Preparation and Characterization of Iodinated Poly(vinyl alcohol) Microfibril

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Summary: Iodination of poly(vinyl alcohol) (PVA) microfibril, which was obtained from saponification of poly(vinyl pivalate), was conducted before and after zone drawing at various conditions. The resulting PVA microfibrils were characterized by differential scanning calorimeter and scanning electron microscopy. Surface morphologies of these PVA microfibrils showed some differences between PVA microfibril 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 on zone drawing. Iodinated PVA microfibrils showed a decrease in crystal melting temperature of about 100 ^{o}C compared to the untreated sample. PVA microfibrils drawn after iodination showed relatively higher crystal melting temperature than those of microfibrils iodinated after drawing. These results were considered as the proofs of the changes in crystalline lattice of the PVA microfibrils. Effects of drawing temperature on sublimation of iodine were also evaluated.

Introduction

Poly(vinyl alcohol) (PVA) obtained by the saponification of poly(vinyl ester) is a linear semicrystalline polymer, which has been widely used as fiber. PVA fibers have high tensile and compressive strengths, tensile modulus, abrasion resistance due to its highest crystalline lattice modulus, and superior biocompatibility.[1-3] Recently, Lyoo *et al.* found that a PVA fiber of well-oriented microfibrillar structure was formed during saponifying poly(vinyl pivalate) (PVPi) to PVA.[4-10] These PVA microfibrils show the appearance and characteristics of natural fibers, such as cotton and jute. PVA microfibrils show more enhanced mechanical properties than spun fibers. Furthermore, PVA microfibrils have abundant microvoids, which are suspected to improve the biocompatibility.

Embolization is the operational therapy of controlling the flow of blood to the specific vein or portion of it to prohibit the supply of nutrition to some kind of cell, such as cancer cell. Another kind of embolization is physical treatment for blood circulation, such as the aneurysm surgery.[11-13] Cancer cell-killing embolic application has been paid attention to for its possibility and effectiveness for replacement of commercialized metallic coil shaped embolic materials; metallic materials have some problems during operation for its sharpness of cut face. PVA microfibrils, in contrast, show superior properties, including enhanced biocompatibility and less risk of scratching, but hard to be detected by X-ray during the operation because of its lack of radio-opacity. Radio-opacity is very important characteristics for embolic materials for the minute positioning control of materials in human organ.

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, as well as amorphous regions, to form new substitution types of crystalline lattice.[14,15] It is valuable to relate the radio-opacity introduced and property changes in operational point of view. In this study, iodination of PVA microfibrils was conducted with varying iodination conditions. For the consideration of the effects of crystalline structure on the formation of iodine-complex, PVA microfibrils were drawn before and after iodination at various conditions. The resulting PVA microfibrils were characterized by differential scanning calorimeter and scanning electron micrograph. Iodinated PVA microfibrils showed a decrease in melting temperature about 100 ^{o}C. Crystalline lattice change and physical and chemical characteristic of iodinated PVA microfibrils were also evaluated according to the amount of iodine sorption.

Experimental

Materials

PVA microfibrils were prepared by saponification of PVPi having number averaged degree of polymerization (P_n) of 25,000. Resulting PVA microfibril had P_n and syndiotactic diad content of 10,000 and 61.0%, respectively. Iodine and potassium iodide (KI) were purchased from Aldrich Co. Extra-pure grade reagents were used without further purification. Water used for all the procedures was deionized.

Iodination of PVA microfibril

Aqueous iodine solution of $4x10^{-1}$ mol/l was prepared by mixing of I_2 and KI at mole ratio of 1 to 2. Drawn and untreated PVA microfibrils were iodinated in this aqueous iodine solution for 48 hours at room temperature. Iodinated PVA microfibrils were washed in water for 1 hour at room temperature to wash off the adhesive iodine. Iodinated PVA microfibrils, then, were dried at room temperature without vacuum to prevent the sublimation of iodine.

Zone drawing of PVA microfibril

Iodinated and untreated PVA microfibrils were drawn by zone drawing method. Drawing temperatures were changed from 100 to 200 ^{o}C at fixed drawing rate and weight. Draw ratio was measured as the length gain and ranged from 2 to 4 times.

Desorption of iodine

Iodinated PVA microfibrils were treated with water for 2 hours at 40 ^{o}C. Amount of water was controlled to 1,000ml/1g of PVA microfibrils. Finally, PVA microfibrils were dried at room temperature in atmosphere.

Characterization

Appearances of PVA microfibrils were observed by scanning electron microscopy (SEM). Thermal characteristics of PVA microfibrils were evaluated by using differential scanning calorimeter (DSC).

Results and Discussion

Zone drawing, due to short residence time within a heated drawing zone, has many advantages such as: fewer possibilities of back folding of molecular chain, of microcrystallite formation, of thermal degradation, and of energy loss.[16-23] Zone drawing condition, therefore, can affect amount of iodine sorption of PVA microfibrils. Fig. 1 shows the iodine adsorption of zone drawn PVA microfibril according to drawing temperature and resulting draw ratio. Iodine adsorptions were decreased with increasing zone drawing temperature. Decreases in iodine adsorption can be explained as the increases of regularities of PVA microfibrils by drawing. In addition, effect of draw ratio on iodine adsorption showed the expected tendency; PVA microfibril of higher draw ratio, and resulting higher degree of molecular regularity, showed lower iodine adsorption. Especially, PVA microfibril drawn 4 times at 200 °C showed steeply decreased amount of adsorption. It is well known that crystalline structure of PVA can be penetrated by iodine. In this study, it is assumed that drawing can effectively prevent the penetration of PVA crystalline structure by iodine.

Iodine has high degree of sublimation. The heat on drawing, therefore, evaporated the iodine resulting in weight loss of iodinated PVA microfibrils. Weight losses of iodinated PVA microfibril (weight gain for iodination 39.29%) versus drawing temperature and resulting draw ratio were shown in Fig. 2. Weight losses were calculated with respect to absorbed iodine. Increase in drawing temperature results in the increase of the weight loss of iodinated PVA microfibril. PVA microfibrils drawn 4 times show much higher weight loss than those of drawn twice at same temperature. It is ascribed that hot zone duration time of PVA microfibril drawn 4 times is much more than that of drawn twice.

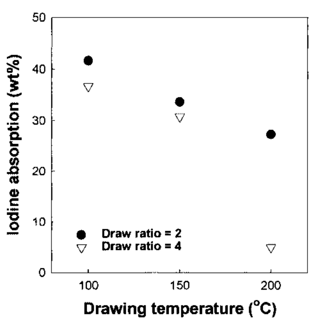


Fig. 1. Iodine adsorption of PVA microfibril according to drawing temperature. (Draw ratio were controlled to 2-4)

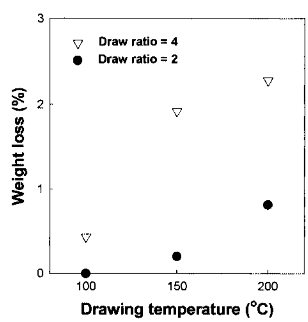


Fig. 2. Weight loss of iodinated PVA microfibril vs. drawing temperature. (Draw ratio were controlled to 2-4)

Iodine desorption of PVA was an important subject for its usage as a polarized film.[24,25] To use iodinated PVA microfibrils as embolic materials, water resistance of iodine desorption should be improved as well. (a) and (b) of Fig. 3 show the amounts of iodine desorption of PVA microfibrils drawn before and after iodination, respectively. Iodine desorption can be depressed by increasing drawing temperature at both cases. Iodine desorption of pre-drawn PVA microfibrils, however, decreased much faster. But this cannot be a clue of fastness of iodine because PVA microfibril drawn 4 times at 200 °C absorbed so less iodine. PVA microfibrils iodinated after drawing show relatively stable iodine desorption values of *ca.* 20%. This result can be related to the penetration depth of iodine. PVA microfibril drawn before iodination should have tighter internal structure than microfibrils drawn after iodination at iodination stage. Therefore, iodine cannot penetrate to the depth enough for drawn PVA microfibrils. This loose-penetrated iodine can be evaporated much more easily.

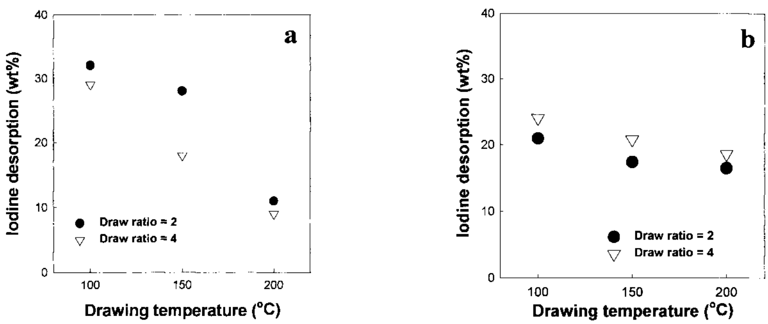


Fig. 3 Iodine desorption of PVA microfibrils versus drawing temperature; (a) drawn before iodination, (b) drawn after iodination. (2 hours in water at 40 °C)

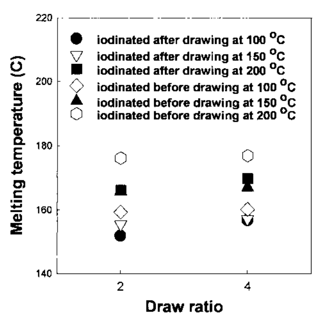
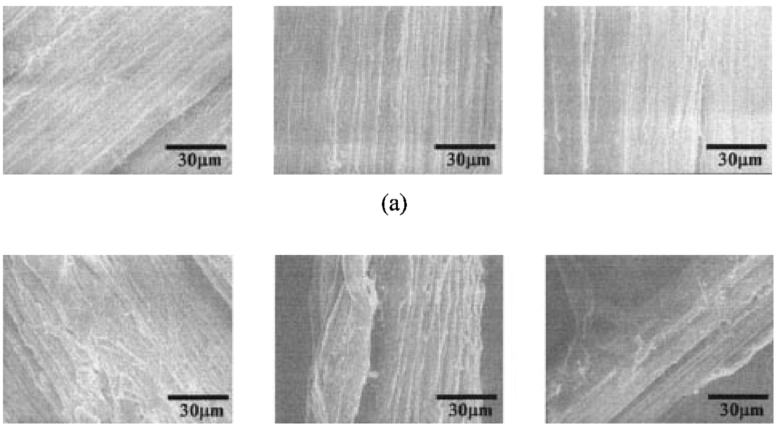


Fig. 4. Crystalline melting temperatures of PVA microfibrils versus draw ratio.

Changes of crystalline structure can be indicated by crystalline melting temperature (T_m). Fig. 4 shows T_m of PVA microfibrils drawn before and after iodination. Temperature was scanned from room temperature to 300 °C at 10 °C/min of heating rate. T_m of untreated PVA microfibril is about 260 °C.[4] On the other hand, PVA microfibrils of this study show (T_m)s of ranging from 150 °C to 180 °C. These changes can be attributed to the reduction in structural regularity by the penetration of iodine.

Surface morphologies of iodinated PVA microfibril were shown in Fig 5. Iodinated PVA fibrils after zone drawing showed much crude surface than fibrils iodinated before drawingn. From this result, it can be confirmed that iodine can also penetrate the PVA crystalline oriented by drawing effectively.



(b)

Fig. 5. SEM photographs of PVA fibrils; (a) drawn after iodination, (b) drawn before iodination (x1,000).

Conclusion

In this study, iodination and zone drawing of PVA microfibrils were conducted at various conditions. Iodine adsorption of undrawn PVA microfibril reaches to 39.29% and iodine evaporations in following zone drawing were ranging from 0% to 2.3 wt% of iodinated PVA microfibrils. Weight loss by iodine evaporation increased with the increase in drawing temperature and this tendency was enlarged for PVA microfibrils of higher draw ratio. Iodination of drawn PVA microfibril was also performed and the amount of iodine adsorption reduced from 42% to 5% with increasing drawing temperature. Iodinated PVA microfibrils were steeped in water at 40 °C for 2 hours. PVA microfibrils iodinated after drawing showed drastic decrease in iodine desorption ranging from 33% to 9% with increasing in drawing temperature. However, PVA microfibrils iodinated before drawing showed the value of about 20% for all drawing temperature. (T_m)s of PVA microfibrils increased with increasing drawing temperature and draw ratio, ranging from 150 °C to 180 °C. But these values were about 100 °C lower than those of untreated PVA microfibrils, *ca.* 260 °C.

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[1] K. Toyoshima, in "*Polyvinyl Alcohols*", C. A. Finch, Ed., John Wiley and Sons, New York 1973, pp. 339-388.
[2] I. Sakurada, in "Polyvinyl Alcohol Fibers", M. Lewin, Ed., Marcel Dekker, New York 1985, pp. 3-9 and pp. 361-386.
[3] M. Masuda, in "Polyvinyl Alcohol-Development", C. A. Finch, Ed., John Wiley and Sons, New York 1991 pp. 403-422 and p. 711.
[4] W. S. Lyoo, W. S. Ha, *Polymer* **1996**, *37*, 3121.
[5] W. S. Lyoo, W. S. Ha, *J. Polym. Sci., Polym. Chem. Ed.* **1997**, *35*, 55.
[6] W. S. Lyoo, J. Blackwell, H. D. Ghim, *Macromolecules* **1998**, *31*, 4253.
[7] W. S. Lyoo, S. N. Chvalun, H. D. Ghim, J. P. Kim, J. Blackwell, *Macromolecules* **2001**, *34*, 2615.
[8] W. S. Lyoo, J. H. Kim, J. H. Choi, B. C. Kim, J. Blackwell, *Macromolecules* **2001**, *34*, 3982.
[9] W. S. Lyoo, B. J. Kim, W. S. Ha, *J. Korean Fiber Soc.* **1996**, *33*, 231.
[10] W. S. Lyoo, J. H. Yeum, H. D. Ghim, B. C. Ji, W. S. Yoon, J. P. Kim, *J. Korean Fiber Soc.* **2000**, *37*, 487.
[11] V. P. Chuang, S. Wallace, *Radiology* **1980**, *135*, 2959.
[12] V. P. Chuang, C. S. Soo, S. Wallace, *AJR* **1981**, *136*, 729.
[13] H. Demachi, O. Matsui, T. Takashima, *Cardiovasc. Intervent. Radiol.* **1991**, *14*, 158.
[14] W. O. Hermann, W. Haehnel, *Ber. Dtsch. Chem. Ges.* **1927**, *60*, 1658.
[15] H. Staudinger, K. Frey, W. Starck, *Ber. Dtsch. Chem. Ges.* **1927**, *60*, 1782.
[16] S. S. Han, W. S. Yoon, W. S. Lyoo, C. J. Lee, B. C. Ji, *J. Macromol. Sci.-Phys.* **1997**, *B36*, 1.
[17] S. S. Han, W. S. Yoon, J. H. Choi, S. Y. Kim, B. C. Ji, W. S. Lyoo, *J. Appl. Polym. Sci.* **1997**, *66*, 1583.
[18] B. C. Ji, G. S. Jeong, W. S. Yoon, S. S. Han, W. S. Lyoo, *Polymer Testing* **1999**, *18*, 299.
[19] W. S. Lyoo, S. S. Han, W. S. Yoon, B. C. Ji, J. Lee, Y. W. Cho, J. H. Choi, W. S. Ha, *J. Appl. Polym. Sci.* **2000**, *77*, 123.
[20] B. C. Ji, E. K. Kim, C. J. Lee, W. S. Lyoo, W. S. Yoon, S. S. Han, *Polymer(Korea)* **1995**, *19*, 846.
[21] W. S. Lyoo, S. S. Han, J. H. Choi, Y. W. Cho, W. S. Ha, *J. Korean Fiber Soc.* **1995**, *32*, 1023.
[22] B. C. Ji, W. S. Yoon, S. Y. Kim, *J. Korean Fiber Soc.* **1993**, *30*, 328.
[23] S. S. Han, S. Y. Kim, *J. Korean Fiber Soc.* **1994**, *31*, 1012.
[24] W. S. Lyoo, J. H. Yeum, J. H. Choi, B. C. Ji, H. D. Ghim, J. P. Kim, T. H. Noh, W. J. Yoon, *Polymer Testing* **2001**, *20*, 503.
[25] W. S. Lyoo, J. H. Yeum, J. H. Choi, H. C. Song, B. C. Ji, J. P. Kim, T. H. Noh, W. J. Yoon, T. S. Cheong, *J. Appl. Polym. Sci.* **2001**, *82*, 108.