

Improvement of Autohesive and Adhesive Properties of Polyethylene Plates by Photografting with Glycidyl Methacrylate

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ABSTRACT: Glycidyl methacrylate (GMA) was photografted with the low- and high-density polyethylene (LDPE and HDPE) plates to provide their surfaces with autohesive and adhesive properties. The chemical composition and wettability of the GMA-grafted LDPE and HDPE (LDPE-g-PGMA and HDPE-g-PGMA) plates remained constant above full coverage of the surfaces with grafted PGMA chains. Autohesive strength obtained with 1,4-dioxane as a good solvent of PGMA increased with an increase in the grafted amount and substrate breaking was observed at the grafted amount of 117 $\mu\text{mol}/\text{cm}^2$. The grafted amount at substrate breaking was decreased by increasing the temperature and load during heat pressing. Adhesive strength was effectively enhanced by use of multi-functional amine compounds

because of the increase in the reaction between primary or secondary amine groups and epoxy groups appended to the grafted PGMA chains. In addition, the decrease in the amine compound concentration and the increase in the number of amino groups in the amine compounds used led to the decrease in the grafted amounts at substrate breaking. Substrate breaking occurred at lower grafted amounts for the HDPE-g-PGMA plates than for the LDPE-g-PGMA plates because the location of the photografting was restricted to the outer surface region for the HDPE plate. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 493–500, 2007

Key words: photografting; polyethylene; glycidyl methacrylate; adhesion; amine compound; autohesion

INTRODUCTION

The characteristic low surface energy and the resulting poor adhesion of polyolefin materials such as polyethylene (PE) and polypropylene (PP) have created numerous technical challenges, while they exhibit a wide range of outstanding properties including excellent chemical resistance and low water adsorption.^{1,2} Many studies have been carried out extensively on their surface modification.

The hydrophilicity of the PE surfaces modified by plasma treatment with non-polymer-forming gases such as O₂, N₂, He, and Ar^{3–5} or ultraviolet (UV) irradiation^{6,7} regresses as a function of time elapsed because polar functional groups formed on the surfaces tend to overturn readily in the outer surface region and migrate into the bulk of the polymer substrates mainly due to a local motion of polymer segments.^{8–11} Therefore, such poor durability of the modified surface properties has frequently limited the application of polyolefin materials. To the contrary, the surface properties of the polyolefin materials modified by the

grafting techniques should be preserved more durably than the surface modified by the techniques mentioned above. The grafting of various monomers on the polyolefin materials are initiated through plasma treatment¹² and irradiation with UV^{13,14–18} or Co⁶⁰ radiation^{19–22} as an energy source.

Of these approaches, the photografting technique initiated by the UV irradiation is the most effective procedure in several respects: investment in equipment expansion is relatively low, a variety of monomers are chosen for each purpose, the procedure is very simple, and the location of the photografting is restricted to the outer surface regions of the polymer substrates because of the low energy of the UV rays and the bulk properties of the polymer substrates are left unchanged.^{14,23–26} The enhancement of autohesive and adhesive strength is one of the properties modified by the surface-grafting. So far, only a few studies have been reported on autohesion of widely used polymer materials by the surface grafting,¹² compared with the large number of studies on surface modification and improvement of adhesivity.^{13,14,27–35} Pioneering studies on autohesion, or self-adhesion (adhesive-free adhesion), were carried out by Voyutskii and coworkers during the 1950–1960s.^{36–38} These investigators concluded that autohesion was caused by self-diffusion of polymer segments from one layer into another of the same polymer across the interface. The

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migrated polymer segments entangle with other ones, randomizing to fuse the surface.

We have investigated the surface modification of the low- and high-density PE (LDPE and HDPE), polypropylene (PP), and poly(tetrafluoroethylene) (PTFE) by photografting and enhancement of their adhesive and autohesive properties.^{23–26} Since one end of a grafted polymer chain is bonded covalently to the polymer substrate and the other end is not put under restraint, the grafted polymer chains show high mobility in a good solvent. Therefore, grafted polymer chains in the swollen grafted layers can be entangled with each other through self-diffusion, when the two grafted plates are brought into close contact by heat-pressing, leading to bond formation without any adhesives. For the LDPE and HDPE plates photografted with methacrylic acid (MAA), acrylic acid (AA), 2-(dimethylamino)ethyl methacrylate (DMAEMA), and methacrylamide (MAAm), substrate breaking was observed without any adhesives at autohesive strength measurements.^{14,25,26}

In this study, we turned our attention to the fact that an epoxy group readily reacts with a primary or secondary amino group under mild conditions. Glycidyl methacrylate (GMA) as an epoxy group-carrying monomer was photografted onto the LDPE and HDPE plates. The enhancement in autohesive strength of the LDPE plates was investigated by varying the heat-pressing conditions such as the temperature, load, and time. In addition, the adhesive properties of the LDPE and HDPE plates were followed up with multi-functional amine compounds in place of a commercially available two-component-type epoxy adhesive, Araldite, used for adhesive strength measurements in our previous studies.^{14,25,26}

EXPERIMENTAL

Materials

LDPE and HDPE plates of 1.0-mm thickness were used as a polymer substrate for photografting. Their crystallinity was calculated from their densities determined by a flotation or buoyancy method with acetone and glycerol at 25°C using the densities of the completely amorphous and pure crystalline parts of PE, as shown in Table I.^{39,40} The LDPE and HDPE

plates cut into 6-cm length and 3-cm width were washed with methanol and acetone and then dried under reduced pressure. GMA (Tokyo Kasei Kogyo, Tokyo, Japan) was used as received without further purification.

Photografting

The photografting procedure was described in detail in our previous articles.^{23–26} First, the photografting of GMA was carried out using aqueous ethanol solutions of different volume fractions as a solvent to determine the optimum ethanol concentration for preparing GMA-grafted LDPE and HDPE (LDPE-g-PGMA and HDPE-g-PGMA) plates with higher grafted amounts. The LDPE and HDPE plates were dipped for 1 min in an acetone solution containing 0.25 g benzophenone (BP) as a photosensitizer (0.5 w/v%) to coat their surfaces. GMA monomer solutions at a monomer concentration of 1.0 M were prepared with aqueous ethanol solutions of different volume fractions. The photografting was carried out at 60°C by applying UV rays emitted from a 400-W high-pressure mercury lamp to the GMA monomer solutions in which the BP-coated LDPE and HDPE plates were immersed. The LDPE-g-PGMA and HDPE-g-PGMA plates were washed with acetone for 24 h to exclude PGMA homopolymers, and then dried under reduced pressure. The grafted amounts in $\mu\text{mol}/\text{cm}^2$ were calculated from the weight increase of the LDPE and HDPE plates after photografting according to eq. (1), as described previously.¹⁴

Surface and bulk properties of grafted layers

The photoelectron spectra for the LDPE-g-PGMA and HDPE-g-PGMA plates were recorded on a Shimadzu ESCA-3400 type spectrophotometer with the MgK α (1253.6 eV) source operating 7 kV and 30 mA.^{13,14} The O1s/C1s values were then calculated from the O1s and C1s peak areas measured at a take-off angle of 90° and the ionized cross-sections^{41–43} to determine the chemical compositions of the surfaces of the grafted layers. The contact angles of water on the LDPE-g-PGMA and HDPE-g-PGMA plates were measured with a sessile drop method at 25°C under an atmosphere of saturated water vapor by a Kyowa Kagaku TYP-QI-type goniometer.^{23–26}

Autohesive strength measurements

For autohesive strength measurements, 1,4-dioxane was used as a good solvent for PGMA, as it had a relatively low boiling point (101.1°C). Two pieces of the LDPE-g-PGMA and HDPE-g-PGMA plates with the same grafted amount cut into 30-mm length and 10-mm width were immersed in 1,4-dioxane at 25°C for 24 h, and then put together with their surfaces

TABLE I
Determination of Degree of Crystallinity and Ultimate Strength of the LDPE and HDPE Plates Used in This Study

Substrate	Density (g/cm ³)	Degree of crystallinity (%)	Ultimate strength (N/cm ²)
LDPE	0.926	50.8	112.3
HDPE	0.958	69.7	317.7

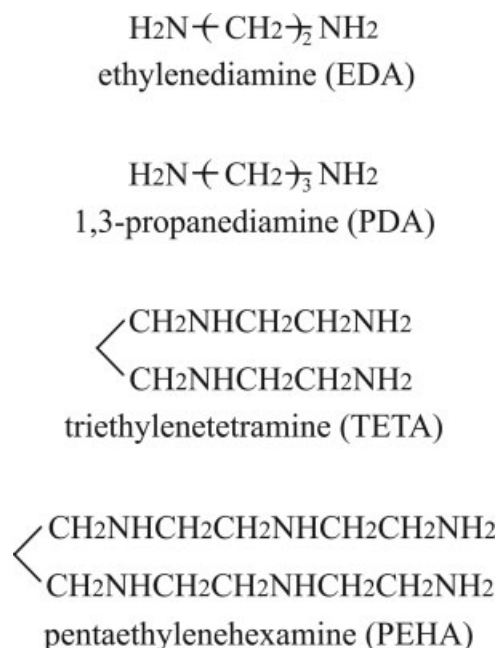


Figure 1 Chemical structures of the multi-functional amine compounds used in this study.

facing each other with a 10×10 -mm overlap. The overlapped samples were heat-pressed by adding a load of 0.5 kg/cm^2 for 24 h at 60°C , unless otherwise noted.

Autohesive and adhesive strength measurements

Multi-functional amine compounds such as ethylenediamine (EDA), 1,3-propanediamine (PDA), triethylenetetramine (TETA), and pentaethylenehexamine (PEHA) were used as a binding agent (Fig. 1). First, the EDA concentration dependence of adhesive strength was assessed by using EDA solutions of different concentrations. One of the amine compound solutions were applied to the surfaces of two pieces of the LDPE-g-PGMA and HDPE-g-PGMA plates with the same grafted amount to provide a 10×10 -mm overlap. The reaction of amino groups of the amine compounds with epoxy groups appended to grafted PGMA chains was completed for 24 h at 60 or 80°C , while the load of 0.5 or 2.0 kg/cm^2 was kept on the overlapped LDPE-g-PGMA and HDPE-g-PGMA plates.

Both ends of the bonded samples were attached to the load cell and base of a tensile testing instrument. The tensile shear autohesive and adhesive strengths were measured with a strain rate of 3 mm/s at 25°C .

RESULTS AND DISCUSSION

Photografting and surface properties of LDPE-g-PGMA and HDPE-g-PGMA plates

Photografting of GMA onto the LDPE plates was carried out for the UV irradiation time of 360 min at 60°C , using aqueous ethanol solutions of different

volume fractions as the solvent. Figure 2 shows the variation in the amount of grafted GMA with the ethanol volume fraction of the solvent. The amount of grafted GMA reached the maximum value at 80 vol%. GMA was barely soluble at the volume fractions of <35 vol%. In addition, it was more difficult to remove PGMA homopolymers from the LDPE surfaces by washing with acetone when the solutions of lower ethanol volume fractions were used as a solvent for the photografting. Therefore, photografting of GMA was carried out by varying the irradiation time with a GMA monomer solution prepared in an aqueous ethanol solution of 80 vol%. It has been reported by Irwan et al.^{44–46} and other researchers⁴⁷ that grafting behavior depends on the balance between the two effects of the mixed solvent consisting of water and an organic solvent. A positive effect of an increasing concentration of the organic solvent component in the mixed solvent is an increase in the solubility of the monomer used. This will lead to a stimulation of the monomer supply for the radicals on the growing grafted polymer chains, leading to the increase in the grafted amount. However, the organic solvent used is involved in the chain transfer and termination of growing grafted polymer radicals.

Figure 3 shows the changes in the amount of grafted GMA with the irradiation time. The amount of grafted GMA increased with an increase in the irradiation time, and then leveled off at longer irradiation times because the monomer solutions were gelled due to the formation of considerable amounts of PGMA homopolymers. The amount of grafted GMA for the LDPE plates was higher than that for the HDPE plates like the photografting of MAA, AA, MAAM, and DMAEMA^{14,28} because of high crystallinity of the HDPE plates.

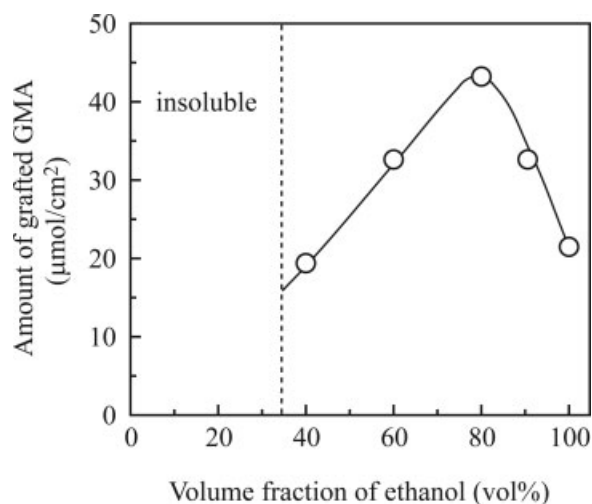


Figure 2 Variation in the amount of grafted GMA with the volume fraction of ethanol in the solvent on the photografting of GMA onto the LDPE plates at 60°C . GMA monomer concentration: 1.0 M ; irradiation time: 6 h.

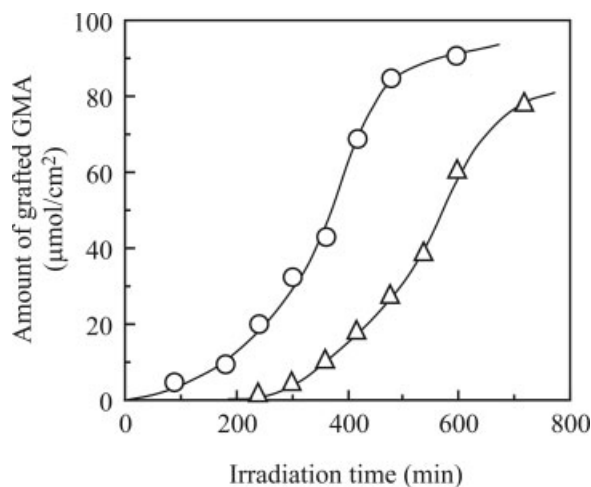


Figure 3 Changes in the amount of grafted GMA with the irradiation time on the photografting of GMA onto the LDPE (○) and HDPE (△) plates in an aqueous solution of 80 vol% ethanol at 60°C. GMA monomer concentration: 1.0 M.

The surface properties of the LDPE-g-PGMA and HDPE-g-PGMA plates were estimated from the surface analysis by ESCA and the measurement of contact angles of water. Figure 4 shows the changes in the intensity ratio, O1s/C1s, and $\cos \theta$ value with the grafted amount for the LDPE-g-PGMA and HDPE-g-PGMA plates. The intensity ratio increased with an increase in the grafted amount, and then stayed constant above the grafted amounts of 35 $\mu\text{mol}/\text{cm}^2$ for the LDPE-g-PGMA plates and 12 $\mu\text{mol}/\text{cm}^2$ for the HDPE-g-PGMA plates, respectively. The constant intensity ratio for the HDPE-g-PGMA plates was a little higher than that for the LDPE-g-PGMA plates. This indicates that grafted PGMA chains are more highly present in the outermost grafted layers of the HDPE-g-PGMA plates than in those of the LDPE-g-PGMA plates. In addition, the constant intensity ratio for the HDPE-g-PGMA plates was obtained at lower grafted amount than for the LDPE-g-PGMA plates. This shows that the location of photografting of GMA onto the HDPE plates is restricted to the outer surface regions of the substrates and the HDPE surface are fully covered with grafted PGMA chains at lower grafted amount than the LDPE surface. Although the grafted layers formed on the LDPE and HDPE plates are considered to consist of grafted PGMA and PE chains, the sampling depth of C1s, which was calculated by the densities of the LDPE and HDPE plates according to the equation presented by Seah and colleagues⁴⁸ and were 11.1 and 10.7 nm, respectively. Therefore, the grafted layers thicker than the sampling depth at C1s orbit were considered to be formed on the LDPE and HDPE plates. In addition, since the surfaces of the LDPE and HDPE plates were fully covered with grafted PGMA chains in the range of the grafted amounts at which the intensity ratio remained

constant, the grafting onto grafted PGMA chains would also take place. Therefore, the grafted layers with more highly branched PGMA chains would be formed at higher grafted amounts.

The $\cos \theta$ value also increased with an increase in the grafted amount and then became constant at the grafted amounts at which the constant intensity ratios were obtained. This shows that the wettability of the LDPE and HDPE surfaces was enhanced by the photografting of GMA. The wettability for the HDPE-g-PGMA plates was a little higher than that for the LDPE-g-PGMA plates. This difference can be explained in terms of the results of surface analysis by ESCA described above. However, the $\cos \theta$ values for the LDPE-g-PGMA and HDPE-g-PGMA plates were lower than those for the LDPE and HDPE plates grafted with hydrophilic monomers such as MAA, DMAEMA, and MAAm.^{13,14,25} The amount of absorbed water was measured to estimate the hydrophilicity of the whole grafted layers formed on the LDPE and HDPE plates according to the procedure described in reference 25. Although the amount of absorbed water gradually increased over the grafted amount for both GMA-grafted plates, the amount of absorbed water was considerably low and limited to

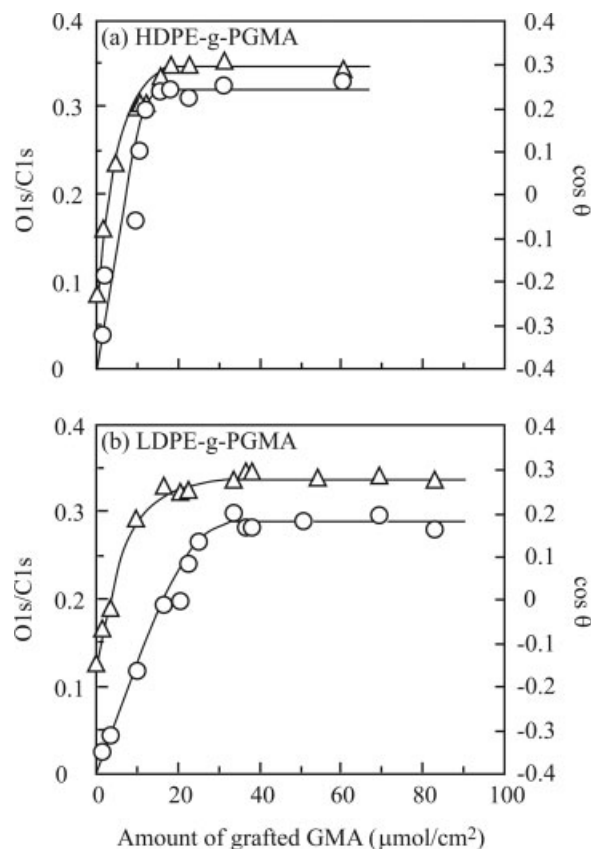


Figure 4 Changes in O1s/C1s (○) and the $\cos \theta$ values (△) with the amount of grafted GMA for the (a) LDPE-g-PGMA, and (b) HDPE-g-PGMA plates.

0.4 mg/g and 1.5 mg/g for LDPE-g-PGMA and HDPE-g-PGMA plates, respectively.

Autohesive (adhesive-free adhesion) properties

The LDPE-g-PGMA plates immersed in 1,4-dioxane for 24 h were put together with the surfaces facing each other with 10×10 -mm overlap, and the overlapped samples were heat-pressed at 60°C under a constant load of 0.5 kg/cm^2 . This condition was used in the present study because substrate breaking occurred under these conditions on the autohesive strength measurements for the LDPE and HDPE plates photografted with hydrophilic monomers such as MAA, AA, and DMAEMA.²⁵ Figure 5 shows the change in autohesive strength with the grafted amount for the LDPE-g-PGMA plates. Autohesive strength increased with an increase in the grafted amount, and the LDPE plate was broken at the grafted amount of $117 \text{ }\mu\text{mol/cm}^2$. This means that autohesive strength goes beyond the ultimate strength of the LDPE plate used in this study. It can be safely said that the bulk properties of the LDPE plates are highly preserved, since autohesive strength at substrate breaking is identical to the ultimate strength of the LDPE plates used in this work.

Grafted PGMA segments will thermally motion in the grafted layers swollen in 1,4-dioxane during heat-pressing, so the self-diffusion of grafted PGMA chains effectively occurs across the interfaces between the grafted layers. If this is the case, then entanglement and/or contraction of grafted PGMA chains will occur favorably cause the increase in autohesive strength. Subsequently, the temperature and load during heat-pressing were increased to decrease the grafted amount at which substrate breaking occurs.

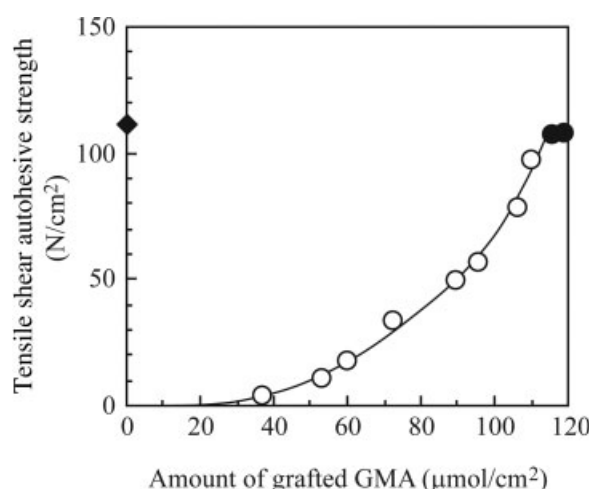


Figure 5 Change in tensile shear autohesive strength with the amount of grafted GMA for the LDPE-g-PGMA plates heat-pressed at 60°C under a load of 0.5 kg/cm^2 (failure: ○, cohesive failure; ●, substrate breaking; ◆, ultimate strength of LDPE).

TABLE II
Amounts of Grafted GMA at Substrate Breaking on Autohesive Strength Measurements for the LDPE-g-PGMA Plates*

Temperature ($^\circ\text{C}$)	Load (kg/cm^2)	Grafted amount ($\mu\text{mol/cm}^2$)
60	0.5	117
80	0.5	115
60	2.0	110
80	2.0	108

* LDPE-g-PGMA plates coated with an aqueous EDA solution of 0.5 M were heat-pressed under different conditions for 24 h.

The grafted amounts at substrate breaking are summarized in Table II.

When the temperature and load were increased during heat pressing, the grafted amount at substrate breaking slightly decreased. For the LDPE plates photografted with hydrophilic monomers such as MAA, AA, DMAEMA, and MAAM, the increase in the temperature and load during heat-pressing after immersion in water lead to the decrease in the grafted amounts at substrate breaking. Thus, the increase in the temperature and load during heat-pressing favors closer contact between the swollen grafted layers and causes more effective self-diffusion of grafted polymer chains across the interfaces of the swollen grafted layers.^{23–26} These results indicate that the use of good solvents such as 1,4-dioxane for the PE-g-PGMA plates and water for the PE plates photografted with the hydrophilic monomers mentioned above is of major importance in the development of autohesive strength.

Adhesion properties with amine compounds

In the present work, the enhancement in adhesive strength was assessed using the multi-functional amine compounds shown in Figure 1. First, the effect of concentration of EDA in 1,4-dioxane on adhesive strength was investigated for the LDPE-g-PGMA plates. The surfaces of the LDPE-g-PGMA plates were coated with EDA solutions of different concentrations. Then, curing after overlapping the LDPE-g-PGMA plates was carried out at 60°C under a load of 0.5 kg/cm^2 for 24 h. The conditions used on the adhesive strength measurements for the LDPE and HDPE plates photografted with MAA, AA, or DMAEMA in our previous paper²⁵ were set up here because adhesive strength increased over the grafted amounts, and substrate breaking was obtained at higher grafted amounts under these conditions. Figure 6 shows the changes in adhesive strength with the grafted amount for the LDPE-g-PGMA plates coated with EDA solutions of different concentrations. Although adhesive strength increased over the grafted amount irrespec-

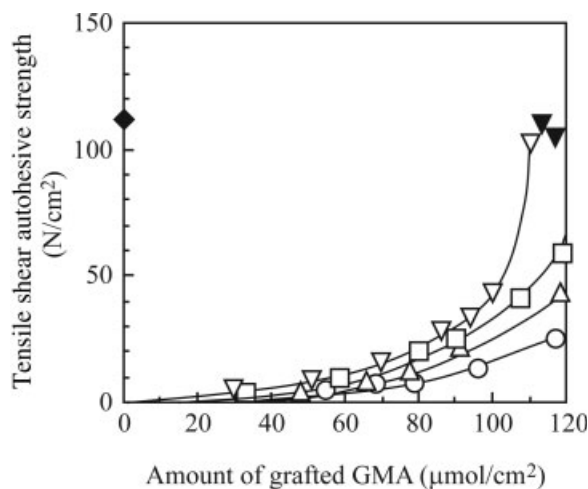


Figure 6 Changes in tensile shear adhesive strength with the amount of grafted GMA for the LDPE-g-PGMA plates coated with aqueous EDA solutions of 15 (original) (○), 8.0 (△), 2.0 (□), and 0.5 (▽, ▼) M. The curing was carried out at 60°C under a load of 2.0 kg/cm² (failure: open, cohesive failure; shaded, substrate breaking; ◆, ultimate strength of LDPE).

tive of the EDA concentration, the substrate breaking was not observed for the LDPE-g-PGMA plates coated with EDA solutions of >2.0 M.

When the surfaces of the LDPE-g-PGMA plates were coated with an EDA solution of 0.5 M, the LDPE-g-PGMA plates were broken at 117 μmol/cm². Here, since 1,4-dioxane is a good solvent of both EDA and PGMA, EDA would penetrate the grafted layers and the reaction would occur between amino groups of EDA molecules and epoxy groups affixed to the grafted PGMA chains in addition to evaporate 1,4-dioxane molecules during heat-pressing. Both amino groups in an EDA molecule need to react with epoxy groups of a grafted PGMA chain so as to crosslink grafted PGMA chains. However, entangling EDA side chains with one unreacted amino group are also formed on grafted PGMA chains at higher EDA concentrations. On this point, the decrease in the EDA concentration to 0.5 M is one of the important factors to increase the reaction of amine groups with epoxy groups. Since both values of autohesive and adhesive strength at substrate breaking shown in Figures 5 and 6 were almost in agreement with the value of the ultimate strength of the LDPE plate used here, the photografting of GMA will have little influence on the bulk properties of the LDPE plate.

Subsequently, adhesion between the LDPE-g-PGMA plates was investigated by use of the 1,4-dioxane solutions of other multi-functional amine compounds such as PDA, TETA, and PEHA on the basis of the above experimental results. Figure 7 shows the changes in adhesive strength with the grafted amount for the LDPE-g-PGMA plates coated with the PDA,

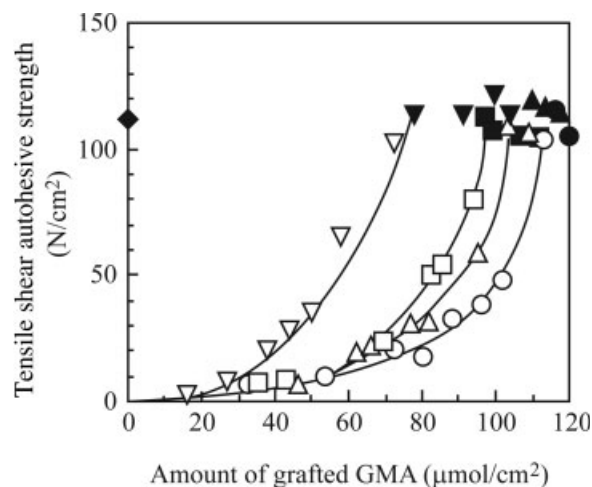
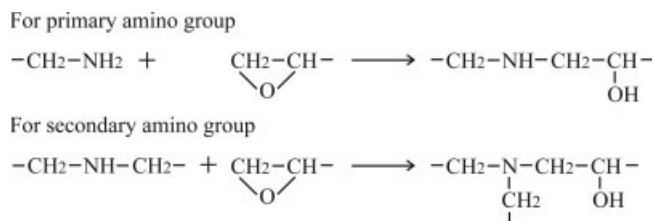


Figure 7 Changes in tensile shear adhesive strength with the amount of grafted GMA for the LDPE-g-PGMA plates coated with the aqueous solutions of EDA (○, ●), PDA (△, ▲), TETA (□, ■), and PEHA (▽, ▼) of 0.5 M. Curing was carried out at 60°C under a load of 2.0 kg/cm² (failure: open, cohesive failure; shaded, substrate breaking; ◆, ultimate strength of LDPE). Heat-pressing time: 24 h for EDA, PDA, and TETA, and 120 h for PEHA.

TETA, and PEHA solutions of 0.5 M. The heat-pressing time was extended up to 120 h to complete the curing reaction for PEHA. Adhesive strength increased with an increase in the grafted amount irrespective of the amine compounds used. The increase in the number of amino groups in an amine compound led to the substrate breaking at lower grafted amounts. These results suggest that the reaction between the primary or secondary amino groups of the multifunctional amine compounds used here and epoxy groups appended to the grafted PGMA chains would occur at the interface between the overlapped LDPE-g-PGMA plates as shown in Scheme 1. The increase in the number of amino groups in an amine compound and the molecular chain length will effectively works on the enhancement of adhesive strength. We tried to decrease the grafted amounts at substrate breaking by adjusting the temperature and load during heat-pressing.

The grafted amounts at the substrate breaking were summarized in Table III for the LDPE-g-PGMA plates



Scheme 1 Reaction between the primary or secondary amino groups of multifunctional amine compounds and the epoxy groups appended to the grafted PGMA chains.

TABLE III
Amounts of Grafted GMA at Substrate Breaking on Adhesive Strength
Measurements for the LDPE-g-PGMA and HDPE-g-PGMA Plates under Different
Conditions*

Amine compound	Temperature (°C)	Load (kg/cm ²)	Time (h)	Grafted amount (μmol/cm ²)
LDPE-g-PGMA plates				
EDA	60	0.5	24	115
PDA	60	0.5	24	110
TETA	60	0.5	24	97
PEHA	60	0.5	96	85
	60	0.5	120	77
EDA	80	0.5	24	113
PDA	80	0.5	24	107
TETA	80	0.5	24	90
EDA	60	2.0	24	100
PDA	60	2.0	24	92
TETA	60	2.0	24	80
EDA	80	2.0	24	95
PDA	80	2.0	24	90
TETA	80	2.0	24	78
HDPE-g-PGMA plates				
EDA	80	2.0	24	85
PDA	80	2.0	24	80
TETA	80	2.0	24	55

* LDPE-g-PGMA and HDPE-g-PGMA plates coated with the multi-functional amine compound solution of 0.5 M.

heat-pressed under different heat-pressing conditions. When the temperature during heat-pressing increased from 60 to 80°C, the grafted amount at substrate breaking slightly decreased. In addition, it was found from Table III that the increase in the load from 0.5 to 2.0 kg/cm² was one of the favorable procedures to enhance adhesive strength. When the curing was carried out at 80°C under a load of 2.0 kg/cm², the

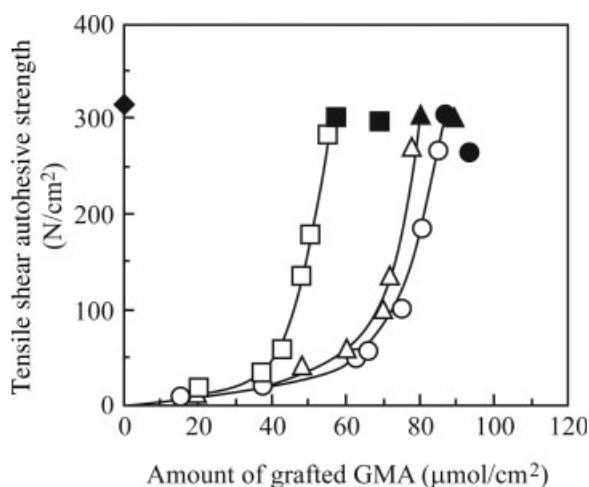


Figure 8 Changes in tensile shear adhesive strength with the amount of grafted GMA for the HDPE-g-PGMA plates coated with the aqueous solutions of EDA (○, ●), PDA (△, ▲), and TETA (□, ■) of 0.5 M. The curing was carried out at 60°C under a load of 2.0 kg/cm² (failure: open, cohesive failure; shaded, substrate breaking; ◆, ultimate strength).

grafted amounts at substrate breaking decreased further, and the substrate breaking occurred at 78 μmol/cm² by coating the TETA solution.

Since the LDPE plates coated with the amine compound solutions of 0.5 M were broken at lower grafted amounts by curing at 80°C under a load of 2.0 kg/cm², adhesion between the HDPE-g-PGMA plates was carried out under the same conditions. Figure 8 shows the changes in the adhesion strength with the grafted amount for the HDPE-g-PGMA plates coated with the EDA, PDA, and TETA solutions of 0.5 M. Although the ultimate strength of the HDPE plates was higher than that of the LDPE plates, the HDPE-g-PGMA plates were broken at lower grafted amounts than the LDPE-g-PGMA plates probably because the location of the photografting of GMA was restricted to the outer surface regions for the HDPE plates and grafted PGMA chains were more densely present at the surfaces of the grafted layers as seen from the results of surface analysis by ESCA in Figure 4.

CONCLUSIONS

This article details the photografting of GMA onto the LDPE and HDPE plates and the enhancement in adhesive properties of the obtained LDPE-g-PGMA and HDPE-g-PGMA plates through the chemical reaction between grafted PGMA chains and amine compounds.

In the case where an aqueous ethanol solution of the volume fraction of 80 vol% was used as a solvent for

the photografting of GMA onto the LDPE plates, the amount of grafted GMA sharply increased with an increase in the irradiation time. Surface analysis by ESCA and contact angle measurements reveal that the wettability of the LDPE-g-PGMA and HDPE-g-PGMA plates stayed constant above the grafted amounts at which the LDPE and HDPE surfaces were fully covered with grafted PGMA chains. The LDPE plates were broken at $117 \mu\text{mol}/\text{cm}^2$ for autohesion (adhesive-free adhesion) with 1,4-dioxane, as shown in Figure 5. Subsequently, we followed up adhesion with the multi-functional amine compounds for the LDPE-g-PGMA and HDPE-g-PGMA plates. The increase in the number of amino groups in the multi-functional amine compounds used led to the decrease in the grafted amounts at substrate breaking because cross-linking between grafted PGMA chains through the reaction between amine groups in the multi-functional amine compounds and epoxy groups appended to the grafted PGMA chains. The increase in the number of amino groups in an amine compound, in addition to the temperature and load during curing, was also a favorable factor to increase adhesive strength. In addition, the location of the photografting of GMA onto the HDPE plates is restricted to the outer surface regions of the substrates, and the substrate breaking occurred at lower grafted amounts for adhesion between the HDPE-g-PGMA plates with amine compounds. In near future, we will focus on the decrease in the grafted amount at substrate breaking by using the amino groups containing polymers such as linear and branched poly(ethylenimine) (LPEI and BPEI), poly(allylamine) (PAAm), and poly(vinylamine) (PVAm) in place of the multi-functional amine compounds.

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