

Preirradiation Grafting of Acrylic and Methacrylic Acid onto Polyethylene Films: Preparation and Properties

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Synopsis

The method of preirradiation grafting of acrylic acid and methacrylic acid onto polyethylene films was studied. The trapped radicals and hydroperoxides or diperoxides appeared to be able to induce graft polymerization. Mohr's salt was added to depress homopolymerization. The influences of crystallinity, dosage, and storage period on the grafting behavior were investigated from the viewpoint of practical application. At elevated temperature, the degree of grafting increased rapidly with reaction time initially, and then leveled off to the value of final percent grafting. Dosage and storage periods had greater extent of influence on the final percent grafting of LDPE than on that of HDPE. Electrical properties, transport properties, and mechanical properties were measured to compare the differences between acrylic-acid- and methacrylic-acid-grafted copolymer films. It was found that the properties of methacrylic-acid-grafted copolymer film was superior to those of acrylic-acid-grafted copolymer film, especially in electrical conductivity. The KOH diffusion test confirmed that grafting occurred not only on the surface but also in the interior of the polymer matrix, and the grafting is believed to proceed from the surface to the interior of the matrix.

INTRODUCTION

Graft polymerization provides a convenient method for the synthesis of semipermeable membranes since commercially available polymer film can be used as a substrate. Co⁶⁰- γ -ray-induced grafting of hydrophilic monomer onto hydrophobic substrate is one of the more promising methods. The grafting of acrylic acid onto polyethylene have been studied by many workers.¹⁻¹³ These include both the direct grafting method and the preirradiation method. In this study, the preirradiation method was utilized to synthesize ion exchange membranes for alkaline battery separator. Methacrylic acid and acrylic acid were used in our experiment to study the properties of these grafted copolymer films.

Cellulose films have long been used as a separator in alkaline batteries. However, they suffer from significant degradation as a result of reaction with battery constituents, thus limiting battery life and performance. The acrylic-acid-grafted polyethylene film has been found to be quite useful as a battery separator in the alkaline batteries.^{14,15} In this study, the methacrylic-acid-grafted polyethylene film was found superior to the acrylic-acid-grafted one. Essentially, the separator or membrane is situated between the electrodes to provide a path for ions. Besides, it is also required to restrict the transference of ionic species which, if deposited on an electrode, will give rise to undesirable side reactions. To prepare such an excellent material, three kinds of polyethylene films were used as substrate and

grafted with acrylic acid and methacrylic acid separately. The grafting behavior was investigated from the practical point of view.

EXPERIMENTAL

Materials

Polymers. The materials used as grafting substrates included: (1) high density polyethylene film (HDPE) with density 0.953 g/cm³, melt index 0.1 g/10 min, and thickness 0.020 mm; (2) low density polyethylene film (LDPE) with density 0.921 g/cm³, melt index 3.0 g/10 min, and thickness 0.120 mm.; (3) blended polymer film consisting of equal parts of HDPE and LDPE (abbreviated as MDPE) with thickness 0.030 mm.

These films were obtained from USI Far East Corp. The films were washed with acetone, immersed in *n*-hexane for 48 h, dried under reduced pressure at 50°C for 24 h, and then stored in a vacuum oven before grafting.

Monomers. Reagent grade acrylic acid methacrylic acid (Wako Pure Chem. Ind., Ltd.) were used as received. Other chemicals used were reagent grade and thus used without further purification.

Irradiation

Weighed polyethylene films were irradiated in the air at room temperature with cobolt 60 source at Union Industrial Research Laboratory, Hsin-Chu, Taiwan.

The dose rate was 0.187 Mrad/h throughout this study. The polyethylene films investigated were stored for either 2 h or 100 h after the irradiation. Unless otherwise indicated, the one with two hours storage time was used.

Grafting Procedure

Weighed and preirradiated polyethylene films were first immersed in aqueous monomer solution with 50 wt % of acrylic acid or methacrylic acid and 0.25 wt % of Mohr's salt (ferrous ammonium sulfate). The solution was deaerated by bubbling nitrogen which had been purified. The reaction kettle was then immersed in a thermostated water bath at 90°C for a specified period of time. After thoroughly cleaning in warm water with ultrasonic cleaner, the films were dried under reduced pressure at 60°C for 24 h.

The degree of grafting was obtained through the weight increase of the films according to the following equation:

$$\% \text{ graft} = \frac{W_1 - W_0}{W_0} \times 100$$

where W_0 is the initial weight of parent film and W_1 is the weight of grafted film.

Electric Resistance

The electric resistance of the grafted film was measured in 40% KOH solution at 25°C using an Ohmmeter (LCR meter ZM-341 NF Electronic

Instruments) working at 1000 Hz. Samples were soaked for 24 h in potassium hydroxide of the same concentration to be used prior to interpose between two platinized platinum electrodes. The test cell¹⁶ was designed to make the area of exposed separator surface approximately 1 cm².

Electrolyte Diffusion Test

KOH diffusion tests¹⁷ were performed on samples clamped between the two compartments of a simple diffusion cell made of acrylate. One half cell was filled with 10M KOH solution, and the other filled with water and indicator. The KOH diffusion rate was determined by noting the time taken for neutralization of the initial amount of acid and subsequent additions of 1M HCl.

Transport Number

The grafted film was conditioned in 0.75N KCl solution for 1 day at room temperature and then placed in between two compartments and Ag–AgCl electrodes to measure the electromotive force of chemical cell. KCl solutions of 0.5 and 1.0N were made to flow individually through the compartments until equilibrium was reached. The membrane potential was measured at 25°C using DC Potentiometer (Yokogawa Electric Works Model 2723). The transport number (\bar{t}) of counterions in the membrane was calculated from the value of the measured potential (E_m) by the following equation:

$$\bar{t} = E_m/2E_0 + 0.5$$

where E_0 is the theoretical potential calculated by the Nernst equation

$$E_0 = (RT/F) \ln(C_2\gamma_2/C_1\gamma_1)$$

where γ_1 and γ_2 are the activity coefficients of KCl at concentrations C_1 and C_2 , respectively.

Mechanical Properties

Tensile strength and elongation at break were determined by using an Instron Tensile Tester (Model 1123). Tests were made on parent polyethylene and grafted polyethylene films including both dry and wet sample. Tests were performed as closely as possible to ASTM standards.¹⁸

Thermal Measurements

Thermal measurements were undertaken by using a Perkin-Elmer Model DSC-2 at a heating rate of 10°K/min going up to 430°K. Several layers of samples were pressed in the sample cups to obtain a reasonable weight of sample for the DSC measurement. The instrument calibration constant was determined by using indium prior to the experiments. A value of 68.4 cal/g was used in the calculations for the heat of melting of completely crystalline polyethylene.¹⁹ The degrees of crystallinity of the films were calculated from the area under the thermogram curve.

RESULTS AND DISCUSSION

Thermal Measurement

As shown in Figure 1, the MDPE (a blend of LDPE and HDPE) gave two endothermic peaks on thermogram, each representing thermal behavior of individual constituent polymer. Because branching will restrict crystal perfection, the low density material melts at a lower temperature, and being almost completely resolved from melting of the crystallites of HDPE. Annealing of MDPE shifted the transition point of HDPE to the higher temperature shown in the upper curve. The crystallinity was calculated to be 58 ± 2 wt %.

Grafting Behavior

Typical graft polymerization curves for low density polyethylene (LDPE) at different dosage are shown in Figure 2. The degree of grafting increased with reaction time then levels off to the value of final percent grafting. Similar results were obtained for high density polyethylene (HDPE) and medium density polyethylene (MDPE). Either acrylic acid or methacrylic acid was used in grafting solution, but no appreciable difference in grafting behavior was found.

Both the dosage and storage period before post-irradiation grafting polymerization have some effects on the grafting behavior; such effects can be explained by the relative data of Table I. In the crystalline region the chain

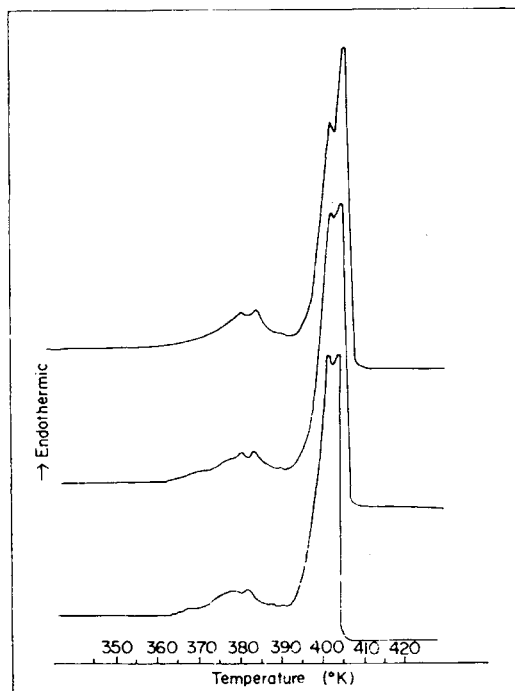


Fig. 1. Endothermic curves of MDPE by differential scanning calorimetry.

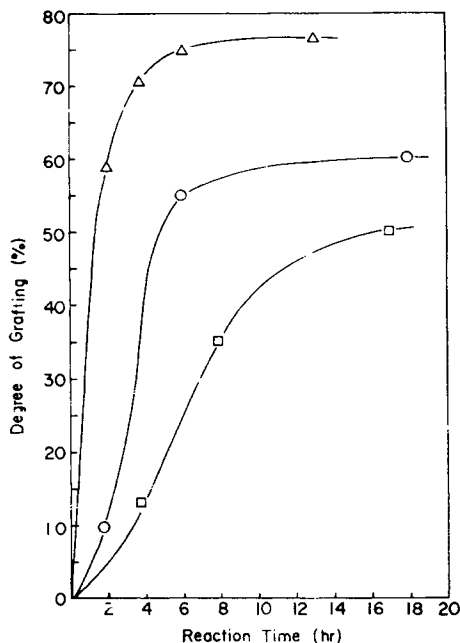


Fig. 2. Degree of grafting at various dosage for LDPE-AAc system. Grafting temperature 90°C; dosage N(Mrad): (□) 1.122; (○) 2.992; (△) 4.488.

segments were so regularly folded that the monomer molecules could hardly diffuse in. Therefore, it was believed that in our grafting system, the grafting polymerization occurred mainly on the surfaces of crystallite and in amorphous regions where the hydroperoxide or diperoxide could decompose to form radicals and initiate the graft polymerization.

The effects of dosage on final percent grafting were also shown in the third and fourth row of Table I. As the radiation dosage increases, the final

TABLE I
Effect of Dosage and Storage Period on the Grafting of Methacrylic Acid (MAA) and Acrylic Acid (AA) onto Polyethylene Film

Grafting monomer	Base film										
	LDPE					MDPE				HDPE	
	AA		MAA			AA		MAA		AA	
Ratio of dosage	1	2.67	4	1	2.67	1	4	1	2.67	1	2.67
Ratio of final percent graft	1	1.20	1.50	1	1.20	1	1.71	1	1.75	1	1.1
Ratio of final percent graft ^a	1	—	3.85	—	—	1	4.9	—	—	—	—
$\frac{\text{(final \%)} 100 \text{ h}^b}{\text{(final \%)} 2 \text{ h}}$	0.26	—	0.67	—	—	0.23	0.65	—	—	—	0.95
= <i>R</i>											

^a The irradiated films was stored at room temperature for 100 h.

^b *R* refers to the ratio of final percent grafting with irradiated films stored for 100 and 2 h, respectively, before grafting polymerization.

final percent grafting increases but not in a linear manner; the increment of final percent graft is not obvious beyond a dosage of 1 Mrad. This may be due to the decay of the trapped radicals either by recombination or chain transfer with the surroundings. Further, since the irradiation was carried out in air, free radicals formed in the matrix may react with oxygen to form diperoxides and/or hydroperoxides which can initiate graft polymerization at elevated temperature,^{20,21} especially in the presence of Mohr's salt. Thus for the irradiated films stored for 100 h before grafting, the grafting is initiated predominately by decomposition of peroxides. Therefore, the fifth row of Table I could be reasonably explained by the fact that the diffusion rate of oxygen into the matrix is linearly proportional to the irradiation time, which was also related to dosage linearly.

From the viewpoint of application, the index R was suggested to be the measurement of the effect of storage period on the final grafting percentage. It is clear that, with an R value close to 1 for HDPE, the irradiated films could be stored for as long as 100 h without significantly influencing the final percent graft. This may be attributed to higher concentration of radicals trapped in the crystalline region.²⁰ It is also found that the grafting behavior of methacrylic acid is similar to that of acrylic acid.

Electrolyte Diffusion Test

This test measures directly the rate at which hydroxyl ion diffuses through a separator under a constant concentration gradient.²² The significance of the diffusion rate is that it is a measure of the ease with which local electrolyte concentrations within a cell can be equalized, and it may also be related to the current carrying ability of the separator as reflected in its electrolytic resistance.

The relationship between the electrolyte diffusion rate and degree of grafting is shown in Figures 3, 4, and 5. For different monomers and the

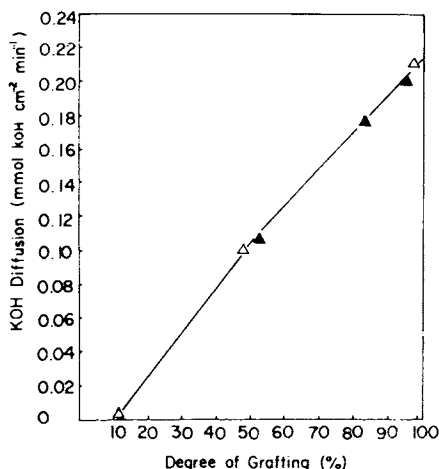


Fig. 3. Variation of KOH diffusion with degree of grafting for a 10*m* KOH concentration gradient at 25°C. Average membrane thickness 0.155 mm; (△) LDPE-*g*-PAA; (▲) LDPE-*g*-PMAA.

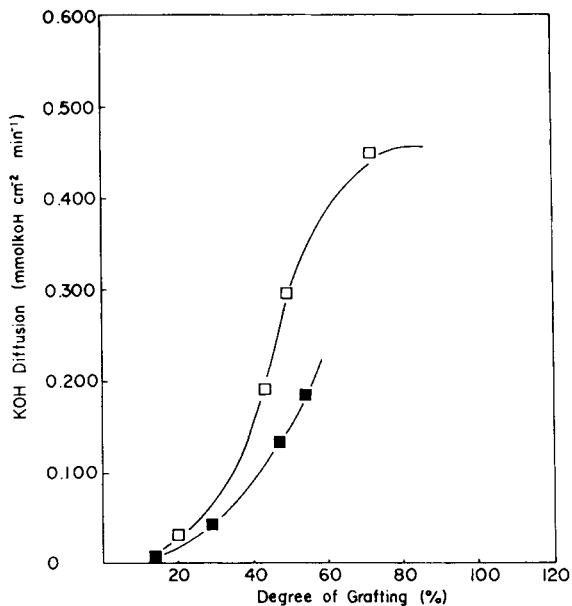


Fig. 4. Variation of KOH diffusion with degree of grafting (MDPE base). Average membrane thickness 0.045 mm; (□) MDPE-g-PMAA; (■) MDPE-g-PAA.

parent polyethylene, there exists a common phenomenon; i.e., up to a certain level of grafting, the KOH diffusion rate increases rapidly with the degree of grafting. This phenomenon was believed to be the result of the fact that the grafting occurred not only at the surface but also in the interior

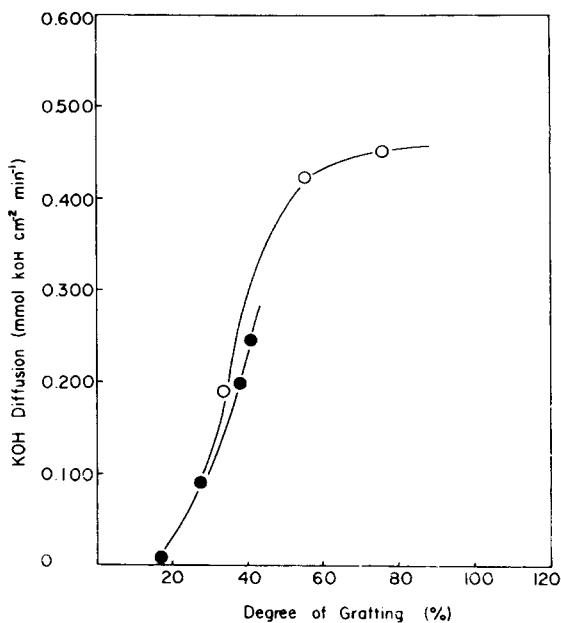


Fig. 5. Variation of KOH diffusion with degree of grafting (HDPE base). Average membrane thickness 0.025 mm; (○) HDPE-g-PMMA; (●) HDPE-g-PAA.

of the polymer matrix, i.e., the grafting may proceed from the surface to the interior of the matrix. It was observed that MDPE grafted with methacrylic acid had a higher diffusion rate than that with acrylic acid did. The pendant methyl groups of polymethacrylic acid, which may swell to a larger extent, are believed to be responsible for such a difference.

Electric Resistance

Figures 6 and 7 show the relationship between specific electric resistance and degree of grafting of acrylic acid and methacrylic acid, respectively. The specific electric resistance decreases exponentially with increasing degree of grafting within the range in which KOH diffusion becomes appreciable. This indicated that only beyond a certain degree of grafting did the grafting proceed to the center of the matrix. It is also important to find that the electric resistance of the HDPE and MDPE grafted with methacrylic acid may be descended to that of LDPE grafted with methacrylic acid.

Transport Number

The permselectivity of membrane is one of the most important properties for ion exchange membrane. The transport number of counterions in the grafted polyethylene films were measured in our experiment. Table II shows the transport numbers of the membranes with different crystallinity and degree of grafting. The permselectivity and fixed ion concentration are also calculated from the transport number and ion exchange capacity, respectively.

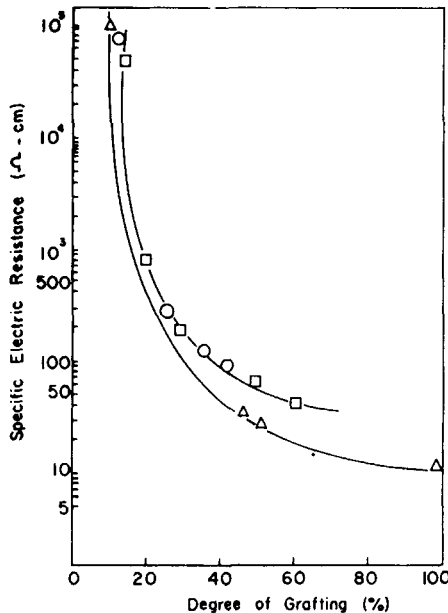


Fig. 6. Specific electrical resistance vs. degree of grafting for various polyethylene grafted with acrylic acid. (Δ) LDPE; (□) MDPE; (○) HDPE.

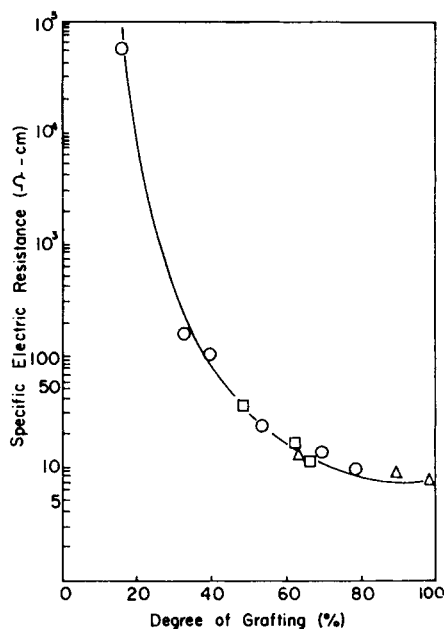


Fig. 7. Specific electrical resistance vs. degree of grafting for various polyethylene grafted with methacrylic acid. (Δ) LDPE; (\square) MDPE; (\circ) HDPE.

It can be seen that membranes with higher degree of grafting do not render higher permselectivity due to successive swelling by water. Generally, membranes with higher fixed-ion concentration should exhibit higher permselectivity, the deviations may be ascribed to electroosmotic transport of water across the membrane²³ and the crystallinity of the parent film.

Mechanical Properties

The effects of grafting on tensile properties were shown in Table III. It can be seen that the membranes containing gel water like LDPE-*g*-PAA in the table will decrease the tensile strength with increasing degree of grafting. This is also believed to be due to the effect of imperfections in the crystallites caused by grafted side chains. The X-ray diffractograms in Fig-

TABLE II
Transference Numbers (t_+) and Permselectivity for Membranes in 1.0N/0.5N KCl Solutions at 25°C

Membranes	Degree of grafting (%)	Transport number t_+	Permselectivity	Fixed ion concn (eq/L imbibed water)
MDPE- <i>g</i> -PAA	50	0.920	0.843	4.43
	32	0.898	0.801	3.85
LDPE- <i>g</i> -PAA	76	0.816	0.640	4.35
	54	0.867	0.740	4.87
HDPE- <i>g</i> -PMAA	75	0.748	0.507	7.7
	53	0.778	0.566	7.0

TABLE III
Mechanical Properties of Base Film and Acrylic Acid Graft Copolymer Film

Film (degree of grafting)	Base film LDPE	LDPE- <i>g</i> -PAA ^a			Base film MDPE	MDPE- <i>g</i> -PAA ^b		Base film HDPE	HDPE- <i>g</i> - PAA ^b
		13%	47%	70%		48%	54%		33%
Tensile strength (kgf/cm ²)	168 ^{Mc} (120 T ^d)	155 ^M	130 ^M	120 ^M	220	296	290	296	290
Elongation (%)	320 ^M (430T)	>160	>160	>160	300	>100	>100	>100	>100

^a After swelling with water, it was surface dried and stored in a desiccator for 24 h before testing.

^b Vacuum dried at 70°C.

^c M: machine direction.

^d T: transverse direction.

ure 8 did confirm that the degree of crystallinity in polymer film was reduced by grafting. Besides, gel water contained in grafted film will swell the matrix and reduce the possibility of hydrogen bonding. In order to investigate the effect of gel water, MDPE- and HDPE-based copolymer films were exhaustively dried before testing, and the result showed that grafted film based on MDPE has tensile strength as strong as that of HDPE-based film. The result may be due to the fact that MDPE is a blend of HDPE and LDPE; thus a great number of small crystallites are dispersed around large crystallites of HDPE. These small crystallites afford much more surface for grafting so that the grafted side chains have greater opportunity for intermolecular or intramolecular hydrogen bonding which could enhance the tensile strength.

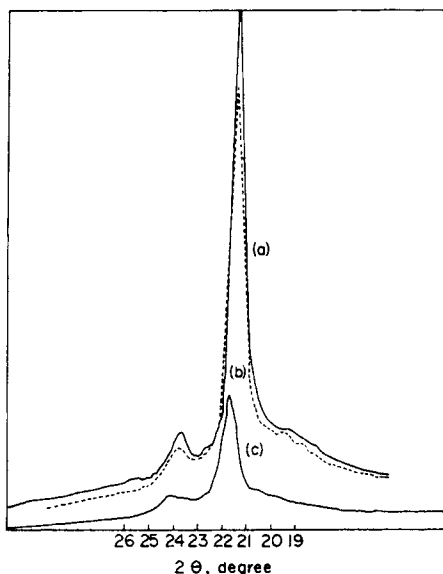


Fig. 8. X-Ray diffractograms of LDPE: (a) machine direction; (b) transverse direction; (c) polyacrylic-acid-grafted copolymer film (47%).

It may be noted that the membranes thus obtained have acceptable mechanical properties whether in a wet or dried state, and this is very important in practical use.

CONCLUSIONS

A convenient method of synthesizing grafted copolymer membranes by preirradiation technique is presented and discussed. Our investigations on the grafting behavior and the properties of the methacrylic acid grafted polyethylene have shown the possibility for practical application as separator of alkaline battery. Blended polymer film of high density polyethylene and low density polyethylene exhibits better improvement in mechanical properties after grafting polymerization. It was also found that the methacrylic acid grafted polyethylene film was better than acrylic-acid-grafted polyethylene, especially in electrical conductivity.

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