

Introduction of Carboxylic Acid Group to Polypropylene Fabric for Battery Separator

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Abstract—Carboxylic acid group was introduced by radiation-induced grafting of acrylic acid (AAc) onto a polypropylene (PP) nonwoven fabric for a battery separator. The AAc-grafted PP nonwoven fabric was characterized by IR, SEM, and TGA. The wetting speed, electrolyte retention, electrical resistance, and tensile strength were evaluated after grafting of AAc. It was found that the wetting speed, electrolyte retention, thickness, and ion-exchange capacity increased, whereas the electrical resistance decreased with increasing grafting yield. The elongation of AAc-grafted PP nonwoven fabric decreased with increasing grafting yield in dry state, whereas the elongation increased in wetting state.

Key words : Polypropylene Nonwoven Fabrics, Radiation-Induced Graft Copolymerization, Acrylic Acid, Ion-Exchange Capacity, Electrolyte Retention, Electrical Resistance

INTRODUCTION

Storage batteries are generally composed of at least one pair of electrodes of opposite polarity and an electrolyte. The battery may employ an acid or an alkaline electrolyte. Conventional acid batteries are exemplified by the lead-acid (sulfuric acid) batteries used in automobiles and the like. Rechargeable batteries include secondary batteries such as nickel-zinc, nickel-cadmium, mercury-zinc and the like [Meeus et al., 1991; Hishimura et al., 1990; Hosako et al., 1989; Sakai et al., 1990; Suzuki et al., 1988].

In addition to the electrodes and electrolyte, one of the recognized key components in a battery is the separator. Separators are elements located between electrodes to prevent direct contact between plates of opposite polarity. The separator permits the free flow of electrolyte and requires a large electrolyte retention volume while inhibiting active materials from passing through it, causing unwanted bridging of plates of opposite polarity [Giovannoni et al., 1989; Wen-Tong, 1988].

Graft polymerization has been considered as a general method for the modification of the physical and chemical properties of polymer materials, and is of particular interest for synthesis of hydrophilic membranes. Polymers such as polyethylene, polypropylene and their copolymer for a battery separator require a large electrolyte retention, excellent chemical and thermal stability in electrolyte and high electrical conductivity [Kaur et al., 1998; Ishigaki et al., 1982].

In this study, polypropylene nonwoven fabric was modified by radiation-induced grafting of acrylic acid (AAc) to introduce hydrophilic group. The AAc-grafted PP nonwoven fabric was characterized by IR, SEM, and TGA. The wetting speed, electrolyte retention, electrical resistance, and tensile strength were eval-

uated after grafting of AAc.

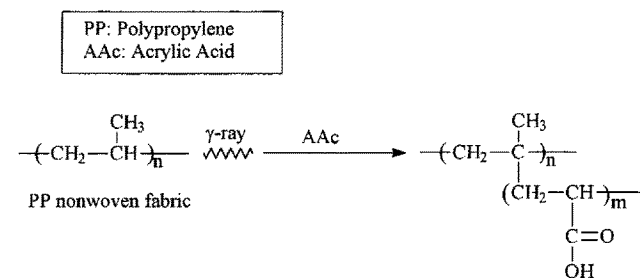
EXPERIMENTAL

1. Materials

Polypropylene nonwoven fabric (PP) 0.40 mm thickness, weighing about 7.0 g/m² was pressed with the pressure of 1,000 kg/cm² at 125 °C for 2 min using hot press (Carver Co. in USA). The PP nonwoven fabric with 0.20 mm thickness, weighing 7.0 g/m² was used as a based material for the grafting, washed with methanol and dried in vacuum oven at 50 °C for 8 h. Reagent-grade acrylic acid (AAc, Junsei, 99 %) was used as received. The other chemicals were reagent grade.

2. Grafting Procedure

Scheme 1 shows the preparation procedure of PP nonwoven fabric separator by the radiation grafting of AAc onto PP. The PP of 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 PP were immediately reacted with monomer. The monomer and homopolymers after grafting of AAc were removed with hot water, subsequently with MeOH. PP obtained by grafting copolymerization was dried in vacuum



Scheme 1. Preparation of PP nonwoven fabric separator for the secondary battery.

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oven at 50 °C for 12 h. 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 PP, respectively.

3. Ion-Exchange Capacity (mmol/g)

The content of the ion-exchange group was determined from the measurement of the total ion-exchange capacity by back titration method. AAc-grafted PP fabric was immersed in 0.05 N NaOH aqueous solution at room temperature for 12 h, and then the hydroxyl ion remaining in the solution was titrated with 0.025 N HCl aqueous solution.

4. Electrolyte Retention (%) and Wetting Speed (mm/min)

The electrolyte retention of AAc-grafted PP nonwoven fabric of size 2×10 cm was measured in 35 % KOH solution.

$$\text{Electrolytic Retention (\%)} = [(W_w - W_g) / W_g] \times 100 \quad (2)$$

where W_w is the weight of the grafted fabric in the wetting condition.

The wetting speed (mm/min) of AAc-grafted PP fabrics of size 2×10 cm was measured in 35 % KOH solution for 30 min.

5. Electrical Resistance (Ω cm)

The electrical resistance of the grafted PP was measured in 0.5 M NaCl solution at 25 °C using an Millicell-ERS apparatus (Millipore Co. in USA). The specific electric resistance, R_p (Ω cm), was calculated by the next equation :

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

where R_{sample} denotes the electrical resistance of 0.5 M NaCl solution in the presence of PP separator, and R_{blank} denotes the electrical resistance of 0.5 M NaCl solution without the separator. The T and S are the thickness and surface area of PP separator.

RESULTS AND DISCUSSION

Several types of additives are currently being used in a wide range of the radiation graft polymerization process. In the graft polymerization of monomers, they increase grafting yield and reduce homopolymerization [Choi et al., 1998; Dworjanyn et al., 1993; Gupta et al., 1989; Haddadai et al., 1995]. In the presence of sulfuric acid, the grafting reaction can be enhanced by partitioning effect [Nho et al., 1997; O'Neill, 1972]. However, little has been reported on the grafting condition of AAc onto PP nonwoven fabric.

Fig. 1 shows the effects of AAc concentration and additive on the grafting of AAc onto PP nonwoven fabric in MeOH or H_2O at 50 °C for 3 h. The PP nonwoven fabric in this experiment was preirradiated with a total dose of 50 kGy. As shown in Fig. 1, with the addition of sulfuric acid and $FeSO_4$, the grafting yield was much enhanced.

When polypropylene is subjected to ionizing radiation in air, trapped radicals or peroxy radicals are generally formed. The

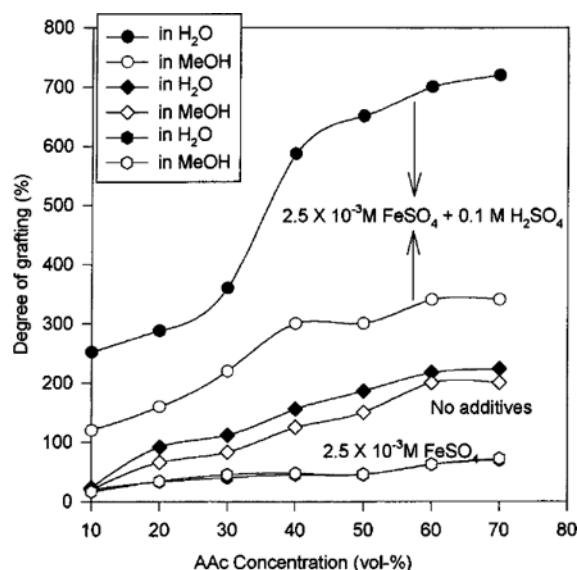


Fig. 1. Effects of AAc concentration and additive on the grafting of AAc onto PP nonwoven fabric at 50 °C for 3 h. Total dose : 50 kGy.

yield of free radicals and peroxy radicals is varied depending on the presence of oxygen when polypropylene is irradiated. The schematic mechanism of polypropylene during irradiation is as follows :



In these schemes, P and P^{\cdot} represent the polypropylene chain and polypropylene radicals produced by irradiation, respectively. Irradiation in air leads to the formation of hydroperoxide species. The $^{\cdot}OH$ radicals formed from hydroperoxide species in the thermal decomposition reaction initiate homopolymerization. It is possible to obviate this problem by using a reducing agent, e.g., metallic salt, which decomposes the peroxy species. In a previous work [Choi et al., 1998], only Fe^{2+} ions were used as the reducing agent to decompose the hydroperoxides, thereby converting hydroxyl radicals to inactive hydroxide ions.



Metallic salt plays a important role in decomposing the hydroperoxides by a redox reaction, as shown in Eq. (10). As shown Fig. 1, with the addition of both sulfuric acid and salt, the grafting was much enhanced. Metallic salt also takes part in the deactivation process of the PO^{\cdot} radical as follows :



This reaction leads to a reduction in the grafting reaction. Therefore, it was examined in this experiment whether FeSO_4 leads to a synergic effect on grafting in the presence of sulfuric acid. From the result it was assumed that sulfuric acid accelerated the decomposition of hydroperoxide in the presence of a metallic salt such as Fe^{2+} , in which backbone radicals are formed and initiated the grafting reaction, as shown in Eq. (10). By the addition of sulfuric acid in the grafting solution, the OH^- accumulated in Eq. (10) can be consumed by the reaction with H^+ , which is dissociated from sulfuric acid. Therefore, Eq. (10) can progress in the presence of acid by the principle of Le Chatelier.

Fig. 2 shows the relationship between the solvents (water, methanol, and water-methanol mixture) and monomer concentration. The PP nonwoven fabric used in this experiment was irradiated by a total dose of 50 kGy. The degree of grafting increased with increasing AAc concentration. Large grafting yield was obtained in H_2O only. This is explained by the fact that acrylic acid is more soluble in water than in methanol and water-methanol mixture. On the other hand, the backbone radical (POO^\bullet) may undergo swelling in water which facilitates accessibility of the monomer to the active sites. Water has a zero chain transfer, constant and consequently various chain transfer reactions are minimal. Decrease of grafting of AAc in MeOH is due to the fact that some unwanted reactions involving chain transfer with MeOH occur. Grafting yield of AAc onto PP by diluent is in the following order :

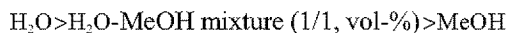


Fig. 3 shows the effects of reaction temperature and reaction time on the grafting of AAc onto nonwoven PP fabric at the reaction temperature of 30, 50, 70 °C in MeOH. The grafting at 70 °C was high, compared to 30 °C and 50 °C. The reason for this is due to radicals formed when the peroxide formed during irradiation in air is decomposed at a temperature of 70 °C. Therefore, a relative-

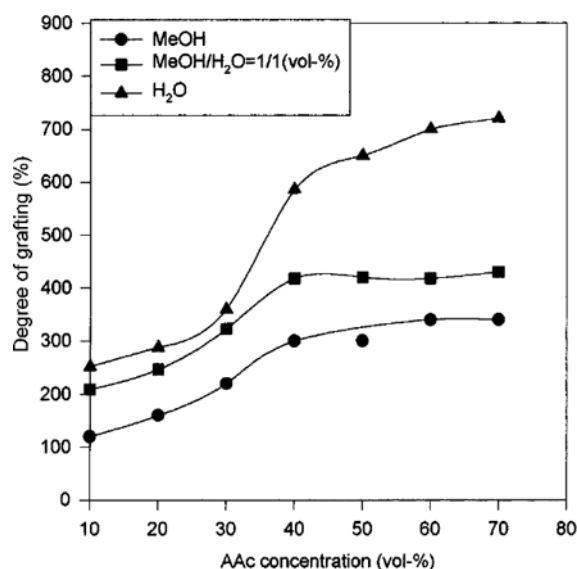


Fig. 2. Effects of AAc concentration and solvent on the grafting of AAc onto PP nonwoven fabric at 50 °C for 3 h. Total dose: 50 kGy; $\text{FeSO}_4=2.5 \times 10^{-3}$ M; $\text{H}_2\text{SO}_4=0.1$ M.

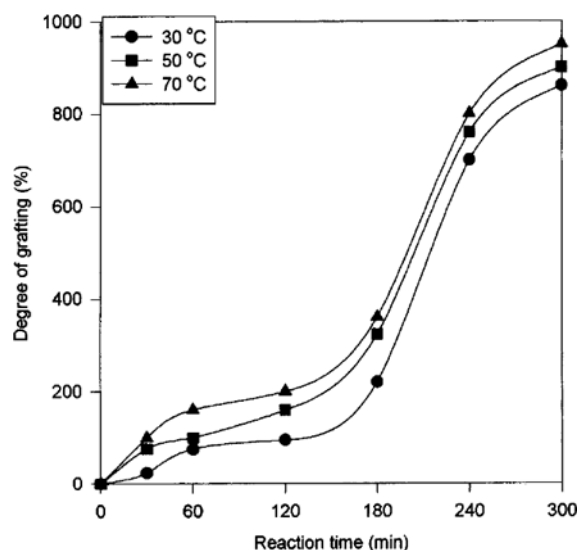


Fig. 3. Effects of reaction temperature and reaction time on the grafting of AAc onto PP nonwoven fabric in H_2O . Total dose: 50 kGy; $\text{FeSO}_4=2.5 \times 10^{-3}$ M; $\text{H}_2\text{SO}_4=0.1$ M; AAc concentration=30 % (vol%).

ly higher temperature is required to obtain a high grafting yield, indicating that it is an important factor for controlling grafting yield. Fig. 4 shows the effects of AAc concentration and total radiation dose on the grafting of AAc onto PP nonwoven fabric. In the presence of metallic salt and sulfuric acid, the reaction temperature was set at 50 °C for 3 h. Grafting increased with increasing total radiation dose.

In a previous work [Choi et al., 1998], the grafting of AAc onto polyethylene film in the presence of ferrous salt, and sulfuric acid was examined. It was found that the grafting yield in the presence of additives was enhanced. However, little has been reported on

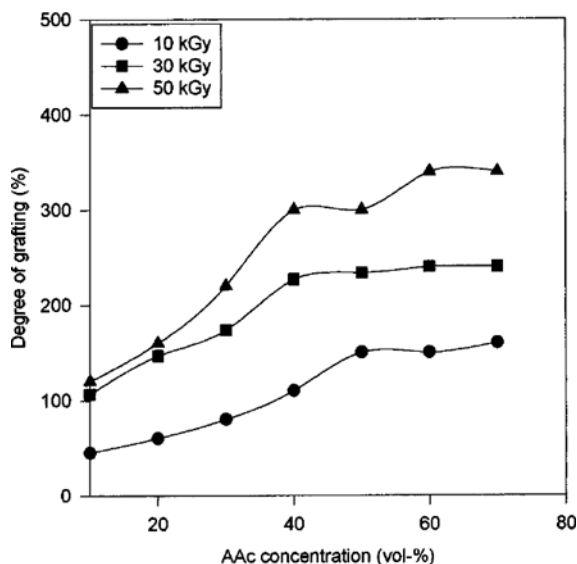


Fig. 4. Effects of AAc concentration and total radiation dose on the grafting of AAc onto PP nonwoven fabric in MeOH at 50 °C for 3 h. $\text{FeSO}_4=2.5 \times 10^{-3}$ M; $\text{H}_2\text{SO}_4=0.1$ M.

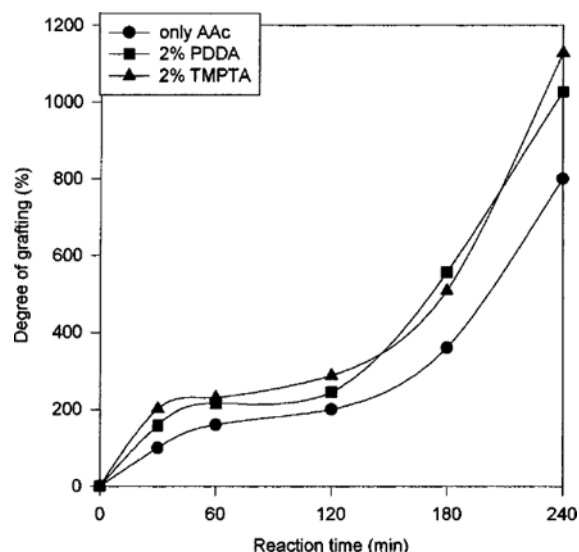


Fig. 5. Effects of additive and reaction time on the grafting of AAc onto PP nonwoven fabric at 50 °C in MeOH.

$\text{FeSO}_4 = 2.5 \times 10^{-3}$ M; $\text{H}_2\text{SO}_4 = 0.1$ M; AAc concentration = 30 % (vol %).

the grafting condition of AAc onto PP nonwoven fabric in the presence of hydrophilic additives such as 1,3-propanediol dimethacrylate (PDDA) and trimethylol propane triacrylate (TMPTA), ferrous salt.

Fig. 5 shows the effects of additive and reaction time on the grafting of AAc onto PP nonwoven fabric in MeOH at 50 °C. PDDA and TMPTA having two and three vinyl groups were used for examination of the effect of multifunctional monomer on the grafting yields. The addition of PDDA and TMPTA to the grafting solution enhanced the grafting yield. The inclusion of PDDA, TMPTA, in the presence of sulfuric acid and ferrous salt increased the grafting yield for all solutions studied. The enhancement of grafting yield by multifunctional monomer appeared to accelerate grafting chain branching.

Fig. 6 shows the IR spectra of the original PP and the grafted PP. The IR sample was prepared at 150 °C in the pressure 5,000 kg

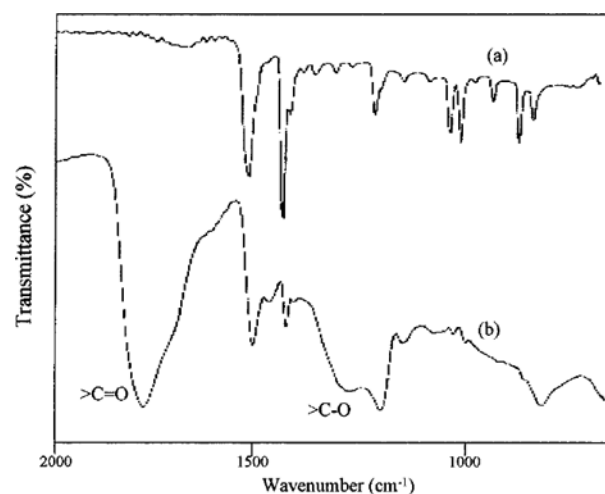


Fig. 6. FTIR-ATR spectra of (a) base PP and (b) 200 % AAc-grafted PP nonwoven fabric.

per cm^2 for 15 min by hot press. The infrared spectra of original PP film and 200 % AAc-grafted PP film were compared. In the IR spectrum of AA-grafted PP film, a characteristic peak at 1,730 cm^{-1} assigned to carbonyl group of poly(AAc) was observed. No such peak was observed in IR spectrum of the original PP film.

Fig. 7 shows the surface morphology of (a) original PP and (b) 200 % AAc-grafted PP nonwoven fabric. The increase in diameter is due to the growth of graft chains inside the polymer matrix. 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.

Fig. 8 shows the TGA curves of (a) ungrafted PP and (b) 200 % AAc-grafted PP nonwoven fabrics. The considerable change in the thermal behavior of PP nonwoven fabric occurred after grafting. In Fig. 8(b), three weight losses with temperature were shown. The 1st weight loss under 100 °C can be interpreted as the loss of moisture, the 2nd weight loss at 268 °C can be explained as the dehydration of grafted poly(AAc), and the 3rd weight loss at 397 °C can be due to a decarboxylation of grafted poly (AAc) onto polymer back-bone as shown below scheme.

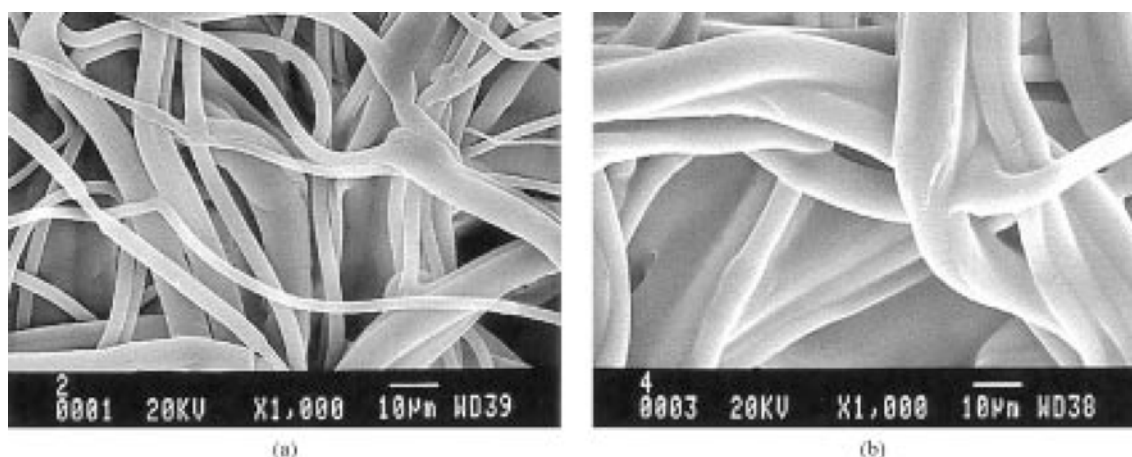


Fig. 7. Surface morphology of (a) base PP and (b) 200 % AAc-grafted PP nonwoven fabric.

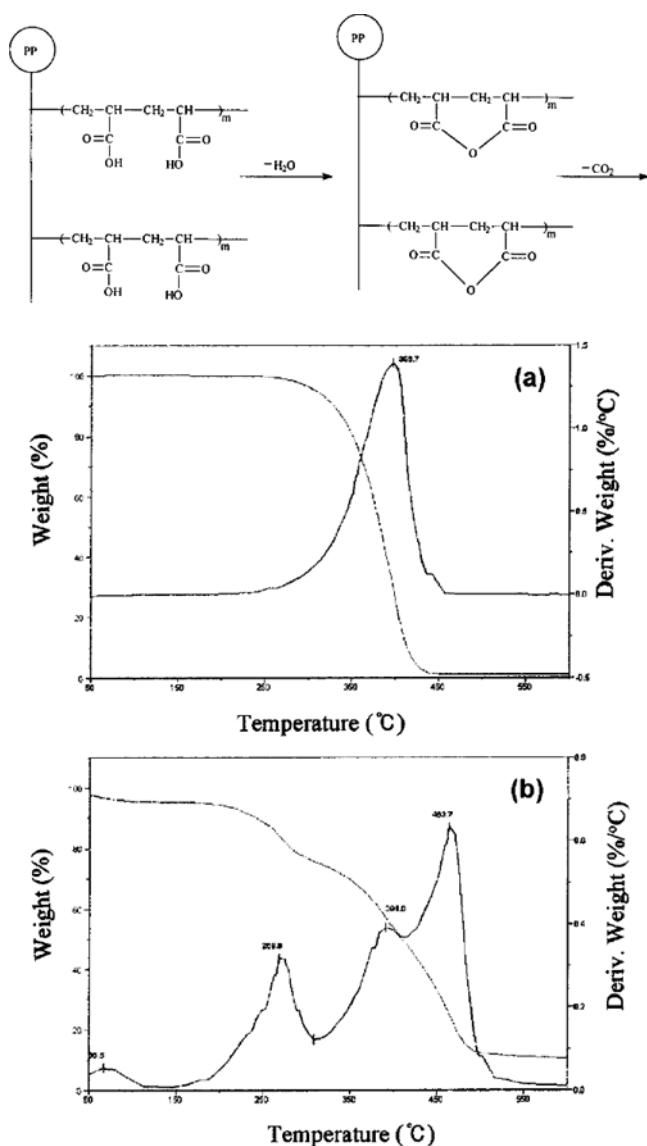


Fig. 8. TGA curves of (a) base PP and (b) 200 % AAC-grafted PP nonwoven fabric.

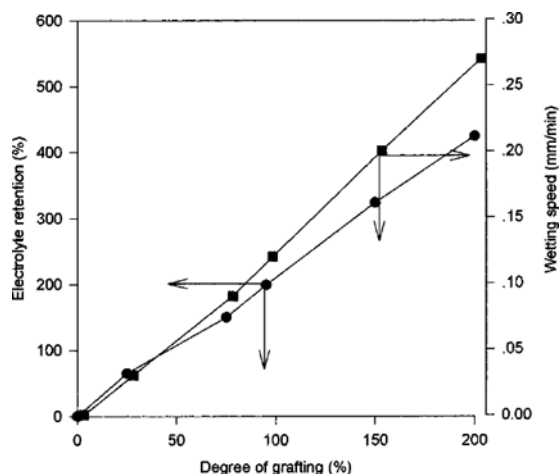


Fig. 9. Electrolyte retention and wetting speed of AAC-grafted PP nonwoven fabric.

Table 1. Mechanical properties of PP and AAC-grafted PP nonwoven fabric^{a)}

Degree of grafting (%)	Thickness (mm)	Tensile strength (kgf/cm ²)	Elongation ^{b)} (%)
0	0.20	12.5	59.2
24	0.22	11.4	45.0(75.0)
75	0.26	9.6	35.2(82.8)
95	0.32	7.8	59.2(117.0)
150	0.32	7.8	30.2(157.0)
200	1.32	1.8	19.6(195.5)

^{a)}Preirradiated by total dose 50 kGy.

^{b)}In parentheses are shown elongation data of determination in wetting state.

Fig. 9 shows the relationship between the electrolyte retention and the degree of grafting, between the wetting speed and the degree of grafting, respectively. The electrolyte retention increased with increasing the degree of grafting. The wetting speed increased with increasing the degree of grafting.

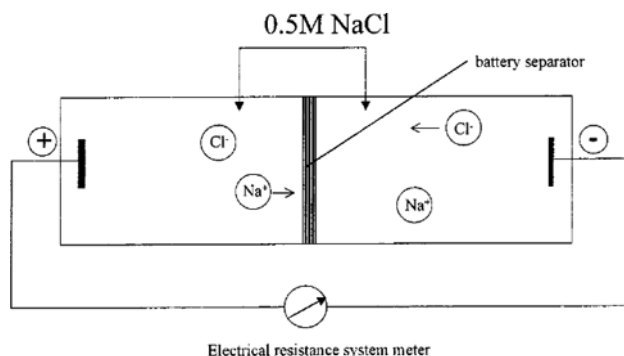
Table 1 shows the mechanical properties such as thickness, tensile strength, and elongation of PP and AAC-grafted PP nonwoven fabric. The tensile strength was decreased with an increase in the degree of grafting. On the other hand, elongation of AAC-grafted PP nonwoven fabric decreased with increasing grafting yield in the dry state, whereas the elongation increased in the wetting state. The increase of elongation of AAC-grafted PP nonwoven separator is due to the hydrogen bonding between the carboxylic acid on the grafted AAC.

Table 2 shows the electrochemical properties such as ion-

Table 2. Electrochemical properties of base PP and AAC-grafted PP nonwoven fabric^{a)}

Degree of grafting (%)	Swelling thickness (mm)	Ion-exchange capacity (mmol/g)	PP separator resistance (Ω/cm ²)
0	0.20	0	Not reading
24	0.26	0.9	120
75	0.38	1.4	36
95	0.75	1.9	21
150	1.05	2.3	32
200	2.30	3.6	30

^{a)}Preirradiated by total dose 50 kGy.



Scheme 2. Apparatus for electrical resistance measurement to battery separator.

exchange capacity and specific electrical resistance of AAc-grafted PP nonwoven fabric. It was found that the ion-exchange capacity of AAc-grafted PP nonwoven fabric increased with increasing grafting yield. The specific resistance decreased with increasing degree of grafting.

CONCLUSIONS

PP battery separators having carboxylic acid group for the secondary battery were prepared by radiation-induced grafting of acrylic acid onto a polypropylene nonwoven fabrics. From the results, the conclusion was as follows :

(1) The PP nonwoven fabric grafted with AAc was successfully prepared.

(2) It was found that the wetting speed, electrolyte retention and thickness increased with increasing the degree of grafting, whereas the electrical resistance decreased.

(3) The elongation of AAc-grafted PP nonwoven fabric decreased with increasing grafting yield in dry state, whereas the elongation increased in wetting state.

(4) The ion-exchange capacity of AAc-grafted PP nonwoven fabric increased with increasing grafting yield.

ACKNOWLEDGEMENT

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