Polymer 149 (2018) 294–304

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Wet spun polyacrylontrile-based hollow fibers by blending with alkali lignin

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ARTICLE INFO

Article history:
Received 31 March 2018
Received in revised form
14 June 2018
Accepted 4 July 2018
Available online 5 July 2018

Keywords:
Alkali lignin (AL)
Polyacrylonitrile (PAN)
Hollow fiber
Phase diagram
Wet-spinning technique
Blending

ABSTRACT

Alkali lignin, a by-product of commercialized paper making process, is an abundant and environmental-friendly material. In this paper, polyacrylontrile (PAN) -based hollow fiber was fabricated by one-step wet-spinning technique through blending with alkali lignin at different ratios. The phase diagram of the blends was determined by titration method. When alkali lignin is added into the PAN solution, the clouding points move away from polymer-DMSO axis, and miscibility gap increases. The phase separation of PAN was slowed down by mixing with alkali lignin which resulted in the formation of hollow structure and promoted the pore formation in the wall. This work clearly explains the roles that alkali lignin plays in the system consisting of polymer, solvent and nonsolvent, and provides a feasible method to produce PAN-based hollow fibers.

1. Introduction

Due to its large surface area, light weight, high permeability and absorption capacity, hollow fiber has been widely used for gas separation, effluent disposal, biofuel production and pervaporation, energy storage, purification and so on [1]. The first commercial hollow fiber product was manufactured by DuPont in 1960s. Most hollow fibers are melt spun through a spinneret with unique geometry design, such as a single-hole tube-in-orifice type spinneret [2]. The hollow portion can be maintained by either blowing nitrogen or using bore liquids [3–5]. Also, bi-component spinning through coaxial electro-spinning or dry-wet spinning can be used to make a sheath-core fiber, and hollow fibers can be obtained by removing the core component [6,7]. Although melt spinning is the most convenient method to make hollow fibers, many polymers would degrade before melting and could only be solution spun into fibers, for example, PAN and polyvinyl alcohol. For solution spun hollow fibers, bi-component spinning is the most widely adopted method; however, the preparation of hollow fibers requires multiple processing steps and the recycling of the core component is difficult. It's desired to develop a simple one-step spinning method to achieve hollow structure.

The fiber formation inside the coagulation bath is controlled by double-sided solvent diffusion and non-solvent induced polymer phase separation (NIPS). When non-solvent diffuses into the extruded spinning dope, the PAN solution separates into polymer-lean phase which forms voids or pores and polymer rich phase which forms the solid portion of fibers. The formation of pores or voids might be affected by the concentrations of spinning dope and non-solvent [8]. There are reports on the formation of hollow fibers by mixing polymer dope with other component [9], such as, high boiling solvent (HBS) lignin. As an effective and facial way to alter the solution properties of polymeric materials [9–13], blending HBS lignin into PAN makes it possible to obtain a hollow geometry through conventional wet-spinning technique; however, the purification of HBS lignin is complicated and time-consuming. By comparison, alkali lignin (AL) [14–17], one of lignin derivatives, is an abundant, cheap, and environmentally friendly material. It's the by-product of commercialized paper making process, and can be dissolved in many polar solvents, such as, dimethyl sulfoxide (DMSO) and water. Thus, AL is a possible alternative to replace HBS lignin for making hollow fiber, and the miscibility of PAN and AL

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https://doi.org/10.1016/j.polymer.2018.07.019
0032-3861/

and how AL affects the fiber structures need to be evaluated. Besides, the usage of DMSO, which is less toxic than DMF and NMP, is beneficial to the possible industrialization of hollow fiber preparation by this method [18,19].

In this paper, the phase diagram of PAN/AL-DMSO-Water quaternary-system was determined by linearized cloud-point curve correlation method (LCP). The thermodynamic properties of the system and the roles of AL were also investigated. We were able to fabricate PAN-based hollow fiber by one-step wet-spinning technique after blending with AL at different contents, and the fiber morphologies, tensile properties and thermal behaviors were compared.

2. Experimental

2.1. Materials

AL (M_w~2700 g/mol, CAS: 8068-05-1, ash content: 21.8%) was obtained from Tokyo Chemical Industry Corporation. DMSO was purchased from Aladdin Industrial Corporation. The atactic PAN (M_w~120000 g/mol, Gangke Carbon Material LTD Corp., Taiyuan, China)/DMSO solutions had a solid content of 20 wt %. Deionized water was used as non-solvent. All chemicals were reagent grade and used without further purification.

2.2. Quaternary phase diagram

Quaternary phase diagram was constructed using the titration method [20–23]. The polymer solutions with an overall solid content of 20 wt% were prepared and the AL/PAN ratio was varied from 0/100 to 50/50. The rest of the solutions are the DMSO. 5 wt% PAN solution was obtained by diluting 20% PAN dope with DMSO, and the 5 wt% PAN solution was further diluted into 2.0, 1.0, 0.5 and 0.1 wt%, respectively. Each solution was stirred vigorously for 24 h to ensure good homogeneity. For titration measurement, a mixture of water/DMSO (70/30 wt%) was added dropwise into PAN solution at 30 °C under constantly magnetic stirring until the solution became cloudy. The clouding points were determined by measuring the amount of PAN, DMSO and water. The clouding points of PAN solutions consisting 0, 2.5% and 7.5% AL were measured. The clouding points of each solution were measured for three times. Also, the clouding points of PAN solutions consisting 20%, 30%, 40% and 50% AL were measured at 0.5% solid content.

Miscibility gap (MG) and degree of shift in bimodal curve (DSBC) were used to analyze the thermodynamic effect. MG was defined as the distance between binodal line and polymer/solvent axis and the DSBC was calculated based on eq (1) [21].

$$\mathrm{DSBC} = \frac{MG_{additive} - MG_{without\ additive}}{MG_{without\ additive}} \times 100\% \quad (1)$$

2.3. Hollow-fiber preparation

The spinning dopes were transferred into a 50 ml stainless-steel syringe preheated at 50 °C and then degassed for 6 h under vacuum. For one-step wet-spinning (Figure S1), the solution was extruded through a blunt tip needle (30G, inner diameter = 0.16 mm) into a coagulation bath consisting DMSO and water. The temperatures of spinning dope and coagulation bath were maintained at 50 °C. The detailed spinning conditions are listed in Table 1.

The as-spun fibers were soaked in hot water (80 °C) for 12 h, and then washed for three times by deionized water at 60, 50, and 40 °C, in sequence. Next, the fibers were soaked in water at ambient temperature for 24 h. Finally, the PAN-based fibers were dried at 30 °C for 24 h in an oven.

2.4. Characterizations

The dynamic rheological measurements were conducted by a parallel plate rotational rheometer (Anton Paar, MCR302, plate diameter: 50 mm). In order to minimize solvent evaporation, a thin layer of silicone oil was applied surrounding the edge of solutions. The surface tension was tested by Force Tensiometer-K100 (KRÜSS GmbH, German). Conductivity meter (INESA, Shanghai, China) was adopted to measure the electrical conductivity of spinning dope. The dispersion status of AL in PAN solution was observed under Optical Microscope (CX31-P, Olympus Co.).

Scanning electron microscope (SEM) (JSM-7001F, Japanese electron) was used to observe the surface and wall-structure of the fibers after being coated with gold sputters. The fibers were immersed into a mixture containing Epoxy resin and its hardener for a while and pulled out to solidify in 50 °C oven for 5 h [24]. After that, the same procedure was used to view the cross-section as above.

The tensile strength of the fibers was measured by a tensile tester (XQ-1C, Shanghai New Fiber Instrument Co.). The gauge length was 20 mm and the extension rate was changed according to the testing method for tensile properties of man-made staple fibers (ICS: 59.060.01). Each sample was tested for 20 times. During tensile testing, the fineness of each fiber was determined by a vibrating fineness meter (XD-1, Shanghai New Fiber Instrument Co.).

A thermogravimetric analyzer (TGA, Q600, TA Instrument) was introduced to measure the thermal properties of the fibers. The fibers were heated from 35 to 800 °C at a heating rate of 10 °C/min under nitrogen.

The porosity of fiber (P_f) was calculated from density measurement based on eq (2) [5,25].

$$P_f(\%) = \left(1 - \frac{\rho_f}{\rho_p}\right) \times 100\% \quad (2)$$

Where, ρ_f and ρ_p are fiber density and polymer density (kg/m^3),

Table 1
Spinning conditions and sample abbreviations.

sample abbreviation	spinning dope		coagulation bath	extrusion rate (mL/min)
	solid content (wt%)	AL:PAN ratio	DMSO/H_2O	
F-1	20	0:100	20/80	0.10
F-2	20	20:80	20/80	0.10
F-3	20	30:70	20/80	0.10
F-4	20	40:60	20/80	0.10
F-5	20	50:50	20/80	0.10