

## Durable, hydrophilic surface modification of polypropylene films by plasma graft polymerization of glycidyl methacrylate

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### SUMMARY

The plasma graft polymerization of glycidyl methacrylate (GMA) was investigated to obtain hydrophilic surface. The combination of the argon plasma and GMA vapor exposures led to graft polymerization of GMA at the surface of polypropylene films. This graft polymerization was initiated by the argon plasma exposure for 2 min, and was accomplished with the GMA vapor exposure for 2 min. The GMA graft polymerization made polypropylene surface hydrophilic. The surface energy was  $55.8 \text{ mJ/m}^2$ . The hydrophilicity introduced by the GMA graft polymerization remained for at least 3 weeks. The graft polymerization of hydrophilic monomers was a good means of hydrophilic surface modification.

### INTRODUCTION

Surface modification of polymers calls a great deal of attention because of the formation of functionality. The objective of the attention is to bring about functional surface properties such as adhesion, wettability, printing, and blood compatibility, without changing the bulk properties of the polymers. These properties are closely related to hydrophilicity of the polymer surface. From this sense hydrophilic surface modification is of interest. Oxidation by flame, chemicals, and corona discharge, in general, is commercially used for the purpose [1]. Plasma treatment also is an attractive technique for hydrophilic modification.

The surface modification by the oxidation leads to the introduction of polar groups such as carbonyl, carboxyl, and hydroxyl groups at the surface of polymers and makes it hydrophilic. However, the hydrophilicity begins to decrease just after the finishing the modification, and is completely lost after 2 - 3 weeks [2]. The loss of the hydrophilicity is due to moving and diffusing of the polar groups into the bulk of the polymer [3]. The movement and diffusion of the polar groups are related to the thermal motion of the polymer chains. Therefore, the thermal motion should be restricted for the maintenance of the hydrophilicity for long times. When long chains containing hydrophilic groups are introduced at the surface of the polymer the movement and diffusion may be hindered by the introduction of the long chains, and the hydrophilicity is expected to be kept for long times. The aim of this investigation is to obtain the hydrophilic surface of polymers without decrease in hydrophilicity when stored for long time. For the purpose, the graft polymerization of glycidyl methacrylate (GMA) was carried out. The activated sites to initiate the graft polymerization were generated by argon plasma. GMA possesses two functionalities, vinyl and epoxide groups. The graft polymerization of GMA in radical reactions proceeds through the vinyl groups, and graft polymers having epoxide groups are formed. Reactions of the epoxide groups in the GMA graft polymers with nucleophilic reagents such as amines and alcohols brings about specific surface properties [4-7].

The GMA graft polymerization at the surface of polyethylene films has been investigated by Allmer et al. [4]. They directed the graft polymerization in the presence of benzophenone as an initiator by the UV photoinitiation. We used the argon plasma to generate the radical sites which initiate the GMA graft polymerization. The argon plasma irradiation is

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able to generate effectively radicals at the surface of polymers without an initiator such as benzophenone. This is an advantage of the argon plasma irradiation.

## EXPERIMENTAL

### Materials:

Polypropylene film (Idemitsu Kosan Co., Japan, PU-M-40) with a thickness of 200  $\mu\text{m}$  was used as a material for graft polymerization. Glycidyl methacrylate (GMA) (Tokyo Kasei Co., Japan) was used as a monomer for graft polymerization.

### Plasma Graft Polymerization:

Plasma graft polymerization was performed in a reaction chamber with a plasma generator. The plasma generator was an inductively coupled system operating at a frequency of 13.56 MHz (rf). The reaction chamber consisted of a Pyrex glass tube (35 mm inner diameter, 593 mm long, a chamber volume of 420.5  $\text{cm}^3$ ) with a monomer reservoir and a plasma gas inlet, a pressure gauge, a ribbon heater to control the temperature of the reaction chamber, a vacuum system (a combination of rotary and diffusion pumps), and a matching network for the inductive coupling of the rf power source. The details of the reaction chamber is illustrated in Fig. 1.

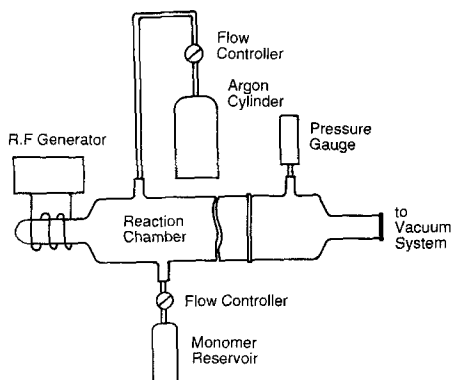


Fig. 1 Schematic Illustration of Reaction Chamber for Graft Polymerization.

In the reaction chamber the polypropylene film (10 x 30 mm) was placed, and the reaction chamber was evacuated to 0.13 Pa. Argon gas was introduced into the reaction chamber at a flow rate of 4  $\text{cm}^3(\text{STP})/\text{min}$  at a pressure of 13.3 Pa, and the rf power was turned on to initiate argon plasma. The polypropylene film was exposed to the argon plasma operated at 25 W for a given duration (0.5 - 2 min), and then, the reaction chamber was once again evacuated to 0.13 Pa. Afterward the GMA vapor was introduced into the reaction chamber at 13.3 Pa from the GMA reservoir, and graft polymerization of GMA at the surface of the polypropylene films was performed at 60  $^{\circ}\text{C}$  for a given duration (0.5 - 30 min). Before the graft polymerization GMA stored in the reservoir was frozen and thawed under vacuum to degas air dissolved in the GMA. Three times repetition of the freezing and thawing was done. All treated films were Soxhlet extracted with acetone for 12 h to remove residual monomer and homopolymer.

### Infrared Spectra of Plasma-Graft-Polymerized Polypropylene Film:

Infrared analysis was made with the attenuated total reflection technique (ATR) using a Nihon Bunko Fourier transform spectrometer FT/IR-3. The crystal of KRS-5 was used for ATR. The purity of the crystal surface was monitored before each analysis by recording spectrum of the bare crystal. The incidence angle of infrared light was 45 $^{\circ}$ . The sampling

depth which is functions of the infrared wavelength, the reflective index (2.4 for KRS-5 crystal, 1.5 for polypropylene which is calculated from the Lorentz-Lorenz formula), and the incidence angle of infrared light ( $45^\circ$ ) is calculated to be  $0.5 - 5 \mu\text{m}$  in the range from  $2.5 (4000 \text{ cm}^{-1})$  to  $25 \mu\text{m} (400 \text{ cm}^{-1})$ . The spectral resolution was  $2 \text{ cm}^{-1}$  and 500 scans were recorded on each sample in order to improve the signal to noise ratio.

#### Contact Angle of Water and Surface Energy:

The advancing contact angles of water, glycerol, formamide, diiodomethane, and tricresyl phosphate on the treated polypropylene surfaces were measured at  $20^\circ\text{C}$  using an Erma contact angle meter with a goniometer, model G-1.

The receding contact angle of water was measured according to the bubble method. The polypropylene film was immersed in water at  $30^\circ\text{C}$ , and a constant volume ( $1 \mu\text{l}$ ) of air bubble was introduced at the lower surface of the polypropylene films using a microsyringe. The contact angle of the air bubble against the polypropylene surface was measured using the Erma contact angle meter.

The surface energy of the plasma-graft-polymerized polypropylene surface was estimated from the data of the advancing contact angles of the five liquids according to Kaelble's method [8].

## RESULTS AND DISCUSSION

### Plasma Graft Polymerization of Polypropylene with GMA

The contact angle of water against polymer surface provides information about polymer chains being present near the outermost layer of the polymer surface. Although ATR IR and XPS spectra also are useful means of surface analysis, the information obtained from the spectra includes not only polymer chains at the surface but also those existing in some depth (sampling depth) from the surface. The sampling depth ( $d_p$ ) is functions of the energy of the incident light and electron, the incident angle of the light, and polymer substrate properties.

$$d_p = \frac{\lambda}{2\pi n_1 \{ \sin^2 \theta - (n_2/n_1)^2 \}^{1/2}} \quad \text{for ATR IR [9]}$$

$$d_p = \frac{2.55 \times 10^{-3} E_0 A}{\rho \sum (N_i/\Delta E_i) \ln(4E_0/\Delta E_i)} \quad \text{for XPS [10]}$$

where  $\lambda$ ,  $n_1$ ,  $n_2$ , and  $\theta$  for ATR IR are the wave length of the incident IR light, the refractive index of the crystal, the refractive index of the polymer, and the incident angle of IR light, respectively; and  $E_0$ ,  $A$ ,  $\rho$ ,  $N_i$ ,  $\Delta E_i$  for XPS are the incident electron energy, the atomic weight of the polymer, the density of the polymer, the number of electrons in the  $i$ -th shell available for the excitation, and the average excitation energy, respectively. From the viewpoint the contact angle is an advantageous means rather than ATR IR and XPS to detect changes in polymer properties at the surface. However, the contact angle is influenced by the surface roughness, and in discussing on the contact angle we should take the effect of the surface roughness into consideration.

Polypropylene surface is hydrophilic and the advancing contact angle of water is  $98^\circ$ . When GMA are graft-polymerized at the surface of polypropylene films the surface would change from hydrophobic to hydrophilic, and some decreases in advancing contact angle may be observed. We watched the contact angle of the polypropylene films in order to detect the occurrence of the graft polymerization of GMA. The SEM (scanning electron microscopy) observation (magnification,  $\times 5000$ ) showed that the graft-polymerized polypropylene films had smooth surface. Therefore, the decrease in contact angle results from changes in chemical composition at the polypropylene surface by the graft polymerization.

Table 1 Advancing Contact Angle of Water against Polypropylene Surface modified by GMA-Plasma-Graft Polymerization and by Plasma Treatment

Surface Modification			Advancing Contact Angle of Water (degree)
Plasma	Plasma Exposure Time (min)	GMA Exposure Time (min)	
Ar	2	-	50
Ar	0.5	10	52
Ar	1	10	40
Ar	2	10	38
Ar	5	10	38
Ar	2	0.5	38
Ar	2	2	38
Ar	2	5	36
Ar	2	30	36
Polypropylene			98

Table 1 shows the advancing contact angle of water against the plasma-graft-polymerized polypropylene films as functions of the exposure time to the argon plasma and the exposure time to the GMA vapor. The argon plasma exposure time gives large influence on the contact angle. When the polypropylene films were exposed to the argon plasma for 0.5 - 5 min, and then exposed to the GMA vapor for 10 min, the advancing contact angle of water decreases from 98° with increasing the argon plasma exposure time, and reaches 38° at exposure times of more than 2 min. The argon plasma exposure also leads to the decrease in advancing contact angle, but the decrease is smaller than that by the combination of the argon plasma and GMA vapor exposure. The advancing contact angle of water is 50° for the polypropylene surface exposed to the argon plasma for 2 min, and is 38° for the polypropylene surface treated by the combination of the argon plasma and GMA vapor exposure. Therefore this comparison indicates that the combination of the argon plasma and GMA vapor exposure makes polypropylene surface more hydrophilic. The exposure time of the GMA vapor gives less influence on the contact angle. When the polypropylene films were exposed to the argon plasma for 2 min and then exposed to the GMA vapor for 0.5 - 30 min, the advancing contact angle of water against the treated film surfaces is 38 - 36° which is changeless within an observational error. The surface energy of the GMA-graft-polymerized polypropylene is estimated to be 55.8 mJ/m<sup>2</sup>. This advantage contact angle corresponds to that of GMA homopolymer (38°) which was radical-polymerized. From the results we conclude that the combination of the argon plasma and GMA vapor exposures leads to the graft polymerization of GMA at the surface of polypropylene films. This graft polymerization is initiated by the argon plasma exposure for 2 min, and is accomplished with the GMA vapor exposure for 2 min.

Allmer et al. have reported that the UV irradiation in the presence of benzophenone can initiate GMA graft polymerization at the surface of polyethylene films. The polyethylene films GMA-graft-polymerized by the photoinitiation showed an advancing contact angle of water of 77.6°, which is fairly larger than the polypropylene films GMA-graft-polymerized by the argon plasma irradiation. The difference in advancing contact angle may be due to hydroxyl groups which were formed by the ring-opening reaction of epoxide groups in the graftpolymer chains of GMA. The reaction will be discussed from results of IR spectra.

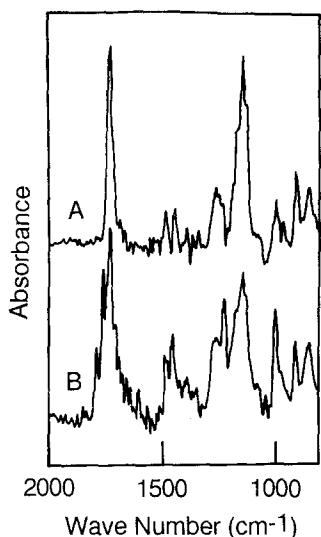


Fig. 2 Difference IR Spectrum between GMA-Graft-Polymerized Polypropylene and Polypropylene (A) and IR Spectrum of GMA Homopolymer (B).

Fig. 2 shows a difference ATR IR spectrum between the GMA-grafted polypropylene and ungrafted polypropylene and an IR spectrum of GMA homopolymer which was radical-polymerized. On the difference IR spectrum (spectrum A) characteristic absorption peaks due to carboxylate and epoxide groups appear at 1737 ( $\nu\text{C}=\text{O}$  in ester), 1494 ( $\delta\text{CH}_3$ ), 1455 ( $\delta\text{CH}_2$ ), 1378 ( $\delta\text{CH}_3$ ), 1231 (epoxide), 1141 ( $\delta\text{C}-\text{O}$  in ester), 1128 ( $\delta\text{C}-\text{O}$  in  $-\text{CH}_2\text{OH}$ ), 1000 ( $\delta\text{C}-\text{O}$  in  $-\text{CHOH}$ ), 917 (epoxide), and  $857\text{ cm}^{-1}$  (epoxide) [11], which correspond essentially to those of GMA homopolymer (spectrum B). This correspondence suggests the possibility that GMA could be graft-polymerized at the surface of the polypropylene films. The relative intensity ratio ( $I_{\text{C}=\text{O}}/I_{\text{CH}_2}$ ) of the absorptions at 1737 ( $\text{C}=\text{O}$  groups) and  $1455\text{ cm}^{-1}$  ( $\text{CH}$  groups) is calculated to be 0.21, which corresponds to the Allmer's results [4] (the ratio is 0.2 in the graft polymerization in the acetone solution, and 0.21 in the graft polymerization in ethanol solution). They calculated that the percentage of the surface covered with the GMA graft polymers from the XPS spectra was 46 % for the specimen having a  $I_{\text{C}=\text{O}}/I_{\text{CH}_2}$  ratio of 0.21 [4].

The appearance of the absorption peaks at 1128 and  $1000\text{ cm}^{-1}$  assigned to  $\delta\text{C}-\text{O}$  in alcohol shows that a part of epoxide groups in the GMA-graft-polymer reacted with water in air during the Soxhlet extraction to form hydroxyl groups. This hydroxyl formation could contribute mainly to decrease in advancing contact angle of water.

### Durability of GMA-Graft-Polymerized Polypropylene Surface

Polymer Surface modified by oxygen plasma treatment begins loss of its hydrophilicity just after accomplishing the treatment. The loss is due to the moving and diffusing of polar groups which were introduced at the polymer surface by the plasma treatment into the bulk of the polymer. The polymer surface can't exclude the loss because of the thermal motion of the polymer chains. If the moving and diffusing of polar groups can be restricted the stability of hydrophilic surface will be improved. The formation of crosslinking at the polymer surface is a possible way of the restriction [2], and the grafting of polymer chains containing polar groups may be another way.

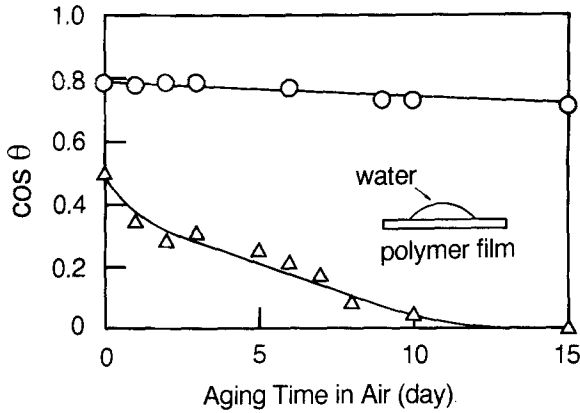


Fig. 3 Advancing Contact Angle of Water ( $\theta$ ) against GMA-Graft-polymerized Polypropylene (○) and Oxygen-Plasma Treated Polypropylene (△) as a function of Aging Time in Air.

Fig. 3 shows the advancing contact angle of water against GMA-graft-polymerized polypropylene surface as a function of the aging time after the grafting. The figure includes the oxygen-plasma-treated polypropylene film as a contrastive specimen. The GMA-graft-polymerized polypropylene film shows a gradual decrease in  $\cos \theta$  with increasing the aging time. The advancing contact angle of water increases from  $38^\circ$  (as grafted) to  $45^\circ$  (after 15 days). On the other hand, the oxygen-plasma-treated polypropylene film shows a rapid decrease in advancing contact angle. At 15 days after the plasma-treatment the advancing contact angle is  $90^\circ$  which is almost equal to that of the untreated polypropylene film ( $98^\circ$ ).

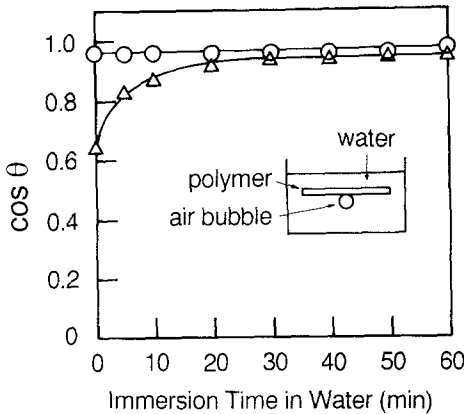


Fig. 4 Receding Contact Angle of Water ( $\theta$ ) against GMA-Graft-Polymerized Polypropylene (○) and Oxygen-Plasma-Treated Polypropylene (△) as a function of Immersion Time in Water.

Fig. 4 shows the receding contact angle of water against the GMA-graft-polymerized and oxygen-plasma-treated polypropylene surfaces as a function of the immersion time in water. The two polypropylene specimens were stored at  $80^\circ\text{C}$  for 3 weeks which was sufficient duration for the polar groups to move and diffuse from the surface layer into the bulk of the polymer. Thereafter, the specimens were immersed in water at  $30^\circ\text{C}$  and the contact angle of air bubble ( $1\ \mu\text{l}$ ) against the surface of the specimen was measured as a function of the immersion time. The GMA-graft-polymerized polypropylene film shows no change in receding contact angle even when immersed in water. The receding contact angle is  $17^\circ$  and  $16^\circ$  at 0 and 60 min after the water immersion, respectively. On the other hand, the oxygen-plasma-treated polypropylene film shows large decreases in receding contact angle

with increasing the water immersion time. The receding contact angle is 50, 30, 24, and 19° at 0, 10, 20, and 60 min after the water immersion, respectively. This figure suggests that the GMA-graft-polymerized polypropylene possesses good stability of its hydrophilic surface.

In conclusion, the combination of the argon plasma and GMA vapor exposures leads to graft polymerization of GMA at the surface of polypropylene films. This graft polymerization is initiated by the argon plasma exposure for 2 min, and is accomplished with the GMA vapor exposure for 2 min. The GMA graft polymerization makes polypropylene surface hydrophilic. The surface energy is 55.8 mJ/m<sup>2</sup>. The hydrophilicity introduced by the GMA graft polymerization is not lost when the film is stored in air for at least 3 weeks. The graft polymerization of hydrophilic monomers is a good means of hydrophilic surface modification.

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