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Analyses of closed porosity of carbon fiber precursors using a robust thermoporosimetric method

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ABSTRACT

We investigated a major fiber spinning process parameter, the coagulation bath concentration, which has a critical effect on the porosity of the polyacrylonitrile (PAN) fibers. Utilizing thermoporosimetry, a calorimetric method based on the Gibbs–Thomson effect, this work details the correlation between coagulation bath concentration, porosity and pore size distribution. Pore size, as well as the pore size distribution, of the fibers throughout the wet spinning process were determined in detail. Moreover, the changes in the number of porous zones, pore size and fiber morphology during the wet spinning process were also examined by changing the coagulation bath composition. Two coagulation bath compositions, 77.5 wt% and 80 wt% DMAc/deionized water were considered. The fibers spun at 80 wt% coagulation bath solvent concentration displayed skinless rough surfaces with high porosity values compared to the fibers spun at 77.5 wt%. Attempts to spin into slightly more concentrated DMAc baths were unstable due to reduced tow tenacity, leading to fiber failure. The study showed that even minor changes in the coagulation bath composition can have a pronounced effect on the fiber properties such as cross-sectional shape, the integrity of the external skin, and the number and size of pores.

1. Introduction

Porosity in precursor fibers has been a subject of interest since the 1960s [1–3]. In wet-spun PAN fibers, pores are one of the structural components that can develop longitudinally or transversely along the fiber axis and occupy the space between microfibrils, negatively impacting the final tensile properties of the fiber [4]. It has been reported that the coagulation process plays a key role in the development of these pores.¹ The main parameters affecting the size, distribution and morphology of the pores depends directly on the diffusion rates of solvent and non-solvent with respect to the fiber surface during the coagulation process, and the pores elongate and/or collapse during the heated drawing process after coagulation [5]. The pores can be cylindrical or irregular with pore sizes ranging from micro pores ($r < 2$ nm) and mesopores ($r < 100$ nm) to macro pores ($r > 100$ nm) [6].

Many approaches have been considered to characterize the porosity of the PAN fibers such as nitrogen-desorption and mercury intrusion methods [7], small angle-X-ray scattering [8], electron microscopy [9] and optical microscopy. However, the major challenge here is that the samples used for the analyses must be dry, and the drying process results in irreversible pore collapse affecting the accuracy of the results,

[9]. Thermoporosimetry [10] is an alternative method to overcome this difficulty, allowing pore size measurement on undried fiber based on the melting or freezing point depression of a liquid confined in the pores, thereby avoiding the need to dry (or freeze-dry) the fiber. The major advantages of this method include short measurement times, use of non-toxic chemicals and the ability to examine wet samples to detect closed pores which are not accessible with other standard porosimetry methods. Thermoporosimetry has been underutilized [11], however this technique has the potential to be used as a simple and cost/time effective method for detecting the porosity of fibers with high accuracy. It is important to note, however, that thermoporosimetry is unable to measure pore diameter beyond 200 nm (macro pores) if water is used as the probe liquid [12]. When measuring large pores, hydrocarbons can be used because of the larger temperature depression versus water.

High quality precursor fibers possess fewer defects, consistent circular cross sectional shape and small diameter. If the diffusion processes during coagulation are not controlled properly, the fibers will develop macro pores which decrease fiber strength. The coagulation process and temperature play vital roles in the development of internal fiber structure and surface properties. There are many studies reported on the effect of coagulation bath temperature on the fiber shape [13]. It has also been reported that the pore size and volume increase with

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increase in coagulation bath temperature [14]. Previous work done by Morris et al. [15] demonstrated the influence of high coagulation bath composition (> 70 wt% solvent/non-solvent) on resulting fibers. They observed numerous advantages by utilizing high solvent concentration in water (79 wt% DMAc/water), including the production of round fiber with high density and low diameter and an increase in molecular orientation and tensile properties. Due to the favorable effects found at high solvent concentrations, in the present study we have focused our attention on two high coagulation bath compositions, 77.5 wt% and 80 wt% DMAc/water.

Nascent fibers were collected from the spinning line during the wet spinning process and the influence of coagulation bath concentration on porosity development was analyzed. The effect of bath concentration on the fiber shape, density, orientation and porosity was investigated by scanning electron microscopy (SEM), and the quantitative information of the pores in the fibers was obtained via thermoporosimetry. As stated previously, thermoporosimetry utilizes the Gibbs–Thomson effect, whereby solidified crystals contained in a porous material melt at a lower temperature than the bulk solid-to-liquid. By indirectly measuring the radius of curvature of the ice-water interfacial tension with thermoporosimetry, the diameter of the voids can be measured. In this work, we have detailed the precise calculation of internal surface area and the distribution of porous regions within PAN fibers.

2. Experimental and characterization

2.1. Materials and methods

Polyacrylonitrile (PAN) terpolymer, poly(acrylonitrile (AN)-co-methyl acrylate (MA)-co-methyl acrylic (MAA) (P(AN-co-MA-co-MAA)) with a molecular weight of approximately 300,000 g/mol was used. Reagent grade N, N-Dimethylacetamide (DMAc) was purchased from Fischer chemical (Pittsburg, PA, USA) and employed in the dissolution of the PAN terpolymer, as well as in the coagulation bath to control fiber formation. Deionized water was used as the non-solvent.

2.2. Wet spinning

Continuous fibers were prepared by wet spinning two sets of P(AN-co-MA-co-MAA) terpolymer/DMAc dope by utilizing the multifilament solution spinning facility at the University of Kentucky Center for Applied Energy Research (UKY CAER). The spinline set up is schematically shown in Fig. 1. A polymer dope with a concentration of 13.5 wt % in N,N-dimethylacetamide (DMAc) was prepared and deaerated under vacuum (~ -29.9 in Hg). The filtered solution was then spun into a DMAc/H₂O coagulation bath. The spinneret contained 500 holes with 60 μm capillary diameters. The fibers were spun at two coagulation bath compositions, 77.5 wt% (sample A) and 80 wt% (sample B) DMAc/H₂O, at a bath temperature of 15 °C. Fiber residence time within the coagulation bath was 50 s, with a calculated extrudate jet velocity of 1.2 m/min (not accounting for die swell). The take-up of the fibers following the washing, stretching and drying process was at a velocity

Table 1
Fiber processing parameters.

Fiber code	Coagulation bath composition (DMAc/H ₂ O)	Coagulation bath temperature (°C)	Locations of the fiber collections			
Sample A	80/20	15	C1	C2	C3	C4
Sample B	77.5/22.5	15	C1	C2	C3	C4

of 6.0 m/min. During coagulation bath composition adjustment, excess heat of mixing from DMAc and water was dissipated using a circulating water/glycol external bath (heat sink). The details of the fiber used in this study are shown in Table 1. After achieving spinning stability, fiber samples were collected at various collection points along the spin line: after coagulation (C1); after washing (C2); after hot stretching (C3); and at the traversing take-up (C4), washed and stored in a bottle filled with deionized water (Table 1), shown in Fig. 1.

2.3. Scanning electron microscopy (SEM)

The surface and cross-sectional morphologies of the fibers were investigated using a Hitachi S-4800 field emission SEM (Hitachi High-Technologies Corporation, Tokyo, Japan). Samples were collected from deionized water and subjected to lyophilisation to preserve the pore structure. Cryostat microtomed fiber bundles were positioned vertically in a thin specimen split mount SEM sample holder (Ted Pella, Redding, CA, USA). The samples were gold coated for 120 s using a Hummer 6.2 Sputter system (Anatech USA, Union City, CA, USA) using 20 mA current. Fibers were imaged with 3 kV accelerating voltage and 5 μA beam current, using the secondary electron detector.

2.4. Thermoporosimetry (TPM)

Fiber thermoporosimetry experiments were conducted using a TA Instruments Q200 differential scanning calorimeter (DSC) calibrated with deionized water. Water saturated nascent fibers (4–6 mg) were cut to 1 mm lengths and placed in hermetically closed aluminum DSC pans, immediately cooled to -60 °C to freeze internal water, and heated to 5 °C at 0.1 °C/min rate. For each sample, these measurements were repeated at least three times to indicate reproducibility.

The pore radius of the fibers was calculated considering the depression of the equilibrium melting temperature of water by using the following equation [11,17].

$$\Delta T \cong \frac{4T_0\gamma_s \cos\theta}{\rho\Delta H_f D_p} \quad (1)$$

where ΔT is the melting point depression, T_0 is the melting temperature of water (273.15 K), D is the pore diameter, θ is the contact angle assumed to be 180°, γ is the surface energy of the solid-liquid interphase, H_f is the specific heat of fusion and ρ is the density of the bound water.¹⁷ The pore size distribution (PSD), dV_p/dR_p , of the fibers was calculated

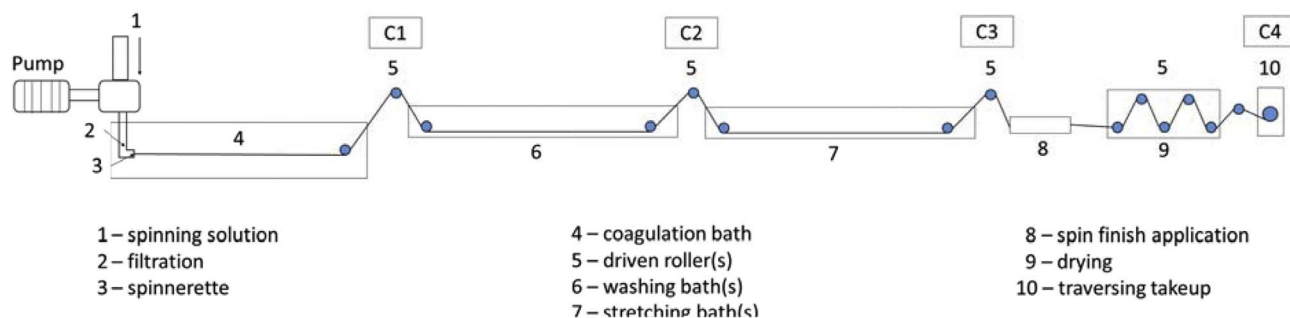


Fig. 1. Schematic representation of the locations of the fiber samples collected along the spinline at various coagulation conditions.

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