

Surface Modification of Polyethylene by Radiation-Induced Grafting for Adhesive Bonding. I. Relationship Between Adhesive Bond Strength and Surface Composition

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Synopsis

A number of vinyl monomers have been surface grafted onto a polyethylene sheet by the mutual irradiation in monomer vapor and by a trapped-radical technique. The surface composition of the grafted sheets has been determined by means of ATR infrared spectrophotometry and compared with the peel strength of the joints bonded with conventional structural adhesives. In the methyl acrylate grafts followed by a saponification treatment, only the surfaces having graft compositions of more than 80 mole-% methyl acrylate give a high peel strength. A similar relationship between peel strength and surface composition is found in the surface grafts of vinyl acetate, acrylic acid, acrylamide, and methylolacrylamide. It is concluded that the formation of a surface with such a high monomer content is a necessary condition for the strong adhesive bonding of grafted polyethylenes at bonding temperatures below the softening point. Moreover, the adhesive bondability of the highly modified surfaces with epoxy adhesives is significantly enhanced by the introduction of carboxy and carbamyl radicals.

INTRODUCTION

Surface modification of polyethylene (PE) is a prerequisite for its successful structural adhesive bonding at temperatures below the softening point of PE. Among many surface treatments proposed,^{1,2} the most effective techniques are³ CASING (Crosslinking with Activated Species of Inert Gases),⁴ oxidative treatments using activated oxygen gas plasma,^{5,6} and chromic acid.⁷ However, these techniques have some serious drawbacks: For instance, the adhesive bondability of the surfaces prepared by oxidative treatments is easily lost by heat aging,⁸ Weather-Ometer exposure,⁸ and rubbing⁹ with papers or clothes. Also when the pretreated sheets are bonded with epoxy adhesives and the bond strength of their joints is evaluated by the T-peel test, it has been found⁸ that CASING treatment of low-density PE results in low peel strength (less than 1 kg/25 mm), whereas that of medium- or high-density PE produces relatively high peel strengths.

Very few studies on the surface modification of PE by radiation grafting for adhesive bonding have been published. Though work has been done on the adhesive properties of radiation-grafted polyolefin powders^{10,11} and thin

films,^{12,13} these are not surface grafts. We have found several surface grafts¹⁴ having a high bondability with epoxy adhesives as a result of extensive investigations on a number of grafting systems. A preliminary paper has been published.¹⁵ The present paper is concerned with the relationship between the adhesive bond strength and the surface composition of surface grafts.

EXPERIMENTAL

Materials

A low-density PE, DFD-6005 (density 0.919 g/cm³, melt index 0.25 g/10 min, Nippon Unicar) was used. A sheet of 0.7 mm thickness was prepared by compression molding at 150°C. The sheet was cut into a rectangular shape measuring 10 mm wide and 80 mm long, treated with reagent-grade cyclohexanone at 55°C for 50 hr to extract antioxidant, washed repeatedly with methanol at 60°C, and then dried under vacuum at 60°C for more than ten days.

A commercial vinyl acetate (VAc) was purified according to a procedure similar to that described by Matsumoto and Maeda.¹⁶ The purified VAc was then prepolymerized with N,N'-azoisobutyronitrile and distilled under vacuum before use. Acrylamide (AM), methylolacrylamide (MAM), and methacrylamide were purified by recrystallization from a benzene solution. The other monomers were distilled in nitrogen or under vacuum before use.

Graft Polymerization

Two grafting techniques were performed: (1) mutual irradiation of the PE sheet in the saturated vapor pressure of monomer at room temperature, and (2) preirradiation of the PE sheet in air at -78°C followed by contact with monomer or monomer solution. The mutual grafting in monomer vapor was carried out by a method similar to that reported by Takamatsu and Shinohara.¹⁷ The dose rate from a Co-60 source was 0.5-1.7 × 10⁵ rad/hr. In the preirradiation method the PE sheet was placed in a glass ampoule¹⁵ with a taper joint at the top. After a calcium chloride tube was attached to the top, the ampoule was irradiated at -78°C at a dose rate of 5.2 × 10⁴ rad/hr. The irradiated ampoule was filled with monomer or monomer solution, connected to a vacuum line, and then sealed off at a pressure below 1 × 10⁻³ mm Hg after the monomer was degassed. The graft polymerization was carried out by keeping the ampoules at a certain temperature.

The grafted sheets were extracted at 55-60°C with suitable solvents to remove the homopolymers and then dried *in vacuo* at 60°C. The overall graft composition was expressed as per cent graft calculated from the equation

$$\% \text{ graft} = \frac{\text{final sheet weight} - \text{initial sheet weight}}{\text{initial sheet weight}} \times 100$$

ATR Infrared Spectroscopy

Attenuated total reflection (ATR) infrared analysis was carried out by using a Model EPI-S2 Hitachi infrared spectrometer and a Model ATR-1 Hi-

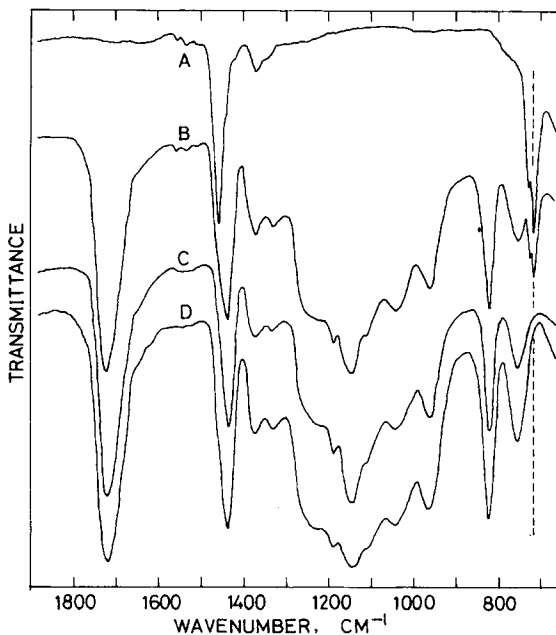


Fig. 1. ATR spectra of methyl acrylate-grafted polyethylene sheets: (A) polyethylene; (B) grafted by preirradiation to 0.86 Mrad and subsequent contact with liquid monomer at 30°C for 18 hr, 500% graft; (C) grafted by vapor-phase mutual irradiation to 0.38 Mrad at 5.2×10^4 rad/hr, 13% graft; (D) poly(methyl acrylate).

tachi ATR attachment. The reflector element consisted of KRS-5 prisms, giving three reflections. The reflected energy was at a maximum at an angle of incidence of 40 degrees.

Interference Microscopy

The composition distribution in grafted PE sheets and the thickness of the grafted layer were observed with an interference microscope (Leitz, Germany). Diallyl phthalate ($n = 1.517$) was used as immersion liquid for low-density PE ($n = 1.51$).

Adhesive Bond Strength

A peel specimen consisting of graft-adhesive-graft was prepared to evaluate the adhesive bondability of the grafted sheets. An aminopolyamide-modified epoxy adhesive and a polyester acrylate adhesive (Bond ML, Konishi Gissuke) were used. The epoxy adhesive consists of 70 parts by weight of a liquid epoxy resin (Epicote 828, Shell Chemical) and 30 parts by weight of an aminopolyamide resin (amine value = 330, Sanyo Chemical Industry). The assembly was lightly weighted (1 kg/cm^2), and the adhesive was allowed to cure at 80°C for at least 3 hr. The thickness of the adhesive layer was maintained constant by insertion of a stainless steel wire 100 μm in diameter. The 180-degree peel strength at 23°C was measured by an Instron Universal Testing Machine (at a cross-head speed of 10 cm/min) according to ASTM D903-49.

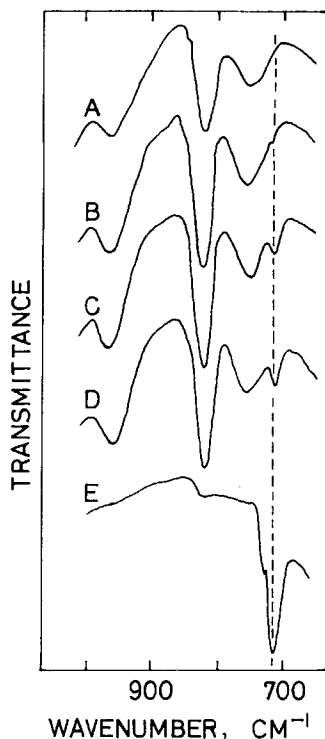


Fig. 2. Changes of ATR spectrum with abrasion of the surface of methyl acrylate graft corresponding to spectrum C in Fig. 1: (A) unabrased; (B), (C), (D), and (E) abraded; the extent of abrasion is $E > D > C > B$.

RESULTS AND DISCUSSION

Methyl Acrylate Grafts

The ATR spectra of the PE sheets grafted with methyl acrylate (MA) by two different grafting techniques are shown in Figure 1 together with the spectra of PE and poly(methyl acrylate) (PMA). By comparing spectrum A with spectrum D, it is seen that the absorption peaks of PE at $720\text{--}730\text{ cm}^{-1}$ overlap, with no peak of PMA. Thus, these bands can be used as a reference band for the PE component. Spectrum B, which was grafted by preirradiation and subsequent contact with liquid MA, has both the PE and PMA bands. On the other hand, spectrum C, which was grafted by vapor-phase mutual irradiation, has only the PMA bands but no PE band (e.g., at $720\text{--}730\text{ cm}^{-1}$). When the surface corresponding to spectrum C is gradually abraded with sand paper and KBr powder, the bands of $720\text{--}730\text{ cm}^{-1}$ appear and increase with abrading. The increase accompanies the decrease of the PMA bands (Fig. 2). These results indicate that the surface composition of spectrum C reaches 100% MA. The interference micrographs of a cross section of the grafts corresponding to spectra B and C are given in Figure 3. The interference fringe corresponds to the composition distribution in the grafts when the thickness of the cross section is constant over the section. In Figure 3, it is seen that the composition of the graft corresponding to spectrum B is ho-

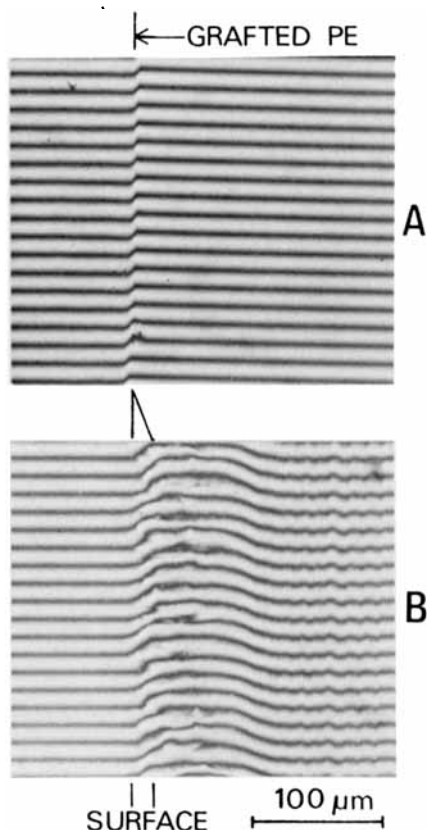


Fig. 3. Interference micrographs of a cross section of the methyl acrylate grafts corresponding to those in Fig. 1: (A) spectrum B; (B) spectrum C.

mogeneous throughout the sample, viz., homogeneous graft, and that of spectrum C is confined to the surface region, viz., surface graft. At the surface of the latter, a drop in fringe is observed; this drop does not arise from the decrease in grafted MA content since its ATR spectrum exhibits 100% MA. A detailed study¹⁸ of the surface topography has shown that the drop is due to a rough or macroscopically porous surface structure. From these results, it is evident that mutual grafting produces a surface graft having a surface layer consisting of only MA component, viz., homopolymer layer; whereas the preirradiation method results in a homogeneous graft having a low MA content in the surface region in spite of the high overall MA content (500% graft).

When the grafted sheets are saponified and bonded to each other with an epoxy adhesive, the sheets grafted by mutual irradiation yield a high peel strength (>5 kg/cm, adherend failure); whereas those grafted by the preirradiation method result in a low peel strength (0.6 kg/cm).¹⁵ Therefore, it seems likely that the formation of the PMA homopolymer layer (100% MA) on the surface is responsible for the high bondability with the epoxy adhesive.

Vinyl Acetate Grafts

Figure 4 shows the ATR spectra of the PE sheets grafted with VAc by three different grafting techniques, together with the spectra of PE and poly(vinyl

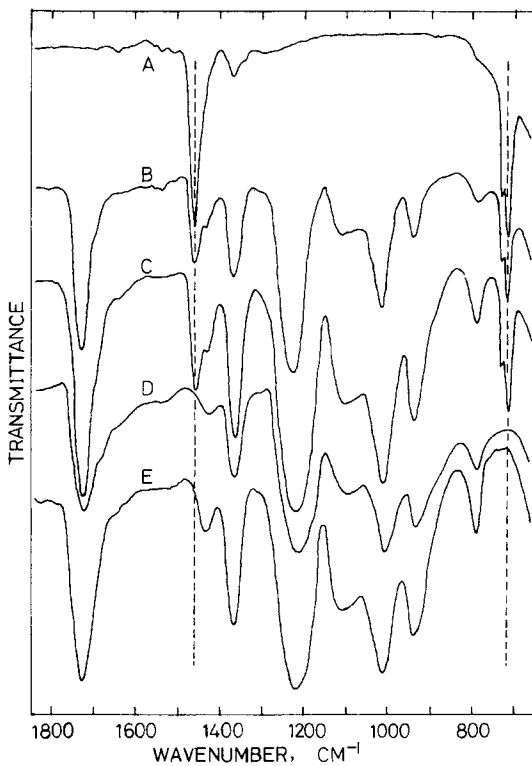


Fig. 4. ATR spectra of vinyl acetate-grafted polyethylene sheets: (A) polyethylene; (B) grafted by preirradiation to 0.86 Mrad and subsequent contact with liquid monomer at 50°C for 3 hr, 45% graft; (C) grafted by preirradiation to 2.14 Mrad and subsequent contact with monomer vapor at 23°C for 21 hr, 136% graft; (D) grafted by vapor-phase mutual irradiation to 1.98 Mrad at 1.1×10^5 rad/hr, 20% graft; (E) poly(vinyl acetate).

acetate) (PVAc). Figure 5 gives the interference micrographs of a cross section of the grafts corresponding to Figure 4. The absorption peaks of PE at 720–730 and 1470 cm^{-1} overlap, with no peak of PVAc (Fig. 4). Spectrum D, which was grafted by vapor-phase mutual irradiation, has only the peaks of PVAc, and no peak of PE at 720–730 and 1470 cm^{-1} . On the other hand, spectra B and C grafted by the preirradiation method have both the PE and PVAc bands. Abrasion of the surface, corresponding to spectrum D, resulted in the appearance of the 720–730 and 1470 cm^{-1} peaks. The graft corresponding to spectrum D exhibits a surface graft, and the grafts corresponding to spectra B and C, a homogeneous graft (Fig. 5). Because of the smoothness of the surfaces of spectra B and C, the sharp drop in fringe at these surfaces seems to arise from the decrease of monomer content; this decrease is the same as that due to the retardation effect reported by Matsuo, Iino, and Kondo.¹⁹ On the other hand, the drop in the surface region of spectrum D arises from a rough surface structure similar to that of the MA graft. When the grafted sheets are bonded with epoxy and polyester acrylate adhesives, only the graft corresponding to spectrum D exhibits a high peel strength.¹⁵ All the results lead to the same conclusion as that in the MA grafts: only vapor-phase mutual grafting produces a surface graft having the PVAc homo-

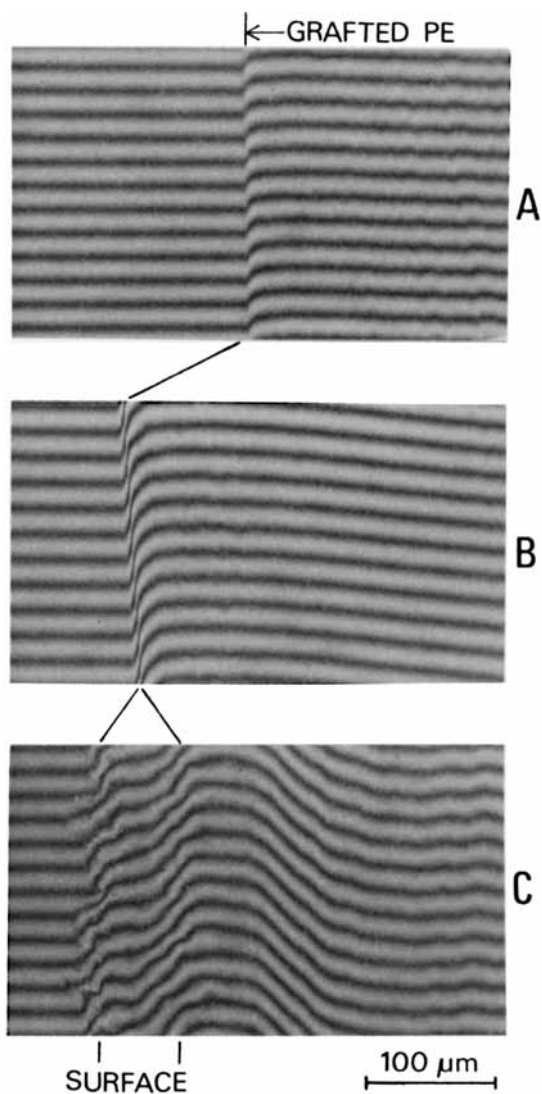


Fig. 5. Interference micrographs of a cross section of vinyl acetate grafts corresponding to those in Fig. 4: (A) spectrum B; (B) spectrum C; (C) spectrum D.

polymer layer on the surface. The formation of the layer is responsible for the strong adhesive bonding.

Relation Between Peel Strength and Surface Composition

In order to obtain a calibration curve for the ATR spectrophotometric determination of the surface composition of the MA grafts, a series of homogeneous graft copolymers of known composition were prepared by mutual irradiation of the PE sheet in a methanol solution of MA and by subsequent mixing on a two-roll mill. The polyblends of the grafts and the homopolymer (PMA) were used for the calibration in the range of 60–100% MA. The ATR spectra of the homogeneous grafts and the blends are shown in Figure 6. The

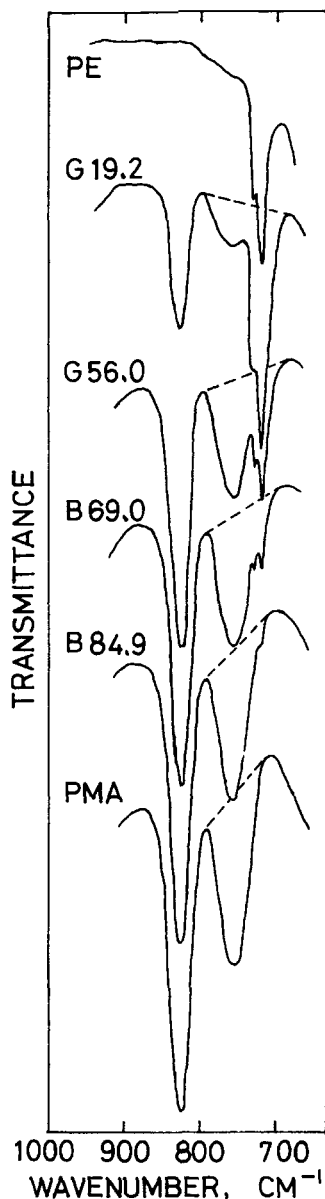


Fig. 6. Typical ATR spectra of homogeneous poly(ethylene-*g*-methyl acrylate) copolymers (G) and polyblends (B) of grafts and poly(methyl acrylate). Numbers on the spectra refer to methyl acrylate content (mole-%).

ATR spectra of the VAc grafts and the blends are shown in Figure 7. It can be seen that the doublet of PE at 720–730 cm^{-1} decreases and the bands of PMA and PVAc increase with corresponding monomer content. The 730 cm^{-1} component is associated with CH_2 rocking in the crystalline region of PE, and the 720 cm^{-1} component is associated with CH_2 rocking in the amorphous region, with some contribution from the crystalline region.^{20,21} In addition, the absorbance ratio of the 720–730 cm^{-1} band was used as a measure of the relative changes in crystallinity.²² When the grafting disrupts the

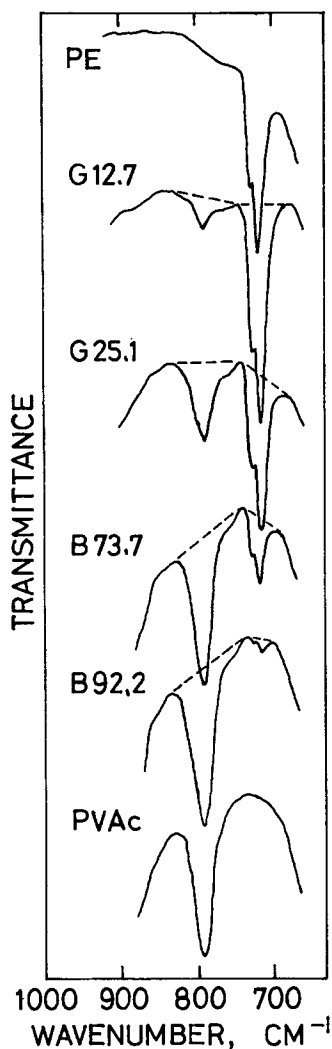


Fig. 7. Typical ATR spectra of homogeneous poly(ethylene-*g*-vinyl acetate) copolymers (G) and polyblends (B) of grafts and poly(vinyl acetate). Numbers on the spectra refer to vinyl acetate content (mole-%).

crystallites of PE, accordingly, the 730 cm^{-1} band should decrease with grafting more rapidly than the 720 cm^{-1} band and finally disappear. For the quantitative determination of the composition in the range of high monomer content, therefore, the use of the 720 cm^{-1} band as a reference band of the PE component seems to be more suitable than the 730 cm^{-1} band. In this work, the absorbance ratio of the 720 to 750 cm^{-1} band was used for the determination of MA content in the MA grafts, and the ratio of the 720 to 795 cm^{-1} band for the determination of VAc content in the VAc grafts, respectively. The absorbances were determined by the baselines as shown in Figures 6 and 7. A calibration curve from Figures 6 and 7 is given in Figure 8. By using these calibration curves, the monomer content in the surface region of the unsaponified grafts was determined.

The surface grafts, having a series of surface compositions, were prepared

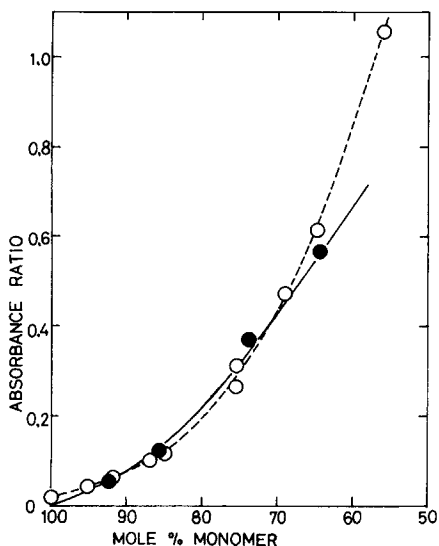


Fig. 8. Calibration curve for ATR spectrophotometric determination of surface composition of grafted polyethylene sheets: (O) A_{720}/A_{750} vs. methyl acrylate content; (●) A_{720}/A_{795} vs. vinyl acetate content.

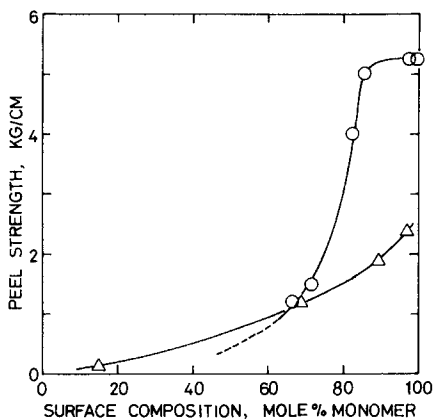


Fig. 9. Relationship between peel strength and surface composition of surface-grafted polyethylene sheets: (O) methyl acrylate grafts; (Δ) vinyl acetate grafts.

by vapor-phase mutual irradiation. The MA grafts were partially saponified with a 0.5N KOH solution in methanol at 50°C for 4.0 hr, neutralized with an aqueous solution of HCl (acetone/water = 1/1), washed with distilled water, and then extracted at 56°C with an acetone/water = 1/1 solution and acetone. After being dried, the saponified grafts were bonded to each other with the epoxy adhesive. The relations between peel strength of the saponified grafts and surface composition of the unsaponified grafts are illustrated in Figure 9 together with that in the VAc grafts, which were bonded with the polyester acrylate adhesive without saponification. The peel strength of the MA grafts increases with surface monomer content and reaches adherend failure (>5.0

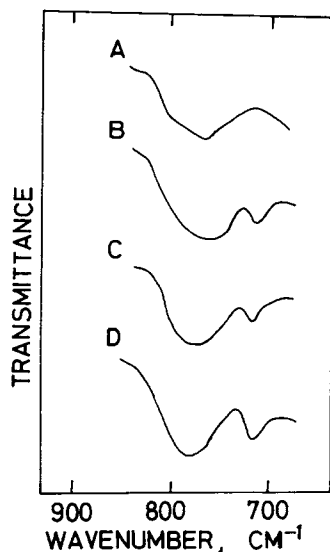


Fig. 10. Changes of ATR spectrum with abrasion of the surface of a polyethylene sheet grafted by preirradiation to 0.85 Mrad and subsequent contact with acrylic acid at 50°C for 1.7 hr: (A) unabraded; (B), (C), and (D) abraded; the extent of abrasion is $D > C > B$.

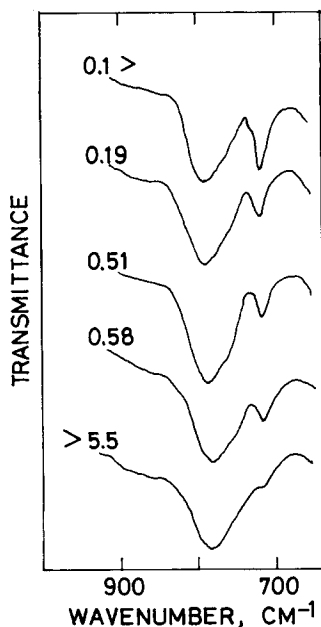


Fig. 11. Relationship between peel strength and the 720 cm^{-1} band of acrylic acid grafts having various surface compositions, which were grafted by preirradiation to 0.30–1.8 Mrad and subsequent contact with liquid monomer at 50°C for 0.6–15.0 hr. Numbers on the spectra refer to peel strength (kg/cm).

kg/cm) at surface compositions of more than 80 mole-% monomer (Fig. 9). If the surface monomer content (MA + AA) does not change during the saponification process, this result indicates that this extremely high monomer content at the surface is responsible for the high bondability with the adhesive.

The VAc grafts give a similar result, where the peel strength increases with surface monomer content up to 100% VAc. In conclusion, formation of surfaces with monomer contents of more than 80 mole-% seems to be a necessary condition for a strong bonding of the grafts with the adhesives, even if it is not a sufficient condition.

Acrylic Acid, Acrylamide, and Methylolacrylamide Grafts

Surface grafts with acrylic acid (AA), acrylamide (AM), and methylolacrylamide (MAM) by preirradiation and subsequent contact with the monomer in liquid phase or in solutions have been found¹⁵ to have a high surface monomer content and bondability with the epoxy adhesive. On the other hand, preirradiation followed by contact with the vapor-phase monomer and vapor-phase mutual irradiation did not produce such a surface graft because of the low volatility of these monomers. Further, mutual irradiation in liquid AA and in methanol solutions of AM and MAM resulted in rapid homopolymerization and a low extent of grafting. In conclusion, only the preirradiation method followed by contact with liquid-phase monomer or monomer solution can produce surfaces having high content of AA, AM, and MAM.

In Figure 10, the ATR spectrum (A) of AA graft having a high bondability with the epoxy adhesive exhibits no 720–730 cm^{-1} band of PE. Abrasion of this surface results in the appearance of the 720 cm^{-1} peak. AA grafts having various surface compositions were prepared by changing the total dose and the contact time. The ATR spectra and the peel strengths of the surface grafts are shown in Figure 11. It can be seen that the peel strength increases with decreasing 720 cm^{-1} peak and reaches adherend failure with the disappearance of the peak. A similar relation between peel strength and the peak was observed in the surface grafts of AM and MAM. These results lead to the same conclusion as those for the MA and VAc grafts: the formation of surfaces having a high monomer content is a necessary condition for strong adhesive bonding of AA, AM, and MAM grafts.

Monomer Dependence of Formation of Homopolymer Layer by Vapor-Phase Mutual Grafting

As shown above, vapor-phase mutual grafting of MA and VAc yields surface grafts with surface composition of 100% monomer. The other grafting methods, including preirradiation and liquid-phase mutual grafting, did not produce a surface graft with these monomers.

According to Harrick's calculations²³ concerning the penetration depth of the incident beam, it can be estimated that the penetration depth into low-density PE ($n = 1.51$) at 720 cm^{-1} and PMA ($n = 1.48$) at 750 cm^{-1} are about 9 and 6 μm , respectively. Therefore, the disappearance of the 720 cm^{-1} peak in the ATR spectra of the surface grafts indicates the presence (on the surface) of the homopolymer layer at least 6 μm in thickness. The grafted sheets were extracted with acetone in a Soxhlet extractor until there was no further decrease in weight. A further extraction with the other solvents which dissolve PMA, but not PE, resulted in no weight loss of the sheets. Moreover, the homopolymer layer containing stabilizers is relatively stable to

heat aging and Weather-Ometer exposure followed by acetone extraction treatment, whereas the layer containing no stabilizer results in a rapid removal of the layer from the surface.²⁴ These results indicate that the PMA chains in the homopolymer layer are linked by chemical bonds to the PE chains and/or the grafted side chains in the interior graft copolymer layer. To the author's knowledge, no paper has been published on the formation of such a homopolymer layer.

In order to clarify the monomer dependence of the formation of the homopolymer layer, a number of vinyl monomers were surface grafted onto the PE sheet by vapor-phase mutual grafting. The results are summarized in Table I. All the monomers in Table I yielded a surface graft under appropriate grafting condition. Only MA, VAc, and methyl methacrylate, however, produced the homopolymer layer within 1.0 Mrad of the total dose.

The following processes can contribute to an increase of monomer content on the surface: (1) primary graft copolymerization from the PE radicals, (2) secondary graft copolymerization from the grafted side chains, (3) concurrent homopolymerization followed by recombination with the grafted side chain and PE radicals. In process 1, the grafting rate increases with increasing initiation and propagation rates and with decreasing termination rate according to kinetics²⁵ similar to those for homogeneous homopolymerization. It is unlikely, however, that a homopolymer layer as thick as 6 μm is formed only by the direct propagation of grafting chains from the PE radicals. Processes 2 and 3 must also contribute to the formation of the homopolymer layer. The relative *G*-values for radical formation of PMA (MA), PVAc (VAc), and poly(methyl methacrylate) (methyl methacrylate) are higher than those of PE, poly(acrylonitrile) (acrylonitrile), and polystyrene (styrene).^{26,27} In addition, a thin film of PMA and PVAc was deposited on the wall of the glass ampoule during grafting; such a deposition can also occur on the grafting surfaces. These facts support the view that processes 2 and 3 play an important role in

TABLE I
Formation of Homopolymer Layer by Vapor-Phase Mutual Irradiation^a

Monomer	<i>G</i> -Value of monomer (polymer) ^b	Formation of the homopolymer layer ^c
Vinyl acetate	33.0	yes
Methyl acrylate	23.5	yes
Ethyl acrylate	—	yes
Methyl methacrylate	27.5	yes
Acrylonitrile	2.7	no
Methacrylonitrile	—	no
Styrene	1.6	no
4-Vinylpyridine	—	no
(Polyethylene)	5-6	—

^a The polyethylene sheet was irradiated in the saturated vapor pressure of the monomer at room temperature to 1.0 Mrad at $0.5\text{--}1.7 \times 10^5$ rad/hr.

^b Taken from ref. 26.

^c Determined from the disappearance of the 720 cm^{-1} peak in the ATR spectra.

the formation of the homopolymer layer. The monomer dependence of the formation of the layer may arise from the difference in the G -values for the radical formation of the monomers, grafted side chains, and homopolymers.

Monomer Dependence of Surface Formation Having High Monomer Content by Trapped Radical Technique

A number of vinyl monomers were grafted onto the PE sheet by the preirradiation method. The results are summarized in Table II. The penetration rate of the grafting front or the resulting composition distribution throughout the grafted sheets depends on whether the grafted side chains are soluble in the grafting medium or not. A similar dependence has been observed in other grafting systems^{28,29,30} and explained in terms of whether the diffusion of the monomer through the grafted layer decreases³¹ or increases^{28,29} as the grafting proceeds. Surfaces having high monomer content and adhesive bondability, however, were formed only in the grafting of AA, AM, and MAM. The grafting of methacrylamide, methacrylic acid, acrylonitrile, and methacrylonitrile, which was confined to the surface region, resulted in low peel strength and monomer content on the surface. Apparently, whether the grafting front proceeds to the inner part of the sheet or not is not a determining factor for the formation of surfaces having a high monomer content. Thus, on the considerations of the monomer dependence of the formation of such surfaces, the graft copolymerization occurring only at the surface, to

TABLE II
Formation of Surfaces Having High Monomer Content, by Preirradiation Method^a

Monomer or monomer solution	$(k_p/k_t) \times 10^{*b}$	$k_p,^b$ l./mole·sec	Rate of penetration of grafting front ^c	Maximum peel strength ^d	Maximum monomer content on the surface ^e
Acrylamide-water	1240	18,000	medium	high	high
Acrylamide-methanol	—	—	very slow	high	high
Methylolacrylamide-water	—	—	medium	high	high
Methylolacrylamide-methanol	—	—	very slow	high	high
Acrylic acid	—	—	slow	high	high
Acrylic acid-water	—	—	medium	high	high
Vinyl acetate	14-17	1000-1100	rapid	low	low
Methyl acrylate	28-168	720-1580	rapid	low	low
Methacrylamide-water	48	800	medium	low	low
Methacrylamide-methanol	—	—	very slow	low	low
Methacrylic acid	—	—	slow	low	low
Methyl methacrylate	4.7-14	140-513	rapid	low	low
Acrylonitrile	10.4	52-127	very slow	low	low
Methacrylonitrile	1.0-1.2	26	very slow	low	low
Styrene	0.54-4.9	24-55	medium	low	low
4-Vinylpyridine	4	12	medium	low	low
N-Vinylpyrrolidone	—	—	medium	low	low

^a The polyethylene sheet was preirradiated in air at -78°C to 0.8-4.0 Mrad and then contacted with the liquid monomer or the monomer solution (40 wt-%) at $30-50^\circ\text{C}$.

^b Taken from ref. 36. The values were determined at $20-30^\circ\text{C}$ by the rotating sector technique, except those of 4-vinylpyridine and acrylonitrile.

^c Determined from the interference micrographs of cross sections of the grafted sheets.

^d Bonded with the epoxy adhesive. High and low peel strengths refer to peel strengths of more than 2.0 kg/cm and less than 0.8 kg/cm, respectively.

^e Determined from the disappearance of 720 cm^{-1} peak in the ATR spectra.

first approximation, can be taken into account; in this case, the effects of monomer diffusion on the grafting can be neglected.

In trapped-radical grafting, in which the effects of monomer diffusion are neglected, the amount of the grafted monomer G can be given by the following equation:³²

$$G = k_p k_t^{-1} [M] \ln (1 + k_t [P\cdot]_0 t) \quad (1)$$

where $[P\cdot]_0$ is the initial concentration of the trapped PE radicals, $[M]$ is monomer concentration, and k_p and k_t are the rate constants for propagation and termination, respectively. According to eq. (1), the grafting amount G at the surface increases with increasing k_p and with decreasing k_t of the monomer, when $[P\cdot]_0$, $[M]$, and t are constant among the grafting systems of the various monomers. The rate constants for propagation and termination of AM have been reported.³³ The ratio k_p/k_t exceeds that reported for any other monomer, k_p being exceptionally high and k_t rather low, as shown in Table II. Further, the k_p value of AM is much higher than methacrylamide.³⁴ In addition, it is well known³⁵ that the radical polymerization of high-purity AA can begin spontaneously at room temperature or lower and can become extremely violent, whereas that of methacrylic acid is milder than that of AA. This indicates that the ratio $k_p/k_t^{1/2}$ of AA is very high and exceeds that of methacrylic acid. The k_t value depends significantly on whether the grafted side chains are soluble in the grafting medium or not. However, whether surfaces having a high monomer content are formed or not is independent of the medium. Therefore, the monomer dependence of the formation of such surfaces may not arise from the difference in termination rate but from the difference in propagation rate of the growing chains; the relatively high propagation rates of AA, AM, and MAM can contribute to raise the monomer content on the surfaces through the direct graft copolymerization from the PE radicals and the homopolymerization followed by recombination with the grafted side chain radicals.

Adhesive Bondability of Surfaces Having High Monomer Content

For strong adhesive bonding of the surface grafts with epoxy adhesives, the formation of surfaces having a high monomer content is a necessary, but not sufficient, condition. The maximum peel strength of unsaponified MA and methyl methacrylate grafts (bonded with the epoxy adhesive) was less than 0.6 kg/cm, and that of the VAc grafts was 2.0–2.5 kg/cm, even when the surface compositions were 100% monomer. The peel strength of the MA grafts increases¹⁵ abruptly with saponification and reaches adherend failure; this increase is attributed to a change from $-\text{COOCH}_3$ to $-\text{COOH}$. The maximum peel strength of AA, AM, and MAM grafts exceeds 5 kg/cm (adherend failure). Apparently, the adhesive bondability of the highly modified surfaces with the epoxy adhesives is extremely enhanced by the introduction of carboxy and carbamyl radicals but not by acetoxy and carbomethoxy radicals.

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