrogen- bonding network is characterized with the employment of Fourier transform infrared spectroscopy (FT-IR). Then, the thickening and thinning processes for the blend films are observed in the water media. The effects of temperature and surfactant on these processes are evaluated, and the essence of the thickening and thinning of the films is also discussed.

Experimental Section

Materials. Atactic poly(*R*,*S*-3-hydroxybutyrate) (a-PHB; diad isotacticity determined by ^{13}C NMR is 0.5) was synthesized through anionic polymerization in bulk with potassium oleate/18-crown-6 ether complex as an initiator.[7,8] The weight-averaged molecular weight (M_w) and the molecular weight distribution (M_w/M_n) of a-PHB, estimated by GPC measurement, are 4.55 × 10^4 and 1.17, respectively.

Syndiotactic poly(*R*,*S*-3-hydroxybutyrate) (s-PHB; diad syndiotacticity is 0.6; $M_w = 9.20 \times 10^4$, $M_w/M_n = 1.64$, lot no.

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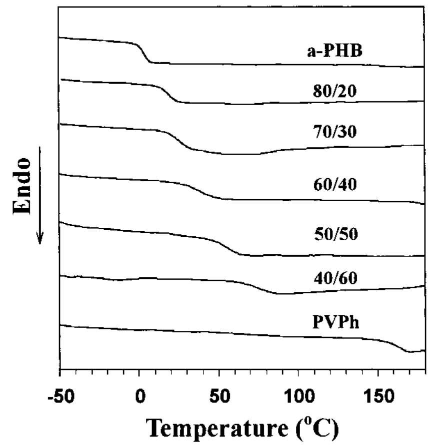

Figure 1. First-run DSC traces of pure a-PHB, PVPh, and their blends with PVPh content of 20 (80/20), 30 (70/30), 40 (60/40), 50 (50/50), and 60 wt % (40/60).

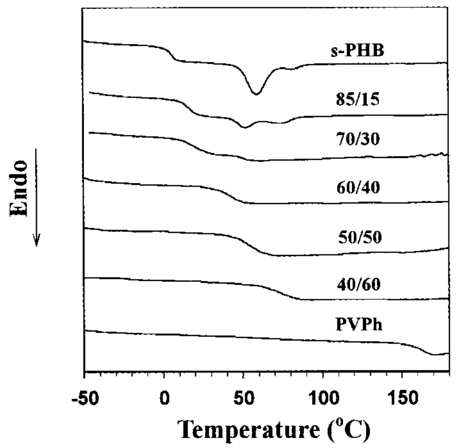

Figure 2. First-run DSC traces of pure s-PHB, PVPh, and their blends with PVPh content of 15 (85/15), 30 (70/30), 40 (60/40), 50 (50/50), and 60 wt % (40/60).

YH000626)[9] and atactic poly(4-vinylphenol) (PVPh, $M_w = 1.08 \times 10^4$, $M_w/M_n = 2.25$, lot no. 16824361) were supplied by the courtesy of Takasago International Corporation and Maruzen Petrochemical Co. Ltd., respectively.

Surfactants, sodium *n*-dodecyl benzene sulfonate (SDBS) and sodium *n*-dodecyl sulfate (SDS), were purchased from Nacalai Tesque, Co. Ltd..

Preparation of Blends. The blend films of a-PHB/PVPh and s-PHB/PVPh were prepared by casting the 5 wt % MEK (methyl ethyl ketone) solution to the Teflon Petri dish, allowing the solvent to evaporate at room temperature for 3 days, then drying in a vacuum for 1 week to remove the residual solvent at 50°C. The cast films were subsequently compression molded between two Teflon sheets with an appropriate spacer at 160−180°C (according to the blend composition) and under a pressure of 5MPa for 2 min, using a Toyoseiki laboratory press (Mini Test Press-10). The thickness of the molded films was about 120 μm. To eliminate the effect from the relaxation of polymer chains, the molded films were annealing at 50 °C for 1 day following with a slow cooling to room temperature in the oven before use.

Thermal Property Characterization. Differential scanning calorimetry (DSC) analysis was performed on a SEIKO DSC 220 system. The polymer sample packed in an aluminum pan was heated from −80 to +195 °C at a heating rate of 20 °C/min. The glass transition temperature (T_g) was taken as the value of the middle point of the transition.

FT-IR Characterization. The films of the blends with a thickness suitable for measurements were prepared by dropping the polymer blend solution to the surface of silicon wafer. Silicon wafer is transparent for IR incident beam and was used as substrate. The thickness of the cast film was carefully controlled to be thin enough to ensure that the studied absorption was within the linearity range of the IR detector. IR measurements were carried out on a single-beam IR spectrometer, Perkin-Elmer Spectra 2000. All the spectra were recorded under a resolution of 4 cm^{-1} and an accumulation of 16 scans.

Thickening and Thinning of the Blend Films. The test film of initial dimension 10 × 10 × 0.12 mm was placed in the small bottle containing 2.0−4.0 mL distilled water or surfactants/water solution. The thickness change of the film at a given temperature was recorded as a function of experimental time.

Contact Angle Characterization. Contact angles of the blend films were measured using a FACE CA-X angle meter equipped with a video camera. The contact angles were determined by the sessile-drop method, assuming that the outline of the drop forms part of a true sphere. The mean value obtained from five experimental values was calculated as the contact angle.

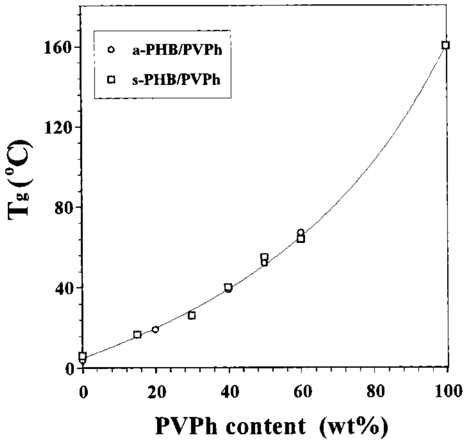

Figure 3. Relationship between the glass transition temperature (T_g) and the composition of the blends of a-PHB/PVPh (○) and s-PHB/PVPh (□). The solid line is the calculated results from Wood's equation (eq 1) with *K* value of 0.42.

Photographs Taking. The photographs of sample films were taken by a Nikon digital camera (COOLPIX 990E, Nikon Co.).

Results and Discussion

Miscibility of a-PHB/PVPh and s-PHB/PVPh Blends. The miscibility of a-PHB/PVPh and s-PHB/PVPh blends was investigated by DSC. The DSC curves are summarized in Figures 1 and 2 for a-PHB/PVPh and s-PHB/PVPh blends, respectively. Except plain s-PHB and s-PHB/PVPh blends with compositions of 85/15 and 70/30, no melting peak appears in the thermograms, which suggests the others are amorphous blends.

As shown in Figures 1 and 2, a single composition dependent glass transition temperature (T_g) is observed for both a-PHB/PVPh and s-PHB/PVPh blends. At the same PVPh content, the value of the T_g of a-PHB/PVPh blend is almost the same as that of the s-PHB/PVPh blend (Figure 3). The glass transition temperature of the blends increases with the content of PVPh and the value of T_g are in good agreement with that calculated from Wood's equation[10] (Equation.1) with *K* value of 0.42 (Figure 3):

$$T_g = (w_1 T_{g1} + K w_2 T_{g2})/(w_1 + K w_2) \qquad (1)$$

This result indicates that the studied systems are miscible blends.

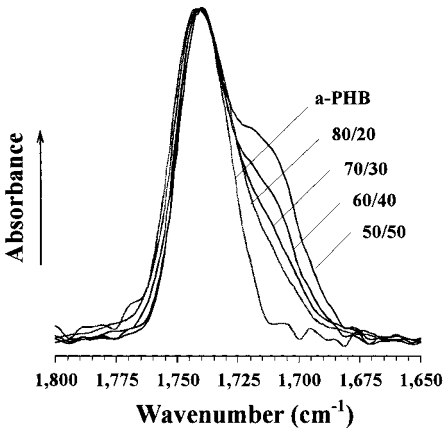

Figure 4. Carbonyl vibration bands in the FT-IR spectra of pure a-PHB and its binary blends with PVPh. The content of PVPh in the blends is 20 (80/20), 30 (70/30), 40 (60/40), and 50 wt % (50/50).

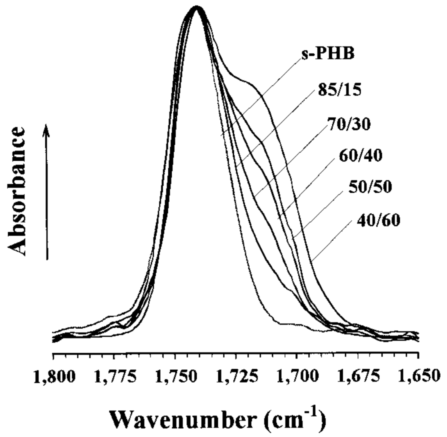

Figure 5. Carbonyl vibration bands in the FT-IR spectra of pure s-PHB and its binary blends with PVPh. The content of PVPh in the blends is 15 (85/15), 30 (70/30), 40 (60/40), 50 (50/50), and 60 wt % (40/60).

Xing et al have systematically studied the miscibility, crystallization, and morphology of isotactic poly(R-3-hydroxybutyrate) (i-PHB)/PVPh blends and reported that i-PHB and PVPh form miscible blends in the whole composition range in melt state.[11] Thus, it seems that the miscibility of poly(3-hydroxybutyrate)/PVPh in the amorphous state is independent of the tacticity of poly(3-hydroxybutyrate).

Hydrogen-Bonding Network in the Blends. FT-IR spectroscopy is a particularly suitable technique to investigate the specific intermolecular interaction. For the a-PHB/PVPh and s-PHB/PVPh blends studied here, the components of a-PHB and s-PHB contain carbonyl groups, yielding a carbonyl stretching mode at about 1741 cm^{-1}, while PVPh shows no absorption in the carbonyl vibration region ranging from 1650 to 1800 cm^{-1}. Therefore, any change of FT-IR spectrum in this region should be directly attributed to the change in the carbonyl group environment, such as the formation of hydrogen bonds.

The FT-IR spectra of a-PHB/PVPh and s-PHB/PVPh blends in the carbonyl vibration region are shown in Figures 4 and 5, respectively, as a function of PVPh content. For pure a-PHB and s-PHB, the carbonyl vibration band centered at 1741 cm^{-1}. Blending with PVPh, a second band appears at a lower wavenumber (about 1716 cm^{-1}) beside the band centered at about 1741 cm^{-1}. The second band should be attributed to the hydrogen bonded carbonyl vibration, indicating the formation of intermolecular hydrogen bonds between a-PHB and PVPh, s-PHB and PVPh. It is clearly indicated that, with the increase of PVPh content in the blends, the relative absorbance of the hydrogen bonded carbonyl vibration increased, indicating the reduction of the percentage of "free" carbonyl groups relative to the hydrogen bonded ones.

Employing the Beer–Lambert law permits a quantitative analysis of the fraction of the carbonyl groups in the inter-associated hydrogen bonds between PHB and PVPh using FT-IR spectroscopy. As a fact, the quantitative evaluations of similar systems have been discussed in a lot of literatures.[1,12−16]

The spectra of PHB/PVPh blends in the carbonyl region exhibit two distinct components.[17] The component approximately at 1741 and 1716 cm^{-1} are attributed to the "free" and inter-associated carbonyl groups, respectively. By a curve-fitting program,[18−20] quantitative data regarding the integrated intensity of the two separated bands are obtained (Tables 1 and 2). During the fitting, the peak positions (ν) of the free and hydrogen bonded bands were fixed, but left the peak shape, widths, and heights of the two bands as the adjustable parameters. As an example, Figure 6 illustrates the experimental and the fitted spectra in the carbonyl vibration region for a-PHB/PVPh blend with PVPh content of 40 wt %. The excellent agreement between the experimental and fitted spectra indicates the reliability of this curve-fitting technique. In this way, quantitative data regarding the integrated intensity of the amorphous, crystalline and associated bands are obtained. The results of the curve fitting (vibration position ν, absorption intensities A and peak widths at half-height $W_{1/2}$) are listed in Tables 1 and 2 for PHB/PVPh blends. It is noteworthy that Gaussian line-shape was obtained for the two bands in all cases.

Then the fraction of the carbonyl groups involved in the intermolecular hydrogen bond ($F_{(\mathrm{B,CO})}$) can be calculated from eq 2:[19,20]

$$F_{(\mathrm{B,CO})} = A_{(\mathrm{B,CO})} /(A_{(\mathrm{B,CO})} + \gamma_{\mathrm{B/F}}\, A_{(\mathrm{F,CO})}) \tag{2}$$

where $A_{(\mathrm{B,CO})}$ and $A_{(\mathrm{F,CO})}$ are the integrated intensity corresponding to the hydrogen-bonded and free carbonyl bands, respectively. $\gamma_{B/F}$ is the absorption ratio which takes into account the differences between the absorptivities of the hydrogen-bonded and free carbonyl groups:

$$\gamma_{\mathrm{B/F}} = \int_0^{+\infty} \epsilon_{\mathbf{B}}(\nu)\, \mathrm{d}\nu \Big/ \int_0^{+\infty} \epsilon_{\mathbf{F}}(\nu)\, \mathrm{d}\nu \tag{3}$$

where ϵ (ν) is the absorption coefficient and ν is the wavenumber. Taking the value of $\gamma_{\mathrm{B/F}}$ as 1.5, which is comparable with the published data for similar systems,[12,13,16] Equation 2 can be simplified as

$$F_{(\mathrm{B,CO})} = A_{(\mathrm{B,CO})} /(A_{(\mathrm{B,CO})} + 1.5A_{(\mathrm{F,CO})}) \tag{4}$$

In principle, the number of the hydroxyl group ($N_{(\mathrm{B,OH})}$) involved in the inter-associated hydrogen bonds formed between PHB and PVPh in the blend should be equal to that of the hydrogen bonded carbonyl group ($N_{(\mathrm{B,CO})}$), that is

$$N_{(\mathrm{B,OH})} = N_{(\mathrm{B,CO})} \tag{5}$$

Based on eq 5, the fraction of the hydroxyl group

Table 1. Analysis Result of FT-IR Spectra of a-PHB/PVPh Blends

	PVPh	band of the free carbonyl			band of the bonded carbonyl				
sample	content/wt %	ν_F/cm^{-1}	$W_{1/2}$/cm^{-1}	A_F/%	ν_B/cm^{-1}	$W_{1/2}$/cm^{-1}	A_B/%	$F_{(B,CO)}$	$F_{(B,OH)}$
a-PHB	0	1741	26.8	100					
80/20	20	1741	25.8	78	1716	27.4	22	0.16	0.89
70/30	30	1741	23.8	68	1716	29.4	32	0.24	0.78
60/40	40	1741	22.0	60	1716	29.2	40	0.31	0.65
50/50	50	1741	22.4	49	1716	31.2	51	0.41	0.57

Table 2. Analysis Result of FT-IR Spectra of s-PHB/PVPh Blends

	PVPh	band of the free carbonyl			band of the bonded carbonyl				
sample	content/wt %	ν_F/cm^{-1}	$W_{1/2}$/cm^{-1}	A_F/%	ν_B/cm^{-1}	$W_{1/2}$/cm^{-1}	A_B/%	$F_{(B,CO)}$	$F_{(B,OH)}$
s-PHB	0	1741	26.4	100					
85/15	15	1741	25.8	84	1716	31.8	16	0.11	0.87
70/30	30	1741	24.2	69	1716	29.0	31	0.23	0.75
60/40	40	1741	24.2	61	1716	29.0	39	0.30	0.63
50/50	50	1741	23.2	54	1716	30.0	46	0.36	0.50
40/60	60	1741	23.0	47	1716	31.2	53	0.43	0.40

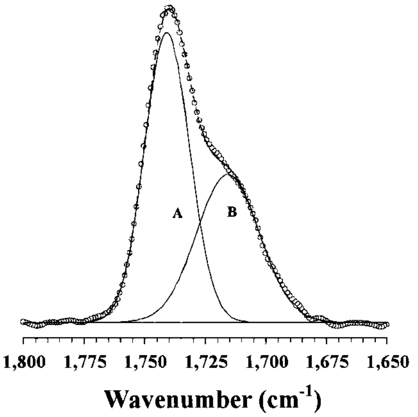

Figure 6. Experimental and curve-fitting FT-IR spectra in the carbonyl vibration region of 60/40 a-PHB/PVPh blend: open circle, experimental points; broken line, fitting results; **A**, amorphous part; **B**, hydrogen-bonded part.

involved in the inter-associated hydrogen bond ($F_{(B,OH)}$) can be expressed as

$$F_{(B,OH)} = F_{(B,\,CO)}\{(1 - w)/\,w\}(M_{PVPh}/M_{PHB}) \qquad (6)$$

where w is the weight content of PVPh in the blend and M_{PHB} and M_{PVPh} are the molecular weights of PHB and PVPh units, respectively.

From eqs 4 and 6, the values of $F_{(B,CO)}$ and $F_{(B,OH)}$ for the PHB/PVPh blends are calculated and listed in Tables 1 and 2. It is clear that $F_{(B,CO)}$ increases while $F_{(B,OH)}$ decreases with the increase of PVPh content. The values of $F_{(B,CO)}$ and $F_{(B,OH)}$ are 0.41 and 0.57, respectively, for a-PHB/PVPh with PVPh content of 50 wt % (Table 1).

On average, there are about 452 carbonyl groups in each a-PHB chain and 40 hydroxyl groups in each PVPh chain studied here (estimated from M_n). For 50/50 a-PHB/PVPh blend, $F_{(B,CO)}$ of 0.41 and $F_{(B,OH)}$ of 0.57 indicates that there are about 185 carbonyl groups in an a-PHB chain and about 23 hydroxyl groups in a PVPh chain involved in the intermolecular hydrogen bond. These numbers strongly suggest that there is a hydrogen-bonding network in 50/50 a-PHB/PVPh blend. The case is similar for other blends. The hydrogen-bonding network should act as physical cross-link in the blend and then exert a great influence on the properties of the blend.

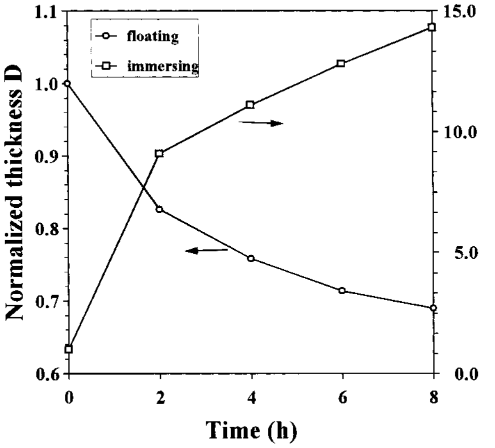

Figure 7. Normalized thickness change of 60/40 a-PHB/PVPh films floating on the surface of water (○) and immersing in the water (□) at 37°C.

Thickening and Thinning in Water Media. The films of 60/40 a-PHB/PVPh and 60/40 s-PHB/PVPh blends tend to float on the surface of distilled water due to the interfacial tension. However, once the films are immersed compulsorily in the water, the films can be kept in the water (the density of the blend film (about 1.1 g/cm^3) is larger than that of water) if they are free from shaking.

The thickness changes of 60/40 a-PHB/PVPh and 60/40 s-PHB/PVPh blends at 37 °C are plotted in Figures 7 and 8, respectively, as the normalized thickness (D) vs experimental time. In this study, the normalized thickness D is defined as:

$$D = d_t/d_0 \qquad (7)$$

where d_t and d_0 are the thickness of a film at experimental time t and 0, respectively.

It is quite interesting that after the experiment of 8 h (Figure 7) the normalized thickness of 60/40 a-PHB/PVPh blend decreases from 1 to 0.69 when the film floats on the water surface, however, while it increases from 1 to 14.3 when the film is immersed in the water. The case is similar to the 60/40 s-PHB/PVPh film (Figure 8). Clearly, the normalized thickness of the film decreases with the experimental time when the film floats on the water surface, while it increases drastically with experimental time when the film immerses in water. In other words, floating on the surface of water thins the films while immersion in the water thickens the films. This thickening/thinning phenomenon could

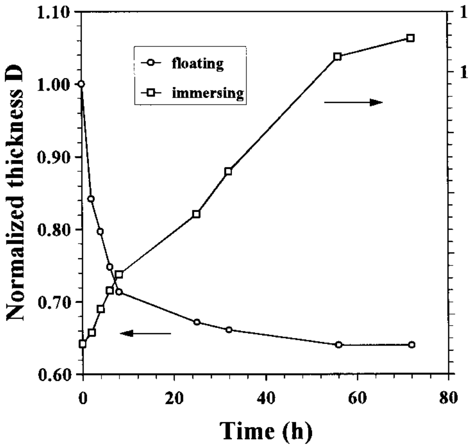

Figure 8. Normalized thickness change of 60/40 s-PHB/PVPh films floating on the surface of water (○) and immersing in the water (□).

be well repeatedly observed, when the blend film was repeatedly moved from the water surface to the water and from the water to the surface, respectively.

This thickening and thinning of polymer films should not be attributed to the swelling of the film in distilled water, which would increasing the weight of the films, because the weight of the test film hardly changed after the experiment and the difference of weight is less than 0.5%. The deformation of the films should not be attributed to the dissolving of blend in the water because both of PHB (a-PHB and s-PHB studied here) and PVPh are not to some degree water-soluble. In the study of the enzymatic degradability for a-PHB[8] and s-PHB,[21] it was found that the control sample did not dissolve in water. It was also reported that PVPh does not dissolve in water.[22] The deformation of the films should not be attributed to the relaxation of the polymer chains, too. The molded films have been annealed at 50 °C for 1 day following with a slow cooling to room temperature in the oven before the measurements carried out. This phenomenon might mainly come from the effects of interfacial tension. In the case of floating, the films should tend to spread over the surface of water just like oil due to the quite large surface tension of water. As a result, the floating thins the films. In the case of immersion, the interfacial tension between water and the films tries to decrease the interface area and thus thickens the films.

On the other hand, the characteristics of the 60/40 a-PHB/PVPh and 60/40 s-PHB/PVPh blends should be considered as the internal factor of the phenomenon of thickening and thinning. In the past few years, we have studied the nonenzymatic and enzymatic hydrolytic degradation of a variety of polymer and polymer blend films in water media.[8,23−27] However, the phenomenon of thickening and the thinning has only been observed for the film of a-PHB/PVPh and s-PHB/PVPh blends. The films of 60/40 a-PHB/PVPh and 60/40 s-PHB/PVPh blends differ from other polymer films in that these blends are free from crystalline phase, with a hydrogen-bonding network and with a T_g of (40 °C) close to the experimental temperature (37 °C). These characteristics allow the segments of the polymer chains move cooperatively on some extent so that the large deformation of the films becomes possible.

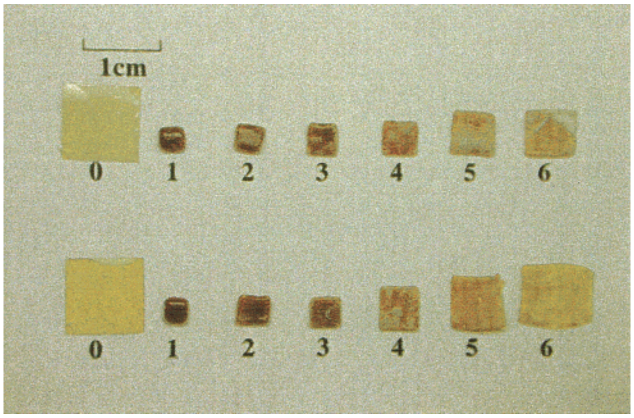

Figure 9. Photographs of 60/40 s-PHB/PVPh blend films after immersing in SDS and SDBS solution at 37°C for 72 h. The top row is the photographs of films immersed in SDS solution. The SDS concentration (mmol/L) is as follows: **0**, control test; **1**, 0.00; 2, 0.40; 3, 1.60; **4**, 8.00; **5**, 40.00; **6**, 80.00. The bottom row is the photographs of films immersed in SDBS solution. The SDBS concentration (mmol/L) is as follows: **0**, control test; **1**, 0.00; **2**, 0.25; **3**, 1.00; **4**, 5.00; **5**, 25.00; **6**, 50.00.

Table 3. Contact Angle of the SDS Solution on the Surface of 60/40 s-PHB/PVPh Blend Film and the Normalized Thickness of the Film after Exposure to SDS Solution at 37 °C

SDS concen/mmol/L	contact angle/deg	normalized thickness after exposure to SDS solution		
		8 h	32 h	72 h
0.00	107.4	3.3	6.7	11.1
0.40	91.4	2.4	5.2	8.7
1.60	81.3	2.2	4.5	6.3
8.00	54.0	1.9	3.7	5.2
40.00	47.1	1.7	2.5	3.4
80.00	42.1	1.4	2.0	2.1

Table 4. Contact Angle of the SDBS Solution on the Surface of 60/40 s-PHB/PVPh Blend Film and the Normalized Thickness of the Film after Exposure to SDS Solution at 37 °C

SDBS concen/mmol/L	contact angle/deg	normalized thickness after exposure to SDS solution		
		8 h	32 h	72 h
0.00	107.4	3.3	6.7	11.1
0.25	88.5	2.8	5.2	6.3
1.00	72.4	2.5	4.5	5.6
5.00	36.0	1.8	2.5	3.1
25.00	29.2	1.7	2.0	2.2
50.00	26.0	1.5	1.6	1.6

Effects of the Surfactants. As discussed above, the interfacial tension should be a main factor of the phenomenon of thickening and thinning. To confirm this point, the thickening behavior was investigated for 60/40 s-PHB/PVPh films in water solution of SDS and SDBS.

The contact angles of the solution SDS and SDBS on 60/40 s-PHB/PVPh film are listed in Tables 3 and 4, respectively. The contact angle decreases with the concentration of the surfactant increasing, indicating that the interfacial tension between the surfaces of the film and surfactant solution decreases with the surfactant concentration increasing.

After exposure to the surfactant solution, the area of 60/40 s-PHB/PVPh film decreases and the thickness increases just as exposure to distilled water (Figure 9 and Tables 3 and 4). However, the change of normalized thickness is observed to decrease with the increase of surfactant concentration for a given experimental time, that is, it increased with the interfacial tension, suggesting that the interfacial tension is a key factor of the thickening of the film.

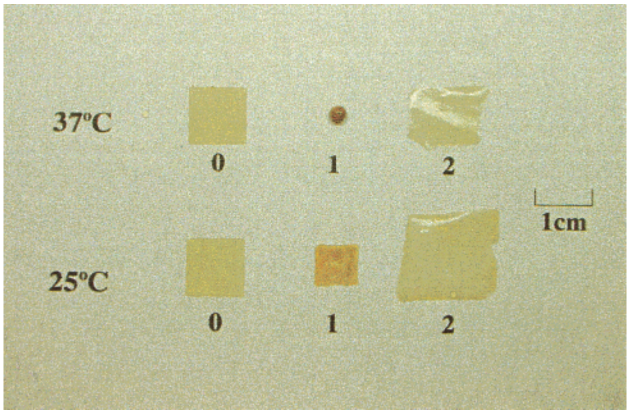

Figure 10. Photographs of 60/40 a-PHB/PVPh blend films immersed in distilled water (**1**) and floated on the water surface (**2**) at 37 and 25°C for 8 h.

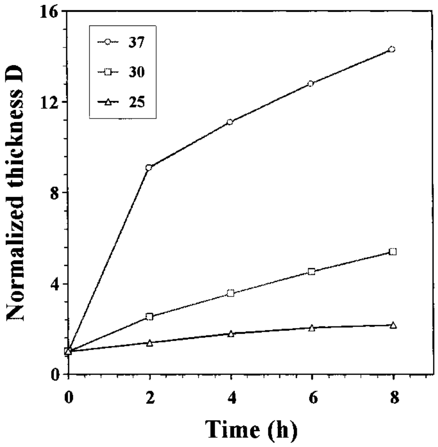

Figure 11. Normalized thickness of 60/40 a-PHB/PVPh films immersed in distilled water at 25 (△), 30 (□), and 37 °C (○).

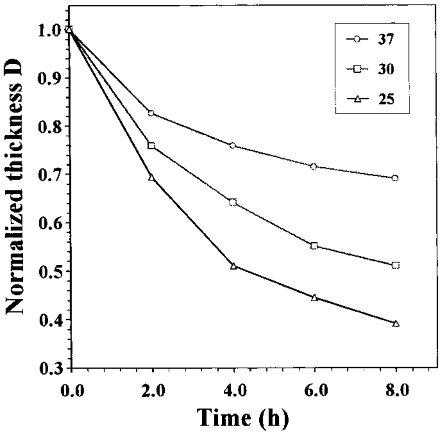

Figure 12. The normalized thickness of 60/40 a-PHB/PVPh films floated on the surface of distilled water at 25°C (△), 30°C (□) and 37°C (○).

Effect of Experimental Temperature. The temperature affects the interfacial tension and the mobility of polymer chains. Thus, it is expected that the thickening and thinning of the polymer film should directly relate to the experimental temperature.

The thickening and thinning behavior of 60/40 a-PHB/PVPh film at 25, 30, and 37 °C in distilled water is compared in Figures 10−12. The thickening extent and rate of 60/40 a-PHB/PVPh film in distilled water increases with the experimental temperature (Figures 10 and 11). Conversely, the thinning extent and rate decreases with the temperature (Figures 10 and 12). It is quite surprising that the normalized thickness of 60/40 a-PHB/PVPh film drops from 1 to 0.39 after floating on the surface of distilled water for 8 h even at 25 °C, which is 15 °C lower than its glass transition temperature (40 °C).

In general, the increase of the temperature lowers the interfacial tension, the power of the thickening and thinning. On the other hand, the increase of the temperature heightens the mobility of the polymer chains to promote the thickening and thinning of film. The two aspects work together to affect the process of the thickening and thinning. It seems the first aspect is the main one for the thinning while the second is for the thickening.

Conclusion

The thermal analysis reveals that PHB (a-PHB and s-PHB) and PVPh are miscible in the amorphous state. Except for s-PHB/PVPh 85/15 blend, the other studied blends are free from crystalline phase. From FT-IR and a curve-fitting program, a hydrogen-bonding network is concluded to be formed in the blends.

The thickness of a-PHB/PVPh 60/40 and s-PHB/PVPh blend films drastically changes in the water media. Floating on the surface of water thins the films while immersion in the water thickens the films. The concentration of SDS and SDBS and the experimental temperature greatly affect the thickening and thinning process of the polymer films. In essence, the interfacial tension is the power and the characteristics of the polymer films should be considered as the internal factors of the thickening and thinning.

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