Thermally Induced Phase Separation Followed by *in situ* Sol–gel Process: A Novel Method for PVDF/SiO_2 Hybrid Membranes

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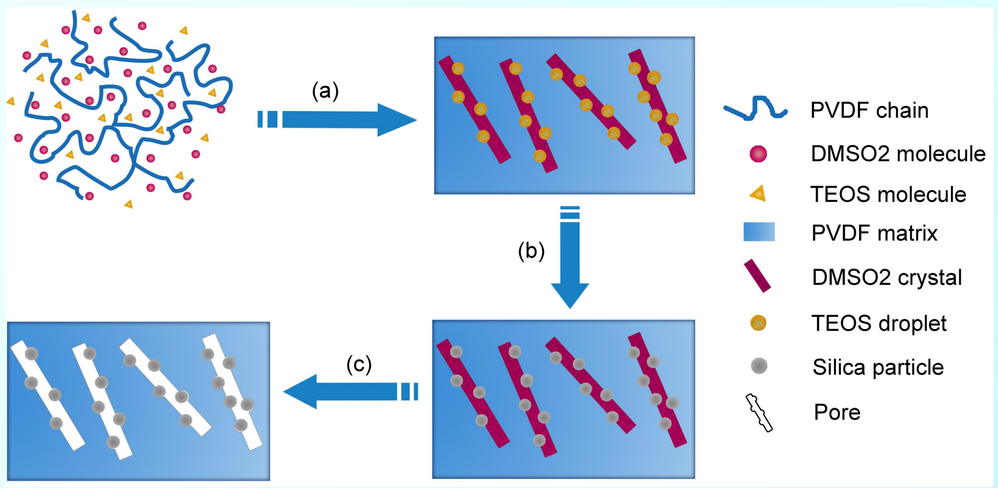
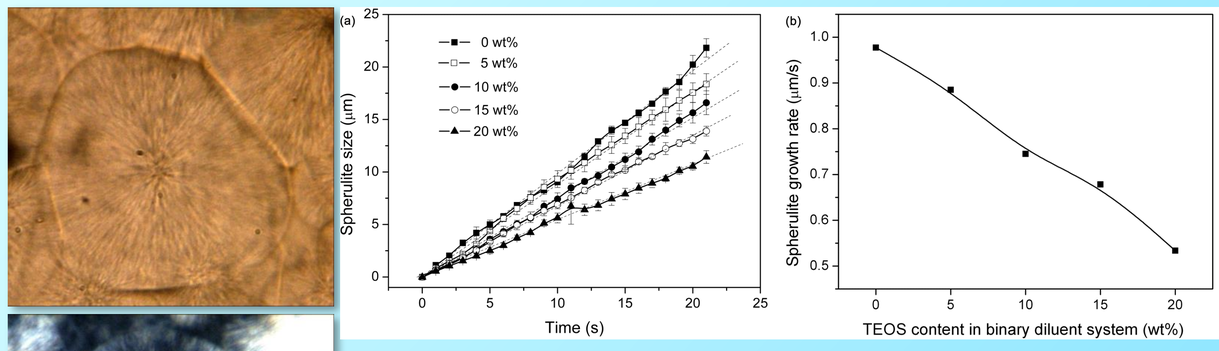
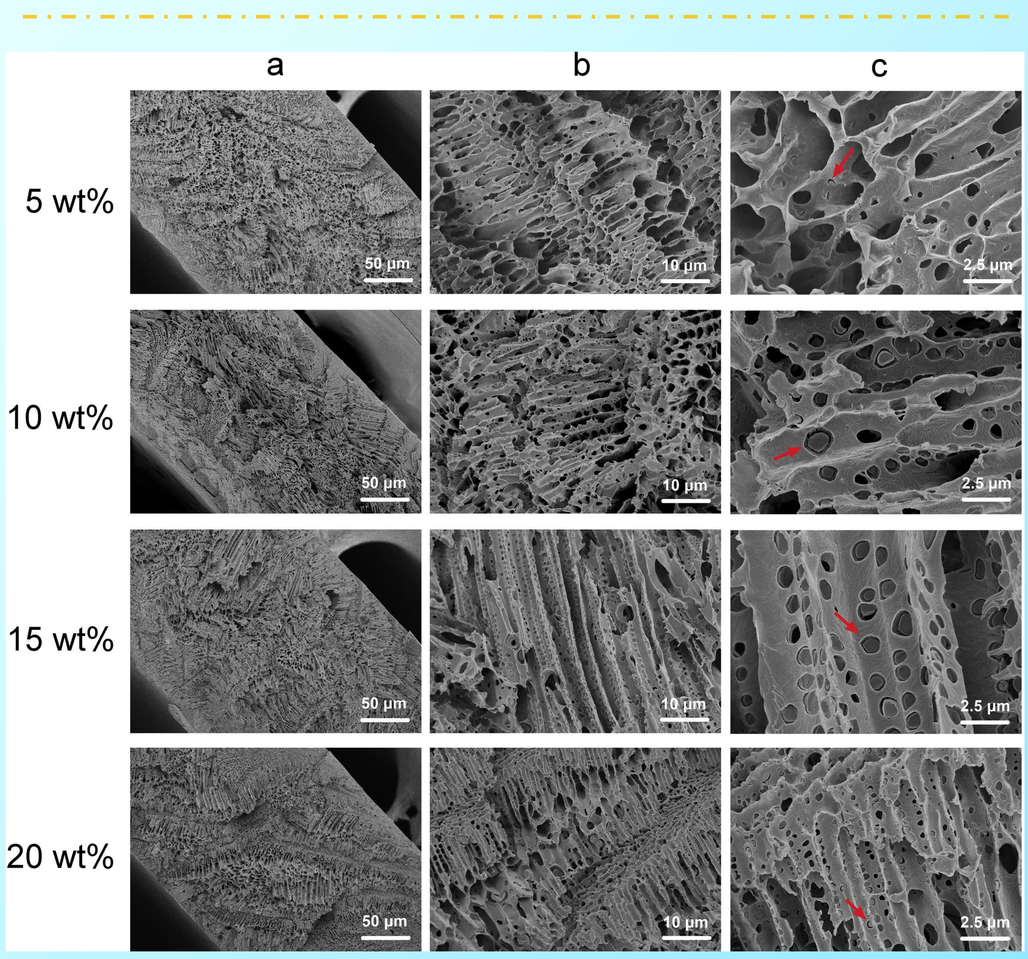
Organic−inorganic hybrid materials have been extensively investigated as a promising choice for separation membranes. The hybrid membranes can combine the advantages of inorganic material and organic polymer, and exhibit excellent separation performances, mechanical properties, and high thermal and chemical stabilities. In this work, poly(vinylidene fluoride) (PVDF)/silica (SiO_2) hybrid membranes were prepared by the thermally induced phase separation (TIPS) of PVDF/dimethyl sulfone (DMSO2)/tetraethoxysilane (TEOS) followed by an in situ sol–gel process of TEOS. The fabricated hybrid membranes possess excellent anti-compression property, and can be used to separate protein mixtures of bovine serum albumin (BSA) and bovine hemoglobin (BHb) efficiently.



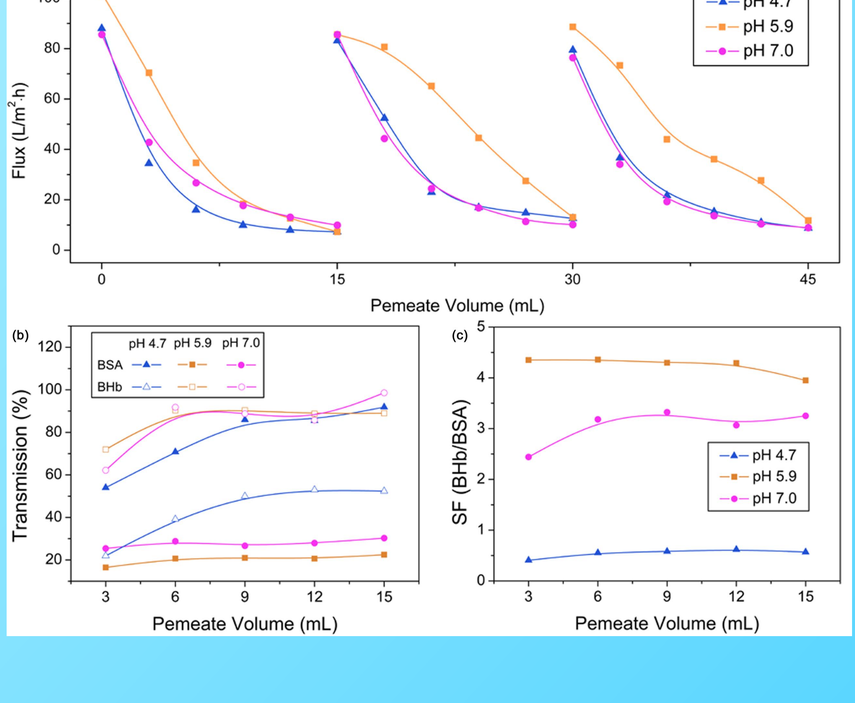
Schematic representation of the membrane formation fabricated via TIPS combining with sol−gel process: (a) Cooling process. solid–solid phase separation takes place to form a nascent membrane; (b) sol−gel process, and (c) extraction process.



The phase separation mechanism of PVDF/DMSO2/ TEOS ternary system is solid–solid TIPS. Upon cooling, no liquid–liquid phase separation takes place. The samples start to solidify and giant spherulites form once the temperature reaches the crystallization point of DMSO2. The growth rate of giant spherulites decreases significantly with TEOS.



Cross-sectional morphologies of the PVDF/SiO_2 hybrid membranes prepared from PVDF/DMSO2/TEOS ternary system with 20 wt% PVDF. Two types of pores are obtained in the membranes: large tubular pores shaped by DMSO2 crystals and small round pores stemmed from TEOS droplets. SiO_2 particles are uniformly dispersed inside the PVDF/SiO_2 hybrid membranes. Their size and shape are in well consistent with those of the small round pores.



Pure water flux of the hybrid membranes as a function of measuring time under high pressure (0.5 MPa) . The anti-compression property improves significantly due to the supporting effect of SiO_2 particles.

It is difficult to separate BSA and BHb, as they have nearly identified molecule weight. The separation results of BSA and BHb at pH 4.7, 5.9 and 7.0 was shown in the left figure. The flux can recover to almost the initial value after washing with PBS (0.5 M). pH 5.9 is the optimal condition. The separation factor of BHB/BSA reaches as high as 4.3.

Conclusion

- **A new method is proposed to prepare PVDF/SiO_2 hybrid membranes by TIPS followed by sol–gel process.**
- **The phase separation mechanism is solid–solid TIPS.**
- **The prepared hybrid membranes exhibit excellent antic-compression property, and can be used to efficiently separate protein mixtures.**

***References*:**

[1] H. Q. Liang, Q. Y. Wu, L. S. Wan, X. J. Huang and Z. K. Xu, *J. Membr. Sci.*, 2013, 446, 482.

[2] X. Y. Qiu, H. Z. Yu, M. Karunakaran, N. Pradeep, S. P. Nunes, K. V. Peinemann, *ACS Nano.*, 2013, 7, 768.

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