

PREPARATION OF MICROPOROUS ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE (UHMWPE) BY THERMALLY INDUCED PHASE SEPARATION OF A UHMWPE/LIQUID PARAFFIN MIXTURE*

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Abstract Ultra-high molecular weight polyethylene (UHMWPE) with a microporous structure was prepared *via* thermally induced phase separation (TIPS). Liquid paraffin (LP) was used as a diluent in the preparation of microporous UHMWPE. Small angle laser light scattering (SALLS) and differential scanning calorimetry (DSC) were used to determine the phase separation temperatures, *i.e.* the cloud points and the dynamic crystallization temperatures, respectively. It was found that the cloud points were coincident with the crystallization temperatures, indicating that a solid-liquid phase separation occurred during thermal quenching of the UHMWPE/LP solution, while, no liquid-liquid phase separation above the crystallization temperature was observed. The effects of the content and the molecular weight of UHMWPE on the morphology and average pore size were investigated with field emission scanning electron microscopy (FE-SEM) and mercury porosimetry. With the increase of the content of UHMWPE, the average pore size of the microporous material decreased and the molecular weight of UHMWPE could also influence the pore size slightly.

Keywords: Ultra high molecular weight polyethylene; Thermally induced phase separation; Liquid paraffin.

INTRODUCTION

Due to its excellent physico-chemical properties such as wear resistance, impact resistance, corrosion resistance, self-lubrication and so on, ultra high molecular weight polyethylene (UHMWPE) was called as supernatural plastic. Microporous UHMWPE is a new type of functional material that can be used widely for heterogeneous phase separation filtration in chemical, medical and energy fields^[1].

As one of the most effective ways to prepare microporous materials, thermally induced phase separation (TIPS) technique has received extensive interest^[2–5]. TIPS is related to the temperature-dependent solubility of polymers. For a polymer/diluent mixture with upper critical solution temperature (UCST), at elevated temperatures, the polymer can be dissolved to form a homogeneous solution, while with the decrease of temperature, the solubility of polymer decreases. At a certain temperature the polymer is no longer soluble, and phase separation is induced. After the polymer is solidified by crystallization or vitrification, a phase-separated structure with a diluent-rich phase and a polymer rich-phase is formed. The residual diluent can be extracted to produce microporous materials. A lot of studies have been reported on the microporous membrane formation *via* TIPS mainly from the basic standpoint of thermodynamics and kinetics^[3–10]. The phase diagrams and structure growth mechanism have been clarified in many UCST systems. For example, Matsuyama and his coauthors^[6] have prepared microporous high density polyethylene (HDPE) hollow fibers *via* TIPS of the HDPE solution in liquid paraffin (LP) and diisodecyl phthalate. The nonisothermal crystallization kinetics of UHMWPE in liquid paraffin has been reported by Zhang^[11]. However, to our knowledge, preparation of microporous UHMWPE from UHMWPE/LP mixture *via* TIPS has not been studied.

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In this work, the microporous material of UHMWPE was prepared from UHMWPE/LP mixture *via* TIPS. The effects of contents and molecular weights of UHMWPE on the cloud points and crystallization temperatures and the morphology of the microporous material were investigated. Results in this study not only enhance our knowledge of TIPS, but also contribute to efforts to prepare high performance porous membranes for appropriate applications.

EXPERIMENTAL

Materials

UHMWPE with two different molecular weights ($M_w = 3.5 \times 10^6$ and $M_w = 2.5 \times 10^6$, abbreviated as UHMWPE35 and UHMWPE25, respectively) were supplied from Beijing No.2 Auxiliary Agent Factory, China. Liquid paraffin with an average molecular weight of 500 was used as the diluent and *n*-heptane was used as an extractant. They were both from Hangzhou chemical agent Co. Ltd, China and used without further purification. Antioxidant 1010 was from Shanghai chemical agent Co. Ltd, China.

Preparation of UHMWPE/LP Mixture

Homogeneous polymer-diluent mixture was prepared by mixing UHMWPE and LP at various ratios in the mixing chamber of a Haake torque rheometer (Rheomix 600, Thermal Haake, Germany) at a rotating rate of 60 r/min and a temperature of 160°C for 15 min in the existence of antioxidant, and then being cooled to room temperature in the air.

Determination of the Crystallization Temperatures and Cloud Points

The cloud points of the UHMWPE/LP mixture was determined by a laboratory-made small angle laser light scattering (SALLS) apparatus. The details on the apparatus of SALLS have been reported previously^[12]. A He-Ne laser generator with a power of 5 mW (Opt. Inst. Plant, Zhejiang University, Hangzhou, China) was used as the light source. A hot stage with a power of 100 W is controlled by an intelligent controller (AI-700, Yuguang, Xiamen, China). Thin sample films were placed between two glass cover slides with a 100 μm Teflon spacer inserted between the two slides. The samples were heated on the hot stage at 160°C for 5 min and then cooled at the cooling rate of 2 K/min. The scattering light impinged on an opaque screen was captured in real time by a CCD camera (MTV-1802CB, MINTRON, Taiwan, China) at a time interval of 0.22 s, then, imported into the computer memory through a video capturing board (Daheng, Beijing, China). The integral scattering intensity Q , a parameter reflecting the density heterogeneity, as defined in Eq. (1), is recorded in real time.

$$Q = \int I(q) q^2 dq \quad (1)$$

in which, q and $I(q)$ are the scattering vector and the scattering intensity at scattering vector q , respectively. Upon phase separation, the intensity of the scattering light increased abruptly. The onset of the increase of scattering intensity was regarded as the cloud points.

The dynamic crystallization temperatures of the samples with various UHMWPE/LP ratios were measured by DSC (Q100 Perkin-Elmer, USA). The samples were heated to 160°C at a heating rate of 10 K/min, held at 160°C for 5 min, and then cooled at a rate of 2 K/min. The onset of the exothermic peak during the cooling process was taken as dynamic crystallization temperature.

Characterization of Average pore Size and Morphology

LP in the UHMWPE/LP mixture was removed by extended Soxhlet extraction in *n*-heptane for about 48 h, then, the residual *n*-heptane was removed by evaporation under vacuum at 50°C. The average pore diameters of the samples were measured by mercury porosimetry using a Micromeritics Autopore IV 9500 (Micromeritics, USA). For SEM observation, the microporous material was fractured in liquid nitrogen. The cross-section of the sample was sputter-coated with Au in vacuum and observed on a SIRION FE-SEM (FEI, The Netherlands) operated at an accelerating voltage of 25 kV.

RESULTS AND DISCUSSION

The cloud points of the UHMWPE/LP system were determined by SALLS. A typical scattering intensity versus temperature curve of the UHMWPE/LP mixture containing 23.6% UHMWPE35 at a cooling rate of 2 K/min was presented in Fig. 1. During the cooling process, TIPS can be divided into three stages according to the change rate of scattering intensity. At stage I with relatively high temperatures, the scattering intensity is low and remains constant, because the mixture is homogeneous and no phase separation happens. At stage II, scattering light intensity increases sharply. The onset temperature for the increase of intensity is defined as the cloud temperature, T_{cp} . During this stage, phase separation starts and proceeds very quickly. At stage III, scattering light intensity increases less rapidly. With the decrease of temperature, the viscosity of the system increases consequently, resulting in the decrease of phase separation rate. More important, during phase separation, the system contains a less viscous LP-rich phase (that is, diluted phase) and a viscoelastic UHMWPE-rich phase. As a dynamically asymmetric phase separation system, the viscoelastic UHMWPE-rich phase forms continuous networks in the system and the diluted phase dispersed as droplets in the UHMWPE-rich matrix. Therefore, the phase separation rate decreases apparently at stage III. At stage IV, the scattering light intensity reaches the maximum, indicating the end of phase separation.

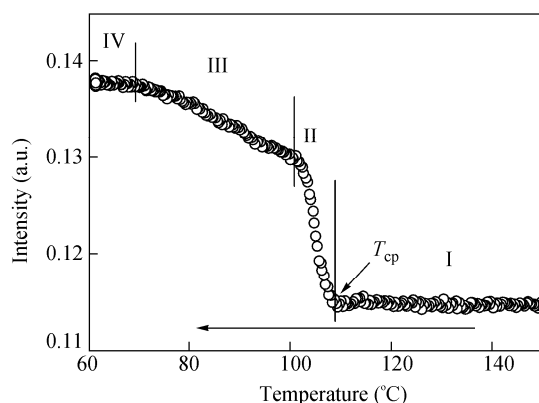


Fig. 1 Scattering light intensity versus temperatures of the system containing 23.6% UHMWPE35 in the cooling rate of 2 K/min

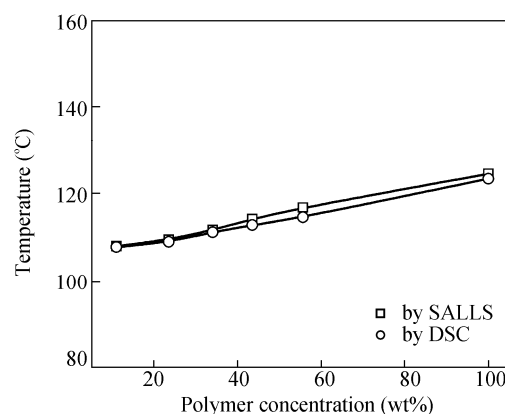


Fig. 2 Comparison of cloud points and the dynamic crystallization temperatures in UHMWPE/LP systems with different concentration of UHMWPE35

Previous studies have indicated that for crystalline polymer-diluents systems, the TIPS mechanism is determined by the competition between liquid-liquid phase separation and crystallization (*i.e.* solid-liquid phase separation). Below the melting point, crystallization is the favorable process unless the nucleation barrier associates with polymer crystallization existed^[13, 14].

Figure 2 presents the phase separation temperatures obtained by SALLS and the dynamic crystallization temperatures obtained by DSC analysis of the UHMWPE35/LP mixtures at various UHMWPE concentrations. It is shown that with the increase of UHMWPE contents, both the phase separation temperatures and the crystallization temperatures increase. More important, for all the samples, no significant difference between the phase separation temperatures and the dynamic crystallization temperatures is observed. Same phenomenon has also been observed for the UHMWPE25/LP mixtures. This indicates that the observed cloud points are in fact resulted from the crystallization of UHMWPE and so a solid-liquid TIPS rather than a liquid-liquid phase separation during the cooling process. The true cloud points (or in other words, the temperatures for liquid-liquid phase separation) are probably below the crystallization temperature so not observable in our experiments. This means that the compatibility between UHMWPE and LP is very good. Similar phenomenon has also been reported by Matsuyama *et al.* for a high-density polyethylene/LP mixture^[6].

Now, we discuss the influence of UHMWPE contents in UHMWPE/LP mixtures on the crystallinity and the pore size of the final porous UHMWPE. Enthalpy of polymer melting is proportional to its crystallinity. If the enthalpy of 100% crystalline polymer melting is known, crystallinity of polymer that is partly crystalline can be calculated according to the following function:

$$\theta = \frac{\Delta H_f}{\Delta H_f^*} \times 100\% \quad (2)$$

where θ is crystallinity, ΔH_f is enthalpy of polymer melting, ΔH_f^* is enthalpy of 100% crystalline polymer melting, equal to 288.42 J/g^[15].

The crystallinity values for UHMWPE35/LP systems with different polymer concentration calculated are given in Table 1. The results indicate that the normalized crystallinity values are roughly equal. That is to say, the crystallinity values are hardly influenced by the amount of LP.

Table 1. Crystallinity of UHMWPE35/LP systems with different polymer concentration

Mass content of UHMWPE (%)	ΔH_f (J/g)	Normalized crystallinity (%)
23.6	44.4	65.2
34.1	62.3	63.3
43.6	87.9	69.9
55.7	111.5	69.4
100	185.7	64.4

Figure 3 gives the morphology of the microporous UHMWPE, which sheds light on the effect of UHMWPE contents on the morphology and pore size of the microporous material. The pore sizes are heterogeneous for the microporous material with 23.6 wt% UHMWPE35 and 23.1 wt% UHMWPE25. However, the microporous material with 43.6% UHMWPE35 and 46.2% UHMWPE25 has smaller pore sizes. The average pore size of microporous UHMWPE decreases with the increase of the content of polymer (Table 2). This is similar to the mixture of HDPE/LP as reported by Matsuyama^[16].

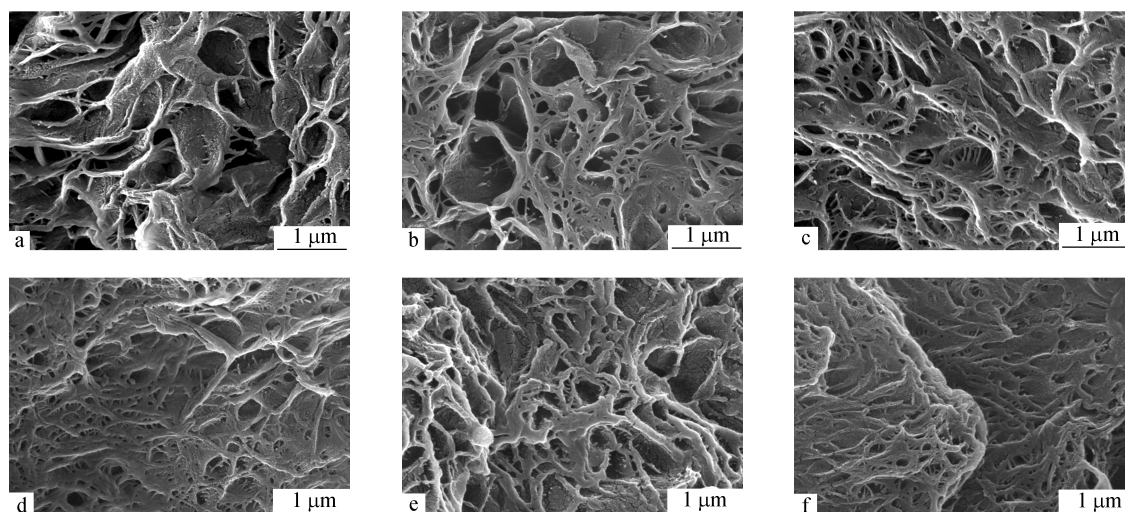


Fig. 3 SEM images of the microporous material prepared from UHMWPE35/LP and UHMWPE25/LP mixtures with similar polymer concentration: (a) 23.6% UHMWPE35, (b) 23.1% UHMWPE25, (c) 43.6% UHMWPE35, (d) 46.2% UHMWPE25, (e) 55.7% UHMWPE35 and (f) 55.6% UHMWPE25

Table 2. Pore size of UHMWPE/LP systems with different polymer concentration

UHMWPE35/LP		UHMWPE25/LP	
Polymer concentration (wt%)	Average pore diameter (μm)	Polymer concentration (wt%)	Average pore diameter (μm)
23.6	0.1211	23.1	0.1134
43.6	0.0583	46.2	0.0571
55.7	0.0480	55.6	0.0450

It is shown in Fig. 3 that the average pore size of UHMWPE35/LP system is slightly larger than those of UHMWPE25/LP system by comparing the microstructure with similar polymer concentration. But it seems that the influence of molecular weight on the average pore size is not significant. The concentration of UHMWPE plays a more important role in determining the pore sizes. This phenomenon is different from porous HDPE and *i*PP exhibiting a significant dependence of molecular weight on average pore sizes^[6, 17]. A possible explanation to this is that the molecular weights of the two kinds of UHMWPE are so high that the comparative difference in the viscosity of the UHMWPE/LP mixtures with similar UHMWPE contents is small, so the phase separation rate is similar. For the solution- or melt-crystallized UHMWPE, the random arrangement of curved lamellae consists of a spherulite structure. The lamellar thickness is between 10 nm and 30 nm^[18]. Because of the limitation of SEM the representative structures resulted from solid-liquid phase separation, such as spherulite structures, cannot be seen in Fig. 3.

CONCLUSIONS

We have prepared microporous UHMWPE materials *via* TIPS of UHMWPE/LP mixtures. It was found that for the polymer concentration region investigated in this article, the TIPS mechanism of UHMWPE/LP system was the solid-liquid phase separation due to UHMWPE crystallization. Moreover, the mechanism was almost independent of the molecular weight of UHMWPE. However, the microstructure of microporous UHMWPE depended on the content and the molecular weight of UHMWPE. The average pore size of UHMWPE/LP system decreased and the microspore uniformity increased with the increase of the content of UHMWPE. The results also indicated that the pore size of the system containing larger molecular weight UHMWPE was larger when the polymer concentration was similar.

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