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Rapid communication

Micelle-like macrovoids in mixed matrix PVDF-PTFE hollow fiber membranes

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ABSTRACT

Unique ‘micelle-like’ macrovoids have been observed for the first time in the polyvinylidene fluoride-polytetrafluoroethylene (PVDF-PTFE) hollow fiber membranes. FESEM results show that the incorporation of 30 and 40 wt% PTFE particles (<1 μm) reduces the number of finger-like macrovoids in the membrane matrix, while micelle-like marcovoids (about 10 μm in size) are formed when PTFE loading is increased to 50 wt% or higher. 50 wt% PTFE is the critical particle concentration for micelle-like macrovoid formation. The origins of micelle formation may be attributed to the adhesion and cohesion forces between air bubbles and particles in the supersaturated PTFE solution. A more rigorous degassing of the PVDF-T50 polymer dope solution may enhance the suspension homogeneity and eliminate the micelle-like macrovoid formation. It is therefore concluded that the micelle-like macrovoid formation arises from the agglomeration of gas bubbles upon PTFE particles with the aid of water diffusion and convection during the phase inversion of membrane formation.

1. Introduction

Loeb and Sourirajan [1] developed the fabrication method of asymmetric membranes via phase inversion in late 1950s. Most asymmetric membranes prepared by their approach consist of macrovoids in membrane cross-sections if the casting solutions contain low and medium polymer concentrations. The origins of macrovoid formation have been intensively debated and studied by membrane scientists [2–14]. Some researchers believed these structures originally from thermodynamic aspects of chemical potential gradient [2–5]. Others deemed that macrovoid formation begun from the local surface instability as well as material and stress imbalances [6–9]. Moreover, Marangoni effects [10], solutocapillary convection mechanism [11,12] as well as osmotic pressure [13] have also been proposed as the formation mechanisms. Obviously, macrovoids formation is an intricate study and several mechanisms may occur concurrently as reported by Widjojo and Chung [14].

Basically, there are four types of marcovoids reported namely teardrop, elliptical, and finger-like (inward- and outward-points) macrovoids [14]. For teardrop and elliptical macrovoids, the possible formation mechanisms are through solutocapillary convection [11,12] and/or osmotic pressure [13]. Alternatively, the solution intrusion followed by membrane contraction for teardrop formation has been proposed by Cabasso [9]. On the other hand, the finger-like macrovoids may form originally by the solvent intrusion, local surface instability, skin rupture or convective flow during a rapid precipitation and lead to nucleation of droplets at the polymer-lean phase [6–9,15]. The residual trace of non-solvent intrusion can be clearly observed by these inward- or outward-points in the finger-like macrovoids [6,14].

The discovery of “micelle-like” macrovoids was unexpected when we prepared mixed matrix polyvinylidene fluoride (PVDF) hollow fibers embedded with PTFE particles (<1 μm) to enhance membranes’ hydrophobicity, mechanical stability and reduce marcovoids [16] for other applications. During the spinning process, we surprisingly observed a novel spherical shaped macrovoid structure when the PTFE particle loading reached 50 wt%. The spherical shaped macrovoid is alike to the micelle structure formed in the oil emulsion process. Therefore, the aim of this rapid communication is to report, for the first time, the discovery and possible origins of micelle-like macrovoid in mixed matrix PVDF-PTFE membranes. We believe that this investigation may advance the science and understanding of membrane formation.

2. Experimental

2.1. Materials

A copolymer polyvinylidene fluoride (PVDF) T #2300 was kindly provided by Kureha Corporation and PTFE particles (<1 μm) was purchased from Sigma–Aldrich. The solvent *N*-methyl-2-pyrrolodinone (NMP, >99.5%), non-solvent ethylene glycol (EG, >99.5%) and external coagulant isopropanol (IPA) were purchased from Merck, Panreac and Fisher Scientific, respectively. All chemical were used as received.

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Table 1
Spinning parameters of PVDF hollow fibers with different PTFE loadings.

	Hollow fiber ID				
	Pure-PVDF	PVDF-T30	PVDF-T40	PVDF-T50	PVDF-T60
Dope composition (wt%)	PVDF/NMP/EG: 15/70/15				
PTFE loading in total solid (wt%)	0	30	40	50	60
Bore fluid (wt%)	NMP/water: 85/15				
Dope flow rate (ml/min)	5				
Bore flow rate (ml/min)	3				
External coagulant (wt%)	IPA/water: 40/60				
Take up speed	Free flow				
Dope and bore fluid temperature (°C)	25 ± 1				
Air gap (cm)	0.5				
Room humidity (%)	65–70				
Post-treatment	3 days store in tap water, freeze drying				
Spinneret dimension (cm)	OD/ID/*L*: 1.6/1.05/6.5				

2.2. Polymer dope preparation and PVDF hollow fiber fabrication

The dry-jet wet phase inversion for hollow fiber spinning process is schematically described elsewhere [8]. The PVDF and PTFE were dried overnight at 100 ± 2 °C in a vacuum oven (2 mbar) to remove moisture content before use. The formulated dope solutions were stirred to homogeneity, degassing for half day before loading into the syringe pump (ISCO 500D). However, another set of PVDF-T50 polymer dope was degassed for 3 days to eliminate the micelle formation. A mixture of 85/15 wt% of NMP/water was employed as the bore fluid while 40/60 wt% IPA/water mixture was utilized as the external coagulant. Then, the nascent fibers went into the coagulation bath freely without additional drawing. Lastly, the hollow fibers were post-treated by solvent exchange in tap water for 3 days to remove the residual NMP, EG and IPA before drying in freeze dryer. The spinning conditions are tabulated in Table 1.

2.3. Characterization

The morphology of the resulting membranes was examined by field emission scanning electron microscopy (FESEM, JEOL JSM-6700F). Samples were prepared in liquid nitrogen followed by platinum coating using a JEOL JFC-1100E ion sputtering device.

The rheological properties of polymer solutions were determined by using an ARES Rheometric Scientific Rheometer. The steady-state shear viscosity was measured by a 25 mm cone-plate fixture at 25 °C in the range of 1–100 s^{-1}. The rheology data are summarized in Table 2.

The mechanical properties of as-spun hollow fiber membranes were conducted by an Instron tensiometer (Model 5542, Instron Corp.). The fiber sample was clamped at both ends and pulled in tension at a constant elongation rate of 10 mm min^{-1} with an initial gauge length of 50 mm. Tensile stress at break, tensile strain, and Young's modulus were obtained from the stress–strain curves. Five readings were measured and an average was obtained from the results.

The elemental analysis of PTFE particles was measured by scanning electron microscope-energy dispersive X-ray (SEM-EDX, JEOL JSM-5600LV). The mapping mode was performed on the PTFE particles surface to detect the existence of certain elements, such as platinum (coating), carbon, fluorine and sulfur. On the other hand, the PTFE particles were compressed into a pellet by a hydraulic press (Graseby Specac) for qualitative elemental analysis through BRUKER X-ray fluorescence spectroscopy (XRF, S2 Ranger).

3. Results and discussion

3.1. Morphologies of PVDF and PVDF-PTFE mixed matrix hollow fiber membranes

Fig. 1 illustrates the morphology of asymmetric hollow fiber membranes spun from pure-PVDF and mixed matrix PVDF-PTFE with different PTFE loadings. The incorporation of PTFE particles with 30 and 40 wt% loadings suppresses macrovoid formation and reduces the number of finger-like macrovoids as compared to the pure-PVDF membrane. This phenomenon is mainly due to the effect of increased viscosity on membrane formation [14,17–20]. As shown in Table 1, the shear viscosity of spinning solutions increases from 1500 to 6500 cP at 10 s^{-1} when the PTFE loading increases from zero to 40 wt%. Therefore, an increase in PTFE loading leads to a higher dope viscosity that impedes the penetration of internal and external coagulants, and impairs conventional macrovoid formation under the same spinning conditions.

Surprisingly, an unusual macrovoid configuration, namely "micelle-like" macrovoids, observes in the PVDF-T50 fibers that were spun from a dope containing 50 wt% PTFE particles, as shown in Fig. 1 (left-hand side and middle of the second row). Similar patterns of micelle-like structure can also be observed in the PVDF-PTFE mixed matrix fiber with 60 wt% particles loading.

Table 2 summaries the mechanical properties of the as-spun membranes in terms of extension at break, tensile at break and Young's modulus. The membrane elasticity (extension at break) and tensile stress (tensile at break) decrease gradually with an increase in PTFE loading. Conversely, the membrane rigidity (Young's modulus) increases for the PVDF-PTFE fibers compared to pure-PVDF fibers. It can be observed that the micelle-like macrovoid fibers have the lowest membrane elasticity, rigidity and tensile stress among the membranes possibly due to the irregular macrovoids across the whole membrane structure.

Table 2
Rheology and mechanical properties of PVDF and PVDF-PTFE hollow fiber membranes.

	Hollow fiber ID					
	Pure-PVDF	PVDF-T30	PVDF-T40	PVDF-T50-sponge-like	PVDF-T50-micelle-like	PVDF-T60-micelle-like
Dope viscosity (cP)	1500	4800	6500	9200	9200	11000
Tensile strain at break (%)	345 ± 34	247 ± 12	129 ± 16	57 ± 12	27 ± 5	21 ± 2
Tensile stress at break (MPa)	2.43 ± 0.17	1.77 ± 0.10	1.70 ± 0.15	1.56 ± 0.09	1.05 ± 0.11	0.56 ± 0.02
Young's modulus (MPa)	82.4 ± 3.0	81.9 ± 0.8	96.3 ± 5.2	100.1 ± 8.5	60.9 ± 4.0	34.3 ± 4.9