

Improvement in Adhesive-Free Adhesion by the Use of Electrostatic Interactions between Polymer Chains Grafted onto Polyethylene Plates

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ABSTRACT: The tensile shear adhesive-free adhesion properties induced by electrostatic interactions between poly(acrylic acid) (PAA) and poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) chains grafted onto polyethylene (PE) with low-density (LDPE) or high-density (HDPE) plates were studied. PAA- or PDMAEMA-grafted PE plates were immersed in a HCl or NaOH solution or water for 24 h, and their electrostatic properties were changed before they were overlapped with each other and heat-pressed. The breaking of the substrate between the two plates with water-swollen grafted layers was observed in the low range of grafted amounts in comparison with immersion in the acidic and basic solutions. The ability of the two plates with grafted polymer chains swollen in water to strongly bond with each other was a result of electrostatic interactions formed by positively charged PDMAEMA and negatively

charged PAA chains. The breaking of the substrate in the case of adhesive-free adhesion between quaternized PDMAEMA-grafted and PAA-grafted PE plates immersed in the basic solution occurred with lower grafted amounts of PAA. This came from the strong attractive force between dissociated anionic PAA chains and quaternized cationic PDMAEMA chains in the basic solution. In addition, the adhesive-free adhesion strength of HDPE plates with the same grafted polymer chains encountered the breaking of the substrate with lower grafted amounts than that of LDPE plates. It was concluded that the grafting of polymer chains onto HDPE plates with high crystallinity was considerably restricted to the outer surface regions. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2632–2638, 2006

Key words: adhesion; polyethylene; photopolymerization

INTRODUCTION

Polyethylene (PE) materials have been used in a whole range of fields because of their excellent properties, such as toughness, durability, density, permittivity, and solvent resistance. Although the water repellency of PE surfaces, which comes from the hydrophobic properties of PE, is one of their excellent properties, poor wettability has considerably restricted their applications to coating and adhesive fields. Recently, a number of techniques have been devoted to the surface modification of PE materials for wettability and adhesion improvement. Many researchers have reported the surface modification of PE substrates through plasma treatment, glow discharge, corona discharge, UV irradiation, and so forth.^{1–4}

We have for more than 10 years attempted to modify hydrophobic surfaces of PE, polypropylene, and poly(tetrafluoroethylene) without changing their bulk properties by means of photografting hydrophilic

monomers and to extend their possibilities to other new fields.^{5–7}

The tensile shear adhesive strength between two grafted polymer substrates has been remarkably enhanced even with low grafted amounts, and in addition, autoadhesion or adhesive-free adhesion properties were observed in a considerably high range of grafted amounts.

The adhesive-free adhesion between hydrophilic monomers and photografted PE substrates is considered to be a mechanism based on entanglements formed via thermal motion of grafted polymer chains. For grafted polymer chains to entangle with one another across the interface between grafted layers of two plates, the grafted amounts have to be allowed to increase to some extent. Although adhesive-free adhesion may extend new applications in the field of adhesives, it is preferable that such adhesive behavior appear for a lower range of grafted amounts.

This work was aimed at achieving adhesive-free adhesion caused by electrostatic interactions between two polymer-grafted PEs with different charges against each other in a range of lower grafted amounts.

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TABLE I
Physical Properties of the Polymer Substrates

Substrate	Density (g/cm ³)	Degree of crystallization (%)	Ultimate tensile strength (N/cm ²)
LDPE	0.917	45.2	107
HDPE	0.946	62.7	312

EXPERIMENTAL

Materials

The densities of the low-density polyethylene (LDPE) and high-density polyethylene (HDPE) plates used as polymer substrates in this study were determined with a specific gravimeter, and their crystallinities were calculated from the specific densities of the crystalline and amorphous parts.^{8,9} These results are summarized in Table I, including the ultimate strength of the polymer substrates, that is, their substrate breaking, obtained from the tensile strength measurements.

PE plates, 60 mm long, 30 mm wide, and 1.0 mm thick, were washed with water, methanol, and acetone in that order and then dried under reduced pressure before each photografting. The monomers acrylic acid (AA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA), used for photografting, were purified by distillation under reduced pressure.¹⁰

Photografting

The LDPE and HDPE plates were immersed in 50 cm³ of an acetone solution containing 0.25 g of benzophenone (BP) as a sensitizer for 1 min. The photografting on the BP-coated PE plates in Pyrex tubes containing the respective monomer solutions fixed at 1.0 mol/cm³ was carried out at 60°C by the application of UV rays emitted from a 400-W high-pressure mercury lamp. The pH value of the DMAEMA aqueous solution before the photografting was adjusted to 8.0 with HCl to increase the solubility of the poly[2-(dimethylamino) ethyl methacrylate] (PDMAEMA) homopolymers formed in the medium at 60°C because the PDMAEMA homopolymers were water-insoluble on account of the hydrophobic interaction between the dimethylamino groups affixed to the DMAEMA monomers. However, the AA aqueous solution was not pH-adjusted because the poly(acrylic acid) (PAA) homopolymers that formed during the photografting were kept water-soluble.

After the photografting, the grafted PE plates were washed with water and methanol to remove unreacted monomers and homopolymers from the grafted layers of the PE surfaces and were held *in vacuo* at room temperature for 24 h. The grafted amount ($\mu\text{mol}/\text{cm}^2$) was calculated from the weight increase in the PE substrates:

$$\text{Grafted amount } (\mu\text{mol}/\text{cm}^2) = \frac{(M_g - M_0) \times 10^6}{AM} \quad (1)$$

where M_g is the mass of the grafted PE substrate, M_0 is the mass of the PE substrate before photografting, A is the surface area of the PE plate, and M is the molar mass of the monomer.¹¹

Surface compositions and hydrophilic properties

The chemical compositions of the PE surfaces with different grafted amounts prepared by UV irradiation were analyzed by means of electron spectroscopy for chemical analysis (ESCA). The photoelectron spectra for the grafted layers were recorded on a Shimadzu ESCA-3400 type spectrometer (Tokyo, Japan) with a Mg K α (1253.6 eV) source operating at 8 kV and 20 mA under a vacuum of at least 5×10^{-5} Pa. The measured binding energies were adjusted to C1s = 285.0 eV or Au4f_{7/2} = 83.8 eV.^{12,13} The ratio of the two intensities, i and j , measured under identical conditions (i.e., the intensity ratio) is given by

$$\frac{n_i}{n_j} = \frac{I_i/\sigma_i}{I_j/\sigma_j} \quad (2)$$

where n is the atomic density, I is the peak intensity, and σ is the photoionization cross section. The values of the photoionization cross section for C1s, O1s, and N1s are 1.00, 1.77, and 2.85, respectively.

The amount of absorbed water, used to investigate the water absorptivity as one of the hydrophilic properties of the grafted layers, was calculated from the weight increase in the grafted PE plates immersed in water for 24 h at 25°C.

Tensile shear adhesive-free adhesion strength measurements

The PAA chains formed on the PE plates were weak anionic electrolytes in aqueous solutions, whereas the PDMAEMA chains were weakly cationic. To investigate the tensile adhesive-free adhesion strength due to the difference in the degree of dissociation between swollen grafted PAA and PDMAEMA chains, individual grafted plates were immersed in HCl or NaOH solutions or water for 24 h before being overlapped with one another and heat-pressed. In an attempt to impart strong cationic electrolytic properties to PDMAEMA chains, dimethylamino groups of the repeat units were quaternized by the immersion of the PDMAEMA-grafted PE plates in a solution containing dimethyl sulfate, ethanol, and NaOH at 60°C.¹⁴

The grafted PE plates were cut (25 mm long and 10 mm wide) and then immersed in water at 25°C for

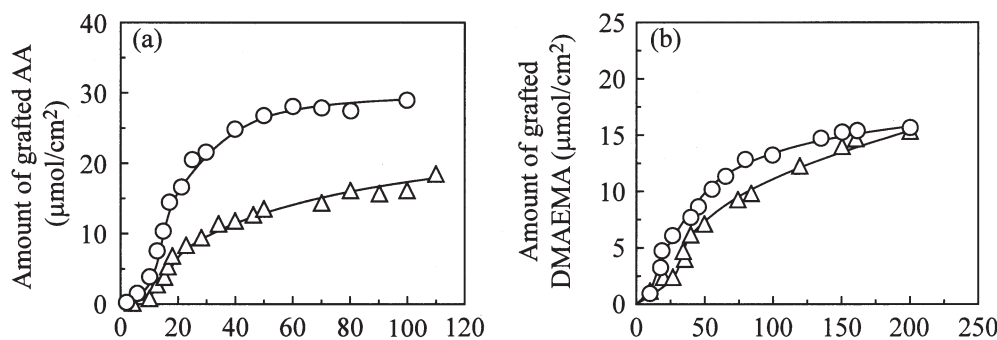


Figure 1 Changes in the grafted amount with the UV irradiation time for (a) the photografting of AA and (b) the photografting of DMAEMA onto (O) LDPE and (Δ) HDPE plates.

24 h, and the two plates were put together with their surfaces facing each other with a 10×10 mm overlap. The overlapped samples were subjected to a load of $2.0 \text{ kg}/\text{cm}^2$ at 80°C , and their tensile shear strength with no adhesives was measured at a shear rate of $3.0 \text{ mm}/\text{s}$.¹⁵

RESULTS AND DISCUSSION

Photografting

The changes in the amounts of the AA and DMAEMA monomers photografted onto the LDPE and HDPE plates are shown in Figure 1(a,b). The grafted amounts increased with an increase in the UV irradiation time but leveled off with a longer irradiation time because AA and DMAEMA were consumed during the formation of their homopolymers in the medium. These monomers grafted onto the HDPE plates less than the LDPE plates with the same irradiation time. This resulted from the tendency for the grafting of these monomers onto HDPE with high crystallinity to be restricted to the outer surface regions, whereas the grafting onto LDPE with less crystalline or larger

amorphous parts could progress from the surface to the bulk inside.

Surface compositions and hydrophilic properties

The degrees of coverage of the PE surfaces with grafted PAA or PDMAEMA polymer chains were followed on the basis of the O1s/C1s or N1s/C1s intensity ratio obtained from ESCA, as shown in Figure 2. An increase in the grafted amount was accompanied by an increase in the O1s/C1s and N1s/C1s intensity ratios, which then leveled off at higher grafted amounts. The increase in the intensity ratios indicated increasing coverage of the PE surfaces with the grafted polymers. Constant intensity ratios mean that the chemical compositions of the outer surface regions of the grafted layers remained unchanged, regardless of the formation of thicker grafted layers.

Figure 3 shows an increase in the amount of water absorbed by poly(acrylic acid)-grafted low-density polyethylene (LDPE-*g*-PAA) and poly[2-(dimethylamino)ethyl methacrylate]-grafted low-density polyethylene (LDPE-*g*-PDMAEMA) plates with the grafted amount. There appeared to be a significant difference

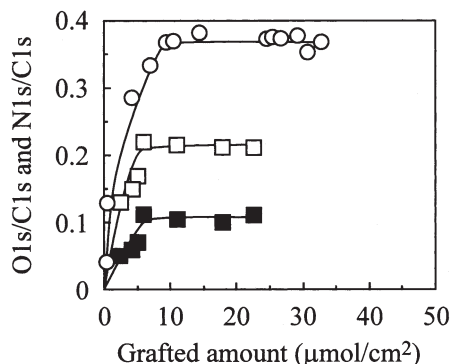


Figure 2 Changes in the (O, \square) O1s/C1s and (\blacksquare) N1s/C1s intensity ratios with the amount of the grafted monomer for the grafted LDPE plates: (O) AA and (\square , \blacksquare) DMAEMA.

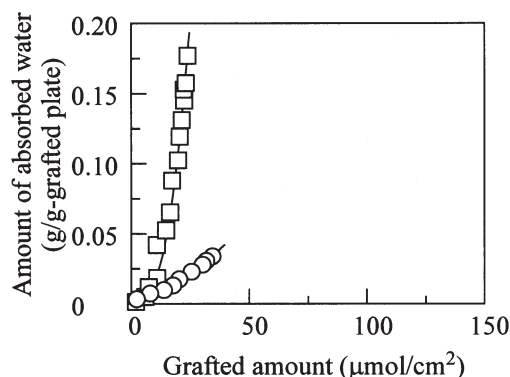


Figure 3 Changes in the amount of absorbed water with the amount of the grafted monomer for the grafted LDPE plates: (O) AA and (\square) DMAEMA.

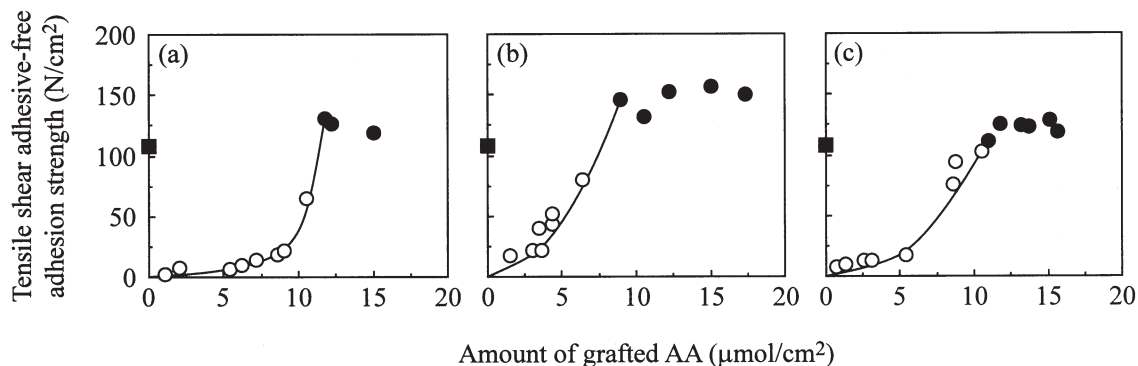


Figure 4 Changes in the tensile shear adhesive-free adhesion strength with the amount of grafted AA for the bonding between LDPE-g-PAA and LDPE-g-PDMAEMA plates immersed in (a) aqueous HCl (pH 3.0), (b) water, and (c) aqueous NaOH (pH 11.0): (■) the ultimate tensile strength of the substrate (per 0.1 cm^2), (○) the cohesive failure, and (●) the substrate breaking. The amount of grafted DMAEMA was $5 \mu\text{mol}/\text{cm}^2$.

in water absorption between LDPE-g-PAA and LDPE-g-PDMAEMA plates, which indicated clearly that the grafting of the hydrophilic monomers onto LDPE surfaces could transform the hydrophobic properties into hydrophilic ones. Grafted polymer chains in water-swollen layers are considered to be in active thermal motion. Therefore, if a swollen layer of one grafted PE surface is heat-pressed to get in close contact with another, the grafted polymer chains will be entangled with one another, and so the bonding strength between the two plates having grafted polymers with charges opposite to each other will be expected to be more potent.

In the next section, we discuss the adhesive-free adhesion on the basis of attractive electrostatic interactions between PE-grafted polymer chains with charges opposite to each other in addition to entanglements among grafted polymer chains due to their thermal motion.

Adhesive-free adhesion or autoadhesion strength

We obtained LDPE plates with the desired grafted amounts by changing the irradiation time from Figure 1. The measurements of the tensile shear adhesive-free adhesion strength were made between the LDPE plates with a constant grafted amount of about $5 \mu\text{mol}/\text{cm}^2$ of DMAEMA and with different grafted amounts of AA. Both LDPE-g-PDMAEMA and LDPE-g-PAA plates were immersed in water, an aqueous HCl solution with pH 3.0, or an aqueous NaOH solution with pH 11.0 for 24 h before being heat-pressed.

Figure 4 shows the change in the tensile shear autoadhesion strength between LDPE-g-PAA plates and LDPE-g-PDMAEMA plates. The adhesive-free adhesion strength increased with an increase in the grafted amount of AA and reached the value of the LDPE substrate breaking, regardless of the pH conditions, immersed in aqueous solutions. As can also be seen

from Figure 4, the adhesive-free adhesion properties were most enhanced between LDPE-g-PDMAEMA plates and LDPE-g-PAA plates immersed in water; that is, the adhesive-free adhesion strength between the grafted PE plates immersed in water started to increase in the lower grafted amount range, and so the substrate breaking occurred at the lowest grafted amount of the three immersion conditions. The adhesive-free adhesion between plates grafted with hydrophilic polymers stems from entanglements due to polymer segments diffusing from one grafted layer into another in addition to occasional hydrogen bonding between the polymer segments.¹¹ However, if both PE plates grafted with weak electrolytic monomers such as AA and DMAEMA are immersed in water, then PAA chains and PDMAEMA chains grafted onto PE are partly ionized; that is, some carboxyl groups and (dimethylamino)ethyl groups are dissociated and protonated, respectively (their extents of ionization are estimated to be ca. 50%¹⁶). As a result, an electrostatic attractive force, that is, an ionic bond, between anionic PAA chains and cationic PDMAEMA chains will play an important role in adhesive-free adhesion. On the other hand, although both PDMAEMA chains of LDPE-g-PDMAEMA plates in an acidic solution (pH 3.0) and PAA chains of LDPE-g-PAA plates in a basic solution (pH 11.0) are almost ionized, neither the PDMAEMA chains in the basic solution nor the PAA chains in the acidic solution are ionized. This means that polymer chains grafted onto the two PE plates will not ionize simultaneously under the acidic or basic conditions; that is, no attractive electrostatic force between the grafted polymer chains will be at work effectively, but only entanglements due to the segmental motion mentioned previously will contribute to the appearance of the adhesive properties. Therefore, the autoadhesion strength between the LDPE plates with nonionized grafted polymer chains and with ionized polymer chains becomes low in com-

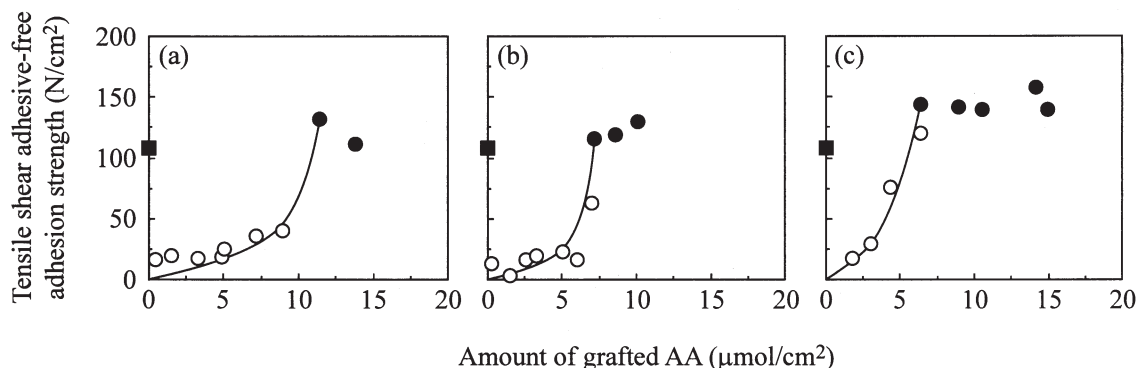


Figure 5 Changes in the tensile shear adhesive-free adhesion strength with the amount of grafted AA for the bonding between LDPE-*g*-PAA and LDPE-*g*-*q*-PDMAEMA plates immersed in (a) aqueous HCl (pH 3.0), (b) water, and (c) aqueous NaOH (pH 11.0): (■) the ultimate tensile strength of the substrate (per 0.1 cm^2), (○) the cohesive failure, and (●) the substrate breaking. The amount of grafted DMAEMA was 5 $\mu\text{mol}/\text{cm}^2$.

parison to that between the LDPE plates with negatively ionized grafted polymer chains and with positively ionized chains. In other words, even if PE plates grafted with weak electrolytic monomers such as AA and DMAEMA are only immersed in water, their autoadhesive properties can be clearly improved.

These results can be summarized as follows:

1. If LDPE-*g*-PAA plates and LDPE-*g*-PDMAEMA plates are immersed in water before heat pressing, the adhesion system can be composed of LDPE-*g*-PAA plates with ionized PAA chains and LDPE-*g*-PDMAEMA plates with ionized PDMAEMA chains. Consequently, electrostatic forces and entanglements among polymer chains as the main attractive forces will lead to considerably high adhesive-free adhesion strength.
2. If both plates are immersed in a basic solution or an acidic solution before heat pressing, one adhesion system can be composed of LDPE-*g*-PAA plates with ionized PAA chains and LDPE-*g*-PDMAEMA plates with nonionized PDMAEMA chains, or another one can be composed of LDPE-*g*-PAA plates with nonionized PAA chains and LDPE-*g*-PDMAEMA plates with ionized PDMAEMA chains. Consequently, entanglement alone among the polymer chains as a main attractive force is operative, and the autoadhesion is not so strong as that of the first case.

We have just shown that in an attempt to increase the adhesive-free adhesion strength between LDPE plates that are grafted with different weak electrolytic monomers, the grafted polymer chains on the two LDPE plates should have charges opposite to each other. Therefore, PE plates grafted with strong electrolytic polymers are expected to show high adhesive-free adhesion strength in a wide pH range. Figure 5

shows the adhesive-free adhesion strength between the LDPE plates with quaternized PDMAEMA chains (degree of quaternization $\sim 80\%$) and those with AA chains immersed in water or an acidic or basic solution. The combination of quaternized poly[2-(dimethylamino)ethyl methacrylate]-grafted low-density polyethylene (LDPE-*g*-*q*-PDMAEMA) plates and LDPE-*g*-PAA plates immersed in the basic solution caused the breaking of the substrate at the lowest grafted amount of PAA chains, as shown in Figure 6(c). The cationic properties of quaternized PDMAEMA chains of the LDPE-*g*-*q*-PDMAEMA plate were quite independent of the pH level of the medium in which they were immersed; on the other hand, PAA chains of the LDPE-*g*-PAA plate were fully anionically ionized in the basic solution. Consequently, it was concluded that the strong attractive interactions of cationic PDMAEMA chains with anionic PAA chains brought the combination to the substrate breaking at the lowest grafted amount of PAA, referring to the highest adhesive-free adhesion strength.

Because about all PAA chains grafted onto LDPE plates do not ionize in an acidic solution and no electrostatic interaction of PAA chains of LDPE-*g*-PAA plates with quaternized PDMAEMA chains of the LDPE-*g*-*q*-PDMAEMA plate is effectively operative, the highest amount of grafted AA is needed to reach the substrate breaking, as shown in Figure 5(a).

Some PAA chains of LDPE-*g*-PAA will ionize even in water, and so quaternized PDMAEMA chains of LDPE-*g*-*q*-PDMAEMA can interact with anionically ionized PAA chains of LDPE-*g*-PAA immersed in water. Therefore, the combination of LDPE-*g*-*q*-PDMAEMA plates and LDPE-*g*-PAA plates in water shows an intermediate strength between the two combinations described previously [Fig. 5(b)].

In what follows, we describe the results of the measurements of the autoadhesion strength between the quaternized poly[2-(dimethylamino)ethyl methacry-

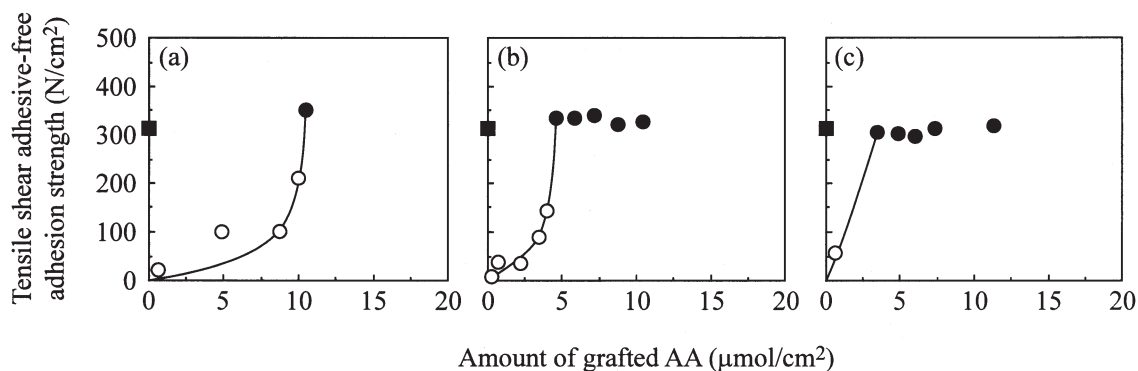


Figure 6 Changes in the tensile shear adhesive-free adhesion strength with the amount of grafted AA for the bonding between HDPE-g-PAA and HDPE-g-q-PDMAEMA plates immersed in (a) aqueous HCl (pH 3.0), (b) water, and (c) aqueous NaOH (pH 11.0): (■) the ultimate tensile strength of the substrate (per 0.1 cm^2), (○) the cohesive failure, and (●) the substrate breaking. The amount of grafted DMAEMA was $5 \mu\text{mol}/\text{cm}^2$.

late]-grafted high-density polyethylene (HDPE-g-q-PDMAEMA) and poly(acrylic acid)-grafted high-density polyethylene (HDPE-g-PAA) plates obtained in a fashion similar to the measurement made of the adhesive-free adhesion strength of the LDPE plates grafted with DMAEMA and AA monomers. Figure 6 shows the tensile shear adhesive-free adhesion strength between HDPE-g-q-PDMAEMA with a constant grafted amount of about $5 \mu\text{mol}/\text{cm}^2$ and HDPE-g-PAA with different grafted amounts. The values of the autoadhesion strength of all the HDPE plates grafted with DMAEMA and AA monomers were higher with the same grafted amount than those of the LDPE plates, and the substrate breaking, the values of which were higher by factors of 2 or more in comparison with the LDPE plates, also appeared in the lower range of the grafted amounts. These appreciable differences are considered due to the high crystallinity of the HDPE plates. That is, first, the higher autoadhesion strength comes from the higher ultimate strength of the HDPE plate in comparison with that of the LDPE plate. Second, because the grafting of the monomers onto HDPE is usually restricted to the outer surface regions, these grafted polymer chains can interact more effectively with one another when heat-pressed than grafted polymer chains onto LDPE, which are partly occluded inside the bulk. Therefore, the combination of HDPE plates grafted with quaternized DMAEMA and AA monomers, although it takes a longer time to obtain the desired grafted amount for grafting with such monomers in comparison with LDPE plates, can be successfully used to obtain higher adhesive-free adhesion strength in the low range of grafted amounts.

CONCLUSIONS

The adhesive-free adhesion induced between PAA and PDMAEMA chains grafted on PE was studied from an electrostatic viewpoint of the grafted polymer chains and on the basis of the crystallinity of PE as the substrate:

1. The adhesive-free adhesion between LDPE-g-PDMAEMA and LDPE-g-PAA plates immersed in water before being heat-pressed showed the highest strength. The electrostatic interaction contributed to the adhesive-free adhesion because the PDMAEMA and PAA chains were partly ionized in water.
2. The substrate breaking of LDPE-g-PAA plates with LDPE-g-q-PDMAEMA occurred at the lowest grafted amount in the case of immersion in a basic solution. Because the cationic properties of the quaternized PDMAEMA chains were quite independent of the pH level in the medium and the PAA chains were fully anionically ionized in the basic solution, the electrostatic force between the polymeric chains with opposite charges worked by entering an ionic bond to form a strong adhesive-free adhesion system.
3. The autoadhesion strength of all the HDPE plates grafted with DMAEMA and AA monomers and the substrate breaking were high by factors of 2 or more in comparison with the LDPE plates because of the high crystallinity of HDPE. These results were due to fact that the grafted polymers were mainly restricted to the outer surface regions of the HDPE plates and could interact more effectively with one another.

It must be stressed that the electrostatic properties of grafted polymer chains play an important role in the autoadhesion between grafted layers on PE plates in addition to entanglements because of segmental motion of the grafted polymer chains.

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