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Optimization of dyeing poly(lactic acid) fibers with vat dyes

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Abstract

Optimization of dyeing poly(lactic acid) fibers with vat dyes has been investigated. Conventional method for dyeing cellulose fibers with vat dyes was able to be applied for dyeing poly(lactic acid) fibers. It has become obvious that higher dyeing temperature and concentration of auxiliaries have negative effects on the dyeability of dyes on poly(lactic acid) fibers. Determination of optimal dyeing condition has also been investigated. We found that optimal concentrations of dyes and auxiliaries could be estimated through simple linear experimental equation.

Keywords: Poly(lactic acid); Vat dye; Dyeing

1. Introduction

In recent years, the poly(lactic acid) as a fiber material is widely noticed in the industrial fields [1–3]. The most attractive characteristic of poly(lactic acid) fibers would be biodegradation. Biodegradable polymers such as poly(lactic acid), aliphatic polyester, polycaprolactone, etc. have a property to degrade into carbon dioxide and water by an action of suitable fungi. This means that biodegradable poly(lactic acid) fibers are suitable for the harmony with an environment even if the fiber is left in the natural environment. Another attractive characteristic would be starting materials. The poly(lactic acid) fiber is synthesized from a starch of a dent corn that harvests at the cycle of a year and does not require any fossil fuels. At this time, the amount of consumption of a dent corn for the synthesis of poly(lactic acid) fibers is less than 0.02% of the total amount of the production in the world. Therefore, the production of poly(lactic acid) fibers would not cause food crisis even if the production of them will be sharply increased in the future. Further, recent high technology enables the production of poly(lactic acid) fibers from other plants such as sweet potato. The production of poly(lactic acid) fibers is, therefore, suitable for a future era of limited natural resources.

In such a situation, the demand of poly(lactic acid) fibers as a substitute for the present synthetic fibers would be greatly increased. In fact, the characteristic of poly(lactic acid) fibers is similar to that of representative synthetic fibers. For example, initial fiber properties such as density, glass transition temperature, fiber strength, Young's modulus, etc. resemble to those of PET and nylon [4]. In addition, dyeing process of poly(lactic acid) fibers is also similar to those of synthetic fibers. Dyeing of poly(lactic acid) fibers is generally carried out with disperse dyes under high temperature and pressure because poly(lactic acid) fibers have low affinity to conventional water soluble dyes. But the dyeing of poly(lactic acid) fibers with dyes for natural fibers has not been attained. Considering future increase in the demand of poly(lactic acid) fibers, the production of composite or union clothes with natural fibers would also be increased. Therefore, functional processing of poly(lactic acid) fibers and the dyeing with dyes for natural fibers are the important subjects that must be solved out. In the former case, textile processing of poly(lactic acid) fibers is beginning to be

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investigated in recent years [5–7]. Our previous reports also discussed the possibility of enzyme processing of poly(lactic acid) fibers [8]. In the latter case, on the other hand, there is only a little report about the possibility of dyeing poly(lactic acid) fibers with vat dyes [9]. But the detailed information about the dyeing condition of poly(lactic acid) fibers is still unclear.

The purpose of the present study is an accumulation of fundamental knowledge about the dyeing of poly(lactic acid) fibers with conventional vat dyes. In order to achieve this, the dyeability of indigo dyes on poly(lactic acid) fibers has been investigated. In this paper, effects of auxiliary and dyeing conditions on dyeing property were discussed.

2. Experimental

2.1. Chemicals

Poly (lactic acid) fabrics that had already been scoured were obtained from Kanebo GOHSEN Ltd. These were prepared for each experiment by boiling in water for 1 h before use. The indigo dye and auxiliaries were obtained from Nacalai Tesque Co. Ltd. and were used as received. All other chemicals (Kanto Chemical Co. Inc.) used were of reagent grade.

2.2. Procedures

The prescribed amount of indigo dyes was previously dissolved in the same quantity of ethanol. Then exact amount of NaOH, $Na_2S_2O_3$ and boiled distilled water was added with stirring. After the indigo dye was reduced to a leuco-form, the dye solution was poured into a stainless steel dyeing vessel until the dyeing vessel was filled with the dye solution. The volume of the dyeing vessel was 500 ml. After the dye solution became fixed temperature, poly(lactic acid) fabric specimens were then immersed into the dyeing vessel and completely sealed to avoid gases. Dyeing was carried out using MINI-COLOUR 12E (TEXAM Co. Ltd.) dyeing machine under exact temperature and time. The bath ratio was adjusted to 1:50. After dyeing, a fabric specimen was dried overnight under the stream of air for the complete oxidation. The removal of un-dyed dyes on the fabric was attained by soaping in boiled water for 10 min under the presence of Marseille soap (1 g/l). The color depth of the dyed fabrics was estimated from the reflectance of the dyed fiber measured with the Minolta CM-1000 spectrophotometer (illumination diameter: 12 mm) under illuminant D65 using 10° observer. The color depth, *K/S* value, was calculated using the Kubelka–Munk equation:

$$K/S = (1 - R)^2/2R$$

where R is the reflectance of the fiber at the wavelength of maximum absorption.

3. Results and discussion

Fig. 1 shows variations of the color depth of dyed poly(lactic acid) fabrics as a function of dyeing temperature. In this case, the dyeing was carried out for 1 h. The color depth of dyed poly(lactic acid) fabrics increased from ca. 330 K and leveled off at higher temperature. The temperature that improves the dyeability completely agrees with the glass transition temperature of the poly(lactic acid) fiber [4]. An activation of molecular dynamics in an amorphous region by an increase in temperature obviously supports access of dye molecules into fibers. When the fiber gaps spread in the degree which does not have evil for the penetration of dyes, further spread of them do not provide marked improvement of the dyeability of dyes. From these results, the dyeing at 373 K that is the lowest temperature to obtain high color yield seems to be suitable from the view point of energy saving.

Fig. 2 shows the effects of dyeing time on the dyeability of dyes at 373 K. The color depth of the dyed poly(lactic acid) fabric gradually decreased with increasing dyeing time. These results are quite different from dyeing behaviors of conventional dyeing processes. In general, the color depth of a dyed fabric would increase with increasing dyeing time until equilibrium dyeing is attained. After the dyeing reaches equilibrium, the color depth of a dyed fabric does not vary. A decrease in the color depth of dyed fabric obtained in this study may relate a drop in the affinity of fibers on dyes or its contrary. Dealing with the first issue of a drop in the affinity of fibers, prolonged dyeing under high temperature may cause variations of the surface property of poly(lactic acid) fibers. As is generally known, softening temperature of a poly(lactic acid) fiber at atmospheric pressure is ca. 400 K. On the other hand, the apparent softening temperature of a poly(lactic acid) fiber may be reduced in this experimental condition because the pressure in a closed dyeing vessel is supposed to be high compared to that in an open vessel. As a result, prolonged dyeing under unsuitable dyeing condition may cause a drop in the dyeability of dyes. The second factor to be considered is a drop in the affinity of dyes on fibers. A part of a leucocompound may be decomposed in this dyeing condition. Chemical reactions with oxygen may be the most leading factor for a decomposition of a leucocompound. However, the dyeing in this

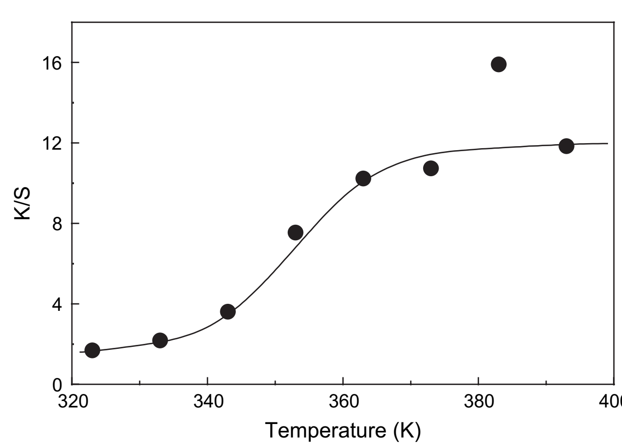

Fig. 1. Effects of dyeing temperature on the color depth of dyed poly(lactic acid) fabrics. Dyeing time: 1 h, [Indigo]: 5% owf, [$Na_2S_2O_3$]: 0.5% w/v, [NaOH]: 0.05% w/v.

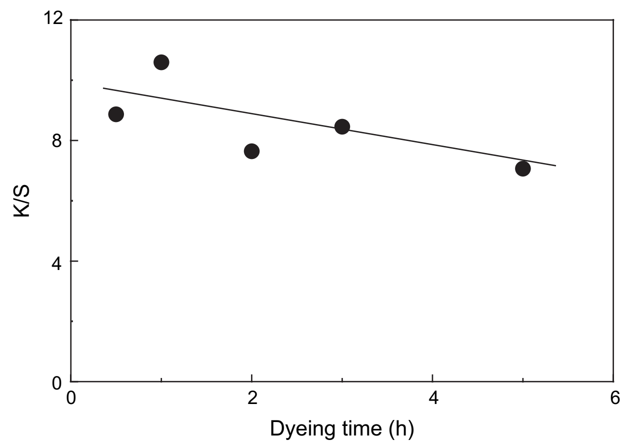

Fig. 2. Effects of dyeing time on the color depth of dyed poly(lactic acid) fabrics. [Indigo]: 5% owf, [$Na_2S_2O_3$]: 0.5% w/v, [NaOH]: 0.05% w/v, temperature: 373 K.

study was carried out under closed system, which avoids gases. Therefore, the possibility for a decomposition of a leucocompound by chemical reactions with gases would be low. Alternatively, a thermal decomposition may have arisen. Prolonged dyeing under high temperature condition may cause a drop in the stability of a leucocompound. In order to avoid thermal decomposition of a leucocompound without causing a drop in the dyeability of dyes, adjustment between dyeing temperature and dyeing time may be necessary.

Fig. 3 shows variations of the color depth of dyed poly(lactic acid) fabrics as a function of dye concentration. In this case, concentrations of auxiliaries (NaOH and $Na_2S_2O_3$) were kept at constant. As shown in Fig. 3, *K/S* value turns into the maximum, when dye concentration is ca. 5% owf. And then, the color yield decreases at higher concentration of dyes. These results are quite different from the dyeing behaviors of conventional dyeing processes. Stoichiometric relationship between the dye and the auxiliary seems to determine the dyeability of dyes in this system. In order to evaluate the effects of the auxiliary on dyeing poly(lactic acid) fabrics, similar investigations were carried out changing the concentration of auxiliaries.

Fig. 4 shows the influences of the concentration of $Na_2S_2O_3$ on the dyeing property at the constant NaOH concentration. The amount of $Na_2S_2O_3$ that is required to obtain the deepest color depth increased with increasing concentrations of indigo. It is natural that higher amounts of $Na_2S_2O_3$ are required to reduce higher amounts of indigo molecule. However, further addition of $Na_2S_2O_3$ causes negative effects on the dyeing property. The color depth of dyed poly(lactic acid) fabrics decreased after reaching the maximum and became constant. These results would relate the over reduction of indigo molecules. The leucocompound in the system may be over reduced by the presence of excess amount of $Na_2S_2O_3$. As a result, a drop in the affinity or the destruction of a leucocompound may occur. In addition, dyeing under high temperature may also participate in the decomposition of the dye. These assumptions are supported from the similar experimental results at the time of changing the amount of NaOH. Fig. 5 shows the effects of the concentration of NaOH on dyeing poly(lactic acid) fabrics at the constant $Na_2S_2O_3$ concentration. As shown in Fig. 5, an appearance in the variation of the color depth seems to be similar to that in Fig. 4. However, a drop in the color depth of dyed fabrics in the range of high concentration of NaOH was remarkable. In particular, the color depth of the fabric dyed with 5% owf of the indigo dye has fallen to nearly 0. These results suggest that a leucocompound in the system is completely decomposed to the extent at which it cannot be developed again. From these results, stoichiometric relationship between indigo dyes and auxiliaries seems to be very important to attain successful dyeing of poly(lactic acid) fabrics.

Fig. 6 shows the relationships between optimum concentration of indigo and auxiliaries (NaOH, $Na_2S_2O_3$). The optimum concentration of auxiliaries was determined for obtaining the deepest color depth of the fabric at the time of a fixed dye concentration. As shown in Fig. 6, linear relationships between the dye concentration and the auxiliaries were observed. In addition, extrapolation of the filled plots (NaOH) completely agrees with the coordinate axes. This suggests that reduction

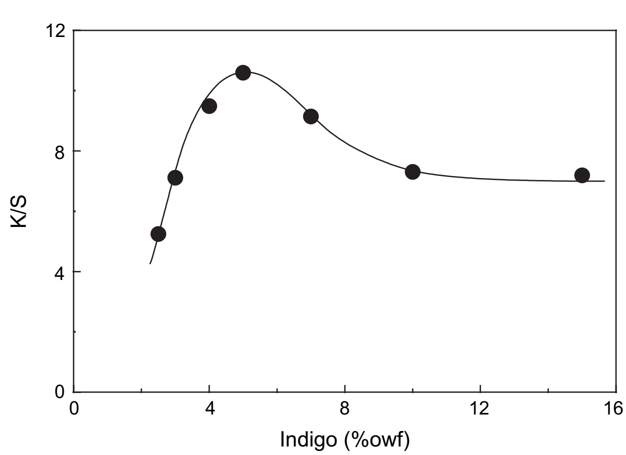

Fig. 3. Effects of dye concentration on the color depth of dyed poly(lactic acid) fabrics. Dyeing time: 1 h, [$Na_2S_2O_3$]: 0.5% w/v, [NaOH]: 0.05% w/v, temperature: 373 K.

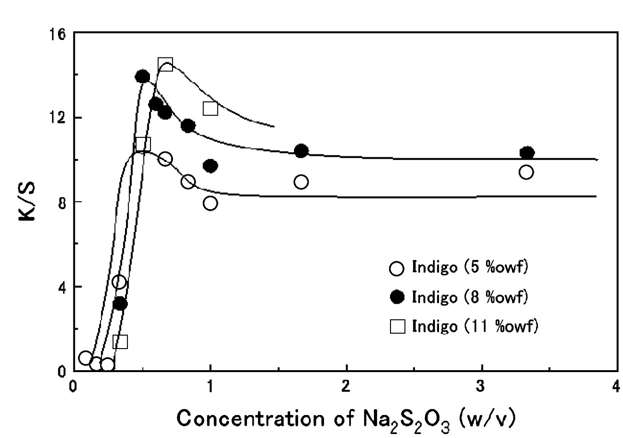

Fig. 4. Effects of the concentrations of $Na_2S_2O_3$ on the color depth of dyed poly(lactic acid) fabrics. Dyeing time: 1 h, [NaOH]: 0.05% w/v, temperature: 373 K.

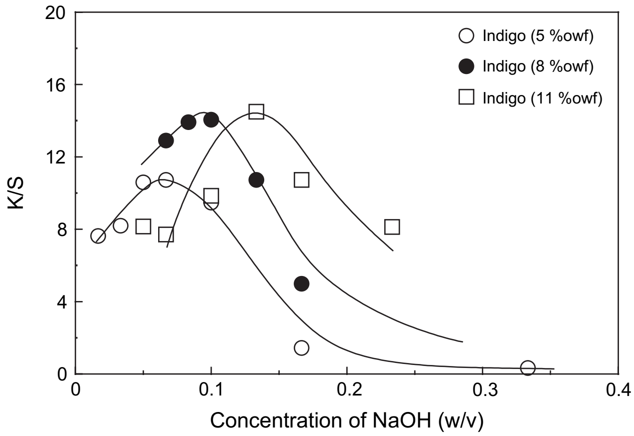

Fig. 5. Effects of the concentrations of NaOH on the color depth of dyed poly(lactic acid) fabrics. Dyeing time: 1 h, [$Na_2S_2O_3$]: 0.05% w/v, temperature: 373 K.

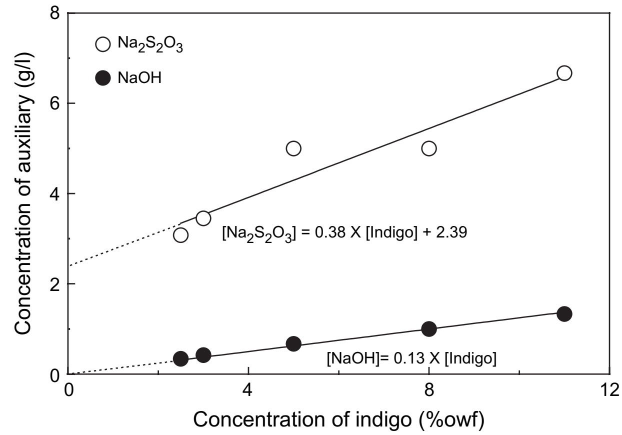

Fig. 6. Relationships between optimum concentration of indigo dye and auxiliaries. Dyeing time: 1 h, temperature: 373 K.

of the dye and subsequent adsorption onto the poly(lactic acid) fiber can be attained without requiring strong alkaline condition when concentration of the dye is low. On the other hand, extrapolation of the open plots ($Na_2S_2O_3$) does not pass through the coordinate axes and has positive intercept. $Na_2S_2O_3$ consumption by a reaction with oxygen in the dye solution may cause an increase in the apparent demand of $Na_2S_2O_3$. In addition, thermal decomposition of $Na_2S_2O_3$ may also be related.

From these results, optimum dyeing condition of poly(lactic acid) fabrics seems to be determined with simple experimental equation. The more reliable empirical equation would be obtained by the further investigation by considering the dyeing temperature and time.

4. Conclusions

The possibility of dyeing poly(lactic acid) fabrics with conventional indigo dyes was investigated. The poly(lactic acid) fabrics could be dyed in deep shade by a similar method of dyeing cellulose fibers with vat dyes. Effects of auxiliaries on the dyeability of dyes were remarkable and were negative at the range of high concentration. Optimal concentrations of dyes and auxiliaries could be estimated with simple experimental equation.

The demand of the poly(lactic acid) as a fiber material would be increased in the future because of the excellent characteristics such as fine fiber property and environmental friendship. Fundamental data obtained in this study would become valuable knowledge in dyeing variety of poly(lactic acid) fiber materials.

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