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Preparation and Performance Characteristics of Resin-filled EVAL Hollow Fiber Membrane

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Abstract

Take the ethylene-vinyl alcohol (EVAL) copolymer as the infrastructural material, the anion exchange resin D301R as the functional grains, adopt dry-wet method to make resin-filled EVAL hollow fiber membrane, test the pure water flux of the membrane, the rejection rate of the bovine serum albumin (BSA) and the static absorption performance of BSA. Check the influences of coagulation bath temperature and copolymer mass fraction to pure water flux and rejection rate. The experimental results indicate that the mass fraction of EVAL is 18%, the mass fraction of resin is 24%, and when the temperature of coagulation bath is in 40~50°C , the prepared resin-filled EVAL hollow fiber membrane has good mechanical intensity, high pure water flux, better BSA adsorption performance that the adsorption capacitance can achieve 25.04mgBSA/g membrane.

Keywords: EVAL, Hydrophilia, Ion exchange resin, Hollow fiber membrane

1. Introduction

As the hydrophilic membrane material, EVAL has its special advantages. EVAL is the crystal atactic polymer composed by hydrophilic vinyl alcohol unit and hydrophobic ethylene unit, which polymer chain has certain proportional hydroxide radical, so it has certain hydrophilia, and the experiment of contact angle (Matsuyama H, 2001, p.2583-2589 & Young T H, 1998, p.717-724) also invalidates EVAL is the hydrophilic material, and this sort of material is not easy to be polluted when the albumens are separating, and CH_2 unit endow it better mechanical intensity (T. Okaya, 1992), and it possesses good bio-compatibility and chemical stability, so it is fit for being infrastructural materials. As the filled grains, the ion exchange resin has certain adsorption capability to protein. This experiment takes EVAL as the infrastructural material, ion exchange resin as filled grains to spin hollow fiber membrane, and the prepared resin filled EVAL hollow fiber membrane albumen has large adsorption capacitance, combining the characteristics of large exterior area of hollow fiber membrane and hydrophilia of EVAL, which is not easy to be polluted.

M.E. Avramescu et al (M.E. Avramescu, 2003, No.218. p.219-233 & M.E. Avramescu, 2003, p.177-193 & M.E. Avramescu, 2002, p.155-173.) prepared resin-filled EVAL flat membrane adsorbent which had good adsorption capacitance and higher desorption rate for BSA, and changed the nature of the membrane for the affinity separation of protein. Zhang, Yuzhong et al adopted controlled phase separation method to prepare resin-filled EVAL fiber adsorbent which had good albumen adsorption capacitance and higher desorption rate, and formed coarse opening structure on the surface and with the increase of filling of resin, the coarseness degree and opening degree on the fiber surface was increased (Zhang, 2005, p.224-232).

This work takes EVAL as the infrastructural material, alkalescence anion exchange resin D301R as the functional grains and adopts dry-wet method to prepare resin-filled EVAL hollow fiber membrane and described its performances.

2. Experiment

2.1 Raw materials

The infrastructural material is EVAL with 44% of ethylene content, and is made by Japan Kuraray Co., Ltd.

The filled grain is alkalescence anion exchange resin D301R made by Tianjin Nankai University Chemical Plant.

The solvent is DMSO made by Tianjin BODI Chemical Co., Ltd.

The additive is CP made by Tianjin Kermel Chemical Reagent Co., Ltd.

The model material is BSA made by China United Stars Industry Co., Ltd.

2.2 Experimental apparatus

(1) The spinning machine of chemical fiber made by Tianjin Motimo Membrane Eng. & Tech. Co., Ltd.

(2) The QUANTA 200 scanning electron microscope made by Holland FEI Company.

(3) The UV2450 ultraviolet and visible spectrophotometer made by SHIMADZU Company.

(4) HZQ-C air bath agitator made by Harbin Donglian Electronic & Technology Development Co., Ltd.

2.3 Preparation of resin-filled EVAL hollow fiber membrane

2.3.1 Preparation of micron-sized ion exchange resin

Because the granularity of the resin grain made by the factory is too large and the obtained filature liquid is not stable and easy to deposit and has only small adsorption capacitance, so we need to perform subsequent machining.

(1) Drying

The water content of the resin just out of the factory is higher, so we need to dry it and then crush it. Put the resin in the vacuum oven to dry it at 80°C until its weight doesn't change.

(2) Crushing

We can adopt rubbing crushing method to obtain the micron-sized ion exchange resin.

2.3.2 Preparation of resin-filled EVAL hollow fiber membrane

To make resins evenly distribute in the filature liquid, with mixing around by the magnetic force, first put solvent, polymer and additive into three flasks, increase the temperature to about 60°C and continue to mix until dissolved, then put in resin several times and mix to stable filature liquid, and put in filature jar to be marinated for 24 hours. The prepared process to adopt dry-wet method to prepare resin-filled EVAL hollow fiber membrane is seen in Figure 1. The filature liquid is extruded from the tube spinneret, and the interior pore is filled with core liquid to make fiber form hollow. The thin flow of filature liquid directly enters into the coagulation bath through certain altitudinal air clearance and separation happens. The prepared fiber wipes off additive and solvent through bath, and is marinated in the 30% glycerite for 48 hours, and then is aired and stored.

2.4 Performance characteristics

2.4.1 Mensuration of pure water flux

We use the ultrafilter evaluation device made by Tianjin Motimo Membrane Eng. & Tech. Co., Ltd. to mensurate the pure water flux. Adjust the pressure to 0.1MPa, maintain the temperature at 25°C , and mensurate the membrane flux when the system is stable. Take the average through tests of several times, and compute the water flux according the following formula.

$$Q = \frac{V}{At}$$

Where, Q represents the water flux (L/m^2.h), V represents the volume of the filtered liquid (L), A represents the effective area of the membrane (m^2) and t represents the testing times (s).

2.4.2 Mensuration of rejection rate

Choose BSA which molecular weight is 67 thousands to dissolve in the cushion liquid which pH value is 7.4, confect 0.1% solution, maintain the solution temperature at the lower temperature, filtrate this solution by the prepared EVAL membrane small sample, take the original liquid and the corresponding filtered liquid, then measure the absorbencies of the original liquid and the filtered liquid by the UV2450 ultraviolet spectrometer. The computation formula of rejection ratio is

$$R = \frac{E_o - E_S}{E_o} \times 100\% .$$

Where, R represents the rejection ratio, E_o represents the absorbency of the original liquor and E_s represents the absorbency of the sieved liquor.

2.4.3 Observation of membrane structure

We observe the membrane structure using QUANTA200 scanning electron microscope. Break the membrane in the liquid nitrogen, fix the sample in the clamp and dry it in the vacuum and at room temperature, then deposit a thin layer of gold on the surface in the vacuum, then we can observe the membranes section structure.

2.4.4 Static adsorption capacitance of protein

The protein static adsorption capacitance of resin-filled EVAL hollow fiber membrane can be confirmed by the BSA interim adsorption experiment. The sorbent sample which we have know its quantity is marinated in the BSA cushion solution until it balances (in this experiment, we adopt 24 hours), and we compute the static adsorption capacitance of resin-filled EVAL hollow fiber membrane to the protein through measuring the changes of BSA concentration. In the adsorption experiment, the pH values of the cushion solution we use are 7.4 and 9.1, and the material liquid protein BSA concentration is 1mg/ml. The protein static adsorption capacitance of resin-filled EVAL hollow fiber membrane (Q) can be computed by this formula.

$Q = (C_0 - C) V / W$

Where, Q represents protein static adsorption capacitance (mgBSA/g membrane), C_0 represents the initial concentration of material liquid protein BSA (mg/ml), C represents the concentration when the material liquid protein BSA has implemented adsorption for 24 hours (mg/ml), V represents the volume of the material liquid (ml), and W represents the weight of the membrane sample (g).

3. Results and discussions

3.1 Structure analysis of resin-filled EVAL hollow fiber membrane

Figure 2 is the SEM photo of the resin-filled EVAL hollow fiber membrane structure. From the exterior in Figure 2, we can see that there are micropore-structures in the exterior which can make BSA contact with resin through micropore. From the section in Figure 2, we can see the resin enwrapped by the polymer, and when the BSA material liquid fills EVAL hollow fiber membrane through resin, it contacts the resin and achieves the function of adsorption. From the interior in Figure 2, we can see many protuberances, because in the membrane forming process, due to high speed separation, resins are assembled to the interior in the exchange process of solution and water, many protuberances and stains are formed.

3.2 Influence of coagulation bath temperature to the performance of resin-filled EVAL hollow fiber membrane

Fix the mass fractions of resin and the EVAL, control the temperature of coagulation bate is in 20~60°C , we will check the influences of coagulation bath temperature to the pure water flux and rejection rate.

The temperature of coagulation bath is an important factor to influence the membrane structure and performance. From Figure 3, we can see that with the gradual increase of coagulation bath temperature, the pure water flux of resin-filled EVAL hollow fiber membrane gradually increases, and the rejection rate gradually reduces. After the thin flow of filature enters into the coagulation bath, the solvent in the casting membrane liquid begins transferring to the coagulation bath, which makes the concentration of the polymer in the casting membrane liquid gradually increase, and polymers begins to assemble each other, so the membrane is finally formed (Gao, 1989). When the temperature of coagulation bath increases, the exchange speed between solvent and nonsolvent quickens and first the compact layer rapidly forms, and coagulation bath quickly immerges in the interior of the membrane, and the mixing speed of the dense and rare phases in the membrane interior becomes quick, which makes the membrane interior form more big cavums, accordingly make water flux continually increase and the rejection rate gradually reduce. Too high or low temperature of coagulation bath temperature is not propitious to the molding of the membrane, and when the temperature is too high, the exchange speed of solvent and nonsolvent is quick and the membrane is easy to induce stains, and when the temperature is too low, the formed membrane is dense, which induces the flux is very low. This experiment selects the temperature of 40~50°C as the best coagulation bath temperature.

3.3 Influence of EVAL mass fraction to the performance of resin-filled EVAL hollow fiber membrane

Take DMSO and CP respectively as the solvent and the additive, fix the mass fraction of the resin D301R in 16%, increase the mass fraction of EVAL to 13%~19%, we will check the influences of EVAL mass fraction to the pure water flux and rejection rate.

As seen in Figure 4, when the concentration of EVAL increases from 13% to 19%, the pure water flux of resin-filled EVAL hollow fiber membrane will reduce with it and the rejection rate will increase with it. When the mass fraction of EVAL is in 13%~19%, with the increase of EVAL mass fraction, the performance of forming membrane gradually becomes better. With the increase of polymer concentration in the filature liquid, the voluble degree among macromolecule chains increases, but the polymer poor phases which can form membrane exterior pores and channels relatively reduce, so with the increase of polymer concentration, the pure water flux of the membrane reduces and the rejection rate increases. But when the content of high polymer EVAL is lower, the agglutinate degree of the filature liquid is lower, which makes the spun hollow fiber configuration is difficult to be controlled and has lower intensity. Therefore, synthetically considering two factors including pure water flux and hollow fiber membrane intensity, this experiment take the best concentration 18% as the emphasis to study.

3.4 Influence of resin mass fraction to the performance of resin-filled EVAL hollow fiber membrane

3.4.1 Influence to BSA rejection rate

When the pH value of BSA solution is 7.4, the rejection performance of resin-filled EVAL hollow fiber membrane is best, so we only study the rejection rate of the membrane when the pH value is 7.4.

Table 1 shows the rejection data of the resin-filled EVAL hollow fiber membrane with different resin-filled quantities. As viewed from the data, when the mass fraction of the polymer is fixed, with the increase of resin mass fraction, the rejection rate of hollow fiber membrane increases, the resin content increases, the adsorption ability to the albumen also increases, the albumen concentration in filtered liquid reduces, the rejection rate increases. But as viewed from the integration, the rejection rate is very low, and when pH value is 7.4, the fiber mainly depends on the aperture to reject the BSA molecules, which causes maybe is that the aperture of the hollow fiber membrane is too big, or the membrane has stains, which will induce lower rejection rate.

3.4.2 Influence to BSA static adsorption capacitance

One important function of the resin mass fraction to resin-filled EVAL hollow fiber membrane is that it fair influences the adsorption capacitance of the protein. This experiment chooses the cushion liquids which pH value are respectively 7.4 and 9.1.

Fix the 18% of mass fraction of EVAL polymer, increase the mass fraction of resin D301R, from Figure 6 we can see that with the increase of resin mass fraction, the adsorption capacitance of BSA will increase. When filling the resin grains to the membrane, because of the increase of adsorption function radicel in the membrane radicel, the static adsorption capacitance of membrane to BSA will be enhanced. Combining Figure 5, we can see that with the increase of resin mass fraction, the adsorption spots will increase, and the adsorption capacitance to BSA will also increase.

3.4.3 Influence to structure

From Figure 7, we can see that with the increase of resin mass fraction, the resin grains obviously increase on the section of resin-filled EVAL hollow fiber membrane, and exterior and interior gradually become uneven because of the resin grains existed in the high polymer. When the resin content is lower, the resin grains in EVAL present single individuals which are distributed evenly and enclosed by polymers and in the forming process of the membrane, the high polymers begin separation, the disturbed function of the resin grains is not obvious, and when the resin content further increases, the disturbed function of the resin grains increase, and the stains on the interior of the hollow fiber membrane also increase with it. When the resin content is low, the high polymer EVAL in the resin-filled EVAL hollow fiber membrane has less structure deficiencies. With the increase of resin content, though the distribution of the solid grains inclines to even, but the whole structure inclines to loosening, and the deficiencies such as the microcracks and hollow pores become more.

4. Conclusions

(1) This experiment adopts the dry-wet method to prepare resin-filled EVAL hollow fiber membrane, and the prepared hollow fiber membrane has higher pure water flux and good BSA static adsorption capacitance.

(2) The pure water flux increases with the increase of coagulation bath temperature and reduces with the increase of EVAL content of the polymer, and when the temperature of the coagulation bath is in 40~50°C and the mass fraction of the polymer is 18%, the every sort of performance of the resin-filled EVAL hollow fiber membrane is excellent.

(3) With the increase of mass fraction of the ion exchange resin, the static adsorption capacitance of BSA increases, and when the resin mass fraction is 24% the adsorption performance and mechanical intensity are good.

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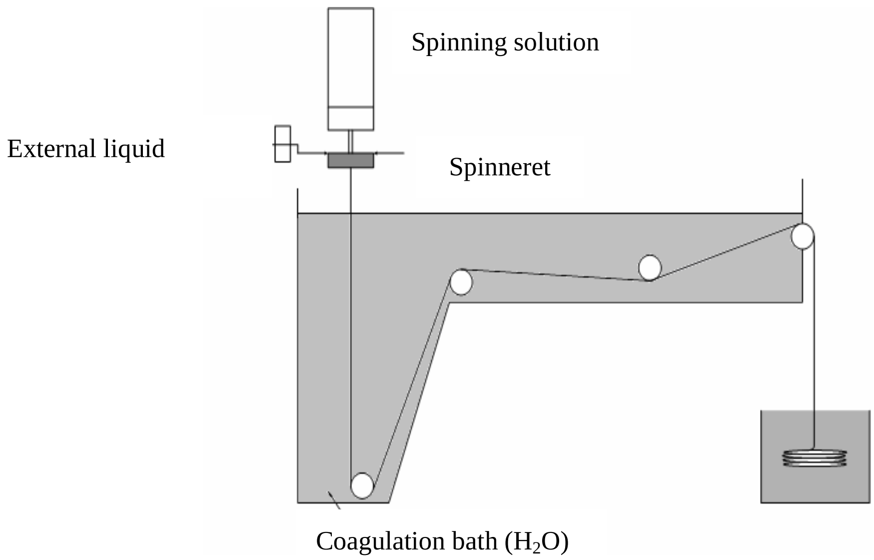
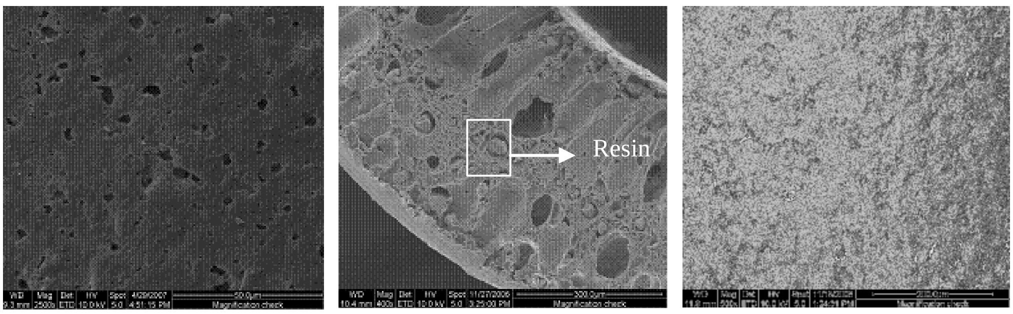


Figure 1. Preparation Equipment of Resin-filled EVAL Hollow Fiber Membrane by Dry-wet Method



Exterior Section Interior

Figure 2. SEM Photo of Resin-filled EVAL Hollow Fiber Membrane Configuration

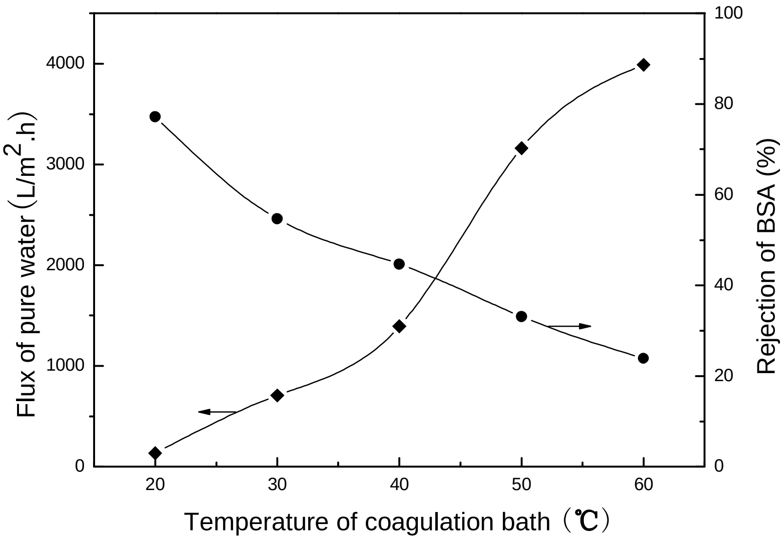


Figure 3. Influence of Coagulation Bath to Pure Water Flux and BSA Rejection Rate

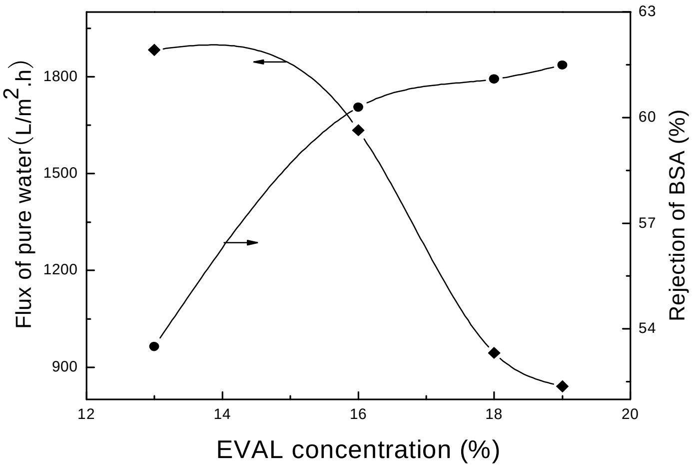
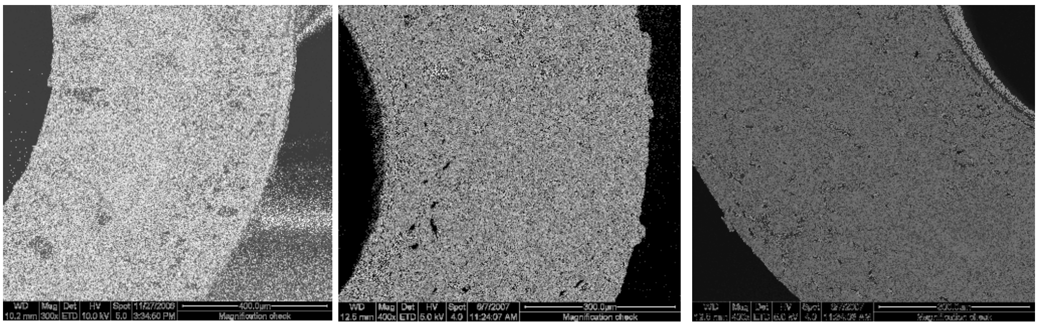


Figure 4. Influence of EVAL Mass Fraction to Pure Water Flux and BSA Rejection Rate



Resin content 10% Resin content 15% Resin content 24%

Figure 5. Section SEM Photo of Resin-filled EVAL Hollow Fiber Membrane with Different Mass Fractions

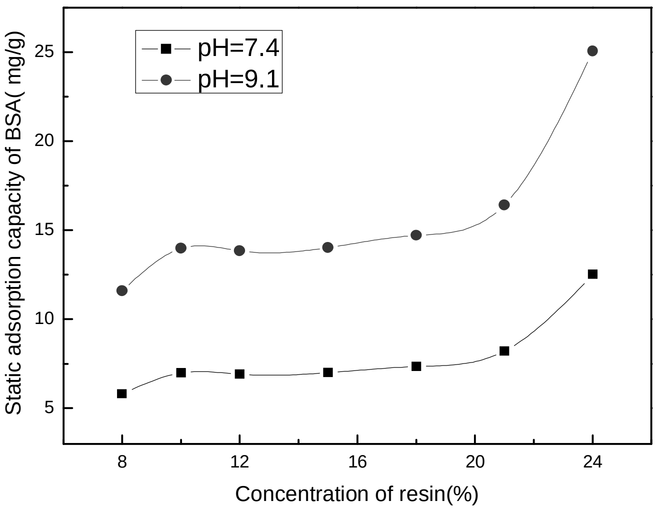


Figure 6. Influence of Resin Mass Fraction to BSA Static Adsorption Capacitance

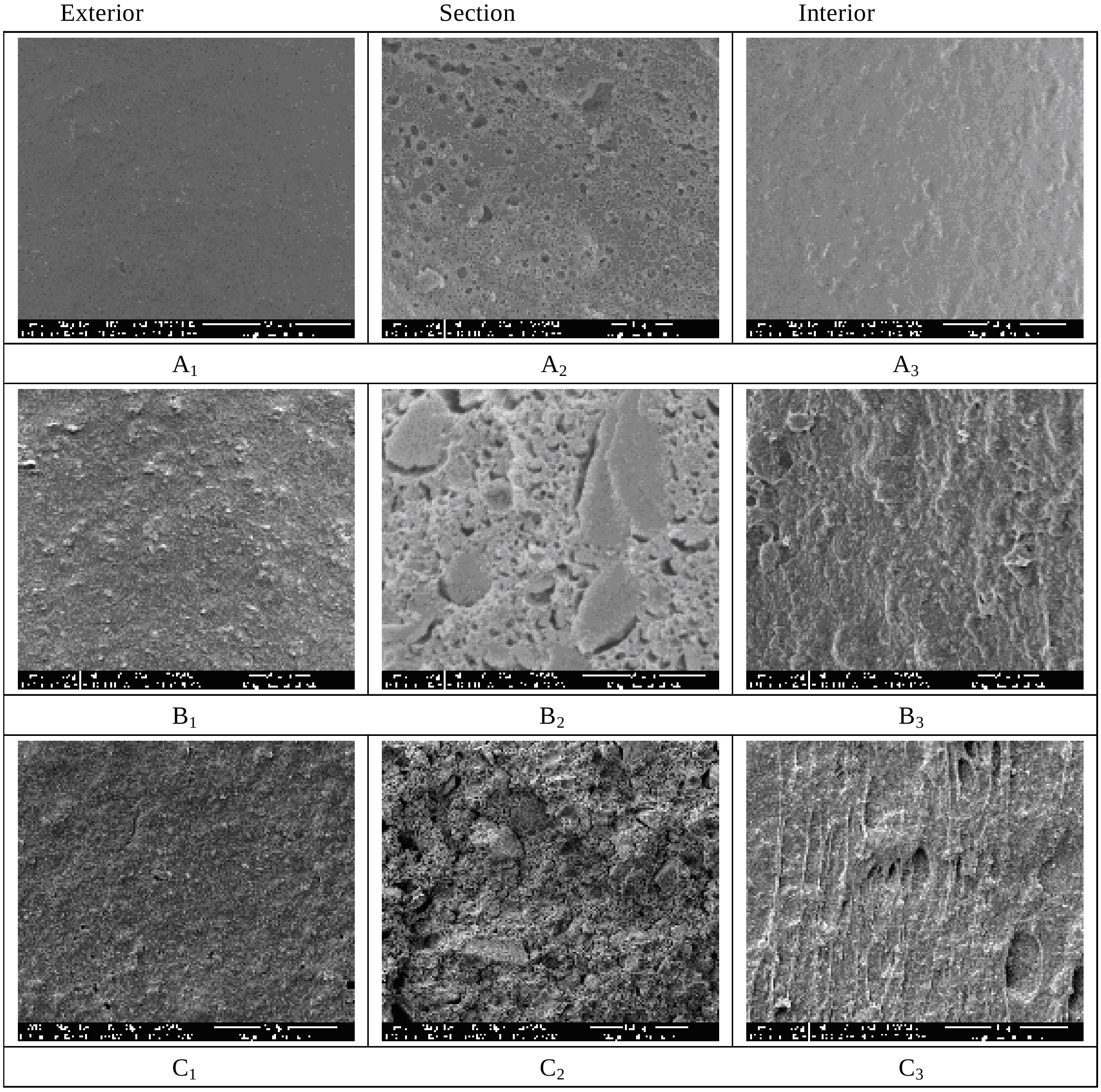


Figure 7. SEM Photo of Resin-filled EVAL Hollow Fiber Membrane with Different Mass Fractions (Mass fraction of EVAL is 18%. In $A_1 \sim A_3$, the mass fraction of resin is 10%. In $B_1 \sim B_3$, the mass fraction of resin is 18%. In $C_1 \sim C_3$, the mass fraction of resin is 24%.)

Table 1. Rejection performance of resin-filled EVAL hollow fiber membrane with different resin mass fractions

D301R/EVAL	10/18	12/18	15/18	18/18	21/18
Rejection Rate (%)	5.6	13	18	43	55