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# Preparation and characterization of polyalkene membranes modified with four different ion-exchange groups by radiation-induced graft polymerization

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## Abstract

Three different cation-exchange membranes with carboxylic acid, phosphoric acid, and sulfonic acid groups, and one anion-exchange membrane with a triethylamine group were prepared by radiation-induced graft polymerization. The maximum capacities of the carboxylic acid, phosphoric acid, sulfonic acid, and triethylamine groups were 3.0, 2.30, 2.43, and 1.42 mmol/g, respectively. The physico-chemical properties of the polyalkene non-woven fabric membrane with four different ion-exchange groups were examined by thermogravimetric analysis, X-ray photoelectron spectrometry (XPS), and scanning electron microscopy. The prepared ion-exchange membrane was applied to the removal of terephthalic acid in dyeing wastewater. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Membranes; Polymerization; Terephthalic acid

## 1. Introduction

Radiation-induced graft polymerization (RIGP) is a useful method for chemical modification of existing polymers because of its wide applicability to various shapes and quantities of base polymer [1–5]. The pre-irradiation grafting technique of RIGP shows practical applicability because storage at a lower temperature enabled us to separate the irradiation process from the grafting process [6].

Ion-exchange membranes have been widely used in various industrial fields. Their electrochemical properties, such as transport number and electrical resistance, have been vastly improved. At the same

time, the ion-exchange membrane is a typical functional polymer and can be used not only as a separation membrane, but also as a new functional material. Consequently, many ion-exchange membranes have been made [7–10], and further efforts to find new applications should be continued.

Polyalkene non-woven fabrics (PNF) have been widely used in battery separators because of low cost, good mechanical properties, and strong properties for electrolyte. For this reason, the preparation and application of ion-exchange membranes has been widely studied using PNF as the base material [11–13]. However, little has been reported on the grafting of vinyl-type monomer onto PNF, the skin-core structure (polyethylene is the skin and polypropylene is the core).

In this study, three different cation-exchange membranes including carboxylic acid, phosphoric

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acid, and sulfonic acid groups, were prepared by RIGP. The carboxylic acid group was introduced by radiation-induced grafting of acrylic acid (AAc) onto PNF. The phosphoric acid and triethylamine groups were also introduced by radiation-induced grafting of glycidyl methacrylate (GMA) and subsequent phosphonation and amination of epoxy groups of poly-(GMA) graft chains, respectively. The sulfonic acid group was introduced by radiation-induced grafting of styrene (St) and subsequent sulfonation of poly-(St) graft chains. The chemical and electrochemical properties of the three different ion-exchange membranes were investigated. The prepared PNF membrane was applied to the removal of a terephthalic acid (TPA) in dyeing wastewater obtained from the Taegu Dyeing Complex in South Korea.

## 2. Experimental

### 2.1. Materials

PNF with a thickness of 0.50 mm and a calculated

density of  $161.6 \text{ g/m}^2$  was washed with methanol and dried in a vacuum oven at  $50^\circ\text{C}$  for 12 h. Reagent grade acrylic acid (AAc, Jusei, 99%), styrene (St, Merck, 99%), glycidyl methacrylate (GMA, Aldrich, 99%), phosphoric acid (Aldrich), and chlorosulfuric acid (Aldrich) were used as received. All the other chemicals of reagent grade were used without further purification.

### 2.2. Grafting procedure

Fig. 1 shows the preparation procedure for the four different ion-exchange membranes by RIGP. A  $10 \times 10\text{-cm}$  sample of PNF was irradiated by  $\gamma$ -rays from a Co-60 source (Co-60 Gamma-ray Irradiator, dose rate:  $0.7 \cdot 10^5 \text{ Gy/h}$ ) under atmospheric pressure and ambient temperatures, and then reacted with the monomer. The unreacted monomer and homopolymers after grafting of AAc, GMA, and St were removed with Soxhlet apparatus using hot water, tetrahydrofuran (THF), and benzene, respectively. The PNFs obtained by the RIGP method were dried in a vacuum oven at  $60^\circ\text{C}$  for 12 h. For the effects of

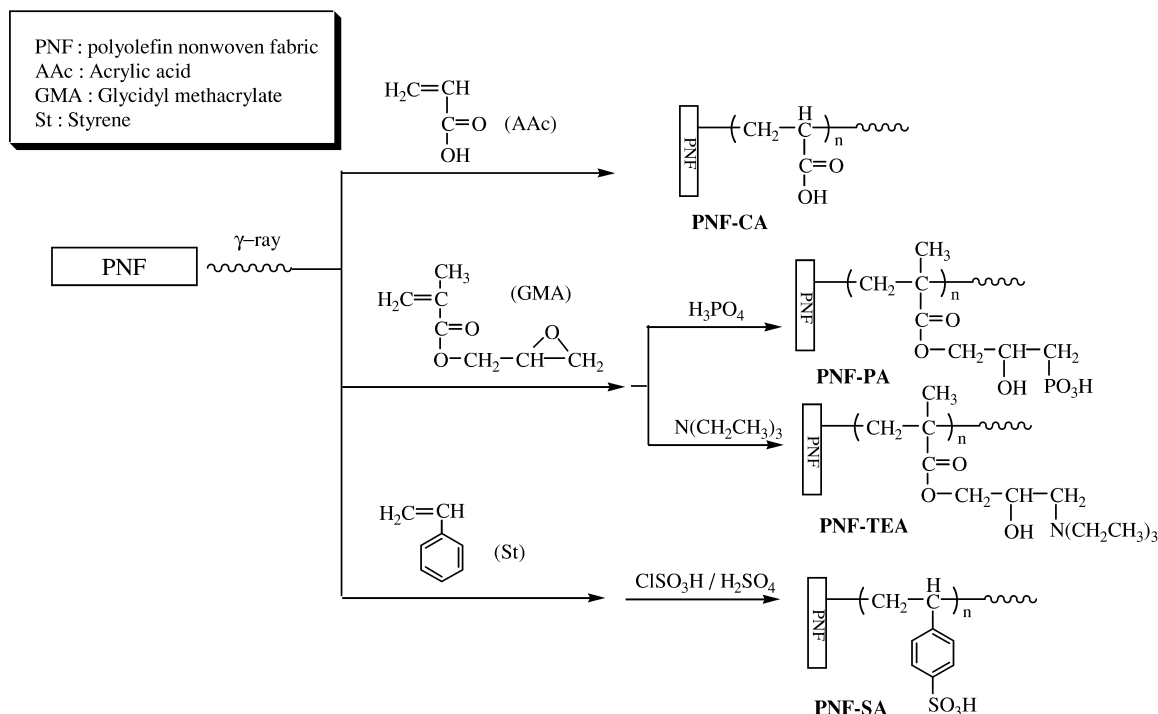


Fig. 1. Preparation procedure for the four different ion-exchange PNF membranes by RIGP. AAc: acrylic acid; GMA, glycidyl methacrylate; PNF, polyalkene non-woven fabric; St, styrene.

various parameters on the grafting copolymerization, the degree of grafting (d.g.) is defined as:

$$\text{Degree of grafting (d.g.) (\%)} = [(W_g - W_0)/W_0] \cdot 100 \quad (1)$$

where  $W_g$  and  $W_0$  denote the masses of the grafted and the ungrafted PNF, respectively.

### 2.3. Phosphonation and amination of the GMA-grafted PNF and sulfonation of St-grafted PNF

The epoxy group of the GMA-grafted (GMA-g) PNF was converted into a  $-\text{PO}_3\text{H}$  group by immersing GMA-grafted PNF in 85% phosphoric acid aqueous solution at  $80^\circ\text{C}$  and varying the reaction time. The triethylamine group was also introduced onto PNF in triethylamine solution at  $80^\circ\text{C}$  by varying the reaction time. After phosphonation and amination, the PNF membrane was washed with deionized water.

Polystyrene in St-grafted PNF reacted with  $\text{ClSO}_3\text{H}$  in  $\text{H}_2\text{SO}_4$  in a glass ampoule for various periods of time and various concentrations. After sulfonation, the PNF membrane was washed in the order of  $99\% \text{H}_2\text{SO}_4 > 50\% \text{H}_2\text{SO}_4 > 20\% \text{H}_2\text{SO}_4 >$  deionized water and was dried under reduced pressure.

The content (mmol/g),  $X_{\text{group}}$ , of the  $-\text{PO}_3\text{H}$ ,  $-\text{N}(\text{CH}_2\text{CH}_3)_3$ , and  $-\text{SO}_3\text{H}$  groups was determined from total ion-exchange capacity by the following equation:

$$X_{\text{group}} = [(W_s - W_g)/W_s] \cdot (1000/M_r) \quad (2)$$

where  $W_s$  is the mass of the PNF with  $-\text{PO}_3\text{H}$ ,  $-\text{N}(\text{CH}_2\text{CH}_3)_3$ , or  $-\text{SO}_3\text{H}$  group and  $M_r$  is the molecular mass of  $\text{H}_3\text{PO}_4$ ,  $\text{N}(\text{CH}_2\text{CH}_3)_3$ , or  $-\text{SO}_3\text{H}$  group.

### 2.4. Electrical resistance

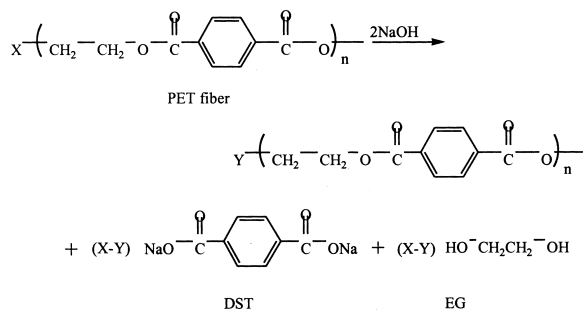
The electrical resistances of the PNF with  $-\text{COOH}$ ,  $-\text{PO}_3\text{H}$ , and  $-\text{SO}_3\text{H}$  groups were measured in  $0.1 \text{ M}$  KCl solution at  $25^\circ\text{C}$  using an Millicell-ERS apparatus (Millipore, USA). The specific electric resistance,  $R_{\text{sp}}$  ( $\Omega \text{ cm}$ ), was calculated using the following equation:

$$R_{\text{sp}} = \{[(R_{\text{sample}} - R_{\text{blank}})]/T\} \cdot S \quad (3)$$

where  $R_{\text{sample}}$  denotes the electrical resistance of  $0.1 \text{ M}$  KCl solution in the presence of PNF membrane, and  $R_{\text{blank}}$  denotes the electrical resistance of  $0.1 \text{ M}$  KCl solution without PNF membrane.  $T$  and  $S$  denote thickness (cm) and surface area ( $\text{cm}^2$ ) of the membrane, respectively.

### 2.5. Removal of TPA in dyeing wastewater

Fig. 2 shows a schematic diagram of the electro-dialysis apparatus for removal of TPA in dyeing wastewater. To examine the efficiency of the ion-exchange membrane, the TPA ( $0.5 \text{ M}$ ) solution was prepared for reaction of TPA ( $0.5 \text{ mol}$ ) and NaOH ( $1.0 \text{ mol}$ ) in  $1000 \text{ ml}$  deionized water. The conductivity change in diluting compartment was measured until there was no further change. The prepared TPA solution was circulated ( $15 \text{ ml/min}$ ) in two pathways as shown in Fig. 2: between the cathode and anion-exchange membrane, and between the anion-exchange membrane and the cathode-exchange membrane. The effective areas of both membranes were  $10 \times 10 \text{ cm}^2$ . The dyeing wastewater (pH 14, biochemical oxygen demand (BOD)  $20\,000 \sim 30\,000 \text{ mg/l}$ , chemical oxygen demand (COD)  $10\,520 \text{ mg/l}$ , total organic carbon (TOC)  $14\,770 \text{ mg/l}$ , TPA concentration  $20\,000 \text{ ppm}$ , ethylene glycol (EG)  $10\,000 \text{ ppm}$ ) obtained from the Taegu Dyeing Complex in South Korea was applied for the removal of TPA. Disodium terephthalate (DST) and EG were obtained from the preparatory processing of tender polyester fiber as show in the following scheme:



### 2.6. Characterization of the four different ion-exchange membranes

For scanning electron microscopy (SEM), a  $0.5 \times$

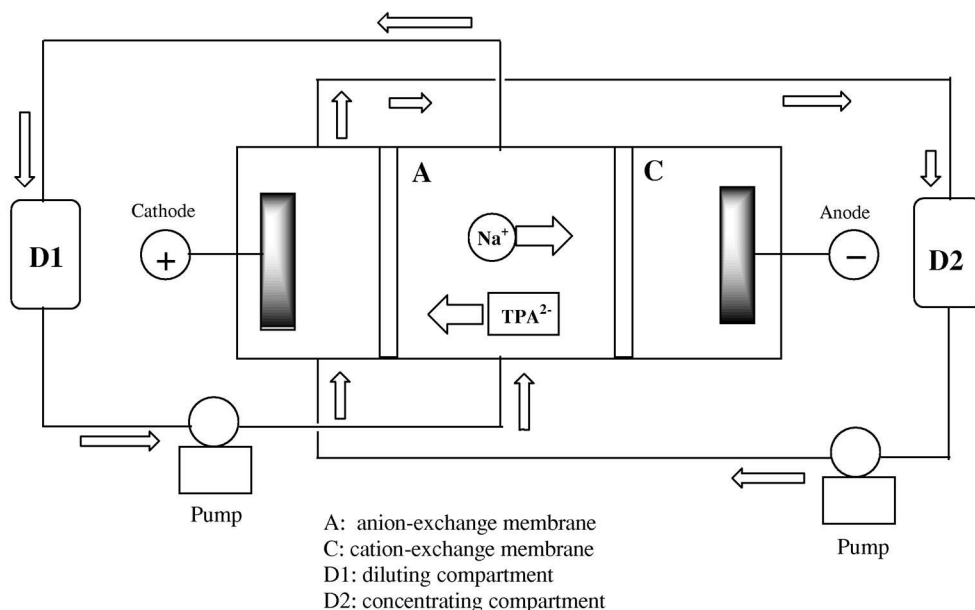


Fig. 2. Schematic diagram of the electro dialysis apparatus for removal of TPA.

0.5-cm sample was coated with gold–palladium alloy prior to measurement. The sputtered sample was then scanned by the electron beam in the scanning electron microscope (JSM-840A, JEOL, Japan).

X-ray photoelectron spectrometry (XPS) results were obtained using an ESCALab 220i instrument (VG Scientific) equipped with a full  $180^\circ$  hemispherical electrostatic analyzer to examine the chemical state of the constituent elements. Al  $K\alpha$  radiation (1486.6 eV) was used as a photon source. The half-width at half-maximum of the  $4f_{7/2}$  line in the XPS spectrum of gold obtained with our XPS instrument was smaller than 1.0 eV. The energy scale of the spectrometer was calibrated using the lowest BE component of C 1s peak (285.0 eV). The C 1s spectra were deconvoluted using a Gaussian-Lorentzian model to obtain the best binding energy values.

Thermogravimetric analyses (TGA) of the PNF and four different ion-exchange membranes were made using two thermal analysis (TA) instruments: TGA 2950 model (DuPont) (Fig. 6a,b), and TA4000/Auto DSC 2910 system (Seiko) with heating rate of  $10^\circ\text{C min}$  in the temperature range  $50\text{--}700^\circ\text{C}$ .

### 3. Results and discussion

In a previous paper [3], the carboxylic acid group was introduced by radiation-induced grafting of acrylic acid (AAc) and methacrylic acid (MAc) onto polyethylene (PE) film for use as a battery separator. It was found that an AAc-grafted PE membrane had a higher diffusion flux than a MAc-grafted PE membrane. The specific electrical resistance of two cation-exchange membranes modified with AAc and MAc decreased rapidly with increase in the range of grafting.

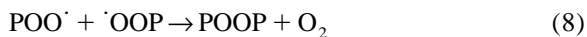
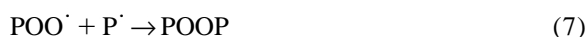
Phosphoric and sulfonic acid groups were also introduced by radiation-induced grafting of GMA onto polypropylene non-woven fabric and PE hollow fiber membrane, and subsequent phosphonation and sulfonation of graft chains, respectively, for the removal of heavy metal ions [2]. Furthermore, the sulfonic acid group was also introduced by radiation-induced grafting of styrene (St) onto PE hollow fiber membrane and subsequent sulfonation of graft chains for the removal of heavy metals [4]. However, the grafting of AAc, GMA, and St onto PNF, where the PNF structure is the skin-core structure (PE is the skin and polypropylene is the core), had not yet been

studied. In addition, the prepared PNF membrane was not applied for the removal of TPA in dyeing wastewater.

### 3.1. Grafting of AAc, GMA, and St onto PNF

Fig. 3 shows the effects of AAc concentration and total irradiation dose on the grafting of AAc onto PNF at 60°C in MeOH for 3 h in the presence of FeSO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>. The grafting yield (%) increased with increased irradiation dose. Ferrous sulphate (FeSO<sub>4</sub>) and Mohr's salt [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·FeSO<sub>4</sub>] are two of the most commonly used compounds for inhibiting homopolymerization of vinyl monomer during grafting polymerization [14].

When PNF is subjected to ionizing radiation in air, trapped radicals or peroxy radicals are formed. In the presence of oxygen, the schematic reaction mechanism of PNF during irradiation is as follows:



In this scheme, P and P<sup>·</sup> represent the PNF chain and PNF radicals produced by irradiation, respectively. Irradiation in air leads to the formation of hydroperoxide species which may result in undesirable homopolymerization initiated by the mobile <sup>·</sup>OH radical formed in the thermal decomposition reaction. It is possible to avoid this problem by using a reducing agent, e.g. metallic salt, to decompose the peroxy species. O'Neill [15] used Fe<sup>2+</sup> ion as the reducing agent to decompose the hydroperoxides, thereby converting hydroxyl radicals to inactive hydroxide ions:

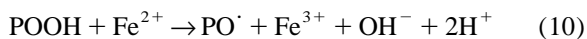


Fig. 4 shows the effect of GMA concentration and total irradiation dose on the grafting of GMA onto PNF at 60°C in MeOH for 3 h. It was found that the grafting yield increased with increased irradiation dose. Maximum grafting yield was obtained around 60% GMA concentration. In general, additives such as salts and acid were added to grafting polymerization because of increasing grafting yield and

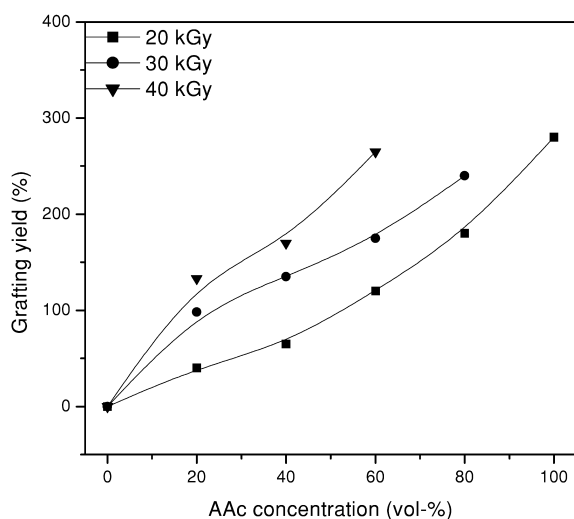


Fig. 3. Effects of AAc concentration and total irradiation dose on the grafting of AAc onto PNF at 60°C in MeOH for 3 h in the presence of FeSO<sub>4</sub> (2.5·10<sup>-3</sup> M) and H<sub>2</sub>SO<sub>4</sub> (0.1 M).

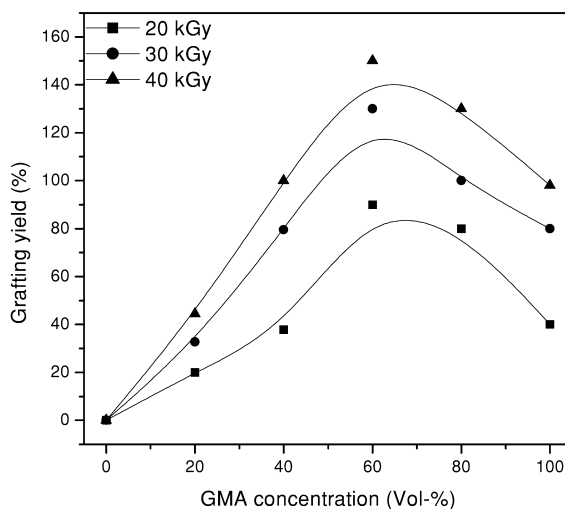


Fig. 4. Effects of GMA concentration and total irradiation dose on the grafting of GMA onto PNF at 60°C in MeOH for 3 h.

reduction of homopolymer. However, the additives were not used in GMA grafting because the epoxide group of GMA was not stable. In a previous paper [16], the effects of additives and solvents were described in detail. It was found that the epoxide group of GMA-grafted polymer chains in the presence of  $\text{H}_2\text{SO}_4$  was changed to diol group.

Fig. 5 shows the effects of St concentration on the grafting of St onto PNF at  $60^\circ\text{C}$  for 14 h as a function of irradiation dose. The degree of grafting (%) increased with increased irradiation dose. The maximum grafting yield was observed at  $\sim 70\%$  monomer concentration at  $60^\circ\text{C}$ , presumably due to Trommsdorff-type effects.

### 3.2. Properties of PNF with ion-exchange groups

Fig. 6 shows the XPS spectra of the survey scan spectra of (a) original PNF, (b) PNF with 1.80 mmol/g carboxylic acid (CA), (c) 1.30 mmol/g phosphoric acid (PA) (d.g. = 95%), (d) 2.30 mmol/g sulfonic acid (SA) (d.g. = 72%), and (e) 1.02 mmol/g triethylamine group (d.g. = 95%). In Fig. 6c, the characteristic band was recorded at 133 eV due to phosphoric acid group. In Fig. 6e, an additional peak was also observed at 399.0 eV due to N 1s. These results also clearly indicated the introduction of

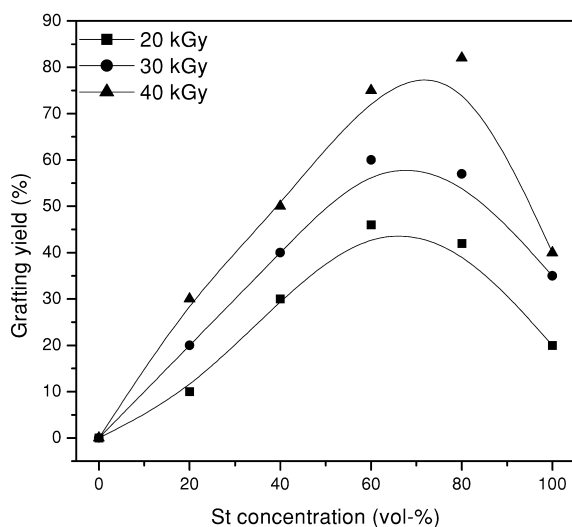


Fig. 5. Effects of St concentration and total irradiation dose on the grafting of St onto PNF at  $60^\circ\text{C}$  in MeOH for 14 h in the presence of  $\text{FeSO}_4$  ( $2.5 \cdot 10^{-3} \text{ M}$ ) and  $\text{H}_2\text{SO}_4$  (0.1 M).

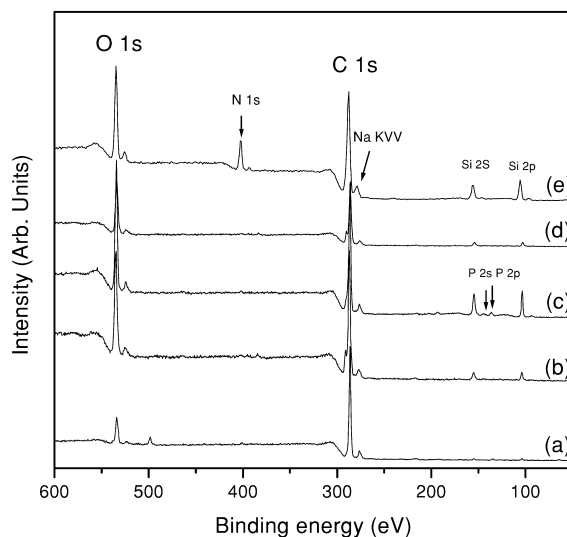


Fig. 6. XPS spectra of the survey scan spectra of the four different ion-exchange PNF membranes. (a) Original PNF; (b) PNF-CA (1.80 mmol/g); (c) PNF-PA (1.30 mmol/g); (d) PNF-SA (2.30 mmol/g); (e) PNF-TEA (1.02 mmol/g).

phosphoric acid and TEA group, respectively, onto the GMA-grafted polymer chains. However, in Fig. 6d, the sulfonic acid group was not recorded by XPS analysis. In order to examine the introduction of the sulfonic acid group, PNF-SA was analyzed by elemental analysis (EA) method. The results for PNF-SA (d.g. = 72%) by the EA method are shown in Table 1.

Fig. 7 shows the surface morphology of (a) original PNF, (b) PNF-CA (1.80 mmol/g), (c) PNF-PA (1.30 mmol/g), (d) PNF-SA (2.30 mmol/g), and (e) PNF-TEA (1.02 mmol/g). The PNF structure used in this study was the skin-core structure (PE is the skin and polypropylene is the core) as shown in Fig. 7a. The cross-sections of the four different PNF

Table 1  
Results of PNF-SA (d.g. = 72%) by EA method

$-\text{SO}_3\text{H}$ content (mmol/g) <sup>a</sup>	Carbon (%)	Hydrogen (%)	Sulphur (%)
0	85.1	14.4	0
0.85	58.7	9.6	1.2
1.80	57.6	8.8	2.6
2.30	56.1	8.4	5.9
2.60	55.6	8.1	6.0

<sup>a</sup> The  $-\text{SO}_3\text{H}$  group content was determined by mass gain.

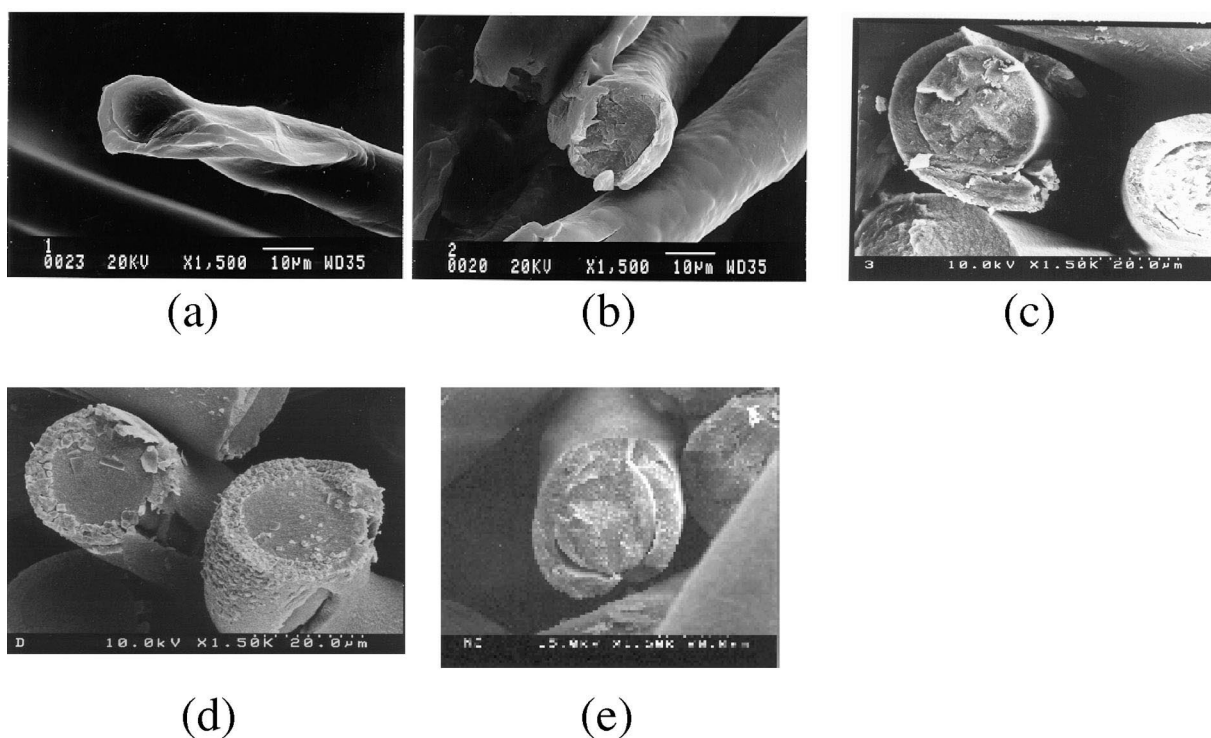


Fig. 7. Surface morphology of the four different ion-exchange PNF membranes. (a) Original PNF; (b) PNF-CA (1.80 mmol/g); (c) PNF-PA (1.30 mmol/g); (d) PNF-SA (2.30 mmol/g); (e) PNF-TEA (1.02 mmol/g).

membranes are shown as skin-core structures in Fig. 7b–e. In Fig. 7b–d, the increase in diameter is due to the growth of graft chains inside the polymer matrix. Because graft polymerization occurs mainly in the amorphous region of the matrix, the graft chain is thought to expand the amorphous region of the matrix.

Fig. 8 shows the TGA curves of (a) original PNF, (b) PNF-CA (1.80 mmol/g), (c) PNF-PA (1.30 mmol/g), (d) PNF-SA (2.30 mmol/g), and (e) PNF-TEA (1.02 mmol/g). In Fig. 8a, the first mass loss at 374°C may be considered as the polyethylene, and the second mass loss at 458°C as the polypropylene. In Fig. 8b, the mass loss was observed from 200 to 450°C. The mass loss at 250°C was due to dehydration of AAC-grafted chains, around 400°C due to decomposition of backbone polymer. In Fig. 8c–e, the difference pattern of the mass loss was observed compared to Fig. 8b.

Fig. 9 shows the relationships between the wetting (%) and the content of ion-exchange groups. The

wetting (%) increased with increased content (mmol/g) of ion-exchange groups. This indicated the introduction of hydrophilic group onto hydrophobic polymer matrix.

Fig. 10 shows the specific electrical resistance of carboxylic, sulfonic and phosphoric acid groups containing PNF as the function of the content of ion-exchange group. The specific electrical resistance decreased with increasing carboxylic, phosphoric, and sulfonic acid content. These results may indicate that the ion transfer depends on the ion-exchange capacity.

### 3.3. Application of the prepared PNF membrane

In order to examine the efficiency of the prepared PNF membrane, 0.5 M TPA solution was prepared. Fig. 11 shows the changes of the conductivity in the diluting compartment as a function of time. The PNF-CA, PNF-PA, PNF-SA, and PNF-TEA contents were 1.80, 1.30, 2.30, and 1.02 mmol/g, respective-

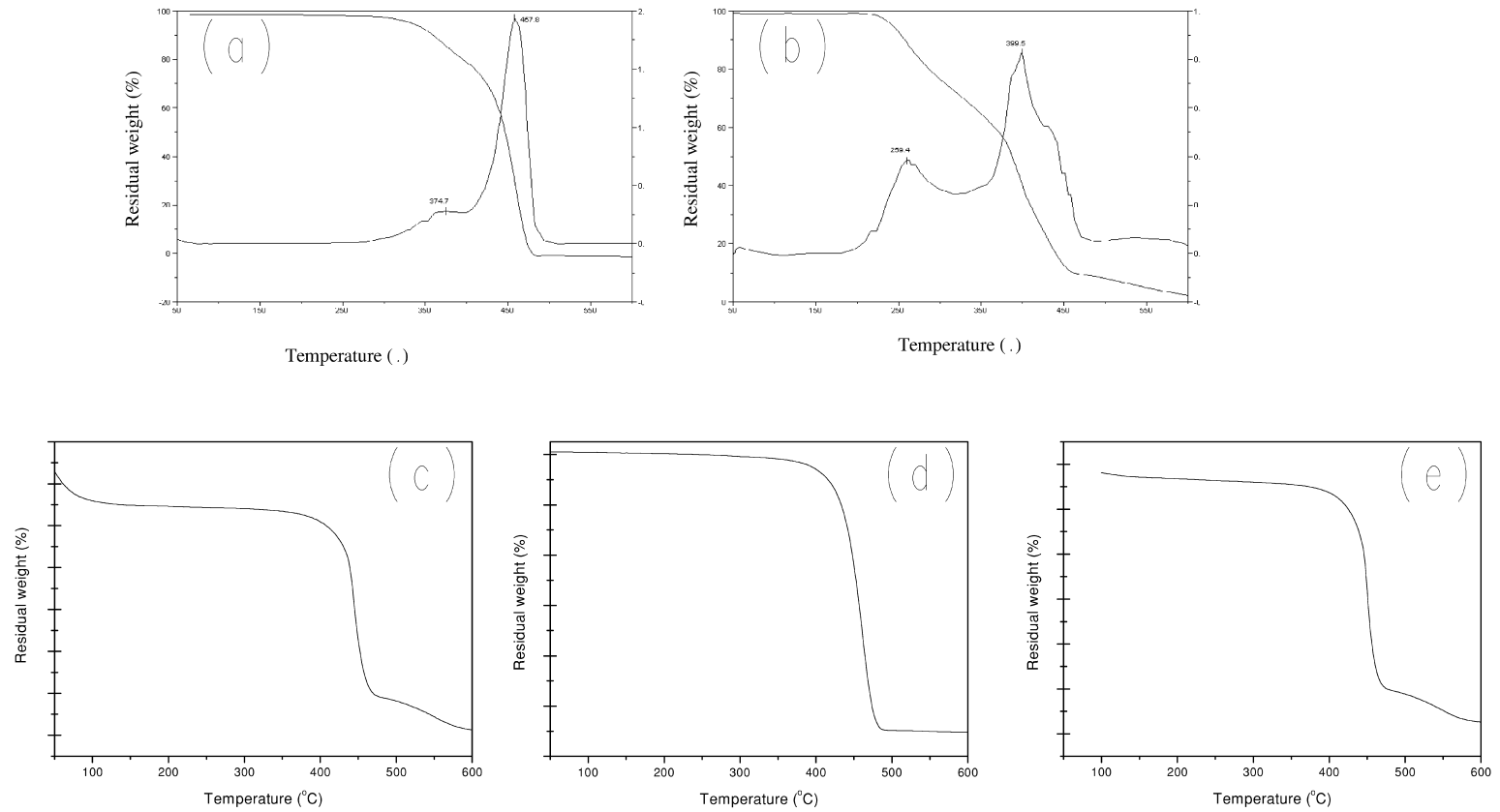


Fig. 8. TGA curves of the four different ion-exchange PNF membranes. (a) original PNF; (b) PNF-CA (1.80 mmol/g); (c) PNF-PA (1.30 mmol/g); (d) PNF-SA (2.30 mmol/g); (e) PNF-TEA (1.02 mmol/g).



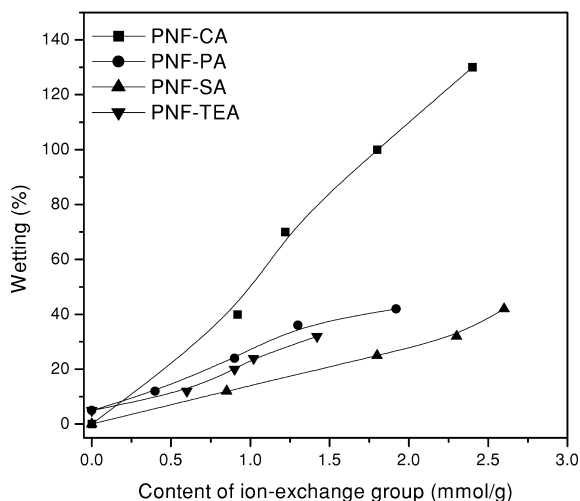


Fig. 9. Degree of wetting of the four different ion-exchange PNF membranes.

ly. In combination of cation-exchange PNF/PNF-TEA, the conductivity of the TPA solution decreased with increased desalination time. The degree of reduced conductivity in PNF-SA/PNF-PEA was  $\sim 77.8\%$  at 210 min.

In order to remove TPA from dyeing wastewater, the prepared PNF membrane was applied in dyeing wastewater obtained from the Taegu Dyeing Complex in South Korea. Fig. 12 shows the changes of

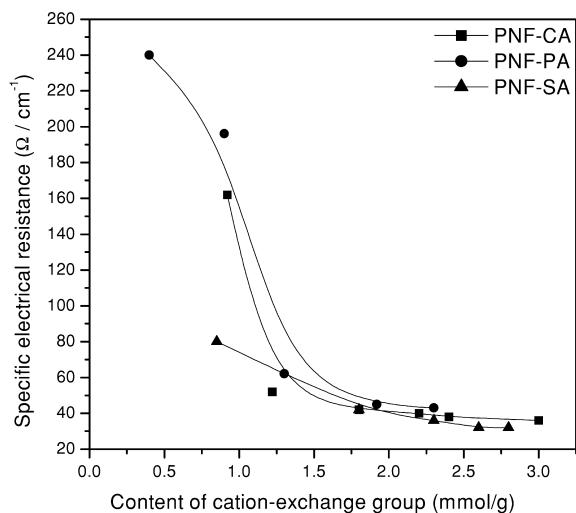


Fig. 10. Specific electrical resistance of the three different cation-exchange PNF membranes.

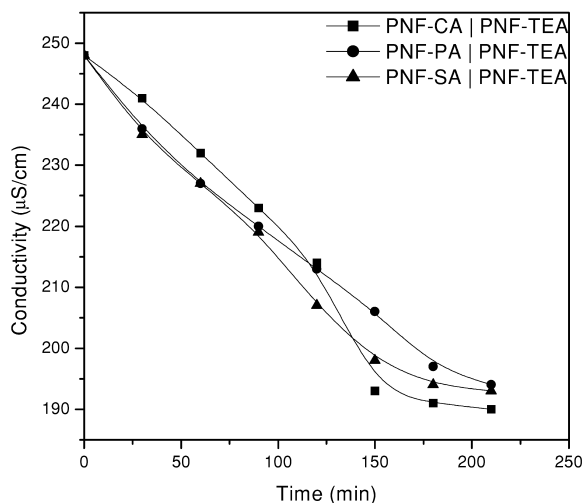


Fig. 11. Changes of conductivity in diluting compartment as a function of time.

the conductivity in diluting compartment as a function of time. PNF-CA, PNF-PA, PNF-SA, and PNF-TEA with 1.80-, 1.30-, 2.30-, and 1.02-mmol/g contents, respectively, were also used. In combination of cation-exchange PNF/PNF-TEA, the conductivity of the TPA solution decreased with increased desalination time. The degree of reduced conductivity in dyeing wastewater using PNF-SA/PNF-PEA was  $\sim 85.3\%$  at 210 min.

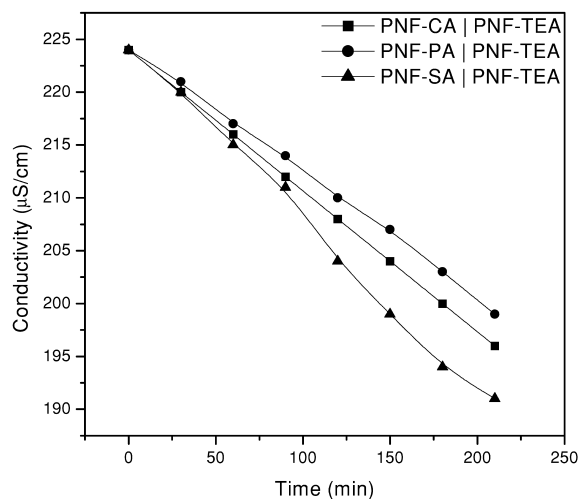


Fig. 12. Conductivity change of dyeing wastewater as a function of time.

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