

Preparation and Characterization of Poly(vinyl chloride)-graft-Acrylic Acid Membrane by Electron Beam

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ABSTRACT: Poly(vinyl chloride) (PVC) was irradiated by electron beam in vacuum at 20 KGy to produce living free radicals, and then reacted with acrylic acid (AA) in solution to obtain the PVC-g-AA copolymers. The copolymers were characterized by Fourier transform infrared spectroscopy. Porous membranes were prepared from copolymers by the phase inversion technique. The morphology of PVC-g-AA membranes was studied by field emission scanning electron microscopy. The mean pore size and pore size distribution were determined by a mercury porosimeter. The mean pore

size was 0.19 μm , and the bulk porosity was 56.02%. The apparent static water contact angle was 89.0°. The water drop penetration rate was 2.35 times to the original membrane. The maximum stress was 4.10 MPa. Filtration experiments were carried out to evaluate the fouling resistance of the PVC-g-AA membrane. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 291–296, 2007

Key words: irradiation; poly(vinyl chloride) (PVC); hydrophilic polymers; membranes

INTRODUCTION

PVC has been widely applied in membrane separation as one of the most abundant synthetic polymers. PVC ultrafiltration membrane with the characteristic skinned structure can be prepared by the phase inversion technique.¹ However, the application of PVC membrane is limited to some extent due to the hydrophobic nature. Protein fouling occurs easily both on the membrane surface and within the pores during the filtration process especially in protein-containing solutions, thus decreasing the permeate flux. Hydrophilic PVC membranes modified by chemical or physical method have been studied. Among these modification methods, grafting is a versatile method in which monomers are covalently bonded onto the polymer chain.² A common grafting approach with γ -ray, plasma, ultraviolet, or electron beam irradiation has been used to bind hydrophilic monomers to the surface of hydrophobic polymers with the aim to improve the surface characteristics, such as wettability, adhesion, adsorption, printability, chemical reactivity, and biocompatibility.^{3–9} For example, F.Vigo improved the surface characteristics of asymmetric PVC ultrafiltration membranes by high frequency discharge and glow discharge treatment.^{10,11} A photochemical method was also often adopted for surface modification of PVC, for example, *O*-butyrylchitosan, *N*-vinyl-2-pyrrolidone, or glycidyl methacrylate are grafted onto the

porous surface of PVC membrane to improve blood compatibility, surface wettability, or immobilize heparin, respectively, by the UV-irradiation.^{12–14} However, surface modification often fails to modify the membrane pores. The long grafted chains laid over the membrane surface may change the pore size and pore size distribution, leading to reduced permeability.

Unlike the chemical initiation process, radiation-grafting method is free from catalyst or additives contamination, and the initiation process is also temperature independent.¹⁵ The preirradiation and peroxy/hydroperoxy methods are convenient in such a way that the polymer substrate can be irradiated and stored for some time before grafting. Both methods have a less problem of homopolymer formation than simultaneous method, since the monomers are not directly exposed to the radiation.¹⁶ The irradiation grafting seems to depend on the chemical composition, the crystalline structure of the polymer, and the irradiation method. The stable radicals of irradiated PVC mainly occur in PVC main chain from cleavage of carbon–chlorine bonds. Allyl and polyenyl free radicals are usually converted into peroxy or hydroperoxy radicals in air,¹⁷ whereas these radicals will decompose again when heated.

In present article, the aim is to obtain a hydrophilic and fouling resistance PVC membrane. The bulk-modified PVC powders were synthesized from grafting copolymerization of PVC and AA, then hydrophilic PVC porous membrane was prepared through phase inversion method. The graft copolymers are promising to prepare porous hydrophilic membranes with well-defined pore sizes and fouling resistance.

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EXPERIMENTAL

Materials

PVC powders ($M_n = 187,500$) were purchased from HangZhou SanXin chemical. Acrylic acid was purified before use. Albumin, bovine serum (BSA, BP0081) was purchased from Sino-American Biotechnology. *N,N*-Dimethylacetamide (DMAc) was obtained from ShangHai 3S.

Grafting polymerization of PVC with AA by electron beam irradiation

PVC powders were preirradiated at room temperature in vacuum using a 2.0 MeV GJ-2 dynamitron electron beam accelerator. The adsorbed dose was 20 kGy and the beam current was 5 mA. Five grams of irradiated PVC was reacted with 0.2M acrylic acid monomer in a flask under stirring. The flask was evacuated at 50°C. After the desired grafting time, the reaction solution was cleaned with excess ethanol and subsequently with deionized water for 24 h at 50°C to remove the residual homopolymers. Then the copolymers were filtrated and dried at 50°C under vacuum. The bulk degree of grafting of the copolymer determined by the weight increase of PVC was 5.2% in this experiment.

Preparation of porous membranes

Asymmetric porous membranes were prepared via the phase inversion method from a casting solution (PVC/CH₃OH/DMAc = 10/5/85, PVC-g-AA/CH₃OH/DMAc = 10/5/85). The solution cast by a pipette onto a glass plate was immediately immersed in deionized water at 25°C. Wet membranes were directly used for filtration experiments. Some membranes were dried in vacuum at 60°C for 24 h for further characterization.

Characterization of porous membranes

FTIR spectra of the PVC or PVC-g-AA were obtained from a BRUKER VECTOR 22 spectrophotometer in a transmission mode. Field emission scanning electron microscopy was obtained using a SIRION-100 (America FEI) electron microscope. Static and dynamic water contact angles of the membranes were measured at 25°C using a contact angle measuring device (OCA20, Germany Dataphysics). One microliter of deionized water was dropped onto the membrane upper surface, which has smaller pore size and decides the separation performance. The mean pore size, bulk porosity, and the pore size distribution were measured with a mercury porosimeter (Auto-Pore IV 9500, micromeritics). The mechanical properties were determined using a tensile tester (Shimadzu

AG-1) using a stretching rate in 10 mm/min at room temperature.

Filtration experiments

Water flux experiments were performed in a 25-mm diameter dead-end ultrafiltration apparatus lab-self made, similar to the one described previously.¹⁸ The experimental protocol was as follows: For the first 30 min, the membrane was precompact at 0.15 MPa. Then the pure water flux (J_0) was recorded at 0.1 MPa every 5 min. After the pure water flux measurements, the deionized water was exchanged with a 0.1 g/L BSA solution in PBS (0.01M, pH = 7.4) for the fouling test performed at 0.1 MPa.

RESULTS AND DISCUSSION

Irradiation grafting of PVC with acrylic acid: PVC-g-AA copolymers

PVC powders will become deep brown under high dose. It is because the high dose may induce the main chain cleavage or the dehydrochlorination to form unsaturated double bond structure. So PVC was preirradiated in a low dose 20 kGy in this experiment. When the grafting time is longer, the AA homopolymerization will become severe. Especially when the temperature is above 50°C, the viscosity of the reaction solution increases obviously. This phenomenon can be explained by the fact that there is a homopolymerization reaction in the grafting systems. The homopolymerizations of AA increase the solution viscosity and hinder the monomers diffusing into free radicals in PVC. In addition, the improvement of PVC macromolecular chain segments movement ability at high temperature accelerates the mutual recombination between primary radicals and growing chain radicals. The trapped radicals have shorter lifetime and vanish more rapidly, and the growing chains terminate faster leading to shorter grafted chains. When the AA concentration was above 0.2M, according to the monomer diffusion-controlled mechanism, homopolymerization will increase the viscosity of the reaction solution and limit monomers mobility, thus it retards the degree of grafting. So a grafting time of 5 h at 50°C was sufficient to ensure the grafting reaction and avoid the homopolymerization of AA. And no gelation was observed during the whole reaction process.

FTIR spectra analysis of PVC-g-AA copolymers

The IR spectrum of the original PVC in Figure 1(a) shows the characteristic absorption bands 2911, 1426, 1330 and 1251, 1098, 690 cm⁻¹ is assigned to the —CH₂ stretching vibration, —CH₂ deformation

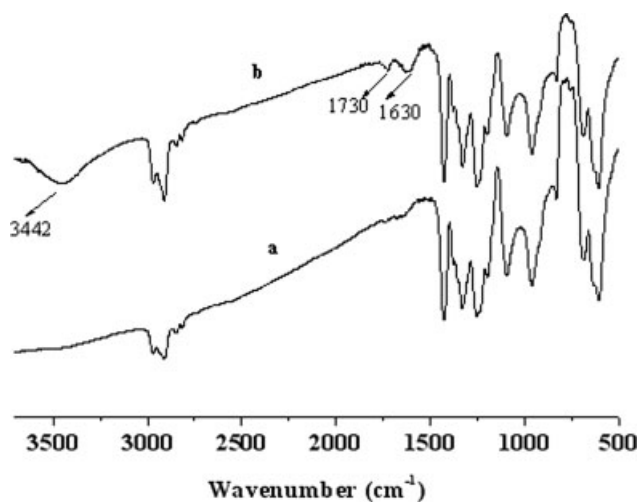


Figure 1 FTIR spectra of (a) original PVC (b) PVC-g-AA.

vibration, C—H bending vibration, C—C vibration, C—Cl vibration separately.¹⁹ A characteristic band at 1730 cm^{-1} in Figure 1(b) is assigned to the carbonyl

stretching vibration (O—C=O groups) associated with the grafted AA chains. The band at 3442 cm^{-1} supports the appearance of —OH. The AA homopolymers were excluded by excess ethanol cleaning (a good solvent for the AA homopolymers). So the FTIR spectra changes confirm the successful grafting of AA onto PVC powders. The unsaturation double bond may be produced during the irradiation process and it can be verified from the emergence of the band at 1630 cm^{-1} .

SEM morphologies of the porous membranes prepared from the PVC-g-AA copolymers

Figure 2 shows the surface and cross section SEM morphologies for the original and grafted PVC membrane. Both the membranes have the similar pore structures because of the similar chemical composition. Both surfaces have a homogeneous morphology and a uniform pore size distribution. No obvious surface changes can be seen in the grafted PVC mem-

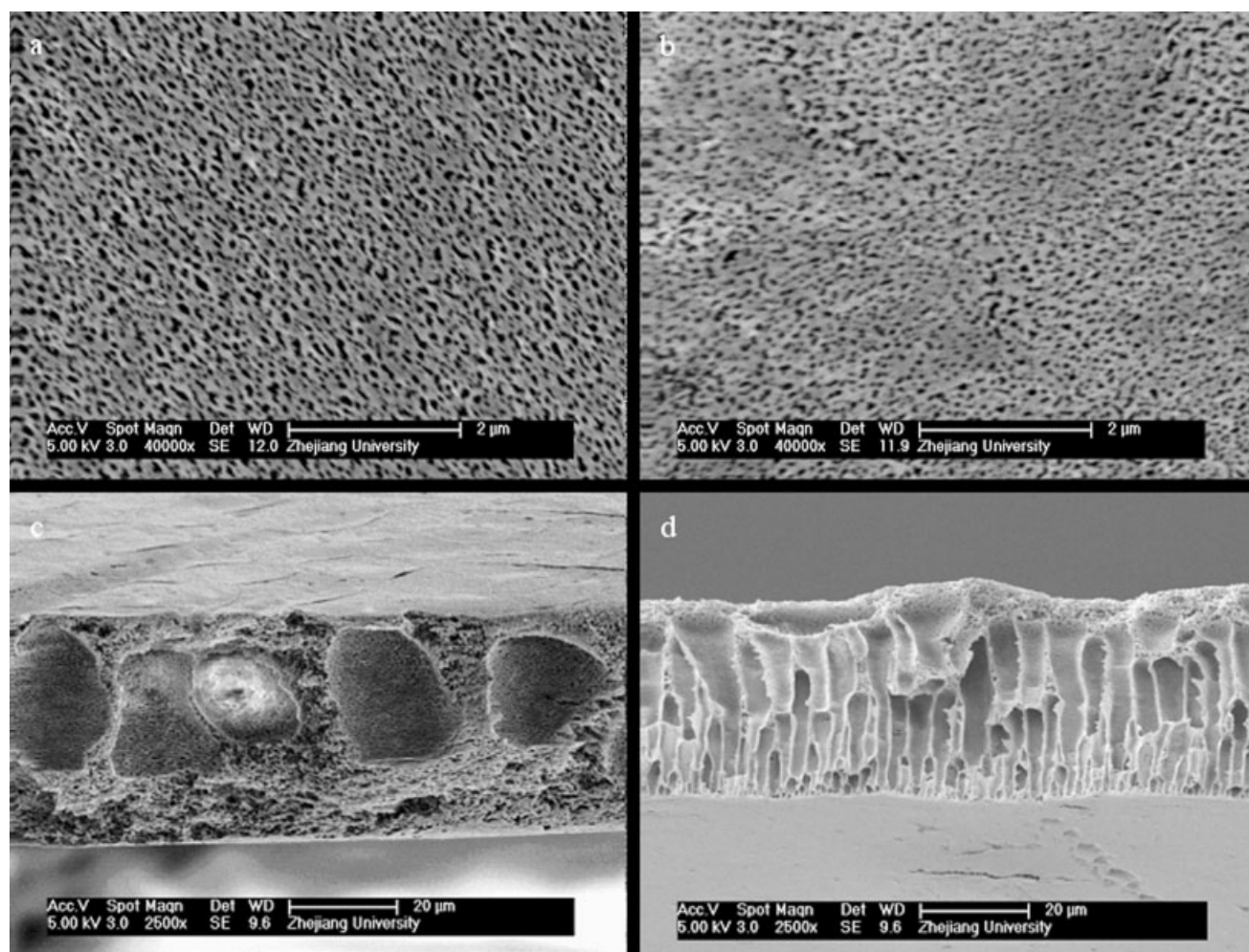


Figure 2 The surface (a,b) and cross section (c,d) SEM micrographs of the PVC porous membrane cast with phase inversion from (a,c) original PVC to (b,d) PVC-g-AA.

TABLE I
Performance Parameters of Both Original PVC and PVC-g-AA Membranes

	Static CA (degree)	Pure water flux L/(m ² h)	Mean pore size (μm)	Porosity (%)	Maximum stress (MPa)
PVC	95.5	107.9	0.13	48.05	5.23
PVC-g-AA	89.0	187.0	0.19	56.02	4.10

brane. The cross section of the original PVC membrane shows a denser skin layer and irregular macrovoids, whereas the cross section of the grafted PVC membrane has a typical asymmetric structure consisting of a thin selective skin layer and a uniform finger-type pore structure. The repulsive forces between carboxylic acid groups of PVC-g-AA copolymers in the solution as well as in the gelation media result in the larger macromolecular chain distance, which gives a highly porous membrane.^{20,21}

Pore size distribution of PVC-g-AA membrane by analysis of a mercury porosimeter

Table I shows the membrane mean bulk pore size, porosity, and bulk pore size distribution. The mean bulk pore size of PVC-g-AA membrane increases from 0.13 to 0.19 μm, and the bulk porosity increases from 48.05% to 56.02%. The SEM images can also support this result. From Figure 3, we can see that the PVC-g-AA membrane has a fewer mercury intrusion than the original PVC membrane, which means a narrower pore size distribution.

Contact angle measurements

Contact angle measurements have been commonly used to characterize the polarity or surface energy of polymeric surface.^{22,23} However, such measurements

are difficult to interpret for porous membrane because of capillary forces in pores, contraction in the dried state, heterogeneity, roughness, and restructuring of the surface.²⁴ Nevertheless, the relative hydrophilicity or hydrophobicity of each sample can be easily obtained by water contact angle measurements. For the porous membrane, the dynamic contact angle can indicate the membrane pore structure more reliably as the water drop can penetrate into the membrane.²⁵ The initial static contact angles are summarized in Table I. The original PVC membrane showed 95.5°, which was considered as a hydrophobic membrane, whereas the PVC-g-AA membrane decreased to 89.0°, suggesting a less hydrophobic membrane. This trend can be clearly observed from the contact angle changes with drop age in Figure 4. The water contact angles of PVC-g-AA membranes are apparently lower than the original PVC membrane at the same drop age. The grafted membrane has a steeper slope ($k_g/k_0 = 2.35$, k_g , k_0 represents the linear slope), and the water drop adsorption time is shorter. This phenomenon is attributed to the hydrophilic nature of the grafted AA polymer chains and the corresponding surface morphologies. The ionic character of the grafting chains also plays an important role in decreasing the contact angles. The hydrophilic AA polymer chains exhibit a lower chemical potential in water than hydrophobic PVC, so the hydrophilic grafted chains are easily segregated at the membrane surface

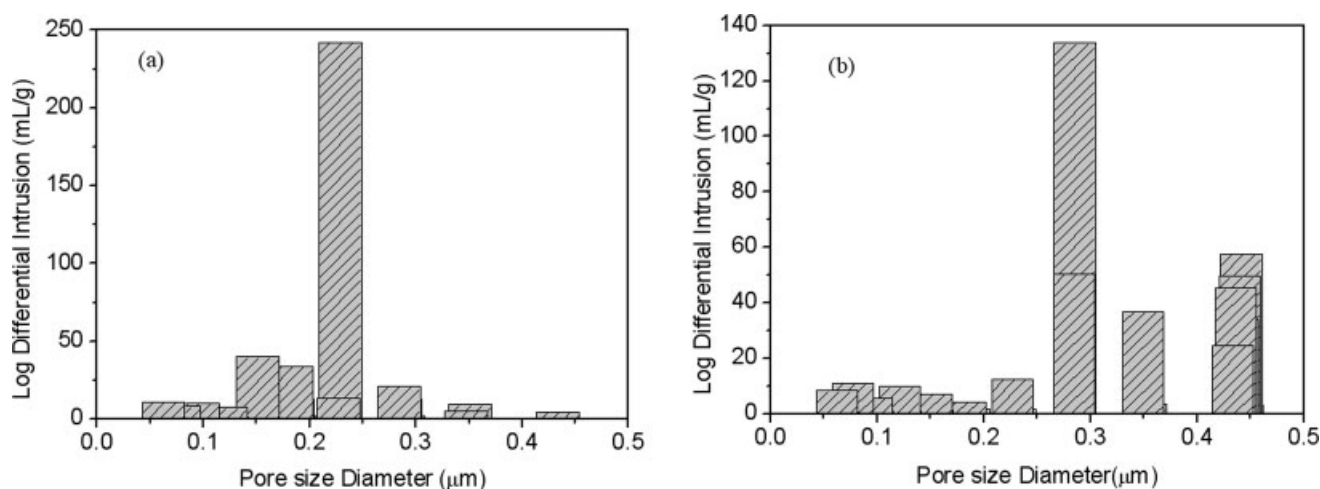


Figure 3 Pore size distribution of (a) the original PVC membrane and (b) PVC-g-AA membrane.

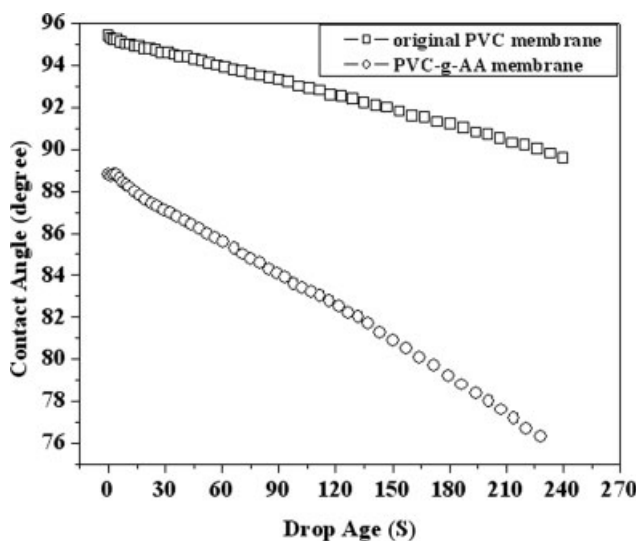


Figure 4 Water contact angle as a function of the drop age for the surface of original and PVC-g-AA membrane.

during gelation. These changes of water contact angles mean that the hydrophobic PVC has been effectively hydrophilized by the grafting of AA.

Mechanical properties

The mechanical properties of a polymeric membrane are the result of its structure and crystalline level. The experimental result in Table I showed that the maximum stress decreased slightly from 5.23 to 4.10 MPa, which was strong enough for commercial application. It may be due to the PVC molecule decomposition or the formation of the unsaturation double bond in high-energy electron beam irradiation.

Filtration performance

To study the effect of the improving hydrophilicity on the performance of the membrane, the pure water and BSA solution fluxes of the original and grafted PVC membranes were measured. In Table I, the pure water flux of PVC-g-AA membrane increased from 107.9 to 187.0 L/(m² h). It may be because of the improvement of the PVC membrane hydrophilicity, pore size, and porosity. In nature the grafted hydrophilic AA chains endow the PVC hydrophilicity, therefore higher water flux is obtained. In Figure 5, we showed the absolute BSA solution (0.1 g/L) flux (*J*) as a function of time through the original PVC membrane and PVC-g-AA membrane. The BSA solution flux of grafted membrane decreased slightly from 187.0 to 120 L/(m² h) in 100 min, whereas the original membrane decreased from 107.9 to 50 L/(m² h). Figure 6 showed the BSA flux ratio normalized by the initial pure water flux to compare flux reductions of the original and grafted membranes

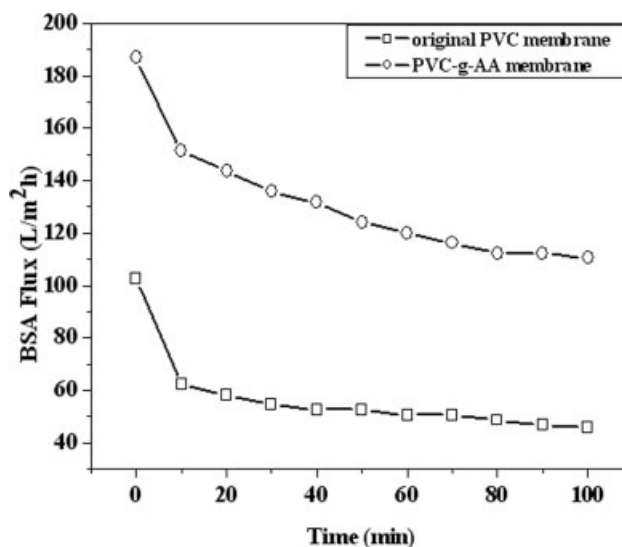


Figure 5 BSA solution (0.1 g/L) flux (*J*) as a function of time through the original PVC membrane and PVC-g-AA membrane.

because of BSA fouling. Protein fouling of the original PVC membrane resulted in a rapid decline of the flux to less than 40% of the initial pure-water flux within 100 min. The PVC-g-AA membrane still had more than 60% of the initial pure-water flux during 100 min operating time. This may be explained because the grafted AA chains weaken the hydrophobic interactions between BSA molecules and PVC membranes. Both the surface and bulk of the PVC-g-AA membrane bearing the polar acrylic groups can effectively prevent protein adsorption, aggregation, and denaturation, which are thought to arise from its

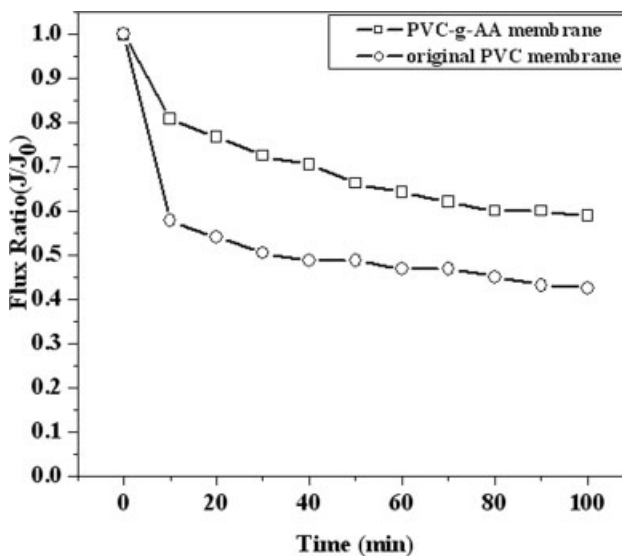


Figure 6 Flux ratio of 0.1 g/L BSA solution (*J*) divided by initial pure water flux (*J*₀) as a function of time for the original PVC membrane and PVC-g-AA membrane.

hydrophilicity, large excluded volume, and unique coordination with surrounding water molecules in BSA aqueous solution.²⁶ These changes of BSA solution flux clearly indicated the improvement of the PVC-g-AA membrane fouling resistance.

CONCLUSIONS

A graft copolymer PVC-g-AA was successfully synthesized through preirradiation grafting method with little reducing the mechanical properties. The porous membranes were prepared from DMAc solutions of copolymers by the phase inversion method. The membrane surface had a better hydrophilicity because of the grafted AA chains, and it was promising to prepare a well-controlled pore size, uniform surface composition, and fouling-resistant PVC membrane combining the superior bulk properties of the hydrophobic PVC with the surface chemistry of the hydrophilic AA polymers. Filtration tests showed that the modification PVC membrane had relative high flux of pure water and BSA solution, demonstrating the better fouling resistance. It proved that preirradiation grafting copolymerization prior to membrane fabrication is a relatively simple approach to prepare a hydrophilic PVC porous membrane using a single step.

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