Effects of 4A Zeolite Additions on the Structure and Performance of LDPE Blend Microfiltration Membrane through Thermally Induced Phase Separation Method

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Abstract: Microfiltration membranes, 4A zeolite/LDPE, were prepared by blending low density polyethylene (LDPE) and 4A zeolite through thermally induced phase separation (TIPS) process with diphenyl ether (DPE) as diluent. The effects of 4A zeolite loading on the pore structure and water permeation performance of the 4A zeolite/LDPE blend membranes were investigated. The incorporation of 4A zeolite particles greatly enhanced the connectivity of membrane pores, the pore size, and thus the water flux of 4A zeolite/LDPE blend membranes due to the gradually stronger DPE-zeolite affinity with the increase of the 4A zeolite loading. The water flux increased from 0 of LDPE control membrane to 87 L/m^{2}h of 4A zeolite/LDPE blend membrane with 4A zeolite loading of 10 wt%. In addition, increasing the DPE content and cooling bath temperature is in favor of the water flux of 4A zeolite/LDPE blend membranes.

Keywords: Low density polyethylene, 4A zeolite, Microporous membrane, Thermally induced phase separation.

INTRODUCTION

With the expanding application of membrane separation technology in chemical industry, urgent needs of strategies to increase the performance of membrane materials, such as precise control of membrane structures, cost reduction of membrane preparation and improvement of membrane strength, has prompted actions of many researchers [1, 2]. Low density polyethylene (LDPE) is an outstanding membrane material because of its nontoxicity, excellent mechanical strength, physical and chemical stability, high anti-degradation as well as low cost [3]. Unfortunately, up to now, LDPE has not been successfully fabricated into microfiltration membranes in industry as other polyolefins like high density polyethylene (HDPE), poly polyvinylidene fluoride (PVDF), polypropylene (PP) and so on. This is mainly due to its lower crystallinity and the lackage of solvent for LDPE at room temperature, both the conventional methods of melt-spinning & stretching (MS-S) and immersion precipitation (IP) cannot be used to prepare LDPE membrane. Thermally induced phase separation (TIPS) [4-8], based on the dependence of polymer solubility on temperature, offers an attractive way to prepare LDPE porous membranes where a homogeneous LDPE solution is formed by dissolving LDPE in diluent above the melting temperature of pure LDPE, and then phase separation is induced by cooling the LDPE solution. Zhang *et al*. [9, 10] have prepared hydrophobic polyethylene microporous membranes *via* the liquid-liquid TIPS process using the system of LDPE/diphenyl ether (DPE) and they found that, with the increase of LDPE mass fraction, the pore size decreased and the membranes microstructure varied due to different phase separation mechanisms. Unfortunately, the LDPE membranes prepared *via* TIPS suffer from extremely low permeability due to the poor pore connectivity. In this regard, membrane modification is expected to bring desired changes in structure and permeability to LDPE membrane without losing inherent characteristics.

Compared to the pure polymer membrane, the polymer/inorganic particle blend membrane has the advantages of pore structure tunability, better mechanical strength and significantly improved anti-fouling performance [11, 12]. Different with other commonly used inorganic particles, such as calcium carbonate ($CaCO_3$) [13], silica (SiO_2) [14], aluminium oxide (Al_2O_3) [15] and titanium dioxide (TiO_2) [16], 4A zeolite possesses the merits of large surface area, high thermal stability and good adsorption ability, and so on. For example, Funk *et al*. [17] prepared isotactic polypropylene/zeolite blend membrane *via* TIPS method. They found that the incorporation of zeolite particles played a very important role in the growth of diluent-rich droplets during liquid-liquid TIPS process and the ultimate pore size of the final membranes.

Therefore, in the present study, to improve the structure and permeability of LDPE, nano-sized 4A

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zeolite particles was used as filler to prepare 4A zeolite/LDPE blend membranes *via* TIPS process. Specifically, this study focuses on the effect of 4A zeolite loading on the morphology, mechanical and thermal properties of 4A zeolite/LDPE blend membranes. In addition, the effects of the composition of the initial casting solution and the temperature of cooling bath on the permeability of 4A zeolite/LDPE blend membranes were also investigated.

EXPERIMENTAL

Materials

Low density polyethylene (LDPE) with melting index of 1.5g/10min was supplied by Petrochina Daqing Petrochemical Company, Heilongjiang China. 4A zeolite with average particle size of 3.5 µm was purchased from Sigma Aldrich, USA. To remove water adsorbed on the particle surface, 4A zeolite powder was held at 200 ^{o}C in a vacuum oven for 48 h and then cooled down to room temperature in a dryer before the membrane preparation. Diphenyl ether (DPE), cyclohexane and ethanol were obtained from Sinopharm Chemical Reagent Co. Ltd., China and used and used without further purification.

Preparation of Membranes

The premixed LDPE/DPE blend systems were melted for 1 h at 170 ^{o}C in a glass vessel with stirring. After that, certain amounts of 4A zeolite were added into the LDPE/DPE solution and the mixtures were further melt for at least 5 h until homogeneous solution were formed. After degassed to remove bubble, the mixtures were quenched in liquid nitrogen and the solid LDPE/zeolite/DPE blend samples were obtained.

The process of membrane preparation was carried out as described in our previous work [18]. Briefly, a portion of the above sample was placed between a pair of stainless steel plate. A Teflon film with a square opening in the center was inserted between them to adjust the thickness of membranes to about 100 µm. The sample was heated up to 170 ^{o}C for 3 minutes on a heater and then pressed into thin film. After that, the stainless steel plate containing the film was taken out quickly and quenched in a cooling bath at different temperature for 10 minutes. The diluent in the film was extracted by immersing the membrane in ethanol for 48 hours. The final membrane was dried under vacuum at room temperature for 24 hr.

Scanning Electron Microscopy (SEM)

The surface and cross-section (fractured in liquid nitrogen) morphologies of 4A zeolite/LDPE membranes were inspected by a Hitachi S4800 scanning electron microscope (SEM) after being coated with gold, the final gold thickness on the membrane is 15 nm.

Differential Scanning Calorimetry (DSC)

The crystallization of 4A zeolite/LDPE membranes was characterized by DSC (PerkinElmer, DSC-7) at a heating rate of 10 ^{o}C/min. The crystallinity (X_c) was calculated based on equation (1) from the DSC curves [14]:

$$X_c = \frac{\Delta H / \phi}{\Delta H_m} \times 100\% \qquad (1)$$

where ΔH_m is the melting enthalpy for a 100% crystalline LDPE and the value is 273 J/g [19], ΔH is the melting enthalpy of the prepared membrane measured in DSC and ϕ is the weight fraction of LDPE in 4A zeolite/LDPE blend membranes.

Mechanical Properties Studies

Stretching testing of 4A zeolite/LDPE membranes were performed at room temperature using an electronic universal testing machine (WCT-10, Shenzhen, China) with a crosshead speed of 5 mm/min. The width and length of the sample was 10 mm and 50 mm, respectively [20]. Five measurements were done for each sample to get the average value.

Static Contact Angle Measurement

Static contact angles for water of 4A zeolite/LDPE membranes were measured by sessile drop method [21] using a Contact Angle Meter (OCA 20, Dataphysics Instruments GmbH Germany) at 25 ^{o}C and about 65 % relative humidity. The volume of the ultrapure water drop used was always 2 µL. All reported values were the average of at least eight measurements taken at different locations of the membrane surface and had a typical mean error of ±1^{o}.

Pure Water Flux and Porosity

Water flux experiments were performed at 25ºC on a dead-end membrane evaluation cell with an effective filtration area of 12 cm^{2}, as shown in Figure **1**. Water permeation tests cannot be run on a LDPE membrane without first pre-wetting the membrane because LDPE is a hydrophobic material. So, the water permeation experiments were carried out using a two-step process [22]. That is, after being pre-wetted with an ethanol/water solution (85 wt%, ethanol) for 30 min, the 4A zeolite/LDPE membrane sample was stabilized at 0.15 MPa for at least 30 min with deionized water. Then the operation pressure was reduced to 0.1 MPa and the water flux was obtained from the volume of the permeated water with 1 h. The flux of pure water (*F*) was calculated as following equation:

$$F = \frac{V}{At} \tag{2}$$

where *V* is the volume of the permeated water during the experiment (L), *A* represents the effective membrane area (m^2), and *t* denotes the operation time (h). Three measurements were done for each sample to get the average value.

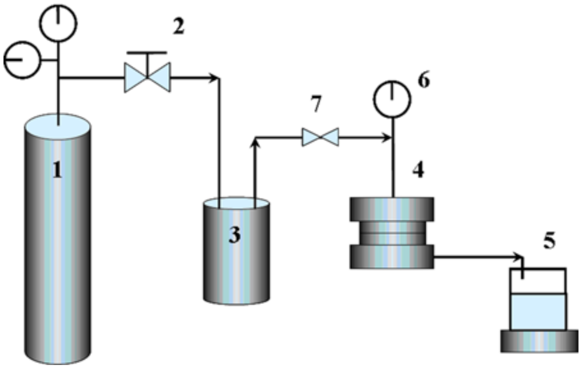

Figure 1: Schematic illustration of the filtration apparatus: (1) nitrogen cylinder; (2) precise value; (3) water reservoir; (4) filtration cell; (5) beaker; (6) pressure gauge; (7) value.

The membrane porosity (ε) is defined as the pores volume divided by the total volume of the porous membrane. It can be determined by gravimetric method and calculated as equation (3) [14]:

$$\varepsilon(\%) = \left(1 - \frac{\rho_f}{\rho_p}\right) \times 100\% \tag{3}$$

where ρ_f is membrane apparent density (kg/m^3, determined by gravimetric method), ρ_p is LDPE density ($0.924 kg/m^3$). The reported data were the average values of triplicate samples for each membrane.

RESULTS AND DISCUSSION

Effect of 4A Zeolite Loading on the Morphology and Performance of 4A Zeolite/LDPE Blend Membranes

4A zeolite/LDPE membranes were formed at a fixed cooling bath temperature of 25 ^{o}C and LDPE:DPE ratio of 1:3 (w/w) with the 4A zeolite loading of 0, 2, 6 and 10 wt% according to the whole weight of a 4A zeolite/LDPE/DPE mixture. That means the weight ratios of 4A zeolite:LDPE:DPE are 0:25:75, 2:24.5:73.5, 4:24:72, 6:23.5:70.5 and 10:22.5:67.5 (w/w/w), respectively.

Morphology

The morphology of 4A zeolite/LDPE membranes were determined by SEM from both the surface and cross-section, as shown in Figure **2**. Both the pure LDPE and 4A zeolite/LDPE blend membranes showed the typical symmetrical morphology with cellular pores which resulted typically from liquid-liquid phase separation *via* nucleation and growth of diluent-rich droplet. In addition, zeolite obviously plays a very important role in the pore size of 4A zeolite/LDPE blend membranes. The cellular pore size of 4A zeolite/LDPE blend membrane decreased initially and then increased with the increase of 4A zeolite loading. This observation can be attributed to the fact that the affinity among polymer, 4A zeolite and DPE changed with the increase of 4A zeolite loading in the LDPE/zeolite/DPE system. The LDPE-zeolite and DPE-zeolite interactions were not quantified in this study, however, SEM micrographs taken during this study clearly showed the affinities changes, the similar phenomena were also observed by Douglas R. Lloyd and co-workers when they prepared 4A zeolite/polypropylene blend microfiltration membranes [17]. At low 4A zeolite loading (2 wt%), the 4A zeolite particles were surrounded by voids, which indicated a strong DPE-zeolite affinity. This strong DPE-zeolite affinity resulted in the migration of DPE to the 4A zeolite particle surface during the phase separation process. Consequently, the increase of polymer concentration in a 4A zeolite-polymer-diluent system brought about a thicker polymer solution which would slow down the phase separation rates, in another word, the droplet growth rates. Thus the resulted pores of 4A zeolite/LDPE membranes should be smaller after the diluent was extracted out. Conversely, at high 4A zeolite loading (6 wt%), the 4A zeolite was coated with polymer, which can be attributed to the fact that the polymer-zeolite affinity is stronger than that of DPE-zeolite. This strong polymer-zeolite affinity resulted in the dissolved polymer migrating to the 4A zeolite particle surface during the phase separation process. Therefore, the bulk polymer concentration and viscosity decreased and droplet growth rates increase [17]. This is why the pore size of 4A zeolite/LDPE blend membrane with 6 wt% 4A zeolite loading is larger than

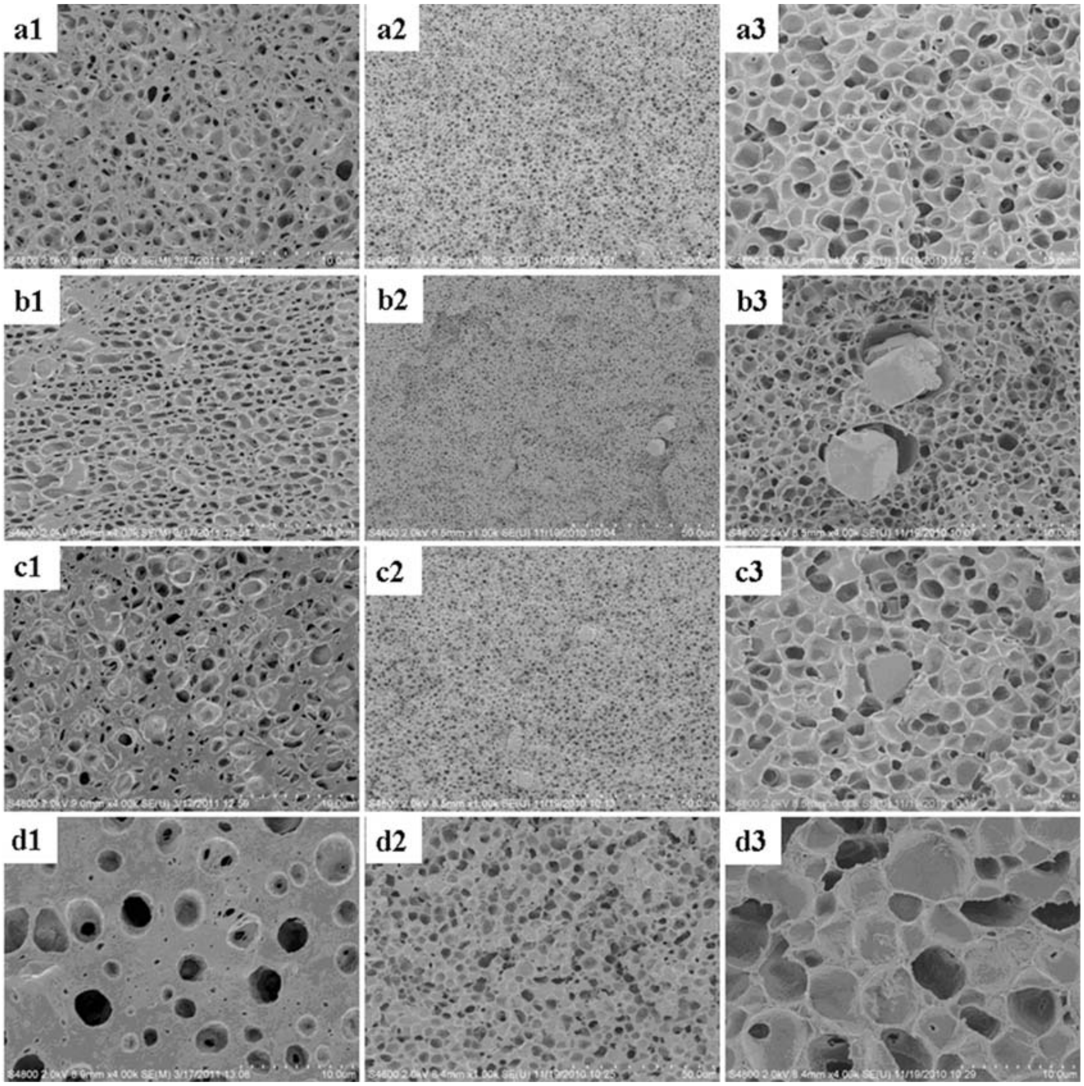

Figure 2: Effect of 4A zeolite loading on the morphology of 4A zeolite/LDPE blend membranes (**a**) 0%, (**b**) 2%, (**c**) 6% and (**d**) 10%. 1, 2, 3 represented surface 4000×, cross section 1000× and cross section 4000×, respectively.

that of the pure LDPE membrane. As the 4A zeolite loading further increased (10 wt%), the stronger polymer-zeolite affinity make more polymer migrate out of the bulk solution to form the compact coating at the zeolite surface. As a result, the 4A zeolite is buried deep in the matrix of LDPE segments as can be seen from Figure **2** (d4). Meanwhile, the pore size of 4A zeolite/LDPE blend membrane with 10 wt% 4A zeolite is the largest among all the 4A zeolite/LDPE membranes.

Thermal and Crystalline Properties

The melting temperature and crystallinity of 4A zeolite/LDPE blend membranes with different 4A zeolite loading are shown in Figure **3**. It can be seen that the crystallinity of 4A zeolite/LDPE blend membrane increased initially, passed through a maximum and then dropped down with increasing 4A zeolite loading. The observation can be attributed to affinity change in the LDPE/zeolite/DPE system again, that is, the variety of 4A zeolite loading brought about the affinity change among LDPE, 4A zeolite and DPE. As for low 4A zeolite loading, the affinity of DPE-zeolite is stronger than that of LDPE-zeolite [17]. It is hypothesized that the strong DPE-zeolite affinity resulted in an increasing polymer concentration in the bulk solution prior to and during phase separation due to diluent migration. More LDPE in solution facilitates the formation of crystal nuclei, which in turn increase the crystallinity of membrane. Conversely, the LDPE-zeolite affinity is greater than the DPE-zeolite affinity at high 4A zeolite loading, which induces a decreasing polymer concentration in the bulk solution. Less LDPE in solution brought about the decrease of the crystallinity.

In addition, according to Figure **3**, the melting temperatures of 4A zeolite/LDPE blend membrane increase with increasing the 4A zeolite loading. The presence of 4A zeolite particles in the LDPE/4A zeolite/DPE system can be regarded as the heterogeneous nucleating agent during the formation of 4A zeolite/LDPE blend membranes [14]. Consequently, LDPE at the LDPE/4A zeolite/DPE system with higher 4A zeolite loading inclines to crystallize at higher temperature compared to that with lower 4A zeolite loading, thus leading to a higher melting temperature of the corresponding 4A zeolite/LDPE blend membrane.

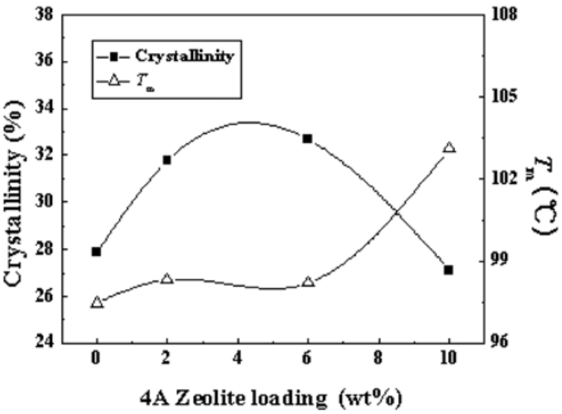

Figure 3: Effect of 4A zeolite loading on melting temperature and crystallinity of 4A zeolite/LDPE blend membranes.

Mechanical Properties

Figure **4** showed the effect of 4A zeolite loading on the mechanical strength of the 4A zeolite/LDPE blend membranes. Both the tensile strength and elongation-at-break increased with the enhancement of 4A zeolite loading. These behaviors indicate that more 4A zeolite in LDPE/4A zeolite/DPE system can result in a better mechanical property of 4A zeolite/LDPE blend membrane at the studied 4A zeolite loading range in this paper. 4A zeolite particles could be regarded as physical cross-linkages in the 4A zeolite/LDPE blend membranes [17]. So a higher 4A zeolite loading is favor to the mechanical property of 4A zeolite/LDPE blend membranes.

Nonetheless, a 4A zeolite loading range of 0-10wt% was chosen in this report because preliminary experiments indicated that it is too difficult to process LDPE/4A zeolite/DPE samples with 4A zeolite loading higher than 10 wt% due to the poor dispersibility of 4A zeolite in LDPE/DPE system.

Hydrophilicity

Generally, the introduction of hydrophilic inorganic particles to hydrophobic polymer membrane can improve the hydrophilicity of the membrane surface and pore walls [23]. The adsorbed foulants on the polymer/inorganic particles blend membranes could be more readily dislodged by shear force than those on a pure polymer membrane, and thus improving the anti-fouling performance of the membranes [24]. Since 4A zeolite used in this work is of very hydrophilic [25], an additional measurement of contact angle was performed to investigate the effect of 4A zeolite loading on the membrane hydrophilicity. Figure **5** shows the values of static water contact angle of 4A zeolite/LDPE blend membranes with different 4A zeolite loading. It can be seen that all of 4A zeolite/LDPE blend membranes are very hydrophobic. With increasing 4A zeolite loading from 0 to 10 wt%, the contact angle of 4A zeolite/LDPE blend membranes declines slightly from 133.4° to 122°. The decrease of contact angle can be attributed to the hydrophilicity of zeolite powder, which results in the improvement of hydrophilic properties with increasing of 4A zeolite loading for 4A zeolite/LDPE blend membranes.

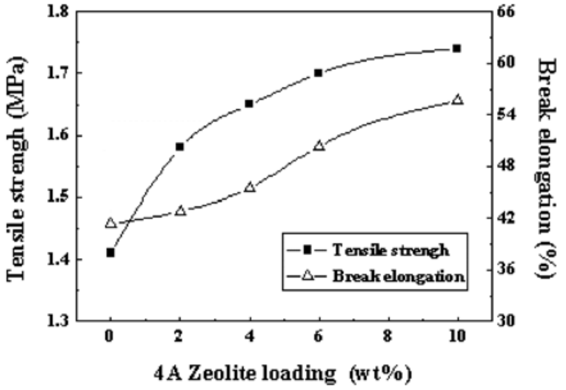

Figure 4: Effect of 4A zeolite loading on the mechanical properties of 4A zeolite/LDPE blend membranes.

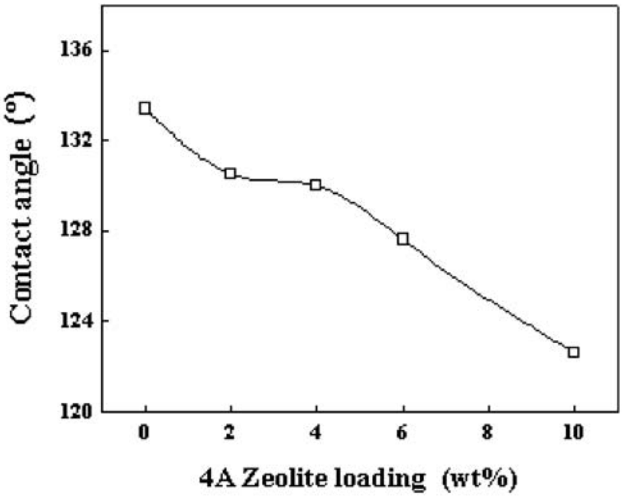

Figure 5: Effect of 4A zeolite loading on the contact angle of 4A zeolite/LDPE blend membranes.

Water Flux

The water flux and porosity of 4A zeolite/LDPE blend membranes with different 4A zeolite loading were shown in Figure **6**. It could be seen that the water flux demonstrated uptrend, while the porosity showed downtrend, with increasing 4A zeolite loading. Generally, the water flux of a porous membrane is depended on its porosity, pore size, the connectivity of membrane pores and the hydrophilicity of surface. Among them, the connectivity of membrane pores is the vital factor to higher water flux regardless the porosity and the pore size is larger or not. From the SEM images (Figure **2**), we can see that the higher 4A zeolite loading result in the larger pore sizes in blend membrane, which partly contributed to the higher water flux of 4A zeolite/LDPE blend membranes. On the other hand, the hydrophilicity of the 4A zeolite/LDPE blend membranes is slightly improved by the addition of 4A zeolite (see Figure **5**). More important, the connectivity of pores of the 4A zeolite/LDPE blend membranes is improved. Therefore, the permeability of the 4A zeolite/LDPE blend membranes were greatly enhanced with the increase of 4A zeolite loading although the porosity of membranes decreased, as shown in Figure **6**.

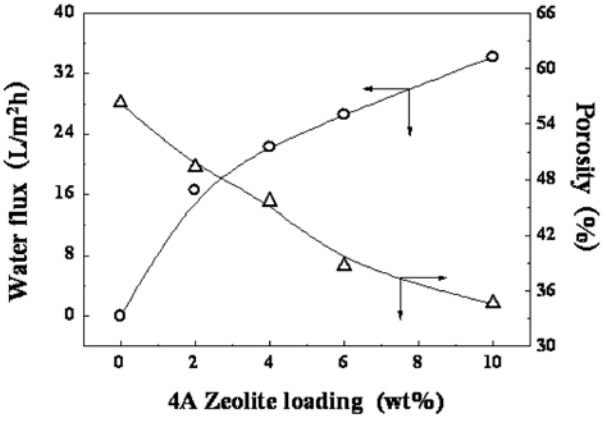

Figure 6: Effect of 4A zeolite loading on the water flux and porosity of 4A zeolite/LDPE blend membranes, the applied pressure for water flux measurements is 0.1 MPa.

Effect of DPE Content on Water Flux of 4A Zeolite/LDPE Blend Membranes

The effect of DPE content on the water flux and porosity of 4A zeolite/LDPE blend membrane is shown in Figure **7**, in which the weight ratio of LDPE:zeolite and the temperature of cooling bath were fixed at 22.5:10 (w/w) and 25 °C, respectively. DPE content of 56-80 wt% were studied because it is difficult to form a 4A zeolite/LDPE membrane with desirable mechanical strength when DPE weight fraction is higher than 80 wt%, while with DPE weight fraction lower than 56 wt% the casting solution is too viscous for 4A zeolite powder to incorporate into the system. From Figure **7**, it is clearly evident that the water flux and porosity increases with increasing DPE content due to decreased viscosity and more diluent, which brought about the larger droplets generated by phase separation and thus the larger pores in membrane structure. This observation is in keeping with the finding of numerous previous L-L TIPS studies in the absence of particulate filler [26, 27].

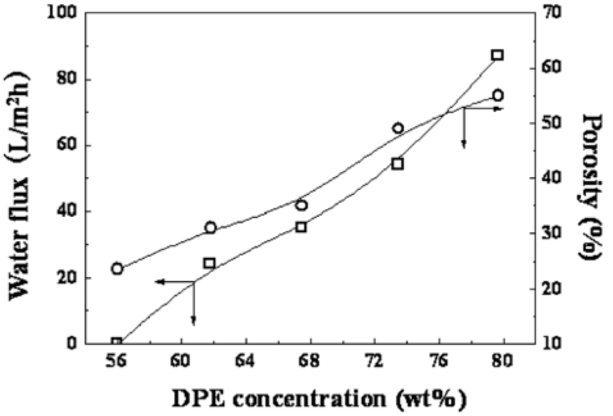

Figure 7: Effect of DPE content on the water flux and porosity of 4A zeolite/LDPE blend membranes.

Effect of Cooling Bath Temperature on Water Flux of 4A Zeolite/LDPE Blend Membranes

Figure **8** shows the values of water flux and porosity of 4A zeolite/LDPE blend membranes with different cooling bath temperature, the weight ratio of 4A zeolite:LDPE:DPE were fixed at 10:22.5:67.5, respectively. It can be seen that the water flux of 4A zeolite/LDPE blend membranes decreased with increasing the cooling bath temperature, but the

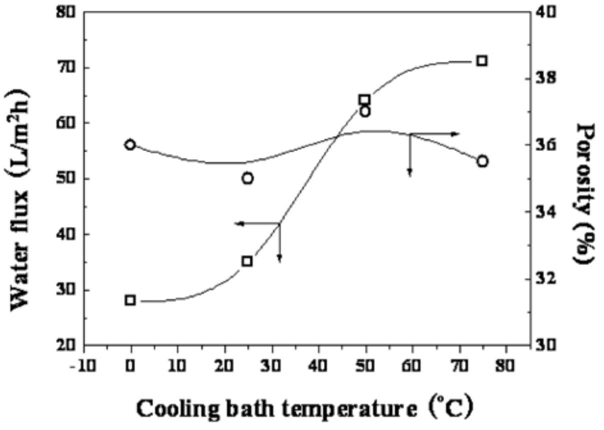

Figure 8: Effect of cooling bath temperature on the water flux and porosity of 4A zeolite/LDPE blend membranes.

porosity changed slightly. The higher water flux is corresponding to the larger pore size. The solidification of 4A zeolite/LDPE/DPE system at higher cooling bath temperature means an decreasing cooling rate, which leads to a prolonged period for droplets to grow in the two phase liquid-liquid suspension [17]. So the pore size of 4A zeolite/LDPE blend membranes increased with increasing the cooling bath temperature. While the nearly unchanged porosity is due to the same DPE content in the LDPE/zeolite/DPE mixtures, so, after extracting DPE, there should be a theoretical equal space left in the 4A zeolite/LDPE blend membranes.

CONCLUSIONS

Microfiltration membranes, 4A zeolite/LDPE, were firstly prepared by blending low density polyethylene and 4A zeolite nanoparticles through thermally induced phase separation process with DPE as diluent. All the 4A zeolite/LDPE blend membranes showed good film-forming property and robust mechanical strength. The incorporation of 4A zeolite particles greatly enhanced the connectivity of membrane pores and thus the water flux of 4A zeolite/LDPE blend membranes which can be attributed to the gradually stronger DPE-zeolite affinity with the increase of the 4A zeolite loading. On the other hand, the water flux and porosity increases with increasing DPE content due to the decreased viscosity. Further, with the increase of cooling bath temperature, the water flux of 4A zeolite/LDPE blend membranes increased, but the porosity changed slightly which can be attributed to the longer growth time of droplets at a fixed diluent content.

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