

Article

Development of Water-Resistant Autohesive Strength of Polyethylene Plates with Photografting of Alkyl (Meth)Acrylates

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Abstract: This study aims to confer autohesive strength to polyethylene (PE) plates by swelling the grafted layers, which were formed on the PE plates grafted with alkyl (meth)acrylate monomers, with 1,4-dioxane, and subsequently heat-pressing them. For the methyl methacrylate (MMA)-grafted PE (PE-g-PMMA) plates, the location of grafting was restricted to the outer surface region and the grafted layer with higher densities of grafted PMMA chains was composed. When the grafted PE plates were immersed in 1,4-dioxane, and then heat-pressed while applying the load, autohesion was developed. The substrate failure was observed for the PE-g-PMMA plates and the grafted amount at which the substrate failure was observed decreased with the procedures that decreased the methanol concentration of the solvent, the MMA concentration, the grafting temperature, and the heat-press temperature, and/or increased the load. The lowest grafted amount of 45 $\mu\text{mol}/\text{cm}^2$ for the substrate failure was obtained under the conditions where the PE-g-PMMA plate prepared at 0.75 M and 60 °C in a 70 vol% aqueous methanol solution was heat-pressed at 60 °C while applying the load of 2.0 kg/cm². The swelling of the grafted layers with 1,4-dioxane considerably contributed to the development of autohesion, bringing the inter-diffusion of grafted PMMA chains and coincident entanglement of grafted PMMA chains during the heat-pressing. The fact that the substrate failure occurred indicates that an autohesive strength higher than the ultimate strength of the used PE plate was obtained. Our approach provides a novel procedure to develop the water-resistant autohesion of PE plates.

Keywords: adhesive strength; autohesive strength; photografting; polyethylene; methyl methacrylate; substrate failure



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1. Introduction

Polyethylene (PE) and polypropylene (PP) have been used in many industrial fields, as they have a high resistance against chemical compounds, such as organic solvents, acids, and bases. However, the poor wettability, or high hydrophobicity, of the polyolefins gives rise to problems that limit their practical applications [1]. Therefore, to overcome them, it is essential to modify the surfaces chemically or physically without changing their bulk properties to expand their practical use [2]. Autohesion is one of the surface properties produced by the surface modification and defined as self-diffusion, which occurs when chemically identical polymers get in contact under the conditions where they have a high mobility and can generate the attractive interaction between polymer chains at the interface [3]. This can be applied to the joining/bonding of polymer materials without any adhesives. Pioneering studies on autohesion were theoretically and empirically started for cotton fabrics coated with polyisobutylene by Voyutskii and coworkers in the 1950s [4–6]. These studies showed that autohesion is caused by the self-diffusion of polymer chains

from one into another layer of the identical polymer across the interface. Some of the migrated polymer segments entangle with others, randomizing to fuse the interface [5,6].

In the middle of the 1980s, Roland et al. reported that the autohesion of 1,4-polybutadiene sheets was enhanced using modification with an azoester compound [7,8]. Since then, many studies have been reported on the development of the autohesion of polymer materials with various surface modification methods, including the introduction of oxygen-containing functional groups with a plasma treatment [9–11], grafting of a zwitterionic monomer [12,13], coating with a polymeric adhesive component [14], plasticization with a plasticizer [15], and formation of water-absorbing polymer layers using the grafting of hydrophilic monomers [16,17].

In terms of the mobility, the formation of graft polymers on the polymer substrate has come up with a new hope. A graft polymer is made up of polymer branches covalently bonded to a backbone polymer chain and the backbone polymer is different from the branch chains in chemical structure. A graft copolymer will exhibit specific properties of each of both polymer segments in some cases and may encompass intermediate properties between them in others. Therefore, a graft copolymer can be considered as a polymer alloy. In general, since many of the polymers are incompatible with each other, it is difficult to blend them homogeneously without any additives. The process to bind together two kinds of polymers through covalent bonds and a composite of a polymer material with other low-molecular-weight compounds overcomes chemical repulsion and can produce new materials [18,19]. This accounts for a general interest in graft copolymers. One of the procedures to create a graft copolymer is to activate a trunk polymer and subsequently initiate the polymerization of a monomer corresponding to the branched polymer, whereby the resulting branched branches are covalently bound to the trunk polymer [20,21]. The photografting technique is particularly suited for the generation of polymeric free radicals under UV irradiation, leading to the grafted polymer materials [22].

In our previous articles, the photografting of hydrophilic and functional monomers, such as acrylic acid, methacrylic acid, methacrylamide, 2-(dimethylamino)ethyl methacrylate, and glycidyl methacrylate, was performed on PE and PP plates and adhesive strength was enhanced and autohesive strength was developed for the grafted PE and PP plates [16,17,23,24]. Based on these results, our interest was piqued in the development of autohesion by grafting water-insoluble monomers, which became the main subject of this study. So far, many studies on the development of the autohesion of polymer materials have been reported [13,16,17,23,25]. However, little was reported on the conference of water-resistant autohesion with the PE plate using the grafting of water-insoluble monomers.

In this study, we make an attempt to develop autohesion for a PE plate grafted with alkyl (meth)acrylate monomers. The tensile shear autohesive strength of the grafted PE plates obtained was systematically estimated as a function of the methanol concentration of the solvent, monomer concentration, and grafting temperature on the photografting and of the load and heat-pressing temperature during the heat-pressing. Furthermore, their autohesive strength is discussed in relation to 1,4-dioxane absorptivity and surface compositions of the grafted layers formed and the water resistance of autohesion was also estimated.

2. Materials and Methods

2.1. Chemicals and Materials

The PE plate of a 1.0 mm thickness ($\rho = 0.921 \text{ g/cm}^3$; crystallinity = 47.7%) was used as a polymer substrate for photografting. Out of the alkyl (meth)acrylate monomers, methyl methacrylate (MMA), ethyl methacrylate (EMA), methyl acrylate (MA), and ethyl acrylate (EA) were selected as a grafting monomer. They were purchased from FUJIFILM Wako Pure Chemical Co., Ltd. (Tokyo, Japan) and used as received. Three kinds of adhesives were used to investigate the adhesive strength of the MMA-grafted PE (PE-g-PMMA) plates. A two-component epoxy adhesive, Araldite[®], (AR-R30) was purchased from Nichiban Co., Ltd. (Tokyo, Japan). The two kinds of solvent-type adhesives, a chloroprene rubber (CR)

adhesive and styrene–butadiene rubber (SBR) adhesive, were purchased from Konishi Co., Ltd. (Osaka, Japan).

2.2. Photografting

The PE plates grafted with (meth)acrylate monomers were prepared using the photografting technique with a 400 W high-pressure mercury lamp. It had a spectral range between 350 and 450 nm, containing 365, 405, 420, and 436 nm. The PE plates were cut into the dimensions of a 65 mm length and 24 mm width and immersed in an acetone solution of benzophenone (BP) at 0.50 *w/v*%. Then, the PE surfaces were coated with BP by evaporating acetone in air. The solutions of MMA, EMA, MA, and EA at the monomer concentration of 0.50 to 2.0 M were prepared with the aqueous methanol solution at 50–90 vol% as a solvent, and then degassed under a reduced pressure for a few minutes. The BP-coated PE plates were immersed in the monomer solution (65 cm³) in Pyrex glass tubes, and UV rays from the high-pressure mercury lamp were applied to the Pyrex glass tubes at 40–60 °C. Unless otherwise described, the photografting was performed at 1.0 M and 60 °C using a 70 vol% aqueous methanol solution as a solvent. After grafting, the PE plates were washed with excess acetone several times to remove the homopolymers, and then dried under a reduced pressure. The grafted amount was calculated in μmol/cm² from the weight increase in the PE plates using Equation (1) [24,26–28].

$$\text{Grafted amount } (\mu\text{mol}/\text{cm}^2) = \frac{(W_g - W_0)/M_M}{31.2} \cdot 10^6 \quad (1)$$

where W_g is the weight of a grafted PE plate, W_0 is the weight of an ungrafted PE plate, and M_M is the molar mass of a monomer (100.12 for MMA and EA, 114.14 for MA, and 86.09 for MA). The quantity of 31.2 is the surface area of the PE plate.

2.3. Contact Angle Measurements

The surface wettability of the grafted PE plates was estimated with the sessile drop method. The contact angles of water on the grafted PE plates were measured at 25 °C with a Kyowa Kagaku TYP-QI-type goniometer (Saitama, Japan).

2.4. XPS Analysis

The XPS high-resolution spectra of C_{1s} and O_{1s} for grafted PE plates were measured on a Shimadzu ESCA-3400 X-ray photoelectron spectrometer (XPS) (Kyoto, Japan), operating at 8 kV and 20 mA. The intensity ratio value was calculated from the peak areas of C_{1s} and O_{1s} for the estimation of the surface composition of the grafted layer [16,23,29].

2.5. Solvent Absorption

The 1,4-dioxane absorptivity of the grafted layers formed was estimated by immersing the grafted PE plates in 1,4-dioxane at 25 °C for 24 h. The grafted PE plates were taken off from 1,4-dioxane, and then the weight was measured after removing 1,4-dioxane attached to their surfaces with a filter paper. The amount of absorbed 1,4-dioxane and n_{dioxane} value, defined as the number of 1,4-dioxane molecules assigned to a monomer segment of grafted polymer chains, were calculated using Equations (2) and (3), respectively [16].

$$\text{Amount of absorbed 1,4-dioxane (g/g)} = \frac{W_w - W_g}{W_g} \quad (2)$$

$$n_{\text{dioxane}} = \frac{(W_w - W_g)/88.11}{(W_g - W_0)/M_M} \quad (3)$$

where W_w is the weight of a grafted PE plate immersed in 1,4-dioxane.

2.6. Autohesive Strength

The grafted PE plates were cut into the dimensions of a 30 mm length and 12 mm width and immersed in organic solvents, such as 1,4-dioxane, acetone, methyl acetate, ethyl acetate, and methyl ethyl ketone, as a good solvent for PMMA, PEMA, PMA, and PEA, for 24 h at 30 °C to swell the grafted layers. After swelling, two pieces of the grafted PE plates with the same grafted amounts were overlapped with a 12 × 12 mm facing area. The overlapped samples were heat-pressed at 60–80 °C by applying the loads of 0.5–2.0 kg/cm² for 24 h. Unless otherwise described, the heat-pressing was performed under the load of 2.0 kg/cm² for 24 h at 80 °C. The tensile shear strength was measured with a strain rate of 3 mm/s at room temperature using the Orientec universal testing machine STA 1225 (A&D company Ltd., Tokyo, Japan) and the tensile shear autohesive strength was obtained by dividing the tensile shear strength by the overlapped area of 1.44 cm².

2.7. Water Resistance of Autohesion

The PE-g-PMMA plates with the grafted amount of 65 μmol/cm² immersed in 1,4-dioxane were overlapped in the same manner described above and heat-pressed at 80 °C for 24 h under the load of 2.0 kg/cm². After autohesion, the PE-g-PMMA plates were immersed in water for 1–5 days and the tensile shear autohesive strength was measured.

2.8. Adhesive Strength

Each adhesive component was applied to the surfaces of the PE-g-PMMA plates with the same grafted amounts and overlapped with a 12 × 12 mm facing area. The adhesive components were cured under the load of 2.0 kg/cm² for 24 h at 80 °C. The tensile shear adhesive strength was measured as mentioned above.

3. Results and Discussion

3.1. Photografting

The photografting of MMA onto the PE plate was performed under different grafting conditions and the water wettability of the grafted PE plates obtained was measured. The changes in the grafted amount with the irradiation time are shown in Figure S1 for the PE-g-PMMA plates prepared by varying the methanol concentration of the solvent, monomer concentration, and grafting temperature. The results in Figure S1 indicate that as the photografting of MMA was performed at lower methanol concentrations, at higher monomer concentrations, or at higher grafting temperatures, the induction period was shortened and the grafted amount sharply increased at shorter irradiation times. In particular, the increase in the monomer concentration and grafting temperature considerably contributed to the increase in the grafted amount. Here, the rate of grafting can be calculated from the slope of the line under the steady conditions, as shown in Figure S2. The photografting is initiated in the free radical mechanism in this study. Therefore, the length of grafted polymer chains can be predicted from the rate of grafting. Here, there is an additional reason that the length, and that the molecular weight, of grafted polymer chains are not empirically determined [21]. Figure 1 shows the changes in the grafted amount at the irradiation time of 4 h and the rate of grafting with the (a) methanol concentration of the solvent, (b) monomer concentration, and (c) grafting temperature. For free radical polymerization, the average molecular weight of polymers is related with the monomer concentration using Equation (4),

$$\frac{1}{\bar{n}} = \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} + \frac{k_{tr}}{k_p} \frac{[S]}{[M]} \quad (4)$$

where \bar{n} is the average molecular weight of polymers, $[M]$ is the monomer concentration, $[S]$ is the solvent concentration, R_p is the propagation rate, k_t is the termination rate constant, k_p is the propagation rate constant, and k_{tr} is the chain transfer rate constant.

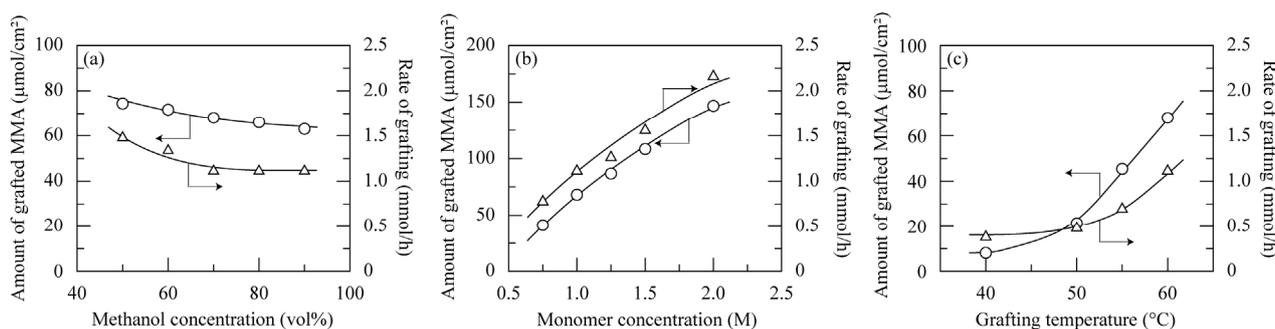


Figure 1. Changes in the grafted amount (O) and rate of grafting (Δ) with the (a) methanol concentration of the solvent, (b) monomer concentration, and (c) grafting temperature for the photografting of MMA on the PE plate. Unless otherwise described, the photografting was performed by using a 70 vol% aqueous methanol solution as a solvent at 1.0 M and 60 °C.

The length of grafted PMMA chains formed under different conditions is discussed from the results shown in Figure 1 and with Equation (4) as follows. The rate of grafting increased as the methanol concentration of the solvent decreased, the monomer concentration increased, or the grafting temperature increased. In particular, the monomer concentration and grafting temperature had a great effect on the rate of grafting. In addition, the length of grafted PMMA chains was also deduced from the above kinetic equation, since the 1,4-dioxane absorptivity would depend on the length and number of grafted PMMA chains as well as their density in the grafted layers. These factors can exert an influence on the development of autohesive strength. The decrease in the methanol concentration of the solvent will cause the solubility of PMMA chains to decrease, consequently generating shorter grafted PMMA chains. In contrast, the rate of the propagation reaction increased with the increase in the monomer concentration, leading to the formation of longer grafted PMMA chains. In addition, since the increase in the grafting temperature results in the increase in the chain transfer reaction, shorter grafted PMMA chains were generated.

3.2. Water Wettability

Figure 2 shows the changes in the $\cos \theta$ value with the grafted amount for the PE-g-PMMA plates prepared by varying the (a) methanol concentration of the solvent, (b) monomer concentration, and (c) grafting temperature on the photografting. As the methanol concentration of the solvent, monomer concentration, or temperature decreased, the grafted amount at which the $\cos \theta$ value sharply increased decreased. This indicates that although the location of grafting is restricted to the outer surface region of the PE plate, it depends on the grafting conditions. The constant $\cos \theta$ values and the grafted amounts at which the $\cos \theta$ value becomes constant are organized in Table 1. Higher constant $\cos \theta$ values were obtained by photografting at lower methanol concentrations and at lower monomer concentrations, whereas the grafting temperature had little effect on the constant $\cos \theta$ value. Also, the constant $\cos \theta$ value means a full coverage of the PE surface with grafted PMMA chains [16,17,23,26]. These results indicate that the surface composition of the grafted layer formed as well as that the location of grafting depends on the grafting conditions. The grafted layer with higher densities of grafted PMMA chains was formed when MMA was photografted on the PE plate in the solvents of lower methanol concentrations and at lower monomer concentrations.

3.3. Determination of a Solvent for Autohesion

First, the effect of a solvent on the photografting on autohesion was investigated. The PE-g-PMMA plates with the grafted amount of 70 $\mu\text{mol}/\text{cm}^2$ were immersed in five kinds of good solvents for PMMA, and then heat-pressed at 80 °C while applying the load of 2.0 kg/cm^2 . Table 2 compares autohesive strength with the solubility parameters and boiling points of the solvents used. In general, in the case when the difference in the solubility parameter between a solvent and a polymer is less than about 1 $(\text{cal}/\text{cm}^3)^{1/2}$, or 2.05 $\text{MPa}^{1/2}$,

the dissolution process is possible and favorable and the dissolution will proceed upon the contact and mixing of both substances together [30,31]. When a polymer chain is dissolved in a solvent under the conditions where the polymer–solvent affinity is higher than the solvent–solvent and polymer–polymer affinities, it can be presented in a relatively expanded conformation with a longer end-to-end distance [32], conferring a high mobility to grafted polymer chains. Such behavior is considered to be favorable for the inter-diffusion of grafted PMMA chains in the swollen state.

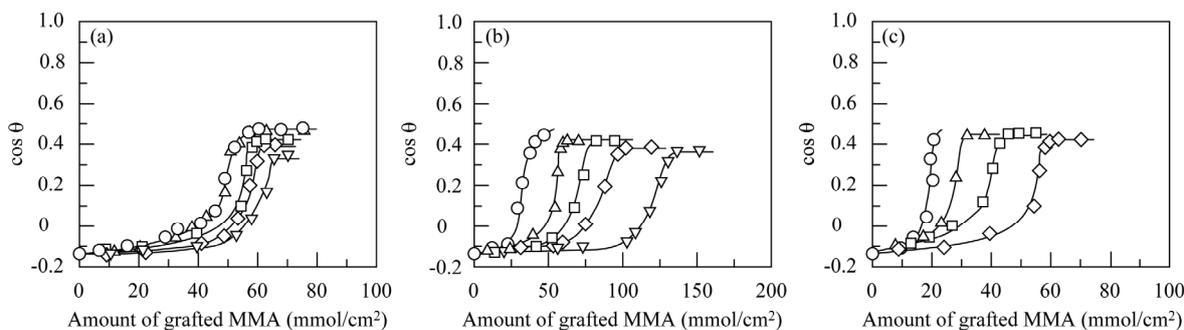


Figure 2. Changes in the $\cos \theta$ value with the grafted amount for the PE-g-PMMA plates prepared (a) at the methanol concentration of the solvent of 50 (○), 60 (△), 70 (□), 80 (◇), and 90 (▽) vol%; (b) at the monomer concentration of 0.75 (○), 1.0 (△), 1.25 (□), 1.5 (◇), and 2.0 (▽) M; and (c) at the grafting temperature of 40 (○), 50 (△), 55 (□), and 60 (◇) °C.

Table 1. The water wettability of the PE-g-PMMA plates prepared under different grafting conditions.

Methanol Conc. (vol%)	Monomer Conc. (M)	Grafting Temp. (°C)	Grafted Amount ($\mu\text{mol}/\text{cm}^2$)	Constant $\cos \theta$
50	1.0	60	57	0.47
60	1.0	60	57	0.47
70	1.0	60	60	0.42
80	1.0	60	66	0.40
90	1.0	60	66	0.33
70	0.75	60	47	0.43 (max.)
70	1.0	60	60	0.42
70	1.25	60	82	0.42
70	1.5	60	132	0.38
70	2.0	60	137	0.37
70	1.0	40	18	0.44 (max.)
70	1.0	50	32	0.40
70	1.0	55	45	0.43
70	1.0	60	60	0.40

Table 2. Autohesive strength of PE-g-PMMA plates with the grafted amount of 70 $\mu\text{mol}/\text{cm}^2$ immersed in different solvents for 24 h at 30 °C.

Solvent	Solubility Parameter ($\text{MPa})^{1/2}$	Boiling Point (°C)	Autohesive Strength (kPa)
ethyl acetate	18.2	77.1	495 ± 67
methyl acetate	18.7	57.1	128 ± 36
PMMA	19.0		
methyl ethyl ketone	19.1	79.6	678 ± 66
acetone	19.9	56.5	113 ± 27
1,4-dioxane	20.5	101.1	substrate failure

Heat-pressing at 80 °C for 24 h under the load of 2.0 kg/cm².

Based on the solubility parameters of PMMA and the solvents used, grafted PMMA chains will exhibit an expanded conformation in the solvents used. However, there was no noticeable tendency between autohesive strength and the difference between the solubility parameter of PMMA and those of the solvents. The substrate failure, or substrate

breaking, was observed only when 1,4-dioxane was used. Grafted PMMA chains are allowed to inter-diffuse across the interface of the swollen grafted layers for longer contact times during the heat-pressing, as the boiling point of 1,4-dioxane is higher than that of the other organic solvents, as shown in Table 2. The strength development can be explained in terms of the heating process, whereby the interface gradually disappears and mechanical strength builds up [33–35]. The reptation model of polymer chains can be applied to the inter-diffusion at the polymer/polymer interface, representing that the strength develops with the contact time to the one fourth power in the scaling law [36,37]. The results shown in Table 2 demonstrate that the buildup of contact time dependent on autohesive strength is confirmed with experimental study. From these results, 1,4-dioxane was selected as a solvent for autohesion.

3.4. 1,4-Dioxane Absorptivity

The mobility of grafted polymer chains in a good solvent plays a significant role in developing autohesion. Therefore, the 1,4-dioxane absorptivity of the grafted layers formed on the PE plates was estimated. Figure 3 shows the changes in the amount of absorbed 1,4-dioxane with the grafted amount for the PE-g-PMMA plates prepared by varying the methanol concentration of the solvent, monomer concentration, and grafting temperature. The amount of absorbed 1,4-dioxane increased with increasing the grafted amount and passed through the maximum value at $60 \mu\text{mol}/\text{cm}^2$ with little dependence on the above grafting conditions. This indicates that the amount of absorbed 1,4-dioxane is dominated mainly by the amount of grafted PMMA chains and independent from the number and length of grafted PMMA chains and their density in the grafted layer. It was found from Figures 2 and 3 that the water wettability is related with the surface composition of the grafted layer, whereas the 1,4-dioxane absorptivity reflects the whole amount of grafted polymer chains in the grafted layer [28,30,31].

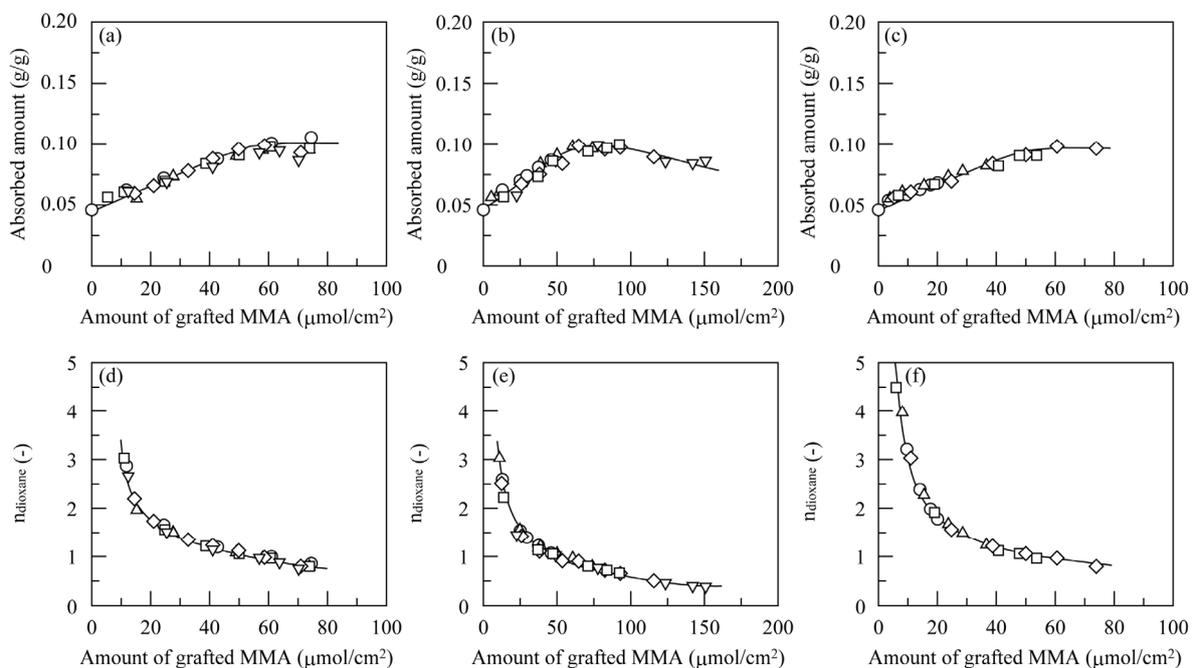


Figure 3. Changes in the amount of absorbed 1,4-dioxane (upper) and n_{dioxane} value (lower) with the grafted amount for the PE-g-PMMA plates prepared (a,d) at the methanol concentration of the solvent of 50 (O), 60 (Δ), 70 (\square), 80 (\diamond), and 90 (∇) vol%; (b,e) at the monomer concentration of 0.75 (O), 1.0 (Δ), 1.25 (\square), 1.5 (\diamond), and 2.0 (∇) M; and (c,f) at the grafting temperature of 40 (O), 50 (Δ), 55 (\square), and 60 (\diamond) $^{\circ}\text{C}$.

3.5. Effect of Grafting Conditions on Autohesion

PE-g-PMMA plates prepared by varying the grafting conditions, such as the methanol concentration of the solvent, monomer concentration, and grafting temperature, were heat-pressed at 80 °C and 2.0 kg/cm². Figure 4 shows the changes in autohesive strength with the grafted amount for the PE-g-PMMA plates prepared under different grafting conditions.

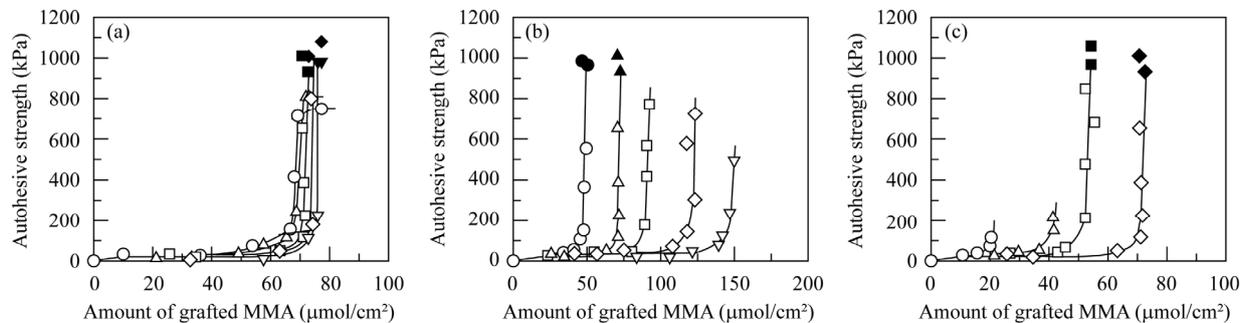


Figure 4. Changes in autohesive strength with the grafted amount for the PE-g-PMMA plates prepared (a) at the methanol concentration of the solvent of 50 (○), 60 (△), 70 (□, ■), 80 (◇, ◆), and 90 (▽, ▼) vol%; (b) at the monomer concentration of 0.75 (○, ●), 1.0 (△, ▲), 1.25 (□), 1.5 (◇), and 2.0 (▽) M; and (c) at the grafting temperature of 40 (○), 50 (△), 55 (□, ■), and 60 (◇, ◆) °C. Failure-open: cohesive failure, filled: substrate failure. The PE-g-PMMA plates were heat-pressed at 80 °C and 2.0 kg/cm².

3.5.1. Effect of Methanol Concentration

Figure 4a shows the changes in autohesive strength with the grafted amount for the PE-g-PMMA plates prepared in the monomer solutions with aqueous methanol solutions of different concentrations. Autohesion was minorly developed below about 65 μmol/cm². This suggests that grafted PMMA chains would not undergo the inter-diffusion due to the fact that the density of grafted PMMA chains at the PE surface is still low. On the other hand, autohesive strength went up sharply at lower grafted amounts for PE-g-PMMA plates prepared by photografting with aqueous methanol solutions at lower concentrations. In particular, the substrate failure occurred for the PE-g-PMMA plates prepared at the methanol concentrations higher than 70 vol %, and the grafted amount at which the substrate failure was observed, which corresponds to the failure point, slightly decreased from 75 to 70 mmol/cm² as the methanol concentration decreased. This shows that autohesive strength went over the ultimate strength of the used PE plate. Since the location of grafting is restricted to the outer surface region with grafting in the solvents of lower methanol concentrations, as shown in Figure 2, the above results can suggest that this procedure facilitates the inter-diffusion of grafted PMMA chains across the interface of the grafted layers.

3.5.2. Effect of Monomer Concentration

The changes in autohesive strength with the grafted amount are shown in Figure 4b for PE-g-PMMA plates prepared at different monomer concentrations. A sharp increase in autohesive strength was observed at lower grafted amounts for the PE-g-PMMA plates prepared at lower monomer concentrations. The substrate failure occurred for the PE-g-PMMA plates prepared at 0.75 and 1.0 M. For the photografting at lower monomer concentrations, as shown in Figure 2b, the location of photografting is restricted to the outer surface region, and the grafted layer with higher densities of grafted PMMA chains is formed. Therefore, this can suggest that the photografting at lower monomer concentrations also facilitates the inter-diffusion of grafted PMMA chains across the interface of the grafted layers to develop autohesion.

3.5.3. Effect of Grafting Temperature

The changes in autohesive strength with the grafted amount are shown in Figure 4c for the PE-g-PMMA plates prepared at different temperatures. As the grafting temperature decreased, adhesive strength sharply increased at lower grafted amounts. However, at 40 and 50 °C, a high autohesive strength could not be obtained due to a low grafted amount. On the other hand, the PE-g-PMMA plates prepared at 55 and 60 °C underwent the substrate failure. The PE-g-PMMA plates prepared at 55 °C failed at the lower grafted amount compared to those prepared at 60 °C.

Since the grafted polymer chains become more likely to suffer from chain transfer reactions at higher grafting temperatures, shorter grafted polymer chains are generated and grafted layers with a lower density of grafted polymer chains are formed. However, the surface composition of the grafted layer is considered to be minorly affected by the grafting temperature in the range of the grafted amounts at which the $\cos \theta$ value was constant, since the constant θ value is almost the same as seen in Table 1. Therefore, the inter-diffusion of shorter grafted polymer chains would be more effective for the development of autohesion. From these results, the dependence of heat-pressing conditions on autohesive strength is investigated for the PE-g-PMMA plates obtained at 1.0 M and 60 °C in a 70 vol% aqueous methanol solution.

3.6. Effect of Heat-Pressing Conditions on Autohesion Strength

Figure 5a,b shows the changes in adhesive strength with the grafted amount under heat-pressing at different temperatures under the load of 2.0 kg/cm². In the heat-pressing temperature ranging from 40 to 55 °C, the higher the heat-pressing temperature, the lower the grafted amount at which adhesive strength sharply increased. However, no substrate failure occurred. On the other hand, at temperatures higher than 60 °C, the substrate failure was observed and the grafted amount at which the substrate failed, which is the failure point, increased with increasing the heat-pressing temperature. Although the increase in the heat-pressing temperature can enhance the mobility of grafted PMMA chains in the water-swollen state, the inter-diffusion of grafted PMMA chains is depressed due to a fast evaporation of 1,4-dioxane.

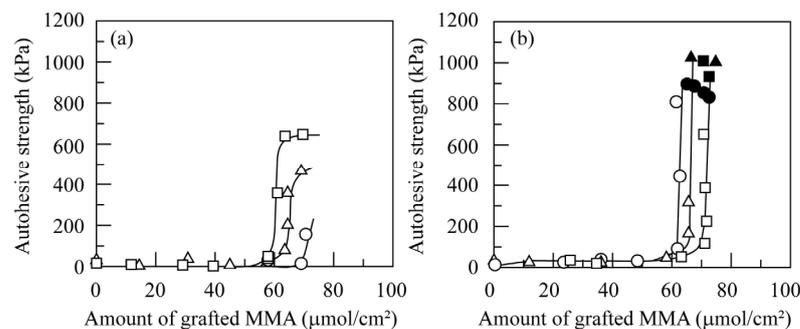


Figure 5. Changes in autohesive strength with the grafted amount for autohesion of the PE-g-PMMA plates heat-pressed (a) at 40 (○), 50 (△), and 55 (□) °C and (b) 60 (○,●), 70 (△,▲), and 80 (□,■) °C under the load of 2.0 kg/cm² after the immersion in 1,4-dioxane at 30 °C. The PE-g-PMMA plates were prepared at 1.0 M and 60 °C in a 70 vol% aqueous methanol solution. Failure-open: cohesive failure, filled: substrate failure.

Taking into consideration the above results, the autohesive strength measurements were also performed at the heat-pressing temperature of 60 °C. First, the PE-g-PMMA plates prepared at 60 °C and 1.0 M were heat-pressed at 60 °C by varying the load. As shown in Figure 6, the PE plate failed at the grafted amounts of 68 and 65 μmol/cm², respectively, when the load of 1.0 and 2.0 kg/cm² was applied during the heat-pressing. On the other hand, the substrate failure did not occur under the load of 0.5 kg/cm². Next, the PE-g-PMMA plates were heat-pressed at 60 °C under the load of 2.0 kg/cm². Figure 7a,b shows the changes in autohesive strength with the grafted amount for PE-g-PMMA plates pre-

pared at different monomer concentrations and at different temperatures, respectively. Autohesive strength was developed even at the heat-pressing temperature of 60 °C, leading to the substrate failure for the PE-g-PMMA plates prepared at 0.75–2.0 M and at 55 and 60 °C.

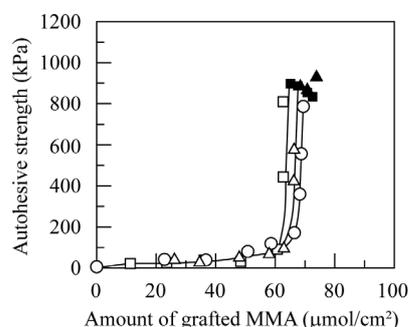


Figure 6. Changes in autohesive strength with the grafted amount for the PE-g-PMMA plates heat-pressed at 60 °C under the load of 0.5 (○), 1.0 (△, ▲), and 2.0 (□, ■) kg/vcm². Failure-open: cohesive failure, filled: substrate failure.

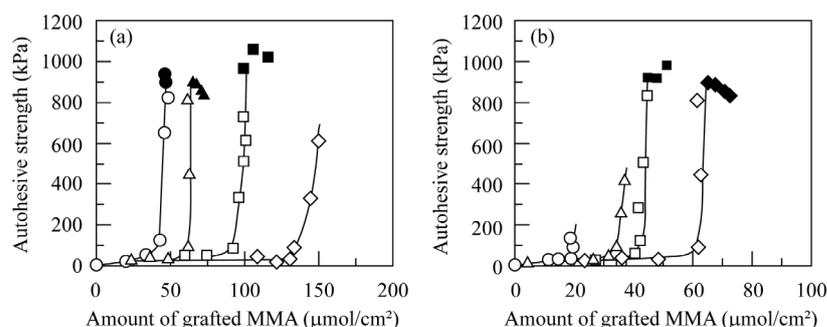


Figure 7. Changes in autohesive strength with the grafted amount for the PE-g-PMMA plates prepared (a) at the monomer concentration of 0.75 (○, ●), 1.0 (△, ▲), 1.5 (□, ■), and 2.0 (◇) M and (b) at the grafting temperature of 40 (○), 50 (△), 55 (□, ■), and 60 (◇, ⊙) °C. Heat-pressing at 60 °C and 2.0 kg/cm². Failure-open: cohesive failure, shaded: substrate failure.

The grafted amounts at which the substrate failure occurred (Figures 4–6) are summarized in Table 3. The comparison of the values shown provides the fact that both the grafting conditions and heat-pressing conditions influenced the failure point. Of them, the monomer concentration and grafting temperature are the factors most involved in the decrease in the failure point. The lowest grafted amount, 45 μmol/cm², showing the failure point, was obtained under the conditions that MMA was photografted onto the PE at 0.75 M in a 70 vol% aqueous methanol solution at 60 °C and the PE-g-PMMA plates obtained were heat-pressed at 60 °C under the load of 2.0 kg/cm².

3.7. Autohesion of PE Plates Grafted with Alkyl (Meth)acrylates

Another three kinds of alkyl(meta)acrylates, MA, EA, and EMA, were also photografted on the PE plate in a 70 vol% aqueous methanol solution at 60 °C and 1.0 M, and then the resulting grafted PE plates were heat-pressed at 80 °C and 2.0 kg/cm² after the immersion in 1,4-dioxane. Figure 8a shows the changes in the cos θ value with the grafted amount for the PE-g-PMMA, PE-g-PEMA, PE-g-PMA, and PE-g-PEA plates. For all these grafted PE plates, the water wettability increased with increasing the grafted amount and then leveled off. The grafted amounts at which the constant cos θ value was obtained for the PE plates grafted with the alkyl acrylates were lower than those at which the constant cos θ value was obtained for the PE plates grafted with the alkyl methacrylates (PE-g-PMA < PE-g-PMMA and PE-g-PEA < PE-g-PEMA). In addition, the cos θ values of the PE plates grafted with the methyl (meth)acrylates became constant at lower grafted amounts compared with the PE plates grafted with the ethyl (meth)acrylates (PE-g-PMA < PE-g-PEA and PE-g-PMMA < PE-g-PEMA). This indi-

cates that the alkyl acrylates are photografted onto the outer surface region compared to the alkyl methacrylates due to an increased hydrophilicity in the structure. In addition, the hydrophilic/hydrophobic interaction of a monomer with the PE plate is also involved in the photografting. In other words, EMA, the most hydrophobic in structure of the used monomers, is most readily grafted onto the PE plate and MA, the most hydrophilic of the used monomers, is least readily grafted onto the PE plate [30,32].

Table 3. The grafted amounts at which the substrate failure occurs under different heat-pressing conditions for PE-g-PMMA plates prepared under different grafting conditions.

Grafting Conditions			Heat-Pressing Conditions		
Methanol Conc. (vol%)	MMA Conc. (M)	Grafting Temp. (°C)	Load (kg/cm ²)	Heat-Pressing Temp. (°C)	Grafted Amount (μmol/cm ²)
70	1.0	60	2.0	80	70
80	1.0	60	2.0	80	72
90	1.0	60	2.0	80	75
70	0.75	60	2.0	80	47
70	1.0	60	2.0	80	70
70	1.0	55	2.0	80	55
70	1.0	60	2.0	80	70
70	1.0	60	2.0	60	62
70	1.0	60	2.0	70	65
70	1.0	60	2.0	80	70
70	1.0	60	1.0	60	68
70	1.0	60	2.0	60	65
70	0.75	60	2.0	60	45
70	1.0	60	2.0	60	64
70	1.5	60	2.0	60	99
70	1.0	55	2.0	60	54
70	1.0	60	2.0	60	64

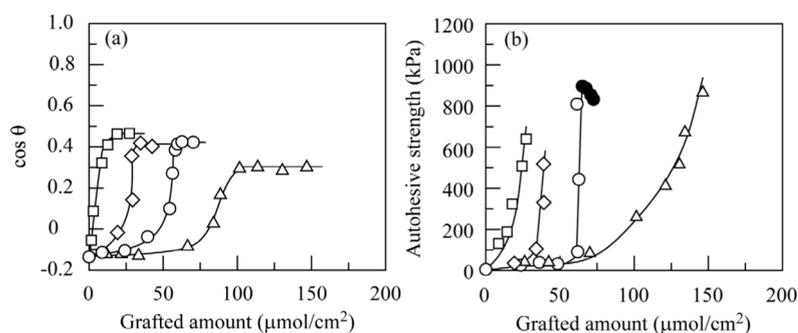


Figure 8. Changes in (a) the $\cos \theta$ value and (b) autohesive strength with the grafted amount for the PE-g-PMMA (○,●), PE-g-PEMA (△), PE-g-PMA (□), and PE-g-PEA (◇) plates prepared at 1.0 M and 60 °C in 70 vol% aqueous methanol solutions. The grafted PE plates were heat-pressed at 80 °C and 2.0 kg/cm². Failure-open: cohesive failure, filled: substrate failure.

The high-resolution spectra of C_{1s} and O_{1s} for grafted PE plates were measured. As a typical example, the C_{1s} and O_{1s} spectra for the PE-g-PMMA plate are shown in Figure S3. The C_{1s} and O_{1s} spectra were analyzed with the deconvolution process [38,39]. The C_{1s} spectrum was divided into a peak at 289 eV corresponding to -C-OOH at 289 eV and one at 287 eV corresponding to -CH-COOH in addition to a main -CH₂-CH- peak at 285 eV. In the O_{1s} spectrum, two peaks arising from -C=O and -C-O- at 532 and 533.5 eV, respectively, were observed [38,39]. The high-resolution spectra with a similar shape were obtained for the other grafted PE plates. In addition, the density of grafted polymer chains in the grafted layers was estimated by dividing the intensity ratio, O_{1s}/C_{1s}, calculated with the XPS measurements, by the atomic ratio, the O/C value, of the corresponding monomer, and the results are summarized in Table 4. The surface composition of the PE-g-PMMA plates, that is, the density of grafted polymer chains in the grafted layer, was rather higher

than that of the other grafted PE plates, indicating that the grafted layer containing grafted polymer chains at higher densities was formed for the PE-g-PMMA plate. Figure 8b shows the changes in autohesive strength with the grafted amount for the grafted PE plates. For all these grafted PE plates, autohesive strength increased with the grafted amount, and the order of the grafted amount at which autohesive strength sharply increases was the same as the order of that at which the wettability increases (PE-g-PMA < PE-g-PEA < PE-g-PMMA < PE-g-PEMA). This is the same order as the results of the water wettability shown in Figure 8a. However, the substrate failure was observed only for the PE-g-PMMA plates. Here, the 1,4-dioxane absorptivity for the grafted PE plates was measured. As shown in Figure 9a, the amount of absorbed 1,4-dioxane increased with an increase in the grafted amount and the 1,4-dioxane absorptivity of the PE-g-PEA is a little higher than the other grafted PE plates at the same grafted amount in a range lower than 50 $\mu\text{mol}/\text{cm}^2$. However, the n_{dioxane} value sharply decreased with an increase in the grafted amount and leveled off at higher grafted amounts. This behavior is independent from the kind of grafting monomers. Therefore, the results shown in Table 4 suggest that the density of grafted polymer chains is also involved in the increase in autohesive strength. In conclusion, the above results empirically convey that the grafting of MMA plays a significant role in the conferment of autohesive strength to the PE plate.

Table 4. The water wettability and surface analysis with XPS of the PE-g-PMAA, PE-g-PEMA, PE-g-PMA, and PE-g-PEA plates prepared at 1.0 M and 60 °C in a 70 vol% aqueous methanol solution.

Sample	Grafted Amount ($\mu\text{mol}/\text{cm}^2$)	Constant $\cos \theta$	$\text{O}_{1s}/\text{C}_{1s}$	Atomic Ratio	Composition
PE		-0.14	0.027		
PE-g-PMMA	60	0.42	0.158	0.400	0.395
PE-g-PEMA	100	0.28	0.117	0.333	0.351
PE-g-PMA	20	0.46	0.176	0.500	0.352
PE-g-PEA	35	0.42	0.145	0.400	0.363

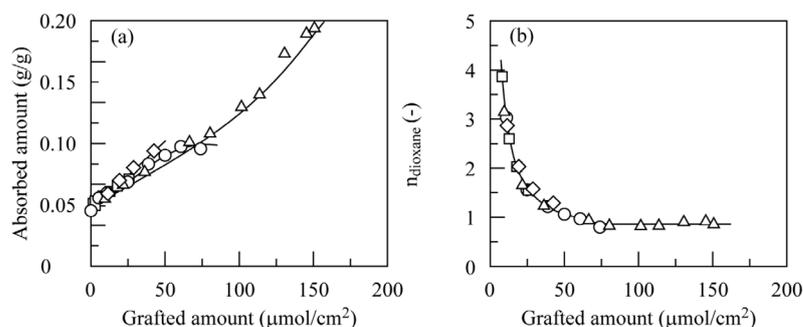


Figure 9. Changes in (a) the amount of absorbed 1,4-dioxane and (b) n_{dioxane} value with the grafted amount for the PE-g-PMMA (○), PE-g-PEMA (△), PE-g-PMA (□), and PE-g-PEA (◇) plates prepared at 1.0 M and 60 °C in 70 vol% aqueous methanol solutions.

3.8. Water Resistance of Conditions

The PE-g-PMMA plates with the grafted amount of 70 $\mu\text{mol}/\text{cm}^2$ joined together using heat-pressing at 80 °C were immersed in water for 1–5 days. As shown in Figure 10, the PE-g-PMMA plates failed even after the immersion. This indicates that autohesion is unimpaired with immersing in water. It should be noted that our developed procedure confers the water-resistant autohesion to the PE plate. Also, the high resistance to water can be potentially applied to electronic, wood, and building fields.

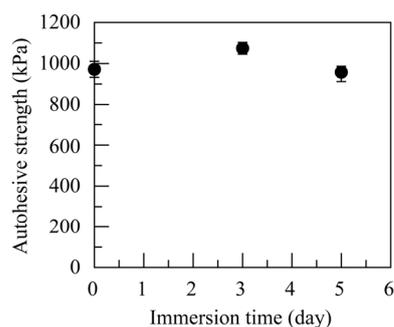


Figure 10. Change in autohesive strength with the immersion time for the PE-g-PMMA plates heat-pressed at 80 °C under the load of 2.0 kg/cm². The PE-g-PMMA plates were prepared at 1.0 M and 60 °C in 70 vol% aqueous methanol solutions.

3.9. Comparison with Adhesive Strength

The PE-g-PMMA plates were bonded with three kinds of commercially available adhesives. Figure 11 shows the changes in adhesive strength with the grafted amount. For all of the adhesives used, adhesive strength increased with the grafted amount. Only the PE-g-PMMA plate bonded with the CR adhesive failed at grafted amounts higher than 55 $\mu\text{mol}/\text{cm}^2$. It should be noted that the grafted amount of 45 $\mu\text{mol}/\text{cm}^2$, at which the substrate failure was observed in the autohesive strength measurements for the PE-g-PMMA plates prepared at 0.75 M, was lower than that at which the substrate failure was observed in the adhesive strength measurements with the CR adhesive.

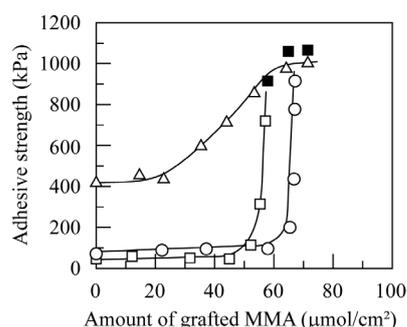


Figure 11. Changes in adhesive strength with the grafted amount for the PE-g-PMMA plates bonded with a two-component-type epoxy adhesive, Araldite® (○), SBR adhesive (△), and CR adhesive (□,■). The adhesives were cured at 80 °C and 2.0 kg/cm². Failure-open: cohesive failure, filled: substrate failure.

4. Conclusions

In this study, we investigated the conferment of autohesion to a PE plate photografted with alkyl (meth)acrylates under different conditions through the swelling of grafted layers with 1,4-dioxane and subsequent heat-pressing. The location of the grafting of MMA was restricted to the outer surface region of the PE plate and the grafted layer that was more rich in grafted PMMA chains was formed, as the experimental factors at the photografting, such as the methanol concentration of the solvent, monomer concentration, and grafting temperature, were decreased. The use of 1,4-dioxane to swell the grafted layer led to the autohesion of the PE-g-PMMA plates, since the inter-diffusion of grafted PMMA chains and coincident entanglement of grafted PMMA chains are caused by a slow evaporation of 1,4-dioxane during the heat-pressing, leading to the substrate failure only for the PE-g-PMMA plates. This means that autohesive strength exceeds the ultimate strength of the used PE plate. In particular, the autohesion of the PE-g-PMMA plates possessed water resistance and the grafted amounts at which the substrate failure was observed for autohesive strength were lower than those at which the substrate failure was observed for

adhesive strength with CR adhesives. In conclusion, our investigation provides a possible alternative to construct the bonding of polymer materials with better mechanical and water-resistant characteristics without using adhesives. Although the experimental results of this study provide some beneficial aspects on the bonding of polymer materials through autohesion, more investigations on the enhancement and development of autohesion at lower grafted amounts and application of this procedure to other polymer/polymer composites will be performed in the near future.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/macromol3030032/s1>, Figure S1. Changes in the grafted amount with the irradiation time for the photografting of MMA on the PE plate (a) at the methanol concentration of the solvent of 50 (○), 60 (△), 70 (□), 80 (◇), and 90 (▽) vol%; (b) at the monomer concentration of 0.75 (○), 1.0 (△), 1.25 (□), 1.5 (◇), and 2.0 (▽) M; and (c) at the grafting temperature of 40 (○), 50 (△), 55 (□), and 60 (◇) °C. Unless otherwise described, the photografting was performed by using a 70 vol% aqueous methanol solution as a solvent at 1.0 M and 60 °C. Figure S2: Determination of the rate of grafting under the steady conditions. Figure S3: The high-resolution spectra of C_{1s}, O_{1s}, and N_{1s} for the PE-g-PMMA plate.

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