

Polymer Surface Reconstruction by Diffusion of Organic Functional Groups from and to the Surface

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Synopsis

Three nonpolar organic polymers containing small amounts of polar functionality were studied with regard to their surface characteristics. Two of the materials, potassium chlorate/sulfuric acid-oxidized polyethylene and poly(ethylene-co-acrylic acid) display variable surface polarities which can be reversibly accessed by heating films of the polymers in air or aqueous sodium hydroxide. Sodium-reduced Teflon-FEP did not exhibit this characteristic. A combination of contact angle, ESCA, and ATR IR data are used to display that the surface changes are caused by migration of functional groups within the outer few tens of angstroms of the surface.

INTRODUCTION

The molecular composition of a polymer surface can be markedly different than that of the bulk. Surfaces of homopolymers are often modified to impart specific surface properties (normally adhesive). Incorporation of additives,¹ chemical treatments,² surface grafting,³ physical abrasion,⁴ flame treatment,⁵ and corona discharge treatment⁶ are techniques of commercial utility. Copolymers and blends often exhibit surfaces with a preponderance of one component.⁷⁻¹⁶ Hydrogels of crosslinked methacrylates containing as much as 98% water exhibit hydrophobic surfaces.¹⁷

There are several reports of materials that change surface composition spontaneously: Potassium chlorate/sulfuric acid-oxidized low-density polyethylene was shown to have "temperature-dependent contact angles."¹⁸ Contact angles (water) of sodium-reduced Teflon-FEP changed from $\theta_{adv} = 52^\circ$, $\theta_{rec} = 16^\circ$ to $\theta_{adv} = 101^\circ$, $\theta_{rec} = 74^\circ$ on heating at 200°C for 96 h.¹⁹ Polyvinyl chloride (co-vinyl acetate), poly(vinyl chloride) containing plasticizers and low-density polyethylene that have been compression molded against gold have surface energies "in excess of the equilibrium values."²⁰ The surface energies "relax to equilibrium values" after removal of the gold foil. The contact angles of water on polypropylene and glow discharged-polymerized polypropylene increase during storage over several weeks.¹⁷ Chromic acid-oxidized polyethylene rapidly becomes hydrophobic when heated in air.²¹ Each of these spontaneous changes in surface composition can be explained by the process depicted in Figure 1. Polar functionality, introduced during treatments of the polymers, diffuses away from the polymer surface into the bulk. The magnitude of the driving force for this reaction, i.e., minimization of surface energy, is most dramatically demonstrated by the hydrogel data mentioned above¹⁷ and the work of LeGrand and Gaines,²² who showed that polycarbonates containing 0.1 wt % of a polycarbonate-di-

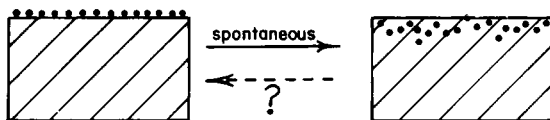


Fig. 1. Diffusion of functional groups (●) from and to the surface.

methylsiloxane block copolymer exhibit siliconelike surfaces.

The process depicted in Figure 1 should be reversible under conditions which counteract surface energy minimization. Indeed, in glow discharge plasma-modified polyethylene, amines migrate from a hydrophilic surface phase to a hydrophobic bulk phase during 2-propanol extraction and return to the surface upon protonation with sulfuric acid.^{23,24} This paper describes a procedure designed to force the diffusion of polar organic functional groups from the bulk to the surface of polymers by taking advantage of interactions between polymer functional groups and a polar condensed phase in contact with the polymer. Three materials were chosen as substrates: two of the surface-modified polymers described above and a random copolymer containing a known concentration of polar functional groups.

EXPERIMENTAL

Polyethylene (d. 0.915) and poly(ethylene-co-acrylic acid) (8% acrylic acid) were obtained from Polysciences. Teflon-FEP (1 mil) was a sample obtained from DuPont. Films of polyethylene and poly(ethylene-co-acrylic acid) (2 mil) were compression-molded between mylar at 15,000 psi and 150°C in a Pasadena hydraulic press. Polyethylene films were extracted with refluxing dichloromethane; poly(ethylene-co-acrylic acid) films and were rinsed with ethanol. Advancing and receding contact angles were determined using a Gilmont syringe and a home-built telescopic goniometer. ESCA (Electron Spectroscopy for Chemical Analysis) spectra (Mg $K\alpha$) were recorded on a Kratos XSAM 800 Spectrometer. Base pressures of 5×10^{-11} torr were typically achieved during analysis. ATR IR spectra were recorded on a Perkin-Elmer 283 Spectrometer using a 45° KRS-5 crystal and Perkin-Elmer MIR accessory.

Polyethylene Film was oxidized by placing 3×3 cm samples in a solution of 1.25 g potassium chlorate in 12 mL sulfuric acid for 30 s at 22°C. The film was kept submersed by agitating the beaker containing the solution. The film was removed from the oxidizing solution, rinsed with three 600 mL portions of distilled water, and dried between filter paper in a vacuum dessicator.

Teflon-FEP was reduced by submersion in a green solution of sodium (excess) and naphthalene (5 g) in THF (200 mL) for 60 s at room temperature. The film was removed from the reducing solution, rinsed with copious THF and then water, and dried between filter paper in a vacuum dessicator.

Heating of polyethylene and poly(ethylene-co-acrylic acid) samples both in air and in sodium hydroxide solution was carried out in glass bottles in a thermostatically controlled oil bath. Heating of Teflon-FEP samples was carried out in a Teflon-TFE beaker in a Parr bomb submersed in a thermostatically controlled sand bath.






RESULTS AND DISCUSSION

Potassium Chlorate/Sulfuric Acid-Oxidized Polyethylene. The surface of this material, originally described by Baszkin and Ter-Minassian-Saraga,^{18,25} exhibits water contact angle and ESCA spectral changes which are consistent with the reported data and the process depicted in Figure 1 when the modified material is heated. Treatment of this "relaxed-surfaced" film with warm aqueous sodium hydroxide followed by dilute hydrochloric acid then water rinses causes the contact angles to decrease and the oxygen concentration in the ESCA sampling depth to increase. This data is summarized in Table I and is consistent with the reverse of the process depicted in Figure 1, i.e., polar surface reconstruction by diffusion of functional groups from the bulk to the surface. The contact angles of unoxidized polyethylene did not change under these conditions. As indicated in Table I this material can be recycled through this process. The ATR IR spectra of samples did not change, indicating that these diffusion processes occur close to the surface relative to the sampling depth of this spectroscopy.²⁶

Sodium/Naphthalene Reduced Teflon-FEP. This material, described by Dwight and Riggs,¹⁹ does not respond to the aqueous base treatment in the manner that oxidized polyethylene does. The most extreme conditions tried were 192 h at 225°C. Contact angle data is summarized in Table II.

Poly(ethylene-co-Acrylic Acid). Surface behavior of this material has not been reported. As a substrate for this study, it has one advantage in particular: The structure and concentration of polar functionality is known (the polymer can be regarded as low-density polyethylene with a carboxylic

TABLE I
Contact Angle (Water) and ESCA (Ratios of Oxygen 1s/Carbon 1s Peak Areas) Data
for Oxidized Polyethylene

Material	θ_{adv}	θ_{rec}	O_{1s}/C_{1s}
PE	95°	68°	0.05
 KClO ₃ /H ₂ SO ₄ PE[Ox]	45°	0°	0.37
 90°C in air 60 min PE[Ox] ↓ ^a	93°	62°	0.25
 30% aq NaOH 80°C, 60 min PE[Ox] ↓ ↑	69°	0°	0.36
 90°C in air 60 min PE[Ox] ↓ ↑ ↓	92°	65°	0.26
 30% aq NaOH 80°C, 60 min PE[Ox] ↓ ↑ ↓ ↑	70°	0°	0.37

^a ↓/↑ indicate direction of functional group movement.

TABLE II
 Contact Angle (Water) for Reduced Teflon-FEP

Material	θ_{adv}	θ_{rec}
FEP	110°	95°
Na/naphthalene		
FEP[red]	55°	0°
200°C in air 96h		
FEP[red] ↓ ^a	105°	71°
30% aq NaOH 225°C, 192 h		
FEP[red] ↓	107°	74°

^a See footnote in Table I.

acid group on 1/60 of the chain carbons). Films of this material exhibit two distinct surfaces as oxidized polyethylene does. Table III summarizes contact angle and ESCA data. Molecular processes consistent with this data are depicted in Figure 2. Carboxylic acid groups that migrate to the surface become ionized and hydrated, forming an ionic surface which, when washed with dilute acid, forms a surface containing carboxylic acid groups. Heating this material in air causes diffusion of the polar groups back into the bulk of the polymer. ATR IR reveals that more is at play beneath the ESCA sampling depth: A strong absorbance centered at 1550 cm^{-1} indicates that the material is not unchanged by the base treatment and that many of the carboxylic acid groups in the outer $2\text{ }\mu\text{m}$ are irreversibly (at least with respect to room temperature dilute acid rinses) deprotonated. The minute amount of sodium present in the ESCA spectrum suggests that Figure 2 accurately represents the outer 50 or so Å of the material.

 TABLE III
 Contact Angle (Water) and ESCA (Ratios of Oxygen 1s/Carbon 1s Peak Areas) Data
 for Poly(ethylene-co-Acrylic Acid)

Material	θ_{adv}	θ_{rec}	O_{1s}/C_{1s}
PEcoAA	93°	62°	0.104
30% aq NaOH 80°C, 30 min			
PEcoAA ↑ ^a	69°	0°	0.208
80° in air 60 min			
PEcoAA ↑ ↓	91°	55°	0.102
30% aq NaOH 80°C, 30 min			
PEcoAA ↑ ↓ ↓	68°	0°	0.214

^a See note in Table I.

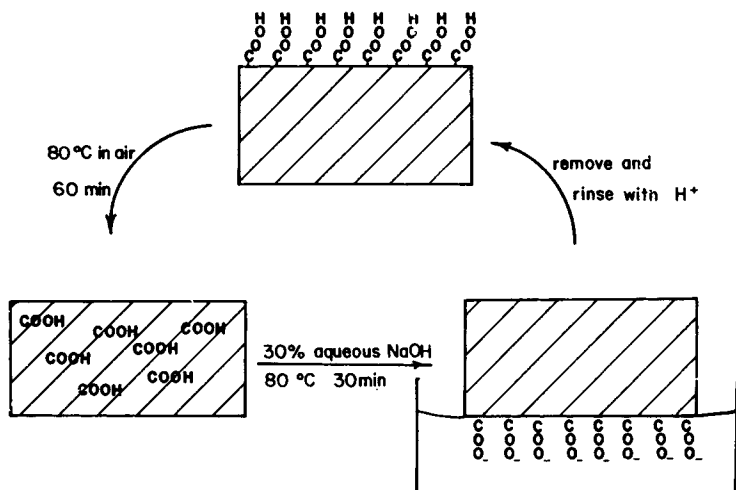


Fig. 2. Migration of carboxylic acid groups when in contact with aqueous sodium hydroxide and air.

CONCLUSION

The results reported here demonstrate that it is possible to *rationally* control the polarity of polymer surfaces by concentrating polar functional groups at the surface or away from the surface, i.e., materials with one bulk composition can display different, addressable surfaces.

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