Fabrication of the Colored PMIA Fibers by Wet Spinning: Effect of Spinning Parameters on the Coagulation Process

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ABSTRACT

The poly (m-phenylene isophthalamide) (PMIA) fiber, which can be prepared by wet spinning, is a kind of aromatic polyamide fiber. The spinning parameters could influence the performance and structure of the colored PMIA fiber such as the diffusion coefficient and coagulation bath. In this study, the PMIA spinning solutions doped with Color Inde purple 120 were first commixed in a pressurizer and then spun into a coagulation bath under a pressure about 0.3 MPa. In the coagulation bath, the pure or dope-dyed PMIA fibers were prepared by wet spinning at 323 K, and then the as-spun fibers were extracted by an ultrasonic oscillation method. The effects of jet stretch ratio, temperature, and concentration of the coagulation bath on the ratio of diffusion coefficient of solvent to coagulator were analyzed during the spinning process of dope-dyed PMIA fibers. The properties and structures of the colored PMIA fibers were characterized by SEM. Finally the most optimized spinning technology of the dope-dyed PMIA fiber was obtained and the dope-dyed PMIA fibers were successfully fabricated through wet spinning.

INTRODUCTION

The Poly (m-phenylene isophthalamide) (PMIA) fiber, which was first prepared in 1962, has been widely used in the textile industry because of its excellent properties, such as thermal stability, fire resistance, and chemical resistance [1]. The products of PMIA fibers have been widely used in the fields of protective apparatus, filtration, insulation materials, and the aero industry. This material played an irreplaceable role in high temperature resistance applications. With the increased requirement for high temperature resistance of fibers, PMIA fiber developed rapidly [2]. However, it is difficult to dye PMIA fiber due to its compact molecular structure and high crystallization, which impedes its further development for highly value-added product. Both, wet spinning and dry spinning can be used to prepare PMIA fiber, but most of the recent literatures focused on the study of wet spinning. In general, wet spinning involves extruding a polymer solution through capillary holes for coagulation, followed by washing, drawing, and heat setting [3-5].

In view of the above problem of PMIA fibers, researchers [6] have studied polymer synthesis, fiber production, and fiber properties intensively to obtain organic synthetic fibers that were not firmly fused to each other upon combustion and also had with excellent dyeing properties that do not require solution dyeing with pigments as with PMIA fibers.

A process for continuously or semi-continuously dyeing and simultaneously improving the flame retardant properties of PMIA fiber is described by Cates and colleagues [7]. The process includes the introduction of the fiber into a swelling agent contained preponderantly of a polar organic solvent, at least one dye, and one flame retardant. Thereby, both the dye and the flame retardant could be introduced into the fiber in the swollen state. The flame retardant properties of dyed fabrics were significantly improved. However, this process involved some special equipment that was not routinely available in most existing processing lines.

In this study, the dope-dyed PMIA fibers were prepared by wet spinning. The effects of jet stretch ratio, temperature, and concentration of the coagulation bath on the ratio of diffusion coefficient were investigated during the spinning process. The internal structure of dope-dyed PMIA fiber was also analyzed, and the most optimized spinning technology of the dope-dyed PMIA fiber was obtained. By studying the wet spinning of dope dyed

PMIA, jet stretch ratio, temperature of coagulation bath, components of coagulation bath, diffusion coefficient ratio of solvent to coagulator; high-performance dope dyed PMIA fiber could be prepared and the optimized preparation technology of dope dyed PMIA fiber was obtained. The study provided a theoretical basis as well as knowledge of the effects of draw down, temperature, composition of coagulation bath on the solvent and the coagulant ratio of diffusion coefficients on the preparation of high-performance PMIA colored fiber. Finally, the properties and structures of colored PMIA fibers were characterized by SEM. Based on the results of the above tests, it was demonstrated that the most optimized spinning technology of the dope-dyed PMIA fiber was obtained.

EXPERIMENTAL

Spinning Process of Dope-Dyed PMIA Fiber

The PMIA spinning dope with or without Color Inde purple 120 (BASF Co. Ltd., Luduigshafen, Germany) were first commixed in a pressurizer and then spun to a coagulation bath with 47.5wt% water and 52.5wt% DMAc under the pressure about 0.3 MPa. In the coagulation bath at 318 K, the pure or dope-dyed PMIA fibers were prepared by wet spinning.

The inherent viscosity of PMIA polymer was 1.91 $dL\cdot g^{-1}$. The weight concentration of the PMIA dope (SRO Materials Safety Co. Ltd., Suzhou, China) was 18wt%. The pigment content was 3wt% based on the polymer mass.

Characterization

A series of capillary dies with the same diameter and different ratios of length to diameter (L/D) were selected. The die diameter was 0.25 mm, and the L/D was 3, 5, 7 and 9, respectively.

The radius of the colored PMIA fiber is defined by the Eq. (1).

$$r = \sqrt{\frac{{R_p}^2 \cdot V_p}{V_r}} \qquad (1)$$

Where r is the radius of the colored PMIA fiber, R_p is the radii of spinneret, V_p is the spinning speed of colored PMIA fiber ($m\cdot min^{-1}$), V_r is the winding speed of colored PMIA fiber ($m\cdot min^{-1}$). The Ds is the diffusion coefficient of solvent and Dn is the diffusion coefficient of coagulant [8], and they are defined by Eq. (2) and Eq. (3).

$$\frac{{M_t}^s}{{M_\infty}^s} = 4\sum_{n-1}^{\infty} \frac{1}{{\lambda_n}^2} e^{-{\lambda_n}^2 D_s t / r^2} \qquad (2)$$

$$\frac{M_t^{\mathrm{n}}}{M_\infty^{\mathrm{n}}} = 1 - 4\sum_{n=1}^{\infty} \frac{1}{\lambda_n^2} \mathrm{e}^{-\lambda_n^2 D_n t / r^2} \qquad (3)$$

Where ${M_t}^s$ is the solvent content in colored PMIA fiber at the moment t second, ${M_\infty}^s$ is the solvent content in colored PMIA fiber at the moment equilibrium, M_t^n is the coagulant content in colored PMIA fiber at the moment t second, M_∞^n is the coagulant content in colored PMIA fiber at the moment equilibrium, t(s) is the time of diffuse, r(cm) is the radius of the colored PMIA fiber, λ_n is constant.

The morphology of the colored PMIA fiber was observed by using scanning electron microscopy (SEM, Pattern: HITACHI S-3000N, Manufacturers: Japan Hitachi Ltd.).

Measurement of the Apparent Colored Depth

The apparent colored depth was the permeating depth in an opaque solid material. The value of the permeating depth could be calculated according to Kubelka-Munk formula [9-10], which was shown as follows:

$$K / S = \frac{(1 - R_\infty)^2}{2R_\infty} \qquad (4)$$

Where K was the absorption coefficient, S was the dispersion coefficient; R_∞ was the reflectivity of a certain wavelength. K/S was generally used to determine the apparent depth and the brightness of colored fibers. Higher K/S value, darker dyed color.

The colored PMIA fibers were exposed to simulated sunlight environment for 10, 20, 25, 30, 40, and 50 h, respectively. The five samples were put into the simulated sunlight environment simultaneously. Then the colored depths of the colored PMIA fibers were tested in order to sign the color fastness of the colored PMIA fibers.

RESULTS AND DISCUSSION

Effect of the Jet Stretch Ratio on the Ratio of Diffusion Coefficient between the Solvent and the Coagulant

Die-swell was a unique phenomenon when visco-elastic polymer solution was extruded from a die [11]. In order to avoid this phenomenon, the negative tension was used in the spinning process, where the spinning speed was faster than the speed of the draft roll. In the solidification process, the speed of the spun yarn would put towards the orientation and increase the fiber strength.

TABLE I. Different draw down of the process conditions.

Experimental conditions	Experimental data
Liquid concentration /%	14.15
Salt /%	7.8
Coagulation Bath	DMAc/H_2O
The concentration of coagulation bath /%	50
Coagulation bath temperature /K	298
Spinning temperature /K	313
Spinneret	5 holes, 0.25mm
Spinning speed/m·min^{-1}	10.73
jet stretch /%	-46，-38，-29，-20
Winding speed / m·min^{-1}	5.83
Clotting time /s	10

Table I shows the effect of different draw down on the diffusion coefficient in the process conditions, and the colored PMIA fibers were produced using those experimental conditions.

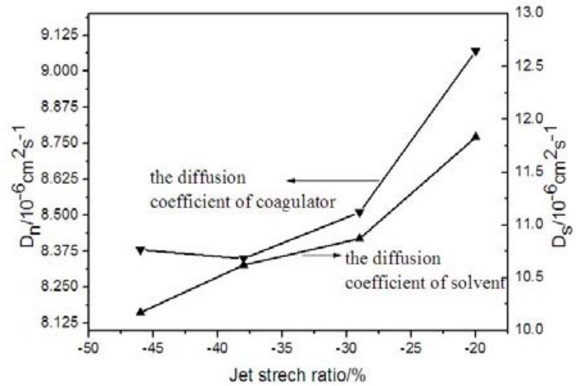

FIGURE 1. Relationship between the jet stretch ratio and the diffusion coefficient of solvent and coagulator.

As shown in *Figure 1*, with the increase of the jet stretch, the fiber radius decreased, the solvent and precipitating agent of the diffusion coefficient increased in the wet spinning system at the same time.

These results were caused by two main factors led to these results: the jet stretch and the fiber radius. On one hand, when the jet stretch was large, stretching made the skin produce stripes, thus facilitated the passage of small molecules and induced the diffusion spread faster. On the other hand, with the increase of spinning tension, the fiber radius of the filament decreased, leading to the increased surface area section of the filament, and the diffusion rate of small molecules became larger.

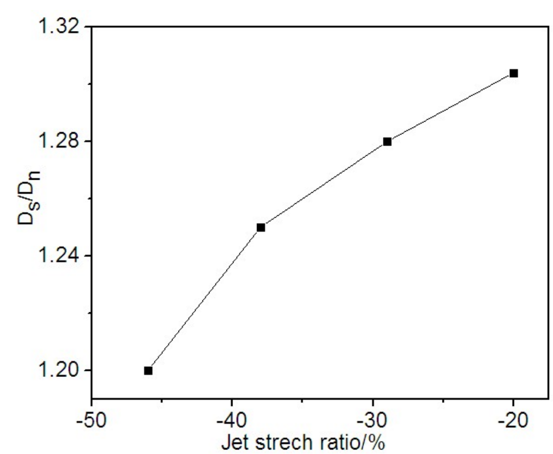

FIGURE 2. Relationship between the jet stretch ratio and the diffusion coefficient ratio (Ds/Dn)

Figure 2 shows that the ratio (Ds/Dn) of diffusivity coefficient of solvent and coagulant increases with the increase of the jet stretch ratio. Considering that other parameters remained unchanged, the adequate solidification of the primary filament was depended on the residence time in the coagulation bath. To obtain high-quality fiber, the moderate solidification rate was needed. It could be abated by increasing the draw down to get good solidification of primary filament from *Figure 2*. However, overstretching could easily make the fiber appear transverse striation, even break, or the circular fiber could not be obtained, so all factors should be taken into account to get the practical spinning condition when determining the spinning condition in the coagulation bath.

The spinning conditions should be taken into account to determine the coagulation bath of realistic spinning conditions.

Effect of the Coagulation Bath Temperature on the Ratio of Diffusion Coefficient between the Solvent and the Coagulant

In wet spinning, the coagulation bath temperature is an important variable to control the spread of the coagulation between solvent and coagulant [12-13]. The conditions of spinning techniques were the same as shown *Table I.* The coagulation bath temperature was set as 298, 318, 328, and 338 K. when the jet stretch was fixed at -46%.

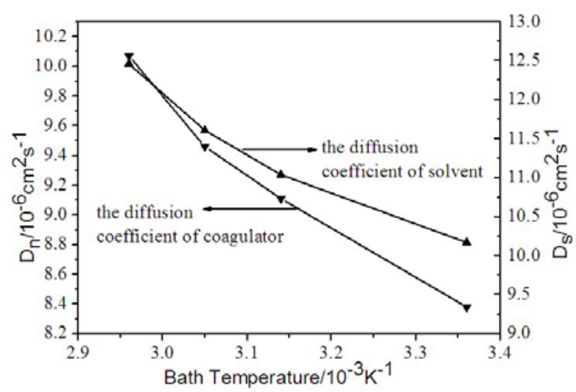

FIGURE 3. Relationship between the coagulation bath temperature and the diffusion coefficient of solvent and coagulator.

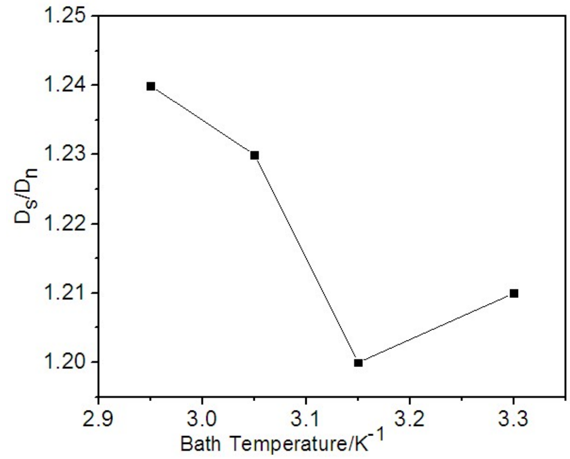

FIGURE 4. Relationship between the coagulation bath temperature and the diffusion coefficient ratio (Ds/Dn).

With the increase of temperature, the diffusion coefficient of solvent and coagulant increased, meanwhile the diffusion coefficient of solvent and coagulant ratio (D_{s1}/D_n) decreased from *Figures 3 and 4*. The increase of temperature affected the diffusion in two aspects. Firstly, the increased temperature impeded the moving capacity of small molecules, and enhanced the diffusion coefficient ability; Secondly, the increased temperature resulted in increased polymer free volume, which created enough space for diffusion of small molecules. D_s/D_n ratio increased with the increased temperature, which was probably due to the significant influence of temperature on the solvent.

Moreover, the solidification process of fiber in addition to the transfer of all substance, the existence of heat transfer, and the temperature differences lead to nascent filament during solidification and heat exchange between the coagulation baths were also different [14]. It can be seen from *Figure 4* that when the coagulation bath temperature approached to the temperature of spinning solution, the diffusion coefficient of the regional flat rate became gentle. This may be due to the effect of heat exchange of the materials. In the m-aramid fiber wet spinning system, D_s/D_n ratio increased with the increase of temperature, indicated that the effect of temperature on the rate of diffusion was different for each component. The diffusion coefficient of solvent increased faster than that of coagulant.

Effect of the Concentration of Coagulation Bath on Diffusion Coefficient Ratio between the Solvent and the Coagulant

The conditions of spinning techniques were the same as listed in *Table I*, except the concentration of coagulation bath was 40wt%, 50wt%, and 60wt%, and the jet stretch was -46 %. The concentration of coagulation bath played an important role in the fiber coagulation. The effect of the concentration on the diffusion of coagulation bath coefficient was studied by varying the solidification process parameters, the results were shown in *Figure 5*.

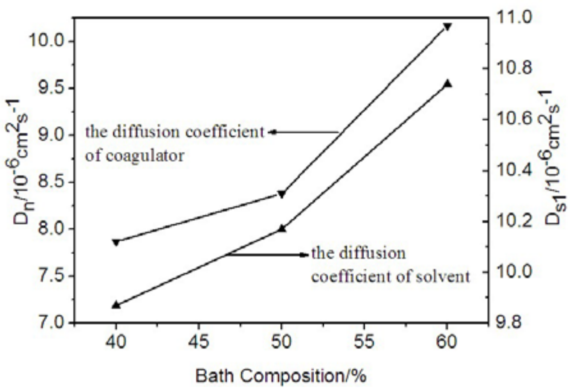

FIGURE 5. Relationship between the concentration of coagulation bath and the diffusion coefficient of solvent and coagulator.

Figure 5 shows the diffusion coefficients of solvent and coagulant increase gradually with increasing solidification bath concentration. When the concentration of solidification bath was low, the fiber surface coagulated dramatically and formed rigid epidermis very easily [15]. It not only led to the decreased tensile performance of nascent filament, but also produced more cavities because of the different delinking solvation speed of external layer and the non-uniform shrinkage internal stress. As a result, the structure and performance of colored PMIA fiber were affected.

Effect of the Purple Pigment on the Dope-Dyed PMIA Fiber

Figure 6 shows the optical images of PMIA fibers and colored PMIA fibers with the purple pigment. As shown in *Figure 6*, the PMIA fibers exhibited obvious color change from white (*Figure 6a*) to purple (*Figure 6b)* with the addition of purple pigment in the PMIA solutions.

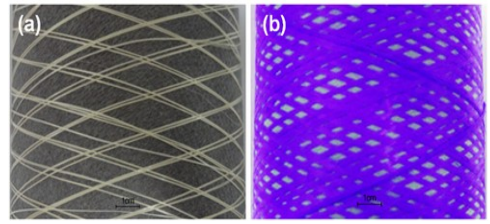

FIGURE 6. Optical images of the PMIA fibers (a) and colored PMIA fibers with (b) purple pigment.

Z-Average (X_{PCS}) and polydispersity index (PDI) [16] are considered to be two important parameters for the characterization of particle dispersion. PDI, a dimensionless constant, represents the dispersion of particle size distribution of the pigment particles. X_{PCS} can be determined through cumulative analysis formula:

$$\chi_{PCS} = \frac{16\pi}{3} \times \frac{kT}{\eta} \left(\frac{n \sin\frac{\theta}{2}}{\lambda_0} \right)^2 \qquad (5)$$

Where k is the Boltzmann's constant, T is the temperature, η (mPa·s) is the viscosity, n is the refractive index, θ (°) is the scattering angle, and λ_0 (nm) is the optical wavelength.

The Z-Average of the purple pigment was 110.1 and the PDI was 0.975. The mean grain sizes of the pigments were all less than 150 nm. The PDI of purple pigments (0.975) was close to 1, indicating the good dispersion state of the pigments in the solution. Because of the largest decomposition temperature and PDI value of the purple pigment, the purple pigment colored PMIA fibers were used in the subsequent study.

Effect of Jet Stretch on the Internal Structure of Dope-Dyed PMIA Fiber

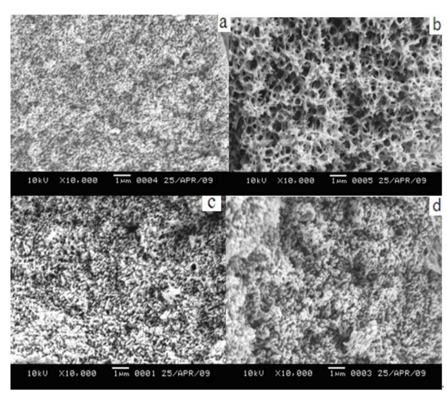

FIGURE 7. Effects of jet stretch on the interior structure of colored PMIA fiber (a:2.5 b:3.0 c:3.3 d:3.7).

As shown in *Figures 7a and 7b,* we can see that with the increase of jet stretch, the volume of internal cavities and other defects increased, the structure became looser. This is because of the double diffusion between solvent and coagulant of the fiber occurred in the coagulation process, the diffusion speed could affect the internal structure of fibers indirectly. When the jet stretch was low, the diffusion coefficient between solvent and coagulant was small, and spinning solution of the solidification was also small, leading to the formation of a dense fibrous internal structure. When the jet stretch rose, the diffusion coefficient between solvent and coagulant changed substantially [17]. Therefore, spinning solution of the coagulation accelerated so that the internal structure of loose fibers further increased.

The effect of the concentration of coagulation bath on the internal structure of dope-dyed PMIA fiber can be seen from *Figure 7c* and *Figure 7d*. It was evidenced that the colored PMIA fibers showed obvious improvement in the color fastness. With the increase of coagulation bath concentration, the defects of colored PMIA fibers, such as internal cavities were reduced, and the structure became more compact. When the concentration was low, the cortices were formed rapidly on surface of primary fibers. It not only led to the decreased mechanical properties of spun fiber, but also led to a large empty induced by the different solvent removal rate of the internal and external layers and the contraction caused by uneven internal stress [18]. When the concentration was higher, the solidification process tended to be easier than a fiber with more compact internal structure, which was the high-strength colored PMIA fiber.

The Apparent Colored Depth of Colored PMIA Fiber

The effects of solarization time and sunlight wavelength on the dye level of fibers were characterized, as shown in *Figure 8.*

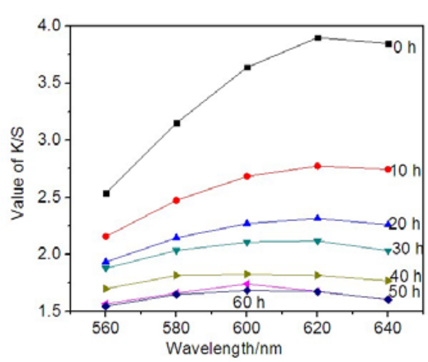

FIGURE 8. Value of K/S of the colored fiber for different solarization time and wavelength.

The dope-dyed PMIA fiber with 3 wt% pigment was measured at different exposure times of 10, 20, 25, 30, 40, and 50 h. The color of colored fiber became thinner and the value of K/S decreased significantly in the first 10 h. The solarization time was longer and the color was shallower. The main absorption of light took place at short wavelength from 620-640 nm, and also the value of K/S was the biggest. The peak values of K/S curves moved to the short wavelength with the increase of sun-baked time. The peak value of colored fiber occurred at 640 nm without solarization and 630 nm for the solarized sample with the solarization time of 10 h. The curves of 40 and 50 h overlapped and the peaks appeared at the same place.

The dyeing depth descended evidently with the ascension of the sun-baked time. The curve reduced significantly at the initial period of time, illustrating the great influence of sunlight on colored fiber. The value of K/S stabilized at 2.3 for 25 h and near to 2.0 for 50 h. It illuminated the determinate dye level of colored PMIA fiber.

CONCLUSION

In this work, the dope-dyed PMIA fibers were successfully developed through wet spinning with the optimized spinning technology. During the process of wet spinning dope-dyed PMIA fiber, the diffusion coefficients of non-solvent and solvent decreased as the time of coagulation extended and increased with the increment of stretch ratio. The higher temperature of dope resulted in bigger Dn and Ds values, but smaller Ds/Dn value, which also meant the values of Dn and Ds were similar. The higher temperature of coagulation bath resulted in smaller Dn, Ds and Ds/Dn values. The fibers became much thinner and no obvious voids were formed as the jet stretch ratio increased. The dyeing depth descended evidently with the ascension of the sun-baked time, it illuminated the determinate dye level of colored PMIA fiber. Based on the results of tests, it was demonstrated that the colored PMIA fibers showed obvious improvement in the color fastness.

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