

Adhesion of Ultrahigh Molecular Weight Polyethylene Plates Photografted with Hydrophilic Monomers and Evaluation of Failure Location by X-ray Photoelectron Spectroscopy

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ABSTRACT: In this study, methacrylic acid (MAA) and acrylic acid (AA) were photografted onto the ultrahigh molecular weight polyethylene (UHMWPE) plates at different monomer concentrations and temperatures, and the grafted UHMWPE plates were bonded with aqueous polyvinyl alcohol (PVA) solutions. The tensile shear adhesive strength of both grafted UHMWPE plates was also discussed in relation to wettability and water absorptivity. The location of failure was also estimated by X-ray photoelectron spectroscopy (XPS). Wettability of the MAA-grafted UHMWPE plates became constant, when the UHMWPE surface was fully covered with grafted PMAA chains. Conversely, wettability of the AA-grafted UHMWPE plates passed through the maximum value and then gradually decreased against the grafted amount probably due to aggregation of grafted PAA chains. Water absorptivity of the grafted layers formed at lower monomer concentrations or temperatures sharply increased at lower grafted amounts. The adhesive strength increased with the grafted amount and substrate breaking was observed at higher grafted amounts, indicating that a main factor to increase the adhesive strength is the formation of a grafted layer by shorter grafted polymer chains and/or the restriction of the location of photografting to the outer surface region. In addition, surface analysis by XPS showed that failure occurred in the boundary between the layer composed of grafted polymer chains and PVA chains and the ungrafted layer at a low adhesive strength, and the location of failure was shifted to the grafted layer containing PVA chains at the grafted amount increased. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40133.

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INTRODUCTION

Ultrahigh molecular weight polyethylene (UHMWPE) as one of the engineering plastics possesses the highest impact resistance and abrasion resistance of the thermoplastic resins, and these properties exceed those of polycarbonate as a most-used engineering plastic. Conversely, as the surface of a UHMWPE material is chemically inert and hydrophobic, adhesion and compatibility to various organic and inorganic materials are poor. These properties have put a restriction on the use of UHMWPE. Therefore, to resolve these problems, many studies have been performed on surface modification of UHMWPE plates and sheets,^{1–3} powder,^{4,5} and fibers,^{6,7} by plasma treatment,^{1,7} grafting,^{4–6} light ion bombardment,² corona discharge,³ and glow discharge.³

The photografting technique has been used to modify the polyolefin materials such as low-density and high-density polyethylene (LDPE and HDPE) and polypropylene (PP). As the energy of UV rays emitted from a 400 W high-pressure mercury lamp

as an energy source of the photografting technique is lower than those of other grafting techniques, the location of grafting is restricted to the outer surface region of the polymer materials and surface properties of the polymer materials are modified at low grafted amounts without changing any bulk properties.^{8,9} In addition, the substrate surfaces modified by the grafting technique can be durably retained. Conversely, while hydrophilic properties gradually regress by turnover or migration of polar functional groups generated, when the surfaces were modified by plasma treatment^{10,11} or UV irradiation.^{12–14}

We have studied surface modification of the LDPE, HDPE, and PP plates by the photografting technique for more than a decade.^{15–18} Wettability of these polyolefin surfaces was enhanced by the photografting of hydrophilic monomers such as methacrylic acid (MAA), acrylic acid (AA), methacrylamide (MAAm), and 2-(dimethylamino)ethyl methacrylate (DMAEMA). In addition, the tensile shear adhesive strength of the LDPE, HDPE,

and PP plates also remarkably increased by photografting hydrophilic monomers and substrate breaking occurred at higher grafted amounts, indicating that adhesive strength exceed the ultimate strength of each polymer materials.^{15,17,19} However, few studies were published on surface modification of UHMWPE plates by the photografting technique compared with that of LDPE, HDPE, and PP plates.

Conversely, it is an important factor to select an adhesive in increasing the adhesive strength. The main components in most of the commercially available adhesives are insoluble or poorly soluble in water except for polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP) and many commercially available adhesives are dissolved in volatile organic solvents. From these perspectives, we focused attention on the photografting of hydrophilic monomers onto UHMWPE plates and enhancement of adhesive strength of the resultant grafted UHMWPE plates. In this study, hydrophilic monomers were photografted onto the UHMWPE plates at different monomer concentrations and temperatures, and the grafted UHMWPE plates were bonded with aqueous PVA solutions under different conditions to discuss their adhesive strength properties in relation to wettability and water absorptivity. In addition, the relation between the location of failure and adhesive strength was discussed from surface analysis of failed surfaces by X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Materials

An UHMWPE plate of 1.0-mm thickness was purchased from Mitsubishi Belting (Kobe, Japan) and used as a polymer substrate for photografting. The density of the UHMWPE plate used was determined to be 0.924 g/cm³ by a flotation, or buoyancy, method with methanol and water at 25°C.^{15,18} The UHMWPE plates cut into 6.5-cm length and 2.4-cm width were washed with water, methanol, and acetone by turns, and then dried under reduced pressure. MAA, AA, MAAM, acrylamide (AAm), 2-hydroxyethyl methacrylate (HEMA), and 2-hydroxyethyl acrylate (HEA) were purchased from Wako Pure Chemical and used as received without further purification. PVA samples with the average degrees of polymerization of 500, 1500, 2000, and 3500 were purchased from Wako Pure Chemical Industries, and named 0.5K-PVA, 1.5K-PVA, 2.0K-PVA, and 3.5K-PVA, respectively.

Photografting

The monomer solutions at the concentrations of 1.0–2.0 M were prepared in water. As solubility of HEMA and HEA was relatively low in water, an aqueous methanol solution of 20 vol % was used as a solvent. The UHMWPE plates were immersed in 50 cm³ of an acetone solution containing 0.25 g of benzophenone (BP) as sensitizer for 1 min and acetone was evaporated from their surfaces at room temperature to coat the UHMWPE surfaces with BP. Then, the BP-coated UHMWPE plates were immersed in each monomer solution in the Pyrex glass tubes and UV rays emitted from a 400 W high-pressure mercury lamp were irradiated at 50–70°C.^{15–18} After photografting, the grafted UHMWPE plates were immersed in water for

24 h to remove unreacted monomers and formed homopolymers, and then dried under reduced pressure. Although some of the grafted UHMWPE plates were further washed with water, their weight remained almost unchanged. This means that most of unreacted monomers and formed homopolymers were removed from the grafted layers formed on the UHMWPE surfaces. The grafted amount, which corresponded to the amount of monomer grafted onto the UHMWPE plates, was calculated in $\mu\text{mol}/\text{cm}^2$ from the weight increase after photografting according to eq. (1).

$$\text{Grafted amount } (\mu\text{mol}/\text{cm}^2) = \frac{(W_g - W_0)/M}{6.5 \times 2.4 \times 2} \cdot 10^6, \quad (1)$$

where W_g is weight of the grafted UHMWPE plates (g); W_0 , weight of the ungrafted UHMWPE plates (g); and M , molar mass of the monomers used (g/mol).

Characterization of Grafted UHMWPE Plates

Surface composition and hydrophilic properties of the grafted UHMWPE plates were estimated from surface analysis by XPS, cross-section observation, wettability, and water absorptivity, respectively.

Surface Analysis by XPS

The C1s and O1s spectra of the grafted UHMWPE plates were recorded on a Shimadzu ESCA-3400 type spectrophotometer with the MgK α (1253.6 eV) source operating at 8 kV and 20 mA.⁸ Then, the intensity ratio, O1s/C1s, was calculated from the core peak areas measured at a take-off angle of 90° and the ionized cross-sections^{15,19,20} to estimate the surface chemical compositions of the grafted UHMWPE plates.

Cross Section Observation

The thickness of the grafted layers was determined by observing the cross section of the grafted UHMWPE plates with a VH-5500 optical microscopy. The grafted UHMWPE plates cut into about 5 mm² were immersed in an aqueous methylene blue solution at 25 mg/100 cm³ for 24 h to stain the grafted layers. After immersion, the samples were washed with water several times and then dried under reduced pressure. The cross sections of the immersed grafted UHMWPE plate samples were photographed through an optical microscope of 200 magnifications. Then, the thickness of the grafted layers was measured and the thickness of the ungrafted layers was calculated from the difference in the thickness of the UHMWPE plates before and after the photografting. The thickness of the original UHMEPE and grafted UHMWPE plates was measured by a micrometer at least five times and the average values were calculated.

Contact Angle Measurements

The contact angles of water on the grafted UHMWPE plates were measured by a sessile drop method at 25°C with a Kyowa Kagaku TYP-QI-type goniometer to estimate their wettability.^{18,19} At least 10 contact angles were averaged to obtain the reliable data to calculate the $\cos \theta$ values.

Water-Absorptivity Measurements of the Grafted Layers

The amount of absorbed water for the grafted UHMWPE plates was measured to estimate the hydrophilic properties of the whole grafted layers. The grafted UHMWPE plates were immersed in distilled water at 25°C for 24 h. Then, the grafted

Table I. Surface Analysis by XPS and Wettability for Water of the UHMWPE-g-PMAA Plates Prepared at Different Monomer Concentrations or Temperatures

Sample	Temperature (°C)	Monomer concentration (M)	Grafted amount ($\mu\text{mol}/\text{cm}^2$) ^a	O1s/C1s	cos θ
UHMWPE					-0.135
UHMWPE-g-PMAA	50	1.0	9	0.35	0.65
	60	1.0, 1.5, and 2.0	12	0.32	0.60
	70	1.0	14	0.32	0.60

^aThe grafted amounts at which the O1s/C1s and cos θ values became constant.

UHMWPE plates were taken out of water, blotted with filter paper to remove water attached to their surfaces, and weighed as quickly as possible. Water absorptivity was estimated from the amount of absorbed water according to eq. (2).

$$\begin{aligned} &\text{Amount of absorbed water (g/g-grafted UHMWPE plate)} \\ &= \frac{W_w - W_g}{W_g}, \end{aligned} \quad (2)$$

where W_w is weight of the grafted plates immersed in water (g).

Tensile Shear Adhesive Strength Measurements

PVA powder was dispersed bit by bit in water and dissolved thoroughly by constantly stirring the solutions at temperatures higher than 85°C. Finally, the solutions were taken to a 100 cm³ volume. The PVA solutions prepared had the concentrations of 2–10 wt %.

The grafted UHMWPE plates were cut into 3.0-cm length and 1.2-cm width. One of the PVA solutions was applied to both surfaces of two pieces of the grafted UHMWPE plates with the same grafted amount to provide a 1.2 × 1.2 cm² overlapping surface area. Unless otherwise noted, the 3.5K-PVA solutions were cured by applying the load of 0.5 kg/cm² at 60°C for 24 h. Tensile strength was measured at the strain rate of 3 mm/s by an Orientec universal testing machine STA 1225. One end of each grafted UHMWPE plate was attached to the load cell and the other end to the actuator of the machine. Here, the experimental factors, such as the degree of polymerization of PVA, concentration of 3.5K-PVA, and temperature and load during the curing were varied to determine the optimum conditions of adhesion of an MAA-grafted UHMWPE (UHMWPE-g-PMAA) plate with the grafted amount of 40 $\mu\text{mol}/\text{cm}^2$ prepared at 2.0 M and 60°C. The values of shear strength were calculated by dividing the force to separate the bonded UHMWPE samples by the overlapping surface area.^{15–17}

Surface Analysis of Failed Surfaces by XPS

After the adhesive strength measurements, the C1s and O1s core spectra of both failed surfaces were recorded for UHMWPE-g-PMAA plates with different adhesive strengths to discuss the relation of the adhesive strength with the location of adhesive failure.

The presence of PVA chains on the failed surfaces was confirmed by treatment of trifluoroacetic anhydride (TFAA) because TFAA selectively reacts with alcoholic hydroxy groups

on PVA.^{21–23} Failed surface samples cut into about 5 mm wide were exposed to vapor in a closely stopped vessel containing 2 cm³ of TFAA for 3 h at room temperature, and then the samples were preserved under reduced pressure at least for 12 h. The C1s, O1s, and F1s core spectra of both failed surfaces were recorded under the same conditions above mentioned.^{15,19,20}

RESULTS AND DISCUSSION

Surface Composition and Wettability

MAA and AA were photografted onto the UHMWPE plate at different monomer concentrations and temperatures. Both grafted amounts increased with the irradiation time, and then tended to level off at longer irradiation times due to an increase in the viscosity of the reaction medium caused by formation of a considerable amount of homopolymers in analogy with the photografting of MAA, AA, and MAAM onto the LDPE, HDPE, and PP plates.^{15–19} In addition, the grafted amounts of MAA and AA increased at shorter irradiation times, as the initial monomer concentration or grafting temperature increased. Wettability and surface composition were estimated for the UHMWPE-g-PMAA and AA-grafted UHMWPE (UHMWPE-g-PAA) plates.

The results of surface analysis by XPS and wettability for water were summarized in Tables I and II for the UHMWPE-g-PMAA and UHMWPE-g-PAA plates prepared at different monomer concentrations or temperatures, respectively. The cos θ value of the UHMWPE-g-PMAA plates increased with the grafted amount, and then became constant at the grafted amounts shown in Table I. At these grafted amounts the O1s/C1s value became constant irrespective of the monomer concentration.

Table II. Surface Analysis by XPS of the UHMWPE-g-PAA Plates Prepared at Different Monomer Concentrations or Temperatures

Sample	Temperature (°C)	Monomer concentration (M)	Grafted amount ($\mu\text{mol}/\text{cm}^2$) ^a	O1s/C1s
UHMWPE-g-PAA	50	1.0	5	0.44
	60	1.0, 1.5, and 2.0	7	0.40
	70	1.0	10	0.40

^aThe grafted amounts at which the O1s/C1s values became constant.

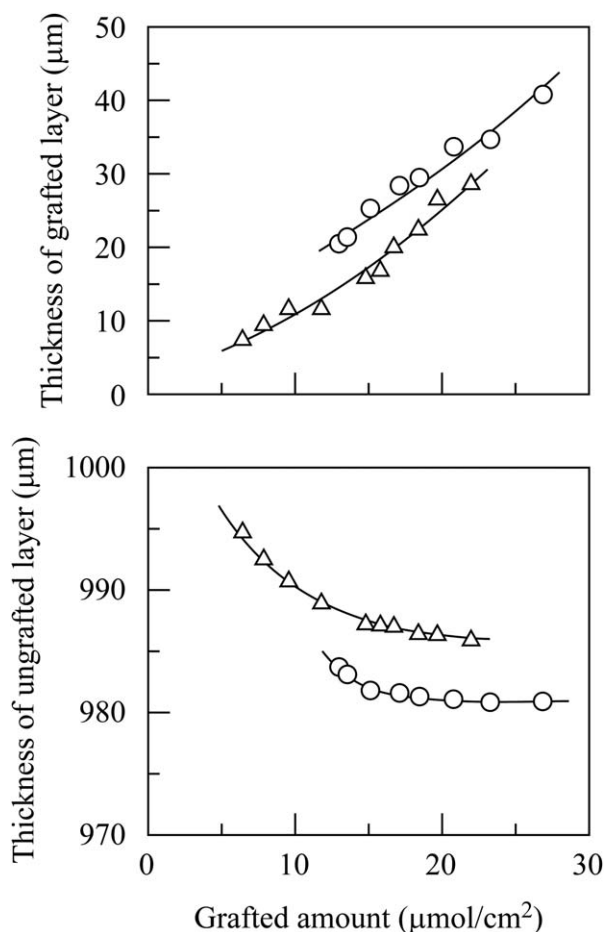


Figure 1. Changes in the thickness of the grafted and ungrafted layers with the grafted amount of the UHMWPE-g-PMAA (○) and UHMWPE-g-PAA (△) plates prepared in the monomer solutions of 1.0 M at 60°C.

This result showed that wettability was controlled by the amount of carboxy groups present on the UHMWPE surface. Wettability of the UHMWPE-g-PMAA plate was independent of the monomer concentration on photografting in analogy with the LDPE, HDPE, and PP plates photografted with MAA and other hydrophilic monomers such as MAAm, HEMA, and DMAEMA.^{15,18,19} According to the kinetics of radical polymerization, the degree of polymerization, or length of polymer chains, was directly proportional to the monomer concentration.^{17,24} Therefore, the above results showed that wettability was independent of the length of grafted polymer chains.¹⁸ For the UHMWPE-g-PAA plates prepared at different monomer concentrations, the intensity ratio became constant at 5 $\mu\text{mol}/\text{cm}^2$. This grafted amount was lower than that for the UHMWPE-g-PMAA plates, indicating that the location of the photografting of AA was restricted to the outer surface region than that of MAA. This is attributed to a little higher hydrophilicity caused by the absence of an α -methyl group in the monomer structure of AA.

Thickness of Grafted Layers

The UHMWPE became thicker by photografting of MAA and AA, while the dimension, such as the width and length, of UHMWPE plates remained unchanged irrespective of the pho-

tografting conditions. The grafted layers were stained blue with methylene blue and thickness of the stained layers was measured through the optical microscopy. Figure 1 shows the change in the thickness of the grafted and ungrafted layers for the UHMWPE-g-PMAA and UHMWPE-g-PAA plates prepared at 1.0 M and 60°C as a typical result. No ungrafted UHMWPE plate was stained. At the grafted amounts higher than 12 and 7 $\mu\text{mol}/\text{cm}^2$ for the UHMWPE-g-PMAA and UHMWPE-g-PAA plates, respectively, the surfaces of both grafted UHMWPE plates were uniformly stained. The thickness of the grafted layers increased with an increase in the grafted amount and the grafted layer of the UHMWPE-g-PMAA plates was a little thicker than that of the UHMWPE-g-PAA plates. Conversely, the thickness of the ungrafted layers decreased with an increase in the grafted amount. The thickness of the ungrafted layer of the UHMWPE-g-PAA plates was a little lower than that of the UHMWPE-g-PMAA plates probably due to higher hydrophilicity of AA. At higher grafted amounts, only the grafted layer became thicker, while the thickness of ungrafted layers remained almost unchanged.

In addition, the O1s/C1s values of PMAA and PAA homopolymers prepared by the photografting techniques were 0.384 and 0.512, respectively.²⁵ The constant intensity ratios shown in Tables I and II were a little lower than these values. So, although the UHMWPE surfaces are fully covered with grafted polymer chains of PMAA or PAA, a small amount of PE chains are intermingled with grafted polymer chains of PMAA or PAA in the grafted layers formed on the UHMWPE plates. Unfortunately, however, PE chains cannot be detected by surface analysis by XPS.

Wettability

As an example, wettability passed through the maximum value, and then gradually decreased with the grafted amount for the UHMWPE-g-PAA plates prepared at 1.0 M and 60°C as shown in Figure 2. Similar behavior was observed for the UHMWPE-g-PAA plates prepared at other monomer concentrations or temperatures. This is considered to be caused by aggregation of

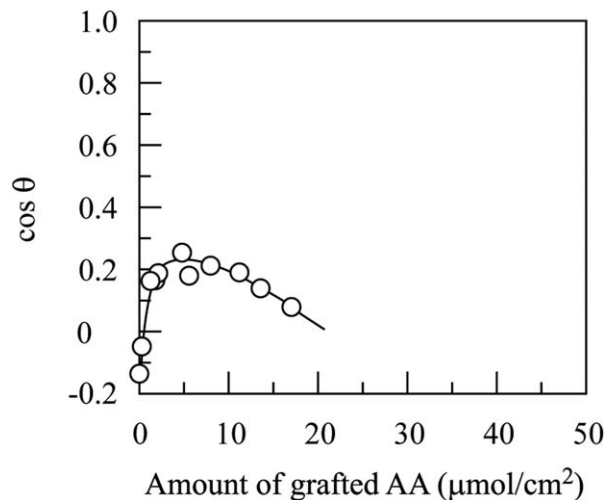


Figure 2. Wettability for water of the UHMWPE-g-PAA plates prepared in a monomer solution of 1.0 M at 60°C.

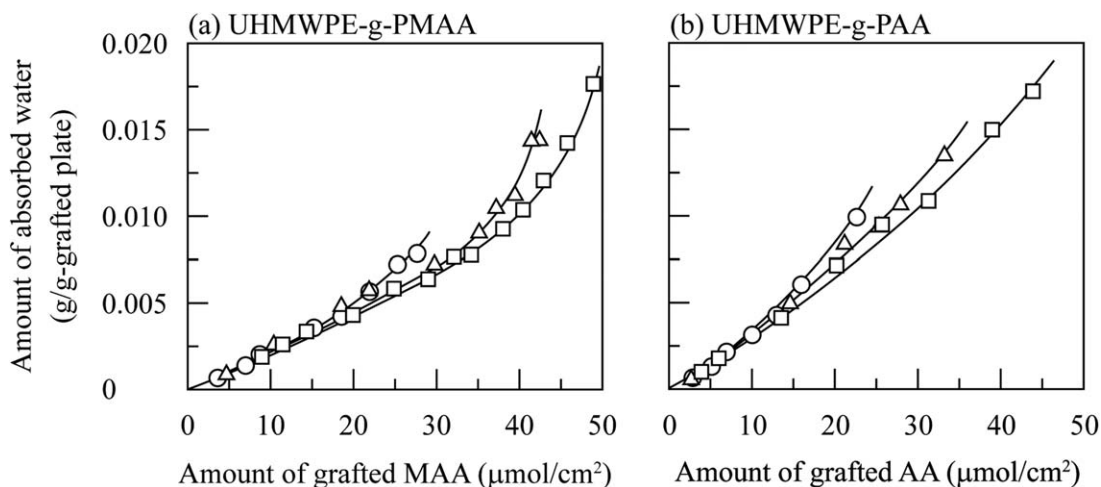


Figure 3. Water absorptivity of the (a) UHMWPE-g-PMAA and (b) UHMWPE-g-PAA plates prepared in monomer solutions of different concentrations at 60°C. Monomer concentration: (○) 1.0, (△) 1.5, and (□) 2.0 M.

grafted PAA chains through hydrogen bonding. This behavior was observed for the LDPE, HDPE, and PP plates photografted with AA in the same procedure and not for the LDPE, HDPE, and PP plates photografted with other hydrophilic monomers in our previous articles.^{15,18,19} In addition, to our knowledge, such behavior was not observed for PE and PP plates grafted with AA by other grafting techniques.^{26–28} Therefore, wettability is considered to vary by the grafting technique which influences characteristics of the grafted layers, such as the length of grafted polymer chains, the density of grafted polymer chains in the grafted layer, and so on.

Wettability of the UHMWPE-g-PMAA plates prepared at different temperatures became constant at the grafted amounts at which the intensity ratio became constant in analogy with the UHMWPE-g-PMAA plates prepared at different monomer concentrations. As the grafting temperature increased, the intensity ratio became constant at higher grafted amounts. When the UHMWPE surface was covered with grafted polymer chains,

wettability became constant, and the grafted amount at which the intensity ratio became constant increased with the grafting temperature. This indicates that the photografting more preferentially progresses into the inside of the UHMWPE plate.

Water Absorptivity

Figures 3 and 4 show the changes in the amount of absorbed water with the grafted amount for the UHMWPE-g-PMAA and UHMWPE-g-PAA plates prepared at different monomer concentrations and temperatures, respectively. As water absorptivity represents hydrophilicity of the whole grafted layer, the length of grafted polymer chains and their density in the grafted layer can be discussed from this value.^{15,16,18} As the monomer concentration or grafting temperature decreased, water absorptivity sharply increased at lower grafted amounts for both grafted UHMWPE plates.

Longer grafted polymer chains are formed at higher monomer concentrations as above mentioned.^{18,24} In addition, it was found from surface analysis by XPS as shown in Table I that the

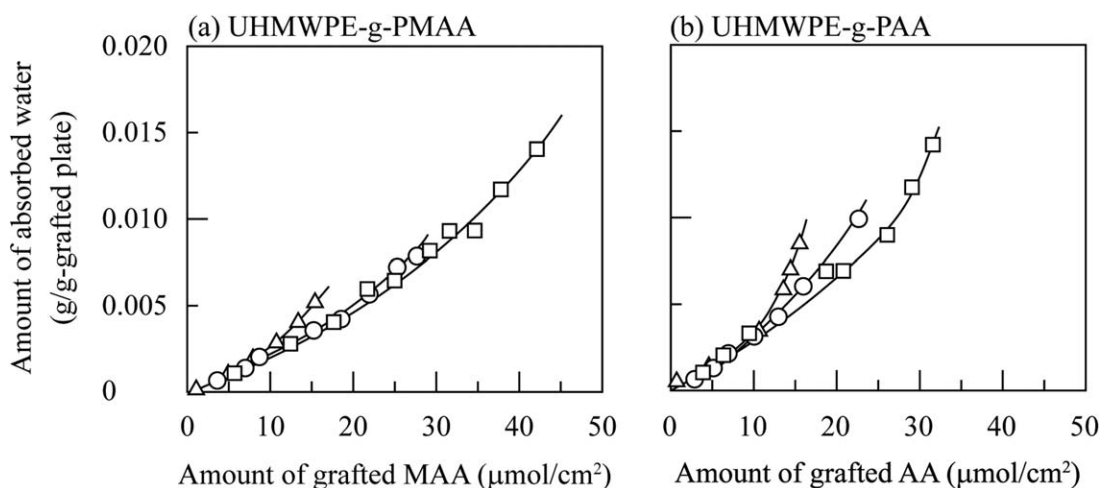


Figure 4. Water absorptivity of the (a) UHMWPE-g-PMAA and (b) UHMWPE-g-PAA plates prepared in a monomer solution of 1.0 M at different temperatures. Temperature: (△) 50, (○) 60, and (□) 70°C.

location of photografting is independent of the monomer concentration. From a comprehensive viewpoint above mentioned, the grafted layers formed by shorter grafted polymer chains possessed higher water absorptivity. However, as the location of photografting is restricted to the outer surface region at lower grafting temperatures as shown in Table II, the density of grafted polymer chains in the grafted layers formed at lower grafting temperatures increases. Therefore, the grafted layers formed at lower temperatures possessed higher water absorptivity.

Tensile Shear Adhesive Strength

The effects of some factors, such as the degree of polymerization of PVA, 3.5K-PVA concentration, and temperature and load during the curing on the adhesive strength were investigated for a UHMWPE-g-PMAA plate with about $40 \mu\text{mol}/\text{cm}^2$ prepared at $2.0 M$ and 60°C . Unless otherwise noted, the conditions of the adhesive measurements were [3.5K-PVA]: 5.0 wt %, load: $0.5 \text{ kg}/\text{cm}^2$, and temperature: 60°C . Figure 5 shows the effects of these factors on the adhesive strength. First, the effects of the degree of polymerization of PVA and 3.5K-PVA concentration on the adhesive strength were discussed. The adhesive strength increased with an increase in the degree of polymerization of PVA or PVA con-

centration. These results indicate that an increase in the adhesive strength is caused by hydrogen bonding between hydroxyl groups appended to PVA chains and carboxy groups appended to grafted PMAA chains and additional entanglement between PVA chains and grafted PMAA chains. Particularly, the substrate breaking occurred at 10 wt %, indicating that the adhesive strength exceeded the ultimate strength of the UHMWPE plate used. Second, the dependence of the load and temperature during the curing on the adhesive strength was discussed. The adhesive strength increased with an increase in the load and became almost constant under the load higher than $0.5 \text{ kg}/\text{cm}^2$. An increase in the load is considered to lead to an increase in penetration of PVA solutions in the grafted layer. The adhesive strength increased with the curing temperature, and then had the maximum value at 60°C . This is considered to be due to higher permeability of a PVA solution at higher curing temperatures. However, the penetration of PVA solutions is restricted at temperatures higher than 60°C because evaporation of water as a solvent is too fast. From the above results, the adhesive strength of the UHMWPE-g-PMAA and UHMWPE-g-PAA plates prepared at different monomer concentrations and temperatures was investigated under the conditions that curing was performed at 60°C for 24 h under the

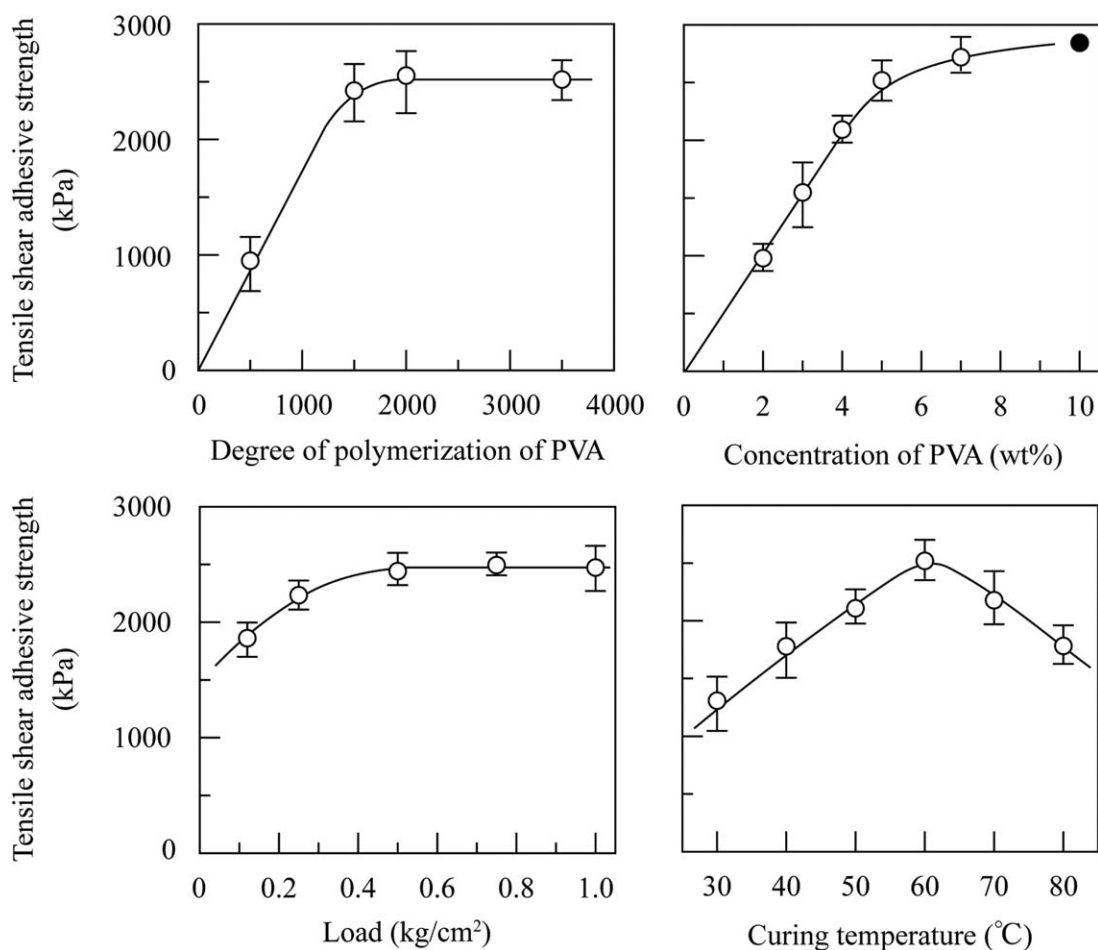


Figure 5. The effects of the degree of polymerization of PVA, 3.5K-PVA concentration, and the load and temperature during the curing on the tensile shear adhesive strength for a UHMWPE-g-PMAA plate with about $40 \mu\text{mol}/\text{cm}^2$ prepared at $2.0 M$ and 60°C . The parameters except for the factor in the X axis were [3.5K-PVA] = 5.0 wt %, load = $0.5 \text{ kg}/\text{cm}^2$, and temperature = 60°C . Failure: open, cohesive strength; shade, substrate-breaking.

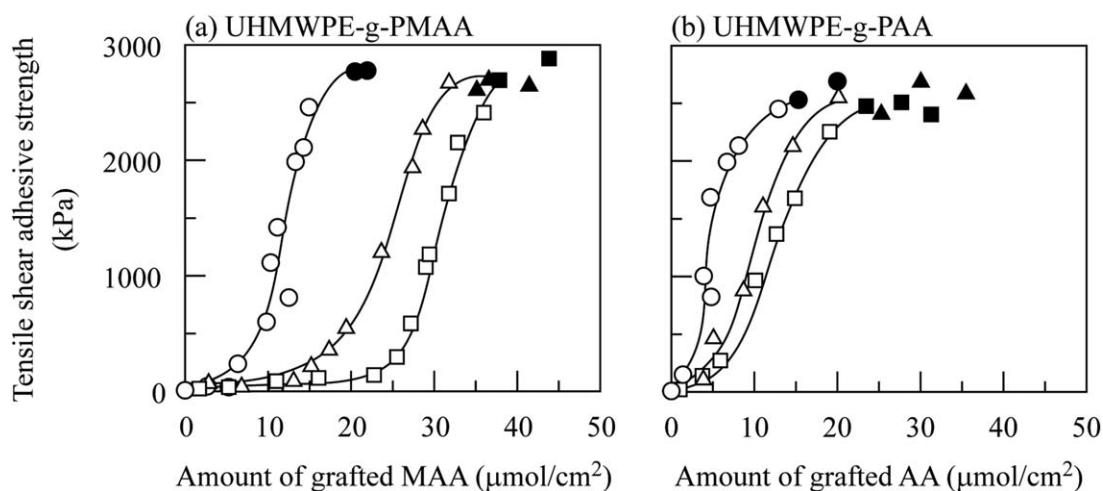


Figure 6. Changes in the tensile shear adhesive strength with the grafted amount of the (a) UHMWPE-g-PMAA and (b) UHMWPE-g-PAA plates prepared in monomer solutions of different concentrations at 60°C. Monomer concentration: (○, ●) 1.0, (△, ▲) 1.5, and (□, ■) 2.0 M. Failure: open, cohesive strength; shade, substrate-breaking.

load of 0.5 kg/cm² with a 3.5K-PVA solution at 10 wt %. The amount of a 3.5K-PVA solution coated between the overlapping surface areas was about 3.5–4.5 mg/cm² irrespective of the grafted amount for the UHMWPE-g-PMAA plates prepared at 1.0 M and 60°C. Figure 6 shows the changes in the adhesive strength with the grafted amount for UHMWPE-g-PMAA and UHMWPE-g-PAA plates prepared at different monomer concentrations. The adhesive strength increased with an increase in the grafted amount. And both grafted UHMWPE plates prepared at lower monomer concentrations were fractured at lower grafted amounts. It was found from this result that the adhesive strength depends on the length of grafted polymer chains, as the location of photografting is independent of the monomer concentration as shown in Table I. The results obtained from Table I and Figure 6 can suggest that the grafted layers consisting of shorter grafted polymer chains possess higher permeability to PVA solutions. In addition, the grafted amount at which substrate breaking occurred for the UHMWPE-g-PAA plates was lower than that for the UHMWPE-g-PMAA plates, when the grafted UHMWPE plates were prepared at the same monomer concentration. This is attributable to higher water absorptivity for the UHMWPE-g-PAA plates as shown in Figure 3, which is caused by the formation of the grafted layer rich in grafted polymer chains.

In addition, some methacrylic and acrylic monomers, such as MAAm, AAm, HEMA, and HEA, were photografted onto the UHMWPE plate at 1.0 M and 60°C. In the case that the monomers have the same functional group, the grafted amounts of acrylic monomers were lower than those of methacrylic monomers (AAm < MAAm, and HEA < HEMA). Even when the irradiation time was prolonged to 150 min, the grafted amounts of AAm and HEA were limited to 0.4 and 2.7 μmol/cm², respectively.

For MAAm-grafted UHMWPE (UHMWPE-g-PMAAm) plates, wettability was enhanced at a low grafted amount, and became constant at the grafted amount of 12 μmol/cm² at which the UHMWPE surface was fully covered with grafted PMAAm

chains ($\cos \theta = 0.92$). This value was considerably higher than those of the UHMWPE plates grafted with other hydrophilic monomers.

In addition, HEMA-grafted UHMWPE (UHMWPE-g-PHEMA) plates with high grafted amounts prepared at long irradiation times possessed high water absorptivity than other UHMWPE plates prepared in this study. From the above results, a high adhesive strength was expected to be obtained for the UHMWPE-g-PMAAm and UHMWPE-g-PHEMA plates. UHMWPE-g-PMAAm and UHMWPE-g-PHEMA plates with different grafted amounts were bonded with 10 wt % of an aqueous 3.5K-PVA solution. The adhesive strength of the UHMWPE-g-PMAAm plates increased with a grafted amount and reached about 1000 kPa at 16 μmol/cm². In addition, for the UHMWPE-g-PHEMA plates, the adhesive strength increased with the grafted amount and a constant adhesive strength of about 1400 kPa was obtained at higher than 50 μmol/cm². However, for the UHMWPE-g-PMAAm and UHMWPE-g-PHEMA plates, substrate breaking was not observed.

Subsequently, the adhesive strength of UHMWPE-g-PMAA and UHMWPE-g-PAA plates prepared at different temperatures will be discussed. Figure 7 shows the changes in the adhesive strength with the grafted amount for UHMWPE-g-PMAA and UHMWPE-g-PAA plates prepared at different temperatures. For the UHMWPE-g-PMAA plates prepared at 50°C, the adhesive strength increased with the grafted amount, but substrate breaking was not observed. The substrate breaking was observed for the UHMWPE-g-PMAA plates prepared at 60 and 70°C and UHMWPE-g-PAA plates prepared at 50–70°C. The grafted amount at which substrate breaking was observed increased, when the grafting temperature increased except for the UHMWPE-g-PMAA plates prepared at 50°C. As the grafting temperature increased, the photografting progressed into the inside of the substrate as shown in Tables I and II. Therefore, the grafted layers that possess higher water absorptivity are formed at lower grafting temperature as shown in Figure 4.

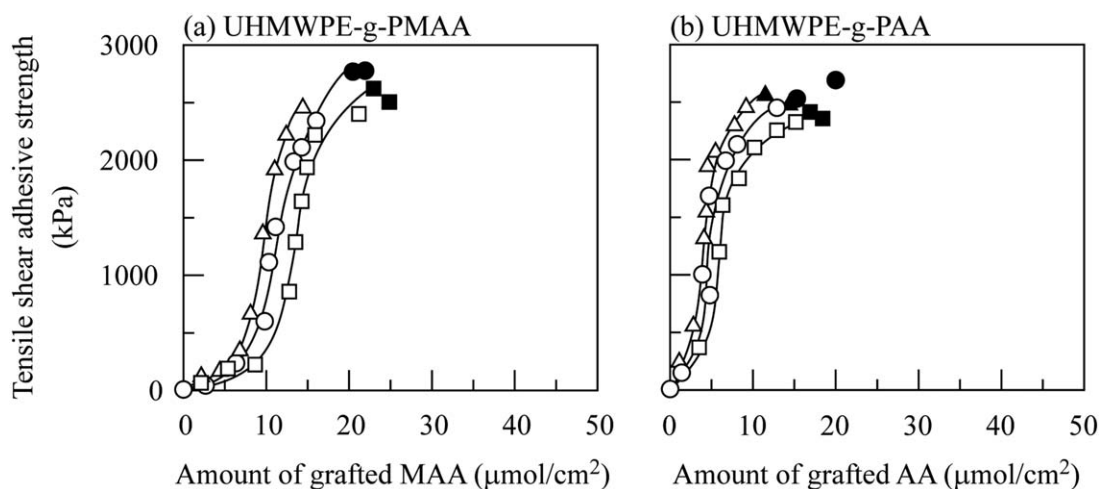


Figure 7. Changes in the tensile shear adhesive strength with the grafted amount of the (a) UHMWPE-g-PMAA and (b) UHMWPE-g-PAA plates prepared in a 1.0 M monomer solutions at different temperatures. Grafting temperature: (Δ , \blacktriangle) 50, (\circ , \bullet) 60, and (\square , \blacksquare) 70°C. Failure: open, cohesive strength; shade, substrate-breaking.

However, enough grafted amount for substrate breaking was not obtained for the UHMWPE-g-PMAA plates prepared at 1.0 M and 60°C. These factors can control the magnitude of the adhesive strength of the grafted UHMWPE plates.

Surface Analysis of Failed Surfaces

Failed surfaces obtained for UHMWPE-g-PMAA plates prepared at 1.0 M and 60°C were analyzed by XPS to discuss the relation between the adhesive strength and the location of failure. First, some control samples were measured by XPS for assignment of the obtained C1s peaks. The PVA-coated UHMWPE plate was prepared by applying a 3.5K-PVA solution to the surface of a UHMWPE plate and drying it at 60°C. Figure 8 shows the C1s, O1s, and F1s core spectra of the surfaces of an UHMWPE-g-PMAA plate with 15 $\mu\text{mol}/\text{cm}^2$, the surface of which is fully covered with grafted PMAA chains, and the PVA-coated UHMWPE plate before and after the TFAA treatment. For the UHMWPE-g-PMAA plate, a peak assigned to a carbon in a carboxy group ($-\text{COOH}$) and an overlapped peak emerged at 289 and 287 eV, respectively, in addition to a main peak at 285 eV. For the PVA-coated UHMWPE plate, a peak assigned to a carbon adjacent to an alcoholic hydroxy group of a PVA chain ($>\text{CH}-\text{OH}$) appeared at 287 eV. However, the peak at 287 eV is assigned to both a carbon adjacent to an alcoholic hydroxy group of a PVA chain ($>\text{CH}-\text{OH}$) and a carbon adjacent to a carboxy group ($>\text{CH}-\text{COOH}$). An additional peak assigned to a terminal trifluoromethyl group ($-\text{CF}_3$) at 293 eV and an F1s peak at 690 eV were observed for the PVA-coated UHMWPE plate was treated with TFAA. However, this peak was not observed for the TFAA-treated UHMWPE-g-PMAA plate. As a result, both assignments can be distinguished if it remained untreated by the TFAA treatment.

Figure 9 shows the C1s, O1s, and F1s core spectra of the failed surfaces of three kinds of UHMWPE-g-PMAA plates with different adhesive strengths before and after the TFAA treatment. Of two failed surfaces, the surface with a higher O1s/C1s value was referred to as the surface (A) and one with a lower O1s/

C1s value to as the surface (B). For a UHMWPE-g-PMAA plate with the adhesive strength of 36 kPa (grafted amount = 5.3 $\mu\text{mol}/\text{cm}^2$), a peak at 289 eV and an overlapped peak at 287 eV were observed in addition to a main peak at 285 eV at the surface (A).^{18,19} These two peaks were little observed at the surface (B). When both failed surfaces were treated with TFAA, an additional peak at 293 eV appeared at the failed surface (A).^{21–23} As this peak was not observed for a TFAA-treated UHMWPE-g-PMAA plate, the above result indicates that PVA chains are present only on the surface (A). So, failure occurred

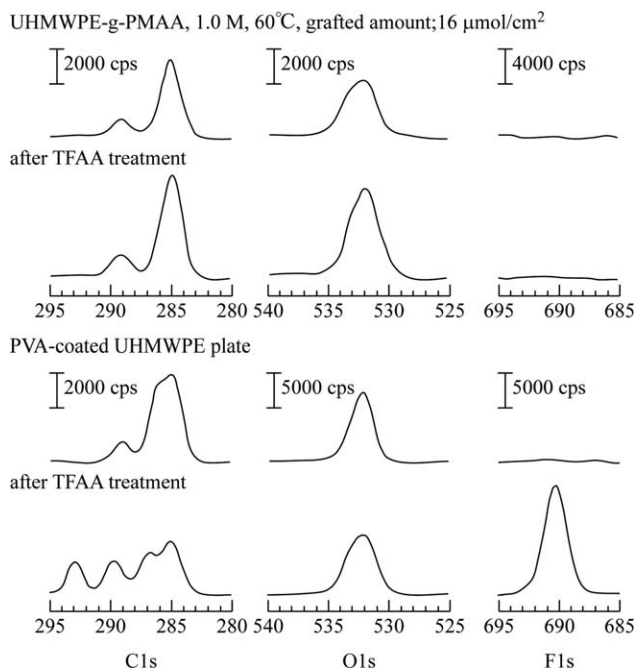


Figure 8. C1s, O1s, and F1s core spectra of a UHMWPE-g-PMAA plate with 16 $\mu\text{mol}/\text{cm}^2$ and a PVA-coated UHMWPE plate before and after TFAA treatment.

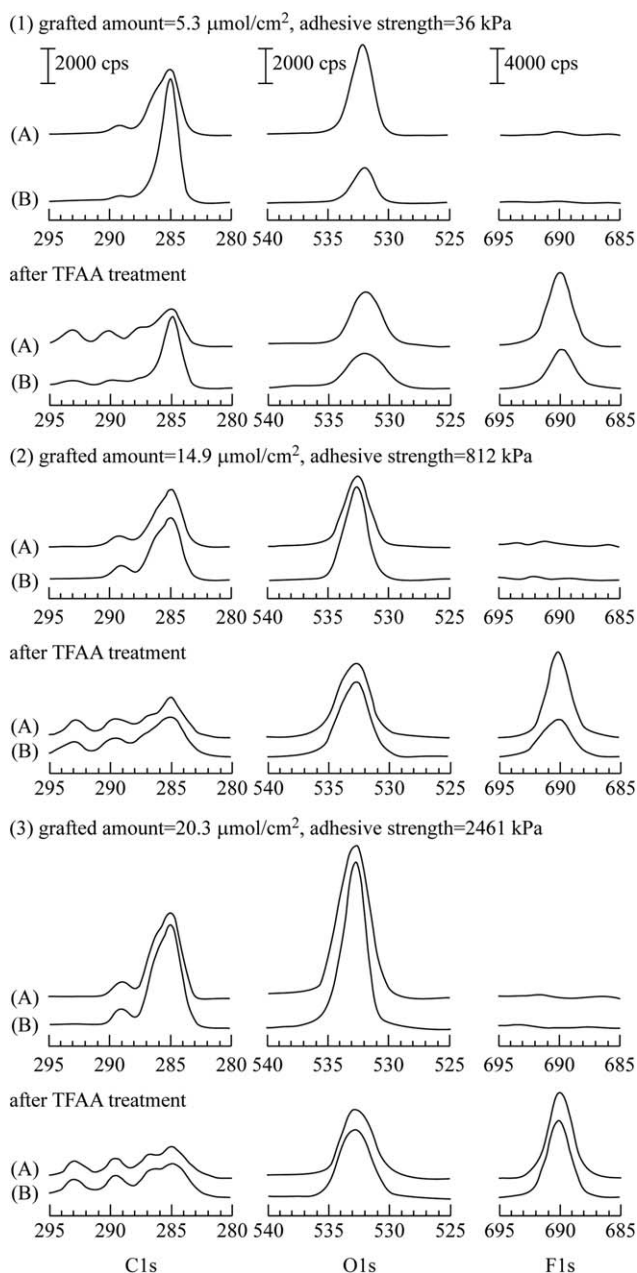


Figure 9. C1s, O1s, and F1s core spectra of the failed surfaces after the adhesive strength measurements for UHMWPE-g-PMAA plates with different adhesive strengths prepared at 1.0 M and 60°C. Grafted amount ($\mu\text{mol}/\text{cm}^2$) and adhesive strength (kPa): (1) 5.3 and 36, (2) 13.5 and 812, and (3) 14.9 and 2461.

at the boundary between the polymer layer consisting of grafted PMAA chains and PVA chains and the ungrafted layer of the UHMWPE plate, as the UHMWPE surface is still not fully covered with grafted PMAA chains for this sample.

An overlapped peak was observed at both failed surfaces in addition to a main peak at 285 eV for a UHMWPE-g-PMAA plate with the adhesive strength of 812 kPa (grafted

amount = $12.5 \mu\text{mol}/\text{cm}^2$). When the failed surfaces were treated with TFAA, a peak at 293 eV appeared at both failed surfaces. As the surface is not covered with grafted PMAA chains yet, the above result shows that failure occurred in the polymer layer consisting of grafted PMAA chains and PVA chains. Both failed surfaces of a UHMWPE-g-PMAA plate with the adhesive strength of 2460 kPa (grafted amount = $14.9 \mu\text{mol}/\text{cm}^2$) also had a peak at 289 eV, and an additional peak at 293 eV after the TFAA treatment. This result shows that failure occurred in the grafted layer into which aqueous PVA solution was penetrated, as the UHMWPE surface is fully covered with grafted PMAA chains at this grafted amount. Consequently, it was found that the location of failure was shifted from the boundary between the polymer layer consisting of grafted PMAA chains and PVA chains and the ungrafted layer to the inside of the grafted layer into which aqueous PVA solution was penetrated with an increase in the adhesive strength.

CONCLUSIONS

An investigation was performed on hydrophilization of the UHMWPE plate by photografting of MAA and AA at different monomer concentrations and temperatures and enhancement in the adhesive strength of the grafted UHMWPE plates with PVA solutions. We drew the following conclusions from the above experimental results. Wettability of the UHMWPE-g-PMAA plates increased with the grafted amount, and became constant when the UHMWPE surface was fully covered with grafted PMAA chains. Conversely, wettability of the UHMWPE-g-PAA plates gradually decreased against the grafted amount probably due to aggregation of grafted PAA chains. Water absorptivity sharply increased at lower grafted amount for both grafted UHMWPE plates prepared at lower monomer concentrations due to formation of shorter grafted polymer chains and for ones prepared at lower temperatures due to the restriction of the location of photografting. The tensile shear adhesive strength sharply increased at lower grafted amounts and substrate breaking was observed at higher grafted amounts. A sharp increase in the adhesive strength at lower grafted amounts was attributed mainly to the formation of shorter grafted polymer chains by photografting at lower monomer concentrations and/or the restriction of the location of grafting to the outer surface region by photografting at lower temperatures. It was found that the photografting of carboxy group-containing hydrophilic monomers such as MAA and AA was a key role in an increase in the adhesive strength, as the UHMWPE-g-PMAAm and UHMWPE-g-PHEMA plates had even lower adhesive strength than expected. An increase in the adhesive strength was caused by the penetration of aqueous PVA solutions into the grafted layer and the hydrogen bonding of PVA chains with grafted polymer chains. Surface analysis of failed surfaces by XPS showed that failure occurred at the boundary between the polymer layers consisting of PVA chains and grafted polymer chains and the ungrafted layer at a lower adhesive strength, as the UHMWPE surfaces were not fully covered with grafted PMAA chains. The location of failure shifted to the grafted layers containing PVA chains, as the adhesive strength increased.

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