

Chapter 10

Exploring the Thermodynamic Aspects of Structure Formation During Wet–Spinning of Polyacrylonitrile Fibres

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ABSTRACT

Wet-spun polyacrylonitrile fibres are the main precursor for high strength carbon fibres. The properties of carbon fibres strongly depend on the structure of the precursor fibre. Polyacrylonitrile fibres were spun from solutions with varying solvent/nonsolvent content and different draw ratios. Wet-spinning is an immersion precipitation process, thus thermodynamic affinity of spinning dope to the coagulation medium was considered as the driving force of phase-separation, while viscosity of the solution accounted for the resistive force against phase separation and growth of the nucleated voids. Thermodynamic affinity was estimated by modifying Ruan's theory and viscosity of the solution was assessed on-line by measuring flow rate and back pressure at the spinneret. Hence, the parameter $X\eta^{-1}$ (thermodynamic affinity/viscosity) was introduced to predict the porous morphology of the fibres. Generally, an increase in $X\eta^{-1}$ led to fibres with higher porosity. A combination of electron scanning microscopy (SEM), porosimetry and thermoporometry was applied to fully characterize microstructure of fibres. Based on image analysis of SEM micrographs and data obtained from thermoporometry and porosimetry fractions

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of dense polymer ligament, micrometer size voids (macrovoids) and nanometer size voids (nanovoids) were estimated. Increasing polymer content or nonsolvent content in the spinning dope caused an increase in the solution viscosity and resulted in fibres with lower porosity. Imposing drawing on the as-spun fibres further decreased the porosity. Drawing also shifted the size distribution of nanovoids toward smaller values.

INTRODUCTION

In recent years there has been an increasing demand for acrylic fibres due to their extensive application as the main precursor for high strength carbon fibres (Paiva, 2003). It has been shown that the properties of carbon fibres strongly depend on the structure of the initial precursor (Mital, 1998; Thunemann, 2000). Hence, understanding the mechanisms of structure development of acrylic fibre during spinning is a key to design better precursors and improve mechanical properties of the resulting carbon fibre (Mital, 1998; Paiva, 2003; Thunemann, 2000). The acrylic fibres used in carbon fibre industry are mainly produced by wet-spinning process (Salem, 2001). Wet-spinning is an immersion precipitation process in which the extruded polymer solution (spinning dope) precipitates as a porous fibre in the coagulation bath (Chen, 2006; Masson, 1995; Wang, 2007). It is a complex process, including phase separation, rheological and diffusion phenomena (Hou, 2005, 2006; Ziabicky, 1976). Phase separation occurs through nucleation and growth of the polymer lean phase leading to void formation with controlled morphology. Solvent/nonsolvent exchange rate between fibre precursor and coagulation medium has been mentioned as the main parameter affecting void size, size distribution and morphology (Knaul, 1997; Lai, 1999; Li, 2004; Lin, 2002; Liu, 1990; Oh, 1996; Um, 2004). Nonsolvent inflow leads to nucleation of the polymer lean phase often surrounded by polymer rich phase forming core-shell nuclei (Mckelvey, 1996). Osmotic pressure difference between the polymer lean phase and coagulation medium drives an intrusive mass into the fibre and thus core of nuclei grows against the polymer rich

shells (Lin, 2002). Therefore, the mixing affinity between fibre precursor and nonsolvent on one hand and the mechanical resistance of the polymer reach phase against deformation on the other hand, determines the kinetics of phase separation (exchange rate and demixing time) and the corresponding void structure. Smolders et al. (1992) conclude that instantaneous and delayed demixing often yield finger-like and sponge-like structures, respectively. Phase separation kinetics can be manipulated in many ways such as variation of spinning dope composition, coagulation bath composition and spinning temperature. For example, increasing polymer concentration in the spinning dope, reduces solvent concentration gradient between fibre and coagulation bath and consequently solvent/nonsolvent diffusion coefficient decreases, solution viscosity increases and growth of the nucleated voids is inhibited (Hou, 2005, 2006). Won et al. (1999) investigate the effect of dope viscosity on void formation. They notice that low solution viscosity results usually to macrovoids formation. But, increasing solution viscosity via increasing polymer concentration leads to a significant reduction in size and number of macrovoids. They attribute this effect to gelation of the polymer phase. Gelation onset causes a reduction in the rate of phase separation and prevents voids growth. Van de Witte et al. (1996) attribute macrovoids reduction to the increase of phase separation delay time as a result of increasing solution concentration or viscosity. Precipitant addition to dope or spinning solution also affects demixing time via reducing the rate of solvent outflow and nonsolvent inflow both rheologically and thermodynamically. In other words, assuming constant exchange rate of solvent outflow and nonsolvent inflow, dope containing less

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