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Elimination of die swell and instability in hollow fiber spinning process of hyperbranched polyethersulfone (HPES) via novel spinneret designs and precise spinning conditions

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ABSTRACT

This study has successfully demonstrated that a proper combination of novel spinneret designs and spinning parameters can effectively counteract the die swell as well as flow instability phenomena, i.e. extrudate distortion, in the hyperbranched polyethersulfone (HPES) hollow fiber spinning. Attempts are also made to unravel the die swell and flow behavior differences between HPES and linear polyethersulfone (LPES) membranes spun using various spinneret designs and spinning conditions. In terms of flow stability, it is revealed that short conical spinnerets with a flow angle of 60° as well as short round flow channel spinneret with a flow angle of 30°, can reduce or eliminate extrudate distortions. Apart from spinneret designs, this study also accentuates the importance of a proper choice of spinning conditions for each specific spinneret to achieve flow stability and reduce die swell, namely: (1) bore fluid composition; (2) dope flow rate; (3) spinning temperature; and (4) take-up speed. Experimental results concluded that a proper combination of spinneret design and these four spinning parameters is the key to stabilize the spinning process. It is found that a high take-up speed spinning and a high non-solvent concentration in the bore fluid can fully eliminate die swell and enhance flow stability in the HPES hollow fiber spinning using short and conical or round spinnerets.

1. Introduction

The importance of hollow fiber spinning technology for vast membrane applications has been well recognized for decades. To date, both melt and solution spinning are the most widely implemented techniques in hollow fiber membrane fabrication [1–13]. Due to the complexity of spinning processes, the understanding of material rheology and its flow behavior through an orifice die are utmost critical to obtain desirable hollow fiber membranes at a reasonable production rate. Clearly, from an economical point of view, the fiber's production rate is one of the major parameters to determine maximum production capacity and profitability in the membrane industry. However, limitations caused by instabilities in the polymer flow will lead to technical problems within the production line itself or fabricate undesirable final products which possess the potential to increase production costs. Thus, advances in spinning technology and knowledge on polymeric materials are the keys to overcome the instability problem.

Some of the issues encompassed within the fiber spinning instability include: (1) draw resonance; (2) necking; (3) capillary break-up; (4) irregular cross-section and (5) melt fracture or extrudate distortion [14–21]. The first four phenomena, which have been investigated previously by many researchers [4,14,15], most likely lead to fiber breakage during the spinning process or generate a non-uniform cross-sectional diameter along the spun fibers. It is believed that their mechanisms are exacerbated by the fluctuations in polymer jet flows, which are themselves resultant of drawing or capillary forces.

The last type of spinning instability, which will be the focus of this manuscript, normally takes place in the form of a distorted, gross or wavy polymer flow [14–16]. The first melt fracture instability was investigated by Nason who observed a wavy polystyrene extrudate at Reynolds numbers in the range of 800–1000 [22]. In fact, the mechanism of extrudate distortion in melt spinning is one of the most controversial issues in fiber spinning and has been heavily debated among rheological scientists [5,14–17,23]. It can be summarized that the proposed mechanisms of extrudate distortion implicate one or more of the following parameters [15]: (1)

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fracture; (2) Reynolds turbulence; (3) thermal effects; (4) die entry and exit effects; (5) rheological effects; and (6) slip at the die wall. As a rule of thumb, most researchers agree that the distortions of polymer extrudate most likely appear when the recoverable shear s_R, which is defined as the ratio of the die wall shear stress to the elastic shear modulus, reaches a critical value of 1–10 [14,15]. Therefore, any effort to reduce or completely eliminate the distortions in the polymer flow must take into consideration some major parameters when spinning hollow fibers from a polymer solution, namely: (1) spinneret designs; (2) dope solution flow rate and rheology; (3) spinning temperature; (4) air gap distance; and (5) take-up speed.

Apart from the technical related parameters, the extrudate flow behavior is very much depending on the polymer material characteristics. In particular, the extrusion behavior of linear and branched polymers with nearly identical viscosity functions demonstrates major qualitative flow distinctions [5,24–26]. Generally, polymers tend to relax by motion along their backbones. However, in the branched polymers, this motion is hindered by branch points, thus the relaxation time increases dramatically [27]. The magnification of polymer chain relaxation time can possibly amplify flow instability and also can be a major contributor to the die swell effect [24,25]. For reader's information, the term flow instability used in the later discussion in this manuscript refers to the extrudate distortion behavior.

In the recent years, polymers with highly branched structures are gaining more popularity due to their large number of functional groups and high surface reactivity in contrast to their linear analogues [28]. Among the various classes of branched polymers, hyperbranched materials, an outgrowth of the invention of dendrimer, are considerably new materials, and little is known of their rheological properties [27]. Although much progress has been achieved in the structural understanding and the synthesis of hyperbranched polymers, much of the fundamental understanding, especially the industrial application of these hyperbranched polymers are still in a stage of infancy [28–30]. In addition, few studies were conducted to systematically compare hyperbranched polymer properties with their linear analogues [31], but the differences between hollow fiber membranes spun with the linear and hyperbranched counterparts were not clearly indicated. The hyperbranched polymers possessing higher intrinsic solubility, lower melt or solution viscosity and lower entanglement in their structures have been expected to be easier to process [32], which is extremely important for hollow fiber membrane spinning in large scale.

Our group conducted an investigation previously [24,25] to identify the unique properties of hyperbranched polyethersulfone (HPES) as compared to linear polyethersulfone (LPES). Rheological studies on the molten HPES and LPES materials show that HPES has a larger molecular weight and a wider molecular weight distribution compared to its linear analogue. Furthermore, the rheological characterization reveals that the HPES dope solution has a longer relaxation time than its linear counterpart. Hence, the HPES nascent fiber spun with conventional straight spinnerets shows a more pronounced die swell and flow instability, i.e. flow distortion, occurring at the spinneret's exit.

Although the residence time of a polymer solution flowing through the annular channel of spinneret (a few millimeters long) is very short, the flow-induced shear stress can affect the rheological behavior of the polymeric solution, i.e. relaxation time, die swell effect, and molecular orientation [8,25,33–37]. For straight annular spinnerets, the highest shear stress usually occurs along the die wall since the dope solution is normally a polymeric non-Newtonian fluid [38]. Therefore, it is crucial to understand the design principles behind engineering a spinneret for spinning a hyperbranched polymer for improved flow stability and reduced die swell effect. To the present, membrane researchers have attempted to modify their spinneret designs for multiple purposes, namely: (1) to tailor pore size distribution and control pure water permeability of ultrafiltration hollow fiber membranes by fabricating spinnerets with different flow angles [8]; (2) to approximately double the surface area of hollow fiber membrane for gas separation by designing a spinneret with microfabricated inserts to create corrugated patterns in the outer fiber perimeter [20]; (3) to induce interlayer diffusion in the interface of dual-layer hollow fiber membrane in order to eliminate delamination [39].

Based on the fundamental understanding of relaxation mechanism in the HPES polymer, other than the common spinneret with a L (die length)/ΔD (die channel) ratio of approximate 10, we have fabricated various other spinnerets with modified exit channels to reduce shear rate (stress) towards polymer solution inside the spinneret. Furthermore, the flow and shear behaviors inside the common and modified spinneret designs were simulated. In this regard, our objectives are: (1) to extensively examine and compare the effects of spinning parameters on the die swell effect and flow stability of LPES and HPES polymer solutions; (2) to overcome the die swell and flow instability problem with the aid of modified spinneret designs, particularly in the HPES hollow fiber membrane fabrications. It is believed that the fundamental knowledge obtained in this study not only provides useful guidelines for academia and industries in fabricating hollow fiber membranes from hyperbranched polymers but also introduces state-of-art spinneret designs to counteract die swell and flow instability in fiber spinning.

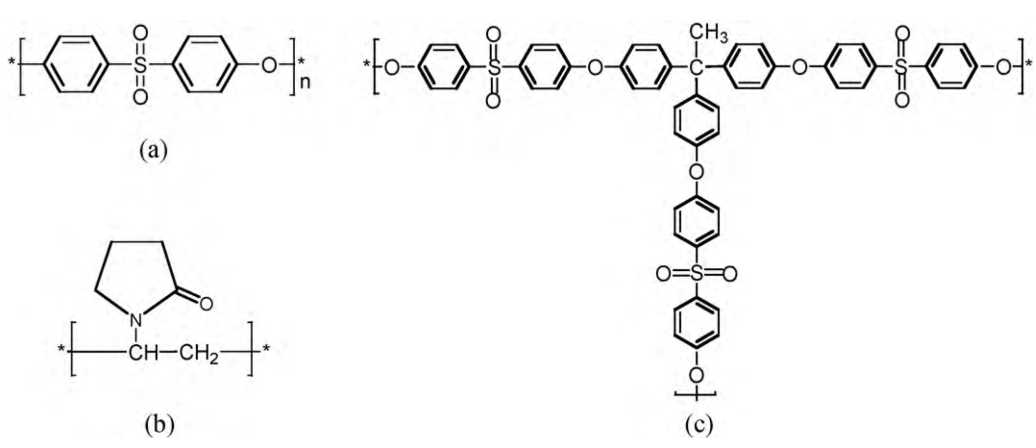

Fig. 1. The chemical structures of: (a) linear polyethersulfone (LPES); (b) hyperbranched polyethersulfone (HPES); (c) polyvinylpyrrolidone (PVP).