

矽酸鹽—尼龍/6 多孔型薄膜之成膜機構探討

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中文摘要

吾人利用恆溫浸漬沉澱以矽酸鹽—尼龍/6 納米複合材料為原料，研製多孔型薄膜，薄膜不具皮層結構上由胞孔及束狀結晶交織成共連續之型態，DSC 分析顯示薄膜之結晶度略高於複材原料，且具雙熔解峰，此外膜材之孔隙度隨製膜液水含量升高而提高，此點可由抗張強度測試及水透過率實驗得到驗證。

ABSTRACT

Microporous membranes were made from a polymeric nano-composite material, mica-intercalated Nylon6, by isothermal immersion-precipitation into water bath. The formed membranes were skinless and composed of cellular pores and sheaf-like crystallites, which interwove into a bi-continuous structure. DSC analysis of the membranes revealed a slightly higher degree of crystallinity than the nano-composite pellet and also a double melting peaks behavior was observed. In addition, porosity of the membrane was found to increase with increasing water content in the dope. This was evidenced by the tensile strength and the water permeability measurements.

INTRODUCTION

Preparation of Nylon 6 membrane by immersion-precipitation method is a challenging task. In general, an appropriate preparation procedure of the dope comprises forming a solution of Nylon 6 in a solvent (e.g., formic acid), inducing nucleation of polymer crystallization by a controlled addition of nonsolvent (e.g., water) to obtain a visible precipitate, and then re-heating it to complete dissolution. Such a dope is commonly referred to as been in a state of 'incipient precipitation' that contains a high population of pre-nucleation embryos [1]. The other critical component for preparing a uniform microporous membrane is to inhibit the liquid-liquid demixing process by precipitation in a soft nonsolvent bath (e.g., 40 wt. % formic acid in water) [1].

Given the aforementioned complicate procedure for the synthesis of microporous Nylon 6 membranes, it is desirable to develop a system whereby the complex dope formation procedures can be simplified and the high formic acid bath can be avoided, while the membrane's microporous character was maintained. Quite interestingly, on our investigation toward unravel the 'art' behind membrane formation, we have found a useful material, a nanocomposite of Nylon 6 and synthetic mica, with which water-wettable skinless membranes can be prepared

simply by precipitation of formic acid-polymer dope solutions in pure water bath. As the membrane is microporous, it may serve as a potential substitute for conventional Nylon 6 membranes.

EXPERIMENTAL

1. Material

Nylon 6 (A1025, MI=23, Mn = 14,000) and mica-Nylon 6 nanocomposite (M1030D, MI=19, Mn = 15,000 g/mol, termed m-Nylon 6, hereinafter) were obtained from Unitika Corp., Japan, in pellet form. Both polymeric materials are semi-crystalline. m-Nylon 6 has a nano-scale-intercalated structure wherein the Nylon 6 molecules intertwined in the space (on the order of one nano meter) between mica laminates. The X-ray diffraction pattern of m-Nylon is shown in Figure 1. The diffraction peak at ca. 4° corresponds to an inter-lamellar distance of 2.2 nm. The m-Nylon 6 used in the present research contains 4.2 wt % mica. Formic acid (purum, Fluka, 98 wt. %, $\rho_2=1.22 \text{ g/cm}^3$) was used as the solvent for Nylon 6 and dispersing agent for mica-Nylon 6. Double distilled-deionized water was used as the precipitant for both polymers.

2. Membrane formation and SEM examination

A specific amount of polymer (dried in vacuum at 50°C) was blended with a known quantity of formic acid to form dopes. Membranes were prepared by spreading the dope on a glass plate, and then immersed rapidly in a nonsolvent bath. After precipitation has finished, the membranes were removed, rinsed in distilled water and then dried at $45\text{-}50^\circ\text{C}$. Various amounts of water were added to the dope solution (cf. Table 1) to see its effects on the permeation properties of the formed membrane. Dried membranes were fractured in liquid nitrogen and then coated under vacuum with gold-palladium. Scanning electron microscopy photomicrographs were taken in top, bottom, and edge views.

3. DSC analysis

DSC (Netzsch, DSC 200) scans for both Nylon 6 and m-Nylon 6 samples (pellets and membranes) were performed to obtain the melting point and heat of fusion data. All experimental were carried out in perforated sample pans over the temperature range $40\text{-}250^\circ\text{C}$ at various rates.

4. Tensile strength

Dried membranes were cut into the standard shape for tensile strength measurements, according to the ASTM (D 638 IV) method. The strength and elongation at break were measured in ambient condition for at least 3 samples and the average value

was reported.

5. Water wettability and water flux

Wettability of the membranes was qualitatively characterized by using the method described by Pall [2]. Pure water permeation fluxes of the prepared membranes were measured with a dead-end type Amicon cell (effective area = 11.95 cm²) at different trans-membrane pressures over the range suitable for microfiltration.

RESULTS AND DISCUSSION

1. Morphologies of the membranes

In the discussion that follows, morphologies of Nylon 6 and m-Nylon 6 membranes prepared by immersing a 20 wt. % dope in water bath will be compared in terms of the cross section and the top surface, respectively.

(i) Cross section

The cross section of the Nylon 6 membrane exhibits an asymmetric structure, as shown in Figure 2(a), consisting of a thin dense skin and a cellular bulk. This morphology is ordinarily observed in amorphous membranes (e.g. PMMA, PC, and cellulose acetate membranes) that are prepared by the immersing precipitation procedure. The pores in this membrane are nearly spherical with sizes decreasing gradually from the top surface toward the bottom surface. There is only little inter-connection between individual pores (termed closed pore in the literature). The presence of skin and closed pores is known to reduce significantly the hydraulic permeability of this membrane. As Nylon 6 has a rather high level of crystallinity, it is expected to crystallize in the course of the precipitation process. This is evident from the X-ray diffraction spectrum (Figure 3(a)) of the membrane. The peak at ca. 20.1° depicts the α -type crystal, whereas the peak at ca. 22.5° depicts β -type crystal [3]. The fact that crystallization-oriented morphology (e.g., crystalline particles) was not obvious in Figure 2(a) suggests that liquid-liquid demixing has taken place much earlier than crystallization. And the former rapidly fixed the cellular structure before initiation of crystallization in the gel layer surrounding the formed liquid pores. This sequential phase separation process has also been observed in several other membrane forming systems containing a crystalline polymer [4,5].

The cross section of the m-Nylon 6 membrane is presented in Figures 2(b)-(d). Unlike the Nylon 6 membrane, this cross section exhibits considerable vestige of crystallization. The pores here are all open (interconnected) and highly distorted with a size much smaller (2 mm dia.) than those shown in Figure 2(a). The pore walls evolve into a dendritic structure being composed of sheaf-like crystallites, which correspond to the intermediate stage of spherulite growth. X-ray diffraction spectrum of this membrane, as shown in Figure 3(b), is similar to that of pure Nylon 6 membrane, except a more obvious α -crystal peak at ca. 23.9° [3]. This particular mixed structure of crystalline

particles and cellular pores represents a situation where crystallization and liquid-liquid demixing have occurred concurrently. Based upon Bulte, Witte, and our previous studies of various crystalline membranes [1,4,5], the role of crystallization during the precipitation process could be enhanced if the dope was made supersaturated with respect to crystallization; i.e., the dope was in an 'incipient precipitation' state. The m-Nylon 6 casting dope in the present case was formed following this guideline, and the preparation procedure was much simpler than those for the other Nylon dopes.

(ii) Top surface

The top surface of the Nylon 6 membrane, as presented in Figure 4(a), forms a continuous skin composed of intersecting polygonal plates with approximately linear boundaries. These crystalline plates resemble the two-dimensional spherulites commonly observed in melt-crystallized films and in the top surfaces of various Nylon (Nylon 66, 46, 4, and 610) and PVDF membranes. Since the spherulites were quite large (ca. 20 mm dia.), the nucleation density for crystallization was low. This is consistent with the general observation that the top gel layer reaches a very high concentration during the initial stage of the immersion precipitation procedure. The top surface of m-Nylon 6 membrane differs markedly from that of pure Nylon 6. As shown in Figures 4(b), this surface is virtually skinless, composed of 'sheaf-like' crystallites, as in the membrane interior. The sizes of the crystallites are considerably smaller than those in Figure 4(a), suggesting that there is a much higher nucleation density during precipitation in this top surface. This agrees with the fact that the dope was in a supersaturated condition containing a high population of pre-nucleation aggregates. Because this surface is open, it is wettable by water due to the microcapillary forces. The wettability test given in Table 2 illustrates this point.

2. DSC analysis

The DSC scans of Nylon 6 and m-Nylon 6 in both membrane and pellet forms are shown in Figure 5. Curves A and B depict the endotherms for m-Nylon6 and Nylon6 pellets, respectively. Curves C and D denote those for m-Nylon6 and Nylon6 membranes, respectively. The m-Nylon 6 pellet has a T_m slightly lower than that of Nylon 6 pellet while the heat of fusion of these polymers are similar. Curves C and D indicate that both membranes possess a significant level of crystallinity. The enthalpy of fusion of Nylon 6 membrane is even higher than that of Nylon 6 in its pellet form. The melting peaks of the membranes are also different from those of the pellets. Instead of being melted at a single temperature for the pellets, there exist a second smaller melting peak at ca. 212° C in front of the major peak at ca. 226° C. This suggests that the crystal structure might have changed during the immersion precipitation procedure. This phenomenon has also been observed in PVDF

membranes prepared by precipitation from various water-solvent systems. Wunderlich described the multi-melting peak behavior in terms of an irreversible melting process [6]. In general, it was attributed to (1) perfection of metastable crystals during heating, (2) melting of crystallites in different crystal forms (e.g., α -, β - forms of Nylon 6), and (3) bi-modal or multi-modal crystal size distribution in the sample. To find out whether the first melting peak corresponds to the fusion of certain imperfect crystallites or some different forms of crystallographic structure requires further research, which is the subject of our future work.

3. Tensile strength and the water permeability of the membranes

The tensile strength and the elongation at break of several membranes are given in Table 2. Among all tested samples, the Nylon 6 membrane has the largest tensile strength and the longest elongation. This is associated with the dense skin and the tight interior structure in this membrane (cf. Figure 2(a)). The m-Nylon 6 membrane prepared with the same dope and bath concentrations (i.e., membrane 'mN6' in Table 2) exhibits a smaller mechanical strength due to its bi-continuous structure shown in Figure 2(b). m-Nylon 6 membranes can be made more porous by addition of water into the dope. This is evident both from the tensile strength and the water permeability data. Table 2 shows that the tensile strengths of the membranes decrease progressively as water contents in the dope increase. The water permeation fluxes for various membranes also increase in the same trend, as indicated in Table 2 and Figure 6. The relatively large increase in water flux for membrane 'mN6-17' is associated with the membrane structure, which is considerably more porous than those prepared using dopes containing small amount of water

CONCLUSION

Nylon 6 and a new type of polymer nanocomposite material, mica-intercalated Nylon 6, were precipitated isothermally in pure water to form porous membranes. The Nylon 6 membrane exhibited an asymmetric morphology with a tight skin and a cellular sublayer. It was, therefore, non-wettable by water and not suitable for microfiltration applications. By contrast, m-Nylon-6 precipitated into a skinless microporous membrane featuring an open bi-continuous structure. DSC measurement of this membrane indicated a significant level of crystallinity. The porosity of the membrane could easily be adjusted by varying the water content in the dope, which was in evidence both from the water permeation flux and tensile strength data.

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LIST OF TABLES

Table-1 Preparation condition of casting dopes

Membrane	thickness (μm)	Dope Composition (Wt. %)		
		Water	Formic acid	Polymer
N6	65	0	80	20
N6-22	60	22	52	16
mN6	58	0	80	20
mN6-9	62	9	73	18
mN6-17	60	17	66	17
mN6-22	68	22	52	16

N6: Nylon 6 membrane

mN-6: mica Nylon-6 nanocomposite membrane

Table-2 Properties of membranes

Membrane	Tensile strength at break (Kgw)	Elongation ($\Delta L/L_0$) (%)	Water wettability (sec)	
			Top	Bottom
N6	0.789	45	> 1000	> 1000
N6-22	0.455	85	> 1000	217
mN6	0.522	30	231	37
mN6-9	0.376	33	100	34
mN6-17	0.317	33	73	32
mN6-22	0.271	30	37	29

LIST OF FIGURES

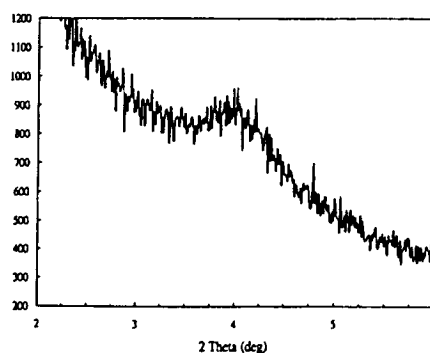


Fig. 3: X-ray diffraction pattern of m-Nylon 6 pellet.

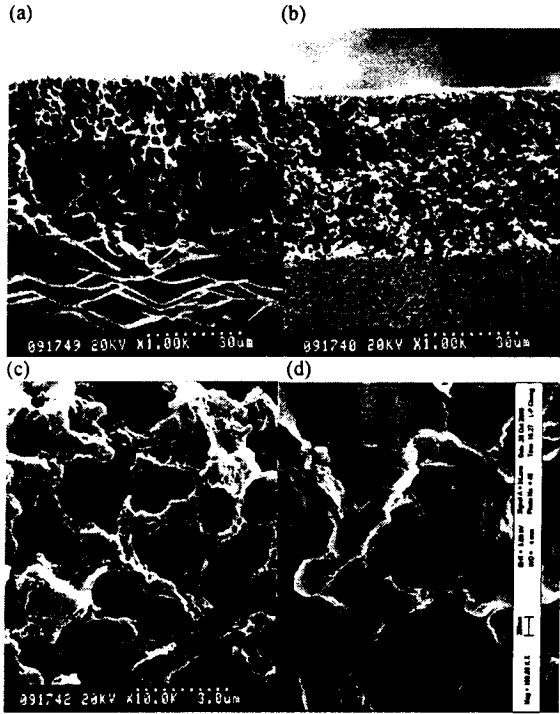


Fig. 2: SEM photomicrographs of the cross sections of the membranes. (a) Nylon 6; (b) m-Nylon 6; (c), (d) magnification of (b).

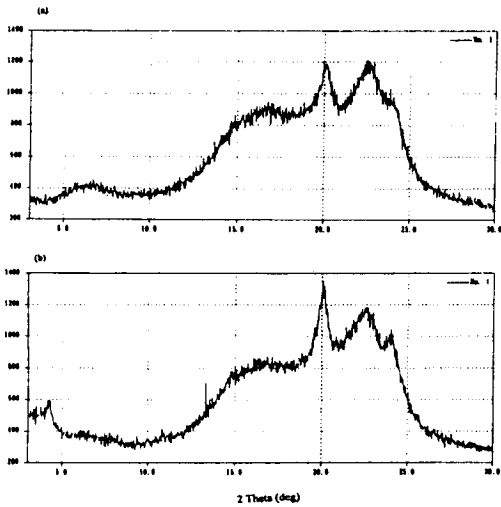


Fig. 3: X-ray (Cu K α , $\lambda=0.15406$ nm) diffraction spectra of Nylon 6 and m-Nylon 6 membranes.

Fig. 3: X-ray diffraction spectrum of Nylon 6 and m-Nylon 6 membranes. (a) (b)

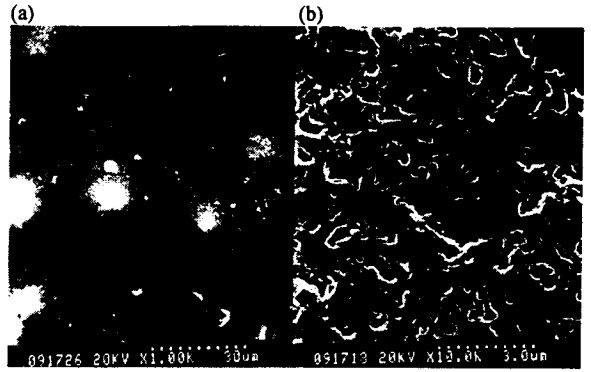


Fig. 4: SEM photomicrographs demonstrating the top surface of (a) Nylon 6; (b) m-Nylon 6 membranes.

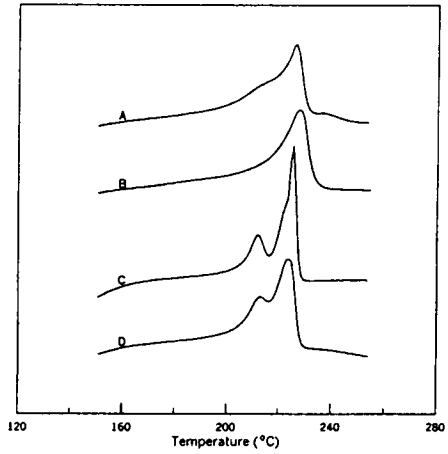


Fig. 5: DSC thermograms of Nylon 6 and m-Nylon 6 pellets and membranes. A: m-Nylon 6 pellet; B: Nylon 6 pellet; C: m-Nylon 6 membrane; D: Nylon 6 membrane, $T_m = 224.1$, $\Delta H = 49.7$ J/g.

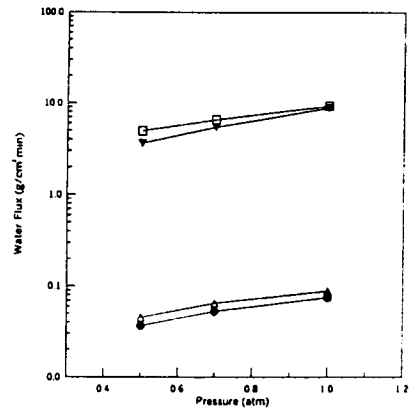


Fig. 6: Pure water fluxes of m-Nylon 6 membranes prepared with different dope water content (cf. Table 1). ●: 0% water; Δ : 9% water; ∇ : 17% water; \square : 22% water.