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A novel process for preparing expanded Polytetrafluoroethylene(ePTFE) micro-porous membrane through ePTFE/ePTFE co-stretching technique

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Abstract Co-stretching processing technique was adopted in this paper for reducing ePTFE membrane pore size in hopes of bringing it the excellent retention property of very small particles. The ePTFE porous membrane were prepared from ePTFE powder through mechanical operations: extrusion, rolling, co-stretching of double-layer sheet in longitudinal direction, and transverse direction respectively and then thermosetting. The porous structures of ePTFE membrane were studied through SEM and Coulter Porometer. The results show that each layer of the double-layer ePTFE sheet can be joined together above 2.5 MPa stress at 210 °C, or 3.5MPa stress at above 190 °C in longitudinal stretching operation. The transition interface between the each layer in the base sheet (after longitudinal stretching operation) and in the membrane (after thermosetting operation) was formed, which contributes to the reduction in the pore size of ePTFE membrane.

Introduction

Polymeric porous membranes, such as Polyethylene (PE), cellulose, Polyacrylonitrile (PAN), Polystyrene(PP), Polyamide(PA), Polyester(PES) etc, have been widely used in engineering fields, in particular, in separation operations. The ePTFE porous membrane, with a microstructure of billions of interconnected continuous fibrils, has a clean non-shedding surface, chemical resistance, thermal stability. So, it plays an important role in liquid and air filtration applications. The ePTFE micro-filtration system features the membrane laminated to a support material, such as felt, woven, and spunbond nonwoven products for a wide range of conditions and applications.

Obviously, as a separation media, the porous structure of polymeric membrane have great effects on the separation efficiency and precision. It is well known that a variety of techniques have been adopted in the production of these membranes. One widely employed method of producing porous ePTFE membrane is a series of mechanical operations, viz. extrusion, rolling, stretching and thermosetting [1, 2]. Ken-ichi Kurumada [3] reported that the method of producing ePTFE porous membrane depends on mechanical transformation to yield the desired porous structure, which is realized via macroscopically controlled mechanical operations, not on heat treatment, because high heat treatment temperature can soften ePTFE leading to a smaller specific surface area with a less fine porous structure. So, some literatures [4–6] have been published on the effects of stretching conditions, including the temperature during stretching, stretching ratio and rate, on ePTFE porous structure. We found that the pore diameter can change in the range 0.3–5 micron through the aforementioned mechanical operations, and the membrane with micro-pores diameter under 0.3 micron cannot be produced [6].

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In this paper, a new method in regard to the reduction in the pore size of ePTFE membrane to bring it excellent retention property of very small particles, such as bacteria retention, through ePTFE/ePTFE co-stretching technique was put forward. The approach adopted is well-known industrial processes (shown in Fig. 1), but the remarkable difference is that the double-layer ePTFE sheet is longitudinally co-stretched in the oven. The attention has been focused mainly on the joining of the ePTFE layers of the double-layer sheet, and how the pore diameter is affected by stretching stress and temperature in the oven. The joining mechanism of the ePTFE layers was also discussed.

Experimental

The ePTFE powder produced by emulsion polymerization (CD123, Asahi Fluoropolymers Co.) was mixed with naphtha as a lubricant (20%), and then extruded into a rod of 13 mm in diameter by an extruder. Thereafter, this rod was rolled between two metal rollers to an ePTFE sheet with thickness of 120 micron. The double-layer sheet was longitudinally stretched by the rollers in the oven at a predetermined temperature, and at the same time, naphtha is removed, which is called ePTFE base sheet in this paper. Then, the ePTFE base sheet was transversely stretched. Finally, to keep dimensional stability, this membrane was heated in an oven at 360 °C (shown in Fig. 1).

The direction of the longitudinal stretching stress is indicated by the arrow, as shown in Fig. 1(3), and the stress is measured at point “A”. The temperature measured in the oven is considered as the longitudinal stretching temperature.

Characterizations

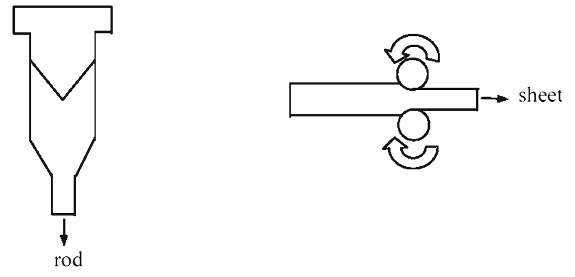
Observation of membrane morphological structure

The ePTFE base sheet and membrane were coated with metal of Au for SEM observation using the Amary-1845FE.

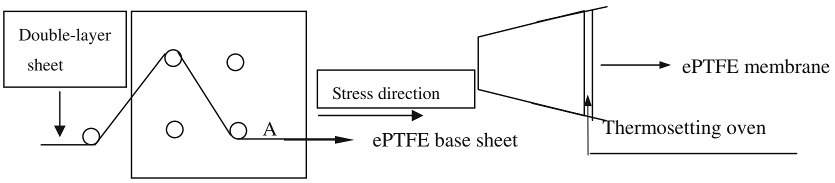
Measurement of pore diameter

Pore sizes were determined by liquid displacement techniques utilizing a Coulter Porometer and Coulter POROFILTM test liquid available from Coulter Electronics Limited, Luton, England, which has a very low surface tension, 40 mN/m. Air pressure is applied to one side of the sample. Eventually, as the air pressure is increased, the capillary attraction of the fluid in the largest pores is overcome, forcing the liquid out and allowing air to pass through the sample. With further increases in the air pressure, progressively smaller and smaller holes will clear. A flow versus pressure relationship for the wet sample can be established and compared to the results for the dry sample. The mean flow pore size is measured at the point where the curve representing 50% of the dry sample flow versus pressure intersects the curve representing wet sample flow versus pressure. The diameter of the pore which opens at that particular pressure (i.e., the mean flow pore size) can be determined from the following expression:

Fig. 1 Processing of co-stretching ePTFE porous membrane



(1) extrusion (2) rolling



(3) longitudinal stretching in oven (4) transverse stretching and thermosetting

$$2\pi r\gamma\cos\theta = \pi r2P$$

where r = radius of capillary(pore) γ = surface tension of liquid θ = contact angle P = hydrostatic pressure. For a fully wetted sample, this equation may be simplified to:

$$r = 2\gamma/P$$

Results and discussion

Effect of longitudinal stretching stress on pore size of co-stretching ePTFE membrane

The ePTFE membrane prepared by the aforementioned mechanical operations has two remarkable characters. One is the solid agglomerates of particles, called "nodes"; the other is a crack in which fine threads called "fibrils" are formed, bridging the two adjoining nodes. We found that the thread-like structures are not formed in ePTFE sheet by rolling operation, but basically formed in ePTFE base sheet by longitudinal stretching operation, and the fibrils and nodes are oriented in the direction of the stretching operation [6]. So, it could be guessed that the longitudinal stretching stress will largely affect the pore size of ePTFE membrane.

Under 210 °C, the double-layer ePTFE sheet was longitudinally stretched together in the oven. The dependence of the pore diameter of ePTFE membrane on the longitudinal stretching stress is shown in Fig. 2. Each layer of the double-layer ePTFE sheet cannot be joined with each other in the case of 1 MPa stretching stress, and the pore diameter of ePTFE membrane thus obtained, 0.29 micron, is similar to that of ePTFE membrane, 0.27 micron, by stretching only single layer with the same process conditions.

From Fig. 2, it can also be seen that the pore size of ePTFE membrane decreases with an increase of longitudinal stretching stress up to 3.5 MPa, and abruptly increases at the stress beyond 3.5 MPa. At the same time, the longitudinal stretching ratio increases from 210% under 1–3.5 MPa to 320% under 4 MPa stretching stress. When the stretching stress is 4 MPa, the longitudinal stretching ratio cannot be controlled to 210% wonderfully through adjusting the experimental equipment. In this case, the fibrils will be elongated, and pore size of ePTFE membrane increases.

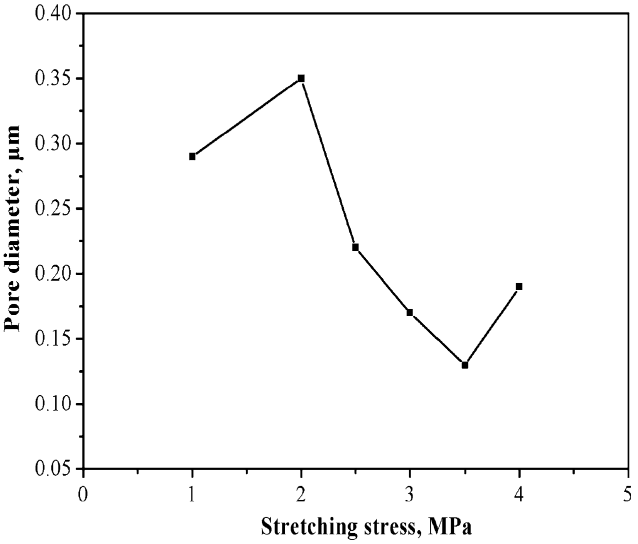


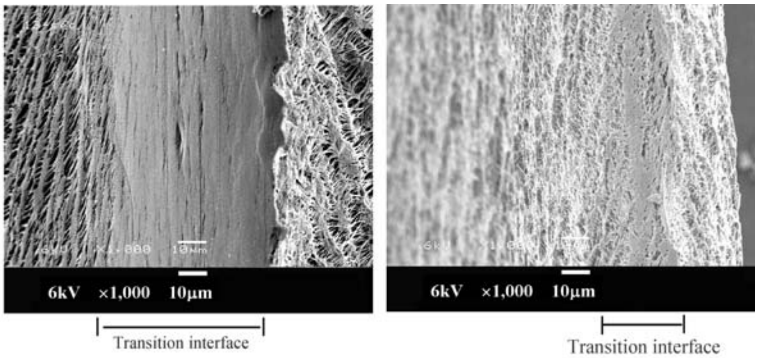
Fig. 2 Pore diameter of co-stretching ePTFE membrane versus longitudinal stretching stress (Stretching temperature: 210 °C; longitudinal stretching ratio: 210% with 1–3.5 MPa stress and 320% with 4 MPa stress)

Within the range of 2–4 MPa stretching stress, we found that the layers of the double-layer sheet can be tightly joined together, which can be judged from Fig. 3, the SEM of the base sheet and the membrane of double-layer ePTFE prepared with 3.5 MPa longitudinal stretching stress and 210 °C temperature. From the figure, the transition interface in the base sheet and membrane could be seen. The fibril length of the transition interface in ePTFE membrane is remarkable smaller than that in other parts, and the density of nodes are larger than that in other parts, which are the causes that the pore size of membrane decrease by means of co-stretching the ePTFE/ePTFE sheet.

Effect of longitudinal stretching temperature on pore diameter of co-stretching ePTFE membrane

During the longitudinal stretching operation, with the constant stretching stress of 3.5 MPa, temperature has remarkable effect on pore diameter of ePTFE membrane, as shown in Fig. 4. Within the range of 170–190 °C temperature, the two layers of the double-layer sheet cannot be joined together, but the pore size of the membrane drops with an increase of stretching temperature. From Fig. 5, it can be seen that some cracks were formed on the base sheet owning to stretching at lower temperature, and the cracks size decreases with an enlarged stretching

Fig. 3 The SEM of ePTFE/ ePTFE (cross section) (Longitudinal stretching stress: 3.5 MPa, temperature: 210 °C)



(1)base sheet(after longitudinal stretching) (2)membrane(after thermosetting)

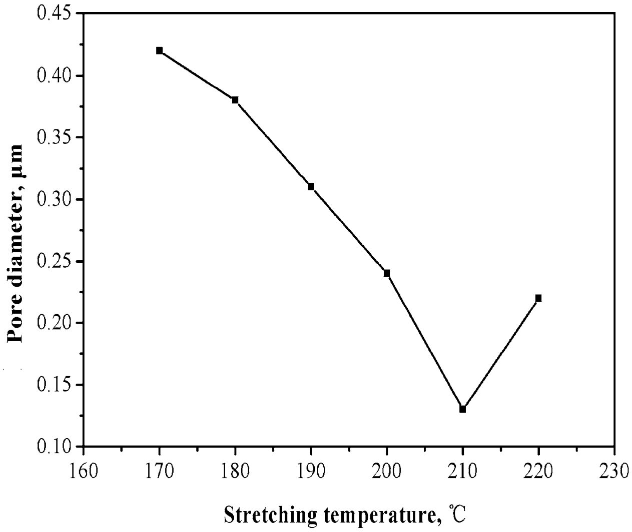


Fig. 4 Pore diameter of co-stretching ePTFE membrane versus longitudinal stretching temperature (Longitudinal stretching stress: 3.5 MPa; longitudinal stretching ratio: 210% at 170–210 °C and 280% at 220 °C)

temperature. Enlargement of cracks size will increase the pore size of ePTFE membrane, which contributes to the result that the pore size of the membrane drops with an increase of stretching temperature within the range of 170–190 °C.

In experiment, we found the two layers of the double-layer sheet can be joined at the stretching temperature above 190 °C. From Fig. 4, it could be seen that the pore size of the ePTFE membrane is reduced with an increase of stretching temperature, and reach a minimum up to 210 °C.

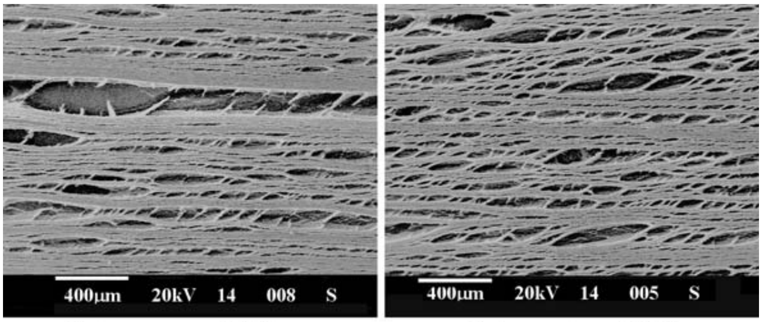
Above 220 °C, the pore size enlarges due to two factors: (1) the fibrils can be easily broken down above 220° C; (2) at the temperature of 170–210 °C, the longitudinal stretching ratio of sheet can be adjusted to 210%. While, above 220 °C, the ePTFE sheet is so soft that the longitudinal stretching ratio, 280%, cannot be controlled to 210% by adjusting the experimental equipment. So, the fibrils will be largely elongated and the pore size will be increased.

Joining mechanism of ePTFE layers

Commonly there are two means for PTFE joining: One is the thermo-pressure way under shearing stress at the temperature near to melting point of PTFE, about 327 °C; The other is the heating way by using PFA (copolymer of tetrafluoroethylene and fluoropropyl ethylene ether) rod as a welding material.

The ePTFE particles for porous membrane are made by emulsion polymerization, whose primary particle diameters is 0.2–0.3 micron, and after

Fig. 5 The SEM of ePTFE base sheet (after longitudinal stretching)



(1) temperature: 170℃ (2) temperature: 180℃

agglomerating, the superior particle size increases up to about 500 micron. With a certain shearing stress, the particles will form porous membranes having a highly ordered periodicity characterized by nodes and fibrils. For the ePTFE sheets mixed with lubricant, we found that the two layers of the double-layer sheet can be joined with above 2.5 MPa at 210 °C, or 3.5 MPa at above 190 °C. The temperature is remarkable below the melting point of PTFE resin. In the longitudinal stretching operation, the nodes and fibrils are basically formed, meanwhile fibrils intertangle and nodes interblend under shearing stress at lower temperature. So, the two ePTFE layers will be joined together. For PTFE joining, PTFE must melt beforehand, whereas ePTFE could be joined at lower temperature due to the combined effects of heat, stress, special structure of the emulsion polymerized ePTFE particles and the stretching operation, which has never been reported.

Conclusion

The pore size of ePTFE membrane could be reduced by means of a series of mechanical operation: extrusion, rolling, co-stretching of double-layer sheet in longitudinal direction, stretching in transverse direction and thermosetting. In longitudinal stretching operation, the temperature and stress have greatly influence on the joining property of the two ePTFE layers, which in turn affects the pore diameters of the ePTFE membrane. The two layers of the double-layer ePTFE sheet can be joined together above 2.5 MPa at 210 °C, or 3.5 MPa stretching stress at above 190 °C. The transition interface in the base sheet and membrane has been formed, which leads to the decrease of the pore diameters of ePTFE membrane. The reasons for jointing of ePTFE layers are fibrils intertangling and nodes interblending under heat and stretching stress.

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