Hydrophilic and Adhesive Properties of Polyethylene Plates Grafted with Hydrophilic Monomers

KAZUNORI YAMADA,* HIDEYO TSUTAYA, SHIGEAKI TATEKAWA, and MITSUO HIRATA

Department of Industrial Chemistry, College of Industrial Technology, Nihon University, Izumi-cho, Narashino-shi, Chiba, 275, Japan

SYNOPSIS

The photograftings of methacrylic acid (MAA), acrylic acid (AA), methacrylamide (MAAm), and acrylamide (AAm) as hydrophilic monomers onto polyethylene (PE) plates were carried out in the liquid phase. The contact-angle measurement and the surface analysis by ESCA reveal that the grafted amount at which the PE surface was fully covered with grafted chains increased in the order of MAA > AA > MAAm and was almost the same as that at which contact angles became constant. The grafting of AAm was not sufficient to modify the surface properties of PE. But AAm required the smallest grafted amount to obtain the same adhesive strength as that of the other monomers. The α-methyl and/or carboxyl groups were required to obtain a high grafted amount. The cos θ value of water on AA-g-PE surfaces reached a maximum around 0.02 mmol/cm^2 and then decreased. It was confirmed to be caused by cohesion of grafted poly(acrylic acid) (PAA) chains due to the hydrogen bond. For all the monomers used, the adhesive strength increased with the grafted amount. As the concentration of the MAA monomer increased on grafting, at a higher grafted amount, the grafted layer absorbed water more rapidly and the PE plates themselves broke. For AA- and MAAm-g-PE plates, the amount of absorbed water increased linearly with the grafted amount irrespective of monomer concentration.

INTRODUCTION

Much work has been carried out on graftings of hydrophilic monomers onto hydrophobic polymers such as polyethylene (PE), polypropylene (PP), and polytetrafluoroethylene (Teflon). Usually, UV- and γ-rays have been used as a source of energy to initiate grafting. Recently, Ikada et al. grafted acrylamide (AAm) onto the oxygen- and argon-plasma-treated PE films and reported that the introduction of active sites onto the PE surfaces was effective in initiating grafting. Though wettabilities of the oxygen-plasma-treated PE and PP surfaces with water declines gradually because of overturn and migration of generated oxygen-containing groups into the inside of the films,[1,2] surface properties of the grafted polymer samples are considered to be stable over a long time. In addition, the location of grafting can be restricted to the polymer surfaces without affecting any bulk properties by using the photografting technique. The chemical composition at the outermost surface of the grafted layer reflects surface properties. Therefore, to discuss the modified polymer surfaces, it is important to follow up the composition of the outer surface layers. ESCA (Electron spectroscopy for chemical analysis or X-ray photoelectron spectroscopy) used here is very effective in estimating the surface composition to 5 nm in depth. On the other hand, the swelling behavior depends on not only the grafted amount but also on structural properties of the grafted layer, since it is reflected by properties of the whole grafted layer.[3]

In this study, methacrylic acid (MAA), acrylic acid (AA), methacrylamide (MAAm), and acrylamide (AAm) as hydrophilic monomers were photografted onto PE surfaces, the hydrophilic properties of which were estimated as a function of the grafted amount on the basis of both contact angle and swelling measurements. Furthermore, their adhesive properties were examined by means of the
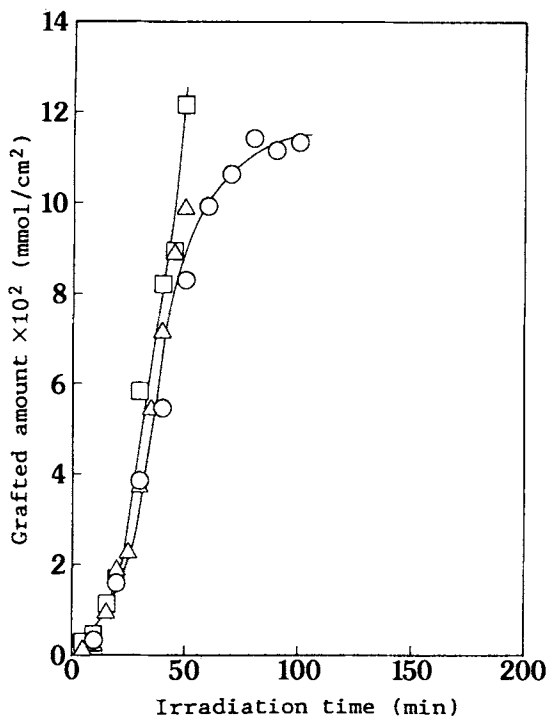
Figure 1   Changes in amount of MAA grafted on PE plates with irradiation time. Monomer concentration (mol/dm^3): (○) 0.9; (△) 1.2; (□) 1.5.

tensile shear adhesive strength measurement. In addition, the compositions of the grafted PE surfaces and their failed surfaces after the adhesive strength measurement were analyzed by means of ESCA.
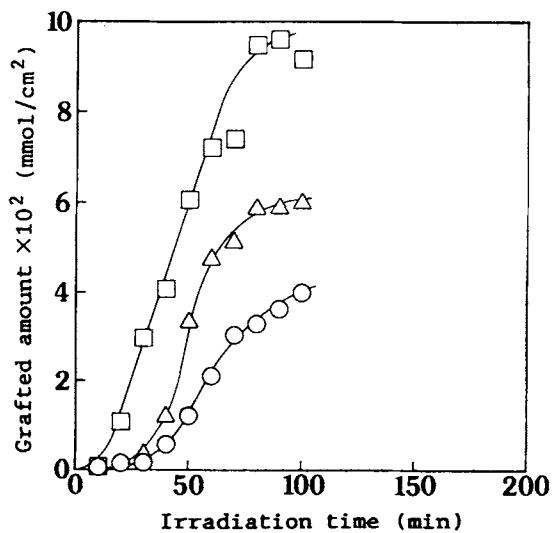

Figure 2   Changes in amount of AA grafted on PE plates with irradiation time. Monomer concentration (mol/dm³): (○) 0.9; (△) 1.2; (□) 1.5.
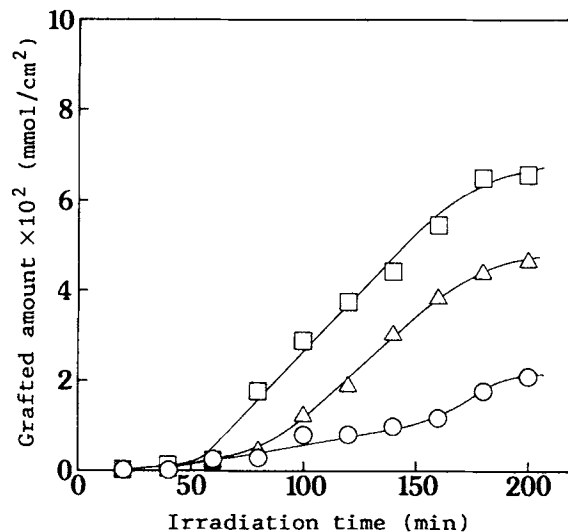

Figure 3   Changes in amount of MAAm grafted on PE plates with irradiation time. Monomer concentration (mol/dm^3): (○) 0.9; (△) 1.2; (□) 1.5.

EXPERIMENTAL

Photografting

MAA and AA were purified by distillation under reduced pressure. MAAm and AAm were recrystallized from benzene at 80°C. 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). Preparation of PE plates, coat-
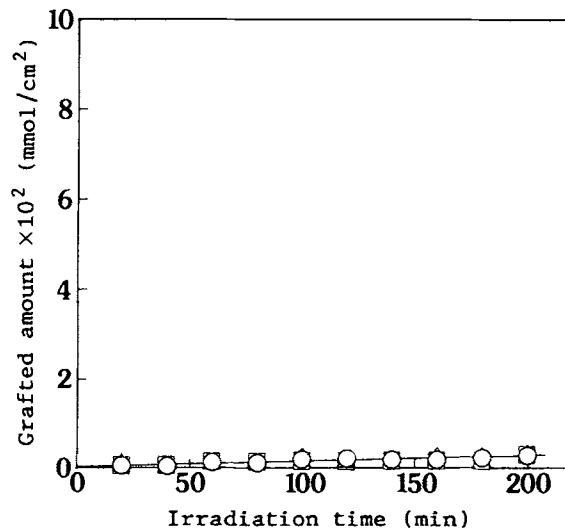

Figure 4   Changes in amount of AAm grafted on PE plates with irradiation time. Monomer concentration (mol/dm^3): (○) 0.9; (△) 1.2; (□) 1.5.

ing of benzophenone as a sensitizer, and photografting were done by the same procedures described in the previous study.[3] The photografting on the sensitizer-coated PE plates was carried out using a 400 W high-pressure mercury lamp at 60°C. The grafted PE plates were washed with hot water at 60–70°C to exclude homopolymers formed in the media and then dried under reduced pressure for 48 h. The grafted amount was calculated from the weight increase of the samples in mmol/cm² using eq. (1):

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

$$= \left(\frac{\text{grafted PE (g)} - \text{ungrafted PE (g)}}{\text{surface area (cm}^2) \times M} \right)$$

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

where M is the molecular weight of the monomer used for grafting.

Surface Analysis by ESCA

The photoelectron spectra were recorded on a Shimadzu ESCA750-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. Binding energies were adjusted to Cls = 285.0 eV for ungrafted PE.[4]
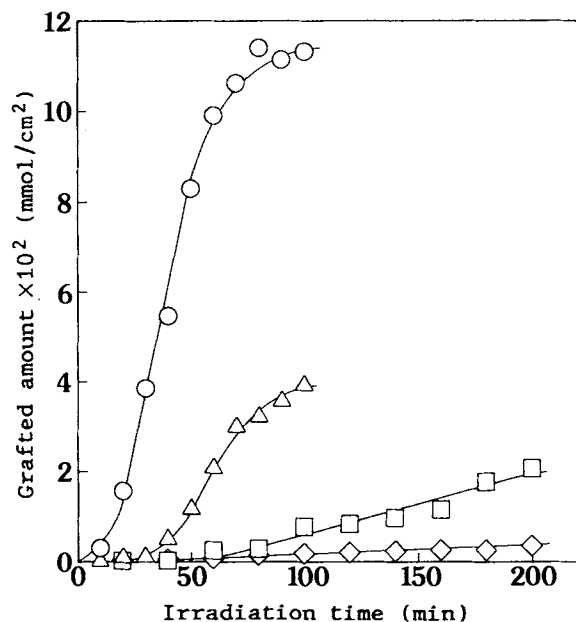
Figure 5 Changes in grafted amount with irradiation time at monomer concentration of 0.9 mol/dm³. Monomer: (O) MAA; (△) AA; (□) MAAm; (◇) AAm.
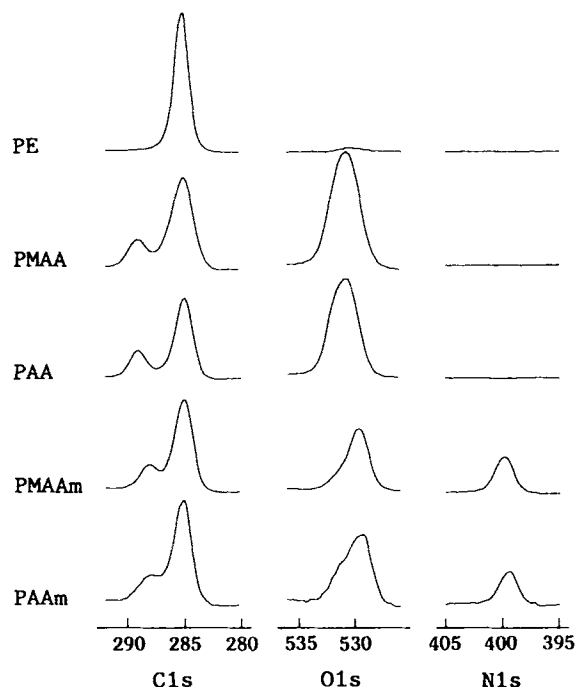
Figure 6 ESCA spectra on Cls, Ols, and Nls for the grafted and ungrafted PE plates.

Contact-angle Measurements

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

Swelling Measurements

The amount of absorbed water, W, and swelling ratio, q, were calculated from the weight increase of the grafted PE plates immersed in water for 48 h at 30°C using eqs. (2) and (3), respectively:

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

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

and

$$q = \frac{W \ (\text{mmol/cm}^2) + G \ (\text{mmol/cm}^2)}{G \ (\text{mmol/cm}^2)} \quad (3)$$

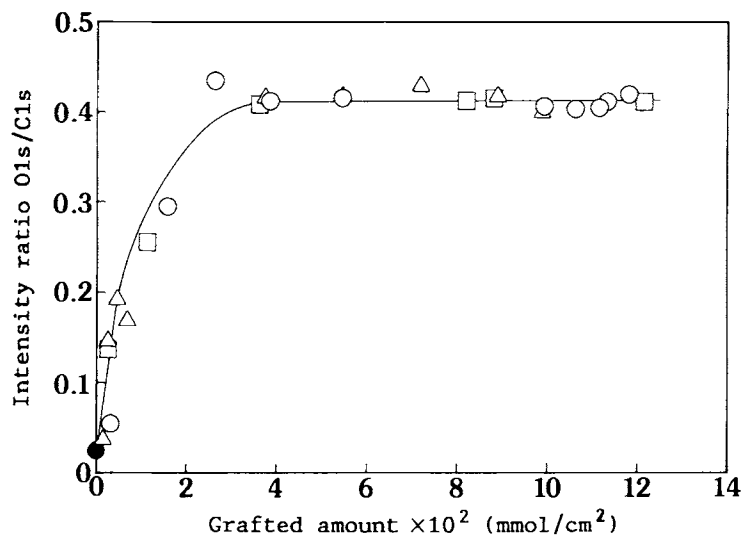where the quantity of 18.016 is the molecular weight of water. In addition, the amount of water bonded

Figure 7   Change in intensity ratio with grafted amount for MAA-g-PE plates. Monomer concentration (mol/dm^3): (○) 0.9; (△) 1.2; (□) 1.5. Sample: (open) grafted PE; (shaded) ungrafted PE.

per monomer segment, in other words, per functional group, n, was calculated using eq. (4):

$$n = \frac{W\,(\mathrm{mmol/cm^2})}{G\,(\mathrm{mmol/cm^2})} = q - 1 \qquad (4)$$
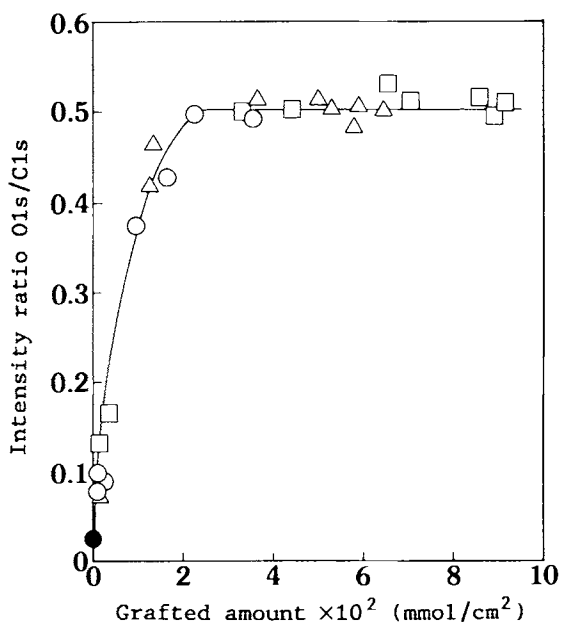

Figure 8   Change in intensity ratio with grafted amount for AA-g-PE plates. Monomer concentration (mol/dm^3): (○) 0.9; (△) 1.2; (□) 1.5. Sample: (open) grafted PE; (shaded) ungrafted PE.

Tensile Shear Adhesive Strength

PE plates of 60 mm length and 10 mm width were used as grafting samples for the tensile shear adhesive strength measurements. After the grafted PE plates were cut widthwise into half, two pieces of the grafted PE plates of the same grafted amount were bonded with a 10 × 10 mm overlap with "Araldite" made by Ciba-Geigy Ltd. as the adhesive. The adhesive was cured for 24 h at 30°C under con-
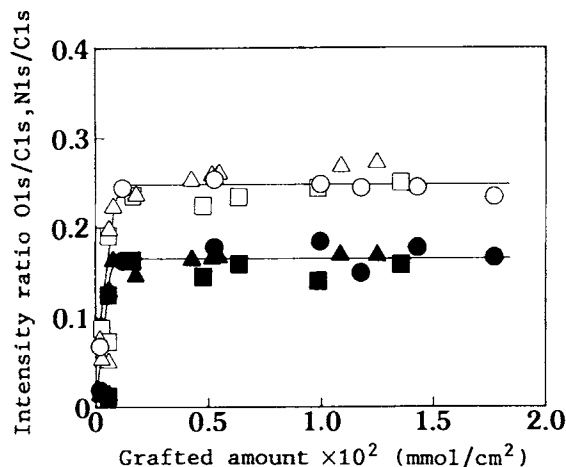

Figure 9   Changes in intensity ratio with grafted amount for MAAm-g-PE plates. Monomer concentration (mol/dm^3): (○) 0.9; (△) 1.2; (□) 1.5. Intensity ratio: (open) O1s/C1s; (shaded) N1s/C1s.

Table I   Surface Properties for the Homopolymers Used and Their Grafted PE Plates

Sample	Intensity Ratio		Grafted amount[a] $\times 10^2$ (mmol/cm^2)	$\cos \theta$[b]
	O1s/C1s	N1s/C1s		
Homopolymers				
PMAA	0.384	—	—	0.74
PAA	0.518	—	—	0.19
PMAAm	0.276	0.218	—	Spreading
PAAm	0.366	0.228	—	Spreading
Ungrafted PE	0.027	—	—	−0.177
Grafted PE plates				
MAA-g-PE	0.42	—	3.0	0.62
AA-g-PE	0.51	—	2.0	0.60 (max)
MAAm-g PE	0.25	0.18	0.2	0.95
AAm-g-PE[c]	0.31	0.17	0.35	0.62 (max)

[a] Grafted amount at which intensity ratios and contact angles become constant.
[b] Contact angles for water.
[c] Maximum values.

stant pressure of 0.5 kg/cm^2. The tensile shear adhesive strength was measured at 25°C with a strain rate of 1 mm/s.

RESULTS AND DISCUSSION

Photografting

The photograftings of four kinds of hydrophilic monomers (MAA, AA, MAAm, and AAm) onto PE surfaces were carried out at monomer concentrations of 0.9–1.5 mol/dm^3. Figures 1–4 show the changes in the grafted amount with irradiation time. For the graftings of MAA, AA, and MAAm, the grafted amount increased with UV irradiation time and monomer concentration.

The grafting of AAm unfavorably took place, and the amount of grafted AAm was limited to 0.003 mmol/cm^2 even at the high monomer concentration of 1.5 mol/dm^3. The grafted amount tended to level off in longer irradiation time, and a considerable amount of homopolymers formed in the reaction media during grafting of MAA, AA, and MAAm. On the other hand, such behavior for the grafting of AAm was never observed even in a longer time at higher monomer concentrations. Uyama and Ikada carried out the grafting of AAm onto PP films UV-irradiated in air for ca. 4 h and reported that the maximum grafted amount reached 130 μg/cm^2 (0.0018 mmol/cm^2).[5] It is inferred from these results

that AAm is hard to graft onto PE and PP in comparison with the other three kinds of hydrophilic monomers.

The induction periods for graftings could be observed except for MAA. After the induction periods, some grafting onto grafted chains themselves such as autocatalysis, autoacceleration, and so on may take place after a longer time period.[6,7] The induction
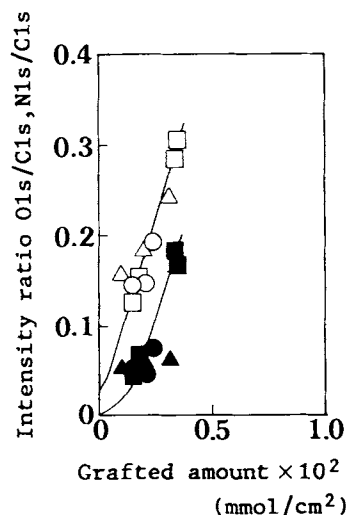

Figure 10 Changes in intensity ratio with grafted amount for AAm-g-PE plates. Monomer concentration (mol/dm^3): (○) 0.9; (△) 1.2; (□) 1.5. Intensity ratio: (open) O1s/C1s; (shaded) N1s/C1s.
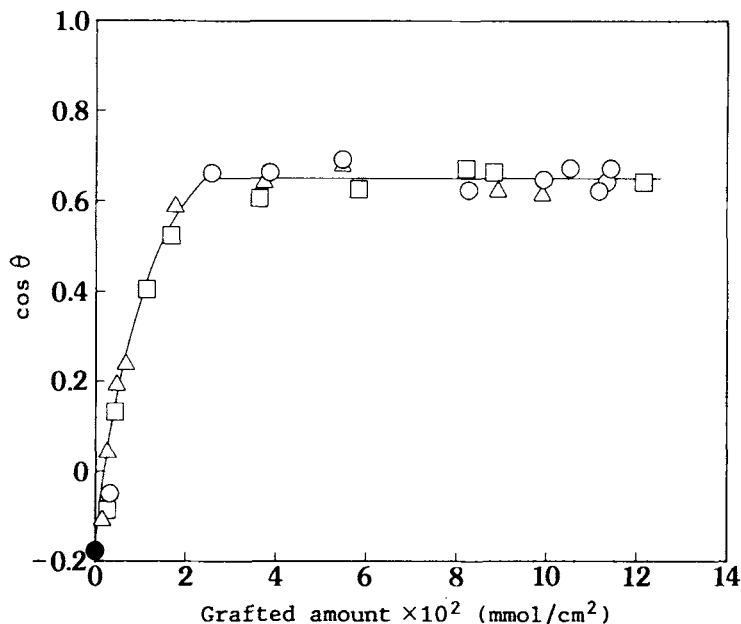
Figure 11 Contact angles for water on MAA-g-PE plates. Monomer concentration (mol/ dm^3): (O) 0.9; (△) 1.2; (□) 1.5. Sample: (open) MAA-g-PE; (shaded) ungrafted PE.

period for AA shortened with the monomer concentration and, on the other hand, that for MAAm was constant around 60 min irrespective of monomer concentration. This is ascribed to the poor affinity of hydrophilic monomers for hydrophobic PE sur-

faces. If the affinity of hydrophilic monomers for PE surfaces is enhanced in the course of grafting, the grafting will further proceed.

Figure 12 Contact angles for water on AA-g-PE plates. Monomer concentration (mol/dm^3): (O) 0.9; (△) 1.2; (□) 1.5. Sample: (open) AA-g-PE; (shaded) ungrafted PE.

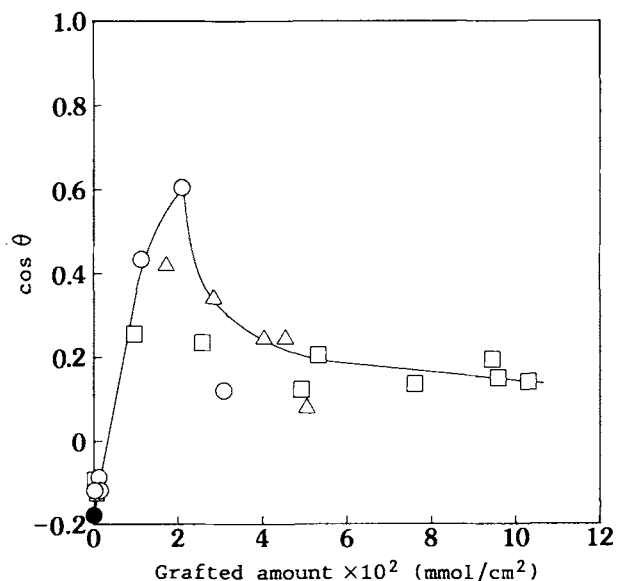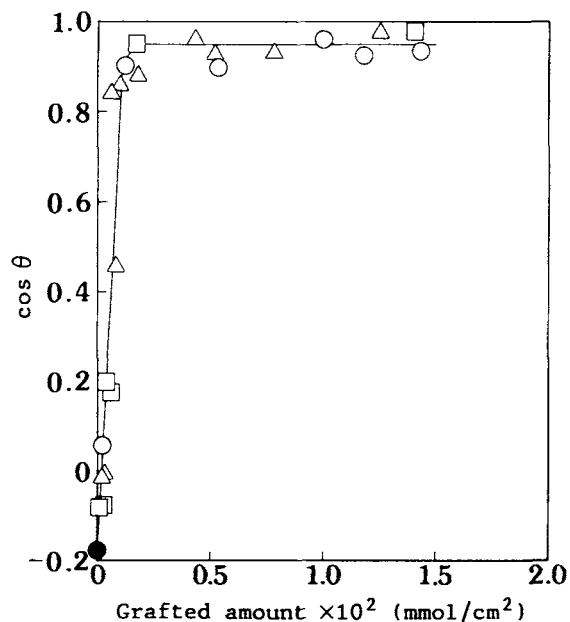**Figure 13** Contact angles for water on MAAm-g-PE plates. Monomer concentration (mol/dm^3): (O) 0.9; (△) 1.2; (□) 1.5. Sample: (open) MAAm-g-PE; (shaded) ungrafted PE.
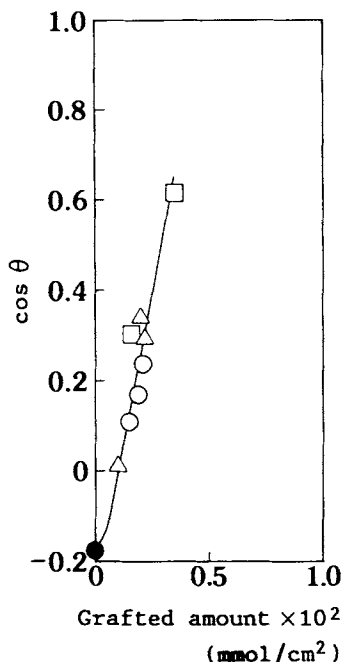
Figure 14 Contact angles for water on AAm-g-PE plates. Monomer concentration (mol/dm^3): (O) 0.9; ($\triangle$) 1.2; ($\square$) 1.5. Sample: (open) AAm-g-PE; (shaded) ungrafted PE.

Figure 5 shows the changes in the grafted amount with UV irradiation time for the graftings of four kinds of hydrophilic monomers at 0.9 mol/dm^3. The

Figure 16 Contact angles for formamide on AA-g-PE plates. Monomer concentration (mol/dm^3): (O) 0.9; ($\triangle$) 1.2; ($\square$) 1.5. Sample: (open) AA-g-PE; (shaded) ungrafted PE.

shorter induction periods corresponded to the higher grafted amounts, and the grafted amount increased in the order of MAA > AA > MAAm > AAm. Therefore, α-methyl or carboxyl group on the monomer better facilitates the grafting onto PE

Figure 15 Contact angles for glycerol on AA-g-PE plates. Monomer concentration (mol/dm^3): (O) 0.9; ($\triangle$) 1.2; ($\square$) 1.5. Sample: (open) AA-g-PE; (shaded) ungrafted PE.
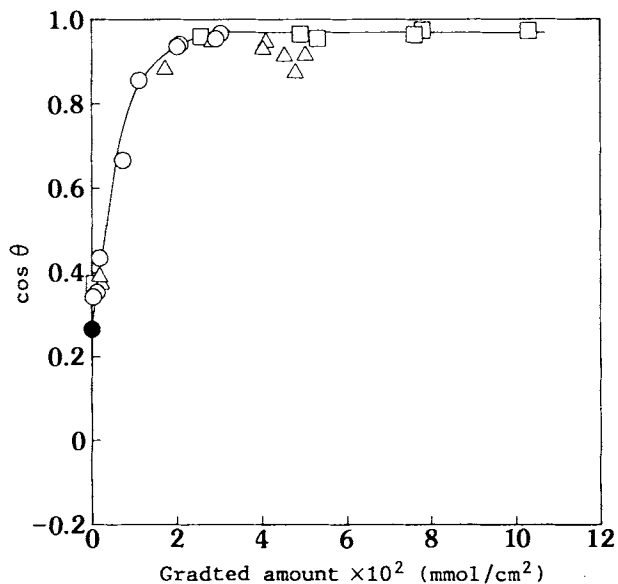
Figure 17 Contact angle for β-thiodiglycol on AA-g-PE plates. Monomer concentration (mol/dm^3): (O) 0.9; ($\triangle$) 1.2; ($\square$) 1.5. Sample: (open) AA-g-PE; (shaded) ungrafted PE.

Table II Contact Angles for Water and Some Organic Solvents on the AA-g-PE Plates

Liquid	Surface Tension (dyne/cm)	cos θ
Water	72.8	0.60 (max)
Glycerol	63.4	0.70
Formamide	58.2	0.79
β-Thiodigrycol	54.0	0.95

surfaces. Ranby et al. and Ogiwara et al. also studied the photografting of hydrophilic monomers onto sensitizer-coated PE films in the liquid phase and reported that grafting % increased in the order of MAA > AA > AAm.[8,9] Their results are in good agreement with ours.

Surface Analysis by ESCA

The grafted PE surfaces were analyzed by ESCA. For the samples with similar geometry and orientation, the ratio of two intensities, I and J, under identical conditions is given by

$$\frac{n_I}{n_J} = \frac{I_I/\sigma_I}{I_J/\sigma_J} \tag{5}$$

where n is the atomic density; I, the peak intensity; and σ, the cross section for photoionization.[10] The cross sections of Cls, Nls, and Ols for ionization are 1.00, 1.77, and 2.85, respectively. Figure 6 shows the Cls, Nls, and Ols spectra for the PE plates grafted with four kinds of hydrophilic monomers together with the ungrafted PE plate. The spectra for the ungrafted PE plate show symmetrical Cls and small Ols peaks. In the Cls spectra for MAA- and AA-g-PE plates, the peak at 289.0 eV assigned to the carbon in the carboxyl group appeared in addition to the peak at 285.0 eV assigned to C—C and C—H bonds. The Cls peaks at 288.5 eV for MAAm- and AAm-g-PE plates correspond to the carbon in the aminocarbonyl group. This chemical shift value was lower than that for the carbon in the carboxyl group. These chemical shift values agree well with those determined by Clark and Thomas.[11]

Figures 7–10 show the changes in intensity ratio with the grafted amount for the grafted PE plates. The intensity ratios for MAA-, AA-, and MAAm-g-PE plates increased with the grafted amount and

then leveled off. As a reference, the surface compositions for individual homopolymers photopolymerized from the monomers used for grafting were analyzed by ESCA. The intensity ratios for the homopolymers and the grafted amounts at which the intensity ratios become constant are summarized in Table I. The intensity ratios for MAA-, AA-, and MAAm-g-PE plates almost agreed with those of their homopolymers. These constant intensity ratios indicate that the grafted layers thicker than the sampling depth of ESCA form on the PE surfaces. The intensity ratio for the AAm-g-PE plate increased with the grafted amount but did not reach a constant value corresponding to that for PAAm homopolymer. This means that the grafting of AAm does not take place sufficiently to cover up the PE surfaces and then the PE surfaces have some scattered distribution of grafted PAAm chains. The values of Ols/Cls were higher than those of Nls/Cls for MAAm- and AAm-g-PE plates. These tendencies agreed with those obtained by Tazuke and Kimura.[12] This suggests that the —NH₂ groups orient toward the interface between air and the grafted layers more easily than do the C=O groups. The grafted amount at which the intensity ratios became constant increased in the order of MAA > AA > MAAm.

Contact-angle Measurements

The surface properties of PE plates grafted with four kinds of hydrophilic monomers were estimated on the basis of the contact-angle measurement. Figures 11–14 show the change in contact angle of water with the grafted amount. Wettabilities of the grafted PE plates were improved at lower grafted amounts of all the monomers used. Wettabilities for MAA-g-PE plates were kept constant above the grafted amount of 0.02 mmol/cm² (cos θ = 0.63). The contact angles became constant around 0.001 mmol/cm² for MAAm-g-PE plates, but it was impossible to measure the contact angles above 0.015 mmol/cm² because water drops swiftly spread on the grafted PMAAm layers. The grafting of MAAm onto PE surfaces seems to be effective in remarkably enhancing their wettabilities. The MAAm-g-PE plates can possess more hydrophilic surfaces than can the MAA-g-PE plates. Therefore, it is considered that an aminocarbonyl group has a closer affinity for water than does a carboxyl group. The contact angles of water on the AAm-g-PE surfaces decreased as the grafted amount increased, but they did not reach a constant value. The maximum of the cos θ value for the AAm-g-PE plate was lower than the value

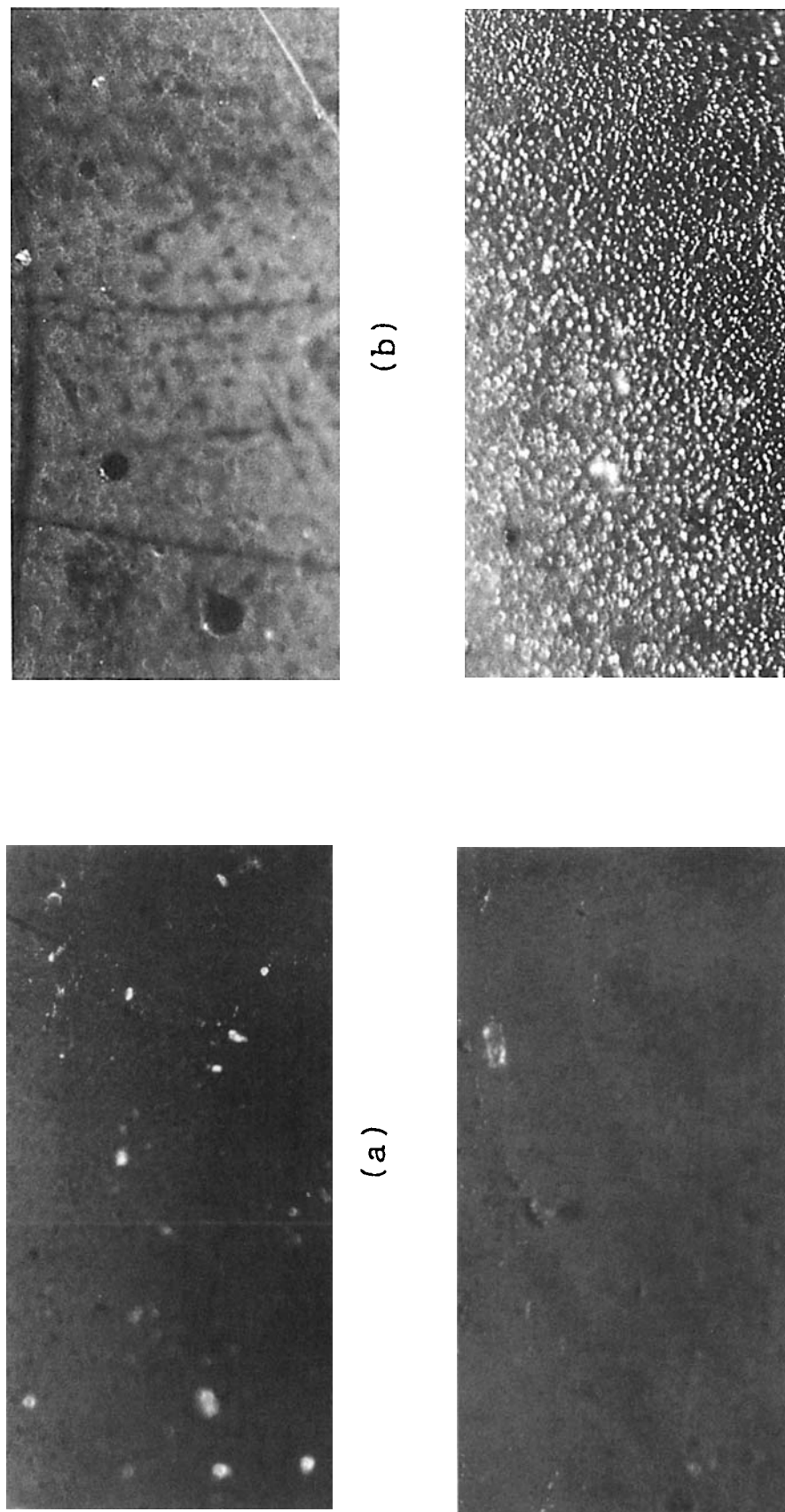**Figure 18** Microphotographs of grafted PE surfaces: (a) MAA-g-PE grafted amount = 3.01×10^2 (mmol/cm^2); (b) MAAm-g-PE, 0.25×10^2 (mmol/cm^2); (c) AA-g-PE, 0.68×10^{-2} (mmol/cm^2); (d) AA-g-PE, 2.10×10^2 (mmol/cm^2).

Figure 19 Changes in amount of absorbed water with amount of MAA grafted on PE plates. Monomer concentration (mol/dm^3): (O) 0.9; ($\triangle$) 1.2; ($\square$) 1.5.
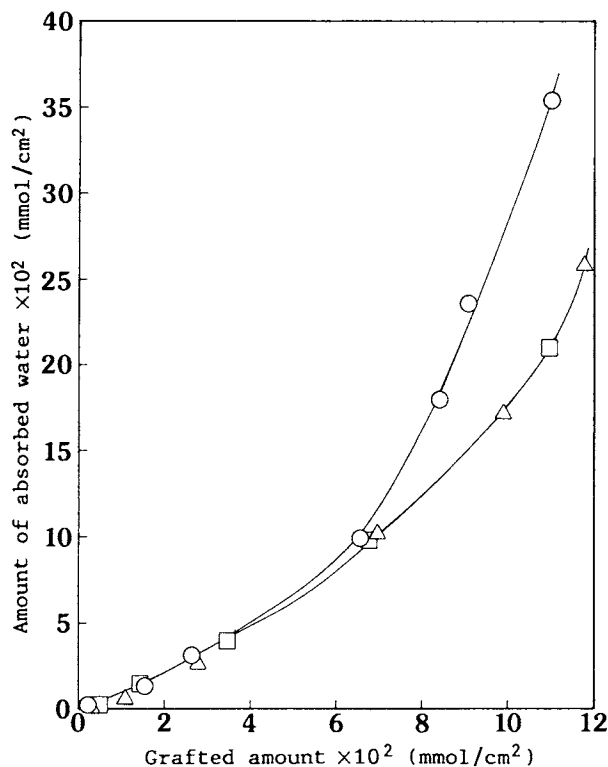

Figure 20 Change in amount of absorbed water with amount of AA grafted on PE plates. Monomer concentration (mol/dm^3): (O) 0.9; ($\triangle$) 1.2; ($\square$) 1.5.

of cos θ for the AAm homopolymer. This is in agreement with a tendency obtained from the surface analysis by ESCA, and so we can make the same point as above, that is, that the PE surfaces are not yet fully covered with grafted PAAm chains.

Wettabilities for AA-g-PE plates went through a maximum value and then decreased to cos θ = 0.17, which is almost equal to the cos θ value for the AA homopolymer prepared by photopolymerization. To understand the anomalous behavior of the contact angle of water, we have investigated some physicochemical properties of the grafted surface such as grafted structure, surface tension (surface free energy), and contact angles of some organic liquids (glycerol, formamide, β-thiodigrycol) with different surface tensions of the grafted layer. Figures 15–17 show the changes in contact angles of some organic liquids with the grafted amount on the AA-g-PE surfaces. Wettabilities of all the organic liquids increased with the grafted amount and then remained constant above 0.02 mmol/cm^2.

As can be seen from Table II, the lower the surface tensions of the organic liquids used, the higher the cos θ values. The contact-angle measurement for the

organic liquids and the surface analysis by ESCA indicate that the density of carboxyl groups are kept constant on the grafted PAA layers above 0.02

Figure 21 Change in amount of absorbed water with amount of MAAm grafted on PE plates. Monomer concentration (mol/dm^3): (O) 0.9; ($\triangle$) 1.2; ($\square$) 1.5.
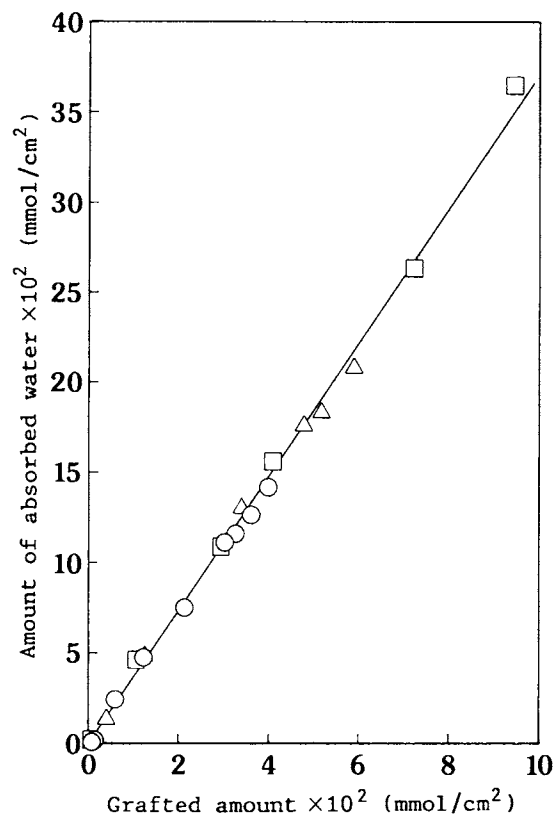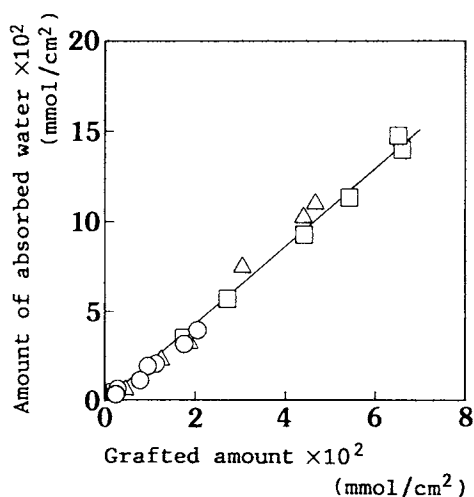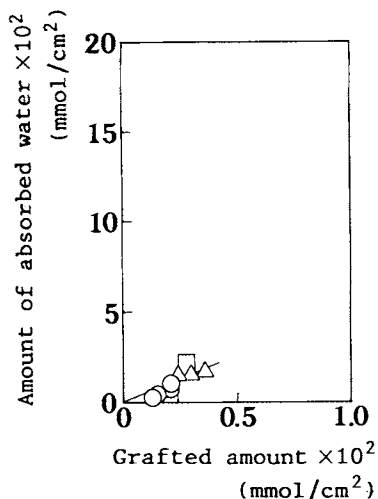
Figure 22   Change in amount of absorbed water with amount of MAAm grafted on PE plates. Monomer concentration (mol/dm³): (O) 0.9; (△) 1.2; (□) 1.5.

mmol/cm² and therefore the decline in contact angle of water is not due to the reaction of carboxyl groups with water.

Figure 18 shows the microscopic photographs of the MAA, AA, and MAAm-g-PE surfaces stained in an aqueous solution of 0.1 wt % toluidine blue (TB). The values in (a), (b), and (d) of Figure 18 are the grafted amounts at which the PE surfaces were fully covered with grafted chains. It is found

Figure 24   Change in swelling ratio and n with amount of AA grafted on PE plates. Monomer concentration (mol/dm³): (O) 0.9; (△) 1.2; (□) 1.5.

that the grafted PE surfaces are stained with TB and that the MAA- and MAAm-g-PE surfaces are flat. The comparison of photographs (c) with (d) for AA-g-PE plates shows that the surface with a lower grafted amount is flat and the grain structure is formed on the surface with the grafted amount of 0.02 mmol/cm².

Chapiro showed that the radiation polymerization of AA led to PAA of the high molecular weight of

Figure 23   Changes in swelling ratio and n with amount of MAA grafted on PE plates. Monomer concentration (mol/dm³): (O) 0.9; (△) 1.2; (□) 1.5.
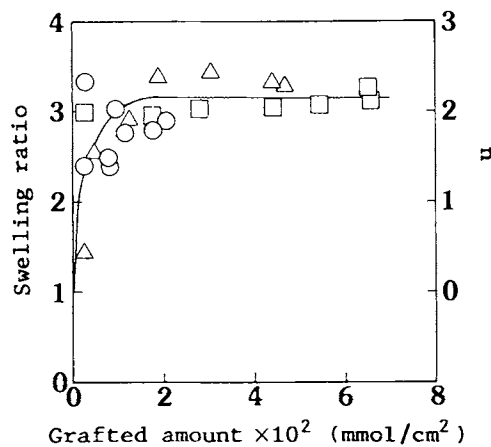
Figure 25   Change in swelling ratio and n with amount of MAAm grafted on PE plates. Monomer concentration (mol/dm³): (O) 0.9; (△) 1.2; (□) 1.5.
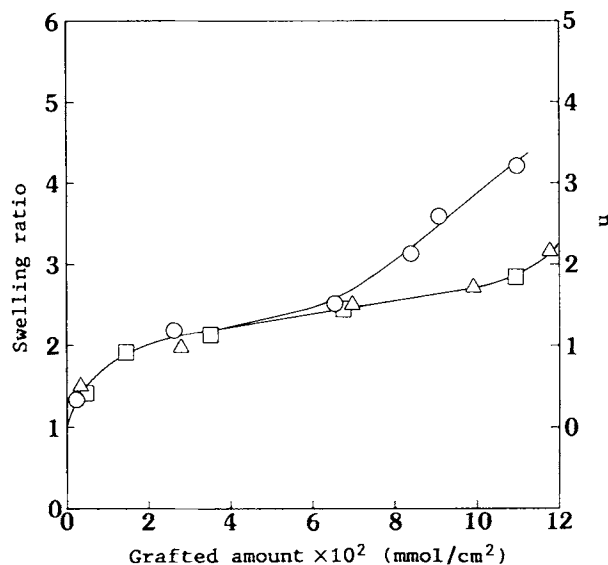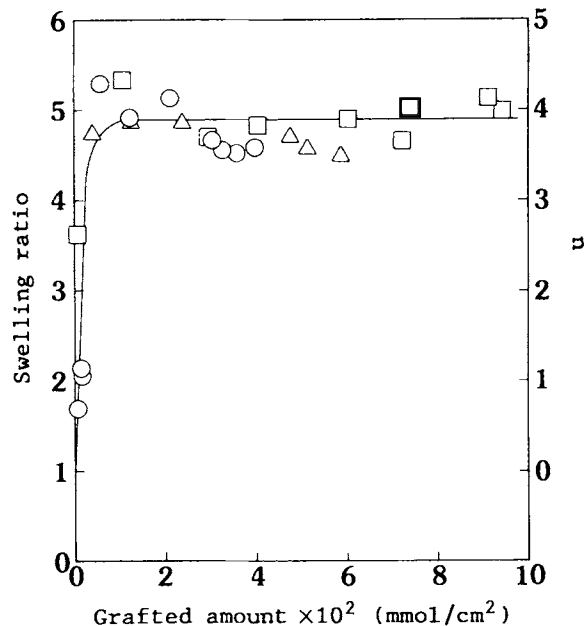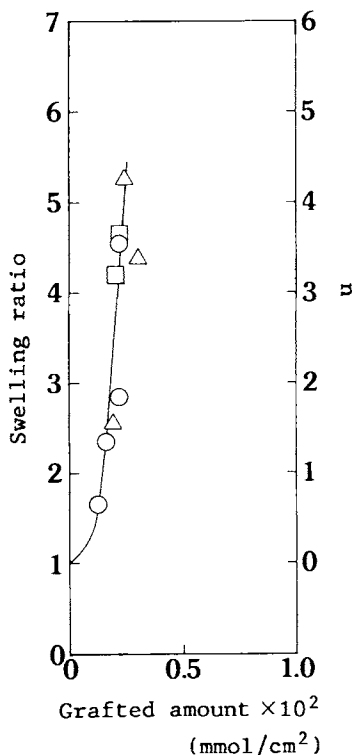
Figure 26 Change in swelling ratio and n with amount of AAm grafted on PE plates. Monomer concentration (mol/dm³): (O) 0.9; (△) 1.2; (□) 1.5.

Figure 28 Change in tensile shear adhesive strength with amount of AA grafted on PE plates. Monomer concentration (mol/dm³): (O) 0.9; (△) 1.2; (□) 1.5. Adhesive situation: (open) adhesives failed; (shaded) PE plates broken.

$1-3 \times 10^6$.[13] It is also possible for grafted PAA chains of high molecular weight to be formed on the PE surfaces even by the photografting. Lawler and

Charlesby showed that PAA chains of molecular weight of 5×10^6 were insoluble in water, i.e., hydrophobic, and formed in powder.[7] Grafted PAA chains cannot usually reorient within such a short

Figure 27 Changes in tensile shear adhesive strength with amount of MAA grafted on PE plates. Monomer concentration (mol/dm³): (O) 0.9; (△) 1.2; (□) 1.5. Adhesive situation: (open) adhesives failed; (shaded) PE plates broken.

Figure 29 Change in tensile shear adhesive strength with amount of MAAm grafted on PE plates. Monomer concentration (mol/dm³): (O) 0.9; (△) 1.2; (□) 1.5. Adhesive situation: (open) adhesives failed; (shaded) PE plates broken.

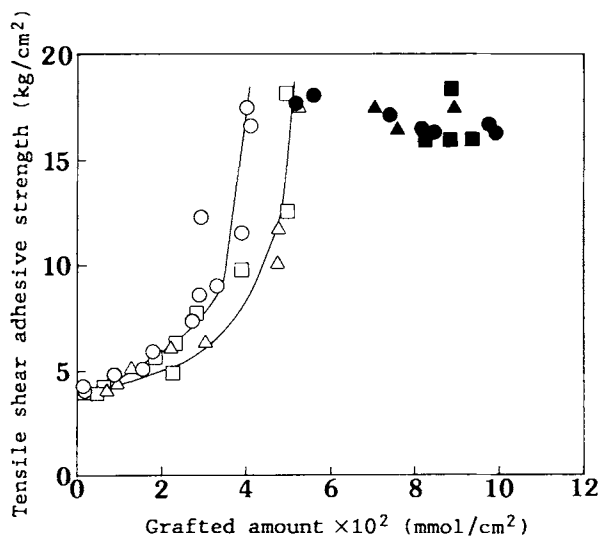**Figure 30** Change in tensile shear adhesive strength with amount of AAm grafted on PE plates. Monomer concentration (mol/dm^3): (O) 0.9; (△) 1.2; (□) 1.5. Adhesive situation: (open) adhesives failed; (shaded) PE plates broken.
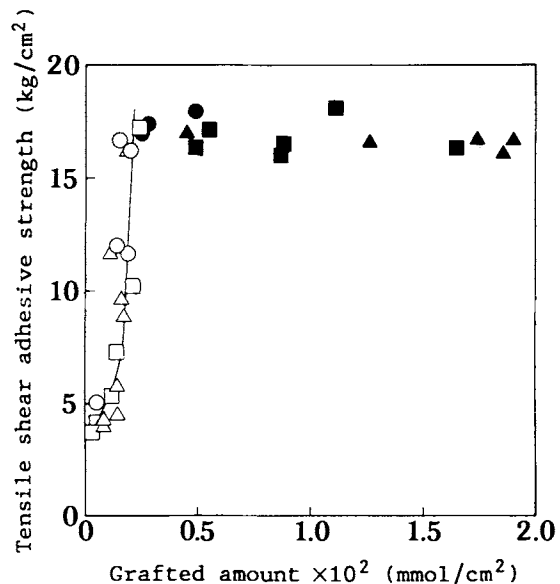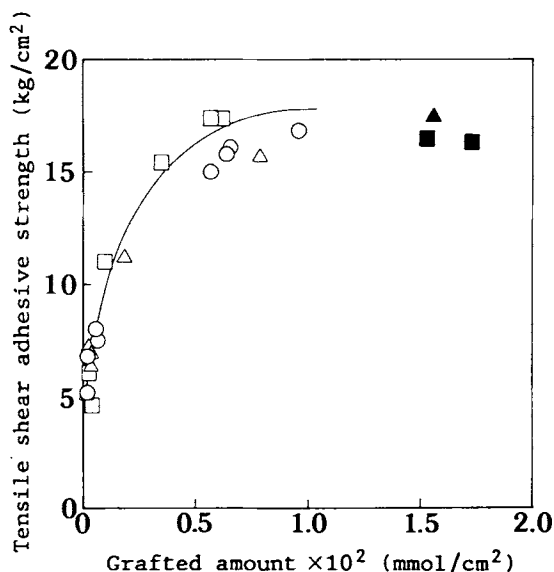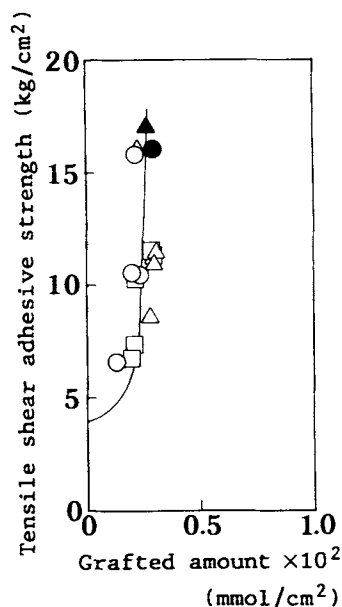
time during measuring a contact angle. Therefore, we consider that the decline in hydrophilicity of the surface of the grafted PAA layer comes from the roughness of surface due to the grain structure formed through the cohesion of grafted PAA chains by a molecular hydrogen bond.

For MAA- and MAAm-g-PE plates, the grafted amounts at which the contact angles of water became constant almost agreed with those at which intensity ratios became constant. The contact angles of the three organic liquids on AA-g-PE plates showed behavior similar to those of water on three other grafted PE plates. The thickness of the grafted layers that dominate the wettabilities of the grafted PE surfaces is almost equal to the sampling depth of ESCA irrespective of the monomer. The grafted amount at which intensity ratios and wettabilities became constant increased in the order of MAA > AA > MAAm, which was the same as the order of the increase in the grafted amount. As the grafted amount at which wettabilities and surface composition become constant increases, the internal grafting proceeds more preferentially.

Table III ESCA Measurements of Failed Surfaces for MAA-grafted PE Plates

Monomer Concentration (mol/dm^3)	Tensile Shear Adhesive Strength (kg/cm^2)	Grafted Amount $\times 10^2$ $(mmol/cm^2)$	Intensity Ratio		
			O1s/C1s	N1s/C1s	S2p/C1s
		Adhesive	0.165	0.022	0.024
		Ungrafted PE	A 0.117	0.022	0.022
			B 0.015	—	—
0.9	4.31	0.15	A 0.128	0.022	0.017
			B 0.045	—	—
	8.41	2.09	A 0.203	0.049	0.010
			B 0.048	—	—
	16.63	4.09	A 0.217	0.025	0.010
			B 0.104	—	—
1.2	5.14	0.41	A 0.128	0.037	0.018
			B 0.070	0.030	—
	11.33	2.22	A 0.138	0.050	0.009
			B 0.060	0.030	0.003
	16.85	5.22	A 0.113	0.035	0.011
			B 0.095	0.039	—
1.5	4.64	0.16	A 0.163	0.042	0.029
			B 0.048	0.032	0.009
	10.81	3.42	A 0.202	0.056	0.015
			B 0.069	0.031	0.008
	18.22	4.94	A 0.182	0.077	0.030
			B 0.137	0.067	0.031

Table IV ESCA Measurements of Failed Surfaces for AA-grafted PE Plates

Monomer Concentration (mol/dm³)	Tensile Shear Adhesive Strength (kg/cm²)	Grafted Amount × 10² (mmol/cm²)	Intensity Ratio		
			O1s/C1s	N1s/C1s	S2p/C1s
		Adhesive	0.165	0.022	0.024
		Ungrafted PE	A 0.117	0.022	0.022
			B 0.015	—	—
0.9	6.30	0.02	A 0.155	0.021	0.027
			B 0.043	—	—
	11.66	0.19	A 0.127	0.023	0.021
			B 0.046	—	—
	16.26	0.20	A 0.129	0.027	0.012
			B 0.055	—	—
1.2	4.56	0.04	A 0.132	0.022	0.015
			B 0.034	0.012	—
	11.73	0.11	A 0.141	0.063	0.024
			B 0.078	0.039	—
1.5	5.00	0.04	A 0.154	0.041	0.019
			B 0.091	0.029	—
	7.34	0.14	A 0.121	0.017	0.013
			B 0.072	0.011	—
	17.26	0.24	A 0.118	0.044	0.019
			B 0.051	0.040	—

Swelling Measurements

The amount of absorbed water was measured as a function of the grafted amount to estimate structural and hydrophilic properties of the whole grafted layers, and those results are shown in Figures 19–22. The amount of absorbed water for MAA-g-PE plates increased with the grafted amount and, especially, it is noteworthy that those prepared at 0.9 mol/dm³ increased sharply above 0.6 mmol/cm³. The concentration of MAA monomer on grafting may be considered to affect the structural properties of the grafted layers. We reported in the previous paper that the PMAA chains grafted at lower monomer concentrations could swell more in water at the lower grafted amount.[3] Then, we considered that the photografting first takes place at the PE surface, followed by both the internal and surface graftings. In the case of lower MAA concentrations, the surface grafting preferentially takes place. Consequently, grafted PMAA chains existing on the PE surface are directly involved in the swelling behavior and so the amount of absorbed water increased rapidly at lower grafted amounts. However, an increase in MAA monomer concentration results in the pref-

erential inside grafting. Since the PMAA chains grafted on the inside of the PE surface have less mobility than do those on the PE surface, the amount of absorbed water becomes relatively lower for MAA-g-PE plates obtained at higher concentrations.

As can be seen from the contact-angle measurement and the surface analysis by ESCA, such grafting behaviors do not affect any wettabilities that depend on the number of functional groups on the outermost surface of the grafted layer, but do affect the swelling properties that depend on both the structure of the grafted layers and the number of functional groups in the whole grafted layer. Ogiwara et al. also reported that under a condition where grafting proceeded favorably the grafted chains distributed inside the PE film.[14] The amount of absorbed water for AA- and MAAm-g-PE plates increased linearly with the grafted amount and was independent of monomer concentration. The amount of absorbed water for AAm-g-PE plates also increased with the grafted amount in the limited range of swelling measurement. Water uptake and the dimension for hydrophobic films radiation-

grafted with hydrophilic monomers increased linearly with the degree of grafting.[15-17] Hegazy et al. reported that the swelling behavior depended on the number of hydrophilic groups.[18]

For the radiation-grafting, the internal grafting proceeds preferentially because of stronger radiation energy, and, consequently, the swelling behavior is independent of grafting conditions. Since the energy of UV lights generated from the high-pressure mercury lamp is lower than that of radiation, the surface grafting preferentially occurs compared to the internal grafting. However, we consider that the higher concentration of MAA monomer offers the possibility of the internal grafting. Consequently, the swelling behavior of the MAA-g-PE plate depends on the grafting conditions.

The changes in swelling ratio with the grafted amount are shown in Figures 23–26. The symbol n denotes the number of water per monomer segment, that is, per polar group. The swelling ratio for MAA-g-PE plates increased sigmoidally with the grafted amount. Both wettabilities and the intensity ratio

increased below the 0.03 mmol/cm^2 grafted amount, indicating that as the PE surface was covered with grafted PMAA chains the swelling ratio increased.

The results from contact-angle measurement and surface analysis by ESCA show that when the amount of grafted MAA exceeds 0.03 mmol/cm^2 the grafted PMAA layer thickens without affecting any bulk properties. No significant increase in the swelling ratio was observed in the range of 0.02–0.06 mmol/cm^2, indicating that the internal grafting proceeded considerably. The n values for MAA-g-PE plates prepared at 0.9 mol/dm^3 increased from 1.5 to 4.0, and for those prepared above 1.2 mol/dm^3, they increased gradually. As the grafting of MAA was carried out at higher monomer concentrations, the swelling ratio increased rapidly at higher grafted amounts. This also suggests that MAA monomers at higher concentrations progressively graft on the inside of the PE surface. The swelling ratio for AA- and MAAm-g-PE plates remained constant irrespective of monomer concentration ($n = 4.0$ for AA-g-PE plates and $n = 2.0$ for

Table V   ESCA Measurements of Failed Surfaces for MAAm-grafted PE Plates

Monomer Concentration (mol/dm^3)	Tensile Shear Adhesive Strength (kg/cm^2)	Grafted Amount $\times 10^2$ (mmol/cm^2)	Intensity Ratio		
			O1s/C1s	N1s/C1s	S2p/C1s
		Adhesive	0.165	0.022	0.024
		Ungrafted PE	A 0.117	0.022	0.022
			B 0.015	—	—
0.9	6.83	0.02	A 0.118	0.035	0.020
			B 0.033	—	—
	8.04	0.06	A 0.151	0.039	0.015
			B 0.053	—	—
	16.09	0.66	A 0.227	0.158	—
			B 0.222	0.047	0.039
1.2	5.40	0.02	A 0.100	0.022	0.017
			B 0.066	—	—
	10.03	0.03	A 0.166	0.027	0.016
			B 0.105	—	—
	15.75	0.53	A 0.240	0.040	0.037
			B 0.188	0.116	—
1.5	6.46	0.04	A 0.103	0.016	—
			B 0.057	0.028	—
	11.02	0.10	A 0.117	0.043	0.013
			B 0.035	—	—
	16.05	0.64	A 0.227	0.076	—
			B 0.222	0.038	0.046

Table VI   ESCA Measurements of Failed Surfaces for AAm-grafted PE Plates

Monomer Concentration (mol/dm³)	Tensile Shear Adhesive Strength (kg/cm²)	Grafted Amount × 10² (mmol/cm²)	Intensity Ratio		
			O1s/C1s	N1s/C1s	S2p/C1s
		Adhesive	0.165	0.022	0.024
		Ungrafted PE	A 0.117	0.022	0.022
			B 0.015	—	—
0.9	6.56	0.12	A 0.136	0.021	0.015
			B 0.061	—	—
	10.48	0.22	A 0.151	0.056	0.028
			B 0.078	—	—
	15.82	0.21	A 0.161	0.048	0.030
			B 0.110	—	—
1.2	7.63	0.28	A 0.058	0.014	0.014
			B 0.049	—	—
	11.00	0.30	A 0.105	0.044	0.017
			B 0.080	—	—
	16.09	0.23	A 0.251	—	0.039
			B 0.082	—	—
1.5	6.71	0.20	A 0.156	0.078	0.023
			B 0.098	—	—
	10.23	0.22	A 0.157	0.044	0.046
			B 0.072	—	—

MAAm-g-PE plates). This reveals that the swelling ratios for AA- and MAAm-g-PE plates depend on only the number of the polar groups and that the structural properties and morphology for grafted PAA and PMAAm chains are independent of monomer concentration. The swelling ratio of AAm-

g-PE plates increased rapidly at a low grafted amount and the n value reached 5.5. In the case where grafting was carried out above 0.9 mol/dm³, the swelling ratio for AAm-g-PE plates was higher than that for MAA-g-PE plates. Therefore, if the AAm-g-PE plates of higher grafted amounts were
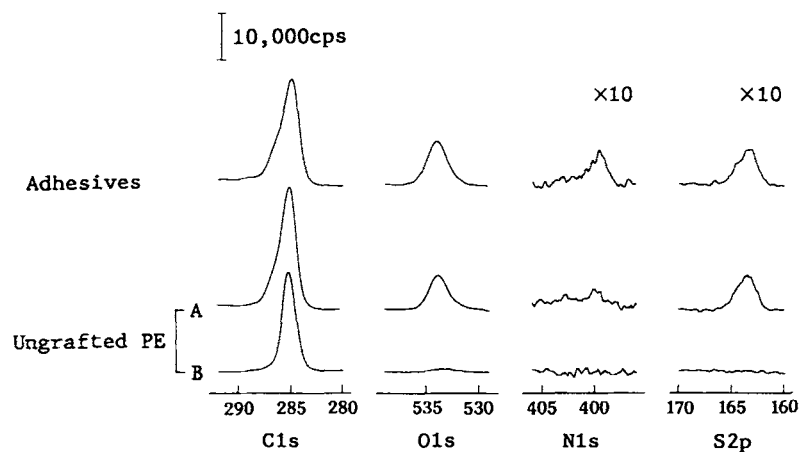

Figure 31   ESCA spectra on C1s, O1s, N1s, and S2p for adhesives and failed surfaces of ungrafted PE plates.

prepared, they could absorb more water. On the basis of the swelling measurement, we can discuss not only the structural properties of the grafted layers but also the mechanism of grafting.

Adhesive Properties for Grafted PE Plates

Figures 27–30 show the changes in the tensile shear adhesive strength with the grafted amounts of individual monomers. The adhesive strength for MAA-g-PE plates increased with the grafted amount. It is found by comparison of these results with those in the previous paper[3] that the adhesive strength for MAA-g-PE plates prepared at lower monomer concentrations increased rapidly in the range of lower grafted amounts. The monomer concentration dependence of adhesive strength is similar to that of the swelling behavior. The internal grafting at higher monomer concentrations tended to decrease the adhesive strength. The adhesive strength for AA-g-PE plates was effectively improved at lower grafted amounts. The AA-g-PE plates broke above

the grafted amount of 0.002 mmol/cm², corresponding to one-tenth as low as the grafted amount of 0.02 mmol/cm² at which the PE plates were covered with grafted PAA chains. The adhesive strength for MAA-g-PE plates increased rapidly above the grafted amount of 0.03 mmol/cm², at which the PE plates were fully covered with grafted PMAA chains. For MAAm-g-PE plates, the adhesive strength increased rapidly below the grafted amount of 0.003 mmol/cm², at which the PE plates were covered with grafted PMAAm chains. However, even if the grafted layer became thicker in the range of 0.003–0.01 mmol/cm², no significant increase in the adhesive strength was observed.

Comparison between the results in Figures 28 and 30 shows that the changes in the adhesive strength with the grafted amount for AAm-g-PE plates are similar to those for AA-g-PE plates. It is evident from the above results that the grafting of hydrophilic monomers onto PE surfaces can enhance their adhesive properties. The grafted amount at which the grafted PE plates broke increased in the order
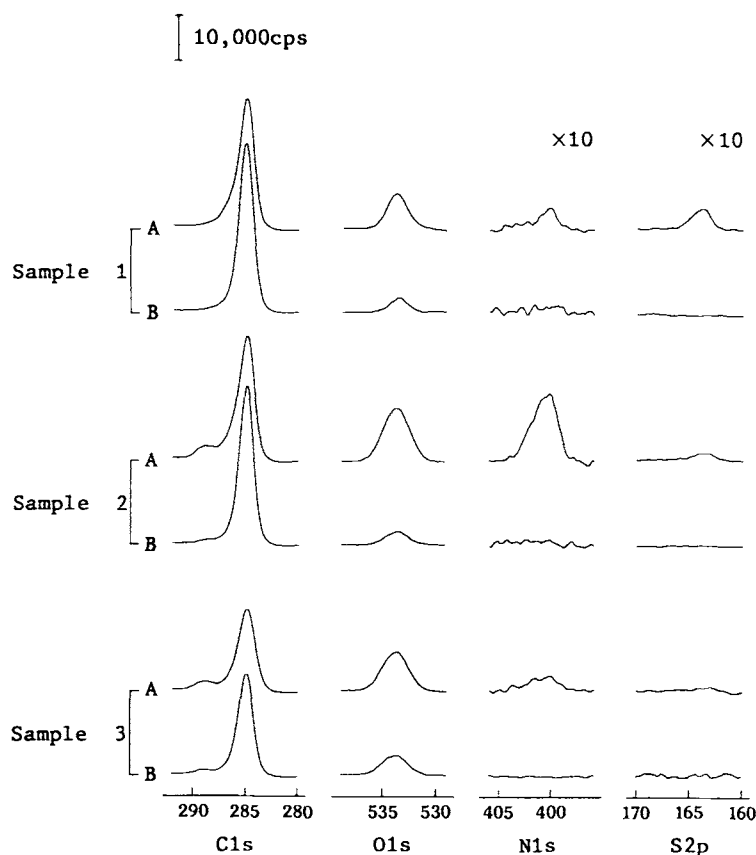

Figure 32   ESCA spectra on C1s, O1s, N1s, and S2p for failed surfaces of PE plates grafted with MAA at 0.9 mol/dm³.

of MAA > AA > MAAm. As the monomers used have poorer affinity for PE plates, it is more difficult for the grafted chains to penetrate into PE plates, and, consequently, the grafted chains existing on the PE surfaces can improve considerable adhesive properties. The grafted PE plates with higher adhesive strength failed at around 17 kg/cm², where the ungrafted PE plate broke on being subjected to the strain under the same conditions, following some necking and elongation.[19] Then, this value is the ultimate tensile strength of the ungrafted PE plate.[10] Since the adhesive strength for the ungrafted PE plate was 3.8 kg/cm², the surface properties of the plates used could be modified without affecting any bulk properties. In addition, the adhesive strength as well as swelling properties reflects structural properties of the grafted layers.

The compositions of failed surfaces after the measurement of adhesive strength were estimated to elucidate the failure mechanism on the basis of the analysis by ESCA. The intensity ratios, O1s/C1s, N1s/C1s, and S2p/C1s, were calculated from

eq. (5). The cross sections of N1s and S2p for ionization are 1.77 and 1.74, respectively.[10] The values of the intensity ratios for the failed surfaces of the grafted PE plates are summarized in Tables III–VI and their C1s, O1s, N1s, and S2p spectra are shown in Figures 31–35. The C1s spectrum for the adhesives used shows an overlapping peak, which divides into two peaks at 285.0 and 287.0 eV. N1s at 399.8 eV and S2p at 170.0 eV were also confirmed. The states of failure can be estimated by using these peaks characteristic of the used adhesives. It was confirmed from Figure 31 that nitrogen and sulfur remained only on Surface A for the ungrafted PE plate. This shows that the failure occurred at the interface between the PE surface and the adhesives and that the adhesives never penetrated into PE plates. The C1s, O1s, N1s, and S2p spectra for MAA-g-PE plates with different adhesive strengths are shown in Figure 32. N1s and S2p peaks appeared only at the Surface A for Sample 1 of the grafted amount of 0.0015 mmol/cm², and the value of O1s/C1s was higher at Surface A than at Surface B.
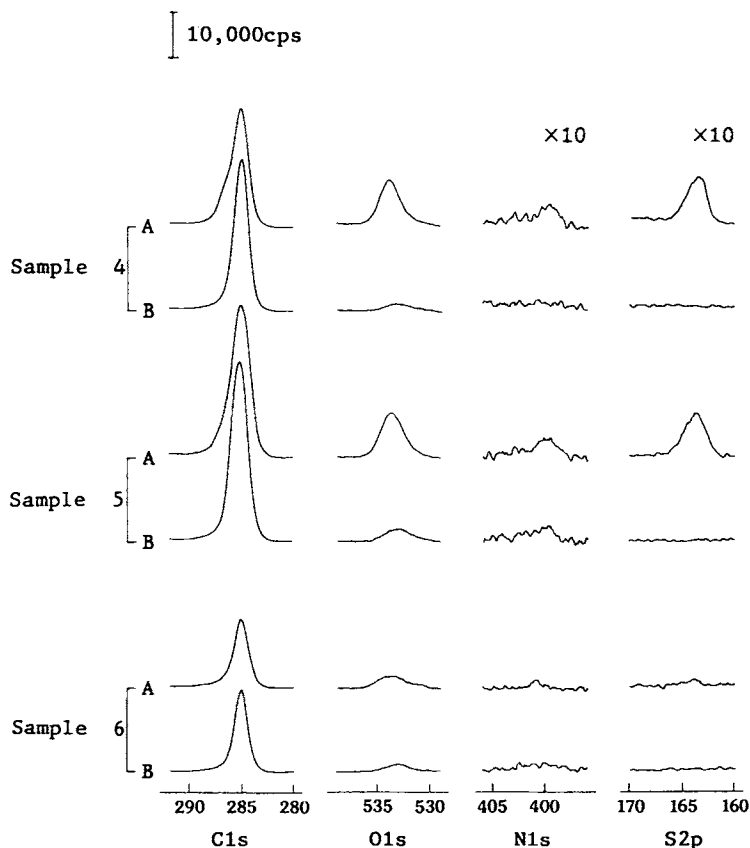

Figure 33   ESCA spectra on C1s, O1s, N1s, and S2p for failed surfaces of PE plates grafted with AA at 0.9 mol/dm³.

These show that the failure occurred between the PE surface and the layer in which grafted PMAA chains and the adhesives mixed. Below the grafted amount at which the PE surface is fully covered with grafted PMAA chains, the layer in which grafted chains coexist with the adhesives is formed on the PE surface. In the C1s spectrum for Surface A of Sample 2, the peak at 289.0 eV appeared distinctly. The difference in O1s/C1s values between Surfaces A and B for Sample 2 is higher than that for Sample 1.

For Sample 2, the interface failure occurred between the PE surface and the layer in which grafted chains and the adhesives mixed the same as for Sample 1. The spectra for C1s and O1s indicate that some grafted PMAA chains exist on Surface B. The peak at 289.0 eV was observed in the C1s spectra for both surfaces of Sample 3 and a relatively higher O1s/C1s value was obtained at Surface B of Sample 3, indicating that the failure occurred inside the grafted PMAA layer. Similar results were obtained for both failed surfaces of MAA-g-PE plates pre-

pared at 1.2 and 1.5 mol/dm³. The lower adhesive strengths for the MAA-g-PE plates of lower grafted amounts can be ascribed to the shortage of fully intimate contact including entanglements in the layer of grafted PMAA chains mixed with PE chains. An increase in the amount of grafted MAA reinforces the bond strength among grafted PMAA and PE chains.

Figures 8 and 33 show that since all the PE surfaces were not yet covered with grafted PAA chains the failure occurred between PE surfaces and the mixed layers. Because of a low grafted amount, PAA grafted chains were distinctly confirmed from C1s spectra. We can suggest from Table IV that the failure for AA-g-PE plates obtained at 1.2 and 1.5 mol/dm³ occurs inside the grafted PAA layer mixed with the adhesives. The O1s/C1s values for failed surfaces were higher than the quantity of 0.021 for the ungrafted PE plate. This indicates a small amount of grafted PAA chains remaining on Surface B. Grafted PAA chains on Surface B tend to increase with adhesive strength.
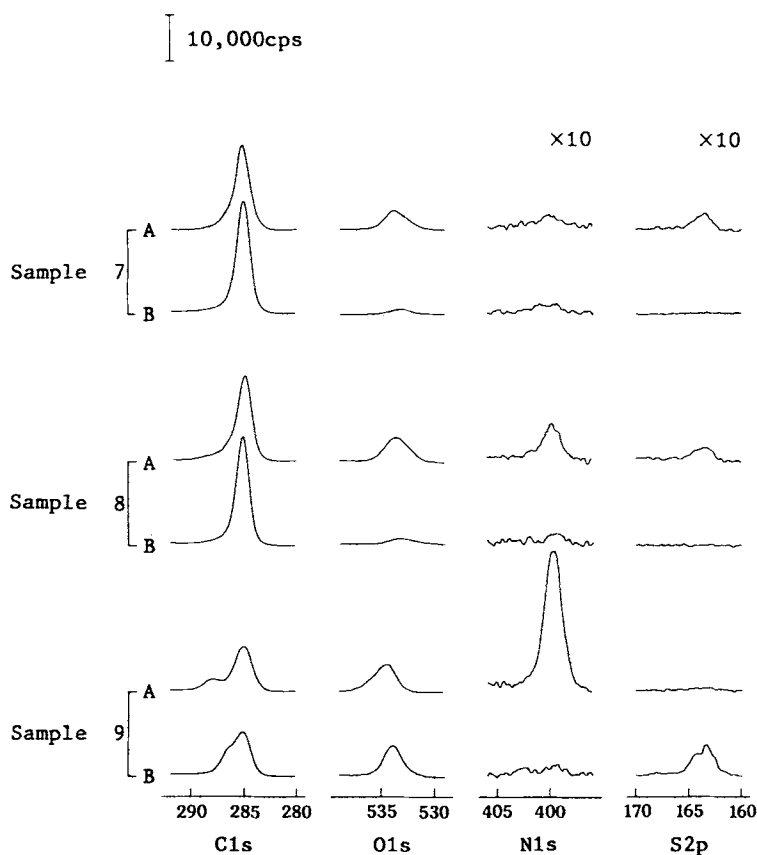

Figure 34   ESCA spectra on C1s, O1s, N1s, and S2p for failed surfaces of PE plates grafted with MAAm at 0.9 mol/dm³.

Figure 34 shows that for Samples 7 and 8 the failure occurred between the PE surface and the layer of grafted PMAAm chains and adhesives. The C1s peak at 288 eV and the N1s peak at 400 eV were confirmed at Surface A of Sample 9. The adhesives left on Surface B was confirmed from the C1s peak at 286 eV and S2p peak at 170 eV. Therefore, it is considered that for Sample 9 the failure occurred between the grafted PMAAm layer and the adhesives.

Figure 35 shows that since all the PE surfaces were not yet covered with the grafted PAAm amount the failure occurred between the PE surfaces and the mixed layers, the same as for AA-g-PE plates. It is confirmed that both grafted PAAm chains and adhesives remain at Surface B for Samples 10–12. The O1s/C1s values were higher than the quantity for ungrafted PE plates, indicating that there are a few grafted PAAm chains left on Surface B. Similar results were also obtained for both failed surfaces of PAAm-g-PE plates prepared at 1.2 and 1.5 mol/dm^3.

CONCLUSION

We studied the surface properties of the PE plates grafted with four kinds of monomers such as wettabilities, water absorptivities, and adhesive properties. From the experimental results discussed above, we can conclude the following:

1. The grafted amount increases in the order of MAA > AA > MAAm > AAm, and the α-methyl or carboxyl group in the monomer segment favors grafting processes.
2. The grafted amount at which wettabilities become constant almost agrees with that at which the surface composition of the grafted layer becomes constant and the wettabilities increase in the order of MAA > AA > MAAm. The grafting of AAm is not sufficient to modify the PE surface. A decline in cos θ of water on AA-g-PE plates is ascribed to roughness of surface of grafted PAA layer through
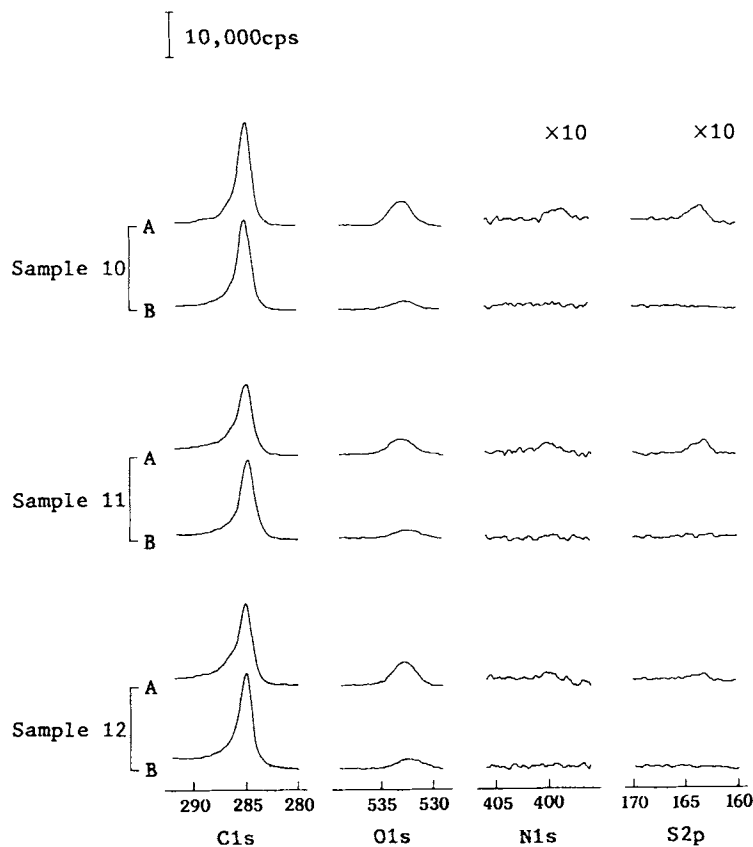

Figure 35   ESCA spectra on C1s, O1s, N1s, and S2p for failed surfaces of PE plates grafted with AAm at 0.9 mol/dm^3.

cohesion of grafted PAA chains by the hydrogen bond.

3. The amount of absorbed water increases linearly with the grafted amount and depends on only the number of functional groups on AA- and MAAm-g-PE plates. In the case of a high MAA concentration, the internal grafting occurs and the amount of absorbed water with the grafted amount deviates from the linearity.

4. The tensile shear adhesive strength increases with the grafted amount in all monomers. The grafted amount at which the grafted PE plates break is the order of MAA > MAAm > AA-AAm. At a low grafted amount, the failure occurs between the PE surface and the layer mixed with grafted chains and the adhesives, whereas at a high grafted amount, the failure occurs between the grafted layer and the mixed layer.

REFERENCES

1. H. Yasuda, and A. K. Sahrma, *J. Polym. Sci. Polym. Chem. Ed.,* **19,** 1285 (1981).
2. Y. Ikada, T. Matsunaga, and M. Suzuki, *Nippon Kagaku Kaishi (J. Chem. Soc. Jpn. Chem. Ind. Chem.),* 1079 (1985).
3. K. Yamada, T. Kimura, H. Tsutaya, and M. Hirata, *J. Appl. Polym. Sci.,* **44,** 993 (1992).
4. R. Holm, and S. Storp, *Surf. Interface Anal.,* **2,** 96 (1980).
5. Y. Uyama, and Y. Ikada, *J. Appl. Polym. Sci.,* **36,** 1087 (1988).
6. A. Safranji, H. Omichi, and J. Okamoto, *Radiat. Phys. Chem.,* **27,** 477 (1986).
7. J. P. Lawler and A. Charlesby, *Radiat. Phys. Chem.,* **15,** 595 (1980).
8. B. Ranby, Z. M. Gao, A. Hult, and P. Y. Zhang, ACS Symposium Series 364, American Chemical Society, Washington, DC, 1988, p. 1980.
9. Y. Ogiwara, M. Kanda, M. Takumi, and H. Kubota, *J. Polym. Sci. Polym. Lett. Ed.,* **19,** 457 (1981).
10. D. R. Miller, and N. A. Peppas, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.,* **C26,** 33 (1986).
11. D. T. Clark, and H. R. Thomas, *J. Polym. Sci. Polym. Lett. Ed.,* **16,** 791 (1978).
12. S. Tazuke, and H. Kimura, *Makromol. Chem.,* **179,** 2603 (1978).
13. A. Chapiro, *Pure Appl. Chem.,* **30,** 77 (1972).
14. Y. Ogiwara, N. Koide, and H. Kubota, *J. Appl. Polym. Sci.,* **35,** 1473 (1988).
15. A. M. Dessouki, E. A. Hegazy, N. B. El-Assy, and H. A. El-Boohy, *Radiat. Phys. Chem.,* **27,** 431 (1986).
16. E. A. Hegazy, I. Ishigaki, A. Rabie, A. M. Dessouki, and J. Okamoto, *J. Appl. Polym. Sci.,* **28,** 1465 (1983).
17. H. Omichi, D. Chundury, and V. T. Stannett, *J. Appl. Polym. Sci.,* **32,** 4827 (1986).
18. E. A. Hegazy, N. B. El-Assy, N. H. Taher, and A. M. Dessouki, *Radiat. Phys. Chem.,* **33,** 539 (1989).
19. M. L. Miller, *The Structure of Polymers,* Reinhold, New York, 1966.