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Gelling and phase inversion preparation for Al_2O_3/PVDF hybrid membrane

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ABSTRACT

The casting solution for forming Al_2O_3/PVDF hybrid membrane (APHM) was prepared using polyvinylidene fluoride (PVDF) modified by KOH in the solution of methanol as a membrane-forming polymer, using vinyl-trimethoxy-silicane as a coupling agent and using aluminum isopropoxide (AIP) as an inorganic precursor, respectively, and APHM linking with chemical bond was obtained by the phrase inversion method. The effects of AIP on the phase behavior and gelling kinetics of the casting solution were studied so as to explore the mechanism of the influence of AIP on the microstructure of the APHM. Results showed that the change in the phase equilibrium of casting solution was encouraged by an increase in AIP concentration and casting solution became thermodynamic unstable, so that compatibility of the casting solution with non-solvent was decreased and the gelling velocity of casting solution was accelerated. The gelling velocity was the during the initial period of membrane formation, and then slowed down. The gelling velocity varied with different casting solutions. Both the gelling velocity and phase separation rate for the casting solutions were improved by the increases in AIP contents, however, the gelling velocity decreased when AIP concentration reached to 20% by weight.

Keywords: APHM; Kinetics; Phase equilibrium; Gelling velocity; Phase inversion

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1. Introduction

Polyvinylidene fluoride (PVDF) is known as one of the most attractive polymer materials in microporous membrane industry. It is widely used in the manufacturing of reverse osmosis, microfiltration, ultrafiltration (UF), nanofiltration, and pervaporation membranes due to its extraordinary properties, such as excellent thermal stability and mechanical properties, high chemical resistance to aggressive reagents like organic solvents, acid, and bases, and excellent membrane forming abilities [1–6]. However, due to the hydrophobic nature of PVDF, membranes fabricated from PVDF polymer have a high fouling tendency and declined permeability when they are exposed to protein-containing solutions, which leads to a sharp drop of the membrane's pure water flux and has become a severe drawback for their applica-

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tion in water treatment [7–10]. So, in order to improve the hydrophilicity of PVDF, it is necessary for us to have PVDF modified.

Several strategies to improve the hydrophilicity of PVDF membranes have, therefore, been investigated such as physical blending, chemical grafting, and surface modification [11,12]. Recent studies on PVDF-blending modification mainly focused on blending polymers with hydrophilic materials for it has the advantage of easy preparation using phase inversion. Several hydrophilic organic materials have reported to modify PVDF, and they can increase the water permeability of a membrane with similar pore size and pore distribution due to due to an increase in pore density as well as in the hydrophilicity of the membrane surface and inside the pores, but the addition of organic hydrophilic materials reduces membrane strength [13–16].

Inorganic materials have been known as a prospective additive for membrane separation processes due to its excellent mechanical properties and remarkable thermal properties, and these extraordinary properties of inorganic materials can be maintained under a wide variety of conditions, leading to good separation performance [17–19]. Inorganic materials that can be blended with PVDF include SiO_2, ZrO_2, TiO_2, Al_2O_3, and some small molecule inorganic salts, such as lithium salts [20–23]. PVDF can be used as composites with these inorganic nanoparticles to improve the membrane separation performance, thermal ability, and membrane forming ability by the combination of the basic properties of organic and inorganic materials. The strong affinity to water makes Al_2O_3 nanoparticles the best candidate material for hydrophilic modification of PVDF membrane [24]. We drew a conclusion that PVDF and Al_2O_3 are not connected by chemical bonds from the previous report, that is to say, they have insufficient combination strength in membrane, which results in low tensile strength of the membrane. What is more, most of previous research works focused on the organic-blends membrane and there are few reports on inorganic-blends membrane [11,12,24], in addition, gelling process and phase inversion mechanism of forming membrane have not been reported as yet.

In this work, we used PVDF modified by KOH in the solution of methanol as a membrane-forming polymer and used vinyl-trimethoxy-silicane as a coupling agent and aluminium isopropoxide (AIP) as an inorganic precursor to prepare the casting solution, then the Al_2O_3/PVDF hybrid membrane (APHM) linking with chemical bond was obtained by the phrase inversion method. And the influences of AIP contents on the phrase inversion and gelling process kinetics of casting solution system were studied. Moreover, the membrane forming mechanism of the APHM was discussed, which provides theoretical basis for the preparation of organic–inorganic hybrid membrane.

2. Materials and methods

2.1. Materials

PVDF (FR904) was purchased from New Materials Co. Ltd. (Shanghai, China). *N*,*N*-dimethylacetamide (DMAc, purity >99%) was obtained from Fuyu Fine Chemical Co. Ltd. (Tianjin, China) as the solvent. AIP was from Sinopharm Chemical Reagent Co. Ltd. Polyvinylpyrrolidone (PVP, K30) was imported from Germany. A mixture of distilled water and ethanol was used as the non-solvent for the membrane precipitation.

2.2. Preparation of APHM

2.2.1. Process technology of APHM

2.2.2. Alkali modification of PVDF polymer

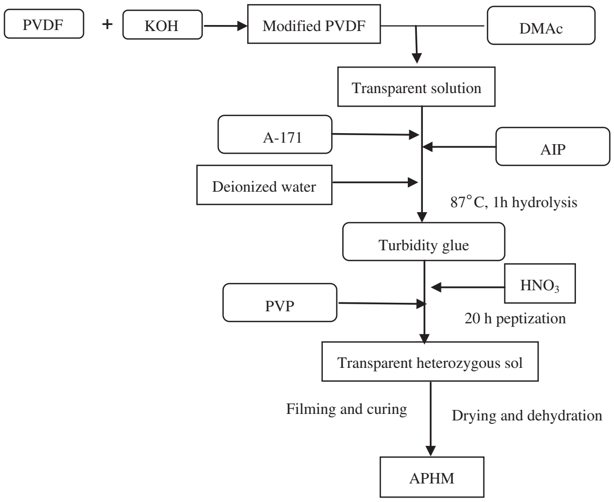

Fig. 1. Preparation route of modified APHM.

KOH methanol solution of 5% (wt) was prepared and then mixed with PVDF. The reaction was under the circumstances of 60℃ water-bath and magnetic stirring; the reaction time was kept 30 min. Finally, the disposed PVDF membrane was washed repeatedly neutral using methanol and dried about 24 h in the vacuum drying oven of 70℃.

2.2.3. Cross-linking of PVDF polymer and AIP

PVDF was dissolved in DMAc solvent to prepare a solution of certain concentration, then a defined amount of coupling agent and different contents of AIP were put into it, the PVDF polymer and AIP were cross-linked after the solution was dissolved (Fig. 1).

2.2.4. Preparation of APHM

The above mixture was constant stirred for 20 h at 87°C to obtain a homogeneous casting solution. The solution was standing for 24 h to remove air bubbles and then was poured onto a glass plate with the casting knife at room temperature. After exposed to air for 15 s, the casting solution on the glass was immediately immersed in the deionized water-bath for 5–7 days, then the APHM was obtained.

2.3. Characterization of APHM

2.3.1. FT-IR characterization

FT-IR (Vector 33, Germany) was employed to probe the chemical composition of prepared membranes. The membrane samples were analyzed by transmission beam method.

2.3.2. Measurement of absolute viscosity

In this study, the casting solution with different AIP contents was prepared and standing for 24 h to remove the air bubbles, then the absolute viscosity of casting solution was measured by a numeral rotational viscometer (NDJ-5S, Shanghai, China) at room temperature.

2.3.3. Phase graph of casting solution of APHM

The phase diagram of the casting solution was observed by the cloud-point titration method [25], and the testing device shown in Fig. 2 was employed to measure the cloud-point of the casting solution with different AIP contents.

2.3.4. Observation of gelling kinetics process and measurement of gelling velocity

The casting solution was dropped on the glass slide, then the cover glass was lidded on the glass slide in order to form a liquid membrane of uniform thickness from the solution between the glass slide and cover glass. A drop of the non-solvent was dropped in the lacune of two glasses using a needle tubing and was allowed to diffuse along the lacune of two glasses to have the gelling process with the casting solution. Gelling kinetics process of APHM was observed by a polarization microscope (E600, Japan), and the gelling front motion and corresponding gelling time were recorded. At last, the gelling speed curve was drawn.

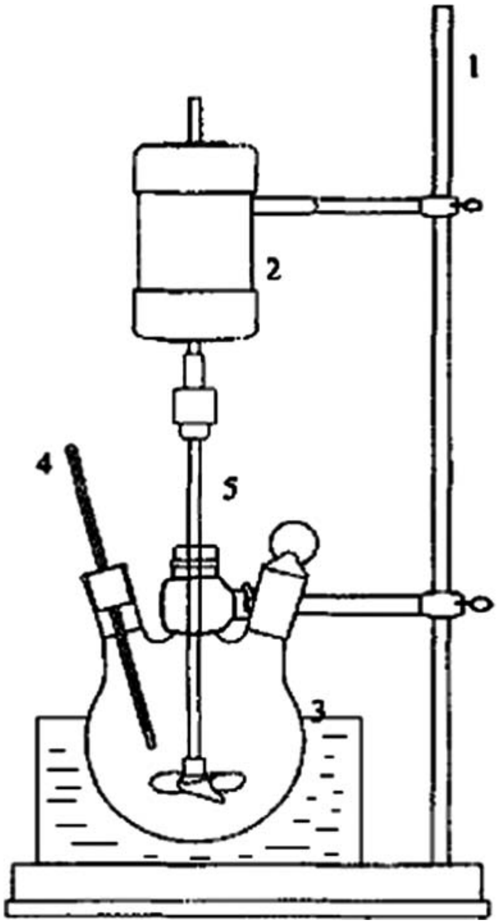

Fig. 2. Schematic representation of the experimental apparatus for phase diagram. (1) iron stand; (2) motor stirrer; (3) water bath; (4) thermometer; (5) burette.

3. Results and discussion

3.1. FT-IR spectra analysis of modified PVDF and APHM

Fig. 3 presents the typical FT-IR spectra of the modified PVDF. As indicated in Fig. 3, the peaks appearing at 1,643.74 cm^{-1} derive from the stretching vibration of C=C double bond, revealing the formation of the C=C double bond. So the surface of PVDF

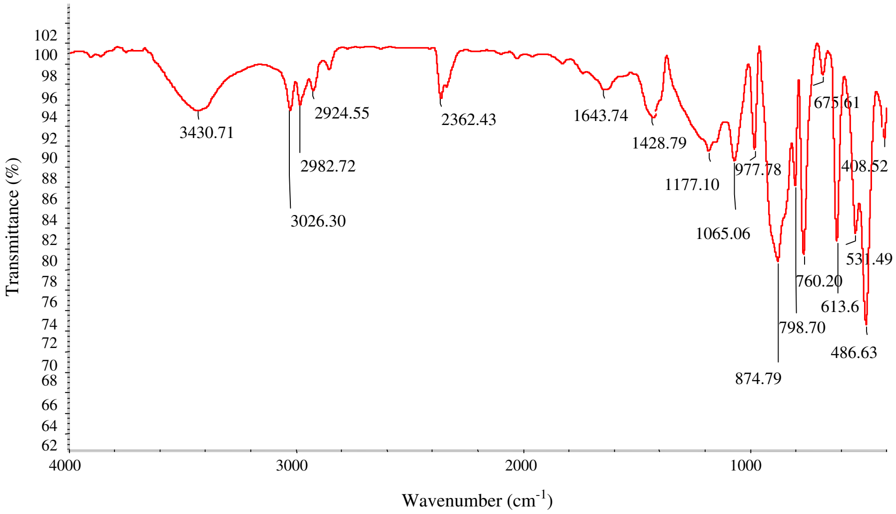

Fig. 3. FT-IR spectra of modified PVDF.

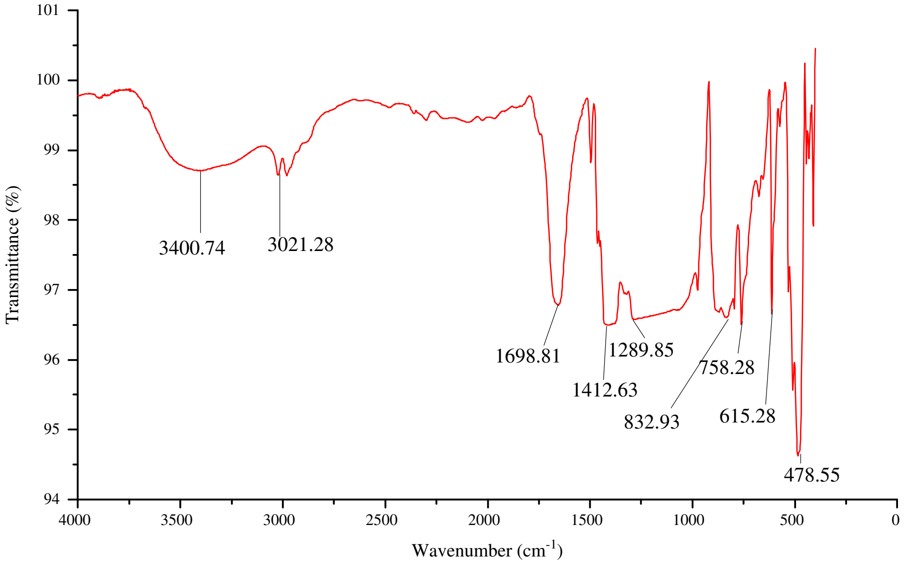

Fig. 4. FT-IR spectra of modified APHM.

processed by alkali can bring in the C=C double bond, and this laid a foundation for the further modification of PVDF membrane. Meanwhile, the modified FT-IR spectra of the modified PVDF surfaces reveal the appearance of the peak at 3,000–3,500 cm^{-1}, which are associated with the hydroxyl group [26–29]. This is because when PVDF is disposed by lye, its defluorination was accompanied with an oxidizing reaction [30,31]. It is thought that the primary reason for why the contact angle of modified PVDF membrane decreased was the formation of the carbonyl group and the hydroxyl group, which can improve the hydrophilicity of the surface of membrane. As shown in Fig. 4, the appearance of the peak at 1,698.81 indicates that the carbonyl group was successfully introduced in APHM. What is more, the peaks at 832.93 and 758.28 cm^{-1} are the stretching vibration peaks of Si–O–Al, and the peak at 615.28 cm^{-1} is the bending vibration peak of Si–O–Al, thus it can be manifested that coupling agent was involved in the hybrid reactions via the hydrolysis with AIP.

3.2. Effect of AIP contents on the viscosity of casting solution

The membrane forming process and structure of polymer membrane have an important correlation with the viscosity of the casting solution. What is more, the viscosity of casting solution can also have an effect on the mass transfer velocity between the solvent and non-solvent in the membrane forming process, and the microstructure of UF membrane was decided by the gelling process, therefore, the existential state of polymer in the casting solution and basic information of membrane, such as structure and properties can be judged by the viscosity of the casting solution. Fig. 5 shows the effect of AIP contents on the viscosity of the casting solution. As shown in Fig. 5, along with the increase in AIP contents, the viscosity of the casting solution increased accordingly. This is mainly because the viscosity of the Al_2O_3 turbidity glue was fairly high after the hydrolytie polycondensation of AIP, and the hydroxyl group on its surface can form hydrogen bond with PVDF and additive (PVP). When AIP was added into the casting solution, the concentration of the solute increased, thus intensified the aggregation of PVDF macromolecules, which can increase the viscosity of the casting solution system. During the measurement process, we also found that the viscosity of the casting solution increased, along with the increases in the standing time and the reduction in the casting solution's temperature.

3.3. Cloud-point phase diagram of hybrid system with different AIP contents

With the deionized water as the titration fluid, the cloud-points with different AIP contents in the casting solution system of APHM were measured in the condition of 50℃ and the ternary phases diagram was drawn in Fig. 6. As shown in Fig. 6, with the increase in AIP contents, the cloud-point curve gradually approaches to the solvent axis. This is because, there are a mass of hydroxyl groups in the Al_2O_3 turbidity glue, which can form hydrogen bond with PVDF and have a strong adsorption to the molecular chain of PVDF. Meanwhile, the alcohol hydroxyl groups in the Al_2O_3 turbidity glue can also form hydrogen bond with the solvent, thus can weaken the appetency between PVDF and the solvent, and make the macromolecule chains gathered, which can accelerate the phase separation of the casting solution [32]. For this reason, the accommodate capacity of the casting solution to the non-solvent decrease, along with the increase in AIP contents, that is to say, a small amount of the non-solvent can make PVDF solidified, so the adding of AIP accelerates the gelling process of the casting solution.

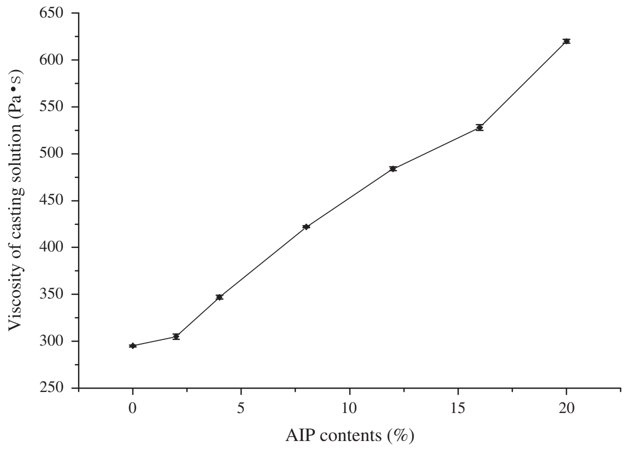

Fig. 5. Effect of AIP contents on the viscosity of casting solution.

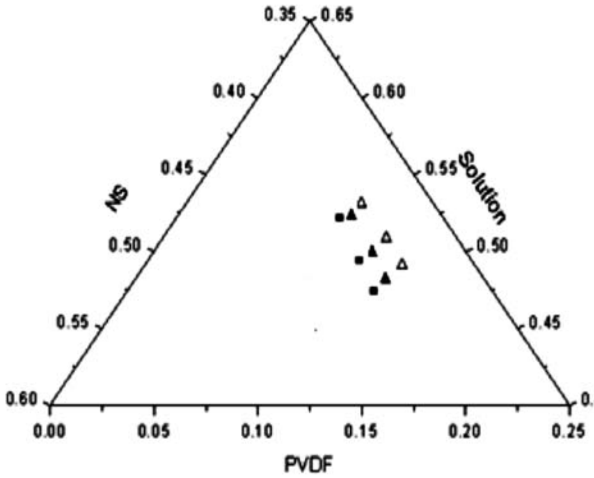

Fig. 6. Cloud-point phase diagram of Al_2O_3/PVDF-S-NS system with different AIP contents at 50℃. Δ—w(AIP) = 0%; ▲—w(AIP) = 4%; ■—w(AIP) = 12%

3.4. Observation of gelling kinetics

Fig. 7 comprises of a group of photos of gelling kinetics with PVDF concentration of 17% and AIP addition of 4%. Evolution processes of membrane structure can be seen in the picture, as shown in Fig. 7, the gelling front motion (L) increases, along with the increase in gelling time (t).

3.5. Effect of AIP contents on gelling kinetics

Fig. 8 shows the gelling kinetics curves of hybrid systems with different AIP contents (0, 4, 12, and 20%). As shown in Fig. 8, the gelling velocity of membrane forming process in the initial period was the largest, then slowed down with the extension of time. And, different casting solution systems at the same moment has different gelling velocity, the casting solution

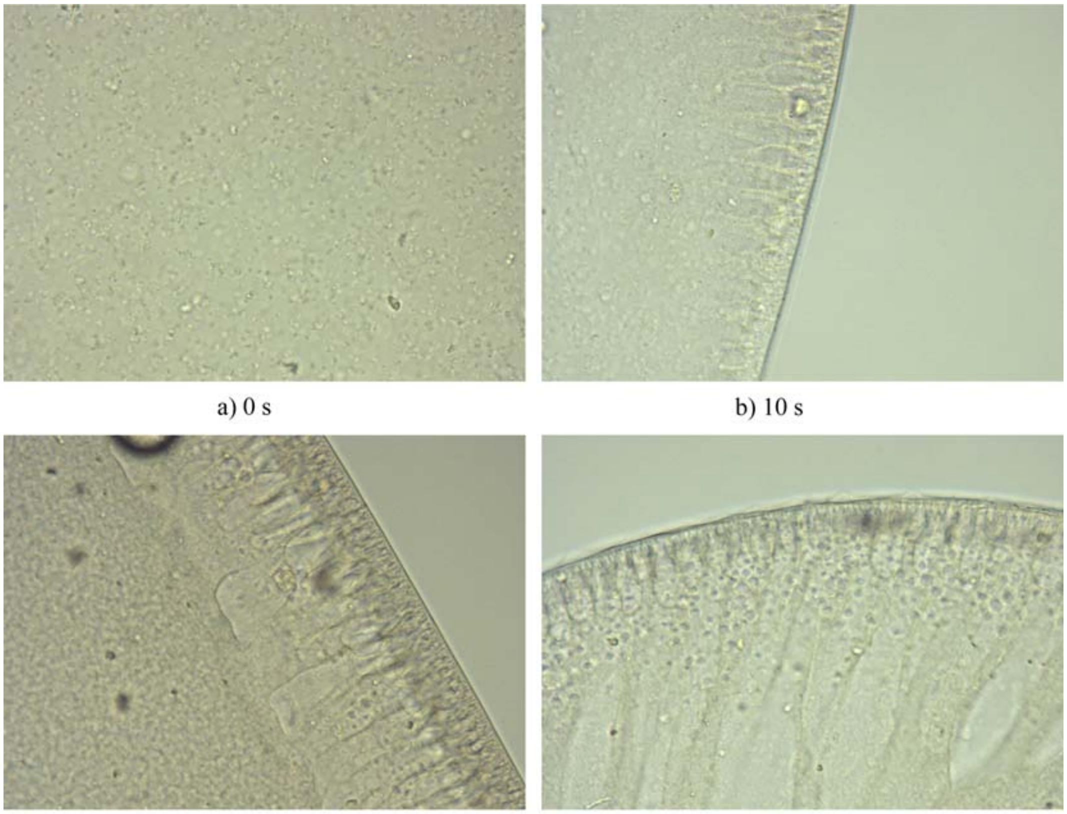
a) 0 s
b) 10 s
c) 25 s
d) 70 s

Fig. 7. Photos of gelling kinetics.

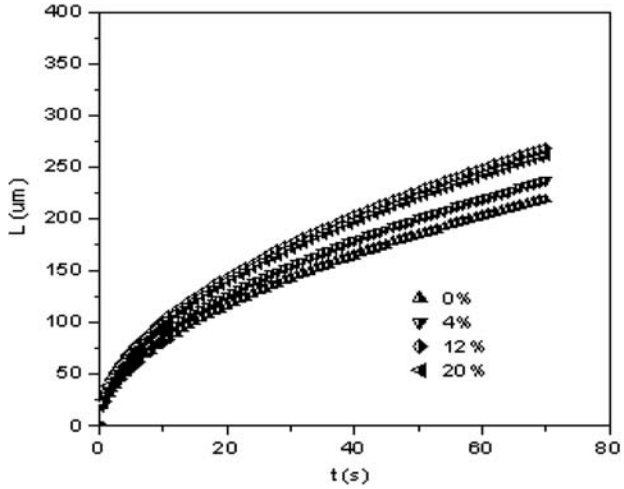

Fig. 8. Gelling kinetics curves of hybrid systems with different AIP contents.

system with more AIP contents has a higher gelling velocity, which means the velocity of phase separation in this system was faster. But when the AIP contents reached to 20%, the gelling velocity decreased. This is because AIP has a double-effect on the gelling velocity of the casting solution, with the addition of AIP, the Al_2O_3 turbidity glue, a kind of hydrophilic substance was formed in the casting solution, and the hydroxyl groups on its surface can form the hydrogen bond with the carbonyl group oxygen atom in the molecule of solvent. Then a composite substance with strong hydrophilicity was formed via the hydrogen bonding interaction, which have an effect on the phase inversion process, on the one hand, it results in the descend of solvents to the dissolving capacity of PVDF and the increase in the phase inversion velocity, on the other hand, the interaction between water and solvent was changed and the velocity diffused from non-solvent to the system was accelerated due to the strong hydrophilicity of the Al_2O_3 turbidity glue, which can also accelerate the phase inversion process. What is more, the hydroxyl groups in the Al_2O_3 turbidity glue can also form the hydrogen bond with the F atoms in the PVDF molecule, then a kind of bridge form complex was built, the dissolving capacity and conformation of polymer in the solution was changed due to the stereo-hindrance effect, thus makes the solution gelated with a small quantity of non-solvent. With the other conditions the same, the tendency of the phase separation will increase along with the increase in AIP contents, and thus makes the gelling velocity faster. But, on the other hand, the adding of AIP can also increase the viscosity of the casting solution, thereby, the motion of the polymer chain in the casting solution was restricted and the time of phase separation was extended. So, the effect of AIP on the gelling velocity of the casting solution is the result of mutual competition between these two factors, and when the AIP contents approached to 20%, the reduction of the gelling velocity was mainly resulted from the second factor.

3.6. The correlation between the square of gelling front motion (L^2) and gelling time (t)

The gelling kinetics curves of the casting solution systems with different AIP contents (4 and 12%) in Fig. 8 were chosen to study the correlation between L^2 and t. As shown in Fig. 9, the correlation between L^2 and t is not a simple linear relation, and the gelling process is incompletely affected by Fick scattering law. Theoretically, as the cross-section structure of membrane is unsymmetrical and uneven, and the structures of the surface layer and the porous support layer are different, which results in different poriness and bending factor, so, the correlation between L^2 and t is not a simple linear relation. In addition, as the thermodynamics and dynamics factors, such as polymer concentration, gelling medium, solvent concentration, viscosity, the mass transfer process and direction of solvent and gelling medium have a big diversity, the alteration of the gelling velocity cannot be uniform.

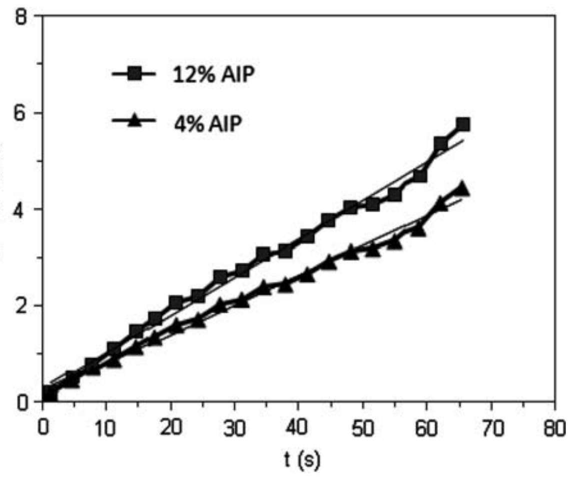

Fig. 9. The correlation between the square of gelling front motion and gelling time.

4. Conclusions

The APHM linking with the chemical bond was prepared by the phase inversion method. FT-IR spectroscopy proved that the C=C double bond was brought in on the surface of modified PVDF and the hydrophilic groups, such as hydroxyl group and carboxyl group were successfully brought in on the surface of APHM. Along with the increase in AIP contents, the viscosity of the casting solution increased accordingly, and the cloud-point curve approached to the solvent axis gradually, indicating the phase separation process of the casting solution was accelerated with the addition of AIP. The study of the gelling kinetics of the casting solution showed that the gelling velocity was the largest in the initial period of membrane formation, and then slowed down. Both gelling velocity and phase separation rate for the casting solutions were improved by the increases in AIP contents, however, the gelling velocity decreased when AIP concentration reached to 20% by weight.

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References

[1] S.S. Madaeni, S. Zinadini, V. Vatanpour, A new approach to improve antifouling property of PVDF membrane using *in situ* polymerization of PAA functionalized TiO_2 nanoparticles, J. Membr. Sci. 380 (2011) 155–162.

[2] B. Deng, M. Yu, X.X. Yang, B.W. Zhang, L.F. Li, L.D. Xie, J.Y. Li, X.F. Lu, Antifouling microfiltration membranes prepared from acrylic acid or methacrylic acid grafted poly (vinylidene fluoride) powder synthesized via pre-irradiation induced graft polymerization, J. Membr. Sci. 350 (2010) 252–258.

[3] Yen-Che Chiang, Yung Chang, Akon Higuchi, Wen-Yih Chen, Ruoh-Chyu Ruaan, Sulfobetaine-grafted poly(vinylidene fluoride) ultrafiltration membranes exhibit excellent antifouling property, J. Membr. Sci. 339 (2009) 151–159.

[4] E. Yuliwati, A.F. Ismail, T. Matsuura, M.A. Kassim, M.S. Abdullah, Effect of modified PVDF hollow fiber submerged ultrafiltration membrane for refinery wastewater treatment, Desalination 283 (2011) 214–220.

[5] M. Khayet, T. Matsuura, Preparation and characterization of polyvinylidene fluoride membranes for membrane distillation, Ind. Eng. Chem. Res. 40 (2001) 5710–5718.

[6] Yong Wei, Hua-Qiang Chu, Bing-Zhi Dong, Xuan Li, Sheng-Ji Xia, Zhi-Min Qiang, Effect of TiO_2 nanowire addition on PVDF ultrafiltration membrane performance, Desalination 272 (2011) 90–97.

[7] J. Wei, G.S. Helm, N. Corner-Walker, X.L. Hou, Characterization of a non-fouling ultrafiltration membrane, Desalination 192 (2006) 252–261.

[8] L. Yan, Y.S. Li, C.B. Xiang, S. Xianda, Effect of nano-sized $Al2O_3$-particle addition on PVDF ultrafiltration membrane performance, J. Membr. Sci. 276 (2006) 162–167.

[9] Chanjuan Liao, Ping Yu, Jianquan Zhao, Liming Wang, Yunbai Luo, Preparation and characterization of NaY/PVDF hybrid ultrafiltration membranes containing silver ions as antibacterial materials, Desalination 272 (2011) 59–65.

[10] ZhaoHong Meng, HuiLing Liu, Yan Liu, Jian Zhang, ShuiLi Yu, FuYi Cui, NanQi Ren, Jun Ma, Preparation and characterization of Pd/Fe bimetallic nanoparticles immobilized in PVDF·Al2O3 membrane for dechlorination of monochloroacetic acid, J. Membr. Sci. 372 (2011) 165–171.

[11] X.L. Li, K.J. Xiao, S.Y. Guo, Preparation and characterization of hybrid PVDF/Al_2O_3 membrane, J. South China Univ. Technol. (Natual Science Edition). 38(7) (2010) 112–116.

[12] Lu Yan, Yu Shui Li, Chai Bao Xiang, Preparation of poly (vinylidene fluoride)(pvdf) ultrafiltration membrane modified by nano-sized alumina (Al_2O_3) and its antifouling research, Polymer 46 (2005) 7701–7706.

[13] B. Jung, Preparation of hydrophilic polyacrylonitrile blend membranes for ultrafiltration, J. Membr. Sci. 229 (2004) 129–136.

[14] J. Marchese, M. Ponce, N.A. Ochoa, P. Prádanosb, L. Palacio, A. Hernández, Fouling behaviour of polyethersulfone UF membranes made with different PVP, J. Membr. Sci. 211 (2003) 1–11.

[15] A.L. Ahmad, M.A. Majid, B.S. Ooi, Functionalized PSF/SiO_2 nanocomposite membrane for oil-in-water emulsion separation, Desalination 268 (2011) 266–269.

[16] A. Rahimpour, S.S. Madaeni, Polyethersulfone (PES)/cellulose acetate phthalate (CAP) blend ultrafiltration membranes: preparation, morphology, performance and anti-fouling properties, J. Membr. Sci. 305 (2007) 299–312.

[17] W.H. Yuan, Y.S. Lin, W.S. Yang, Molecular sieving MFI-type zeolite membranes for pervaporation separation of xylene isomers, J. Am. Chem. Soc. 126 (2004) 4776–4777.

[18] M.A. Carreon, S. Li, J.L. Falconer, Alumina-supported SAPO-34 membranes for CO_2/CH_4 separation, J. Am. Chem. Soc. 130 (2008) 5412–5413.

[19] Kai-Shiun Chang, Tomohisa Yoshioka, Masakoto Kanezashi, Toshinori Tsuru, Kuo-Lun Tung, Molecular simulation of micro-structures and gas diffusion behavior of organic-inorganic hybrid amorphous silica membranes, J. Membr. Sci. 381 (2011) 90–101.

[20] L.Y. Yu, Z.L. Xu, H.M. Shen, Y. Hu, Preparation and characterization of PVDF-SiO_2 composite hollow fiber UF membrane by sol–gel method, J. Membr. Sci. 337 (2009) 257–265.

[21] X.C. Cao, J. Ma, X.H. Shi, Z.J. Ren, Effect of TiO_2 nanoparticles size on the performance of PVDF membrane, J. Appl. Surf. Sci. 253 (2006) 2003–2010.

[22] A. Bottino, G. Capannelli, A. Comite, Preparation and characterization of novel porous PVDF-ZrO_2 composite membranes, Desalination 146 (2002) 35–40.

[23] D.J. Lin, C.L. Chang, F.M. Huang, L.P. Cheng, Effect of salt additive on the formation of microporous poly(vinylidene fluoride) membranes by phase inversion from $LiClO_4$/water/DMF/PVDF system, J. Polym. 44 (2003) 413–422.

[24] M. Shojaie-Bahaabad, E. Taheri-Nassaj, Economical synthesis of nano alumina powder using an aqueous sol-gel method, Mater. Lett. 62 (2008) 3364–3366.

[25] J. Hu, X.M. Zeng, R.J. Dong, Y.W. Zhang, J.X. Zhao, C.X. Wu, D. Pan, Study on phase behavior of PAN-DMSO-H_2O ternary system by cloud-point titration method, China Synth. Fiber Ind. 31(4) (2008) 5–8.

[26] Jian-qiang Meng, Chun-lin Chen, Li-ping Huang, Qi-yun Du, Yu-feng Zhang, Surface modification of PVDF membrane via AGET ATRP directly from the membrane surface, Appl. Surf. Sci. 257 (2011) 6282–6290.

[27] X.D. Zhao, L.Z. Song, J. Fu, P. Tang, F. Liu, Adsorption characteristics of Ni(II) onto MA-DTPA/PVDF chelating membrane, J. Hazard. Mater. 189 (2011) 732–740.

[28] L.Z. Song, C.Y. Dong, J. Li, Application of the PAA-PVDF microfiltration composite membrane for municipal wastewater advanced treatment, Toxicol. Environ. Chem. 89 (2007) 223–232.

[29] V.L. Silva, R. Carvalho, M.P. Freitas, C.F. Tormena, W.C. Melo, Structural determination of Zn and Cd-DTPA complexes: MS, infrared, 13C NMR and theoretical investigation, Spectrochim. Acta A 68 (2007) 1197–1200.

[30] M. Shojaie-Bahaabad, E. Taheri-Nassaj, Economical synthesis of nano alumina powder using an aqueous sol-gel method, Mater. Lett. 62 (2008) 3364–3366.

[31] Q. Zhao, S.L. Yu, H. Lv, Study on preparation of PVDF hybrid membrane and its fouling by humic acid solution, J. China Water Wastewater 19(26) (2010) 147–151.

[32] X.Y. Wang, L. Zhang, H.L. Chen, Effect of maturation time of dopes on the morphology and crystallization of PVDF membranes, Polym. Mater. Sci. Eng. 25(7) (2009) 57–60.