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Dyeing Properties of Nylon 66 Nano Fiber with High Molecular Mass Acid Dyes

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Abstract: Research and development of nano fiber products is very active over the world. Physical characteristics and dyeing properties of nylon 66 nano fiber were investigated in this study. X-ray diffraction, DSC, analysis of amino end group, and water absorption were performed to get information concerning physical properties of nano fiber. Nylon 66 nano fiber was dyed with high molecular mass acid dyes. Effects of dyeing temperature, pH of dyeing solution, and concentration of acid dyes on dyeing properties such as rate of dyeing and the extent of exhaustion, were examined and compared to those of regular fiber. It was found that nano fiber adsorbed acid dyes at lower temperature, got rapidly dyed, and its extents of exhaustion at specific dyeing temperature were higher than regular fiber. It was also observed that nano fiber could adsorb a large amount of acid dye without a significant loss in the extent of exhaustion. Washing fastness of the dyed nano fiber was lower by 1/2~1 grade, light fastness by 1 grade than the dyed regular fiber.

Keywords: Nylon 66 nano fiber, Electro-spinning, Dyeing property, High molecular mass acid dye

Introduction

Recently nano fiber is developed very actively, and it is used for manufacturing artificial skin, medical fiber, barrier protection fabric against chemical and biological attack, electrolytic material of battery, and so on.

The barrier protection fabric based on nano fiber is being commercialized because nano fiber has a breathable characteristic not only protecting fine particles or bacteria but also permeating moisture vapor from perspiration. It is well known that the US Pentagon has developed and used it as a military outwear for the protection against biological attack. Also, NASA, MIT, and some research institutes enter a competition for development of nano fiber products. Nano fiber has submicron diameter, which is made under the action of an electrical force with high voltage. Since internal electrical repulsion is made inside a polymer raw material, molecules are aggregated and split into nano fiber. As an electrical field strength increases, denier of fiber becomes finer in scale of submicron. Nano fiber can be manufactured into a fabric form without weaving process because of their excellent cohesiveness.

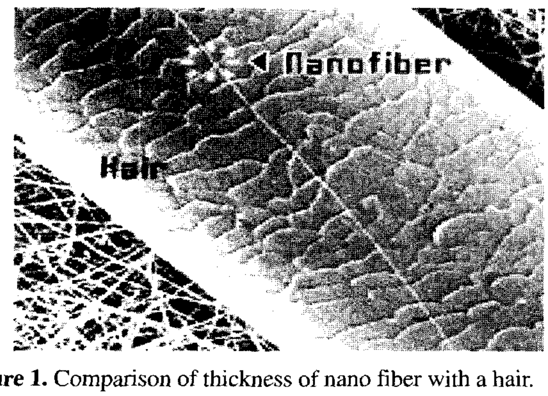

Figure 1. Comparison of thickness of nano fiber with a hair.

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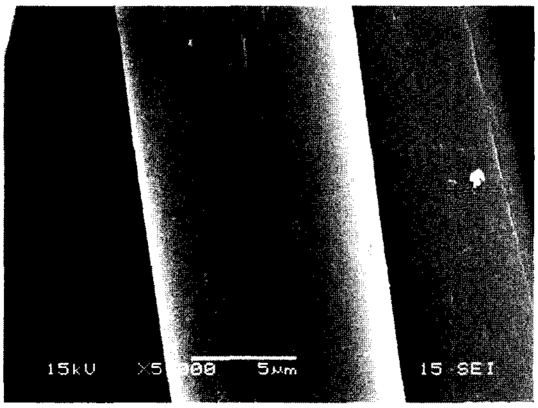
Nano fiber has an excessive specific surface area in comparison with its volume, so it is very suitable to filters used for the prevention against air pollutants and the purification of water. Nano fiber made of electro-conductive polymer is available for coating material on window glass in the field of a smart window that can detect the amount of daylight and change the color of window. Conductive nano fiber is used as an electrolyte of Li ion battery with some merits such as leakage prevention of electrolytic liquid and reduction of size as well as weight of battery. Nano fiber of artificial protein like tissue is helpful to patients due to healing properties and such stitching fiber or bandage is absorbed into the human body without a side effect. Other uses in the medical field are artificial blood vessel, artificial kidney, and so on. In the case of out or inner wear, they have light and comfortable feeling, good thermal insulation, and permeability [1].

There have been several researches for the dyeing of regular and microdenier fibers [2-17], but papers concerning dyeing properties of nano fiber are rare. It is well known that nylon fiber adsorbs acid dye rapidly in the early stage of dyeing causing unlevellness and that this tendency is getting more severe in the case of microdenier fiber. Nano fiber in dyeing solution tends to entangle nano fibers themselves together, so it is necessary to solve this difficulty to get nano fiber dyed successfully. In this paper, dyeing properties of nylon 66 nano fiber were investigated. Nylon 66 regular fiber (1 denier) and nano fiber (approximately 0.003 denier), were used in the dyeing experiment. The samples were dyed with three high molecular mass acid dyes. Effects of dyeing temperature, pH of the dye bath, and dye concentration on dyeing propreties were examined. X-ray diffraction and DSC were performed for measurement of degree of crystallinity. Water absorption and amino end group of nylon fibers were analyzed in order to study their effects on dyeing properties.

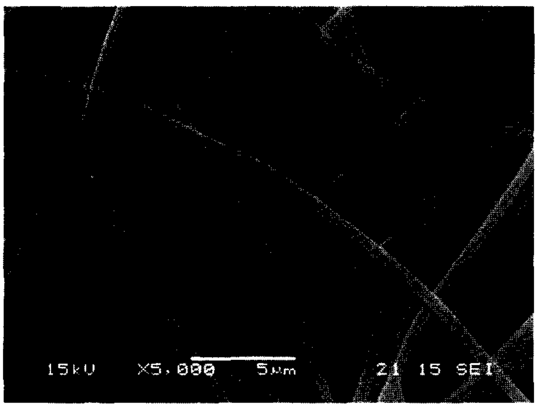
Experimental

Fibers

Nylon 66 nano fiber was a form of non-woven that was electro-spun by Nano Technics Ltd. and nylon 66 regular fiber (50 filaments/48 denier) used was Tactel manufactured by DuPont. The SEM images of the two fibers are shown in Figure 2. Nylon 66 regular fiber was knitted with knitting machine of 28 gauges for dyeing experimental. The samples were scoured with 1 *g/l* of NaOH and 1 *g/l* of Inkanol OL-1 (Poong-Young Chemistry Co.) at 100 °C for 30 minutes. Characteristics of the samples are given in Table 1.



(a) Regular fiber



(b) Nano fiber

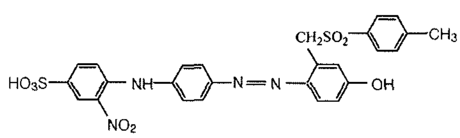
Figure 2. SEM images of regular fiber and nano fiber.

Table 1. Characteristics of nylon 66 regular fiber and nano fiber

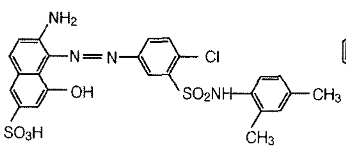
Sample	Type	Counts	Weight
Regular fiber	Knit	50 f/48 d 1 dpf	230 g/m^2
Electro-spun nano fiber	Nonwoven	600 nm in diameter 0.003 dpf	23.1 g/m^2

Table 2. Molecular weight and chemical constitution of acid dyes

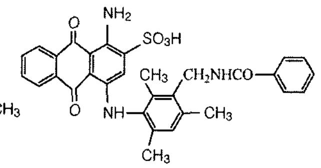
Dyes (C. I. number)	Molecular formula	Molecular weight
C. I. Acid Orange 67	$C_{29}H_{32}N_4O_8S_2$	628.72
C. I. Acid Red 336	$C_{25}H_{23}N_4O_6S_2$	575.06
C. I. Acid Blue 260	$C_{33}H_{23}N_3O_6S$	603.73



(a) C.I. Acid Orange 67



(b) C.I. Acid Red 336



(c) C.I. Acid Blue 260

Figure 3. Chemical structures of acid dyes used.

Acid Dyes

Three high molecular mass acid dyes were used in the experiment. Their molecular weights are shown in Table 2 and chemical structure in Figure 3.

Reagents

Acetic acid, ammonium sulfate, ammonium acetate, and sodium acetate were used as received. Other reagents used were first grade.

Measurement

Degree of crystallinity of nylon 66 nano fiber and regular fiber was examined with DSC (Perkin Elmer GSC-7, USA) at a heating rate of 10 °C/min under nitrogen atmosphere from room temperature to 280 °C. Degree of crystallinity was calculated from equation (1):

$$\text{Degree of crystallinity} = (H_f / H_o) \times 100 \qquad (1)$$

where, H_f (J/g): heat of fusion of specimen
H_o (J/g): heat of fusion of 100 % crystalline nylon 66 (α-form crystal)

X-ray diffractometer (Rigak Rint 200, Japan) was used in order to identify equatorial diffraction profile of specimen that was monitored on wide-angle X-ray diffractometer with reflection of Cu-Ka ray filtered by Ni.

Amino end group in nylon fibers was analyzed with ASTM D-664-8.

Water absorption of specimen was calculated from equation (2):

$$\text{Water absorption (\%)} = \frac{W - W_0}{W_0} \times 100 \qquad (2)$$

where, W(g): weight of fiber wetted with distilled water
W_o(g): weight of dry fiber

Dyeing

The standard dyeing conditions using IR dyeing machine (Daelim Starlet Ltd. Co., Korea) were as follows: dyeing solution was prepared using liquor ratio 1:500, pH of dyeing solution was controlled to 4.0 with acetic acid and ammonium sulfate, temperature was raised from 40 °C to the highest dyeing temperature at the rate of 1 °C/min., and dyeing was continued at the highest dyeing temperature for 60 min.

The highest dyeing temperatures examined were 70, 80, 90, 100, and 110 °C at the dye concentration of 5 % o.w.f. and the rate curve was plotted by measuring dye uptake of the dyed fiber which was taken out from the dyepot at predetermined dyeing times. The pH's of dye bath examined were 3, 4, 5, 6, and 7 at the dye concentration of 3 % o.w.f. and pH was adjusted with buffer solution which was prepared from formic acid, acetic acid, sodium acetate, monosodium phosphate, and disodium phosphate. The dye concentration was changed from 1 % o.w.f. to 11 % o.w.f. to investigate build-up property.

The extent of exhaustion (%) was measured with UV spectrophotometer (Unicam, USA) using equation (3):

$$\text{Extent of exhaustion (\%)} = [1 - (A_t/A_o)] \times 100 \qquad (3)$$

where, A_o: initial optical density of dyeing solution
A_t: optical density of dyeing solution after dyeing time t

Color strength (K/S) was calculated from the well-known Kubelka-Munk equation. Colorfastness to washing and to light was assessed in accordance with KS K 0430 A-1 and KS K 0700 method, respectively.

Results and Discussion

Degree of Crystallinity

Figure 4 shows DSC thermogram of both fibers. Melting peaks of nylon 66 nano fiber and regular fiber were observed at about 260 °C. The melting peak of regular fiber is more sharp and its area is bigger than that of nano fiber, which indicates the cystal of regular fiber is more perfect and the degree of crystallinity is higher than nano fiber. The ratio of degree of crystallinity of regular fiber and nano fiber is 43.1:34.6 according to equation (1). It means that the degree of crystallinity of regular fiber is 25 % higher than nano fiber. Because dyes can be diffused into the amorphous region of fiber, nano fiber whose degree of crystallinity is low is expected to absorb more dye than regular fiber if other conditions are the same.

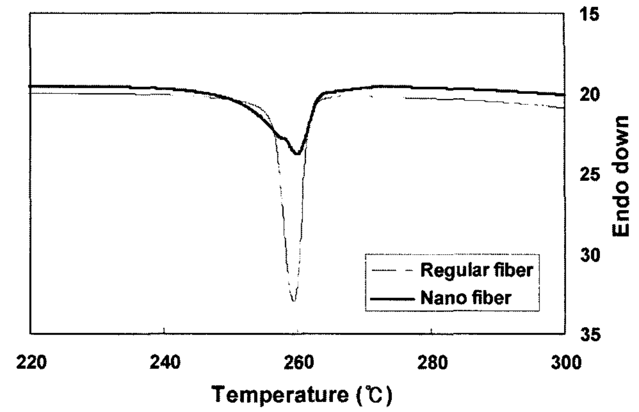


Figure 4. The DSC thermogram of regular fiber and nano fiber.

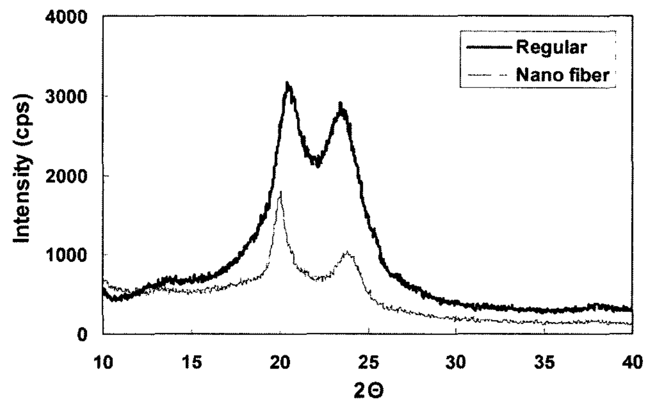


Figure 5. The X-ray diffractograms of regular fiber and nano fiber.

X-ray equatorial diffraction profile is shown in Figure 5, which corresponds well with the result of DSC analysis.

Number of Amino End Group and Water Absorption

Amino end group is an important parameter in the acid dyeing because it acts as a dyeing site and whose quantity is closely related to the amount of acid dye absorbed. Table 3 shows that the number of amino end group of regular fiber is

Table 3. Amino end group and water absorption of regular fiber and nano fiber

Property	Regular fiber	Nano fiber
Amino end group (m equiv./kg nylon)	83.8	32.1
Water absorption (%)	1.9	117.0

2.6 times more than that of nano fiber. This fact suggests that regular fiber can absorb more acid dyes than nano fiber.

Water absorption of nano fiber is 117 % and it is remarkably higher than that of regular fiber. It might be caused by the structure of nano fiber that is a form of web, nano web is regarded as an entanglement of nano fibers, and there are so many empty space between nano fibers that water can penetrate into empty space easily by the capillary action. In dyeing process, high water absorption might be helpful because the large amount of dye solution can penetrate into nano web and contact the fiber surface more widely.

Effects of Dyeing Temperature on Dyeing Property

The rate of exhaustion of C. I. Acid Red 336 on both fibers dyed at 100 °C is shown in Figure 6. This exhaustion curve was plotted by measuring dye uptake of the dyed fiber which was taken out from the dyepot at predetermined dyeing times. Nano fiber starts to absorb dye at lower temperature and gets dyed at a rapid rate as compared with regular fiber. It is generally said that the faster rate of fine-denier fiber is

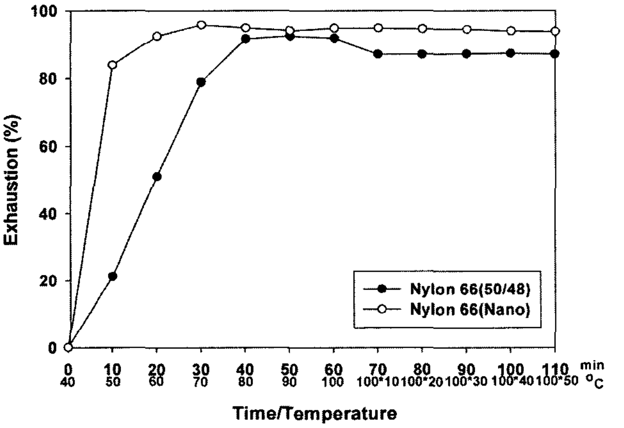


Figure 6. The exhaustion curve of regular fiber and nano fiber dyed at 100 °C.

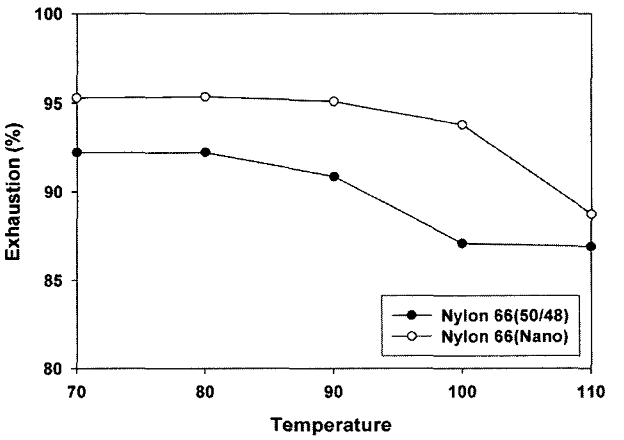


Figure 7. The extent of exhaustion of regular fiber and nano fiber as a function of dyeing temperature.

Table 4. Half-dyeing time and final extent of exhaustion of regular fiber and nano fiber dyed at different dyeing temperature (C.I. Acid Red 336)

Dyeing temperature (°C)	Half-dyeing time (min)		Extent of exhaustion (%)	
	Regular fiber	Nano fiber	Regular fiber	Nano fiber
70	16	4<	92.2	95.3
80	16	4<	92.2	95.4
90	16	4<	90.9	95.1
100	15	4<	87.1	93.8
110	14	3<	86.9	88.7

attributed to its large specific surface area. The exhaustion curves of C. I. Acid Red 336 dyed at 70, 80, 90, 110 °C showed almost the same tendency to that at 100 °C.

Figure 7 shows the final extent of exhaustion obtained at different dyeing temperatures. The extent of exhaustion of regular fiber is in the range of 92-87 %, that of nano fiber is 95-89%. It appears that the extent of exhaustion of nano fiber is slightly higher. The difference between them at specific dyeing temperature is approximately 3 %. The extent of exhaustion on regular fiber seems to reach its maximum value at 70 and 80 °C, that of nano fiber starts to decrease at the temperatures higher than 90 °C, because molecular movement of fiber becomes so active that fiber-dye bonds are breakable at high tempertures. Table 4 shows half-dyeing time and the extent of exhaustion. Half-dyeing time of regular fiber is 16 minutes but that of nano fiber is 4 minutes. It means that dyeing rate of nano fiber is faster about quadruple in the case of C. I. Acid Red 336.

C. I. Acid Blue 260 and C. I. Acid Orange 67 shows the similar trends to C. I. Acid Red 336.

Effects of pH of Dyeing Solution on Dyeing Property

Figures 8 and 9 show the extent of exhaustion of three acid dyes on both fibers at different pH of dyeing solution. It is observed that the extent of exhaustion of dyes decreases as pH increases. Amino groups of nylon are protonated by the addition of acid and they become dyeing sites for the acid dyes which possess negative charge in water. The number of dyeing site decreases with increasing pH of dyeing solution, which results in diminution of the extent of exhaustion.

It can be found by the careful examination of slope of the exhaustion curves that nano fiber is less affected by pH than regular fiber. This might be explained by the number of amino end group in the fiber. Because nano fiber has about 40 % of amino end group in comparison with regular fiber, the decrease of the protonated amino group on fiber surface by increasing pH is less than regular fiber.

The extent of exhaustion of C. I. Acid Red 336 on regular fiber is markedly decreased above pH 6 comparing with two other dyes. Similar phenomenon is shown in the dyeing of nano fiber also. It means that C. I. Acid Orange 67 and Blue

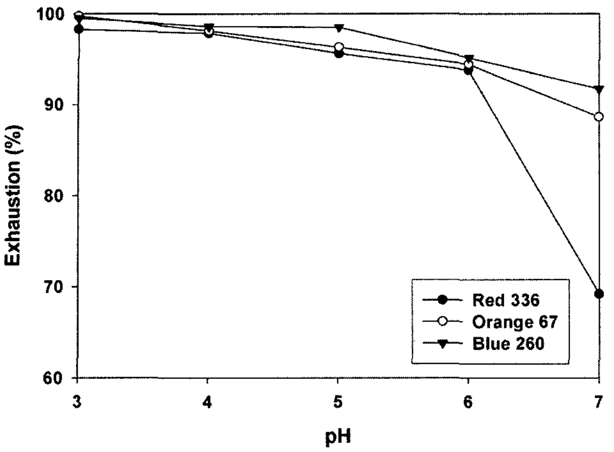


Figure 8. Change of the extent of exhaustion on regular fiber as a function of pH of dyeing solution.

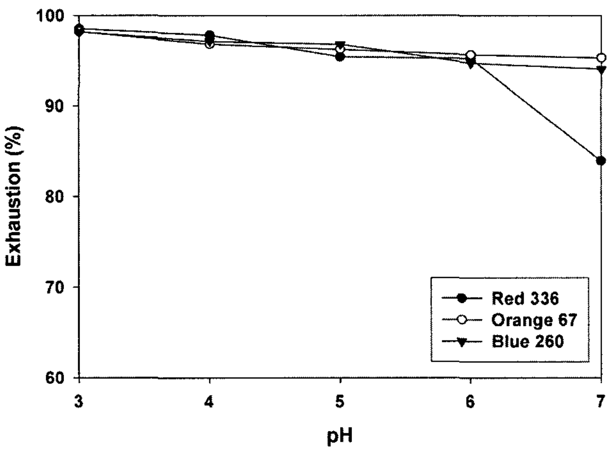


Figure 9. Change of the extent of exhaustion on nano fiber as a function of pH.

260 are less affected by pH of dyeing solution. However this fact does not act harmfully in the dyeing of nylon fibers in dyeing factory because the optimal pH of dyeing solution adopted in dyeing factory is below pH 5.

Effects of Dye Concentration on Dyeing Property

Effects of concentration of C. I. Acid Red 336 on the extent of exhaustion on both fibers are shown in Figure 10. The extent of exhaustion on both fibers decreases as dye concentration increases. This phenomenon is generally known fact, and true in all dyeing system. The extent of exhaustion on regular fiber is 85 % at 5 % o.w.f. and decreases abruptly at dye concentration above 5 % o.w.f. On the other hand the extents of exhaustion on nano fiber are above 90 % at dye concentration from 1 to 11 % o.w.f., suggesting that nano fiber can accommodate a large amount of dye without a significant loss in the extent of exhaustion.

Effects of concentration of C. I. Acid Red 336 on K/S

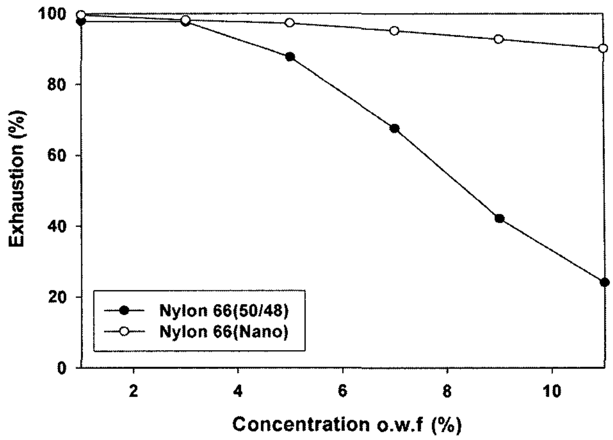


Figure 10. Variation of the extent of exhaustion of C.I. Acid Red 336 as a function of dye concentration.

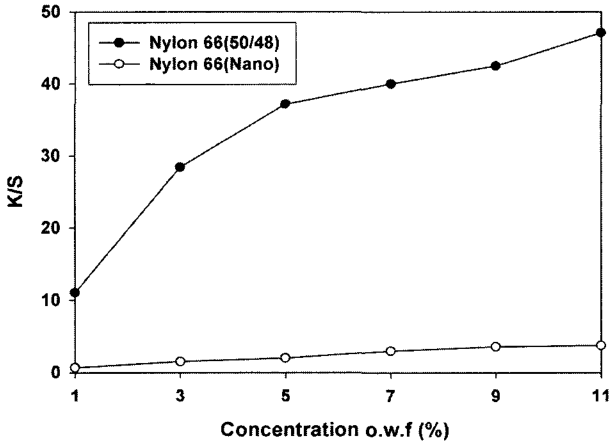


Figure 11. Variation of K/S value of fibers dyed with C.I. Acid Red 336 as a function of dye concentration.

values of the dyed fabrics are shown in Figure 11. K/S value is known to be proportional to apparent color depth of the dyed fabric. The remarkable difference in K/S value between regular fiber and nano fiber is clearly seen, originating from the difference in the specific surface area. The greater extent of surface reflection that ensues from the greater surface area of nano fiber makes the dyed nano fiber visually lighter in shade than regular fiber dyed at the same dye concentration. As dye concentration increases K/S value of the dyed regular fiber increases, but it increases a little above 5 % o.w.f. K/S value of the dyed nano fiber increases very slowly with dye concentration, but it increases gradually up to 11 % o.w.f., suggesting that very high dye concentration is required to give deep color to nano fiber.

Denier of mono filament of nano fiber is 0.003 d and that of regular fiber is 1 d. Apparent color depth of the dyed nano fiber is considerably weaker than that of the dyed regular fiber. Therefore dye concentration must be increased a lot in dyeing of nano fiber to obtain a similar color depth to regular fiber. This relation is expressed by empirical equation (4):

$$C_A/C_B = (d_B/d_A)^{1/2} \quad (4)$$

Where, C_A: the amount of dye used for fiber with d_A denier
C_B: the amount of dye used for fiber with d_B denier

According to equation (4), the amount of dye required for nano fiber to get the same color depth with regular fiber is more than 90 times.

The results obtained with C. I. Acid Orange 67 and Blue 260 are very similar to those of C. I. Acid Red 336.

Colorfastness of the Dyed Samples

Table 5 represents colorfastness of the dyed fibers with dye concentration of 5 % o.w.f. at different dyeing temperatures. Washing fastness of nano fiber has not changed with an increase of dyeing temperature, while that of regular fiber are better by 1/2~1 grade. Light fastness of nano fiber is inferior to that of regular fiber by 1 grade, due to larger surface area through which light can penetrate.

Washing and light fastness of both fibers dyed at different pH are shown in Table 6. Variation of pH of dyeing bath does not seem to affect color fastness of both fibers.

Table 5. Colorfastness of fibers dyed with high molecular mass acid dyes at different dyeing temperature

Dye	Dyeing temp. (°C)	Nano fiber				Regular fiber			
		Washing fastness			Light fastness	Washing fastness			Light fastness
		Cotton	Nylon	Wool		Cotton	Nylon	Wool	
Orange 67	70	3	2	3-4	4	3-4	3-4	3-4	5
	80	3	2	3-4	4	3-4	3-4	3-4	5
	90	3	2	3-4	4	3-4	3-4	3	5
	100	3	2	3-4	4	3-4	3-4	3	5
	110	3	2	3-4	4	4	3-4	3-4	5
Red 336	70	3-4	3-4	3-4	4	3	4-5	3-4	5
	80	3-4	3-4	3-4	4	3	4-5	3-4	5
	90	3	3-4	3-4	4	3	4	3-4	5
	100	3	3-4	3-4	4	2-3	4	3	5
	110	3	3-4	3-4	4	2-3	4	3	5
Blue 260	70	3	2	2-3	4	3-4	2	3	5
	80	3	1-2	2-3	4	3-4	2	3	5
	90	3	1-2	2-3	4	3-4	2	3	5
	100	3	1-2	2-3	4	3-4	2	3	5
	110	3	1-2	2	4	3-4	2	3	5

Table 6. Colorfastness of fibers dyed with high molecular mass acid dyes at different pH

Dye	Dyeing pH	Nano fiber				Regular fiber			
		Washing fastness			Light fastness	Washing fastness			Light fastness
		Cotton	Nylon	Wool		Cotton	Nylon	Wool	
Orange 67	3	3-4	2	3-4	4	4	3-4	4-5	5
	4	3-4	2	3-4	4	4	3-4	4-5	5
	5	3-4	2	3-4	4	4	3-4	4-5	5
	6	3-4	2	3-4	4	4	3-4	4	5
	7	3-4	2	3-4	4	4	3	4	5
Red 336	3	2-3	3	3-4	4	3-4	4	4	4
	4	2-3	3	3-4	4	3-4	3-4	4	4
	5	2-3	3	3-4	4	2-3	2-3	3-4	5
	6	2-3	3	3-4	4	2-3	2-3	3-4	5
	7	3	3	4	4	2-3	2-3	3-4	5
Blue 260	3	3-4	2	2-3	4	4	3	3-4	5
	4	3-4	2	2-3	4	4	3	3-4	5
	5	3-4	2	2-3	4	4	3	3-4	5
	6	3-4	2	2-3	4	4	3	3-4	5
	7	3-4	2	2-3	4	4	3	3-4	5

Table 7. Colorfastness of fibers dyed with high molecular mass acid dyes at 11 % o.w.f.

Color	% o.w.f	Nano fiber				Regular fiber			
		Washing fastness			Light fastness	Washing fastness			Light fastness
		Cotton	Nylon	Wool		Cotton	Nylon	Wool	
Orange 67	11	2	2-3	3-4	4	3	2	2-3	5
Red 336	11	3	2	2	4	3	2	2-3	5
Blue 260	11	2-3	2	2-3	4	3	2	2-3	5

Table 7 shows that washing fastness of the dyed nano fiber with dye concentration of 11 % o.w.f. is similar to regular fiber. Light fastness of regular fiber is better by 1 grade than nano fiber. These fastness grades are regarded to be sufficient for using nano fiber as an apparel.

Conclusions

It was confirmed that degree of crystallinity of nano fiber was lower, amount of amino end group was smaller, but water absorption was much higher than regular fiber.

Examination of half-dyeing time and exhaustion curves revealed that nano fiber absorbed acid dyes at lower temperature, got rapidly dyed, and its extents of exhaustion at specific dyeing temperature were higher by approximately 3 % as compared with regular fiber. It was observed that the extent of exhaustion of dyes on both nylon fibers decreased as pH increased due to the reduction of dyeing sites. Nano fiber, which had smaller number of amino end group, was less affected by pH of dyeing solution than regular fiber. Nano fiber could absorb a large amount of acid dye without a significant loss in the extent of exhaustion. K/S values of the dyed nano fiber, which were much lower than those of regular fiber, increased gradually up to 11 % o.w.f.

Washing fastness of the dyed nano fiber were lower by 1/2~1 grade, light fastness by 1 grade than the dyed regular fiber. Change of the highest dyeing temperature and pH of dyeing solution did not affect colorfastness of the dyed nano fiber.

References

1. http://www.nano21c.com/pressroom.
2. S. M. Burkinshaw, "Chemical Principles of Synthetic Fiber Dyeing", pp.79-86, Chapman & Hall, London, 1995.
3. K. Himeno, *Dyeing Industry, Jpn.*, **40**, 586 (1992).
4. P. Viallier and C. Jordan, *J. Soc. Dyers Colour.*, **117**, 30 (2001).
5. H. Oda, *Dyes and Pigments*, **48**, 151 (2001).
6. S. D. Kim and E. J. Park, *Fibers and Polymers*, **2**, 159 (2001).
7. K. S. Kim, S. D. Kim, J. L. Lee, and K. W. Lee, *J. Korean Fiber Soc.*, **38**, 683 (2001).
8. J. S. Oh, D. S. Jeong, and M. C. Lee, *J. Korea Soc. Dyers and Finishers*, **14**(6), 8 (2002).
9. D. S. Jeong, D. H. Lee, M. C. Lee, and T. Wakida, *J. Korea Soc. Dyers and Finishers*, **14**(6), 15 (2002).
10. D. S. Jeong, D. H. Lee, and M. C. Lee, *J. Korea Soc. Dyers and Finishers*, **14**(6), 24 (2002).
11. S. H. Yoon, T. K. Kim, Y. J. Lim, and Y. A. Son, *J. Korea Soc. Dyers and Finishers*, **14**(6), 31 (2002).
12. H. R. Maradiya and V. S. Patel, *Fibers and Polymers*, **3**, 43 (2002).
13. J. S. Bae and H. S. Freeman, *Fibers and Polymers*, **3**, 147 (2002).
14. J. J. Lee, M. K. Han, W. J. Lee, J. H. Hong, and J. P. kim, *Fibers and Polymers*, **3**(3), 85 (2002).
15. S. D. Kim, Y. S. Lee, B. S. Lee, and J. Y. Jaung, *J. Korean Fiber Soc.*, **39**, 723 (2002).
16. J. J. Lee, W. J. Lee, and J. P. Kim, *Fibers and Polymers*, **4**, 66 (2003).
17. P. Savarino, S. Parati, and R. Buscaino, *Dyes and Pigments*, **60**, 223 (2004).