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FACTORS AFFECTING VAPOR-PHASE PHOTOGRAFTING OF METHACRYLIC ACID ON LOW-DENSITY POLYETHYLENE FILM

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ABSTRACT

Factors affecting photografting ($\lambda > 300$ nm) of methacrylic acid on a low-density polyethylene film (thickness = $70 \mu\text{m}$) were investigated in a vapor-phase system. Xanthone was coated on the film. Factors examined were pressure of the system (1, 20, and 50 mmHg), polymerization temperature (40, 50, and 60°C), and use of monomer mixed with water. It was found that the grafting rate decreases in the following order: 1 mmHg $>$ 20 mmHg $>$ 50 mmHg at 60°C , and $60^\circ\text{C} > 50^\circ\text{C} > 40^\circ\text{C}$ under 1 mmHg pressure. The rate was sharply reduced by using monomer mixed with water (monomer/water = 1/1). The contact angle of water on the grafted films largely depended on the grafting conditions, decreasing in the same order as that of the grafting rate described above. Thus, higher wettability was recorded for grafted films prepared under grafting conditions where the grafting rate is slow. The resultant grafted chains are supposed to localize mainly on the film surface.

INTRODUCTION

Photografting supplying monomers in their gaseous state is applicable to various natures of monomer since it is not necessary to consider monomer solubility in a polymerization solvent. The technique has been successfully utilized for surface modification of polymers by Rånby et al. [1-4]. The authors studied vapor-phase photografting as a means for the functionalization of polymer materials and observed that the grafting is largely promoted by adding a pertinent quantity of solvent [5, 6] to the monomer and using the monomer mixture [7]. Moreover, it was found that catalytic activities of *N*-vinylimidazole-grafted [8] and 4-vinylpyridine-grafted [9] polyethylene samples prepared by using the vapor-phase system toward hydrolysis of *p*-nitrophenylacetate were lower than those prepared by using a liquid-phase system.

In previous papers [10, 11], wettability of methacrylic acid (MAA)-grafted polyethylene film was compared between samples (vapor- and liquid-phase samples) prepared by using the vapor- and liquid-phase systems, respectively. The contact angle of water on the vapor-phase samples was larger than that of the liquid-phase samples. This was ascribed to the fact that the grafted chains of the latter sample are located mainly on the film surface, while those of the former sample are distributed inside the film, resulting in lower wettability. In this paper the effects of pressure, temperature, and the use of a monomer mixed with water on vapor-phase photografting are investigated in order to improve the wettability of MAA-grafted polyethylene film.

EXPERIMENTAL

Sample

Low-density polyethylene (PE) film, which was prepared with a thickness of 70 μm , was dipped in acetone solution containing 0.3 wt% xanthone and 0.5 wt% poly(vinyl acetate) (PVAc, $\bar{M}_w = 100,000$), taken out of the solution, and then dried under reduced pressure to prepare xanthone-coated film. The quantity of xanthone coated on the film was too small to determine gravimetrically. Xanthone was of reagent grade and used without further purification. MAA was purified by distillation under reduced pressure.

Photografting

Vapor-phase photografting was carried out using Pyrex glass tubes. A polymer film (55 \times 70 mm) fixed on a sample holder was set at the center part of the tube, and 1 mL monomer of a solution of 1 mL monomer and 1 mL water was placed in the bottom part. The pressure of the system was adjusted to 1, 20, or 50 mmHg. Irradiation with a high-pressure mercury lamp (400 W) was carried out at 40, 50, or 60°C for various time periods using a Riko rotary photochemical reactor RH400-10W around which the Pyrex glass tubes were rotated. The polymerized film was extracted for 24 hours with hot water to remove the homopolymer of poly(MAA). The percent grafting was taken as the percentage of weight increase of the original

film. The graft efficiency was expressed as the weight percent of grafted polymer relative to total conversion of monomer.

Electron Probe Microanalysis (EPMA)

Grafted poly(MAA) was converted to potassium salts by immersing the grafted film in an aqueous solution of 1% potassium hydroxide at room temperature for 24 hours. The distribution profile of potassium atoms in the grafted film was measured with electron probe microanalyzer model EPM-8000 of Shimadzu Co.

Measurements of Contact Angle and ATR-FT-IR Spectra

Contact angle measurements were made with a contact angle meter type CA-P of Kyowa Kaimenkagaku Co. at ambient humidity and temperature. ATR-FT-IR spectra of the surface layer of grafted film were measured with an infrared spectrometer model JIR-5500 of Japan Electron Optics Laboratory.

RESULTS AND DISCUSSION

Figure 1 shows the effect of pressure on vapor-phase photografting at 60°C. The grafting rate increased when the pressure of the polymerization system was lowered. The vapor pressure of MAA at 60°C is estimated to be about 10 mmHg based on the vapor pressure of 1 mmHg at 25.5°C [12]. Accordingly, it is supposed that the pressures of 20 and 50 mmHg used in this study are not enough to vaporize MAA sufficiently at 60°C, and this may cause the decreased grafting rate. The graft efficiencies of each system were more than 50%, showing a predominant formation of grafted polymer. Thus, vapor-phase grafting was characterized by high grafting efficiency since the formation of homopolymer proceeds mainly on the film surface. Figure 2 shows the contact angle of water on the MAA-grafted PE films. The contact angle gradually decreased with an increase in the percent grafting, but the magnitude differed among the grafting systems. The contact angle decreased in the order 1 mmHg > 20 mmHg > 50 mmHg.

In this study, PVAc was used as the polymeric carrier of the photoinitiator used to hold the photoinitiator homogeneously and tightly on the film surface. An extraction treatment was carried out in order to examine the contribution of PVAc to grafting initiation. MAA-grafted PE films prepared in the system at 60°C under 1 mmHg pressure were further extracted for 24 hours with methanol, which is a solvent for both PVAc and poly(MAA), and the results are shown in Table 1. Only a slight decrease in percent grafting due to the second extraction was observed. This suggests that the grafted poly(MAA) is linked directly to the PE substrate, not to the PVAc carrier.

Figure 3 presents the effect of polymerization temperature on vapor-phase photografting under 1 mmHg pressure. The percent grafting of the system at 60°C increased with irradiation time, while that of the systems at 40 and 50°C leveled off beyond about 40 minutes irradiation. The graft efficiency was also influenced by the polymerization temperature and decreased in the order 60°C > 50°C > 40°C. As shown in Fig. 4, the contact angle tended to decrease in the order 60°C >

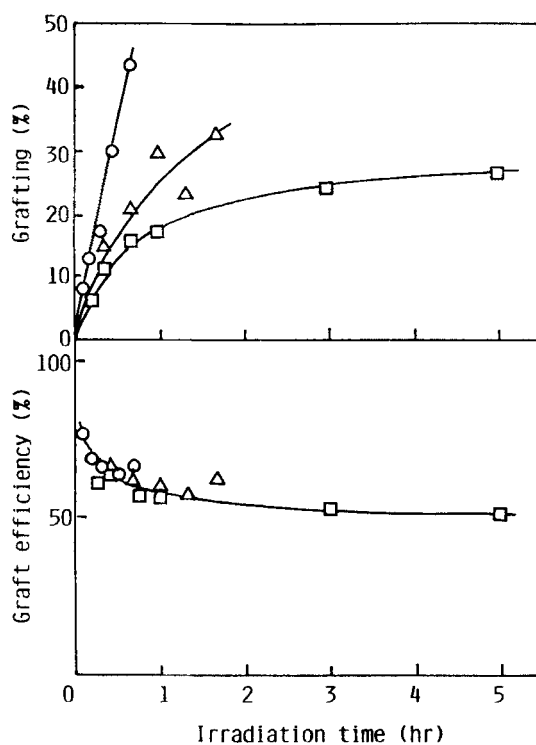


FIG. 1. Effect of pressure on vapor-phase photografting of MAA on PE film at 60°C. Pressure of the system (mmHg): (○) 1, (△) 20, (□) 50.

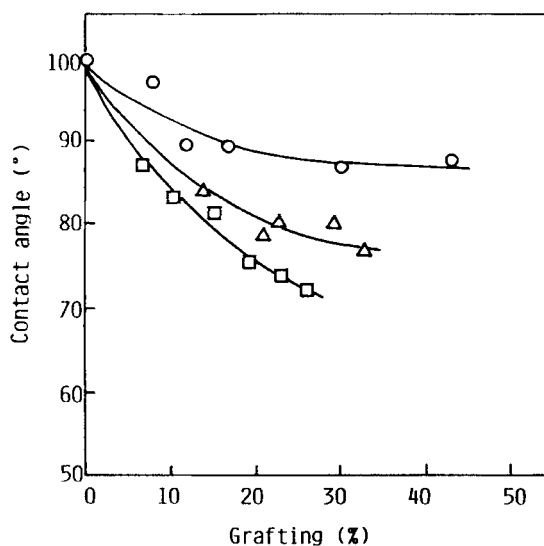


FIG. 2. Contact angle of water on MAA-grafted PE films prepared in the system at 60°C. Pressure of the system (mmHg): (○) 1, (△) 20, (□) 50.

TABLE 1. Second Extraction of MAA-Grafted PE Films with Methanol

Grafting, %	
Before ^a	After ^b
17.3	16.5
30.5	29.0
45.7	44.1

^aPercent graftings obtained by the first extraction with hot water for 24 hours.

^bPercent graftings obtained by the second extraction with methanol for 24 hours.

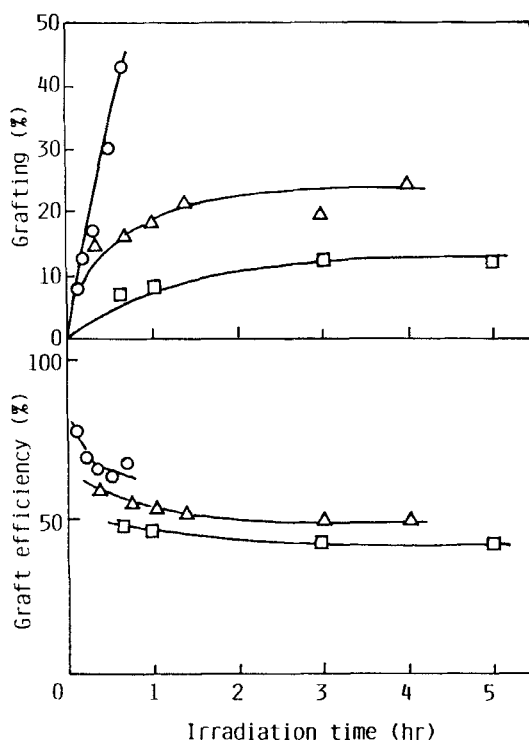


FIG. 3. Effect of polymerization temperature on vapor-phase photografting of MAA on PE film under 1 mmHg pressure. Temperature ($^{\circ}\text{C}$): (\square) 40, (\triangle) 50, (\circ) 60.

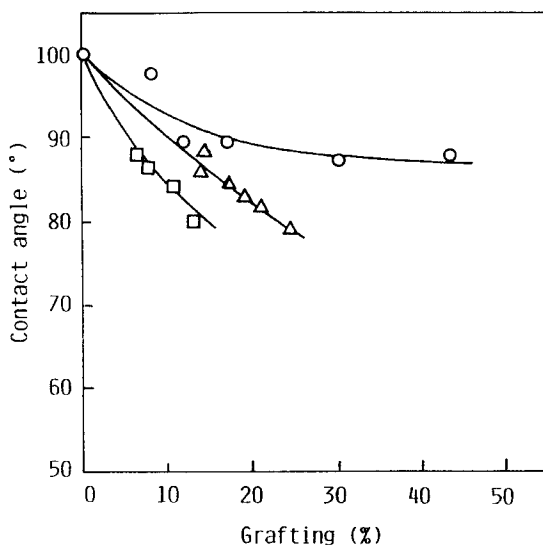


FIG. 4. Contact angle of water on MAA-grafted PE films prepared in the system under 1 mmHg pressure. Temperature ($^{\circ}\text{C}$): (\square) 40, (\triangle) 50, (\circ) 60.

$50^{\circ}\text{C} > 40^{\circ}\text{C}$. It was found, as above, that the pressure and the polymerization temperature greatly influence the grafting reaction and can be factors in controlling the wettability of MAA-grafted PE films.

In previous papers [10, 11] we used water as a polymerization solvent in a liquid-phase system. Therefore, the use of MAA mixed with water was examined in vapor-phase photografting in order to imitate the atmosphere of a liquid-phase system, and the results are shown in Fig. 5. The grafting was carried out at 60°C under 1 mmHg pressure. The percent grafting and the graft efficiency were sharply reduced by adding 1 mL water to 1 mL MAA monomer. As seen in Fig. 6, the contact angle of the sample with water was lower than that of the sample without water, showing an improved wettability due to the use of MAA mixed with water.

Figure 7 shows distribution profiles of the potassium atom in the cross section of MAA-grafted PE film measured by EPMA. The grafted chains of the sample with water seem to appear at the film surface compared to those of the sample without water. The total thickness of the film and the thickness of the ungrafted layer were measured, and the results are shown in Fig. 8. The dashed line represents the thickness of the original film. The sample with water exhibited a larger increase in total thickness with an increase in percent grafting than did that of the sample without water. The thickness of the ungrafted layer decreased with an increase in percent grafting, and the magnitude was small in the sample with water compared to the sample without water. It was therefore found that grafted chains of the sample with water are likely to locate on the film surface, while those of the sample without water are distributed inside the film. As shown in Fig. 5, the use of MAA mixed with water brought about an increased formation of homopolymer in the system, leading to a reduced grafting rate. This is a main reason why the vapor-phase system with water results in a grafted film with a localized distribution of

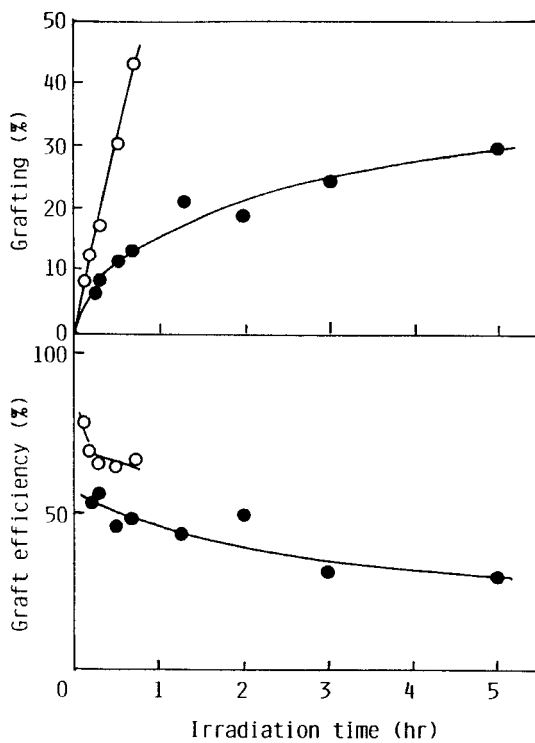


FIG. 5. Effect of water on vapor-phase photografting of MAA on PE film at 60°C under 1 mmHg pressure. (○) Without water, (●) with water.

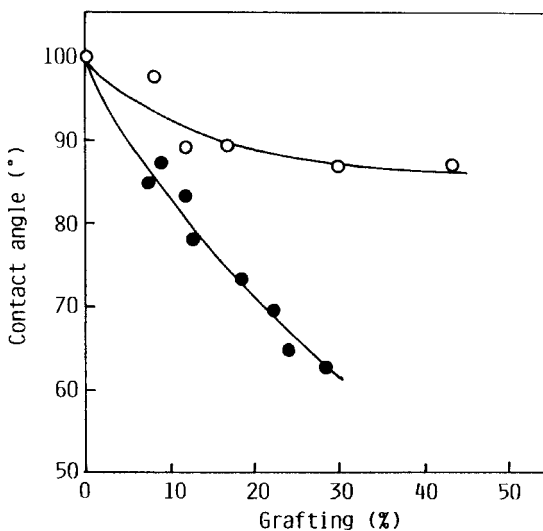


FIG. 6. Contact angle of water on MAA-grafted PE films prepared in the system at 60°C under 1 mmHg pressure. (○) Sample without water, (●) sample with water.

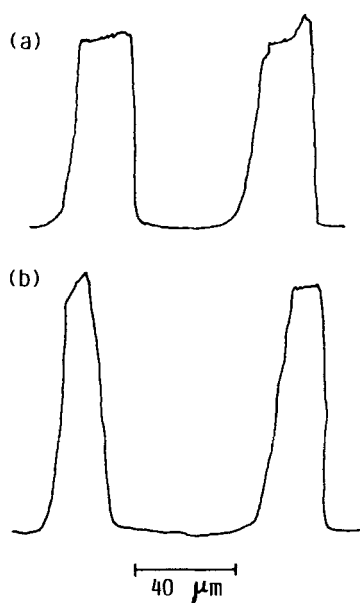


FIG. 7. Distribution profile of potassium atom in the cross section of MAA-grafted PE film measured by EPMA. (a) Sample without water (grafting = 30.1%), (b) sample with water (grafting = 28.3%).

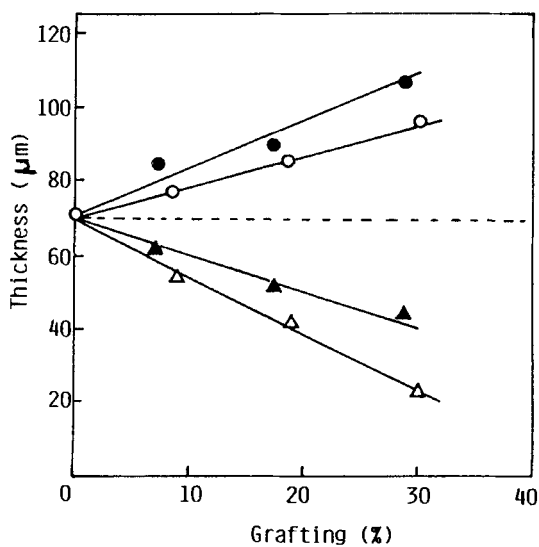


FIG. 8. Relationship between total thickness of the film and thickness of ungrafted layer and percent grafting. Total thickness (μm): (○) sample without water, (●) sample with water. Thickness of ungrafted layer (μm): (△) sample without water, (▲) sample with water. The dashed line represents the thickness of the original film.

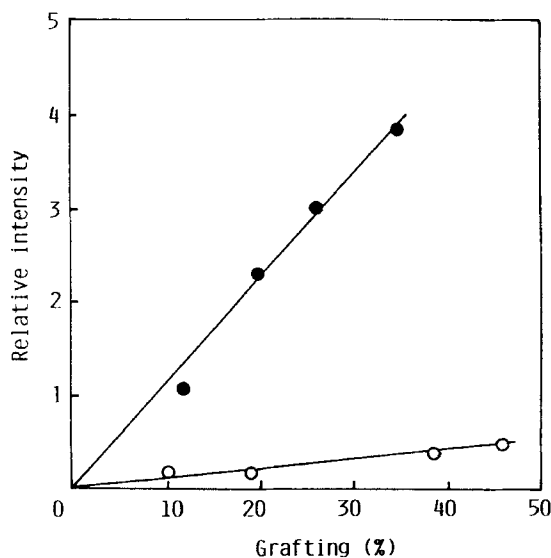


FIG. 9. Change in relative intensity of C=O peak at 1710 cm^{-1} against CH_2 peak at 1470 cm^{-1} as the internal standard with percent grafting in MAA-grafted PE films. (○) Sample without water, (●) sample with water.

grafted chains, which contributes to high wettability. In order to confirm the above result obtained by EPMA, MAA-grafted chains of the surface layer of the grafted film were examined by ATR-FT-IR. Figure 9 shows the relative intensity [3] of the C=O (stretching) peak at 1710 cm^{-1} against the CH_2 (bending) peak at 1470 cm^{-1} as an internal standard. The relative intensity increased with an increase in the percent grafting, and the magnitude was considerably larger for the sample with water than for that without water. This supports the belief that the MAA-grafted chains of the sample with water mainly localize on the film surface compared to those of the sample without water.

CONCLUSIONS

It was proved that such factors as the pressure, the polymerization temperature, and the use of monomer mixed with water greatly influence both the grafting reaction of MAA on PE film and the wettability of grafted film in the following manner. Under grafting conditions where the grafting rate is largely reduced and the grafted chains locate on the film surface, the wettability of the resultant grafted films becomes high. Accordingly, it is concluded that a grafted film with high wettability can be prepared in vapor-phase photografting by the proper choice of pressure and polymerization temperature and the use of a monomer mixed with water.

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