

Estimation of Surface Properties of Grafted Layers Formed on Low- and High-Density Polyethylene Plates by Photografting of Methacrylic Acid and Acrylic Acid at Different Monomer Concentrations and Temperatures

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ABSTRACT: An investigation was carried out on estimation of hydrophilicity, wettability and water-absorptivity, and surface analysis by X-ray photoelectron spectroscopy of the low- and high-density polyethylene (LDPE and HDPE) plates photografted with methacrylic acid (MAA) and acrylic acid (AA) at different monomer concentrations or temperatures. Wettability of the MAA-grafted LDPE and HDPE plates increased with grafted amounts, and became constant when the substrate surfaces were fully covered with the grafted polymer chains. On the other hand, for the AA-grafted LDPE and HDPE plates, wettability had the maximum value, and then gradually decreased against the grafted amount probably due to aggregation of grafted PAA chains, although the surfaces were covered with grafted PAA chains at lower grafted

amounts compared with grafted PMAA chains. Water-absorptivity sharply increased at lower grafted amounts due to formation of shorter grafted polymer chains for photografting at lower monomer concentrations or due to restriction of the location of grafting to the outer surface region for photografting at lower temperatures. Therefore, for photograftings of AA or onto the HDPE plates, the substrate surfaces were covered with grafted polymer chains and the grafted layers formed possessed higher water-absorptivity at lower grafted amounts. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2614–2625, 2012

Key words: ESCA/XPS; graft copolymers; hydrophilic polymers; polyethylene; surface modification

INTRODUCTION

Polyethylene (PE) is a polymer material generally used in diverse fields. However, due to the hydrophobic and inert surfaces, their availability is frequently limited. Up to now, various surface modification techniques have been developed to make their surfaces hydrophilic, including chemical reactions,¹ corona discharge,^{2,3} plasma treatment,^{4–6} and grafting.^{7,8} For example, various oxygen-functional groups are formed on the surfaces of the PE substrates by plasma treatments with generated from non-polymer-forming gases such as O₂, N₂, He, and Ar^{9–13} or UV irradiation.^{14–16} However, hydrophilicity of the PE surfaces modified by these techniques gradually regresses against the time elapsed because polar functional groups formed on the surfaces will tend to readily overturn in the outer surface region or migrate into the bulk of the polymer substrates

mainly due to local motion of substrate polymer segments.^{17–19}

On the other hand, the surface properties of the polymer materials modified by the grafting technique will durably remained because polymer chains were introduced to the surfaces. In fact, the grafting technique is much attractive in modifying surface and functional properties of the polyolefin materials such as low- and high-density polyethylene (LDPE and HDPE) and polypropylene (PP). Many initiation methods of surface grafting have been developed, e.g., chemical reagents,²⁰ electron beam,^{21,22} γ -ray,^{23,24} plasma,^{25,26} and UV-irradiation.^{27–29} Among them, the combined use of UV initiation with a hydrogen-abstraction-type photosensitizer is one of the most attractive procedures.^{30–32} Over two decades, we have investigated surface modification of the LDPE,^{27,29,33–35} HDPE,^{29,33,35} and PP³³ plates by the photografting technique with a 400W high-pressure mercury lamp. The procedure is very simple, and the initial sites for grafting and the density of functional groups can be readily controlled. In addition, since the energy of UV rays is lower than those of other grafting techniques, the location of grafting can be restricted to the outer surface region of the polymer substrates.

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TABLE I
Conditions of Photografting of MAA and AA onto the LDPE and HDPE Plates

Monomer	Substrate	Temperature (°C)	Monomer concentration (M)
MAA	LDPE	60	0.5, 1.0, and 1.5
	HDPE	60	0.5, 1.0, 1.5, and 2.0
AA	LDPE	60	0.5, 1.0, and 1.5
	HDPE	60	0.5, 1.0, 1.5, and 2.0
MAA	LDPE	40, 50, 60, and 70	1.0
	HDPE	40, 50, 60, and 70	1.0
AA	LDPE	40, 50, and 60	1.0
	HDPE	40, 50, and 60	1.0

Adhesive or autohesive strength of a LDPE plate was also considerably improved by the photograftings of hydrophilic monomers such as methacrylic acid (MAA),^{27,29} acrylic acid (AA),^{27,29} and methacrylamide (MAAm)³⁴ and the substrates were broken at higher grafted amounts. This means that adhesive or autohesive strength went over the ultimate strength of the LDPE plate used.^{33–35}

Wettability is a measure of the hydrophilicity of the substrate surface and depends on the surface composition, which is closely related with adhesivity of the modified polymer materials. Therefore, surface analysis by X-ray photoelectron spectroscopy (XPS) has been used to determine the surface composition of the modified polymer materials.^{27,34} Water-absorptivity of the grafted layers formed is also a factor to influence adhesive strength.²⁷ Water-absorptivity as a characteristic of the whole grafted layer depends on the number and length of grafted polymer chains formed, the location of grafting, the density of grafted polymer chains in the grafted layer, and so on.^{27,29,33} These characteristics of the whole grafted layer can be varied by the grafting conditions such as the temperature, kind of monomer, kind and composition of solvent, and so on.^{27,33,36} Many studies have been reported on an effect of the grafting conditions on the degree of grafting and kinetic analysis of grafting.^{37,38,39–42} However, little was reported on an influence of the grafting conditions on the characteristics of the grafted layers formed such as wettability, water-absorptivity, and adhesivity.^{27,29} Adhesivity is enhanced by modifying surface properties of the surfaces of the materials. Wettability strongly depends on the density of polar functional groups on the surfaces. In addition, adhesives can penetrate in the grafted layers formed by photografting of hydrophilic monomers. Therefore, it is of great importance to estimate the characteristics of the grafted layers formed under different conditions in discussing the relation of adhesivity of the grafted polymer substrates with hydrophilic properties of the grafted layers formed.

In this study, the photografting of MAA and AA onto the LDPE and HDPE plates was carried out at

different monomer concentrations and temperatures. Wettability and water-absorptivity of the resultant grafted LDPE and HDPE plates were characterized as function of the grafted amount in relation with the grafting conditions such as the monomer concentration and temperature for the photografting and their surface compositions determined by XPS.

EXPERIMENTAL

Materials

The LDPE and HDPE plates of 1.0-mm thickness were used as a polymer substrate for photografting. Crystallinity was calculated to be 50.8% for the LDPE plate and 69.7% for the HDPE plate from the density measurements by a flotation or buoyancy method with methanol and glycerol at 25°C using the densities of the completely amorphous and pure crystalline parts of PE.^{29,43} The LDPE and HDPE plates of 7.0-cm length and 2.4-cm width were washed with distilled water, methanol and acetone by turns, and then dried under reduced pressure. MAA and AA were purchased from Wako Pure chemical and used without further purification.

Photografting

The solutions of MAA and AA were prepared in water at the monomer concentrations of 0.5–2.0M. In acetone, 0.25 g of benzophenone (BP) as a sensitizer was dissolved and made up to 50 cm³ (0.5 w/v %). The LDPE and HDPE plates were immersed in a BP solution for 1 min, and then acetone was evaporated at room temperature to coat BP on their surfaces. Then, the BP-coated LDPE and HDPE plates (length: 7.0 cm, width: 2.4 cm) were immersed in the respective monomer solutions (65 cm³) in the Pyrex glass tubes and UV rays emitted from a 400W high-pressure mercury lamp were irradiated at 40–70°C.^{29,35,43,44} The grafting conditions were summarized in Table I. The distance between the high-pressure mercury lamp and each Pyrex glass tube was 2.2 cm. During the irradiation of UV rays, the Pyrex

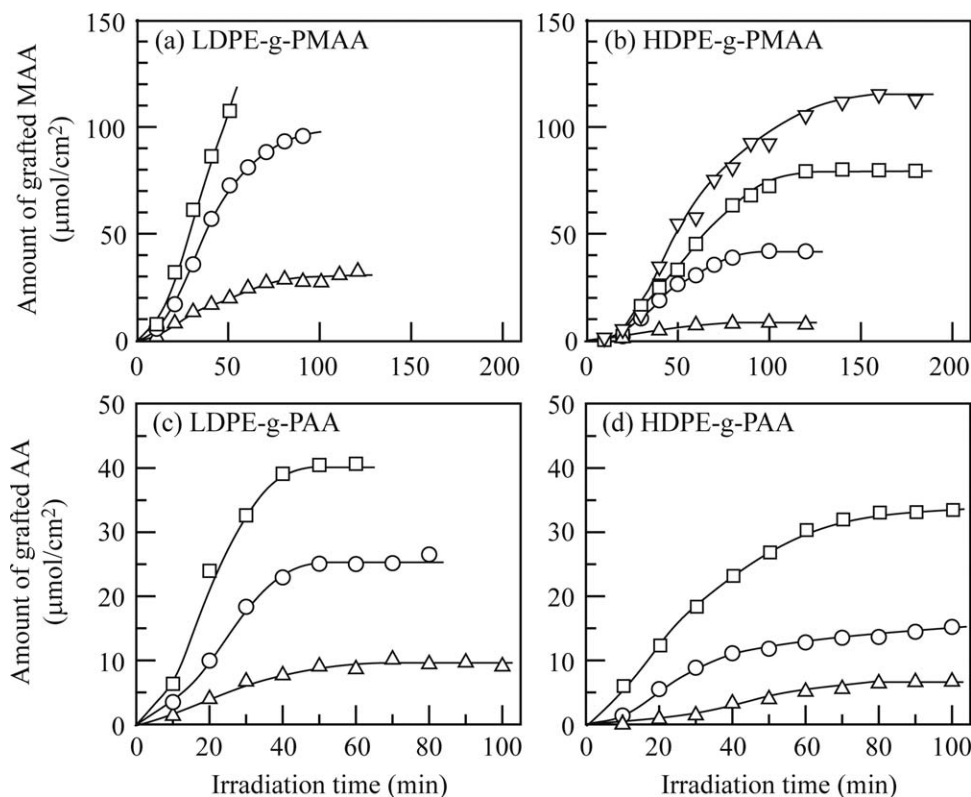


Figure 1 Photografting of (a and b) MAA and (c and d) AA onto the (a and c) LDPE and (b and d) HDPE plates in monomer solutions of different concentrations at 60°C. Monomer concentration (M)- \triangle : 0.5, \circ : 1.0, \square : 1.5, ∇ : 2.0.

glass tubes rotated on its axis every 10 s and revolved around the high-pressure mercury lamp in 1.0 min. After the photografting, the grafted LDPE and HDPE plates were washed with water for 24 h to exclude unreacted monomers and homopolymers, and then dried under reduced pressure. The grafted amount in $\mu\text{mol}/\text{cm}^2$ was calculated from the weight increase of the LDPE and HDPE plates after the photografting according to eq. (1).

$$\text{Grafted amount} = \frac{(W_g - W_0)/M}{33.6} \times 10^6 \quad (1)$$

where W_g is weight of the grafted LDPE and HDPE plates (g); W_0 weight of the ungrafted LDPE and HDPE plates (g); and M molar mass of the monomers used (g/mol). The quantity of 33.6 is the surface area (cm^2) except for the side surfaces for the LDPE and HDPE plates.

In addition, the aliquots of 5 cm^3 were taken from the outer solutions at predetermined time intervals, and then added dropwise in excess methanol. Then, when a NaOH solution at 1M was added so as to reach the pH value to 10 and the solutions were continuously stirred, homopolymers of PMAA or PAA sodium salt were precipitated. The polymer precipitates were filtered out, and then washed throughout

with methanol until the filtrates became neutral. Finally, they were dried under reduced pressure and the weight of formed homopolymers was measured. As shown in eq. (2), the consumption rate of monomer (M/min) is equal to the sum of the formation rates of grafted polymer chains and homopolymers.

$$-\frac{d[M]}{dt} = -\left(\frac{d[M]_{\text{graft}}}{dt} + \frac{d[M]_{\text{homo}}}{dt}\right) \quad (2)$$

The concentrations of monomers consumed by the photografting and formation of homopolymers, $[M]_{\text{graft}}$ and $[M]_{\text{homo}}$, were represented by eqs. (3) and (4), respectively.

$$[M]_{\text{graft}} = \frac{W_g - W_0}{M} / 0.065 \quad (3)$$

$$[M]_{\text{homo}} = \frac{W_{\text{homo}}}{M_{\text{Na}}} / 0.005 \quad (4)$$

where W_{homo} is weight of precipitated homopolymers sodium salt; M_{Na} molar mass of MAA and AA sodium salt. The formation rates of grafted polymer chains and homopolymers were calculated from the slope of their formed amounts against the irradiation time, t , in the initial stage.

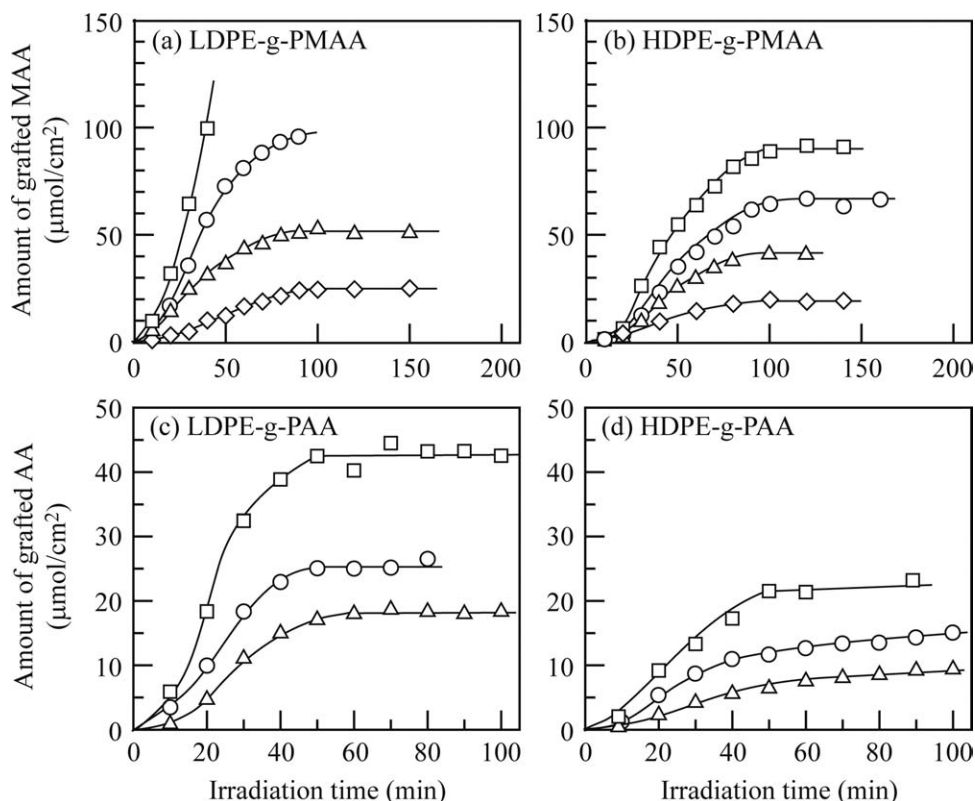


Figure 2 Photografting of (a and b) MAA and (c and d) AA onto the (a and c) LDPE and (b and d) HDPE plates in monomer solutions of 1.0M at different temperatures. Temperature °C-◇: 40, △: 50, ○: 60, □: 70.

Characterization of grafted PE plates

The C1s and O1s core spectra for grafted LDPE and HDPE plates were recorded on a Shimadzu ESCA-3400 spectrophotometer with the MgK α (1253.6eV) source operating at 8 kV and 20 mA.^{27,45,46} The intensity ratio, O1s/C1s, was calculated from the O1s and C1s peak areas measured at a take-off angle of 90° of photoelectrons and the ionized cross-sections to determine the surface compositions of the grafted LDPE and HDPE plates.^{27,47-49} The contact angles for water on the surfaces of the grafted LDPE and HDPE plates were measured by a sessile drop method at 25°C with a Kyowa Kagaku TYP-QI-type goniometer.²⁷

The amount of absorbed water for the grafted LDPE and HDPE plates was measured to estimate the hydrophilic properties of the whole grafted layers. The grafted LDPE and HDPE plates were immersed in distilled water at 25°C for 24 h. Then, the grafted LDPE and HDPE plates were taken out of water, blotted with filter paper to remove water attached to their surfaces, and weighed as quickly as possible. The amount of absorbed water (g/g-grafted PE) was calculated according to eq. (5).

$$\text{Amount of absorbed water} = \frac{W_w - W_g}{W_g} \quad (5)$$

where W_w is weight of the grafted LDPE and HDPE plates immersed in water (g).

RESULTS AND DISCUSSION

Photografting

The photografting of MAA and AA onto the LDPE and HDPE plates was carried out at different monomer concentrations and temperatures as shown in Table I. Figure 1 shows the effect of the monomer concentration on the photografting of MAA and AA onto the LDPE and HDPE plates at 60°C. The amounts of grafted MAA and AA increased against the UV irradiation time irrespective of monomer concentration. Higher grafted amounts were obtained at shorter irradiation times, as the monomer concentration was increased. However, the grafted amounts tended to level off at longer irradiation times except photografting of MAA onto the LDPE plate at 1.5M and 60°C. In addition, the amount of grafted MAA was higher than the amount of grafted AA at the same irradiation time for both polymer substrates. For the photografting of methacrylic and acrylic monomers onto the LDPE and HDPE plates and films, the grafted amounts of methacrylic monomers were higher than those of acrylic monomers such as MAA > AA,²⁷ 2-hydroxyethyl methacrylate (HEMA) > 2-hydroxyethyl acrylate,⁵⁰ and MAAM > acrylamide.^{27,34} This is considered to be attributed to higher affinity of methacrylic monomers toward the PE because the methacrylic monomers have a α -methyl group in the

TABLE II
Grafting of MAA onto the LDPE Plates
Under Different Conditions

Coating of BP	UV irradiation	Irradiation time (min)	Temperature (°C)	Grafted amount ($\mu\text{mol}/\text{cm}^2$)
Yes	Yes	60	60	72.5
Yes	Yes	60	40	17.2
No	Yes	60	60	13.8
No	Yes	120	60	35.7
No	Yes	60	40	2.63
Yes	No	0	60	0.32
Yes	No	0	40	0.17
No	No	0	60	0.08

repeating unit. In other words, the methacrylic monomers are a little more hydrophobic than the acrylic monomers, although these monomers are soluble in water. In addition, the grafted amounts for the HDPE plates were lower than those for the LDPE plates. This is mainly due to higher crystallinity of the HDPE plate. A difference in the grafted amount between the LDPE and HDPE plates was also reported in other articles.^{29,51,52}

Figure 2 shows the effect of the temperature on the photografting of MAA and AA onto the LDPE and HDPE plates at the monomer concentration of

1.0M. As the temperature increased, higher grafted amounts were obtained at shorter irradiation times. However, the grafted amounts tended to level off at longer irradiation times except photografting of MAA onto the LDPE plate at 70°C, since diffusion of monomers in the medium decreased due to formation of a large amount of homopolymers. An increase in the grafted amount at higher temperatures is considered to be due to an increase in active sites through hydrogen-abstraction from PE chains.^{53,54}

Subsequently, grafting of MAA onto the LDPE plate was carried out at different conditions to discuss the effectiveness of coating with BP, irradiation of UV rays, and increase in the temperature. The amounts of grafted MAA obtained under different grafting conditions were summarized in Table II. The grafted amount for photografting without coating with BP at 60°C was limited to 13.8 $\mu\text{mol}/\text{cm}^2$ and the thermal grafting of MAA little occurred at 40°C. When one or two of the three procedures described above was conducted, the grafted amount was successfully increased. It was found from Table II that either coating of the LDPE surface with BP or UV irradiation is effective for an enhancement in the hydrogen-abstraction from PE chains and an increase in the grafted amount.⁵⁰

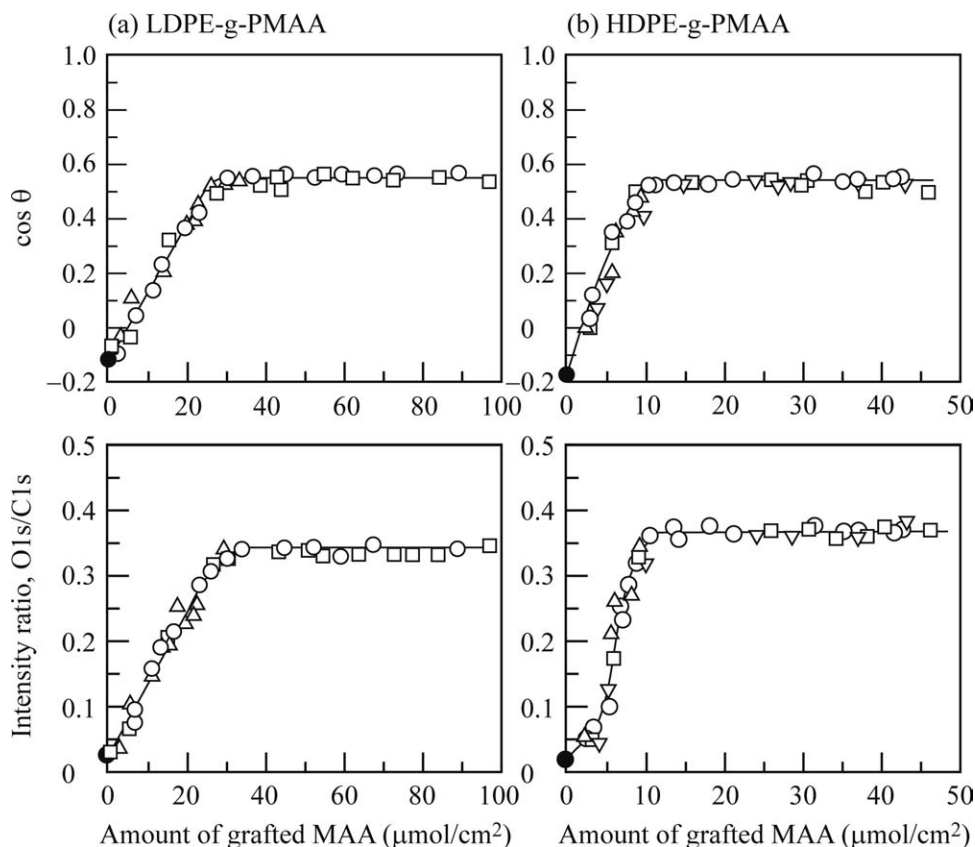


Figure 3 Water wettability and surface analysis by XPS of the (a) LDPE-g-PMAA and (b) HDPE-g-PMAA plates prepared in monomer solutions of different concentrations at 60°C. Monomer concentration (M)- Δ : 0.5, \circ : 1.0, \square : 1.5, ∇ : 2.0.

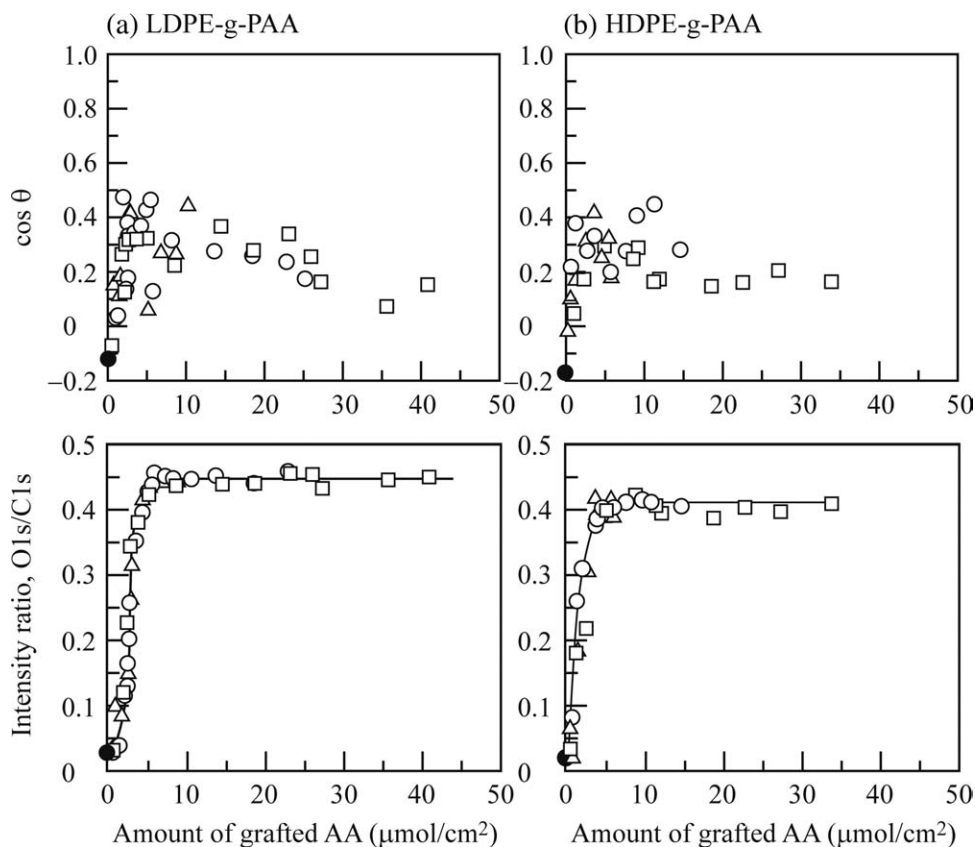


Figure 4 Water wettability and surface analysis by XPS of the (a) LDPE-g-PAA and (b) HDPE-g-PAA plates prepared in monomer solutions of different concentrations at 60°C. Monomer concentration (M)- Δ : 0.5, \circ : 1.0, \square : 1.5, ∇ : 2.0.

Effect of monomer concentration

Wettability and surface composition

The wettability measurements and surface analysis by XPS were carried out for the grafted LDPE and HDPE plates with prepared at different monomer concentrations. Figure 3(a,b) shows the effect of the monomer concentration on the wettability and surface composition for the MAA-grafted LDPE and HDPE (LDPE-g-PMAA and HDPE-g-PMAA) plates prepared at 60°C. The values of $\cos \theta$ and intensity ratio, O1s/C1s, increased with an increase in the grafted amount and leveled off at further grafted amounts. The grafted amounts at which the $\cos \theta$ value became constant were in close agreement with those at which the intensity ratio became constant for both LDPE-g-PMAA and HDPE-g-PMAA plates. Since the constant intensity ratio reflects the density of grafted PMAA chains in the surface region of the grafted layers formed on the LDPE and HDPE plates, the above results indicate that wettability depends on the density of carboxylic groups of grafted PMAA chains present in the surface region of the LDPE and HDPE plates and becomes constant when the LDPE and HDPE surfaces are fully covered with grafted PMAA chains.

Subsequently, Figure 4(a,b) shows the effect of the monomer concentration on the wettability and surface composition for the AA-grafted LDPE and HDPE (LDPE-g-PAA and HDPE-g-PAA) plates prepared at 60°C. The intensity ratio for the LDPE-g-PAA and HDPE-g-PAA plates increased with an increase in the grafted amount and then became constant at further grafted amounts as is the case with the LDPE-g-PMAA and HDPE-g-PMAA plates. However, $\cos \theta$ passed through the maximum value and then gradually decreased against the grafted amount. Since the decrease in wettability was observed in the range of the grafted amount at which the intensity ratio is constant, it could be one of the reasons that grafted PAA chains are aggregated through hydrogen bonding between carboxyl groups.⁵⁵ The results shown in Figures 3 and 4 indicate that both the location of the photografting and the density of carboxyl groups in the surface region of the grafted layers are independent of the monomer concentration for the photografting.

The chemical composition of the surface region of the grafted layers was calculated from the constant intensity ratios of the grafted LDPE and HDPE plates prepared at different monomer concentrations

TABLE III
Water Wettability and Surface Composition of the grafted LDPE and HDPE Plates Prepared at 60°C

Sample	Grafted amount ($\mu\text{mol}/\text{cm}^2$)	O1s/C1s	$\cos \theta$	Composition (%)
LDPE		0.027	-0.120	
HDPE		0.021	-0.180	
PMAA		0.384		
PAA		0.518		
LDPE-g-PMAA	25	0.33	0.55	85.9
HDPE-g-PMAA	10	0.36	0.54	93.8
LDPE-g-PAA	6	0.44	0.4 (max)	84.9
HDPE-g-PAA	3.5	0.42	0.4 (max)	81.1

and the intensity ratios of PMAA and PAA homopolymers prepared,²⁹ and the results were summarized in Table III. The constant intensity ratios of the grafted LDPE and HDPE plates prepared at 1.0M and 60°C were lower than the intensity ratio of the corresponding homopolymers. This indicates that a small amount of PE chains are present in the surface region of the grafted layers. In addition, the intensity ratios became constant at lower grafted amounts for the grafted HDPE plates than for the grafted LDPE plates, indicating that the location of the photografting is restricted to the outer surface region for the HDPE plates than for the LDPE plates. This is considered to be due to a high crystallinity of the HDPE

plate. In this study, water was used as a solvent for the photografting of MAA and AA. Here, if other organic solvents are used in place of water, the monomer medium can penetrate into the surface region of the PE substrate, which is accompanied by the progression of the grafting into the inside of the substrate and a decrease in the density of grafted polymer chains in the grafted layer. This behavior is considered to be disadvantageous in the properties closely related with the surface composition such as wettability and adhesion.

Water-absorptivity

Figure 5(a,b) shows the changes in the water-absorptivity with the grafted amount for the grafted LDPE and HDPE plates prepared at different monomer concentrations. The amount of absorbed water for grafted LDPE and HDPE plates prepared at lower monomer concentrations sharply increased at lower grafted amounts. Surface analysis by XPS (Figs. 3 and 4) showed that the location of the photografting of MAA and AA is independent of the monomer concentration at a constant temperature. Therefore, the monomer concentration dependence of the water-absorptivity is considered to be explained in terms of the kinetics of radical polymerization.⁵⁶⁻⁵⁸ Figure 6 shows the changes in the rates of

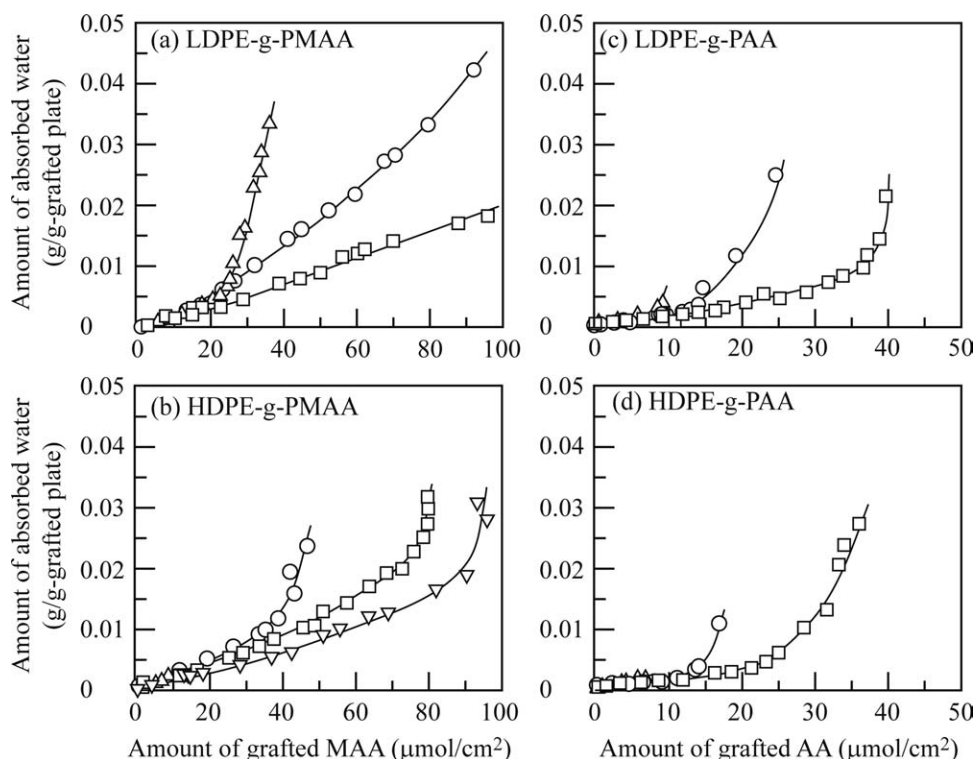


Figure 5 Water-absorptivity of the (a) LDPE-g-PMAA, (b) HDPE-g-PMAA, (c) LDPE-g-PAA, and (d) HDPE-g-PAA plates prepared in monomer solutions of different concentrations at 60°C. Monomer concentration (M)- Δ : 0.5, \circ : 1.0, \square : 1.5, ∇ : 2.0.

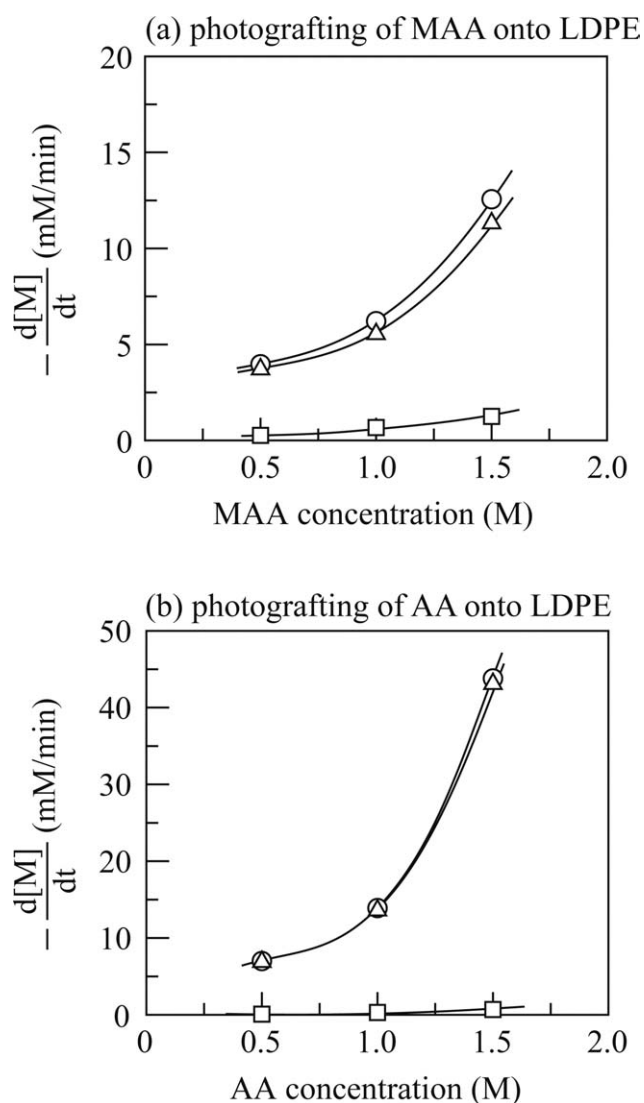


Figure 6 The rates of polymerization (○), grafting (□), and homopolymerization (△) for photografting of (a) MAA and (b) AA onto the LDPE plate in monomer solutions of different concentrations at 60°C.

photografting and homopolymerization with the monomer concentration for the photografting of MAA and AA onto the LDPE plate at 60°C.

The rates of photografting and homopolymerization increased with the monomer concentration for both photograftings of MAA and AA onto the LDPE plates, although most of the monomers consumed were involved in formation of homopolymers. In fact, the medium became highly viscous at longer irradiation times during photografting of AA. An increase in the rate of photografting at a constant temperature results in an increase in the rate of propagation of grafted polymer chains. It is considered that the photografting was initiated from the radical active sites generated mainly by abstraction of hydrogen atoms from PE chains in the range below the grafted amounts at which the surfaces of

the LDPE and HDPE plates are fully covered with grafted polymer chains and longer grafted polymer chains are formed at higher monomer concentrations. On the other hand, since the LDPE and HDPE surfaces are covered with grafted polymer chains in the range of the constant intensity ratio, radical active sites will be formed on grafted polymer chains and the grafting on grafted polymer chains occur. Therefore, from the above results, we can conclude that the grafted layers with shorter grafted chains formed at lower monomer concentrations have the capability to hold more water molecules and possessed high water-absorptivity.

Effect of temperature

Wettability and surface composition

Wettability measurements and surface analysis by XPS were carried out for grafted LDPE and HDPE plates prepared at different temperatures. Figure 7(a,b) shows the effect of the grafting temperature on the wettability and surface composition for the LDPE-g-PMAA and HDPE-g-PMAA plates prepared at a monomer concentration of 1.0M. As the temperature for the photografting increased, the values of $\cos \theta$ and O1s/C1s became constant at higher grafted amounts and their constant values were lower.

Figure 8(a,b) shows the effect of the grafting temperature on wettability and surface composition for the LDPE-g-PAA and HDPE-g-PAA prepared at a monomer concentration of 1.0M. The $\cos \theta$ value went through the maximum and then gradually decreased against the amount of grafted AA irrespective of the temperature during the photografting. On the other hand, the intensity ratio for the LDPE-g-PAA and HDPE-g-PAA plates prepared at higher temperatures became constant at higher grafted amounts in analogy with the LDPE-g-PMAA and HDPE-g-PMAA plates. A decrease in wettability specifically characteristic of the LDPE-g-PAA and HDPE-g-PAA plates wasn't observed for the LDPE plates photografted with MAA and HEMA as well as the LDPE-g-PMAA and HDPE-g-PMAA plates.^{29,34} In addition, since the energy of UV-rays irradiated from a 400W high-pressure mercury lamp is lower than those of other grafting techniques, the location of the grafting can be restricted to the outer surface region of the substrate. Therefore, the grafted layer rich in grafted polymer chains can be formed by the photografting technique with a 400W high-pressure mercury lamp. In addition, through our investigations on the photografting of hydrophilic monomers, the absence of a α -methyl group in the monomer structure can be involved in the aggregation of grafted PAA chains. The surface composition

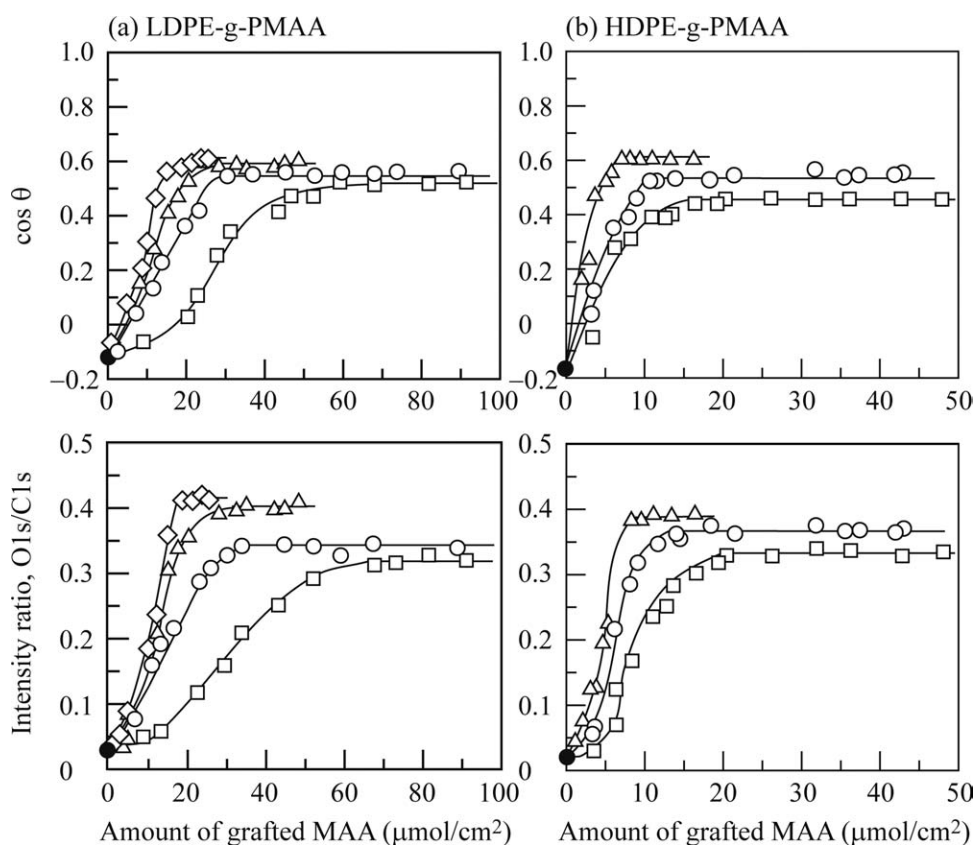


Figure 7 Water wettability and surface analysis by XPS of the (a) LDPE-g-PMAA and (b) HDPE-g-PMAA plates prepared in monomer solutions of 1.0M at different temperatures. Temperature ($^{\circ}\text{C}$)- \diamond : 40, \triangle : 50, \circ : 60, \square : 70.

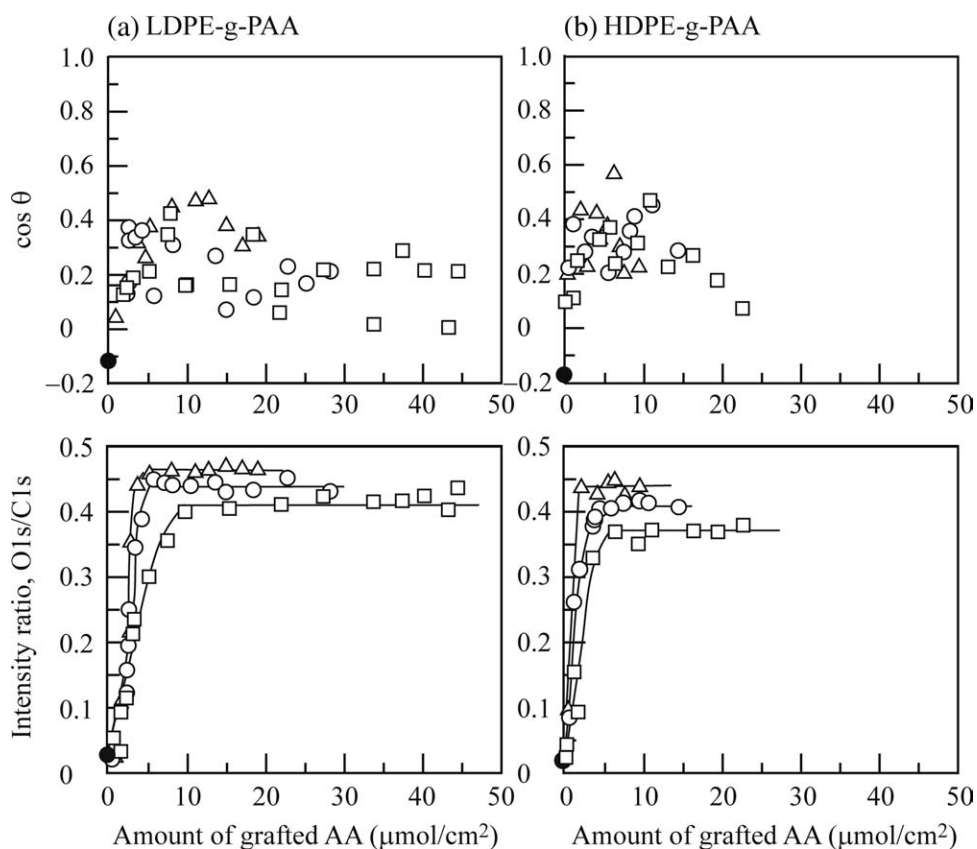


Figure 8 Water wettability and surface analysis by XPS of the (a) LDPE-g-PAA and (b) HDPE-g-PAA plates prepared in monomer solutions of 1.0M at different temperatures. Temperature ($^{\circ}\text{C}$)- \diamond : 40, \triangle : 50, \circ : 60, \square : 70.

TABLE IV
Water Wettability and Surface Composition of the LDPE-g-PMAA and HDPE-g-PMAA Plates Prepared at Different Temperatures

Sample	Temperature (°C)	Grafted amount (μmol/cm ²)	O1s/C1s	cos θ	Composition (%)
LDPE-g-PMAA	40	18	0.38	0.61	98.9
	50	20	0.36	0.58	93.8
	60	25	0.33	0.55	85.9
	70	65	0.31	0.51	80.7
HDPE-g-PMAA	50	7	0.38	0.60	98.9
	60	10	0.36	0.54	93.8
	70	17	0.33	0.45	85.9

obtained for the grafted LDPE and HDPE plates prepared at different temperatures was summarized in Tables IV and V, respectively. As the temperature during photografting was increased, the photografting of MAA and AA more progressed into the inside of the PE substrate. Either lower crystallinity of the LDPE plate or a little less hydrophilicity of MAA will enhance the progress of the photografting into the PE substrate. Therefore, among the grafted PE plates prepared in this study, the substrate surface was fully covered with grafted polymer chains at the lowest grafted amount for the HDPE-g-PAA plate. The results above-mentioned made it clear that the density of grafted polymer chains in the outer surface region of the grafted layer is independent of the monomer concentration and dependent on the temperature during the photografting.

Figure 9(a,b) shows the changes in the water-absorptivity with the grafted amount for the grafted LDPE and HDPE plates prepared at different temperatures. As the temperature of the photografting decreased, the water-absorptivity sharply increased at lower grafted amounts. According to the kinetics of radical polymerization, shorter grafted polymer chains are considered to be formed through higher chain transfer reaction at higher temperatures.⁵⁹ However, since the photografting more progresses into the interior of the substrate at higher tempera-

tures, the grafted layers more rich in grafted polymer chains are formed for grafted LDPE and HDPE plates prepared at lower temperatures. This is one reason for higher water-absorptivity for grafted LDPE and HDPE plates prepared at lower temperatures.

CONCLUSIONS

An investigation was carried out on estimation of hydrophilicity of the grafted layers formed on the LDPE and HDPE plates by photografting MAA and AA at different monomer concentrations and temperatures from the contact angle and water-absorptivity measurements and surface analysis by XPS. We drew the following conclusions from the experimental results obtained in this study. Wettability of the LDPE-g-PMAA and HDPE-g-PMAA plates increased with the grafted amounts, and then became constant when the substrate surfaces were fully covered with grafted PMAA chains. On the other hand, wettability for the LDPE-g-PAA and HDPE-g-PAA plates had the maximum values against the grafted amount, and then gradually decreased at higher grafted amounts. Water-absorptivity of the grafted LDPE and HDPE plates increased over the grafted amount irrespective of the grafting conditions such as the monomer concentration, temperature, and type of substrate. Water-absorptivity sharply increased at lower grafted amounts due to formation of shorter grafted polymer chains at lower monomer concentrations and due to restriction of the location of grafting to the outer surface region for photografting at lower temperatures. Therefore, since photografting of AA or photografting onto the HDPE plates also lead to restriction of the location of grafting to the outer surface region, the substrate surfaces were covered with grafted polymer chains and water-absorptivity sharply increased at lower grafted amounts. Our next step is to follow adhesive properties of the grafted LDPE and HDPE plates prepared at different

TABLE V
Water Wettability and Surface Composition of the LDPE-g-PAA and HDPE-g-PAA Plates Prepared at Different Temperatures

Sample	Temperature (°C)	Grafted amount (μmol/cm ²)	O1s/ C1s	Composition (%)
LDPE-g-PAA	50	4	0.47	91.8
	60	6	0.43	83.0
	70	10	0.41	79.2
HDPE-g-PAA	50	2	0.44	84.9
	60	3.5	0.41	79.2
	70	7	0.37	71.4

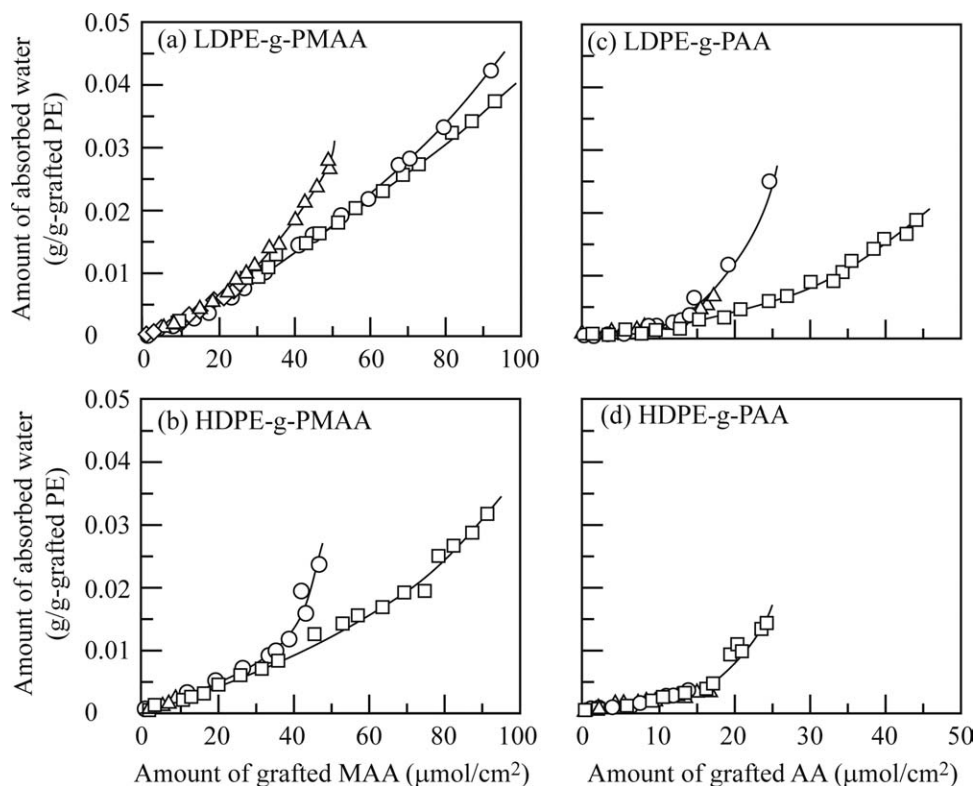


Figure 9 Water-absorptivity of the (a) LDPE-g-PMAA, (b) HDPE-g-PMAA, (c) LDPE-g-PAA, and (d) HDPE-g-PAA plates prepared in monomer solutions of 1.0M at different temperatures. Temperature (°C)-◇: 40, △: 50, ○: 60, □: 70.

monomer concentrations and temperatures with dilute chitosan solutions modified by enzyme tyrosinase in the presence of 3,4-dihydroxyphenethylamine (dopamine) to discuss tensile shear adhesive strength in relation with the surface properties such as wettability, water-absorptivity, and surface composition in addition to the grafted amount.

References

- Bandopadhyay, D.; Tarafdar, A.; Panda, A. B.; Pramanik, P. J *Appl Polym Sci* 2004, 92, 3046.
- Carley, J. F.; Kitz, P. T. *Polym Eng Sci* 2004, 18, 326.
- Ogawa, T.; Mukai, H.; Osawa, S. *J Appl Polym Sci* 2000, 79, 1162.
- Gilliam, M. A.; Yu, Q. S. *J Appl Polym Sci* 2005, 99, 2528.
- Ren, Y.; Hong, Y.; Sun, J.; Qiu, Y. *J Appl Polym Sci* 2008, 110, 995.
- Teodoru, S.; Kusano, Y.; Rozlosnik, N.; Michelsen, P. K. *Plasma Proc Polym* 2009, 6, S375.
- Wang, H.; Brown, H. R. *J Polym Sci Polym Phys* 2003, 42, 253.
- Iqbal, M.; Chuai, C.; Huang, Y.; Che, C. *J Appl Polym Sci* 2010, 116, 1558.
- Kang, M. S.; Chun, B.; Kim, S. S. *J Appl Polym Sci* 2001, 81, 1555.
- Kim, B. K.; Kim, K. S.; Park, C. E.; Ryu, C. M. *J Adhes Technol* 2002, 16, 509.
- Sanchis, M. R.; Blanes, V.; Blanes, M.; Garcia D.; Balart, R. *Eur Polym J* 2006, 42, 1558.
- Zhao G. W.; Chen, Y. S.; Wang, X. L. *Appl Surf Sci* 2007, 253, 4709.
- Masaeli, E.; Morshed, M.; Tavanai, H. *Surf Interface Anal* 2007, 39, 770.
- Irwan, G. S.; Aoyama, Y.; Kuroda, S.; Kubota, H.; Kondo, T. *Eur Polym J* 2004, 40, 171.
- Reddy, P. R. S.; Agathian, G.; Kumar, A. *Radiat Phys Chem* 2005, 73, 169.
- Tang, L.; Yan, M.; Qu, B. *J Appl Polym Sci* 2005, 99, 2068.
- Yasuda, T.; Yoshida, K.; Okuno, T. *J Polym Sci Polym Phys* 1988, 26, 2061.
- Morra, M.; Occhiello, E.; Garbassi, F. *Surf Interface Anal* 1990, 16, 412.
- Morra, M.; Occhiello, E.; Marola, R.; Gargasi, F.; Humphrey, P.; Johnson, D. J. *Colloid Interface Sci* 1990, 137, 11.
- Natta, G.; Severini, F. *Makromol Chem* 1968, 201, 119.
- Lim, S. L.; Fane, A. G. *J Appl Polym Sci* 1990, 41, 1609.
- Marletta, G.; Pignatoaro, S. *Macromolecules* 1991, 24, 99.
- Mahmoud, G. A. *J Appl Polym Sci* 2007, 104, 2769.
- Zu, J.; Wu, M.; Zhang, J.; Yu, C.; Liu, X.; Tong, L. *J Appl Polym Sci* 2006, 99, 3401.
- Huang, J.; Wang, X.; Chen, X.; Yu, X. *J Appl Polym Sci* 2003, 89, 3180.
- Hsiue, G. H.; Wang, C. C. *J Polym Sci Polym Chem* 2003, 31, 3327.
- Yamada, K.; Tsutaya, H.; Tatekawa, S.; Hirata, M. *J Appl Polym Sci* 1992, 46, 1065.
- Yamada, K.; Tatekawa, S.; Hirata, M. *J Colloid Interface Sci* 1994, 162, 144.
- Yamada, K.; Kimura, J.; Hirata, M. *J Appl Polym Sci* 2003, 87, 2244.
- Ikada, Y. *Biomaterials* 1994, 15, 725.
- Rândy, B. *Int J Adhes Adhes* 1999, 19, 337.
- Rândy, B.; Yang, W. T.; Tretinnikov, O. *Nucl Instrum Methods B* 1999, 151, 301.
- Yamada, K.; Kimura, T.; Hirata, M. *J Photopolym Sci Technol* 1998, 11, 263.

34. Yamada, K.; Hirata, M. ACS Symp Ser 2003, 847, 511.
35. Yamada, K.; Takeda, S.; Hirata, M. J Appl Polym Sci 2006, 103, 493.
36. Jeun, J. P.; Hua, Z. J.; Kang, P. H.; Nho, Y. C. J Appl Polym Sci 2009, 115, 222.
37. Zu, J.; Wu, M.; Zhang, J.; Yu, C.; Liu, X.; Tong, L. J Appl Polym Sci 2006, 993401.
38. Jeun, J. P.; Hua, Z. J.; Kang, P. H.; Nho, Y. C. J Appl Polym Sci 2010, 115, 222.
39. Cardona, F.; George, G. A.; Hill, D. J. T.; Perera, S. J Polym Sci Polym Chem 2002, 40, 3191.
40. Gupta, B.; Anjum, N.; Gupta, A. P. J Appl Polym Sci 2000, 77, 1331.
41. Shing, J. B. W.; Baker, W. E.; Russell, K. E.; Whitney, R. A. J Polym Sci Polym Chem 2003, 32, 1691.
42. Koul, V.; Guha, S. K.; Choudhary, V. Polym Int 2007, 30, 411.
43. Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, H. Eds. Encyclopedia of Polymer Science and Engineering; John Wiley & Sons: New York, 1986; Vol. 4, p 482.
44. Noto, N.; Matsumoto, S.; Takahashi, Y.; Hirata, M.; Yamada, K. J Appl Polym Sci 2009, 113, 1963.
45. de Lange, P. J.; Gebben, B.; Elfrink, P. J. Surf Int Anal 1994, 22, 502.
46. Mikhailova, S. S.; Mykhaylyk, O. M.; Dorfman, A. M.; Povstugar, V. I. Surf Int Anal 2000, 29, 519.
47. Ratner, B. D.; Castner, D. G. In Surface Analysis—The principal Techniques; Vickerman, J. C., Ed.; Wiley: New York, 2000.
48. Clark, D. T.; Feast, W. J.; Kilcast, D.; Musgrave, W. K. R. J Polym Sci Polym Chem 1973, 11, 389.
49. Clark, D. T.; Thomas, H. R. J Polym Sci Polym Chem 1978, 16, 791.
50. Yamada, K.; Iizawa, Y.; Yamada, J.; Hirata, M. J Appl Polym Sci 2006, 102, 4886.
51. Han, J.; Wang, H. J Appl Polym Sci 2009, 113, 2062.
52. Zouahri, A.; Assouag, M.; Robin, J. J.; Boutevin, B.; Elbachiri, A.; Elmidaoui, A. J Appl Polym Sci 2006, 101, 4423.
53. Wirsén, A.; Albertsson, A. C. J Polym Sci Polym Chem 1995, 33, 2039.
54. Fang, Y. E.; Lu, X. B.; Cheng, Q. J Appl Polym Sci 1998, 68, 83.
55. Han, J.; Wang, X.; Wang, H. J Colloid Interface Sci 2008, 326, 360.
56. Zhang, G.; Jia, Y.; Sun, S.; Wu, L.; Zhao, G.; An, L. Macromol Theory Simul 2007, 16, 785.
57. Shi, Q.; Zhu, L. C.; Cai, C. L.; Yin, J. H.; Costa, G. Polymer 2006, 47, 1979.
58. White, J. L.; Sasaki, A. Polym-Plast Technol 2003, 42, 711.
59. Kangwansupamonkon, W.; Gilbert, R. G.; Kiatkamjornwong, S. Macromol Chem Phys 2005, 206, 2450.