

Ce(IV)-Induced Graft Copolymerization of Methacrylic Acid on Electrospun Polysulphone Nonwoven Fiber Membrane

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ABSTRACT: Ce(IV)-induced graft copolymerization of methacrylic acid (MAA) on polysulphone (PSU) surface is studied. After pretreatment either by formaldehyde solution or by air glow discharge plasma, the PSU fiber membrane was immersed in MAA solution with Ce(IV) and heated under 80°C under N₂ protection. The MAA was induced by the Ce(IV) redox initiation system to polymerize on the PSU fiber membrane surface. It was found that the pretreatment of the membrane is a very necessary condition for the graft copolymerization to obtain high graft degree. For both the formaldehyde and the air glow discharge plasma pretreated

membrane, the graft degree increase with the reaction time. To study the reaction mechanism, control experiments were carried out. Membrane surfaces were characterized by ATR-FTIR and XPS. The reaction mechanism of the graft copolymerization was discussed based on the experimental data. The effect of the graft copolymerization on the membrane's structure and water permeability was finally studied. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3835–3841, 2006

Key words: graft copolymerization; polysulphone; electrospinning; surface modification; membrane

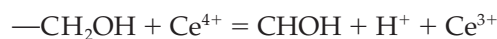
INTRODUCTION

Electrospinning is a polymer processing technique that provides a simple and versatile way to prepare ultrafine polymer fibers with nano/microscaled diameters.¹ In electrospinning, a d.c. voltage sufficient to overcome surface tension force of the polymer solution is used to shoot fine jets of the polymer solution out toward a grounded collector. The jet is stretched before it reaches the collector, dried, and finally is collected as an interconnected nonwoven web of ultrafine fibers. The electrospun polymer nonwoven fabrics possess properties such as high porosity, microscaled pore size and high interconnectivity of the interstitial space, and high surface area due to the small fiber diameter. These properties make the electrospun nonwoven fabric a novel filtration membrane for both gas and liquid filtration.^{2,3}

In recent years, the electrospun polymer nonwoven fabrics have received an extensive research interest for applications in such diverse fields as tissue engineering scaffold,⁴ affinity membrane,⁵ biosensor/chemosensor,⁶ protective cloth,⁷ etc. Most of these applications, however, require that the electrospun polymer

fiber surface be specifically chemically functionalized. For tissue engineering application, for example, adhesion protein molecules need to be immobilized on the fiber surface⁴; for affinity membrane application, specific ligand molecules need to be covalently attached on the fiber surface.⁵ In all these cases, introduction of reactive groups such as —COOH and —NH₂ on the chemically inert polymer fiber surface will be a necessary first step, which can be followed by the covalent attachment of functional molecules using the reactive groups (such as —COOH and —NH₂) as binding sites.

Graft copolymerization is the most common approach to introduce large amount of reactive groups on chemically inert polymer surfaces. Among different graft copolymerization methods, Ce(IV)-induced graft copolymerization is a special and important one. Ce(IV)-alcohol system is a classical redox initiator system capable of initiating radical polymerization of vinyl monomers.⁸ Mino and Kaizerman⁹ observed for the first time that oxidation of alcohols by Ce(IV) ion proceeds by a single electron transfer:



A great limitation of the Ce(IV) redox system is, however, that it can only be used for graft copolymerization on polymers with alcoholic hydroxyl groups, such as polyvinyl alcohol,¹⁰ cellulose,¹¹ chitosan,¹²

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starch,^{13,14} PEG,¹⁵ etc. For common chemically inert polymers, such as polysulphone (PSU), alcoholic hydroxyl groups need to be introduced on the substrate surface prior to the Ce(IV)-induced graft copolymerization.

In this work, the Ce(IV) redox initiation system was used for graft copolymerization of MAA on electrospun PSU nonwoven fiber membrane. The PSU fiber surface is first pretreated with either formaldehyde solution or air glow discharge plasma to introduce alcoholic hydroxyl groups (or other oxygen-containing groups) on the fiber surface, which was followed by the graft copolymerization of MAA induced by the Ce(IV) redox system.

EXPERIMENTAL

Materials and reagents

Polysulphone (PSU, $M_n = 26,000$), ammonium cerium(IV) nitrate, pyridine and toluidine blue O (TBO) were purchased from Sigma–Aldrich (Steinheim, Germany) and used as received. Formaldehyde solution (37%, w/w) from Lancaster (Morecainbe, England) and acetic acid from Merck (Darmstadt, Germany) were used as received. Methacrylic acid (MAA) from Sigma–Aldrich (Steinheim, Germany) was purified by vacuum distillation before use.

Nonwoven PSU fiber membrane preparation by electrospinning

Nonwoven PSU ultrafine fiber membrane was prepared by electrospinning method. Briefly, PSU solution (25 wt %) in pyridine was added into a 10-mL syringe. A syringe pump was used to squeeze out the polymer solution at speed of 3 mL/h through a needle with an inner diameter of 0.21 mm. A 15 kV voltage was loaded between the needle and an aluminum plate (10 cm × 10 cm). The polymer solution was drawn into fibers by the high voltage and deposited on the aluminum plate to give a nonwoven polymer fiber mesh. The as electrospun fiber membrane was subsequently heat treated under 188°C for 6 h, which enhance the adhesion between the fibers to increase the structural integrity and mechanical strength of the membrane. The heat treated membrane was then peeled off from the aluminum plate. The obtained paper-like PSU fiber membrane was cut into 1.5 cm × 2 cm pieces for use. Membrane thickness can be control by changing electrospinning time. Unless stated other wise, the membranes thickness used in this work was 200 μm.

Pretreatment of PSU fiber membrane

The PSU fiber membrane was then pretreated either by formaldehyde or by air glow discharge plasma. For

TABLE I
Notations Used in This Work and Their Specifications

	Pretreatment	Ce ⁴⁺
Control I ^a	No	No ^b
Control II	No	Yes ^b
Sample I	Formaldehyde treated	Yes ^b
Control III	Air plasma treated	No ^b
Sample II	Air plasma treated	Yes ^b

^a It is believed that there is no graft copolymerization reaction occurring on Control I. Therefore, in this work Control I was used as a background for measurement of —COOH group density on the other samples (see experimental part).

^b "Yes" means there was no Ce⁴⁺ in the MAA solution.

pretreatment by formaldehyde, the PSU fiber membrane was exposed to 18.5 vol % formaldehyde in 1M acetic acid solution for 24 h at room temperature to yield —CH₂OH groups on the surface.¹⁶ For pretreatment by air plasma, the PSU fiber membrane was put into the chamber of an inductively coupled (electrodeless) radio frequency glow discharge plasma cleaner (Harrick, PDC-001). The plasma treatment was carried out for 5 min with a gas pressure of 20 Pa and an electrical power of 30 W.

Ce(IV)-induced graft copolymerization of MAA on the PSU fiber membrane

The pretreated membrane was immersed into a glass tube added with 10 mL 10 vol % MAA (Aldrich, purified by vacuum distillation) aqueous solution, 0.4M H₂SO₄, and 0.073M ammonium cerium(IV) nitrate (Fluka). After purging with nitrogen, the tube was heated under 80°C for a given time. After the graft copolymerization reaction, the PMAA-grafted PSU fiber membrane was thoroughly rinsed in 10 mM NaOH solution under stirring to remove the unreacted monomer or homopolymer. The membrane was finally rinsed with DI water.

To study the reaction mechanism, control experiments with different conditions were also carried out. In this article, the PMAA-grafted samples and the controls were represented by notations, as summarized in Table I.

Material characterization

For physical properties characterization, FE-SEM (FEI-QUANTA 200F) was used to observe the microstructure of the PSU membrane; apparent density of the PSU membrane was calculated by dividing the membrane mass by the membrane volume (product of membrane thickness and area); porosity was then calculated using the apparent density and the bulk density of PSU (1.24 g/cm³); specific surface area of the membrane was measured on a N₂ BET system (ASAP

2020 V3.00H, Micromeritics); pore size of the membrane was measured by the Bubble Point method on a Porometer 3G (Xonics, USA).

For surface chemical composition characterization, ATR-FTIR spectra of the PSU membranes were obtained on a Nicolet spectrometer system with an Avatar[™] OMINI-Sampler[™] accessory; XPS spectra were obtained on a VG ESCALAB 2201-XL Base System. Peak fitting of the C1s spectrum and calculation of the atomic ratio (O/C) were both performed by the System software. The calculation of the O/C atomic ratio was based on the peak areas of O1s and C1s and the intensity factors of O and C (2.85 and 1.0, respectively).

Graft degree of the PMAA-grafted PSU fiber membrane was quantified by measuring the COOH density using TBO method.^{17,18} The membrane was immersed in an aqueous solution containing 0.5 mM TBO (Aldrich) and the pH value was adjusted to 10 with NaOH. The formation of ionic complexes between the —COOH groups in the grafted PMAA chains and the cationic dye was allowed to proceed for 6 h. Then the membrane was rinsed with 0.1 mM NaOH solution to remove the free TBO molecules. The combined TBO on the membrane was dissolved in 50 v% acetic acid and the absorbance at 620 nm of the solution was measured on a UV-visible spectrophotometer (UNICAM UV300). The amount of the —COOH groups on the membrane was calculated based on the assumption that the carboxyl groups can combine with equal amount (in mole) of TBO molecules.¹⁹ It is believed that on Control I (see Table I) there should not be any graft copolymerization reaction occurring; therefore, the TBO amount adsorbed on any other samples will be subtracted by that of the Control I to eliminate the effects of the physical adsorption of TBO. The amount of the TBO physically adsorbed on the Control I is 10 nmol/mg. This is not significant compared with the amounts of the TBO bonded on the other samples.

For permeability measurement of both the unmodified and modified PSU membrane, several membranes were stacked with a total thickness of 1 mm. The membranes were then put into a Millipore ultrafiltration cell 8010 (ϕ 25 mm; effective filtration area is 4.1 cm²) equipped with a pressure gauge. DI water was fluxed through the membranes and the flux was recorded under a pressure of 1 psi.

RESULTS AND DISCUSSION

Nonwoven PSU fiber membrane preparation

The Nonwoven PSU fiber membrane was fabricated by electrospinning. After electrospinning, the PSU fiber membrane was subsequently heat treated under 188°C for 6 h. The heat treatment is very important to electrospun polymer fiber membranes because it can

greatly enhance the fusion between the fibers, changing the “fluffy” cotton-like material into a strong membrane with good structural stability and mechanical strength.²⁰ The PSU membrane obtained after heat treatment is shown in Figure 1. The membrane is a high porous material with microscaled interstitial space. Detailed physical properties such as apparent density, special surface area, mechanical strength, etc. are summarized in Table II.

Ce(IV)-induced MAA graft copolymerization on formaldehyde-pretreated PSU membrane

Ce(IV)-induced radical polymerization is widely used for graft copolymerization on polymer surfaces with alcoholic hydroxyl groups. PSU is a mechanically strong polymer widely used for membrane preparations. The chemically inert surface of the untreated PSU, however, makes it difficult to be directly surface modified by the Ce(IV)-induced graft copolymerization because there are no alcoholic hydroxyl groups on PSU surface. To overcome this problem, the PSU membrane was pretreated in formaldehyde solution under acidic conditions. This pretreatment have been demonstrated to be able to introduce —CH₂OH groups in the benzene ring-containing polymer surface, through the reaction between the formaldehyde and the benzene ring of the polymers,¹⁶ as shown below:

XPS analysis (Table III) showed that the O/C atomic ratio on the membrane surface was obviously increased after the pretreatment by formaldehyde, indicating the formation of the —CH₂OH groups. The existence of the —CH₂OH group on the formaldehyde-pretreated PSU surface can be further verified by the analysis of the C1s spectrum. Figures 3(a) and 3(b) show the C1s spectrum of the PSU membrane before and after the formaldehyde treatment. The C1s spectrum of the untreated membrane surface was mostly composed of peak I (at 285.0 eV), which corresponds to carbon atoms without any bond with oxygen atoms. This is in accordance with the chemical structure of PSU because most of the carbon atoms (23 out of 27 in one unit) in PSU do not link with oxygen atom. The C1s spectrum of the formaldehyde-treated PSU surface has a significantly increased peak II at ~287.0 eV which can be assigned to carbon atoms with single bond with oxygen atom (—C*—O—), indicating the existence of the —CH₂OH groups.

The formaldehyde-pretreated PSU fiber membrane was then immersed into MAA solutions containing Ce(IV). The —CH₂OH groups together with the Ce(IV) form the redox-initiating system to induce the graft copolymerization of MAA. To verify this mechanism, both the formaldehyde-treated and the non-treated PSU membrane were immersed into the MAA solution with Ce(IV) for the graft reaction, corre-

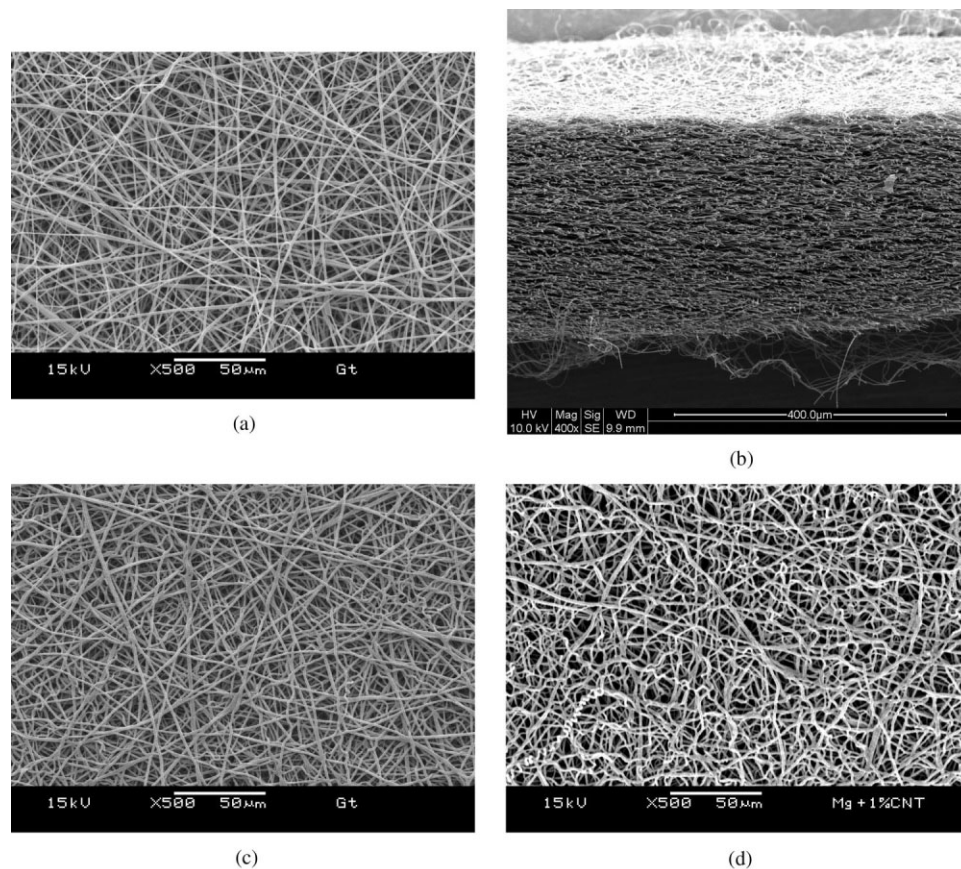


Figure 1 SEM micrographs of the electrospun nonwoven PSU fiber membrane: (a) original PSU membrane; (b) cross section of the original PSU membrane; (c) Sample II (graft time was 1 h); and (d) Sample II (graft time was 2 h).

sponding to Sample I and Control II, respectively (Table I). The results of graft degree measurement are shown in Figure 2(a). The graft degree of the Sample I is significantly higher than that of the Control II, which is in support of the proposed mechanism. ATR-FTIR spectrum of Sample I is shown in Figure 4(b). The appearance of the peak at 1700 cm^{-1} of Sample I is indicative of the —COOH groups in the grafted PMAA. The ATR-IR spectrum of the formaldehyde-treated membrane has no difference with the untreated membrane and so is not shown. The XPS C1s spectrum of the Sample I is shown in Figure 3(c).

Compared with the formaldehyde-treated PSU membrane [Fig. 3(b)], the C1s spectrum of the Sample II has much stronger peak I at 285.0 eV and a new peak III at 290.0 eV. This is in accordance with the existence of PMAA because PMAA has only two kinds of carbon atoms, i.e., carbon atom without link with oxygen corresponding to peak I and carboxyl carbon atom (—C*OOH) corresponding to peak III. The small peak II in the C1s spectrum of the Sample I indicated that the surface still remained some $\text{—CH}_2\text{OH}$ groups and the surface was not totally covered by the PMAA.

TABLE II
Physical Properties of the Electrospun Nonwoven PSU Fiber Membrane

Membrane thickness	50–400 μm can be obtained by controlling electrospinning conditions
Fiber diameter	0.8–2 μm
Apparent density	0.22 g/cm^3
Porosity	82%
Tensile strength	5.7 MPa
Specific surface area (by N_2 BET measurement)	4.0 m^2/g
Pore size (by bubble point method)	Maximum pore size, 9.5 μm Minimum pore size, 4.2 μm

TABLE III
O/C Atomic Ratios on the PSU Membrane Surfaces

	O/C atomic ratio
Untreated PSU membrane	13.3/86.7
Formaldehyde-pretreated PSU membrane	18.7/81.3
Air plasma-treated PSU membrane	25.3/74.7
Sample I (graft time was 2 h)	22.7/77.3
Sample II (graft time was 2 h)	29.3/70.7

The smaller but obvious graft degree of PMAA on the Control II is interesting. Previous work²¹⁻²⁴ has shown that the highly oxidative Ce(IV) can directly attack organic substrate to undergo the electron transfer reaction to give radicals. This is a possible reason for the graft copolymerization on the Control II.

Ce(IV)-induced MAA graft copolymerization on air plasma-treated PSU membrane

To further increase the graft degree of the PMAA on the PSU membrane surface, it is necessary to yield as much oxygen-containing groups as possible on the membrane surface prior to the graft copolymerization. Therefore, we use air glow discharge plasma for the pretreatment of PSU membrane, followed by the Ce(IV)-induced graft copolymerization of MAA. Figure 2(b) showed that the Sample II got a much higher PMAA graft degree than the Sample I. ATR-FTIR spectrum of the Sample II shown a strong peak at $\sim 1700\text{ cm}^{-1}$, also implying the high graft degree [Fig. 4(c)]. The ATR-IR spectrum of the air plasma-treated membrane without PMAA grafting has no difference with the untreated membrane and so is not shown. The C1s spectrum of the Sample II is mostly composed of peak I at 285.0 eV and peak III at 290.0 eV [Fig. 3(e)], which is in accordance with the existence of PMAA containing only these two kinds of atoms. It can be found by comparing Figures 3(c) and 3(e) that Sample II has only two peaks while Sample I has three, indicating that Sample II has higher graft degree and higher cover ratio of PMAA than Sample I. The O/C atomic ratio (Table III) of the PMAA-grafted membrane surface is quite close to the O/C atomic ratio (33.3/66.7) in the PMAA molecules, also verifying the cover of the PMAA on the Sample II.

Reaction mechanism of the Ce(IV)-induced graft copolymerization on air plasma-treated PSU membrane

It has been well known that plasma treatment can produce oxygen-containing groups on polymer surfaces. XPS results showed that the O/C atomic ratio of the air plasma-treated PSU membrane surface is much higher than that of the untreated PSU membrane (Ta-

ble III). It can be inferred that these oxygen-containing groups form redox initiation system with the Ce(IV). However, it is also well known that plasma treatment can also produce some radicals or peroxide groups on polymer surface, which also can induce graft copolymerization of vinyl monomers. This make the problem complicated: whether the radicals (or peroxide groups) or the Ce(IV) is the main reason that cause the high graft degree of Sample II? To find the reason, a control experiment (Control III) in which the air plasma-treated PSU fiber membrane was immersed into the MAA solution without Ce(IV) for the graft copolymerization was performed. The results are shown in Figure 2(b). It can be seen that the graft degree for the Control III is almost zero. This means there is no or

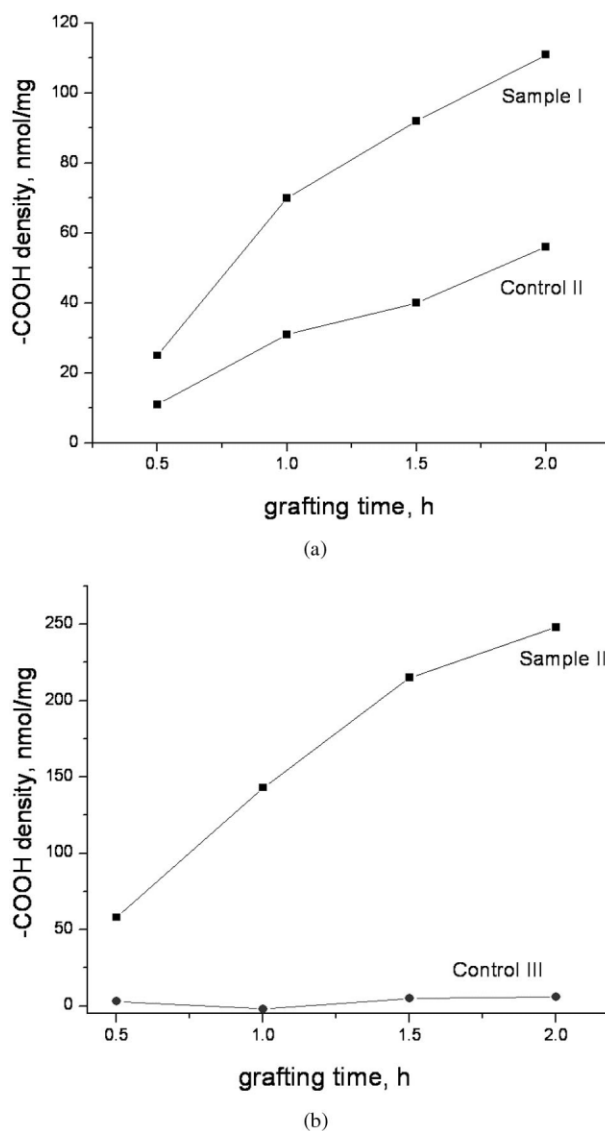


Figure 2 —COOH group density of (a) Sample I and Control II and (b) Sample II and control III at different grafting time. Specifications of Control II, Control III, Sample I, and Sample II are shown in Table I.

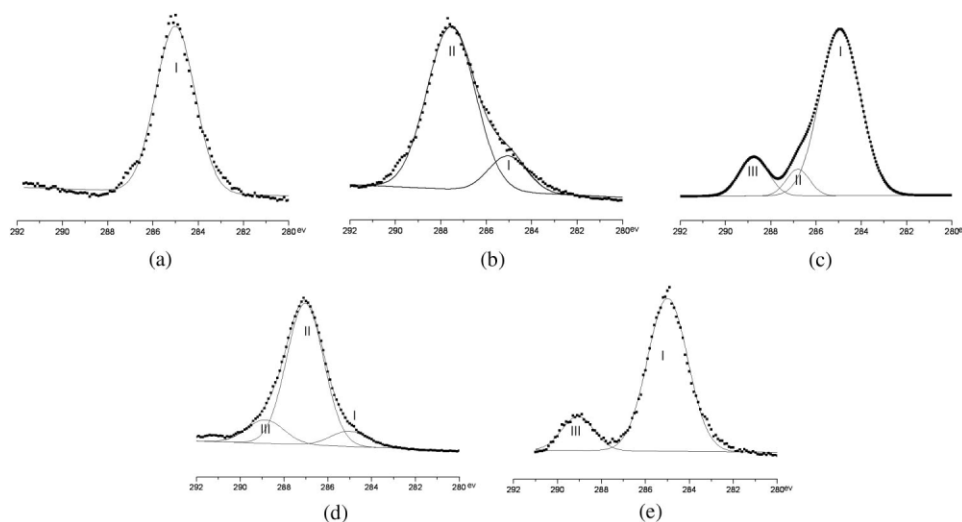


Figure 3 XPS C1s spectra of (a) original PSU membrane; (b) formaldehyde-treated PSU membrane; (c) Sample I (graft time was 2 h); (d) air plasma-treated PSU membrane; and (e) Sample II (graft time was 2 h)

very little radicals or peroxide groups produced on the PSU membrane surface after the air plasma treatment. Thus, it can be said that the high graft degree of the Sample II is due to the Ce(IV) redox system. The large amount of the oxygen-containing groups (the type of the group will be discussed shortly) produced on the PSU surface by the plasma treatment were oxidized by the Ce(IV) to initiate the polymerization reaction.

C1s XPS spectra [as shown in Fig. 3(d)] were used to study the sort of the oxygen-containing groups introduced by the air plasma treatment. In the C1s spectrum of the air plasma-treated PSU, in addition to peak I at 285.0 eV and a strong peak II at 287.0 corresponding to $-\text{C}^*-\text{O}-$, a small peak III at ~ 289.0 eV corresponding to carbonyl carbon atoms ($\text{C}^*=\text{O}$ or $\text{OC}^*=\text{O}$) also appeared. The whole C1s spectrum, however, was mainly composed of peak (II), indicating that the oxygen-containing groups are mainly of $-\text{C}^*-\text{O}-$ kinds. Therefore, it can be inferred that the main oxygen-containing groups on the air plasma-treated PSU is alcoholic hydroxyl groups ($\text{C}-\text{OH}$), which is exactly needed by Ce(IV) to form the initiating system. However, it need to be noted that other oxygen-containing functions such as carbonyl groups introduced by the air plasma treatment may also make contribution to the graft copolymerization. Reddy et al.²⁵ has demonstrated that carbonyl-containing molecules such as methyl ethyl ketone and acetone both can form redox-initiating systems with the Ce(IV).

Membrane structure and permeability

The electrospun PSU fiber membrane is a three-dimensional high porous material. To check whether the grafting reaction is occurred only on the outer surface

of the membrane or on the whole internal surface of the membrane, PSU fiber membranes with different thickness (50, 100, and 200 μm) were prepared and used for the graft copolymerization. No matter what the thickness is, the graft densities of the $-\text{COOH}$ groups normalized by the membrane mass all gave value of 111 ± 10 nmol/mg for Sample I (polymerization time was 2 h), and 248 ± 15 nmol/mg for Sample II (polymerization time was 2 h). This indicated that the graft copolymerization reaction took place on the whole internal surface of the membrane.

The microstructure of the Sample II is shown in Figures 1(c) and 1(d). An interesting phenomenon is that the PSU fibers become obviously curled after the PMAA grafting, as shown in Figure 1(d). As a whole, the nonwoven fibrous morphology of the PSU membrane was not affected significantly by the graft copo-

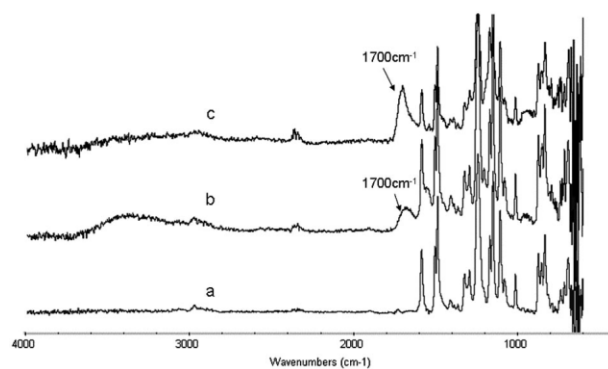


Figure 4 ATR-IR spectra of (a) original PSU membrane; (b) Sample I (graft time was 2 h); and (c) Sample II (graft time was 2 h). The ATR-IR spectrum of the formaldehyde-treated and the air plasma-treated membrane did not show difference with the original membrane, and so were not shown.

lymerization. The permeability of the membrane was not affected by the graft of PMAA either. Water flux through stacked membranes with total thickness of 1 mm under a pressure drop of 1 psi is 3.2 ± 0.2 mL/cm² min for the untreated PSU membrane and 2.9 ± 0.5 mL/cm² min for Sample II (graft time is 2 h).

CONCLUSIONS

Ce(IV)-induced graft copolymerization of MAA can occur on electrospun nonwoven PSU fiber membrane after pretreatment by either formaldehyde or air glow discharge plasma. Formaldehyde pretreatment can produce —CH₂OH groups on the PSU surface, which can form redox-initiating system with the Ce(IV). Air plasma treatment produces large amount of oxygen-containing groups consisting of mainly alcoholic hydroxyl groups, which can form the redox-initiating system with the Ce(IV) to initiate the graft copolymerization. The graft copolymerization can take place evenly on the internal surface throughout the membrane, and does not affect the membrane microstructure and permeability. To conclude, by combination of the air glow discharge plasma treatment and the Ce(IV) redox-initiating system, a very convenient method to graft PMAA on chemically inert polymer surfaces with high graft degree is developed in this work. The work significantly benefits the studies on applications of electrospun polymer fibers by developing an efficient method for their surface modification.

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