한국염색가공학회지
Vol. 21, No. 4, pp.63~67(2009. 8)

〈Research Paper〉

m-Aramid Films in Diverse Coagulants

Ji Young Kim, Ji Won Jung, Sam Soo Kim and Jaewoong Lee[1,†]

School of Textile, Yeungnam University, Gyeongsan, 712-749, Korea
[1]*Kolon Industries, Inc., Gumi, 730-030, Korea*

(Received: July 24, 2009/Revised: August 13, 2009/Accepted: August 18, 2009)

Abstract— *m*-Aramid dissolved in *N,N*-dimethylacetamide (DMAc), were coagulated in different coagulants such as water, methanol, ethanol, propanol and butanol. Various concentrations and temperatures of the coagulants were also used to evaluate dyeing properties of coagulated *m*-aramid films. Field emission scanning electron microscopy (FE-SEM) was employed to investigate the surface morphology of *m*-aramid films. Wide angle X-ray diffraction (WAXD) was conducted in order to measure crystallinity change of *m*-aramid fibers and films. WAXD patterns showed that crystallinity of *m*-aramid fibers was reduced after film formation. In addition, color depth (K/S value) was measured and the results revealed that the film coagulated in water possessed fairly enhanced color depth.

Keywords: *m-aramid film, coagulation, dyeing, coagulant, Nomex, color depth*

1. Introduction

Poly(*m*-phenyleneterephthalamide), *m*-aramid known as Nomex, is a high-performance aromatic polyamide which has wide variety of applications in daily life[1]. Nomex is both thermally and chemically very stable. The amide groups are attached to the phenyl ring at the 1 and 3 positions, and it causes Nomex to a lower modulus and tensile strength and a higher elongation as well as solubility in organic solvents. However, Nomex is difficult to dye because of its highly crystalline structure and very high glass transition temperature[2,3]. In general, dyeing method of Nomex involves high concentrations of a dye carrier in the dyebath, high dyeing temperature, and long dyeing times. Such conditions require substantial amounts of energy to maintain dyeing temperature and for the treatment of waste dye bath. Hence, other research have been studied on the use of solvent[2,4-7] and supercritical fluids[8,9]. However, the additional swelling of *m*-aramid chain using sufficient amount of solvent and dyeing at very high pressure must be required; thus, these methods possess additional limitation caused by the solvent or pressure as well.

The purpose of this study was to evaluate various coagulation parameters including coagulants, concentrations of DMAc, and temperatures in the coagulation bath for the improvement in dye uptake of *m*-aramid under normal dyeing conditions and the effect of these coagulation parameters on the morphological and surface properties of the *m*-aramid films.

2. Experimental

2.1 Materials

N,N-Dimethylacetamide (DMAc) and calcium chloride ($CaCl_2$) were purchased from either Aldrich Chemical Co. or Fisher Scientific Co. They were used as supplied without further purification. The *m*-aramid was a Dupont fiber product. Two commercially available basic dyes, C. I. Basic Red 46 and C. I. Basic Blue 41, were chosen to dye the *m*-aramid films. The molecular structures of the basic dyes are shown in Table 1.

2.2 Preparation of *m*-aramid film

A *m*-aramid fiber was soaked in DMAc (DMAc/*m*-aramid, 100/10, w/w) at 120℃ for 4 h. The soaking *m*-aramid fibers were dissolved in the solvent by adding anhydrous $CaCl_2$ (80 wt% of *m*-aramid) as a catalyst. Coagulated *m*-aramid film was produced using a film maker (Baker Applicator YBA-4). The coagulation parameters are shown in Table 2.

†Corresponding author. Tel.: +82-54-469-3843; Fax.: +82-54-461-6113; e-mail.: leejaew@hotmail.com

Table 1. Structure of the basic dyes

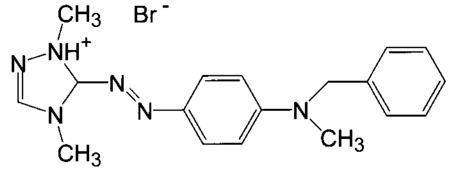
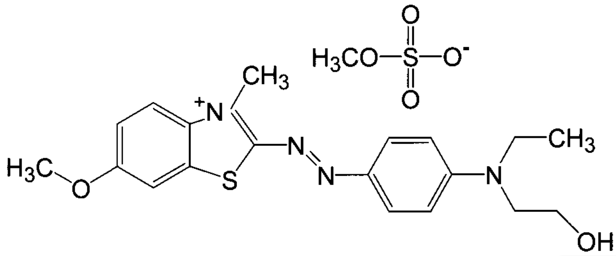
Name of dyes	Structure of dyes
C.I. Basic Red 46	
C.I. Basic Blue 41	

Table 2. The coagulation parameters

Test group	Variables	Contents
Group 1	Coagulants	Water, Methanol, Ethanol, Propanol, Butanol
Group 2	Water/DMAc (v/v) in coagulation bath	99/1, 95/5, 90/10, 80/20, 60/40
Group 3	Temperature of coagulation bath (°C)	5, 10, 20, 40, 80

2.3 Characterization of coagulated *m*-aramid film

2.3.1 Wide angle X-ray diffraction (WAXD)

WAXD patterns were recorded with an X-ray diffractometer (MiniFlex, Rigaku, Japan) with a CuK α radiation source. The diffraction angle was varied from 10 to 40° to identify changes of crystallinity.

2.3.2 Field emission scanning electron microscopy (FE-SEM)

The field emission scanning electron microscopy investigation was conducted with a Hitachi S-4300 at 15 kV accelerating voltage. Samples were coated with gold under argon purge before examination.

2.4 Dyeing procedure

The *m*-aramid fibers and films were dyed with 3% o.w.f. dyebath solution in the presence of acetic acid (pH 4) for 40 min at 80°C.

2.5 Color depth (K/S) of the dyed *m*-aramid films

K/S values were calculated by using a colorimeter (Macbeth Color-Eye 3100) coupled to a PC using illuminant D_{65} and 10° standard observer with the specular component excluded and the UV component included. Each film was folded once so as to give twice the thickness and an average of four readings was taken each time.

$$K/S = (1-R)^2 / 2R$$

where, K is an absorption coefficient of the dyed samples, S is a scattering coefficient of the dyed samples and R is a spectral reflectance at λ_{max}.

3. Results and discussion

3.1 Effect of the various coagulation parameters on the characterization of *m*-aramid film

3.1.1 Wide angle X-ray diffraction of *m*-aramid films

Many of the unique characteristics of *m*-aramid such as highly crystalline structure are attributed to the addition of aromatic rings into the polymer structure. Polymers consist of linear molecules that have crystalline and amorphous region in the polymer. In order for dyeing occur, the dye molecules must penetrate into the polymer by moving through the less dense, low crystalline areas (amorphous areas) of the structure. Hence, optimal dye uptake of *m*-aramid can be accomplished by changing the degree of crystallinity. The use of X-ray diffraction can be used to determine the crystallinity of the *m*-aramid films. Fig. 1 presents the wide angle X-ray diffraction pattern of pure Nomex fiber and *m*-aramid films provided with the various coagulants. The pattern of pure Nomex exhibits four characteristic peaks at 2θ = 13.50, 18.06, 23.04 and 27.14[10]. The peaks are sharper and more intense at higher crystallinity. Compared with the pure *m*-aramid fiber, the diffraction peak of the *m*-aramid films did not show the characteristic peaks of the *m*-aramid fiber. The diffraction curves of the coagulated *m*-aramid films exhibit a significantly larger amorphous region and thus reduced crystallinity regardless of the coagulants. It confirmed that coagulants in this study decrease the crystallinity of *m*-aramid films. Hence, the influence of the coagulants on the crystallinity of *m*-aramid films was significant.

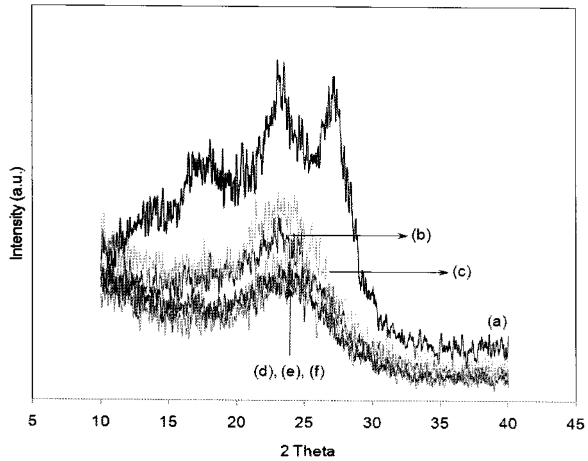


Fig. 1. X-ray diffraction patterns of (a) untreated *m*-aramid fiber, coagulated *m*-aramid films under (b) water, (c) methanol, (d) ethanol, (e) propanol, and (f) butanol.

3.1.2 Surface morphology

Effect of various coagulants on the SEM images of the coagulated *m*-aramid films is shown in Fig. 2. The *m*-aramid film, which was coagulated in water, shows a smooth surface. On the other hand, *m*-aramid films coagulated in propanol and butanol show rough surfaces and have microvoids. However, the difference in the SEM images between propanol and butanol coagulants was not exhibited. A *m*-aramid film which was coagulated in methanol exhibits lots of wrinkles while the SEM image of *m*-aramid film which was coagulated in ethanol was bulky. Fig. 3 shows the SEM images of the *m*-aramid films in the various concentrations of DMAc of the coagulation bath. In terms of water/DMAc volume ratio of 99/1 and 90/10, the SEM image of *m*-aramid film shows wrinkles.

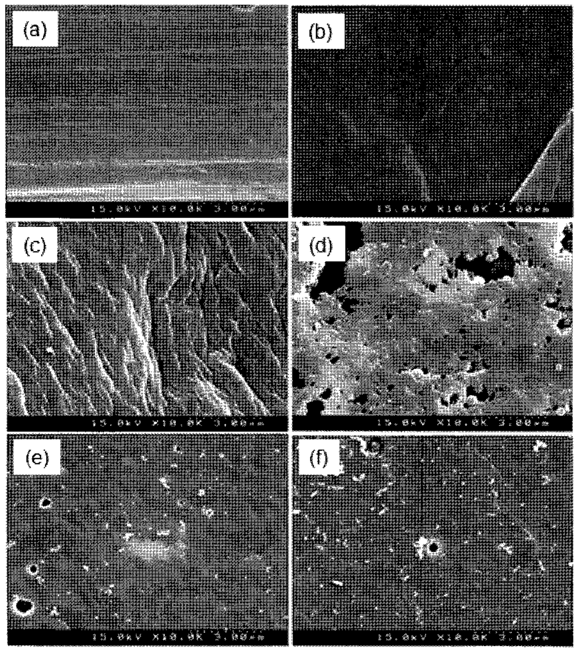


Fig. 2. SEM images of *m*-aramid (a) fiber and films coagulated in (b) water, (c) methanol, (d) ethanol, (e) propanol, and (f) butanol.

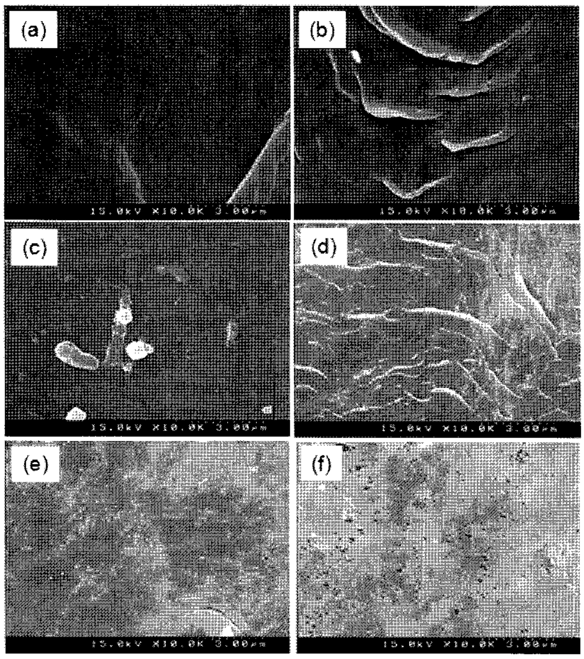


Fig. 3. SEM images of *m*-aramid films coagulated in water/DMAc (v/v) (a) 100/0, (b) 99/1, (c) 95/5, (d) 90/10, (e) 80/20, and (f) 60/40.

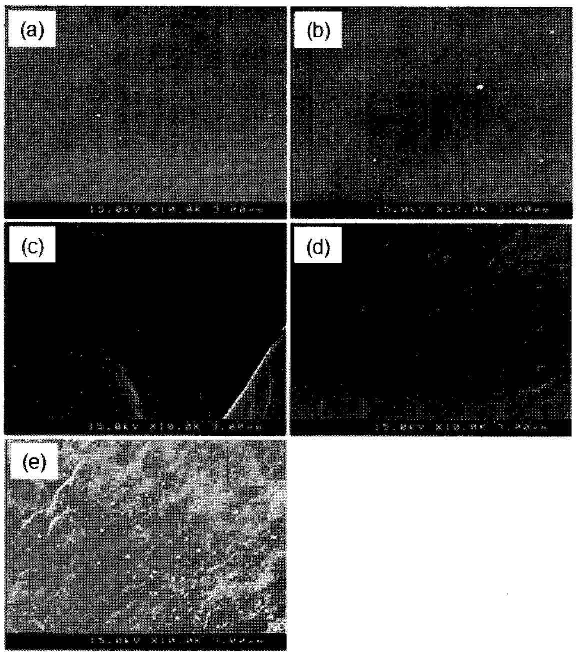


Fig. 4. SEM images of m-aramid films coagulated in water at (a) 5℃, (b) 10℃, (c) 20℃, (d) 40℃, and (e) 80℃.

On the other hand, the SEM images of m-aramid films on the ratios of water/DMAc of 95/5, 80/20, and 60/40 in the coagulation bath exhibit smooth surfaces. However, microvoids were revealed in the water/DMAc ratio of 60/40. The influence of coagulation temperature on the SEM images of m-aramid films is shown in Fig. 4.

The SEM images of m-aramid films were smooth regardless of the temperatures in the coagulation bath.

3.2 Color depth (K/S value) of dyed m-aramid films

To evaluate the effects of each of the coagulation parameters on the dye uptake of m-aramid films, color depth (K/S value) of the dyed m-aramid films was determined. Fig. 5 shows the influence of coagulants on the K/S value of dyed m-aramid films.

The order of decreasing K/S value of the dyed m-aramid films is water, methanol, ethanol, propanol, and butanol. With water, highest K/S value of the dyed m-aramid film is obtained. A considerable decrease in K/S values occurs in methanol and ethanol. A slight decrease in K/S value is observed in propanol and butanol coagulants.

The influence of five concentrations of DMAc in the coagulation bath on the K/S values of m-aramid films is

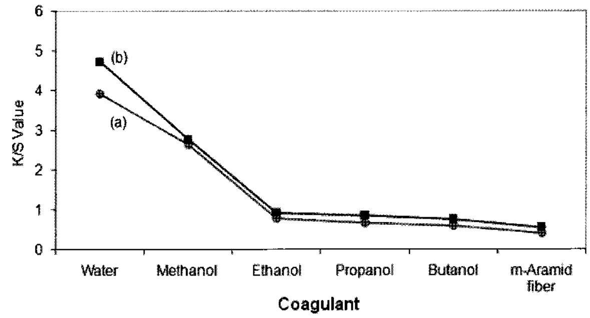


Fig. 5. Coagulants effect of m-aramid films dyed with (a) C. I. Basic Red 46 (540nm) and (b) C. I. Basic Blue 41 (640nm) with 3 % o.w.f. dyebath solution at 80℃ for 40 min.

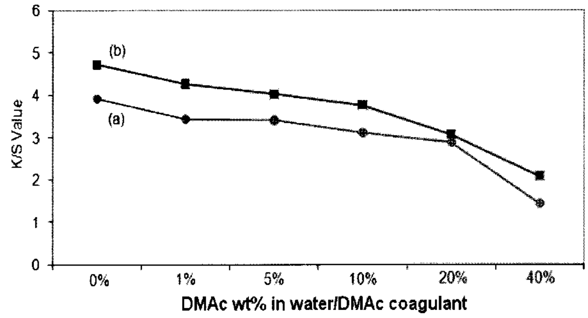


Fig. 6. Water/DMAc ratio effect of m-aramid films dyed with 3% o.w.f. (a) C. I. Basic Red 46 (540nm) and (b) C. I. Basic Blue 41 (640nm) at 80℃ for 40 min.

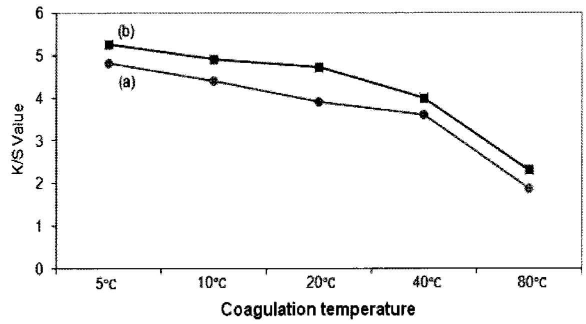


Fig. 7. Coagulation-temperature effect of m-aramid films dyed with 3% o.w.f. (a) C. I. Basic Red 46 (540nm) and (b) C. I. Basic Blue 41 (640nm) at 80℃ for 40 min.

shown in Fig. 6. Increasing concentration of DMAc in the coagulation bath resulted in a decrease in color depth (K/S value) of m-aramid films.

Fig. 7 indicates the influence of temperature in the coagulation bath on the K/S values of m-aramid films. Temperature increase in the coagulation bath leads to decrease in the K/S value of the dyed m-aramid films.

Fig. 7 shows that the coagulation temperature dependence of the K/S value in the m-aramid films is similar for the trend shown in Fig. 6.

4. Conclusions

WAXD revealed that the reduced crystallinity contributed to enhance dyeability of *m*-aramid.

According to SEM images, under ethanol or methanol coagulation, the surface of coagulated *m*-aramid films showed relatively rougher than other coagulants of water, propanol and butanol. Voids in coagulated film surface occurred at the portion of water/DMAc coagulation (w/w) of 60/40. *m*-Aramid films dyed with basic dyes showed that the order of decreasing K/S value was methanol, ethanol, propanol, butanol.

Increased DMAc concentration in the water/DMAc coagulant and higher temperature in water coagulation decreased K/S values.

References

1. P. G. Tortora and B. J. Collier, "Understanding Textiles", Prentice-Hall, New Jersey, pp.153-164, 1997.
2. R. A. F. Moore and H. D. Wigmann, Dyeability of Nomex® Aramid Yarn, *Textile Res. J.*, **56**, 254-260(1986).
3. H. E. Ulery, Sorption of Basic Dyes by Expanded Dispersions of Nomex(DUP) Aromatic Polyamide (Aramid), *J. Soc. Dyers Colour.*, **90**, 389-410(1974).
4. J. Preston and W. L. Hofferbert, A Solvent-Dyeing Process for Aramid Fibers, *Textile Res. J.*, **49**, 283-287(1979).
5. E. A. Manyukov, S. F. Sadova, N. N. Baeva and V. A. Platonov, Study of Dyeing of Thermostable Para/Meta-Aramid Fiber, *Fiber Chem.*, **37**, 54-58(2005).
6. A. S. Ribnick, H. D. Weigmann and L. Rebenfeld, Interactions of Nonaqueous Solvents with Textile Fibers, Part II: Isothermal Shrinkage Kinetics of a Polyester Yarn, *Textile Res. J.*, **43**, 176-183(1973).
7. A. S. Ribnick and H. D. Weigmann, Interactions of Nonaqueous Solvents with Textile Fibers, Part III: The Dynamic Shrinkage of Polyester Yarns in Organic Solvents, *Textile Res. J.*, **43**, 316-325(1973).
8. T. Kim, G. Kim, J. Y. Park, J. S. Lim, and K. P. Yoo, Solubility Measurement and Dyeing Performance Evaluation of Aramid NOMEX Yarn by Dispersed Dye in Supercritical Carbon Dioxide, *Ind. Eng. Chem. Res.*, **45**, 3425-3433(2006).
9. K. J. Yong, Y. H. Park, K. P. Yoo, H. J. Lee, and S. W. Nam, Dyeing Property of Aramid Spun Yarn with Disperse Dyes in Circulated Supercritical Fluid Dyeing, *J. Korea Fiber Soc.*, **40**(5), 463-471(2003).
10. Y. Sun and G. Sun, Novel Refreshable *N*-Halamine Polymeric Biocides: N-Chlorination of Aromatic Polyamides, *Ind. Eng. Chem. Res.*, **43**, 5015-5020 (2004).