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EFFECTS OF SIO_2 NANOPARTICLES ON THE STRUCTURE OF POLYVINYLIDENE FLUORIDE ULTRAFILTRATION MEMBRANE

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ABSTRACT

In this paper we describe the process of adding SiO_2 nanoparticles into a polyvinylidene fluoride (PVDF) casting solution to prepare inorganic-organic hybrid membranes. The hybrid membrane performance was improved compared with that of a pure PVDF membrane. Tests showed that the pure water flux of the membrane was improved without the decrease in the retention rate. The addition of SiO_2 nanoparticles induced a strong increase in the viscosity and made the casting operation easier. The phase diagram shows that the addition of SiO_2 nanoparticles decreases the water tolerance of the solution, and thus speeds up the membrane formation process. The DSC curves also revealed that the degree of crystallinity of PVDF has obviously increased in the hybrid membrane.

Keywords: Polyvinylidene fluoride (PVDF); SiO_2 nanoparticles; inorganic-organic hybrid membranes.

INTRODUCTION

Ceramics are useful due to their high thermal stabilities, strengths, and high modulus, but they are usually very brittle. Polymers, on the other hand, are much easier to process and are very tough, but they are thermally less stable. The introduction of inorganic fillers into a polymer matrix increases its strength and stiffness and sometimes strongly influences the final properties, which are also controlled by the interfacial interactions between the matrix and fillers [1].

In membrane application process, the use of hybrids is a promising strategy, which may combine the advantages of both organic and inorganic polymeric membranes and may contribute to solving some of the problems connected with each of them.

With the development of nanotechnology and materials, many researchers have focused on inorganic nano-particle-organic hybrid membranes. Because the performance of hybrid membranes can be influenced by many parameters such as chemical composition, production technology, nano-particle diameter and concentration of the nano-particle additives, the performance of a membrane can be adjusted using many approaches.

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Genné *et al.*[2] found that the addition of ZrO_2 in a polysulfone casting solution causes a dramatic increase in membrane permeability. The surface porosity, which was about 11% for these membranes, was much higher than the reported values of 2-3% for pure polymeric ultrafiltration membranes. The molecular weight cutoff of these high surface porosity membranes confirmed that there was no significant change in the skin pore size.

Ebert *et al.*[3] found polyamideimide (PAI) membranes with 40 wt% TiO_2 could withstand temperature treatment at 180 °C with only a minor decrease in flux. The pore size distribution of the treated membranes remained practically unchanged. In addition, they found that PVDF/TiO_2 membranes were also less susceptible to compaction than pure PVDF membranes under a pressure of 30 bar.

Jiang *et al.*[4] synthesized nanodispersed silica particles by a Stober method. These silica particles were uniformly dispersed in a solution of polyvinyl alcohol (PVA) in water. Nano-sized silica/PVA composite ultrafiltration (UF) membranes were prepared by a phase-inversion process. The results showed that the mechanical properties of these membranes were significantly improved.

Among the organic membrane materials, polyvinylidene fluoride (PVDF) is a promising material due to its heat resistance, satisfactory elasticity, good mechanical and chemical properties, bioinertness, and film formation ability[5].

Zenon Environmental Inc.[6] produced the PVDF-α-Al_2O_3 porous membrane by reacting and dispersing α-Al_2O_3 particles in a PVDF casting solution. The resulting membrane provided a specific flux that was about 50% higher than that of a membrane made with the same polymer but without the α-Al_2O_3 particles.

Bottino[7] found that the cross-sectional structure of hybrid membranes was not practically affected by the presence of ZrO_2, but was strongly dependent on the solvent. The UF performance of the membrane could be varied by changing the PVDF solvent. Bottino[8] also found that the thermal properties of PVDF/silica hybrid membranes were very similar to those of the PVDF membranes; whereas the mechanical resistance was slightly lower. Increasing the amount of silica in highly diluted PVDF solutions yielded the membranes with a higher permeate flux and lower retention ratio; whereas no effect on the membrane performance was observed by adding the silica to concentrated PVDF solutions. The most relevant and beneficial effect of the silica was due to the increase in viscosity of the casting solutions which made casting operations easier.

To promote the dispersion of the inorganic component in polymers, which are already preformed in many cases, a sol-gel process was used to grow the inorganic phase in the polymer solution. This method was commonly used by the GKSS Research Center [9-13]. For the preparation of the inorganic phase, tetraethoxy silane and an amino silane were added to a solution. The addition of amino silane not only improves dispersion but also assures adhesion between the inorganic phase and the organic polymer matrix. Lack of adhesion, even if the inorganic phase is well dispersed, will result in the formation of defects which are highly undesirable in membrane applications.

The purpose of this study was to prepare a new membrane containing inorganic nanoparticles of SiO_2. We also investigated the influence of these SiO_2 nano-particles on the membrane formation process, membrane structure and mechanical properties.

EXPERIMENTAL

Materials

Polyvinylidene fluoride was obtained from Shanghai New Materials Company Limited (3FNM), (FR-904, intrinsic viscosity = 1.4~1.9 dl/g). N, N-dimethylacetamide (>99%, DMAC) and SiO_2 (A200, 20 nm) were purchased from Aldrich and Degusa, respectively. Egg white protein (43000) was provided from Shuangxuan Microorganism Substrate Plant of Beijing. Lithium chloride (LiCl, reagent grade) and polyvinylpyrrolidone (PVP, 15k) obtained from Beijing Chemical Plant were used as additives. 3-aminopropyltrithoxy silane (KH550) was obtained from Nanjing Crompton Shuguang Organosilicon Specialties Co. Ltd.

Phase Behavior of the SiO_2/ LiCl /PVP/PVDF System

The gelation phase boundaries at 25°C of the quaternary system, SiO_2/LiCl/PVP/PVDF, were determined by the widely used 'cloud point' method. In brief, a specific amount of PVDF (pre-dried at 120°C) was mixed with DMAC, LiCl and PVP and then sealed in a glass bottle. This mixture was blended at 60°C until completely dissolved. The cloud point measurements were carried out by titration of the polymer solutions with a concentration of 4-25 wt% PVDF in DMAC, to which 1 wt% SiO_2 was added. Homogenous dispersions were obtained by stirring with a mixer. The vessels were closed, and put in a thermostatic bath at 60°C. Non-solvent (water) was added with a syringe. The cloud point did not become clear again after 12 h of homogenization and was calculated from the total amount of polymer, solvent and non-solvent present in the vessels.

Viscosity Measurement

The viscosity of the solutions containing different amounts of SiO_2 was measured by a HAKKA-6L rheometer. Measurements were performed at a constant temperature of 25°C and a constant shear rate.

Membrane Preparation and Characterization

PVDF porous membrane was prepared by the phase inversion method. The casting solution was prepared at 60-65°C for dissolution of PVDF in DMAC with the concentration of PVDF, LiCl and PVP at 15%, 2% and 3% (w/w) respectively. A film was casted on a glass plate and, after an evaporation time about 10s, the film was immersed in a coagulation bath at a temperature of 15-20°C. The film was removed from the glass plate and leached overnight in water in order to completely remove any traces of solvent.

By changing the SiO_2 concentration in the casting solution, membranes with various morphologies and separation properties could be obtained. The thicknesses of the membranes were 0.075-0.080mm. To provide dense membranes for the purpose of measuring the contact angle of the hybrid membranes, wet membranes were dehydrated in a vacuum at a temperature of 40°C.

The prepared membranes were then characterized by the following methods:

Scanning Electron Microscope

The samples were fractured in liquid nitrogen and coated with Au/Pd by penning sputtering. They were observed in a Quanta 2000-EDAX Genesis 2000 scanning electron microscope.

Transport and Separation Properties

A self-made ultrafiltration apparatus equipped with a magnetic stirrer was used to evaluate the membrane performance in relation to water or aqueous solutions of macromolecules. The volume of the ultrafilter was 200 ml and the effective membrane area was 24 cm^2. The pressure required for testing the membranes was obtained by compressed air using an air compressor.

The water flux was determined under a pressure of 0.2 MPa at a temperature of 25°C. Before the measurements of membrane flux, the membranes were pressurized by ultrafiltering pure water for three hours under a pressure of 0.2 MPa. The retention ratio of flat membranes was determined by ultrafiltering a solution of 0.1% egg white proteins (M = 43,000), which was calculated according to the concentrations in the feed and permeate solutions. The protein concentration in the permeation and the solution was determined by an HP8451 ultraviolet-visible spectrophotometer at 280nm.

Tensile Strengths

Dried dense and wet porous membranes were cut into the standard dumbbell shape for the measurements of tensile strength and modulus. The tensile strengths at the breaking point were measured using an Instron 4302 universal tensile testing machine under ambient conditions for at least three samples and the average value was recorded.

Porosity

The 24 cm^2 membrane pieces were taken out, the water on the membrane surface was lightly absorbed with filter paper and then the pieces were weighed, the weight, W_1, was recorded. Subsequently, the membranes were put it into an oven to dry at a temperature of 60-70°C. After a constant weight was obtained, the weight, W_2, was recorded again. The porosity of the membrane was calculated according to the following equation:

$$A_k = \frac{W_1 - W_2}{A \times \delta \times \rho_{H_2O}} \times 100\%$$

where, W_1—weight of wet membrane(kg), W_2—weight of dry membrane(kg), A—membrane area(m^2), δ—membrane thickness(m), ρ—density of membrane(kg/m^3).

FTIR Spectra

FTIR spectra were obtained using a P-E FTIR-1730 spectrometer. The samples for the IR studies were dried, mixed with KBr, and then pressed. FTIR spectra were used to identify the formation of covalent bonds or hydrogen bonds between PVDF and SiO_2.

Differential Scanning Calorimetry (DSC)

The thermal behavior of PVDF and PVDF-silica hybrid membranes was determined by using a differential scanning calorimeter (DSC6200) to verify the change in the heat of melting. The

sample (about 5 mg) encapsulated in a platinum pan was heated from 50 to 250°C at a rate of 10 °C/min under an argon atmosphere to measure the heat of melting.

RESULTS AND DISCUSSION

Performances of Ultrafiltration Membrane

Figure 1 shows that the removal of egg protein is relatively constant regardless of the amount of SiO_2. However, the pure water flux of hybrid membranes increased during the initial stage and then declined with the addition of SiO_2 (Figure 2). The initial behavior may be caused by the improved hydrophilicy of the membrane because the hydrophilic SiO_2 containing many available hydroxides, is dispersed on the membrane surface and into the pores. Table 1 shows that the observed values of the contact angle of the hybrid membrane decreased which supports the hypothesis that the hydrophilicy of the hybrid membrane was likely improved. At the same time, the porosity of the hybrid membrane was also improved (Figure 3 and 4(b)). When the added quantity of SiO_2 was too large, the SiO_2-particles apparently agglomerated in the membrane pores (Figure 4(c)), which logically would result in a lowered porosity of the hybrid membrane and a lower pure water flux.

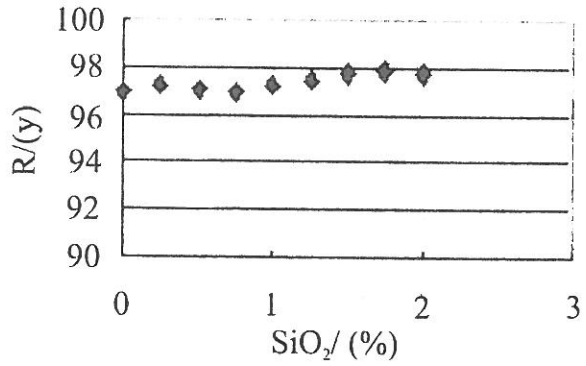


Figure 1: Effect of SiO_2 on Egg protein Removal of Hybrids Membranes

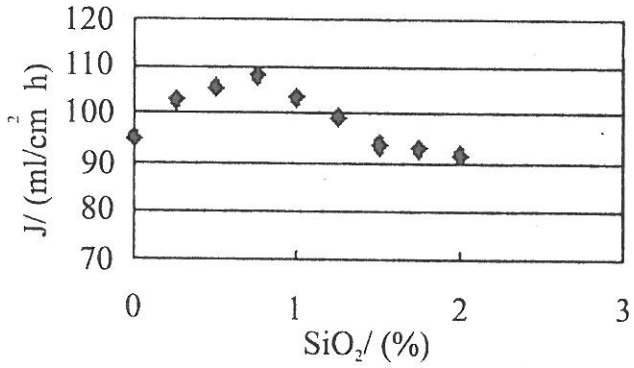


Figure 2: Effect of SiO_2 on the Pure Water Flux of Hybrid Membranes

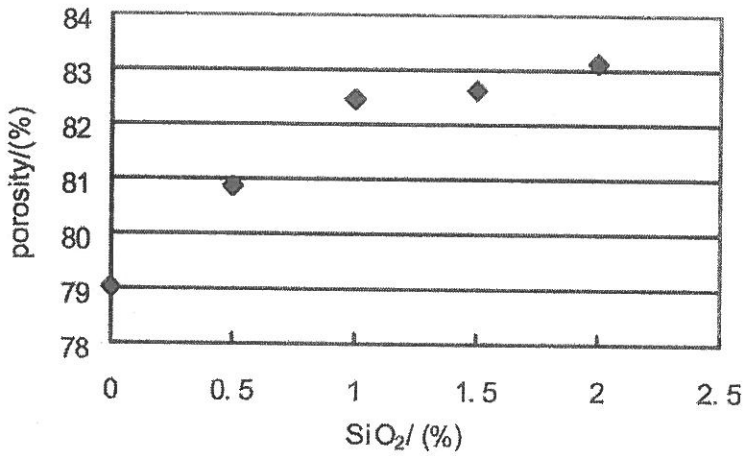
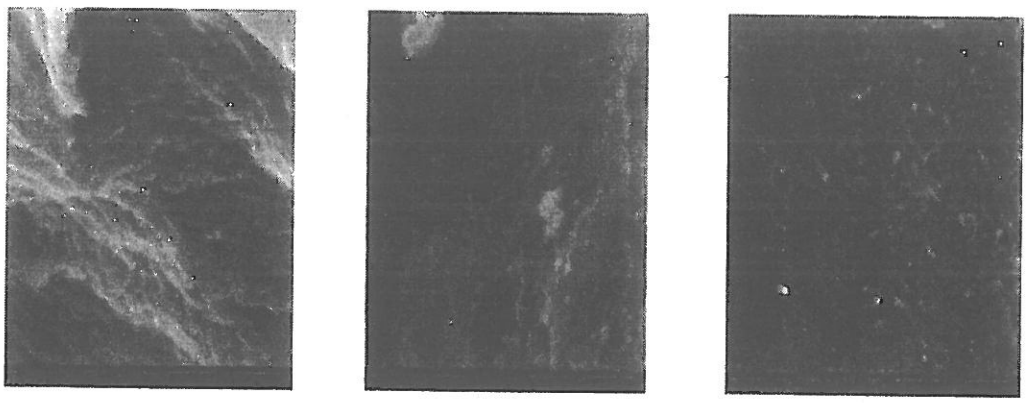


Figure 3: Effect of SiO_2 on the Porosity of Hybrid Membranes



SiO_2 0% SiO_2 1.0% SiO_2 1.5%

Figure 4: SEM Micrographs of Macrovoid Wall

Table1
The Influence of SiO_2 Nano-particles on the Contact Angle of Hybrid Membranes

SiO_2(%)	0	0.25	0.5	0.75	1	1.5	2
Contact angle of hybrid membrane (°)	78	75	73	73	72	71	71

Mechanical Properties

Figures 5 and 6 show the tensile strength and Youngs modulus of the dry membrane and wet membrane. With respect to the dry hybrid membrane (dense membrane), when the content of SiO_2 was kept in the range of 0-2 wt%, the tensile strength and Youngs modulus were greatly improved compared with those of pure PVDF UF membrane. The tensile strength of the dry hybrid membrane with a SiO_2 concentration of 2 wt% was 59 MPa, which was 93% higher than

pure PVDF UF membrane. Meanwhile, the Youngs modulus was observed to reach as high as 957 MPa for some samples. Figure 7 compares the FTIR spectra of PVDF dry membrane and PVDF-SiO_2 hybrid membrane, the result shows no relevant interaction between PVDF and SiO_2.

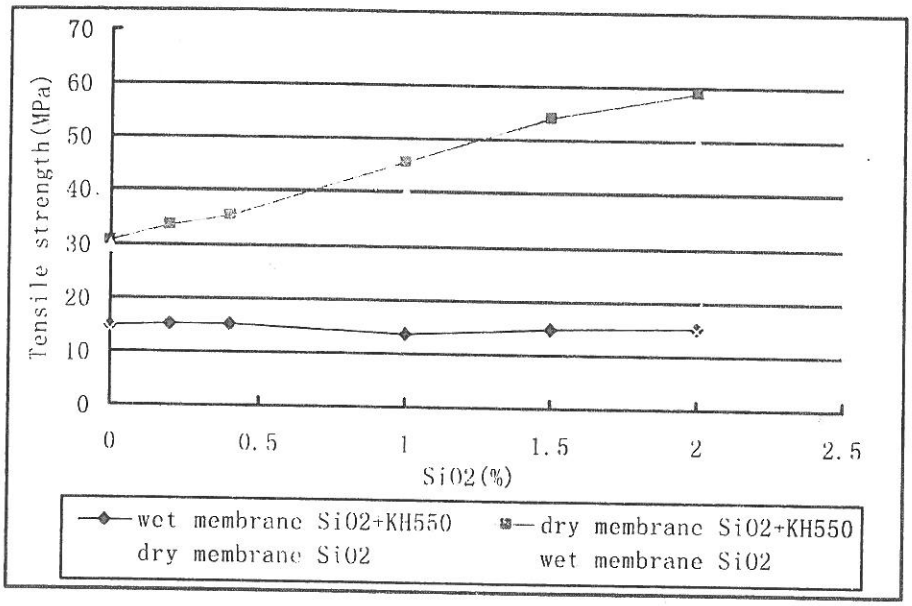


Figure 5: The Influence of nm-SiO_2 Content on the Tensile Strength of the Membrane

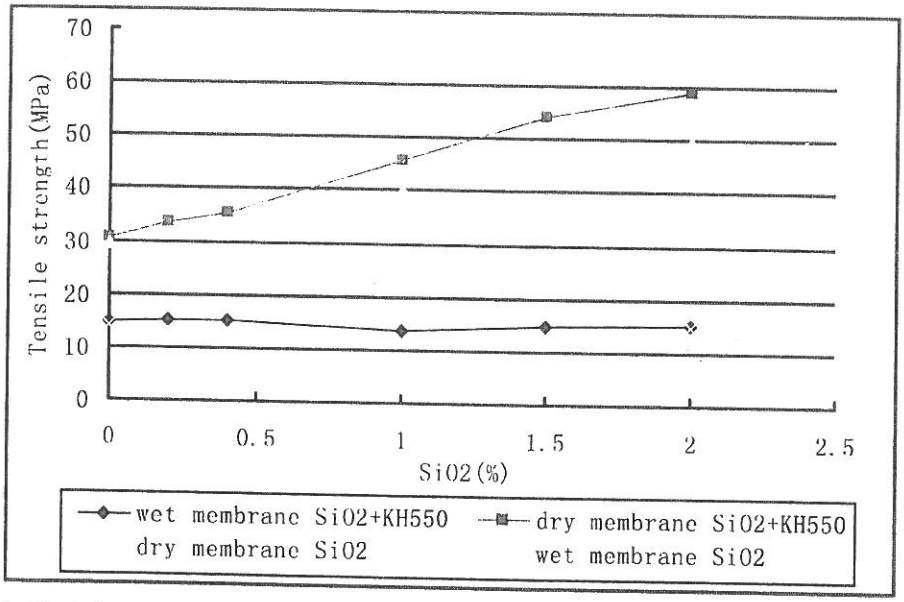


Figure 6: The Influence of nm-SiO_2 Content on the Young Modulus of the Membrane

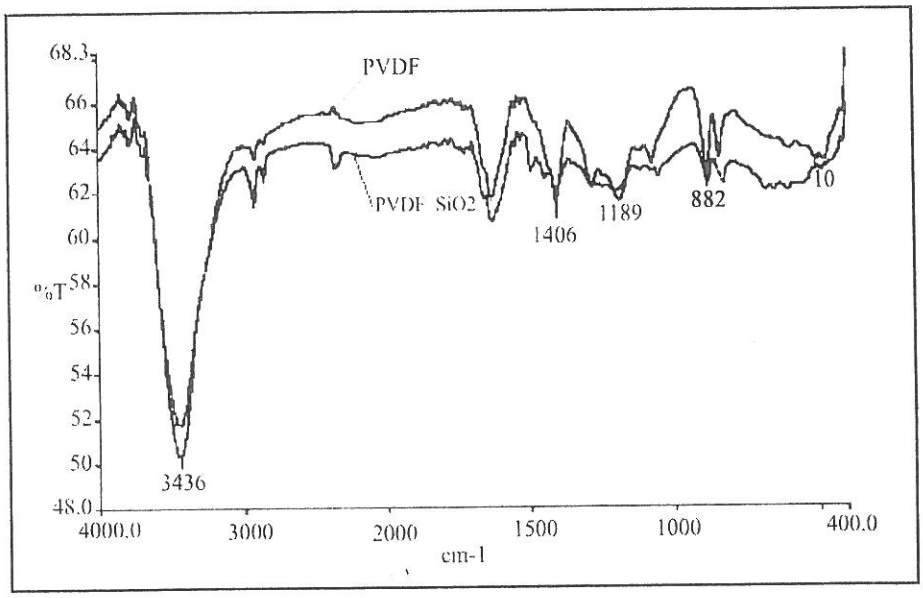


Figure 7: The Infrared Spectrum of PVDF and PVDF-SiO_2 Hybrid Membranes

The tensile strength and Youngs modulus of the wet membrane (porous membrane) changed slightly with the addition of SiO_2. A possible reason is that the wet membrane pores cause mechanical leakage of the ultrafiltration membrane. The mechanical strength of a wet membrane was much lower than that of a dry membrane (dense membrane). The pore size and the resulting porosity of the membrane had a strong impact on the mechanical strength of the membrane showing that the nano-particles were not the main factors responsible for the membrane strength.

When KH550 was added to the casting solution, both the tensile strength and Youngs modulus of membranes (dry and wet) increased. We speculate that the amino silane increased the adhesion between the inorganic phase and the organic polymer matrix.

Process of Membrane Formation

The mechanism of membrane formation is an important issue. Addition of a small amount of SiO_2 nano-particles will produce influences on the membrane formation process, which was shown from the viscosity change and cloud point testing.

Firstly, the addition of silica induced a strong increase in the viscosity. Binary solutions of PVDF and DMAC were clear and had viscosities between 1000 mPa.s to 30000 mPa.s. When SiO_2 particles were dispersed in the DMAC, the binary solution was opalescent. The addition of SiO_2 caused a strong increase in the viscosity for the ternary dispersion. Bottino[8] also found the same phenomena when SiO_2 was added into a PVDF/NMP solution. He suspected that this phenomenon occurred because of the strong interactions between the solvent and the silanol groups, which led to the aggregation of PVDF chains and the formation of macromolecular networks resulting in an increase in viscosity.

We found that the viscosity of the PVDF solution without any SiO_2 did not show any change with the mixing rate, but the viscosity of the PVDF solution with SiO_2 would change, exhibiting the characteristics of a non-Newtonian fluid.

The addition of SiO_2 (represented by triangles in the phase diagram (Figure 8)) shifts the cloud point curve to lower nonsolvent (water) concentrations compared with membranes composed of pure PVDF (represented by circles). That suggests SiO_2 reduces the ability of a PVDF solution to admit water (non-solvent), and thus speeds up the membrane formation process.

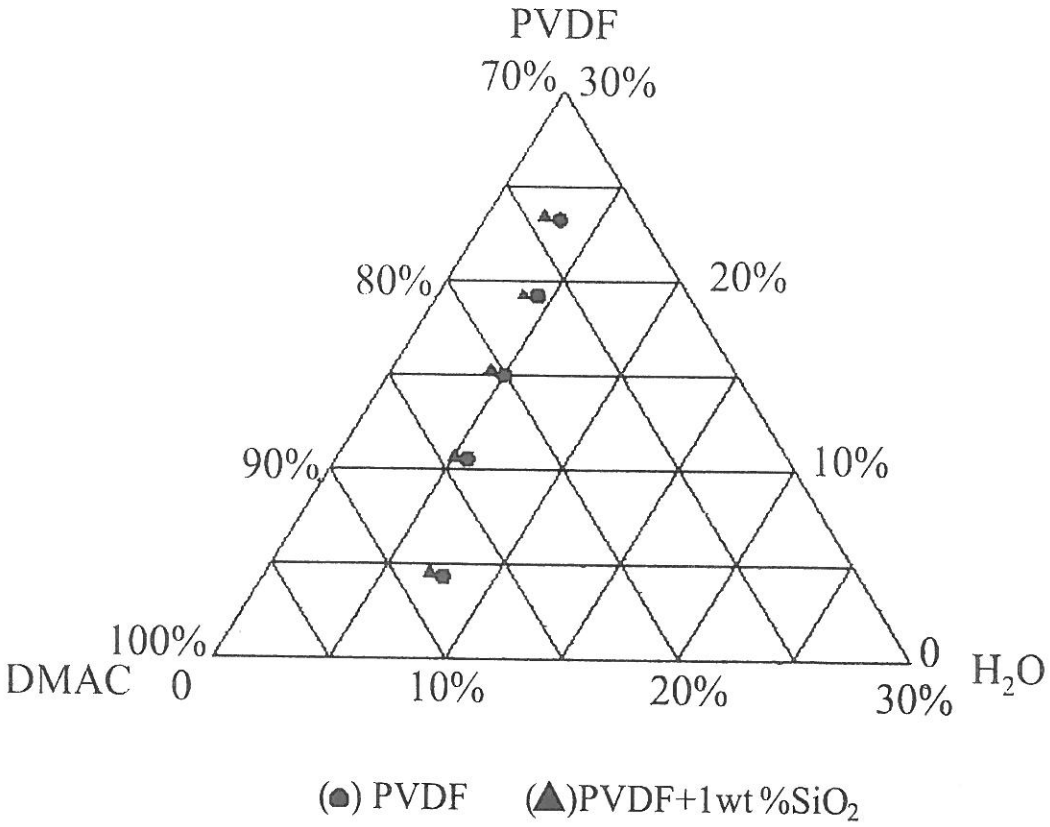


Figure 8: Cloud Point Curves of PVDF-DMAC-H_2O System

When a polymer is melted, its crystallinity will change. The heat of melting reflects the quantity of heat required to destroy the crystal structure. The greater the degree of crystallinity, the greater the heat of melting is[13]. Figure 9 shows the melting enthalpy of three membranes. With an increase in SiO_2 content, the melting points changed a little while the melting enthalpy largely increased. This was caused by an increase of the degree of crystallinity. This result also explained the improvement of the mechanical strength of the hybrid membranes.

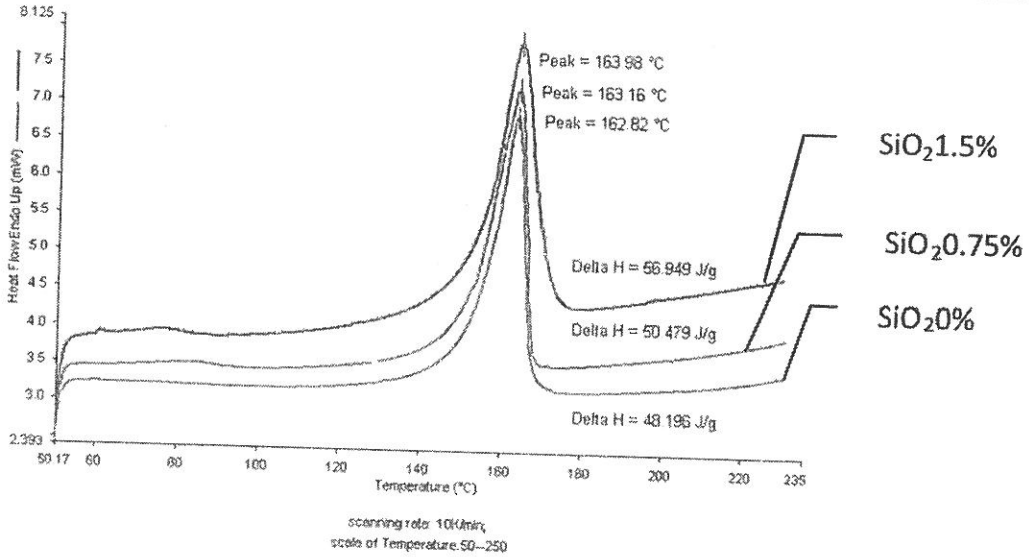


Figure 9: DSC Curves of SiO_2-membrane

CONCLUSIONS

SiO_2 nano-particles can be uniformly dispersed in PVDF solution. The porosity of hybrid membranes increased with the addition of SiO_2. Furthermore, it was noted that the rejection rate of egg protein did not change while the pure water flux of a hybrid membrane was first improved then reduced. The strong interactions between the solvent and the silanol groups led to the aggregation of PVDF chains, the formation of macromolecular networks and, in turn, an increase in viscosity. The cloud point curve supported the hypothesis that SiO_2 could reduce the ability to admit non-solvent molecules. The DSC experimental results further supported an increase in the degree of crystallinity in hybrid membranes compared with non-hybrid membranes.

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