Surface Modification of Polyethylene by Radiation-Induced Grafting for Adhesive Bonding. IV. Improvement in Wet Peel Strength

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Synopsis

Adhesive joints of hydrolyzed methyl acrylate grafts, bonded with epoxy adhesives, yield extremely high peel strength (adherend failure) in dry conditions. However, when the joints are exposed to humid environments, the peel strength rapidly decreases with exposure time and then reaches a constant value (wet peel strength). Since the locus of failure changes from the adherend to the homopolymer layer with decreasing peel strength, the decrease is due to a decrease in mechanical strength of the homopolymer layer itself, which results from its swelling by water absorption. Many attempts to reduce the swelling of the homopolymer layer or to strengthen the swollen homopolymer layer were unsuccessful except (1) priming with epoxy solutions consisting of a base epoxy resin and organic solvents which can dissolve not only epoxy resins but also hydrolyzed poly(methyl acrylate) and (2) partial etching of the homopolymer layer by photo-oxidative degradation. All the results on the improvement in wet peel strength can be explained in terms of the penetration of epoxy resins into the homopolymer layer and subsequent curing of the penetrated epoxy resin.

INTRODUCTION

Vapor-phase mutual grafting of methyl acrylate (MA) onto polyethylene (PE) and subsequent hydrolysis produce a surface graft having high adhesive bondability to epoxy adhesives.[1,2] The grafted surface layer consists of an outer homopolymer layer (only of MA component) and an inner graft copolymer layer (both of PE and MA components).[2] The high stability of the stabilizer-containing homopolymer layer to solvent extraction, thermal-oxidative aging, and accelerated weathering indicates that the homopolymer layer is not only crosslinked but is also linked by chemical bonds to the PE and grafted chains in the contiguous copolymer layer.[2,3] The extremely high dry peel strength of the joints in dry conditions is due to the presence of the hydrolyzed homopolymer layer on the surface.[2,3] Since the homopolymer layer contains carboxyl groups, however, it can swell by the absorption of water when exposed to humid environments. This swelling should lead to a decrease in wet strength of the layer itself and thus a decrease in wet peel strength of the joints, whose failure occurs in the homopolymer layer. This paper is concerned with wet peel strength and its improvement.

EXPERIMENTAL

Polyethylene sheets, 2.0 mm thick, were surface grafted with MA by the vapor-phase mutual irradiation technique using γ-rays from a ^{60}Co source or using 4-MeV electrons from a linear electron accelerator. The details have been

described elsewhere.[3] The PE sheets used[3] were a low-density PE (designated LDPE), a carbon black-containing LDPE (Black LDPE), and a medium-density PE (MDPE). The grafted sheets were partially hydrolyzed under four different conditions: (1) 1.0N KOH methanol solution at 50°C, (2) 1.0N NaOH aqueous solution at 50°C, (3) 0.36N HCl acetone/water (5/1) solution at 60°C, and (4) 1.4N HCl acetone/water (5/1) solution at 50°C. Conditions (1) and (2) were followed by neutralization with a 1N HCl acetone/water (1/1) solution at 56°C. The hydrolyzed surface grafts were treated at 56°C consecutively with water, acetone/water (1/1), and acetone to extract soluble components. The hydrolyzed grafts (LDPE and Black LDPE) used in this work had 15 to 20 μm (γ-ray-in-duced graft) or 5 to 9 μm (electron-induced graft) of the isotropic layer thickness T_i and had 100 $\pm$ 10 μm (γ-ray-induced graft) or 20 $\pm$ 5 μm (electron-induced graft) of the anisotropic layer thickness T_a.[3] When hydrolyzed grafts were bonded with epoxy adhesives, the dry peel strength abruptly increases with T_i and reaches a maximum value (PE adherend failure, more than 30 kg/25 mm or 15 kg/cm) at T_i above 8 μm (γ-ray-induced graft) or 2 μm (electron-induced graft), at which the surface is covered with the homopolymer layer.[2,4] Unless otherwise specified, electron-induced Black LDPE grafts hydrolyzed for 2 or 4 hr under condition (1) were used as a standard sample. A typical surface morphology of the grafts is shown in Figure 1.

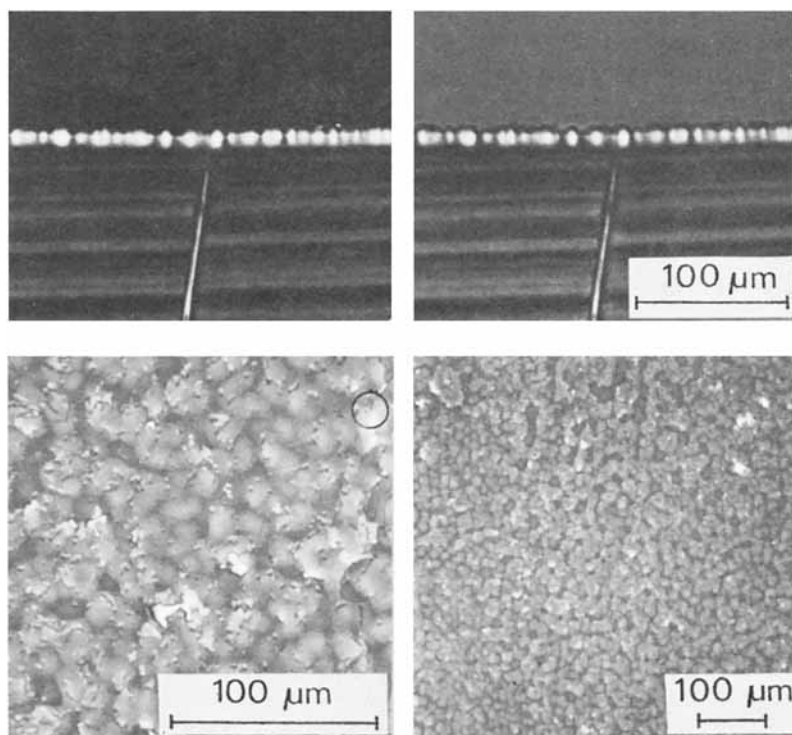Two hydrolyzed grafts were bonded to each other with epoxy adhesives to

Fig. 1. Optical micrographs (top) of a cross section and scanning electron micrographs (bottom) of a typical carbon black-containing low density PE sheet grafted by high energy electrons and partially hydrolyzed. An identical area in a cross section of the graft was photographed between crossed polarizers in the 45° position of the ungrafted PE part (left) and at 85° angle between polarizer and analyzer in the 45° position (right).

prepare a T-peel specimen, consisting of a graft–epoxy–graft "sandwich." Two different formulations of epoxy resins were used: (1) Cemedine No. 1500 (epoxy/polyamide = 10/9, Cemedine Co. Ltd., Tokyo, Japan, designated Adhesive 20) and (2) Epicote 828/Epicote 871/Epicure 103 = 50/50/45 (Shell Chemical, designated Adhesive 20). Adhesive 20 has a higher viscosity and curing rate than Adhesive 10. The assembly was lightly weighted (0.15 kg/cm^2), and the adhesives were allowed to cure at 60°C for 4 hr (Adhesive 20) or for three days (Adhesive 10). Unless otherwise specified, Adhesive 10 was used. After the T-peel specimens were conditioned at 50% R.H. at 23°C, the dry T-peel strength (10 or 25 mm width) was measured at a cross-head speed of 10 cm/min according to ASTM D1876-61T. The wet T-peel strength (10 mm width) was measured at 23°C immediately after immersion in distilled water at 60°C for 264 hr. The average, maximum, and minimum peeling loads were determined from the autographic curve for the first 5 cm of peeling after the initial peaks.

RESULTS AND DISCUSSION

Wet Peel Strength

Figure 2 shows the peel strength of γ-ray-induced graft joints measured at 23°C immediately after exposure to humid environments. When the joints are immersed in distilled water at 60°C, the peel strength rapidly decreases with immersion time and then reaches a constant value in 250 hr. The long-term exposure to distilled water at 22°C or to a humidity of 100% R.H. at 22°C gives a constant peel strength similar to that after water immersion at 60°C. Therefore, the constant value seems to indicate a wet peel strength of the adhesive joint assemblies whose insides have been saturated with water. In addition, electron-induced grafts, having T_i values of more than 5 μm, gave wet peel strengths (0.6–3.0 kg/cm) similar to that of γ-ray-induced grafts. In this work, accordingly, the peel strength after immersion in distilled water at 60°C for 264 hr is called
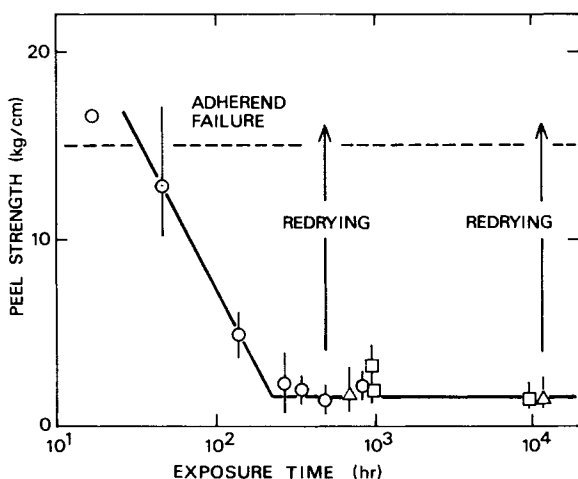

Fig. 2. Changes in peel strength with exposure to humid environments. The joints of γ-ray-induced grafts were exposed to 100% R.H. at 22°C (□), to distilled water at 22°C (△), and to distilled water at 60°C (○).

the wet peel strength, whereas the initial peel strength before water immersion is called the dry peel strength.

The carboxyl-containing homopolymer layer, which consists of hydrolyzed crosslinked PMA, should behave as a polyelectrolyte hydrogel in aqueous solutions, as well as poly(acrylic acid) and poly(methacrylic acid) homopolymer hydrogels, which expand with ionization or dissociation of the carboxyl groups. Figure 3 shows a typical expansion–shrink behavior of the grafted layer, which is immersed in aqueous solutions of $0.1N$ HCl (pH 1) and $0.1N$ NaOH (pH 14). The isotropic and anisotropic layer thicknesses (T_i and T_a) in $0.1N$ NaOH were 4.5 and 1.5 times those in $0.1N$ HCl, respectively. A similar expansion–shrink behavior is observed in the epoxy–graft interphase of the joints (Fig. 4). The T_i and T_a values in $0.1N$ NaOH were 3.1 and 1.3 times those in $0.1N$ HCl, respectively. Apparently, the isotropic or homopolymer layer swells or expands significantly with increasing pH or with ionization of the carboxyl groups even when bonded with epoxy adhesives. This swelling should lead to a decrease in mechanical strength of the homopolymer layer itself and thus a decrease in wet peel strength, where bond failure occurs in the layer. Figure 5 shows a typical change in wet peel strength with pH. The wet peel strength decreases with increasing pH and becomes constant at pH values of more than 7. This decrease in wet peel strength corresponds to the increase[5] in viscosity of dilute aqueous solutions of poly(methacrylic acid) and poly(acrylic acid) with increasing pH
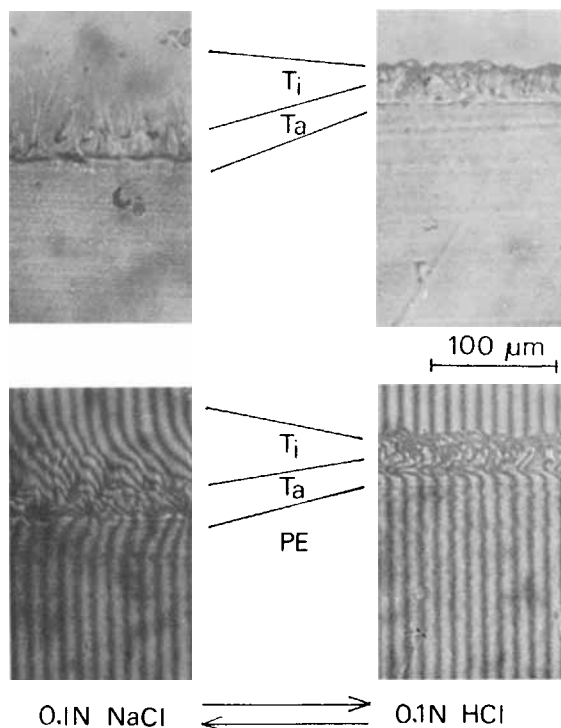

Fig. 3. Typical expansion–shrink beahvior of grafted surface layers. A cross section of γ-ray-induced MDPE grafts was immersed in a $0.1N$ NaOH (left) or a $0.1N$ HCl (right) aqueous solution and then photographed under an unpolarized light (top) and under an interference microscope (bottom).
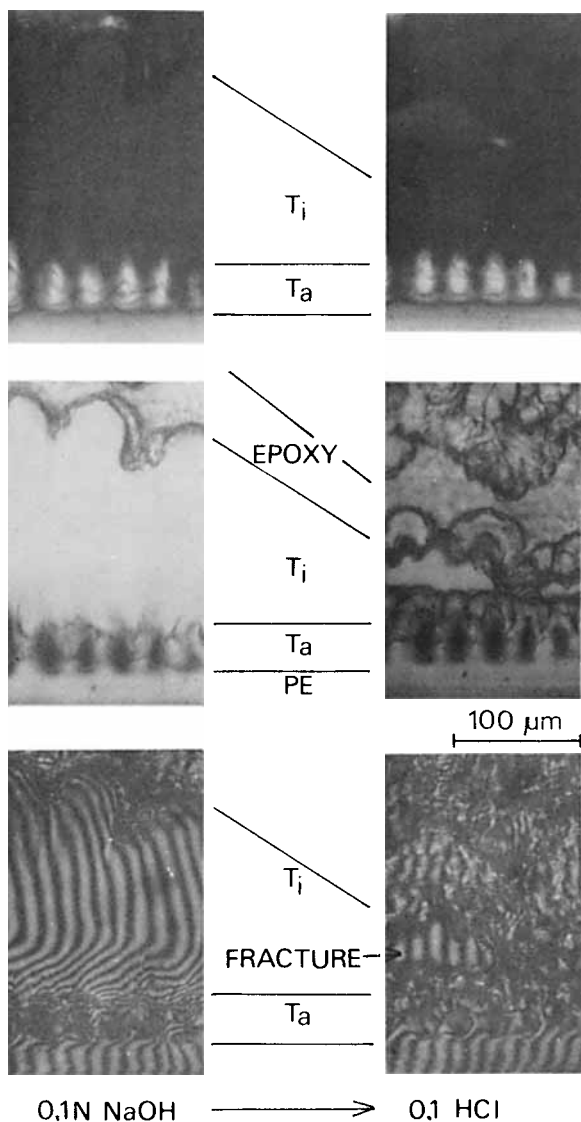
Fig. 4. Typical expansion–shrink behavior of adhesive–graft interphases. A cross section of the joints of γ-ray-induced MDPE grafts was immersed in a $0.1N$ NaOH (left) or a $0.1N$ HCl (right) solution and then photographed at 75° angle between polarizer and analyzer in the 45° position of the ungrafted PE part (top), at 0° angle between polarizer and analyzer in the 45° position (middle), and under an interference microscope (bottom).

or with neutralization of the carboxyl groups, whose increase indicates expansion of the polymer molecules. Therefore, the low wet peel strength in alkaline solutions reflects a low mechanical strength of the homopolymer layer itself, which results from expansion of the layer with increasing neutralization of the carboxyl groups.

Microscopic observations of fractured γ-ray-induced graft joints indicate that the bond failure in wet conditions occurs within the homopolymer layer near the epoxy–homopolymer interface rather than at the interface (e.g., top of Fig. 6). In addition, both sides of the fractured surfaces showed a similar fracture to-
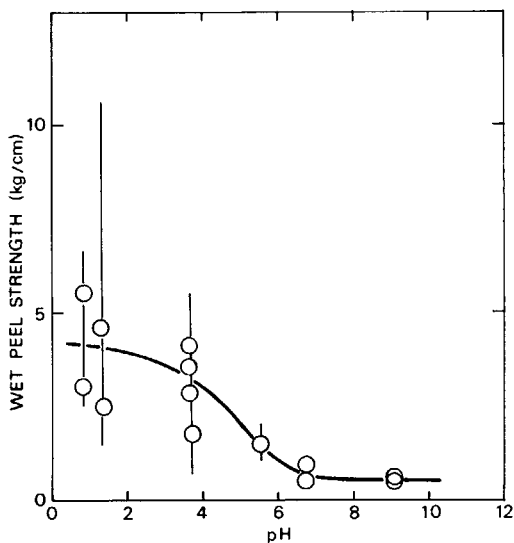
Fig. 5. Wet peel strength of joints immersed in buffer solutions of various pH.

pography (bottom of Fig. 6) and the same overall ESCA spectrum as that[6] of the hydrolyzed PMA homopolymer. Electron-induced grafts, having T_i values of more than 5 μm, gave results similar to those in γ-ray-induced grafts having T_i
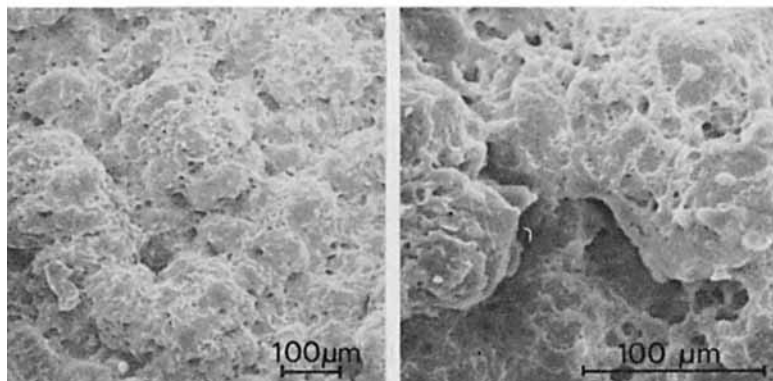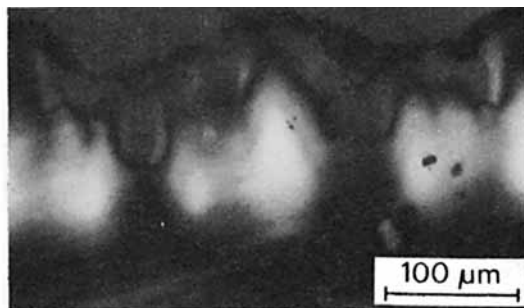

Fig. 6. Optical micrograph of a cross section (top) and scanning electron micrographs (bottom) of fractured wet joints of γ-ray-induced Black LDPE grafts. The average wet peel strength was 1.3 kg/cm. A cross section of the fractured wet joints was photographed at 85° angle between polarizer and analyzer in the 45° position of the ungrafted PE (top). The black region on the surface shows a deposited gold layer.

values of 15–20 μm.   On the other hand, electron-induced grafts, having thinner isotropic layers on T_i values of less than 4 μm, yielded a wide scatter in wet peel strength (0.7–5.2 kg/cm).   Microscopic observations of the fractured joints show that failure occurs in the adhesive, the inner copolymer layer, and the unmodified PE part (i.e., a mixed mode failure) when accompanied by high wet peel strength of approximately 5 kg/cm (Figs. 7 and 8), whereas failure occurs in the homo-polymer layer when accompanied by low peel strength of less than 3 kg/cm.   All the results on wet joints indicate that the locus of failure changes from the PE adherend to the homopolymer layer with decreasing peel strength in humid environments.   Therefore, it is concluded that the decreasing peel strength is due to a decrease in mechanical strength of the homopolymer layer itself, which results from its swelling by water absorption.   This conclusion is also supported by the following results.   Redrying of the joints saturated with water returned the reduced peel strength to the initial high peel strength (Fig. 2).   The exposure of the joints to dry–wet cycles did not result in a decrease in dry and wet peel strengths.

When bond failure occurs in the homopolymer layer, the wet peel strength reflects the wet mechanical strength of the homopolymer layer itself.   Thus, the improvement in wet peel strength requires a decrease in swelling degree of the homopolymer layer or an increase in wet mechanical strength of the layer.   Many attempts to improve the peel strength were unsuccessful except the following results.   The unsuccessful attempts include crosslinking of the grafted layer by high-energy electron irradiations and by bivalent cations (e.g., Ca^{2+} and Ba^{2+}).
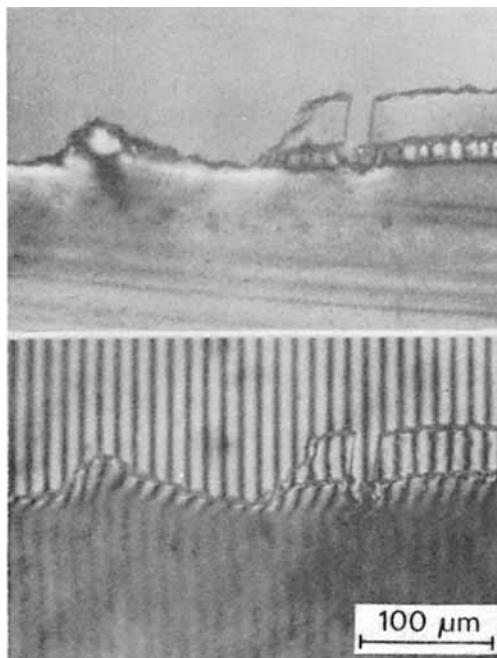

Fig. 7. Optical micrograph of a cross section of fractured wet joints of electron-induced Black LDPE grafts.   The average wet peel strength was 5 kg/cm.   A cross section of the fractured wet joints was photographed at an 85° angle between polarizer and analyzer in the 45° position of the ungrafted PE part (top) and under an interference microscope (bottom).
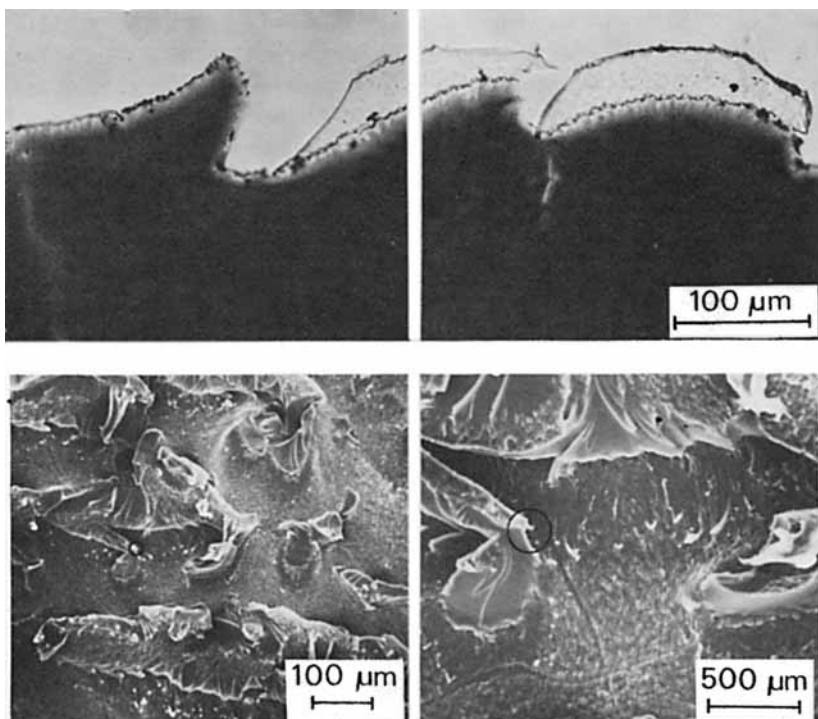
Fig. 8. Optical micrographs (top) of a cross section and scanning electron micrographs (bottom) of the same fractured joints as in Fig. 7.   A cross section of the joints was photographed under an unpolarized light (top).

Priming with Epoxy Solutions

As shown in Figure 4, the immersion of the graft joints in aqueous solutions can cause an appreciable swelling of the isotropic or homopolymer layer but little swelling of the inner anisotropic copolymer layer.   Accordingly, it is convenient to imagine that the grafted surface layer consists of a swelling and a nonswelling layer (i.e., a low wet-strength and a high wet-strength layer), although it is uncertain whether or not the boundary between the two layers coincides with that between the isotropic and anisotropic layers.   The surface layer has a macroscopically rough topography (Fig. 1) and probably a porous structure, which results from the growth process of the homopolymer layer (i.e., secondary grafting from the PMA chains) and the subsequent partial removal of the surface homopolymer during hydrolysis.[2]   Therefore, some adhesives may penetrate into the layer.   If an epoxy adhesive is allowed to penetrate up to the boundary and to cure, the water-resistant cured epoxy can protect the swelling layer against the swelling by water absorption.   This protection or reinforcement may lead to an increase in wet peel strength.   There are two possible means for realizing this situation: (1) enhancement of the adhesive penetration and (2) thinning of the homopolymer or swelling layer.   This section describes the former results. The next section describes the latter.

In order to enhance the adhesive penetration, electron-induced grafts were impregnated or primed with epoxy solutions consisting of a basic epoxy resin and organic solvents, which can dissolve not only the epoxy resin but also hydrolyzed PMA homopolymer (and thus can swell the homopolymer layer). The epoxy solutions contained no curing agent to prevent curing during the application. The primed grafts were bonded with Adhesive 10 containing an amine curing agent. The results are summarized in Table I. The primers increased the wet peel strength of electron-induced grafts (adherend failure) but not that of γ-ray-induced grafts, which had a thicker isotropic layer (15–20 μm) than the electron-induced grafts (5–9 μm). This result can be explained as follows.

The improved wet peel strength of electron-induced grafts indicates reinforcement of the swelling layer, which otherwise becomes a weak boundary layer in wet conditions. The reinforcement requires penetration of the primer epoxy resin up to the boundary between swelling and nonswelling layers and subsequent curing of the penetrated epoxy. The penetration may require the existence of pores through which the epoxy can penetrate to the boundary or a swollen state of the layer through which the epoxy can diffuse. The curing may also require penetration of the curing agent (in the adhesive) into the penetrated primer epoxy. Further, the cured epoxy needs to be resistant to water. An unreinforced swelling layer would lead to unimproved wet peel strength because such a layer becomes a weak layer in the wet joint. The unimproved wet peel strength of γ-ray-induced grafts, having a thick isotropic layer, probably is the case.

Etching of Homopolymer Layer

The surface homopolymer layer is rapidly etched by photooxidative degradation.[3] To obtain a series of electron-induced grafts having different T_i values, a batch of electron-induced grafts, having T_i values of 5–9 μm, was exposed to an artificial weathering apparatus[3] and then partially hydrolyzed. Figures 9 and 10 give the wet peel strength and the amount of grafted monomer versus ultraviolet exposure time for two series of the grafts. It is seen that the wet peel strength increases (Fig. 9) and then decreases (Fig. 10) with exposure time or with decreasing grafted amount. The previous work[3] has shown that the de-

TABLE I
Improvement in Wet Peel Strength by Epoxy Primers

Primer[a]	Wet peel strength, kg/cm	
	γ-Ray-induced graft	Electron-induced graft
Unprimed	0.6–3.0	0.6–5.2
MEK/n-BA = 50/50	0.6–3.0	15–19[b]
Epicote 872/MEK/iso-PA = 13/44/43	0.6–3.0	20[b]
Epicote 872/M-iso-BK/n-BA = 26/37/37	0.6–3.0	22[b]
Epicote 872/M-iso-BK/iso-PA = 26/37/37	0.6–3.0	22[b]

[a] Epicote 872 = a diglycidyl ether of bisphenol A–dimer acid adduct (Shell Chemical); MEK = methyl ethyl ketone; n-BA = n-butyl alcohol; iso-PA = isopropyl alcohol; M-iso-BK = methyl isobutyl ketone.
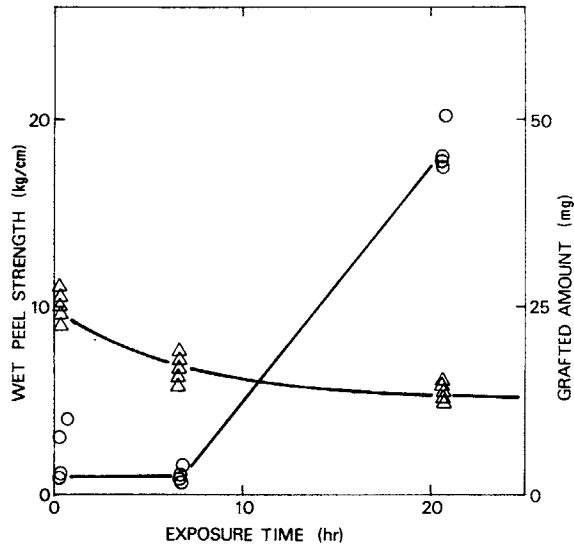
[b] PE adherend failure.

Fig. 9. Wet peel strength and grafted amount vs. ultraviolet exposure time for a batch of electron-induced Black LDPE grafts. The grafts were exposed to an artificial weathering apparatus, hydrolyzed, and then bonded: (O) wet peel strength; (△) grafted amount.

crease in grafted amount reflects the degradative removal of the homopolymer layer[3] and that the complete removal of the homopolymer layer leads to the loss in dry peel strength (thus also in wet peel strength). Therefore, the increase in wet peel strength is probably due to a decrease in the homopolymer or swelling layer thickness, and the subsequent decrease in the wet peel strength is due to
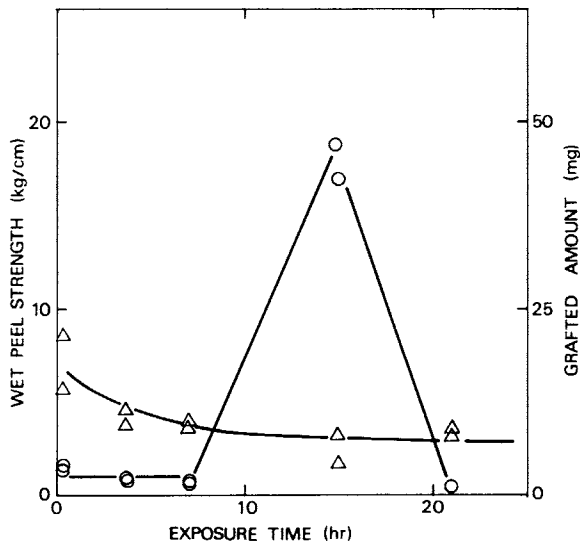

Fig. 10. Wet peel strength and grafted amount vs. ultraviolet exposure time for a batch of electron-induced Black LDPE grafts of a batch different from that in Fig. 9: (O) wet peel strength; (△) grafted amount.

the loss in the dry peel strength as a result of the complete removal of the layer.

Hydrolysis Condition Dependence

In the preceding sections, the results on the effects of priming and etching were obtained by using electron-induced grafts having T_i values of 5–9 μm, which were hydrolyzed in 1.0N KOH methanol solution at 50°C (condition 1) for 2 or 4 hr. However, a different batch of electron-induced grafts, having smaller T_i of less than 4 μm, has been found to give high wet peel strengths without priming and etching, although there is a wide scatter (Fig. 11). The wet peel strength increases with hydrolysis time or degree. This increase in wet peel strength may be due to a decrease in homopolymer layer thickness or T_i and an increase in penetration depth of the adhesive with hydrolysis degree. Figure 12 shows the decrease in grafted amount with hydrolysis. This decrease results mainly from partial removal of the surface homopolymer, which is due to cleavage of ester side chain links by hydrolysis[2]:

$$-CH_2-\underset{\underset{COOCH_2-}{|}}{CH}- \quad \longrightarrow \quad -CH_2-\underset{\underset{COOH}{|}}{CH}- \quad + \quad HO-CH_2-$$
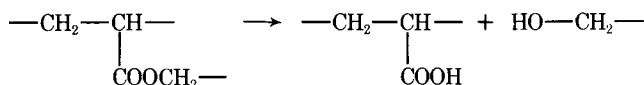
The increase in adhesive penetration can result from the optimization of the surface energetic conditions (e.g., maximum capillary rise and equality of solubility parameter)[6-8] by the introduction of carboxyl groups.

Acid hydrolysis in acetone/water = 5/1 mixture (conditions 3 and 4) gave high wet peel strengths for all the batches of electron-induced grafts used in this work, although there is a wide scatter. A typical result is shown in Figure 13, where the wet peel strength was plotted against the degree of hydrolysis of PMA homopolymer dissolved in the acid hydrolysis solution. The degree of the dissolved
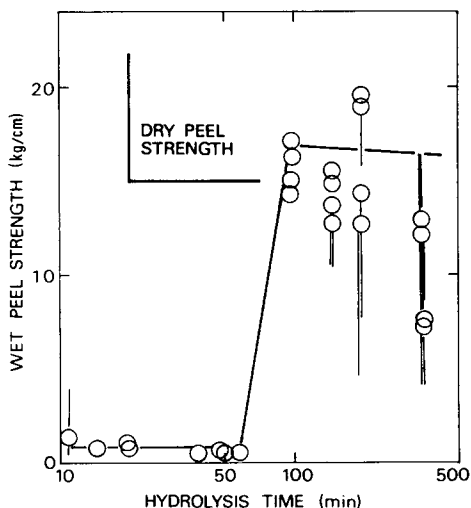

Fig. 11. Wet peel strength vs. hydrolysis time for a batch of electron-induced Black LDPE grafts, which were hydrolyzed in a 1.0N KOH methanol solution (condition 1) and bonded with Adhesive 10.
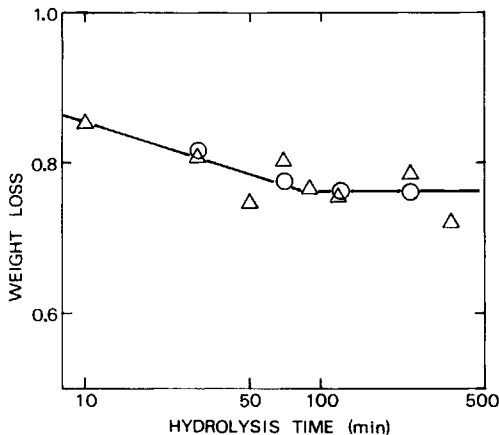
Fig. 12. Weight loss or decrease in grafted amount vs. hydrolysis time for the grafts corresponding to Fig. 11: (O) Black LDPE: (△) LDPE.

PMA homopolymer probably corresponds[9] to the degree of the grafted homo-polymer surface. In this case, the hydrolysis reaction must occur uniformly over the homopolymer layer since the solution dissolves PMA and hydrolyzed PMA over a wide range (0–70 mole%) of hydrolysis degree. This uniformity may promote the partial removal of the homopolymer layer and the adhesive pene-tration. On the other hand, alkaline hydrolysis in water (condition 2) gave low wet peel strengths without exception, whereas the dry peel strength resulted in adherend failure. In this case, the hydrolysis reaction must occur only in the surface region in the initial stages of reaction since the aqueous solution does not dissolve PMA. This nonuniformity may retard the homopolymer removal and the epoxy penetration. With respect to the nonuniform reaction, the al-kaline hydrolysis in methanol (condition 1, Fig. 11) may be intermediate between
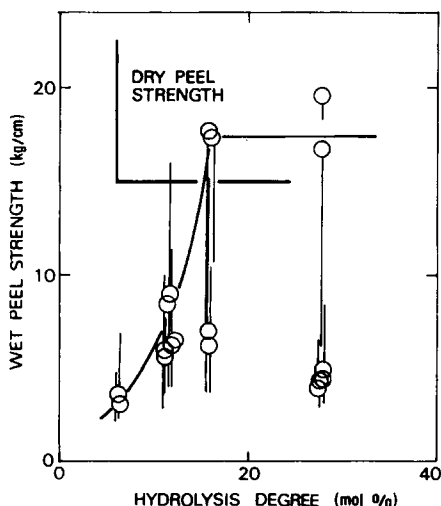

Fig. 13. Wet peel strength of electron-induced Black LDPE grafts vs. hydrolysis degree of PMA homopolymer. Both the grafts and the PMA homopolymer were hydrolyzed in a 0.36N HCl ace-tone/water (5/1) solution (condition 3). The hydrolyzed grafts were bonded with Adhesive 10.

the acid hydrolysis in acetone/water (Figs. 13 and 14) and the alkaline hydrolysis in water since the solubility of PMA and hydrolyzed PMA in methanol is intermediate between those in the acetone/water mixture and water.

The dry peel strength increases rapidly with degree of hydrolysis and reaches a maximum (adherend failure) (Figs. 11, 13, and 14). This increase can be attributed to the optimization of the surface energetic criteria[6-8] by the introduction of carboxyl groups. The wet peel strength also increases with the hydrolysis degree. However, the increase in wet peel strength requires a longer time or a higher degree of hydrolysis than the increase in dry peel strength does (Figs. 11 and 13). This difference probably indicates the importance of the homopolymer removal and the epoxy penetration (which increase with hydrolysis) in the improvement of wet peel strength.

The above results on the hydrolysis condition dependence of wet peel strength can be also explained in terms of the relationship between adhesive penetration and homopolymer layer thickness. The epoxy primers masked the hydrolysis condition dependence by enhancing greatly the epoxy penetration and gave the maximum wet peel strength (adherend failure) without exception in all the samples having the maximum dry peel strength.

Adhesive Dependence

In the electron-induced grafts hydrolyzed under condition 3, the wet peel strength increased with hydrolysis when bonded with Adhesive 10 (Fig. 13). On the other hand, it did not increase when bonded with Adhesive 20, although the dry peel strength increased with hydrolysis (Fig. 14). This difference may be due to a difference in adhesive penetration between the two adhesives because Adhesive 10 has a much lower viscosity and curing rate than Adhesive 20.
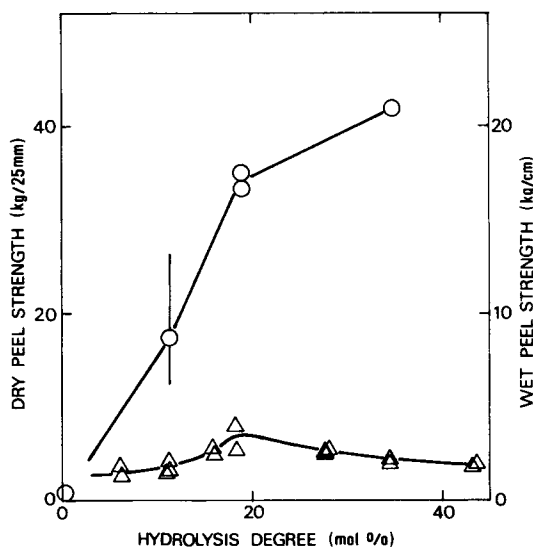

Fig. 14. Dry and wet peel strength of electron-induced Black LDPE grafts vs. hydrolysis degree of PMA homopolymer. The same grafts as used in Fig. 13 were bonded with Adhesive 20: (O) dry peel strength; (△) wet peel strength.

Mechanism of Improvement in Wet Peel Strength

All the results on the improvement in wet peel strength can be explained in terms of penetration of epoxy into the homopolymer or swelling layer and subsequent curing of the penetrated epoxy, although there is no direct evidence for the epoxy penetration. A schematic diagram of the improvement is shown in Figure 15. The grafted surface layer consists of a hydrophilic swelling layer having a low wet mechanical strength and a hydrophobic nonswelling layer having a high wet mechanical strength. The swelling layer probably corresponds to the homopolymer layers, which can appreciably swell by water absorption, and the nonswelling layer may correspond to the inner graft copolymer layer, which can slightly swell. Since the surface layer has a rough, porous surface structure, some epoxys can penetrate into a certain depth of the swelling layer during bonding. When the penetrated epoxy is allowed to cure, the water-resistant cured epoxy reinforces the swelling layer against the attack of water.

In the grafts having a thin swelling layer, the epoxy can penetrate up to the boundary between the swelling and nonswelling layers and reinforce the total depth of the swelling layer. The total reinforcement should lead to an increase in wet peel strength. On the other hand, in the grafts having a thick swelling layer, the epoxy adhesive cannot penetrate up to the boundary but only into a part of the total depth. The remaining unreinforced swelling layer becomes a weak layer in the wet joints, and the result is unimproved wet peel strength. The epoxy primers eliminate the unreinforced layer by enhancing the epoxy penetration. The photodegradative etching eliminates the unreinforced layer by partially removing the swelling layer.
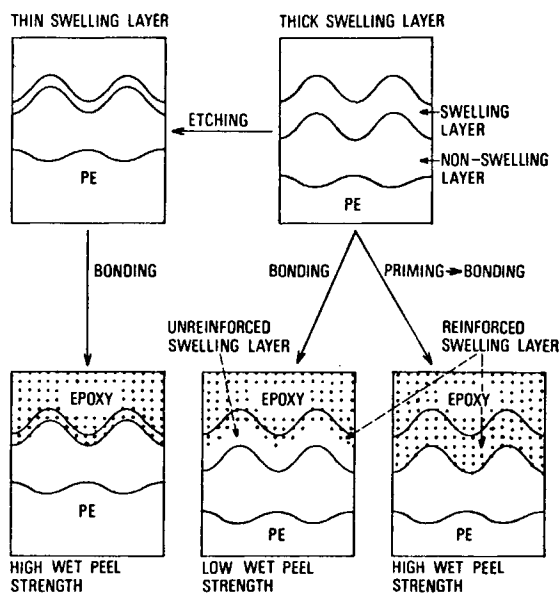

Fig. 15. Schematic diagram of improvement in wet peel strength.

Adhesion Mechanism

The dry strength reaches a maximum (adherend failure) with formation of the homopolymer layer[2] and decreases greatly with removal of the layer,[3] where the layer is hydrolyzed to a hydrolysis degree of more than 20 mole% (Fig. 14). In other words, the attainment of the maximum dry peel strength requires the coverage of the surface with the homopolymer layer. This surface homopolymer requirement cannot be explained in terms of the weak boundary layer theory[10] and the wettability criteria for maximum adhesion.[11] The wettability criteria do not require such a significant modification of the surface because the water contact angle becomes constant at lower grafting stages (i.e., at lower graft compositions) than the homopolymer layer formation (100% monomer). The requirement may correspond to an optimum surface state required for the epoxy penetration. This adhesion mechanism is supported by the results on the improvement in wet peel strength.

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