Hydrophilic and Adhesive Properties of Methacrylic Acid-Grafted Polyethylene Plates

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SYNOPSIS

Methacrylic acid (MAA) was grafted onto polyethylene (PE) surfaces by simultaneous irradiation with UV rays in the liquid phase to estimate hydrophilic and mechanical properties for MAA-grafted PE plates. The amount of grafted MAA increased sigmoidally with UV irradiation time, and the higher grafted amount was obtained at higher monomer concentrations. With an increase in grafting of MAA, the wettabilities from the contact angles of water were enhanced and the refractive indices from the ellipsometry decreased. Though the contact angles remained constant above the grafted amount of 0.02 mmol/cm^2, the refractive indices approached the value of PMAA around 0.009 mmol/cm^2, indicating that the PE surfaces were fully covered with grafted PMAA chains. Then, at a fixed grafted amount, the grafted layer can absorb more water and the grafted PE plates possessed higher tensile shear adhesive strength, in case grafting was carried out at lower monomer concentrations. Surface properties depended on the density of carboxyl group at the surfaces of grafted layers, whereas adhesive properties depended on the structural properties of grafted chains as well as on the density of carboxyl group of the whole grafted layers.

INTRODUCTION

Polyolefins such as polyethylene (PE) and polypropylene (PP) have good mechanical properties, but their surfaces are inert or hydrophobic. Such surfaces will result in poor adhesivities or wettabilities. Therefore, in some cases, the addition of new properties to such polymer substrates is required while concurrently leaving their bulk properties unchanged. Several techniques such as photo-, radiation-, and plasma-initiated graftings are available for modifying polyolefins, of which the photografting is expected to be the most convenient technique. An advantage of this technique is that the location of grafting can be restricted to the polymer surfaces without affecting any bulk properties because of the lower energy of the used UV rays. Many studies have been carried out for the hydrophilization of polymer substrates by means of photografting and radiation-grafting using methacrylic acid (MAA), acrylic acid (AA), and acrylamide (AAm) as hydrophilic monomers.[1,2] The PE plates grafted with such hydrophilic monomers can be used for the hydrogel systems, since they exhibit good mechanical properties even in the swollen state.

The purpose of the present study is to prepare the MAA-grafted PE plates using a 400 W high-pressure mercury lamp and to discuss their hydrophilic and adhesive properties. Their hydrophilic properties were estimated on the basis of both contact angle and swelling measurements as a function of the grafted amount. In order to relate hydrophilic properties with surface compositions, the grafted PE surfaces were analyzed by use of electron spectroscopy for chemical analysis (ESCA). Their adhesive properties were also examined from tensile shear adhesive strength measurements. An ellipsometer was also used to follow the change in refractive indices of the grafted PE surfaces with the amount of grafted MAA.

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EXPERIMENTAL

Materials

MAA was purified by distillation under reduced pressure. Acetone was distilled over potassium permanganate. Purification of poly(vinyl acetate) (PVAc) was carried out by reprecipitation from acetone into petroleum ether. The intrinsic viscosity of PVAc in a benzene solution was measured with an Ubbelhode viscometer at 25°C,[3] and, as a result, the molecular weight of PVAc was roughly 1.2×10^5. Other chemicals were used as obtained.

Photografting

PE pellets manufactured by Sumitomo Chemical Industry Co. were used (molecular weight = 22,000–44,000, density = 0.919 g/cm^3, and MI = 50 g/min). The pellets were washed with water, methanol, and acetone before drying under reduced pressure. Then, the pellets were melted on a glass plate heated to 200°C, and another glass plate at the same temperature was put on the molten PE and pressed to obtain a PE plate of 2 mm thickness. Several of these PE plates were cut into 40 mm lengths and 15 mm widths and then weighed. The PE plates were coated with a sensitizer according to the method of Ogiwara et al.[4]: that is, 0.25 g of benzophenone (1.35×10^{-2} mol, sensitizer) and 0.5 g of PVAc were dissolved in acetone to take the solution to a 50 dm³ volume, and the coating of the sensitizer was made by dipping the PE plates in the solution for 1 min. The photografting was carried out using a Riko rotary photochemical reactor RH400-10W equipped with a 400 W high-pressure mercury lamp. The sensitizer-coated PE plates after being dried were immersed in the aqueous solutions of MAA of a given concentration in the Pyrex glass tubes. MAA was grafted onto PE surfaces at 60°C under a nitrogen atmosphere.[5] The grafted PE plates were washed with hot water (60–70°C) to exclude PMAA homopolymers formed during grafting and then dried under reduced pressure for 48 h at room temperature. The amount of MAA grafted onto PE surfaces was calculated from the weight increase of the samples using eq. (1):

$$G(\text{mmol/cm}^2)$$

$$= \left\{ \frac{[\text{grafted PE(g)} - \text{ungrafted PE(g)}]/86.09}{\text{surface area(cm}^2)} \right\}$$

$$\times 1000 \quad (1)$$

where G is the amount in moles of the MAA monomer grafted per unit area. The quantity of 86.09 is the molecular weight of the MAA monomer.

Surface Analysis by ESCA

The photoelectron spectra were recorded on a Shimadzu ESCA 750-type spectroscopy with a MgKα X-ray source (1253.6 eV) operating at 8 kV and 30 mA. A vacuum of at least 5×10^{-5} Pa in the chamber was maintained for all measurements. Samples were mounted onto the probe tips with double-sided Scotch tape. Binding energies were adjusted to C1s = 285.0 eV for an ungrafted PE.[6]

Contact Angle Measurements

The contact angles of water on the grafted PE surfaces were measured with a sessile drop method at 25°C under an atmosphere of saturated water vapor using a goniometer (Kyowa Kagaku Co., Model TYP-QI). At least 20 contact angles were averaged to get reliable data.

Refractive Index Measurements

A Shimadzu P-10-type ellipsometer was used to measure the phase difference (Δ) and the azimuth angle (Ψ) of the amplitude ratio (ellipsometric parameters) with a He–Ne laser light with a wavelength of 632.82 nm at the incident angle of 70°.[7] The null method was utilized in the measurements.[8] The refractive indices n for grafted PE surfaces were calculated from the ellipsometric parameters (Δ and Ψ) by a computer according to the accepted procedure. Hirata et al. treated PE plates with sulfuric acid–potassium dichromate or fuming sulfuric acid and ellipsometrically determined the thickness of the adsorbed water vapor layer according to the same technique.[9]

Swelling Measurements

The grafted PE plates were immersed in distilled water for 48 h at 30°C. Then, the grafted PE plates were removed from the water, blotted quickly with filter paper to remove the water attached on their surfaces, and weighed quickly. The amount of water absorbed into the grafted layer (W) and swelling ratio (Q) were calculated from the weight increase of the samples using eqs. (2) and (3), respectively:

$W \, (\text{mmol}/\text{cm}^2)$

$$= \left[\frac{\text{wet weight}(g) - \text{dry weight}(g)}{\text{surface area}(\text{cm}^2) \times 18.016} \right] \times 1000 \quad (2)$$

where the quantity of 18.016 is the molecular weight of water:

$$Q = \left[\frac{W(\text{mmol}/\text{cm}^2) + G(\text{mmol}/\text{cm}^2)}{G(\text{mmol}/\text{cm}^2)} \right] \quad (3)$$

In addition, the amount of water bonded per monomer segment, n_{water}, was calculated using eq. (4):

$$n_{\text{water}} = \left[\frac{W(\text{mmol}/\text{cm}^2)}{G(\text{mmol}/\text{cm}^2)} \right] = Q - 1 \quad (4)$$

Tensile Shear Adhesive Strength Measurements

The PE plates of 60 mm length and 10 mm width were used for the measurements of tensile shear adhesive strength and the grafted PE plates were cut widthwise into half. "Araldite" made by Ciba-Geigy Ltd. was used as an adhesive. The base and curing agent were mixed in a ratio of 1 : 1 by weight. Two pieces of the grafted PE plates of the same grafted amount were bonded with a 10 × 10 mm overlap with the adhesive, and the adhesives were cured for 24 h at 30°C under the constant pressure of 0.5 kg/cm^2. Both ends of the jointed samples were attached, respectively, to the load cell and base of a tensile testing instrument. The adhesive strength was measured at 30°C with a strain rate of 1 mm/s.

RESULTS AND DISCUSSION

Photografting

Grafting of MAA onto PE surfaces was carried out at monomer concentrations from 0.3 to 1.5 mol/dm^3. The grafted amount onto PE surfaces was plotted against UV irradiation time in Figure 1. The grafted amount increased sigmoidally with UV irradiation time, that is, a considerable increase in the grafted amount following a gradual increase was observed. This autoaccelation shows the possibility that grafting onto grafted chains also takes place.[10] The higher grafted amount was obtained and the induction period became shorter at higher monomer concentrations. The grafted amount had a tendency to level off in longer irradiation times, because a con-
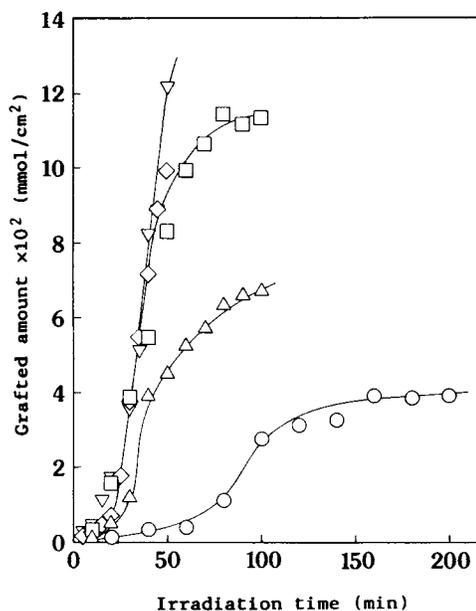
Figure 1 The dependence of grafted amount on monomer concentration; monomer concentration (mol/dm^3) — O: 0.3, △: 0.6, □: 0.9, ◇: 1.2, ▽: 1.5.

siderable amount of PMAA homopolymers was formed in the reaction medium.

Surface Analysis by Means of ESCA

The grafted PE surfaces were analyzed by means of ESCA. Since photoelectrons escape from a short distance of a few nanometers underneath solid surfaces, an ESCA can provide some information on atoms and their bonding types and chemical compositions of polymer surfaces. For a sample with similar geometry and orientation, the ratio of two intensities, I and J, under the identical conditions is given by

$$\frac{n_I}{n_J} = \frac{I_I/\sigma_I}{I_J/\sigma_J} \quad (5)$$

where n is the atomic density; I, the peak intensity, and σ, the cross section for photoionization.[11,12] The cross sections of C1s and O1s for ionization are 1.00 and 2.85, respectively.[13]

Figure 2 shows the C1s and O1s spectra for a grafted PE plate. The C1s spectrum can be resolved into the two compositions: one at 285.0 eV assigned to the hydrogen carbon, and the other at 289.0 eV, to the carbon in the carboxyl group. The peak corresponding to the carbon in the carboxyl group
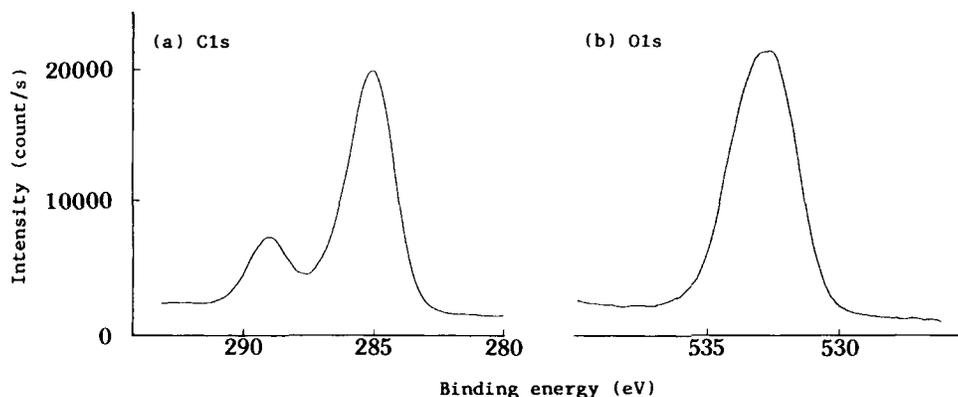
Figure 2 ESCA spectra on C1s (a) and O1s (b) for MAA-grafted polyethylene.

shifted by ca. 4.0 eV from the primary peak at 285.0 eV. The value of the shift was in good agreement with that determined by Clark and Thomas.[14] The O1s spectrum shows a broad and overlapping peak, which is divided into C—O single and C=O double bonds.

Figure 3 shows the changes in the intensity ratio (O1s/C1s) and relative intensity [C1s (C=O)/ΣC1s] with the grafted amount. The relative intensity denotes the concentration ratio of the carbon atom in the carboxyl group to the whole carbon atoms. Both intensity ratio and relative intensity increased with the grafted amount and leveled off at the grafted amount above 0.02 mmol/cm^2. The values of the intensity ratio and relative intensity for PMAA homopolymer measured as a reference were 0.384 and 0.160, respectively. Both values for the PE plates grafted above 0.02 mmol/cm^2 almost agreed with those for the PMAA homopolymer.
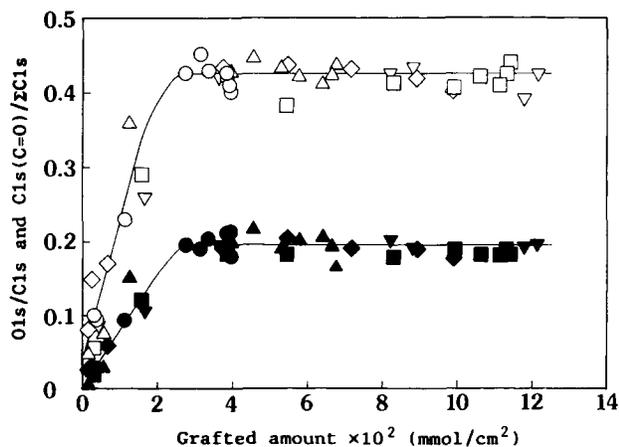
The results of ESCA measurements indicate that when the grafted amount is as high as 0.02 mmol/cm^2 the PE surfaces are fully covered with grafted PMAA chains. It is expected that when the grafted amount exceeds 0.02 mmol/cm^2 the thickness of the grafted layer increases without changing the outermost surface composition.

Surface Properties of Grafted PE Plates

The surface properties of the grafted PE plates were estimated on the basis of the contact angle and refractive index measurements. Figure 4 shows the change in wettability with the grafted amount. Wettabilities increased with the grafted amount. This result indicates that grafting of MAA onto PE surfaces is effective in enhancing their wettabilities.
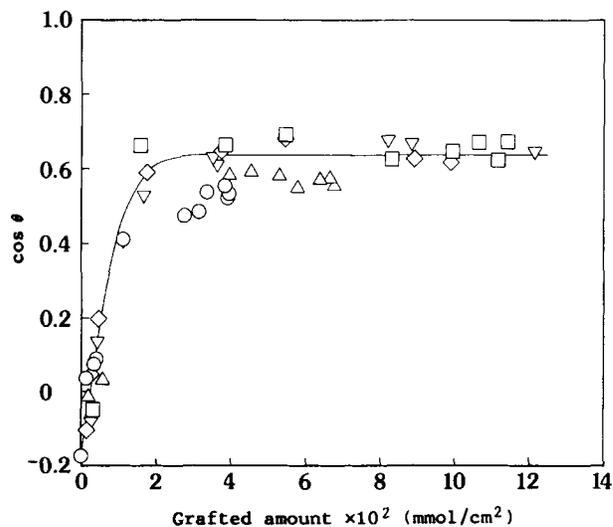

Figure 3 Changes in intensity ratio with grafted amount; monomer concentration (mol/dm^3) — O: 0.3, △: 0.6, □: 0.9, ◇: 1.2, ▽: 1.5; intensity ratio—open: O1s/C1s, shaded: C1s (C = O)/ΣC1s.

Figure 4 Change in wettability with grafted amount for MAA-grafted polyethylene; monomer concentration (mol/dm^3) — O: 0.3, △: 0.6, □: 0.9, ◇: 1.2, ▽: 1.5.

The contact angle reached an almost constant value ($\cos\theta = 0.63$) that was near to or more than the grafted amount of 0.02 mmol/cm² and the tendency was independent of the monomer concentrations applied.

The dependence of contact angle on the grafted amount was in good agreement with that of the intensity ratio determined by ESCA. These results suggest that the thickness of the grafted layer that dominates the contact angles is similar to the sampling depth of ESCA. For ordinary polymers, an ESCA can analyze the surfaces to 3–5 nm in depth.[15] When the grafted amount exceeds 0.02 mmol/cm², thicker grafted layers form as compared to the sampling depth of ESCA.

Figure 5 shows the change in refractive index with the grafted amount. The refractive indices of ungrafted PE and PMAA surfaces were 1.482 and 1.427, respectively. The refractive index decreased slowly in the beginning of grafting and then decreased linearly with the grafted amount. We could not measure the refractive index above 0.01 mmol/cm² because of the surface roughness of the grafted layer. The slow decrease in the beginning indicates that the initiation of grafting of MAA takes place at or underneath the PE surface layers. On the other hand, the linear decrease indicates that the PE surfaces are gradually covered with the grafted chains as the grafted amount increases. The refractive index

for the grafted PE surface with 0.009 mmol/cm² was 1.430, which is almost the same as the value for the PMAA surface. We can conclude from the above results the following: The PE surface was already covered with grafted PMAA chains at 0.009 mmol/cm². The thickness of the grafted layer dominating the refractive index is far smaller than the sampling depth of ESCA. Figure 5, therefore, indicates the refractive indices at the outermost surface layers of the grafted PE plates.

Swelling Behavior of Grafted PE Plates

The swelling measurements were carried out to estimate the hydrophilic properties of the whole grafted layers. Figure 6 shows the changes in the amount of absorbed water with the grafted amount. The amount of absorbed water increased slowly at a lower grafted amount below 0.01 mmol/cm² and then increased rapidly at any monomer concentration. In addition, the amount of absorbed water depended on monomer concentration above the grafted amount of 0.01 mmol/cm². This tendency differs from the contact angle behavior for the grafted amount, because the contact angle is dominated by the amount of the carboxyl group of the surface of grafted layer, while the swelling behavior is affected by the amount of the carboxyl groups in the whole grafted layers. At a fixed amount, the grafted layer prepared at lower monomer concentrations can absorb a large quantity of water, depending on the structural properties such as the differences in the length and the extent of branching of the grafted chains.

Figure 7 shows the changes in the swelling ratio with the grafted amount. The symbol n_{water} denotes the amount of water per monomer segment. If the formation of the grafted layer proceeds without changing the morphology, then the swelling ratio will be proportional to the grafted amount.

Omichi et al. studied the radiation-grafting of MAA to PE films and found that the water uptake increased linearly with the grafting yield.[16] Hegazy et al. studied the preirradiation-grafting of AA into poly (tetrafluoroethylene–hexafluoropropylene) films and reported that no effect of grafting conditions such as preirradiation dose, grafting temperature, and monomer concentration on the swelling behavior was observed and the degree of swelling depended mainly on the amount of the hydrophilic group in the films.[17] For the grafted PE plates prepared at lower monomer concentrations, the amount of water per monomer segment increased gradually and then increased drastically with the
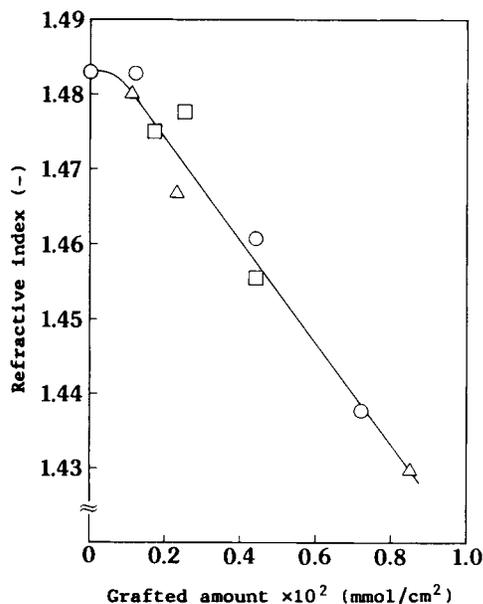
Figure 5   Change in refractive index with grafted amount; monomer concentration (mol/dm³) — O: 0.3, △: 0.6, □: 0.9.
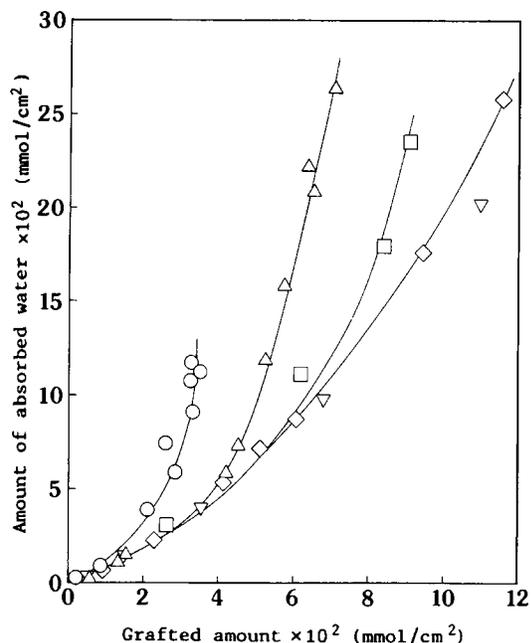
Figure 6 Changes in amount of absorbed water with grafted amount; monomer concentration (mol/dm^3) — O: 0.3, △: 0.6, □: 0.9, ◇: 1.2, ▽: 1.5.

grafted amount. On the other hand, for the PE plates grafted at higher monomer concentrations above 1.2 mol/dm^3, no such behavior was observed. For a fixed grafted amount, therefore, the PE plates grafted at lower monomer concentrations would have longer grafted chains.

Grafting onto the grafted chains can also take place. We can consider from the above results that such grafted chains move and extend more readily than do chains directly grafted onto the PE surfaces. A variety of discussions have been made about mobility of grafted chains. Beddows et al. studied the irradiation-grafting of 2-hydroxyethyl methacrylate and vinyl acetate onto low-density PE powder and reported that it was possible for the hydroxy groups to extend into the aqueous phase and the difference in radical yields of the polyolefin would give a statistical difference in the number of grafted chains. In addition, the chains themselves would be of different lengths and morphology.[18]

## Adhesive Properties of Grafted PE Plates

Figure 8 shows the changes in tensile shear adhesive strength with the grafted amount. The adhesive strength increased with the grafted amount. Grafting at lower monomer concentrations increased the adhesive strength rapidly at a lower grafted amount

range. The adhesive strength for ungrafted PE plates was 3.8 kg/cm^2. Therefore, grafting of MAA onto PE surfaces plays an important role in the formation of strong adhesive joints between the grafted chains and the used adhesives. Furthermore, when the adhesive strength exceeded ca. 17 kg/cm^2, the grafted PE plates broke. The ungrafted PE plates (60 × 10 mm), strained under the same conditions in order to obtain the ultimate tensile strength of the PE substrate, broke at 16.5 kg/cm^2 following some necking and elongation.[19] Since the strength at which the grafted PE plates broke was almost the same value as the ultimate strength of the ungrafted PE plate, the bulk properties of PE plates could be kept unchanged through grafting of MAA.

The monomer concentration dependence of the adhesive strength is similar to that of the swelling behavior. Therefore, we can consider that the adhesives cured after permeating into the grafted layers and the adhesive strength is related to the bulk properties of the whole grafted layers, particularly to the structural properties of the grafted chains. An ESCA has been successfully used to study adhesive failures and surface bondings.[20] The intensity ratios were calculated from eq. (5). The cross sections of N1s and S2p for ionization are 1.77 and 1.74, respectively. The core level spectra for the epoxy adhesive and the failed surfaces of the grafted PE plates with different adhesive strengths are shown in Figure 9 and the intensity ratios are summarized in Table 1. It is found that the used adhesives contain a small quantity of nitrogen and sulfur in addition to carbon and oxygen. The C1s spectrum gives a shift peak at 287 eV, characteristic of the used adhesives. The nitrogen and sulfur atoms exist
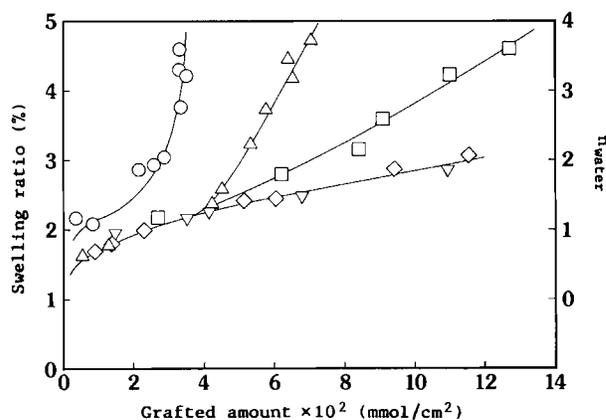
Figure 7 Changes in swelling ratio with grafted amount; monomer concentration (mol/dm^3) — O: 0.3, △: 0.6, □: 0.9, ◇: 1.2, ▽: 1.5.
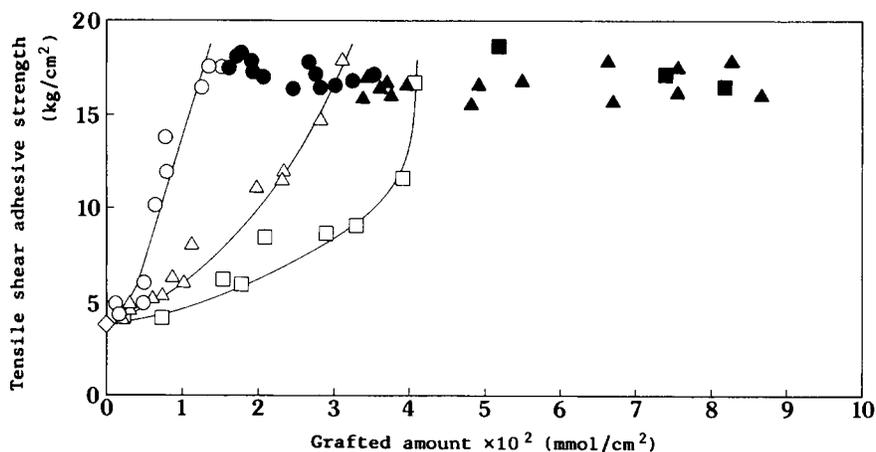
Figure 8 Changes in tensile shear adhesive strength with grafted amount; monomer concentration (mol/dm^3) — O: 0.3, △: 0.6, □: 0.9; adhesion situation—open: adhesives failed, shaded: PE plates broken.

only at surface A for sample ①, and the value of O1s/C1s is higher at surface A than at surface B. It is understood that the failure occurred at a boundary between the grafted layer and PE surface. We can estimate that few grafted chains are located on surface B of sample ① and the bonding strength between grafted chains and adhesives is stronger than that between grafted and PE chains. The peak at 289 eV appeared in the C1s spectrum for sample ②, corresponding to the carbon in the carboxyl group. The difference in values of O1s/C1s between surfaces A and B for sample ② is a little higher than

that for sample ①. A small O1s peak was measured, but no N1s and S2p peaks were.

Some grafted chains were located on surface B, but few adhesives were found. Therefore, for sample ②, the failure occurred at the boundary between the grafted layer and PE surface, the same as for sample ①. For both samples, the penetration of the adhesives into the grafted layer can reach the boundary between the grafted layer and PE surface. The C1s spectrum for sample ③ has two peaks that refer to the existence of the grafted chains and adhesives at 289 and 287 eV, respectively. The appearance of N1s
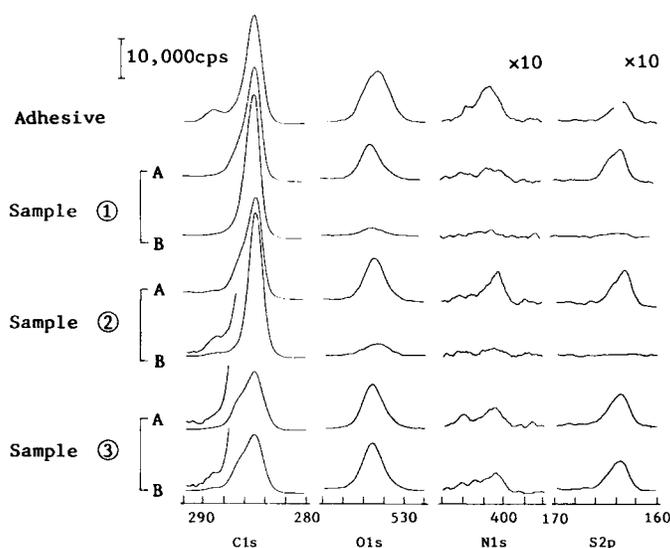
Figure 9 ESCA spectra on C1s, O1s, N1s, and S2p for failed surfaces of polyethylene grafted with MAA at 0.3 mol/dm³.

Table I ESCA Measurements of Failed Surface for MAA-Grafted Polyethylene Plates

Monomer Concentration (mol/dm^3)	Sample	Tensile Share Adhesive Strength (kg/cm^2)	Grafted Amount × 10^2 (mmol/cm^2)		Intensity Ratio		
					O1s/C1s	N1s/C1s	S2p/ C1s
	Adhesive				0.165	0.022	0.024
0.3	3-①	6.06	0.15	A	0.135	0.026	0.024
				B	0.032	—	—
	3-②	10.20	0.64	A	0.230	0.035	0.017
				B	0.050	—	—
	3-③	16.60	1.44	A	0.247	0.033	0.030
				B	0.239	0.032	0.033
0.6	6-①	4.43	0.16	A	0.083	0.021	0.014
				B	0.063	0.021	0.063
	6-②	8.11	1.13	A	0.229	0.054	0.015
				B	0.051	—	—
	6-③	16.70	3.16	A	0.204	0.026	0.094
				B	0.079	—	—
0.9	9-①	4.31	0.15	A	0.128	0.022	0.017
				B	0.045	—	—
	9-②	8.41	2.09	A	0.203	0.049	0.010
				B	0.048	—	—
	9-③	16.63	4.09	A	0.217	0.025	0.010
				B	0.104	—	—

and S2p peaks indicates that there were some adhesives left at the failed surfaces. The comparison between the spectra obtained from both surfaces shows that the failure occurred inside the grafted layer in which the grafted chains and adhesives were mixed together. As the grafted amount increases, the denser grafted layer is formed at the boundary between the grafted layer and PE surface. The grafted chains are entangled with one another or with PE chains.

Dessouki et al. studied the radiation-grafting of AAm into PE films and reported that the rigidity of the polymer increased at very high degrees of grafting; the increase in the adhesive strength is expected at such high degrees of grafting.[21] Therefore, the adhesive strength of the grafted PE plates is considered to become higher than the ultimate strength of the PE plate at higher grafted amounts, where the failure occurred inside the grafted layer. Therefore, the swelling and mechanical properties depend on not only the grafted amount but also on the structural properties of the whole grafted layers.

CONCLUSIONS

Grafting of MAA onto PE plates was studied by using a photografting technique. Based on the above investigations, we can conclude the following:

1. The density of carboxyl groups at the surfaces of the grafted layer increases with the grafted amount and is kept constant above 0.02 mmol/cm^2.
2. Grafting of MAA onto PE plates is effective in enhancing their wettabilities and the grafted amount dependence of wettability is in good agreement with that of the density of the carboxyl group at the surface.
3. The refractive indices for grafted PE surfaces decreases with an increase in the grafted amount and almost agrees with that for PMAA surface around the grafted amount of 0.009 mmol/cm^2, indicating that the PE surfaces is fully covered with grafted PMAA chains.

4. The grafted layer prepared at lower monomer concentrations can absorb a large quantity of water and possesses higher tensile shear adhesive strength.

5. Surface properties depend on the density of the carboxyl group at the surface of grafted layer, and swelling and adhesive properties depend not only on the density of carboxyl group in the whole grafted layers but also on the structural properties such as the length and branching of the grafted chains.

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