



Tuning the water permeability of ultra-high molecular weight polyethylene microporous membrane by molecular self-assembly and flow field



Sijun Liu ^{a,b}, Wei Yu ^{a,*}, Chixing Zhou ^a

^a Advanced Rheology Institute, Department of Polymer Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China

^b National Engineering Research Center for Nanotechnology, Shanghai 200241, PR China

ARTICLE INFO

Article history:

Received 17 August 2013

Received in revised form

24 February 2014

Accepted 28 February 2014

Available online 10 March 2014

Keywords:

Ultra-high molecular weight polyethylene

Dibenzylidene sorbitol

Flow field

ABSTRACT

We have systematically studied phase separation behavior in ultra-high molecular weight polyethylene/liquid paraffin/dibenzylidene sorbitol (UHMWPE/LP/DBS) ternary blends. The aim of this paper is to investigate the combined effect of DBS and flow field on the structure and water permeability of UHMWPE microporous membrane. The experimental results show that DBS molecules self-assemble into fibrils firstly during cooling and the blends exhibit a gel-like state before liquid–liquid phase transition. The relaxation time of DBS fibrils is quite long, which shows a great sensitivity to flow field as compared to UHMWPE chain. UHMWPE microporous membrane was prepared via thermally induced phase separation method. DBS fibrils, as in situ formed nucleating agent, decrease the pore size and water permeability and enhance mechanical properties of membrane remarkably. Shear flow can result in alignment of DBS fibrils, which facilitates the nucleation of UHMWPE and induces the lamellae aligned perpendicular to flow direction. This feature was used to design thermal and mechanical histories and obtained oriented UHMWPE microporous membrane. In comparison to the isotropic UHMWPE microporous membrane, the oriented UHMWPE microporous membrane provides low tortuous paths across the membrane and produces high water permeability.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The thermally induced phase separation (TIPS), firstly suggested by Castro in 1980s, is one of the most useful techniques to prepare polymer microporous membrane [1–9]. In the TIPS process, a homogeneous polymer and diluent blends mixed at a relative high temperature, and then the solution is cooled to induce phase separations. Liquid–liquid phase separation (LLPS) or solid–liquid phase separation (SLPS), or both can happen in such processes. During LLPS, a polymer-rich continuous phase and polymer-poor droplet or the interconnected bicontinuous structure are formed, and then grow as a result of coarsening. A cellular or a lacy structure is obtained after removing the diluent by solvent extraction, and the final membrane shows good porosity and water permeability. In the process of SLPS, a leafy or spherulitic structure is usually obtained as the polymer solidifies or crystallizes prior to LLPS, and

the resulting membrane presents poor porosity and water permeability, but excellent breaking stress and elastic moduli. Therefore, different phase separation behaviors have important effects on the final structures and properties of microporous membrane in the TIPS process.

In polymer–solvent binary system, polymer microporous membrane can be prepared with different pore size, porosity, water permeability and mechanical strength by controlling polymer concentration, cooling rate, quenching temperature or annealing time. In addition, efforts have also been paid to adjust the microstructures by a third component that may affect the process of TIPS. For example, adding zeolite particles [10,11] to liquid–liquid thermally induced phase separation system complicates the droplet growth behavior and significantly influences the final cell size since the strong polymer–zeolite affinity results in the migration of dissolved polymer to the zeolite particle surface. Han [12] studied the effect of polyethylene glycol (PEG) with different molecular weights on pore size and porosity of polyphenylene sulfide (PPS) membrane, and indicated that PEG as a nucleating agent could increase pore density and porosity, and decreases pore size. Cui [13]

* Corresponding author. Tel.: +86 21 54743275; fax: +86 21 54747159.

E-mail address: wyu@sjtu.edu.cn (W. Yu).

prepared poly (vinylidene fluoride) (PVDF) membrane by melt-blending the ternary mixture of PVDF/SiO₂/dibutyl phthalate (DBP), and found that water permeability and tensile strength would reach a maximum at certain SiO₂ content. It can be inferred from all these reports that additive offers a wider route to control the porous structure and property in the process of membrane preparation. Unlike these additive particles that are most isotropic and inert, dibenzylidene sorbitol (DBS), as an amphiphilic molecule derived from the sugar alcohol D-glucitol (Fig. 1), can strongly interact in the presence of various solvents [14,15] and form a physical gel through self-assembling into a fibril network. In fact, the self-assembly of DBS can also happen in the melt of amorphous polymer like polystyrene or polycarbonate [16,17] and crystalline polymer such as polypropylene [18–21]. In the latter case, the DBS fibrils formed from self-assembly can promote heterogeneous crystal nucleation. Many authors have indicated that DBS fibrils of 10 nm in diameter create a polymer/DBS interface as large as 400 m² per gram of DBS [22,23], which assist polymer chains to crystallize into numerous small spherulites and endow the polymer with enhanced mechanical strength and optical clarity [24,25].

In our previous work [26], we systematically studied phase separation behavior in ultra-high molecular weight polyethylene/liquid paraffin (UHMWPE/LP) blends, and found UHMWPE and LP have excellent affinity due to their similar chemical structure and the close solubility parameter ($\delta_{\text{UHMWPE}} \approx 16.12 \text{ J}^{1/2}/\text{cm}^{3/2}$ and $\delta_{\text{LP}} \approx 15.96 \text{ J}^{1/2}/\text{cm}^{3/2}$). In contrast to most of papers which cannot differentiate LLPS from crystallization in this system [27–29], our experimental results showed that it is possible to manipulate different phase separation behaviors by controlling the relative quenching depth and annealing time, which can offer more delicate control on the microporous structure of UHMWPE membrane using the thermally induced phase separation. It is well known that DBS fibrils as a nucleating agent have an important influence on polymer crystallization, while the effect of DBS fibrils on UHMWPE microporous membrane has not been investigated yet. Our recent work has illustrated the effect of DBS on the LLPS and SLPS in UHMWPE/LP system [30]. In this work, we will study the role of DBS fibrils in preparation of UHMWPE microporous membrane. The focus is how to increase the water permeability substantially by controlling the morphology of DBS fibrils and phase transitions of UHMWPE.

2. Experimental

2.1. Materials and membrane preparation

UHMWPE was kindly supplied by Shanghai Chemical Technology Institute, and the number average molecular weight is approximately 2,000,000 g/mol. DBS was obtained in powder form from Miliken chemical. Liquid paraffin, composed of short alkane with the average molecular weight about 150–250 g/mol, was purchased from Shanghai Chemical Reagent Factory and used without further purification.

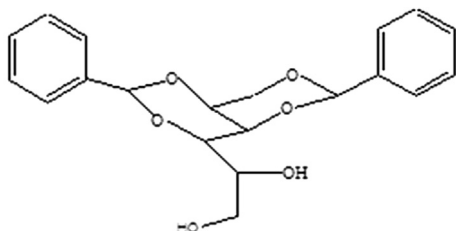


Fig. 1. Chemical structure of dibenzylidene sorbitol (DBS).

First of all, LP/DBS gel was prepared by heating the required quantities of DBS and LP in a glass vessel under nitrogen atmosphere up to a temperature between 180 °C and 220 °C depending on DBS amount. Since the melting point of DBS in LP is greatly depressed, and dependent on the DBS content [15], such temperature range is sufficient for the complete melting of DBS in LP for DBS content less than 0.56 wt%. A clear solution was obtained, and then the sample was cooled down to the room temperature. After that, the predetermined amounts of UHMWPE powders and LP/DBS gel were manually premixed with a glass bar at room temperature for several minutes followed by melt-mixed in a batch mixer (XSS-300, Shanghai Kechang Rubber & Plastic Equipment Co, China) at 165 °C for 10 min with the rotor speed 60 rpm. The UHMWPE/LP weight ratio is fixed as 10/90 and the weight fractions of DBS in the total weight of the ternary blends are 0, 0.05, 0.1, 0.2, 0.3 and 0.5 wt %, respectively.

UHMWPE microporous membranes were prepared by the two experimental procedures described herein. In the first procedure, the homogeneous UHMWPE/LP/DBS small pieces were compressed into film (thickness $\approx 100 \mu\text{m}$) at 165 °C and then cut into a disk of 40 mm in diameter. In order to accurate control cooling rate and shear strain, the disk was heated on a hot stage to 165 °C and kept for 10 min to eliminate thermal history, and then cooled directly to room temperature with cooling rate of 2 °C/min. The disk can also be quenched to the desired test temperature depending on DBS amount where shear flow was applied, subsequently cooled to room temperature. As shown below in Fig. 3, 165 °C is sufficient high for the complete melting of UHMWPE and DBS fibrils. Samples were taken out and solidified in the liquid nitrogen. After LP in the sample was extracted in ethanol for 48 h and dried in vacuum oven for 24 h at 40 °C, UHMWPE microporous membrane was obtained. In the second procedure, the large UHMWPE membranes were prepared for the measurements of porosity, water permeability and mechanical strength. The pre-compressed UHMWPE films with diameter in 100 mm were sealed in a stainless cell developed at our lab. The film was heated to 165 °C for 10 min to eliminate thermal history, and then quenched to the desired temperature and subjected to controlled flow using a parallel plate. Fig. 2 shows a schematic diagram of the shear cell and a diagrammatic representation of a typical experimental procedure. The thickness of film d keeps a constant value depending on the height of cell notch, the distance of up-plate move h is calculated in advance according to the desired strain γ , $h = \gamma \cdot d$. The way to extract LP and obtain microporous membrane is the same as the first procedure.

2.2. Rheological measurements

Rheological measurements were performed on a rotational rheometer (Gemini 200HR, Bohlin Instruments, UK) with parallel plate geometry of 20 mm in diameter and a gap of 1.0 mm. The samples for rheological measurements were obtained by compressing UHMWPE/LP/DBS blends into a sheet with the thickness about 1.0 mm under 165 °C and 10 MPa. Strain sweeps in the range of 0.01–1.0 at frequencies of 0.1–2 Hz were carried out to determine the linear viscoelastic range. The annealing treatment was held at 165 °C for 10 min to eliminate the pristine crystalline structures, and the stability of the sample was checked through the measurement of G' and G'' with 0.1 Hz in the linear viscoelastic region. Little change in G' and G'' was found over a long period (120 min) at 165 °C with a strain amplitude of 1.0%, which illustrated that the effects of LP loss and thermal oxidation can be ignored.

Three rheological experiments were performed to study the viscoelasticity of DBS fibrils and the effect of shear flow on the DBS fibril network. (1) In order to study the relaxation behavior

Download English Version:

<https://daneshyari.com/en/article/5181325>

Download Persian Version:

<https://daneshyari.com/article/5181325>

[Daneshyari.com](https://daneshyari.com)