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Fine structure and crystallinity of porous Nylon 66 membranes prepared by phase inversion in the water/formic acid/Nylon 66 system

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Abstract

Microporous Nylon-66 polymeric membranes were prepared by immersion–precipitation from a ternary system, water/formic acid/Nylon 66. Depending upon the precipitation conditions, membranes with morphologies that reflect the sequence of liquid–liquid demixing (as characterized by cellular pores) and crystallization (as characterized by crystal particles) events during the course of precipitation were obtained. The details of the membrane morphologies were disclosed using a low voltage field emission scanning electron microscope (FESEM) at very high resolutions. In particular, nano-scale fine structures such as dendritic crystal elements, nano-pores, nano-grains, branching lamellae, etc., which were rarely presented in the membrane literature. Wide angle X-ray diffraction analyses indicated that Nylon-66 crystallized into 'α' structure in all prepared membranes. Crystallinities were determined by appropriate deconvolution of the diffraction peaks. The results indicated that membranes prepared by a well-dissolved casting dope had a somewhat higher crystallinity than those prepared by incipient dopes being in metastable states with respect to crystallization. This observation was confirmed by Fourier transform infrared spectroscopy and DSC thermo analyses.

Keywords: Polyamide; Immersion–precipitation; Cellular pores; Spherulites; Crystallinity

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1. Introduction

Nylon 66, a polyamide derived from 1,6-hexamethylene diamine and adipic acid, is a semicrystalline polymer, which possesses good thermal stability and mechanical strength, and is considered to be an important engineering thermoplastic [1–3]. Porous polyamide membrane has been commercialized for many years and is nowadays widely used in fine-separation processes [4,5]. Microporous membranes are often manufactured by the so-called immersion–precipitation process [6], in which a polymer solution is cast on a substrate and then immersed in a nonsolvent bath to induce polymer precipitation by means of crystallization and/or liquid–liquid demixing. Unlike a nonporous Nylon 66 film, which has a water contact angle of ca. 60°, a skinless microporous Nylon 66 membrane is water wettable; i.e., water drops can penetrate into the membrane matrix within a few seconds. This property is associated with the porous morphology of the membrane. It can be

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produced by a fine-tuned immersion–precipitation process, which involves precipitation of an incipient casting dope in a soft coagulation bath [7,8]. Because the casting dope is metastable with respect to crystallization and the bath contains a large amount of solvent, crystallization dominates over liquid–liquid demixing to yield a structure consists of interlinked stick-like crystalline particles.

The formation mechanism of crystallizable polyamide membranes has been investigated by a number of authors. On the basis of phase diagram and mass transfer modeling, Bulte et al. obtained the initial diffusion paths and concentration profiles for various immersion conditions for the preparation of Nylon 46 membranes. These calculated results correlated well with the membrane morphologies [9,10]. Cheng et al. took into consideration the effects of dope's aggregation state (e.g., a supersaturated dope may be prepared which contains a high population of pre-nucleation embryo) and bath strength (e.g., a soft bath containing significant solvent may be used) on the relative level of liquid–liquid demixing and crystallization during the course of precipitation [8,11,12]. A mathematical model was developed to illustrate the concentration evolution of nonsolvent, solvent, and polymer within the membrane prior to phase separation. In conjunction with the phase diagram, these results help to understand the relation between morphology and immersion conditions. Recently, Thomas et al. used confocal microscope to observe scattering profiles of casting dopes during immersion–precipitation, and found that precipitation occurred initially at some distance from the membrane–bath interface, which then propagates both upward and downward through the membrane [13]. Techniques other than immersion–precipitation have also been used to prepare porous polyamide membranes. For example, Kho et al. introduced compressed carbon dioxide as an antisolvent to precipitate Nylon 6 from 2,2,2-trifluoroethanol solutions to form porous membranes. In this way, pressure became an additional effective variable for tailoring the membrane microstructure [14].

Despite that Nylon-66 membrane formation mechanism has been discussed previously [8,11,12,15], the issues concerning nano-scale fine structure of the membrane such as twisted lamellae, nano-grains, etc., and thermal behavior and crystallinity of the membrane have never been presented. These characteristics were investigated using low voltage field emission scanning electron microscopy (LVFESEM, fine structure), differential scanning calorimetry (DSC, thermal behavior and crystallinity), Fourier transform infrared spectroscopy (FTIR, crystallinity) and wide angle X-ray diffraction (WAXD, crystallinity and crystal structure) [16–18]. In particular, a spectrum deconvolution technique based on Gauss and Lorentzian functions were employed to analyze both WAXS and IR spectra, and to determine the degree of crystallinity of the membrane. The results were found to be consistent with those reported in the literature [17,19,20].

2. Experimental

2.1. Materials

Poly(hexamethylene adipamide) (Nylon 66, Zytel 101, Du Pont, measured intrinsic viscosity = 2.68 g/dl, $M_v = 87{,}000$ g/mole) was received in pellet form. Formic acid (Acros, 99%) was used as the solvent and distilled–deionized water was used as the nonsolvent for Nylon 66. All materials were used as received.

2.2. Membrane formation

A dope solution was uniformly spread on a glass surface using a casting knife. It was then immersed at 25 °C into a coagulation bath composed of water and formic acid. After precipitation has completed (typically a few min), a white solid membrane was obtained. The nonsolvent and the residual solvent in the nascent membrane were removed by a sequence of washing steps. Finally, the formed membrane was held tightly in a press between two sheets of filter papers and then dried at 40 °C. The immersion conditions for various membranes are summarized in Table 1. Dope "A" was a homogeneous solution consisting only of polymer and solvent. Dope "B" contained a substantial amount of nonsolvent. It was in a supersaturated state with respect to crystallization (i.e., its composition is located below the crystallization line) and would gel upon standing at 25 °C for an extended period of time. However, prior

Table 1
Preparation conditions and properties of various membranes

Code	Dope composition (%)			Bath FA content (%)	Wettability (s)		Melting point (°C)	ΔH (J/g)
	Water	FA	N-66		Top	Bottom		
AI	0	75	25	10	300	300	264.0	86.4
AII	0	75	25	40	300	2	265.8	85.8
BI	12	63	25	10	264	15	264.7	76.1
BII	12	63	25	40	62	19	265.5	74.0