Effect of Iodine Absorption on the Characteristics of Syndiotacticity-Rich High Molecular Weight Poly(vinyl alcohol) Microfibril

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ABSTRACT: Iodination of syndiotacticity-rich high molecular weight poly(vinyl alcohol) (PVA) microfibril, which was obtained from the saponification of poly(vinyl pivalate) without a spinning procedure, was conducted before and after zone drawing at various conditions. The resulting PVA microfibrils were characterized by differential scanning calorimetry and scanning electron microscopy. Surface morphologies of these PVA microfibrils showed some differences between PVA microfibrils iodinated after and before drawing. Crude shapes of PVA microfibrils iodinated after drawing indicated that iodine decreased the structural regularity severely. On the other hand, PVA microfibrils iodinated before drawing showed relatively ordered surfaces. This was ascribed to the enhanced molecular ordering of PVA microfibrils due to zone drawing. Iodinated PVA microfibrils showed a decrease in the crystal melting temperature of about 100°C compared to the untreated sample. PVA microfibrils drawn after iodination showed a relatively higher crystal melting temperature than those of microfibrils iodinated after drawing. These results were considered as proof of the changes in the crystalline lattice of the PVA microfibrils by iodine absorption. Effects of the drawing temperature on the sublimation of iodine were also evaluated. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1519–1524, 2003

Key words: iodination; PVA microfibril; zone drawing

INTRODUCTION

Poly(vinyl alcohol) (PVA) obtained by the saponification of poly(vinyl ester) is a linear semicrystalline polymer, which has been widely used as a fiber. PVA fibers have high tensile and compressive strengths, tensile modulus, abrasion resistance due to their highest crystalline lattice modulus, and superior biocompatibility.[1–3] Recently, Lyoo et al. found that a PVA fiber of a well-oriented microfibrillar structure was formed during saponifying poly(vinyl pivalate) (PVPi) to PVA.[4–12] These PVA microfibrils show the appearance and characteristics of natural fibers, such as cotton and jute. PVA microfibrils show more enhanced mechanical properties than those of spun fibers. Furthermore, PVA microfibrils have abundant microvoids, which are suspected to enhance the surface area.

Embolization is the operational therapy controlling the flow of blood to a specific vein or portion of it to prohibit the supply of nutrition to some kind of cell, such as a cancer cell. Another kind of embolization is the physical treatment for blood circulation, such as the aneurysm surgery.[13–15] Cancer cell-killing embolic application has been paid attention to for its possibility and effectiveness for replacement of commercialized metallic coil-shaped embolic materials; expensive metallic materials have some problems during operation because of the sharpness of their cut faces. PVA microfibrils, in contrast, show superior properties, including enhanced biocompatibility and less risk of scratching, but are hard to be detected by X-ray during an operation because of their lack of radiopacity. Radiopacity is a very important characteristic for embolic materials for the minute positioning control of materials in human organs. There are several methods endowing radiopacity to organic polymeric materials, including iodination.

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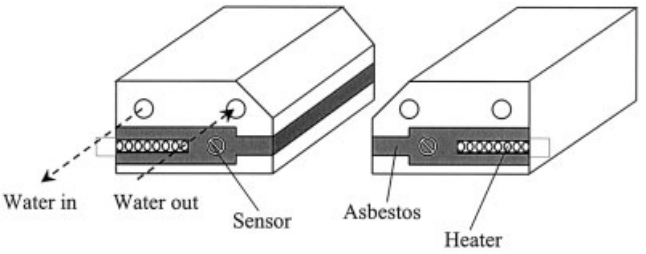

Figure 1 Schematic representation of band heater assembly.

Iodine is reported to reform the crystalline lattice of PVA. Changes in the crystalline lattice of PVA microfibrils by iodine sorption indicated that iodine molecules intruded into crystalline regions, as well as into amorphous regions, to form new substitution types of crystalline lattice.[16,17] It is valuable to relate the radiopacity introduced and property changes from an operational point of view. In this study, the iodination of PVA microfibrils was conducted with varying iodination conditions. For the consideration of the effects of the crystalline structure on the formation of an iodine complex, syndiotacticity-rich high molecular weight PVA microfibrils were drawn before and after iodination at various conditions. The resulting PVA microfibrils were characterized by differential scanning calorimetry (DSC) and scanning electron micrography (SEM). Iodinated PVA microfibrils showed a decrease in the melting temperature about 100°C. The crystalline lattice change and physical and chemical characteristics of iodinated PVA microfibrils were also evaluated according to the amount of iodine sorption.

EXPERIMENTAL

Materials

PVA microfibrils were prepared by the saponification of PVPi with a number-average degree of polymerization (P_n) of 25,000. The resulting PVA microfibril had a P_n and syndiotactic diad content of 10,000 and 61.0%, respectively. Iodine and potassium iodide (KI) were purchased from the Aldrich Co. (Milwaukee, WI). Other extrapure-grade reagents were used without further purification. The water used for all the procedures was deionized.

Iodination of PVA microfibril

An aqueous iodine solution of 4×10^{-1} mol/L was prepared by the mixing of I_2 and KI at a mol ratio of 1:2. Drawn and untreated PVA microfibrils were iodinated in this aqueous iodine solution for 48 h at room temperature. Iodinated PVA microfibrils were washed in water for 1 h at room temperature to wash off the adhesive iodine. Iodinated PVA microfibrils were then dried at room temperature without a vacuum to prevent the sublimation of iodine.

Zone drawing of PVA microfibrils

Iodinated and untreated PVA microfibrils were drawn by the zone-drawing method.[18–25] Zone drawing was carried out at different temperatures of 100, 150, and 200°C by moving a pair of narrow-band heaters with dimensions of 7-cm length, 2.5-cm width, and 1-mm thickness (Fig. 1). The film used for zone drawing was of 210-μm thickness, 5-mm width, and 10-cm length, being drawn under tension controlled by different dead weights, respectively, on an Instron model 4201 (Fig. 2). The draw ratio was measured as the length gain and ranged from two to four times.

Desorption of iodine

Iodinated PVA microfibrils were treated with water for 2 h at 40°C. The amount of water was controlled to 1000 mL/1 g of PVA microfibrils. Finally, PVA micro-

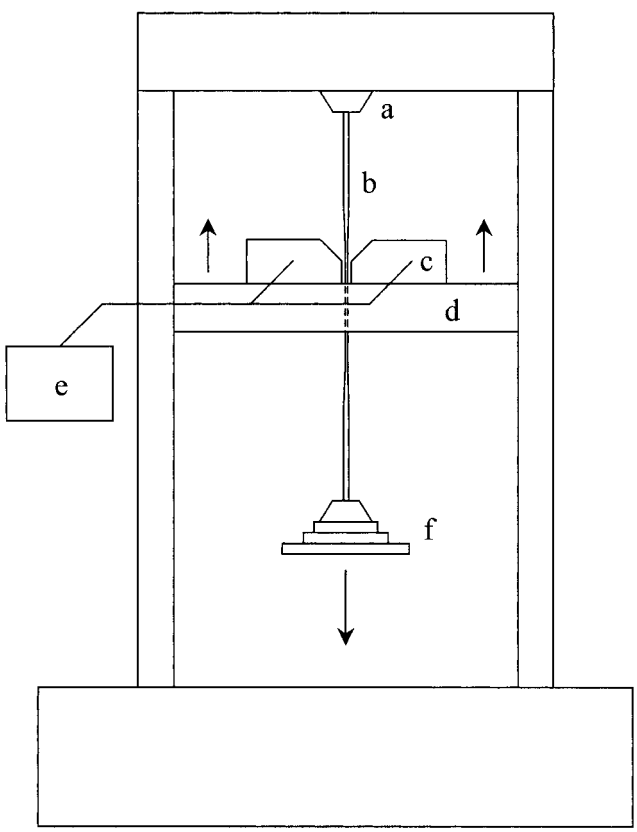

Figure 2 Schematic representation of zone-drawing apparatus.

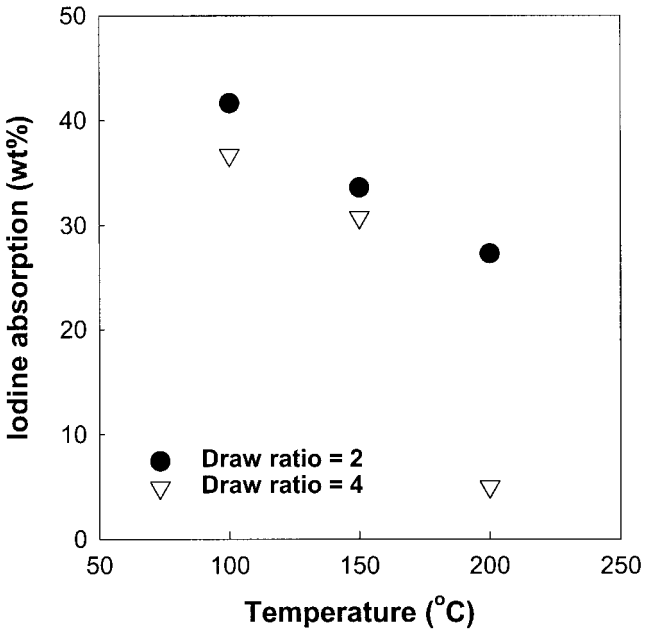

Figure 3 Iodine absorption of zone-drawn PVA microfibril according to drawing temperature. Draw ratios were controlled to 2–4.

fibrils were dried at room temperature in the atmosphere.

Characterization

The appearance of the PVA microfibrils was observed by SEM. The thermal characteristics of the PVA microfibrils were evaluated by using DSC. The temperature was scanned from room temperature to 300°C at a 10°C/min heating rate and the crystal melting temperature (T_m) was evaluated.

RESULTS AND DISCUSSION

Zone drawing, due to the short residence time within a heated drawing zone, has many advantages, such as fewer possibilities of back folding of the molecular chain, of microcrystallite formation, of thermal degradation, and of energy loss.[13–17] The zone-drawing condition, therefore, can affect the amount of iodine sorption of PVA microfibrils. Figure 3 shows the iodine absorption of zone-drawn PVA microfibrils according to the drawing temperature and the resulting draw ratio. Iodine absorptions were decreased with increasing zone-drawing temperature. Decreases in the iodine absorption can be explained as increases of the regularities of PVA microfibrils by drawing. In addition, the effect of the draw ratio on iodine absorption showed the expected tendency: PVA microfibrils of a higher draw ratio, and the resulting higher degree of molecular regularity, showed lower iodine absorption. Especially, PVA microfibrils drawn four times at 200°C showed a steeply decreased amount of absorption. It was well known that the crystalline structure of PVA can be penetrated by iodine. In this study, it is assumed that drawing can effectively prevent the penetration of the PVA crystalline structure by iodine.

Iodine has high degree of sublimation. The heat on drawing, therefore, evaporated the iodine, resulting in weight loss of the iodinated PVA microfibrils. Weight losses of the iodinated PVA microfibrils (weight gain for iodination 39.3%) versus the drawing temperature and resulting draw ratio are shown in Figure 4. Weight losses were calculated with respect to the absorbed iodine. An increase in the drawing temperature results in an increase in the weight loss of the iodinated PVA microfibril. PVA microfibrils drawn four times show a much higher weight loss than that of those drawn twice at same temperature. It is ascribed that the hot-zone duration time of PVA microfibrils drawn four times is much more than that of those drawn twice.

Iodine desorption of PVA has been an important subject for its usage as a polarized film.[26,27] To use iodinated PVA microfibrils as embolic materials, the water resistance of iodine desorption should be improved as well. Figure 5(a,b) shows the amounts of iodine desorption of PVA microfibrils drawn before and after iodination, respectively. Iodine desorption can be depressed by increasing the drawing temperature for both cases. Iodine desorption of predrawn PVA microfibrils, however, decreased much faster. But this cannot be a clue of the fastness of iodine because PVA microfibrils drawn four times at 200°C

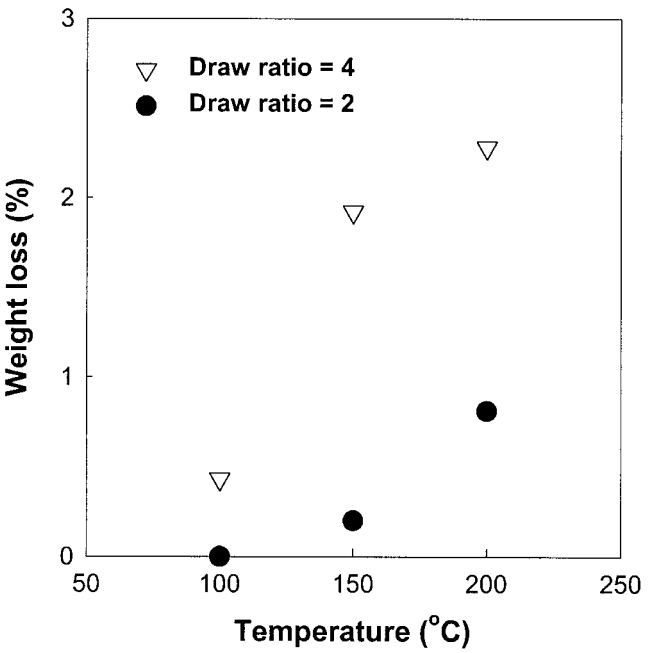

Figure 4 Weight loss of iodinated PVA microfibril versus drawing temperature. Draw ratios were controlled to 2–4.

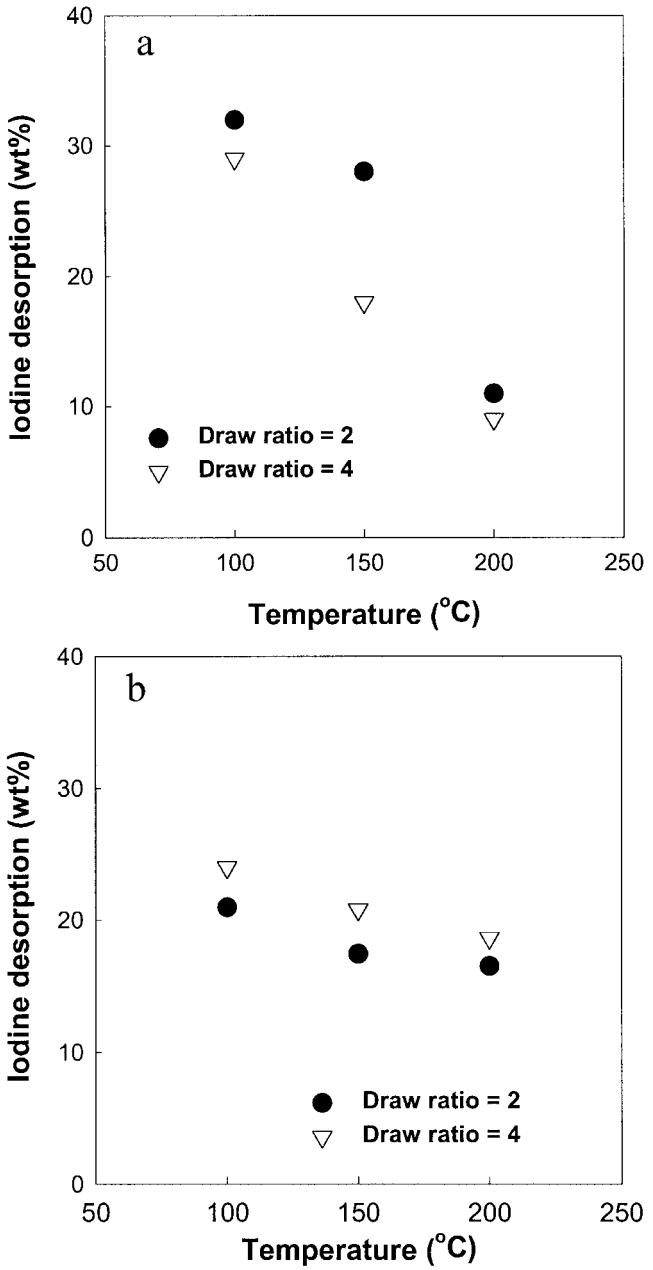

Figure 5 Iodine desorption of PVA microfibrils versus drawing temperature: (a) drawn before iodination; (b) drawn after iodination. Iodine desorption was performed for 2 h in water at 40°C.

absorbed much less iodine. PVA microfibrils iodinated after drawing showed relatively stable iodine desorption values of about 20%. This result can be related to the penetration depth of iodine. PVA microfibrils drawn before iodination should have a tighter internal structure than that of microfibrils drawn after iodination at the iodination stage. Therefore, iodine cannot penetrate into the depth enough for drawn PVA microfibrils. This loose-penetrated iodine can be evaporated much more easily.

Changes of the crystalline structure can be indicated by the T_m. Figure 6 shows the T_m of PVA microfibrils drawn before and after iodination. The T_m of untreated PVA microfibrils is about 260°C.[5] On the other hand, PVA microfibrils of this study show T_m's ranging from 150 to 180°C. These changes can be attributed to the reduction in the regularity of the crystalline regions by the penetration of iodine.

Surface morphologies of the iodinated PVA microfibrils are shown in Figure 7. Iodinated PVA fibrils after zone drawing showed more of a crude surface than that of the fibrils iodinated before drawing. From this result, it can be deduced that iodine can also penetrate the PVA oriented crystalline by drawing effectively.

CONCLUSIONS

In this study, iodination and zone drawing of PVA microfibrils were conducted at various conditions. Iodine absorption of undrawn PVA microfibril reaches 39.29% and iodine evaporations in the following zone drawing ranged from 0 to 2.3 wt% of the iodinated PVA microfibrils. The weight loss by iodine evaporation increased with increase in the drawing temperature and this tendency was enlarged for PVA microfibrils of higher draw ratios. Iodination of drawn PVA microfibrils was also performed and the amount of iodine absorption decreased from 42 to 5% with an increasing drawing temperature of the previously performed zone drawing. Iodinated PVA microfibrils were steeped in water at 40°C for 2 h. PVA microfibrils iodinated after drawing showed a drastic decrease in iodine desorption ranging from 33 to 9% with an increasing drawing temperature. However, PVA mi-

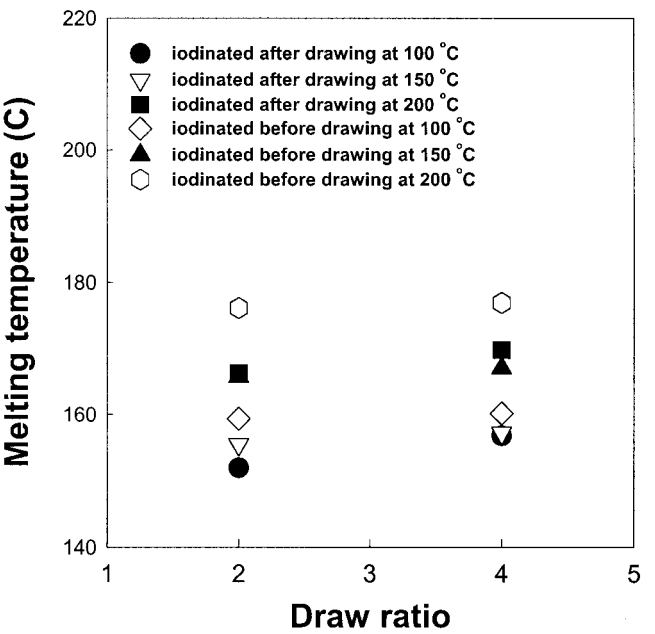

Figure 6 Crystal melting temperatures of PVA microfibrils versus draw ratio.

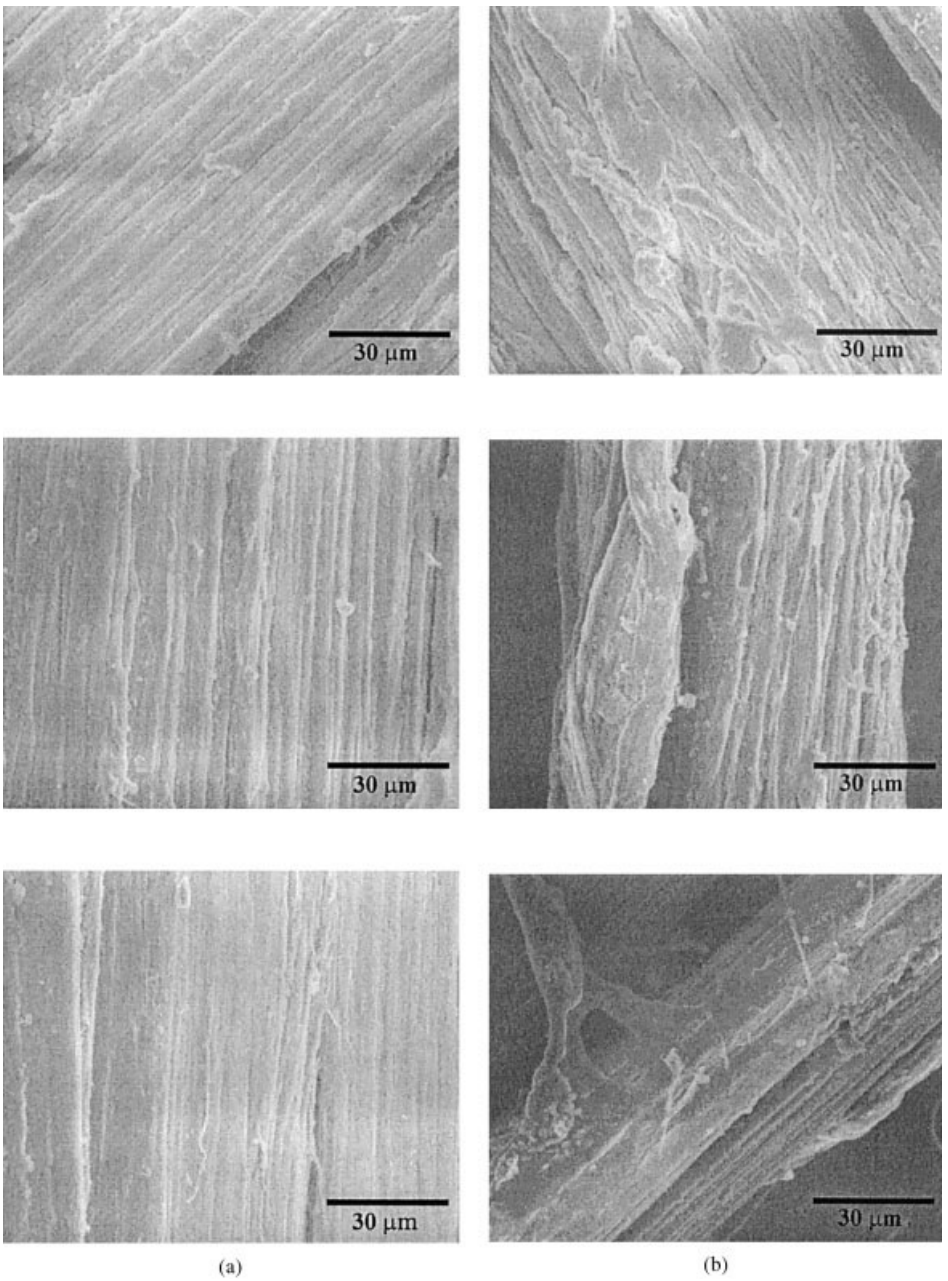

Figure 7 SEM photographs of PVA fibrils: (a) drawn after iodination; (b) drawn before iodination (× 1 K).

crofibrils iodinated before drawing showed a value of about 20% for all drawing temperatures. The T_m's of the PVA microfibrils increased with increasing drawing temperature and draw ratio, ranging from 150 to 180°C. But these values were about 100°C lower than those of the untreated PVA microfibrils, about 260°C. It is expected that these iodinated PVA fibrils can be used as an embolic fiber for biomedical applications, owing to their high fineness, good biocompatibility, and good binding property. In the near future, we will report on the effects of molecular weight and stereoregularity on the structure and properties of iodinated PVA microfibrils.

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