STUDIES ON POLY (VINYL CHLORIDE)/SILICA DIOXIDE COMPOSITE HOLLOW FIBER MEMBRANE

by

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Poly (vinyl chloride)/silica dioxide composite hollow fiber membranes were prepared by using the method of immersion-precipitation process. The influences of stretching ratio on the formation of the interfacial microporous of poly (vinyl chloride)/silica dioxide composite hollow fiber membranes were specifically investigated by scanning electron microscope, dynamic mechanical analysis, and finite element method. Results show that with the stretching ratio increasing, numerous IFM appear on the surface of membranes. Finite element method actually reflects the dynamic change of microporous structure of poly (vinyl chloride)/silica dioxide composite hollow fiber membranes.

Key words: *poly (vinyl chloride), hollow fiber membrane, interfacial microvoids*

Introduction

Polymer separation membranes shaped as porous hollow fibers, are usually prepared via three techniques during evolvement on formation of porous membranes: stretching and heating process method, thermally induced phase separation method, and non-solvent induced phase separation (NIPS) method [1]. Poly (vinyl chloride) (PVC) is an outstanding membrane material, for its low cost, acids, alkalis and solvent resistance, excellent physical and chemical properties, which could be widely subjected to NIPS method. Attention on PVC membranes, researchers have been mainly studied on polymer concentration, the kind and content of additives, the selection and composition of solvent, and coagulation bath. However, the method of fabricating poly (vinyl chloride)/silica dioxide (PVC/SiO_2) composite hollow fiber membranes (HFM) with high performance through phase inversion technique was previously seldom reported.

In this study, the composite membrane with asymmetric structure was obtained from a ternary solution of PVC/SiO_2, and dynamic mechanical analysis (DMA) by NIPS and post-stretching method. There are two kinds of pores in PVC/SiO_2 composite HFM. One is stretching microporous (SMP) induced the microspores during phase separation process, and

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the other is so-called interfacial microvoids (IFM). The effects of stretching ratio (SR) on microporous structure (SMP and IFM) in membranes were discussed. The relationship between the formation of IFM and performance of composite HFM were also studied.

Experimental

Preparations of PVC/SiO_2 composite HFM

To obtain the PVC/SiO_2 blend solution, DMA and SiO_2 were mixed for 30 minute firstly, then PVC was adding to DMA/SiO_2 suspension to get the dope solution. The PVC/SiO_2 concentration was kept at 17%. Dry/wet-spinning technique was used to preparation hollow fibers membranes. Water was used as gelation bath. After the formation process, HFM were stored in water for at least one day, and then immersed into a tank containing 60% glycerol solution for at least one day.

Characterization

The morphology of membranes was observed with FEI Quanta 200 (The Netherlands) scanning electron microscope. The DMA curves of the membranes were obtained by Netzsch DMA242.

Results and discussion

The morphologies of PVC/SiO_2 composite HFM

The cross-section structures of PVC/SiO_2 composite HFM with different SR are shown in fig.1. It can be seen that PVC/SiO_2 composite HFM have similar cross-section structures, which exhibit two-layer finger-like morphologies extended to the middle of cross-section of HFM because water is used as both inner and outer gelation bath. It is also seen that both the internal and external diameters decreased with the increase of SR, fig.1(c) and (d).

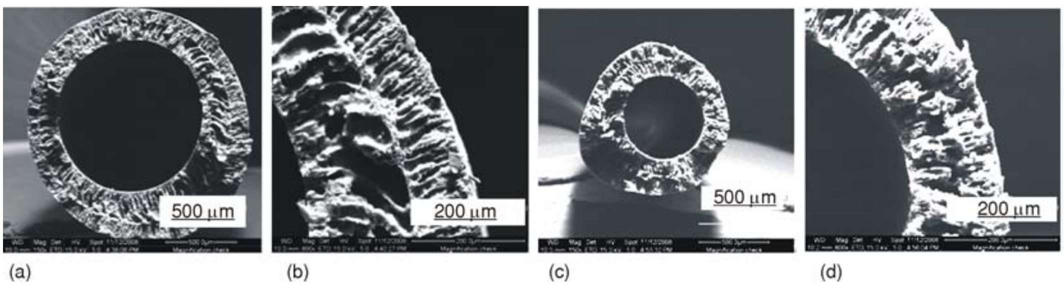

Figure 1. Effect of the SR on the cross-section morphology of PVC/SiO_2 composite HFM; (a) and (b) SR 0, (c) and (d) SR 3

From fig. 2, it is found that the external and internal surface structure of PVC/SiO_2 HFM without stretching is distinct from that with stretching. In figs. 2(a1) and 2(a2), the external and internal surface structure of PVC/SiO_2 composite HFM without stretching seems denser, while membrane with stretching looks more smooth, and has numerous microporous-SMP and IFM, shown in figs. 2(b1) and (b2), which are distinct from the porous prepared from solution phase inversion. The experimental results illustrate that the precipitation membrane formed microporous-SMP and IFM of PVC/SiO_2 composite HFM with stretching, may be affected by the different thermal expansion coefficient between PVC and SiO_2. Under stretching stress, the interlayer in PVC/SiO_2 composite HFM occurs separation in interface easily which leads to IFM.

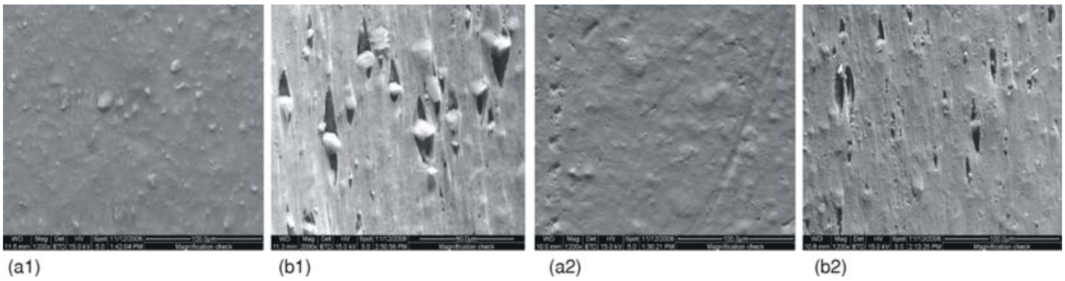

Figure 2. Effect of the SR on the surface of PVC/SiO_2 composite HFM; (a) SR 0, (b) SR 3, (1) the external surface, (2) the internal surface

Mechanical properties of composite HFM

In order to evaluate the effects of microporous on mechanical properties of PVC/SiO_2 composite HFM, the DMA of membranes were determined. The DMA of HFM can be seen in fig. 3. The x-axis value, which indicates the peak of the glass temperature, $\tan\delta$, of membranes moves to the high temperature region with the increasing of SR, in other words, the glass temperature, T_g, of PVC/SiO_2 composite HFM raises with the increasing of SR. The experimental results show that the regularity of PVC chains arrangements becomes more regular, and the degree of PVC macromolecule improves as the increasing of SR, fig. 3. Besides, SiO_2 particles dispersed in the PVC may prevent the movement of PVC macromolecule chains at a low temperature, while enlarge the steric effect of macromolecule chain segment. It is suggestion that microporous structure of the composite HFM mainly include: network porous introduced by double-diffusion, SMP and IFM, where the network porous decrease with the SR increased, meanwhile, SMP and IFM increase. This may denote that the mechanical properties of composite HFM are mainly due to SMP and IFM, while the network porous has little effects.

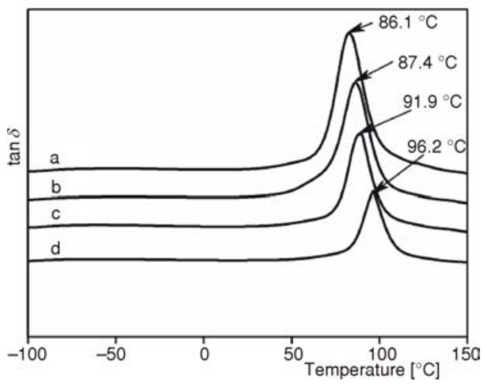

Figure 3. The DMA curve of PVC/SiO_2 composite HFM; (a) PVC, (b) PVC/SiO_2 with SR 0, (c) PVC/SiO_2 with SR 2, (d) PVC/SiO_2 with SR 2.5

Simulation of microporous structure

Changes of microporous structure in composite HFM under tensile were simulated by finite element method (FEM) [2]. The system of composite PVC/SiO_2 HFM is an immiscible system with dispersion of SiO_2 particles in PVC. The adhesive force in the interface is very small due to different mechanical properties between the two-phase materials (SiO_2 particles and PVC polymer), which results the interface separated easily, so the interface is defined by contact element in present study. As shown in fig. 4(a), the circular in the center is SiO_2 particle, the other is PVC polymer. It can be seen from the strain figure of the composite HFM with stretching, fig. 4(b): the radio of interface micro-voids along the stretching direction enlarge with the increase of the stretching stress and this leads to deboning and further enlarging at the

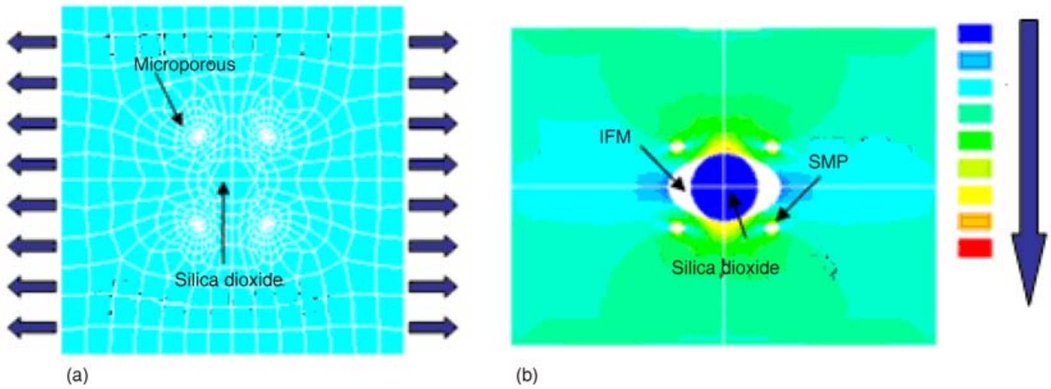

Figure 4. Model of PVC/SiO_2 composite HFM; (a) SR 0,(b) SR 3

PVC-SiO_2 interphase to develop SMP, which is correlated well with experimental observations. This provides a method to simulate the change of membrane.

Conclusion

The PVC/SiO_2 composite HFM obtained with more obvious SMP and IFM were prepared FEM was used to simulate the changing of microporous structure during the stretching process. It is shown that attempts to formulate complete models for the performance of these kinds of composite membrane is important in as much as these predictions are used to guide membrane design and evaluate membrane performance in the future.

Acknowledgment

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