PREPARATION OF PHOTOCHROMIC THERMOPLASTIC POLYURETHANE FIBERS BY ELECTROSPINNING

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Abstract: *In this study, photochromic nanofibers were prepared by electrospinning of the spirooxazine based photochromic dyes loaded thermoplastic polyurethane (TPU) solutions. The morphology of the electrospun fibers were characterized by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The obtained phtochromic nanofiber mats were tested by means of UPF (Ultraviolet Protection Factor) and ΔE color difference after UV irradiation. Photochromic nanofiber mats changed rapidly and reversibly from colorless form to colored state when irradiated by ultraviolet light. Photochromic nanofibers also showed UPF values higher than 50.*
Keywords: *Photochromic dyes, nanofiber, electrospinning, ultraviolet protection.*

1. Introduction

Photochromic dyes undergo a reversible structural and color changing between two forms by the absorption of electromagnetic radiation, where the two forms have different absorption spectra (Figure 1). These dyes can be used to create attention-grabbing effects involving the sudden generation or fading of color in response to ultraviolet (UV) light. Photochromic dyes also provide UV protection due to their absorption of UV radiation to convert it to less harmful energy by change of cis–trans isomerization or intermolecular proton transfer [1-3].

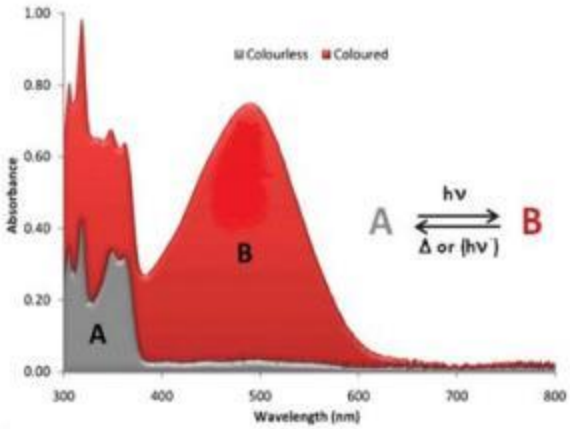

Figure 1: UV-vis-spectra of a photochromic material before (A) and after (B) UV irradiation [4]

In this study, photochromic dye was incorporated into the TPU nanofibers by electrospinning. The principle of electrospinning process is to use electrostatic force as the main driving power for nanofiber formation (Figure 2) [5]. One of the obvious advantages of the electrospinning process is highly porous structure of electrospun nanofiber mats which exhibit much greater surface area and possibility of functionalization [6, 7]. These properties are useful for the applications in many fields, such as sensors, wound dressing materials, nano-composites, artificial blood vessels and many other applications [8].

Electrospun nanofiber mats have been produced from a wide variety of polymers and their blends. Among them, thermoplastic polyurethanes (TPU) are a widely used class of polymer, which have good biocompatibility and high mechanical properties and can be easily electrospun. Therefore electrospun TPU nanofibers are of interest in terms of biomedical applications [9, 10]. Their biocompatibility, non-toxicity, toughness and functionality have led to the widespread use of TPUs in implantable devices (vascular grafts, pacemaker leads, blood bags, bladders and artificial heart valves) and medical applications [11,12].

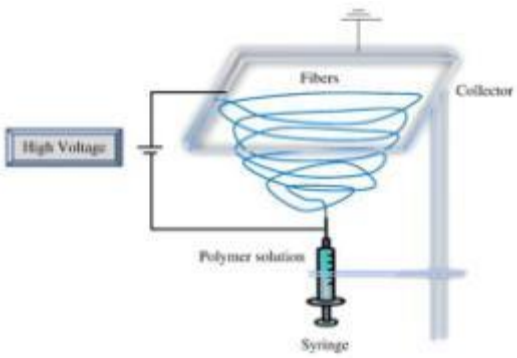

Figure 2: Schematic diagram of electrospinning apparatus [13]

Application of photochromic dyes by electrospinning process provide advantages such as increasing sensitivity of photochromic dyes or reducing the time necessary for photochromic dye to respond to the UV irradiation due to large surface area of the electrospun mats. Photochromic electrospun nanofibers could find applications in areas such as optical sensors, optical data storage devices and processing media [14].

The aim of the study was to develop spirooxazine based photochromic dye incorporated electrospun polymeric matrix. The morphology, color change with UV irradiation and UV protection properties of neat and photochromic dye loaded mats were investigated.

2. Material and Method

2.1 Materials

Spirooxazine based photochromic dye was purchased from Polychrom Co. Ltd. and used as received. TPU (Pellethane 2103-80AE, based on 4,4-methylene bisphenylene isocyanate, polytetramethyleneoxide and 1,4 butanediol) was received from Velox (Lubrizol Advanced Materials). N,N-Dymetilformamid (DMF) was purchased from Sigma Aldrich.

2.2 Electrospinning process

10% (w/v) of TPU stock solutions was prepared by dissolving TPU granules in DMF at room temperature for 24h. Photochromic dye was added into the TPU solution under constant stirring. Photochromic dye was loaded at 5%, 10% and 20% (w/w) (based on the weight of TPU granules).

Electrospinning of the solutions was carried out by connecting the emitting electrode of positive polarity from a high-voltage DC power supply (Simco, MP Series CM5 30 P, Charging Generator Output 30 kV DC) to the solutions contained in a standard 10 ml syringe, the open end of which was attached with 2.5 cm long 22 gauge flat-tipped stainless steel needle used as a nozzle, and the grounding electrode to a stationary rectangular metal collector covered by a piece of aluminum foil used as the fiber collecting area.

The electrostatic field strength was fixed at 13 kV/20 cm. The complete electrospinning apparatus was enclosed in a glass box and the electrospinning of the nanofibers was carried out at room temperature. The photochromic dye-loaded electrospun fibers collection time was about 7 h. The feed rate of the solutions was controlled to about 1 ml h^{-1} using a syringe pump for stable electrospinning jet. Samples were dried to remove the residual solvent at room temperature for a day.

2.3 Characterization

The morphological appearance of electrospun mats were obtained using by a scanning electron microscope (SEM; FEI Quanta 250FEG). All samples were sputtered with a thin layer of gold under vacuum by EMITECH K550X ion sputtering device before assessment.

FTIR spectra were obtained using a Perkin Elmer FTIR spectrometer in a spectral range from 650 to 4000 cm^{-1} with a resolution of 1 cm^{-1}.

UV protection factor (UPF) values of the samples were measured by UV Transmittance Analyzer, UV-2000F (Labsphere Co. USA) according to standard AS/NZ 4399:1996.

Color measurements were carried out according to the CIELab color space using a portable spectrophotometer (ColorLite Sph 870) in a UV cabinet (UVP-UV2/PCR) with a UV light bulb (USHIO G25T8 UVA type bulb, 25 W, maximum wavelength 365 nm). The samples were placed into the UV cabinet and irradiated with UV light for 2 min. After irradiation, the UV light was switched off and color measurement was carried out as immediately as possible (~3 s). The color value of neat electrospun mats was regarded as the standard. Color build-up during sample irradiation was determined by the difference between the standard and irradiated colored samples by using ΔE (color difference) and *L** (lightness/darkness of the color) values.

3. Results

The SEM images of both neat and photochromic dye loaded electrospun mats are displayed in Figure 3. It can be seen from the images that the TPU nanofibers are bead-free; and the incorporation of photochromic dyes in TPU polymer solution did not affect the smooth morphology of the resulting electrospun nanofibers. Based on these SEM images, the average diameter of the neat TPU and photochromic dye loaded as-spun fibers was in the range of approximately 700nm to 900 nm.

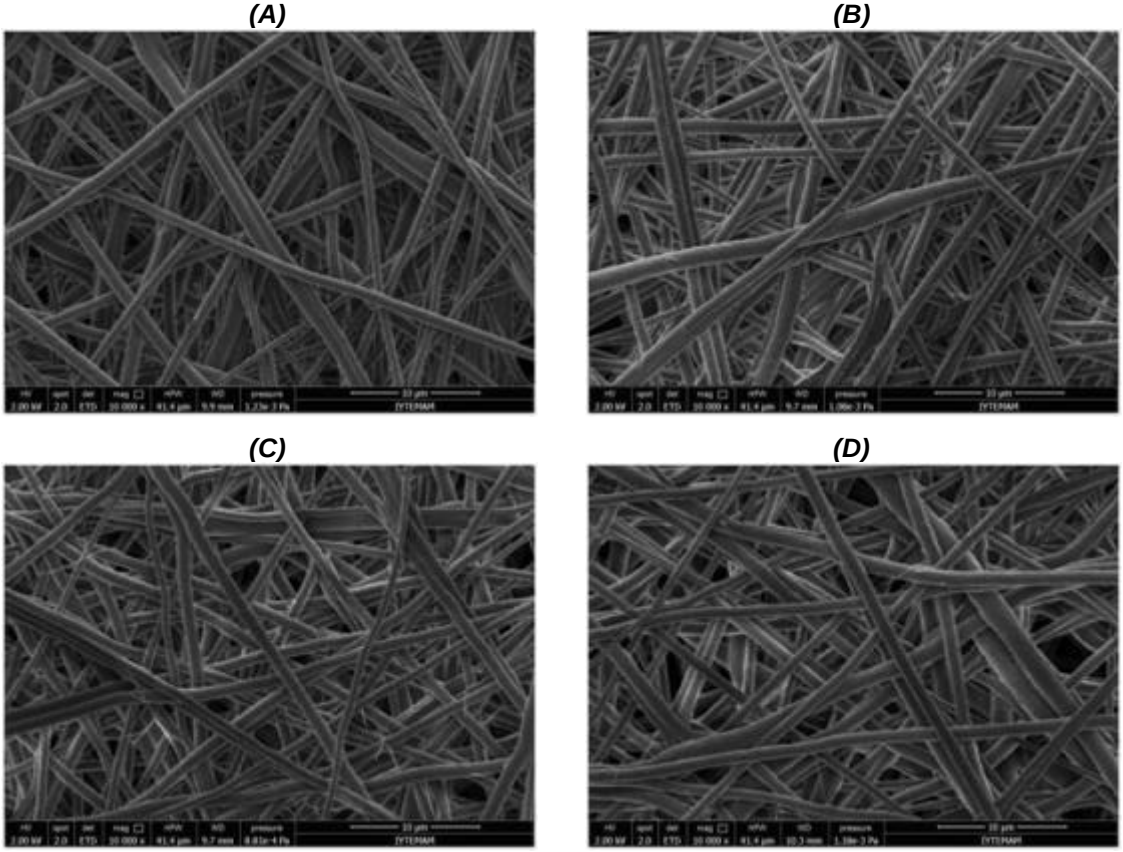

Figure 3: SEM images of (A) neat TPU nanofibers, (B) 5% photochromic dye loaded TPU nanofibers, (C) 10% photochromic dye loaded TPU nanofibers and (D) 20% photochromic dye loaded TPU nanofibers.

The interaction between TPU nanofibers and photochromic dye was investigated through FTIR spectroscopy. Figure 4 illustrates the FTIR spectra of TPU nanofibers and photochromic dye loaded TPU nanofibers. The absorption band at 1036 cm^{-1} correspond to the asymmetric stretching vibration of C_{spiro}-O bond of oxazine ring in the photochromic dye loaded nanofibers.

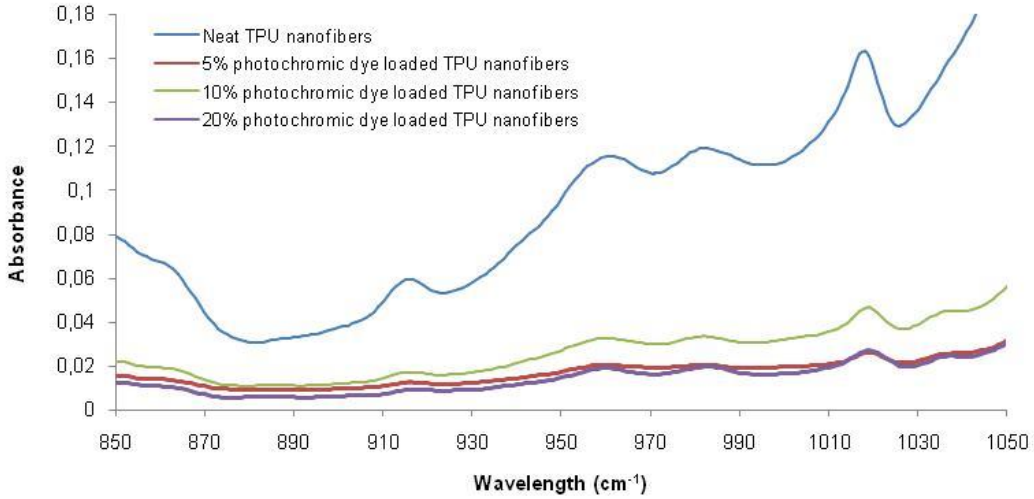

Figure 4: FTIR spectra of neat TPU nanofibers, 5% photochromic dye loaded TPU nanofibers, 10% photochromic dye loaded TPU nanofibers and 20% photochromic dye loaded TPU nanofibers.

UPF values for the samples were also measured since photochromic dye has UV absorption property. Both neat and photochromic dye loaded TPU nanofiber mats showed excellent UV protection properties with 50+ UPF values.

All samples were colorless (white) in the absence of irradiation. A reversible purple color developed after irradiation (Figure 5).

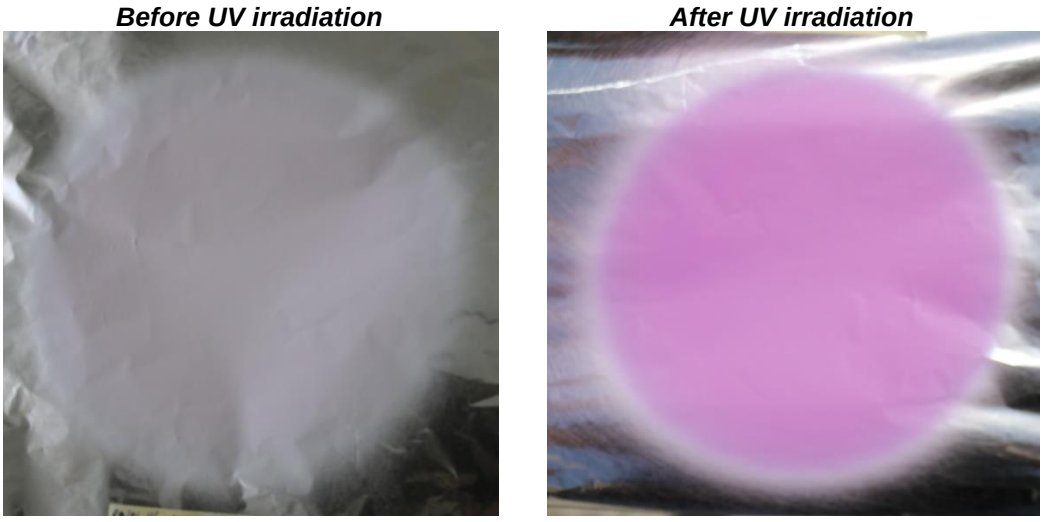

Figure 5: Images of the samples before and after UV irradiation

The *L** values of irradiated photochromic dye loaded nanofiber mats were lower than those of neat nanofiber mats, which confirmed the color build-up under irradiation (Table 1). It was shown that the photochromic dye concentration in the electrospun nanofibers did not have a significant effect on the color values (*L**, ΔE and Remission% values).

Table 1: Color values of the electrospun mats

Samples	*L**	ΔE	R% (560 nm)
Neat TPU nanofibers	101,40	--	--
5% photochromic dye loaded TPU nanofibers	84,54	24,91	54,15
10% photochromic dye loaded TPU nanofibers	83,47	24,58	52,74
20% photochromic dye loaded TPU nanofibers	84,55	23,23	54,99

4. Conclusion

Mats of TPU nanofibers containing spirooxazine based photochromic dye were successfully prepared by electrospinning from 10% w/v TPU solutions in DMF. The results from SEM and FTIR demonstrated the incorporation of the photochromic dye with TPU fibers. Photochromic dye loaded mats exhibited excellent UV protection and changed rapidly and reversibly from colorless form to colored state when irradiated by ultraviolet light. However photochromic dye concentration in the electrospun nanofibers did not affect the color values of the mats. Considering these results, investigation of the fatigue resistance properties of photochromic dye loaded TPU electrospun fibers has been planned to be the further step of the present contribution.

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