



Short communication

Dyeing of electrospun nylon 6 nanofibers with reactive dyes using electron beam irradiation

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ABSTRACT

Nylon 6 nanofibers were prepared by using an electrospinning technique. The dyeing behavior of nylon 6 nanofibers which were dyed with reactive dyes, vinylsulphone type-Remazol Red RR, by electron beam irradiation (EBI) has been investigated. Electrospun nylon 6 nanofibers were irradiated varying EBI doses of 10, 20, 30, 40, 50, 100 kGy and their *K/S* values, Lab values and dyeing equilibrium were observed. No additives and toxic reagents were used for dyeing nylon 6 nanofibers with reactive dyes using radiation. Compared with conventional dyeing method, it is found that irradiated dyeing of nylon 6 nanofibers with reactive dyes has improved not only the color strength and fiber-shrink phenomenon but also the scission reactions of functional groups of Remazol Red RR at EBI dose greater than 10 kGy. This finding suggests that the dyeing by EBI significantly influence the waste-water treatment in a green way. The resulting dyed nylon 6 nanofibers were characterized using scanning electron microscopy (SEM) and UV-Visible spectroscopy.

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Introduction

Dyeing, bleaching, printing and finishing processes generate great amount of wastewater and require large water consumption [1]. Reactive dyes have been popular in dyeing industries of cellulose fibers because of their bright and firm shade. They have wide range of inexpensive brilliant colors with excellent washing fastness. In cotton and wool, as active sites of fiber, hydroxyl group of reactive dyes form covalent bonds with fiber [2–4]. In nylon, terminal amino end groups facilitate dyeing with anionic reactive dyes. Fiber reactive electrophilic groups of reactive dyes, especially chlorotriazines and vinylsulphones form covalent bonds with the nucleophilic amino end groups of nylon during dyeing [5–7]. The presence of water solubilizing sulfonate groups (SO₃⁻) in reactive dyes makes them anionic in nature [2,6]. Monoazo type azo-reactive

dye, Remazol Red RR (Figure S1), possesses vinylsulphonyl and non-halogen triazine reactive groups [8].

Dyeing of 1 kg of cotton with reactive dyes needs about 150 L of water, 0.8 kg NaCl, and about 50 g of dyestuff. More than 80,000 tons of reactive dyes are produced worldwide each year [9], pollution of textile wastewater containing polyaromatic structures with high molecular weight of nitrogen, sulfur and metals in reactive dyes causes serious treatment problems which should be treated by an activated sludge method or any treatment of biological, chemical and physical methods [10].

It is known that reactive dyes were developed for cellulosic fibers and acid dyes are commonly used on nylon. In order to improve the wet fastness properties of nylon dyed with acid dyes, reactive dyes have been developed and covalent bonds which were formed between reactive dyes and the amino groups of nylon can be fixed at the boil to nylon and needed for an alkaline fixation step.

Nanofibers have attracted much research interest and have a wide range of applications due to their outstanding physical, chemical and biological properties [2]. Nanofibers have high porosity due to their small pore sizes between adjacent nanofibers

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and therefore, they show improved breathability [2,11,12]. The thermal insulation, antibacterial performance, mold properties, comfort properties, and durability of nanofibers were reported [2,13–15].

Nylon 6 is a biodegradable and biocompatible semi-crystalline synthetic polymer. It has a wide range of applications in various industrial, especially, in textile and biomedical fields due to its low cost and very good mechanical strength, high chemical resistance, strong thermal stability, and superior fiber forming ability [16–18].

EBI is a well-known eco-friendly technique and it has a wide range of industrial applications. EBI introduces functional reactive groups such as, $-OH$, $-COOH$, $-COO^-$ on the polymer surfaces during irradiation. EBI significantly improves the dyeability of fabrics and EBI dose has great influence on dyeing behavior of fabrics. EBI technique has many advantages over thermal process, it has no solvent release, and it reduces energy consumption [19–21].

Electrospinning is an effective technique to produce polymer nanofibers with excellent structures and properties. These nanofibers have a wide range of applications such as separation filters, sensors, protective clothing, catalysis reaction, wound dressing materials, tissue scaffolds, drug delivery, etc. [16,18,22–24].

In this paper we have dyed electrospun nylon 6 nanofibers with reactive dye, Remazol Red RR by Electron Beam Irradiation (EBI) technique. The dyed nanofibers were characterized by scanning electron microscopy (SEM) and UV–Vis spectroscopy. The dyeing behavior of nylon-6 nanofibers was measured by the color strength (K/S), $CIEL^*a^*b^*$, and $CIELC^*h^o$ values. The objectives of this study were to produce eco-friendly dyeing and simultaneous wastewater purification effects.

Experimental

Materials

All the chemicals were used as received without further purifications. Nylon 6 pellets (KN120 grade) were purchased from Kolon Industries, South Korea, and formic acid (analytical grade, 85%) was obtained from Showa, Japan. Remazol Red RR (reactive dyes, vinylsulphone type) was purchased from DyStar, Germany. Doubly distilled water (DI water) was used in dyeing process.

Electrospinning

22 wt.% of nylon 6 pellets was dissolved in 85% formic acid under magnetic stirring overnight at room temperature to obtain a uniform mixture for electrospinning. The polymer solution was electrospun at 18 kV at a flow rate of 0.8 mL/h and the tip-to-collector distance was kept at 15 cm [25]. After vacuum-drying for 24 h, all of the nanofibers were used for further analysis. The schematic representation of the electrospinning set-up is shown in Fig. 1.

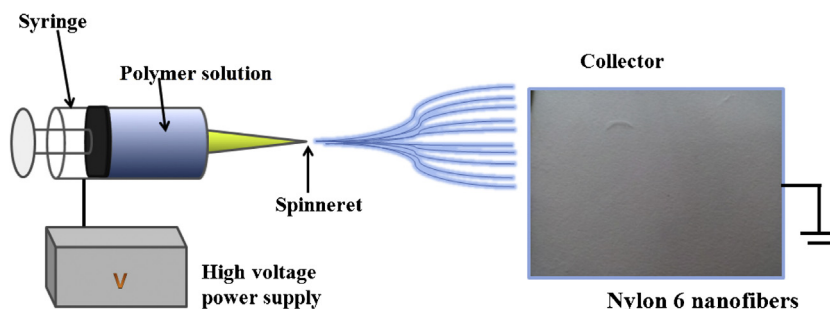


Fig. 1. Schematic representation of the electrospinning set-up.

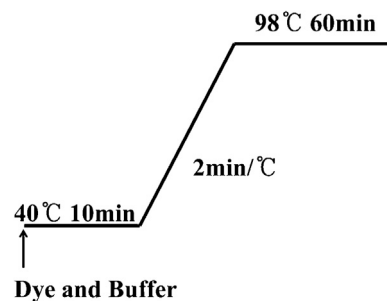


Fig. 2. Used conventional dyeing profile.

Dyeing

Electrospun nylon 6 nanofibers were put in aqueous solution of 2% o.w.f (on the weight of fabric) Remazol Red RR and then, irradiated with an electron-beam at doses of 10–100 kGy; the use of salts and toxic reagents are not necessary when nylon 6 were dyed using radiation. The irradiation of dyeing process was performed by a conveyor type scanned electron beam accelerator with beam energy of 2.5 MeV, beam current of 8.5 mA, irradiation width of 110 cm, conveyor velocity of 10 m/min, and dose rate of 6.67 kGy/s (roller type handling system, EBTECH Co., Ltd., Korea) at room temperature in an air atmosphere. With respect to the radiation dose unit, 1 kilogray (kGy) equals the absorption of 1 kilojoule (kJ) of material. The dose in kilogray is equal to the specific energy (SE) requirement in kilojoules per kilogram (kJ/kg) [21]:

$$SE = D \text{ (kJ/kg)} \quad (1)$$

Fig. 2 depicts the conventional dyeing process used in this work [7]. Nylon 6 nanofibers were placed in the stainless steel dye pot and appropriate buffer solution (McIlvaine buffers used) was added; dyeing was carried out using 2% o.w.f Remazol Red RR at pH 6.

After dyeing, the samples were removed and rinsed in cold tap water for 5 min as much excess liquor as possible and dried in air at room temperature for 24 h.

Characterizations

A standard procedure was used to create samples for SEM measurements. Samples were coated with platinum (ion-sputter, Hitachi E-1010, Japan) under vacuum, and then they were used to investigate the morphology of the electrospun nylon 6 nanofibers before and after dyeing by using scanning electron microscopy (SEM, Jeol JSM-5900) with the accelerating voltage of 15 kV. The UV–Vis spectra were obtained from a UV-Visible spectrometer (Lambda 900, Perkin-Elmer, USA) in the range of 400–700 nm. The

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