



Preparation of polyethylene microporous membranes with high water permeability from thermally induced multiple phase transitions



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ABSTRACT

Thermally induced phase separation (TIPS) has been widely used to prepare microporous membrane. The interaction and dynamic asymmetry between polymer and solvent sometime make the transition happen through viscoelastic phase separation (VPS) mechanism. Under such condition, cell like structure is obtained with low water permeability. In this paper, a new method is proposed to obtain high permeability membranes by TIPS. Dibenzylidene sorbitol (DBS) and HDPE-g-MAH are introduced into the polyethylene/di-iso-decyl phthalate (HDPE/DIDP) system, which exhibits an upper critical solution temperature (UCST) behavior and undergoes VPS mechanism during cooling. DBS can self-assemble and form fibril network both in HDPE and DIDP. The addition of HDPE-g-MAH makes DBS mainly distributed in HDPE-rich domains, while it mostly locates in the DIDP-rich domain in the ternary system due to their similar polarity. The self-assembly of DBS in the HDPE-rich domains can induce the secondary liquid–liquid phase separation, which significantly change the structure in walls between cells. High permeability of pure water and high retention of permeability in silica suspension can be obtained under proper control of the extent of these phase transitions.

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1. Introduction

Thermally induced phase separation (TIPS) has become one of the most popular techniques to prepare the polymer microporous membranes [1–3], especially for polyolefins [1,4–11], which don't have suitable solvent at room temperature. In the TIPS process, the mixture of polymer and diluent is heated to elevated temperature to obtain a homogeneous system and then cooled down to induce the phase separation. After the solvent extraction and drying, a polymer membrane with desired structure is obtained.

By varying the raw material, polymer concentration, cooling rate, quenching depth, annealing time etc., microporous membrane with different pore size, porosity, water permeability and mechanical strength can be prepared. During the cooling process, either solid–liquid phase separation (SLPS) or liquid–liquid phase separation (LLPS) or both take place in the polymer/diluent system. In the case of SLPS, a leafy or spherulitic like structure with lower porosity and water permeability but smaller porous size is usually observed [5,12,13]. As to LLPS through spinodal decomposition

mechanism, the interconnected bicontinuous structure with higher porosity, higher water permeability and larger porous size [14,15] is often obtained. Whereas, if SLPS and LLPS both take place, the final pore structure becomes variable via manipulating the two phase separation processes. In fact, due to the large dynamical asymmetry between polymer and diluent, LLPS through viscoelastic phase separation mechanism is more likely to dominate [16], where the major diluent forms isolated droplets due to the higher elasticity of the minor component. Then, the cellular structure forms [5,13,15,17,18], and the water permeability depends greatly on the porosity on the polymer network, which is usually very low for amorphous polymer and semicrystalline polymer. Decreasing the content of polymer in polymer/diluent solution may possibly increase the water permeability at the cost of mechanical properties. Therefore, although there is a large amount of theoretical investigations on the viscoelastic phase separation [16,19–22], LLPS through spinodal decomposition to form bicontinuous structure is still preferred in application.

In addition, the effect of the third component was also studied to achieve more freedom in control of structure. Funk et al. [23,24] found that adding zeolite particles to liquid–liquid thermally induced phase separation system complicated the droplet growth behavior and greatly influenced the pore size, which was mainly

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ascribed to the strong polymer-zeolite affinity. Cui et al. [25] investigated the influence of SiO₂ particle in the poly (vinylidene fluoride) (PVDF)/dibutyl phthalate (DBP) system, and found the maximum water permeability and tensile strength at certain SiO₂ content. Ma et al. [26] found that adding nanoparticle (MMT and PTFE (Polytetrafluoroethylene)) in PVDF/DPK (diphenyl ketone) system decreased the pore size of membrane, which could be attributed to the short time for the SLPS owing to the fast crystallization in presence of nanoparticle. Li et al. [27] even found that the CdSe nanorods and nanospheres kinetically arrested co-continuous morphologies in demixing polymer blends due to gelation of the nanoparticles within one of the polymer phases. Besides these isotropic or inert additives, self-assembly (or sol–gel transition) has also been adopted recently to form nano-objects in-situ in polymer/diluent system during TIPS. Liang et al. [28] reported an approach to prepare hybrid membranes by sol–gel transition of tetraethoxysilane in PVDF/dimethylsulfone (DMSO₂)/tetraethoxysilane (TEOS) ternary system, where the homogeneously dispersed SiO₂ improve the mechanical properties and water permeation. Liu et al. [29,30] suggested using the dibenzylidene sorbitol (DBS) to control the pore structure in polyethylene/liquid paraffin system. In fact, DBS is widely used as nucleation agent in the polymer system [31–33], which can strongly interact and self-assemble to form a physical gel into fibril network in various matrices [34–36]. The self-assembly of DBS depends on the solvent polarity, DBS concentration, temperature and time [37]. In contrast to the sol–gel transition of TEOS induced by ammonia solution [28], the self-assembly of DBS is also thermally driven. Therefore, the interplay between LLPS, SLPS and self-assembly of DBS becomes crucial for the structural development. Liu [29,30] found that the self-assembly temperature is higher than that of LLPS and SLPS in the UHMWPE/LP/DBS system. Because of the narrow gap between LLPS temperature and SLPS (crystallization) temperature, the self-assembly of DBS and the crystallization of UHMWPE determined the porous structure. Oriented porous structure was obtained by controlling the direction of DBS nanofibrils through shear flow, which could increase the water permeability over five times.

In this paper, the influence of DBS self-assembly on LLPS and SLPS of polyethylene/diluent system will be discussed. Di-iso-decyl phthalate (DIDP) is chosen as the solvent due to their low affinity with PE, which can generate wider range of LLPS as compared to LP in our previous studies [29,30] and make more room to tune phase separation and self-assembly. Also, through heterogeneously self-assembly of DBS from the selectively distribution in phase separated blends, the water permeability of binary PE/DIDP system is improved compared to the traditional viscoelastic phase separation.

2. Experimental section

2.1. Materials and sample preparation

HDPE (Mw~80,000 g/mol, PDI~3.0) was purchased from Taisox Company. DBS powder was obtained from Miliken Chemical. Di-iso-decyl phthalate was purchased from TCI Company. The HDPE-g-MAH (5600D) was obtained from Dupont Company.

For the HDPE/DIDP binary system, the pre-determined quantities of HDPE and DIDP were mixed in a flask using mechanical agitation apparatus under a nitrogen atmosphere at 200 °C, and then the homogeneous solution was cooled down to room temperature to obtain the HDPE/DIDP sample. For the HDPE/DIDP/DBS, the DIDP/DBS gel was obtained by mixing the required quantities of DBS and DIDP in a flask using magnetic stirring apparatus under nitrogen atmosphere at 200 °C. Then the homogeneous solution was cooled down to room temperature to obtain DIDP/DBS gel. The

DIDP/DBS gel and HDPE powder were mixed in a flask using a mechanical agitation apparatus under nitrogen atmosphere at 200 °C, then it was cooled to room temperature. The same process was employed to prepare the HDPE/HDPE-g-MAH/DIDP/DBS system with the addition of HDPE-g-MAH in the second step. For HDPE/DIDP/DBS ternary system, the sample is named as A-B-C, where A, B, C represents the content of HDPE, DIDP, and DBS, respectively. For example, in sample 30-70-1, the ratio between the weight fraction of HDPE and that of DIDP is 30/70, and DBS of 1% weight of total HDPE and DIDP is added. For the system containing HDPE-g-MAH, it is denoted as MAH A-B-C, the content of HDPE-g-MAH was kept constant as 5 wt.% of the HDPE content.

To prepare the HDPE microporous membranes, small pieces of samples were compressed into film (thickness ~ 100 μm) at 200 °C with a pressure of 5 MPa. Three cooling protocols, namely the quick quenching (~50 °C/min), slow quenching (~1 °C/min) or isothermal at certain temperature for certain time (5 min), were adopted to prepare the microporous polymer films. Afterwards, the obtained films were put into ethanol for 48 h to extract DIDP and dried in vacuum oven at 40 °C for 24 h.

2.2. Rheological measurements

The rheological measurements were performed on a rotational rheometer (Bohlin Gemini 200HR, Malvern Instruments, UK) using coaxial cylinder with the cup diameter 38.5 mm and the bob diameter 35 mm. Before the experiments, the sample was heated to 200 °C for 5 min to eliminate the pristine crystalline structures, and the silicone oil was added on the surface of the sample to prevent the volatilization of DIDP. The measurement modes are given below. The strain sweep experiment was conducted to get the linear region of the system. In the linear region, temperature ramp under 1 rad/s from 200 °C to 100 °C with a 2 °C/min rate was conducted to determine the non-isothermal phase separation temperature. Cyclic frequency sweep at specified temperature was used to monitor the time evolution of phase transition in the sample.

2.3. Differential scanning calorimetry

A differential scanning calorimeter (DSC) (Q2000, TA Instruments) was adopted to study the crystallization behavior under the non-isothermal and isothermal condition. Small amount of sample (~8 mg) were sealed in an aluminum DSC pan, which was heated to 200 °C and kept for 5 min to remove thermal history. Then the samples were cooled down to 40 °C with cooling rates of 2 °C/min. Then the onset temperature of the exothermic peak during the cooling period was regarded as the non-isothermal crystallization temperature T_c . To investigate the crystallization behavior in isothermal process, after eliminating the thermal history at 200 °C for 5 min, the samples were quenched to certain temperature (130 °C and 120 °C) and annealed for 60 min. Subsequently, the sample was heated back to 200 °C to monitor the melting behavior.

2.4. Morphological observation

The evolution of morphology during phase separation was observed by optical microscopy. A small amount of sample was sandwiched between two glass coverslips separated by a 50 μm thick polytetrafluoroethylene (PTFE) spacer with a square opening in the center. The PTFE spacer allowed a uniform thickness of the sample as well as restricted DIDP evaporation in the observation. Two protocols were adopted to investigate the phase separation behavior of the sample. (1) In order to obtain the phase separation

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