

Plasma-Induced Graft Polymerization of Poly(ethylene glycol) on Poly(methyl methacrylate) Surfaces for Improving Antistatic Property

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Received 5 November 2009; accepted 14 March 2010

DOI 10.1002/app.32453

Published online 27 May 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Ar plasma-induced graft polymerization of poly(ethylene glycol) (PEG) on Ar plasma pretreated poly(methyl methacrylate) (PMMA) surfaces was carried out to improve the antistatic properties. The surface composition and microstructure of the PEG-grafted PMMA surfaces from plasma induction were characterized by attenuated total reflectance Fourier transfer infrared (ATR-FTIR) spectroscopy, water contact angles (CA), and atomic force microscopy (AFM) measurements. The measurements revealed that the antistatic properties can be

remarkably improved with the surface resistivity of PEG-grafted PMMA surface decreasing significantly by 3–6 orders of magnitude, with the optimum condition for polymerization grafted onto the Ar plasma pretreated PMMA surface being 40 W for RF power and 3 min for glow discharge time. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 943–949, 2010

Key words: plasma treatment; surface modification; PMMA; PEG; antistatic property

INTRODUCTION

Poly(methyl methacrylate) (PMMA) has been widely used in many technological fields for the high insulation,¹ excellent chemical inert,² high mechanical strength,³ lightweight, and high light transmittance.⁴ However, the industrial applications of PMMA have been limited due to the relatively hydrophobic surface^{5–8} and high static charges.^{9,10} Therefore, to improve the poor electrical conductivity, modification of the PMMA surface is necessary. Over the past decade there have been rapid exploration and commercialization of plasma technology, a dry and low temperature process that is environmentally benign and easy to handle,^{11,12} to improve the surface properties of polymeric materials. Among others, cold plasma technique, which is one of the processes allowing covalent grafting of functional groups, monomers or macromolecular compounds to polymeric surfaces,^{13,14} has its own advantages: this technique can be performed on

most substrate surfaces, using both organic molecules and monomers, without affecting the bulk properties of the substrates.^{15,16} On the other hand, Poly(ethylene glycol) (PEG) is one of the most effectively and widely used polymers for surface modification because of its unique properties such as hydrophilicity, flexibility, high exclusion volume in water, non-toxicity, and immunogenicity.^{17–21} Moreover, PEG can provide a polymer with an increased moisture affinity, which in turn, promotes the dissipation of static charges.²² For instance, Kang²³ reported that the electrical conductivity of polypyrrole could be enhanced by using PEG as a polymer additive during the oxidative polymerization. Based on above consideration, coating Ar plasma pretreated PMMA with PEG is an interesting approach to decrease the static charge.

In this work, we carried out the Ar plasma-induced graft polymerization of PEG on the Ar plasma pretreated PMMA surface. The effect of low plasma treatment on the static property was investigated, with the optimum treatment conditions for antistatic property being obtained.

EXPERIMENTAL

Materials

PMMA plates with a thickness of 1 mm and a diameter of 10 mm were obtained from Xi'an Organic

Additional Supporting Information may be found in the online version of this article.

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 10675078.

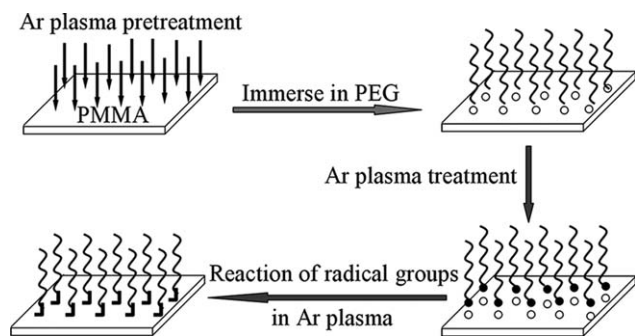


Figure 1 Schematic representation of the process of Ar plasma-induced graft polymerization of PEG on the Ar plasma pretreated PMMA surface.

Chemical Co., (China). PEG with a molecular weight (M_w) of 200 was obtained from Aladdin-reagent Co., (Beijing, China). Argon of purity >99.99% was used to generate the glow discharge for the plasma pretreatment and the graft polymerization of the PEG onto the PMMA surfaces.

Graft polymerization procedure

The process for Ar plasma-induced graft polymerization of PEG onto the Ar plasma pretreated PMMA surface includes three main steps: (a) Ar plasma pretreatment of the PMMA surface; (b) solution coating of PEG on the plasma pretreated PMMA surface; and (c) Ar plasma-induced graft polymerization of PEG on the PMMA surface. After Ar plasma pretreatment and exposure to air for approximate 2 h, the PMMA plates were immersed in a PEG solution for approximate 60 s. After drying for 30 min at 40°C in vacuum, the plates were exposed to the Ar plasma to induce the PEG graft polymerization^{24,25}, as shown in Fig. 1. At the end of the Ar plasma pretreatment or Ar plasma-induced graft polymerization, each plate was immersed in acetone at 45°C with refluxing for at least 12 h, followed by rinsing in copious amounts of distilled water to remove the residual amount of physically absorbed homopolymer and macromonomer.

Plasma reactor

Ar plasma treatments (both for activation and for graft polymerization) were performed in radio frequency (RF) plasma reactor, built of a vacuum chamber (1500 cm³). PMMA samples were fixed to a custom-made sample holder and kept at a distance of 8 cm from the RF electrodes, which were externally connected to a 13.56 MHz radio frequency (RF) generator (SY-300, obtained from the Institute of Microelectronics, Chinese Academy of Science, Beijing, China). The chamber pressure was reduced below 1.0 Pa using a vacuum pump. Argon was

introduced into the chamber under varying pressure by throttling the outlet valve. Figure 2 is the schematic diagram of the plasma treatment system.

Infrared spectroscopy

Attenuated total reflectance Fourier transfer infrared (ATR-FTIR) spectra of the pristine PMMA plate and PMMA with plasma-grafted PEG were obtained from an EQUI NOX55 FTIR spectrometer (Bruker Co., Germany). The samples were equipped with a high pressure clamp and ZnSe crystal plate appropriate for the application. All spectral data were obtained by cumulating 64 scans at a resolution of 4 cm⁻¹.

Water contact angle measurement

The static water contact angles were measured at 25°C and 55% relative humidity by OCA20 video-based contact angle instrument (Dataphysics Co., Germany). Multiple readings of at least five points were obtained with the deviation range within $\pm 0.1^\circ$, and their averaged value was adopted.

Surface resistivity measurement

The surface resistivity of pristine PMMA plates and PMMA with plasma-grafted PEG were measured with a ZC-36 ohmmeter (The Sixth Ammeter Co., Shanghai, China) for 10¹⁷ super high resistivity.

Topography of the surface

The topography of the polymer surface was studied by atomic force microscope (AFM) (WET-SPM-9500J3, Shimadzu Co., Japan). The images were acquired at the room temperature, using a standard silicon micro cantilever (OMCL-TR800 PSA-1) with force of 3 N/m and resonance frequency of 75 kHz in the tapping mode.

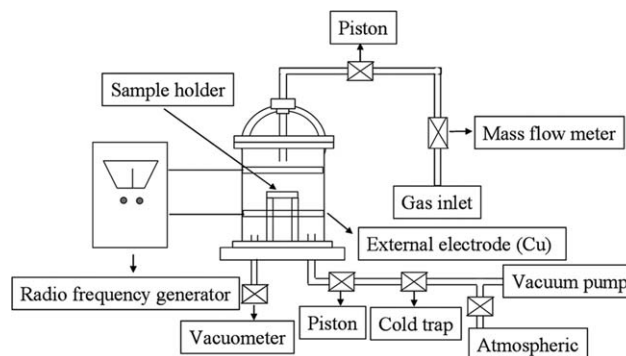


Figure 2 Schematic diagram of plasma treatment system.

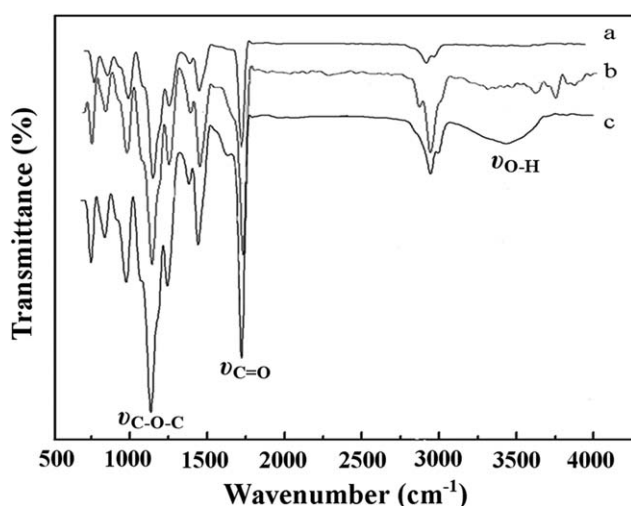


Figure 3 ATR-FTIR spectra of (a) Ar plasma pretreated PMMA, (b) PEG-grafted PMMA without plasma pretreated, and (c) PEG-grafted PMMA with plasma pretreated.

RESULTS AND DISCUSSION

ATR-FTIR analysis

Figure 3 shows the respective ATR-FTIR spectra of the plasma preactivated PMMA (a), unactivated PMMA modified by PEG (b) and preactivated PMMA modified by PEG (c). It is worth noting that the spectra in Figure 3(a) and those in Figure 3(b) are similar, indicating the failure in PEG graft polymerization. We can conclude that a preactivation of the PMMA to increase its surface energy is a necessary step for the uniform sample coverage and for the success of the graft polymerization. In the preactivated PMMA modified by PEG [Fig. 3(c)], the main bands of PEG can be detected at 1140 cm^{-1} (C—O—C stretching vibration) and at 3433 cm^{-1} (O—H stretching vibration), confirming the success in the graft polymerization.

Effect of Ar plasma pretreatment conditions on hydrophilicity of PMMA surface

When the PMMA is treated with the inert gas plasma (in the present case Ar), the chemical bonds break (with consequent formation of low molecular weight segments) due to the plasma species bombardment. Some of these activation radicals decay by crosslinking, but those residues can react with the atmospheric oxygen to form a variety of polar groups such as hydroxyl and carbonyl groups. These polar groups incorporate with moisture through hydrogen bonding and help moisture penetrate and bind on the PMMA surface, to improved the sample's hydrophilicity.²⁶

Figure 4 shows the effect of Ar plasma pretreatment time on the water contact angles of PMMA surface (Ar pressure = 50 Pa and RF power = 40 W).

The original untreated sample exhibits a slightly hydrophilic nature characterized by the high water contact angle of 80° . However, the surface wettability is significantly increased following the plasma treatment. Under the given plasma conditions, a time of 90 s is long enough for good hydrophilicity (water contact angle is 46°). In other words, improving wettability achieves more rapidly during the initial seconds. When the treatment time is longer than 3 min, the contact angle is slightly increased and remains at a relatively constant level, suggesting that the physical and chemical changes induced by plasma treatment are in a balance state. The change in water contact angle with the treatment time should be attributed to both the polar groups introduced onto the PMMA surface and the increased surface roughness. It could be concluded that plasma treatment time shorter than 3 min improves the surface hydrophilicity effectively, and the elongation of treatment time does not bring any further increase of hydrophilicity.

To investigate the effect of Ar pressure on hydrophilicity of PMMA surface, we analyzed the performances of the water contact angle and the working gas pressure (treatment time = 3 min and RF power = 40 W) (Fig. 5). With Ar pressure increasing, the contact angle decreases greatly from 80° to 47° , while there is little change in contact angle above 40 Pa. Such behavior suggests that higher pressure has no significant effect on the wettability of PMMA surface. When the system is under relatively high gas pressure, the extremely dense plasma is produced, resulting in collision of the free radicals. The kinetic energy decreases down to low energy, which is far from the threshold energy E_{th} , thus the ion penetration into the surface being suppressed. As a result, the number of polar groups decreased (the less polar

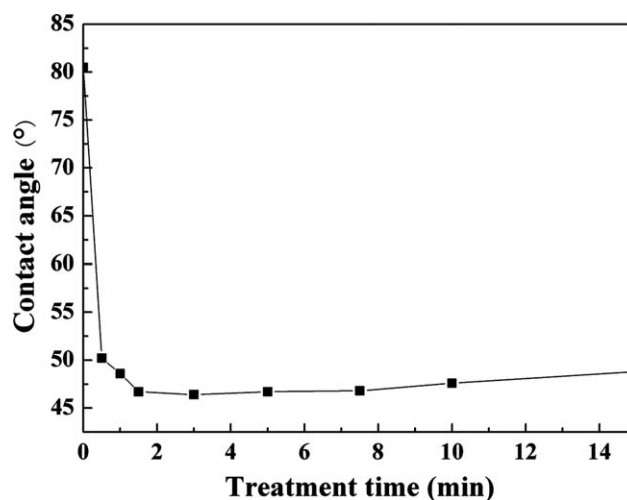


Figure 4 Effect of Ar plasma treatment time on the water contact angle of PMMA surface (RF power = 40 W, Ar pressure = 50 Pa).

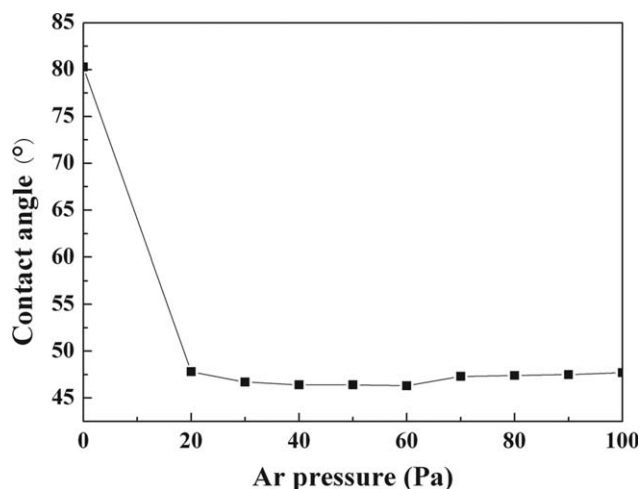


Figure 5 Effect of Ar pressure on the water contact angle of PMMA surface (Treatment time = 3 min, RF power = 40 W).

groups, the higher contact angle). So the appropriate pressure is 40–60 Pa.

Meanwhile, we also study the effect of Ar plasma RF power on the water contact angles of PMMA surface (treatment time = 3 min and Ar pressure = 50 Pa) (Fig. 6). The results indicate that the contact angle decreases gradually with increasing discharge power. A quantity of argon molecules acquired more energy resulting from the increase of discharge power, thus enhancing the ionization of argon and the average energy of active particles, and hence further raising the possibility of the reaction and the intensity of active particles with PMMA. Consequently, the effect of surface modification is reinforced and the surface reaction reaches equilibrium below 40 W.

Based on the above results, Ar plasma pretreatment RF power of 40 W, Ar pressure of 50 Pa and pretreatment time of 3 min may be the optimal condition for improving the hydrophilicity of PMMA surface. With being immersed in the PEG solution, a thin layer of the PEG macromonomer can be coated evenly on the surface of hydrophilic PMMA.

Effects of Ar plasma conditions on hydrophilicity and surface resistivity for PEG-grafted PMMA

PEG has been reported to be good hydrophilicity, high water-solubility for hydroxyl group. Therefore, the surface hydrophilicity can be improved when PEG is grafted onto PMMA surface. When they are grafted onto PMMA surface, hydrophilic groups (indicating —OH) arrayed placing in air can attract water from the environment and combine with water molecules by H-bond. The presence of a thin layer of water on the surface provides the material with a slight conductivity that corresponds to a

decrease in surface resistivity. In previous experiments, it was found that working pressure made no great difference to the surface resistivity of PEG-grafted PMMA surface. So the effects of PEG concentration, plasma treatment time and RF power on the contact angles and surface resistivity are investigated in this experiment.

Figure 7 shows the dependence of the surface resistivity and water contact angles on the Ar plasma-induced graft polymerization concentration (Ar pressure = 50 Pa, polymerization time = 3 min, RF power = 40 W). The surface resistivity decreases to $1.0 \times 10^{10} \Omega/\text{sq.}$ with PEG concentration increased up to about 15 wt %. However, there is no remarkable reduction with PEG concentration increased from 15 wt % to 50 wt %. In fact, Ar plasma treatment increases the surface energy of PMMA, and PEG covers the surface with a uniform thin film after immersion and solvent evaporation. At the high concentration, excessive PEG is weakly bond to the PMMA surface and probably weakly crosslinked, almost totally elute off from PMMA surface during the washing step so that grafting PEG onto PMMA surface is restrained.

Figure 8 shows the dependence of the surface resistivity and water contact angles on the plasma-polymerization time of the Ar plasma-induced graft polymerization of PEG (Ar pressure = 50 Pa, RF power = 40 W). It can be seen that surface resistivity and contact angles on the PMMA surface decrease with increasing Ar plasma-induced polymerization time. At a graft polymerization time longer than 3 min, the surface resistivity is slightly increased, but the water contact angles of the PEG-grafted PMMA surface levels off at approximate 54° . This phenomenon may be attributable to the PEG-grafted degree on the PMMA surface. With increasing Ar

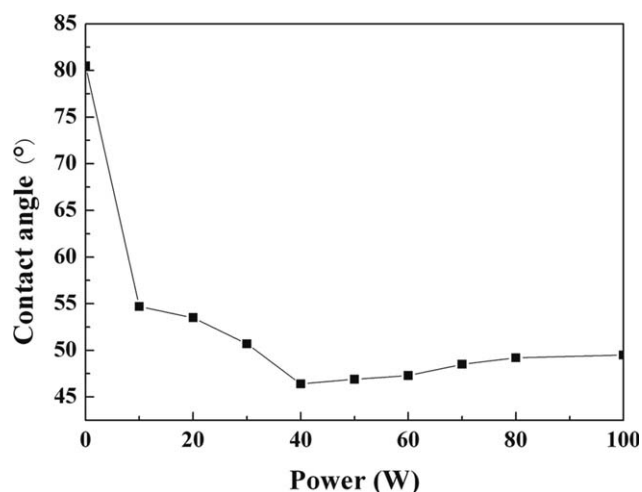


Figure 6 Effect of the RF power on the water contact angle of PMMA surface (Treatment time = 3 min, Ar pressure = 50 Pa).

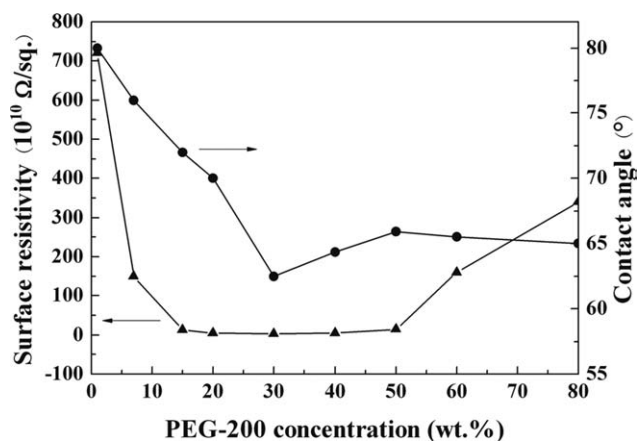


Figure 7 Effect of PEG concentration for polymerization on the water contact angle and surface resistivity of the resulting PEG-grafted PMMA surface (Ar pressure = 50 Pa, polymerization time = 3 min, RF power = 40 W).

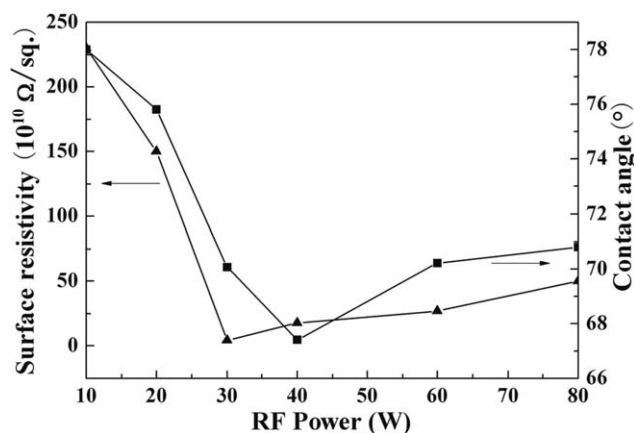


Figure 9 Effect of RF power for polymerization on the water contact angle and surface resistivity of the resulting PEG-grafted PMMA surface (Ar pressure = 50 Pa, polymerization time = 3 min).

plasma-induced polymerization time up to about 3 min, before showing a decrease with further increase in the plasma treatment time, the graft degree on the PMMA surface increases. When the plasma-induced polymerization time is longer than 3 min, the grafting degree basically hold unchanged. This shows that graft already gets saturation. In fact, in the process of plasma-induced polymerization, plasma-etching process and plasma-polymerization process take place simultaneously with mutual competition. When the plasma-induced polymerization time goes beyond some time, the equilibrium between etching and polymerization may become the main process during plasma treatment.

Figure 9 shows the dependence of the surface resistivity and water contact angles on the RF power of the Ar plasma-induced graft polymerization of PEG. The surface resistivity and water contact angles decrease with increasing RF power for polymerization. However, the surface resistivity and water con-

tact angles increase somewhat at RF power higher than 40 W. Too high an RF power used for polymerization may have resulted in an increased extent of crosslinking in the PEG layer and gel fraction. As a consequence, the hydrophilicity of the PEG-grafted PMMA surface is slightly reduced. Along with increasing the discharge power, the activated particles increase, so does the amount of PEG grafted onto the PMMA surface. But too high power will inactivate those activated particles, thus the amount of immobilized PEG decreasing instead.

Based on the Figures from 7 to 9, it can be seen that the trend of surface resistivity is similar to that of contact angle after PEG is grafted onto PMMA surface. This indicates that there are some connections between antistatic property and hydrophilic character. After Ar plasma treatment, the polar groups such as —OH are introduced onto the surface, which will incorporate with moisture through hydrogen bonding and help moisture penetrate and bind on the surface. Under the action of water molecules,

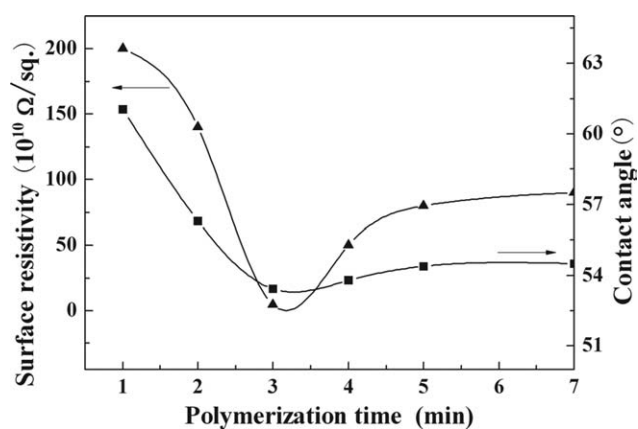


Figure 8 Effect of Ar plasma glow discharge time for polymerization on the water contact angle and surface resistivity of the resulting PEG-grafted PMMA surface (Ar pressure = 50 Pa, RF power = 40 W).

TABLE I
Surface Resistivity Measured on PEG-Grafted PMMA with Ar Plasma Pretreated and PEG-Grafted PMMA Without Plasma Pretreated Under the Different Glow Discharge Conditions

Graft conditions by plasma	Surface resistivity (Ω/sq.)	
	With plasma pretreatment	Without plasma pretreatment
—	—	5.0×10^{15}
—	1.8×10^{15}	—
20%, 3 min, 40 W, 50 Pa	4.5×10^{10}	3.0×10^{12}
30%, 3 min, 40 W, 50 Pa	2.2×10^{10}	2.2×10^{12}
40%, 3 min, 40 W, 20 Pa	8.0×10^9	2.0×10^{11}
40%, 3 min, 40 W, 30 Pa	6.0×10^{10}	3.5×10^{11}
40%, 3 min, 50 W, 50 Pa	4.3×10^{12}	7.0×10^{12}
40%, 3 min, 70 W, 50 Pa	2.1×10^{11}	8.0×10^{11}

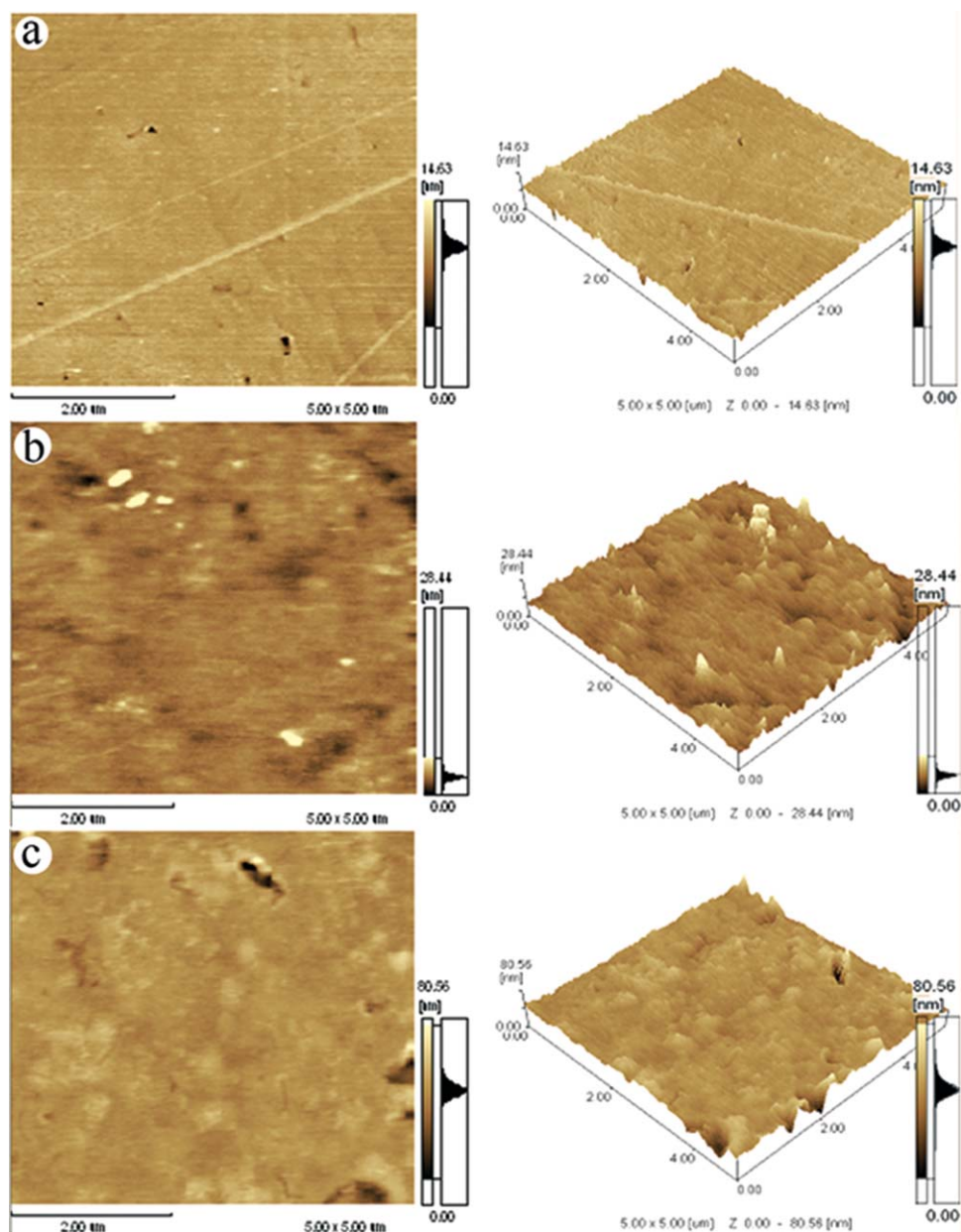


Figure 10 AFM images of (a) the pristine PMMA surface, (b) Ar plasma pretreated PMMA, and (c) the PEG-grafted PMMA surface (Ar pressure = 50 Pa, polymerization time = 3 min, and RF power = 40 W). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

these polar groups will also generate ionization and a structural layer of conduct electricity on the surface, which enhance the electrostatic dissipation. Therefore, the improved surface wettability will decrease the accumulation of electrostatic charges.

Effect of Ar plasma pretreatment on surface resistivity for PEG-grafted PMMA

In the procedure of PMMA surface modification discussed in this article, the preactivation played an important role in surface resistivity. Table I shows the differences between preactivated PMMA surface modified by PEG and unpreactivated PMMA surface

modified by PEG in surface resistivity. The surface resistivity of PEG-grafted PMMA with plasma pretreatment is lower in comparison with that of PEG-grafted PMMA without plasma pretreatment. This phenomenon can be attributed to the diffusion of low mass oxidized degradation products into polymer bulk and the orientation of polar groups on modified macromolecular chains toward the PMMA surface, which is beneficial to release the static charge.

Surface topography of the samples

Figure 10 shows the AFM image of the untreated PMMA surface [Fig. 10(a)], the Ar plasma pretreated

PMMA (Ar pressure = 50 Pa, Treatment time = 3 min, and RF power = 40 W) [Fig. 10(b)] and the PEG-grafted PMMA (Ar pressure = 50 Pa, polymerization time = 3 min, and RF power = 40 W) [Fig. 10(c)]. As seen in Figure 10, the pristine PMMA has a smooth surface with no distinguishable features, with an average surface roughness value, R_a , of approximately a 14.6 nm [Fig. 10(a)], while after plasma treatment a large number of nanoscale depressions are created on the sample surface. The morphology of the PMMA surface exhibits a roughness comparable to that of the pristine PMMA, with a R_a value of approximately 28.4 nm. After the PEG graft polymerization on the PMMA surface [Fig. 10(c)], the morphology of the surface becomes fairly roughened, with R_a values increased to approximately 80.6 nm.

CONCLUSIONS

Ar plasma-induced graft polymerization of PEG macromonomer on the Ar plasma-pretreated PMMA surface has been successfully carried out. The preactivation process was investigated in terms of plasma treatment time, Ar pressure and RF power. The results showed that the optimal conditions for plasma pretreatment were 3 min, 50 Pa, and 40 W. Moreover, it had been systematically investigated the effects of the PEG concentration, polymerization time, and RF power of the plasma graft-polymerized PEG on the PMMA surface on the water contact angle and surface resistivity. Surface resistivity measurements revealed that the surface resistivity of PEG-grafted PMMA surface decreased significantly by 3–6 orders of magnitude in comparison with Ar plasma treated PMMA (about $10^{15} \Omega/\text{sq.}$). The results clearly indicated that plasma-induced graft polymerization of PEG is a practical and successful method for antistatic surface modification of materials.

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