Anti-yellowing Finishing of Nylon Fiber Using a Reaction with Reducing Sugar

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Abstract: It is well known that nylon fibers turn yellow during long storage in wooden boxes or corrugated cartons, where the nylon fibers react with various aromatic aldehydes gradually generated from wood or crude paper. In general, in the textile fields, formaldehyde is a useful reagent to prevent nylon products from turning yellow, but it is also one of the main materials causing the sick building syndrome (SBS). In this paper, we investigated reaction conditions between nylon 6 fibers and various reducing sugars to prevent nylon fibers from turning yellow due to vanillin, which is one of the aromatic aldehydes. Furthermore, their other fiber properties, such as mechanical strength and hygroscopicity, were also examined.

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1. Introduction

Colorless or white nylon fibers and their products usually become yellow during long storage in wooden boxes or corrugated cartons, because of colored materials produced by reactions between the terminal amino groups of nylon polymers and various aromatic aldehydes gradually produced from the lignin in wood or crude paper. Fig. 1 illustrates the reaction of nylon fibers with vanillin, which is an aromatic aldehyde obtained from natural plants such as vanilla beans. The amino groups of nylon fibers are usually protected by chemical methods to maintain their original color, especially their white color. Among the various chemical modifications, formaldehyde had been used for a long time as the best reagent, not only for anti-yellowing finishing but also for dimensional stability finishing for cotton fibers or various polyamide fibers, including nylon and protein, because it shows high reactivity toward the hydroxyl or amino groups of the fibers, high solubility in water or most organic solvents, and very low industrial production cost. However, it is well known that formaldehyde is also one of the main materials causing the sick building syndrome (SBS). Recently, its usage has been strictly controlled in various fields, not only textiles but also building materials, such as wallpaper, lumber, resin board, adhesives, and so on. Now, many Japanese companies have lawfully utilized various alternative aldehydes having a different chemical structure, such as acetaldehyde, propionaldehyde, benzaldehyde, and salicylaldehyde, but these aldehydes are also very doubtful in terms of safety for the human body from the viewpoint of medical

science. On the other hand, some other groups also reported thirty years ago that nylon fibers interacted with (reacted with and/or adsorbed) free formaldehyde generated from toys, household goods, furniture, and building materials, even during short storage [1,2]. These interactions are also largely related to the terminal amino groups of nylon polymers. Since 2001, the Japanese Government has imposed strict legal controls on the storage and selling methods of children's and baby clothes so as not to come in contact with free formaldehyde. Due to the above two problems, the safety of formaldehyde and its re-adhesion to nylon fibers, new harmless protective agents for the amino groups of nylon fibers are needed urgently.

In our laboratory, chemical modifications of synthetic fibers by natural products such as sugars have been investigated for several years [3-7]. Especially, research on the reaction of nylon 6 fibers with sugar lactone to prevent them from turning yellow was done thoroughly in a previous paper [7], where a nucleophilic reaction of the amino groups on nylon 6 fibers toward the lactone ring of sugar chemically introduced sugar hydroxyl groups on their surface and thus prevented the fibers from reacting with vanillin effectively. However,

Fig. 1 Scheme of reaction of nylon 6 fibers with vanillin.

Fig. 2 Scheme of reaction of nylon 6 fibers with D-glucose and their anti-yellowing effects against vanillin.

this method using sugar lactones posed some serious problems for industrial use, such as the very slow reaction speed, the strict limitation of solvent usage (for example, water was not suitable because of hydrolysis of the reactive lactone ring), and the not very low cost of sugar lactones. Usually, most sugar lactones are not obtained from natural products in large quantities, but are synthesized chemically or enzymatically by the oxidation of reducing sugars such as glucose, galactose, or mannose.

In the present paper, we report a new anti-yellowing method using various reducing sugars, which are also natural raw materials of sugar lactones, as described above. A reducing sugar molecule has one reactive hydroxyl group on the anomeric carbon, which can react with amino compounds easily *via* Schiff's base similarly to the above reaction with vanillin. Fig. 2 shows a reaction of nylon fibers with D-glucose and the subsequent prevention reaction with vanillin as the yellowing material. However, it is also well known in the field of food science that heating a mixture including both reducing sugars (such as starch) and amino compounds (such as amino acid and protein) causes a browning

reaction, which is called a melanoidin reaction or a Maillard reaction. The detailed production mechanism of the brown materials is not still clear, because of the complicated multi-step reactions after the formation of Schiff's base and the following Amadori rearrangement (colorless reactions) [8,9]. This side reaction gives good color, flavor, and taste to various foods, but these additional effects, in particular a change of color, are unexpected in the textile field. Therefore, the melanoidin reaction also had to be controlled in addition to the above yellowing reaction by aromatic aldehydes. Furthermore, as sugar compounds have many hydrophilic hydroxyl groups, other fiber properties of nylon fibers bearing a sugar moiety are also reported in this paper.

2. Experimental

2.1 Reagents and nylon 6 fabric

Organic solvents of methanol, dimethylsulfoxide (DMSO), and dimethylformamide (DMF), and reducing sugars of D-glucose, D-galactose, D-mannose, D-xylose, L-arabinose, D-maltose, 2-deoxy D-glucose, and *N*-acetyl D-glucosamine were purchased from Nacalai Tesque Co., Japan. The chemical structures of the above sugars are illustrated in Fig. 3. These solvents and sugars were used without further purification. Distilled water, deionized by ion-exchanging resins, was used as purified water for the following reaction. Nylon 6 fabric (taffeta, standard white) was purchased from Shikisensha Co., Japan. It was washed thoroughly with methanol and distilled water and then dried overnight before the following experiments.

2.2 Surface modification of nylon 6 fabric by reducing sugars

A fixed amount of sugar was dissolved in a 200 ml flask containing 100 ml of heated organic solvent or distilled water (sugar concentration: 25 – 100 mM). However, as some sugars of galactose, maltose, and *N*-acetyl glucosamine did not dissolve fully in the methanol solution, a solution containing a slight insoluble sugar was used for these reactions. After the solution was reached the desired temperature, nylon 6 fabric (10 cm ×

Fig. 3 Chemical structures of various types of reducing sugars. *D-Isomer of arabinose (an L-isomer was used in this work).

10 cm, ca. 0.63 g) was dipped in the flask. After a period of time (1.0 – 8.0 hr), the nylon 6 fabric was taken out and washed with distilled water and methanol. The obtained fabric was dried thoroughly before the next yellowing tests using vanillin.

2.3 Yellowing test with vanillin

A 0.06 g portion of vanillin was dissolved in a 300 ml beaker containing 200 ml of heated distilled water. After the solution was reached at 60 °C, nylon 6 fabric (10 cm × 10 cm) was dipped in the beaker. After 5 min, the nylon 6 fabric was taken out, washed with distilled water thoroughly, and then dried overnight.

2.4 Determination of color of nylon 6 fabric

The color of nylon 6 fabric was estimated by the K/S values, which were calculated from their reflectivity (400 nm), as measured with a UV-VIS spectroscope equipped with an integrating sphere (UV-3100A, Shimadzu Co., Japan). This method was reported as the usual method for the measurement of the dyestuff concentration of dyed fabrics [10]. In this paper, the large K/S values indicated a deep yellow color of nylon 6 fabric, and the K/S values of the original nylon fabrics before and after the reaction with vanillin were 0.05 and 3.16, respectively.

2.5 Other fiber properties of nylon 6 fabric

The mechanical strength of the nylon 6 fabric was evaluated in terms of its measured relative tensile strength, using a tensile test machine (AGS-5kNJ, Shimadzu Co., Japan). Test pieces (2.5 cm × 23 cm) were kept for 24 hr under standard conditions (20 °C, 50RH%) before the measurements. These samples were fixed with a distance of 15 cm between the chucks, and then stretched at a constant speed of 200 mm/min under the same standard conditions. The tensile strength of the original nylon 6 fabric was 162 N/cm. The adsorption-desorption isotherms of water vapor on the nylon 6 fabrics were measured at 25 °C with an automatic vapor adsorption apparatus (BELSORP 18S, Nihon Bell Co., Japan), with the fabric (4.0 cm × 4.0 cm) placed in a sample tube, and dried in a vacuum before the measurements. In the adsorption process, water vapor was automatically added to the tube until the relative vapor pressure (P/Ps) reached 0.99. In the subsequent desorption process, water vapor was gradually removed from the nylon 6 in the tube until the P/Ps reached 0.10. In this paper, the amount of water vapor absorbed onto the nylon 6 fabric during the desorption process (P/Ps = 0.80) was taken as the hygroscopicity index of nylon 6 fabric and is shown as such below. The adsorption-desorption isotherms of water vapor on the original nylon 6 fabrics were already reported in our previous papers [6,7].

3. Results and discussion

3.1 Solvent effect

The reaction time dependency of K/S values of nylon 6 reacted with D-glucose in various solvents is shown in Fig. 4 (A). These K/S values increased slightly with the reaction time in each organic solvent, and then the fabric color changed from original white to light brown. This result seemed to be indicated that the melanoidin reaction between nylon 6 fabric and D-glucose proceeded to produce the color on the fabric. Similar phenomena were observed as a side reaction of unreacted amino groups of aminolyzed PET fibers with various reducing sugars in a DMSO solution, which were already reported in our previous paper [5]. On the other hand, as

Fig. 4 Influence of types of solvents on K/S values of nylon 6 fabrics reacted with glucose (A) before reaction with vanillin and (B) after reaction with vanillin. Reaction conditions : [Glc] = 100 mM, 60 °C, solvents : methanol (●), DMSO (▲), DMF (◆), water (■).

the color of the solution after the reaction with D-glucose did not change, the colored materials were mainly produced not in the organic solvent but on the nylon fabric. This fact was not contradictory to the mechanism of the melanoidine reaction. Furthermore, a yellowing test due to vanillin was undertaken for the nylon fabric reacted with D-glucose, where the reaction of unreacted terminal amino groups of the nylon fabric with vanillin made the yellow color. The obtained results are shown in Fig. 4 (B). The K/S values of nylon 6 fabric after the yellowing test largely decreased in reaction time of D-glucose, and were clearly lower than the value of the original nylon 6 fabric. These results also indicated that the reaction of most terminal amino groups of nylon 6 fabric with D-glucose proceeded to prevent the fabric from turning yellow due to vanillin. Especially, when methanol was used as the reaction solvent, the smallest K/S value was shown in the organic solvents examined in this work. These results indicated that methanol was the most appropriate solvent for anti-yellowing reaction with D-glucose. In addition, it was also clear that this reaction speed in methanol was four times as fast as one with D-gluconolactone examined in a preceding paper [7]. As a result, an important problem of how to enhance the slow reaction speed between sugars and nylon fibers could be solved here.

On the other hand, when water was used as the reaction solvent, these K/S values were almost the same as the original nylon fabric, both before and after the vanillin tests. That is, the reaction of the nylon 6 fabric with D-glucose could not proceed in the water solution thoroughly.

3.2 Reaction temperature

The time dependency of K/S values of nylon 6 fabric due to melanoidin reactions on the temperature and the time dependency of K/S values of nylon 6 fabric after the yellowing test on the temperature are shown in Fig 5 (A) and (B), where methanol and D-glucose were used as the solvent and reducing sugar, respectively. The higher temperature conditions gave both a larger increase in the K/S values due to the melanoidin reaction (Fig. 5 (A)) and a larger decrease in the K/S values after the yellowing test (Fig. 5 (B)). Judging totally from these results of temperature conditions, more appropriate conditions to keep the original fabric color required both the longer reaction time and the lower temperature. In other words, the high temperature could enhance both the melanoidin reaction and the anti-yellowing reaction greatly, whereas the low temperature could suppress the former side reactions more effectively than the latter reaction because

Fig. 5 Influence of reaction temperature on K/S values of nylon 6 fabrics reacted with glucose (A) before reaction with vanillin and (B) after reaction with vanillin. Reaction conditions : [Glc] = 100 mM (in methanol), 64 °C (●), 60 °C (▲), 50 °C (■), 40 °C (◆).

of the different activation energies among these.

3.3 Sugar concentration

The influence of the D-glucose concentration in the methanol solution on K/S values of nylon 6 fabrics was similarly examined, the results of which are shown in Fig. 6 (A) and (B). Consequently, the higher concentration of glucose more effectively enhanced the reaction speed of both the melanoidin reaction and the anti-yellowing reaction of D-glucose for the amino groups, but the effects were smaller compared with the other conditions, such as solvent effects or reaction temperature.

3.4 Influence of types of the reducing sugar

Various sugars, with the exception of glucose, were also examined by the similar method, where a reaction

Fig. 6 Influence of glucose concentration on K/S values of nylon 6 fabrics reacted with glucose (A) before reaction with vanillin and (B) after reaction with vanillin. Reaction conditions : [Glc] = 100 mM (●), 50 mM (▲), 25 mM (■) (in methanol), 64 °C.

was carried out in refluxing methanol (64 °C). In general, it is known that a melanoidin reaction between amino compounds and reducing sugars proceeds *via* the first formation of Schiff's base and the subsequent complex multi-step reactions such as dehydrogenation and transfer reactions among the hydroxyl groups of sugars [10]. Additionally, the reactivity of sugars toward amino groups is largely related to the molecular size of these raw materials. In this paper, both the stereochemistry of the hydroxyl groups and the molecular weight of reducing sugar were mainly examined. As shown in Fig. 7 (A), the K/S values increased in the reaction time of each sugar, but the degree of color change of the nylon fabric was different. Especially, the reaction with D-xylose or L-arabinose having a smaller molecular weight (MW :

Fig. 7 Influence of types of reducing sugars on K/S values of nylon 6 fabrics reacted with reducing sugar (A) before reaction with vanillin and (B) after reaction with vanillin. Reaction conditions : [Sugar] = 100 mM (in methanol), 64 °C, additive : glucose (●), galactose (▲), mannose (■), xylose (○), arabinose (△), maltose (×). *These sugars were not dissolved fully in the methanol solution.

151.12) was enhanced as compared to D-glucose (MW : 180.16), whereas the reaction with D-maltose having the largest molecular weight (MW : 342.30) had the least effect. Interestingly, the reaction with the sugar having the same molecular weight as D-glucose, D-galactose, and D-mannose indicated different results, where using D-mannose maintained the original white color most. Similarly, using L-arabinose maintained a whiter color compared with using D-xylose. These results indicated that the stereochemistry of the hydroxyl groups in the C-2 position might play an important role in the melanoidin reaction between reducing sugars and nylon 6 fibers,

Fig. 8 Influence of 2-position of hydroxyl groups of sugars on K/S values of nylon 6 fabrics reacted with reducing sugars (A) before reaction with vanillin and (B) after reaction with vanillin. Reaction conditions: [Sugar] = 100 mM (in methanol), 64 °C, additive: 2-deoxy glucose (○), *N*-acetyl glucosamine (×), glucose (●), mannose (▲). **N*-Acetyl glucosamine was not dissolved fully in the methanol solution.

especially Amadori rearrangement [8]. On the other hand, the results of the yellowing tests also indicated that the K/S values of the fabrics after reactions with sugars having smaller molecular weight decreased more (Fig. 7 (B)). In particular, the reaction with D-mannose imparted the whitest fabric color among the reducing sugars examined here, even after the vanillin yellowing test.

On the basis of the above results, the similar experiments using 2-deoxy D-glucose or *N*-acetyl D-glucosamine were performed, where the former sugar had no hydroxyl groups and the latter sugar had bulky acetyl amide groups in the C-2 position (ref. Fig. 3). Fig. 8 shows the results of these sugars along with those of

D-glucose and D-mannose. Beyond our expectation, the use of 2-deoxy D-glucose enhanced the melanoidin reaction most in this work, and the obtained fabric became brown without reacting with vanillin. Probably, many factors, such as the electrostatic interaction, hydrogen bonds, or steric hindrance between the hydroxyl group in the C-2 position and other hydroxyl groups, might prevent these hydroxyl groups from dehydrogenating to make colored materials. On the other hand, the use of *N*-acetyl D-glucosamine caused the slowest reaction speed with nylon fibers because of its very bulky substituents. In our next work, other types of deoxy sugars will have to be examined to clarify in more detail the mechanism of the melanoidin reaction between reducing sugars and nylon fibers using not only measurements of the K/S values but also other methods such as IR or NMR spectroscopy.

3.5 Mechanical strength and hygroscopicity

Finally, other fiber properties of the nylon 6 fabric bearing sugar units on its surface were evaluated. Fig. 9 shows the tensile strength of the nylon 6 fabric reacted with D-glucose, D-galactose, or D-mannose. As a result, the mechanical strength did not decrease with the reaction time of each sugar. This did not contradict our proposed reaction mechanism, where reducing sugars can react with their terminal amino groups without breaking the main chains of the nylon polymer. In addition, the results of the hygroscopicity of the nylon 6 fabric after the reactions with these sugars are also summarized in Fig. 10. The amount of water vapor on the nylon fabric increased with the reaction time of each reducing sugar. These results indicated that a chemical reaction with hydrophilic reducing sugars afforded a hydrophilic surface of nylon fabric, and were very similar to the results of sugar lactone reported in our previous paper [7]. In particular, when D-mannose was used as an additive, the highest increase in hygroscopicity was observed in these sugars, and then was about the same as a 20% augmentation of the original nylon fabric. Judging from these results, including the above anti-yellowing effect, the largest number of sugar moieties can be introduced on nylon fibers when D-mannose is used as the anti-yellowing reagents.

4. Conclusion

The anti-yellowing effect of nylon 6 fibers using reducing sugars was investigated in this paper. As a result, the effect was influenced largely by the type of solvent, reaction temperature, sugar concentration, and type of

Fig. 9 Influence of types of reducing sugars on mechanical strength of nylon 6 fabrics reacted with reducing sugars. Reaction conditions : [Sugar] = 100 mM (in methanol), 64 °C, additive : glucose (●), galactose (▲), mannose (■), measurement conditions : 20 °C, 50RH%.

Fig. 10 Influence of types of reducing sugars on hygroscopicity of nylon 6 fabrics reacted with reducing sugars. Reaction conditions : [Sugar] = 100 mM (in methanol), 64 °C, additive : glucose (●), galactose (▲), mannose (■), measurement conditions : 23 °C, P/Ps = 0.80.

reducing sugar. Interestingly, the reaction with mannose, an isomer of glucose, prevented the nylon fibers most effectively from being changed not only to yellow by the reaction with vanillin, but also to brown by the melanoidin reaction as a side reaction. Furthermore, nylon fabrics with an introduced sugar moiety indicated a higher hygroscopicity compared with the original fabrics, in particular, the reaction of nylon 6 fabrics with mannose afforded about a 20% increase in their hygroscopicity.

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