$$I_{1,2i} = \sum_{x=0}^{n-1} \sum_{y=1}^{m} \frac{\sin \{ksa[x + y + (i - 1)(n + m)]\}}{ksa[x + y + (i - 1)(n + m)]}$$

$$I_{1,2i+1} = \sum_{x=0}^{m-1} \sum_{y=1}^{m} \frac{\sin \{ksa[x + y + in + (i - 1)m]\}}{ksa[x + y + in + (i - 1)m]\}}$$

and

$$I_{2,2i+2} = \sum_{x=0}^{n-1} \sum_{y=1}^{n} \frac{\sin \{ksa[x + y + im + (i - 1)n]\}}{ksa[x + y + im + (i - 1)n]}$$

For the asymmetric rodlike molecule with *p* blocks of type A and *p* blocks of type B, the master intensity equation is (15) with t_z, $I_{1,2i}$, $I_{1,2i+1}$, and $I_{2,2i+2}$ as above.

The coil–rod hybrid molecule is treated by the techniques of Adelman and Deutch. For the symmetric case involving *p* units of A coils and $(p - 1)$ units of B rods, the intensity is given by

$$\begin{aligned} I = {} & pf_{\rm a}^2\left\{m + 2\sum_{z=1}^{m-1} (m - z)t_z{}^{\rm A}\right\} + (p - 1)f_{\rm b}^2 \\ & \times \left\{n + 2\sum_{z=1}^{n-1} (n - z)t_z{}^{\rm B}\right\} + 4f_{\rm a}f_{\rm b}\sum_{i=1}^{p-1} (p - i)I_{1,2i} \\ & + 2\left\{f_{\rm a}^2\sum_{i=1}^{p-1} (p - i)I_{1,2i+1} + f_{\rm b}^2\sum_{i=1}^{p-2} (p - 1 - i)I_{2,2i+2}\right\} \end{aligned}$$

where

$$t_z{}^{\rm A} = e^{-bz}$$

$$t_z{}^{\rm B} = \frac{\sin (ksaz)}{(ksaz)}$$

$$I_{1,2i} = \frac{m(1 - e^{-\mu})}{\mu}\left[\sum_{i=1}^{n} \frac{\sin (ksai)}{ksai}\right]\left[e^{-\mu}\frac{\sin (nksa)}{nksa}\right]^{i-1}$$

$$I_{1,2i+1} = m^2\left[\frac{1 - e^{-\mu}}{\mu}\right]^2\left[\frac{\sin (nksa)}{nksa}\right]^i (e^{-\mu})^{i-1}$$

$$I_{2,2i+2} = \left[\sum_{i=1}^{n} \frac{\sin (ksai)}{ksai}\right]^2 (e^{-\mu})^i\left[\frac{\sin (nksa)}{nksa}\right]^{i-1}$$

$$\mu = bm$$

For a molecule of *p* A blocks in a coil configuration and *p* B blocks in a rod configuration the master intensity equation changes to

$$\begin{aligned} I = {} & pf_{\rm a}^2\left\{m + 2\sum_{z=1}^{m-1} (m - z)t_z{}^{\rm A}\right\} + pf_{\rm b}^2 \\ & \times \left\{n + 2\sum_{z=1}^{n-1} (n - z)t_z{}^{\rm B}\right\} + 2f_{\rm a}f_{\rm b}\sum_{i=1}^{p} (2p - 2i + 1)I_{1,2i} \\ & + 2\sum_{i=1}^{p-1} (p - i)(f_{\rm a}^2I_{1,2i+1} + f_{\rm b}^2I_{2,2i+2}) \end{aligned}$$

where the t_z's, $I_{1,2i}$, $I_{1,2i+1}$, and $I_{2,2i+2}$ are the same as for the symmetric case.

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Surface Modification of Polyethylene by Radiation-Induced Grafting for Adhesive Bonding. 2. Relationship between Adhesive Bond Strength and Surface Structure

Shinzo Yamakawa,* Fumio Yamamoto, and Yoshinori Kato

Ibaraki Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corporation, Tokai, Ibaraki 319-11, Japan.

Received March 31, 1976

ABSTRACT: Mutual irradiation of polyethylene (PE) sheets in methyl acrylate (MA) vapor has been found to form an optically isotropic surface layer on an anisotropic graft copolymer layer consisting of PE and MA components. This isotropic layer, which can extend to a thickness of 70 μm, consists of poly(methyl acrylate) (PMA) homopolymer except in the boundary region (6–9 μm) adjacent to the inner anisotropic copolymer layer. The high stability of the former layer to solvent treatments indicates that this homopolymer is not only cross-linked but is also linked by chemical bonds to the PE and grafted PMA chains in the contiguous copolymer layer. In the adhesive joints of the saponified grafts with epoxy adhesives, the peel strength increases abruptly with the formation of the isotropic layer and without exception reaches PE adherend failure at a thickness of more than 10 μm. It is thus proposed that the thickness can be used as a criterion for estimating the resulting bond strength in advance of bonding.

Surface modification of PE is a prerequisite for its strong structural adhesive bonding at temperatures below the softening point. Among many surface pretreatments proposed, the most effective techniques are[1,2] CASING (cross-linking with activated species of inert cases),[3] ablative oxidative treatments using atomic oxygen,[4,5] and chromic acid.[6] Although the increased bond strengths are thought to result from the removal of weak boundary layers or from an increase

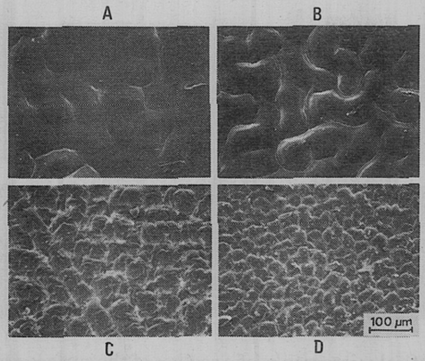


Figure 1. Scanning electron micrographs of a series of surface grafts of a low-density PE sheet which was irradiated in a saturated vapor pressure of MA at 15 °C for 2.0 (A, B), 2.5 (C), and 5.5 h (D).

in wettability, these two factors cannot be used as a criterion for predicting with high reliability before bonding whether or not the surfaces will result in a high bond strength. The wettability is a necessary, but not a sufficient, condition for forming strong joints.[3] Also there are no methods for evaluating the removal of weak boundary layers; this results in some disagreement among groups of workers[3,5,7] about effects arising from CASING. The characterization of the treated surfaces (within 1000 Å from the surface) has been limited by the heterogeneous modification and the lack of adequate analytical tools.

Very few studies have been published on the surface modification of PE by radiation grafting for adhesive bonding. We have found two groups of surface grafts[8,9] having a high adhesive bondability as a result of extensive investigations on a number of grafting systems. One of them involves acrylic acid, acrylamide, and methylolacrylamide grafts prepared by trapped radical technique, and the other involves MA and vinyl acetate grafts prepared by vapor-phase mutual grafting. In the MA graft, 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 surface composition determined by attenuated total reflection (ATR) infrared spectrophotometry was used as a preliminary criterion for good adhesion of the grafted surfaces.[9] Wettability cannot be used as the criterion for good adhesion because the peel strengths increase more abruptly at higher stages of the surface grafting than at the stage of which the water contact angle is saturated.[8] In this work an attempt has been made to characterize the surface structure of the MA graft and to relate it to the adhesive bondability (or the resulting bond strength). This prompts us to find a criterion for good adhesion.

Experimental Section

Materials. The PE samples used were a low-density (0.919 g/cm^3) PE supplied by Nippon Unicar and a medium-density (0.945 g/cm^3) PE supplied by Japan Olefin Chemical. The melt index of the former was 0.25 g/10 min, and that of the latter was 0.30 g/10 min. Sheets, 2 and 3 mm thick, were prepared from the PE pellets by hot-rolling and compression molding at 160 °C (between chromium-plated steel sheets for ferrotyping) followed by quenching to room temperature. The sheets were cut to a rectangular shape measuring 25 mm wide and 115 mm long, treated at 55 °C successively with reagent grade cyclohexanone and methanol to remove low molecular weight ingredients, and then dried under vacuum at 60 °C. A commercial MA was dried over an anhydrous calcium sulfate and then distilled in nitrogen before use.

Surface Grafting. The PE sheets were irradiated in the saturated vapor pressure of MA at 15 or 25 °C except the grafts in Figures 3B and 3C. The vapor-phase mutual grafting was carried out by a method similar to that described by Takamatsu and Shinohara.[10] The dose rate from a ^{60}Co source was 5.0×10^4 rad/h. To remove occluded PMA homopolymer, the grafted sheets were extracted with acetone in a Soxhlet extractor until there was no further decrease in weight.

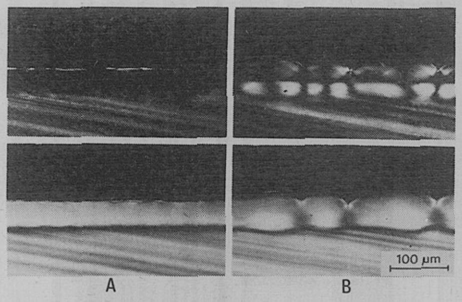


Figure 2. Polarizing micrographs of a cross section of the surface grafts (A and B) corresponding to Figures 1A and 1B. The micrographs were taken between crossed polarizers in the extinction (top) and 45° (bottom) positions of the ungrafted PE part.

Saponification Treatment.[8] For strong adhesive bonding of the MA grafts, the grafted sheets were saponified with a 1 N KOH solution in methanol at 50 °C for 4 h and then treated at 56 °C consecutively with 1 N HCl solution in acetone–water (1:1, v/v), water, acetone–water (1:1), and acetone.

Adhesive Bond Strength. A peel specimen consisting of graft–adhesive–graft was prepared to evaluate the adhesive bondability of the saponified grafts. An aminopolyamide-modified epoxy adhesive[9] was used. The assembly was lightly weighted (0.15 kg/cm^2), and the adhesive was allowed to cure for 4 h at 80 °C. The thickness of the adhesive layer was maintained constant by insertion of a stainless steel wire 100 μm in diameter. The T-peel strength at 23 °C was measured by a tensile test machine (at a cross-head speed of 10 cm/min) according to ASTM D1876-61T.

Microscopy. Cross sections of the grafted sheets were examined with a Leitz interference microscope, with which both interference and polarizing micrographs of the same position in a section can be taken successively. The thickness of microtomed sections, cut perpendicular to the sheet surfaces, was ca. 20 μm. The immersion liquid was diallyl phthalate (n 1.517). The topography of grafted surfaces was observed with a scanning electron microscope.

Surface Composition.[9] The composition in the surface region (6–9 μm from the surface) of the unsaponified surface grafts was determined by ATR infrared spectrophotometry using the 720-cm^{-1} band of PE and the 750-cm^{-1} band of PMA.

Results and Discussion

Growth of Graft Copolymer Layer. Figure 1 shows the scanning electron micrographs of a series of MA grafts, indicating a typical growth of the surface grafting. Figures 2, 3A, and 4 give the optical micrographs of a cross section of the surface grafts corresponding to Figure 1. In the mutual irradiation of PE sheets in the saturated vapor pressure of MA at room temperature, the graft copolymerization is confined to the surface region of sheets (Figure 3A).[9] The grafted MA content in the surface region increases with irradiation time; this increase leads to swelling or expansion of the grafting layer. The expansion of a layer parallel to the surface plane is, however, restricted owing to fixation by the contiguous (inner) ungrafted PE layer. As a result of this limited expansion, the grafted surface layer upheaves at a certain MA composition (Figures 1A → 1B or 2A → 2B), and then the periods of upheaval or upthrust become smaller and more regular with irradiation time (Figures 1C → 1D or 4A → 4B).

Under examination between crossed polarizers in parallel light, cross sections of the PE sheets used in this work (low- and medium-density PE with low melt index, i.e., high average molecular weight) exhibit no apparent spherulic structure but cause an extinction of light when the surface plane of section is parallel to the vibration planes of crossed polarizers (called at the extinction position). Rotation of a section relieves the extinction and gives four distinct changes in brightness from a maximum to a minimum during a 360° rotation. Biaxial rolling and compression molding, which have been carried out for the sheet preparation, can lead to a uniplanar orientation

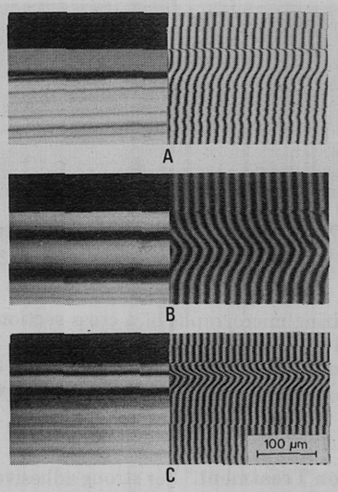


Figure 3. Polarizing (left, in the 45° position) and interference (right) micrographs of a section of surface graft having different distributions of graft composition. Comparison of these micrographs shows the relation between extinction lines (left) and distribution of graft composition: (A) the graft corresponding to Figures 1A and 2A; (B) low-density PE irradiated in the saturated vapor pressure of ethyl acrylate at 25 °C for 3.0 h; (C) medium-density PE irradiated under the same condition as Figure 3B.

of PE molecules in the amorphous regions. According to the row structure mechanism,[11] the PE molecules in the crystalline regions can also orient along the direction of stress, i.e., parallel to the surface plane. Thus this optical anisotropy seems to be due to a uniplanar orientation of PE molecules parallel to the sheet surface (zero amplitude effect, see below).

When a thin section is examined between crossed polarizers in parallel light, the extinction of light passing through the section is generally possible for the following reasons: (1) isotropy effect, (2) thickness compensation effect, (3) zero amplitude effect, (4) zero birefringence effect, and (5) accidental effect.[12,13] A relatively wide extinction line is seen along the grafting front (i.e., borderline between the grafted and ungrafted PE layers) in Figures 2 (bottom) and 3A (left), which were taken between crossed polarizers in the 45° position of the ungrafted PE part. This extinction results from the difference in birefringence (cause 2) because the distribution of MA composition determines its position and width. This is clearly shown from comparison of the polarizing and interference micrographs of surface grafts having a different distribution of graft composition and hence having two extinction lines (Figures 3B and 3C). Narrow and less dark extinction lines, the direction of which coincides with that of microtomy, can also be seen in the ungrafted PE parts of Figures 2 (bottom), 3A (left), 4A (c), and 4B (c). This line is due to the unevenness (resulting from the microtomy) in thickness of these sections (cause 2).

The graft copolymer layer before its upheaval has the same extinction angle as that of ungrafted PE (e.g., the top of Figure 2A); this may indicate the remaining orientation of PE molecules through the grafting. Another possible process for the optical anisotropy is the growth of grafted chains perpendicular to the surface. With the upheaval of the grafted layer, however, a distribution of the extinction angle appears in the graft copolymer layer. A typical feature of resulting extinction patterns (in the extinction position of the ungrafted PE part) is the extinction cross seen in Figure 2B (top). The arms of the cross are parallel or perpendicular to the original sheet surface, i.e., to the planes of polarizer and analyzer. The arms perpendicular to the surface plane indicate the presence of molecules oriented parallel or perpendicular to the surface and coincide in position with the top and the bottom of upheaval.

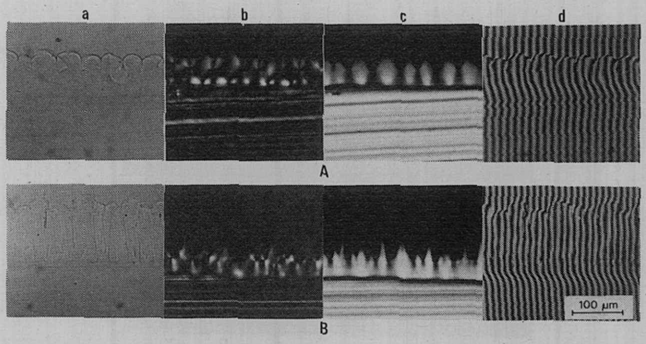


Figure 4. Optical micrographs of a section of the surface grafts (A and B) corresponding to Figures 1C and 1D. An identical area in the sections was photographed under four different conditions: (a) under an unpolarized white light; (b) between crossed polarizers in the extinction position of the ungrafted PE part; (c) between crossed polarizers in the 45° position; and (d) under an interference microscope.

On the basis of these results, the extinction patterns (Figures 2B and 4B) can be explained in terms of distortion of the suggested orientations of PE and grafted chains and in terms of their re-orientation along the upheaval stress. With respect to the growth and the optical properties of grafting surface layer, a more detailed study using uniaxially oriented PE samples will be presented in the near future.

Formation of an Optically Isotropic Layer. Figure 4A (c) shows that bright portions with a shape like candlelight correspond to the upheaval of the grafted layer. The top of the former coincides in position with the top of the latter. Apparently, the former reflects the anisotropy (or orientation) of the upheaved graft copolymer layers and hence may provide a rough indication of the presence of the copolymer consisting of PE and MA components.

Figure 4B shows the optical micrographs of a section of a surface graft (corresponding to Figure 1D) at a much more advanced stage of grafting than that of Figure 4A (corresponding to Figure 1C). In Figure 4B (c), it is noted that an optically isotropic layer, in which no light is transmitted at any microscopic stage between crossed polarizers, is formed on the candlelight (i.e., upheaved copolymer layer); the former reaches more than 70 μm in thickness. The interference fringes (d) are saturated in the isotropic layer, whereas there is an apparent gradient of fringes in the anisotropic layer. From complete disappearance of the 720-cm^{-1} band (of PE) in the ATR spectrum of the graft, it is evident that the outer region of the isotropic layer contains no PE component. In other words, a PMA homopolymer layer is formed on the graft copolymer layer consisting of PE and MA components.

Figure 5 summerizes the thickness (T_i) of the isotropic layer and the surface composition vs. irradiation time. The T_i value was determined from the micrographs taken between crossed polarizers in the 45° position of the ungrafted PE part (Figure 6). The average of thickness at the positions of the top of the candlelight was recorded. Both the surface composition and the T_i value increase with irradiation time. From comparison of these two curves, it can be seen that the surface composition approaches 100 mol % MA at ca. 15 μm of T_i. According to Harrick's calculations[14] concerning the penetration depth of the incident beam under ATR infrared spectrometry, it can be estimated that the penetration depth into low-density PE (n 1.51) at 720 cm^{-1} is ca. 9 μm and that into PMA (n 1.48) at 750 cm^{-1} is ca. 6 μm. On the basis of this estimate, the above relationship between surface composition by ATR and T_i value indicates that the grafted surface (in the literal sense of the term surface) reaches 100 mol % MA just after the formation of 6 or 9 μm of T_i. In other words, an isotropic copolymer region (containing PE molecules) of 6–9 μm exists

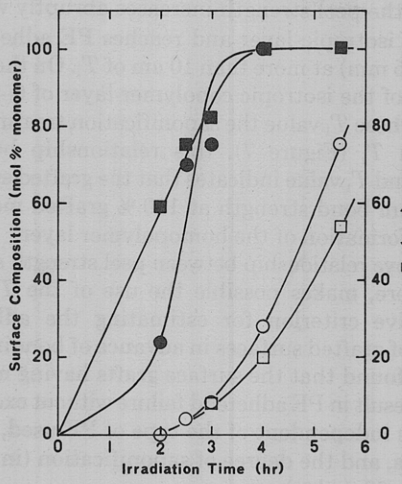


Figure 5. Surface composition and thickness of isotropic layer (T_i) of unsaponified surface grafts vs. irradiation time. PE sheets were irradiated in the saturated vapor pressure of MA at 15 °C: (●) surface composition, low-density PE; (■) surface composition, medium-density PE; (○) T_i, low-density PE; (□) T_i, medium-density PE.

between the PMA homopolymer and the anisotropic layers. This estimate is in good agreement with results[15] obtained by x-ray photoelectron spectroscopy (ESCA, its escape depth is less than 50 Å); the surface composition by ESCA reached 100 mol % MA, with formation of 7–8 μm of T_i. The isotropic copolymer layer probably consists of a highly grafted copolymer, in which the molecular orientations have been destroyed by its extensive grafting.

The grafted sheets were extracted with acetone in a Soxhlet extractor until there was no further decrease in weight. Further extraction with the other solvents, which dissolve PMA, but not PE, resulted in no weight loss of the sheets. Even after these extraction treatments some grafts showed homopolymer layers of more than 60 μm (e.g., Figure 4B). Moreover, the homopolymer layer containing stabilizers was stable to heat aging and Weather-Ometer exposure followed by acetone treatment, whereas the layer containing no stabilizer resulted in rapid removal of the layer.[16] These results indicate that the PMA chains in the homopolymer layer are not only cross-linked to each other but also linked by chemical bonds to the PE and grafted PMA chains in the contiguous (inner) copolymer layer. Only cross-linked PMA homopolymer (not grafted) can be removed by the extraction treatments. To the author's knowledge, no paper has been published on the formation of such a homopolymer layer.

It is unlikely that a homopolymer layer as thick as 60 μm is formed only by the direct propagation of growing graft chains from the PE radicals[17] (process 1). The other processes should also contribute to the formation; the processes involve secondary graft copolymerization from radicals on the grafted PMA chains (process 2) and concurrent homopolymerization followed by recombination with the PE and grafted-PMA radicals (process 3). The grafted PMA radicals can be produced by concurrent radiolysis[18] of the grafted chains and by the chain transfer reactions from the growing graft and homopolymer chains to grafted chains. The view that processes 2 and 3 play an important role in the formation of the homopolymer layer is supported by results concerning the radiation grafting of MA onto PMA[19] and the significant formation of cross-linked insoluble polymers on bulk homopolymerization of MA.[20]

Saponification Treatment. Saponification treatment is necessary for strong adhesive bonding of the MA grafts with epoxy adhesives.[8] This treatment, at the same time, gives a decrease in T_i at the graft stages of more than 10 μm of T_i (Figure 7), whereas it gives no change in thickness of the anisotropic layer ($T_t - T_i$, see Figure 6). At the same stages, the grafted sheets exhibited a greater weight loss than that due to the change from OCH_3 to OH. Because the infrared spectra of the removed contents, which were recovered from the saponification and the subsequent extraction solutions, coincide with those of hydrolyzed PMA, this additional weight loss should correspond to the decrease in T_i and result from the partial removal of PMA chains in the isotropic layer. This removal does not result from extraction of occluded PMA homopolymers but from cleavage of chemical bonds by saponification since the samples were extracted with acetone until there was no further loss in weight.

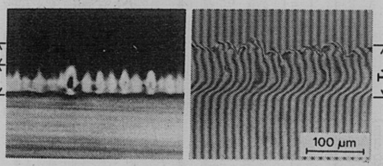


Figure 6. Experimental determination of thicknesses of the total graft layer (T_t) from an interference micrograph (right) and of the isotropic layer (T_i) from the polarizing micrograph in the 45° position (left). A medium-density PE sheet was irradiated in the saturated vapor pressure of MA at 25 °C for 5.0 h and then saponified.

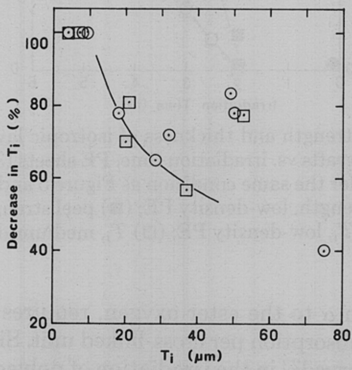
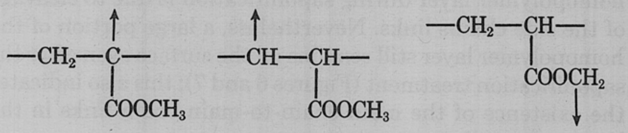


Figure 7. Decrease in thickness of isotropic layer (T_i) with saponification treatment. PE sheets were grafted under the same condition as Figure 5 and then saponified: (○) low-density PE; (□) medium-density PE.

There are three possible cross-link or branch sites in the homopolymer layer:



$$-\mathrm{CH_2}-\underset{\mathrm{COOCH_3}}{\overset{\uparrow}{\mathrm{C}}}- \qquad -\overset{\uparrow}{\mathrm{CH}}-\underset{\mathrm{COOCH_3}}{\mathrm{CH}}- \qquad -\mathrm{CH_2}-\underset{\mathrm{COOCH_2}\downarrow}{\mathrm{CH}}-$$

I II III

MA shows[21] a much greater tendency to form cross-linked insoluble polymers on bulk polymerization than does methyl methacrylate. This difference is thought to depend[20] on whether or not the polymer possesses an active α-hydrogen atom (as a chain transfer site) on the main chain carbon adjacent to the carbonyl carbon. Moreover, methacrylate and acrylate monomers are not radiation grafted onto poly(methyl methacrylate) but onto PMA, which possesses a main chain α-hydrogen atom.[19] These results indicate the contribution of the main chain α-hydrogen atom to processes 2 and 3 (for the formation of the homopolymer layer), leading to branch I.

On the other hand, in a systematic investigation[22] concerning the effects of structure of side chains (i.e., ester groups) on radiation cross-linking of poly(alkyl acrylates), it has been found that poly(*tert*-butyl acrylate), possessing no side chain

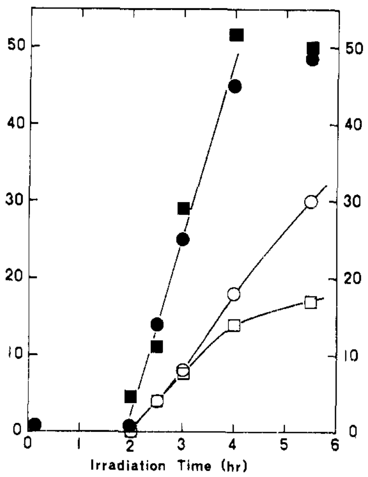


Figure 8. Peel strength and thickness of isotropic layer (T_i) of saponified surface grafts vs. irradiation time. PE sheets (3.0-mm thick) were grafted under the same condition as Figure 5 and then saponified: (●) peel strength, low-density PE; (■) peel strength, medium-density PE; (○) T_i, low-density PE; (□) T_i, medium-density PE.

hydrogen atom α to the ester oxygen, requires a markedly higher energy absorption per cross-linked unit. Similar effects have been observed[23] in the irradiation of polyacrylates containing aromatic rings in the side chain: poly(benzyl acrylate) and poly(β-phenylethyl acrylate) were easily gelled, whereas poly(phenyl acrylate) was very resistant. These results suggest the contribution of the side chain hydrogen atoms in PMA to the radiation cross-linking,[22,23] and hence to processes 2 and 3 (for the formation of the homopolymer layer), leading to branch III.

Although main chain-to-main chain links (including only branches I and II) are nonsaponifiable, side chain-to-side chain and side chain-to-main chain links (including branch III) should be subject to cleavage with saponification. The cross-linked homopolymer films prepared under the same condition as the grafted films were extracted with acetone and trichloroethylene in a Soxhlet extractor until there is no further weight loss. The saponification of the films, followed by acetone extraction, yielded a greater loss than the theoretical loss in weight (83.7 wt %) for 100% saponification; this result indicates the existence of the side chain links in the radiation-polymerized PMA films. Consequently, it can be concluded that the partial removal of PMA component in the homopolymer layer during saponification is due to cleavage of the side chains links. Nevertheless, a large portion of the homopolymer layer still remains on the surface even after the saponification treatment (Figures 6 and 7); this also indicates the existence of the main chain-to-main chain links in the homopolymer layer.

Relationship between Peel Strength and Isotropic Layer. Figure 8 summerizes the peel strength and the T_i value of saponified grafts vs. irradiation time. In Figure 8, it can be seen that the peel strength increases abruptly with the formation of isotropic layer and reaches PE adherend failure (>30 kg/25 mm) at more than 10 μm of T_i. On the basis of the existence of the isotropic copolymer layer of 6–9 μm, in the range of whose T_i value the saponification treatment gives no change in T_i (Figure 7), this relationship between peel strength and T_i value indicates that the grafted surface yields a maximum bond strength at 100 % grafted monomer, i.e., after the formation of the homopolymer layer.

The above relationship between peel strength and T_i value, furthermore, makes possible the use of the T_i value as a quantitative criterion for estimating the adhesive bond strength of grafted surfaces in advance of bonding. In fact, it has been found that the surface grafts having more than 10 μm of T_i result in PE adherend failure without exceptions; this relation is independent of the type of PE used, the grafting conditions, and the degree of saponification (in the range of more than 20 mol %).

Acknowledgment. We are grateful to Drs. K. Nakagawa and K. Kudo for many helpful discussions.

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