



Oxidized polystyrene surfaces produced by plasma and neutral beam methods : an x-ray photoelectron and surface derivatization study
by Terry Lee Thompson

A thesis submitted in partial fulfillment of the requirements for the degree i of Master of Science in Chemistry
Montana State University
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Abstract:

Plasma treatments of polymers are commonly used to alter surface chemical properties, such as surface free energy, reactivity, adhesiveness, and biocompatibility. This study was conducted to investigate the use of neutral molecular beams for controlled surface modification. Detailed investigations of the chemistry of polymer surfaces that have been oxidized by neutral molecular beams have not previously been investigated in depth. Oxygen plasma modifications of polystyrene surfaces have been extensively investigated. Polystyrene was used as a model surface to compare the effects of neutral oxygen beams and oxygen plasmas on polymer surfaces. In an oxygen plasma environment, the surface is exposed to ions, ozone, atoms, electrons, excited states of molecular and atomic oxygen, and to a broad electromagnetic spectrum. The resultant chemistry can be difficult to control. Beams composed primarily of energetic oxygen atoms and molecules may offer the possibility to achieve more controlled surface chemistries.

Polystyrene samples were exposed to hyperthermal neutral oxygen beams composed of an approximately 60/40 mix of oxygen atoms to oxygen molecules traveling at an average velocity of 8 km/sec. Samples were also exposed to radio-frequency oxygen plasmas under commonly used operating parameters. X-ray photoelectron spectroscopy (XPS), surface chemical derivatization, and scanning electron microscopy (SEM) were used to characterize the surfaces.

Both modification methods resulted in similar amounts of surface oxidation that increased with progressively greater intensity or duration of exposure, with different distributions of carbon-oxygen bonding environments. The molecular beam produced unique metastable species that lasted up to two weeks. Once the surfaces had aged, the different beam exposure durations had nearly identical chemistry. The beam exposure resulted in the formation of sub-micron surface features that increased in number with increased exposure duration, while the plasma exposure did not affect surface roughness. The surface roughness could be varied independently of surface chemistry with the molecular beam. Plasma exposure resulted in the destruction of the aromatic structure of the polystyrene, while the beam exposure left the aromatic character intact. Surface derivatization was not effective in obtaining accurate quantitative results in systems with a variety of functionalities in low concentrations because of cross-reaction and yield problems.

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

Plasma treatments of polymers are commonly used to alter surface chemical properties, such as surface free energy, reactivity, adhesiveness, and biocompatibility. This study was conducted to investigate the use of neutral molecular beams for controlled surface modification. Detailed investigations of the chemistry of polymer surfaces that have been oxidized by neutral molecular beams have not previously been investigated in depth. Oxygen plasma modifications of polystyrene surfaces have been extensively investigated. Polystyrene was used as a model surface to compare the effects of neutral oxygen beams and oxygen plasmas on polymer surfaces. In an oxygen plasma environment, the surface is exposed to ions, ozone, atoms, electrons, excited states of molecular and atomic oxygen, and to a broad electromagnetic spectrum. The resultant chemistry can be difficult to control. Beams composed primarily of energetic oxygen atoms and molecules may offer the possibility to achieve more controlled surface chemistries.

Polystyrene samples were exposed to hyperthermal neutral oxygen beams composed of an approximately 60/40 mix of oxygen atoms to oxygen molecules traveling at an average velocity of 8 km/sec. Samples were also exposed to radio-frequency oxygen plasmas under commonly used operating parameters. X-ray photoelectron spectroscopy (XPS), surface chemical derivatization, and scanning electron microscopy (SEM) were used to characterize the surfaces.

Both modification methods resulted in similar amounts of surface oxidation that increased with progressively greater intensity or duration of exposure, with different distributions of carbon-oxygen bonding environments. The molecular beam produced unique metastable species that lasted up to two weeks. Once the surfaces had aged, the different beam exposure durations had nearly identical chemistry. The beam exposure resulted in the formation of sub-micron surface features that increased in number with increased exposure duration, while the plasma exposure did not affect surface roughness. The surface roughness could be varied independently of surface chemistry with the molecular beam. Plasma exposure resulted in the destruction of the aromatic structure of the polystyrene, while the beam exposure left the aromatic character intact. Surface derivatization was not effective in obtaining accurate quantitative results in systems with a variety of functionalities in low concentrations because of cross-reaction and yield problems.

CHAPTER 1

INTRODUCTION

Surface modification and surface engineering are very important for many scientific research areas. Modification of a surface may be advantageous when a bulk material that has some desirable property such as high strength, low cost, or durability is lacking in a surface property that is desired, like adhesion, biocompatibility, or wear resistance. The surface can be treated to obtain the desired surface property while maintaining the desirable properties of the bulk material. Surface modification plays an important role in the search for biologically inert or compatible polymer based materials that are placed in biological environments both long term and permanently [1,2]. For example, the introduction of hydrophilic groups onto the surface of a synthetic implant device reduces the surface induced aggregation of blood platelets on the surface which is believed to initiate events that lead to a negative physiological response [26]. Surface modification also plays a major role in the composite materials field. For example, fibers are treated both to effect processability and their adhesion to

the matrix material, which alters end product properties [3,4]. The largest single use of plastics is for packaging, which often require treatment to achieve satisfactory adhesion of printing and coatings [5].

There are many ways a surface can be modified. Polymer surfaces can be oxidized by exposure to wet chemical oxidizing agents such as chromic acid [27]. They also can be oxidized by environmental exposure to light [8,9]. Exposure to corona discharges is widely used to enhance the adhesion of inks to polyethylene in many commercial applications [28]. Plasma techniques are widely used in many industries. Plasma etching, plasma deposition and polymerization are widely used in the manufacture of integrated circuits [29]. Radio frequency glow discharge oxygen plasmas are a common method used to modify polymer surfaces. In an oxygen plasma environment, the surface is exposed to ions, ozone, atoms, electrons, metastable excited states of molecular and atomic oxygen, and to a broad electromagnetic spectrum [6]. This can make control of the resultant chemistry difficult.

In this study, beams of energetic oxygen atoms and molecules are being investigated as an alternative method to alter surface chemical properties. Polystyrene was used as a model surface to compare the neutral beam technique with plasma oxidation because the plasma oxidation of polystyrene surfaces has been extensively studied [6,7,8,9,10,11]. The interest in the interaction of energetic oxygen atoms with surfaces has mainly been driven by the space effects community. Oxygen atoms present in

low earth orbit (LEO) undergo impact with spacecraft that are moving at orbital velocities of approximately 8 km/sec. These interactions result in significant erosion and oxidation of the materials of the spacecraft [30]. Investigations of the chemistry involved in the oxidation of Kapton and several fluorocarbon polymers have been performed by exposure to atomic oxygen in low Earth orbit on the space shuttle [31]. Beams of atomic oxygen are often used for laboratory studies of space environmental effects [32].

Plasma and hyperthermal neutral molecular beams present two very different exposure environments. Unlike plasmas, where the species present and their kinetic energies are difficult to measure and are not commonly measured during sample exposure. The neutral beams provide the opportunity for easy measurement of the species present and their energies. The oxygen molecular beam used in this study has two main components: hyperthermal neutral oxygen atoms and molecules that have variable velocities in the range of 3-9 km/sec, corresponding to O-atom kinetic energies of approximately 0.7 to 9 eV. The oxygen plasma environment presents many neutral and ionic species with a myriad of excited states and near thermal energies of approximately 0.05 eV for neutrals and energies up to 10^3 eV for ions. Unlike plasmas, beam exposure presents little opportunity for charging effects and bombardment damage with more control over surface temperature. The neutral molecular beam also has good directional control.

In a plasma environment, directional control is potentially good for ionic species.

The polystyrene monomer unit consists of a two carbon backbone with a benzyl ring attached. Exposure of polystyrene surfaces to beams of energetic oxygen atoms and to oxygen plasmas results in the incorporation of oxygen into the polymer surface. The surfaces have been characterized by X-ray photoelectron spectroscopy (XPS) and derivatization techniques that represent the bulk of the work on this thesis. Scanning electron microscopy (SEM) was used to examine surface topography.

CHAPTER 2

EXPERIMENTAL METHODS

Sample Preparation

Polystyrene

Polystyrene (PS) samples used for surface modification were from commercially available 8.5x11 inch sheets provided by Plaskolyte (Columbus, OH). The sheets had a thickness of 0.93 mm with an average molecular weight of approximately 100,000. The polystyrene sheet was cut into 0.5 inch disks. The disks were rinsed with hexane for approximately 20-30 seconds and sonicated in methanol for 5 minutes and finally patted dry. Initial beam samples were soaked in methanol for 15 minutes instead of being sonicated. Both solvents used were HPLC grade, Fisher Scientific, Fair Lawn, NJ. The samples were immediately placed in the plasma or beam apparatus for surface modification. Control samples were analyzed immediately after cleaning.

Reference Polymers

Reference polymer films were prepared to investigate the surface derivatization reactions. Polymers were purchased from either Aldrich Chemical Co. (Milwaukee, WI) or Polysciences Inc. (Warrington, PA).

Poly(vinyl methyl ketone) (PVMK) had a MW of 500,000, Poly(acrylic acid) (PAA) had a MW of 250,000, and Poly(vinyl alcohol) (PVA) had a MW of 50,000-85,000. Poly(epoxy propyl methacrylate) was received as a 10% by weight solution in methyl ethyl ketone.

Solutions of the dry polymers were prepared as follows. Polymer was weighed in a capped glass vial and solvent was added to make a desired weight percentage solution. Guidelines for solvents and weight percentages were taken from reference 21. The vials used were 20-ml scintillation vials: borosilicate glass with polypropylene lined caps (Fisher Scientific, Pittsburg, PA). The analytical scale used was a Mettler AE 200. Polymer solutions were filtered with Millex LCR 0.5 micrometer filters for organic and aqueous solvents. PVMK was dissolved in a 50/50 volume mixture of tetrahydrofuran (99.9+%, Sigma-Aldrich) and chloroform (HPLC grade, Fisher Scientific). The final solution had a 2% weight composition of polymer to solution. PAA was dissolved in methanol to make a 1.6% by weight solution. PVA was dissolved in nano-pure water to make a 1.2% by weight solution.

The polymer solutions were spin-cast onto clean 12 mm glass cover slips/disks. The glass substrates had been previously cleaned by sonication

in acetone in a Branson 2210 Ultrasonic Cleaner. The solutions were spin-cast using a Headway Research instrument at 3000-4000 rpm for periods of 40 seconds

Surface Modification

Plasma Modification

The plasma reactor was designed and built in house by Dongrui Fang [15]. A schematic of the plasma apparatus is shown in figure 1. The entire setup consists of the plasma reactor, rf power generator and matching network, mechanical pump and traps, and gas flow and pressure controllers.

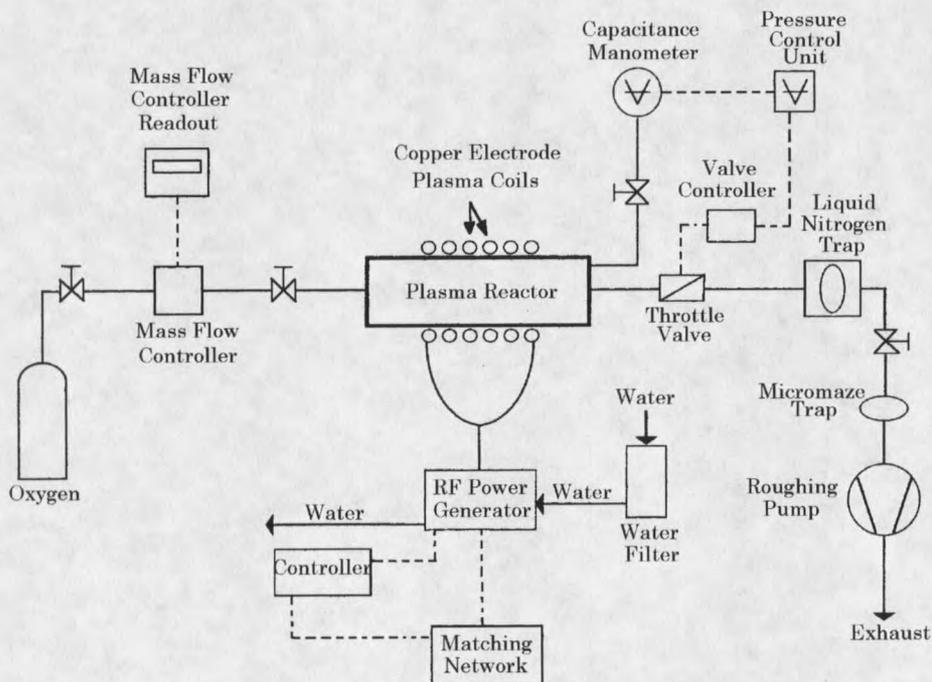


Figure 1. Plasma apparatus

The plasma chamber is composed of a Pyrex glass cylinder that is 24.1 inches long and has an inside diameter of 4 inches and an outside diameter of 4.6 inches. Stainless steel Kurt J. Lester ASA flanges, along with hand cut rubber gaskets, seal each end of the reactor. One flange has two gas feeds and a port for pressure gauges (KJL-205). The other flange has two ports connected to a pressure transducer (Baratron MKS 127A001D) and a pumping line. The flanges are held onto the Pyrex cylinder by four equally spaced bolts that squeeze the cylinder and gaskets between the flanges.

The rf power generator (RF-5S) and matching network (AM-5) are from RF Power Products Inc. The matching network is used to match the impedance of the power amplifier to that of the plasma reactor and is water-cooled. The plasma coil is composed of $\frac{1}{4}$ inch copper tubing which is wrapped in eight coils around the reactor. The power amplifier is microprocessor controlled with simple push-button operation and digital readouts. It is self-protected with automatic shutdown for high-reflected power, under/over voltage, and excessive temperature. The power amplifier can provide up to 500 Watts output power at 13.56 MHz.

The reactor pressure is measured by an MKS PDRC1C power supply with digital readout that reads the pressure from the pressure transducer (Baratron MKS 127A001D). The reactor pressure is automatically regulated by a MKS throttle valve (MKS 253A220401) that is controlled and powered by a MKS type 152 exhaust valve controller. Gas flow into the reactor is

controlled by a mass flow controller (MKS 1259050SV), a four channel readout and power supply, and shutoff valves (Kurt J. Lester SS-4BKT). This system controls two gas feed lines into the reactor.

The vacuum pump used in this system is a mechanical dual stage pump (Leybold LH-91245-1) with a pumping speed of 4 m³/hr and can achieve pressures of 10⁻⁴ torr under ideal conditions. The pumping line has a micromaze trap (Kurt J. Lester MMA-077-2QF), a shutoff valve, and a liquid nitrogen trap. The trap was not used during this study.

Prepared polystyrene samples were placed flat, six at a time, on a horizontal sample tray inside the plasma chamber in the middle of the reactor coil. The chamber was then evacuated for approximately 20 minutes until a vacuum of about 30 mtorr was reached. Oxygen gas was then introduced and allowed to stabilize at a flow rate of 5 sccm at a pressure of 300 mtorr. The rf power amplifier was then turned on to generate the plasma for a period of two minutes. Exposures were made at 20, 100, and 180 Watts rf power. The chamber was then vented to air and the samples were placed in Fluoroware® sample containers.

Molecular Beam Modification

Pulsed beams of energetic oxygen atoms are produced with a laser detonation source [17], which is coupled to a crossed molecular beams apparatus [18,19] for beam diagnostics [20]. A rotatable quadrupole mass

spectrometer is placed in line with the source for beam characterization. Figure 2 shows a schematic diagram of the apparatus. A pulsed CO₂ laser is used to induce a high temperature plasma in a "slug" of O₂ gas that is injected with a pulsed valve into the confined region of a conical nozzle. As a result of efficient electron-ion recombination in the rapidly expanding plasma, an expanding cone of essentially neutral species with hyperthermal velocities is produced.

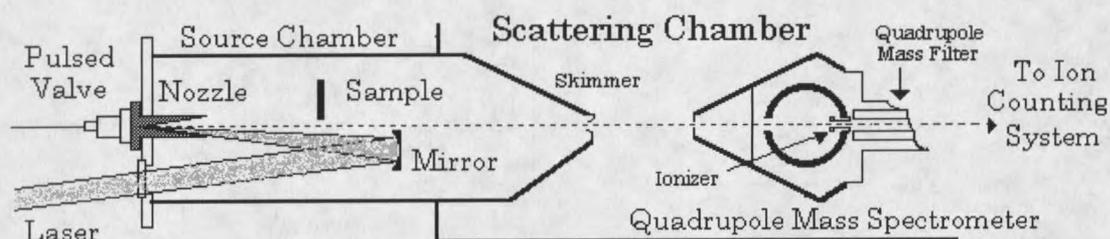


Figure 2. Neutral molecular beam source

A typical pulse contains a mix of atomic and molecular oxygen in a ratio of approximately 60/40, respectively, traveling at an average velocity of about 8 km/s (5 eV of kinetic energy for O atoms). The O/O₂ ratio and the nominal beam velocity can be varied over a wide range by adjusting the valve operating voltage, the time the valve is open, the pressure of the gas behind the valve, the laser power, and the delay in firing the laser.

The source chamber is pumped by a ten-inch oil diffusion pump backed by a Welch Duo-Seal mechanical pump. The laser is an Alltec Al-851 commercial CO₂ laser. An Edwards thermocouple gauge (AIM-S-NW25) and controller (ADG) and a Dunway Stockroom Corp. ion gauge (I-075-N) with a

Granville-Phillips controller are used to monitor pressure. The quadrupole mass spectrometer is from Extranuclear Laboratories. The ion counting system and ionizer are home built and are described in detail in reference [18], and uses a quad discriminator (Leroy 821), log/ln rate meter (Ortec 449), and a PC-mounted multi-channel scaler (EG&G Ortec ACE-MCS).

Prepared polystyrene samples were placed in a sample holder that holds nine samples. The holder was then placed to hold the samples perpendicular to the beam axis at a distance of 31.4 cm from the apex of the source's conical nozzle; see figure 7. The source chamber was then evacuated to a pressure of 10^{-6} torr. The oxygen feed gas to the pulsed valve was set at 125 psig. The pulsed valve was set to operate with 800 volts and a 100 μ sec. wide pulse. The pulsed valve is triggered at $t = 0$. The CO₂ laser was set to fire 245 μ sec. after the pulse valve was triggered. The laser was producing 5.5 joules/pulse. The laser and pulsed valve were operated at a frequency of 1.8 Hz, resulting in an atomic oxygen flux at this distance of approximately one monolayer per second (10^{15} atoms/cm²/s). The time of flight and kinetic energy distributions of the molecular beam used to expose the samples in this study are shown in figure 3. The beam was composed of 59% oxygen atoms with an average kinetic energy of 4.6 eV and 41% oxygen molecules with an average kinetic energy of 9.8 eV. Samples were exposed to durations of 10, 100, 500, 1000, and 10,000 total pulses. The chamber was vented to air and the samples were removed and placed in Fluoroware® sample containers.

