

술폰산기를 갖은 코아-셸형 폴리올레핀 부직포의 전기화학적 성질

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Electrochemical Properties of Core-Shell Polyolefin Nonwoven Fabric Modified with Sulfonic Acid Group

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요 약 : 폴리올레핀 부직포는 녹는점이 ~162 °C며 구성비가 40%인 폴리프로필렌과 녹는점이 ~132 °C며 구성비가 60%인 폴리에틸렌으로 구성된것을 이용하였다. 전지격막을 제조하기 위하여 방사선그래프트 법을 이용하여 이 폴리올레핀에 스티렌을 그래프트 시킨 후 다음으로 술폰산기를 도입하였다. 술폰산기를 갖은 폴리올레핀 부직포를 XPS, SEM, DSC, TGA, 및 Porosimeter를 사용하여 특성 평가 하였다. 술폰화 반응후, 폴리올레핀 부직포에 대한 전해질 보존 (electrolyte retention), 전기저항 (electrical resistance) 및 K⁺에 대한 운반율과 같은 전기화학적 특성을 조사하였다. 그 결과 술폰산기의 함량이 증가하면 할수록 전해질 보존율은 증가하였으며 반면에 전기저항은 감소하는 사실을 알았다. 또한 술폰산기의 함량이 0.22 ~ 3.60 mmol/g 에서 K⁺의 운반율은 0.90 ~ 0.93이었다.

Abstract : The core-shell polyolefin nonwoven fabric (PNF), wherein the PNF comprises at least about 60% of polyethylene having a melting temperature at ~132 °C and no more than about 40% of second polypropylene having a lower melting temperature at ~162 °C. The sulfonic acid group for battery separators were prepared by radiation-induced grafting of styrene onto PNF and by the subsequent sulfonation of polystyrene graft chains. The sulfonated PNF was characterized by XPS, SEM, DSC, TGA and porosimeter. The electrochemical properties such as electrolyte retention, electrical resistance, and transport number of the K⁺ions were evaluated after sulfonation. It was found that the electrolyte retention increased, whereas the electrical resistance decreased with increasing sulfonic acid content. The transport number of K⁺ in PNF with sulfonic acid of 0.22 ~ 3.60 mmol/g was to be 0.90 ~ 0.93.

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Key words : polyolefin nonwoven fabric, sulfonation, battery separator, radiation-induced grafting, styrene, electrical resistance, transport number

1. Introduction

Storage batteries are generally composed of a pair of electrodes with opposite polarity and an electrolyte. In addition to the electrodes and electrolyte, one of the recognized key components in a battery is a separator. Separators are elements located between electrodes to prevent direct contact. The separator permits a free flow of electrolyte and has a large electrolyte retention volume.¹⁻³

Radiation-induced grafting is a good method to introduce functional groups into different polymer materials using a specially selected monomer. There have been many reports on the radiation graft copolymerization of polar monomers onto a hydrophobic polymer matrix to obtain the hydrophilic property for versatile applications.⁴⁻⁹ Ion-exchange membrane can be used for water desalination,¹⁰ as carriers for immobilization of medical products,¹¹ as separators in alkaline batteries,¹² etc.¹³

In a previous study,⁷ the grafting of styrene onto a polyethylene (PE) hollow fiber membrane was carried out by the pre-irradiation grafting technique. The effects of reaction time, reaction temperature, additives such as H₂SO₄ and divinylbenzene on the grafting reaction were studied. From the study, it was found that the role of additives such as ferrous salts, sulfuric acid and divinylbenzene could enhance the grafting yield in the radiation grafting process. We also prepared an ion-exchange membrane having the carboxylic acid group by the radiation-induced grafting of acrylic acid (AAc) and methacrylic acid (MAc) onto a PE film.¹⁴ The surface area, thickness, volume, water uptake, ion-exchange capacity, specific electric resistance and electrolyte flux were evaluated after the PE was grafted with AAc and MAc. It was found that the KOH diffusion flux of an AAc-grafted PE membrane had a higher diffusion flux than an MAc-grafted PE membrane. Electrical resistance of two cation-exchange membranes having AAc and MAc decreased rapidly by increasing the

degree of grafting, though two ion-exchange membranes had almost the same electrical resistance. However, the radiation grafting of styrene onto polymer matrix, wherein the polymer matrix comprises at least about 60% of a polyethylene and no more than about 40% of a second polypropylene, and the application of battery separator polymer have not been reported yet in our knowledge.

In this study, a PNF modified with the sulfonic acid group was prepared by the radiation-induced grafting of styrene and by its subsequent chemical modification for an alkaline battery separator. The electrochemical properties such as transport number and electrical resistance of the PNF modified with the sulfonic acid group were examined. Furthermore, the mechanical properties of the separator were also discussed.

2. Experimental

2.1. Materials.

The PNF with the thickness of 0.50 mm and density of ca. 161.6 gm⁻² was washed with methanol and dried in a vacuum oven at 50 °C for 12 hrs. Reagent-grade styrene (St, Merck, 99%) were used as received. The other chemicals were reagent grade.

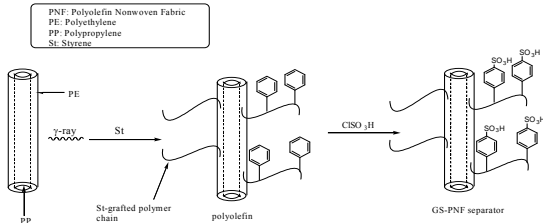
2.2. Grafting Procedure.

Scheme I shows the preparation procedure of the PNF separator by the radiation grafting of styrene (St) onto PNF. The PNF of the area 10 × 10 cm was irradiated by γ -ray from Co-60 source (Co-60 Gamma-ray Irradiator) under atmospheric pressure and ambient temperatures, and then irradiated PNF were immediately reacted with monomer. The monomer and homopolymers after grafting of St were removed with benzene using a Soxhlet apparatus. The PNF obtained by grafting copolymerization was dried in vacuum oven at 50 °C for 12 hrs. In the studies of the effects of various parameters on the grafting copolymerization, the degree of grafting is defined as

$$\text{Degree of grafting (\%)} = [(W_g - W_o) / W_o] \times 100 \quad (1)$$

where W_g and W_o denote the weights of the grafted and the ungrafted PNF separator, respectively.

Scheme I. Preparation of the GS-PNF separator for the secondary battery.



Scheme I. Preparation of the GS-PNF separator for the secondary battery.

2.3. Sulfonation of St-grafted PNF.

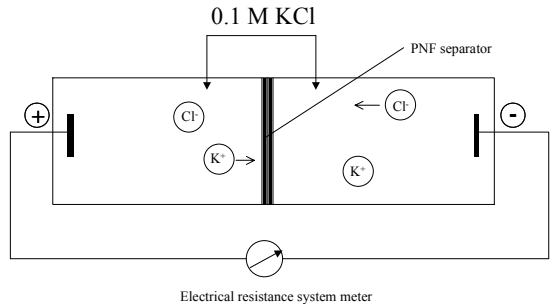
Polystyrene in St-grafted PNF reacted with ClSO_3H in H_2SO_4 or $\text{ClCH}_2\text{CH}_2\text{Cl}$ in a glass ampoule at various periods of time and concentrations. After the sulfonation, the PNF separator was washed in the order of 99% H_2SO_4 > 50% H_2SO_4 > 20% H_2SO_4 > deionized water and was dried under reduced pressure. The $-\text{SO}_3\text{H}$ group content was determined by the measurement of the total ion-exchange capacity by titration. The $-\text{SO}_3\text{H}$ form membrane was immersed in a 5% NaCl aqueous solution at room temperature for 12 hrs, and then the H^+ ion liberated from the PNF membrane was titrated with a 0.05 N NaOH aqueous solution.

2.4. Electrical Resistance

The electrical resistance of the sulfonated PNF was measured in 0.1 M KCl solution at 25°C using an Millicell-ERS apparatus (Millipore Co. in USA) as shown in Scheme II. The specific electric resistance, R_{sp} ($\Omega\text{ cm}$), was calculated by the following equation:

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

where R_{sample} denotes the electrical resistance of 0.1 M KCl solution in the presence of PNF separator, and R_{blank} denotes the electrical resistance of 0.1 M KCl solution without the PNF separator.



Scheme II. Apparatus for Electrical Resistance Measurement of Battery Separator.

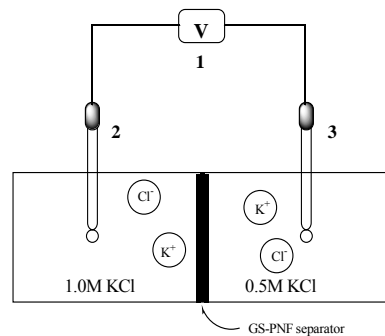
2.5. Transport Number (t_+).

Scheme III shows the apparatus for the transport number measurement of the PNF separator modified with sulfonic acid group. The PNF was placed between two compartments in the cell. KCl solutions of 0.1 M and 0.5 M were allowed to flow through the PNF separator until equilibrium was reached. The potential of sulfonated PNF was measured at 25°C using a digital voltmeter. The transport number (t_+) of K^+ of the PNF separator was calculated from the measured potential (E_m) by the following equation:

$$E_m = (2t_+ - 1) (RT/F) \ln(a_1/a_2) \quad (4)$$

Where a_1 and a_2 are average activity coefficients of KCl and F denotes Faraday's constant.

Scheme III. Apparatus for the Transport Number Measurement of the GS-PNF Separator.



1 Voltmer, 2 and 3: Ag-AgCl electrode, the area of GS-PNF separator, 1.0cm^2 .

Scheme III. Apparatus for the Transport Number Measurement of the GS-PNF Separator.

2.6. Characterization.

For scanning electron microscopy (SEM), sample of 0.5 cm × 0.5 cm size was coated with gold-palladium alloy prior to the measurement. The coated sample was then scanned by the electron beam in scanning electron microscope (JSM-840A, JEOL Co., Japan).

The x-ray photoelectrons spectra (XPS) of the samples have been obtained using ESCALab 220i (VG Scientific) equipped with a full 180° hemispherical electrostatic analyzer to examine the chemical state of the constituent elements. As a photon source, Al K_α radiation (1486.6 eV) was used. The half-width at half-maximum of the 4f_{7/2} line in the XPS spectrum of gold obtained at our XPS spectrometer 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.

The differential scanning calorimeter (DSC) of the sulfonated PNF were measured with DSC-7 Serious Thermal Analysis System (Perkin Elmer) for a heating rate of 10 °C min⁻¹ and the temperature range of 50-200 °C. Thermogravimetric analysis (TGA) of the sulfonated PNF were made on a TA instruments of the TGA 2950 model (Dupont Co.) with a heating rate of 10 °C min⁻¹ in the temperature range of 50-700 °C.

The porosity of St-grafted PNF was measured with Poresizer 9320 model (Micrometrics, 0.0006 ~ 360 mm diameter).

3. Results and Discussion

In a previous paper,⁷ we described the grafting of St onto PE hollow fiber membrane and its sulfonation for removal of heavy metal. It was found that the grafting yield was enhanced with additive such as H₂SO₄ and divinylbenzene. Furthermore, the maximum grafting yield was obtained from 70% styrene monomer concentration at 50 °C for 15 h. In radiation grafting, a role of additives such as ferrous salts and Mohr's salts decreased the homopolymerization, while the additives such as divinylbenzene and H₂SO₄ increased copolymerization.

However, a little has been reported the physical and chemical properties and electrochemical properties of the sulfonated PNF separator. In this study, the PNF separators having various grafting yield were obtained in MeOH in the presence of ferrous salt (2.5×10^{-3} M) and sulfuric acid (0.1 M) at 50 °C by varying the reaction time.

3.1. Sulfonation and Physical and Chemical Properties of the PNF Separator.

The St-grafted PNF (d.g.= 72%) was dipped into a mixture of ClSO₃H/ClCH₂CH₂Cl to make the sulfonated PNF separator, varying the parameters such as ClSO₃H concentration and solvents.

Fig. 1 shows the effects of ClSO₃H in ClCH₂CH₂Cl on the sulfonation as a function of reaction time. The high concentration of ClSO₃H in ClCH₂CH₂Cl is effective for sulfonation. Concerning the sulfonation of 72% St-grafted PNF, the content of sulfonation increased with increasing reaction time.

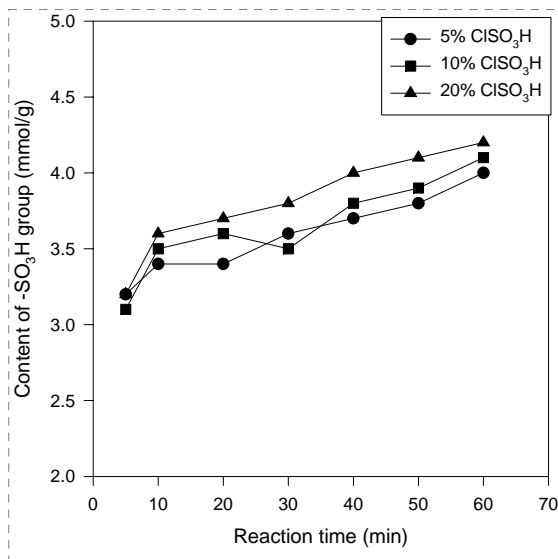


Fig. 1. Sulfonation of 72% St-grafted PNF by ClSO₃H in ClCH₂CH₂Cl.

Fig. 2 shows the effects of ClSO₃H concentration in H₂SO₄ as function of reaction time. The sulfonation of St-grafted PNF increased with increasing ClSO₃H in H₂SO₄. The content of sulfonic acid group was linearly

proportional to the reaction time. The PNF separator having sulfonic acid group above 4.0 mmol/g was damaged in $\text{ClSO}_3\text{H}/\text{H}_2\text{SO}_4$ solution.

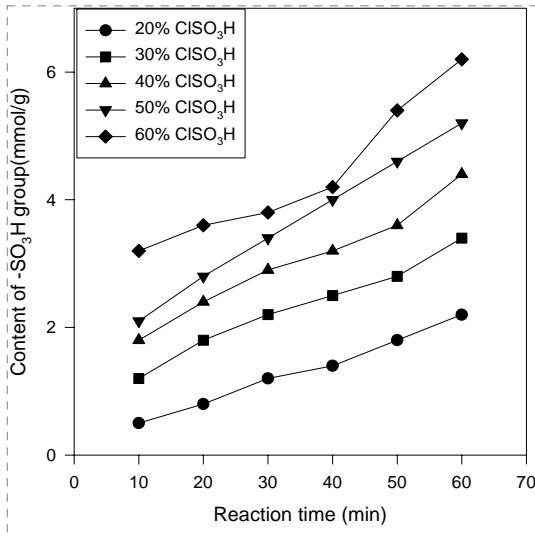


Fig. 2. Sulfonation of 72% St-grafted PNF by ClSO_3H in H_2SO_4 .

The relationship of the grafting yield and sulfonic acid content was shown in Fig. 3. The sulfonic acid group content increased with increasing grafting yield.

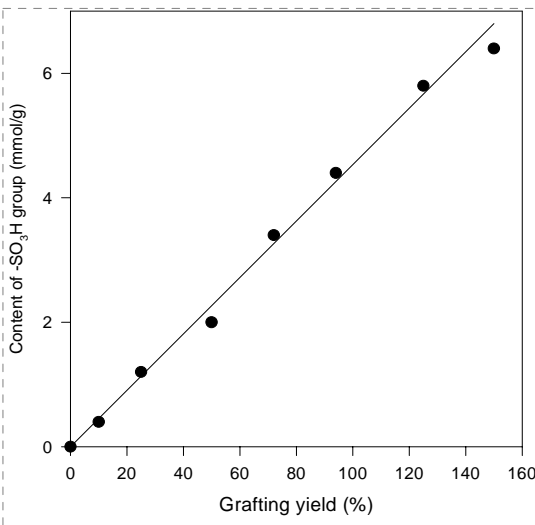


Fig. 3. Relationship between the $-\text{SO}_3\text{H}$ group content and grafting yield with 10% ClSO_3H in $\text{ClCH}_2\text{CH}_2\text{Cl}$ at 25 °C for 30 min.

Fig. 4 shows the comparison of sulfonic acid group content determined from weight gain and titration. It was found that $-\text{SO}_3\text{H}$ content determined by the weight gain accurately coincided with that by titration.

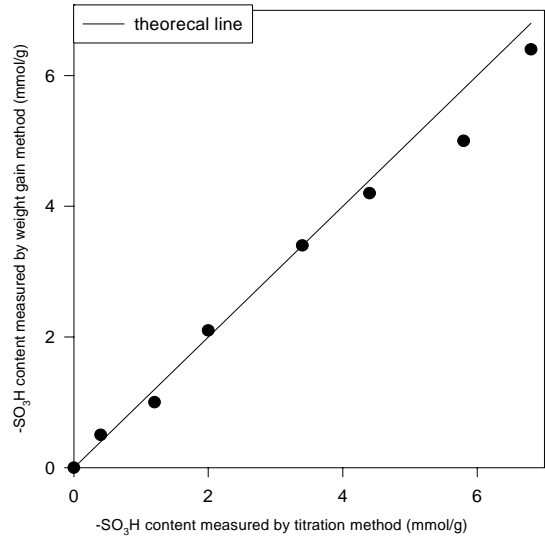


Fig. 4. Comparison of $-\text{SO}_3\text{H}$ group content measured by titration and weight gain methods.

Fig. 5 shows the XPS spectra of (a) original PNF, (b) 72% St-grafted PNF separator and (c) the PNF separator (d.g.=72%) with $-\text{SO}_3\text{H}$ of 3.40 mmol/g. The core level binding energy of C 1s of PNF is calculated to be 285.0 eV. As the PNF was grafted with styrene, an additional peak was observed at 288 - 292 eV because of the vinyl group at the grafted polymer chains. These results clearly indicated that the styrene was introduced onto PNF. The elemental analysis data of the PNF separator with sulfonic acid group are listed in Table 1. The $-\text{SO}_3\text{H}$ group content of 0.40 - 3.60 mmol/g was determined by weight gain, and the sulphur content of 1.2 - 6.0% was measured by elemental analysis. These results indicated that the sulfonic acid group was clearly introduced onto PNF.

Fig. 6 shows the scanning electron micrographs of the cross-section of (a) original PNF, (b) 72% PNF separator, and (c) the PNF separator with $-\text{SO}_3\text{H}$ of 3.40 mmol/g. In Fig. 6 (b) and (c), the increase in diameter is due to the growth of graft chains inside the polymer matrix.

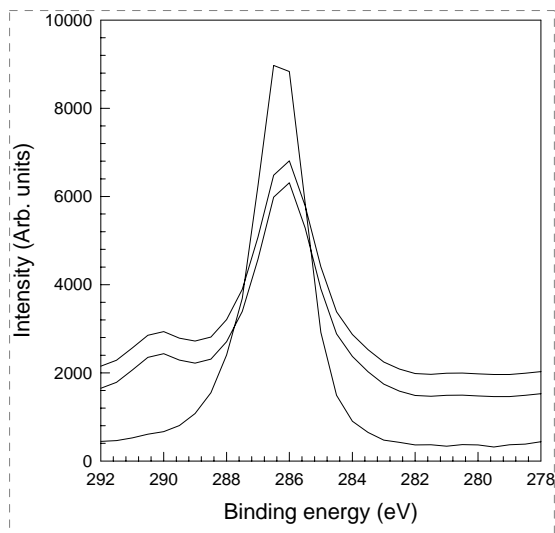


Fig. 5. XPS spectra of Cls of (a) original PNF, (b) 72% St-grafted PNF, and (c) GS-PNF with $-SO_3H$ of 3.40 mmol/g (d.g.=72%).

Table 1. Elemental Analysis of the GS-PNF Separator^{a)}

Grafting yield (%)	$-SO_3H$ Content ^{b)} (mmol/g)	Carbon (%)	Hydrogen (%)	Sulphur (%)
0	0	85.1	14.4	0
11	0.4	58.7	9.6	1.2
52	2.0	57.6	8.8	2.6
72	3.4	56.1	8.4	5.9
76	3.6	55.6	8.1	6.0

^{a)} Preirradiated by total dose=30 kGy

^{b)} The $-SO_3H$ group content was determined by weight gain

Because the graft polymerization occurs mainly in the amorphous region of the matrix, the graft chain is thought to expand the amorphous region of the matrix. In Fig. 6 (c), the outer matrix was modified with $ClSO_3H$, while the inner matrix was not modified with that.

Fig. 7 shows the DSC curves of the (a) original PNF, (b) 72% St-grafted PNF, and (c) the PNF separator (d.g.=72%) with $-SO_3H$ group of 3.40 mmol/g. The sample weights was set 5.0 mg. In Fig. 7(a), (b), and (c), it was found that two melting temperatures due to polyethylene and polypropylene. The first melting temperature was observed at 132 °C due to polyethylene

and the second melting temperature at 162 °C due to polypropylene. In Fig. 7, the area of the first melting temperature and second melting temperature was about ca. 60% and 40%, respectively.

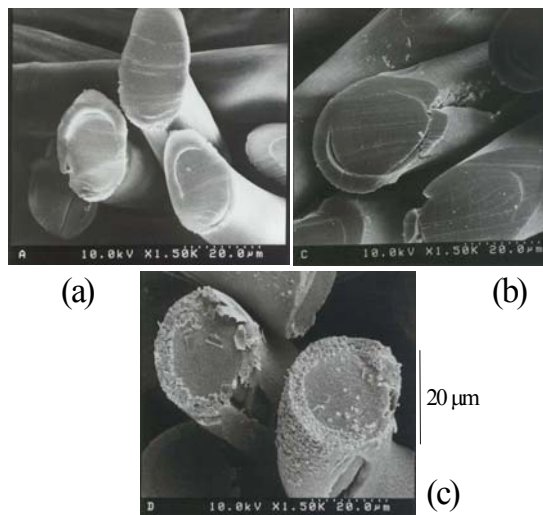


Fig. 6. Scanning electron photomicrograph of the cross-section of (a) original PNF, (b) 72% St-grafted PNF, and (c) S-PNF with $-SO_3H$ of 3.40 mmol/g (d.g.=72%).

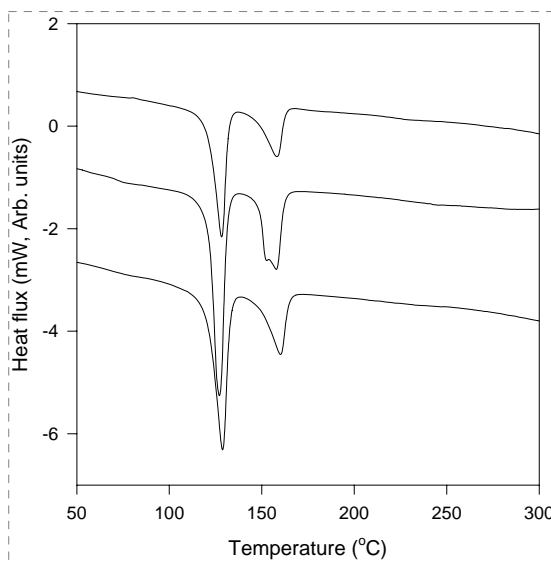


Fig. 7. DSC curves of (a) original PNF, (b) 72% St-grafted PNF, and (c) GS-PNF with $-SO_3H$ group of 3.40 mmol/g (d.g.=72%).

Fig. 8 shows the DTA thermal curves of (a) original PNF, (b) St-grafted PNF, and (c) PNF separator modified with $-SO_3H$ group of 3.40 mmol/g. The three endothermic peaks were observed. The first peak at around 132 °C can be explained as the polyethylene, and the second peak at 162 °C as the polypropylene, third peak around 450 °C due to degradation of polymer backbone.

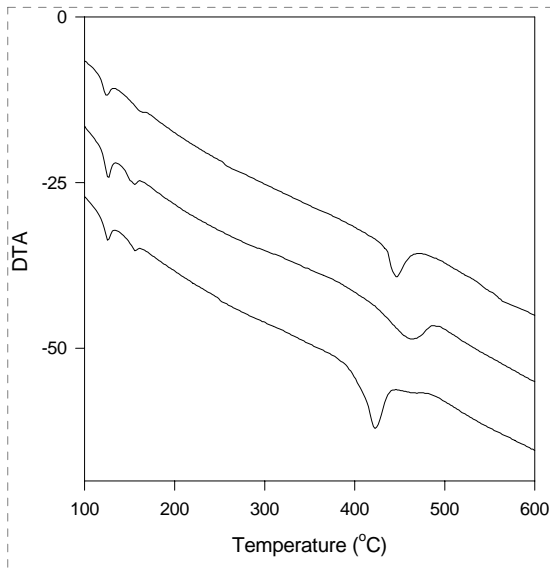


Fig. 8. DTA curves of (a) original PNF, (b) 72% St-grafted PNF, and (c) GS-PNF with $-SO_3H$ group of 3.40 mmol/g (d.g.=72%).

Fig. 9 shows the intrusion data (a) and the pore size distribution (b) of the original PNF, St-grafted PNF, and the PNF separator with $-SO_3H$ group of 3.40 mmol/g by porosimeter, respectively. In Fig. 9(a), the total intrusion volume, total pore area, bulk density, and porosity increased with increasing the grafting yield. In Fig. 9(b), St-grafted PNF consisted mostly of the pore diameters ranging from 10^2 to 10^5 mm. The pore volume of 0.02 mL/g for the ungrafted PNF was expanded to 0.13 mL/g for 72% grafting yield. However, the pore volume of the PNF separator with the $-SO_3H$ group (d.g. = 72%) was suddenly decreased to 0.0015 mL/g. These results seem to be due to introduce of sulfonic acid group onto the pore of PNF.

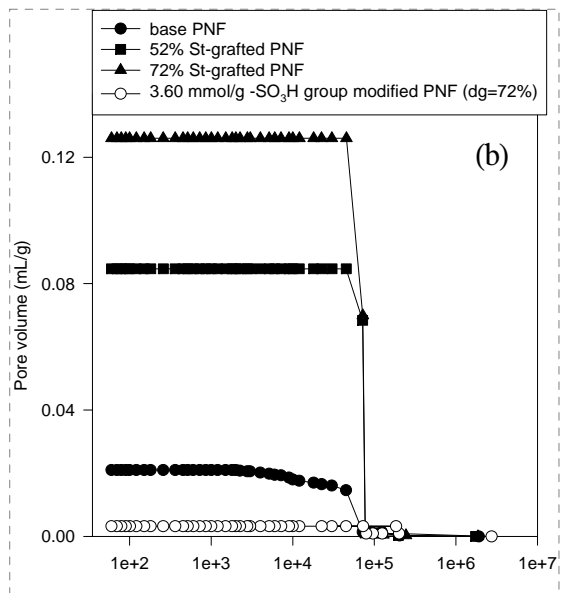
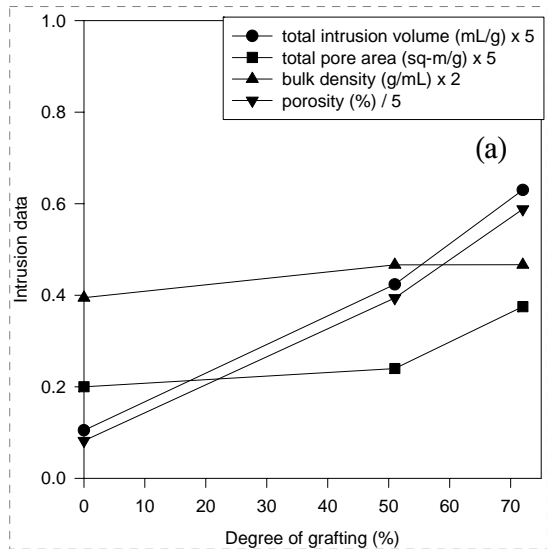


Fig. 9. Intrusion data (a) and pore diameter distribution (b) of the PNF separator.

3.2. Electrochemical properties of the sulfonated PNF separator.

Table 2 shows the electrical properties of specific electric resistance and transport number of PNF separator with $-SO_3H$ group (d.g.=72%). The specific electrical resistance decreased with increasing the content of $-SO_3H$ group. These indicated the introduction of hydrophilic

Table 2. Electrochemical Properties of the GS-PNF Separator^{a)}

Content of -SO ₃ H group (mmol/g)	Specific electric resistance (Ω cm)	Transport number (t ₊) (0.5/1.0 M KCl)	Electrolyte retention ^{b)} (%)
-	Not reading	-	-
0.20	150	0.90	8.7
1.95	54	0.92	16.0
3.40	25	0.93	24.0
3.62	23	0.93	24.8

a) Degree of grafting (d.g.=72%). b) Determined in 30%(wt.%) KOH solution

Table 3. Mechanical Properties of GS-PNF Separator^{a)}

Degree of grafting (%)	Content of sulfonic acid ^{b)} (mmol/g)	Thickness (mm)	Tensile strength ^{c)} (N/m ²)
0	-	0.50	5.8(7.7)X10 ⁶
11	0.22	0.55	4.7X10 ⁶
51	1.97	0.85	4.9X10 ⁶
72	3.40	1.05	4.9X10 ⁶
76	3.60	1.15	5.2X10 ⁶

a) Preirradiated by total dose=30 kGy. b) Condition of sulfonation: 30% CISO₃H in H₂SO₄ for 30 min

c) Peak point. The non-irradiated data is shown in parentheses.

group onto hydrophobic PNF separator. In general, the battery separator is required electrical resistance even with 60 W/cm² in given battery cell. The transport number of K⁺ in the sulfonated PNF separator was in the range of 0.90-0.93.

Table 3 shows the mechanical properties of thickness and tensile strength of the PNF separator with -SO₃H. The electric retention of the PNF separator with -SO₃H group increased with increasing sulfonic acid group content. The tensile strength was in the range of 4.8×10⁶-5.9×10⁶ N/m².

4. Conclusions

The PNF separator having the sulfonic acid group for battery separators were prepared by the radiation-induced grafting of styrene onto the PE/PP separator and their chemical modification. From the results, the conclusions are as follows:

- (1) The surface area and thickness of the PNF separator increased with increasing grafting yield.
- (2) The electrolyte retention (%) of the PNF separator increased by increasing sulfonic acid group content.
- (3) Electrical resistance of the PNF separator decreased by increasing sulfonic acid group content.
- (4) The transport number of K⁺ in the sulfonated PNF separator was in the range of 0.90-0.93.

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