Investigation on Preparation and Porosity of YSZ/PTFE Microporous Membrane Modified by PTFE Resin Emulsion

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Abstract

In this paper, YSZ/PTFE composite microporous membrane was prepared by mechanical tensile method, using PTFE resin emulsion as material and YSZ micro/nanoparticles as reinforcer. The performance of YSZ/PTFE composite microporous membrane was characterized by mechanical property testing. The effects of the dispersant PVA, the draw ratio, YSZ content and calcination temperature on the porosity of composite microporous membrane were systematically investigated. The results showed that the porosity increased significantly as PVA added; with the increase of YSZ content, the porosity gradually increased, but the YSZ content was not over 20%; the porosity reached 73.09% when the draw ratio 3.5 times, YSZ content 8%, and the calcination temperature 320℃.

Keywords: PTFE, YSZ, Microporous membrane, Porosity

1. Introduction

Polytetrafluoroethylene (PTFE) has many excellent characteristics such as low permittivity, (Xie, 2007, pp. 32-39 and Xi, 2008, pp. 7469-7476), high water repellency, high chemical resistance and high heat resistance.(Yuan, 2005, pp. 7-11, Fang, 2001, pp. 13-16, Liu, 2004, pp.340-346, Murali, 2009, pp. 290-295, Kim, 2008, pp. 654-657 and Wang, 2004, pp. 26-28). PTFE membrane is a new membrane material, has become one of indispensable material in the cutting edge of science and modern industry. There are many scholars have studied of microporous membrane, (Wei, 2005, pp. 27-30, Huai, 2010 and Chen, 2003, pp. 20-22), but few people use PTFE resin emulsion as raw material. Recently, imperfect porosity of pure PTFE membrane has greatly limited its scope of application. Thus a lot of efforts have been continuously made to improve the porosity of PTFE membrane by means of inorganic or organic compound inclusion.

Domestic and foreign researchers through the filled methods improve PTFE membrane’s strength, hydrophilicity, abrasion resistance, pressure resistance, or give a special performance to PTFE membrane, such as antibacterial activity. (Sun, 2009, pp. 75-77 and Bao, 2006, pp. 8-11).

Yttria-stabilized zirconia (YSZ) is the most commonly used filler in recent years. YSZ is an important functional oxide for many structural and electronic applications, such as solid oxide fuel cells (Bao, 2007), gas sensor (Liu, 2004, pp. 340-346) and automotive exhaust three-way catalysts (Murali, 2009, pp. 290-295) because of its excellent chemical resistance, refractory character, oxygen ionic conductivity and olymorphous nature. In view of these applications, controlling the porosity of these systems is highly desirable (Hung, 2006, pp. 225-230). So the samples were made by adding micro/nanometer YSZ into PTFE for improving the porosity.

In this article, the purpose of this work is to study the porosity of the PTFE composite microporous membrane filled with YSZ. Some insights into the porosity of YSZ/PTFE composite microporous membrane are also given.

This study may be helpful for investigating potential applications of the composite microporous membrane.

2. Experiments

2.1 Materials

PTFE resin emulsion was obtained fromTianjin chemical reagent Ltd.; YSZ micro/nanoparticle was bought from Cabot Corporation in America, and its average size is 0.08~30μm; PVA was obtained from Beijing Organic Chemistry Company, the degree of polymerization is 1700, and the degree of alcoholysis is 99%.

2.2 Membrane preparing

The specimen compositions were prepared by PTEF resin emulsion, YSZ powders and PVA. First, the mixtures were heated and strived for 30~60min by magnetic stirrer in the range of 60℃ to 90℃ which was not expected to be higher than 100℃in order to remove water. Second, the mixtures were squeezed and turned out to be the dense and smooth thick film. The membrane with a thickness around 0.2~0.4mm was obtained at room temperature by homemade calendar at a rolling speed between 0.5~1.5m/min, and then it was heated at 50~100℃ in the oven. Third, pre-molded YSZ/PTFE composite microporous membrane was prepared with different draw ratio by stretching at a speed of about 0.5~1m/min and heating at approximately 200℃. At last, under a certain tension, the pre-molded membrane was heat-setting by calcinations in the range of 300℃ to 330℃ for 8~10min, and then YSZ/PTFE composite microporous membrane was prepared after natural cooling.

2.3 Studies of DSC curves

DSC curves were produced by a differential scanning calorimetry (DSC-7, Perkin-Elmer Limited, American). The samples were analysed under the N_2 gas atomsphere at the heating rate of 2℃/min between 40℃and 400℃.

2.4 Porosity analysis

Porosity is defined as the percentage of air in the composite membraner. In this study the Saturation weighing method was used to measure the porosity of composite microporous membrane. Ethanol was chosen as the saturated medium in this paper.

3. Results and discussion

3.1 Effect of dispersant on the porosity

The C-F and C-C in the PTFE molecule are hydrophobic groups, so PTFE is incompatible with YSZ powders. Since that the PVA was used as dispersant. PVA was dissolved in hot water at 90℃, and the 2% PVA solution was obtained, and then YSZ powders were added and ultrasonic cleaner was used to mix well for 30min. Finally, PTFE resin emulsion was poured into the solution which was constantly stired by magnetic stirrer. Composite microporous membrane sample was obtained through the steps in *2.2*. The effect of dispersant on the porosity of composite microporous membrane was shown in Table 1. The experiment was carried on the conditions: YSZ content 7%, calcination temperature 320℃, calcination time 8min and heating rate 2℃/min

Table 1 shows that the porosity of composite microporous membrane increased significantly at different draw ratio from 0.5 times to 1 times to 1.5 times when the PVA was added as dispersant, as a result of that condensation reaction was occured between the hydroxyl groups of PVA molecule and a amount of the hydroxyl groups on the surface of YSZ. At the same time, long carbon chains of the membrane combined with the PTFE substrates, by which not only the interface state between inorganics and organics were effectively modified, but also the dispersion and anti-sedimentation of the YSZ particles in PTFE resin emulsion were enhanced, so that the membrane were stretched more easily. Consequently, the prorosity of the membran added PVA was higher.

3.2 The effect of the draw ratio on the porosity

Figure 1 shows the effect of draw ratio on the porosity of composite microporous membrane. The experiment was carried on the conditions: calcination temperature 320℃, calcination time 8min, and heating rate 2℃/min

It is evident in Figure 1 that the porosity of the membrane is improved with the draw ratio increasing. The porosity of the membrane which is not stretched is zero, and reaches 73.09% when the draw ratio 3.5 times and YSZ content 8% are chosen. In addition, pure PTFE membrane was difficult to stretch in the preparation process, and it was likely that the sample fracture would occur when the draw ratio was more than 2 times. From microstructure analysis, the banded structures of PTFE resin are pulled out from the spherical particles when shear stress is applied to them. By increasing draw ratio, the shear force also increases gradually, which promotes more and more band structure undrew and leads to the micro-fiber length increasing. Meanwhile, the average pore size of specimens also increases, so that the porosity increases. (Hao, 2005, pp. 26-29).

3.3 The effect of YSZ content on the porosity

The effect of YSZ content on the porosity of composite microporous membrane is shown in Figure 2. The experiment was carried on the conditions: calcination temperature 320℃, calcination time 8min and heating rate 2℃/min.

The porosity gradually increases with the increase of YSZ content. The explanation over this phenomenon is that the addition of YSZ decreases the bulk desity of PTFE resin baseband, and then reduces the fusion degrees among the resin particles and intermolecular force. So under the same stress, the more YSZ content is, the easyer the microporous can be drawed out, the higher the porosity.

3.4 The effect of Calcination temperature on the porosity

The calcination temperature is an important part to the preparation of composite microporous membrane. In order to determine the calcination temperature, the experiment carried out the DSC analysis of PTFE resin in the range from 25℃ to 400℃. The DSC curve is shown in Figure 3.

From Figure 3, it can be seen that the melting temperature of used PTFE resin is about 329℃. In this paper, YSZ/PTFE composite microporous membrane was prepared, using PTFE resin emulsion as a material. The thickness of sample was 0.2~1mm. Early results showed that when the calcination temperature was more than 329℃, under a certain tension, the sample easily occured to the rupture because the sample was comparative thin. But when the calcination temperature is less than 300℃, crystallization rate is lower and crystal structure is imperfect, following that unstable size and insufficient strength of the sample. Therefore, the calcination temperature should be chosed in the range of 300℃ to 330℃.

Figure 4 shows the effect of calcination temperature on the porosity of composite microporous membrane. The experiment was carried on the conditions: the draw ratio 1.5 times, calcination time 8min and heating rate 2℃/min.

From Figure 4, it can be seen that as the calcination temperature going up within 300~320℃, the porosity of composite microporous membrane gradually increases firstly, and reaches the maximum value at 320℃, then decreases. The reason is that the length of composite membrane sample is fixed, leading to a certain tensile force generating. With the crystal area gradually melting, the amorphous areas become larger, and then more and more macromolecular chains move toward the direction of internal stress eliminated, thus the micro-fibers shrinks. At the same time, the nodes connected with the micro-fibers are gradually undrawed by the tensile force. The bigger nodes decrease, and the small nodes tend to disappear, following that node size decreases and micro-fiber area increases, so the porosity increases. But when the temperature exceeds 320℃, the crystal areas tend to melt, leading to the macromolecular chain mobility increasing. The micro-fibers fuse with each other or ruptured by the large internal stress, resulting in the decrease of the pore size and the membrane porosity.

4. Conclusions

The effects of the dispersant PVA, the draw ratio, YSZ content and calcination temperature on the porosity of composite microporous membrane were systematically investigated using weight method. The main results are summarized as follows:

1) In this paper, YSZ/PTFE composite microporous membrane was prepared by mechanical tensile method, using PTFE resin emulsion as material and YSZ micro/nanoparticles as reinforcer. This method is simple, low cost and so on, having important theoretical significance and practical value.

2) The study analysed the effect of dispersant PVA on the porosity of composite microporous membrane. The result showes that the porosity of composite microporous membrane with dispersant PVA increaseses significantly.

3) The effects of technological sonditions on the porosity of composite microporous membrane were systematically studied. It is indicated that the porosity increases with the increase of YSZ content, but the composite microporous membrane become difficult to stretch when the YSZ content is over 20%; the porosity increases at first and then decreases with the calcination temperature going up, reaching its maximum value at 320℃; the porosities for the membranes doped with different YSZ contents are positive proportional to the draw ratio, and it reaches 73.09% with the draw ratio 3.5 times and YSZ content 8%.

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Table 1. Effect of dispersant on the porosity of composite microporous membrane

draw ratio(times)	without dispersant(%)	with dispersant PVA(%)
0.5	11.74	15.21
1	19.90	28.44
1.5	35.55	46.77

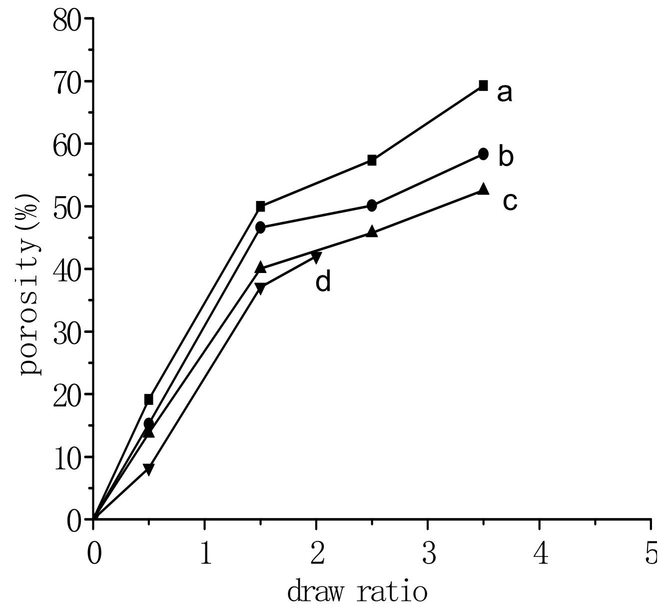

Figure 1. Effect of the draw ratio on the porosity of composite microporous membrane:
YSZ content (a) 8%, (b) 7%, (c) 5% and (d) pure PTFE membrane

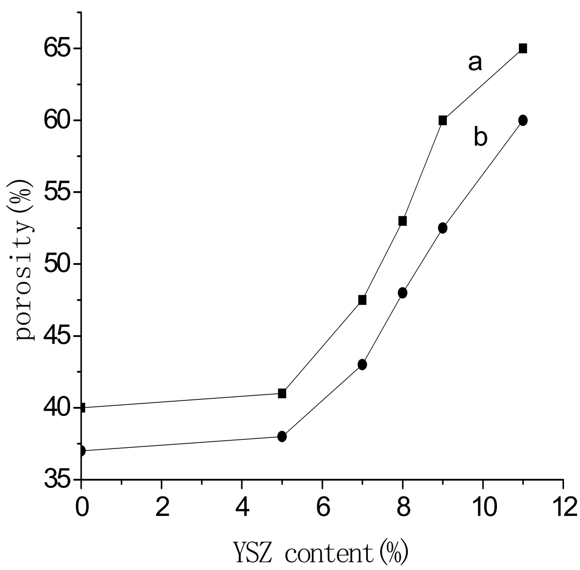

Figure 2. Effect of YSZ content on the microporous of composite microporous membrane:
The draw ratio (a) 2 times and (b) 1.5 times

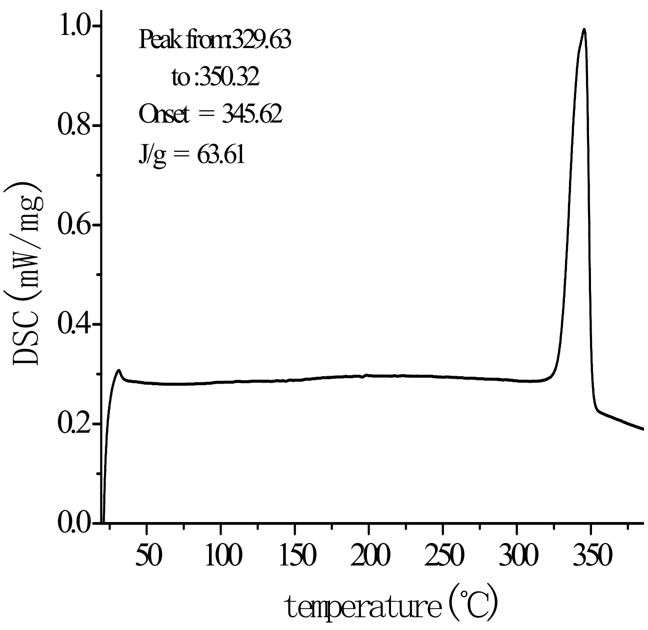

Figure 3. DSC curves of PTFE membrane

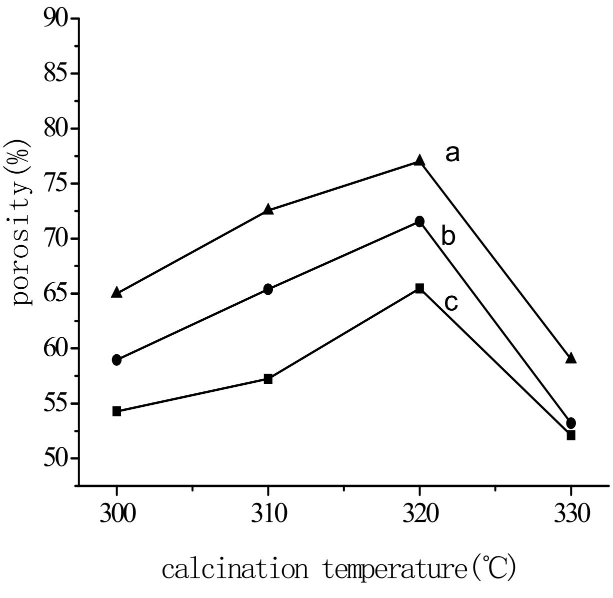

Figure 4. Effect of calcination temperature on the microporous of composite microporous membrane: YSZ content (a) 10%, (b) 7% and (c) 5%