Surface Modification with Acrylic Polyampholytes 1, Adsorption of Acrylic Polyampholytes on Fiberglass Reinforced Plastics, and Characterization of the Polymer Adsorbed Surfaces

Takeshi Terabayashi,[1] Takanobu Maruyama,[1] Yoshio Shimizu,[1] Masanori Komatsu,[1] Toshio Takahashi[2]

[1]*Functional Materials Research Laboratories, Lion Corporation, Hirai, Edogawa-ku, Tokyo 132-0035, Japan*
[2]*Research and Development Headquarters, Lion Corporation, Hirai, Edogawa-ku, Tokyo 132-0035, Japan*

Received 14 June 2005; accepted 9 January 2006
DOI 10.1002/app.24084

ABSTRACT: The adsorption of acrylic polyampholytes on fiberglass reinforced plastics (FRP) was investigated using random copolymers derived from (dimethylamino)ethyl methacrylate (DM), methacrylic acid, and *t*-butyl methacrylate (*t*-BMA). The effect of the copolymer structure changes on the adsorption and the interactions between the copolymers and the surface were assessed using ζ-potential and contact angle measurements, NMR, and ESCA. The copolymer having the composition of 58 mol % pDM, 38 mol % pMMA, and 4 mol % pt-BMA was adsorbed on the FRP surface at pH 7, and it formed the highest hydrophilic surface among the tested copolymers. An analysis by use of atomic force microscope revealed that the copolymer afforded a uniform 4–6 nm thick coverage on the FRP. We concluded that the interactions between the copolymer's cationic sites and the anionic FRP surface are important as well as the hydrophobic interaction for adsorption. Furthermore, it is suggested that the hydrophilicity of the copolymer's adsorbed surfaces is related to the density of the copolymer's anionic sites. These results indicate that the ampholytic structure of the polymers would be essential for the surface modification on the FRP. The effect of functional groups of surfaces on the acrylate adsorption was also assessed using surface plasmon resonance. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4454–4461, 2006

Key words: water-soluble polymers; copolymerization, hydrophilic polymers; adsorption; surfaces

INTRODUCTION

The phenomenon of ampholytic polyelectrolyte adsorption at a solid/liquid interface has received considerable attention because of its importance in biological science and moreover due to various practical applications in industry.[1,2] Concerning biotechnology, the adsorption of natural ampholytic polyelectrolytes such as proteins plays an important role in biological assays and the development of biomaterials.[3,4] Synthetic polyelectrolytes have also been used for many technological processes such as flotation, wastewater treatment, and paper production.[5,6] More recently, the application of synthetic polyampholytes to the surface modification of various hard surfaces has been examined.[7,9] During the past decade, considerable information on ampholytic polyelectrolytes has been accumulated and the properties and behavior of the ampholytic polyelectrolytes in solution have been well investigated.[10–13] Even so, adsorption phenomena are often more complicated than the behavior of related systems in solution,[14] and recent reports have been directed to understanding the adsorption phenomena.[15–18]

In this context, we have undertaken studies of the adsorption behavior of acrylic polyampholytes on fiberglass reinforced plastics (FRPs) and especially the evaluation of the surface properties of the thin polymer films formed from the adsorbed polyampholytes on the FRP surface.[19]

The goal of our studies is to develop novel surface modification agents for hard surfaces as part of a surface modification strategy for toiletry products. The FRP surface is hydrophobic and is negatively charged in an aqueous solution. It was well known that amphoteric compounds, having positive–negative ion pairs, strongly bind to anionic charged mica, and the adsorption of the amphoteric polyelectrolyte depends on the number of discrete ionic bonds.[20] In other words, the adsorption is determined by the details of the charge distributions and not by the net charge carried by the polymer. In addition, changing the hydrophilic/hydrophobic balance would control the polymer solubility and the adsorption on FRP. Therefore, our strategy for the design of the surface

---

Correspondence to: M. Komatsu (mkoma@lion.co.jp).

Journal of Applied Polymer Science, Vol. 101, 4454–4461 (2006)

modification agents involves the use of polyampholytes slightly modified with a hydrophobe. As a first report of our studies, we now report a study of the effects of changes in the polyampholyte structure, i.e., the charges, the hydrophilic/hydrophobic balance, etc., on the adsorption behavior of the copolymers and the characteristics of the copolymer-covered surfaces.

We prepared a series of random copolymers derived from (dimethylamino)ethyl methacrylate (DM), methacrylic acid (MAA), and *t*-butyl methacrylate (*t*-BMA). The adsorption of copolymers with different DM/MAA ratios on the FRP from dilute solutions was studied as a function of pH to assess the effects of the charges on the adsorption. The effect of the hydrophobic interaction was assessed using the copolymers with different *t*-BMA ratios. The interactions between the copolymers and the FRP during the adsorption were assessed using ζ-potential measurement, ^{1}H NMR, and ESCA. The surface properties produced by the copolymer adsorption were also evaluated using atomic force microscope (AFM), contact angle and ζ-potential measurements. In addition, the surface plasmon resonance of an alkanethiol gold surface was used to evaluate the surface effects, especially the importance of the substrate's functional groups on the adsorption phenomena.

EXPERIMENTAL

Materials

All reagents including (dimethylamino)ethyl methacrylate (DM), methacrylic acid (MAA), and *t*-butyl methacrylate (*t*-BMA) were the best grade commercially available and were used without further purification, unless otherwise specified. The FRP plates (Inax) and FRP particles (Matsumura Kasei) consisting of polyester resin and glass fibers were used for the adsorption experiments.

Polymerization procedure

Deionized water (90 g) in a 500 mL separable flask equipped with a reflux condenser, N_2 inlet tube, dropping funnels, and mechanical stirrer was stirred for 30 min at 80°C in a N_2 gas atmosphere. To the flask, 168 g of the aqueous solution containing 83 g of DM, MAA, and *t*-BMA, and 27 g of the aqueous solution containing 1.5 g of sodium persulfate were added dropwise over a 2 h period. The mixture was stirred for an additional 5 h at 80°C and allowed to cool. The product was obtained as a clear and colorless to pale yellow aqueous solution. The composition ratios and the polymerization yields were measured by nuclear magnetic resonance spectrometry (^{1}H NMR). The ^{1}H NMR spectra were recorded at 400 MHz in D_2O on a JOEL GSX-400 NMR spectrometer. The composition was expressed as the ratio of pDM, pMAA, and pt-BMA, which represent the polymerized units of each monomer in the copolymers. The polymerization yields were greater than 99%, and the composition ratios were almost the same as the ratios of the monomer used. The molecular weights of the copolymers were determined by gel permeation chromatography (GPC) based on a pullulan standard.

Methods

ζ-potential of FRP plate surfaces

The ζ-potentials of the untreated FRP plate surface and copolymer **4**-treated FRP plate surface were measured using an ELS-8000 (Otsuka Electronics) with a cell for a flat plate sample with monitor particles[21,22] (monitor particle, Saradyn standard polystyrene latex; *d*, 212 nm; *E*, −33.6 v/cm).

The IEP of the copolymers

Copolymer IEPs were determined by the titration method to assess the degree of dissociation as described in the literature.[23] One mol/L HCl and 1 mol/L NaOH were used to adjust the pH of the copolymer solution. All measurements were carried out in 0.001 mol/L NaCl solutions.

Adsorption of the copolymers on FRP composed of polyester resin

The adsorption of copolymers on the FRP particles (specific surface area: 2.7 m^2/g (BET)) was carried out by treating the FRP particles with an aqueous solution of the copolymer containing 0.01 mol/L NaCl. The copolymer concentrations were varied from 0.01 to 0.1 g/L and pH values were adjusted to 3.8 or 7.2 with NaOH or HCl in amounts that were negligible when compared to the salt concentration. During the measurement, 1 g of the FRP was dispersed in 5 g of the copolymer solution, and the dispersion was stirred for 24 h at 25°C. After filtration, the copolymer concentrations of the initial solution and the treated solutions were measured by GPC. The GPC analyses of the copolymers were performed on a Hitachi LaChrom system with refractive index at 50°C. An Asahipak Ohpak Q-802 as the column and M/15 phosphate buffer (pH 9.2) as an elution solvent were used, the flow rate being 0.5 mL/min in all cases. The adsorbed amount was calculated from the difference in the concentrations.

Repetition method of the copolymer adsorption

The 0.5% aqueous solution of copolymer **4** was sprayed on the FRP plate, 10 ×10 cm^2, followed by drying. The treated FRP plate was then rinsed with water to remove the excess copolymer on the FRP surfaces. The process was repeated to assess the adsorption behavior of the copolymer on the surface. After the repetition, the adsorbed polymer on the surface was extracted with a 2 mol/L methanol solution of HCl. Using the extract, the amount of the copolymer irreversibly adsorbed on the surface was determined by GPC.

Treatment of the FRP plate with copolymers for surface analysis

Two milliliters of a 0.5–1% aqueous solution of a copolymer, adjusted to pH 7, was sprayed on an FRP plate, 10 ×3 cm^2 or 10 ×10 cm^2, and then rinsed with water for 30 s, followed by drying. The plate was used for the analyses of the surface properties.

Surface analysis by using AFM

The surface of the FRP plate treated with copolymer **4** was analyzed using a Digital Instrument NANOSCOPE III a. The measurements were performed in the contact mode.

Surface analysis with ESCA

The surface conditions of the copolymer **4**-treated FRP plate surfaces were analyzed using a Physical Electronics QUANTUM 2000 Scanning ESCA microprobe. The auto Z beam radius was 100 μm, and the irradiation angles were 30°, 45°, and 70°.

Analysis of the adsorption process by using NMR

D_2O solutions (0.025%) of copolymer **4** (0.555 mL) in the absence and presence of FRP powders (particles smaller than 150 μm, 100 mg) were prepared in NMR tubes. The pHs of the solutions were adjusted at pH 2.0, 4.0, and 6.0 using the buffer solutions of potassium hydrogen phthalate. The NMR measurements were performed using a JOEL GSX-400 NMR spectrometer in the SGHMG mode (64 scans) at ambient temperature.

Contact angles of the surfaces

The contact angles were determined with a CAZ contact angle goniometer (Kyowa Surface Science) using water and methyl iodide. In preparation for the measurements, the FRP plates were treated with 0.5% aqueous solutions of the copolymers at pH 7.2. The plates were washed with water to remove any excess copolymer followed by drying.

TABLE I
Copolymers Derived from DM, MAA, and t-BMA, and Their Molecular Weights

	Composition (mol %)	Molecular weight		
Copolymer	pDM/pMAA/pt-BMA	M_n	M_w	M_w/M_n
1	86/10/4	34000	88700	2.61
2	67/29/4	23200	59300	2.56
3	60/40/0	23600	35400	2.35
4	58/38/4	18800	46400	2.47
5	55/36/9	20300	49300	2.43
6	38/58/4	10500	28200	2.69

Preparation of the alkanethiol adsorbed surfaces

The mixed organosulfur monolayers were formed by immersing the gold-coated plates, (SIA Kit Au, Biacore) in 2 mM ethanol solutions of thiol derivatives for 12 h. The plates were rinsed with ethanol and dried. Three surfaces were prepared using three different solutions: (A) $HS(CH_2)_{15}CH_3$ and $HS(CH_2)_{10}COOH(1:1)$, (B) 1 : 1 mixture of $HS(CH_2)_{15}CH_3$ and $HS(CH_2)_{11}OH$, and (C) $HS(CH_2)_{10}COOH$ and $HS(CH_2)_{11}OH$. The contact angles for each plate were determined in water using a CAZ contact angle goniometer (Kyowa Surface Science).

Measurement of the adsorption amount of the copolymers by SPR

The amount of copolymer adsorbed on the thiol-treated surface was determined using a Biosensor Instrument Biacore3000. A phosphoric acid buffer, 10 m*M*, pH 7, was used as the running buffer in the flow-cell of the instrument. A 0.5% aqueous solution of the copolymer was passed through the flow-cell for adsorption followed by the flow of the buffer solution to remove any excess copolymer. The variation in the refractive index before and after the copolymer adsorption was measured as RU. The amount was calculated using the RU value according to the following relationship $1\text{RU} = 1\ \text{pg/mm}^2$.

RESULTS AND DISCUSSION

Copolymer adsorption on FRP as a function of the polymer concentration

The acrylic polyampholytes used in this study and their characteristics are shown in Table I. Based on the initial results, copolymer **4** was used to explore the adsorption behavior. The copolymer **4** has the composition of 58 mol % pDM, 38 mol % pMAA, and 4 mol % pt-BMA, and among the copolymers used (see below), it afforded the most hydrophilic surface on the FRP.

During the adsorption experiments, the FRP particles were treated with aqueous solutions of copolymer

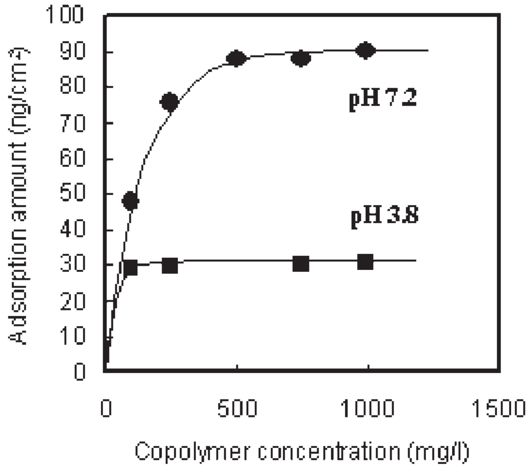

Figure 1 Adsorbed amount of copolymer **4** as a function of copolymer concentrations at different pH values. pH 3.8 (■) and pH 7.2 (●).

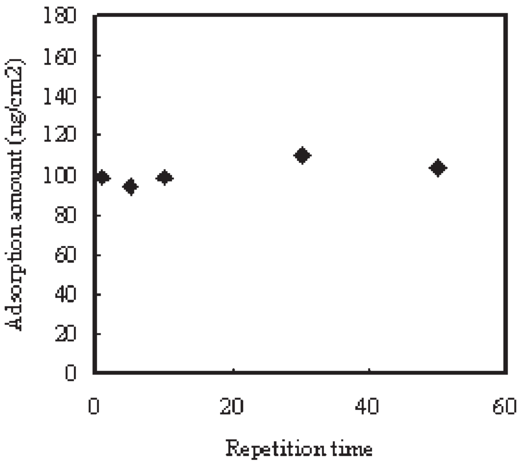

Figure 2 Adsorbed amount of copolymer **4** as a function of repetition times.

4 at pH 3.8, pH 7.2, and ambient temperature. The adsorbed amount of copolymer **4** as a function of the polymer concentration is shown in Figure 1. In each case, the amount reached a plateau value. The saturated amount of the adsorbed copolymer at pH 7.2 was 90 ng/cm^2 and this value was greater than the adsorbed amount at pH 3.8 (30 ng/cm^2). A similar pH dependence of the adsorption was previously observed for other polyampholytes.[15–18] In that case, it was found that the adsorption at the polyampholyte's isoelectric point (IEP) reached a maximum. This increase in the adsorption as the IEP was approached was attributed to a decrease in the polyampholyte's net charge. It seems reasonable that a lower net charge would cause less electrostatic repulsion of the adsorbed aggregates. Less repulsion should lead to a higher adsorption density. Therefore, we determined the IEP of copolymer **4** to be pH 6.6. (see Table III) Since pH 7.2 is much closer to the IEP than is pH 3.8, there should be less repulsion at the higher pH and the greater adsorption of copolymer **4** is in the correct direction.

In view of the application to toiletries, we measured the surface accumulation and saturated amount of the adsorbed copolymer by the following spray and rinse method. A 0.5% aqueous solution of the copolymer was sprayed on an FRP plate, which was allowed to dry. The copolymer-treated FRP plate was rinsed with water to remove the excess copolymer on the FRP surface. After spraying, more than 2000 ng/cm^2 of copolymer **4** remained on the surface and most of the copolymer was removed from the FRP surface after rinsing with water. The residual amount of the copolymer is *ca*. 100 ng/cm^2. This amount agrees with that (90 ng/cm^2) obtained by adsorption from the aqueous solution described above.

A plot of the residual amount versus the repetition time is shown in Figure 2. The amounts of the adsorbed copolymer after rinsing are approximately the same under these conditions showing that the repetition did not cause an accumulation of the copolymer.

Evaluation of the electrostatic interaction between the copolymer and the FRP on the adsorption

To evaluate the interaction during the adsorption process between the FRP surface and copolymer **4** solutions, we determined the IEP of the copolymer in the solution and ζ-potentials of the FRP plate surface as a function of pH. The results of the ζ-potentials of the FRP plate surface are plotted in Figure 3. The IEP of the FRP surface is pH 3.8, so the net charge of the FRP surface should be near zero for the adsorption at pH 3.8. The copolymer's IEP is pH 6.6, and the polymer would be positively charged during the adsorption at a solution pH of 3.8. There should be no strong electrostatic attractive force between the FRP surface and

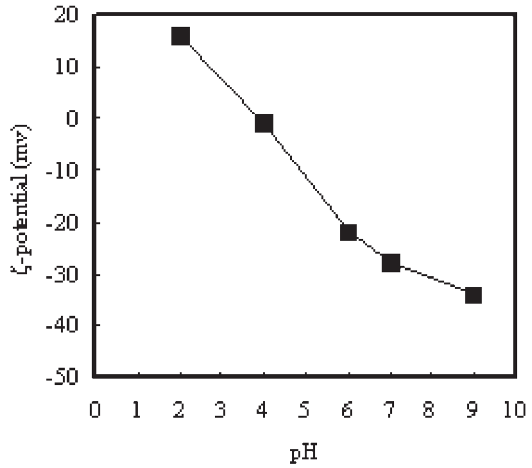

Figure 3 ζ-potential of the nontreated FRP plate surface with pH of the aqueous phase.

TABLE II
Adsorbed Amount of the Copolymers on FRP

Copolymer	*A* (ng/cm^2)
1	115
2	110
3	96
4	100
5	145
6	50

the copolymer in the solution at pH 3.8. At pH 7.2, the FRP would have a negative surface charge and the polymer would be negatively charged, but the density would not be high because pH 7.2 is near the copolymer's IEP. The adsorption interaction between the FRP and the copolymer at pH 7.2 should be unfavorable for adsorption due to the charge. Experimentally, the adsorption is about threefold greater at pH 7.2 than at pH 3.8, suggesting that the hydrophobic interaction or the interaction of the cationic sites on the molecule, not the net charge of the molecule, with the anionic FRP surface plays an important role in the adsorption.

Effects of changes in structure of the copolymers on the adsorption

The effect of copolymer structure on the acrylic polyampholyte adsorption on the FRP was investigated using the compounds listed in Table I. Table II shows the saturated amounts of the adsorbed copolymers at pH 7.2 and Table III shows the IEP of the copolymers.

The ratio of pDM to pMAA and the adsorption diminish in the following order: **1** (pDM/pMAA = 8.6) $>$ **2** (pDM/pMAA = 2.3) $>$ **4** (pDM/pMAA = 1.5) $>$ **6** (pDM/pMAA = 0.65). This implies that the adsorption increases with the increasing density of the dimethylamino groups. Copolymer **6** has the lowest isoelectric point (i.e. pH 5.9) and would have the highest density of the anionic charges (at pH 7) in this group. If the electrostatic repulsion between copolymer **6** and the FRP at pH 7 is the highest, the adsorption should be the lowest. In other cases, the pDM value is higher than that of the pMAA and they would be less repulsion than for copolymer **6** and the FRP.

TABLE III
IEP of the Copolymers

Copolymer	IEP
1	7.1
2	7.0
3	6.6
4	6.6
5	6.6
6	5.9

TABLE IV
Properties of the Thiol-Treated Surfaces

Surface	Functional group	Molar ratio	θ (deg)
A	COOH/CH$_3$	1/1	80
B	CH$_3$/OH	1/1	84
C	COOH/OH	1/1	53

The data obtained for copolymers **3**, **4**, and **5** suggest that the *t*-butyl ester groups also affect the adsorption; the higher the density of the *t*-butyl ester groups, the higher the adsorption. These data imply that both the density of the cationic sites and the hydrophobic nature of the molecule play important roles in the adsorption at pH 7.2, which is near the IEP of the copolymers.

Analysis of the adsorption phenomena of the copolymers using surface plasmon resonance

The surface adsorption of copolymers can be measured by surface plasmon resonance when the polymers are adsorbed on an alkanethiol surface.[24,25] Thus, three different alkanethiols or mixtures were adsorbed on Au plates. The thiol structures and the observed contact angles are recorded in Table IV.

Alkylthiols are well known to form a highly ordered monolayer surface when adsorbed on Au.[26–28] In the three cases summarized in Table IV, the thiol contacts and covers the Au surface revealing hydroxyl or carboxyl substituents on the opposite side of the monolayer. As shown in Table IV, surface A consists of CH$_3$ groups and COOH groups, and surface B possesses CH$_3$ groups and OH groups. The contact angles of the surfaces were 80° and 84°, respectively, and the data imply that these surfaces are hydrophobic. Surface C is the most hydrophilic, having OH and COOH groups on the upper surface of the layer (contact angle = 53°). By using these plates, we evaluated the effects of surface functional groups on the copolymer adsorption. The experiments were carried out at pH 7 and the data were obtained using a Biacore 3000 instrument.

Table V shows that copolymer **1**, which has the highest density of cationic residues in the group **1**, **4**, and **6**, is most strongly adsorbed on A. At pH 7, the

TABLE V
Adsorbed Amount of the Copolymers on the Thiol-Treated Surfaces

	Copolymer					
Surface	**1**	**2**	**3**	**4**	**5**	**6**
A	59[a]		<5	10	66	17
B			48	177	154	
C			169	230	205	

[a] ng/cm^2.

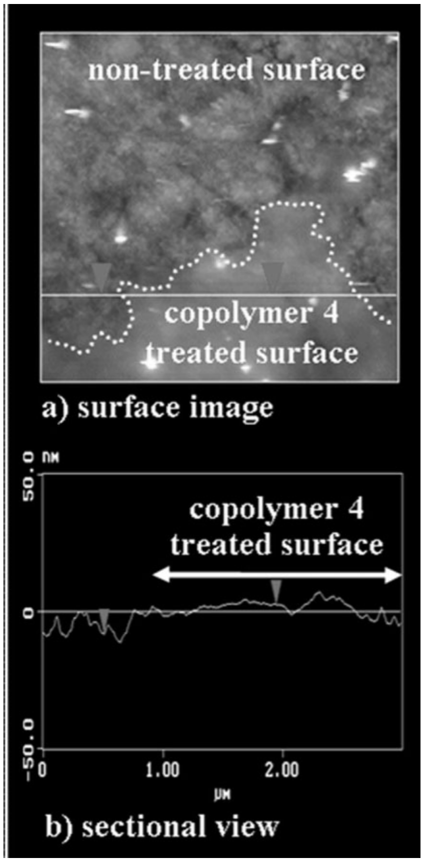

Figure 4 AFM images of the copolymer **4**-treated and nontreated FRP surfaces at a scan area of 3 × 3 μm^2. (a) surface image; (b) sectional view.

surface carboxyl groups on surface A should largely be ionized to COO^- ions, and the net charge on the polymer should be near zero because its IEP (7.1) is nearly identical to the solution pH of 7. We conclude that **1** strongly adsorbs due to the interaction of its cationic residues with the anionic surface. A consideration of the adsorption results for the other polymers (i.e. **3**, **4**, and **5**) suggests that although the charge effect dominates, the hydrophobic property of the copolymer is also significant for the surface adsorption at pH 7 on surface A.

Surface B possesses hydroxyl groups on its surface, and the surface hydroxyl groups should not largely be ionized to RO^- ions at pH 7. In this case, it is seen that the adsorption amounts of the copolymers **3**, **4**, and **5** on surface B were greater than the corresponding adsorption amounts on surface A. It is postulated that the hydrophobic interaction between surface B and the copolymers is more significant compared with that of surface A for the adsorption. On the other hand, in the case of surface C, which is hydrophilic, the three copolymers (i.e. **3–5**) afforded the highest adsorption amounts on surface C among the three surfaces, A–C. Therefore, it is expected that the electrostatic interaction between the hydrophilic surface and the copolymers is much more dominant than those of the hydrophobic surfaces and the copolymers during the adsorption.

Analysis of the copolymer-covered FRP surface by AFM

The surface topography of the FRP surface in the presence and absence of any treatment with copolymer **4** was examined using AFM (Fig. 4). Figure 4(a) shows the AFM image of the surfaces, i.e., the upper side is the nontreated one and the lower side is copolymer **4**-treated. The sectional view showing the height of the layer is also displayed in Figure 4(b). From the data, it was found that the copolymer afforded uniform coverage on the FRP surface with a polymer thickness of about 4–6 nm.

ζ-Potential of the copolymer-covered FRP surface

In an attempt to evaluate the locations of the functional groups on the copolymer-covered surface, we measured the ζ-potential of the copolymer **4**-treated FRP surface at pH 7.[21,22] At pH 7, the ζ-potential of the copolymer **4**-treated FRP surface was −39 mV, which is lower than that of the untreated FRP surface (see Fig. 3). This implies that the density of the negative charges on the copolymer-covered FRP surface is higher than the negative charge density on the untreated FRP surface.

Surface analysis by using ESCA

We measured the C1s, O1s, and N1s ESCA spectra of the FRP surface before and after treatment with copolymer **4**. The nontreated FRP surface exhibited C1s and O1s in a ratio of 85.3 : 14.6. No clear N1s peak was observed. In contrast, the copolymer-covered surface showed two N1s peaks having bond energies of 403 and 399 eV. (see Fig. 5) The former peak is attributed to the ammonium group, and the latter is assigned to the tertiary nitrogen group. Peaks were observed for

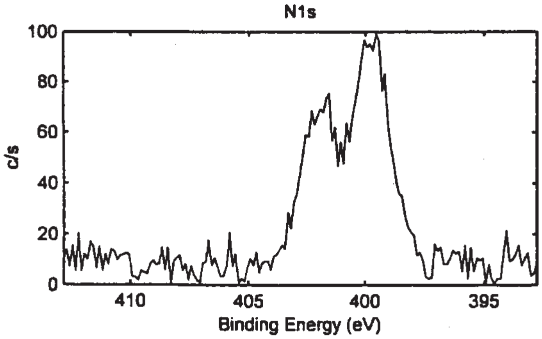

Figure 5 ESCA N1s spectrum of the copolymer **4**-treated FRP surface.

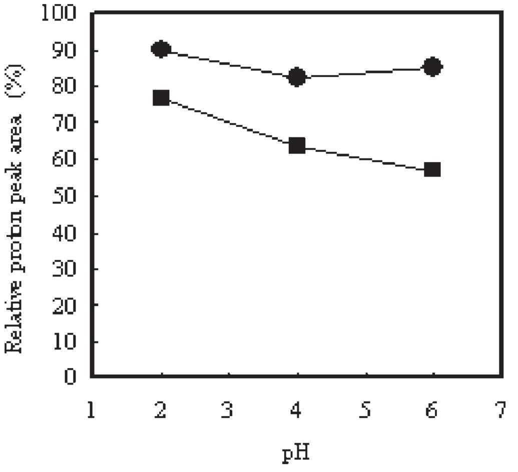

Figure 6 Relative proton peak areas of NCH_3 (■) and main chain (●) as a function of pH in the presence of FRP particles. The value of the ordinate is the relative proton peak area (%) compared with those without FRP.

C1s and O1s; the intensities were in the order C1s 82.0% > O1s 16.7% > N1s 1.3%. The increase in the O1s and N1s peak intensities implies that the copolymer is adsorbed on the FRP surface. Splitting of the N1s peak is probably due to the interaction between the copolymer's $N—CH_3$ moieties and the FRP's anionic sites.

Surface analysis by using NMR

Proton NMR was used to assess the functional group orientation on the surface covered by copolymer **4**. Spectra were obtained in D_2O solutions at different pH values in the presence and absence of the FRP powder. Figure 6 plots the proton peak area for NCH_3 versus solution pH (filled squares) and the main chain protons of the copolymer (filled circles). At each pH, the peak area was lower in solutions with the FRP powder than without the powder. Furthermore, the decrease in the peak area of the protons in NCH_3 was greater than that of the proton in the main chain. We assume that the copolymer interacts with the FRP surface when adsorbed, and this alters the proton environment. The decrease in the $N\text{-}CH_3$ proton intensity was greater than that for the main chain, suggesting that the NCH_3 groups are located at the interface between the FRP surface and the copolymer. The anionic groups would tend to locate in the polymer/water interface on the surface. These observations are consistent with the data on the ζ-potentials of the untreated and treated FRP plate surfaces and ESCA analysis described above. These results imply that the cationic moieties of copolymer **4** interacted with the anionic sites of the FRP to adsorb on the FRP surface, while the anionic sites of the copolymer are predominantly located at or near the copolymer/water interface of the copolymer layer on the FRP.

Contact angle evaluation

The contact angles for pure water against the copolymer-covered surfaces were measured using a contact angle goniometer. The data, summarized in Table VI, show that the copolymer-treated surfaces exhibit lower contact angles compared with the nontreated FRP surface. Copolymer **4** afforded the most hydrophilic surface among the copolymers tested; its water contact angle is 43°.

In the case of the copolymers having the pDM/pMAA ratio of > 1.0 (i.e. **1**, **2**, and **4**), their contact angles decrease in the order **1** (pDM/pMAA = 86/10) > **2** (pDM/pMAA = 67/29) > **4** (pDM/pMAA = 58/38). These values imply that the contact angle decreased with the increasing density of carboxyl groups in the molecular structure, and reached a minimum at the ratio pDM/pMAA = 1.5. Copolymers **3**, **4**, and **5** have the pDM/pMAA ratio of 1.5 and their contact angles were similar to each other. This result suggests that the *t*-butyl ester groups did not strongly affect the surface wettability.

CONCLUSIONS

The present study reports the adsorption of the polyampholytes derived from DM, MAA, and *t*-BMA on the FRP surfaces. The results suggest that the copolymer having the composition of 58 mol % pDM, 38 mol % pMMA, and 4 mol % *p*-t-BMA was adsorbed on the FRP surface at pH 7, and formed the most hydrophilic surface on FRP among the tested copolymers. Analyses of the copolymer-treated surfaces using AFM, NMR, ESCA, ζ-potential, and contact angle measurements showed that the interaction between the copolymers and the FRP surface is primarily electrostatic. The ionic interaction between the cationic sites of the copolymer and the anionic FRP surface is dominant, but the hydrophobic interaction also plays a significant role in controlling the surface adsorption.

TABLE VI
Contact Angles of the Copolymer-Treated FRP Plate Surfaces

Copolymer	θ (deg)
1	66
2	49
3	45
4	43
5	46
6	71
nontreated FRP	78

We thank Dr. A. Igarashi and Mr. A. Hisanaga of the Lion Corp. for the AFM, ESCA, and NMR analyses.

References

1. Dautzenberg, H.; Jaeger, W.; Koetz, J.; Philipp, B.; Seidel, C.; Stschrbina, D. Polyelectrolytes; Hanser Publishers: Munich, 1994.
2. Kudaibergenov, S. E. Adv Polym Sci 1999, 144, 115.
3. Andrade, J. D.; Hlady, V. Adv Polym Sci 1987, 79, 1.
4. Kawasaki, K.; Kambara, M.; Matsumura, H.; Norde, W. Caries Res 1999, 33, 473.
5. Bohm, N.; Kulicke, W. M. Colloid Polym Sci 1997, 275, 73.
6. Watanabe, Y.; Kubo, K.; Sato, S. Langmuir 1999, 15, 4157.
7. Komatsu, M. Ger. Pat. DE10,062,355 A1 (2000).
8. Aubay, E.; Yeung, D. US Pat. 6,593,288 B2 (2003).
9. Durbut, P. PCT Pat. WO03/012021 A1 (2003).
10. Forster, S.; Schmidt, M. Adv Polym Sci 1995, 120, 53.
11. Diehl, A.; Barbosa, M. C.; Levin, Y. Phys Rev E: Stat Phys Plasmas Fluids Relat Interdiscip Top 1996, 54, 6516.
12. Kassapidou, K.; Jesse, W.; Kuil, M. E.; Lapp, A.; Egelhaaf, S.; van der Maarel, J. R. C. Macromolecules 1997, 30, 2671.
13. Harrison, I. M.; Candau, F.; Zana, R. Colloid Polym Sci 1999, 277, 48.
14. Zhang, Y.; Tirrrell, M.; Mays, J. W. Macromolecules 1996, 29, 7299.
15. Walter, H.; Harrats, C.; Mueller-Buschbaum, P.; Jerome, R.; Stamm, M. Langmuir 1999, 15, 1260.
16. Walter, H.; Mueller-Buschbaum, P.; Gutmann, J. S.; Lorenz-Haas, C.; Harrats, C.; Jerome, R.; Stamm, M. Langmuir 1999, 15, 6984.
17. Mahltig, B.; Gohy, J. F.; Jerome, R.; Bellmann, C.; Stamm, M. Colloid Polym Sci 2000, 278, 502.
18. Vermohlen, K.; Lewandowski, H.; Narrer, H.-D.; Schwuger, M. J. Colloids Surf A 2000, 163, 45.
19. Komatsu, M. Proc 6th Surfactant Congress, Berlin; AOCS Press: Champaign, 2004; p 9. Presented in part at the 6th CESIO meeting.
20. Kamiyama, Y.; Israelachvili, J. Macromolecules 1992, 25, 5081.
21. Oka, K.; Ohtani, W.; Kameyama, K.; Kidai, M.; Takagi, T. Appl Theor Electroph 1980, 1, 373.
22. Mori, H.; Okamoto, T.; Husen (Japan) 1980, 27, 117.
23. Bieringer, R.; Abetz, V.; Muller, A. H. E. Eur Phys J E 2001, 5, 5.
24. Rich, R. L.; Myszka, D. G. Curr Opin Biotechnol 2000, 11, 54.
25. Ito, S. High Polym (Japan) 1999, 48, 702.
26. Nuzzo, R. G.; Dusco, F. A.; Allara, D. L. J Am Chem Soc 1987, 109, 2358.
27. Aramaki, K. J Surface Sci Soc Japan 1998, 36, 279.
28. Stoebe, T.; Hill, R. M.; Ward, M. D.; Davis, H. T. Langmuir 1997, 13, 7276.