Surface Modification of Polyethylene by Radiation-Induced Grafting for Adhesive Bonding. III. Oxidative Degradation and Stabilization of Grafted Layer

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Synopsis

Vapor-phase mutual grafting of methyl acrylate (MA) onto polyethylene (PE) and subsequent saponification treatment produce a surface graft having a high adhesive bondability, which results from the presence of a hydrolized homopolymer layer (consisting of only monomer component) on an inner graft copolymer layer consisting of both PE and monomer components. The oxidative deterioration and the stabilization of the grafted surface layer have been investigated to clarify the long-term stability of the adhesive bondability. The bondability rapidly disappears with accelerated weathering followed by acetone extraction treatment, whereas it is kept unchanged during thermal-oxidative aging at 100°C. Microscopic and ATR infrared spectroscopic observations of the degraded surfaces show that the bondability loss is due to degradative removal of the surface homopolymer layer. The addition of combinations of conventional antioxidants and ultraviolet absorbers stabilizes the grafted surface layer against thermal-oxidative and photo-oxidative degradation and thus extends the bondability retention time. The stabilization is more effective in the grafts of carbon black-containing PE, where carbon black is present in the inner-graft copolymer layer.

INTRODUCTION

Mutual irradiation of polyethylene (PE) in methyl acrylate (MA) vapor with γ-rays from ^{60}Co sources yields a surface graft having a high adhesive bondability.[1,2] The grafted surface layer consists of an outer homopolymer layer (of only MA component) and an inner graft copolymer layer (of both MA and PE components). The high stability of the homopolymer layer to solvent treatments indicates that this homopolymer is not only crosslinked but is also linked by chemical bonds to the PE and grafted PMA chains in the contiguous copolymer layer. The peel strength increases significantly with saponification treatment as epoxy adhesives are used (less than 1 kg/25 mm to more than 30 kg/25 mm). The presence of the hydrolyzed surface homopolymer layer has been found to be a necessary condition for its strong adhesive bonding with epoxy adhesives.[2] Accordingly, the long-term stability of the adhesive bondability may depend on the stability of the homopolymer layer itself; i.e., degradative removal of the layer may lead to a disappearance in adhesive bondability of the grafted surface. This paper is concerned with the oxidative degradation and the stabilization of the grafted layer.

EXPERIMENTAL

Surface Grafts

The polyethylene samples used were of low density (ca. 0.92 g/cm^3, designated as LDPE), a carbon black-containing LDPE (ca. 0.93 g/cm^3, Black LDPE), and a medium-density polyethylene (0.945 g/cm^3, MDPE). Black LDPE consists of LDPE and carbon black of 2.6 wt-%. The melt index of LDPE, Black LDPE, and MDPE was 0.30, 0.25, and 0.25 g/10 min, respectively. Sheets 0.5 and 2.0 mm thick were prepared from the PE pellets by the method previously described.[2] A commercial methyl acrylate (MA) was used after distilled in nitrogen before use.

The PE sheets (25 mm wide and 115 mm long) were surface grafted with MA by vapor-phase mutual irradiation of PE—MA both with γ-rays from a ^{60}Co source and with 4-MeV electrons[3] from a linear electron accelerator. In the γ-ray-induced grafting,[2] the PE sheets (2.0 mm thick alone) were irradiated in the saturated vapor pressure of MA at 25°C at an average dose rate of 8.3×10^2 rads/min. The electron-induced grafting[3] was carried out in a closed 6-liter reactor of stainless steel, having an aluminum (0.3 mm thick) window. The PE sheets were placed in the reactor, evacuated at a pressure of less than 1×10^{-3} mm Hg, and then irradiated in the saturated vapor pressure of MA at ca. 20°C and an average dose rate of 4.7–5.0×10^5 rads/min for 25 min. To remove occluded PMA homopolymer, the grafted sheets were extracted with acetone in a Soxhlet extractor until there was no further decrease in weight. The amount of grafted monomer was expressed as weight increase per initial surface area of sheet. The grafted sheets were partially saponified and solvent extracted by the method[2] previously described.

Accelerated Deterioration Tests

The grafted sheets were oven aged in a circulating-air oven to evaluate the thermal-oxidative stability. In addition, an artificial weathering apparatus (Toyo Rika Kogyo, Type WE-SUN-HC) of sunshine carbon-arc type (ASTM E42-65, Type EH) was used to evaluate the photo-oxidative stability or the weatherability. The grafted surfaces were exposed with a cycle of 20-hr continuous light with intermittent water spray (102-min light followed by 18-min light and spray) and 4-hr darkness unless otherwise noted. When the water spray was off, the temperature and the relative humidity in the chamber were ca. 45°C and ca. 55%, respectively. The black panel temperature was $63° \pm 3°$C. To extract degradation products, all the aged samples were extracted with acetone at 56°C for 20 hr and then dried under vacuum at 55°C.

The progress of degradation in the grafted surface layer was followed by four methods: (a) weight loss per grafted amount, (b) ATR (attenuated total reflection) infrared spectroscopy,[1] (c) isotropic (T_i) and anisotropic (T_a) layer thicknesses determined from interference and polarizing micrographs,[2] and (d) adhesive bondability to epoxy adhesives. The weight loss per grafted amount (%) was calculated from $100 - [100(W_3 - W_0)/(W_1 - W_0)]$ in unsaponified grafts and from $100 - [100(W_3 - W_0)/(W_2 - W_0)]$ in saponified grafts, where W_0, W_1, W_2, and W_3 are the weight of original sheet, after grafting, after saponification, and after aging (or weathering) and subsequent extraction, respectively. In method d, the two degraded sheets (2.0 mm thick) were bonded with an epoxy

adhesive to prepare a T-peel specimen, consisting of graft—adhesive—graft. The epoxy adhesive consists of 50 parts by weight of a diglycidyl ether of bisphenol A (Epicote 828, Shell Chemical), 50 parts of a diglycidyl ether of Linoleic acid dimer (Epicote 871), and 45 parts of an aromatic amine adduct (Epicure 103). The assembly was lightly weighted (0.15 kg/cm^2), and the adhesive was allowed to cure at 50°C for 4 hr in a circulating-air oven. The thickness of the adhesive layer was maintained constant by insertion of a stainless-steel wire 100 μm in diameter. The T-peel strength was measured by a tensile test machine (at a cross-head speed of 10 cm/min) according to ASTM D1876-61T. The average peeling load was determined from the autographic curve for the first 5 cm of peeling after the initial peak.

Stabilization of Grafted Layer

Conventional antioxidants and ultraviolet (UV) absorbers were used to stabilize the grafted layer against oxidative degradation. The grafts were impregnated with stabilizer solutions at 50°C and dried naturally in a room. The antioxidants include 4,4'-thiobis(2-*tert*-butyl-5-methylphenol)(TBBMP), tetrakis[methylene-3(3',5'-di-*tert*-butyl-4-hydroxyphenyl)propionate]methane, and dilauryl thiodipropionate. The UV absorbers include 2-hydroxy-4-*n*-octoxybenzophenone and 2(2'-hydroxy-3',5'-amylphenyl)benzotriazole.

RESULTS AND DISCUSSION

Grafted Layers

Figures 1 and 2 show a typical surface structure of LDPE sheets grafted at low dose rates (ca. 8×10^2 rads/min) from a ^{60}Co source and grafted at high dose rates (ca. 5×10^5 rads/min) from a linear electron accelerator, respectively. Despite significant difference in dose rate between both the radiation sources, both the grafts show a similar surface graft structure. The grafted layers consist of an optically isotropic outer layer and an anisotropic (bright candlelight-shape) inner layer, although their thicknesses are different between both the grafts. By comparing the isotropic layer thickness (T_i) with the surface composition (determined by ATR and ESCA) of a series of grafts with various surface compositions, it has been found that the grafted surface (in the lateral sense of the term surface) actually reaches 100 mol-% MA at 6–9 μm (γ-ray-induced graft)[2] or 2–4
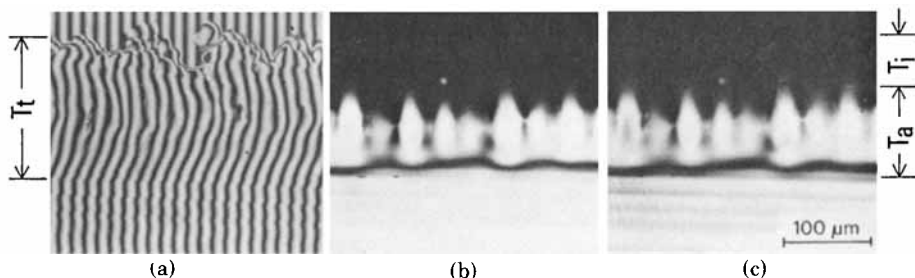

Fig. 1. Typical surface structure of low-density PE sheets grafted by γ-rays and then saponified. An identical area in a cross section of the grafts was photographed under three different conditions: (a) under an interference microscope; (b) between crossed polarizers in the 45° position of the ungrafted PE part; (c) at 85° of angle between polarizer and analyzer in the 45° position.
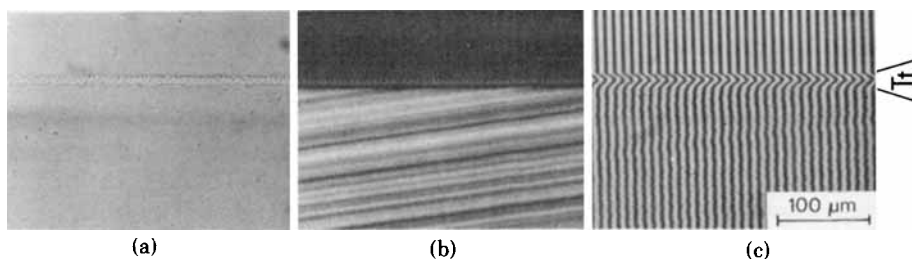
Fig. 2. Typical surface structure of low-density PE sheets grafted by high-energy electrons. An identical area in a cross section of the grafts was photographed under three different conditions: (a) under an unpolarized white light; (b) between crossed polarizers in the 45° position of the ungrafted PE part; (c) under an interference microscope.

μm (electron-induced graft)[3,4] of T_i, at which the surface composition by ATR is 80–85 mol-% MA (γ-ray-induced graft) or ca. 60 mol-% MA (electron-induced graft). This relationship does not change with saponification treatment.[2] As a measure of the surface homopolymer layer, accordingly, the T_i value was determined from the micrograph taken between crossed polarizers [(Figs. 1(b) and 2(b)]. As a measure of the inner graft copolymer layer, the anisotropic layer thickness (T_a) was determined by subtracting the T_i value from the total thickness of outer homopolymer and inner graft copolymer layer (T_t), which was determined from the interference micrograph [(Figs. 1(a) and 2(c)].

As seen in Figure 3, Black LDPE sheets (containing 2.6 wt-% carbon black) yield the same isotropic and anisotropic layers as LDPE sheets (containing no carbon black), although the surface grafting rate in the former is 20–30% lower than that in the latter. In Figure 3(a), it is noted that carbon black is present along the upheaved[2] graft copolymer layer. This presence of carbon black, which is a radical chain terminator[5] against auto-oxidation, may contribute to stabilization of the grafted layer.

The hydrolyzed surface grafts (LDPE and Black LDPE) used in this work had 15–20 μm (γ-ray-induced graft) and 5–9 μm (electron-induced graft) of T_i. The thickness of anisotropic layer (T_a) was 100 ± 10 μm (γ-ray-induced graft) and 20 ± 5 μm (electron-induced graft). The grafted amount was 8–12 mg/cm^2 (γ-ray-induced graft) and 0.5–1.0 mg/cm^2 (electron-induced graft). The grafted surface, which is saponified up to a saponification degree of more than 20 mol-%,
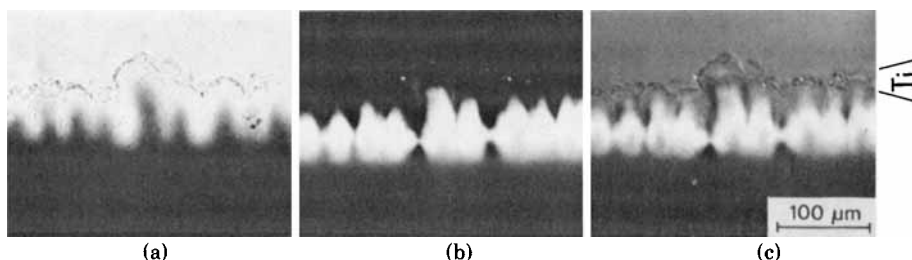

Fig. 3. Typical surface structure of carbon black-containing low-density PE sheets grafted by γ-rays and then saponified. An identical area in a cross section of the grafts was photographed under three different conditions: (a) under an unpolarized white light; (b) between crossed polarizers in the 45° position of the ungrafted PE part; (c) at 80° angle between polarizer and analyzer and in the 45° position.

shows a high adhesive bondability of more than 30 kg/25 mm (adherend failure) in the T_i range of at least more than 10 μm (γ-ray-induced graft) or more than 4 μm (electron-induced graft), in which the surface is 100 mol-% monomer or is covered with the homopolymer layer. According to the above relationship, the retention of the adhesive bondability in oxidative environments will depend largely on the oxidative stability of the homopolymer layer itself; this dependence will hold for both the γ-ray-induced and electron-induced grafts.

Oxidative Stability of Grafted Layer

Table I summarizes preliminary results on the thermal-oxidative and photo-oxidative stability of the γ-ray-induced grafts. The degree of degradation was evaluated by weight loss per grafted amount following acetone extraction treatment at 56°C after aging or weathering. The grafts used for deterioration tests were extracted with acetone until there was no further decrease in weight, where acetone dissolves PMA and partially hydrolized PMA but not PE. Accordingly, the acetone treatment following aging or weathering will extract mainly the PMA component solubilized by chain scission or degradation from the grafts. In fact, the ungrafted PE sheets showed no noticeable weight change during oven aging, whereas some grafts showed a significant weight loss. As shown later, furthermore, stabilized grafts showed no weight loss during oven aging at 80–100°C. In addition, weathering will cause a progressive degradation from the exposed surface rather than homogeneous degradation in the bulk. Therefore, the weight loss values indicate a selective removal of monomer components at least at the initial stages of degradation.

The vapor-phase mutual grafting traps PE and PMA radicals, and the trapped radicals can react with oxygen to yield peroxides or hydroperoxides as the grafted sheets are exposed to air. In order to examine the influences of the remaining hydroperoxides on oxidative degradation, one of the samples grafted under the same condition was heat treated under vacuum at 80°C for 16 hr to terminate the trapped radicals before being exposed to air. Another sample was exposed to air without any radical decay treatment. In Table I, it is apparent that the

TABLE I
Oxidative Stability of Surface Graft Layers Prepared by Gamma Ray-Induced Grafting

Sample	Radical decay treatment[b]	Saponification treatment	Accelerated weathering for 208 hr	Oven aging at 80°C for 228 hr	Oven aging at 80°C for 1000 hr
			Weight loss per grafted amount, %		
LDPE	No	No	89	60	—
LDPE	Yes	No	88	22	—
Black LDPE[a]	No	No	50	22	—
Black LDPE[a]	Yes	No	35	0	—
MDPE	Yes	No	92	3	—
LDPE	No	Yes	87	10	42
LDPE	Yes	Yes	85	10	36
Black LDPE[a]	No	Yes	65	3	15
Black LDPE[a]	Yes	Yes	51	3	14
MDPE	Yes	Yes	86	1	—

[a] The PE sample consists of LDPE and carbon black of 2.6 wt-%.

[b] The grafted PE was heat treated under vacuum at 80°C for 16 hr before being exposed to air.

radical-decayed unsaponified samples show much lower weight loss during oven aging at 80°C up to 208 hr than the nondecayed samples. On the other hand, saponified samples do not show such a difference in weight loss. Since alkyl hydroperoxides decompose in hot alkali,[6] the saponification treatment may decompose the hydroperoxides. It seems unlikely that the carboxyl group introduced by the saponification treatment retards the oxidative degradation. In addition, there is no reason that the hydroperoxides are localized mainly in the surface homopolymer layer, a significant amount of which is removed by saponification treatment.[2]

In Table I, it is also seen that the presence of carbon black in the grafted layer (Fig. 3) is effective to prevent the thermal-oxidative and photo-oxidative degradation of the grafted layer. The effectiveness of the carbon black and the above-mentioned radical decay treatment on the oxidative degradation indicates that the oxidative degradation of the grafted layer also proceeds through the well-known auto-oxidation mechanism[7] of hydrocarbons suggested by Bolland and other workers and that the addition of conventional stabilizers will stabilize the grafted layer against oxidative degradation.

In Table I, all the saponified samples exposed to the weathering apparatus showed an almost complete loss in adhesive bondability (0.5–1.5 kg/25 mm), whereas those aged at 80°C showed no loss (more than 30 kg/25 mm). In addition, the weight loss data show that the grafted layer is resistant to thermal oxidation but not to weathering. This degradative behavior of the homopolymer layer is in agreement with that of poly(alkyl acrylate) homopolymers[8,9] and ethylene–ethyl acrylate copolymers.[10] Conley and Valint[8] observed that poly-(ethyl acrylate), contrary to Steele's early work,[11] was quite stable to thermal-oxidative aging at 100°C. Moreover, Wargotz reported that ethylene–ethyl acrylate copolymer showed the PE-like stability to thermal-oxidative degradation.[10] With respect to the apparent difference between Steele's and Conley's results, Wargotz has suggested[10] that the polymer prepared by redox polymerization (Steele) has a hydroxymethylene group at the end of the polymer chain and, as a result, degrades more rapidly than the polymer containing no such a endgroup (Conley).

Photo-oxidative Degradation

Figure 4 shows the decrease in adhesive bondability of a saponified γ-ray-induced graft (Black LDPE) with accelerated weathering. Figures 5–7 show the ATR spectra, the surface graft structure, the homopolymer layer thickness (T_i), and the weight loss of the degraded grafts corresponding to Figure 4, respectively.

The adhesive bondability to a epoxy adhesive, evaluated by peel strength, rapidly decreases during accelerated weathering (Fig. 4). The ATR spectra (Fig. 5) show a significant decrease in surface graft composition: The 750 cm^{-1} peak of PMA decreases with weathering time (A → B → C), whereas the 720 cm^{-1} peak of PE increases. The optical micrographs of a cross section of the degraded grafts show a progressive degradation from the surface of the grafted layer: the anisotropic copolymer layer is gradually removed along the upheaval structure after rapid removal of the isotropic layer (Figs. 3 and 6). The weight loss occurs rapidly at the initial stages of weathering and then levels off; apparently, this initial weight loss corresponds to the rapid removal of isotropic layer (Fig. 7).
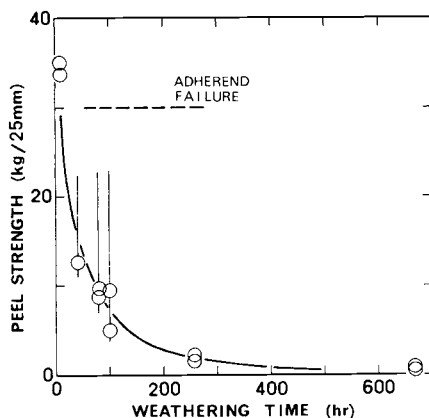
Fig. 4. Changes in adhesive bondability of a grafted surface with accelerated weathering. A γ-ray-induced graft of a carbon black-containing low-density PE (2.0 mm thick) was used.

By comparing the peel strength (Fig. 4) with the T_i value (Fig. 7), it can be concluded that the decrease in adhesive bondability with weathering is due to the degradative removal of the isotropic layer or the surface homopolymer layer. This conclusion is consistent with that obtained from relationship between bond strength and T_i value in undegraded grafts[2]: the high adhesive bondability of the saponified MA grafts is associated with the presence of the surface homopolymer layer.

In the LDPE grafts containing no carbon black, also, the photo-oxidative degradation proceeds selectively along the upheaved graft copolymer layer after
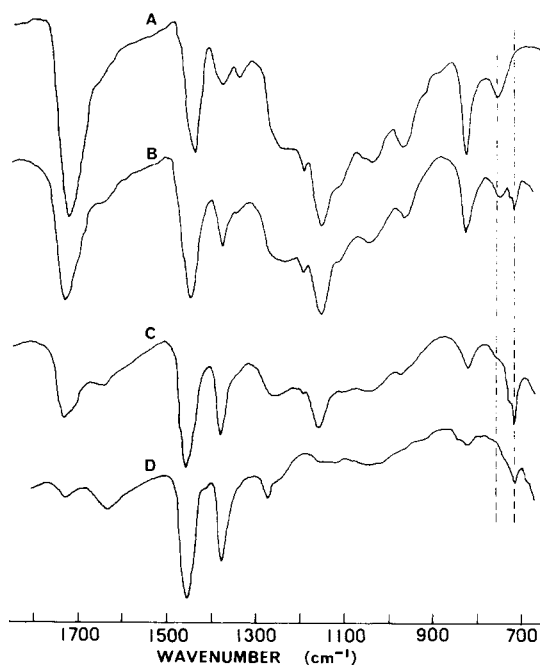

Fig. 5. ATR infrared spectra of the degraded grafts corresponding to Figure 4. Nujol was used in spectra B and C as an immersion liquid: (A) undegraded; (B) 40-hr exposed; (C) 666-hr exposed; (D) nujol.

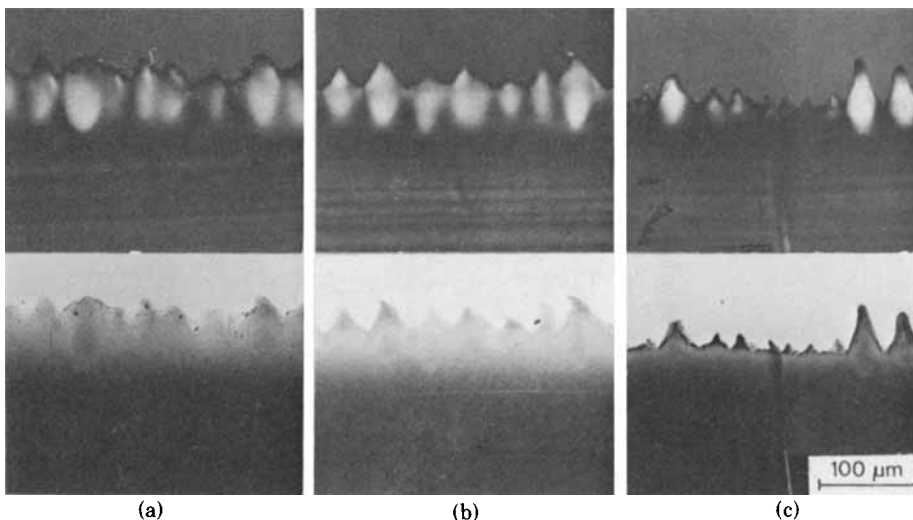(a)   (b)   (c)

Fig. 6. Surface structure of the degraded grafts corresponding to Figure 4. An identical area in the sections was photographed between crossed polarizers (top) and under unpolarized white light (bottom): (a) 40-hr exposed; (b) 100-hr exposed; (c) 666-hr exposed.

the complete removal of the isotropic layer as well as in the Black LDPE grafts containing carbon black (Fig. 6). Accordingly, the selective degradation does not result from the light-screening[12] and antioxidant[13] effects of carbon black (present in the copolymer layer) but from the graft composition distribution. That is, it results from a higher sensitivity of PMA (or hydrolyzed PMA) component in photodegradation than that of PE component since the contour line of graft composition in the grafted layer proceeds along the upheaved structure.

The higher sensitivity of PMA is due to the fact that PMA has a UV-absorbing ester group, whereas PE does not have such a group except traces of carbonyl groups introduced as an inpurity structure. In the photodegradation of PMA[13] and poly(ethyl acrylate),[14] furthermore, the major primary process has been suggested to be splitting-off of the ester side chain. Since the unsaponified homopolymer layer possesses some side chain links,[2] the side-chain scissions can
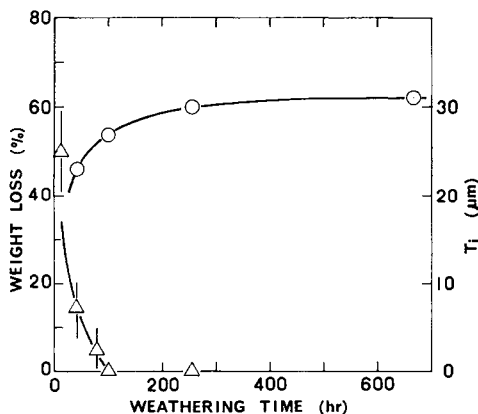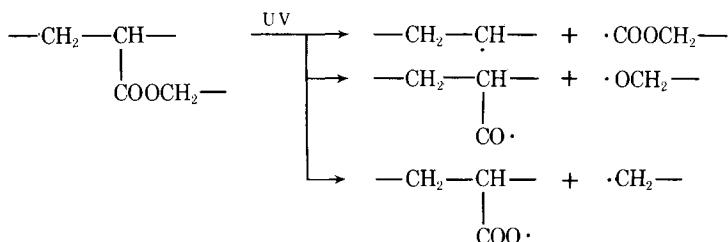

Fig. 7. Isotropic layer thickness (T_i) and weight loss per grafted amount vs weathering time, corresponding to Figure 4: ($\triangle$) T_i; ($\bigcirc$) weight loss.

also contribute to the rapid removal of the unsaponified isotropic layer:

$$—CH_2—CH—\ \xrightarrow{UV}\ \begin{cases} —CH_2—\overset{\cdot}{CH}— & + & \cdot COOCH_2— \\ —CH_2—CH— & + & \cdot OCH_2— \\ \quad\quad\quad\ \ \underset{CO\cdot}{|} \\ —CH_2—CH— & + & \cdot CH_2— \\ \quad\quad\quad\ \ \underset{COO\cdot}{|} \end{cases}$$

The initial side-chain scissions, which are accompanied by hydrogen abstraction from the main chains, lead to the main-chain scissions via the auto-oxidation process.[7]

Stabilization

Figure 8 shows weight loss (per grafted amount) versus oven-aging time at 100°C of the electron-induced grafts stabilized with an antioxidant, TBBMP, which is widely used in cable-sheathed PE and shows a synergism[5] with carbon black. Apparently, the antioxidant stabilizes the grafted layer against oven aging at 100°C. The peel strength data also showed no change in adhesive bondability during the oxidative aging.

In Table I and Figure 7, the weight loss (per grafted amount) during accelerated weathering exceeds 50% despite only one side exposure of sheet. This means that PE component is also removed from the exposed surface or that the thermal-oxidative degradation of PMA component occurs also on the unexposed surface. In order to separate the contribution of thermal oxidation on the unexposed surface to the weight loss, only one surface of PE sheets was selectively surface grafted by masking another side with a paint. Table II summarizes the effects of carbon black and stabilizers on weatherability of the grafted layers. Although the thermal-oxidative degradation occurs even on the unexposed surface, the presence of both carbon black and antioxidant stabilizes almost
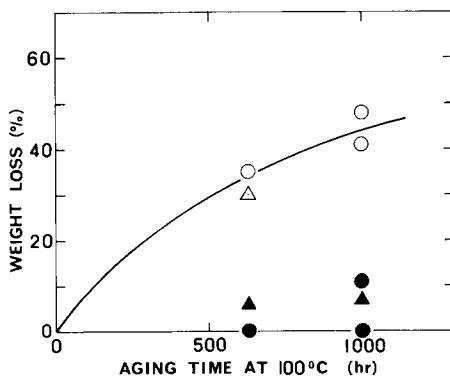

Fig. 8. Effects of antioxidant on the thermal-oxidative degradation of grafted layers. Electron-induced grafts of a low-density PE (LDPE) and a carbon black-containing low-density PE (Black LDPE) sheets were stabilized with 4,4'-thiobis(2-*tert*-butyl-5-methylphenol): (△) LDPE; (▲) LDPE, stabilized; (○) Black LDPE; (●) Black LDPE, stabilized.

TABLE II
Effects of Carbon Black[a] and Stabilizers on Weatherability of Grafted Layers

Sample	Stabilizer[b]	Exposed surface[c]	Weight loss per grafted amount, %[d]	
			γ-Ray-induced.graft	Electron-induced graft
LDPE	Added	Ungrafted	1	19
Black LDPE[a]	None	Ungrafted	6	28
Black LDPE[a]	Added	Ungrafted	0	0
LDPE	None	Grafted	63	221
LDPE	Added	Grafted	10	112
Black LDPE[a]	None	Grafted	36	76
Black LDPE[a]	Added	Grafted	0	56

[a] The original PE sheet contains carbon black of 2.6 wt-%. Black LDPE consists of LDPE and carbon black.

[b] A combination of 2-hydroxy-4-n-octoxybenzophenone and 4,4'-thiobis(2-$tert$-butyl-5-methylphenol).

[c] Only one side of PE sheets was selectively surface grafted. The sheet thickness was 0.5 (electron-induced grafts) and 2.0 mm (γ-ray-induced grafts).

[d] Accelerated weathering for 200 hr followed by acetone extraction treatment.

completely the grafted layer. This coincides with the oven aging results (Fig. 8). Furthermore, the presence retards the photo-oxidative degradation of the exposed surface.

Since saponified PMA is dissolved in water, the water spray washes away continuously the degraded surface to produce a new surface for photodegradation. Further, the stabilizers added into the grafted layer are gradually removed together with the removal of degradation products, even if the stabilizers are not dissolved in water. The progressiveness in degradation causes differences in stabilization effect between weathering tests with water spray and without water spray and between the γ-ray-induced and electron-induced grafts. For example, the bondability of unstabilized grafts disappears more rapidly during weathering with water spray than during weathering without water spray (Fig. 9). In addition, the percent weight loss per grafted amount of the electron-induced grafts becomes more significant than that of the γ-ray-induced grafts (Table II), since
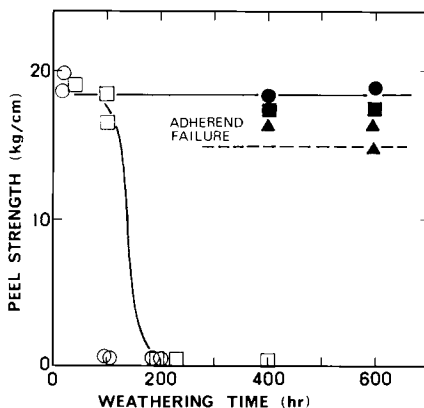

Fig. 9. Stabilization of grafted surface against accelerated weathering without water spray. An electron-induced graft of a carbon black-containing low-density PE sheet was stabilized with three different combinations of antioxidants and ultraviolet absorbers: (O) unstabilized, with water spray; (□) unstabilized, without water spray; (●, ▲, ■) stabilized, without water spray.
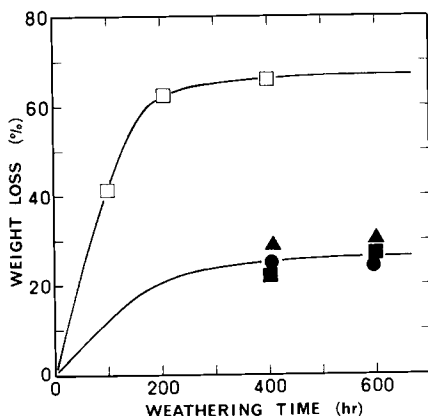
Fig. 10. Weight loss per grafted amount vs weathering time, corresponding to Figure 9.

the grafted layer thickness of the former is much smaller than that of the latter. Figures 9 and 10 show the stabilization effect on an electron-induced graft (Black LDPE) against accelerated weathering without water spray. Apparently, the stabilized graft containing carbon black retains the adhesive bondability at least up to 600-hr exposure with no water spray. On the other hand, there is an weight loss of 20%–30%; this loss may correspond to the degradation of a layer into which the UV light penetrates.

CONCLUSIONS

The rapid bondability loss during weathering is due to the degradative removal of the homopolymer layer, and the bondability retention during thermal-oxidative aging is due to the maintenance of the layer. This relationship between bondability and homopolymer layer in degraded grafts coincides with that[2] in undegraded grafts. The stabilization effects of stabilizers and carbon black support the previous conclusion[2] that the homopolymer is not only crosslinked but is also linked by chemical bonds to the PE and grafted PMA chains in the inner copolymer layer.

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