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EFFECT OF DYEING ON MELTING BEHAVIOR OF POLY(LACTIC ACID) FABRIC

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Abstract

The effect of the dyeing on the melting behavior of poly(lactic acid) fabrics was investigated by differential scanning calorimeter. The DSC melting peaks at 10°C min^{-1} of the untreated poly(lactic acid) fabric were observed at a temperature higher than those of the dyed fabrics. The restricting force from the extended tie molecules along the fiber axis seems to decrease in the dyeing process. When the sample was rapidly heated, the crystallites melted at lower temperatures since recrystallization was restricted. It was estimated, based on the heating-rate dependency of melting behavior, that the original crystallites of the untreated sample melted at 146.1°C and those of the dyed samples melted at higher temperatures, suggesting that their crystallites are grown to be more perfect in the dyeing process.

Keywords: crystallization, double endotherm, DSC, multiple melting endotherm, PLA, poly(lactic acid)

Introduction

Poly(lactic acid) fiber is a new product in the textile market, and has two attractive features: first, it is made from renewable resources such as starch. Second is hydro- and biodegradable material. Currently, this polymer is used only for medical applications, due to its high cost. However, if the production cost becomes compatible with other fiber-forming polymers, poly(lactic acid) is expected to be widely applied to fibers and fabrics.

In spite of the advantageous characteristics of poly(lactic acid), the color fastness of dyed fabrics and thermal stability will be the major factors to be improved. Concerning the color fastness, we investigated the lightfastness of dyed fabrics [1, 2] and reported that lightfastness can be improved if a stable dye is selected. Concerning the thermodynamic properties of poly(lactic acid), many results have already been reported. The equilibrium melting temperature of poly(*L*-lactic acid) was reported to be 215°C by Kalb and Pennings [3], while the melting temperature of the fiber was 178°C by Mochizuki [4]. Although the above data shows a certain variation, it can be

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said that the melting temperature of poly(lactic acid) fiber is lower than that of usual synthetic fibers, but it is relatively high, compared with the melting temperatures of other biodegradable polymers.

When the melting of fiber or fabric is measured by differential scanning calorimetry (DSC), the phenomenon of molecular rearrangement during heating process should be taken into account in the analysis [5]. It is found that the melting–recrystallization–remelting behavior of nylon 6 fiber is influenced by several factors such as the fiber-axis restricting force derived from textile construction. We also established that the DSC melting temperature of the most imperfect crystallites can be estimated as the temperature where the melting curve initially deviates from the baseline, T_{sm}, at high heating rates [5].

Based on our previous results, we consider that the melting behavior of the poly(lactic acid) fiber dose not reflect the melting of original crystallite because of molecular reorganization during heating. In this study, we reanalyzed the untreated and dyed poly(lactic acid) fabrics by DSC to investigate the effect of dyeing on the melting behavior.

Experimental

Materials

Poly(lactic acid) fabrics were woven with the following structure: warp; 83.3 dtex fineness (24 filaments), 37.0 cm^{-1} density, weft; 166.7 dtex fineness (48 filaments), 24.0 cm^{-1} density, plain weave. The untreated fabrics were used as sample 1. Three kinds of sample fabrics were prepared as described in our previous papers [1, 2]. The treating temperature was controlled as follows; maintained at 50°C for 5 min, heated up to 100°C in 20 min and maintained at 100°C for 60 min. Sample 2 was the fabric treated in hot water with no dye. Samples 3 and 4 were treated the fabrics in hot water with Disperse Red 82 (SERILINE Red 3B-LS, Yorkshire Japan plc) and Disperse Violet 27 (FORON Brilliant Violet EBLN, Clariant Japan K.K.) of 2% owf, respectively.

Differential scanning calorimetry (DSC)

The melting behavior of the samples was measured using a differential scanning calorimeter (MAC Science Co., Ltd., DSC3200S). The temperature and enthalpy were calibrated in the usual way by standard materials of indium, tin, lead and zinc, whose purity is ≥99.999%. Samples were packed in open-type aluminium sample pans by the following three techniques. In technique 1, the poly(lactic acid) fabric was cut into a disc of 4 mm diameter and packed in a sample vessel. In technique 2, the fabric was cut to the same size as in technique 1 and unraveled to make short fibers and then packed in a vessel. In technique 3, a fine copper powder of ca 30 mg was added to a disc of the fabric to fill up the openings within it and then packed densely in a vessel, in order to increase the thermal conductivity [6]. Sample mass was 1.5–1.8 mg. The measurements were performed at various heating rates from 10 to 100°C min^{-1} in an atmosphere of nitrogen at 50 mL min^{-1}.

Results and discussion

The melting curves at 10°C min^{-1} of all the samples packed by technique 1 are shown in Fig. 1. The sample 1 shows a double melting behavior at the peak temperatures (T_{pm}) of 159.0 and 169.5°C. On the other hand, the sample 2 shows a broad peak with the T_{pm} of 163.6°C. The sample 3 has a main peak at 166.0°C and a shoulder peak on the low-temperature side. The sample 4 shows a double melting behavior at the T_{pm} of 162.6 and 167.0°C. The main T_{pm} of the sample 1, which was not heat-treated, is the highest temperature of all. The results of the samples 3 and 4 show that the sorbed dye molecules change the melting behavior to double endotherms. This suggests that the melting-recrystallization-remelting behavior of the samples 3 and 4 is remarkable in comparison with the sample 2. Since the sorbed dye molecules reduce the intermolecular or three-dimensional friction between macromolecular chains, the crystallites are promoted to melt, reorganize and become more perfect. The effect of Disperse Violet 27 as a lubricant is thought to be larger than that of Disperse Red 82, considering their melting behavior.

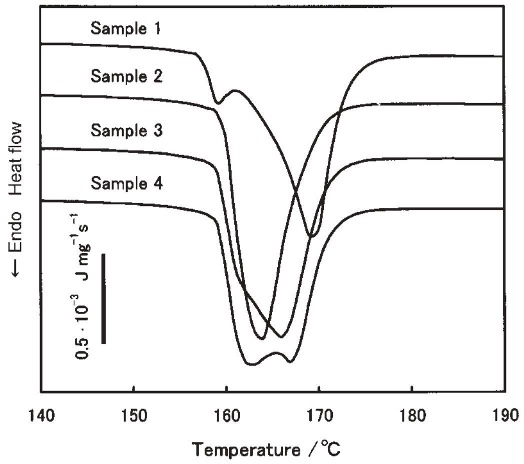

Fig. 1 DSC heating curves measured at 10°C min^{-1} of samples 1–4 packed by technique 1

The melting curves of the samples 1 and 2 packed by techniques 2 and 3 are shown in Fig. 2, in addition to the results by technique 1. In the case of sample 1, the endothermic peak at lower temperature is larger in technique 2 than that of technique 1, while the endothermic peak at higher temperature is smaller. Considering that the T_{pm} of higher peak is lower in technique 2 than that of technique 1 by 1.8°C, the endothermic peak shifts to the low-temperature side. The curve of technique 3 shows that the low-temperature peak shifted to high temperature to become a shoulder peak, and the T_{pm} of the main peak was slightly higher than that of technique 1.

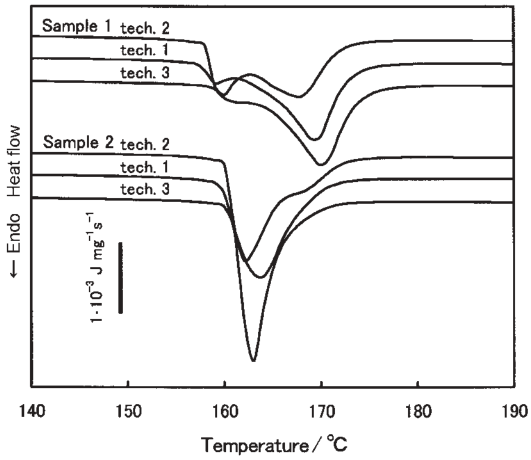

Fig. 2 DSC heating curves measured at 10°C min^{-1} of samples 1 and 2 packed by techniques 1, 2 or 3

The DSC curves of sample 2 were not so strongly affected by the packing techniques in comparison with that of sample 1. In the curve by technique 2, the main T_{pm} is lower than that of technique 1 by 1.5°C, and a shoulder peak is detected clearly on the high-temperature side. The melting peak of technique 3 is extremely sharp, and the T_{pm} is slightly lower than that of technique 1. This difference between techniques 1 and 3 is thought to result from the improvement in the thermal conductivity within the sample by adding copper powder.

As mentioned in Fig. 1, the main T_{pm} of the sample 1 was higher than that of the sample 2. The difference between the samples 1 and 2 seem to show that the melting temperature of poly(lactic acid) fabric was reduced by the heat treatment for dyeing. However, this result is unexpected, since the original lamellar crystallites must become larger in thickness during the heating process of 100°C. Generally, untreated drawn fibers are considered to have a lot of extended tie molecules connecting crystallites. The above results for sample 1 suggest that the melting behavior is strongly affected by the fiber-axis restricting force which transmits through the crystallite networks connected by extended tie molecules, as described in our previous paper [5]. Because of a temporary entropic restriction, the restraint on partial melting is considered to increase the melting point with increasing the force in the following order, technique 2, 1 and 3. As a result, the melting peak became simpler in shape and higher in temperature. In the case of sample 2, the melting behavior suggests that the orientation of crystallites is disarranged, and the number of tie molecules decreases in the heat treatment for dyeing.

From the above facts, it is thought that the melting behavior of all the samples at 10°C min^{-1} does not exactly exhibit their original one. The melting curves were strongly influenced by their higher-order structures composed of crystallites and amorphous region including tie molecules. Therefore, they are variously changed by a fiber-axis restricting force. The melting temperatures of the original crystallites can not be estimated from the data measured at 10°C min^{-1}.

There was no crystallization peak on the curves of samples 1–4 measured by technique 1, but slight exothermic changes were observed. These changes were attributed to their pre-melt crystallization. The enthalpy change of melting, ΔH_m (J g^{-1}), and that of pre-melt crystallization, ΔH_c (J g^{-1}) , are listed in Table 1.

Table 1 Enthalpy change of pre-melt crystallization, ΔH_c, and melting ΔH_m of samples 1–4

	Sample	ΔH_c/J g^{-1} pre-melt crystallization	ΔH_m/J g^{-1} melting
1	Non-treatment	–1.65	53.51
2	Heat-treatment	–0.69	55.86
3	Dyed Dis. Red 82	–0.30	56.11
4	Dyed Dis. Violet 27	–0.24	56.57

This table shows that the absolute value of ΔH_c decreased in the following order, sample 1, 2, 3 and 4, but the ΔH_m value increased in the same order. This result suggests that the crystallization and growth of the existing crystallites occurred during the heating treatment of dyeing. In addition, the slightly higher ΔH_m of the dyed samples, sample 3 and 4, than the value of sample 2 suggests that the dye molecules as a lubricant promote crystallization of poly(lactic acid) in the dyeing process.

The effect of the heating rate on the melting peaks was investigated. Figures 3–5 show the melting curves measured at various heating rates from 10 to 100°C min^{-1} of samples 1–3 packed by technique 1, respectively. Figure 3 shows that the double endothermic peaks at 10°C min^{-1} become simpler and broader in shape with increasing heating rate and shift to the high-temperature side. The results of samples 3 and 4 show a similar tendency. In the case of sample 2, the melting peak becomes broader and shifts to the

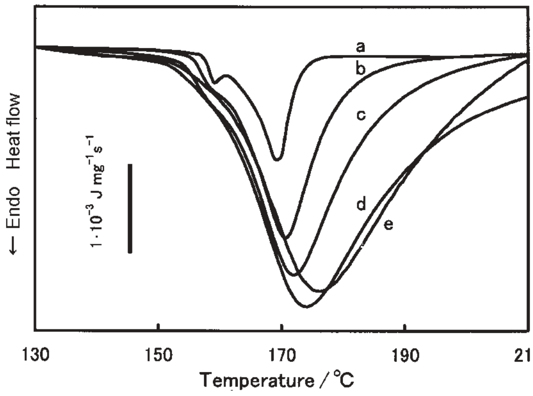

Fig. 3 DSC heating curves measured at various heating rates from 10 to 100°C min^{-1} of sample 1 packed by technique 1: a – 10, b – 30, c – 50, d – 80 and e – 100°C min^{-1}

high-temperature side. The T_{pm} value almost linearly increased with increasing heating rate. This heating rate dependency is thought to result mainly from the thermal lag between the sample-temperature monitoring station and the sample itself.

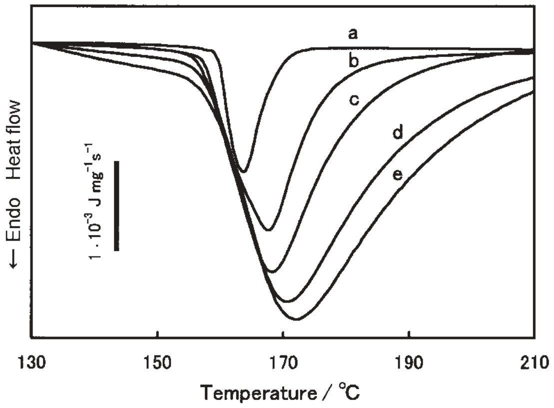

Fig. 4 DSC heating curves measured at various heating rates from 10 to 100°C min^{-1} of sample 2 packed by technique 1: a – 10, b – 30, c – 50, d – 80 and e – 100°C min^{-1}

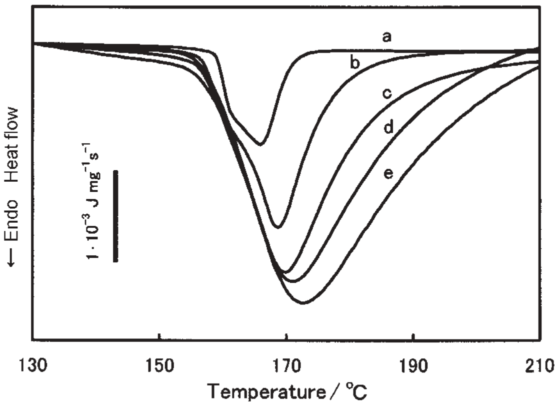

Fig. 5 DSC heating curves measured at various heating rates from 10 to 100°C min^{-1} of sample 3 packed by technique 1: a – 10, b – 30, c – 50, d – 80 and e – 100°C min^{-1}

According to the strict solution [7, 8] based on the theoretical model for a heat-flux DSC investigated by Mraw [9], true melting temperature, T_{fus} is related to the T_{sm} temperature where a melting curve initially departs from its baseline. The relationship between T_{fus} and T_{sm} is given as

$$T_{fus}=T_{sm}-CR\beta \qquad (1)$$

where C is the heat capacity of the sample material itself and its vessel, R is the thermal resistance between the sample-temperature monitoring station and the sample itself and β is the heating rate. This equation indicates that the slope of the straight line drawn through T_{sm} plots is given as CR, and T_{sm} is higher than T_{fus} by $CR\beta$.

Figure 6 shows the relationships between the T_{sm} values of samples 1–4 and the heating rates, β. This figure shows that the T_{sm} values of samples 1 and 2 decrease in the low β region, and then increase linearly with increasing heating rate. Also, the T_{sm} of samples 3 and 4 decrease similarly in the low β region, but they do not show an obvious tendency to increase in the high β region. The T_{sm} values of samples 1 and 2 are thought to show a similar heating-rate dependency to that of nylon 6 fabric. As described in the previous paper [5], the shifts of their T_{sm} to low-temperature side should be attributed to the fact that high-speed heating inhibits the reorganization of their crystallites during heating. In the cases of samples 3 and 4, the sorbed dye molecules may affect their heating-rate dependencies of T_{sm} as a lubricant.

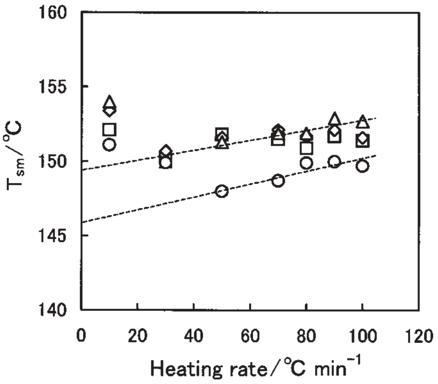

Fig. 6 Relationships between heating rates and T_{sm} values of samples packed by technique 1: o – sample 1, △ – 2, □ – 3 and ◇ – 4

The temperature estimated by linear extrapolation of the T_{sm} to 0°C min^{-1} is supposed to be the temperature of zero-entropy-production melting of the original crystallites [5]. In this study, this estimation was tried in the same manner on the T_{sm} plots in Fig. 6. As a result, the temperatures of samples 1 and 2 were estimated 146.1 and 149.1°C, respectively. It seems to be reasonable that the extrapolated temperature of sample 2 is higher than that of sample 1, because the crystallites had grown to become more perfect during the heat treatment. Therefore, these data must be the exact melting temperatures of their original crystallites, while the data at 10°C min^{-1} are strongly affected by the higher-order structures in the fibers. For samples 3 and 4, the extrapolated temperatures could not be determined, because no linear relationship existed between the linear heating rate and T_{sm} in the high β region. However, the zero-entropy-production melting temperatures of their smallest crystallites must be almost the same degree as sample 2, since they were treated at the same temperature.

Figure 7 shows the relationships between the T_{im} values of samples 1–4 and the heating rates. Since sample 1 clearly showed a double melting behavior at

10°C $\min^{-1}$, two kinds of T_{im} values were determined for the main peak and the side one on all the curves. All the T_{im} values decrease in the lower region but increase in the higher region with increasing heating rate. This result suggests that the heating-rate dependency of T_{sm} strongly affected that of T_{im}, though T_{im} is not related to T_{fus} from a theoretical point of view. In addition, the above consideration on T_{sm} of samples 2 and 3 is supported by the fact that the T_{im} values of samples 2–4 showed an extremely close heating-rate dependency.

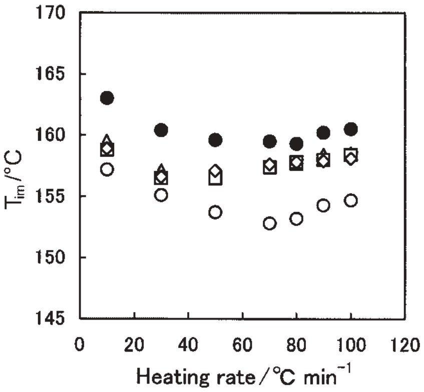

Fig. 7 Relationships between heating rates and T_{im} values of samples packed by technique 1: o – sample 1 (side peak), ● – 1 (main peak), △ – 2, □ – 3 and ◇ – 4

In the case of nylon 6 fabric, T_{im} slightly increased with increasing heating rate, and it was completely different from the T_{sm} behavior [5]. The difference in the T_{sm} behavior between poly(lactic acid) and nylon 6 is thought to result from the difference in strength of intermolecular interaction. Poly(lactic acid) is expected to have a weaker intermolecular interaction than nylon 6 considering their one-order structures. Therefore, the melting of poly(lactic acid) is promoted to occur quickly by the larger motility of polymer, but the reorganization is supposed to occur slowly. Because the reorganization of poly(lactic acid) is retarded in the early stages of melting, the heating-rate dependency of T_{im} is thought to be similar to that of T_{sm}.

Correct T_{sm} value is difficult to obtain, because a slight change of endotherm is difficult to detect the start temperature of melting on a DSC curve. However, the above inference based on the heating-rate dependency of T_{sm} is strongly supported by the fact that the behavior of T_{im} showed a tendency similar to that of T_{sm}.

Conclusions

When poly(lactic acid) fabrics were heated at 10°C $\min^{-1}$, the melting peaks of the untreated sample were observed at a temperature higher than those of the dyed samples. The restricting force from the extended tie molecules along the fiber axis seems to decrease in the dying process. It is considered that the high restricting force tended to shift the melting peak to higher temperature. The data of melting enthalpy showed that the crystallinity of poly(lactic acid) fiber is increased in the dyeing process. When the sample was rapidly heated, the crystallites melted at lower temperatures since recrystallization was restricted. It was estimated based on the heating-rate dependency of T_{sm}, that the original crystallites of the untreated sample melt at 146.1°C. This value is lower than those of the treated samples by ca 3°C, and therefore the crystallites are grown to be more perfect in the dyeing process.

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References

1 K. Mogi, T. Nakamura, H. Kubokawa and H. Komatsu, Sen'I Gakkaishi, 57 (2001) 234.
2 K. Mogi, T. Nakamura, H. Kubokawa and H. Komatsu, Sen'I Gakkaishi, 57 (2001) 239.
3 B. Kalb and A. J. Pennings, Polymer, 21 (1980) 607.
4 M. Mochizuki, Sen'I Gakkaishi, 52 (1996) P-200.
5 H. Kubokawa and T. Hatakeyama, J. Therm. Anal. Cal., in press.
6 T. Hatakeyama, H. Yoshida, C. Nagasaki and H. Hatakeyama, Polymer, 17 (1976) 559.
7 Y. Saito, K. Saito and T. Atake, Thermochim. Acta, 99 (1986) 299.
8 K. Saito, T. Atake and Y. Saito, Netsu-Sokutei, 14 (1987) 2.
9 S. C. Mraw, Rev. Sci. Instrum., 53 (1982) 228.

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