Journal of Membrane Science 405–406 (2012) 275–283

Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Finger-like voids induced by viscous fingering during phase inversion of alumina/PES/NMP suspensions

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ARTICLE INFO

Article history:
Received 6 December 2011
Received in revised form 4 March 2012
Accepted 8 March 2012
Available online 17 March 2012

Keywords:
Ceramic hollow fibre membranes
Phase inversion
Finger-like voids
Viscous fingering

ABSTRACT

The formation mechanism of phase-inversion ceramic hollow fibre membranes has not been well understood. In this paper, we report on the formation of finger-like macrovoids during non-solvent-induced phase inversion of alumina/PES/NMP suspensions. A membrane structure without such finger-like macrovoids was observed when the suspension was slowly immersed into pure ethanol or a mixture of 70 wt% NMP and 30 wt% water, whereas finger-like macrovoids occurred when the suspension was slid into the non-solvents at higher speeds. We found that the formation process of finger-like macrovoids could be fully or partially reversed when nascent membranes were taken out from water shortly after immersion, depending on the duration of the immersion. Splitting of the fingers during the formation of the macrovoids was also observed during the phase inversion of two alumina/PES/NMP suspensions. These experimental observations were not predicted by current theories of finger-like macrovoid formation in polymer membranes, but appear to mimic the well-known viscous fingering phenomenon. We therefore propose that in the phase inversion of ceramic suspensions, the viscous fingering phenomenon is an important mechanism in the formation of finger-like voids.

1. Introduction

Ceramic hollow fibre (HF) membranes fabricated through the combined phase-inversion/sintering method have attracted increasing attention over the past 10 years. By combining the features of ceramic materials with small tubular geometries, ceramic HF membrane modules with high packing densities and high surface-to-volume ratios are able to work under harsh conditions whereas polymeric membranes fail under such conditions. Phase-inversion ceramic HF membranes have been employed for various uses, such as dense perovskite HF membranes for high-temperature oxygen production [1–4], porous alumina HF membranes as substrates for functional layers [5–8], and HF-membrane-based solid oxide fuel cells (SOFC) [9–12].

Phase-inversion ceramic HFs normally contain two regions in their macrostructures. One is a region of finger-like macrovoids, and the other is the macrovoid-free part that sometimes is referred as the “sponge-like structure” [13]. The existence and arrangement of finger-like macrovoids may significantly affect the permeability and the mechanical strength of a ceramic HF membrane [12,13]. To achieve desired properties, tailoring the macrostructure and the microstructure of ceramic HF membranes is necessary. For example, an asymmetric perovskite HF membrane for oxygen separation requires a thin, dense skin layer and a thick, highly porous support layer dominated by finger-like macrovoids [3,14]; while in an anode-supported micro-tube SOFC, an optimized combination of a finger-macrovoid layer and a sponge-like layer is required to achieve both high mechanical strength and good electro-chemical performance [12].

To control the macrostructure of ceramic HF membranes, the occurrence and growth of finger-like macrovoids must be manipulated during the phase-inversion process. Such manipulation requires understanding about the formation mechanism of the macrovoids. The formation of the finger-like macrovoids in polymer membranes has been studied for a long time, and several mechanisms have been proposed to interpret empirical observations of the morphologies of polymer membranes [15,16]. These mechanisms can be roughly classified into two categories. The first category is based on the assertion that the formation of finger-like macrovoids is induced by incoming non-solvent flows [17–21], and the other is based on the assertion that their formation is caused by diffusional flows, i.e., the growth of nucleated polymer-lean phases in polymer solutions [22]. The latter category seems more likely in polymer membranes, though evidence has shown that both mechanisms are possible, depending on the polymer/solvent/non-solvent system involved [23]. The diffusional-flow mechanism from

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doi:10.1016/j.memsci.2012.03.020

polymer membranes was also used to interpret the formation of finger-like macrovoids in ceramic HF membranes [14], although there is a big difference between dual-phase ceramic suspensions and single-phase polymer solutions.

Kingsbury et al. investigated the formation of finger-like voids in alumina HF membranes [13,24,25], and they proposed that the fingers are formed in the spinning process by the well-known "viscous fingering" phenomenon. They were able to qualitatively interpret their results using the "viscous fingering" hypothesis by focusing on the effects of the suspension's viscosity. However, their interpretation did not exclude the possibility that other mechanisms are at work, and stronger evidence distinguishing finger formation in ceramic suspensions from that in polymer solutions is needed to verify the "viscous fingering" hypothesis. In this study, we used flat-sheet alumina membranes as a benchmark to verify the unique features of the viscous fingering phenomenon in alumina/PES/NMP suspensions and to demonstrate that viscous fingering is responsible for the formation of finger-like voids in the phase inversion of ceramic suspensions.

2. Distinguishing characteristics of the viscous fingering phenomenon

Viscous fingering is commonly observed when a less viscous fluid replaces a more viscous fluid, during which uneven fronts of the replacing fluid invade the replaced fluid and form complex patterns, often taking finger-like shapes. Early studies of this phenomenon originated from observations of fluid replacement in porous media [26]. Typical examples of replacing/replaced fluid systems are slurry/water systems [27], which are similar to non-solvent/ceramic suspension systems in which phase inversion occurs. Most investigations on viscous fingering were carried out in a two-dimensional shallow geometry called a Hele-Shaw cell, in which viscous fingering is analogous to the fluid replacement occurring in a porous medium. The onset and growth of fingers rely on the instability of the interface between the replaced fluid and the replacing fluid. These issues have been discussed both theoretically and experimentally in the literature on fluid mechanics [28–30].

There are two main types of viscous fingering processes. One is the immiscible viscous fingering in which there is a distinct interface between the replacing fluid and the replaced fluid, with the interfacial tension playing an important role in the fingering process. The other is the miscible viscous fingering in which the replacing fluid and the replaced fluid are miscible and there is no interfacial tension, but the dispersion of the finger front affects the fingering process [30]. In a system consisting of a displacing non-solvent and a displaced ceramic suspension, both of which are involved in phase-inversion ceramic membrane fabrication processes, the interface between the suspension and the non-solvent is always distinct although the exchange between the solvent of the ceramic suspension and the non-solvent occurs during the whole phase-inversion process. Such a system can thus be treated as an immiscible system with varying interfacial tensions and varying viscosities.

In the immiscible interface between a non-solvent and a ceramic suspension, when it moves towards the suspension side and a periodic disturbance with a wavelength λ is applied on the interface (illustrated in Fig. 1), the disturbance can be either stabilized or amplified depending on the pressure jump across the perturbed interface. The pressure jump comes from the viscosity difference between the non-solvent and the suspension, which can be quantified by assuming that the flux of the non-solvent passing through the interface follows Darcy's law [26,30]:

$$\Delta p_V = k(\mu_1 - \mu_2)U\delta_x \tag{1}$$

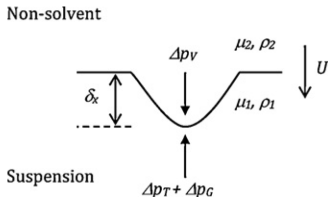

Fig. 1. Illustration of a moving interface between two fluids.

where Δp_V is the pressure jump across the interface due to the viscosity difference, k is the resistance constant of the suspension to the permeation of the non-solvent, μ_1 and μ_2 are the viscosity of the suspension and the non-solvent, respectively, U is the velocity of the moving interface, and δ_x is the variation of the interface. Because the viscosity of the suspension is usually much larger than the viscosity of the non-solvent, we can reduce Eq. (1) to

$$\Delta p_V = k\mu U\delta_x \tag{2}$$

Here, we replace μ_1 with μ for simplicity. This pressure jump tends to amplify the disturbance towards the suspension and thus initiate the fingering process.

In the case of flat-sheet membranes where the non-solvent/suspension interface is horizontal, the influence of gravity cannot be neglected. Then, at the disturbed interface, a pressure jump applies due to gravity:

$$\Delta p_G = (\rho_1 - \rho_2)g\delta_x \tag{3}$$

Here, ρ_1 and ρ_2 are the density of the suspension and the non-solvent, respectively. In the case of ceramic suspensions, normally we have $\rho_1 > \rho_2$. Then, the direction of Δp_G is against Δp_V and tends to flatten the interface.

Another force that produces a pressure jump against Δp_V is the interfacial tension. The pressure jump, Δp_T, produced by the interfacial tension is the product of the interfacial tension, T, and the curvature, κ, of the perturbed interface; that is,

$$\Delta p_T = T\kappa \tag{4}$$

In the onset and growth of fingers, Δp_V must be larger than the sum of Δp_G and Δp_T. Hence, a critical moving velocity of the interface (or finger fronts) is defined by

$$U_c = \frac{\Delta p_G + \Delta p_T}{k\mu\delta_x} \tag{5}$$

The interfacial moving velocity must be higher than the critical velocity to initiate or continue fingering processes [28].

The stability of the interface can be assessed by a dimensionless parameter, the capillary number Ca, which measures the viscous force relative to the interfacial tension by

$$Ca = \frac{k\mu UW}{T} \tag{6}$$

where W is a dimension-related parameter. In the Hele-Shaw cell, this parameter is the width of the cell, but it needs to be clarified in real membrane fabrication cases. The fingering process will occur at a high Ca number when the interface becomes less stable, while it stops or reverses when the Ca is lower than a certain value.

Finger splitting is a commonly observed phenomenon in viscous fingering studies when the capillary number, Ca, is very high. This phenomenon is based on the fact that disturbances also exist on the interface surrounding the moving fingers. It has been found that the minimum required wavelength, l, and the amplitude, A, of a disturbance for initiating fingers are determined by the capillary number, Ca:

$$A \sim \frac{1}{e^{\sqrt{Ca}}} \tag{7}$$