

Autohesive Properties of Polyolefins Photografted with Hydrophilic Monomers

Kazunori Yamada, Jun Kimura, Mitsuo Hirata

Department of Applied Molecular Chemistry, College of Industrial Technology, Nihon University, 1-2-1 Izumi-cho, Narashino, Chiba 275-8575, Japan

Received 31 October 2001; accepted 4 March 2002

ABSTRACT: In an attempt to provide polyolefins such as low- and high-density polyethylene and polypropylene with autohesive properties, hydrophilic monomers such as methacrylic acid (MAA), acrylic acid (AA), and 2-(dimethylamino)ethyl methacrylate (DMAEMA) were photografted onto their surfaces. The wettabilities of the grafted plates stayed constant above full coverage of the substrate surfaces with grafted polymer chains, except for the AA-grafted plates. The amount of absorbed water for the grafted layers formed increased with an increase in the number of grafted polymer chains. The autohesive strength increased with an increase in the wettability and water absorptivity of the grafted plates as well as the temperature and load on heat pressing. For all grafted plates substrate breaking at auto-

hesive strength measurements was observed for grafted amounts 2–3 times as much as those at adhesive strength measurements. The substrate breakings for the HDPE and PP plates photografted with AA and DMAEMA at adhesive strength measurements were observed at lower grafted amounts compared with those photografted with MAA. This study has made it clear that the photografting of hydrophilic monomers onto polyolefin materials can markedly enhance autohesivity without any adhesives as well as the adhesivity for high grafted amounts. Therefore, polyolefin materials with improved autohesivity and adhesivity can be widely applied in adhesive fields, including for novel uses. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 2244–2252, 2003

INTRODUCTION

Polyolefins such as polyethylene (PE) and polypropylene (PP) are extensively used as polymer materials because of their low density, excellent solvent resistance, and availability at low cost. However, their poor wettabilities give rise to problems for practical applications. To overcome these problems, several surface modification techniques have been exploited.^{1,2} Most of them have attempted to introduce polar functional groups on the substrate surfaces to increase their surface free energies, leading to an increase in the wettabilities. Plasma treatment has been widely used to make polymer surfaces hydrophilic, considerably enhancing wettability and adhesivity with non-polymer-forming gases such as O₂, N₂, He, and Ar.^{3–5} However, the surface properties of the modified substrates gradually regressed as a function of time elapsed. This occurred because the polar functional groups that formed on the substrate surfaces tended to readily overturn in the outer surface region and migrate into the bulk of the polymer substrates mainly as a result of local motion of segments of the polymer chains.^{6–9} Thus, the applicability of polyolefins has

frequently been limited due to poor durability of the modified surfaces.

We have investigated the surface modification of PE and polytetrafluoroethylene (PTFE) plates using a photografting technique.^{10–13} The wettability of low-density PE (LDPE) plates was considerably improved at low grafted amounts by the photografting of methacrylic acid (MAA), acrylic acid (AA), and methacrylamide (MAAm), and adhesive strengths higher than the ultimate tensile strength of the LDPE plate used were observed.^{10,11} Because hydrophilic polymer chains with polar functional groups can covalently bond to substrate polymer chains in the surface region, the hydrophilic properties of the substrate surfaces modified by the photografting technique should be better preserved than with other surface modification techniques.

So far, only a few studies have been reported on the autohesion of widely used polymer materials by surface grafting,^{14–17} compared with the larger number of studies on surface modification and improvement in adhesivity^{10,11,18–24} Pioneering studies on autohesion, or self-adhesion, were carried out using cotton fabrics coated with polyisobutylene under various conditions by Voyutskii and coworkers in 1950s.^{25–27} They concluded that autohesion was caused by self-diffusion of polymer segments from one layer into another of the same polymer across the interface. The migrated poly-

Correspondence to: K. Yamada (k5yamada@cit.nihon-u.ac.jp).

TABLE I
Determination of Degree of Crystallinity and Ultimate Strength of Polymer Substrates in This Study

Abbreviation	Density (g/cm ³)	Degree of crystallinity (%)	Ultimate strength (kg/cm ²)
LDPE	0.926	50.8	14.1
HDPE	0.958	69.7	22.2
PP	0.905	66.2	25.0

mer segments entangle with other ones, thus enhancing fracture resistance, and eventually randomize to fuse the surface. We have reported that for photografting of hydrophilic monomers such as MAA, AA, and MAAM onto LDPE and PTFE plates, the location of photografting is restricted to the surface region of the substrates, and the grafted layers formed on the substrate surfaces possess high water absorptivities.^{11,13} The grafted polymer chains would have high mobility in the water-swollen state. Therefore, grafted polymer chains in the water-swollen grafted layers can be entangled with each other via their self-diffusion when the two grafted plates are brought into close contact by heat pressing, leading to bond formation without any adhesives. Also, for PTFE plates grafted with MAA, AA, 2-(dimethylamino)ethyl methacrylate (DMAEMA) by the combined use of plasma treatment and photografting, autohesive strength can be increased to a value equivalent to that of adhesive strength.^{22,23}

This article reports on a study of the improvement in autohesivity and adhesivity of polyolefins such as low- and high-density PE (LDPE and HDPE) and polypropylene (PP) plates that were photografted with MAA, AA, and DMAEMA. Further, the improved surface properties, which was analyzed by ESCA and by measurements of contact angle and water absorption, will be discussed.

EXPERIMENTAL

Materials

The crystallinities of the substrates (thickness : 1 mm) used, LDPE, HDPE, and PP, were estimated from their densities determined by a flotation or buoyancy method with acetone and glycerol at 25°C using the known densities of the completely amorphous and pure crystalline parts as shown in Table I.^{28,29} These polymer plates, which were 6 cm in length and 3 cm in width, were washed with methanol and acetone and then dried under reduced pressure. MAA, AA, and DMAEMA were purified by distillation under reduced pressure.

Photografting

The procedure for photografting was described in detail in our previous articles.^{11,30,31} The polymer plates

were dipped for 1 min in 50 cm³ of an acetone solution containing 0.25 g of benzophenone (BP) as a photosensitizer to coat their surfaces. The BP-coated polymer plates were immersed in the aqueous monomer solutions of MAA, AA, and DMAEMA at a monomer concentration of 1.0 mol/dm³. Before photografting only the pH of the aqueous DMAEMA solution was adjusted, to pH 8.0 using concentrated HCl, to enhance the solubility of PDMAEMA. Photografting was done at 60°C by applying UV-rays emitted from a 400-W high-pressure mercury lamp to the aqueous monomer solutions in which the BP-coated polymer plates were immersed under a nitrogen atmosphere in the Pyrex glass tubes. After grafting, the grafted polymer plates were washed with water for 24 h to exclude homopolymers and then were dried under reduced pressure for 48 h at room temperature. The grafted amounts ($\mu\text{mol}/\text{cm}^2$) were calculated from the weight increases of the plates after photografting.

Surface and bulk properties of grafted layers

The photoelectron spectra for the grafted plates were recorded on a Shimadzu ESCA-750 type spectrometer with the Mg K α (1253.6 eV) source operating at 8 kV and 30 mA.^{10,11} Then the O_{1s}/C_{1s} and N_{1s}/C_{1s} values were calculated from the individual peak areas and ionized cross sections³²⁻³⁴ to determine the chemical compositions of the surfaces of the grafted layers. The contact angles of water on the grafted plates were measured with a sessile drop method at 25°C under an atmosphere of saturated water vapor with a Kyowa Kagaku TYP-QI-type goniometer.^{10,11}

The amount of absorbed water for the grafted plates was measured to estimate the hydrophilicity of the grafted layers. The grafted plates were immersed in distilled water at 25°C for 24 h. Then the grafted plates were taken out of the water, blotted with filter paper to remove water attached to their surfaces, and weighed as quickly as possible. The amount of absorbed water and the moles of water molecules assigned per monomer segment, n_{water} , were calculated.^{10,30}

Adhesive and autohesive strength measurements

A commercial two-component-type epoxy adhesive called Araldite was applied to the grafted surfaces of two pieces of grafted plates with the same grafted amount cut into pieces 30 mm in length and 10 mm in width to provide an overlap of 10 × 10 mm. The adhesives were cured for 24 h at 60°C while the load of 0.5 kg/cm² was kept on the bonded, grafted plates.

For autohesive strength measurements, the grafted plates with the same grafted amount immersed in distilled water at 25°C for 24 h were put together with their grafted surfaces facing each other with a 10 × 10

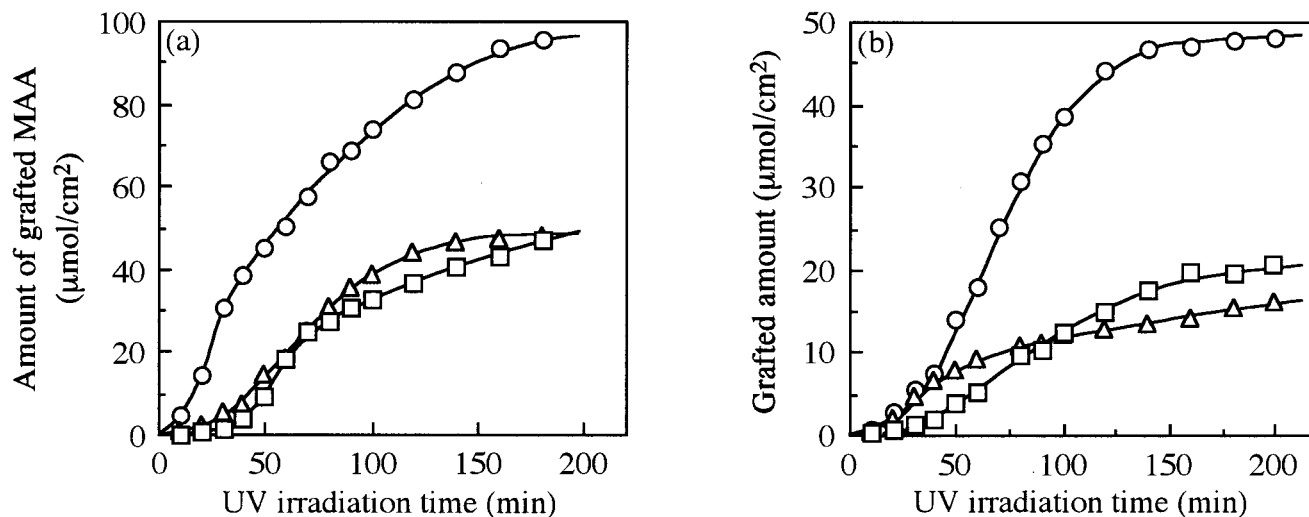


Figure 1 Changes in the grafted amount with UV irradiation time for (a) photografting of MAA onto (○) LDPE, (△) HDPE, and (□) PP plates; and (b) (○) MAA, (△) AA, and (□) DMAEMA on to a HDPE plate

mm overlap. The overlapped samples were heat-pressed by adding a load of $2.0 \text{ kg}/\text{cm}^2$ for 24 h at 80°C , unless otherwise noted.

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 $3 \text{ mm}/\text{s}$ at 25°C .

RESULTS AND DISCUSSION

Photografting

The changes in the grafted amount with the UV irradiation time for the photografting of MAA onto the LDPE, HDPE, and PP plates and of MAA, AA, and DMAEMA onto the HDPE plates are shown in Figure 1(a,b), respectively. The amount of grafted MAA increased with an increase in the irradiation time for all polymer substrates used in this study. Because photografting proceeds primarily in the amorphous part of the outer surface regions, MAA monomers can more easily bond to the LDPE plate with low crystallinity than the HDPE and PP plates [Fig. 1(a)]. AA monomers are considered to be more difficult to bond to HDPE surfaces because of their higher hydrophilicity, or lower affinity, for HDPE [Fig. 1(b)]. The tendency for the grafted amounts to increase with the irradiation time for the photografting of these three kinds of hydrophilic monomers onto LDPE and PP plates was similar to that for the photografting onto the HDPE plate, as shown in Figure 1(a,b).

Surface analysis by ESCA and contact-angle measurements

Surface analysis of the grafted plates by ESCA was carried out to estimate the chemical composition of the

surfaces of the grafted layers. The $\text{O}_{1s}/\text{C}_{1s}$ values for the MAA-grafted and AA-grafted plates and the $\text{O}_{1s}/\text{C}_{1s}$ and $\text{N}_{1s}/\text{C}_{1s}$ values for the DMAEMA-grafted plates increased with the grafted amounts and then leveled off. The increase in the intensity ratios corresponded to that in the wettabilities of the substrate surfaces from the photografting. The intensity ratios being constant for the higher grafted amounts means that the chemical composition of the outer surface regions of the grafted layers stayed unchanged irrespective of the formation of thicker grafted layers. The constant intensity ratios and the grafted amounts at which the intensity ratios leveled off for the grafted plates prepared above are summarized in Table II. The constant values of $\text{O}_{1s}/\text{C}_{1s}$ for the AA-grafted plates were obtained at lower grafted amounts and became higher than those for the MAA-grafted plates. These results show that the location of photografting of AA is restricted to the outer surface regions of the substrates and that grafted PAA chains can cover the substrate surfaces at lower grafted amounts than grafted PMAA chains. The intensity ratios for the DMAEMA-grafted plates stayed constant at the lowest grafted amounts of these three grafted plates. The surface analysis by ESCA of the $30\text{-}\mu\text{m}$ -thick LDPE films photografted with MAA, AA, and DMAEMA and the microscopic observation of their cross sections were reported in detail in our previous article.³⁰ The intensity ratios for the DMAEMA-grafted PE film became constant and the ungrafted layers disappeared at the lowest grafted amount of these grafted films. This indicates that because DMAEMA monomer is more hydrophobic than MAA and AA monomers, the internal grafting, which occurs simultaneously with the surface grafting, progresses for the photografting of DMAEMA. Therefore, it is considered that for the

TABLE II
Surface Compositions and Wettabilities of Grafted Plates Prepared in This Study

Sample	Grafted amount ^a ($\mu\text{mol}/\text{cm}^2$)	Constant intensity ratio		$\cos \theta$
		O1s/C1s	N1s/C1s	
LDPE-g-PMAA	25	0.32		0.5
LDPE-g-PAA	6	0.37		0.4 (max)
LDPE-g-PDMAEMA	5	0.26	0.12	0.15
HDPE-g-PMAA	10	0.31		0.45
HDPE-g-PAA	3	0.36		0.3 (max)
HDPE-g-PDMAEMA	1	0.24	0.09	0.12
PP-g-PMAA	12	0.33		0.5
PP-g-PAA	4	0.38		0.2 (max)
PP-g-PDMAEMA	2	0.23	0.12	0.1
PMAA		0.384		
PAA		0.518		
PDMAEMA		0.253	0.114	
LDPE		0.027		-0.120
HDPE		0.021		-0.180
PP		0.024		-0.090

^a The grafted amount at which the intensity ratios and $\cos \theta$ values become constant.

photografting of DMAEMA onto the LDPE, HDPE, and PP plates, the internal grafting progressed easily compared with the photografting of MAA and AA, and the intensity ratio reached a constant value at the lowest grafted amount of all the grafted plates.

The contact angles of water on the grafted plates were measured to estimate their surface wettabilities. The constant $\cos \theta$ values for the grafted plates are also summarized in Table II. The $\cos \theta$ value increased with an increase in the grafted amount and then stayed constant above the grafted amount at which the intensity ratios became constant for the MAA-grafted and DMAEMA-grafted plates. On the other hand, the $\cos \theta$ values for the AA-grafted plates passed through the maximum values. It was found that in the range of the grafted amount in which the intensity ratio increased, photografting would mainly initiate on substrate surfaces. However, above the grafted amounts

at which the intensity ratios become constant, photografting onto grafted PAA chains would also occur. Thus, it is possible for highly branched grafted PAA chains with high molecular weight to form.³⁵ On the other hand, Lawler and Charlesby reported that high-molecular-weight PAA chains were insoluble in water.³⁶ Therefore, the wettability of the surfaces of the AA-grafted plates is considered to decrease with an increase in the grafted amount after the maximum value because of the aggregation of grafted PAA chains caused by attractive intermolecular interaction such as hydrogen bonding.

Water-absorptivity measurements

Figure 2 shows the changes in the amount of absorbed water with the grafted amount for the grafted plates. The amount of absorbed water increased with an in-

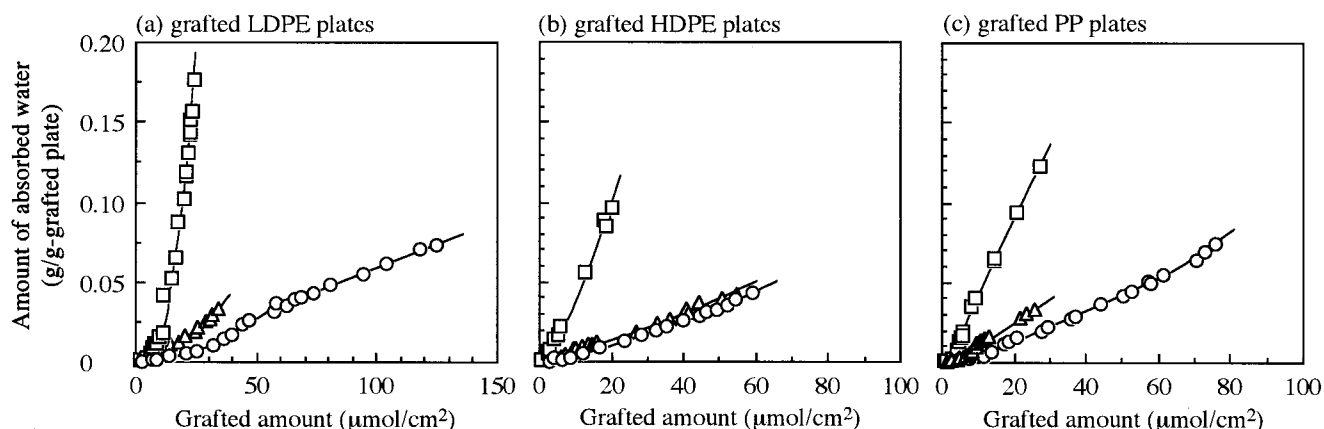


Figure 2 Changes in the amount of absorbed water with the grafted amount for (a) grafted LDPE, (b) grafted HDPE, and (c) grafted PP plates. (grafted monomer—○: HDPE, △: AA, □: DMAEMA).

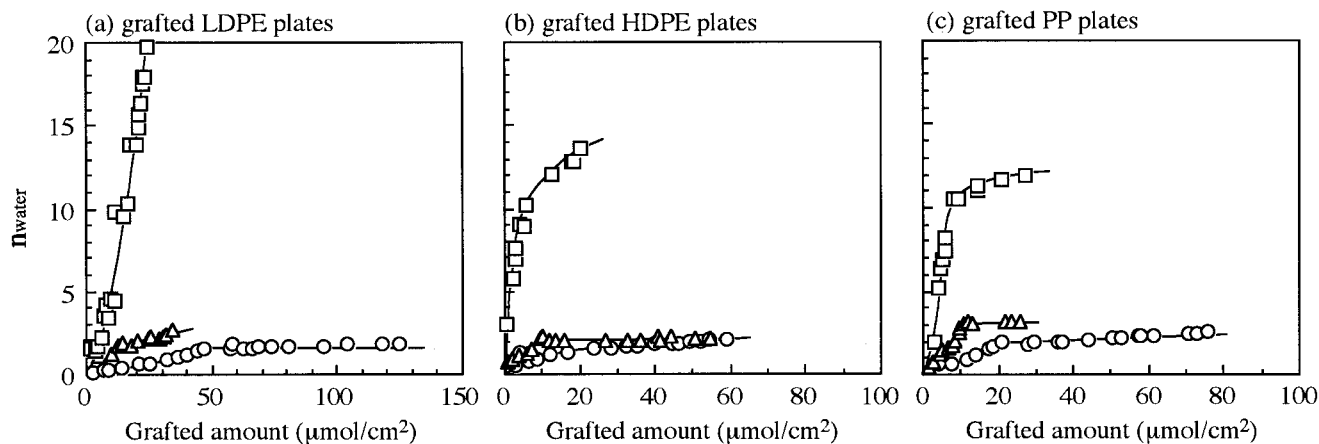


Figure 3 Changes in the n_{water} value with the grafted amount for (a) grafted LDPE, (b) grafted HDPE, and (c) grafted PP plates (grafted monomer—○: MAA, △: AA, □: DMAEMA).

crease in the grafted amount. Of these, the DMAEMA-grafted layers in particular exhibited very high water absorptivity. The grafted layers formed on the HDPE and PP plates had slightly higher absorptivities than those on the grafted LDPE plates because the grafted layers enriched with grafted polymer chains were mainly formed as a result of their high crystallinities. The AA-grafted plates exhibited slightly higher water absorptivity than did the MAA-grafted ones. This can be explained as follows: Surface analysis by ESCA (Table II) showed that the location of the photografting of AA was mainly restricted to the outer surface region of the polymer substrates—that is, the substrate surfaces were covered with grafted PAA chains at lower grafted amounts than with grafted PMAA chains. Therefore, grafted PAA chains can contact more free water molecules than grafted PMAA chains at the same grafted amount in addition to the more hydrophilic structure of the AA monomer.

The DMAEMA-grafted plates absorbed much more water in the range of high grafted amounts than the other two grafted plates. It can also be considered from the results shown in Figure 3 (discussed below) that grafted PDMAEMA chains with rather hydrophobic properties can proceed into the bulk of the substrates with the concomitant breaking of some crystalline regions of the substrates.

The water absorptivities of the grafted layers cannot be satisfactorily explained only by the amount of absorbed water and the monomer structures. The n_{water} values are useful for discussing the water absorptivities in more detail. Figure 3 shows the changes in the n_{water} value with the grafted amount for the grafted plates. The n_{water} values for the MAA-grafted LDPE (LDPE-g-PMAA) plates increased with the grafted amount and then leveled off at the grafted amount of about $50 \mu\text{mol}/\text{cm}^2$, at which the water-absorption curve bent, as shown in Figure 2(a). This means, taking into consideration surface analysis by ESCA, that

the thickness for the MAA-grafted layers continued to increase without any change in their chemical composition in the range where the n_{water} values stayed constant. The constant n_{water} values for the MAA-grafted HDPE and PP (HDPE-g-PMAA and PP-g-PMAA) plates were obtained at lower grafted amounts than for the LDPE-g-PMAA plate. This occurred because the photografting of MAA onto the HDPE and PP plates was restricted to the outer surface regions as a result of their high crystallinity, as pointed out previously, and made it possible for additional grafted polymer chains to come into contact with water molecules.

The n_{water} values for the DMAEMA-grafted plates sharply increased with the grafted amount, especially for the DMAEMA-g-LDPE plates. It has been shown from surface analysis by ESCA that grafted PDMAEMA chains can cover the substrate surfaces at lower grafted amounts than can the other two grafted polymer chains monomers. When hydrophilic monomers were photografted onto the surfaces of the polymer substrates used, the internal grafting more or less occurred simultaneously with the surface grafting. The internal grafting was considered to preferentially progress for the photografting of DMAEMA because a relatively hydrophobic DMAEMA monomer has closer affinity toward polymer chains of the substrates than do MAA and AA monomers. Therefore, the thick grafted layers from the photografting of DMAEMA with the breaking of a part of the crystalline regions, especially for the LDPE plate with low crystallinity, can accommodate more water molecules, leading to higher n_{water} values.

Autohesive strength measurements

The dependence of the tensile shear autohesive strength on temperature and load during heat pressing was investigated for the PMAA-g-HDPE plates.

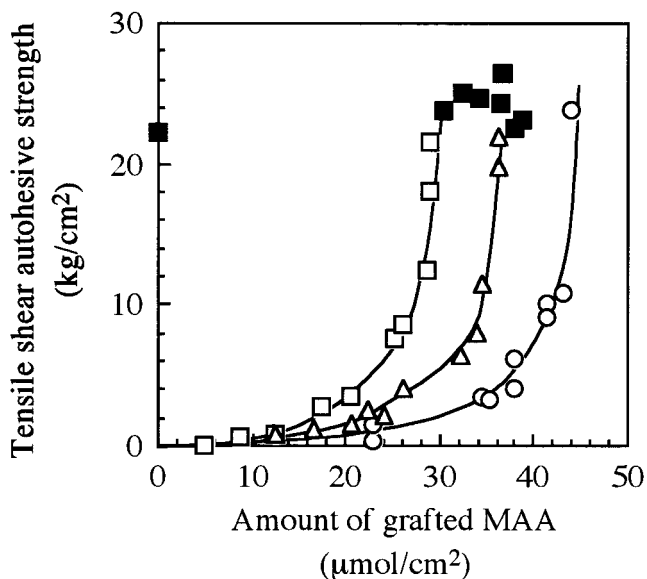


Figure 4 Changes in tensile shear autohesive strength with the grafted amount for HDPE-g-PMAA plates heat-pressed at (○) 40°C, (△) 60°C, and (□) 80°C under a load of 2.0 kg/cm² (failure: open symbol—cohesive failure; shaded symbol—substrate breaking).

Figure 4 shows the changes in autohesive strength with the grafted amount at different heat-pressing temperatures under a constant load of 2.0 kg/cm². As the heat-pressing temperature increased, autohesive strength sharply increased at lower grafted amounts. It is expected that the thermal motion of grafted PMAA segments at increased temperatures becomes

more active in the water-swollen state, and so their self-diffusion across the interfaces between the grafted layers effectively occurs. If this is the case, then intermolecular interactions such as entanglements of grafted PMAA chains will favorably cause an increase in autohesive strength. Although the behavior of autohesive strength against the heat-pressing temperature appeared similar in any condition, it was only at the heat-pressing temperature of 80°C above 24 μmol/cm² that substrate breaking was observed. The autohesive strength at which substrate breaking was observed was almost in agreement with the ultimate tensile strength of the ungrafted HDPE plate shown in Table I. Substrate breaking was observed when autohesive strength was beyond the ultimate tensile strength of the substrate.

Taking the above results into consideration, the autohesive strength of the PMAA-g-HDPE plates at a heat-pressing temperature of 80°C was measured by varying the load in the range of 0.5–4.0 kg/cm². Figure 5 shows the changes in autohesive strength with the grafted amount at different loads on heat pressing. An increase in load led to substrate breaking at lower grafted amounts at loads below 2.0 kg/cm². An increased load favors closer contact between water-swollen grafted layers and the more effective self-diffusion of grafted PMAA chains across the interfaces of the swollen grafted layers. The substrates were broken at the same grafted amount, even if the load increased from 2.0 to 4.0 kg/cm². Therefore, measurements of the autohesive strength of the other grafted

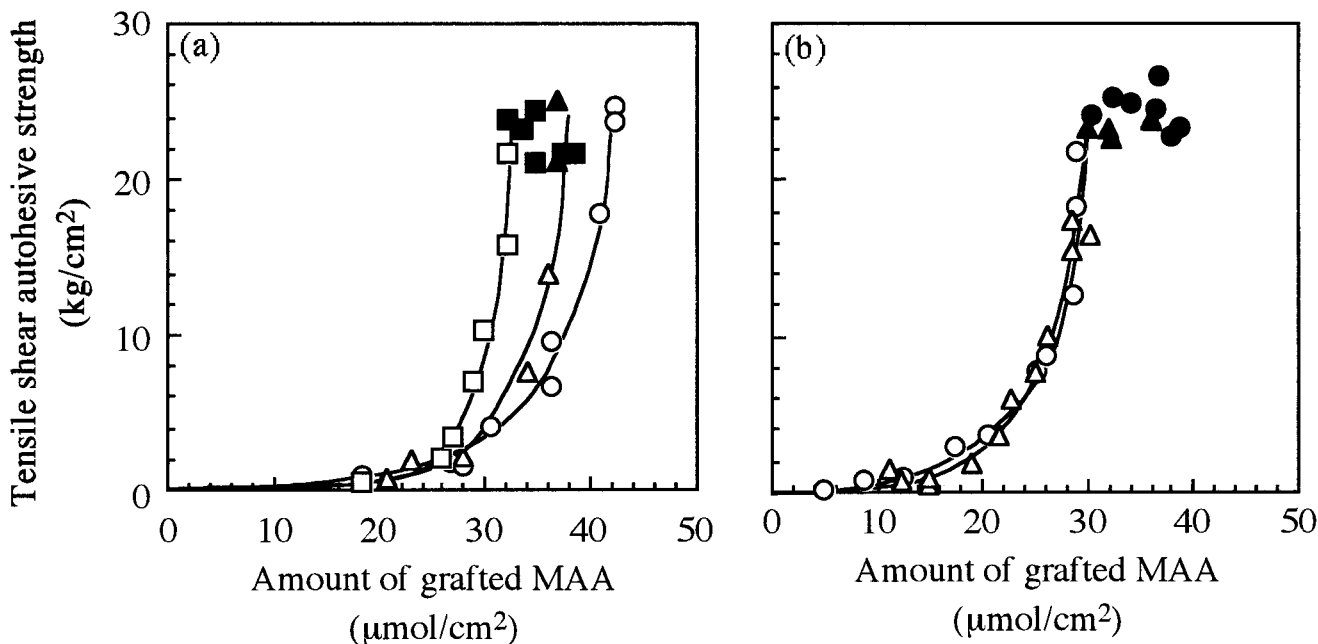


Figure 5 Changes in tensile shear autohesive strength with the grafted amount for HDPE-g-PMAA plates heat-pressed at 80°C under a load of (a) ○: 0.5 kg/cm², △: 1.0 kg/cm², □: 1.5 kg/cm²; (b) ○: 2.0 kg/cm², △: 4.0 kg/cm² (failure: open symbol—cohesive failure; shaded symbol—substrate breaking).

plates were made at a load of 2.0 kg/cm^2 and a heat-pressing temperature of 80°C .

Figure 6 shows the changes in autohesive strength with the grafted amount for the grafted LDPE, HDPE, and PP plates. In addition, the grafted amounts at which autohesive breaking occurred are summarized in Table III. The substrate was broken above the grafted amount of $60 \mu\text{mol/cm}^2$ for the LDPE-g-PMAA plates. The values of autohesive strength at substrate breaking were almost equivalent to the ultimate tensile strength of 14.1 kgf/cm^2 for an ungrafted LDPE plate shown in Table I. This indicates that the LDPE plate can be surface-modified by photografting of MAA without affecting any bulk properties. Substrate breaking was observed at $30\text{--}35 \mu\text{mol/cm}^2$ for the HDPE-g-PMAA and PP-g-PMAA plates. The lower values of the substrate breaking for the LDPE-g-PMAA plate may be a result of the location of photografting being more restricted to the outer surface regions of the HDPE and PP plates with higher crystallinities. It can also be seen from Tables II and III that the grafted amounts at substrate breaking were higher than those at which the substrate surfaces were covered with grafted PMAA chains. The AA-grafted plates were broken at lower grafted amounts than the MAA-grafted plates irrespective of the substrates used because of the photografting of AA to the outer surface region. Intermolecular interactions such as hydrogen bonding between carboxyl groups and the entanglements of grafted polymer chains can be considered as working more effectively for the AA-grafted plates than for the MAA-grafted plates.

Higher autohesive strength for the DMAEMA-grafted plates and substrate breaking were observed at much lower grafted amounts. Because the grafted layers for the DMAEMA-grafted plates possessed high water absorptivity, as shown in Figure 2, the grafted PDMAEMA chains would have considerable mobility in the water-swollen state. In addition, because PDMAEMA behaves as a thermosensitive polymer with a lower critical solution temperature (LCST), solubility in water would be remarkably reduced at higher temperatures.³² Therefore, an increase in autohesive strength would be caused by the entanglements and cohesion of grafted PDMAEMA chains because of their contraction, ascribed to hydrophobic interaction on heat pressing.

The above results suggest that autohesive strength from heat pressing of grafted LDPE, HDPE, and PP plates with water-swollen grafted layers can effectively be enhanced through hydrogen bonding and hydrophobic interaction among functional groups affixed to grafted polymer chains as well as through self-diffusion of grafted polymer segments.

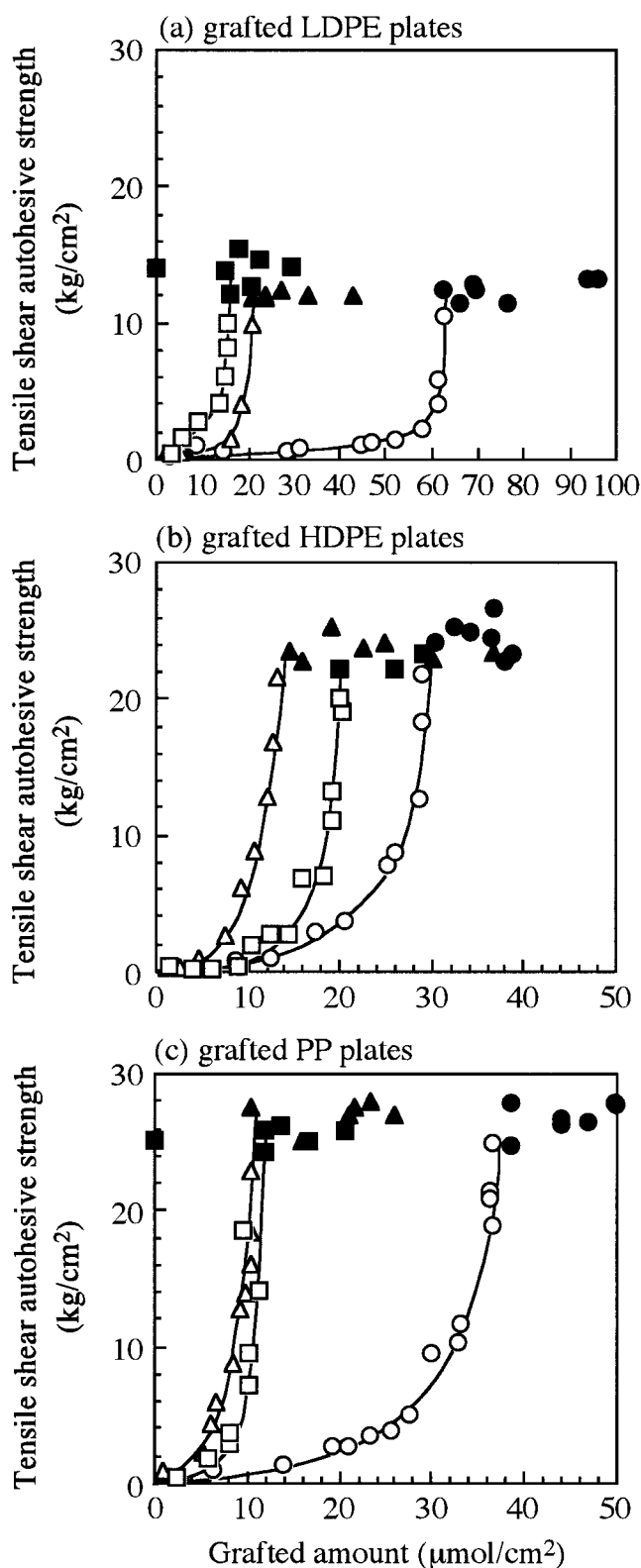


Figure 6 Changes in tensile shear autohesive strength with the grafted amount for (a) grafted LDPE, (b) grafted HDPE, and (c) grafted PP plates heat-pressed at 80°C under a load of 2.0 kg/cm^2 (grafted monomer—○: MAA, △: AA, □: DMAEMA; failure: open symbol—cohesive failure, shaded symbol—substrate breaking).

Adhesive strength measurements

Figure 7 shows the adhesive strengths for three types of substrates, LDPE, HDPE, and PP, photografted with MAA and for HDPE plates photografted with three kinds of monomers, MAA, AA, and DMAEMA, using a commercial two-component-type epoxy adhesive called Araldite. The grafted amounts at substrate breaking are summarized in Table III.

It can be seen from Figure 7 and Table II that the grafted amounts at which substrate breakings in autohesive strength occur are 2–3 times as high as those in adhesive strength, as expected. The increase in adhesive strength is considered to be attributable to the increase in wettability of the modified substrate surfaces and to the permeability of the adhesives into the grafted layers formed. This is in marked contrast with autohesive strength, which was mainly a result of the intermolecular interactions between the grafted polymer chains themselves.

It is of great interest that the autohesive strength of the LDPE, HDPE, and PP plates can be markedly improved by swelling the grafted layers formed on the grafted plates in water and then heat-pressing them together without any adhesives.

CONCLUSION

This article has detailed the autohesive and adhesive properties of LDPE, HDPE, and PP plates photografted with hydrophilic monomers such as MAA, AA, and DMAEMA on the basis of the surface and bulk properties of the grafted layers formed.

Autohesive strength increased with an increase in the wettability of the grafted layers, with the chemical composition with the grafted amount being followed up through ESCA. Water absorptivity of the grafted layers was investigated as a function of the grafted amount and was found to be closely related to an enhancement in autohesivity. On the other hand, the adhesivity of three kinds of grafted plates using

TABLE III
Grafted Amounts at Which Substrate Breaking Occurs on Autohesive and Adhesive Strength Measurements

Sample	Autohesive strength ($\mu\text{mol}/\text{cm}^2$)	Autohesive strength ($\mu\text{mol}/\text{cm}^2$)
LDPE-g-PMAA	60	40
LDPE-g-PAA	20	
LDPE-g-PDMAEMA	15	
HDPE-g-PMAA	30	14
HDPE-g-PAA	15	5
HDPE-g-PDMAEMA	20	6
PP-g-PMAA	35	14
PP-g-PAA	10	
PP-g-PDMAEMA	12	

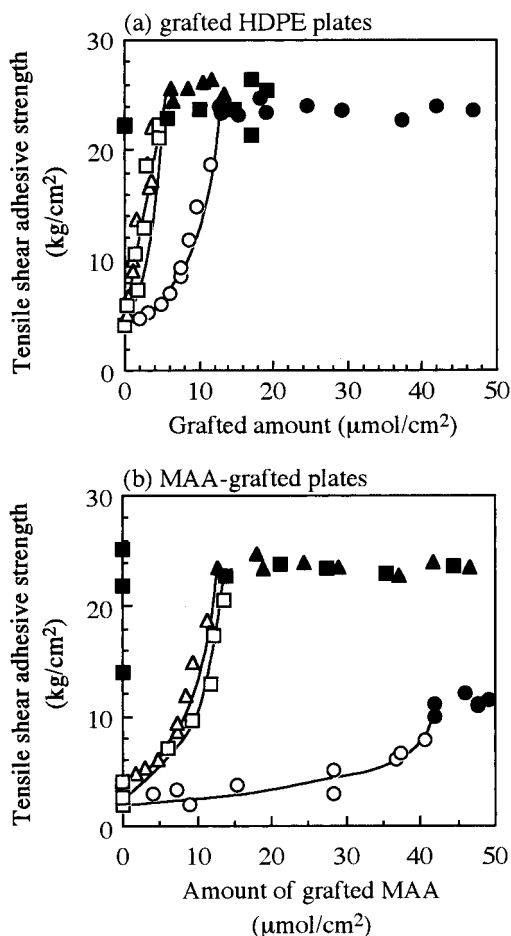


Figure 7 Changes in tensile shear adhesive strength with the grafted amount for (a) MAA-grafted plates and (b) grafted HDPE plates. The adhesives were cured at 80°C under a load of 0.5 kg/cm² (sample: (a) ○: LDPE-g-PMAA, △: HDPE-g-PMAA, □: PP-g-PMAA; (b) ○: LDPE-g-PMAA, △: HDPE-g-PAA, □: HDPE-g-PDMAEMA; failure: open symbol—cohesive failure, shaded symbol—substrate breaking).

Araldite (described above) mainly depended on the wettability of the grafted layers.

References

1. Kolluri, O. S. In Handbook of Adhesive Technology; Pizzi, A., Mittal, K. L., Eds.; Marcel Dekker: New York, 1994; Chapter 3.
2. Chen, K.; Uyama, Y.; Ikada, Y. In Contact Angle, Wettability and Adhesion; Mittal, K. L., Ed.; VSP: Utrecht, 1993; p. 865.
3. Wittenbeck, P.; Wokaun, A. J Appl Polym Sci 1993, 50, 187.
4. Mercx, F. P. M. Polymer 1994, 35, 2098.
5. Tsuchida, M.; Osawa, Z. Colloid Polym Sci 1994, 272, 770.
6. Hirasawa, H.; Ishimoto, R. J Adhesion Soc Jpn 1982, 18, 247 (in Japanese).
7. Yasuda, T.; Yoshida, K.; Okuno, T. J Polym Sci Polym Phys 1988, 26, 2061.
8. Morra, M.; Occhiello, E.; Garbassi, F. Surf Interface Anal 1990, 16, 412.
9. Morra, M.; Occhiello, E.; Marola, R.; Garbasi, F.; Humphrey, P.; Johnson, D. J Colloid Interface Sci 1990, 137, 11.

10. Yamada, K.; Kimura, T.; Tsutaya, H.; Hirata, M. *J Appl Polym Sci* 1992, 44, 993.
11. Yamada, K.; Tsutaya, H.; Tatekawa, S.; Hirata, M. *J Appl Polym Sci* 1992, 46, 1065.
12. Yamada, K.; Hayashi, K.; Sakasegawa, K.; Onodera, H.; Hirata, M. *Nippon Kagaku Kaishi (J Chem Soc Jpn Chem Ind Chem)* 1994, 1994, 427 (in Japanese).
13. Yamada, K.; Ebihara, T.; Gondo, T.; Sakasegawa, K.; Hirata, M. *J Appl Polym Sci* 1996, 61, 1899.
14. Chen, K.-S.; Uyama, Y.; Ikada, Y. *Langmuir* 1994, 10, 1319.
15. Yamada, K.; Isoda, J.; Ebihara, T.; Hirata, M. In *Interfacial Aspects of Multicomponent Polymer Materials*; Sperling, L. H., Ed.; Plenum Press: New York, 1973.
16. Yamada, K.; Kimura, T.; Hirata, M. *J Photopolym Sci Technol* 1998, 11, 263.
17. Yamada, K.; Hirata, M. *Kagaku to Kogyo (Chem Chem Industry)* 1998, 51(1), 68 (in Japanese).
18. Bhowmik, S.; Ghosh, P. K.; Ray, S.; Barthwal, S. K. *J Adhesion Sci Technol* 1998, 12, 1181.
19. Kang, E. T.; Shi, J. L.; Neoh, K. G.; Tan, K. L.; Liaw, D. J. *J Polym Sci Polym Chem* 1998, 36, 3107.
20. Zhang, M. C.; Kang, E. T.; Tan, K. L. *Colloids Surf, A* 2001, 176, 139.
21. Brennan, A. B.; Arnold, J. J.; Zamora, M. P. *J Adhes Sci Technol* 1995, 9, 1031.
22. Brewis, D. M.; Mathieson, I.; Sutherland, I.; Cayless, R. A. *J Adhes* 1993, 41, 113.
23. Morra, M.; Occhiello, E.; Garbassi, F. *J Adhes* 1994, 46, 39.
24. Zhang, J.; Cui, C. Q.; Lim, T. B.; Kang, E.-T.; Neoh, K. G. *J Adhes Sci Technol* 1998, 12, 1205.
25. Voyutskii, S. S.; Zamazii, V. M. *Rubber Chem Technol* 1957, 30, 544.
26. Voyutskii, S. S.; Shtarkh, B. V. *Rubber Chem Technol* 1957, 33, 548.
27. Voyutskii, S. S.; Vakula, V. L. *J Appl Polym Sci* 1963, 7, 475.
28. Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds. In *Encyclopedia of Polymer Science and Engineering*; Wiley: New York, 1986; Vol. 4, p. 482.
29. Billmeyer, Jr., E. W., Ed. *Textbook of Polymer Science*; Wiley: New York, 1984; Chapter 10.
30. Yamada, K.; Tatekawa, S.; Hirata, M. *J Colloid Interface Sci* 1994, 164, 144.
31. Yamada, K.; Sato, T.; Tatekawa, S.; Hirata, M. *Polym Gels Networks* 1994, 2, 323.
32. Clark, D. T.; Feast, W. J.; Kilcast, D.; Musgrave, W. K. R. *J Polym Sci Polym Chem* 1973, 11, 389.
33. Clark, D. T.; Thomas, H. R. *J Polym Sci Polym Chem* 1978, 16, 791.
34. Clark, D. T.; Feast, W. J. *J Macromol Sci Revs Macromol Chem* 1975, C12, 191.
35. Chapiro, A. *Pure Appl Chem* 1972, 30, 77.
36. Lawler, J. P.; Charlesby, A. *Radiat Phys Chem* 1980, 15, 595.