Adhesion of Polyethylene Plates Photografted with Methacrylic Acid and Acrylic Acid with Enzymatically Modified Chitosan Solutions and X-ray Photoelectron Spectroscopy Analysis of Failed Surfaces

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ABSTRACT: An investigation was carried out on the application of dilute chitosan solutions modified by a tyrosinase-catalyzed reaction with 3,4-dihydroxyphenetylamine (dopamine) to the adhesion of low-density polyethylene (LDPE) and high-density polyethylene (HDPE) plates photografted with carboxyl-group-containing hydrophilic monomers, such as methacrylic acid (MAA) and acrylic acid (AA). In the case where photografting was carried out at lower monomer concentrations or at lower temperatures, the adhesive strength sharply increased with lower grafted amounts. A sharp increase in the adhesive strength was found to be due to the formation of shorter grafted polymer chains at lower monomer concentrations and/or the restriction of the location of grafting to the outer surface region at lower temperatures. In addition, the adhesive strength also sharply increased at even lower grafted amounts for photografting onto the HDPE plates and/or that of AA because the location of grafting was restricted to the outer surface region. For the AA-grafted LDPE and HDPE plates, substrate breaking was observed. This was attributed to the coverage of the substrate surfaces with grafted poly(acrylic acid) chains at lower grafted amounts and a high water absorptivity of the grafted layer. X-ray photoelectron spectroscopy (XPS) analysis of the grafted LDPE plates incubated in a dopamine solution containing tyrosinase suggested that the increase in the adhesive strength was caused by the penetration of enzymatically modified chitosan solutions in the grafted layers and the subsequent reaction of quinone derivatives enzymatically generated with grafted polymer chains. In addition, the surface analysis of the failed surfaces by XPS showed that as the adhesive strength increased, the location of failure was shifted from the interface between the layers mixed with enzymatically modified chitosan materials and grafted polymer chains to the inside the grafted layer containing enzymatically modified chitosan materials. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 939–950, 2011

Key words: adhesion; enzymes; ESCA/XPS; graft copolymers; polyethylene (PE)

INTRODUCTION

The surfaces of polyolefin materials, such as polyethylene (PE) and polypropylene (PP), are hydrophobic and chemically inert. To solve this problem, various chemical techniques have been developed to make their surfaces hydrophilic.[1–7] Among them, photografting is one of the most effective techniques for producing modified surfaces.[8–11] The grafted layers formed on the surfaces possess a high water absorptivity in addition to the fact that the wettability is modified when hydrophilic monomers, such as methacrylic acid (MAA),[9,10] acrylic acid (AA),[9,10] methacrylamide (MAAm),[12] and 2-(dimethylamino)ethyl methacrylate,[10] are photografted onto low-density polyethylene (LDPE) plates. The mobility and reactivity of grafted polymer chains in the water-swollen state is also of great importance in the enhancement of the adhesiveness. Therefore, investigations have been also carried out on the surface modification of the polyolefin materials by various photografting techniques.[13–15] The tensile shear adhesive strength of MAA- and AA-grafted LDPE [LDPE-*g*-poly(methacrylic acid) (PMAA) and LDPE-*g*-poly(acrylic acid) (PAA)] plates with a commercially available adhesive increased with an increase in the grafted amount, and substrate breaking was observed at higher grafted amounts.[9] Subsequently, we investigated the adhesive-free adhesion, or *autohesion,* of LDPE plates through hydrogen bonding and ionic bonding between the polar functional groups of the grafted polymer chains or the entanglement of the grafted polymer chains and reported that substrate breaking was observed at higher grafted amounts.[8,9,12,16] These results support our conclusion that the high mobility of the grafted polymer chains is considerably involved in increasing the autohesive strength.

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The kinetic properties of grafted polymer chains, including their length and number, can be controlled by the grafting conditions, such as the kind of solvents, the temperature, the absence or presence of initiators and their concentration, and the monomer concentration. Among them, the temperature and kind of solvents have an influence on the location of grafting and the density of the grafted polymer chains in the grafted layer.[9,10,17,18] However, little has been reported on the effects of the monomer concentration and temperature during grafting on the modified hydrophilic properties.[9,10] We estimated the hydrophilic properties of grafted layers formed on LDPE and high-density polyethylene (HDPE) plates by the photografting of MAA and AA on the basis of the wettability, surface analysis by X-ray photoelectron spectroscopy (XPS), and water absorptivity. The water wettability of the LDPE-*g*-PMAA and LDPE-*g*-PAA and MAA- and AA-grafted HDPE (HDPE-*g*-PMAA and HDPE-*g*-PAA) plates was independent of the monomer concentration. On the other hand, the water absorptivity of the grafted layers prepared at lower monomer concentrations or at lower temperatures sharply increased with lower grafted amounts. The location of the photografting of AA was restricted to the outer surface region compared to that of MAA, and the surfaces were fully covered with grafted polymer chains at lower grafted amounts for photografting onto the HDPE plate than for that onto the LDPE plate.[10,19]

As described previously, the hydrophilization of polyolefin surfaces is highly effective for the enhancement of adhesion.[13–15] However, little attention has been paid to the development or improvement of a novel adhesive. The main component of most of the commercially available adhesives is polymer material, and polymer materials are insoluble or poorly soluble in water. In contrast, the biopolymer chitosan [2-acetamido-2-deoxy-D-glucose-(*N*-acetylglucan)] is insoluble in water and most organic solvents but is soluble in aqueous acidic solutions. Therefore, in an earlier study,[20] we focused attention on the adhesion of LDPE and HDPE plates surface-modified by the photografting technique with a chitosan-based adhesive that we developed.[20]

Chitosan is a deacetylated polymer of acetylglucosamine and is usually prepared by the deacetylation of chitin [2-acetamido-2-deoxy-D-glucose-(*N*-acetylglucosamine)], which is one of the most abundant biopolymers in nature. A main commercial source is the shells of marine or freshwater invertebrates, such as shrimp, crabs, lobsters, and krill. The applications of chitosan include those in the cosmetics, agriculture, food, biomedical, and textiles industries in addition to its use as a chelating agent for the refinement of industrial effluents because of its useful features, such as its hydrophilicity, biocompatibility, biodegradability, and antibacterial properties.[21–23] In collaboration with Payne, Yamada and coworkers[24,25] prepared high-viscosity, gel-like materials from a dilute chitosan solution with 3,4-dihydroxyphenetylamine (dopamine) and the enzyme tyrosinase and reported their applicability to a water-resistant adhesive. The viscosity of the dilute chitosan solutions was considerably increased by the tyrosinase-catalyzed quinone formation from dopamine and the subsequent nonenzymatic quinone crosslinking of chitosan chains. When high-viscosity modified chitosan materials were spread on the surfaces of the glass slides and the glass slides, overlapping and tightly clipped together, were submerged in water, a tensile shear adhesive strength of over 400 kPa was observed.[25] Here, the function of the adhesive protein was mimicked with a different biological analogy and a different biopolymer. Another biological analogy for our study is the process of cuticular sclerotization in insects. The reaction mechanism has been schematically illustrated and is explained in detail in refs. 24–26.

In this study, we investigated the effects of the photografting of MAA and AA, to be more specific, the number and length of the resulting grafted polymer chains, the location of the photografting, and the kind of monomer used, on the adhesion of LDPE and HDPE plates with enzymatically modified chitosan solutions. In addition, the relation of the location of failure with the tensile shear adhesive strength was examined through surface analysis by XPS of the failed surfaces.

EXPERIMENTAL

Materials

LDPE and HDPE plates 1.0 mm thick were used as a polymer substrate for photografting. LDPE and HDPE plates 7.0 cm in length and 2.4 cm wide were washed with distilled water, methanol, and acetone by turns and were then dried under reduced pressure.[9,10,19] Mushroom tyrosinase (EC. 1.14.18.1) and dopamine were purchased from Sigma Chemical (St Louis, MO). The tyrosinase used had a specific activity of 2870 U/mg of solid (determined by the supplier). Chitosan flakes (Chitosan 300) were purchased from Wako Pure Chemical (Tokyo, Japan). The degree of deacetylation of the chitosan sample used was determined by the colloid titration method with potassium poly(vinyl alcohol) sulfate. The viscosity-average molar mass was calculated from the intrinsic viscosity values determined in a 0.1*M* aqueous acetic acid solution containing 0.2*M* NaCl with an Ubbelohde viscometer at 25°C.[26] The constants K and a in the Mark–Houwink–Sakurada equation

were 1.81 $\times$ 10^{-3} cm^3/g and 0.93, respectively.[27,28] The degree of deacetylation and the average molar mass of the chitosan sample used were 0.87 and 1.53 $\times$ 10^6 g/mol, respectively.[29]

Photografting and characterization of the grafted PE plates

The photografting of MAA and AA was carried out onto the LDPE and HDPE plates at different monomer concentrations and temperatures. In our previous article,[19] the effects of the monomer concentration and temperature during photografting on the wettability and water absorptivity of the resulting grafted LDPE and HDPE plates were discussed in relation to the surface composition determined by XPS.

The aqueous solutions of the MAA and AA monomers were prepared at 0.5–1.5*M*. The LDPE and HDPE plates were immersed in a benzophenone (BP; sensitizer) solution of acetone (0.5% w/v) for 1 min to coat BP on the surfaces. Then, UV rays emitted from a 400-W high-pressure mercury lamp were irradiated to the aqueous monomer solutions in which the BP-coated LDPE and HDPE plates were immersed in a Pyrex glass tube at 50–70°C. The grafted amounts in $\mu mol/cm^2$ were calculated as the amount of monomers grafted on the unit surface area from the weight increase of the LDPE and HDPE plates after the photografting.

The intensity ratio, O1s/C1s, was calculated from the O1s and C1s peak areas measured on a Shimadzu ESCA-3400 spectrophotometer (Kyoto, Japan). The contact angles for water on the surfaces of the grafted LDPE and HDPE plates were measured by the sessile drop method at 25°C. The amount of absorbed water was calculated from the weight increase in the grafted LDPE and HDPE plates immersed in distilled water at 25°C for 24 h.

Enzymatic modification of the chitosan solutions and adhesive strength measurements

Chitosan solutions of 1.0–1.5 w/v% were prepared by the dispersion of chitosan flakes into 100 cm^3 of water and intermittent dropping of a 2*M* HCl solution to maintain the pH values at 3–4 with mild stirring. After the mixtures were stirred for 24 h to dissolve most of the chitosan flakes, the insoluble parts were removed by vacuum filtration with a G3 glass filter (As One Corp., Osaka, Japan). The chitosan solutions we obtained were diluted with water to a final amino group concentration of 30 m*M* on the basis of the weight concentration of the prepared chitosan solutions and the degree of deacetylation of the chitosan sample used. The pH values of the chitosan solutions were adjusted to 5.8–6.0 with a 2*M* NaOH solution.[26,29]

The grafted LDPE and HDPE plates were cut into pieces 3.5 cm in length and 1.2 cm wide. The enzymatic reaction was initiated by the addition of dopamine and 1.0 cm^3 of an aqueous tyrosinase solution to the chitosan solutions so as to make the concentrations 10 mM and 60 U/cm^3, respectively. The enzymatically modified chitosan solutions were spread on each surface of the two grafted LDPE and HDPE plates with the same grafted amounts 45 min after dopamine was added, and then, the surfaces were placed in contact with a 1.2 $\times$ 1.2 cm^2 overlapping surface area. The overlapping samples were tightly fixed with two binder clips and laid in an oven at 25°C. The enzymatic reaction time was set at 45 min because, at this enzymatic reaction time, the tensile shear adhesive strength showed the maximum value for the LDPE-*g*-PMAA plate with the grafted amount of 30 $\mu mol/cm^2$ prepared at 1.0*M* and 60°C.[20]

The tensile shear adhesive strength was measured with an Orientec universal testing machine (STA 1225, Tokyo, Japan). One end of each grafted LDPE and HDPE plate sample was attached to the load cell, and the other end was attached to the actuator of the machine. The samples were loaded at a shear rate of 3.0 mm/s until failure. We calculated the values of the shear strength by dividing the force to separate the bonded LDPE samples by the overlapping surface area.[8,10]

Reactivity of quinone with the grafted polymer chains

The LDPE-*g*-PMAA and LDPE-*g*-PAA plates (1.0 $\times$ 1.0 cm^2) were incubated in an aqueous 10 m*M* dopamine solution (50 cm^3) containing tyrosinase (60 U/cm^3). After 30 min, the LDPE-*g*-PMAA and LDPE-*g*-PAA plates were removed from the dopamine solution, thoroughly washed with water to remove unreacted components, and dried under reduced pressure.[20] The photoelectron spectra of the C1s, O1s, and N1s core levels were recorded at a takeoff angle of 90° on a Shimadzu ESCA-3400 type spectrophotometer with a Mg Kα (1253.6 eV) source operating at 8 kV and 20 mA.[20] Then, the intensity ratios of O1s/C1s and N1s/C1s were calculated from the O1s, C1s, and N1s peak areas and the ionized cross sections.[30–32]

Surface analysis of the failed surfaces by XPS

After the adhesive strength measurements, the C1s, O1s, and N1s core spectra of both failed surfaces were measured for the grafted LDPE and HDPE plates with different adhesive strengths to discuss the relation of the adhesive strength with the location of adhesive failure. A chitosan film was prepared as a reference sample for XPS analysis. The chitosan

film was prepared by the procedure described in our previous article.[25] The chitosan film was incubated in an aqueous solution (10 m*M*) containing tyrosase (60 U/cm^3) for 30 min. The enzymatically modified chitosan film was washed with water and then dried under reduced pressure. Alternatively, the enzymatically modified chitosan solution (enzymatic reaction time = 45 min) was spread onto the surface of the LDPE-*g*-PMAA plate with a grafted amount of 40 μmol/cm^2 prepared at 1.0*M* and 60°C, and the LDPE-*g*-PMAA plate was allowed to stand in air at 25°C to evaporate water. The C1s, O1s, and N1s core spectra of these reference samples were recorded in the same manner described in the previous section.[9]

RESULTS AND DISCUSSION

Photografting and hydrophilic properties of the grafted layers

The photografting of MAA and AA was carried out onto the LDPE and HDPE plates at different monomer concentrations or temperatures in our previous study.[19] The hydrophilic properties of the LDPE and HDPE surfaces modified by the photografting of MAA and AA were estimated from the wettability and water-absorptivity measurements and were discussed in relation to the grafted amounts. The results obtained can be summarized as follows.

For the LDPE-*g*-PMAA and HDPE-*g*-PMAA plates, the wettability increased with the grafted amount and then became constant when the surfaces of the LDPE and HDPE plates were fully covered with grafted PMAA chains. Here, both the wettability and coverage of the LDPE and HDPE surfaces with grafted PMAA chains were independent of the MAA monomer concentration during photografting. On the other hand, the wettability of the LDPE-*g*-PAA and HDPE-*g*-PAA plates had a maximum value against the grafted amount, although the O1s/C1s value increased with the grafted amount and then became constant, analogous to the LDPE-*g*-PMAA and HDPE-*g*-PMAA plates. The decrease in the wettability was considered to result from the aggregation of grafted PAA chains by hydrogen bonding. Surface analysis by XPS revealed that the location of the photografting of AA was more restricted to the outer surface region than that of MAA. In addition, the AA-grafted PE plates had a higher water absorptivity than the MAA-grafted PE plates.[33,34]

In addition, as the photografting of MAA was carried out at lower temperatures, the wettability leveled off at lower grafted amounts, and higher values of cos θ were obtained; this indicated that grafted layers with higher densities of grafted polymer chains were formed at lower temperatures. The water absorptivity, which is characteristic of the hydrophilicity of the whole grafted layer, sharply increased at lower grafted amounts for the grafted LDPE and HDPE plates prepared at lower monomer concentrations or temperatures. From the viewpoint of the kinetics of radical polymerization, we found that a higher water absorptivity was obtained when shorter grafted polymer chains were formed on the outer surface region of the substrates. Therefore, the grafted layers formed on the HDPE plates possessed a little higher water absorptivity than those formed on the LDPE plates.[35]

Adhesive strength measurements

The tensile shear adhesive strength of the grafted LDPE and HDPE plates prepared at different monomer concentrations and temperatures was estimated with enzymatically modified chitosan solutions. The enzymatic reaction time was fixed at 45 min in this study because the adhesive strength had a maximum value at this enzymatic reaction time for the LDPE-*g*-PMAA plates with a grafted amount of 30 μmol/cm^2 in our previous study.[20] When tyrosinase was added to chitosan solutions containing dopamine, quinone derivatives were enzymatically generated and subsequently reacted with the amino groups on chitosan. As a result, the chitosan solutions behaved as high-viscosity gel materials. A considerable increase in the viscosity was observed at the enzymatic reaction time of 3–5 h. A considerable increase in the viscosity inhibited the penetration of the modified chitosan solutions in the grafted layers after the spread of modified chitosan solutions onto the surfaces of the grafted PE plates. In addition, the fact that high-viscosity chitosan materials were insoluble in acidic solutions supported the supposition that chitosan underwent a crosslinking reaction. A simplified scheme of the reaction mechanism of the enzymatic modification of chitosan was depicted in ref. 25. Figure 1(a,b) shows the changes in the tensile shear adhesive strength with the grafted amount for the LDPE-*g*-PMAA and HDPE-*g*-PMAA plates prepared in monomer solutions of different concentrations at 60°C. As the monomer concentration decreased, the adhesive strength of the LDPE-*g*-PMAA and HDPE-*g*-PMAA plates increased sharply at lower grafted amounts. These results indicated that the adhesive strength also depended on the length and number of grafted polymer chains formed and the grafted amount in the same manner as the water absorptivity of the grafted layer.[8,19] However, the adhesive strengths of the LDPE-*g*-PMAA and HDPE-*g*-PMAA plates were limited to 600 and 1000 kPa, respectively, regardless of the MAA monomer concentration during photografting. The constant adhesive strength was considered to be

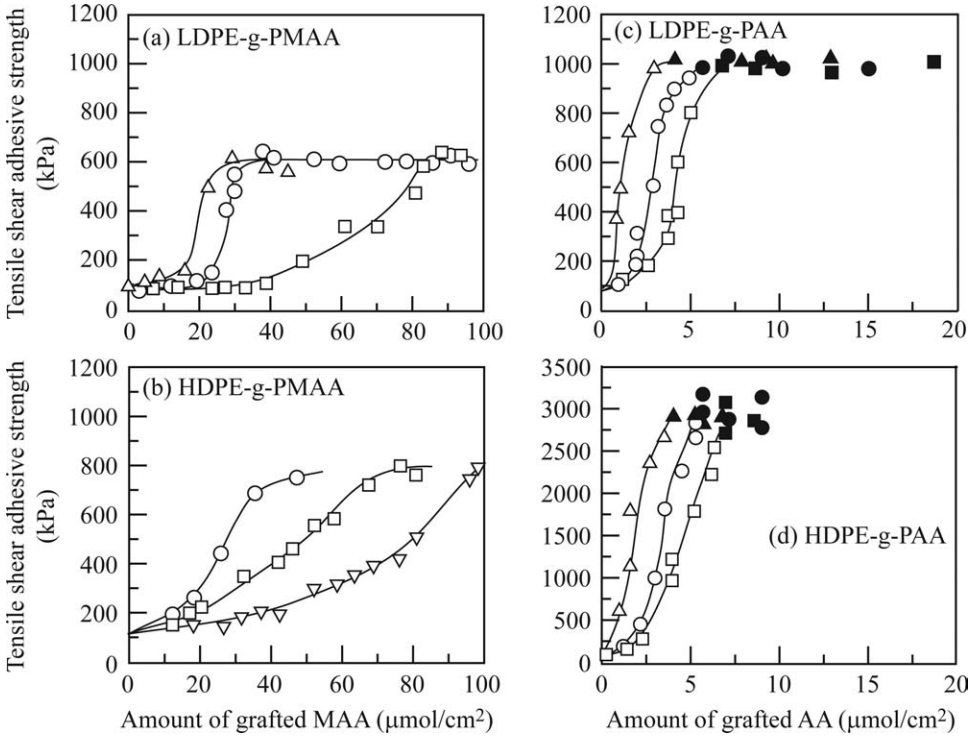

Figure 1 Changes in the tensile shear adhesive strength with the grafted amount of the (a) LFPE-*g*-PMAA, (b) HDPE-*g*-PMAA, (c) LDPE-*g*-PAA, and (d) HDPE-*g*-PMAA plates prepared in monomer solutions of different concentrations at 60°C. Monomer concentration: (△) 0.5, (○) 1.0, (□) 1.5, and (▽) 2.0*M*. Failure: open, cohesive failure; shaded, substrate-breaking.

partly due to the formation of thicker grafted layers and the limited penetration of enzymatically modified chitosan solutions into the grafted layer. This point is discussed in more detailed through the surface analysis of the failed surfaces by XPS in the following section.

Shorter grafted PMAA chains were formed by photografting at lower monomer concentrations, and the resulting grafted layers possessed a higher water absorptivity, as described in our previous article.[19] An increase in the adhesive strength at lower grafted amounts for the LDPE-*g*-PMAA and HDPE-*g*-PMAA plates prepared at lower monomer concentrations was attributed to the high permeability of the enzymatically modified chitosan solutions in the grafted layers. In addition, because the location of the photografting of MAA was restricted to the outer surface region for the HDPE plates,[10,36,37] grafted layers with a little higher density of grafted PMAA chains were formed, as shown in Table III in our previous article.[19] These characteristics of the grafted layers were considered to be favorable for an increase in the adhesive strength at lower grafted amounts for the LDPE-*g*-PMAA and HDPE-*g*-PMAA plates prepared at lower monomer concentrations and higher constant adhesive strengths for the HDPE-*g*-PMAA plates.

Subsequently, Figure 1(c,d) shows the changes in the tensile shear adhesive strength with the grafted amount for the LDPE-*g*-PAA and HDPE-*g*-PAA plates prepared in monomer solutions of different concentrations at 60°C. The adhesive strength of the AA-grafted PE plates sharply increased at lower grafted amounts compared to the MAA-grafted PE plates. This was mainly because the LDPE and HDPE surfaces were covered with grafted PAA cabins at lower grafted amounts compared to those covered with grafted PMAA chains, and the grafted layers of the AA-grafted PE plates had a little higher water absorptivity than the MAA-grafted PE plates. In addition, for both the LDPE-*g*-PAA and HDPE-*g*-PAA plates, substrate breaking was observed at further grafted amounts, regardless of the monomer concentration of photografting. The amounts of grafted AA at which substrate breaking occurred, shown in Figure 1(c,d), are summarized in Table I. The grafted amount at which substrate breaking occurred decreased with decreasing monomer concentration. According to the kinetics of radical polymerization, the formation of shorter grafted polymer chains can be considered effective for increasing the adhesive strength.

Figure 2 shows the changes in adhesive strength with the grafted amounts for the grafted LDPE and HDPE plates prepared at different temperatures. The adhesive strengths of the grafted LDPE and HDPE plates prepared at lower temperatures sharply increased with lower grafted amounts.

TABLE I
Grafted Amounts at Which Substrate Breaking Was Observed for LDPE-*g*-PAA and HDPE-*g*-PAA Plates Prepared in Monomer Solutions of Different Concentrations at 60°C

Sample	Monomer concentration (*M*)	Grafted amount (μmol/cm^2)
LDPE-*g*-PAA	0.5	4
	1.0	6
	1.5	7.5
HDPE-*g*-PAA	0.5	4
	1.0	6
	1.5	7

TABLE II
Grafted Amounts at Which Substrate Breaking Was Observed for LDPE-*g*-PAA and HDPE-*g*-PAA Plates Prepared in Monomer Solutions of 1.0*M* at Different Temperatures

Sample	Temperature (°C)	Grafted amount (μmol/cm^2)
LDPE-*g*-PAA	50	4
	60	6
	70	7
HDPE-*g*-PAA	50	4
	60	6
	70	7

Substrate breaking was observed for the LDPE-*g*-PAA and HDPE-*g*-PAA plates prepared at different temperatures, as was the case for the ones prepared at different monomer concentrations. The amounts of grafted AA at which substrate breaking occurred, obtained from Figure 2(c,d), are summarized in Table II. The grafted amount at which substrate breaking occurred decreased with decreasing temperature during the photografting. Such behavior was caused by the fact that the location of photografting was restricted to the outer surface region of the substrates for the photografting at lower temperatures. However, we considered that the formation of a thick grafted layer limited an increase in the adhesive strength for both MAA-grafted PE plates. Further discussion of the failure is made from the surface analysis by XPS.

In addition, MAAm and HEMA were selected as hydrophilic monomers with other polar functional groups than a carboxyl group, and these monomers were photografted on the LDPE plates at 1.0*M* and 60°C. Figure 3 shows the change in the adhesive strength with the grafted amount for the HEMA-grafted LDPE (LDPE-*g*-PHEMA) and MAAm-grafted LDPE [LDPE-*g*-polymethacrylamide (PMAAm)] plates. The adhesive strength of the LDPE-*g*-PHEMA plates gradually increased over the grafted amount, and the adhesive strength went up to 400 kPa. Also, for the LDPE-*g*-PMAAm plates, the adhesive strength increased little, even when the grafted amount

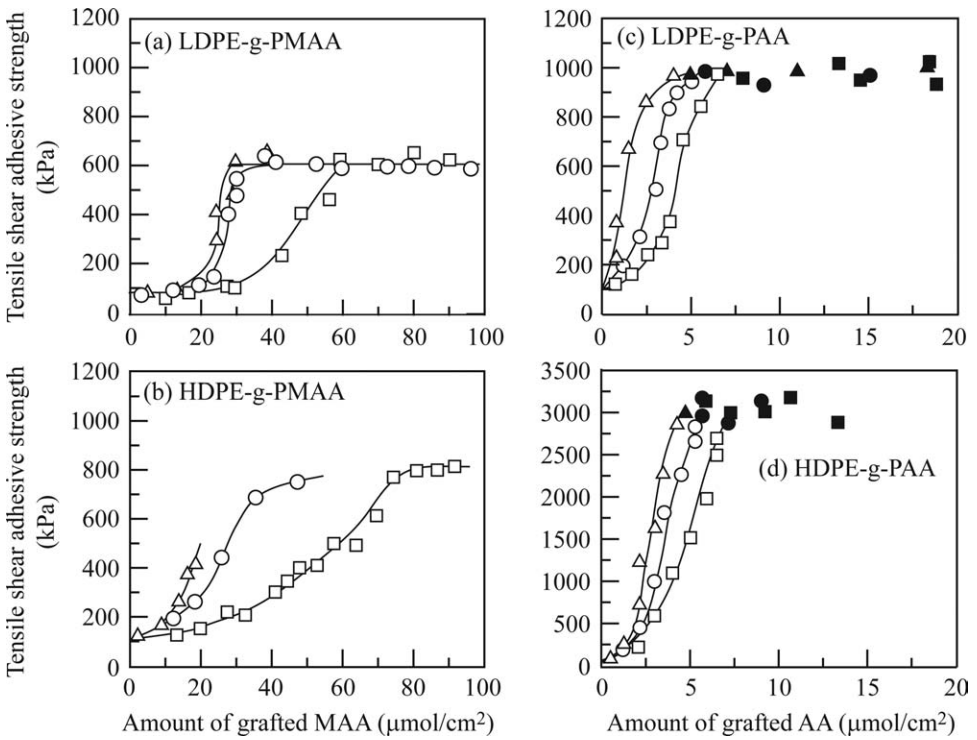

Figure 2 Changes in the tensile shear adhesive strength with the grafted amount of the (a) LFPE-*g*-PMAA, (b) HDPE-*g*-PMAA, (c) LDPE-*g*-PAA, and (d) HDPE-*g*-PMAA plates prepared in 1.0*M* monomer solutions at different temperatures. Temperature (°C): (◇) 40, (△) 50, (○) 60, and (□) 70. Failure: open, cohesive failure; shade, substrate-breaking.

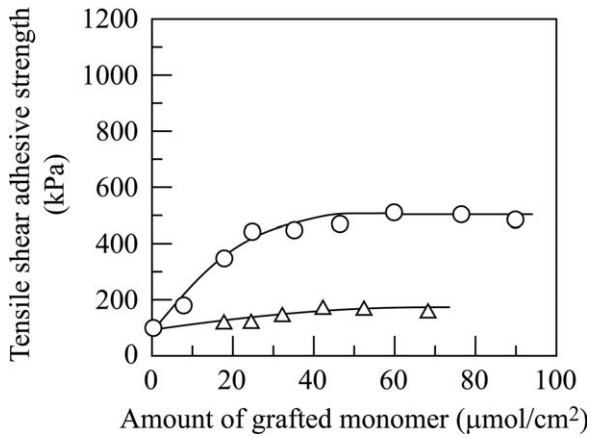

Figure 3 Changes in the tensile shear adhesive strength with the grafted amount of the LFPE-*g*-PHEMA (○) and HDPE-*g*-PMAAm (△) plates prepared at 1.0*M* and 60°C.

increased to 70 μmol/cm^2. The results in Figure 3 show that the presence of carboxyl groups was of great importance in the enhancement of the adhesive strength in this study. To further elucidate the difference in the adhesive strength of these grafted LDPE plates, the quinone reactivity was investigated for these four kinds of grafted LDPE plates.

Quinone reactivity of the grafted polymer chains

Four kinds of grafted LDPE plates were incubated in a dopamine solution containing tyrosinase for 30 min. The visual observations showed that the surfaces of the LDPE-*g*-PMAA and HDPE-*g*-PAA plates were brown and that the color developed over the immersion time. Here, the C1s, O1s, and N1s core spectra were measured for these four kinds of grafted LDPE plates incubated by XPS. Figure 4 shows the C1s, O1s, and N1s core spectra of the incubated LDPE-*g*-PMAA plate. A peak at 289 eV assigned to the carbon atom in the carboxyl group (—COOH) went down, and a new peak at about 288 eV, overlapping with a main peak at 285 eV, emerged by incubation.[9,10,33,34] The C1s at 288 eV corresponded to the carbon atom (—CH_2—NH_2) next to an amino group in the quinone derivative binding to the grafted PMAA chains. In addition, an N1s peak at 400 eV was also observed.

On the other hand, such color development was not observed for the incubated LDPE-*g*-PHEMA and LDPE-*g*-PMAAm plates. Also, no considerable change in the XPS spectra was observed after incubation for the LDPE-*g*-PHEMA and LDPE-*g*-PMAAm plates (not shown). These results indicate that quinone derivatives enzymatically generated from dopamine reacted with a carboxyl group and not with other functional groups, such as amido or alcoholic hydroxyl groups. To explain the dependence of the monomer concentration and temperature during the photografting on adhesive strength, LDPE-*g*-PMAA and LDPE-*g*-PAA plates with different grafted amounts prepared at 0.5–1.5*M* were incubated in a dopamine solution containing tyrosinase (60 U/cm^3) at 25°C. A clear difference was observed in the shape of the C1s spectra before and after incubation, and an N1s peak emerged, although little valuable information was obtained from the O1s spectra.

The N1s/C1s value increased with the immersion time and then leveled off at 10–20 min, depending on the grafting conditions and the grafted amount. Figure 5 shows the change in the constant N1s/C1s value with the grafted amount for the LDPE-*g*-PMAA and LDPE-*g*-PAA plates prepared in monomer solutions of different concentrations at 60°C. The N1s/C1s value of the LDPE-*g*-PMAA plates prepared at lower monomer concentrations increased at lower grafted amounts. This result indicates that the grafted layers prepared at lower monomer concentrations possessed a higher reactivity with quinone derivatives enzymatically generated from dopamine.

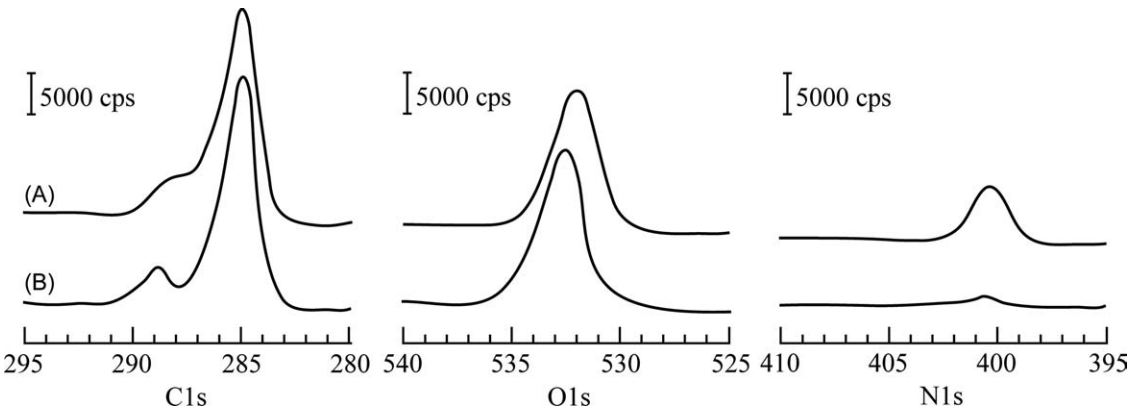

Figure 4 Photoelectron spectra of the C1s, O1s, and N1s core levels of the LDPE-*g*-PMAA plate of 40 μmol/cm^2 incubated in a dopamine solution containing tyrosinase. Sample: (A) after incubation and (B) before incubation.

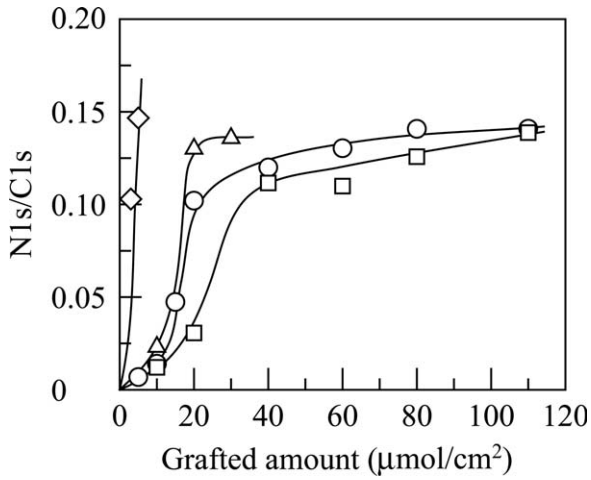

Figure 5 Changes in the constant N1s/C1s values with the grafted amount for LDPE-*g*-PMAA and LDPE-*g*-PAA plates prepared in monomer solutions of different concentrations at 60°C. Monomer concentration: (△) 0.5, (○, ◇) 1.0, and (□) 1.5*M*. Sample: (△, ○, □): LDPE-*g*-PMAA, and (◇) LDPE-*g*-PAA. These LDPE-*g*-PMAA and LDPE-*g*-PAA plates were prepared at 60°C.

In particular, the N1s/C1s value sharply increased for the LDPE-*g*-PAA plates prepared at 1.0*M* and 60°C. As shown in Figure 9 of our previous article, the high water absorptivity of the formed grafted layers was also involved in an increase in the reactivity of quinone derivatives with grafted chains of PMAA or PAA.[19] The monomer concentration dependence of the quinone reactivity of the grafted PMAA chains shown in Figure 5 was similar to the monomer concentration dependence of the adhesive strength of the LDPE-*g*-PMAA plates shown in Figure 1. From these results, we found that the reaction of the quinone derivatives enzymatically generated with grafted polymer chains played a primary role in increasing the adhesive strength.

Surface analysis of the failed surfaces by XPS

The failed surfaces obtained after the adhesive strength measurements were analyzed by XPS to determine the relation between the adhesive strength and the location of failure for the LDPE-*g*-PMAA and LDPE-*g*-PAA plates prepared at 60°C and 1.0*M*.[38] First, some control samples were measured by XPS for assignment of the obtained C1s peaks. Figure 6 shows the C1s and N1s core spectra of the chitosan film [Fig. 6(a)], the incubated chitosan film [Fig. 6(b)], and the LDPE-*g*-PMAA plate coated with enzymatically modified chitosan solution [Fig. 6(c)] as the control samples.

A peak at 286.7 eV, assigned to a carbon binding to one alcoholic —OH group (—CH_2—OH) and overlapping with a main peak at 285 eV, was detected in

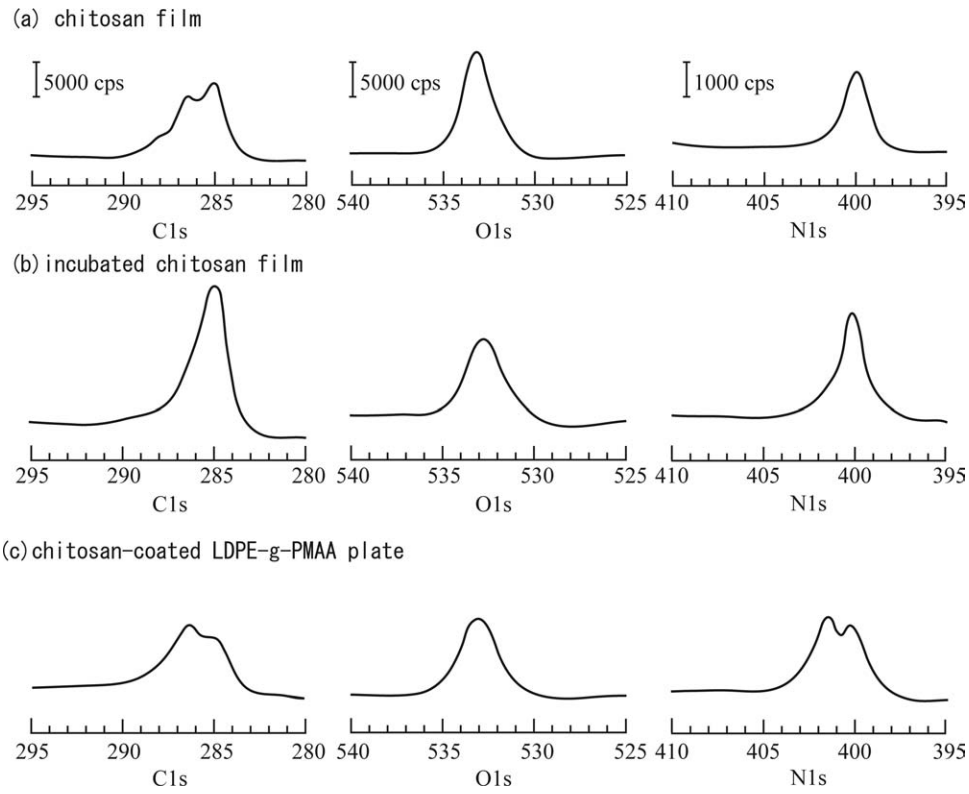

Figure 6 C1s, O1s, and N1s core spectra of (a) a chitosan film, (b) an incubated chitosan film, and (c) the LDPE-*g*-PMAA plate coated with an enzymatically modified chitosan solution.

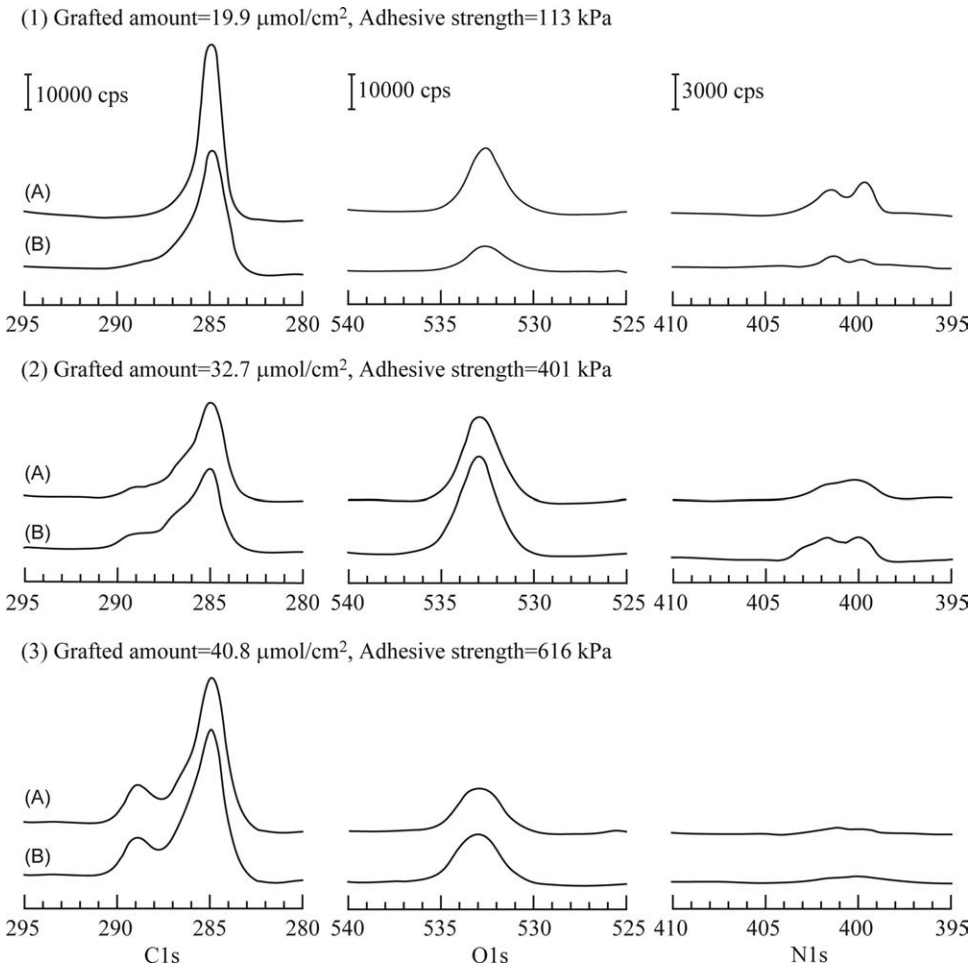

Figure 7 C1s, O1s, and N1s core spectra (A) of the failed surfaces and (B) after the adhesive strength measurements for LDPE-*g*-PMAA plates with different adhesive strengths. The LDPE-*g*-PMAA plates was prepared at 1.0*M* and 60°C. Grafted amount (μmol/cm^2) and adhesive strength (kPa): (1) 19.9 and 113, (2) 27.5 and 401, and (3) 40.8 and 616.

the C1s spectrum for the chitosan film. A small overlapping peak corresponding to a carbon atom in —O—*C*—O— in the chitosan or chitin segments, a carbon atom adjoining a —NH_2 group in the chitosan segment, or a carbon atom in —CONH— in the chitin segment was also observed at about 288 eV.[39,40] For the incubated chitosan film, an asymmetric C1s peak was obtained in addition to distinct O1s and N1s peaks. When the enzymatically modified chitosan solution was coated on the surface of the LDPE-*g*-PMAA plate, the C1s peak at 289 eV (—COOH) disappeared, and a little broad N1s peak emerged. This N1s peak was assigned to different nitrogen-containing moieties present in the reaction system, such as untreated dopamine, enzymatically generated quinone derivatives, quinone derivatives bound to chitosan or grafted PMAA chains, and free amino groups on chitosan.

The location of failure for the LDPE-*g*-PMAA and LDPE-*g*-PAA plates prepared at 1.0*M* and 60°C was determined from surface analysis by XPS on the basis of the results shown in Figure 6.[41] The C1s, O1s, and N1s core spectra of the failed surfaces of both the LDPE-*g*-PMAA and LDPE-*g*-PAA plates were compared on the basis of the peak components assigned for the aforementioned reference samples, shown in Figures 4 and 6.[42] Figure 7 shows the C1s, O1s, and N1s core spectra of the failed surfaces for LDPE-*g*-PMAA plates with different adhesive strengths. For the LDPE-*g*-PMAA plate (grafted amount = 19.9 μmol/cm^2) with an adhesive strength of 113 kPa, a tailed C1s peak at 287–288 eV and a small overlapping N1s peak were observed at both failed surfaces in addition to the peak at 289 eV. These peaks at the surface [Fig. 7(A)] were higher than those at the surface [Fig. 7(B)]. Here, the relative intensity, C1s (—COOH)/ΣC1s, was calculated and represented the ratio of the area of the C1s peak at 289 eV to the area of the whole C1s peak.[42] The relative intensity values of 0.059 and 0.028 for both failed surfaces were lower than the value of 0.15 of the LDPE-*g*-PMAA plate of 19.9 μmol/cm^2. The N1s/C1s values of 0.053 and 0.013 obtained at both failed surfaces were also much lower than the N1s/

C1s value of 0.132 for the LDPE-*g*-PMAA plate coated with the enzymatically modified chitosan solution. Because the LDPE surface was not fully covered with grafted PMAA chains at this grafted amount, the failure could be estimated to occur at the boundary between the grafted layer mixed with enzymatically modified chitosan and grafted PMAA chains and the ungrafted layer.

For the LDPE-*g*-PMAA plate of 27.5 μmol/cm^2 with an adhesive strength of 400 kPa, a C1s peak at 289 eV was observed at both failed surfaces, and the relative intensity values of the failed surfaces were 0.130 and 0.088. These values were lower than the relative intensity of 0.205 for the LDPE-*g*-PMAA plate before the adhesive joint. In addition, overlapping C1s peaks at 287–288 eV and a small N1s peak were also observed. These results demonstrate that the LDPE-*g*-PMAA plates failed in the grafted layer in which enzymatically modified chitosan solutions penetrated during curing. Therefore, we can safely say that strength between the grafted layer and the ungrafted layer increased because the location of failure was shifted from the boundary between the grafted layer and ungrafted layer to inside the grafted layer. The shift of failure location was considered to be caused by an increase in the strength of the grafted layers through the quinone reaction with the grafted PMAA chains.

For both failed surfaces of the LDPE-*g*-PMAA plate of 40.8 μmol/cm^2 with an adhesive strength of 616 kPa, peaks at 289 eV were obvious, and intensity ratios of 0.426 for surface A and 0.460 for surface B were obtained. The relative intensities of 0.169 for surface A and 0.178 for surface B were almost the same as those of the LDPE-*g*-PMAA plate before the adhesive joint. In addition, a N1s peak was little. Therefore, from these results, we concluded that failure occurred in the grafted layer that was free of the components of the enzymatically modified chitosan solution. A similar failure in the grafted layer was observed for the LDPE-*g*-PMAA plates with an adhesive strength of about 600 kPa. The shift of failure location in the grafted layer with an increase in the adhesive strength, as shown in Figure 7, was also observed for the LDPE-*g*-PMAA plates prepared at other monomer concentrations and temperatures.

Next, Figure 8 shows the C1s, O1s, and N1s core spectra of both failed surfaces of the LDPE-*g*-PAA plates prepared at 1.0*M* and 60°C after the adhesive strength measurements. For the LDPE-*g*-PAA plate at the grafted amount of 0.94 μmol/cm^2 with an adhesive strength of 119 kPa, an overlapping peak at 287–288 eV and an obvious peak at 289 were observed in the C1s spectrum in addition to a small N1s peak at the failed surface B. In addition, the relative intensity of 0.037 at the failed surface A was lower than that of 0.105 at the failed surface B. Therefore, it appeared that small amounts of grafted PAA chains, chitosan chains, and nitrogen-containing components were present on the failed surface A. Because the LDPE plate did not have enough grafted PAA chains yet to fully cover the surface at this grafted amount, this result indicates that failure occurred at the boundary between the layer mixed with modified chitosan chains and grafted PAA chains and the ungrafted PE layer.

Both failed surfaces A and B of the LDPE-*g*-PAA plates of 2.98 μmol/cm^2 with 768 kPa had almost the same C1s, O1s, and N1s core spectra. A high O1s peak and an overlapping N1s peak were observed on both failed surfaces. The appearance of the C1s peak at 289 eV signified the presence of grafted PAA chains on the failed surfaces. In addition, a considerable increase in the overlapping C1s peak at 287 eV and the appearance of an N1s peak showed that enzymatically modified chitosan chains and other nitrogen-containing components were present on both failed surfaces.[40] Therefore, these results support the fact that failure occurred in the layer consisting of the grafted PAA chains and components of the enzymatically generated chitosan materials. Finally, as the amount of grafted AA increased, the peak at 289 eV in the C1s core spectra became significant. The relative intensities of both failed surfaces were 0.198 and 0.176. The amount of grafted AA of 4.95 μmol/cm^2 was a little higher than that at which the LDPE surface was fully covered with grafted PAA chains. Therefore, these results indicate that failure occurred in the grafted layer containing the components of enzymatically generated chitosan materials for the LDPE-*g*-PAA plates of 4.95 μmol/cm^2 with 944 kPa. A shift in the failure location with an increase in adhesive strength was also observed for LDPE-*g*-PAA and HDPE-*g*-PAA plates prepared at different monomer concentrations or temperatures.

The LDPE plate was covered with grafted PAA chains at a low grafted amount, and a grafted layer with a higher water absorptivity was formed.[19] This was favorable for the penetration of the enzymatically modified chitosan solutions into the grafted layer. In addition, when the enzymatically generated quinone derivatives reacted with the chitosan chains, the chitosan solutions became highly viscous fluid or gelled materials.[25] However, the behavior of the shift of the failure location observed for the LDPE-*g*-PAA plates was quite different compared to that of the LDPE-*g*-PMAA plates. The enzymatically generated quinone derivatives also reacted with the grafted PMAA and PAA chains, as shown in Figure 4.[20] These previously described factors led to an increase in the adhesive strength and the occurrence

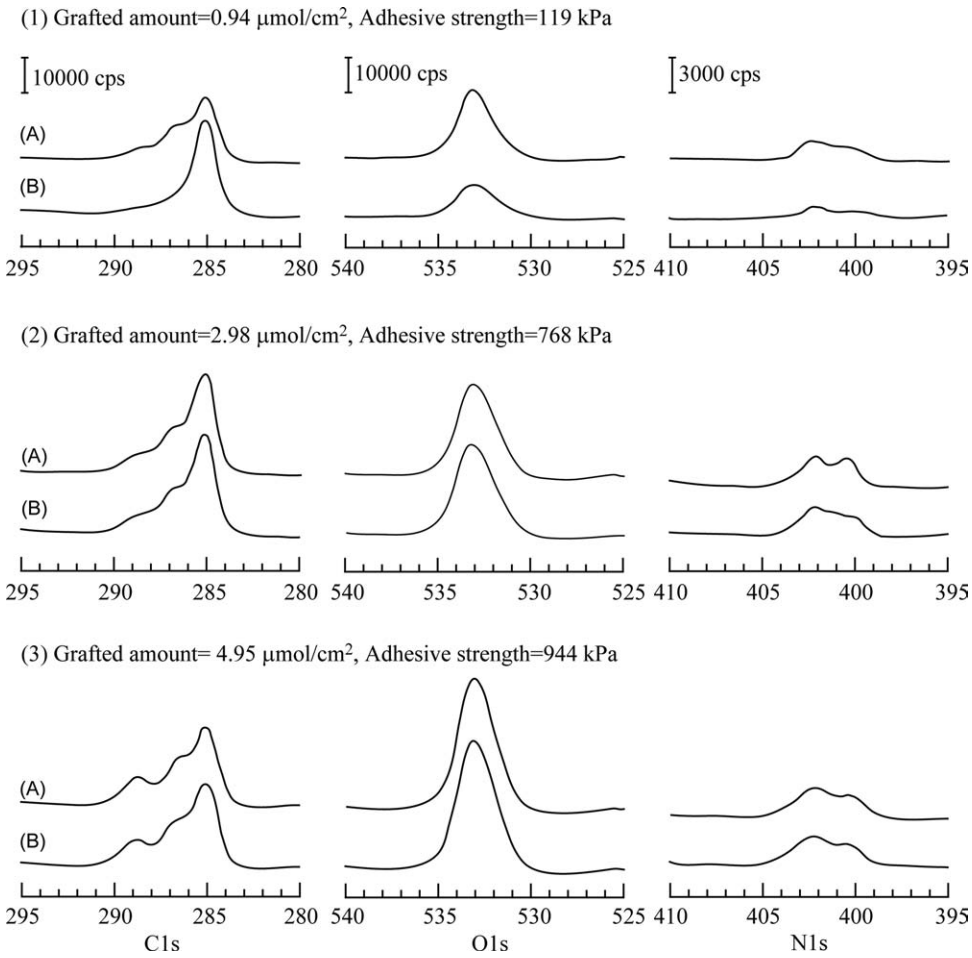

Figure 8 C1s, O1s, and N1s core spectra (A) of the failed surfaces and (B) after the adhesive strength measurements for LDPE-*g*-PMAA plates with different adhesive strengths. The LDPE-*g*-PAA plates was prepared at 1.0*M* and 60°C. Grafted amount (μmol/cm^2) and adhesive strength (kPa): (1) 0.94 and 119, (2) 2.98 and 768, and (3) 4.95 and 944.

of substrate breaking for the LDPE-*g*-PAA and HDPE-*g*-PAA plates. On the other hand, a higher grafted amount was required to obtain a higher adhesive strength for the LDPE-*g*-PMAA and HDPE-*g*-PMAA plates; this resulted in the formation of fairly thick grafted layers. So, the portion without components of the modified chitosan solution was left in the grafted layer. The adhesion of the LDPE and HDPE plates with enzymatically modified chitosan solutions was enhanced by the photografting of MAA. However, an increase in the thickness of the grafted layers for the LDPE-*g*-PMAA and HDPE-*g*-PMAA plates was disadvantageous for an increase in the adhesive strength.

CONCLUSIONS

In this study, we studied the application of dilute chitosan solutions modified by a tyrosinase-catalyzed reaction with dopamine to the adhesion of LDPE and HDPE plates surface-grafted with MAA and AA. In addition, the relation of the location of failure and adhesive strength was examined through surface analysis by XPS of the failed surfaces after tensile shear adhesive strength measurements.

For the LDPE and HDPE plates grafted with MAA and AA at lower monomer concentrations or at lower temperatures, the adhesive strength increased sharply at lower grafted amounts. A sharp increase in the adhesive strength was caused by the formation of shorter grafted polymer chains by photografting at lower monomer concentrations and the restriction of the location of grafting to the outer surface region by photografting at lower temperatures. In addition, the adhesive strength increased sharply at even lower grafted amounts for photografting onto the HDPE plates or that of AA because the location of grafting was restricted to the outer surface region. For the LDPE-*g*-PAA and HDPE-*g*-PAA plates, substrate breaking was observed. The fact that the substrate surfaces were fully covered with grafted polymer chains and that grafted layers with a little higher water absorptivity were formed was effective for increasing the adhesive strength. In addition, from

XPS analysis, we found that the increase in the adhesive strength was due to the penetration of the enzymatically modified chitosan solutions into the grafted layers and the reaction of generated quinone derivatives with the grafted polymer chains. Subsequently, after the adhesive strength measurements, the failed surfaces were analyzed by XPS. Failure occurred at the boundary between the layers mixed with enzymatically modified chitosan and grafted polymer chains and the ungrafted layer for grafted LDPE and HDPE plates with a lower adhesive strength. The location of failure shifted to the layers mixed with components of enzymatically modified chitosan solutions and grafted polymer chains for the LDPE-*g*-PAA and HDPE-*g*-PAA plates with higher adhesive strength. Finally, in this study, we determined the usability of enzymatically modified chitosan solutions for an adhesive to joint LDPE and HDPE plates photografted with MAA and AA. A high adhesive strength was attributed to the restriction of photografting in the outer surface region, the formation of short grafted polymer chains, and the formation of grafted layers with a higher water absorptivity.

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