Journal of Applied Polymer Science

Adhesion of Grafted Polypropylene Plates with Enzymatically Modified Chitosan Solutions and Analysis of Failed Surfaces by X-ray Photoelectron Spectroscopy

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ABSTRACT: In this study, hydrophilic monomers were photografted onto the PP plates at different monomer concentrations and temperatures, and grafted PP plates were bonded with enzymatically modified chitosan solutions. Their adhesive strength properties were discussed in relation to the grafting conditions and hydrophilic properties such as wettability and water-absorptivity. In addition, the location of failure was investigated by X-ray photoelectron spectroscopy analysis of failed surfaces. Wettability of the grafted PP plates except for the PP grafted with acrylic acid (PP-g-PAA) plates remained constant above the grafted amounts at which the PP surfaces were fully covered with grafted polymer chains. On the other hand, wettability of the PP-g-PAA plates passed through the maximum value and then gradually decreased with the grafted amount probably because of the 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 an increase in the grafted amount and substrate breaking was observed for PP-g-PAA plates because enzymatically modified chitosan solutions were successfully penetrated in the grafted layers and quinone derivatives reacted with carboxy groups of grafted PAA chains. Failure occurred in the layers composed of grafted PAA chains and components containing in enzymatically modified chitosan solutions and the location was shifted to the inside of grafted layer, as the grafted amount increased. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 1369–1376, 2013

KEYWORDS: adhesives; biopolymers & renewable polymers; grafting; polyolefins; spectroscopy

Received 7 August 2012; accepted 19 March 2013; Published online 25 April 2013
DOI: 10.1002/app.39301

INTRODUCTION

The polyolefin materials such as polyethylene (PE) and polypropylene (PP) have hydrophobic and chemically inert surfaces. As these surface properties are unfavorable to their application related with surface properties, the use of the polyolefin materials was frequently limited. To solve this problem, many researchers have carried out investigations on their surface modification[1–5] and development of novel adhesives.[6–8] In our previous article,[6] highly viscous solutions prepared from dilute chitosan solutions containing 3,4-dihydroxyphenetylamine (dopamine) and an oxidoreductase tyrosinase were applied to adhesion of low- and high-density PE (LDPE and HDPE) plates photografted with hydrophilic monomers, such as methacrylic acid (MAA) and acrylic acid (AA).[7,8] Here, chitosan was selected as a main polymer component because chitosan is prepared by deacetylation of chitin that is the main component of the exoskeletons of arthropods such as crustaceans, chitosan possesses amino groups as a reactive functional group, and chitosan solutions were more viscous than other polymer solutions.

Chemical treatments to enhance the adhesive strength of the polyolefin materials include corona discharge,[9] plasma treatment,[1] plasma polymerization,[10] grafting of hydrophilic monomers,[7,8] and grafting of a hydrophilic polymer segment.[11,12] Their surfaces are hydrophilically modified by the chemical treatments mentioned above. Of them, the photografting technique with a 400-W high pressure mercury lamp is the most potential procedure. An empirical reason is that the energy of the high pressure mercury lamp is considerably lower than the energy sources of other grafting techniques, and consequently the polymer materials can be modified at low grafted amounts without changing any bulk properties. Surface properties modified by a variety of grafting techniques are durably stable, whereas surface properties hydrophilically modified with non-polymerizable plasmas[13,14] or by UV irradiation[15] gradually regressed mainly because of the gradual overturn or migration

of oxygen-containing functional groups generated into the bulk inside.[16,17]

In addition, wettability for water is enhanced by these surface modification techniques and one of the important surface properties related with wettability is the adhesive strength. In particular, photografting of hydrophilic monomers is an effective procedure to modify the adhesive strength of polyolefin materials as mentioned above. We have reported that not only the adhesive strength is enhanced[7,8,18,19] but also the autohesive strength, or adhesive-free adhesion strength, is developed[19] by photografting hydrophilic monomers, such as MAA, AA, and methacrylamide (MAAm) onto the LDPE and HDPE plates. So far, insofar as the photografting technique, few articles have been reported on surface modification of PP plates compared with surface modification of the LDPE and HDPE plates mainly because of their higher crystallinity and stability.[20,21] Next, our focus was turned on the polymeric component in adhesives. As most of the main components of commercially available adhesives are insoluble or poorly soluble in water except for poly(vinyl alcohol), these components are dissolved in volatile organic solvents.

When chitosan solutions modified by tyrosinase in the presence of dopamine was applied to adhesion of LDPE and HDPE plates surface-modified by the photografting technique, substrate breaking was observed at higher grafted amounts.[22] The reaction mechanism of the high-viscosity, gel-like materials from chitosan solutions is tyrosinase-catalyzed quinone oxidation of dopamine and subsequent nonenzymatic quinone crosslinking between chitosan chains,[7] which has been schematically illustrated and explained in detail in Refs. 6, 23, and 24. In this case, quinone derivatives enzymatically generated react with either amino groups on chitosan chains or carboxy groups on grafted PMAA and PAA chains. These reactions are essential to the enhancement in the adhesive strength.[7]

In this study, enzymatically modified chitosan solutions were applied to adhesion of the PP plates photografted with hydrophilic monomers. The tensile shear adhesive strength of the grafted PP plates was measured as a function of the grafted amount to discuss the effects of the monomer concentration and temperature on the photografting and kind of functional groups on adhesion of the PP plates. In addition, the location of failure was determined through surface analysis of failed surfaces obtained by X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Materials

A PP plate of 1.0-mm thickness was used as a polymer substrate for photografting. The crystallinity for the PP plate used was determined by a flotation or buoyancy method with methanol and glycerol at 25°C.[18,22] The specific gravity of a mixture solution in which PP samples cut into about 1 mm pieces were floated was measured with a gravimeter. The crystallinity for the PP plate used was calculated to be 53.0% from the specific gravity value and the densities of the completely amorphous and pure crystalline parts of PP.[25] The PP plates were cut into 6.0-cm length and 2.4-cm width, washed with water, methanol, and acetone by turns, and then dried under reduced pressure.

Mushroom tyrosinase (EC. 1.14.18.1) of the specific activity of 2850 U/mg solid (determined by supplier) and dopamine were purchased from Sigma Chemical (St Louis, USA). Chitosan flake (chitosan 300) was purchased from Wako Pure Chemical (Tokyo, Japan). The viscosity-average molar mass was calculated from the intrinsic viscosity value determined in an aqueous acetic acid solution of 0.1*M* containing NaCl of 0.2*M* with an Ubbelohde viscometer at 25°C.[26,27] The constants K and a in the Mark–Houwink–Sakurada equation were 1.81×10^{-3} cm^3/g and 0.93, respectively. Average molar mass of the chitosan sample used was calculated to be 1.24×10^6 g/mol from the intrinsic viscosity of 893 cm^3/g.[28,29] The degree of deacetylation of the chitosan sample was determined by the colloid titration method. Diluted chitosan solutions were titrated with an aqueous solution of potassium poly(vinyl alcohol) sulfate at pH values of 3–4. The degree of deacetylation of the chitosan sample was determined to be 0.87 form the equivalent point of the colloid titration.[28,30] MAA, AA, MAAm, and 2-hydroxyethyl methacrylate (HEMA) were purchased from Wako Pure chemical and used as received without further purification.

Photografting

The solutions of MAA, AA, and MAAm were prepared with water at a monomer concentrations of 0.5–2.0*M*. As solubility of HEMA was relatively low in water, an aqueous methanol solution of 20 vol% was used as a solvent for photografting of HEMA. The PP plates were immersed in 50 cm^3 of an acetone solution containing 0.25 g of benzophenone (BP) as a sensitizer for 1 min and acetone was evaporated from their surfaces at room temperature to coat the PP surfaces with BP. Then, the BP-coated PP plates were immersed in each monomer solution in the Pyrex glass tubes and UV rays from a 400-W high-pressure mercury lamp were irradiated at 40–70°C. After photografting, the grafted PP plates were washed with water for 24 h to exclude unreacted monomers and formed homopolymers thoroughly, and then dried under reduced pressure. The grafted amount in μmol/cm^2 was calculated from the weight increase of the PP plates after photografting according to the following equation:

$$\text{Grafted amount } (\mu\text{mol/cm}^2) = \frac{(W_g - W_0)/M}{6.0 \times 2.4 \times 2} \cdot 10^6 \qquad (1)$$

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

Characterization of Grafted PP Plates

The photoelectron spectra for the grafted PP plates were recorded on a Shimadzu ESCA-3400 type spectrophotometer with the MgKα (1253.6 eV) source operating at 7 kV and 30 mA.[8] Then, the intensity ratios, O1s/C1s and N1s/C1s, were calculated from the O1s, C1s, and N1s peak areas measured at a take-off angle of 90° and the ionized cross-sections[19,32,33] to determine the surface chemical compositions of the grafted PP plates. The contact angles of water on the grafted PP plates were measured by a sessile drop method at 25°C with a Kyowa Kagaku TYP-QI-type goniometer.[22,31]

The amount of absorbed water for the grafted PP plates was measured to estimate the hydrophilic properties of the whole grafted layers. The grafted PP plates were immersed in distilled water at 25°C for 24 h. Then, the grafted PP plates were taken out of water, blotted with filter paper to remove water attached to their surfaces, and weighed as quickly as possible. The amount of absorbed water was calculated the according to the following equation:

$$\text{Amount of absorbed water (g/g-grafted plate)} = \frac{W_w - W_g}{W_g} \quad (2)$$

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

Enzymatic Modification of Chitosan Solutions and Adhesive Strength Measurements

Chitosan solutions of 1.6–2.0 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 to dissolve most of the chitosan flakes added, 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 30 m*M* on the basis of the weight concentration of the chitosan solutions and the degree of deacetylation of chitosan used. The optimum pH value of activity of tyrosinase ranges from 6.5–7.5, depending on the substrate used. However, as chitosan is insoluble at pH values above 6.0, the pH values of the chitosan solutions were adjusted to 5.8–6.0 by adding small amounts of 2*M* NaOH solution.[6]

The grafted PP plates were cut into 3.0-cm length and 1.2-cm width. The enzymatic reaction was initiated by adding 1.0 cm^3 of an aqueous tyrosinase solution to 100 cm^3 of a chitosan solution containing 10 m*M* of dopamine so as to make the tyrosinase concentration at 60 U/cm^3. Chitosan solutions were spread on both surfaces of two grafted PP plates 45 min after the enzymatic reaction was initiated, and then the surfaces were placed in contact with a 1.2 × 1.2 cm^2 overlapping surface area. The overlapped samples were tightly fixed with two binder clips and laid on an oven for 24 h at 25°C. The enzymatic reaction time was set at 45 min because at this enzymatic reaction time, the maximum tensile shear adhesive strength was obtained for MAA-grafted LDPE (LDPE-g-PMAA) plates with the grafted amount of 30 μmol/cm in our previous articles.[2,17]

The tensile shear adhesive strength was measured on an Orientec universal testing machine STA 1225. One end of each grafted PP plate samples was attached to the load cell 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 shear strength were calculated by dividing the force to separate the bonded PP samples by the overlapping surface area.[15–17]

Surface Analysis of Failed Surfaces by XPS

The C1s, O1s, and N1s core spectra of both failed surfaces were measured for PP-g-PAA plates with different adhesive strengths to discuss the relation of the adhesive strength with the location of adhesive failure. A chitosan film was prepared by the procedure described in our previous article as a reference sample for XPS analysis.[22,31,32] The chitosan film was incubated in an aqueous solution (10 m*M*) containing tyrosinase (60 U/cm^3) for 30 min. Then, the enzymatically modified chitosan film was washed with water and then dried under reduced pressure. Alternatively, enzymatically modified chitosan solution (enzymatic reaction time of 45 min) was spread on the surface of a PP-g-PAA plate with the grafted amount of 7.6 μmol/cm^2 prepared at the monomer concentration of 1.0*M* and the grafting temperature of 60°C, and then the PP-g-PAA plate was allowed to stand in air at 25°C to evaporate water. The C1s, O1s, and N1s core spectra of a chitosan film, a chitosan film incubated in a dopamine solution containing tyrosinase, chitosan-coated LDPE-g-PMAA plate as a reference, were recorded.[8]

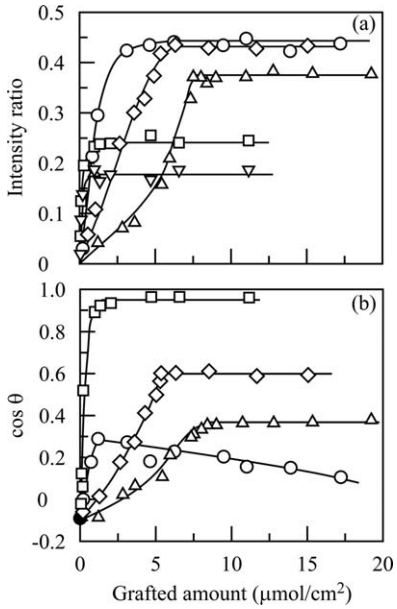

Figure 1. Changes in (a) the intensity ratios, O1s/C1s (○, △, □, ◇) and N1s/C1s (▽), and (b) cos θ values with the grafted amount for PP-g-PAA (○), PP-g-PMAA (△), PP-g-PMAAm (□, ▽), and PP-g-PHEMA (◇) plates prepared at 1.0*M* and 60°C.

Reactivity of Quinone with Grafted Polymer Chains

Grafted PP plates (1.0 × 1.0 cm^2) were incubated in an aqueous dopamine solution (10 m*M*) containing tyrosinase at 60 U/cm^3. After incubation for 30 min, the grafted PP plates were thoroughly washed with water, and dried under reduced pressure. The C1s, O1s, and N1s core level spectra were recorded in the same manner described above.[8] Then, the intensity ratios, O1s/C1s and N1s/C1s, were calculated from the O1s, C1s, and N1s peak areas and the ionized cross-sections.[22,31,32]

RESULTS AND DISCUSSION

Surface Composition and Wettability of the Grafted Surfaces

MAA, AA, MAAm, and HEMA were photografted on the PP plate at 1.0*M* and 60°C. The grafted amount increased over the irradiation time and leveled off at further increased irradiation times irrespective of the kind of monomers because of the gelation of the medium by the formation of large amounts of homopolymers. Figure 1 shows the change in the intensity ratios and cos θ value with the grafted amount for the grafted

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PP plates prepared at 1.0*M* and 60°C. The intensity ratios and cos θ value increased with the grafted amount and the cos θ value became constant at the grafted amounts at which the intensity ratios became constant for the grafted PP plates except for the PP-g-PAA plate. This indicates that when the PP surfaces were fully covered with grafted polymer chains, wettability became constant. On the other hand, the cos θ value for PP-g-PAA plate passed through the maximum and gradually decreased against the grafted amount, although the PP surface were fully covered with grafted PAA chains. It could be one of the reasons that grafted PAA chains are aggregated through hydrogen bonding between carboxy groups. A factor of the aggregation of grafted PAA chains is considered to be the absence of α-methyl groups from the above experimental results. A decrease in the cos θ value at higher grafted amounts was also observed for LDPE-g-PAA and HDPE-g-PAA plates and both for LDPE and HDPE plates photografted with other hydrophilic monomers.[7,22,31] It is a characteristic behavior for the AA-grafted polyolefin plates prepared by the photografting technique.

The grafted amounts at which the constant intensity and cos θ value became constant and the constant intensity ratios were summarized in Table I. The outer surface compositions of the grafted layers formed were estimated by dividing the constant intensity ratios obtained from Figure 1 by the intensity ratios of the corresponding homopolymers prepared.[18,22] The constant intensity ratios of the PP-g-PMAA and PP-g-PAA plates obtained from Figure 1 were lower than the intensity ratios of the corresponding homopolymers (0.389 for PMAA and 0.518 for PAA), indicating that even if the PP surface was fully covered with grafted polymer chains, a small amount of PP chains were present at the surfaces of the grafted layers formed. In other words, a small amount of PP chains were mixed with grafted polymer chains in the grafted layers. The PP surface was covered at a lower grafted amount with grafted PAA chains than with grafted PMAA chains. A little increase in hydrophobicity because of the presence of an α-methyl group will lead to a progress of photografting of methacrylic monomers into the inside of the PP substrate.

When hydrophilic monomers such as methacrylic and acrylic monomers were photografted to a PE film of 30-μm thickness, the PE grafted with methacrylic monomers were more expanded than PE grafted with acrylic monomers.[33] This result supports the consideration above mentioned.

Table I. Water Wettability and Surface Composition of the Grafted PP Plates Prepared at 1.0*M* and 60°C

Sample	Grafted amount[a] (μmol/cm^2)	Constant intensity ratio		cos θ
		O1s/C1s	N1s/C1s	
PP-g-PAA	3	0.43		0.3 (max)
PP-g-PMAA	7.5	0.37		0.35
PP-g-PMAAm	1	0.24	0.18	0.93
PP-g-PHEMA	6	0.42		0.6

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

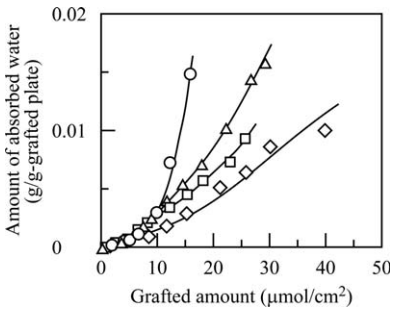

Figure 2. Changes in the amount of absorbed water with the grafted amount for PP-g-PAA (○), PP-g-PMAA (△), PP-g-PMAAm (□), and PP-g-PHEMA (◇) plates prepared at 1.0*M* and 60°C.

Water-Absorptivity of Grafted Layers

The amount of absorbed water of the grafted PP plates prepared at 1.0*M* and 60°C was measured to estimate hydrophilicity of the whole grafted layers. Figure 2 shows the changes in the amount of absorbed water with the grafted amount. The amount of absorbed water increased over the grafted amount and the PP-g-PAA plates had higher water absorptivity than the other grafted PP plates prepared in this study, although the cos θ value decreased at higher grafted amounts. Hydrogen bonding between carboxy groups on grafted PAA chains is considered to be gradually broken during immersion in water, although the time course of the amount of absorbed water was not measured in this study. The results obtained from Figure 2 will be attributed to more restriction of photografting of AA to the outer surface region of the PP substrate and higher composition of grafted PAA chains in the grafted layer.

Adhesive Strength and Quinone Reactivity

Grafted PP plates with different grafted amounts were bonded with enzymatically modified chitosan solutions. The reaction of enzymatically generated quinone derivatives with chitosan was shown in Ref. 24. Figure 3 shows the changes in the adhesive strength with the grafted amount for the grafted PP plates prepared at 1.0*M* and 60°C. The adhesive strength of PP-g-PMAA plates increased with the grafted amount, and then remained

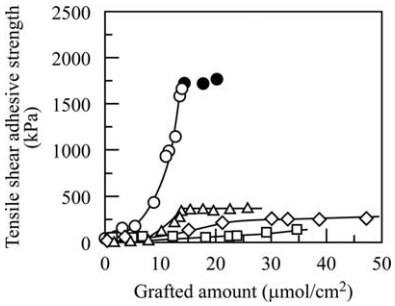

Figure 3. Changes in the adhesive strength with the grafted amount for PP-g-PAA (○), PP-g-PMAA (△), PP-g-PMAAm (□), and PP-g-PHEMA (◇) plates prepared at 1.0*M* and 60°C. Failure: open, cohesive failure; shaded, substrate-breaking.

Table II. Adhesion of PP-g-PAA 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	20	Substrate breaking
Chitosan solution containing dopamine and tyrosinase	45	Ungrafted	43
Chitosan solution containing dopamine	0	20	992
Chitosan solution containing tyrosinase	0	20	1005
Chitosan solution containing tyrosinase	45	20	1048
Chitosan solution	0	20	848
Chitosan solution	0	Ungrafted	38
Mixture of dopamine and tyrosinase	45	20	350
Mixture of dopamine and tyrosinase	0	20	369

PP-g-PAA plates were prepared at 1.0*M* and 60°C. Concentration of each component: amino group concentration = 30 m*M*, dopamine = 10 m*M*, tyrosinase = 60 U/cm^3.

almost constant at more than 15 μmol/cm^2. On the other hand, the adhesive strength of PP-g-PAA plates sharply increased at low grafted amounts and substrate breaking was observed at higher grafted amounts. However, for MAAm-grafted PP (PP-g-PMAAm) and HEMA-grafted PP (PP-g-PHEMA) plates, a predominant increase in the adhesive strength was not observed, although they possessed a high water-absorptivity and wettability. The grafted PP plates were immersed in a dopamine solution (10 m*M*) containing tyrosinase (60 U/cm^3). An N1s peak emerged after incubation for PP-g-PMAA and PP-g-PAA plates. Appearance of the N1s peak indicates that an enzymatically generated quinone derivative reacted with a carboxy group of grafted PMAA or PAA chains.[7,8] The reaction of enzymatically generated quinones with grafted PMAA or PAA chains was shown in Ref. 7. On the other hand, the N1s/C1s value remained almost unchanged after incubation for PP-g-PMAAm plates. In addition, no additional N1s peak was also observed after incubation for PP-g-PHEMA plates. These results indicate that a quinone derivative reacts with a carboxy group and did not do with an amino or an alcoholic hydroxy group.[7] The reaction of quinone derivatives enzymatically generated with grafted polymer chains is involved in an increase in the adhesive strength in addition to an increase in wettability and water-absorptivity. The N1s/C1s value increased with the grafted amount in the range of the grafted amounts below 5 and 2 μmol/cm^2 for PP-g-PMAA and PP-g-PAA plates, respectively. In addition, availability of enzymatically modified chitosan solutions as a water-soluble adhesive was estimated from the adhesive strength of PP-g-PAA plates at the grafted amount of 20 μmol/cm^2 with different reference solutions. As show in Table II, the adhesive strength of 850–1050 kPa was obtained for chitosan solutions containing dopamine or tyrosinase. These values were much lower than the adhesive strength obtained by enzymatically modified chitosan solutions. The adhesive strength for a mixture of dopamine and tyrosinase was as low as 350–369 kPa. Low adhesive strength obtained for these reference solutions will open up the possibility of chitosan materials modified by enzymatic reaction toward the practical application as an adhesive.

Determination of Failed Location by XPS

The location of failure for PP-g-PAA plates after adhesive strength measurements was estimated from detailed assignment of peaks in the C1s and N1s spectra of the reference samples shown in reference 8. The C1s and N1s spectra of a PP-g-PAA plate coated with enzymatically modified chitosan solution were almost the same as those of a LDPE-g-PMAA plate coated with enzymatically modified chitosan solution. Figure 4 shows the C1s, O1s, and N1s spectra of the failed surfaces of PP-g-PAA plates with different adhesive strengths prepared at 1.0*M* and 60°C. The failed surface at which higher O1s/C1s and N1s/C1s values were obtained was denoted as the surface A. For a PP-g-PAA plate with the adhesive strength of 156 kPa (grafted amount = 3.11 μmol/cm^2), an overlapped C1s peak at 287–288 eV and an N1s peak were observed on the both failed surfaces. Appearance of these peaks indicates that failure occurred in the layer formed by mixture of grafted PAA chains with components of enzymatically modified chitosan solutions, as the PP plate was not fully covered with grafted PAA chains at this grafted amount. An overlapped C1s peak at 287–288 eV and an N1s peak were also observed for a PP-g-PAA plate (grafted amount = 11.0 μmol/cm^2) with 932 kPa, although the intensity of these peaks became weaker than that of the PP-g-PAA plate with 156 kPa. In addition, the relative intensity [C1s(-COOH)/$\sum$C1s], which represented the ratio of the area of the C1s peak at 289 eV corresponding to a carbon atom in a carboxy group to the area of the whole C1s peak, was 0.122 for a PP-g-PAA plate with 2.9 μmol/cm^2. This value was a little higher than the relative intensities (0.114 and 0.106) of the both failed surfaces. A similar result was also obtained from the failed surfaces of a PP-g-PAA plate (grafted amount = 13.9 μmol/cm^2) with 1663 kPa. The N1s/C1s values obtained from both failed surfaces were lower than the N1s/C1s value of 0.106 for the PP-g-PAA plate coated with enzymatically modified chitosan solution irrespective of the grafted amount. This indicates that failure occurred in the parts containing components of enzymatically modified chitosan solutions in the grafted layers with a shift from the contact surface to the inside of the grafted layer for

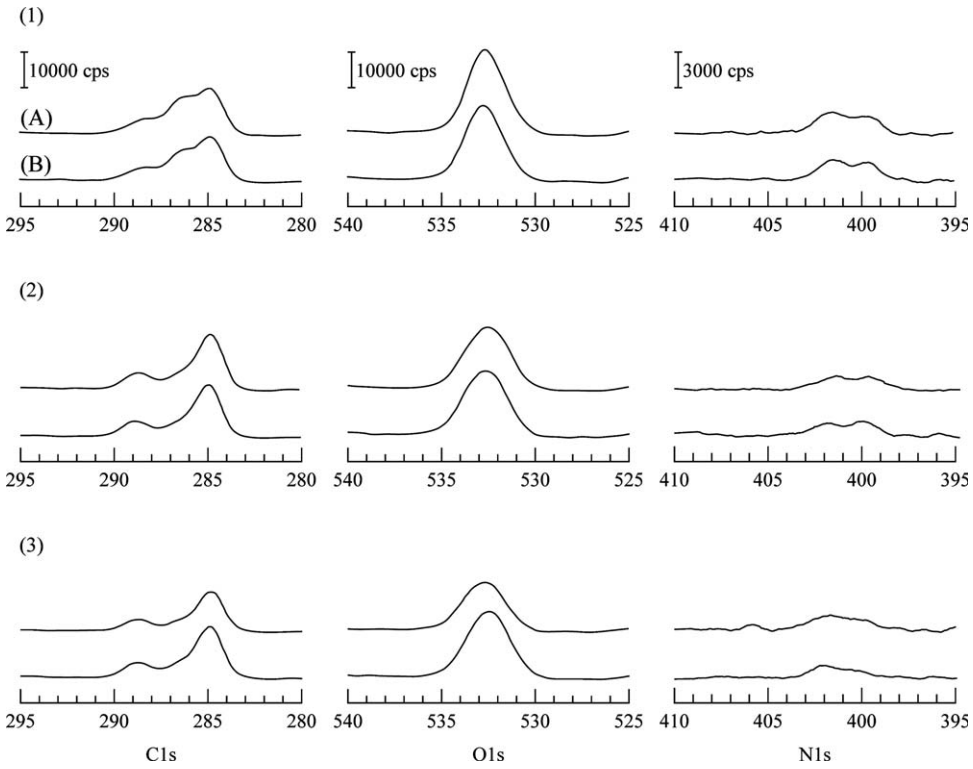

Figure 4. C1s, O1s, and N1s core spectra of the failed surfaces after adhesive strength measurements for PP-g-PAA plates with different adhesive strengths. The PP-g-PAA plates were prepared at 1.0*M* and 60°C. Grafted amount (μmol/cm^2) and adhesive strength (kPa): (a) 3.11 and 156, (b) 11.0 and 932, and (c) 13.9 and 1663.

the PP-g-PAA plates prepared at 1.0*M* and 60°C, as the PP surfaces were fully covered with grafted PAA chains at the grafted amounts higher than 3 μmol/cm^2.

Effect of Monomer Concentration for PP-g-PAA Plates

As substrate breaking was observed for PP-g-PAA plates prepared at 1.0*M* and 60°C, the effects of monomer concentration and temperature on the photografting on the adhesive strength were investigated. The amount of grafted AA increased at shorter irradiation time, as the monomer concentrations increased. However, coverage of the PP surfaces with grafted PAA chains was independent of the monomer concentration on the photografting.[18,22] In addition, wettability toward water for PP-g-PAA plates passed through the maximum value, and then gradually decreased against the grafted amount irrespective of the monomer concentration. Behavior of surface coverage with grafted PAA chains and wettability for PP-g-PAA plates prepared at 1.5 and 2.0*M* was almost the same as the ones prepared at 1.0*M*.[18,22] However, the grafted amount enough to cover the PP surface was not obtained for the PP-g-PAA plates prepared at 0.5*M*. Figure 5 shows the changes in water-absorptivity and adhesive strength with the grafted amount for PP-g-PAA plates prepared at 0.5–2.0*M*. Water-absorptivity for PP-g-PAA plates prepared at lower monomer concentrations sharply increased at lower grafted amounts. Surface analysis by XPS showed that progress of photografting of hydrophilic monomers in the inside of the PP plate was independent of monomer concentration as is the case with photografting onto the LDPE and HDPE plates.[22] Therefore, the dependence of the monomer concentration on water-absorptivity is considered to be attributed to the number and length of grafted polymer chains formed on the surface. From the viewpoint of the kinetics of

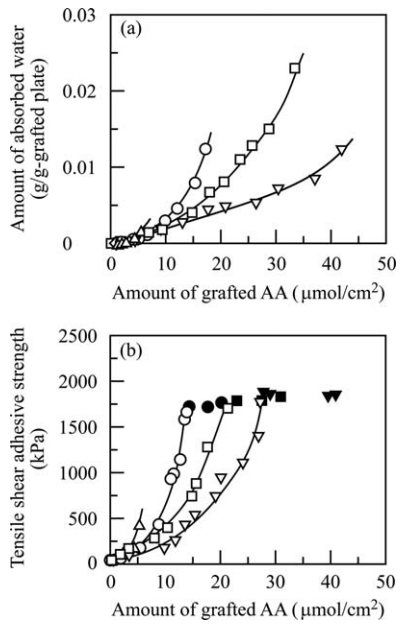

Figure 5. Changes in (a) the amount of absorbed water and (b) adhesive strength with the grafted amount for PP-g-PAA plates prepared in monomer solutions of different concentrations at 60°C. Monomer concentration: 0.5 (△), 1.0 (○), 1.5 (□), and 2.0 (▽)*M*. Failure: open, cohesive failure; shaded, substrate-breaking.

radical polymerization, longer grafted polymer chains are formed at higher monomer concentrations because of the higher rates of chain propagation.[8] In other words, formation of shorter grafted polymer chains is of advantage for an increase in water-absorptivity of the grafted layers. In addition, the adhesive strength of the PP-g-PAA plates prepared at lower monomer concentrations also sharply increased at lower grafted amounts and the grafted amount at substrate breaking decreased. These results indicate that the grafted layers formed at lower monomer concentrations are susceptible to penetration of enzymatically generated chitosan solutions. This behavior will facilitate the reaction of quinone derivatives enzymatically generated with grafted PAA chains. The location of failure for PP-g-PAA plates prepared at 1.5 and 2.0*M* was also estimated by XPS analysis (not shown). An overlapped C1s peak at 287–288 eV and an N1s peak were also observed for the failed surfaces of these PP-g-PAA plates and the intensity of these peaks decreased with an increase in the grafted amount, or adhesive strength. This indicates that failure occurred in the parts highly containing components of enzymatically modified chitosan solutions and the location of failure was shifted into the inside of the grafted layer.

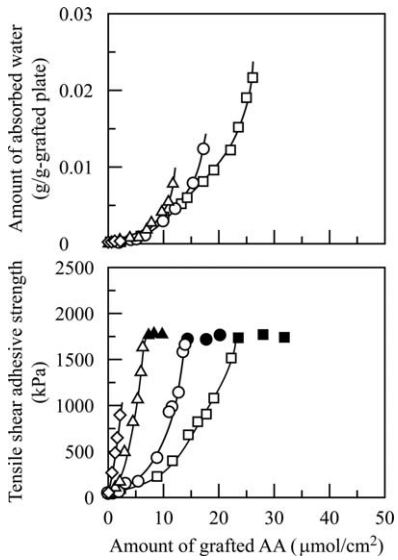

Figure 6. Changes in (a) the amount of absorbed water and (b) adhesive strength with the grafted amount for PP-g-PAA plates prepared in 1.0*M* monomer solutions at different temperatures. Temperature (°C): 40 (◇), 50 (△), 60 (○), and 70 (□). Failure: open, cohesive failure; shaded, substrate-breaking.

Effect of Temperature for PP-g-PAA Plates

Surface composition for PP-g-PAA plates prepared at 40–70°C was summarized in Table III. As the temperature on photografting was increased, the O1s/C1s value became constant at higher grafted amounts and the constant intensity ratio was a little increased. However, the cos θ value went through the maximum, and then gradually decreased against the grafted amount irrespective of the grafting temperature. The location of the photografting was restricted to the outer surface region of the PP plate and the grafted layer rich in grafted PAA chains was formed at lower temperatures. In addition, the absence of an α-methyl group in the monomer structure is a main factor to restrict the location of the photografting to the outer surface region. The results above-mentioned indicate that the density of grafted PAA chains in the outer surface region of the grafted layer is independent of the monomer concentration and dependent on the grafting temperature. Figure 6 shows the changes in the water-absorptivity and adhesive strength for PP-g-PAA plates prepared at different temperatures. As the temperature decreased, the water-absorptivity sharply increased at lower grafted amounts. This tendency can be explained according to the experimental results and the kinetics of radical polymerization. Shorter grafted PAA chains are formed at higher temperatures mainly because of higher chain transfer reaction. However, as the photografting of AA more progresses into the interior of the PP plate at higher temperatures, the grafted layers more rich in grafted PAA chains are formed at lower temperatures. This is a main reason for higher water-absorptivity for PP-g-PAA plates prepared at lower temperatures.

Table III. The Constant Intensity Ratios and Surface Composition of the PP-g-PAA Plates Prepared in Monomer Solutions of 1.0*M* at Different Temperatures

Temperature (°C)	Grafted amount[a] (μmol/cm^2)	O1s/C1s	Composition (%)
40	1.5	0.51	98.5
50	2	0.5	96.5
60	3	0.43	83
70	5	0.4	77.2

[a] The grafted amounts at which theO1s/C1s values become constant.

The adhesive strength of PP-g-PAA plates prepared at lower temperatures sharply increased at lower grafted amounts. For PP-g-PAA plates prepared at 50–70°C, substrate breaking was observed, and the grafted amount at substrate breaking occurred decreased from 23 μmol/cm^2 at 70°C to 6 μmol/cm^2 at 50°C, as the grafting temperature increased. This behavior was also caused by the fact that the location of photografting was restricted to the outer surface region of the PP plate at lower temperatures as mentioned above. In addition, the failed surfaces obtained for PP-g-PAA plates prepared at 50°C and 70°C are also analyzed by XPS. Although the results obtained by the XPS measurements were not shown here, a peak at 286–287 eV and N1s peak were observed on both failed surfaces, and the intensity of their peaks gradually decreased as the grafted amount, or adhesive strength, increased. It was found from surface analysis by XPS that failure occurred in the parts containing components of enzymatically modified chitosan solutions and the location of failure was shifted into the inside of the grafted layer irrespective of the conditions of preparation of the PP-g-PAA plates such as the monomer concentration and temperature.

CONCLUSIONS

We drew the following conclusions from the above experimental results. Wettability of the grafted PP plates except for the PP-g-

PAA plates increased with the grafted amounts, and then became constant when the PP surfaces were fully covered with grafted polymer chains. Water-absorptivity of the grafted PP plates increased over the grafted amount irrespective of the grafting conditions such as the monomer concentration and temperature. In addition, water-absorptivity sharply increased at lower grafted amounts because of the formation of shorter grafted polymer chains for the grafted PP plates prepared at lower monomer concentrations and because of the restriction of the location of grafting to the outer surface region for the grafted PP plates prepared at lower temperatures. For the PP-g-PAA plates, the adhesive strength sharply increased and substrate breaking was observed at lower grafted amounts, as the monomer concentration or temperature on photografting was lower. Such behavior was caused by the formation of shorter grafted polymer chains and restriction of the location of grafting. The facts that the PP surface was fully covered with grafted polymer chains and that grafted layers with higher water absorptivity were formed play an important role in an increase in adhesive strength. In addition, XPS analysis showed that the increase in the adhesive strength was attributed to the penetration of enzymatically modified chitosan solutions into the grafted layers and the reaction of generated quinone derivatives with grafted polymer chains. Subsequently, failure occurred in the layers mixed with enzymatically modified chitosan and grafted polymer chains at a low adhesive strength. For PP-g-PAA plates with higher adhesive strength, the location of failure shifted to the grafted layers containing components of enzymatically modified chitosan solutions. Consequentlly, in this study, we determined the usability of enzymatically modified chitosan solutions for an adhesive to adhere the PP plate.

REFERENCES

1. Gomathi, N.; Neogi, S. *Appl. Surf. Sci.* **2009**, *17*, 7590.
2. Li, Z.; Zhang, W.; Wang, X.; Mai, Y.; Zhang, Y. *Appl. Surf. Sci.* **2011**, *17*, 7600.
3. Ren, J.; Hua, X.; Zhang, T.; Zhang, Z.; Ji, Z.; Gu, N. *J. Appl. Polym. Sci. B* **2011**, *121*, 210.
4. Suresh, B, Maruthamuthu, S.; Kannan, M.; Chandramohan, A. *Polym. J.* **2011**, *43*, 398.
5. Tretinnikov, O. N.; Pilipenko, V. V.; Firsov, S. P. *Polym. Sci.* **2011**, *53*, 171.
6. Yamada, K.; Chen, T.; Kumar, G.; Vesnovsky, O.; Topoleski, L. D.; Payne, G. F. *Biomacromolecules* **2000**, *1*, 252.
7. Noto, K.; Matsumoto, S.; Takahashi, Y.; Hirata, M.; Yamada, K. *J. Appl. Polym. Sci.* **2009**, *113*, 3963.
8. Yamagami, S.; Kanama, W.; Yamada, K. *J. Appl. Polym. Sci.* **2011**, *121*, 939.
9. Carrado, A.; Sokolova, O.; Donnio, B.; Palkowski, H. *J. Appl. Polym. Sci.* **2011**, *120*, 3709.
10. Wickson, B. M.; Brash, J. L. *Colloid Surf. A* **1999**, *156*, 201.
11. Balcı, M.; Allı, A.; Hazer, N.; Güven, O.; Cavicchi, K.; Cakmak, M. *Polym. Bull.* **2010**, *64*, 691.
12. Kalaycı, Ö. A.; Cömert, F. B.; Hazer, B.; Atalay, T.; Cavicchi, K. A.; Cakmak, M. *Polym. Bull.* **2010**, *65*, 215.
13. Garcia, D.; Fenollar, O.; Lopez, R.; Sanchis, R.; Balart, R. *J. Appl. Polym. Sci.* **2008**, *110*, 1201.
14. Teodoru, S.; Kusano, Y.; Rozlosnik, N.; Michelsen, P. K. *Plasma Process. Polym.* **2009**, *6*, S375.
15. Costamagna, V.; Wunderlin, D.; Larrañaga, M.; Mondragon, I.; Strumia, M. *J. Appl. Polym. Sci.* **2006**, *102*, 2254.
16. Morra, M.; Occhiello, E.; Garbassi, F. *Surf. Interface Anal.* **1990**, *16*, 412.
17. Morra, M.; Occhiello, E.; Marola, R.; Gargasi, F.; Humphrey, P.; Johnson, D. *J. Colloid Interface Sci.* **1990**, *137*, 11.
18. Yamada, K.; Kimura, J.; Hirata, M. *J. Appl. Polym. Sci.* **2003**, *87*, 2244.
19. Yamada, K.; Takeda, S.; Hirata, M. *J. Appl. Polym. Sci.* **2007**, *103*, 493.
20. Xing, C. M.; Deng, J. P.; Yang, W. T. *Macromol. Chem. Phys.* **2005**, *206*, 1106.
21. Balart, J.; Fombuena, V.; Espana, J. M.; Sanchez-Nacher, L.; Balart, R. *Mater. Des.* **2012**, *33*, 1.
22. Yamada, K.; Yamagami, S.; Naohara, Y. *J. Appl. Polym. Sci.* **2012**, *125*, 2614.
23. Yamada, K.; Aoki, T.; Ikeda, N.; Hirata, M.; Hata, Y.; Higashida, K.; Nanamura, Y. *J. Appl. Polym. Sci.* **2008**, *107*, 2723.
24. Kumar, G.; Bristow, J. F.; Smith, P. J.; Payne, G. F. *Polymer* **2000**, *41*. 2157.
25. Mark, H. F.; Bikales, N.; Overberger, C. G.; Menges, G., Eds. Encyclopedia of Polymer Science and Engineering; Wiley: New York, **1986**; Vol. *4*, p 482.
26. Painter, P. C.; Coleman, M. M. In Fundamentals of Polymer Science; Painter, P. C., Coleman, M. M., Eds.; Technomic Publishing: Lancaster, **1997**; Chapter10.
27. Maghami, G. G.; Roberts, G. A. F. *Macromol. Chem. Macromol. Chem. Phys.* **1988**, *189*, 195.
28. Yamada, K.; Aoki, T.; Ikeda, N.; Hirata, M. *J. Appl. Polym. Sci.* **2007**, *104*, 1818.
29. Yamada, K.; Aoki, T.; Ikeda, N.; Hirata, M.; Hata, Y.; Higashida, K.; Nanamura, Y. *J. Appl. Polym. Sci.* **2008**, *107*, 2723.
30. Kokufuta, E. *Macromolecules* **1979**, *12*, 350.
31. Yamada, K.; Tsutaya, H.; Tatekawa, S.; Hirata, M. *J. Appl. Polym. Sci.* **1992**, *46*, 1065.
32. de Lange, P. J.; Gebben, B.; Elfink, P. J.; *Surf. Interface Anal.* **1994**, 22,*502*.
33. Yamada, K.; Tatekawa, S.; Hirata, M. *J. Colloid Interface Sci*, **1994**, *162*, 144.