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Preparation of Nano Disperse Dyes from Nanoemulsions and Their Dyeing Properties on Ultramicrofiber Polyester

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Abstract: Six nano disperse dyes were prepared using corresponding O/W nanoemulsions which were obtained with sodium laurylsulphate and caprylic triglyceride. The average particle size of the dyes prepared were in the range of 110~130 nm. Exhaust dyeing using nano dyes resulted in low exhaustion yields of 17~26 % on regular polyester fiber and 28~38 % on ultramicrofiber polyester. The observed low exhaustion yields of nano disperse dye can be explained by the solubilization of dye particles into surfactant micelles as well as the high stability of the nanoemulsions, these might reduce the capacity of dye uptake onto the fibers. However, higher K/S values of dyeings with nano dyes on ultramicrofiber sites compared to those on regular polyester sites suggested their potential to be more efficient dyes for finer denier microfiber polyesters.

Keywords: Nanoemulsion, Nano disperse dye, Ultramicrofiber, Exhaust dyeing

Introduction

Nanotechnology has become one of the most important and exciting fields of recent times since it promises to change the direction of technological advances in a wide range of applications. In particular, there have been some revolutionary products based on nanotechnology in the textile market, for instance nano fiber for air filter and optical fiber, Morphotex from Teijin [1], fiber finishing agents from Nano-Tex [2], as well as dyeing technology for nylon 6,6 nano fiber [3].

Disperse dyes have extremely low solubility in water and therefore give an affinity for hydrophobic fibers such as polyester, nylon and acetates. For exhaust dyeing, commercial disperse dyes are normally applied from fine aqueous dispersions in which the average particle sizes are typically in the region of 800~1,000 nm. In this study, it has been investigated the new method to prepare a nanoemulsion system containing much smaller dye particles of nano size in the range 110~130 nm. To evaluate their dyeing properties, the emulsion has been applied onto regular polyester (75 d/ 24 f) and island-in-the-sea type ultramicrofiber polyester [4] by an exhaust dyeing.

Conventional milling method using a glass or sand bead, which is a typical a top-down process, is generally used to manufacture insoluble dye dispersions, but their average particle size exceeds 200 nm although Zirconium bead used. Therefore, there have been very limited research results to prepare nano sized disperse dyes of 100 nm by utilizing a bottom-up process.

Nano disperse dyes were prepared in an aqueous nanoemulsion of sodium laurylsulphate (SLS) and caprylic triglyceride by direct precipitation of dye in oil cores under continuous ultrasound treatment.

Nanoemulsions [5,6] consist of very fine emulsions with droplet sizes that are typically between 20 and 500 nm. Nanoemulsions are thermodynamically stable, like as micro-emulsions, but require a low concentration of surfactant in contrast to microemulsions. In recent years, attentions have been focused on nanoemulsions of droplet sizes in the submicrometer region, which is below those of conventional emulsions and microemulsions.

Nanoparticles can be prepared by directly adding a material (for reaction or simple precipitation) in the form of liquid solution or a gas to the primary reactant that is present in the

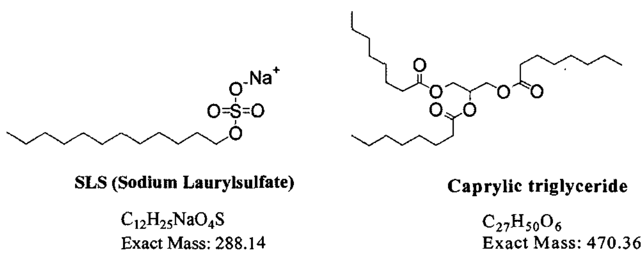

Figure 1. Structures of the surfactant and oil used in this study.

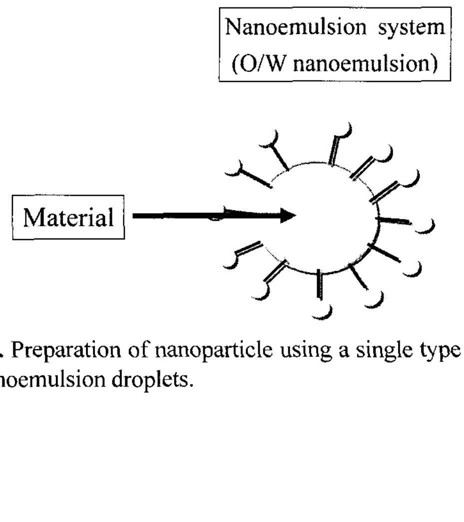

Figure 2. Preparation of nanoparticle using a single type of oil-in-water nanoemulsion droplets.

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nanoemulsion droplet [7], as shown in Figure 2. Initially, the material collects in the oil core of the nanoemulsion. Subsequently, nuclei are formed inside the oil core, which eventually grow until precipitation occurs inside the nanoemulsion droplet. Consequently, the extent of particle growth will be limited by the size of the oil droplets within the nanoemulsion.

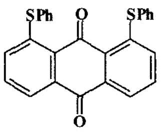
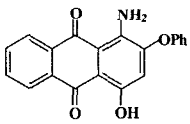
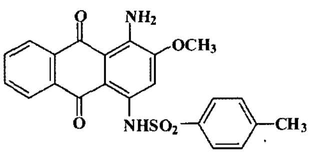
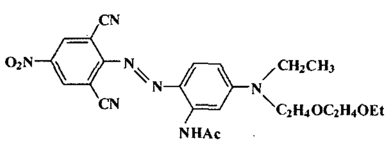
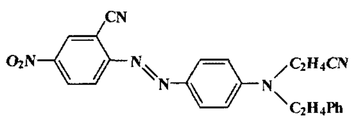
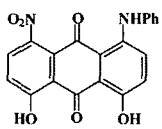
Disperse dyes with average particle sizes in the nanometer range have been prepared using nanoemulsion system, then these were examined their dyeing properties on polyester fiber in comparison with those of conventional disperse dyes.

Experimental

Materials

Nano disperse dyes were prepared in an oil-in-water nanoemulsion system prepared from 30 % SLS (Taedong Chemical, Korea), caprylic triglyceride (Uniqema) and distilled water. Six dyes as dried press cake supplied from M. Dohmen Korea Co. were listed in Table 1. To investigate the dyeing properties of nano dyes, tricot knit composed of regular polyester and Island-in-the-Sea type ultramicrofiber blend (surface : 0.05 d, back : 2 d), was supplied from Kolon Co. Ltd.

Table 1. Dyes used in this study

Dye	Structure	Molecular weight
Solvent Yellow 163		424.5
Disperse Red 60		331.3
Disperse Red 86		422.5
Disperse Blue 337		493.5
Disperse Red 184		424.5
Disperse Blue 62		376.3

Preparation of Nano Disperse Dyes

The preparation of nano disperse dyes consists of several stages: firstly, a nanoemulsion was prepared by dissolving 3 parts SLS in 87 parts distilled water. Ten parts caprylic triglyceride were added to the surfactant solution at 60~70 °C. This mixture was treated for 5 min at 70 °C using a Homomixer (TOKUSHC KIKAS Co., Model ROBOMICX) at 4,000 rpm, then treated for three times with a Microfluidizer high shear emulsifier (Microfluidics Co. 110EH) at a pressure of 1,000 bar.

Dried press cake of dyes was dissolved in DMF and the solution added dropwise to the nanoemulsion at 80 °C with stirring, followed by a stirring for 5 min. Continuous ultrasound treatment was then applied for 15 min using a Sonicator UP 200s (Ultraschollprozessor). A flow chart for the preparation of nano disperse dyes is shown in Figure 3.

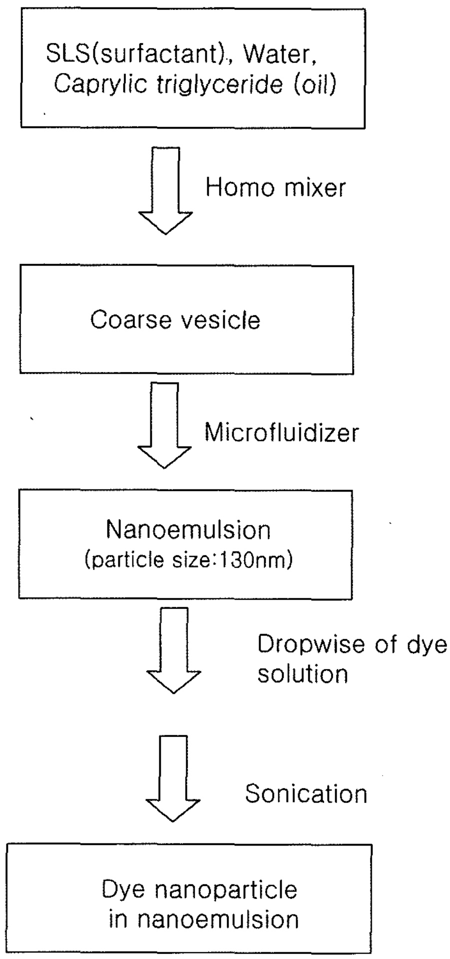
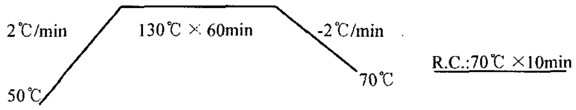


Figure 3. Process for the preparation of nano disperse dyes.



NaOH 0.5g/l and $Na_2S_2O_4$ 0.5g/l were used for a reduction clear process.

Figure 4. Diagram of the exhaust dyeing process with nano disperse dyes.

The average particle sizes of nanoemulsion and nano disperse dye were measured by a Particle size analyzer (OTSUKA ELEC. Co. Ltd., ELS 8000). Zeta potential of nano disperse dyes was also determined by a particle size analyzer (OTSUKA ELEC. Co. Ltd., ELS 8000).

Dyeing Procedure

Dye baths were prepared from pre-formed nano disperse dye-containing emulsions with distilled water, which adjusted to pH 4 by the addition of acetic acid. Regular polyester (75 d/24 f) or an island-in-the-sea type microfiber was immersed in the dye bath. Dyeing was carried out in a KS-W24 Inter Cooler IR dyeing machine (Korea Scientific Co.), as shown in Figure 4.

Colorimetric Measurements

The Colorimetric properties of the dyeings were determined on a Datacolor SF 600 plus spectrophotometer (Datacolor International) using a D_{65} illuminant and 10 ° observer, UV excluded and specular component included.

Determination of Dye Exhaustion Yields

Exhaustion of nano disperse dye from the dyeing bath was determined using a UV-visible spectrophotometer where the absorbance was measured at the absorption maxima of the dye.

The exhaustion percentage (%E) was calculated using the following equation:

$$\text{Exhaustion (\%)} = (A_0 - A_1)/A_0 \times 100$$

where A_0 and A_1 are the absorbance of the maximum wavelength of dyes in original dyeing bath and of that in the residual dyeing bath, respectively.

Results and Discussion

Hypothesis for the Mechanism of Nano Disperse Dye Formation

This hypothesis has been previously proposed [8-10]. As it is shown in Figure 5, initially, the oil cores are surrounded by the excess surfactant (SLS). The dye as a press cake dissolved in DMF is added drop by drop into an empty nanoemulsion under continuous ultrasound treatment. The dye diffuses into the oil core so that the dye builds up in the

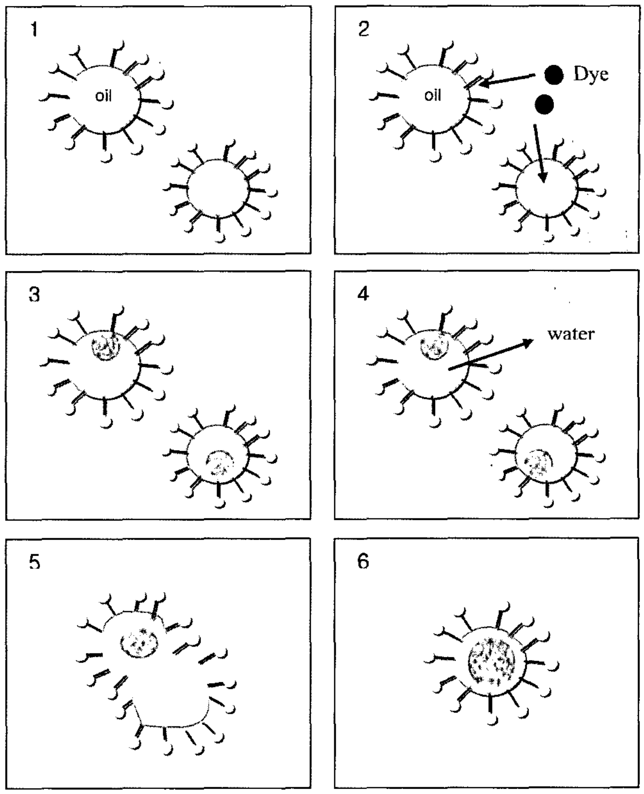


Figure 5. Hypothesis for the mechanism of nano disperse dye formation.

oil phase. Finally, exchange of dye particles takes place between the oil cores as a result of collisions between the droplets, enabling the nuclei to grow.

In this study, all 6 dyes gave corresponding emulsion system in which dye particles were dispersed as much as commercial disperse dyes were evenly dispersed in water. A stable dispersion was obtained by the addition of the emulsion prepared into water, which proved the presence of dye particles inside the emulsion system.

Analysis of Particle Size and Zeta Potential

Average particle sizes for each of the nano dyes are shown in Table 2.

Table 2. Average particle size and zeta-potential

Organic molecules	Average particle size (nm)	Zeta potential (mV)
SLS/Water/Caprylic triglyceride	137.8	−37.37
C.I. Solvent Yellow 163	113.3	−37.79
C.I. Disperse Red 60	135.0	−40.43
C.I. Disperse Red 86	110.5	−38.80
C.I. Disperse Red 184	131.2	−38.66
C.I. Disperse Blue 62	117.6	−38.99
C.I. Disperse Blue 337	133.8	−37.46

Table 3. Exhaustion yields of nano dye emulsions

Dye	Exhaustion yield (%)	
	Regular polyester	Ultramicrofiber (Islands-in-the-Sea type)
C.I. Solvent Yellow163	20.1 %	28.2 %
C.I. Disperse Red 60	20.0 %	31.8 %
C.I. Disperse Red 86	17.3 %	36.9 %
C.I. Disperse Red 184	19.8 %	32.6 %
C.I. Disperse Blue 62	26.7 %	34.0 %
C.I. Disperse Blue 337	23.8 %	38.2 %

As the average particle size of the nanoemulsion was 138 nm, it could be assumed that maximum particle size of dyes were between 110~133 nm, since the particle size of the dye has to be limited by the size of the oil droplets in the nanoemulsion.

To evaluate the stability of nano dye particles, corresponding zeta potentials were measured. As it can be seen from Table 2, the nanoemulsion and each of the nano disperse dyes were negatively charged, the zeta potentials being −37~−40 mV, indicating their good stability.

To investigate the dyeing properties of nano disperse dye emulsions, the exhaustion yields (%) for six dye emulsions were examined. As summarized in Table 3, results of the exhaustion yields by an exhaust dyeing were just 20~30 % of the total nano dye applied both on regular and microfiber polyester. As commercial disperse dyes exhibit exhaustion of 90~95 %, these results were extremely lower than conventional disperse dyes.

In general, the dyeing mechanism of the disperse dye on polyester fiber involves mainly hydrophobic interaction between fiber and disperse dye [11]. It is assumed that, in the nanoemulsion system prepared, the dye particles are partitioned between the oil phase of the emulsion, aqueous phase and the fiber phase. It would be appeared that the strong tendency of the dyes to be solubilized inside the surfactant micelles of the nanoemulsion made adsorption of dye molecules to the hydrophobic surface of the fiber to be less favourable. Consequently, the observed low exhaustion of nano dye emulsions could be attributed to the solubilization effect of the nano dye particles in surfactant micelles, reducing the uptake of nano dyes by the polyester fiber. In addition, the inherent thermodynamic stability of the nanoemulsion might also contribute to their low exhaustion levels.

Nano dye emulsions exhibited much higher exhaustion yields on ultramicrofiber in comparison with that of regular polyester, indicating a greater substantivity of nano dyes for ultramicrofiber than for regular denier polyester. Difference depended on the dye structure, for instance C.I. Solvent Yellow 163 showed just 20 % exhaustion yield on regular polyester compared to 28 % on ultramicrofiber. For C.I. Disperse Red 86, two times higher exhaustion yield was observed with ultramocrofiber than regular polyester.

These outstanding properties should be closely related to the possibility to improve the dyeability on much finer denier microfiber with nano disperse dyes, irrespective of its low exhaustion yield.

Table 4. K/S values of dyeings with nano dye emulsions

Dye	K/S value (check-sum)			
	Regular polyester	Island-in-the-Sea type ultramicrofiber		
		Micro-fiber site (0.05d)	Reg. PET site (2 d)	Difference of K/S values
Solvent Yellow 163	12.7	16.7	12.9	22.4 %
Disperse Red 60	69.4	61.9	60.9	1.5 %
Disperse Red 86	38.9	40.3	35.2	12.6 %
Disperse Red 184	69.5	73.3	59.1	19.4 %
Disperse Blue 62	62.6	62.6	53.7	14.2 %
Disperse Blue 337	174.9	281.1	235.9	16.1 %

Colorimetric Properties between Regular and Ultramicrofibre

The shade depths of the dyeings with nano dye emulsions were obtained in terms of the K/S values as calculated from the reflectance data according to the Kubelka-Munk equation (Table 4).

In the case of islands-in-the-sea type ultramicrofiber blended fiber, we measured the K/S values of the ultramicrofiber site (0.05 d) and regular polyester site (2 d), respectively. In general, for commercial disperse dyes, depths of shade tended to be much lower on ultramicrofiber compared to that obtained with regular denier fiber depending on the difference of their fineness. By contrast, in the case of the nano disperse dyes, K/S values were significantly higher on the ultramicrofiber site than those of the regular polyester site (e.g. 22 % higher for C.I. Solvent Yellow 163) except C.I. Disperse Red 60 which gave similar K/S values for both sites. Although it was not certain, the observed higher K/S values on finer denier site might be correlated with higher affinity of nano dyes on ultramicrofiber site rather than regular denier site, as explained in Table 3.

To verify the relationship between colorimetric properties and dye particle size, dyeings on islands-in-the-sea type ultramicrofiber blended polyester with nano sized C.I. Disperse Blue 337 were compared with dyeings with commercial C.I. Disperse Blue 337. In the case of the commercial dye, regular polyester site showed higher K/S values (393.6 in check-sum) than microfiber site (310.2 in check-sum), as shown in Figure 6, whereas the dyeing with the nano dye exhibited higher K/S values (281.1 in check-sum) at microfiber site compared with that of regular polyester site (235.9 in check-sum, as shown in Figure 7.

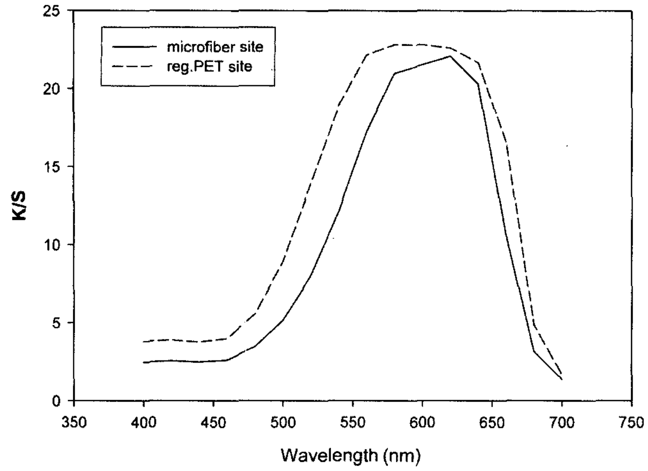


Figure 6. K/S value curve of C.I. Disperse Blue 337 (a commercial dye) at microfiber and regular denier sites.

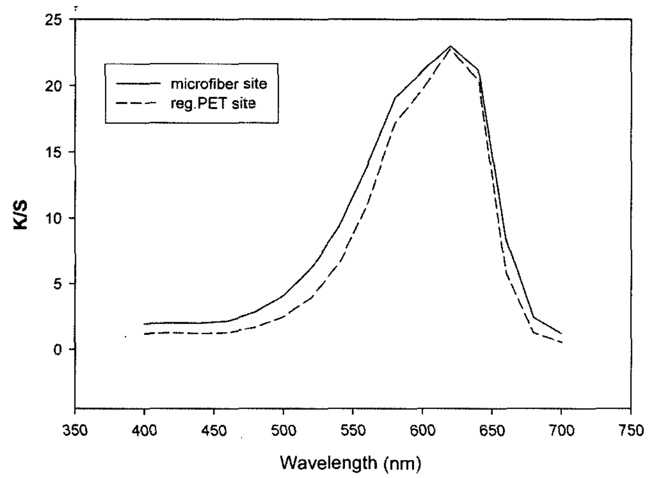


Figure 7. K/S value curve of C.I. Disperse Blue 337 (nano dye) at microfiber and regular denier sites.

Conclusions

Six nano disperse dyes were prepared using corresponding O/W nanoemulsions. The average particle size of the dyes prepared in this study were 110~130 nm.

When the nano dye emulsions were applied onto the regular polyester fiber and the ultramicrofiber polyester, exhaustion yields were just less than 40 % of the applied dye, these were lower compared to those of commercial disperse dyes. The observed low exhaustion yields of nano disperse dye emulsions could be attributed to the solubilisation of dye particles into surfactant micelles, which retarded uptake of dyes by polyester fibre. The high stability of the nanoemulsions might also be responsible for the low exhaustion yields.

However, in the case of dyeings with nano dyes prepared on ultramicrofibers, it was observed that microfiber site exhibited higher K/S values than those of regular polyester site, in the range of 1.5 %~22.4 %, which was promising a possibility to perform higher efficiency on ultramicrofiber.

Acknowledgement

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