

Full Research Paper

## The Preparation and Characterization of Poly(m-phenyleneisophthalamide) Fibers Using Ionic Liquids

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**Abstract:** A process to produce fibers from Poly(m-phenyleneisophthalamide)(PMIA) solution in an ionic liquid via wet-spinning technology are described. The spinning process was investigated on a small laboratory scale. Ionic liquid spinning solutions were first prepared for PMIA fibers, followed by wet spinning. In the course of this research, the physical properties of the PMIA fibers were estimated. We studied the dependence of the mechanical properties of the obtained PMIA fibers on the composition of the coagulation bath, and on the choice of solvent in spinning solution. The morphology of the fibers from ionic liquid and traditional DMAc solvents via wet-spinning process were observed by scanning electrical microscopy(SEM). The differences of morphologies and properties of the PMIA fibers obtained from two different solvents are discussed.

**Keywords:** poly(m-phenyleneisophthalamide), ionic liquid, wet-spinning.

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### 1. Introduction

Poly(m-phenyleneisophthalamide)(PMIA) is well known as fire resistant material. It is a kind of high-crystallinity fibrous polymers and neither soluble nor fusible easily because of the high rigidity and conjugation of its backbone which cause difficulty to process. At present, PMIA has poor solubility in organic solvents such as dimethylformamide(DMF) and dimethylacetamide(DMAc) [1-3].

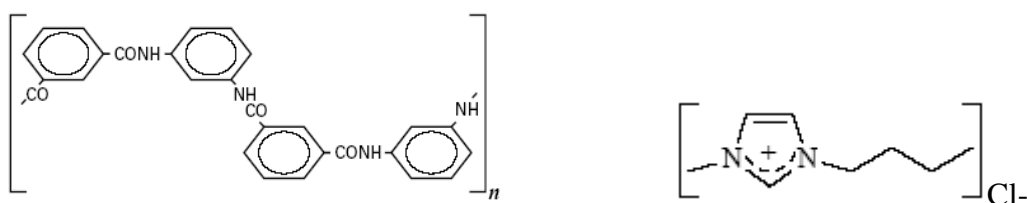
For several years, investigations aimed at developing new environment-friendly technologies to produce PMIA fibers. The processes elaborated here are based on ionic liquid as a PMIA solvent.

Ionic liquids are salts that are liquids at room temperature. Usually composing of a bulky organic cation such as imidazolium or pyridinium cation and a smaller inorganic ion such as Cl<sup>-</sup>, PF<sub>6</sub><sup>-</sup> or BF<sub>4</sub><sup>-</sup>, they can be customized like organic solvents. However, ionic liquids are considered “green” because, unlike the volatile organic compounds (VOCs), they are many of these compounds have negligible vapor pressure and can be recycled and reused repeatedly [4-7]. Recent research has focused on the wet-spinning formation of regenerated silk using ionic liquids as a solvent [8,9].

In our current research, we have investigated the dissolution and wet-spinning formation of PMIA fiber in and from ionic liquids. The research included the following aspects: estimation of the properties of the PMIA fibers, preparation and quality assessment of spinning solutions prepared using ionic liquid, the impact of the coagulation bath’s composition and temperature upon the mechanical properties of the fibers obtained.

## 2. Materials and Methods

PMIA (Mw  $\approx$  140,000 gmol<sup>-1</sup>), DMAc and LiCl were provided from the DuPont China Holding Co., Ltd, the Shanghai Chemical Company and the J&K Chemical Ltd respectively. Ionic liquid 1-n-butyl-3-methylimidazolium chloride ([Bmim]Cl) was synthesized and purified using the method by Seddon K.R [10]. The schematic representation of PMIA and [Bmim]Cl were shown in Figure 1. PMIA-IL mixtures were prepared via mechanical stirring at elevated temperatures (90 - 100 °C). Characterization of the fibers was performed using SEM.



**Figure 1.** The schematic representation of Poly(m-phenyleneisophthalamide) (PMIA) and 1-n-butyl-3-methylimidazolium chloride [Bmim]Cl.

Temperature of PMIA solution was kept at 80 °C by circular water. Filtration film was placed on the spinneret, and the spinning solution was extruded through a spinneret to form a PMIA fiber at an ambient temperature. The PMIA fiber was then immersed into nonsolvent (water) coagulation bath for wet separation and then the washing treatment bath. The coagulation bath temperature was controlled at 40 - 60 °C by a refrigeration/heating unit to ensure rapid solidification, while the washing bath was kept at ambient temperature. The spun fibers are stretched ( $R_{max} = 50 - 100\%$ ) in water at 100 °C, rinsed with water at 40° C, and finally tension-collected on spools as multifilament yarn.

The mechanical properties of the as-spun fibers were tested in accordance with suitable standards [11, 12]. Cross-section and surface images of the fibers were taken with the use of the Quanta 200 scanning electron microscope made by FEI Co, USA.

### 3. Results and Discussion

Because of its high viscosity, the temperature of PMIA/[Bmim]Cl solution must be kept at 80 °C. In consecutive trials, the temperature of the cooling medium was kept at 40 - 60 °C. The spinning solution manifested good properties; filtration, for example, proceeded smoothly at a pressure of about 0.3 - 0.5 MPa.

In this phase of the research, the effects of the composition of the spinning bath, the composition of coagulation bath and the temperature of coagulation bath upon the mechanical properties of the formed PMIA fibers were presented in Table 1, 2 and 3.

**Table 1.** Effect of PMIA concentration in spinning solution on mechanical properties of as-spun fibers.

mechanical properties	PMIA concentration in spinning solution □ wt% □		
	14	16	18
linear density (dtex)	9.2	9.6	10.5
tenacity conditioned (cN/dtex)	1.26	1.38	1.45
elongation at break conditioned (%)	18.8	19.2	20.7
sound velocity (km/s)	0.98	1.08	1.13

**Table 2.** Effect of the composition of coagulation bath on Mechanical properties of as-spun fibers.

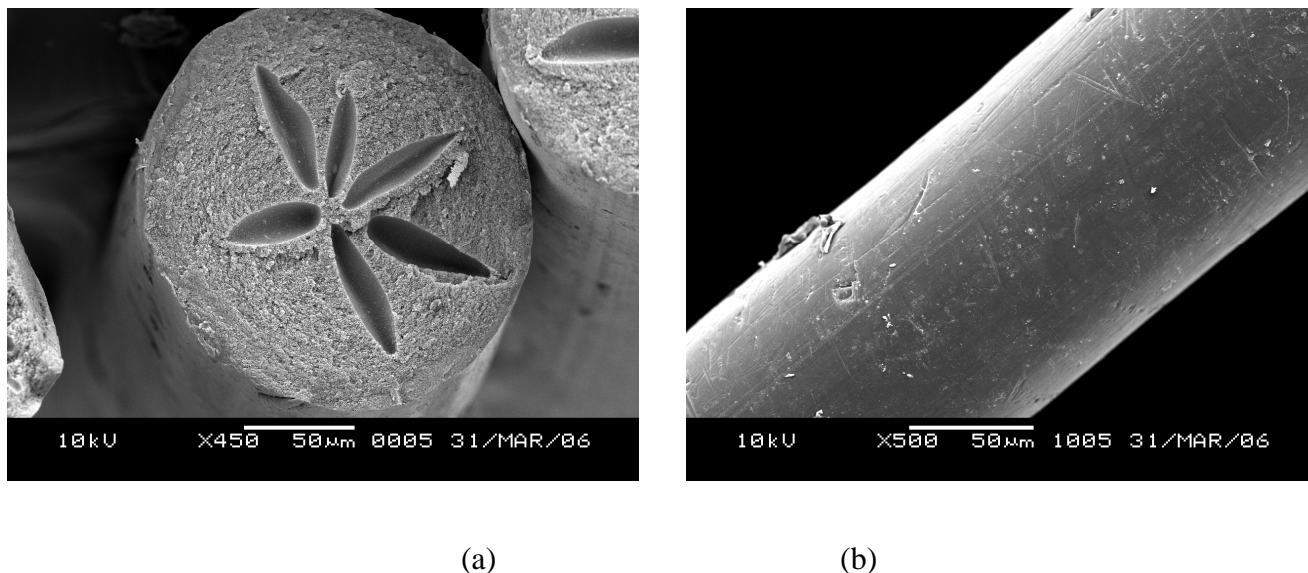
mechanical properties	the content of [Bmim]Cl in coagulation bath □ wt% □	
	0	10
linear density (dtex)	10.5	13.2
tenacity conditioned (cN/dtex)	3.27	2.79
elongation at break conditioned (%)	20.7	18.9
sound velocity (km/s)	1.13	1.02

**Table 3.** Effect of the temperature of coagulation bath on Mechanical properties of as-spun fibers.

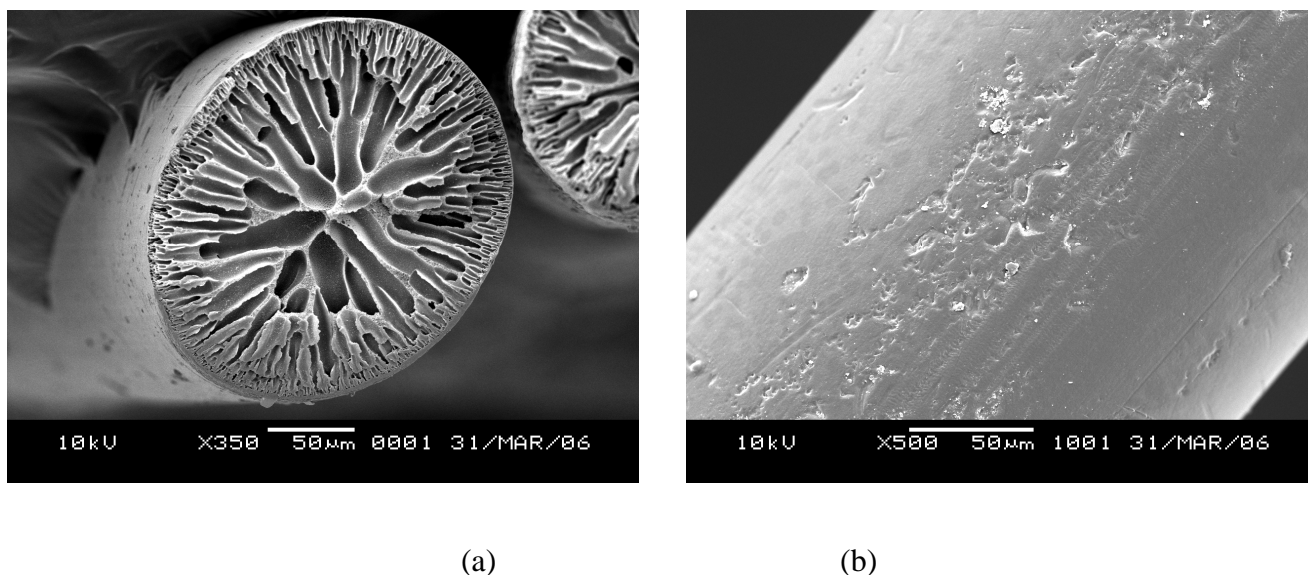
mechanical properties	the temperature of coagulation bath □ ° C □	
	40	60
linear density (dtex)	10.5	11.8
tenacity conditioned (cN/dtex)	3.27	3.18
elongation at break conditioned (%)	20.7	19.8
sound velocity (km/s)	1.13	1.09

As shown in Table 1, mechanical properties of as-spun fibers are improved with the increasing concentration of PMIA. From the results presented in Table 2, it may be concluded that the concentration of [Bmim]Cl in the coagulation bath does not radically influence the fibers' conditioned

tenacity. The highest value of the parameter appeared in fibers that were spun to a coagulation bath containing 100 % water. In Table 3, the temperature of coagulation bath actually has no influence on the mechanical properties of the fibers obtained. The tensile properties of the samples were a little poor compared to that of Nomex. The poor properties were due to the low spin draw ratios (and therefore low degrees of orientation)



**Figure 2.** SEM photos of PMIA fibers from ionic liquid [Bmim]Cl; a) cross-section, b) outer surface.



**Figure 3.** SEM photos of PMIA fibers from DMAc; a) cross-section, b) outer surface.

Figure 2 and 3 show SEM images of the as-spun fibers from two different solvents. These SEM images presented display a circular shape of the cross-section. While much more holes, differentiated in dimensions, can be seen on the cross-section of fibers from DMAc, and some micro pores are presented on the outer fiber surface. The reason of that phenomenon can be due to much rapid solidification during the process of wet separation. These images indicate that the fiber had an outer

dense skin responsible for the retention, which confirm our design objective that water as a strong coagulant started to precipitate the nascent fiber from the outside and the precipitation moved to the inside until the completion of whole fiber matrix while a bore fluid with high solvent concentration was used to delay the liquid-liquid phase inversion at the inner surface of the nascent fiber.

Figure 2 shows SEM images of the as-spun fibers from [Bmim]Cl. It could be evidently seen that from [Bmim]Cl, thickness of the dense region near the outer edge of the fiber enhanced comparing Figure 3(a) to Figure 2(a), the network pore size on the inner surface decreased comparing Figure 3(a) to Figure 2(a) and especially the outer surface from microporous became dense comparing Figure 3(b) to Figure 2(b), which supported the results of mechanical properties measured above. These changes in the fibers surface morphology could be attributed to the warm solidification during the process of wet separation.

#### 4. Conclusions

In this work, PMIA fibers were first prepared from ionic liquid spinning solutions by wet-spinning process on a small laboratory scale. The experimental results showed that the highest value of the parameter appeared in fibers that were spun to a coagulation bath containing 100 % water at 40 °C. The SEM images revealed that the as-spun fibers from [Bmim]Cl had much denser outer skin and less micro pores in cross-section than that from DMAc. Future work will focus on process analysis, increased productivity, and optimization of processing operating regimes to produce fibers of high orientation, well-controlled size, good mechanical properties and other target characteristics.

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