

## Articles

## Surface Functionalization of Polyethylene for Magnetic Resonance Signal-Enhancing Coating Materials

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Contrast enhancement for magnetic resonance imaging of polyethylene films is achieved by surface amination with hydrazine plasma treatments followed by covalent attachment of a cation chelator, diethylenetriaminepentaacetic acid (DTPA), which is then allowed to complex with gadolinium(III) ion. First, we investigated the effects of plasma conditions, that is, plasma treatment time and power. Polyethylene surfaces after the treatment to link primary amine groups, attachment of DTPA via amide linkage, and complexation with  $Gd^{3+}$  were characterized by X-ray photoelectron spectroscopy, water contact angle, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and atomic force microscopy. A maximum surface density of primary amine group is found by the plasma treatment at low power (15 W) and short treatment time (5 min) under the continuous wave conditions. ATR-FTIR confirms that the amine and amide groups are formed on the PE surface after the hydrazine plasma treatments, which is also shown to have a smoothing effect for polymer surface morphology as examined by AFM. Finally, the magnetic resonance imaging of the DTPA– $Gd^{3+}$  complexed surface of polyethylene produces clear magnetic resonance signals with significant contrast over the background.

## Introduction

Surface modifications of polymer materials have received much attention recently since surface properties play an important role in many technological applications such as in coatings, lamination, composite blending, and biocompatibility of these materials. Surface functionalization with specific chemical groups is known as a facile route for subsequent chemical reactions at the surface (e.g., binding of biomolecules, surface-initiated polymerization, and surface grafting) and for providing desired changes in physical properties of the substrate surface (e.g., wettability, adhesion, and biocompatibility).<sup>1–3</sup> Surface functionalization of a polymer can be achieved by a chemical reaction with a contacting solution,<sup>4,5</sup> self-assembled monolayers,<sup>6</sup> ra-

diation,<sup>7</sup> photochemical grafting,<sup>8</sup> and plasma treatment.<sup>9–11</sup> Among them, the plasma treatment has been of special interest in theoretical and technological investigations because plasma processes are generally free of byproducts left on the surface, and only the surface layers of substrates are altered.<sup>12</sup> Polyethylene is one of the most commonly used commodity polymers in biomedical applications such as hip-joint implants and catheters; hence, its surface functionalization by plasma treatment constitutes a timely and highly relevant subject matter. The attachment of a primary amine group to the PE surface is particularly useful, for the primary amine group is relatively reactive nucleophiles, useful either for the covalent binding of a great variety of chemical compounds or for providing reactive sites for interfacial bonding. A convenient means for the amine group functionalization is ammonia plasma treatments and a number of reports can be found in the literature.<sup>13–16</sup>

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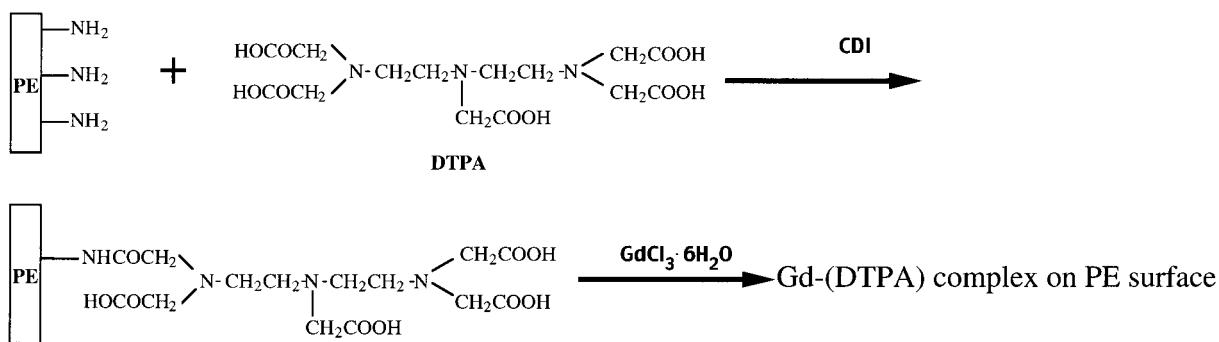
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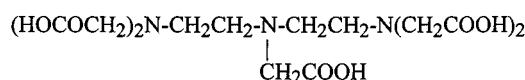
**Scheme 1. Chemical Attachment of DTPA–Gd<sup>3+</sup> on a Hydrazine Plasma Treated PE Surface**

However, there is a dearth of work that deals with surface amination of PE with hydrazine plasma treatments, which appear to be less invasive to the substrates than ammonia plasma treatments.

For our purpose in attaching a cation chelator, diethylenetriaminepentaacetic acid (DTPA), we start with the surface amination of PE by hydrazine plasma. Once amine groups are so implanted on the surface, DTPA is linked via amide linkage and then coordinated with Gd<sup>3+</sup>, which provides the necessary contrast by a hyperfine field of highly magnetic Gd<sup>3+</sup> upon shortening *T*<sub>1</sub> relaxation time of protons for nuclear magnetic resonance imaging (MRI) of devices made of PE. The current limits in the development and applications of endovascular MRI is the difficulty in readily detectable endovascular devices without active elements interacting with external magnetic field because almost all devices, such as catheter and guide wire, do not give rise to intrinsic detectable signal contrast on clinical MRI equipment. Thus, there exists a dire need for making these devices detectable within the equipment. We have developed a class of coatings on the PE surface, by covalently attaching the DTPA–Gd complex, a MR signal enhancer in clinical practice. Once attached, Gd<sup>3+</sup> through interactions with water molecules near the complexed surface provides a significant contrast for a MR signal for the endovascular devices. A brief preliminary account of this study appeared elsewhere.<sup>17</sup>

## Experimental Section

**Materials.** PE films used in this study were 25-μm thick and contained no additives. Hydrazine with a purity of 98%, 4-trifluoromethylbenzaldehyde (TFBA), dimethyl sulfoxide (DMSO), methanol, and gadolinium (III) chloride hexahydrate were purchased from Aldrich and used as-received. A commonly employed Gd<sup>3+</sup> chelator, diethylenetriaminepentaacetic acid (DTPA), was purchased from Sigma.



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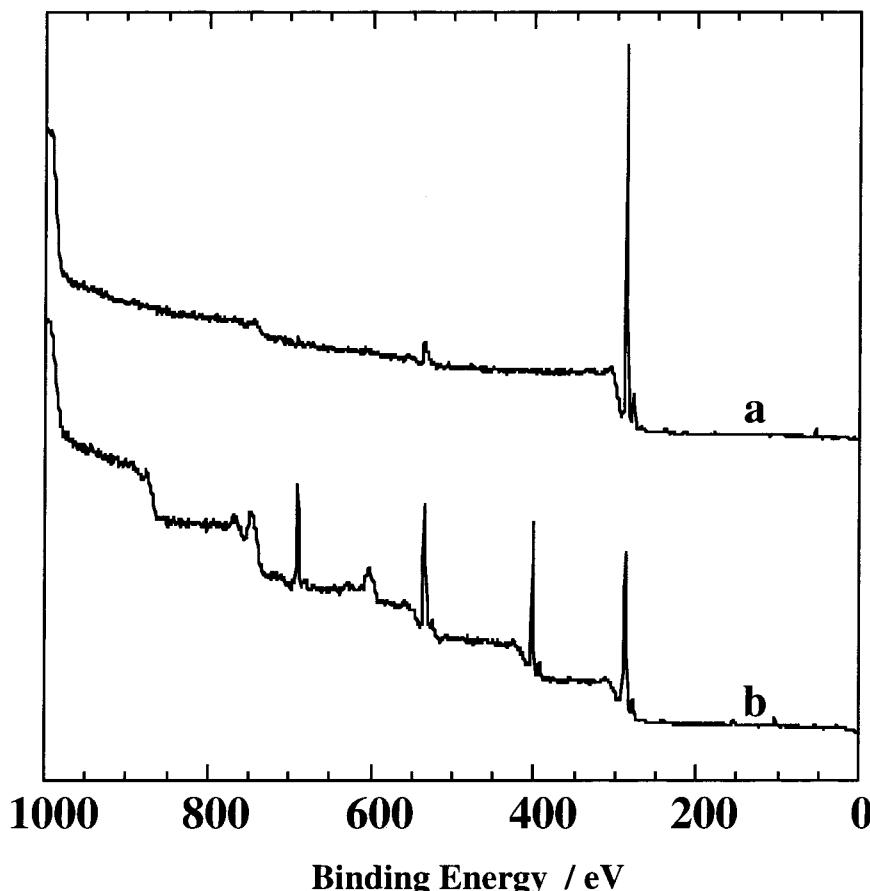
**Hydrazine Plasma Treatments.** The PE films were ultrasonically cleaned successively in tetrahydrofuran, methanol, and deionized water. Each wash took 15 min. After the cleaning, the films were dried overnight with dry nitrogen. Since the details of the plasma apparatus have appeared elsewhere,<sup>18</sup> only a brief description is provided here for the sake of brevity. The plasma system is a capacitively coupled, parallel-plate glass reactor. The reactor is composed of a cylindrical stainless steel reaction chamber wherein the stainless steel removable electrodes are located in the upper and lower regions with a dimension of 20-cm diameter and 0.8-cm thick. The upper electrode is connected to the RF-power supply and the lower electrode is a part of the vacuum line through its supporting conical-shaped and circularly perforated stainless steel tubing. The space between the upper electrode and upper wall of the chamber is occupied by three 1-cm-thick and 20-cm-diameter Pyrex-glass removable disks. These disks insulate the electrode from the stainless steel top of the reactor and allow the adjustment of the electrode gap. A controlled frequency of 50 kHz was employed for all the experiments.<sup>17</sup> The following treatment procedure was adopted. The clean PE film was placed in the center region of the lower electrode and the reactor was evacuated to a base pressure of 15 mTorr. Subsequently, hydrazine pressure was established (350 mTorr) through the reactor by opening the valve to a liquid hydrazine reservoir. After the hydrazine pressure was established, the film was treated by the hydrazine plasma under varying powers and treatment times. Then, the reactor was brought to atmospheric pressure with air and the film was taken out.

**Surface Derivatization Reaction.** Because the fluorine atom is efficient in producing photoelectrons under X-ray excitation, the quantification of surface density of the implanted amine group by the hydrazine plasma was effected by labeling with 4-trifluorobenzaldehyde (TFBA). The plasma-treated PE films were exposed to vapors from two drops of TFBA placed on the glass beads in a glass vial at room temperature. The reaction to form benzylidene linkage between the amine group on the surface with the aldehyde group of TFBA was allowed to take place for 60 min. After derivatization, the samples were pumped overnight to remove any unreacted TFBA. Since the reaction proceeded almost quantitatively, three fluorine atoms per –NH<sub>2</sub> group should be detected, which permits us to determine the ratio of amine group to total nitrogen, NH<sub>2</sub>/N.<sup>19</sup>

**Attachment of DTPA–Gd to the PE Surfaces.** The DTPA–Gd complex was coated onto the amine-functionalized PE surface as shown in Scheme 1. In a 25-mL dry flask, 50 mg of DTPA was added to 10 mL of anhydrous DMSO. In a small vessel, 21 mg of carbonyldiimidazole (CDI), as a coupling agent, was dissolved in 4 mL of anhydrous DMSO. The CDI solution was slowly added into the reaction flask while stirring, and the mixture was further stirred at room temperature for 2 h. The solution then was injected into a dry glass tube sealed

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**Figure 1.** X-ray photoelectron spectra of the PE surface (a) before plasma treatment and (b) after hydrazine plasma treatments for 5 min at a power of 25 W.

with a rubber septum which had a piece of the hydrazine plasma treated PE film. After being allowed to react for 20 h, the PE sample was carefully washed sequentially with DMSO, methanol, and water, each three times. Next, the DTPA-treated PE film was soaked in a solution of 0.5 g of  $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$  in 50 mL of deionized water for 24 h at room temperature. Finally, the PE sample was washed thoroughly with water.

**XPS Measurements.** XPS measurements were performed with a Perkin-Elmer Phi 5400 apparatus. Unmonochromatized  $\text{Mg K}\alpha$  X-ray was utilized at 15 W and 20 mA, and photoelectrons were detected at a takeoff angle of  $45^\circ$  (sampling depth  $\approx 5\text{--}6$  nm). The pressure in the analysis chamber was  $10^{-8}$  Torr. The survey spectra were run in the binding energy range 0–1000 eV, followed by high-resolution spectra of  $\text{C}_{1s}$ ,  $\text{N}_{1s}$ ,  $\text{O}_{1s}$ ,  $\text{F}_{1s}$ , and  $\text{Gd}_{4d}$  regions. The  $\text{C}_{1s}$  neutral carbon peak was assigned a binding energy of 285.0 eV, according to the routine procedure in the XPS analysis of polymers, and it was used as the reference binding energy for other signals.

**Contact Angle Measurements.** Static water contact angles were measured using the sessile drop method with a Rame-Hart goniometer at room temperature. The angles were recorded within 10 s after the drop was placed on the film surface. The reported contact angle value represents an average of at least six different measurements.

**ATR-FTIR.** ATR-FTIR spectra were obtained on a ATI-Mattson, Research Series IR instrument by using a KRS-5 crystal at an incident angle of  $45^\circ$  (analysis depth of about 1.5 mm). The sample size was  $7 \times 70$  mm. The apparatus was purged with  $\text{N}_2$  and the frequency scale calibrated with a He–Ne laser to an accuracy of  $0.01\text{ cm}^{-1}$ . In a typical measurement, 250 scans were collected with a  $2\text{-cm}^{-1}$  resolution.

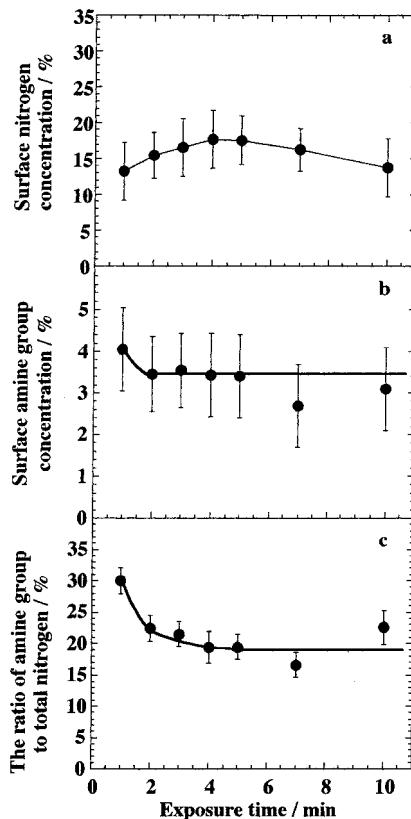
**Surface Roughness Evaluation.** The surface roughness was determined using AFM in the Nanoscope III instrument. The constant force mode was used. The commercially etched silicon tips were employed for morphology evaluation. The

mean roughness of each film was determined by measuring surface vertical height variation relative to the geometric center plane of the AFM imaging; hence each surface roughness value represents an average of three separate measurements from different areas.

**MR Scanner Measurements.** MR signal enhancement by the DTPA–Gd complex-coated PE film was assessed by MR scanner measurements. Fatfree yogurt was used as a tissue-mimic, commonly called a phantom in the MRI literature, to perform in vitro evaluation of the coating for MRI. The coated PE films were held stationary in beakers filled with the phantom. The samples were imaged using both 2D spin-echo (SE) and 2D spoiled gradient-recalled echo (SPGR) sequences on a 1.5 T scanner (Signa, GE Medical Systems, Milwaukee, WI). 2D SE scan parameters were  $\text{TR/TE} = 200/15$  ms (time of repetition/time of echo),  $30^\circ$  flip angle, field of view (FOV) =  $20 \times 20$  cm, acquisition matrix =  $160 \times 256$ , receiver bandwidth (RBW) =  $\pm 16$  kHz, and slice thickness = 5 mm, where TR and TE stand for the times for repetition and echo, respectively. Spatial resolution was between 0.625 and 0.781 mm. MR signal intensities from the region of interest (ROI) of images were measured by the 2D SPGR sequence. 2D SPGR scan parameters were the same as those with 2D SE except  $\text{TR/TE} = 7.1/3.6$  ms and  $10^\circ\text{--}60^\circ$  flip angle. Contrast enhancement by the coating was obtained by normalizing the signals arising from the vicinity of the objects by the phantom background signal.

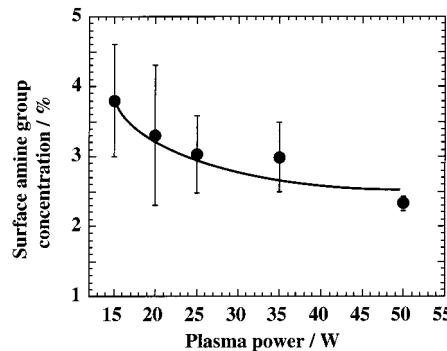
## Results and Discussion

**Surface Atomic Composition of the PE Surface Treated by Hydrazine Plasma.** The XPS survey spectra of PE at a takeoff angle of  $45^\circ$ , before and after the hydrazine plasma treatments are shown in Figure 1. There are only one dominant  $\text{C}_{1s}$  peak at the binding



**Figure 2.** Surface nitrogen concentration as a function of hydrazine plasma treatment time (a), surface primary amine group concentration as a function of plasma treatment time (b), and the ratio of primary amine group to total nitrogen as a function of plasma treatment time (c), all at a plasma power of 25 W.

energy of 285.0 eV and one minor O<sub>1s</sub> peak at 532 eV without any indication of nitrogen for the sample without the plasma treatments. The surface atomic composition for carbon and oxygen was 97.4% and 2.6%, respectively. After the hydrazine plasma treatments and the subsequent derivatization with TFBA, the XPS spectrum (trace b) shows a significant fluorine signal at 699 eV and nitrogen signal at 400 eV. The relative surface atomic compositions for nitrogen and fluorine were 17.3% and 10.2%, respectively. We present this as clear evidence for surface amination on PE by the hydrazine plasma. In Figure 2 are displayed three profiles of surface concentrations as functions of the plasma treatment time. They are the surface nitrogen concentration (a), surface primary amine group concentration (b), and the ratio of amine group to total nitrogen (c) from the top to the bottom, respectively. The surface nitrogen concentration is found in a range of 13–17%; it increases slightly with the treatment time initially and reached a maximum between 4 and 5 min and then decreases at longer treatment times. This seems to indicate that the surface nitrogen content is the result of a competition between the hydrazine plasma induced amine group implantation and plasma etching of the surface. At the early stages of the plasma treatment, it is likely that the surface group implantation is dominant because of a low surface group concentration, whereas the etching effect becomes progressively dominant in the later stages with a possible saturation of implantable groups, resulting in a decrease of surface nitrogen group.



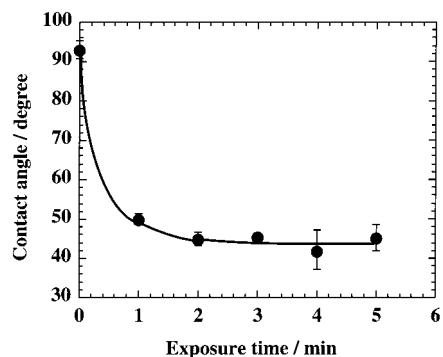
**Figure 3.** Surface amine group concentration as a function of plasma power after 5 min of exposure.

The profile of the surface primary amine group concentration, shown in (b), is estimated by converting from the observed surface fluorine concentration resulting from the derivatization with TFBA. The amine group concentration is in the range from 3% to 4%; it reaches about 4% after 1 min and then settles down to a plateau value around 3%. The ratio of primary amine group to total nitrogen is displayed at the bottom (c), which can be regarded as a measure of the amine group implantation selectivity. It decreases from 32% at 1 min of the plasma treatment to a plateau value around 21% within 2 min. These values are slightly higher than those obtained by the treatment with ammonia plasma.<sup>13</sup> We can surmise from these results that amine group implantation takes place after only a brief period of exposure of a few minutes to the hydrazine plasma, and further exposure just results in a greater extent of etching.

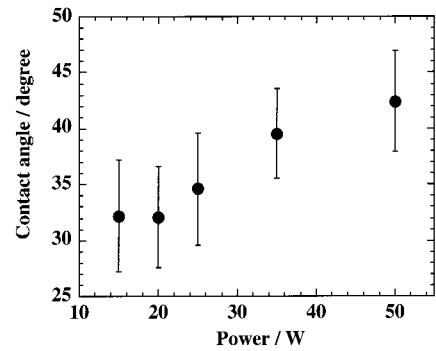
Next, we examine the effect of the plasma power. The amine group concentration profile relative to the plasma power is shown in Figure 3. It is rather clear that the efficiency of amine group implantation decreases with increasing plasma power, presumably owing to the greater role of etching by positive ion bombardment whose intensity increases with plasma power. Hence, the trend is seen rather parallel to that with the treatment time.

To quantify the absolute surface density of amine group, a separate experiment with ion exchange was performed. A fluorescence dye, sodium salt of 2-*N*-(7-nitrobenz-2-oxa-1,3-diazol-4-yl)aminoethanesulfonic acid (NBD taurine), was used to exchange the counterion on ammonium salt on the surface, whereby we could estimate the surface densities of amine groups. They were found to be in a range of 8–19 groups/nm<sup>2</sup> for the plasma power of 100–25 W, respectively. It should be emphasized that these estimates are based on the assumption that only ion-exchangeable cations under the conditions are ammonium ions arising from the implanted amine groups.

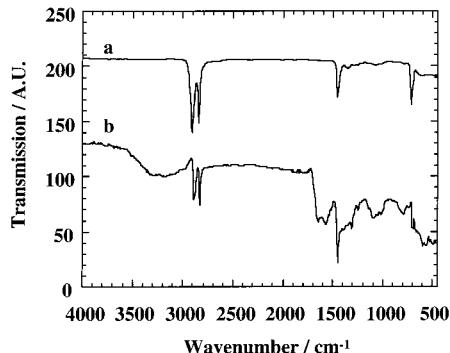
**Wettability of the Film Surface.** To gauge the water wettability, a measure of hydrophilicity, of the film surface, static water contact angles were measured for the film samples with different plasma treatment times and plasma powers. Figure 4 shows the static water contact angles as a function of plasma treatment time. Before the plasma treatment, the water contact angle was 92°. After the treatment for 1 min, the contact angle decreased significantly to about 50°. The ensuing longer treatment time had only a minor effect in



**Figure 4.** Water contact angle on PE as a function of hydrazine plasma treatment time at a power of 25 W.



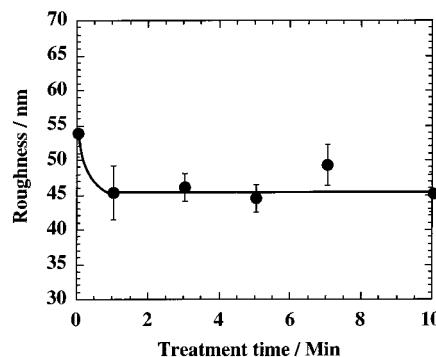
**Figure 5.** Water contact angle on PE as a function of plasma power after 5 min of exposure.



**Figure 6.** ATR-FTIR spectra of PE film: (a) untreated PE film and (b) differential spectrum between PE film treated with hydrazine plasma for 3 min and untreated PE film.

decreasing the contact angle. Thus, it is reasonable to conclude that the PE surface transformed from a hydrophobic to a moderately hydrophilic surface with the hydrazine plasma treatments. Figure 5 shows the contact angle as a function of plasma power. With increasing plasma power, the contact angles of PE increased slightly but it is apparent that the surface still remains moderately hydrophilic, even in higher plasma treatment powers. These results can only mean that the lower is the plasma power; the more favorable is the formation of a hydrophilic surface by the hydrazine plasma.

**ATR-FTIR Spectroscopy.** To investigate the chemical moieties formed on the PE surface after the plasma treatments, ATR-FTIR measurements were carried out. Figure 6 shows the ATR-FTIR spectra of the untreated and treated surfaces. The spectrum of untreated PE (trace a) shows characteristic peaks of PE ascribed to asymmetric  $\text{CH}_2$  stretching, symmetric  $\text{CH}_2$  stretching,

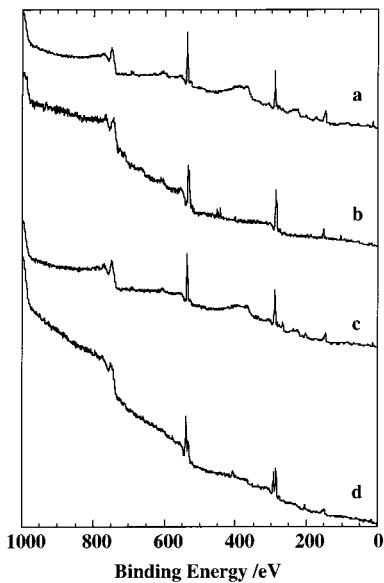


**Figure 7.** Root-mean-square surface roughness of PE films as a function of hydrazine plasma treatment time.

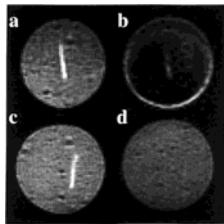
asymmetric  $\text{CH}_3$  bending, and  $\text{CH}_2$  rocking at 2914, 2846, 1462, and  $731\text{ cm}^{-1}$ , respectively. After the plasma treatment for 3 min, several small broad peaks appeared at 3300, 1664, and  $1554\text{ cm}^{-1}$ , which are assigned to N–H stretching, amide C=O stretching, and N–H rocking and C–N stretching of the amine group, respectively. Upon subtraction of the untreated PE spectrum from the treated PE one, the differential spectrum (trace b) shows clearly the characteristic peaks from amine and amide groups at 3328, 1664, and  $1557\text{ cm}^{-1}$ , indicating that the surface is mainly comprised of primary amine and amide groups, both hydrophilic, which is consistent with the contact angle results.

**Surface Roughness.** Changes in the surface roughness of the samples with respect to the treatment duration were probed by AFM. A plot of the root-mean-square surface roughness as a function of treatment time at a constant plasma power of 25 W is displayed in Figure 7. The surface roughness is shown to decrease abruptly from the untreated sample within a short initial period of 1 min and then quickly settles to an asymptote. Apparently, plasma etching to be dominant after the first few minutes has a smoothing effect even at a power of 25 W by removal of weak boundary layers. The AFM images for the untreated PE film and the plasma-treated one for 5 min also show that the surface morphology has undergone changes after the plasma treatment, graphically demonstrating the smoothing effect of the plasma treatment. Simultaneously, it is entirely possible that some low molecular weight species deposit on the polymer surface. This has a deleterious effect on surface functionalization since some of the implanted groups on the surface composed of these low molecular weight species are not completely removed by solvents in further purification steps.

**Chemical Attachment of DTPA–Gd to the Aminated Surface.** The chemical attachment of DTPA to the aminated PE surface was carried out by the formation of amide linkage between the implanted primary amine group and one of five carboxyl groups of DTPA, catalyzed by a coupling agent. The coordination of DTPA with  $\text{Gd}^{3+}$  follows subsequently by incubating in an aqueous solution of  $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ . Figure 8 shows the XPS spectra of PE films coated with DTPA–Gd complex (traces a, b, and c) and that of pure DTPA–Gd complex (trace d). The appearance of a Gd photoelectron peak at a binding energy of 146 eV confirms the chemical attachment of DTPA–Gd complex on the treated surfaces, and we collect the relative atomic compositions of PE films before and after attachment of DTPA–Gd



**Figure 8.** X-ray photoelectron spectra of PE film coated with DTPA-Gd: (a) PE film treated by hydrazine plasma for 5 min at power of 15 W and coated with 4.1%  $\text{Gd}^{3+}$ , (b) PE film treated by hydrazine plasma for 5 min at power of 25 W and coated with 1.1%  $\text{Gd}^{3+}$ , (c) PE film treated by hydrazine plasma for 5 min at a power of 50 W and coated with 1.8%  $\text{Gd}^{3+}$ , and (d) pure DTPA-Gd complex.

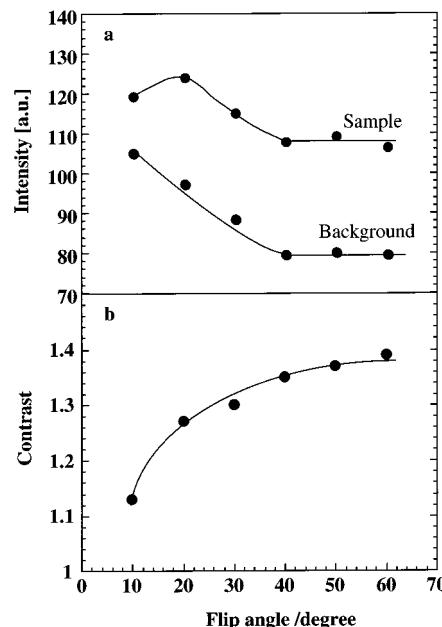


**Figure 9.** Typical MR images of PE samples in a phantom by using spin-echo technique: (a) PE film treated by hydrazine plasma for 5 min at a power of 15 W and coated with 4.1%  $\text{Gd}^{3+}$ , (b) PE film treated by hydrazine plasma for 5 min at a power of 25 W and coated with 1.1%  $\text{Gd}^{3+}$ , (c) PE film treated by hydrazine plasma for 5 min at a power of 50 W and coated with 1.8%  $\text{Gd}^{3+}$ , and (d) the control PE film without plasma treatment.

**Table 1. Surface Chemical Composition of PE Films before and after Attachment of DTPA-Gd**

CW plasma power/time	before attachment			after attachment			Gd%
	C%	O%	N%	C%	O%	N%	
15 W/5 min	73.0	10.2	16.7	61.1	32.5	2.3	4.1
25 W/5 min	70.6	8.5	20.8	60.3	34.9	3.7	1.1
50 W/5 min	71.4	9.3	16.7	61.9	30.7	5.6	1.8

complex in Table 1. On comparison of the samples before and after the attachment, it is quite obvious that the surface chemical compositions of PE films have undergone a substantial change; the carbon atomic concentration decreased from about 70% to about 61% and that of oxygen increased from around 10% to 31%, while that of nitrogen decreased from 17% to 3%. The observed similarity of all four spectra makes it clear that the surface compositions of the coated films are close to that of pure DTPA-Gd complex. These data are taken then as evidence that the coatings of DTPA-Gd complex on the surface of PE film were formed after the covalent linking of DTPA and subsequent coordination with  $\text{Gd}^{3+}$ .



**Figure 10.** (a) MR signal intensity measured for PE film with 1.1%  $\text{Gd}^{3+}$  at the surface and the background as a function of flip angle; (b) MR signal contrast in the vicinity of the same sample as a function of flip angle.

**MR Imaging Evaluation of Coated Samples.** All samples were placed in a yogurt-filled beaker and then MR images were acquired. Food-grade fatfree yogurt as a tissue-mimicking material (phantom) was chosen because its relaxation rates are roughly equivalent to those of human tissues. The results of in vitro tests are displayed in Figure 9. All three PE films coated by DTPA-Gd complex show clear MR signals by using the spin-echo technique with  $\text{TR}/\text{TE} = 200/15$  ms where  $\text{TR}$  and  $\text{TE}$  are the times for repetition and echo, respectively, while controlled, bare PE film does not give rise to any MR signal. The sample with Gd atomic concentration of 4.1% shows the strongest MR signal, indicating that the enhancement of the MR signal is dependent on the concentration of  $\text{Gd}^{3+}$  ion. The MR signal intensity measured in a region of interest in the phantom and that measured in the background as a function of flip angle for the 1.1% Gd sample is shown in Figure 10a. It can be seen that the MR signal intensity of the sample reaches its maximum at around a flip angle of 20°. The relationship between the image contrast and flip angle is also displayed in Figure 10b. The contrast increases monotonically with increasing flip angle in the range of 10°–60° and reaches an optimum angle in a range of 50°–60°. The flip angle ( $\theta$ ) at which the signal intensity reaches a maximum is related to  $\text{TR}$  and  $T_1$  values of the sample by the Ernst equation:<sup>20</sup>

$$\cos \theta = \exp(-\text{TR}/T_1) \quad (1)$$

By determination of the  $\text{TR}$  value and the flip angle at which the maximum signal intensity occurred,  $T_1$  relaxation time can be estimated. The flip angle at which the peak signal intensity occurred was 20° for a sample at a  $\text{TR}$  of 7.1 ms. Hence, the  $T_1$  relaxation time is determined as 114 ms. Since the scans were obtained

over a range of flip angle from 10° to 60° in 10° increments, the error in  $T_1$  determined by the Ernst angle should be taken into account. Thus, the  $T_1$  relaxation time for the sample is found to be in a range of 114–383 ms corresponding to 20° and 11° of the Ernst angle. These results indicate that the MR signal was significantly enhanced and  $T_1$  relaxation time shortened in the vicinity of the coated PE samples compared to the corresponding  $T_1$  relaxation time of about 1200 ms for the phantom.

### Conclusions

The surface amination of PE was carried out by the hydrazine plasma treatments. XPS results revealed that lower power (10–15 W) and shorter treatment time (1–2 min) gave rise to greater concentrations of amine group on the PE surface. Surface wettability with water for the PE surface clearly demonstrates that the initial hydrophobic surface transforms to a moderately hydrophilic one after the plasma treatments. ATR-FTIR results confirm that amine and amide groups, both hydrophilic, were formed on the PE surface after the plasma treatments. Surface roughness by AFM indicates that the plasma treatment has a smoothing effect for the PE surface up to a power of 25 W.

The MR signal-enhancing coating materials were prepared by chemical attachment of DTPA–Gd complex to the surface of PE film treated with the plasma. XPS measurements confirm that the DTPA–Gd<sup>3+</sup> complex is successfully attached to the PE surface. In the phantom experiments with fatfree yogurt, the DTPA–Gd complex coated samples showed a strong MR signal and a clear contrast between the coated material and the background. Moreover,  $T_1$  relaxation time in the vicinity of the surfaces of coated samples was shown to decrease significantly. Thus, we have successfully demonstrated the focal point of this study, namely, making PE catheters visible by MRI used for endovascular interventions or therapy.

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