Adhesion of Surface-Grafted Low-Density Polyethylene Plates with Enzymatically Modified Chitosan Solutions

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ABSTRACT: An investigation was undertaken on application of dilute chitosan solutions modified by tyrosinase-catalyzed reaction with 3,4-dihydroxyphenetylamine (dopamine) to adhesion of the low-density polyethylene (LDPE) plates surface-grafted with hydrophilic monomers. Tensile shear adhesive strength effectively increased with an increase in the grafted amount for methacrylic acid-grafted and acrylic acid-grafted LDPE (LDPE-g-PMAA and LDPE-g-PAA) plates. In particular, substrate breaking was observed at higher grafted amounts for LDPE-g-PAA plates. The increase in the amino group concentration of the chitosan solutions and molecular mass of the chitosan samples led to the increase in adhesive strength. Adhesive strength of the PE-g-PMAA plates prepared at lower monomer concentrations sharply increased at lower grafted amounts, which indicates that the formation of shorter grafted PMAA chains is an effective procedure to increase adhesive strength at lower grafted amounts. Infrared measurements showed that the reaction of quinone derivatives enzymatically generated from dopamine with carboxyl groups was an important factor to increase adhesive strength in addition to the formation of the grafted layers with a high water absorptivity. The above-mentioned results suggested that enzymatically modified dilute chitosan solutions can be applied to an adhesive to bond polymer substrates. The emphasis is on the fact that water is used as a solvent for preparation of chitosan solutions and photografting without any organic solvents. J Appl Polym Sci 113: 3963–3971, 2009

Key words: adhesion; biopolymers; enzymes; graft copolymers; polyethylene (PE)

INTRODUCTION

The characteristic low surface energy and the resulting poor adhesion of polyolefin materials such as polyethylene (PE) and polypropylene (PP) have created numerous technical challenges, while they exhibit a wide range of outstanding properties including excellent chemical resistance and low water adsorption. Many researchers have diligently engaged in studies on surface modification of polyolefin materials by various chemical techniques. Their surfaces were made more hydrophilic by introducing oxygen-containing functional groups on the surfaces through plasma treatment with nonpolymer-forming gases such as O_2, N_2, He, and Ar,[1–5] or UV irradiation.[6–8] However, the surface properties modified by these chemical techniques regressed over time because oxygen-containing functional groups generated on the surfaces gradually overturn or migrate into the bulk inside because of local thermal motion of the substrate polymer chains.[9–12] Such poor durability of the modified surface properties has frequently put a restriction on the use of polyolefin materials.

In contrast to this, the surface properties modified by the grafting techniques will be durably preserved because grafted polymer chains covalently bond to the polymer substrate and intramolecular thermal motion is considerably limited because of their large molecular size.[13] Surface modification of polyolefin materials by grafting techniques has been also widely investigated by many researchers. The grafting polymerization was initiated by plasma treatment[14–17] or by irradiation with UV[18–21] and Co^{60} radiation.[22-26] Because the energy of UV rays emitted from a 400W high-pressure mercury lamp used 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 substrates and the surface properties are modified at lower grafted amounts.

For about two decades, we have investigated surface modification of the hydrophobic polymer substrates such as low- and high-density PE (LDPE and HDPE) and polytetrafluoroethylene (PTFE) plates and films by the photografting technique.[27-37] The photografting with a 400W high-pressure mercury lamp is an effective and practical means in the fact that this procedure is very simple and the initial sites for

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grafting and the density of functional groups can be readily controlled.[27,31,33,37] The wettability of the surfaces of the LDPE, HDPE, PP, and PTFE plates was enhanced by the photografting of hydrophilic monomers such as methacrylic acid (MAA), acrylic acid (AA), methacrylamide (MAAm), and 2-(dimethylamino)ethyl methacrylate (DMAEMA).[27,31,33] Furthermore, tensile shear adhesive strength of the grafted LDPE plates remarkably increased in lower grafted amounts.[27,31] Autohesion, or adhesive-free adhesion, was also developed by overlapping two grafted LDPE plates immersed in water, and then heat-pressing them.[31,33,37] Substrate breaking was observed at higher grafted amounts on both adhesive and autohesive strength measurements. These results indicate that tensile shear strength exceeded the ultimate tensile strength of the LDPE plate used.

However, most of the main components in commercially available adhesives are insoluble or poorly soluble in water expect for polyvinyl alcohol. Therefore, many commercially available liquid-type adhesives are dissolved in volatile organic solvents. We have also made investigation on construction of water-resistant adhesives with enzyme tyrosinase and chitosan.[38-40] The viscosity of dilute chitosan solutions considerably increased by the tyrosinase-catalyzed quinone oxidation of 3,4-dihydroxyphenetylamine (dopamine) and subsequent nonenzymatic quinone reactions with amino groups of chitosan. When high-viscosity modified chitosan materials were spread on the surfaces of the glass slides and the glass slides overlapped and tightly clipped together were submerged in water, tensile shear adhesive strength of over 400 kPa was observed. The function of the adhesive protein was mimicked using 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 explained in detail.[38,39] On the basis of these results, we considered that enzymatically modified chitosan materials had a potential for an alternative water-soluble adhesive in the fact that chitosan is soluble in the pH range lower than 6.0.

It is important to develop a novel water-solvent polymeric adhesive without organic solvents in environmental preservation. So, we focused attention on chitosan because it is produced in large amounts by deacetylation of chitin that is contained in the shells of the crustaceans such as crabs and prawns. However, the use of chitosan is limited mainly to wastewater treatment to capture heavy metal ions.[41] Therefore, if enzymatically modified chitosan materials are used for an adhesive, an alternative usage of chitosan will come out.

In this study, dilute chitosan solutions modified by tyrosinase-catalyzed reaction with dopamine were applied to adhesion of the LDPE plates photografted with different hydrophilic monomers. The effects of the enzymatic reaction time, amino group concentration and molar mass of chitosan, and grafted amounts on adhesive strength of the LDPE plates were investigated from the tensile shear adhesive strength measurements.

EXPERIMENTAL

Materials

A LDPE plate of 1.0-mm thickness was used as a polymer substrate for photografting. The crystallinity was calculated to be 50.8% from the density determined by a flotation or buoyancy method with acetone and glycerol at 25°C using the densities of the completely amorphous and pure crystalline parts of PE.[27,31,33] The LDPE plates cut into 7.0-cm length and 2.5-cm width were washed with methanol and acetone, and then dried under reduced pressure. The hydrophilic monomers used in this study, MAA, AA, and MAAm, were used without further purification.

Mushroom tyrosinase (EC. 1.14.18.1) and dopamine were purchased from Sigma Chemical (St Louis, MO). The specific activity of mushroom tyrosinase used was 2870 U/mg-solid (determined by supplier). Four kinds of chitosan samples were purchased from Sigma Chemical and Wako Pure Chemical (Tokyo, Japan). One wt% chitosan solutions were prepared in an aqueous acetic acid solution of 1.0 w/v% and their viscosities were measured by a Brookfield DV II+ viscometer with S18, S25, or S34 spindles at a rotation speed of 1 rpm.[38-40]

The degrees of deacetylation and viscosity-average molecular mass of the chitosan samples used were determined according to the procedures described in detail in previous articles.[38,40,42-44] The degrees of deacetylation of the chitosan samples used were determined by the colloid titration method with an aqueous solution of potassium poly(vinyl alcohol) sulfate (KPVS). Molecular mass was calculated from the values of intrinsic viscosity determined using an Ubbelohde viscometer in an aqueous acetic acid solution of 0.1*M* containing NaCl of 0.2*M* at 25°C. The degrees of deacetylation and viscosity-average molecular mass of the chitosan samples used in this study are summarized in Table I.

Photografting

The photografting of MAA, AA, and MAAm onto the LDPE plates was carried out by the same procedure in our previous articles.[26-28] First, solutions of MAA, AA, and MAAm were prepared in water at a monomer concentration of 1.0*M*. The LDPE plates were

TABLE I
The Degrees of Deacetylation and Viscosity-Average Molecular Mass of the Chitosan Samples Used in this Study

Sample	Degree of deacetylation (%)	viscosity (mPa·s)	[η] (cm^3/g)	$\overline{M_\eta}$ (g/mol)
C560	81.3	561	672	9.75×10^5
C890	87.3	888	893	1.24×10^6
C1100	87.3	1119	1020	1.53×10^6
C2500	89.8	2500	1072	1.62×10^6

immersed in 50 cm^3 of an acetone solution containing 0.25 g of benzophenone (BP) as a sensitizer for 1 min to coat the LDPE surfaces with BP. The BP-coated LDPE plates were immersed in the respective monomer solutions (65 cm^3) in the Pyrex glass tubes, and then UV rays emitted from a 400W high-pressure mercury lamp were irradiated at 60°C. After the photografting, the grafted LDPE plates were washed with water for 24 h to exclude unreacted monomers and generated homopolymers, and then dried under reduced pressure. The grafted amount (μmol/cm^2) was calculated from the weight increase of the LDPE plates according to eq. (1) in Ref. 45.

Preparation of chitosan solutions

Chitosan solutions were prepared from four kinds of chitosan samples shown in Table I. Chitosan solutions of 1.0-1.2 w/v% were prepared by dispersing chitosan flakes to 100 cm^3 of water and intermittently dropping 2*M* HCl solution to maintain the pH values at 3-4. After the mixtures were stirred for 24 h, insoluble parts were removed by vacuum filtration with a G3 glass filter. The chitosan solutions obtained were diluted with water so that the amino group concentration was adjusted to 10-40 m*M* on the basis of the weight concentration of the chitosan solutions and degree of deacetylation of each chitosan sample.[38-40] Then, the pH values of the chitosan solutions were adjusted to 5.8-6.0 with small amounts of 2*M* NaOH solution.

Enzymatic modification of chitosan solutions

The enzymatic reaction was initiated by adding 1.0 cm^3 of an aqueous tyrosinase solution to 100 cm^3 of the chitosan solutions containing dopamine (10 m*M*) to reach the final concentration of 60 U/cm^3. Reacted chitosan solutions were spread on each surface of two grafted LDPE plates with the same grafted amount cut into 3.5 × 1.25 cm^2, and then the surfaces were placed in contact with a 1.25 × 1.25 cm^2 overlapping surface area. In this procedure, the majority of the reaction mixture applied to the grafted LDPE plates was extruded when the surfaces were clipped. Weight measurements indicated that 10-18 mg of the reaction mixture remained between the grafted LDPE plates after clipping the samples together, and this value could not be rigorously controlled.[38] The overlapped samples were tightly fixed with two binder clips and laid on an oven at 25°C for 24 h.

Adhesive strength measurements

Tensile shear adhesive strength was measured by an Orientec universal testing machine STA 1225. One end of each sample was attached to the load cell in the lower side and the other end to the actuator of the machine. The samples were loaded at a shear rate of 3.0 mm/s until failure. The values of tensile shear strength were calculated by dividing the force to separate the bonded LDPE samples by the overlapping surface area.[29,37,39]

IR spectrum measurements

LDPE-g-PMAA and LDPE-g-PAA plates were incubated in 10 m*M* dopamine solutions containing tyrosinase (60 U/cm^3) for 6 and 3 hr at 25°C, respectively. The LDPE-g-PMAA and LDPE-g-PAA plates incubated were washed with water, and then dried under reduced pressure. Grafted layers were whittled away from the surfaces of both grafted LDPE plates incubated with a sharp blade, and then mixed with KBr powder in the composition of correctly 1.5 wt %, and compressed to get them into thin pellets. Infrared spectra were measured on a JASCO FT/IR-4200 spectrophotometer (Tokyo, Japan) ranging from 400 to 4000 cm^{-1} at a resolution of 2 cm^{-1}.

RESULTS AND DISCUSSION

Effect of enzymatic reaction time

The hydrophilic monomers such as MAA, AA, and MAAm were photografted on the LDPE plates at 60°C and the grafted amounts were varied by changing the UV irradiation times.[27,31,33,36,37] The enzymatic reaction was initiated by adding mushroom tyrosinase to C1100 chitosan solutions at the amino group concentration of 30 m*M* containing dopamine. Enzymatically modified chitosan solutions were spread on the surfaces of the LDPE-g-PMAA plates at different enzymatic reaction times. Figure 1 shows the effect of the enzymatic reaction time on adhesive strength for LDPE-g-PMAA plates at the grafted amount of 30 μmol/cm^2. Surface analysis by ESCA showed that the intensity ratio, O1s/C1s, stayed constant in the range of the grafted amounts higher than 25 mmol/cm^2. The LDPE surfaces were fully

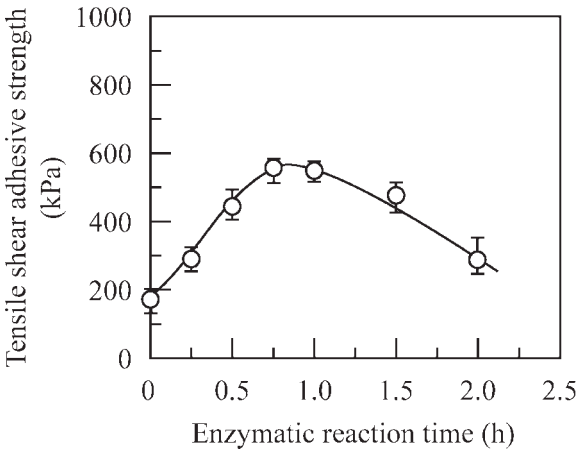

Figure 1 Variation in tensile shear adhesive strength of the LDPE-g-PMAA plates (G = 30 μmol/cm^2) coated with enzymatically modified chitosan solutions with the reaction time. The overlapped LDPE-g-PMAA plates were held at 25°C. G is grafted amount.

covered with grafted PMAA chains at this grafted amount.[31] Adhesive strength increased with an increase in the enzymatic reaction time, and then had the maximum value at 45 min. Successive reactions related with quinone derivatives can be explained on the basis of the schematic representation.[38,39] The viscosity of the solution sharply increased 1.5 h after the enzymatic reaction was initiated because chitosan chains were crosslinked through the quinone linkage.[38] In addition, when a chitosan film is incubated in a dopamine solution containing tyrosinase, the chitosan film is colored blackish brown because of quinone-tanning.[39,40,45,46] These results also indicate that quinone derivatives enzymatically generated reacted with chitosan's amine groups.[38]

Therefore, chitosan solutions were still low viscosity at the enzymatic reaction time of 45 min. Since enzymatically modified chitosan solutions are allowed to penetrate into the grafted layers during the curing, the quinone generation and subsequent gelation will progress in the grafted layers. This behavior plays an important role in the enhancement of adhesive strength of the LDPE plates in addition to the photografting of MAA. However, a gradual decrease in adhesive strength at further increased reaction times is considered to be because of a considerable increase in the viscosity caused by gelation.[38,39] In other words, the increase in gelation will restrain the penetration of chitosan materials into the grafted layer.

C1100 chitosan solutions at amino group concentrations of 10-40 m*M* and chitosan solutions of 30 m*M* with different molecular mass were modified with tyrosinase in the presence of dopamine. Enzymatically modified chitosan solutions were spread on LDPE-g-PMAA plates of 30 μmol/cm^2 at the enzymatic reaction time of 45 min, and then the enzymatically modified chitosan solutions were cured between the overlapped LDPE-g-PMAA plates at 25°C. The effects of molecular mass of chitosan and amino group concentration of C1100 chitosan on adhesive strength were shown in Figure 2. As the amino concentration of C1100 chitosan increased from 10 to 30 m*M* or molecular mass of chitosan increased from C560 to C1100, adhesive strength increased. These results indicate that the increases in the concentration of amino groups and molecular mass of the chitosan samples effectively led to the increase in the viscosity through quinone linkage.[39,40] However, adhesive strength values for solutions of C1100 chitosan of 40 m*M* and C2500 chitosan of

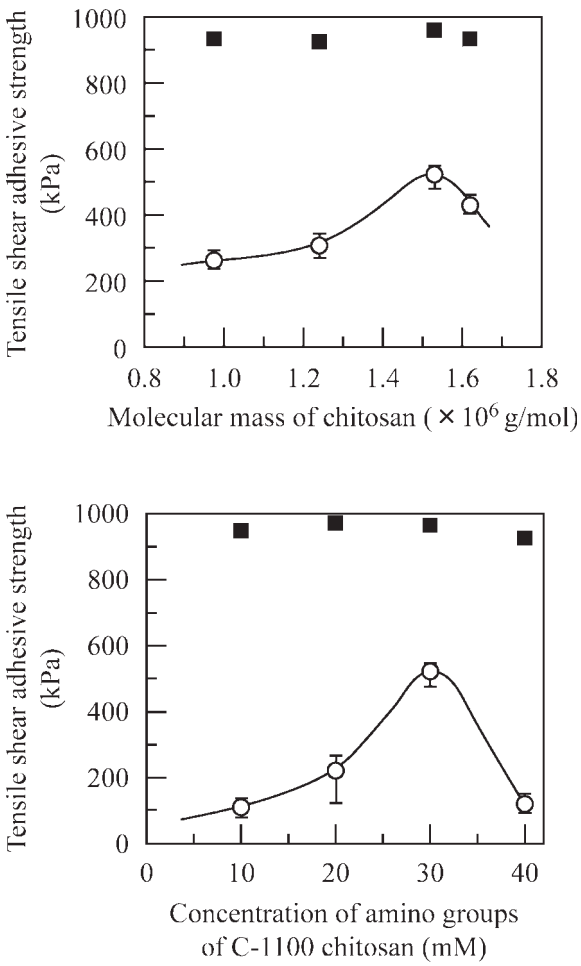

Figure 2 The effects of (a) molecular mass of chitosan samples and (b) concentration of amino groups of C1100 chitosan on tensile shear adhesive strength of the LDPE-g-PMAA (○, grafted amount = 30 μmol/cm^2) and PE-g-PAA plates (■, grafted amount = 20 μmol/cm^2). Enzymatically modified chitosan solutions were coated at the enzymatic reaction time of 45min. The overlapped LDPE-g-PMAA and LDPE-g-PAA plates were held at 25°C (failure: open, cohesive failure; shaded, substrate breaking).

TABLE II
Adhesion of LDPE-g-PMAA Plates with Different Reference Solutions

Reference solution	Reaction time (min)	Grafted amount (μmol/cm^2)	Adhesive strength (kPa)
Chitosan solution containing dopamine and tyrosinase	45	30	586
Chitosan solution containing dopamine and tyrosinase	45	Ungrafted	88
Chitosan solution containing dopamine	45	30	325
Chitosan solution containing tyrosinase	45	30	324
Chitosan solution	0	30	326
Mixture of dopamine and tyrosinase	45	30	78
Mixture of dopamine and tyrosinase	0	30	98

The overlapped LDPE-g-PMAA plates were held at 25°C. Concentration of each component: Amino group concentration of C1100 = 30 m*M*; dopamine = 10mM; tyrosinase = 60 U/cm^3.

30 m*M* were lower than those we expected, probably because the viscosity of the chitosan solution was too high and/or crosslinking reaction heterogeneously occurred.

In addition, adhesive strength measurements were carried out with reference solutions to emphasize the enzymatic modification of chitosan solutions for adhesion of the LDPE-g-PMAA plates. Adhesive strength obtained with different reference solutions was summarized in Table II. Adhesive strength was limited to 320-330 kPa for a chitosan solution or chitosan solutions containing either dopamine or tyrosinase. These values of adhesive strength were much lower than that obtained with the enzymatically modified chitosan. Adhesive strength of LDPE-g-PMAA plates coated with dopamine solutions containing tyrosinase was as low as 78-98 kPa. Low values of adhesive strength for these reference solutions will open up the possibility of chitosan materials modified through the enzymatic reaction toward the practical application as an adhesive.

Effect of photografting of hydrophilic monomers

An enzymatically modified chitosan solution was spread on LDPE-g-PMAA plates with different grafted amounts at the enzymatic reaction time of 45 min, and the enzymatically modified chitosan solutions were cured between the overlapped LDPE-g-PMAA plates at 25°C. The effect of the grafted amount on adhesive strength was shown in Figure 3 for LDPE-g-PMAA plates prepared at a monomer concentration of 1.0 *M*. When the amount of grafted MAA exceeded 25 μmol/cm^2, adhesive strength sharply increased. However, adhesive strength stayed constant at higher grafted amounts. Our previous articles reported the surface modification of the LDPE plates by the photografting of MAA and their surface characteristics.[31] The LDPE surface was made hydrophilic by the photografting of MAA and the modified surface wettability was kept constant in the range of the grafted amounts higher than 25 μmol/cm^2 irrespective of monomer concentrations on the photografting (cos θ = 0.5). However, the water absorptivity of the grafted layers of PMAA formed on the LDPE surfaces increased over the grafted amount. In addition, adhesive strength was limited to 88 kPa for an ungrafted LDPE plate coated with an enzymatically modified chitosan solution as shown in Table II. These results support our conception that hydrophilization of the LDPE surfaces by the photografting also plays an important role in the increase in adhesive strength of the LDPE plate.

In addition, LDPE-g-PMAA plates were also prepared at 0.5 and 1.5 *M* to assess the effect of grafting kinetics such as the number and length of grafted polymer chains prepared on adhesive strength. An enzymatically modified C1100 chitosan solution at 30 m*M* was spread on LDPE-g-PMAA plates

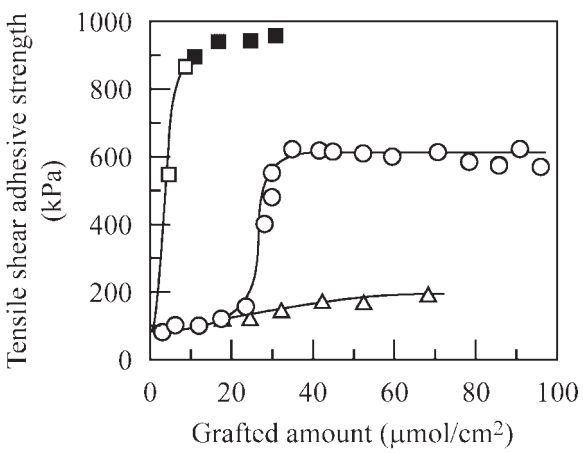

Figure 3 Changes in tensile shear adhesive strength of the LDPE-g-PMAA (○), LDPE-g-PAA (□,■), and LDPE-g-PMAAm (△) plates coated with enzymatically modified chitosan solutions with the grafted amount (failure: open, cohesive failure; shaded, substrate breaking). The enzymatic reaction time was 45 min. The overlapped grafted LDPE plates were held at 25°C.

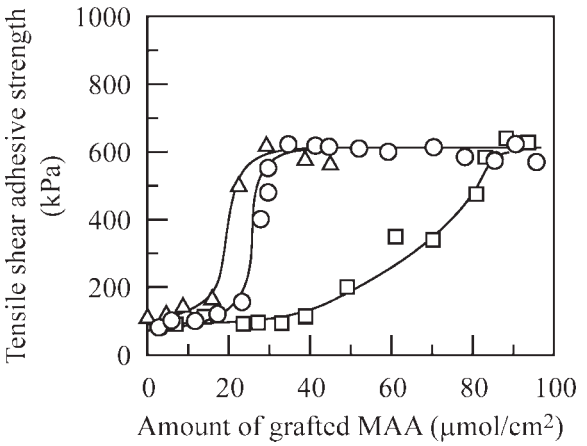

Figure 4 The effect of monomer concentration on the photografting on tensile shear adhesive strength of the LDPE-g-PMAA plates. Enzymatically modified chitosan solutions were coated at 45 min. The overlapped LDPE-g-PMAA plates were held at 25°C. MAA concentration (M)- △: 0.5, ○: 1.0, □: 1.5.

prepared at different monomer concentrations, and the modified chitosan solutions were cured at 25°C. The effect of the MAA monomer concentration on the photografting on adhesive strength was shown in Figure 4. As the MAA monomer concentration on the photografting was lower, adhesive strength sharply increased at lower grafted amounts. The dependence of monomer concentration on the photografting on adhesive strength was also observed for adhesion of the LDPE-g-PMAA plates with a commercially available two-component-type epoxy adhesive, Araldite, in our previous article.[27] In addition, the kinetics of radical polymerization represents that the rate constant of propagation increases with an increase in the monomer concentration. Therefore, the increase in the monomer concentration leads to the formation of longer grafted polymer chains. So, the number of grafted PMAA chains increases and shorter grafted chains are formed at the LDPE surfaces, when the LDPE-g-PMAA plates are prepared at lower monomer concentrations. However, above this grafted amount at which the LDPE surfaces are fully covered with grafted PMAA chains, grafting of MAA onto the grafted PMAA chains will occur, generating highly branched grafted PMAA chains. The water absorptivity as one of the hydrophilic properties of the whole grafted layers also depended on the MAA monomer concentration on the photografting of MAA.[27] These results support our conception that adhesive strength depends on the monomer concentration on the photografting and on the grafted amount. It was found from the above-mentioned results that adhesive strength sharply increased at lower grafted amounts, as the monomer concentration on the photografting of MAA was lower.

Subsequently, the effect of photografting of other hydrophilic monomers, AA and MAAm, on adhesive strength was estimated. The hydrophilic properties of the AA-grafted and MAAm-grafted LDPE (LDPE-g-PAA and LDPE-g-PMAAm) plates are also summarized in Table III.[27,31,33] Since an AA monomer has no α-methyl (-CH_3) group in the structure, the location of photografting of AA was restricted to the outer surface region and the LDPE surface was fully covered with grafted PAA chains than with grafted PMAA chains at lower grafted amount.[31] In addition, the grafted layers of PAA possessed higher water absorptivity than the grafted layers of PMAA. However, grafted PMAAm chains fully covered the LDPE surface at much lower grafted amount and the LDPE-g-PMAAm plates possessed a considerably higher surface-wettability than the LDPE-g-PAA and LDPE-g-PMAA plates. However, water absorptivity for LDPE-g-PMAAm plates was lower than those for LDPE-g-PMAA and LDPE-g-PAA plates.[33] Adhesive strength of these three kinds of grafted LDPE plates was compared in relationship with the hydrophilicity of their grafted layers. Although adhesive strength of the LDPE-g-PMAAm

TABLE III
The Hydrophilic Properties and Surface Compositions of the LDPE-g-PMAA, LDPE-g-PAA, and LDPE-g-PMAAm plates Prepared in this Study

Sample	Grafted amount[a] (μmol/cm^2)	Constant intensity ratio		cos θ
		O1s/C1s	N1s/C1s	
LDPE-g-PMAA	25	0.32		0.5
LDPE-g-PAA	6	0.37		0.4 (max)
LDPE-g-PMAAm	0.25	0.25	0.15	0.5
PMAA		0.384		
PAA		0.518		
PMAAm		0.253	0.153	
LDPE		0.027		−0.120

[a] The grafted amounts at which the intensity ratios and cos θ values become constant.

plates gradually increased with an increase in the grafted amount, a sharp increase in adhesive strength was not observed at higher grafted amounts. Adhesive strength of LDPE-g-PAA plates sharply increased at lower grafted amounts and higher adhesive strength was obtained at higher grafted amounts compared with LDPE-g-PMAA plates. In particular, for LDPE-g-PAA plates substrate breaking was observed in the range of the grafted amounts higher than 10 μmol/cm^2. This result indicates that adhesive strength higher exceeded the ultimate strength of the LDPE plates used at higher grafted amount for LDPE-g-PAA plates. This can be explained in terms of the fact that the location of photografting of AA is restricted to the outer surface region of the LDPE plate than that of MAA and the grafted layers rich in grafted PAA chains possess high water absorptivity.[27] These characteristics peculiar to the LDPE-g-PAA plates are attributed to the absence of α-methyl groups in monomer structure.

Subsequently, LDPE-g-PMAA, LDPE-g-PAA, and LDPE-g-PMAAm plates were incubated in a dopamine solution containing tyrosinase. The LDPE-g-PMAA and LDPE-g-PAA plates were colored blackish brown because of quinone tanning, whereas no color development was observed for the LDPE-g-PMAAm plates as well as an ungrafted LDPE plate. This difference in color development indicates that enzymatically generated quinone derivatives react with grafted PAA and PMAA chains. Such color development has been observed for the reaction of chitosan with quinone derivatives enzymatically generated from dopamine,[38-40] chlorogenic acid,[47] phenol,[48] alkylphenols,[45,46,49] and other enzymatic substrates.[48] The instrumental approach to provide evidence that enzymatic reaction results in the covalent modification of the surface grafted layers of the LDPE-g-PMAA and LDPE-g-PAA plates was carried out to monitor changes in the IR spectra of these grafted LDPE plates which were incubated in a dopamine solution containing tyrosinase. Figure 5 shows IR spectra of grafted chains obtained from LDPE-g-PMAA and LDPE-g-PAA plates incubated. There are definite changes in NH stretching and NH bending regions of the IR spectra. A broad increase in the NH stretching region (3100–3300 cm^{-1}) was observed. Figure 5 also shows the emergence of a peak in the NH bending region at 1540 cm^{-1}.[49] These results supports the fact that PMAA and PAA chains underwent quinone reaction, which led to an increased adhesive strength for LDPE-g-PMAA and LDPE-g-PAA plates.

In these two decades, we have carried out studies on adhesion of the LDPE and HDPE plates photografted with hydrophilic monomers such as MAA, AA, MAAm, and DMAEMA with a commercial two-component-type epoxy adhesive or by autohesion, adhesive-free adhesion, of them through hydrogen bonding between polar functional groups, ionic bond between negatively and positively chargeable ionic groups, and entanglement of grafted polymer chains.[27,31,33] Adhesive and autohesive strength went over the ultimate strength of the LDPE plate and substrate breaking was observed at higher grafted amounts. It is particularly worth noting that the amount of grafted AA at which substrate breaking was observed in this study is as low as or lower than these grafted amounts. In addition, it is environmentally favorable that water is used as a solvent without organic solvents for the photografting of hydrophilic monomers onto the LDPE plates and enzymatic modification of dilute chitosan solutions.

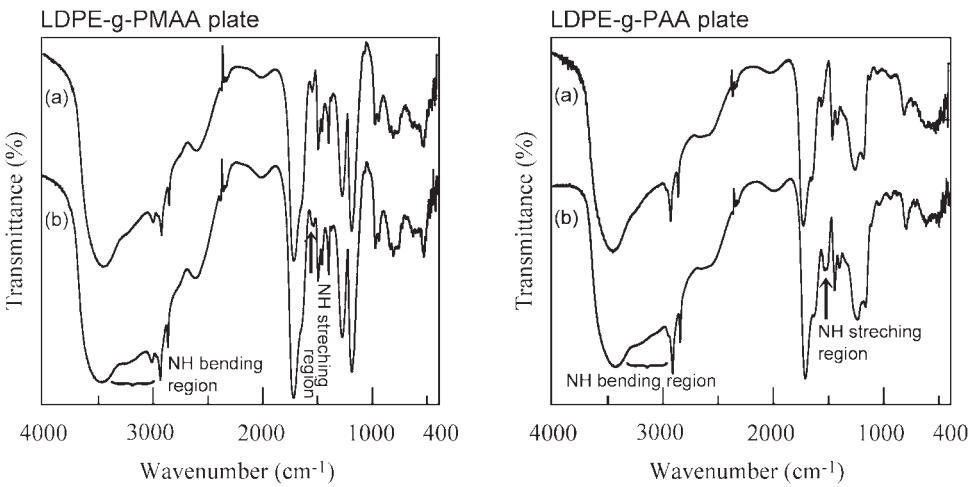

Figure 5 IR spectra (a) before and (b) after incubation in a dopamine solution containing tyrosinase for grafted chains obtained from LDPE-g-PMAA (left) and LDPE-g-PAA (right) plates.

In this study, the photografting of hydrophilic monomers was carried out as a surface modification to improve adhesive strength of the LDPE plates with enzymatically modified chitosan solutions. Since the grafted amount at which adhesive strength sharply increased was higher than those at which the LDPE surface was covered with each grafted polymer chain for LDPE-g-PMAA and LDPE-g-PAA plates, a certain grafted amount was required to penetrate enzymatically modified chitosan solutions. However, the grafted amount at which LDPE-g-PAA plates bonded with enzymatically modified chitosan solutions failed was half as much as that at which LDPE-g-PAA plates bonded through adhesive-free adhesion, or autohesion and approximately equivalent to that at which LDPE-g-PAA plates bonded with a commercially available epoxy adhesive.[31]

CONCLUSIONS

It was found from the above-mentioned results that the adhesive properties of the LDPE plate grafted with MAA and AA were considerably enhanced with enzymatically modified chitosan solutions. However, adhesive strength was incomparably lower for an ungrafted LDPE plate coated with enzymatically modified chitosan solutions and for the LDPE-g-PMAA plates coated with chitosan solutions containing either tyrosinase or dopamine. These results support that both photografting of hydrophilic monomers and tyrosinase-catalyzed modification of chitosan solutions play an important role in increasing adhesive strength of the LDPE plates. Substrate breaking was observed at higher grafted amounts for LDPE-g-PAA plates and the grafted amount at which substrate breaking obtained for LDPE-g-PAA plates in this study was as low as or lower than those at which substrate breaking was observed at adhesive strength measurements with a commercially available two-component-type epoxy adhesive and at autohesive strength measurements.

In addition, water was used as a solvent for the photografting of hydrophilic monomers onto the LDPE plates and preparation of chitosan solutions. Here, the absence of organic solvents is very favorable from an environmental point of view. This technique is environmentally friendly in that chitosan typically obtained from wastes generated from crustacean processing is used as a main low material. We will examine adhesion of other hydrophobic polymer substrates such as HDPE, PP, and PTFE plates by this procedure.

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