Polymer Surfaces and Interfaces: Characterization, Modification and Application, pp. 83–90
K. L. Mittal and K.-W. Lee (Eds)

Tenaciously bound hydrophilic coatings on polymer surfaces

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Revised version received 18 March 1996

Abstract—Hydrophilic polymer surfaces are desirable for many applications, such as adhesion and wettability. In this study, we have developed a tenaciously bound hydrophilic surface coating which can be applied to a hydrophobic polymer using a plasma treatment process. In this process, porous polyethylene (PE) was used and pretreated with the plasma discharge of an oxidizing gas, e.g. carbon dioxide. The treated surface, containing mainly anionic groups, was then soaked in a polycation solution, e.g. polyethyleneimine (PEI). A tenaciously bound hydrophilic coating was formed due to multiple anchors (ionic interactions) between PEI and the plasma-treated surface. The coated surface was characterized using water contact angle goniometry and X-ray photoelectron spectroscopy (XPS). Both the stability and the durability of the coating have been evaluated using various storage conditions and repeated washing in water. The coating process developed in this study is useful in many applications which require a permanent and lasting wettable polymer surface.

Keywords: Surface modification; hydrophilic coating; plasma surface treatment.

1. INTRODUCTION

There has been a dramatic increase in the use of polymeric materials in both consumer and industrial products during the last few decades. Their wide range of applications is due to their ease of fabrication into complex shapes; their low cost; wide ranges in chemical, physical, optical, and mechanical characteristics, and flexibility to modify both bulk and surface properties. In general, polymers with desired physical and mechanical properties are hydrophobic in nature. Such hydrophobic polymers often exhibit poor surface adhesion and limited applications when surface wettability is required. Thus, surface modification of polymers to improve wettability becomes important. As a result, many surface modification methods have been developed [1, 2], such as physical adsorption [3], corona discharge, plasma discharge

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treatment [4, 5], ozone exposure [6], flame treatment [7], and acid etching [8]. These processes often cause surface oxidation and create hydrophilic polar groups. However, in most cases, the modified surfaces are unstable and become hydrophobic after storage in air for several days or weeks [9–12]. The instability of the modified surface is believed to be due to the reorientation of the surface polar groups and migration of the modified polymer chains from the surface towards the bulk phase of the material [10].

The objective of this study was to develop a stable hydrophilic surface coating for polymeric materials using plasma treatment [13]. A hydrophilic polymer surface is first generated with conventional plasma discharge of oxidizing gases, such as oxygen, carbon dioxide or air. Such oxidation may create an acidic surface, containing carboxylates, ethers, and ketone groups. To stabilize this plasma-oxidized surface layer, the surface is then soaked in a solution of polycations, such as polyethyleneimine (PEI). The polycations tenaciously adsorb onto the acidic (anionic) surface, primarily via ionic interactions. The multiple anchors of the polycations to the polymer surface may prevent polymer surface reorientation and/or migration, as well as the removal of polycations from the polymer surface. As a result, a stable hydrophilic coating is obtained. The coating process, called HydroLAST™ coating, developed in this study has many advantages, such as the simplicity of the process, the ease of scale-up, no volatile organic solvents, wide applicability to most hydrophobic polymers, and stable and durable coatings.

Porous polyethylene (PE) was selected to demonstrate this tenacious, hydrophilic coating, due to its increasing demand in filters, membrane supports, wicks, and medical/diagnostic components. Some of these applications require a stable hydrophilic surface. In this study, porous PE sheets were first treated with CO_2 plasma followed by adsorption of PEI. After the coating, the retention of PEI on the coated PE was characterized using X-ray photoelectron spectroscopy (XPS). The wettability of the modified PE was characterized using water contact angle measurements. The stability of the hydrophilic coating was evaluated after storage in both dry and wet conditions at room temperature and at an elevated temperature. The durability of the coating was examined by repeated washing in water. In addition to an untreated control, a conventional hydrophilic treatment of PE using oxygen plasma was also prepared for a comparison study.

2. MATERIALS AND METHODS

2.1. Materials

Porous PE sheets with an average pore size of 15 μm and a thickness of 1.6 mm were received as a gift from Interflo Technology, Brooklyn, NY. Samples were cut into 2.5 × 5.0 cm and pre-cleaned by sonication in H_2O/isopropyl alcohol (50 : 50) solution three times for 10 min each at room temperature. The CO_2 and O_2 used in the plasma treatments were purchased from Wesco, Billerica, MA.

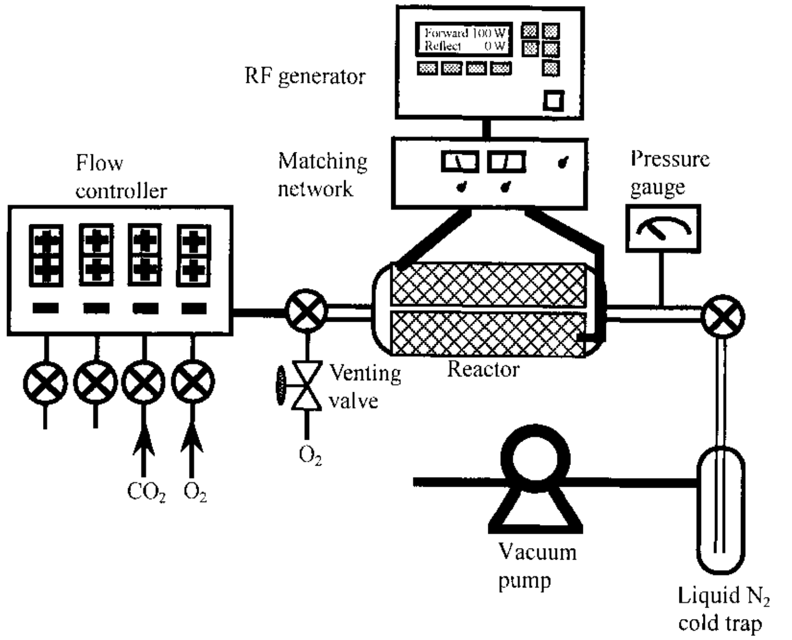

Figure 1. Plasma system for the polymer surface treatment.

PEI (Polymin® SNA, BASF Corp.) was obtained as a gift from the manufacturer and used as received. A 3% (w/v) PEI solution was prepared in deionized (DI) water. The pH of the solution was adjusted to 7.0 using 0.1 N HCl.

2.2. *Surface coating*

A radio-frequency (RF) plasma system was used for the surface treatments (see Fig. 1). The gas plasma was produced by an RF power generator at 13.56 MHz (RF5S, RF Plasma Products, Inc., Voorhees, NJ) with an automatic matching network (AMNPS-2A, RF Plasma Products, Inc., Voorhees, NJ) to minimize reflecting power (usually zero). The samples were first placed in a quartz reactor and evacuated. After flushing with CO_2 and re-evacuating three times, the reactor pressure was controlled at 8 Pa using a mass flow controller (model 247C, MKS, Burlington, MA). A plasma treatment was then applied at 250 W for 15 min. After the plasma treatment, the samples were soaked in the PEI solution at room temperature under vacuum for 5 min to remove trapped air from the porous substrates. The samples were then soaked in the solution at atmospheric pressure for an additional 20 min. After incubation, the CO_2/PEI-treated samples were air-dried prior to surface characterization. For the comparison study, O_2 plasma treatment was applied at 200 W for 30 min.

2.3. *X-ray photoelectron spectroscopy (XPS or ESCA)*

XPS measurements were carried out in an SSX-100 spectrometer (Surface Science Instruments, Mountain View, CA) using a monochromatic Al K_α X-ray source, a detection system with a 30° solid angle acceptance, and a hemispherical analyzer. A 5 eV floodgun was applied to compensate for the surface charging of polymer samples. The X-ray spot size (area analyzed) on the sample surfaces was approximately 1 mm in diameter. A standard 55° take-off angle (the angle between the surface normal and the axis of the analyzer lens) was used for surface scans. Surface compositions determined from XPS spectra were used to examine the existence of PEI on the plasma-treated PE surfaces.

2.4. *Contact angle goniometry*

The wettability of the samples was evaluated using water contact angle measurements. A computer-video processed goniometer, VCA-2000 (Advanced Surface Technology, Billerica, MA), was used to take the measurements. A sessile drop of DI water was dispensed and its image was captured by a video camera and displayed on a computer monitor. The contact angle of the water drop was then determined using computer software.

2.5. *Stability study*

The stability of the hydrophilic coating was examined in aqueous and dry storage conditions at both room temperature and 50°C. The treated samples were first washed ultrasonically in DI water three times for 10 min each. After drying, the samples were stored in DI water or air at both room temperature and 50°C. After storage for a certain period of time, the samples were ultrasonically washed (three times for 10 min each) and dried in air prior to surface characterization using water contact angle measurements. The characterized samples were stored again at the same conditions for additional time. Storing and washing were repeated to evaluate the stability of the coatings.

2.6. *Durability study*

The durability of the coating was evaluated by repeated washing in water. In each washing cycle, samples were sonicated in DI water for 10 min at room temperature. After certain washing cycles, samples were air-dried and examined using XPS and contact angle goniometry.

3. RESULTS AND DISCUSSION

3.1. *Wettability of the hydrophilic-modified PE*

Porous PE sheets were plasma-treated and then PEI-coated to improve surface wettability. A conventional hydrophilic surface treatment using an O_2 plasma was also performed for comparison. Table 1 shows the water contact angles of the

Table 1.
Water contact angles on the treated porous PE

Sample	Before washing	After washing[a]
Untreated	109°	109°
O_2 plasma-treated	cwo[b]	83°
CO_2-treated/PEI-coated	cwo	cwo

[a]Washing ultrasonically in DI water three times for 10 min each.
[b]cwo — completely wets out: the PE sheet absorbs the water drop.

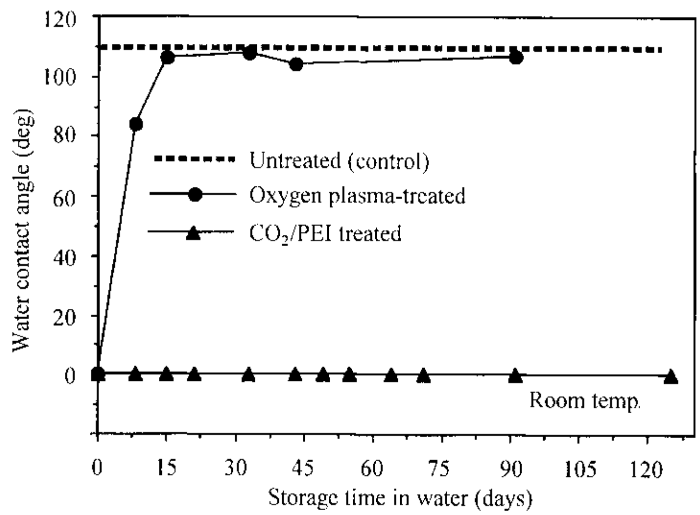

Figure 2. Water contact angles for hydrophilic-treated PE stored in water at room temperature.

hydrophilic-modified PE and the untreated control. Before and after washing with DI water, the untreated control showed a hydrophobic surface with a water contact angle of 109°.

Both surfaces treated with the O_2 plasma or the CO_2/PEI process, on the other hand, completely wet out immediately after treatment (before washing). Water drops were instantly absorbed by the treated PE sheets, due to the hydrophilic porous structure of the material. Therefore, no contact angles were measured. However, after washing in water and drying in air, the O_2 plasma-treated surface became hydrophobic with a contact angle of 83°, while the CO_2/PEI-treated surface remained unchanged in surface wettability. The results reveal that the CO_2/PEI-treated PE surfaces are extremely hydrophilic. Further surface analysis using XPS was carried out to characterize the retention of the PEI on the CO_2-treated PE surfaces.

3.2. Stability of the hydrophilic coatings

The stability of the hydrophilic-treated surfaces in various storage conditions was studied. Figure 2 shows the treated samples stored in DI water at room temperature for various times. Untreated PE was hydrophobic and consistently maintained high

Table 2.
Stability (in terms of water contact angles) of the hydrophilic-treated PE in various storage conditions

Sample	0 day	1 week	2 weeks	1 month	2 months	4 months
Untreated control	109°	109°	110°	109°	109°	110°
O_2 plasma-treated[a]	cwo[e]	83°	108°	108°	109°	109°
CO_2/PEI-treated[a]	cwo	cwo	cwo	cwo	cwo	cwo
CO_2/PEI-treated[b]	cwo	cwo	cwo	cwo	cwo	cwo
CO_2/PEI-treated[c]	cwo	cwo	cwo	cwo	cwo	cwo
CO_2/PEI-treated[d]	cwo	cwo	cwo	cwo	cwo	cwo

[a]Stored in water at room temperature.
[b]Stored in water at 50°C.
[c]Stored in air at room temperature.
[d]Stored in air at 50°C.
[e]cwo — completely wets out: the PE sheet absorbs the water drop.

water contact angles of approximately 109° over a 4-month period of storage in water. The O_2 plasma-treated PE completely wets out immediately after treatment. However, the surface became hydrophobic within 2 weeks. On the other hand, the CO_2/PEI-treated PE surface completely wets out even after repeated washing in a 4-month stability study, indicating that a stable and durable hydrophilic coating was obtained.

The stability of the CO_2/PEI-treated surfaces was further evaluated in various storage conditions with repeated washing for 4 months. Table 2 shows the water contact angles of the hydrophilic-treated PE surfaces. The CO_2/PEI-treated PE surfaces remained hydrophilic after a 4-month storage in air or water at both room temperature and 50°C. These results suggest that the PEI coating is both hydrophilic and stable.

3.3. *Durability of the hydrophilic coatings*

The durability of the coatings on plasma-treated porous PE has been determined by repeated rinsing in water. After washing in water for 30 cycles, the coated/rinsed PE surfaces still completely wet out. Figure 3 shows the surface nitrogen to carbon ratios, N/C, of the coated and water-washed porous PE surfaces from XPS measurements. No nitrogen was shown on the untreated/uncoated and treated/uncoated PE surfaces. On the treated/coated/unrinsed PE, a high N/C ratio of 0.28 was observed, indicating the presence of PEI. After repeated rinsing with water, surface N/C ratios decreased with the number of rinsing cycles, indicating the removal of coated PEI from the PE surfaces. However, after rinsing over six cycles, the surface N/C ratio reached a constant value of 0.18. These results suggested that approximately 65% of coated PEI was tenaciously bound to plasma-treated PE and could not be removed by repeated washing in DI water. In addition, the N/C ratios for all coated samples were less than 0.5, the theoretical ratio for PEI. This result indicates that the coated PEI layer is less than 5 nm, which is about the XPS sampling depth, and/or the coverage of PE by PEI is incomplete. To determine the uniformity

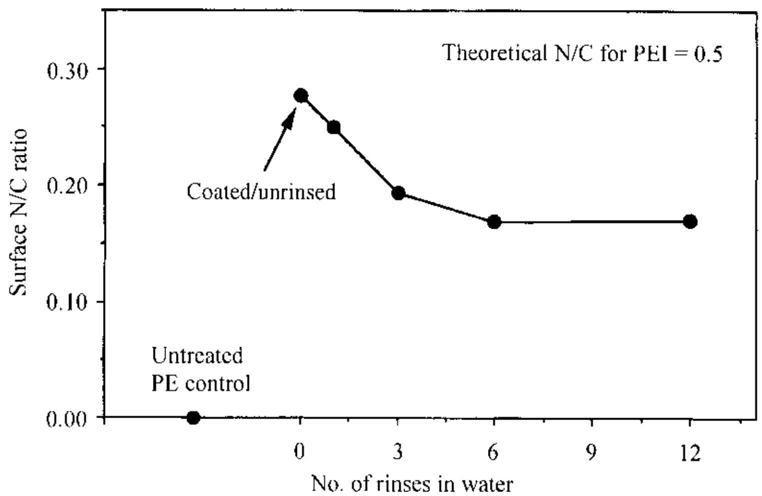

Figure 3. XPS results of the water-rinsed HydroLAST™ coatings on porous PE.

of the PEI coating further surface analysis using time-of-flight secondary ion mass spectrometry (TOF-SIMS) is needed to image the coated surface.

The durability of the coatings was also examined using solvent extraction and sterilization. After extraction with methanol for 18 h, the extracted PE surfaces were still wettable. The modified PE samples were also sterilized using e-beam and g-radiation treatments at normal dosages, 2.0 and 2.4 Mrad, respectively. After sterilization and further rinsing with water, the PE surfaces remained wettable. These studies also support the durability of PEI coatings.

4. CONCLUSIONS

In this study, a tenaciously bound hydrophilic coating was demonstrated on a porous PE sheet when the surface was treated with a CO_2 plasma followed by dip-coating with PEI. This simple process provides a stable and durable hydrophilic coating unlike conventional plasma surface treatments, such as an O_2 plasma. This coating process may have wide applications in many fields to improve surface wettability, wicking, and/or adhesion.

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