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〈Research Paper〉

Coloration of Pure Polypropylene Fiber with Super Hydrophobic Dyes; Application of Anthraquinone Derivatives with Linear Alkyl Substituents

Taekyeong Kim*, **Seokhan Yoon**[1], **Jinpyo Hong**[1], **Hongje Kim**[1] **and Jinseok Bae**[1]

Dept. of Textile System Engineering, Kyungpook National University
[1]*Korea Dyeing Technology Center*

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Abstract— Polypropylene fiber was dyed with 4 super hydrophobic dyes having different alkyl derivatives on the same chromophore. Double-tailed cationic surfactant, didodecyldimethylammonium bromide(DDAB), was used to make dye-dispersant complex to improve the dispersion of dyes. As the alkyl groups are longer and the hydrophobicity is increased, the dyeability onto polypropylene fiber was improved and deep coloration was obtained. As for the fastness properties, wash fastness was relatively good, while light fastness was bit low.

Keywords: *polypropylene, hydrophobic dyes, cationic surfactant, dyeing, fastness*

1. Introduction

Polypropylene fiber has the strength of 4.5~9.0g/d and the elasticity of 25~60%. They have similar mechanical properties of polyester fibers. It is the most widely used fibers in the industry and has excellent chemical-resistant properties as well. They are also known as a floating fiber since the density is 0.90~0.92[1-3], the lowest of all kinds of fibers, and expected for the usage for sportswear[4]. Polypropylene fiber can be used in the fields of fast drying and heat insulation material applications as moisture regain and thermal conductivity is as low as 0.05% and 0.12W/mK respectively[2,5]. However, it is impossible to dye polypropylene fiber at any dyeing systems because of the extreme hydrophobicity of the fiber[6-8].

In order to dye this polypropylene fiber, two kinds of coloration methods are being considred. One is adding pigment at the stage of fiber formation, and the other is the blending with dyeable polymer or the chemical modification of the polypropylene fiber. The first method is possible to dye polypropylene fibers by adding pigment at fiber formation but the application is relatively restricted since the color is determined at the stage of fiber formation. The second method is also possible to dye polypropylene fibers but there are disadvantages such as the loss of the typical properties of polypropylene fibers by chemical modification[6-8].

This study shows that dyeing of polypropylene fibers without any physical and chemical modifications is possible at the established process by selecting dyes having affinity to polypropylene fibers. For the dyes to have affinity to polypropylene fibers having extreme hydrophobicity, they need to have extreme hydrophobicity. In this regard, solvent dyes and oil dyes, the more hydrophobic, were used to dye polypropylene fibers. Different alkyl derivatives of anthraquinone dyes were selected to

*Corresponding author. Tel.: +82-53-950-5639; Fax: +82-53-950-6617; e-mail: taekyeong@knu.ac.kr

investigate the change of dyeability of polypropylene fibers according to the degree of hydrophobicity. Cationic surfactant having two long alkyl substituents was used to form dye-dispersant complex for the dispersion of hydrophobic dyes and their properties were examined.

2. Experimental

2.1. Materials

100% pure polypropylene fabrics and 4 anthraquinone dyes having different alkyl substituents were selected and their names and structures are shown in Fig. 1. The purity of the dyes was at least 97% and they were used without further purification. The cationic surfactant, didodecyldimethylammonium bromide(DDAB, $[CH_3(CH_2)_{11}]_2(CH_3)_2N^+Br^-$), having 2 long alkyl substituents was used for the dispersion of dyes.

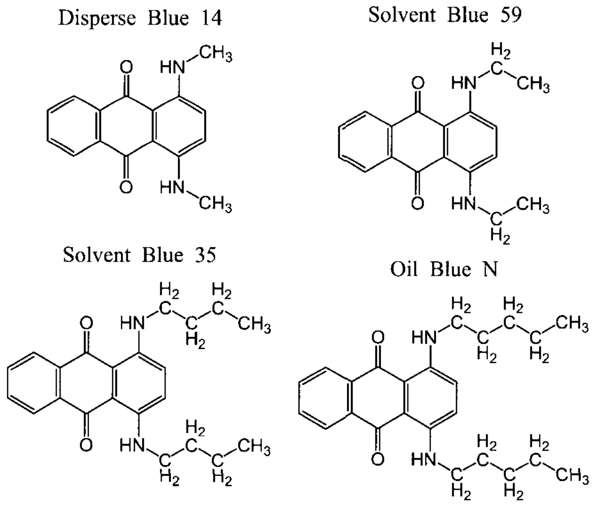


Fig. 1. Dyes used in this study.

2.2. Preparation of dye-dispersant complex and dye solution

A certain amount of dye was dissolved with 50ml tetrahydrofuran(THF) and then mixed with the solution of DDAB in 50ml tetrahydrofuran(THF). The mixture was evaporated and dried in vacuum for 24 hours to remove THF entirely. In this procedure, the uniform mixture of dyes and dispersant(DDAB) was prepared. 1~2 hour exposure of ultrasonic apparatus after the addition of water to this mixture makes uniform and stable dye solution of super hydrophobic dyes by the dispersion activity of DDAB. This solution was finally used for dyeing.

2.3. Dyeing

Pure polypropylene fibers(1.0g) were added to 5% owf dye dispersion solution at the liquor ratio of 1:50 and dyed at 130℃ for 1 hour. The amount of DDAB used for dye dispersion solution was 1.5 molar ratio compared to the amount of dyes. The dyeing was carried out at different conditions as necessary. The dyed materials were washed with acetone three times to remove dyes remained at the surface of fabrics.

2.4. Measurement of dye uptake

Dyed polypropylene fiber(0.05g) was extracted at 90℃ for 2 hours by using 10ml 100% *N,N*-dimethylformamide(DMF). The absorbance of this extract was measured by UV-VIS spectrophotometer and dye uptake was calculated using calibration curve made previously. In order to obtain the color strengths of dyed fabrics, a color measurement instrument, *datacolor 650^{TM}*, was used. The K/S values were taken at every 10nm in the range of 400~700nm and all the values were summed into total K/S.

2.5. Fastness properties

Oil Blue N, shows the best dyeability, 3% owf dye dispersion solution was used to investigate the fastness of dyed materials.

The wash fastness, rubbing fastness, and light fastness were measured by KS K 0430 A-1, KS K 0650, and ISO 015 B02(63℃, 20hrs, water-cooled xenon-arc lamp, continuous light) respectively.

3. Results and Discussion

3.1. Dyeability of dyes

The dyeability onto polypropylene fiber was examined for 4 kinds of super hydrophobic dyes according to the length of alkyl chains. In case of super hydrophobic dyes, since stable dispersion of dyes is very important, cationic surfactant(DDAB) having 2 long chain alkyl groups was utilized in this study. This surfactant has excellent solubility in organic solvent like hydrophobic dyes and it is possible to make dye-DDAB complex from uniform mixture solution of dye and DDAB. Also, by adding water and ultrasonic exposure, it is known that a certain stable vesicle like cell membrane can be formed through self-assembling process. The characteristic of this vesicle is that stability is excellent and it is possible to incorporate any material captured inside[9~11]. In this experiment, the super hydrophobic dyes were dispersed by vesicle formation method.

To examine the dyeability of each dye, dyeing was carried out in 5% owf dye dispersion solution at the liquor ratio of 1:50 and 130℃ for 1 hour. The amount of DDAB used for dye dispersion solution was 1.5 molar ratio compared to the amount of dyes. The results are shown in Fig. 2. As the length of alkyl substituents increased, the dyeability for polypropylene fiber tends to be improved

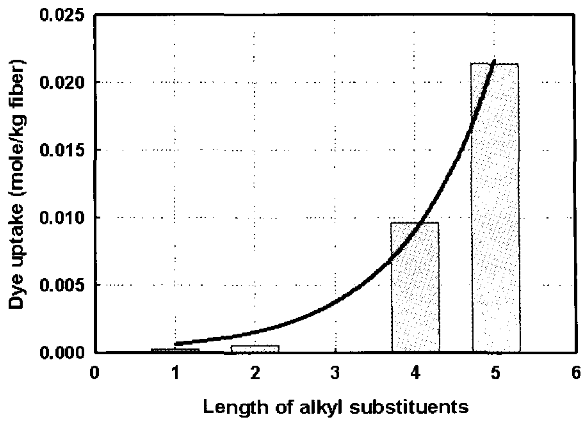


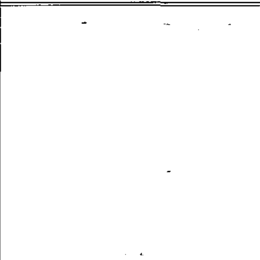
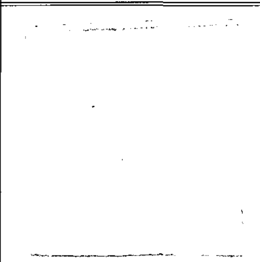
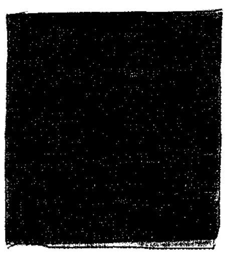
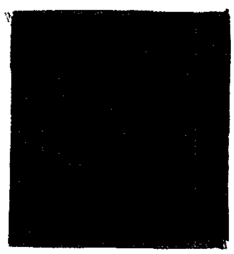
Fig. 2. Effect of alkyl substituents on dye uptakes.

dramatically. This can be explained that the hydrophobicity of dyes extremely increases according to the length of alkyl substituents. Especially, Oil Blue N having pentyl group shows deep colors($\sum_{\lambda=400}^{700}(K/S)_\lambda = 218$). This explains that, for polypropylene fibers to be dyed, super hydrophobic dyes which are much more hydrophobic than conventional disperse dyes are necessary. The photos of fabrics dyed with the 4 super hydrophobic dyes are shown in Table 1 to visualize color strength of them.

3.2. Effect of DDAB on dyeability

DDAB was employed for the dispersion of super hydrophobic dyes and the relation between dyeability and the amount of DDAB was examined. Polypropylene fibers were dyed in these dye dispersion solution having different amount of DDAB and the results are

Table 1. Photos and color strengths of the fabrics dyed with 5% owf of super hydrophobic dyes at 130℃

Dye	Blue 14	Blue 59	Blue 35	Blue N
Sample				
Total K/S*	12	17	112	218

*Total K/S : sum of K/S values obtained at every 10nm in the range of 400~700nm.

shown in Fig. 3. It can be noticed that the maximum dye uptake was shown when 1.5 molar ratio of DDAB compared to dyes was used. This is ascribed that uniform and stable dispersion is impossible and dye particle is aggregated if the amount of DDAB is too small. On the other hand, the dyeability is decreased if the amount of DDAB is large because dye dispersion becomes too stable in dyeing liquor to be adsorbed and penetrated into fabrics from the liquor[12,13]. In this regard, the relative amount of DDAB was fixed to 1.5 molar ratio in further experiments.

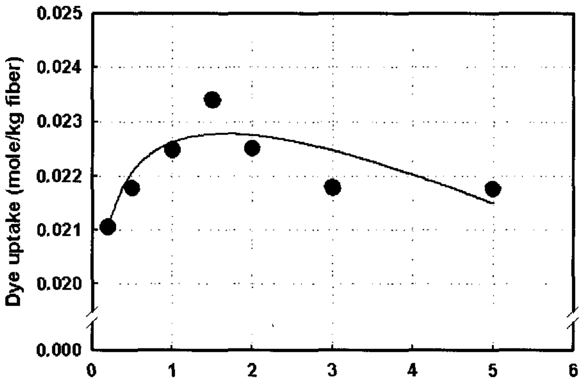


Fig. 3. Effect of molar ratio of DDAB on dyeability of Oil Blue N.

3.3. Optimum dyeing condition

Dyeability depending on dyeing temperature and dye amount was investigated in the base of the best dye and dispersion condition already determined in series of experiments previously. Fig. 4 indicates the dyeability according to the dyeing temperature at 100~130℃. As temperature increased, the amount of dyeing increased continuously. However, optimum dyeing temperature should be decided considering the poor thermal property of polypropylene since the higher dyeing temperature gives the worse touch of polypropylene fibers. From the Fig. 5, maximum build-up was shown at 2~3% owf dye amount. Therefore, the optimum dyeing condition was decided to be 100~110℃ and 2~3% owf.

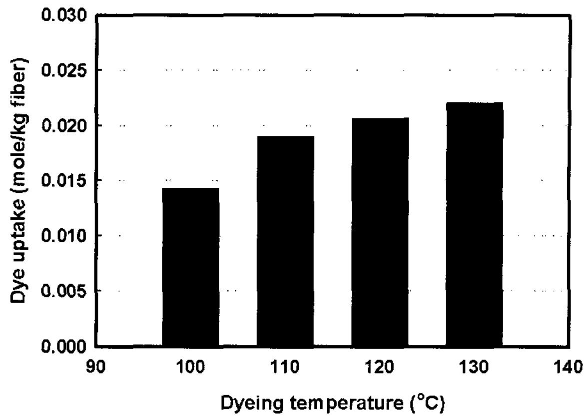


Fig. 4. Effect of dyeing temperature on dye uptakes of Oil Blue N.

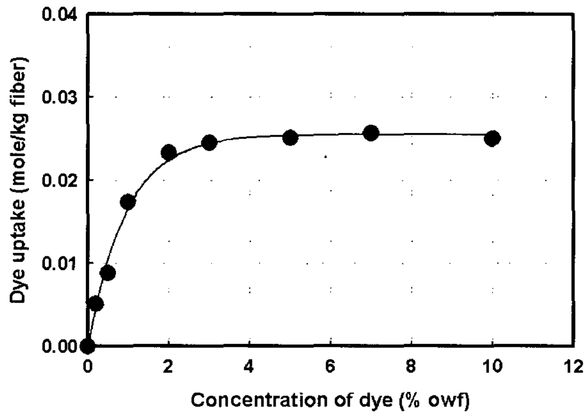


Fig. 5. Build-up property of Oil Blue N at 130℃.

3.4. Fastness properties

Table 2 shows the results of color fastness to washing, rubbing and light of dyed fabrics by Oil Blue N. In general, overall color fastness

Table 2. Color fastness of the fabric dyed with Oil Blue N

Color fastness			Rating
Washing	Change in color		4~5
	Staining	Acetate	4~5
		Cotton	4~5
		Nylon	3~4
		Polyester	4
		Acrylic	4~5
		Wool	4
Rubbing	Staining	Dry	5
		Wet	5
Light	Change in color		4

of dyed polypropylene fibers were moderately good to excellent and the ratings of color fastness to washing were in the range of 4 to 5 except staining on nylon (3~4). In the case of nylon, the staining seems to be due to the affinity between the alkyl group of dye molecules and that of nylon.

The rubbing fastness and light fastness were good enough for the practical usage; the rubbing fastness and light fastness were 5 and 4, respectively.

4. Conclusions

Super hydrophobic dyes were applied for the coloration of pure polypropylene fibers, which is known as an undyeable polymer. The hydrophobicity of the dyes are increased as the length of alkyl substituents on the same chromophore is increased. Dye-DDAB complex method was employed for the dispersion of dyes and dye dispersion solution by this mixture was prepared and used. As the length of alkyl substituents is increased, the dyeability onto polypropylene fiber tends to improve dramatically. Especially, Oil Blue N having pentyl group achieved very deep color. In the case of the amount of didodecyldimethylammonium bromide, molar ratio of 1.5 showed the best dyeability of polypropylene. The overall fastness properties of dyed polypropylene were moderately good to excellent.

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