

Structure and Properties of Dope-Dyed Poly(*m*-phenylene isophthalamide) Fibers By Wet Spinning

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(Received: 6 April 2012;

Accepted: 18 January 2013)

AJC-12730

Poly(*m*-phenylene isophthalamide) (PMIA) fiber was usually difficult to dye due to their rigid molecular structure and high crystallinity. In this study, the dope-dyed PMIA fibers with different amounts of pigment were prepared by wet spinning. The properties of the pigment were analyzed, including molecular structure, size distribution and dispersive properties. Measurements showed that the average diameter of pigment was no more than 100 nm, so pigments were easy to disperse in the fibers. The colour fastness of the coloured PMIA fibers was tested and their thermal properties and mechanical properties were also analyzed. The results of thermal gravity analysis (TGA) indicated that the coloured PMIA fibers maintained nice thermal performance. Compared to PMIA fibers, the coloured PMIA fibers became lighter after exposing to simulated sunlight for 50 h. The breaking tenacity of fibers exceeded 1.9 cN/dtex and the retentivity was above 85 % after being exposed to simulated sunlight for 50 h. The breaking tenacity of fibers exceeded 2.0 cN/dtex and the retentivity was above 80 % after being exposed to simulated sunlight for 50 h. These suggested the good mechanical performance of coloured PMIA fibers. This study successfully developed the dope-dyed PMIA fibers through wet spinning. The dyed performance of the coloured PMIA fibers was improved, while the thermal performance was also very nice. The mechanical properties of coloured fibers were similar to PMIA fibers.

Key Words: Poly(*m*-phenylene isophthalamide), Wet spinning, Dope-dyed, Coloured fiber.

INTRODUCTION

Poly(*m*-phenylene isophthalamide) (PMIA) fiber was fabricated as a member of the aramid fibers in 1962 and has been used in a variety of areas, such as aerospace industry, heat protective clothing, flame resistance, radiation protection, etc.^{1,2}. Its excellent thermal, mechanical and chemical resistance properties make it one of most important materials used in high-temperature resistance area. The fabrication technique of PMIA fiber developed rapidly in the past decade³. However, it is still fairly difficult to dye the PMIA fiber due to its rigid molecular structure and high crystallinity, which inhibits its application in protection fabric area.

In view of above problems of PMIA fibers, many researchers have studied intensively from the viewpoints of polymer synthesis, fiber production and fiber properties to obtain organic synthetic fibers with excellent form stability at a high temperature. A process has been described by Cates and others⁴ for continuous or semi-continuous dyeing poly(*m*-phenylene isophthalamide) fibers, simultaneously improving its flame-resistant properties that the fibers immersed in a swelling agent, containing at least one dye and one flame retardant. So both the dye and the flame retardant were introduced into the

swollen fiber. However, those processes involved some equipments that are not routinely available on most existing processing lines.

In this study, the properties of the pigment were analyzed, including heat resistance, molecular structure and size distribution. The coloured PMIA fibers contained 3 wt % colour Inde Red were obtained by wet spinning dyed PMIA spinning dope and then these fibers were exposed to simulated sunlight environment. The colour fastness of the coloured PMIA fibers was tested. Based on the results of mechanical tests, thermogravimetry analysis (TGA) and the coloured depths test, it was found that the colour fastness of the coloured PMIA fibers was greatly improved.

EXPERIMENTAL

17 wt % PMIA spinning solution was provided by SRO Materials Safety Co. Ltd. (Suzhou, China). The inherent viscosity was 1.97 dL g⁻¹. Dimethyl acetamide (DMAc) and the pigment Red-180 (Colour Inde) were supplied by BASF Co. Ltd. (Ludwigshafen, Germany). Coloured spinning dope was prepared that the pigment content was 3 wt % with respect to PMIA.

Spinning process: The PMIA spinning dope with or without Red-180 (Colour Inde) was first stirred in a pressurizer and then spun into a coagulation bath containing 47.5 wt % water and 52.5wt % dimethyl acetamide under the pressure of 0.3 MPa. The spinning speed was controlled at 10.7 m min⁻¹. The temperature of coagulation bath was 45 °C. The fibers were stretched to the draw ratio from 1.5-1.8 in a boil water bath and then washed in a water bath at 90 °C. Finally the fibers were stretched in dry at 290 °C in the hot air.

Measurement and characterization: Mechanical property of the fibers was measured using an XQ-1 fiber strength and elongation measuring instrument (New Fiber Instrument, Shanghai, China). The pre-tension was 0.05 c N/dtex and gauge length was 10 μm. The speed of tensile testing was 10 μm min⁻¹. Each sample was tested 20 times under like conditions. Nuclear magnetic resonance analysis of the samples was performed using a NMR spectrometer (AVANCE-400, BRUKER, Fremont, America). Nanometer particle size and zeta potential analysis of the samples was performed by using a Malvern Zetasizer Nano ZS analyzer (Malvern Instruments Ltd., Worcestershire, UK). Thermal stability of coloured PMIA fibers and PMIA fibers were measured using thermal gravimetric analysis (TGA, NETZSCH, Archer Berg, Germany). The morphology of the coloured PMIA fiber samples was observed using scanning electron microscopy (SEM, HITACHI S-3000N, Hitachi, Japan).

Measurement of the apparent coloured depth: The colour fastness of fibers was tested using Light Fastness Tester Specifications (ATLAS-150ST, Data colour, New Jersey, United states) with the lamp power of 1500 W at air condition.

The apparent coloured depth was the permeating depth in an opaque solid material. The value of the permeating depth can be calculated according to Kubelka-Munk formula^{5,6}, as follows:

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

where K is the absorption coefficient, S is the dispersion coefficient, R_∞ is the reflectivity on a certain wavelength. K/S is generally used to determine the apparent depth and the brightness of coloured fibers. K/S value was bigger, dyed colour was darker.

RESULTS AND DISCUSSION

Pigment particles size: In this experiment, the particle size of the pigment was mainly in the range of 150-400 nm, as

shown in Fig. 1. The distribution width was 250 nm and the aggregate pigments size was less than 300 nm. The Z-Average size (zatasizer nano series average size, X_{PCS}) could be calculated to be 110.1 nm by the following equation^{7,8}

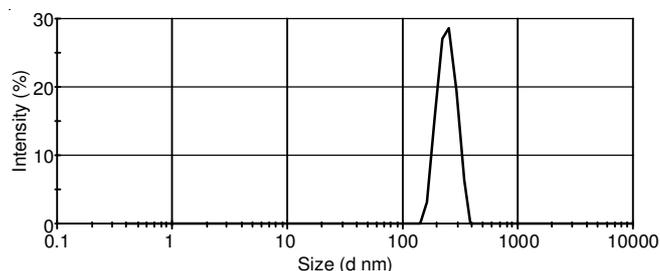


Fig. 1. Size distribution of the pigment particles

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

where, k (1.38 × 10⁻²³ J K⁻¹) is Boltzmann constant, T (K) is temperature, η (mPa s) is viscosity, n is refractive index, θ (°) is scattering angle, λ₀ (nm) is incident wavelength.

The above results indicated that the pigment was small and uniform and stably and homogeneously distributed in the coloured spinning solution. This would facilitate that the well dispersion of pigment in fibers was obtained and the aggregation of pigment was suppressed even with high loading because the diameter of the PMIA fiber was usually 15 μm, which was 50 times higher than the diameter of the pigment with size of below 300 nm. The coloured PMIA fiber which was prepared by this method had a high colour fastness, which can meet the requirements of long-time using.

Colour fastness of coloured PMIA fibers: The ¹³C NMR spectrum of the pigment was shown in Fig. 2. When the magnetic frequency was less than 50 ppm, two sharp peaks were appeared at 14.3 and 35.5 ppm chemical displacements, respectively, -CH₂ and -CH₃. Some sharp resonance peaks were appeared between 100-160 ppm. This area was main the basic aromatic carbon resonance peaks. Resonance peaks were not obviously existed above 150 ppm.

Through the analysis of the pigment NMR spectrum, the molecular structure contained mostly aromatic structure and the side contained small amount of -CH₂, -CH₃ and aryl ether structure⁹. The intermolecular forces were existed between those molecular groups and the fiber molecular, which enhanced the colour fastness of the coloured PMIA fibers.

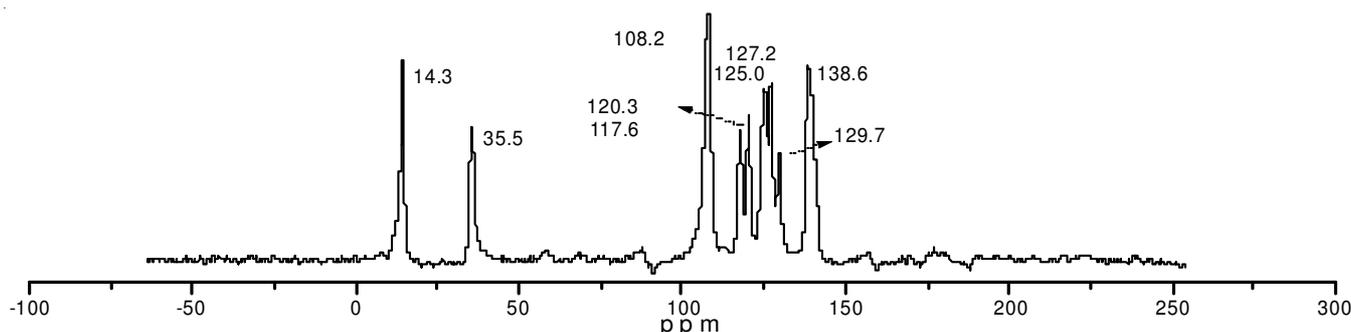
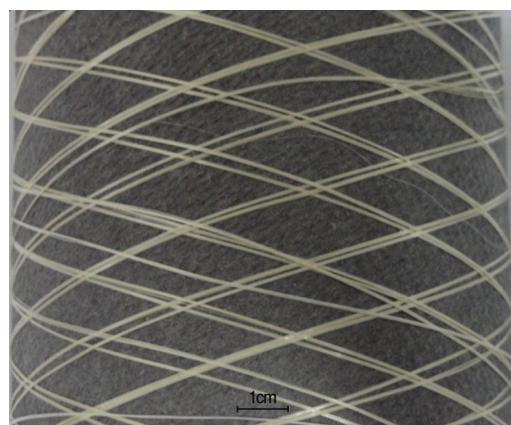
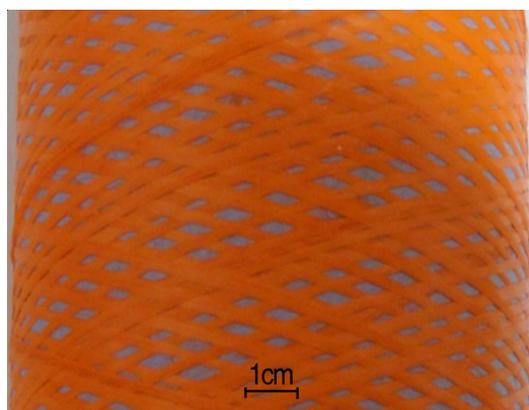


Fig. 2. ¹³C NMR spectroscopic analysis of pigment structure

Fig. 3 showed the optical images of PMIA fibers and coloured PMIA fibers with the red pigment. As shown in the figure, the PMIA fibers exhibited obvious colour change from white (Fig. 3a) to red (Fig. 3b) with the red pigment added into the PMIA solutions.



(a)



(b)

Fig. 3. Digital photographs of the uncolored PMIA fibers (a) and the colored PMIA fibers (b)

A bunch of uncoloured fibers and coloured fibers was consisted of 100 and 800 single fibers with about 12 μm of diameter, respectively. Fig. 3 showed that the coloured fibers showed a bright and uniform salmon pink. In addition, the colour of fibers hasn't obvious change even after stretching at a high temperature of 290 $^{\circ}\text{C}$. This result indicated that there is strong interaction between pigment particle and PMIA matrix, causing the colour stability of fibers.

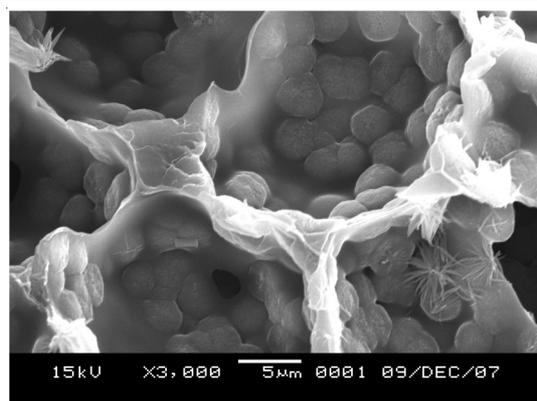
Mechanical properties of dope-dyed PMIA fiber: The mechanical properties of dope-dyed PMIA fibers with different draw ratios were measured and the results are listed in Table-1.

The doped-dye fiber was drawn above the glass transition temperature (T_g) of the fiber. The segment motion of the fibers occurred and the molecular chains aligned along the fiber axis under the tensile force¹⁰. The tenacity of the PMIA fibers improved obviously with the increase of draw ratio in the dry drawing. The strength of the fiber increased gradually as the drawing ratio increased. However, the fiber elongation and the fiber breaking tenacity decreased when the draw ratio increased to a large value. Optimal spinning parameters were that the strength was 5.73 cN/dtex, the jet stretch ratio was 40 %, the boiling water draw ratio was 1.8 and the dry drawing ratio was 3. The coloured PMIA fibers broke when the drawing ratio was fairly large in the dry-drawing process¹¹. Therefore, the draw ratio of the dry drawing should be controlled within the range of suitable values.

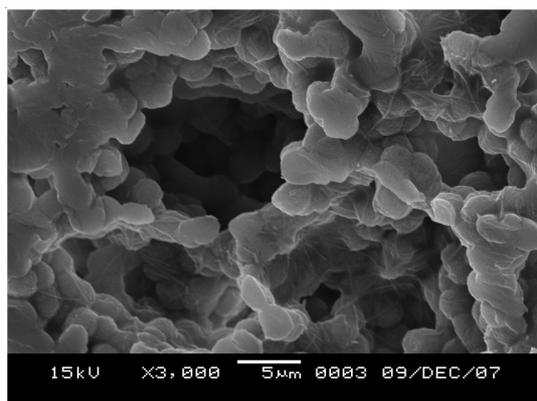
Morphology of dope-dyed PMIA fiber section: The dope-dyed PMIA fibers were drawn under different draw ratios (draw ratios = 2.0, 3.0, 3.2) in dry drawing. Fig. 4 showed SEM micrographs of the fiber internal structure. We could find that the fiber volume of internal structure increased with increasing draw ratios, so the molecular structure became more compact¹². We also found that the pigment was uniformly dispersed in the fiber. After a 3-time drawing, the strength of the coloured fiber was very high, reaching 5.73 cN/dtex (Table-1) and the dyeing depth was also very satisfactory (Fig. 4b).

TABLE-1
MECHANICAL PROPERTIES OF DOPE-DYED PMIA FIBER

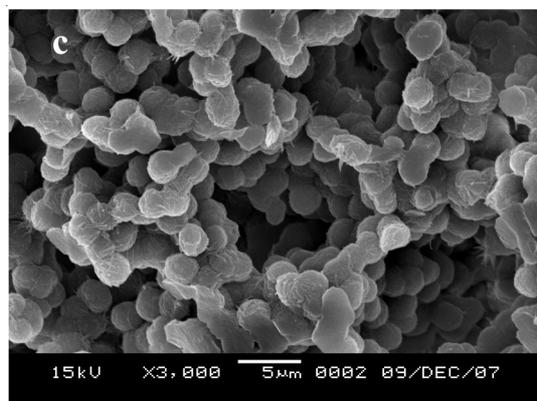
Process parameters			Mechanical properties			
Jet stretch ratio	Second draw ratio	Draw ratio of dry drawing	Titer (dtex)	Breaking tenacity (cN dtex ⁻¹)	Elongation at break (%)	
-0.4	1.5	1.0	9.08	0.9	96.40	
		2.0	4.19	2.65	51.78	
		2.5	3.2	3.77	37.17	
		3.0	2.47	5.25	24.28	
		3.2	2.46	5	21.81	
-0.6	1.8	1.0	9.15	1.01	92.96	
		2.0	3.92	2.74	59.88	
		2.5	2.72	4.53	36.99	
		3.0	2.59	5.73	23.94	
		3.2	2.56	4.86	22.74	
-0.3	1.5	1.0	8.4	0.83	64.29	
		2.0	4.02	2.24	44.2	
		2.5	3.1	2.98	26.58	
		3.0	2.45	4.13	19.35	
		3.2	2.35	4.50	26.94	
-0.3	1.7	1.0	8.72	0.92	87.32	
		2.0	3.54	2.93	45.49	
		2.5	2.81	4.60	30.32	
		3.0	2.66	4.28	18.66	



(a)



(b)



(c)

Fig. 4. SEM micrographs of the colored PMIA fiber section (draw ratio: a = 2.0, b = 3.0, c = 3.2)

However, we could see that the mostly pigment particles produced aggregate in Fig. 4c, leading to the decrease of fiber strength. The dyeing depth of coloured fiber was highest when the draw ratio was 3.

Thermal stability property: Thermal stability property of three pigments was measured using TGA and DSC at a heat rate of 20 °C/min from 3-900 °C under air atmosphere, as shown in Fig. 5.

The onset decomposition temperatures of the red pigments were all higher than PMIA fibers. The red pigment was pyrolyzed in the presence of oxygen at 467 °C, respectively. The onset decomposition temperature of the red pigment was higher than PMIA fibers. Therefore, the red pigment had potential

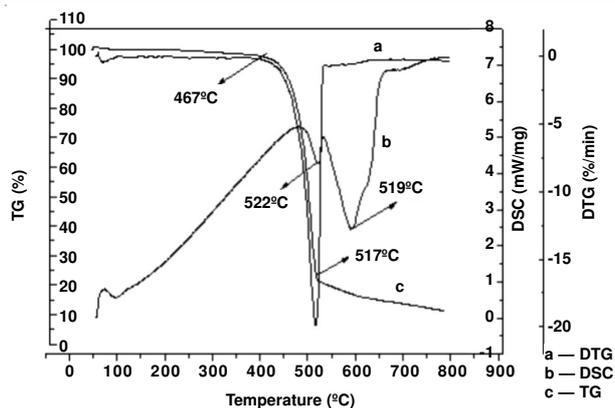


Fig. 5. TG and DSC curves of the red pigment

application in fabricating dye coloured PMIA fibers with good thermostability.

Thermal stability property of the coloured PMIA fibers and the uncoloured fibers were measured using TGA at a heat rate of 20 °C min⁻¹ from 40-650 °C under nitrogen atmosphere (Fig. 6). The weight loss trend of the uncoloured PMIA fibers declined more quickly than that of the coloured PMIA fiber. The onset degradation temperature T_d of coloured fibers was obviously improved from Fig. 6 (T_d of coloured fibers was 506.5 °C, T_d of uncoloured fibers was 430.9 °C). So the coloured PMIA fibers had a higher thermal stability. The coloured PMIA fibers exhibited three distinct decomposition stages¹³. The first step of degradation occurred roughly at the temperature lower than 100 °C, corresponding to the degradation of adsorbed water. The second T_d was 260 °C, corresponding to the decomposition of the pigment. The last step at 490.2 °C might be assigned to coloured PMIA degradation. The mass remains of the coloured PMIA fibers were 41.5 % when the degradation temperature was at 600 °C. The results indicated that the coloured PMIA fibers had good thermal stability at high temperatures.

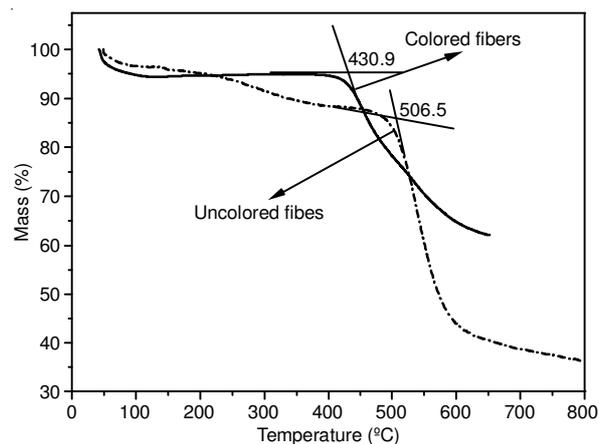


Fig. 6. TGA curves of the red colored PMIA fibers and the uncoloured fibers. The red pigment content was 3 wt % and the draw ratio was 3.0

Mechanical property of coloured and uncoloured PMIA fiber after solarization: The dyeing deepness decreased evidently with the increase of sun-baked time. This illustrated great influence of sunlight on the dyeing deepness of the coloured fibers¹⁴.

The breaking tenacity of uncoloured fiber decreased with increasing solarization time (Fig. 7). In the start 10 h, the drop-out trend of the uncoloured PMIA fiber declines quickly than that of the coloured PMIA fiber, its because the initial intensity of uncoloured PMIA fiber was too high for 2.5 cN dtex^{-1} , after 10 h irradiation for $2.38 \text{ cN dtex}^{-1}$, its strength decreased by 5 %, while the coloured PMIA fiber starting strength only of $2.36 \text{ cN dtex}^{-1}$, after 10 h of $2.34 \text{ cN dtex}^{-1}$, drop only of 2.5 %. The breaking tenacity retentivity of uncoloured fiber was close to 85 % after 50 h sun-baked time. It demonstrates a certain gap between these two fibers. The better pigment would be selected to improve the retentivity of fiber mechanical property in the future work.

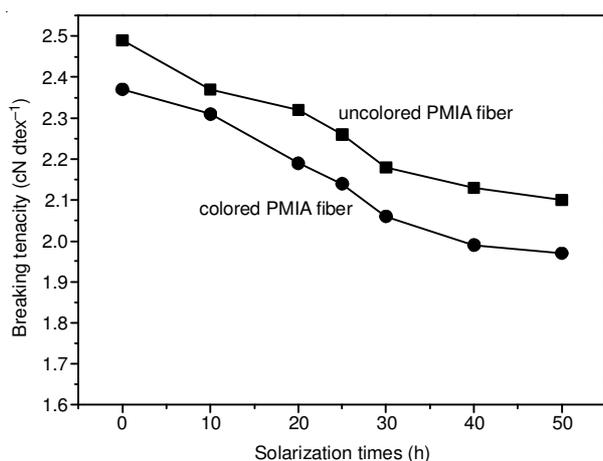


Fig. 7. Mechanical property of red colored and uncoloured PMIA fiber after solarization

We could also see that the breaking tenacity of the coloured fiber decreased significantly with the increase of solarization time. The breaking tenacity decrease of the uncoloured PMIA fiber was more than that of the coloured PMIA fiber during the first 10 h. The breaking tenacity retentivity of uncoloured fiber was close to 85 % after sun-baked time was 50 h.

Conclusion

In this study, the dope-dyed PMIA fibers were fabricated by wet spinning. The optimal spinning processing parameters:

jet stretch ratio was -0.6, jet stretch ratio was 40 wt %, boiling water draw ratio was 1.8 and dry drawing ratio was 3. The dyed performance of coloured PMIA fibers was improved and meanwhile the mechanical and thermal performance of the PMIA fibers was maintained at a high level. The introduction of the pigment had little influence on the properties of PMIA fibers and the coloured PMIA fibers with excellent performance were obtained.

ACKNOWLEDGEMENTS

This work was financially supported by China National 973 Project (No. 2011CB606103), China National 863 Project (No. 2012AA03212) and the Fundamental Research Funds for the Central Universities (No. 11D10625) and the Research and Innovation Project of Shanghai Education Committee, China, No.11CX30.

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