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INVESTIGATION ON DYEABILITY OF NYLON 6 NANOFIBRES WITH REACTIVE DYE

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Resumen: La capacidad de las nanofibras ha sido un desafío importante para todo el polímero y el químico textil de la última década. Los nuevos enfoques para proporcionar teñibilidad de nanofibras aumentan considerablemente el costo de la operación de teñido. En este sentido, se produjo nanofibra electrospun nylon 6. Se estudió la morfología de las nanofibras resultantes utilizando microscopio electrónico de barrido (SEM) antes y después de teñir con colorante reactivo (C.I. Reactive Violet 3) y luego se evaluó la capacidad de teñido de nanofibras electrospun de nylon 6. Los colorantes reactivos son compuestos orgánicos capaces de formar enlaces covalentes con los grupos nucleófilos de la cadena de polímero de fibra. Cuando un tinte se une con fibra, el tinte se convierte en parte de la fibra. Los resultados SEM de nylon 6 nanofibras antes y después del teñido con colorante reactivo, la extensión del agotamiento y el grado de fijación mostraron que las nanofibras de nylon 6 se pueden teñir con colorante reactivo mediante la fabricación de banda covalente.

Palabras clave: Dyeability, Reactive dye, Nanofiber, Nylon 6

Abstract: The Dyeability of nanofibres has been an important challenge to the entire polymer and textile chemist for last decade. The new approaches to provide dyeability of nanofibres increase the cost of the dyeing operation considerably. In this regard nylon 6 electrospun nanofiber was produced. The morphology of resultant nanofibers was studied using scanning electron microscope (SEM) before and after dyeing with reactive dye (C.I. Reactive Violet 3) and then dyeability of nylon 6 electrospun nanofibers was evaluated. Reactive dyes are organic compounds capable of forming covalent bonds with the nucleophilic groups of fiber polymer chain. When a dye bonds with fiber the dye becomes part of fiber. The SEM results of nylon 6 nanofibers before and after dyeing with reactive dye, extent of exhaustion and extent of fixation showed that nylon 6 nanofibers are dyeable with reactive dye via making covalent band.

Keywords: Dyeability, Reactive dye, Nanofiber, Nylon 6

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1- INTRODUCTION

The dyeability of nanofibres have been an important challenge to the entire polymer and textile chemist for last decade <http://www.nano21c.com/pressroom>. New approaches were investigated for dyeing of nanofibers such as mixture of polymers, plasma finishing and new designed dyes particularly. These approaches in which dyeing of nanofibers is performed, increase costs of dyeing operation considerably. Therefore, those approaches were not economically successful for dyeing of nanofibers. This issue is due to factors followed below:

1. Increasing in nanofibers viscosity
2. Reduction of mechanical properties of nanofibers
3. Variable and weak operation
<http://www.nano21c.com/pressroom>

New researches have been showed that nanofibers containing of dye can produce (Lee K. et al, 2005). There are various ways for preparation of colloid solutions containing dye. Easier method for this is Mechanical blending of polymer solution with dye powder that substantial problem of this method is aggregation of nanoparticles. The resultant Colloid solution is transformed into nanofiber by using of electrospinning process. Electrospinning is a widely and effective technology for producing long polymeric nanofibers with diameters ranging from several nanometers to micrometers. In electrospinning process, a liquid polymer with suitable viscosity is forced to pass through a nozzle with small diameter to produce a polymeric semisolid nanofiber continual. Varied applications have been defined for nanofibers such as composites, medical and hygienic fields because of its high specific surface area in comparison with its volume and with adding different dyes to nanofiber, different properties such as antibacterial activity will be achievable (Lee K. et al, 2005). Dyeing process consists of adsorbing dye from solution to the fiber surface, flowing dye into the fiber and moving of dye molecule from one point to another. This process will continue until nanofibers remain inside the dye bath. (Zhang S, et al, 2009)

Amino groups of dye structure are capable of forming bonds with anionic dyes such as acid, direct and reactive dyes. Reactive dyes have a structure similar to the acid dyes except for the electronegative groups in the reactive dyes structure and for that reason, these dyes are called reactive. Conventional stages for dyeing with reactive dyes are including:

1. Exhaustion of dye from dyebath to fiber surface
2. Adsorption of dyes to fiber surface
3. Diffusion of dye into the fiber
4. Migration of dye for creating uniformity
5. Dye fixation through forming of covalent bond between dye and fiber (Shore J, 1992)

In this research, dyeability of nylon 6 nanofiber has been investigated. Hence, at first nylon 6 nanofiber was electrospun at optimum concentration. Morphology of resultant nanofibers was evaluated through scanning electron microscopy (SEM) before and after dyeing with selected reactive dye (C.I. Reactive Violet 3) and then dyeability of nylon 6 nanofibers was studied by using of resultant extent of exhaustion and extent of fixation of dye. (Soleimani-Gorgani A, Taylor J. A, 2006)

2- EXPERIMENTAL

2.1. Materials and apparatus

All chemical which have been used in this article were in analytical grade. Formic acid, acetic acid and ammonium sulphate purchased from Merck. Nylon 6 (MW=25000-27000 Da) prepared from commercial producer and used as received.

2.2. Electrospinning

Polymer solutions with different concentrations (10-20%) were prepared to know which condition provides smooth and uniform nanofibers. First polymer chips weighted precisely then added to 5 ml formic acid (98%) and stirred until having uniform polymer solution. Solution viscosity measured using a Brookfield DVII+ viscometer. Gamma research high voltage was used to provide the electrospinning electrical field. Samples were transferred to New Eva pump and collector was placed in front of the pump.

Electrospinning was performed with 15 kV voltage and 0.5 ml/hour feeding rate at 10 cm collector distance.

2.3. Dyeing of nanofiber web

Table 1. Material used for each dye bath

Bath number	1	2	3	4	5	6
Initial dye concentration (%)	0.05	0.1	0.2	0.5	0.8	1
Acetic Acid (%)	0.5	0.5	0.5	0.5	0.5	0.5
Ammonium sulphate (%)	0.25	0.25	0.25	0.25	0.25	0.25
L:R	20:1	20:1	20:1	20:1	20:1	20:1

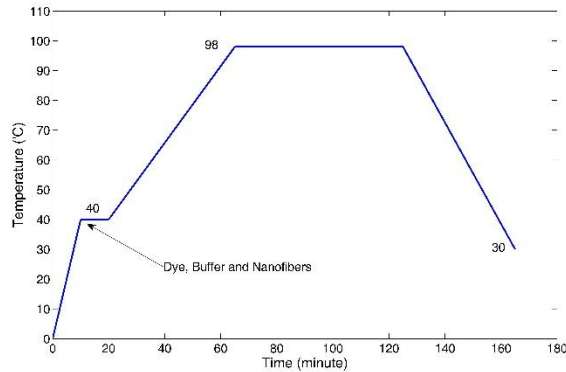


Figure 1. Dyeing diagram of nylon

First dye, buffer (a mixture of acetic acid and ammonium sulphate) and nanofiber web were added to dye bath at 40 °C and pH=4. Then bath was heated to 98 °C in 45 minutes. Dyeing process was performed at this temperature for 60 minutes. Finally samples were cooled to ambient temperature and nanofiber mats were collected for further tests.

2.3. Dyeing of nanofiber webs

Specific adsorption coefficient of this dye was measured using adsorption of known concentrations. Cintra 10 transmittance UV-Visible spectrophotometer was used for measuring

Cibacron violet TB-D (reactive violet 3) was used for nylon 6 nanofiber dyeing. Dyeing performed at different initial dye concentration according to table 2 and based on dyeing diagram (Figure 1).

adsorption coefficient. Then initial and final dye concentrations at different bath were measured according to beer-lambert law. Exhaustion measured using Equation 1:

$$\%E = \frac{A_0 - A_1}{A_0} \times 100 \quad (1)$$

Where A_0 and A_1 are adsorption of dye solution before and after dyeing procedure respectively. High washing fastness is the main advantage for reactive dyes due to introduction of covalent bond between dye and polymer chain. But some of dye molecules are absorbed to fabric because of ionic and Van der Waals bonds. The amount of covalent bonded dyes to overall absorbed dye is known as dye fixation factor. Samples were boiled in 150 ml pyridine solution (20%) for 30 minutes to remove unreacted dye molecules. This factor calculated using Equation 2 and 3.

$$K/S = \frac{(1-R)^2}{R^2} \quad (2)$$

$$\%F = \frac{(K/S)_2}{(K/S)_1} \times 100 \quad (3)$$

Where $(K/S)_1$ and $(K/S)_2$ are calculated using Xrite reflectance spectrophotometer before and after pyridine treatment.

2.4. Scanning electron microscopy (SEM)

Electrospun and dyed nanofibers were selected for SEM imaging. First samples were prepared by gold coating to make their surfaces conductive. This step performed by Bal-Tec sputter coater. Then SEM images recorded using Philips XL30.

3- RESULTS AND DISCUSSION

3.1. Electrospinning

Results obtained from SEM images show that 10% polymer solution is not appropriate for electrospinning. In this condition polymer solution

viscosity is not enough to produce continuous flow which leads to reduction in fiber diameter and bead formation. Polymer entanglement is increased and viscosity is raised at higher polymer solution concentration which results in more stable jet and better nanofibers. Electrospun nanofibers using 15% polymer solution were better in quality compared to 10% sample due to better rheological properties of polymer solution; but some beads observed in SEM images. The best nanofiber produced with 20% polymer solution without any bead which has been showed in Figure 2. Diameter distribution for electrospun nanofiber using 20% polymer solution at 0.5 ml/hour feeding rate is shown in figure 3. Fiber distribution was between 40-220 nm with maximum at 120-140 nm and the average diameter for fibers was 121 nm.

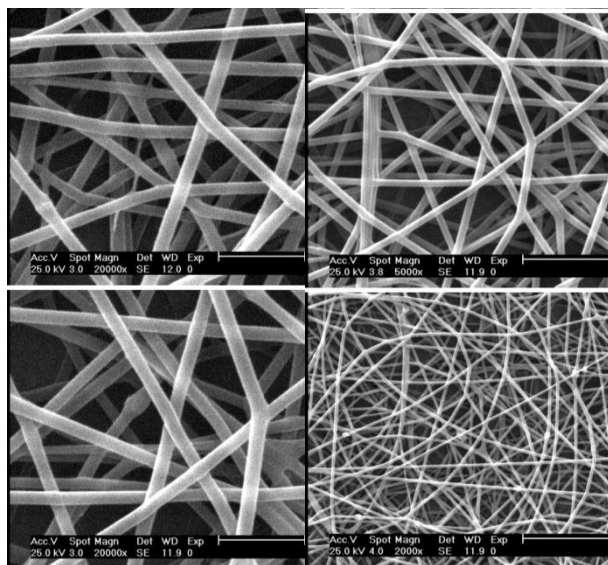


Figure 2. SEM image of nanofibers obtained from electrospun 20% solution

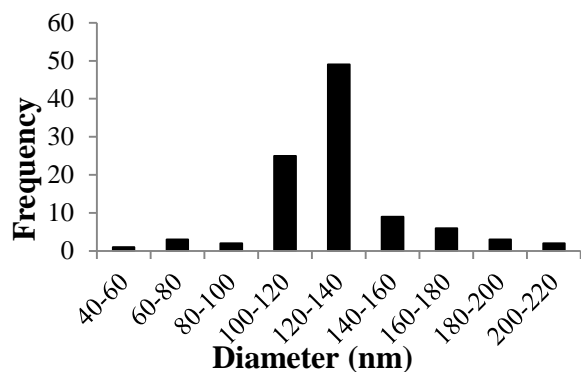


Figure 3. Fiber diameter distribution for nanofibers obtained from electrospun 20% solution

3-2- Dyeability properties of nanofiber

Only a part of reactive dyes establish covalent bonds with nylon amine groups during the dyeing procedure and the rest are absorbed by ionic and Van de Waals bonds. Reactive dyes with trichlorotriazine functional groups can react with nylon amine groups toward nucleophilic substitution (SN₂). This reaction has been showed in Figure 4.

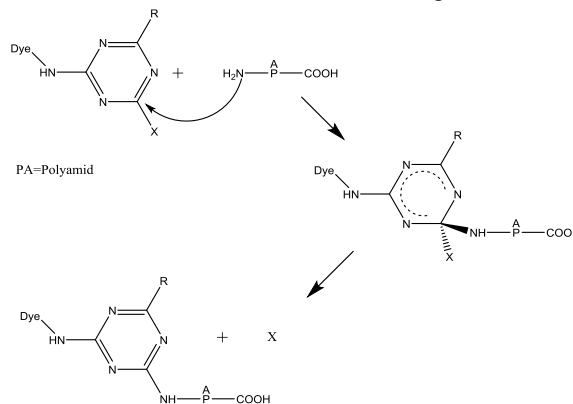


Figure 4. Reaction mechanism between reactive dye and nylon amine group

Nylon 6 dyeing with commercial reactive dyes have been investigated widely and pH=4 have been reported as the optimal condition. In this pH amine groups in nylon is converted to its cationic format (PA-NH₃⁺) which is an absorbing site for dyes with sulfonic functional groups (Dye-SO₃⁻). Also, there are some unprotonated amine groups in nylon polymer chain, since this reaction is an equilibrium one (Figure 5). Therefore, the chemical reaction can perform between dye and nylon.

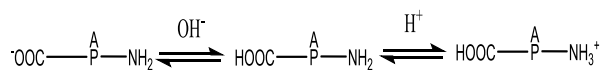


Figure 5. Equilibrium reaction of nylon at different pH

Dye exhaustion, (K/S) and fixation factor calculated according to the experimental which its results are reported in table 2. Also exhaustion plot at different dye concentration is shown in figure 6. According to results, exhaustion for nanofiber is relatively low compared with nylon fiber dyeing. This phenomenon happens due to the small size of the pores in the

nanofibers. When first dyes are absorbed to nanofibers, these sites are blocked and doesn't let other dyes absorbed by these sites. Also the repulsion between adsorbed surface dyes may cause low exhaustion by nanofibers. It can be seen that exhaustion is decreased with increase in initial dye concentration which have been reported in previous researches.

Table 2. Calculated amounts for exhaustion (E %), (K/S) before and after pyridine treatment and the fixation factor (F %) at different initial dye concentration

Initial dye concentration	0.05	0.10	0.20	0.50	0.80	1.00
E (%)	6.28	6.03	5.83	4.46	3.23	2.55
(K/S) ₁	0.08	0.16	0.23	0.50	0.65	0.86
(K/S) ₂	0.03	0.06	0.09	0.21	0.29	0.39
F (%)	33	36	39	42	45	45

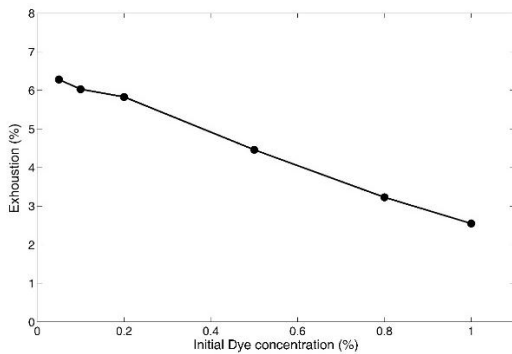


Figure 6. Exhaustion at different initial dye concentration

The plots of (K/S) after dyeing and pyridine treatment at different dye concentrations have been reported in figure 7. These results show that (K/S) increased slightly at higher dye concentration which is similar to results reported by Li et. al. This happens due to high surface area of nanofibers which leads to high surface reflection. Also (K/S) of dyed nanofibers is decreased after pyridine treatment, due

to removal of unreacted dyes.

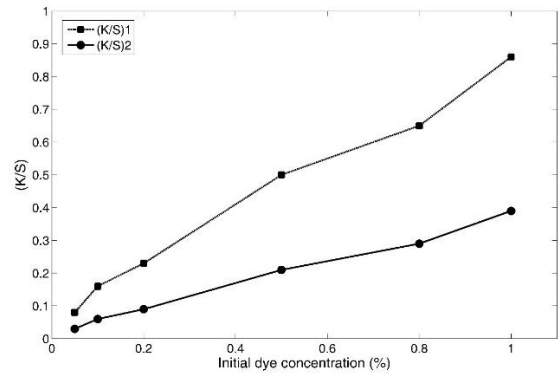


Figure 7. (K/S) values for different initial dye concentration before and after pyridine treatment

Fixation factor in different initial dye concentration is reported in Figure 8. According to these results fixation is relatively increase at higher dye concentrations. This phenomena happens because of higher amount of dye available for chemical reaction and covalent bonding.

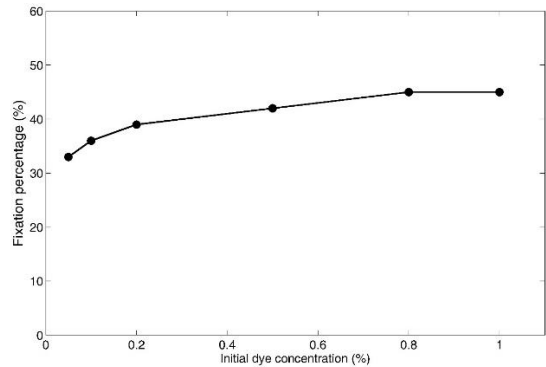


Figure 8. Fixation factor for different initial dye concentration

Results obtained from SEM images (Figure 9) shows that significant changes in morphology has happened. Fibers shrunk and stuck after dyeing process. Also there are some particles in surface of nanofibers which are surficial dyes which are absorbed by Van der Waals forces.

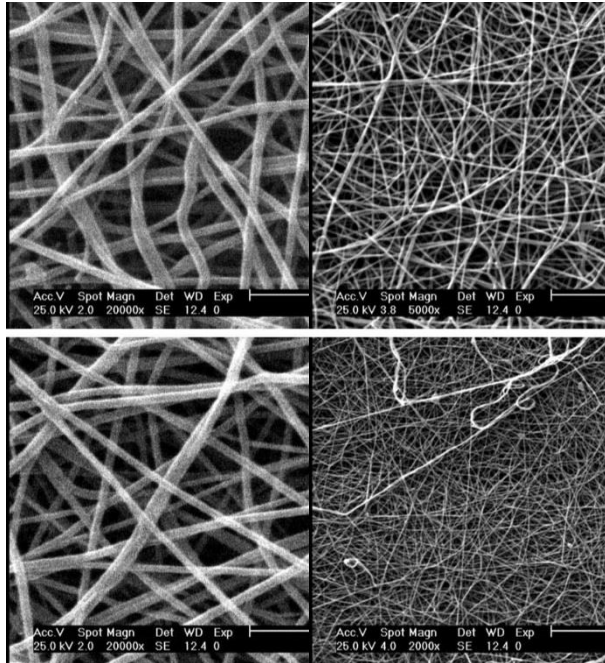


Figure 9. SEM images of nanofibers after dyeing process

Exhaustion and fixation factor results declares that nylon 6 nanofibers are dyeable. The low amount of exhaustion and fixed dyes can be related to following reasons.

- 1- High solubility of dye because of presence of various sulfonic acid functional groups in dye structure which results in less affinity to nylon 6 nanofibers.
- 2- High electrostatic repulsion between dye (Dye-SO₃⁻) and nylon 6 (-COO⁻)
- 3- Dye agglomeration in dyeing bath
- 4- Web structure of nanofibers which leads to high free space.
- 5- Oxidation of amine functional groups in nylon during the electrospinning process.

- 6- Large chemical structure of dyes which alters the penetration of dyes into the nanofibers.
- 7- Porous structure of nanofibers which shrinks during dyeing process and prohibits further dye adsorption

4- CONCLUSION

In this article nylon 6 nanofibers were successfully produced by electrospinning of 20% polymer solution. Produced nanofibers was smooth without any bead and the average diameter of nanofibers were 121nm. Then nanofibrous mats were dyed using reactive violet 3 dye at different concentrations. Obtained results show that dye exhaustion decreased with increase in dye bath concentration, on the other hand (K/S) and fixation factor increased gradually. It can be concluded that according to nanofibers are dyeable based on proposed method.

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