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SHORT COMMUNICATIONS

The Effect of Crystallization on the Thinning-Thickening Phenomena of Plastic Blend Film in Water Media

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Accidentally, we have found a plastic blend film of highly syndiotactic poly[(R,S)-3-hydroxybutyrate] (s-PHB; diad syndiotacticity is 0.6) and atactic poly(4-vinylphenol) (PVPh), which shows spontaneous and reversible thinning-thickening phenomenon in the aqueous media.[1] When the film with the thickness of 0.1–0.2 mm was put on the water surface, the film can float on water just by the surface tension even if it has a little higher density than that of water. It was observed that the frontal dimension of the film became larger and the film became thinner in course of time. However, when the film with the same dimension was sunk in water, the frontal dimension became smaller and the film became thicker. Furthermore, the film has the ability to transfer between the thinned and thickened states.

Shape-memory alloys are the materials that can produce some deformation and then return to its original shape. With so special properties, shape-memory alloys have been widely studied and used in various fields, such as automatic control. Shape memory alloys rely on plastic deformation caused at a given ambient temperature, which then become elastic on heating allowing the alloy to return (spring back) to its original shape.[2] It means that the shape-memory alloys can take two states, *i.e.*, plastic and elastic states, and the conversion between two states is controlled by the temperature. In the case of PHB/PVPh blends, although finally the materials also have two states, *i.e.*, thinning and thickening states, they have essential difference compared with plastic and elastic states. The conversion between thinning and thickening states may be controlled by many factors such as temperature, surface tension and the composition in the blend film. It is obvious that the deformation of shape-memory alloys and that of PHB/PVPh blend films should have different mechanism.

So far as we know, the PHB/PVPh blend is the first example of plastic materials, which show reversible deformation in the aqueous medium. This blend system with so special and excellent property would be expected to have a wide application in various fields. If its memory function is further paid enough attention to, it would have uncountable value in a variety of fields, such as the application for future chemical actuators. What is more gratifying is that the component materials (PHB and PVPh) of the blend film are biodegradable,[3,4] which offers potential advantages in the biomedical field.

In this communication, the structural features, which affect the reversible thinning-thickening phenomenon, will be investigated by ATR FT-IR, X-Ray diffraction and DSC.

EXPERIMENTAL

Materials

Chemosynthesized highly-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. YH000626),[5] biosynthesized isotactic poly[(R)-3-hydroxybutyrate] (i-PHB; $M_w = 5.86 \times 10^5$, $M_w/M_n = 2.35$) 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 (Japan), Mitsubishi Gas Co., Ltd. (Japan), and Maruzen Petrochemical Co., Ltd. (Japan), respectively. Solvents methyl ethyl ketone (MEK) and 1,4-dioxane were purchased from Nacalai Tesque, Inc. (Japan). Solvent chloroform was purchased from Kanto Chemical Co., Inc. (Japan).

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Preparations

The blend films of s-PHB/PVPh were prepared by casting the 5 wt% MEK solution to the Teflon® petri dish, allowing the solvent to evaporate at 60°C for three days, and drying in vacuum for further three days to remove the residual solvent at 60°C. The blend films of i-PHB/PVPh were prepared by casting the mixture of i-PHB chloroform solution (5 wt%) and PVPh dioxane solution (5 wt%) to the Teflon® petri dish, allowing the solvent to evaporate at room temperature for one week, and drying in vacuum for three days to remove the residual solvent at 60°C. The cast films were subsequently compression molded between two Teflon® sheets with an appropriate spacer at 200°C and under a pressure of 5 MPa for 2 min, using a laboratory press (MINI TEST PRESS-10, Toyoseiki, Co., Tokyo, Japan). The thickness of the molded films was 0.1–0.2 mm. In order to eliminate the effect of relaxation of polymer chains, the molded films were annealed at 60°C for one day following with a slow cooling to room temperature in the oven before use.

Measurements

The test film of initial dimension 10 × 10 mm (thickness: 0.1–0.2 mm) was placed in a small Teflon® bottle containing 10 mL distilled water.

The photographs of sample films were taken by a digital camera (Nikon COOLPIX 990E, Nikon Corp., Japan).

The measurements of attenuated total reflectance Fourier-transform infrared (ATR FT-IR) spectra of blend films were carried out on an ATR Objective optical system ATR-8800 M, P/N 206-70450-91 (Shimadzu, Corp., Kyoto, Japan) mounted on infrared microscope AIM-8800 (Shimadzu, Corp., Kyoto, Japan). All the spectra were recorded under an accumulation of 64 scans.

The wide angle X-Ray diffraction (WAXD) patterns of the blend films were recorded by a RINT-2000 X-Ray diffractometer (Rigaku Corp., Japan) using Nickel-filtered Cu-$K\alpha$ radiation ($\lambda = 0.154$ nm; 40 kV; 200 mA) with the 2θ angle ranging from 10 to 35 degree at a scanning rate of 1 degree min^{-1}.

Differential scanning calorimetry (DSC) analysis was performed on a SEIKO DSC 220 system (Seiko Instruments, Inc., Tokyo, Japan). The polymer sample packed in an aluminum pan was heated from −20°C to 200°C at a heating rate of 20°C min^{-1}.

RESULTS AND DISCUSSION

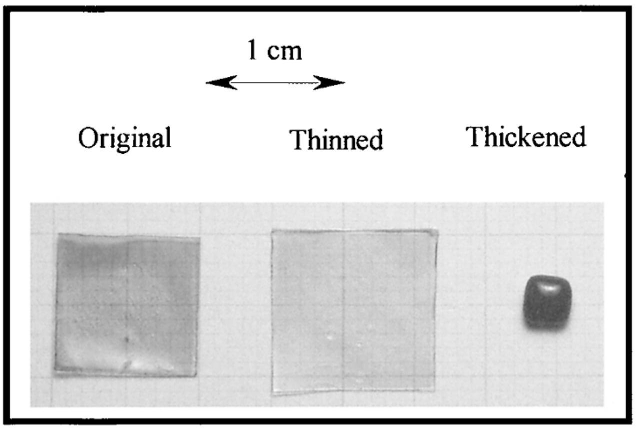

Figure 1. The photograph of original, thinned and thickened 50/50 (wt/wt) s-PHB/PVPh blend cast films.

When a cast film with the standard size (1.0 cm × 1.0 cm) and the thickness of 0.1–0.2 mm of the 50/50 (wt/wt) blend of s-PHB and PVPh was put on the surface of water (water/air interface) at 37°C, after 8 h the frontal dimension of the film became larger (1.1 cm × 1.1 cm) and the film became thinner with the lapse of time, while when the film with the same dimension was sunk in water at 37°C, after two weeks the frontal dimension of the film became smaller (0.3 cm × 0.3 cm) and the film became thicker as shown in Figure 1. The ratio of maximum and minimum frontal dimension of the film could become up to 25±2 for a longer time. The changes in dimension could not be induced by the dissolution of polymer or by the absorption of water, since no obvious change either in volume or in weight of the sample is observed after the experiment. It should be emphasized that both of the two components in the blend film are not dissolvable in water. These phenomena are similar to the spreading of a drop of oil lying on water surface. In the case of oil, the molecules of oil form monolayer. However, in this case, it is impossible for the film to become a monolayer. There would be a balance between the interfacial tension and intermolecular interaction.

What is more magical is that memory effect has been observed. When the as-cast original film was put on the water surface, it became larger in course of time. Then, when this enlarged film was sunk in water, it could reduce its frontal dimension and become thicker as shown above. A similar but very reverse phenomenon was observed, *i.e.*, if the film was firstly sunk in water, it became smaller in course of time. Then, this thickened film became larger, when it was put on the surface of the water again.

It was well known that strong intermolecular hydrogen bonds were formed between the carbonyls of PHB and the hydroxyls of PVPh.[1,6,7] The measurements of attenuated total reflectance Fourier-transform infrared (ATR FT-IR) spectra of the blend film before and after deformation show no obvious changes in the stretch-

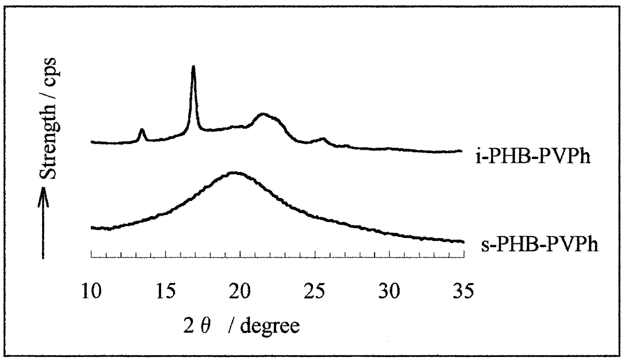

Figure 2. The Wide Angle Diffraction X-Ray patterns for i- and s-PHB/PVPh blends 50/50 (wt/wt), respectively.

ing vibration region (1650–1800 cm^{-1}) of the PHB carbonyls, a part of which formed strong hydrogen bonds with the PVPh phenol hydroxyls. It was concluded that the deformation is induced by the motion of not the groups only but the whole molecular chains.

Atactic PVPh used here is a fully amorphous polymer and its glass transition temperature (T_g) is relatively high (164°C) in the pure state. Bacterially synthesized poly[(*R*)-3-hydroxybutyrate] (i-PHB) is a highly crystalline polymer while s-PHB is an almost amorphous polymer. The T_g values of i- and s-PHB are similar, namely, about 7°C. They share the same chemical structure but have different stereochemical structures. However, no deformation was observed for the i-PHB/PVPh blend film under the same experimental conditions. The wide angle X-Ray diffraction (WAXD) patterns indicate that i-PHB forms the crystal phase even in the 1 : 1 blend with PVPh but s-PHB in the blend does not form crystalline phase and presents as the fully amorphous state as shown in Figure 2. The rigid crystal phase should hinder the great movement of macromolecular chains, which would induce the thinning-thickening deformation of film in aqueous media.

In the Figure 3 are shown the differential scanning calorimetry (DSC) thermograms indicating that the two blend samples have the similar glass transition temperature (T_g) at about 50.5°C. Although this midpoint T_g was higher than 37°C, it is also found that the glass transition of the amorphous phase of both *i*- and s-PHB/PVPh 1 : 1 blends start at the same temperature region, *i.e.*, at about 30–40°C. At least part of the macromolecular chains can change their conformation in the fully amorphous blend at 37°C, the temperature the thinning-thickening phenomena were observed.

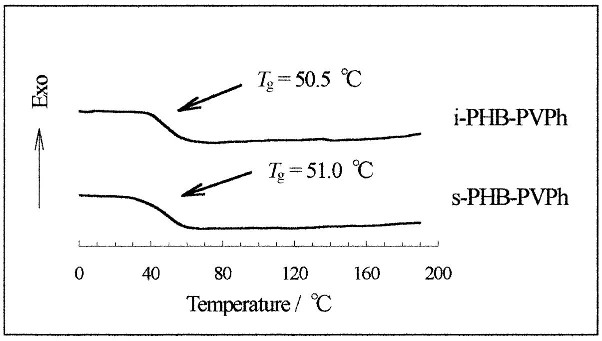

Figure 3. The DSC curves for the blends i- and s-PHB/PVPh 50/50 (wt/wt), respectively, recorded in the second heating scan.

It could be concluded that the amorphous nature and the molecular mobility of the PHB component were much important factors controlling the deformation. The study of the molecular mechanism, which induces reversibly thinning-thickening phenomena of plastic films, is in progress in our laboratory.

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