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〈Research Paper〉

Dyeing Properties of Nylon Fabric with Reactive Dyes Having Different Reactive Group

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Abstract— The dyeing properties of the several reactive dyes possessing different types of the reactive group on nylon 6 fabric have been investigated. Dyeing of nylon fiber with commercial reactive dyes was dependent on the dye bath pH. As pH increased, the extent of exhaustion decreased due to the deprotonation of the amino end group. But, the extent of fixation increased because of the enhanced reactivity with nylon fiber. It was found that all reactive dyes could be applied to nylon 6 reasonably at pH 5-6. But, the conflicting requirements of dye exhaustion and covalent bond formation limited the extent of fixation efficiency. The best method to improve the extent of the fixation efficiency of the reactive dyes was the conversion of sulphatoethylsulphone group to vinylsulphone group before dyeing with trisodium phosphate. The converted Supra type reactive dye gave the highest extent of fixation efficiency, which was about 90%.

Keywords: *dyeing, nylon, reactive dye, reactive group, dye bath pH*

1. Introduction

Coloration of nylon fabrics are usually performed with various types of acid dyes. The presence of terminal amino end groups in nylon fibers provides substantivity toward acid dyes, which have anionic sulphonate groups. However, wash fastness of non-metallized acid dye is often unsatisfactory. 1:2 metal complex acid dye and mordant acid dye display reasonable wash fastness. But these dyeings can also cause some staining of adjacent fabrics during laundering and wastewater is contaminated by heavy metal like chrome. While an after-treatment of the dyed nylon can give fairly improved wash fastness, repeated washing can still result in loss of color 1). Loss of color and staining of adjacent fabrics arises from the facile partial dissociation of ionic linkage between acid dye and nylon fiber.

Reactive dyes were commercially developed for cellulosic fibers and now become the most important dye for those fibers. The substantivity and reactivity of the reactive dyes have been widely studied. The mechanism of the formation of covalent bond between the reactive group in the reactive dye and the hydroxy group in cellulosic fiber is well understood 2-5). The high wash fastness is most often achieved by the use of fiber reactive dyes. The high wash fastness of the dyed cellulosic fabrics is derived from the covalent links between the fiber and dye. Hence, it can be said that one of the methods to improve the wash fastness is the formation of the covalent bond between any fiber/dye systems.

While reactive dyes designed for application to cellulosic fibers display very high wash fastness on nylon in low to moderate depths of shade. In deep shades, presence of unreacted dye results in only poor to moderate wash fastness 2). The application of reactive dyes to nylon 66 fabrics was intensely investigated in the United Kindom

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recently[6-8]. Ciba specialty chemical launched Eriofast series i.e., bifunctional reactive dyes and developed for applying to nylon. According to Ciba specialty chemicals, these dyes are applied simply in acidic condition due to their high exhaustions and out standing wash and light fastness. Y.A. Son et al found that heterobi functional reactive dyes provided great opportunity for efficient dye-fiber reaction due to the mixed double-anchors such as sulphato ethylsulphone and monochloro-triazinyl reactive groups[9]. The effect of molecular size and shape, degree of sulphonation on the application properties of reactive dyes on nylon have been reported[10].

The reactive dyes are very sensitive to chemical and physical variations in the substrate. Hence, owing to their low migrating power, careful control of dye exhaustion, usually by means of temperature control, must be exercised.

Aim of this work is to investigate the dyeing properties of reactive dyes having different reactive groups on nylon 6 fabrics.

2. Experimental

2.1. Materials

Nylon filament fabric(70d/24f, 214/5cm x 150/5cm) was used for dyeing. All chemicals used in the dyeing and reactions were laboratory grade reagents. Uniclear AST(Shin Young Chemicals, non-ionic) was employed as a soaping agent and AATCC Standard Reference Detergent WOB was used in wash fastness test.

Five reactive dyes were used and their chemical structures are shown in Fig. 1. C. I. Reactive Red 195(heterobifunctional; sulphatoethylsulphone and monochlorotriazine), C. I. Reactive Red 24 (monofunctional; monochlorotriazine), C. I. Reactive Red 120(bifunctional; two monochlorotriazines), C. I. Reactive Red 21(monofunctional; sulphatoethylsulphone), C. I. Reactive Blue 203(bifunctional; two sulphatoethylsulphones) were named as Dye 1, Dye 2, Dye 3, Dye 4 and Dye 5, respectively. These dyes were commercial samples that were not purified before use.

2.2. Dyeing procedure

Dye bath pH was adjusted to 3~7 by employing McIlvaine buffer system that consists of 0.2M Na_2HPO_4 and 0.1M citric acid.

Dyeing was carried out in a sealed, 150 cm^3 capacity, stainless steel dyepots(Labomat, Mathis).

Samples were placed in a 40 ℃ dyebath of liquor ratio 30:1. Temperature was raised to 100 ℃. At this temperature, the reactive dyeing was continued for 60 min. Dyed fabric was soaped in an bath containing 2g/l Na_2CO_3 and 2g/l Uniclear AST and allowed to dry in open air.

The conversion of sulphatoethylsulphone group into vinylsulphone group was carried out at room temperature in alkaline bath whose pH was adjusted to 10 by the addition of Na_3PO_4. The completion of the reaction was monitored using HPLC(YoungLin, Korea) with Nava-Park silica 60 Å 4 ㎛ column and methanol was used as mobile phase.

2.3. Evaluation

Absorbance measurements of the dye bath were performed on a UV/VIS spectrophotometer (Helios, Unicam). The extent of exhaustion (%E) of dye was calculated using Eq. (1) and pre-determined calibration curve. Unfixed dye from the samples was extracted using 25% pyridine solution and then measured spectrophotometrically. The extent of dye fixation (%F) and dye fixation efficiency (%FE) were calculated using Eqs. (2) and (3).

$$\%E = \left(\frac{D_0 - D_t}{D_0}\right) \times 100 \qquad (1)$$

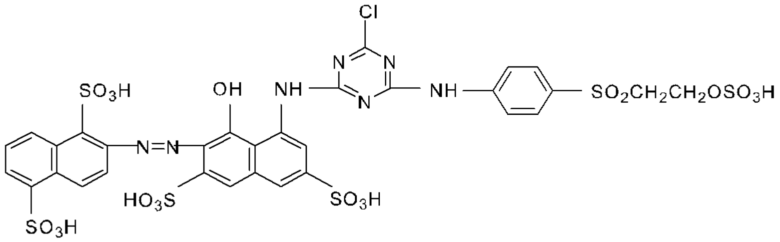
$$\%F = \left(\frac{D_0 - D_t - D_e}{D_0 - D_t}\right) \times 100 \qquad (2)$$

$$\%FE = \left(\frac{E \times F}{100}\right) \qquad (3)$$

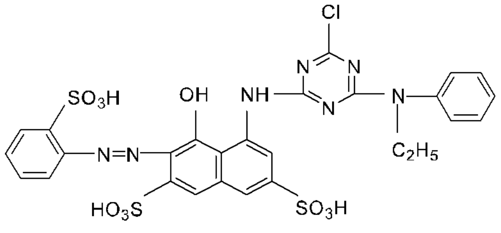
where, D_0 : Quantity of dye initially in the dye bath

D_t : Quantity of residual dye in the dye bath after dyeing time t

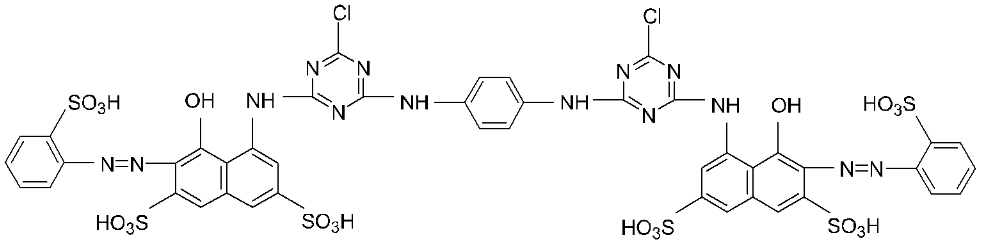
D_e : Quantity of extracted dye with 25% pyridine solution



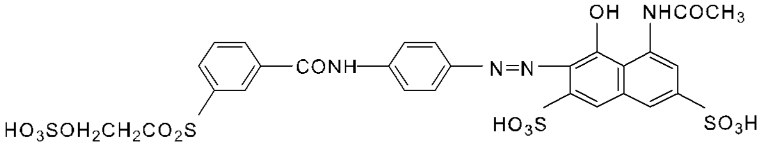
Dye 1 (C. I. Reactive Red 195)



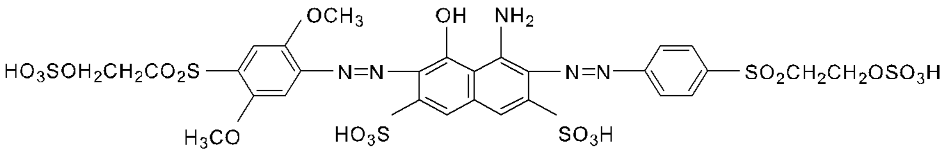
Dye 2 (C. I. Reactive Red 24)



Dye 3 (C. I. Reactive Red 120)



Dye 4 (C. I. Reactive Red 21)



Dye 5 (C. I. Reactive Blue 203)

Fig. 1. Chemical structure of reactive dyes used in the experiment.

3. Results and Discussion

3.1. Effect of pH on dyeing properties

The dye bath pH is known to be a very important factor in nylon dyeing. Dyeings are performed at 100℃ varying pH from 3 to 7 to investigate the effect of pH on the dyeing properties of reactive dye on nylon. Fig. 2 shows the extent of exhaustion of reactive dyes at various pH. It is obvious that the extent of exhaustion increases while decreasing pH. As pH decreases, amount of protonated amino group increases, subsequently increase in dyeing site can absorb more reactive dye which is anionic. The extent of exhaustion are in the order of Dye 5 > Dye 4 > Dye 1 > Dye 3 > Dye 2. Dyeing properties of the reactive dyes are closely related to the type of reactive group and chemical structure of the chromogen. Dyes used in the experiments are different in type and number of reactive group and molecular structure of the chromogen. Even the experimental results shown in Fig. 2 does not result exclusively from the reactive group. Hence, it can be cautiously said that the reactive dyes possessing sulphatoethylsulphone group have higher affinity to nylon fiber due to its anionic character than dyes having monochlorotriazine.

Fig. 3 represents the extent of fixation. Extent of fixation means how many % of absorbed dye is reacting with nylon fiber. It shows that the extent of fixation increases with increasing the dye bath pH. Nylon fiber can form covalent bond through nucleophilic substitution reaction or nucleophilic addition reaction. It is not the protonated amine, but the free amine that reacts with the reactive dye. At lower pH values, the amount of free amine is so small that the extent of fixation decreases. Because three reactive dyes such as Dye 1, Dye 3 and Dye 5 have two reactive groups, they exhibit higher extent of fixation than monofunctional Dyes 2 and 4.

Fig. 4 shows the extent of fixation efficiency which means how many % of initial dye form covalent bond with nylon fiber. Dyes 2 and 3 having monochlorotriazine group show the highest extent of fixation efficiency at pH 4, and Dye 1 containing heterobifunctional groups at pH 5, and Dyes 4 and 5 having sulphatoethylsulphone group at pH 6. The maximum extent of fixation efficiency are in the order of Dye 5 > Dye 3 ≃ Dye 1 >> Dye 2 > Dye 4. So, it can be said that reactive dyes having two reactive groups have better dyeing properties than monofunctional reactive dyes.

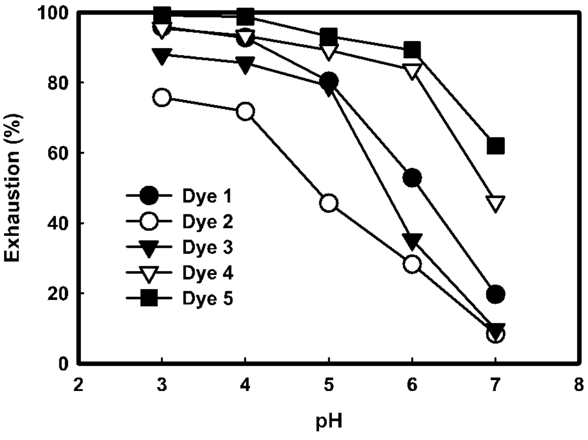


Fig. 2. Effect of dye bath pH on the extent of exhaustion.

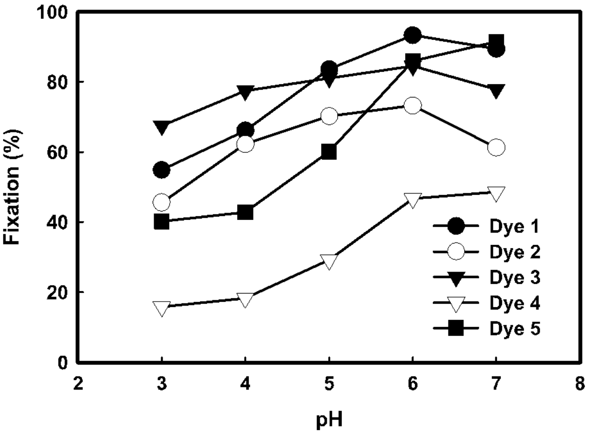


Fig. 3. Effect of dye bath pH on the extent of fixation.

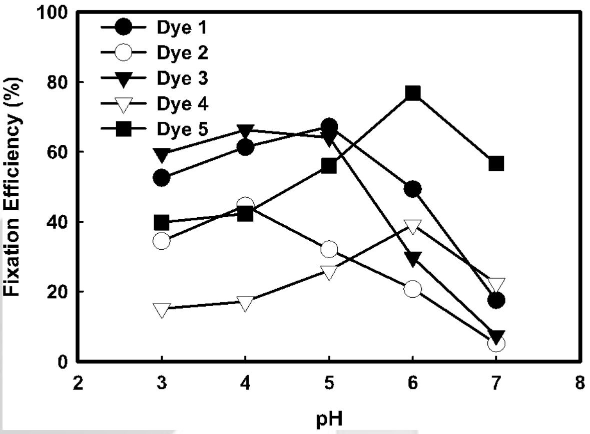


Fig. 4. Effect of dye bath pH on the extent of fixation efficiency.

3.2. Effect of temperature on dyeing properties

The extent of fixation efficiency of the reactive dyes on nylon are not as high as that in cellulosic dyeing. Hence, It is required to enhance the extent of fixation efficiency for practical dyeing of nylon fabric. The plausible methods to improve the extension of fixation efficiency is the application of high dyeing temperature, or conversion of sulphato-ethylsulphone group to vinylsulphone group before dyeing.

Fig.s 5~7 shows variations of the extent of exhaustion, fixation and fixation efficiency of the five reactive dyes as a function of dyeing temperature. Dyeing with each reactive dye was carried out at the dye bath pH, which give the highest extent of fixation efficiency.

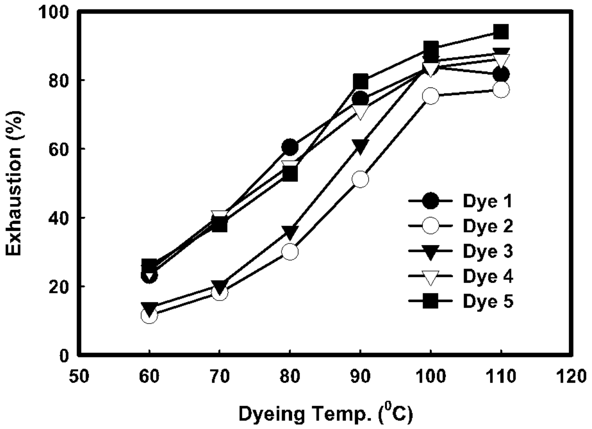


Fig. 5. Effect of application temperature on the extent of exhaustion.

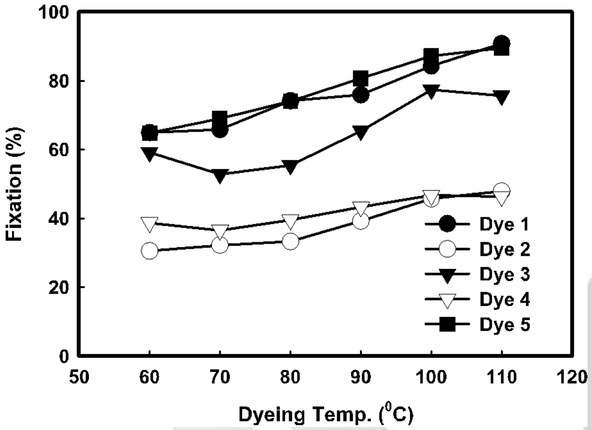


Fig. 6. Effect of application temperature on the extent of fixation.

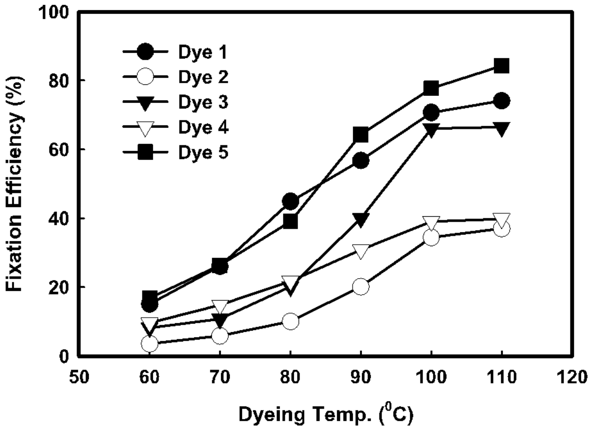


Fig. 7. Effect of application temperature on the extent of fixation efficiency.

As the dyeing temperature increases, the extent of exhaustion tends to increase due to more relaxation of fiber structure, and the extent of fixation shows the same tendency because of the increased reactivity at the elevated temperature. As a result, the extent of fixation efficiency reaches the maximum value at the highest dyeing temperature. Although the extent of fixation efficiency at 110℃ dyeing is slightly higher than at 100℃ dyeing, we decide to choose 100℃ as the appropriate dyeing temperature, considering that increase in dyeing temperature above 100℃ is not very effective and that the practical dyeing temperature of nylon fabric.

3.3. Dyeing properties of the reactive dyes having vinylsulphone group

Since the vinylsulphone group reacts with amino group in nylon, further study was carried out to convert sulphatoethylsulphone group to vinylsulphone group before dyeing[8] so as to enhance the extent of fixation efficiency. Reactive dyes having sulphatoethylsulphone group such as Dye 1, Dye 4 and Dye 5 were dissolved in water, and trisodium phosphate was added up to pH 10. This reaction mixture was stirred at room temperature for two hours in order to convert sulphatoethylsulphone group to vinylsulphone group as shown in Scheme 1. The converted reactive dyes having vinylsulphone group are names as Dye 1′, Dye 4′, and Dye 5′ respectively.

Fig. 8 shows the difference in extent of exhaustion of the original dyes and the converted ones. At all pH values examined, the converted dyes show higher exhaustion than the corresponding original dyes. This can be attributed to the substantivity of the converted dye having increased by the formation of the new double bond.

$$\text{D-SO}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{Na} \xrightarrow[\text{Na}_3\text{PO}_4]{\text{pH10}} \text{D-SO}_2\text{-CH=CH}_2 + \text{SO}_4^{2-}$$

Scheme 1. Conversion of sulphatoethylsulphone to vinylsulphone group.

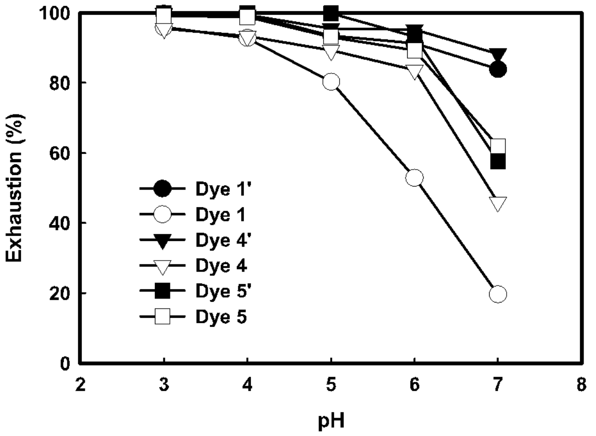


Fig. 8. Comparison of the extent of exhaustion of converted dye with original dye.

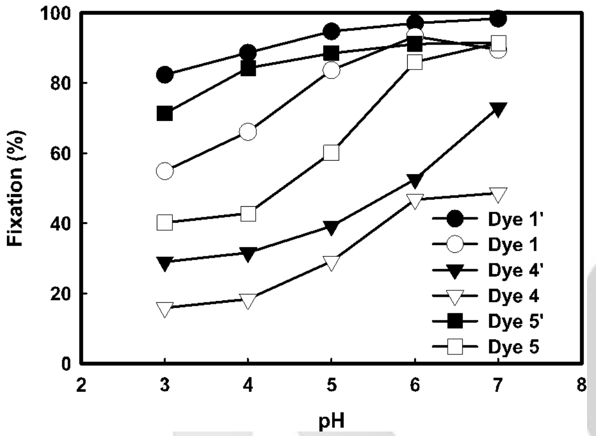


Fig. 9. Comparison of the extent of fixation of converted dye with original dye.

A sulphatoethylsulphone group carries negative charge. Hence, it attracts the positive protonated amino group at low pH, but it loses the attraction power at high pH where the number of the positive charge reduces. On the other hand a vinylsulphone group, which is planar and do not carry charge, probably provides additional affinity to dye molecule through the increased planarity and enhanced hydrophobicity especially at pH 6~7.

The extent of the fixation of the converted dyes, shown in Fig. 9, are also higher than those of the corresponding original dyes at all pHs. This might be caused by the high reactivity of the vinylsulphone group. As a result, it is evident in Fig. 10 that the extent of the fixation efficiency of the converted dyes are higher than the corresponding original dyes. The extent of the fixation efficiency of the Dye 1′ is the highest among dyes examined and it is about 90% which is almost the same value as that of the commercial Supra type reactive dyes on cotton. Based on these dyeing results, we come to conclusion that the converted Supra type reactive dye, Dye 1′, is the most suitable for dyeing of nylon 6 fabric.

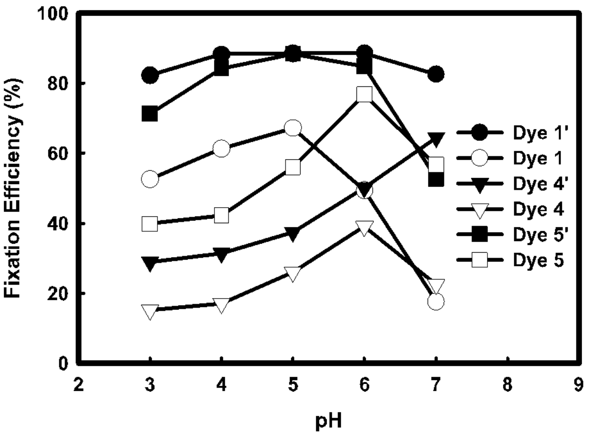


Fig. 10. Comparison of the extent of fixation efficiency of converted dye with original dye.

4. Conclusions

The dyeing properties of five commercial reactive dyes carrying different types of reactive groups on nylon 6 fabric have been investigated. Dyeing of nylon fiber with reactive dyes was highly dependent on the dyeing pH and temperature.

As pH increased, the extent of exhaustion decreased due to the deprotonation of the amino end group, but the extent of fixation increased because of the enhanced reactivity with nylon fiber. The extent of exhaustion, fixation and fixation efficiency increased with increasing the dyeing temperature. It was found that all reactive dyes could be applied to nylon 6 reasonably at pH 5-6, but the conflicting requirements of dye exhaustion and covalent bond formation limited the extent of fixation efficiency. The best method to improve the extent of the fixation efficiency of the reactive dyes was the conversion of sulphatoethylsulphone group to vinylsulphone before dyeing with trisodium phosphate. The converted Supra type reactive dye gave the highest extent of fixation efficiency which was about 90 %.

The commercial Supra type reactive dyes share the same reactive system, but they are different in the chemical structure of the chromogen. Hence in the future it would also be necessary to investigate work the effect of the chemical structure of the chromogen to the dyeing property of the reactive dye on nylon fabric.

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