

Lamination of High-Density Polyethylene by Bulk Photografting and the Mechanism of Adhesion

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ABSTRACT: The photolamination of high-density polyethylene (HDPE) by bulk photografting is described, along with a discussion of the adhesion mechanism. HDPE can be photolaminated very easily with a thin poly(acrylic acid) layer, photopolymerized from acrylic acid, with very strong adhesion obtained after a short time of UV irradiation; the adhesion failure mode is polyethylene breakage. Thicker HDPE sheets require longer irradiation times for strong adhesion. Methacrylic acid or hydroxyethyl methacrylate provides no adhesion of HDPE at all after irradiation. When glycidyl acrylate is used alone between HDPE sheets, the

peel strength of the photolaminated polyethylene is only approximately 320 N/m, but when glycidyl acrylate or hydroxyethyl methacrylate is grafted with acrylic acid, very good adhesion can be obtained. It is proposed that stronger adhesion is produced by a less branched grafted chain structure, which permits much more chain entanglement. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1097–1106, 2005

Key words: adhesion; polyethylene (PE); graft copolymers; hydrophilic polymers

INTRODUCTION

Yang and Rånby^{1–9} developed a method for laminating polymer films with a bulk (no solvent) surface photografting process, in which a thin layer of an acrylic monomer containing a dissolved photoinitiator is sandwiched between two thin films and then photopolymerized. Most importantly, photolamination occurs simultaneously during the photografting process and results in good adhesion of the two films. Kang and coworkers^{10,11} reported the photolamination of ozone-pretreated low-density polyethylene (LDPE) films via a novel technique of UV-induced graft copolymerization with acrylamide or acrylic acid (AA) under atmospheric conditions and in the complete absence of an added initiator or oxygen scavenger.

This photolamination technique can be applied to a wide variety of plastic films and produces laminates of high mechanical strength and high and selective barrier properties toward different gases and vapors. However, this method has an unavoidable drawback, in that it can only be used for thin and UV-transparent films.

Most of the work on photolamination by bulk photografting has been done with LDPE films, for which

enough adhesion can be obtained that sample strips are broken in a peel test rather than the interface failing. In this situation, the reported apparent peel strength at break for a laminate in which both films were 0.188-mm-thick films of LDPE was 1050 N/m.⁸ High-density polyethylene (HDPE) has a surface that is more difficult to graft than that of LDPE because of the linear chain structure of HDPE and its higher degree of crystallinity. The reported apparent peel strength at break for a laminate of two HDPE films 0.04 mm thick was only 290 N/m.³ In the work described here, our efforts were focused on the photolamination of HDPE, and thicker HDPE sheets were used.

In previous work, the photolamination of polymeric films was normally performed with a single monomer. The monomers were usually water-soluble. The most effective monomer was found to be AA, and so it has been most studied. It is likely that the adhesion of polymeric films photolaminated with a water-soluble monomer will become weaker when the films are soaked in water for some time or even when they are held in a humid atmosphere for a long time. Therefore, we studied the use of a mixture of water-soluble and water-insoluble monomers to form less water-soluble grafted copolymers and hence improve the water resistance of photolaminated films.

Yang and Rånby³ suggested that the lamination method involves the formation of hyperbranched graft macromolecules and a crosslinked macromolecular network obtained by the addition of multifunc-

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tional monomers. In this article, we present some work that was designed to determine the true adhesion mechanism of photolamination by bulk photografting.

EXPERIMENTAL

Materials

HDPE was supplied by Nova Chemicals, Ltd. (Sania, Canada); its melt flow index was 0.39 g/10 min, and its density was 0.949 g/cm³. The HDPE film was cut into 2 cm × 10 cm rectangular samples (≈0.5 mm thick, unless otherwise noted) and then was subjected to Soxhlet extraction with acetone for 24 h to remove impurities and additives before use.

Vinyl monomers such as AA, methacrylic acid (MAA), glycidyl acrylate (GA), glycidyl methacrylate (GMA), and hydroxyethyl methacrylate (HEMA) were used without purification; all were analytical-reagent (AR) grade. The photoinitiator benzophenone (BP; chemically pure) was used as received. GA was obtained from Polysciences, Inc. (Warrington, PA); the other chemicals were obtained from Sigma-Aldrich (Milwaukee, WI).

Uv equipment

The UV system with a shutter assembly was supplied by Amba Lamps Australasia Proprietary, Ltd. (Sydney, Australia). The input power of the UV medium-pressure mercury lamp was 2 kW. No filter was used to isolate UV light. The output UV intensity was measured with a UV Power Puck from Electronic Instrumentation and Technology, Inc. (Sterling, VA). The intensities in the ultraviolet A, B and C bands, defined as UVA (320–390 nm), UVB (280–320 nm), and UVC (250–280 nm) were simultaneously measured.

Grafting procedure

The assembly for the photolamination experiments was similar to that used by Yang and Rånby.¹ The monomer, containing 2 wt % BP, was coated onto one HDPE sample, and then the other HDPE film sample was put on top. The sandwich was then pressed with suitable pressure to spread the monomer solution into an even and thin liquid layer. The extra solution squeezed out was removed with a tissue. The weights of the two HDPE samples before and after the application of the solution were measured. The polyethylene (PE) samples were put at a fixed position 4 cm below the focal point of the UV lamp, at which the UVC intensity was 0.024 W/cm². The extent of photopolymerization was altered by changes in the irradiation time. The grafting temperature was not strictly controlled.

After the grafting, the samples were dried in 50°C oven for 48 h for the removal of unreacted monomer, and then their weights were measured. The samples used for the study of the polymerization reaction were washed with 80°C water in an ultrasonic bath for 2 h, Soxhlet-extracted with acetone for at least 48 h for the removal of homopolymer, and then dried at 50°C for 24 h. The weights of the samples after extraction were measured also.

The polymerization conversion of the monomer to the polymer was defined as W_p/W_0 , the grafting conversion was defined as W_g/W_0 , and the grafting efficiency was defined as W_g/W_p , where W_0 is the weight of the monomer and initiator, W_p is the weight of the polymer formed (including the homopolymer), and W_g is the weight of the grafted polymer.

Peel test

The peel strength (N/m) was measured at room temperature with a 180° T peel test with an Instron (Buckinghamshire, England) 4302 instrument at a crosshead speed of 50 mm/min, unless otherwise noted. The average force after the initial peak load was taken as the peel strength.

Rejoining of the samples after the washing

In some cases (discussed later), the laminated samples could be separated under essentially zero force after being soaked in 80°C water and extracted in acetone. The grafted HDPE sheets obtained in this way were immersed in distilled water at 80°C for 24 h, and then two pieces of samples that had originally been irradiated with UV light at the same time were put together with their grafted surfaces facing each other and then heat-pressed under 5000 psi at 60°C for 24 h.

Rejoining of the samples after the peel tests

Several samples after peel testing at a low crosshead speed of 0.5 or 1 mm/min were immersed in distilled water at 80°C for 24 h and then heat-pressed under 5000 psi at 60°C for 24 h.

Water absorption of the grafted samples

The grafted HDPE sheets after washing were immersed in distilled water at 50°C for 48 h to obtain equilibrium of water absorptivity. After the treatment, excess water on the sheet surfaces was wiped with a tissue, and then the weight of the grafted HDPE sheets was measured.

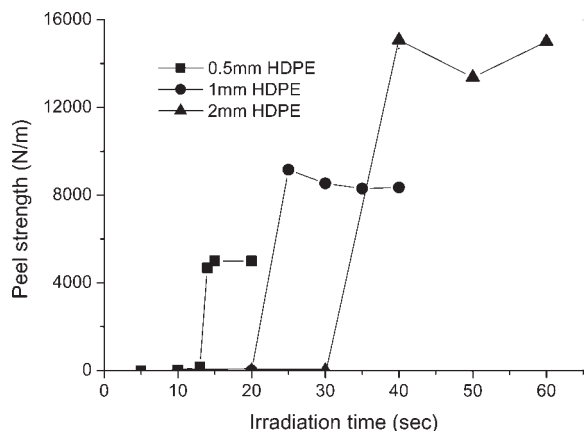


Figure 1 Variation of the peel strength of PE samples photolaminated with AA (2% BP) with the irradiation time.

Microscopy study of the samples after the peel tests

After the peel tests, the surfaces of the peeled samples were examined with a BH2-MJLT optical microscope from Olympus Optical Co., Ltd. (Tokyo, Japan).

RESULTS AND DISCUSSION

Photolamination

Photolamination by AA and MAA

The results of the peel tests of HDPE samples photolaminated with AA (2% BP) are shown in Figure 1. HDPE sheets of different thicknesses were used.

The HDPE sheets were very easy to photolaminate by the bulk photografting of AA, especially the thin sheets. The constant values of the peel strength are in fact apparent peel strengths obtained when the HDPE samples broke. Not surprisingly, these values, which are really just values of the force per unit of width needed to break the samples, vary approximately linearly with the sample thickness. The thicker sheets needed a longer irradiation time to obtain high adhesion strength because of the absorbency of UV light by the top PE sheet that the UV had to traverse before initiating both polymerization and grafting in the monomer.

The previously reported³ apparent peel strength at break of a polymer strip for an HDPE/HDPE (0.04-mm-thick film) laminate was 290 N/m. In our experiments, much higher apparent peel strengths at break were obtained because the strips were much thicker. For 0.5-mm HDPE sheets, the breaking force per width was approximately 5000 N/m; for 1-mm HDPE sheets, it was 9000 N/m; and for 2-mm HDPE sheets, it was approximately 15,000 N/m. A higher apparent peel strength at break was expected for thicker HDPE sheets irradiated for a longer time. These results imply

that very strong adhesion can be obtained by photolamination.

There was almost no intermediate between zero adhesion and maximum adhesion. The peel strength of the 0.5-mm sheet jumped from zero to the maximum in times less than the radiation time intervals employed, in this case less than 1 s. A visual examination of samples that were separated immediately after irradiation suggested that there was a small amount of unreacted liquid AA monomer left on the HDPE sheets that had been irradiated for 13 s. However, for the HDPE sheets irradiated for 14 s, no visible liquid monomer could be found. Presumably by 14 s, enough polymer had formed to adsorb all the monomer. This result suggested that the dramatic change in adhesion came from the interpenetration of grafted layers during polymerization. The grafted layer was glassy after drying, and so when fully entangled it had a higher failure stress than HDPE. The sudden transition probably occurred when the failure stress of the dried glass layer became greater than the yield stress of HDPE, and this caused a change in the failure mechanism.

The changes in the polymerization conversion, grafting conversion, and grafting efficiency with the irradiation time are shown in Figure 2 for both AA and MAA. The polymerization conversion and grafting conversion of both monomers increased with the irradiation time, but the latter lagged the former; therefore, initially the grafting efficiency was low, and it also increased with the irradiation time. After 30 s of irradiation, the polymerization conversion was high, nearly 90% for AA and over 70% for MAA.

A surprising finding was how low the polymerization conversion (28%) and grafting conversion (12%) were after 15 s of irradiation when the photolaminated samples had very strong adhesion. Experiments described later demonstrated that there was no crosslinking between the chains grafted on both sides. Hence, the only possible reason for the strong adhesion was the entanglement of the grafted chains. Of course, strong adhesion could not be obtained if the photolaminated samples were tested immediately after irradiation because of the plasticizing effect of the large amount of unreacted monomers and low-molecular-weight homopolymer. Good adhesion could be obtained only after the evaporation of these small molecules.

Although MAA has a chemical structure very similar to that of AA, HDPE sheets sandwiched with MAA and irradiated with UV light showed almost no adhesion. After UV irradiation, a thin grafted layer was formed on the surface of the HDPE sheet. The polymerization conversion of MAA was lower than that of AA at the same irradiation time; however, with a longer irradiation time, the polymerization conversion of MAA could reach a very high value. The

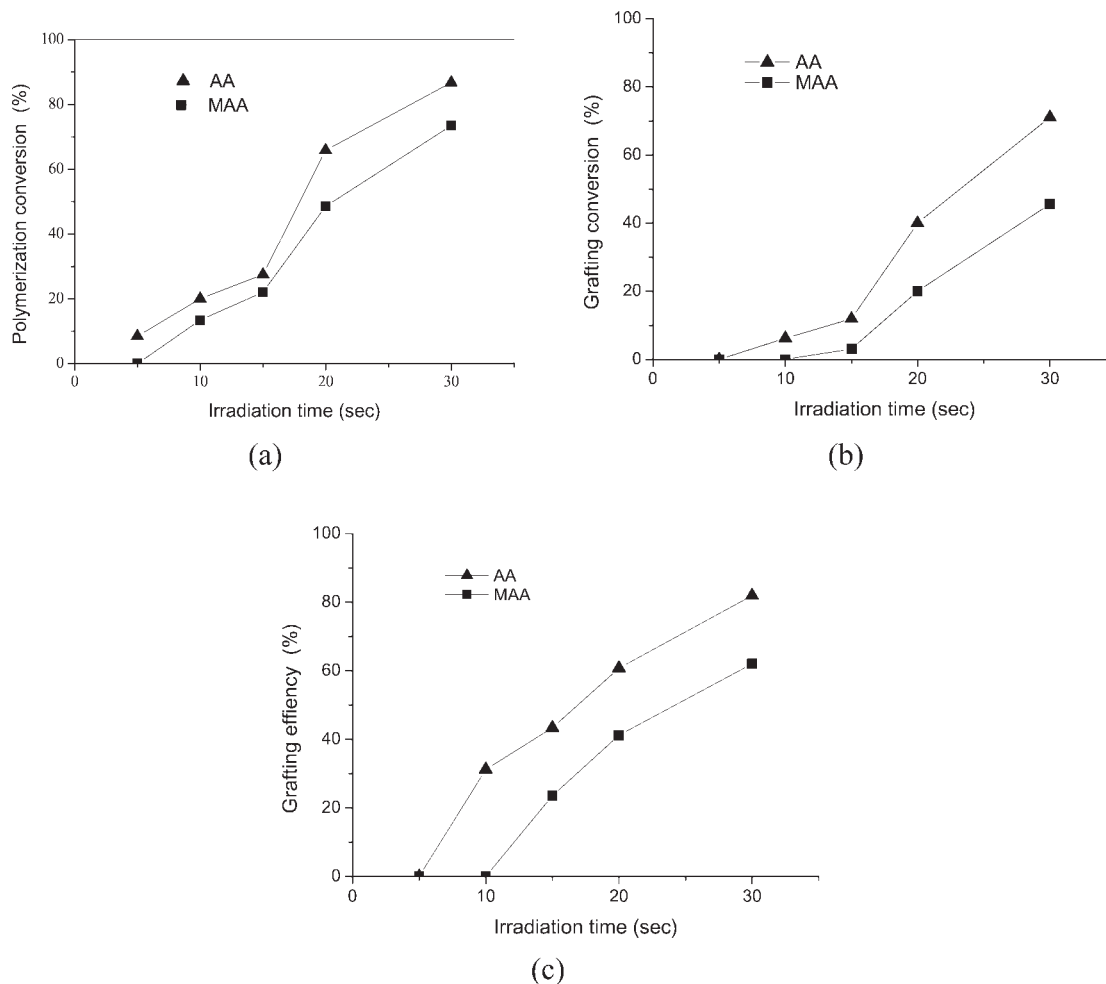


Figure 2 Changes in (a) the polymerization conversion, (b) the grafting conversion, and (c) the grafting efficiency of AA and MAA with the irradiation time.

difference in the grafting conversions of AA and MAA was more significant at longer irradiation times. Even after 30 s of irradiation, the grafting conversion of MAA was only about 45%.

The change in the grafting efficiency with the irradiation time was different from that observed by Yang and Rånby.² They reported that the grafting efficiency of AA onto LDPE at 50°C was between 60 and 80%. However, as shown in Figure 2(c), the grafting efficiency increased with the irradiation time for both AA and MAA. Because the temperature was not strictly controlled in our experiments, there was a temperature increase during irradiation. This was probably one reason for the increasing grafting efficiency. Another possible reason was the branching of grafted chains. Once there were grafted chains, branching could occur very easily because of the existence of tertiary and secondary hydrogen atoms on the grafted poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA). With the increase in the number of grafted chains, there were more and more tertiary and secondary hydrogen atoms that could be abstracted by the

photoinitiator and therefore initiate the branching grafting.

Because of the absence of tertiary hydrogen atoms on the grafted PMAA chains, branching did not occur as easily as it did on the grafted PAA chains. Possibly this was the reason for the difference in the grafting conversion with the irradiation time for AA and MAA.

As discussed previously, very good adhesion was obtained for the HDPE samples photolaminated with AA even when the polymerization conversion and grafting conversion were very low. However, there was no adhesion at all for the samples photolaminated with MAA, even when the polymerization conversion and grafting conversion were rather high. Thus, the grafted amount was not an important parameter controlling adhesion, although of course some grafted material was required to impart adhesion.

Adhesion was mainly influenced by the structure of the grafted chains. The thickness of the liquid layer sandwiched between two HDPE sheets was between 10 and 30 μm . Thus, it was impossible to obtain linear

grafted chains with the molecular weight range of approximately 10^6 – 10^7 to connect the two HDPE surfaces. One possible way of connecting the two surfaces was branching on grafted chains. With an increase in the branching and the propagation of the branched grafted chains, it became possible for the branched grafted chains on both surfaces to mix with each other. Yang and Rånby³ suggested that a branched tree structure rooted onto the polymer substrate and a cured (crosslinked) network structure rooted onto the two different polymer substrates were the lamination mechanism. As discussed before, even at very low polymerization and grafting conversions, the adhesion of HDPE sheets photolaminated with AA was very strong. As shown later, crosslinking did not occur in our system. Thus, there was only one possible mechanism that gave the adhesion, the entanglement of the branched tree structure that grew from each surface. However, for both AA and MAA, a branched structure could be formed during photolamination because of the presence of tertiary and secondary hydrogen atoms on grafted PAA (tertiary and secondary H) and PMAA (secondary H) chains. Therefore, the branched tree structure model is not sufficient to explain the strong adhesion of AA-grafted HDPE sheets, as there was no adhesion for MAA-grafted sheets. The length of the chains between branch points was possibly the important factor that made the difference between AA and MAA. Because the reactivity of AA was higher than that of MAA, the chain lengths between branch points for grafted PAA chains were longer those for PMAA chains. The less densely packed and more swellable grafted chains were more able to entangle with one another. Therefore, better adhesion could be obtained. The strong adhesion of HDPE sheets photolaminated with AA at very low polymerization and grafting conversions suggested that, even at low conversions, there were sufficiently long grafted chains to entangle with the homopolymer or the grafted chains from the opposite HDPE surface.

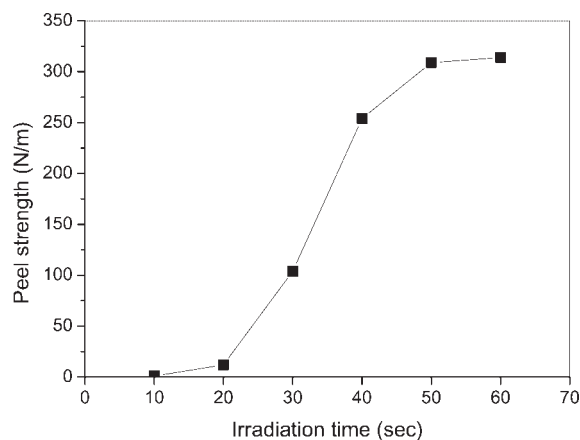


Figure 3 Peel strength of PE samples photolaminated with GA (2% BP) with the irradiation time.

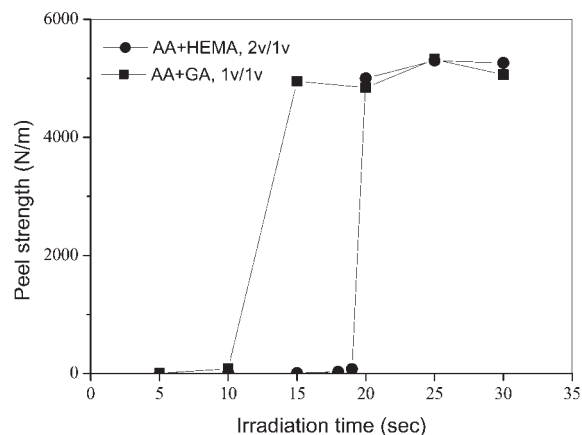


Figure 4 Variation of the peel strength of PE samples photolaminated with AA–GA (1/1 v/v, 2% BP) and AA–HEMA (2/1 v/v, 2% BP) with the irradiation time.

When AA (2% BP) was used, a lightly branched but long grafted chain structure could be expected. First, a high AA concentration was beneficial to the growth of grafting chains. Second, the viscosity of the solution increased with the irradiation time, and so the termination of grafting chains became more difficult; for the same reason, the branching on grafted chains became more difficult.

The formation of this lightly branched structure is thought to be the main reason for the strong adhesion of PE samples photolaminated with AA (2% BP).

Photolamination by mixed monomers

Figure 3 shows the peel test results of PE sheets photolaminated with GA (2% BP). In clear distinction to the situation of HDPE samples photolaminated with AA, the peel strength of HDPE samples photolaminated with GA was very small, only about 320 N/m even after 60 s of irradiation. The peel strength initially increased with the irradiation time (after an induction period) till 50 s and then remained almost constant. Similarly to the case of MAA, there was very little adhesion for the HDPE sheets sandwiched with GMA and irradiated with UV light.

In contrast to the situation with pure GA, when GA was cogenerated together with AA onto HDPE sheets (50 vol % for each), the peel strength of photolaminated HDPE sheets could reach 5000 N/m (PE breaks) after a 15 s of irradiation, as shown in Figure 4. This result was similar to that obtained when AA was photolaminated alone. In a similar way, when HEMA was used alone, there was no adhesion at all. However, when it was photolaminated with AA, as shown in Figure 4, very good adhesion could be obtained, although it took a little longer.

We found that the HDPE sheets photolaminated with a water-soluble monomer (AA) could be pulled

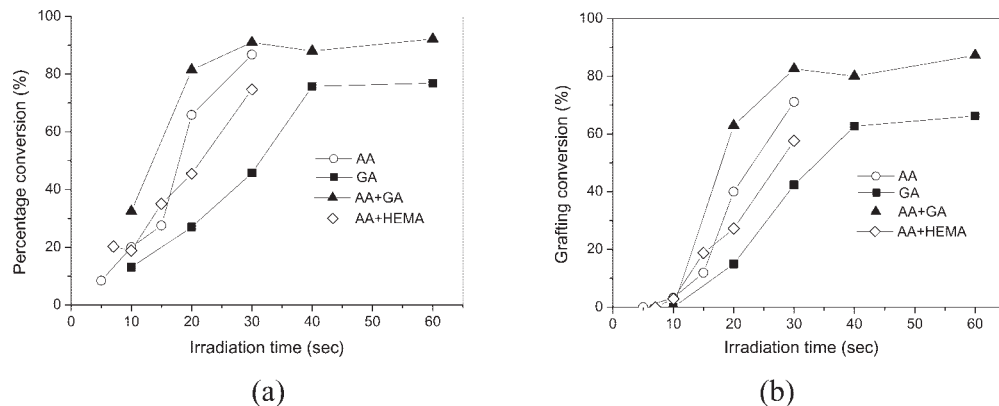


Figure 5 (a) Polymerization and (b) grafting conversion of AA, GA, AA-GA (1/1 v/v), and AA-HEMA (2/1 v/v).

apart when soaked in water or even just left in a humid atmosphere for some weeks. We, therefore, decided to determine if a combination of a water-insoluble monomer and a water-soluble one could improve the water resistance of the photolaminated HDPE sheets.

Figure 5 shows the polymerization conversion and grafting conversion of AA, GA, AA-GA, and AA-HEMA in photolamination.

The polymerization reactivity of GA was lower than that of AA, perhaps because of the steric hindrance of a large pendent group. The lower reactivity made it easier for the propagating chain to be terminated by small free radicals before it became long. The existence of such short branches was probably the reason for the weak adhesion of PE samples photolaminated with GA.

When GA was copolymerized together with AA, the polymerization and grafting conversions were higher at the same irradiation time than those when either AA or GA was used separately. This is a very interesting result. Why did the combined monomers have higher reactivity than a single monomer? The explanation is probably as follows. First, GA is less polar than AA, so its concentration was higher at the HDPE surface, which it may have swelled. Therefore, the grafting could occur more easily. When the grafted chains were initiated, both AA and GA monomers could be added to the growing chains before they were terminated. Second, the GA monomer has a large pendent group, but AA does not. The pendent group in the GA structure sterically hinders the access of GA monomers to a growing GA-grafted chain, but no similar problem occurs for the attachment of an AA monomer to a growing GA-grafted chain or a GA monomer to a growing AA chain.

When only HEMA was used, there was almost no grafting. However, when HEMA was used together with AA, the polymerization and grafting conversions were slightly lower than those when only AA was grafted. This result can be explained similarly to the

case of AA-GA. However, because of the quite low grafting efficiency of HEMA, a longer irradiation time was required to reach a critical grafting conversion to photolaminate the HDPE samples.

Adhesion mechanism

The following tests were performed to further elucidate the adhesion mechanism and to test the hypothesis that a less branched chain structure was required for good adhesion.

Peel strength of the laminated samples after washing with water and acetone

The HDPE samples laminated with AA (20 s of irradiation) no longer adhered after they were immersed in 80°C water in an ultrasonic bath for 2 h and then Soxhlet-extracted with acetone for 48 h. The HDPE samples laminated with AA-GA (30 s of irradiation) similarly lost adhesion. These results suggest that there was no significant crosslinking between the grafted chains on both sides. Thus, the adhesion between the two pieces of photolaminated HDPE samples was mainly due to the entanglement of grafted chains, which separated easily upon swelling, rather than covalent bonds formed by the crosslinking between the grafted chains attached to the two sides (forming a continuous network). Although swelling would reduce the adhesion for a network, it would not go to zero as failure would still require chain scission.

In contrast, the HDPE samples laminated with AA-GA (50 s of irradiation) still had very weak adhesion (60 N/m), even after long extraction (and swelling). This result shows there was some crosslinking between the grafted chains when the samples were irradiated for much longer times. However, the adhesion due to the crosslinking of grafted chains was very weak and could be ignored.

Water absorbency of the grafted samples

Figure 6 shows the water absorbency of PE samples grafted with different monomers. The samples grafted with AA had much higher water concentrations than others with the same amount of grafting. The water absorption of the samples grafted with AA (2% BP) was 120%, whereas that of the samples grafted with MAA (2% BP) was only about 21%, which was same as that observed for HDPE grafted by MAA in organic solvents.¹² We expected the degree of swelling of grafted chains to be controlled by their length, their grafting density, and their degree of branching. The higher the degree of branching was, the less they were able to swell. Hence, the high water absorption of the samples grafted with AA suggested the existence of long, lightly branched grafted chains.

When AA was cografted with a water-insoluble monomer (GA) or weakly water-soluble monomer (HEMA), the water absorption of the grafted samples was similar to that of the samples grafted with MAA and much lower than that of the samples grafted with only AA. This suggests that the combination of AA with a water-insoluble monomer could improve the water resistance of the photolamination. It was shown by the peel testing of samples soaked in water for a week that the adhesion of samples photolaminated with AA-GA was higher than that of samples photolaminated with AA.

Rejoining of the samples after the washing

Yamada and coworkers¹³⁻¹⁶ grafted hydrophilic monomers, such as MAA, AA, 2-dimethylaminoethyl-methacrylate, and methacrylamide, onto LDPE and HDPE. They then joined the samples, showing that the grafted chains in the water-swollen grafted layers could be entangled with one another through their self-diffusion when the two grafted polymer plates

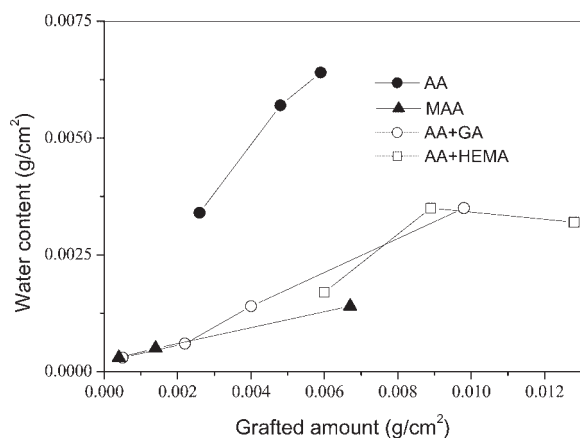


Figure 6 Water absorbency of PE samples grafted with different monomers.

TABLE I
Peel Strength of Rejoined PE Samples

Solution	Irradiation time (s)	Peel strength (N/m)
AA (2% BP)	15	>5000, PE broke
AA (2% BP)	20	>5000, PE broke
MAA (2% BP)	30	0

were forced into contact; this led to bond formation via heat pressing without any adhesives.

Some of the laminated and separated HDPE sheets were immersed in distilled water at 80°C for 24 h after they were washing. Two samples irradiated for the same time (specified in Table I) were rejoined by heat pressing under 5000 psi at 60°C for 24 h. Table I shows the peel test results of the samples after rejoining.

The HDPE sheets photolaminated with AA could be rejoined to produce excellent adhesion, perhaps as strong as that of the samples after the initial photolamination; the rejoined PE samples broke during peel tests. For the rejoined samples, the adhesion could only be attributed to the entanglement of the grafted chains.

For the samples photolaminated with MAA, the initial poor adhesion could have been caused by the presence of low-molecular-weight homopolymer, which could not evaporate during drying but still could act as a plasticizer. These results eliminated this possibility because there could be no homopolymer left after washing. One would expect that long, lightly branched grafted chains would give good adhesion after washing, so these results suggest the existence of a less branched but longer chain structure for the samples photolaminated with AA (2% BP) and a more hyperbranched structure with short chains for the samples photolaminated with MAA (2% BP).

Peel tests of the laminated samples at different crosshead speeds

The grafted layers, after drying, were expected to be in their glassy state. The glass-transition temperature of PAA was 103°C, and that of PMAA was over 200°C. Hence, the failure of these layers, if fully entangled or crosslinked, was expected to change very little with the testing (crosshead) rate. Strongly rate-dependent failure was only expected (1) if the coupling layer was marginally entangled (but glassy), so chain pullout was an important failure mechanism, or (2) if the layer was plasticized, so the glass-transition temperature was close to room temperature.

Peel test results for HDPE samples photolaminated with AA (20 s of irradiation) and AA-GA (50 s of irradiation) at different crosshead speeds are listed in Table II.

TABLE II
Peel Strength of PE Samples Tested at Different Crosshead Speeds

	Crosshead speed (mm/min)				
	50	20	5	1	0.5
AA, 20 s	PE broke	PE broke	PE breaks	4820	4240
AA-GA, 50 s	PE broke	PE broke	PE breaks	4720	1790

As shown in Table II, when the crosshead speed was 5 mm/min or greater, the HDPE itself broke rather than the joining layer. However, when the crosshead speed was 1 or 0.5 mm/min, the joining layer could be pulled apart without HDPE failure. The samples laminated with AA-GA (50 s of irradiation) were a little easier to pull apart than the samples laminated with AA (20 s of irradiation).

Because the tested samples had very strong adhesion, they were not suitable for a study of the effect of the crosshead speed on the peel strength. Therefore, samples laminated with AA-GA (30 s of irradiation) were used in the following tests. The peel strengths of samples immediately after irradiation, samples dried 2 days at room temperature, and samples dried 2 days in a 50°C oven were measured at different crosshead speeds.

As shown in Figure 7, the peel strength increased with the crosshead speed. For the samples tested immediately after irradiation, the peel strength was very low when the crosshead speed was low. The laminated samples could be pulled apart without the failure of HDPE itself even at a 20 mm/min crosshead speed. The samples dried 2 days at room temperature had peel strengths almost double those of the samples tested immediately after irradiation when the crosshead speed was low. At a 20 mm/min crosshead speed, HDPE itself broke instead of the adhesive fail-

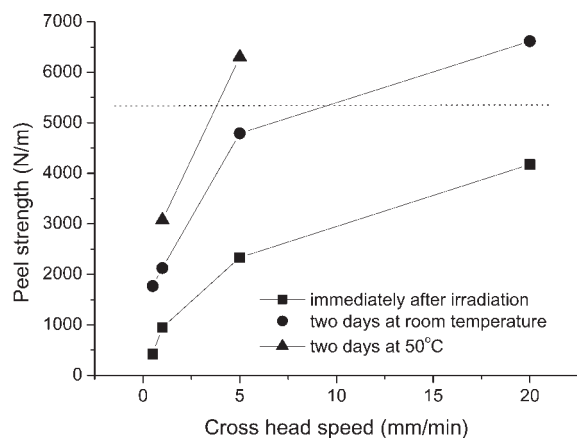


Figure 7 Peel strength of PE samples photolaminated with AA-GA (30 s of irradiation) at different crosshead speeds. The dotted line shows the minimum apparent peel strength for the failure of HDPE samples.

ing. For the samples dried at 50°C for 2 days, HDPE itself broke when the crosshead speed was just 5 mm/min.

The samples tested immediately after irradiation still contained some unreacted monomers and oligomers. The latter materials acted as plasticizers and reduced the glass-transition temperature of the entangled grafted layers; this permitted them to move easily. Therefore, the photolaminated HDPE sheets could be pulled apart easily, especially at low crosshead speeds. However, with an increase in the crosshead speed, the entangled grafted chains did not have enough time to move, and the peel strengths increased because of the breakage of entangled chains. When the samples were dried at room temperature or at a higher temperature for some time, the unreacted monomers and small oligomers evaporated. As a result of the reduction of the plasticizer content, the movement of the entangled chains became much more difficult. HDPE itself broke at a lower crosshead speed for the samples dried at 50°C for 2 days than for those dried at room temperature (both sets were dried for the same time) because the former material was less plasticized.

These results show that the adhesion can be attributed to the entanglement of the grafted chains.

Optical microscopy study

Figure 8 shows the significant differences in the optical microscopy images of surfaces of HDPE samples after peel tests at different crosshead speeds. These samples were photolaminated with AA-GA and tested immediately after irradiation.

The surface roughness of the tested samples increased with the crosshead speed. When the crosshead speed was 0.5 mm/min, the fracture surface of the sample was smooth and semitransparent. However, for the sample tested at 20 mm/min, the surface was rough and white.

As discussed before, when the samples were tested at lower crosshead speeds, there was enough time for the entangled chains to pull apart at a relatively low stress, and this caused low crack tip deformation. However, at higher crosshead speeds, the local stress for pulling out the entangled grafted chains was higher, and some may have broken; therefore, there was much more crack tip deformation.

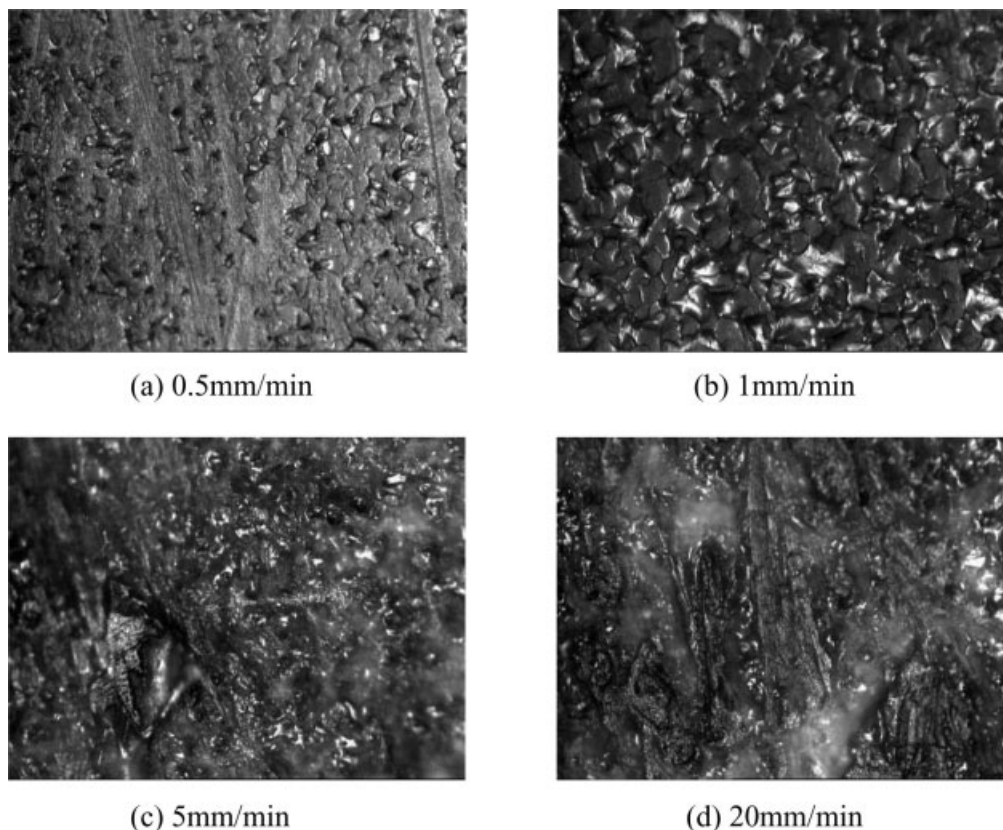


Figure 8 Optical microscopy images (magnification = $10\times$, image width = 0.534 mm) of the surfaces of HDPE samples photolaminated with AA-GA (tested immediately after 30 s of irradiation) after peel tests at different crosshead speeds: (a) 0.5, (b) 1, (c) 5, and (d) 20 mm/min.

When the HDPE samples photolaminated with AA (dried at 50°C for 2 days after irradiation) were tested at a 0.5 mm/min crosshead speed, the failure mode of the adhesion was probably mainly breakage of the grafted chains at the position at which they were entangled, with a fracture surface similar to that shown in Figure 8(d). After the peel tests, the samples were put in 80°C water for 24 h and then heat-pressed under 5000 psi for 24 h. They rejoined with very strong adhesion; the adhesion was strong enough that PE broke during the peel test at a 50 mm/min crosshead speed. The strong adhesion after rejoining indicated that the grafted chains were long enough to become entangled again.

The samples tested at a 1 mm/min crosshead speed behaved quite differently, as shown in Figure 9. Here the failure occurred by the breakage of the grafted chains at the position at which they attached to the PE surface. The dark part in Figure 9 is the grafted material; the bright part is the surface of PE. After the tests, these samples could not be rejoined.

All the test results show that the mechanism of strong adhesion for the photolaminated HDPE samples was entanglement between the chains in the grafted layers that grew from each PE surface. Entan-

glement requires a less branched chain microstructure.

CONCLUSIONS

We have demonstrated that photolamination with AA or mixtures of AA with other acrylics can be an effec-



Figure 9 Optical microscopy image (magnification = $5\times$, image width = 1.06 mm) of the surface of an HDPE sample photolaminated with AA (dried at 50°C for 2 days after 20 s of irradiation) after a peel test at a crosshead speed of 1 mm/min. The opposing surface looked similar.

tive and rapid way of joining thin HDPE sheets. Surprisingly, MAA is quite ineffective under similar circumstances, even though that its polymerization and grafting rates are only a little lower than those of AA. PE sheets joined by AA can be separated in water and then rejoined to give good adhesion, and this shows that the main adhesion mechanism is chain entanglement rather than crosslinking. We suggest that the main difference between AA and MAA is that the latter produces a grafted layer with a highly branched, perhaps hyperbranched, structure that cannot entangle, whereas the grafted layer of AA has a more lightly branched structure.

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