# Surface Modification of Polyethylene by Radiation-Induced Grafting for Adhesive Bonding. V. Comparison with Other Surface Treatments

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## Synopsis

Helium gas plasma treatment of low-density polyethylene (LDPE) yields much lower peel strength than oxidative treatment using chromic acid and oxygen gas plasma. The practical adhesion, the bondability retention, and the bond durability of oxidatively treated LDPE sheets, bonded with epoxy adhesives, have been compared with those of partially hydrolyzed LDPE–methyl acrylate surface grafts. The oxidized surfaces easily lose the bondability by light rubbing with tissue paper, solvent extraction, heat aging, and artificial weathering, whereas the grafted surfaces retain the bondability. The bondability loss is due to removal of the oxidized layer, and the bondability retention is due to retention of the surface homopolymer layer. Conventional antioxidants stabilize the grafted but not the oxidized surfaces against thermal oxidative degradation. The grafted LDPE joints have much higher bond durability in humid environments than those of the oxidized LDPE joints. The dry and wet peel strengths of oxidized LDPE joints are greatly improved by application of primers consisting of a base epoxy resin and organic solvents. An adhesion mechanism involving penetration of epoxy adhesives into the oxidized layers and subsequent reinforcement of the layers by curing of the penetrated epoxy is proposed.

## INTRODUCTION

It is necessary to pretreat the surfaces of polyethylene (PE) to achieve strong adhesive joints at bonding temperatures below the softening point. However, there is still controversy as to the mechanisms of bond improvement by the pretreatment. In addition, very few papers have been published on the stability of the treated surfaces and the bond durability of the adhesive joints in spite of the practical importance of their environmental properties. Among many surface pretreatments proposed,[1,2] the most extensively investigated techniques for structural adhesive bonding are CASING[3] and oxidative treatments using atomic oxygen (or oxygen gas plasma)[4,5] and chromic acid.[6–8] In this paper, the practical adhesion, the bondability stability, and the bond durability of the treated PE joints bonded with epoxy adhesives are compared with those of hydrolyzed methyl acrylate (MA) surface grafts.[9–13] In addition, the adhesion mechanisms of oxidatively treated surfaces to epoxy adhesives are discussed in comparison with that of the grafted surfaces.

## EXPERIMENTAL

Three different PE samples, previously described,[11] were used: (1) low-density PE (designated LDPE); (2) medium-density PE (MDPE); (3) carbon black-containing low-density PE (Black LDPE). The preparation of PE

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sheets[9,10] and partially hydrolyzed (electron-induced) MA grafts[11] are described elsewhere.  A plasma reactor (PR-503, Yamato Scientific Co. Ltd.) was used for helium (He) and oxygen ($O_2$) gas plasma treatments of PE sheets.  The standard conditions were 25–50 W ($O_2$ plasma) or 75–100 W (He plasma) at a 20 ml/min flow rate and 0.3–1.0 torr.  A chromic acid solution[6] and an acid paste were used for chromic acid treatment of PE sheets.  The acid paste consists of 11 g potassium dichromate, 170 g lead sulfate, and 100 g concentrated sulfuric acid (sp. gr. 1.84).

The bond strength or practical adhesion of surface-modified PE joints was evaluated by the 180° peel test,[9] the T-peel test,[10,11] and the tensile lap shear test.  For the lap shear test, composite test pieces consisting of steel (2.0 mm)–epoxy (0.05 mm)–PE (0.5 mm)–epoxy (0.05 mm)–steel (2.0 m) were prepared, similar to the aluminum test pieces used in previous works.[3,5]  Four different formulations of commercial epoxy resins were used:  (1) Epicote 828/polymide L-25 = 7/3 (designated adhesive S-1),[9,10] (2) Epicote 828/Versamide 140 = 7/3 (adhesive S-2), (3) Epicote 828/Epicote 871/Epicure 103 = 50/50/45 (adhesive 10),[11,13] and (4) Cemedine No. 1500 (epoxy/polyamide = 10/9, adhesive 20).[13]  Adhesive S-2 was allowed to cure for 16 hr at room temperature and then for 8 hr at 60°C.

## RESULTS AND DISCUSSION

### Practical Adhesion

The most effective pretreatments for structural adhesive bonding of PE are CASING and oxidative techniques such as the use of chromic acid, $O_2$ plasma, and flame.[2,14]  Table I shows the effects of these pretreatments on T-peel strength of PE–epoxy–PE joints and also shows a comparison between the treated PE joints and the PE–MA surface graft joints.  Flame treatments yielded peel strengths similar to those obtained by chromic acid and $O_2$ plasma, although the former required careful process control to prevent overoxidation and warpage. High-energy electrons, $\gamma$-rays, and ultraviolet irradiation in air yielded low peel strengths of less than 0.5 kg/25 mm.  In He and $O_2$ plasma-treated PE joints, the peel strength increased rapidly with exposure time and leveled off within 5 min, which is in agreement with previous works.[3,5]  The leveled-off values are shown in Table I.  On the other hand, in chromic acid-treated LDPE and Black

TABLE I
T-Peel Strength of Treated PE Joints Consisting of PE–Epoxy–PE[a]

| Treatment | T-Peel strength (average–maximum–minimum), kg/25 mm | |
|---|---|---|
|  | LDPE | MDPE |
| Control | < 0.1 | < 0.1 |
| Hydrolyzed MA graft | > 30[b] | > 40[b] |
| Acid solution, 30 min, 70°C | 2.1–7.4–0.6 | 4.0–20–1.7 |
| $O_2$ plasma, 5–30 min, 25–50 W | 6.0–38[b]–3.7 | 5.0–20–2.3 |
| He plasma, 5–30 min, 75–100 W | 0.4–0.8–0.1 | 2.9–5.3–2.2 |

[a] Bonded with adhesive S-2.
[b] PE adherend failure.

LDPE joints, the peel strength increases, passes through a maximum, and then decreases with treatment time (Figs. 1 and 2); whereas the tensile lap shear strength levels off after an initial rapid increase (Fig. 3). This initial increase is probably due to the introduction of polar groups. The subsequent decrease in peel strength, which was also observed by other workers,[15] reflects an increase in thickness of the oxidized layer because the infrared absorption peaks of carbonyl groups at 1710–1730 cm$^{-1}$ showed a monotonous increase with treatment time. In this case, the thickened oxidized layer becomes a weak boundary layer
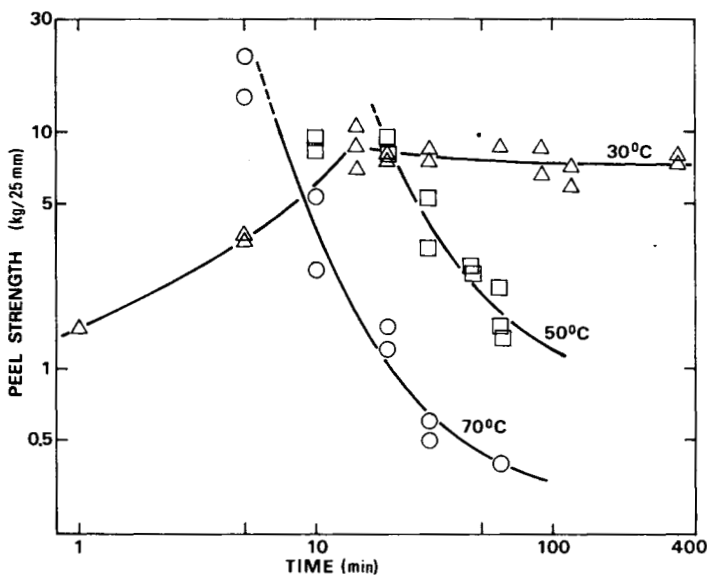


Fig. 1. Average T-peel strength vs. treatment time of acid solution-treated Black LDPE joints bonded with adhesive S-1.
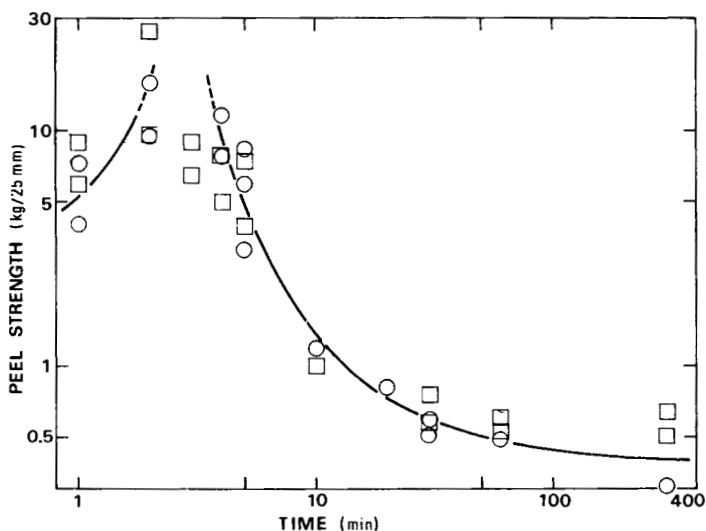


Fig. 2. Average T-peel strength vs. treatment time of acid paste-treated Black LDPE joints bonded with adhesive 20:  (O) 70°C; (□) 90°C.
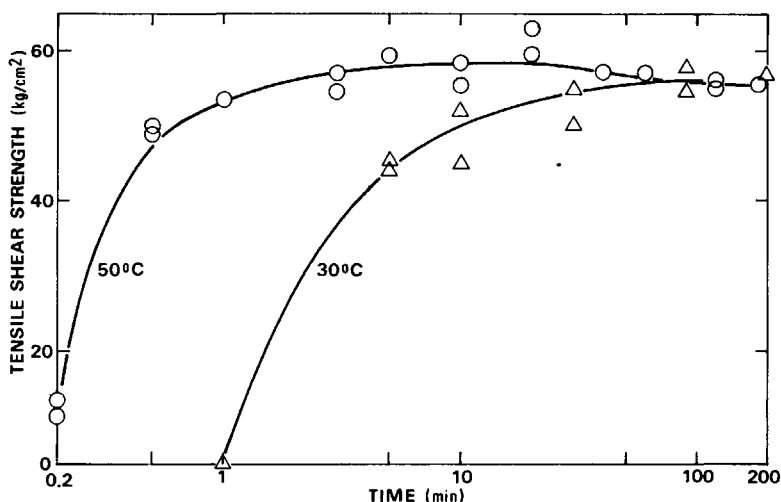
Fig. 3. Tensile lap shear strength vs. treatment time of acid solution-treated Black LDPE joints bonded with adhesive S-1.

in the joint, and the peel strength depends on the mechanical (or cohesive) strength of the oxidized layer. Acetone extraction of the excessively oxidized surfaces increases the peel strength (Fig. 4). This increase is due to partial removal of the oxidized layer because the carbonyl absorption peaks decreased with acetone extraction.

Oxidative treatments give much higher peel strength than He plasma treatment (Table I and Fig. 1). In particular, He plasma-treated LDPE sheets give a low peel strength of less than 1 kg/25 mm, whereas He plasma-treated HDPE sheets give a high peel strength of 2–5 kg/25 mm. On the other hand, He plasma-treated LDPE and MDPE sheets give high tensile lap shear strengths
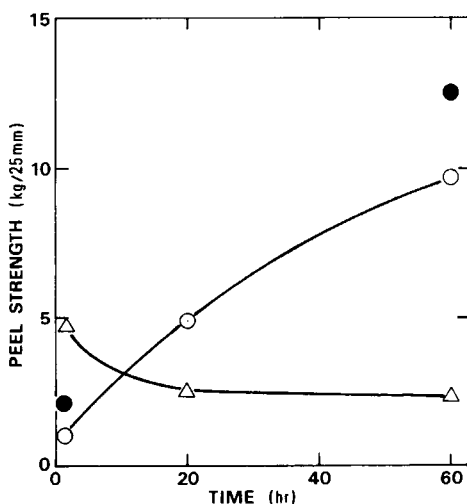


Fig. 4. Average T-peel strength vs. acetone immersion time at 55°C of acid solution-treated PE joints bonded with adhesive S-1 after acetone immersion: (●) LDPE; (O) Black LDPE; (△) MDPE.

(Table II) in conformity with previous works.[3,5] Since brittle epoxy adhesives usually yield high shear strength and low peel strength, it seems likely that the peel strength is more sensitive to changes in surface properties with treatment than the tensile shear strength. Moreover, the peel test evaluates a wider range of the changes than the tensile shear test. Thus, the He plasma or CASING treatment is not effective for the improvement in practical adhesion of LDPE. No results have been published on the peel strength of CASING- or He plasma-treated LDPE joints. Previous works[1–3,5] have evaluated the practical adhesion by lap shear strengths bonded with epoxy adhesives. The grafted joints give the highest peel strength and bond reliability among the surface-modified PE joints (Table I). The grafts having the surface homopolymer layer gave adherend failure without exception, whereas the treated PE sheets gave wide scatter in peel strength.

## Stability of Treated Surfaces

Light rubbing of oxidatively treated surfaces with cloth or tissue paper causes loss in bond strength (Table III), in agreement with previous work.[16] This bondability loss is due to removal of the oxidized surface layer because rubbing also causes a decrease in wettability and in the infrared absorption peaks for carbonyl groups. This easy removal of the layer by rubbing suggests that the oxidized layers are rather unstable and can be easily removed when exposed to

TABLE II

Tensile Lap Shear Strength of Helium Plasma-Treated PE Joints Consisting of Steel–Epoxy–PE–Epxoy–Steel[a]

| | | Tensile shear strength, $kg/cm^2$ | | | |
|---|---|---|---|---|---|
| PE | Treatment | Average | Maximum | Minimum | Locus of failure |
| LDPE | control | < 10 | | | interfacial failure from PE |
| LDPE | He plasma[b] | 78 | 88 | 70 | interfacial failure from steel |
| MDPE | control | 28 | 30 | 26 | interfacial failure from PE |
| MDPE | He plasma[b] | 106 | 130 | 78 | interfacial failure from steel |

[a] Bonded with adhesive S-2.

[b] 5–30 min, 75 W.

TABLE III

Effects of Rubbing of Oxidatively Treated LDPE Surfaces on 180° Peel Strength[a]

| | 180° Peel strength (average–maximum–minimum), kg/cm | |
|---|---|---|
| Treatment | Before rubbing | After rubbing |
| Control | < 0.1 | < 0.1 |
| Hydrolyzed MA graft | > 5.0[b] | > 5.0[b] |
| Tesla coil | 1.7–2.0–1.5 | < 0.1 |
| Flame | > 5.0[b] | < 0.1 |
| Acid solution, 120 min, 30°C | > 5.0[b] | < 0.1 |
| Acid solution, 30 min, 70°C | > 5.0[b] | 1.2–1.5–1.0 |
| $O_2$ plasma, 5 min, 25 W | > 5.0[b] | 0.2–0.4–0.15 |
| $O_2$ plasma, 15 min, 25 W | > 5.0[b] | 0.15–0.3–0.1 |

[a] Two LDPE sheets (0.7 mm thick) were bonded with adhesive S-1.

[b] PE adherend failure.

various environments.   Table IV summarizes the bondability stability or retention of oxidatively treated Black LDPE surfaces, compared with that of the graft.   Apparently, the oxidized surfaces easily lose the adhesive bondability by cyclohexanone extraction, heat aging, and artificial weathering, whereas the grafted surface retains the bondability.   This bondability loss of the former is probably due to removal of the oxidized layers because the layers also lose their wettability.   The bondability retention of the latter is due to retention of the homopolymer layer.[11]   Conventional antioxidants stabilize the grafted surfaces, but not the oxidized surfaces, against thermal oxidative degradation.   This may be a serious drawback of the oxidative treatments.

## Bond Durability in Humid Environments

Table V shows the bond durability of oxidatively treated PE joints, compared with the graft joints.   When the graft joints are immersed in water at 60°C, the peel strength decreases rapidly with immersion time and then reaches a constant value in 250 hr.[13]   The peel strength after water immersion for 264 hr (Table V) indicates the wet peel strength of the joint assembly.   When the grafts are primed with epoxy solutions consisting of a base epoxy resin and organic solvents, which can dissolve not only epoxy resins but also hydrolyzed FMA (e.g., Epicote 872/methyl ethyl ketone/isopropyl alcohol = 13/44/43), the wet peel strength reaches PE adherend failure without exception.[13]   This primer was also effective in improving dry and wet peel strengths of the oxidized PE joints, although there was a wide scatter in wet peel strength (Table V).   The graft joints have much higher bond durability than those of the oxidized PE joints.

## Adhesion Mechanisms

The improved practical adhesion (or bond strength) of PE by oxidative treatment is thought to result from the elimination of weak boundary layers (i.e., low-strength regions on the original PE surfaces)[3] or from improved wettability[17]

TABLE IV
Bondability Retention of Treated PE Surfaces Exposed to Various Environments[a]

| Environment | T-Peel strength (average–maximum–minimum), kg/25 mm | | |
| --- | --- | --- | --- |
| | MA-grafted | Acid-treated | $O_2$ plasma-treated |
| Control | > 35[b] | 2.0–3.0–0.5 | 10.6–17–7.0 |
| Acetone, 60 hr, 55°C | > 35[b] | 9.5–14.5–4.5 | 12.0–17–7.0 |
| Cyclohexanone, 40 hr, 55°C → methanol, 20 hr, 55°C | > 35[b] | 0.2–0.4–0.1 | 2.8–5.1–1.6 |
| Distilled water, 65 hr, 80°C | > 35[b] | 1.1–2.7–0.7 | 7.4–10.6–6.1 |
| Heat aging, 500 hr, 80°C → acetone, 20 hr, 55°C | > 35[b] (>35[b])[c] | 0.4–0.7–0.1 (< 0.1)[c] | < 0.1 (< 0.1)[c] |
| Artificial weathering, 40 hr → acetone, 20 hr, 55°C | > 35[b] | 0.1 > | 1.6–2.8–0.7 |
| Artificial weathering, 100 hr → acetone, 20 hr, 55°C | (> 35[b])[c] | (0.1–0.2–0.05)[c] | (5.7–8.2–3.5)[c] |

ᵃ Treated Black LDPE sheets were bonded with adhesive 10 after exposure to environments.
ᵇ PE adherend failure.
ᶜ Stabilized with antioxidants and ultraviolet absorbers.[11]

TABLE V
Bond Durability of Treated PE Joints[a]

| | T-Peel strength (average–maximum–minimum), kg/cm | | |
|---|---|---|---|
| Environment | MA-grafted | Acid-treated | O$_2$ plasma-treated |
| Control | > 16[c] | 5.0–7.0–3.0 | 6.0–8.0–4.0 |
| Distilled water, 264 hr, 60°C | 2.0–3.5–0.5 (> 18[c])[d] | 2.4–4.2–0.9 (16–18[c]–10.0)[d] | 3.0–4.4–1.6 |
| Flexural fatigue test in air[e] at 23°C | > 16[c] | 2.1–3.3–1.4 | 2.3–3.6–1.4 |
| Flexural fatigue test in water[e] at 55°C | (> 16[c])[d] | 3.0–4.5–2.0 | 0.1–0.1–0.05 |

[a] The same PE sheets and adhesive as in Table IV.
[b] Followed by acetone treatment for 66 hr at 56°C.
[c] PE adherend failure.
[d] Primed.
[e] The T-peel specimens were exposed to a fatigue testing machine (ASTM D671-63, Method A) for 1 × 10$^6$ cycles.

by the introduction of polar groups. However, neither of these mechanisms of bond improvement provides an interpretation consistent with the following results. In chromic acid-treated LDPE and Black LDPE joints, the dry peel strength increases, passes through a maximum, and then decreases with treatment time (Figs. 1 and 2). The peel strength of the excessively oxidized PE increases again with partial removal of the oxidized layer by acetone extraction (Fig. 4) and decreases greatly with complete removal of the layer by rubbing (Table III). The epoxy primers enhance the dry and wet peel strengths. These results can be explained by an adhesion mechanism similar to that[13] of the grafted surfaces to epoxy adhesives, which involves penetration of epoxy resins into the modified surface layer and subsequent reinforcement of the layer by curing of the penetrated epoxy. A schematic diagram is shown in Figure 5.

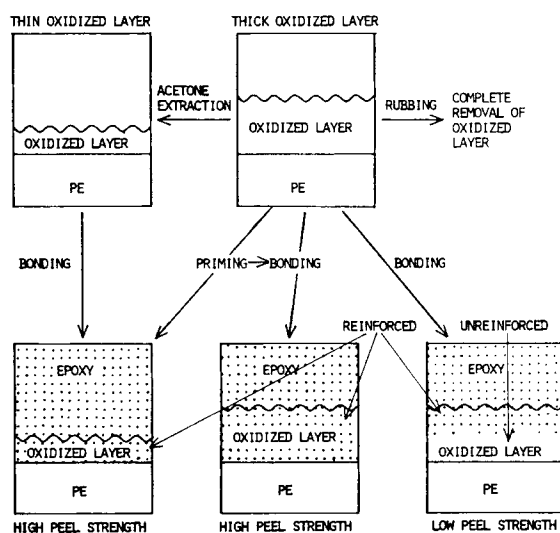Oxidative treatment of PE forms an oxidized surface layer having lower me-



Fig. 5. Schematic diagram of peel strength of acid-treated LDPE joints.

chanical (or cohesive) strength than the PE bulk. The lowered strength results from the oxidative degradation of PE molecules, which is concurrent with the introduction of polar groups. A sufficient wetting or an intimate contact is attained between the oxidized surfaces and epoxy adhesives. Moreover, some epoxy adhesives penetrate to a certain depth in the layer during bonding because the oxidized layer has a rough, porous structure, shown by scanning electron micrographs of the oxidized surfaces.[18] When the penetrated epoxy is allowed to cure, it can reinforce the weak oxidized layer. The adhesives may also partially remove the outer section of the oxidized layer by dissolution or displacement. A displacement mechanism has been suggested by Brewis.[19] Bonding of excessively oxidized surfaces, having a thick oxidized layer of low cohesive strength, leaves a depth of the unreinforced oxidized layer in the joint. The remaining unreinforced layer becomes a weak point in the joint. The result is a limited peel strength, which depends on the cohesive strength of the layer. Epoxy primers eliminate the unreinforced layer by enhancing the epoxy penetration or by partially dissolving the oxidized layer. Rubbing leads to a loss in wettability and peel strength by completely removing the oxidized layer.

The initial increase in practical adhesion with acid treatment (Figs. 1 and 2) is not due to the elimination of weak layers on the original surface, but rather to the introduction of polar groups. The removal of the oxidized layer by light rubbing leads to a loss in practical adhesion. This result supports the above conclusion against the weak boundary layer concept[3,20] because the rubbing does not form another new region of low strength on the surface. The introduction of polar groups can lead not only to improved contact between PE surfaces and epoxy adhesives, but also to an increased attractive force at the interface. As discussed above, however, the further increase in polarity with longer treatment time is not reflected in practical adhesion. The limiting factor is the cohesive strength of the oxidized surface layer, which decreases with further treatment or oxidative degradation.

The weak boundary layer concept[3,20] and the wettability criteria for maximum adhesion[17] provide no answer to the question why oxidized PE gives relatively high peel strength despite the easy removal of the oxidized layer or despite the presence of the mechanically weak oxidized surface layer. An answer can be given by the above-mentioned reinforcement or displacement mechanism. The oxidized PE joints give a wide scatter in peel strength, whereas the grafted PE joints with the surface homopolymer layer give adherend failure without exception. The scatter in peel strength of the former reflects the variation in thickness or cohesive strength of the oxidized layer. The extremely high peel strength and bond reliability of the latter reflect complete coverage of the surface with the homopolymer layer possessing high cohesive strength and high interfacial force between the homopolymer layer and the unmodified PE bulk. The high interfacial force results from chemical linkages through the graft copolymer layer, which exists between the homopolymer layer and the unmodified PE bulk.[10]

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