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Preliminary exhaustion studies of spiroxazine dyes on polyamide fibers and their photochromic properties

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Abstract

The photosensitive spiroxazine dyes have been prepared to examine the practical dyeing feasibilities and behaviors. An interest on direct spiroxazine exhaustion to the polyamide substrates and its photochromism effects within the fiber molecules were investigated. The exhaustion (%) of the spiroxazine dyeings increased with increasing application temperatures. Successful spiroxazine exhaustion within the fiber molecules was determined from the photographs of the photochromism of the dyed substrates. When UV irradiation was subjected to the spiroxazine dyeings, the absorption spectra generated by photochromic reaction were clearly observed and its reversible decoloration behaviors responded rapidly in the dark.

Keywords: Spiroxazine; Photochromism; Polyamide; Exhaustion; UV irradiation

1. Introduction

A functional finishing introducing photosensitive color-producing property is quite an attractive research subject in many application fields for coloration purposes. Especially, fiber substrates, the most widely used materials in our circumstances, enjoy considerable usage in many coloration areas using dyeing and printing methods. In order to apply insoluble solid particles to the fiber substrates, in general, the most commonly used applications have been carried out using solution dyeing and microcapsule binding methods [1–3]. In solution dyeing method, the dyes are added at the extrusion state so that the fiber substrates have a consistent dye solid throughout. Microcapsules containing a color-producing material or a developer have been prepared with resin by in situ polymerization method. However, in solution dyeing, the excessive dyes added to polymer dope could make a problem during spinning process. For microcapsule application, the following factors are carefully attended as the characteristics required for microcapsules. The color contents must be held in microcapsules stably until it is required. Also, the binding microcapsules within the fiber substrates can impart a harsh handle to the treated substrates due to the usage of binder. In this context, the direct application of colorants to the substrates using exhaustion method is commonly considered as the most convenient way.

In general, the application of dye types, and indeed all dyes for substrates, relies on the reciprocal reaction

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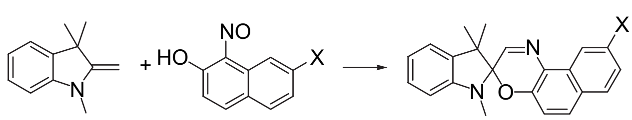
characteristics between the substrates and dye molecules [4,5]. Although polyamide fibers have been dyed dominantly using ionic dyes for textile purposes and over the years a number of studies had been carried out to examine the exhaustion properties, little attention has been focused on the application of non-textile dye such as spiroxazine on to polyamide fibers. This approach could provide interesting photochromic reaction properties of spiroxazine dyes within the fiber substrates. Thus, in this experiment, an interest on spiroxazine exhaustion and its photochromism effects on the polyamide fibers were attended. The three spiroxazine dyes were prepared and then the preliminary exhaustion behaviors of spiroxazine dyes were investigated.

2. Experimental

Melting points were determined using an Electrothermal IA 900. Elemental analyses were recorded on a Carlo Elba Model 1106 analyzer. Mass analysis was recorded using a Shimadzu QP-1000 spectrometer with an electron energy of 70 eV and direct sample introduction.

2.1. Materials

The spiroxazine dyes **3a–c** were prepared using previously described procedures [6,7]. Polyamide filament taffeta (warp 75 denier/yarn 107 yarns/in., weft 75 denier/yarn 97 yarns/in., 70 ± 5 g/m^2) was used in this experiment. All other chemicals used were laboratory grade reagents.



1 **2a**, X=H **2b**, X=OH **2c**, X=OCH$_3$ **3a**, X=H **3b**, X=OH **3c**, X=OCH$_3$

2.2. Exhaustion

Polyamide fiber was dyed in sealed, stainless steel dye pots of 120 cm^3 capacity in a laboratory-scale dyeing machine (ACE-6000T). Samples were placed in a 40 °C dyebath of 50:1. After 10 min, the temperature was raised until reaching the range of temperatures of 80–120 °C. At these temperatures, the exhaustion of spiroxazine dyes was continued for 1 h. At the end of exhaustion, the dyed samples were removed, rinsed thoroughly in tap water and allowed to dry in the open air.

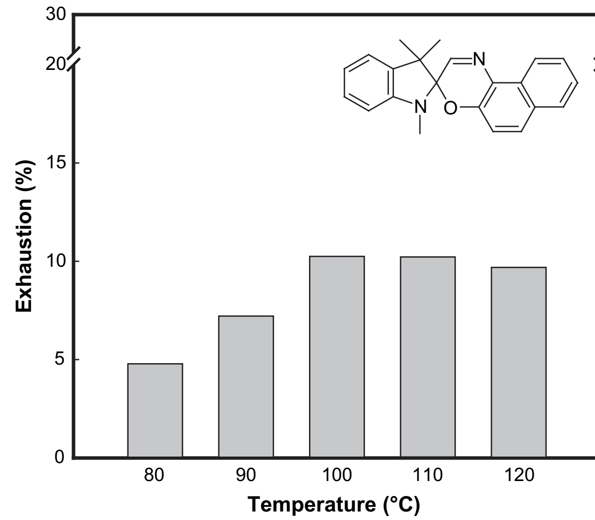


Fig. 1. Effect of temperatures on exhaustion with spiroxazine dye **3a**.

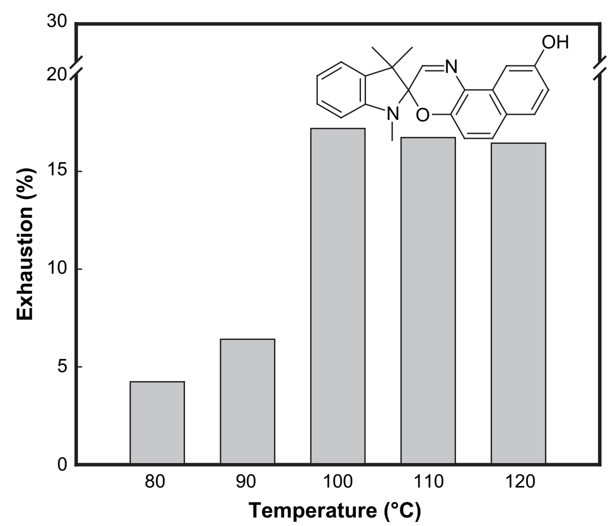


Fig. 2. Effect of temperatures on exhaustion with spiroxazine dye **3b**.

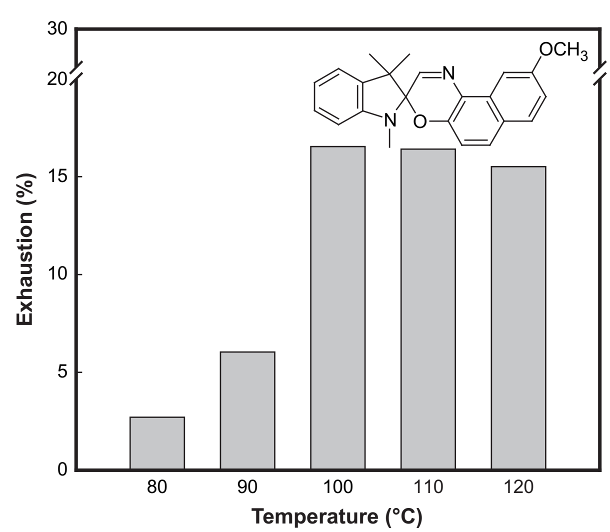


Fig. 3. Effect of temperatures on exhaustion with spiroxazine dye **3c**.

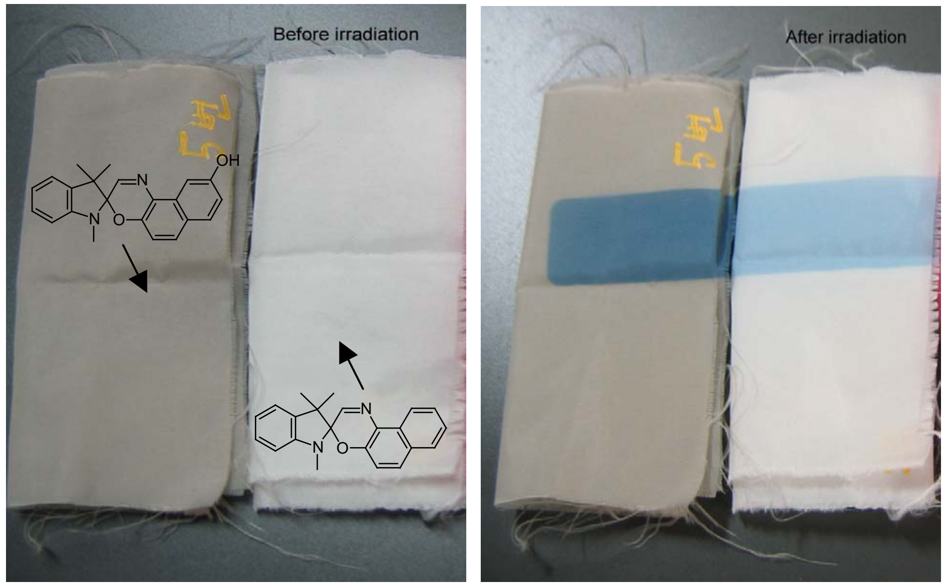


Fig. 4. Photographs of photochromism behavior on polyamide substrates using spiroxazine.

2.3. Absorbance measurement

Absorbance of spiroxazine dyeings was determined using a *Datacolor SF 600 plus* spectrophotometer interfaced to a PC.

3. Results and discussion

3.1. Effect of exhaustion temperature

The spiroxazine dyes **3a–c** are generally prepared by condensing Fisher's base, **1**, with various types of nitrosonaphthols, **2a–c**.

In order to examine the effect of temperatures on exhaustion behaviors, polyamide fibers were dyed with three spiroxazine dyes at various temperatures (80–120 °C). The 6% owf of spiroxazines was used for this work. Employed exhaustion method was followed as mentioned above. Figs. 1–3 show the exhaustion (%) of spiroxazine dyeings on polyamide fibers. Generally, the exhaustion (%) of the dyeings increased with increasing application temperatures. The adsorption was more favorable at higher temperature than at lower temperature. Within the lower range of dyeing temperatures (80–90 °C), these conditions had little effect on the spiroxazine dye uptake by the substrates. Especially, higher dyeing exhaustions were obtained in the range of temperatures 100–110 °C.

However, the exhaustion (%) values of three spiroxazine dyes were very low. This exhaustion behavior was attributed to the low diffusional power of spiroxazine dyes within the higher crystalline structure of fiber molecules and the weak attractive forces between dyes and substrates. The observed results indicate that the dye exhaustion of spiroxazine dyeings which increased with increasing application temperatures was attributed to the higher kinetic energy of the spiroxazine molecules, the greater diffusional power within the polymer substrates and the higher fiber swelling effect. In this context, it is thought that in terms of exhaustion temperature, the adsorption behavior of spiroxazine on polyamide substrates is following a similar dyeing mechanism as commercial non-ionic dyes, which involved a high-pressure and a high-temperature dyeing system. The result of dye exhaustion within the fiber molecules can be also supported from the photographs of the photochromism of the dyed substrates (Fig. 4). These photographs were very useful to determine the spiroxazine penetration within the substrates and to confirm the photochromic reaction.

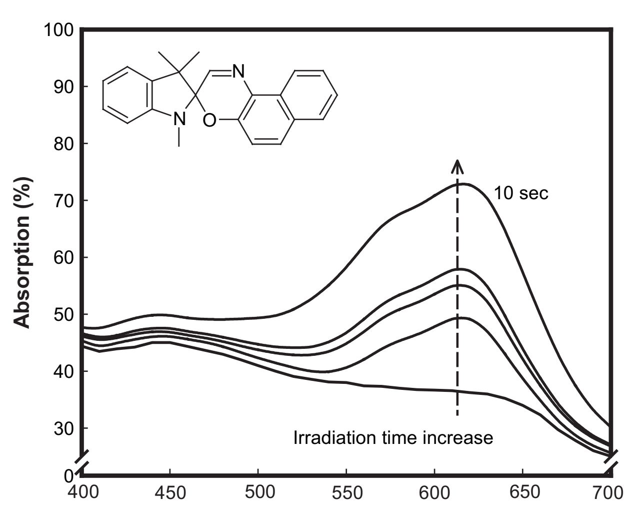


Fig. 5. Visible spectral changes of spiroxazine dyeing **3a**.

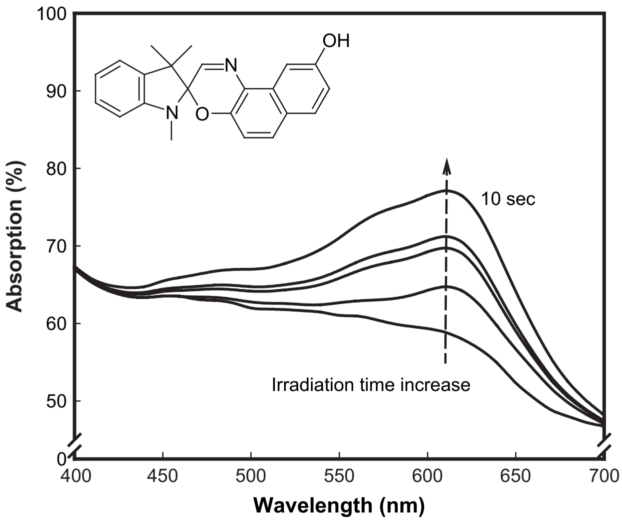


Fig. 6. Visible spectral changes of spiroxazine dyeing **3b**.

3.2. Absorbance of color-produced substrates

The photochromic reaction is caused by the reversible heterocyclic cleavage of the C(spiro)–O bond under UV irradiation, yielding the colored form that can return to the colorless form by ring closure under visible light irradiation or in the dark. Photochromic absorption spectral changes of spiroxazine dyeings on UV irradiation are shown in Figs. 5–7. When UV ray of 365 nm was irradiated to the spiroxazine dyeings, the corresponding absorption properties by photochromic reaction were mainly observed at the range of 610–620 nm from all spiroxazine dyeings and their intensities increased with irradiation time. The increased band is ascribable to the generation of the open merocyanine form resulting from the closed spiro form. This finding can also support the results that exhaustion of the spiroxazine dyes was successfully completed using conventional dyeing method.

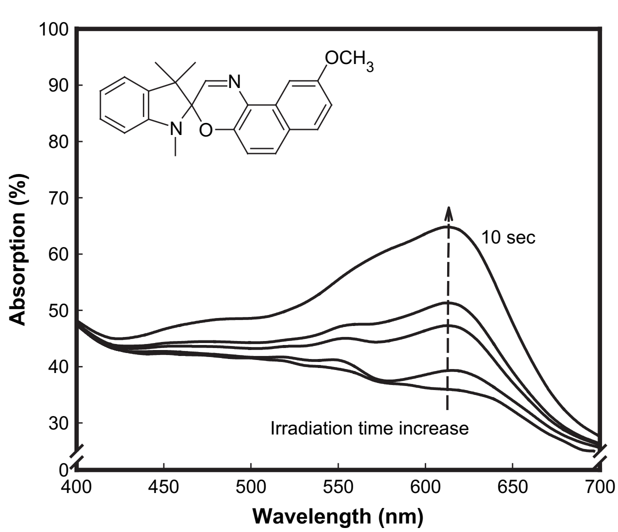


Fig. 7. Visible spectral changes of spiroxazine dyeing **3c**.

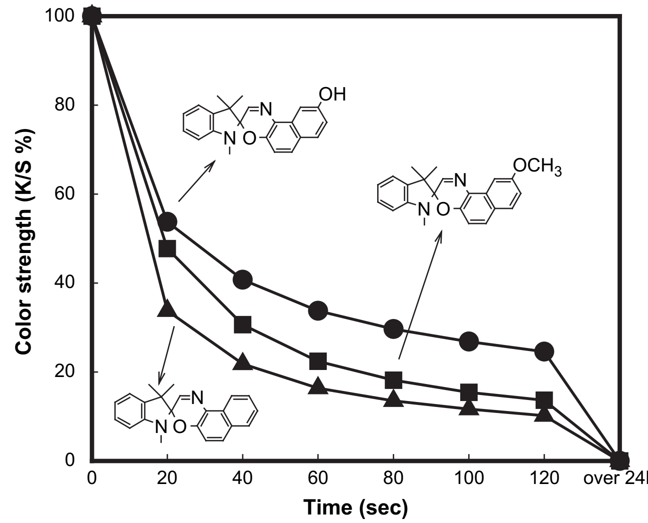


Fig. 8. Decoloration of colored spiroxazine dyeings as a function of time.

3.3. Decoloration

Fig. 8 shows the decoloration (%) behaviors of the photochromic color generated by spiroxazine dyeings according to the time in the dark. Photochromism in spiroxazine compounds generally involves the UV-induced dissociation of the spiro C–O bond and the reversible ring closure reaction. The color-produced photomerocyanine form is usually unstable and returns to the closed form photochemically. The color strength (K/S%) of color-produced spiroxazine dyeings decreased with increasing storage duration. Especially, the decoloration (K/S%) rate decreased by 30–50% within initial 20 s, which could represent the original closed spiro form was rapidly recovered from the open merocyanine form. This observed quick reversible response within the fiber substrates clearly represents the photochromic reaction and leaves a potential possibility in exhaustion method in terms of easy application.

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