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Surface Modification of Polystyrene with O Atoms Produced Downstream from an Ar/O₂ Microwave Plasma

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Abstract: Because discarded polystyrene (PS) is little affected by degrading agents, PS was treated with a remote microwave (MW) plasma discharge of an Ar/O₂ mixture in the absence of radiation to increase wettability and introduce functional groups which make the waste more liable to degradation and useful for technological applications. X-ray photoelectron spectroscopy (XPS) detected decreases in the aromatic sp² and aliphatic sp³ carbons with treatment and, initially, increases in C–O and carbonyl groups, present in the formation of ethers, epoxides, alcohols, ketones and aldehydes. At longer treatment times, ester, O–C=O; carbonate-like, O–(C=O)–O; and anhydride, O=C–O–C=O; moieties are observed with an overall oxygen saturation level of 23.6 ± 0.9 at% O. Atomic Force Microscopy (AFM) measurements detected little change in surface roughness with treatment time. Advancing water contact angle decreased by ca. 50% compared to pristine PS indicating an increase in hydrophilicity because of oxidation. Washing the treated samples in deionized water decreased the oxygen concentrations at the saturation treatment times down to 18.6 ± 1 at% O due to the washing away of a weak boundary layer.

Keywords: polystyrene; microwave plasma of Ar/O₂; XPS; surface modification; AFM; water contact angle; hydrophilicity

1. Introduction

Since polystyrene (PS, Figure 1) has limited water adsorption, and physical and chemical properties that make it relatively non-biodegradable [1], pretreatment of its surface is often done to increase wettability and introduce reactive functional groups to enhance degradation and usefulness for technological applications [2,3].

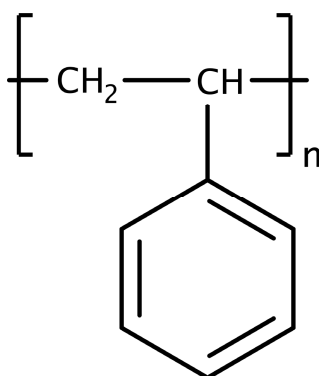


Figure 1. Molecular structure of polystyrene. Reproduced with permission from Taylor & Francis Ltd. www.tandfonline.com [4].

One way to increase the hydrophilicity of the PS surface is to use vacuum UV (VUV) photo-oxidation where a remote microwave (MW) plasma is employed to produce excited atoms, such as Ar (which emits 104.8 and 106.7 nm VUV radiation), which is then photo-absorbed by gaseous oxygen flowing over the PS surface [4]. The oxidation of the surface may occur because oxygen molecules photo-absorb in the VUV region of the electromagnetic spectrum [5], resulting in photo-dissociation forming reactive ground state, ^3P , and electronically excited, ^1D and ^1S , oxygen atoms which are energetically possible with threshold wavelengths of 242.4, 175.0 and 133.2 nm, respectively [6]. When this VUV photo-oxidation experimental set-up [4] was used to treat poly(ethylene terephthalate) (PET) [7], the results were in good agreement with a previous study where the oxygen was separated from the radiation emitted from MW plasmas of He- H_2 and H_2 by a MgF window having a cut-off wavelength of 112 nm [8]. The reaction time associated with the distance from the remote MW plasma results in negligible contributions from charged particles and metastables because of recombination and deactivation processes occurring in transit to the sample [9,10].

Since VUV radiation is capable of $\sigma \rightarrow \sigma^*$ alkyl chain excitation to produce free radical centers in the near-surface region of the polymer [4], which may initiate the incorporation of polar oxygen-containing functional groups, this study was done using a remote MW discharge of an Ar/ O_2 mixture where the samples were not exposed to radiation from the plasma. The operating techniques were similar to that used in a standard procedure for producing ground state $\text{O}(^3\text{P})$ atoms as, for example, in the EPR chemical kinetic study of $\text{O} + \text{HBr}$ [11].

2. Materials and Methods

2.1. Materials, X-ray Photoelectron Spectroscopy (XPS), Contact Angle Goniometry, Atomic Force Microscopy (AFM)

The materials, and surface characterization using X-ray photoelectron spectroscopy (XPS), water contact angle (CA), and Atomic Force Microscopy (AFM) measurements to determine surface composition of the top 2–5 nm, increases in hydrophilicity, and changes in surface roughness, respectively, were conducted as a function of treatment time, as described in ref. [4]. Commercially available 0.125 mm thick biaxially oriented PS film (Goodfellow Corp., Huntington, UK), $(\text{C}_8\text{H}_8)_n$, was cleaned with KOPTEC 200 proof (100%) anhydrous ethanol (Decon Labs Inc., King of Prussia, PA) in an ultrasonic bath for 15 min and stored in a desiccator, that contained calcium sulfate, for at least 24 h.

2.2. Production of Oxygen Atoms

A mild MW plasma system [7] was used to study the surface modification of PS as a function of treatment time. The MW plasma of an Ar/ O_2 mixture, having flow rates of 50 and 10 sccm, respectively, was generated in an Evenson cavity (Opthos Instruments, Inc., Rockville, MD) which was powered by

a 2.45 GHz MW generator (Kiva Instrument Corp, Kensington, MD). The experiments were conducted with MW absorbed power of ca. 25 W and pressure of $(2.1\text{--}2.9) \times 10$ Pa. The vacuum system was designed so that the discharge was located ca. 41 cm upstream from the PS and the radiation from the discharge was not directed at the sample [12].

3. Results

3.1. Treatment with a O Atoms Downstream from an Ar/O₂ MW Plasma

3.1.1. PS Quantitative Analyses and Contact Angle Measurements

Carbon, oxygen and sometimes a trace amount of nitrogen were detected on the surface of every PS sample. When pure Ar MW plasma was used, XPS detected no change in the surface composition of PS. The quantitative analyses for the PS samples treated in the absence of radiation are summarized as a function of treatment time in Figure 2. Initially, the concentration of oxygen increased rapidly and then saturated at an atomic percentage of 23.6 ± 0.9 at % O for six sets of samples which resulted in a decrease of the advancing water contact angle (CA) (increase in hydrophilicity) of ca. 50%.

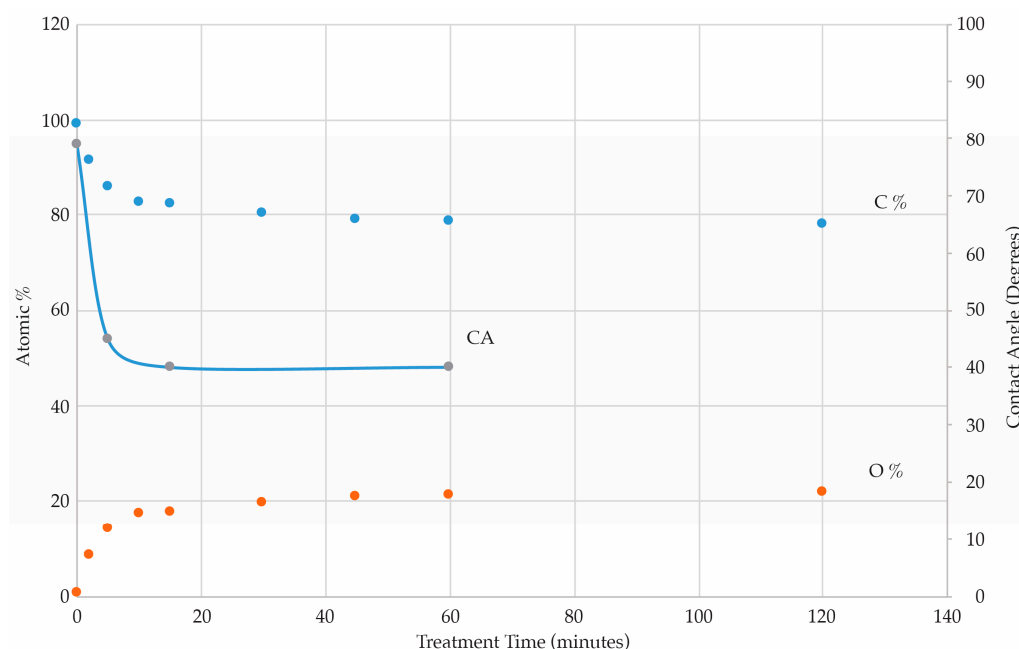


Figure 2. Quantitative X-ray photoelectron spectroscopy (XPS) (at%) and contact angle (CA) results for polystyrene (PS) as a function of treatment time with O atoms downstream from an Ar/O₂ microwave (MW) plasma.

3.1.2. XPS Chemical State Analyses

Figure 3 shows an example of the high resolution C 1s spectra obtained for the control and treated samples which were normalized to peak intensity at the main hydrocarbon peak (284.6 eV). Using the binding energies from the literature [7,13], the curve fitting results for the C 1s spectra are reported in Table 1.

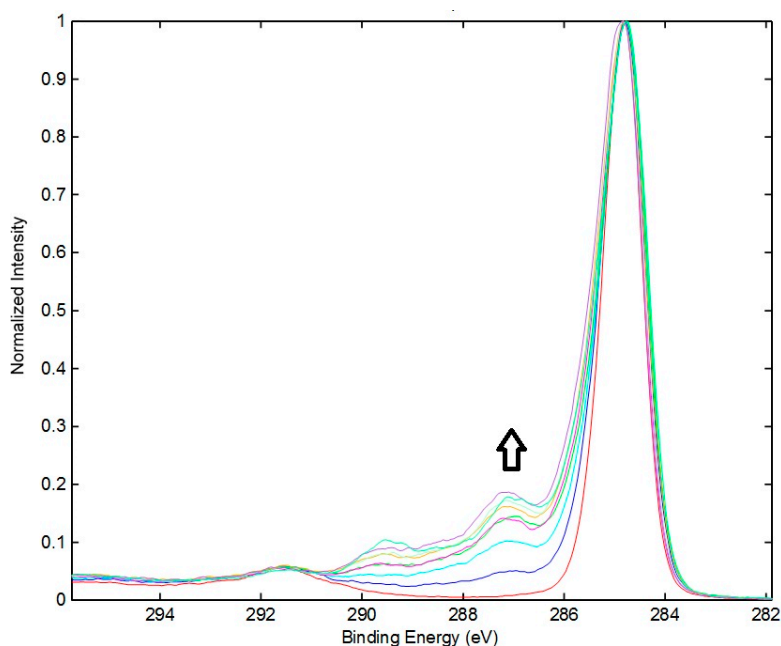



Figure 3. Overlapped C 1s spectra for control and treated polystyrene films for 0, 2, 5, 10, 15, 30, 45, 60 and 120 min using a remote MW discharge of Ar/O₂ mixture. The arrow indicates increasing treatment time.

Table 1. Curve Fitting for C 1s Area Peaks of Polystyrene as a Function of Treatment Time with a Remote MW Discharge of Ar/O₂. Binding Energies and species were reproduced with permission from Taylor & Francis Ltd. www.tandfonline.com [4].

Binding Energy (eV)	Species	Control	2 min	5 min	10 min	15 min	30 min	45 min	60 min	120 min
284.6	C–C sp ²	78.0	72.3	64.5	60.4	53.5	56.0	53.1	46.1	51.7
285.1	C–C sp ³	17.7	13.8	10.6	8.1	11.3	7.1	7.3	10.3	6.6
286.0	C–O–C,  , phenolic OH	0	8.5	11.1	14.1	16.0	17.0	18.2	20.1	19.3
287.0	C=O, aldehyde	0	1.9	8.1	11.0	11.8	12.3	13.4	14.1	13.7
288.6	O–C=O, carboxylic acid	0	0	1.7	2.5	2.7	3.4	3.7	4.6	4.5
289.8	O=C–O–C=O, O–(C=O)–O	0	0	1.1	1.9	2.4	2.6	2.7	3.3	3.3
292.0	Energy Loss	4.3	3.4	3.0	2.1	2.3	1.8	1.6	1.6	1.0


The binding energies for phenolic hydroxyl and carboxylic acid are at 286 and 288.6 eV, respectively [14]. As shown in the molecular structure of PS (Figure 1), the C 1s peak for the control sample consists of three distinct components: the aromatic sp² carbon peak at 284.6 eV, the aliphatic sp³ carbon peak at 285.1 eV, and the energy loss structure associated with the $\pi \rightarrow \pi^*$ transition, which is characteristic of the pendant phenyl group, at about 292 eV. Curve fitting six sets of data for pristine PS gave the following results: sp² ($76.7 \pm 1.8\%$), sp³ ($19.0 \pm 1.5\%$) and energy loss ($4.3 \pm 0.4\%$) which is good agreement with the published analysis for PS: 71.4%, 21.8% and 6.8% [15], respectively, considering the close proximity of the aromatic and aliphatic peaks.

With increasing treatment time, there are decreases in the aromatic sp² and aliphatic sp³ carbons and, initially, increases in C–O and carbonyl groups due to possible formation of ethers, epoxides, alcohols, ketones and aldehydes. At longer treatment times, ester, O–C=O; carbonate-like, O–(C=O)–O; and anhydride, O=C–O–C=O; moieties are formed. The $\pi \rightarrow \pi^*$ energy loss satellite becomes weaker with treatment time as new carbon-oxygen bonds are created.

The overlapped O 1s spectra for the samples (not shown here) were broad Gaussian peaks and, due to the lack of energy resolution, the O 1s spectra did not provide much additional information.

Two experiments were done by treating PS with O atoms for 60 min and then placing the samples in deionized water for 1h while bubbling with gaseous Ar. These washed samples showed a decrease in the surface oxygen saturation level of 5 ± 1 at % O down to 18.6 ± 1 at % O. Analysis of the XPS spectra after washing (Table 2) showed washing had its biggest effect by decreasing the presence of carbonate/anhydride; C–O; and C=O functional groups.

Table 2. Curve Fitting of C 1s Area Peaks for Untreated PS (Control), 60 min O atom Treated PS, and two 60 min O atom Treated PS Samples after Washed with Deionized Water. Binding energies and species were reproduced with permission from Taylor & Francis Ltd. www.tandfonline.com [4].

Binding Energy (eV)	Species	Control	60 min	60 min Washed	60 min Washed
284.6	C–C sp ²	78.0	46.1	67.7	61.3
285.1	C–C sp ³	17.7	10.3	12.5	16.2
286.0	 C–O–C, C–C, phenolic OH	0	20.1	8.4	7.2
287.0	C=O, aldehyde	0	14.1	6.2	7.1
288.6	O–C=O, carboxylic acid	0	4.6	3.1	5.0
289.8	O=C–O–C=O, O–(C=O)–O	0	3.3	0.8	1.4
292.0	Energy Loss	4.3	1.6	1.3	1.9

3.1.3. Surface Topography for O Atom Treatment

Figure 4 shows the AFM images and root mean squared (RMS) roughness factor (R_q) for PS samples before (0 min) and after 5, 15 and 60 min of treatment. The changes in surface roughness were found to be insignificant.

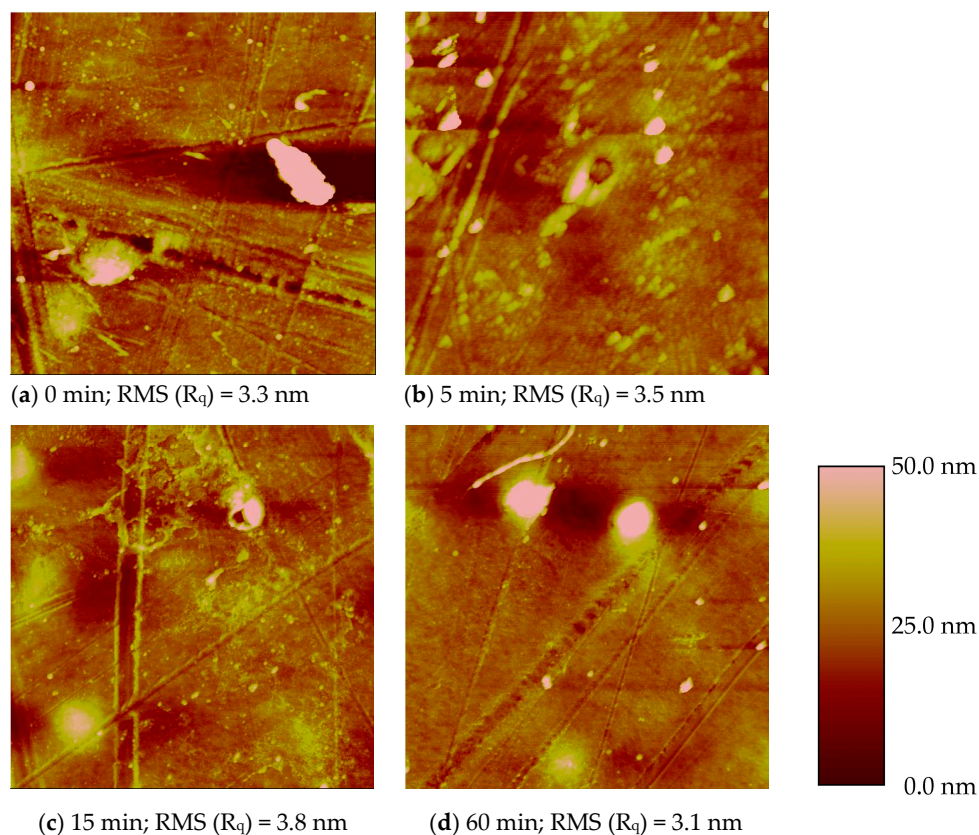


Figure 4. AFM surface topographic images after treatment of PS for (a) 0; (b) 5; (c) 15 and (d) 60 min with O atoms.

4. Discussion

The treatment of PS with O atoms in the absence of radiation showed a controlled increase in the concentration of oxygen with treatment time up to a saturation level of 23.6 ± 0.9 at % O compared to ca. 20 at % observed by VUV photo-oxidation [4]. A remote oxygen 300 W MW plasma study observed that the level of oxidation was dependent on the flow rate and reached an O/C saturation of 0.65, which corresponds to 39 at % O, at 600 sccm [16] compared to the 60 sccm and 25 W used in this study.

The carbonyl, ether, and alcohol functional groups observed in Table 1 may be formed by mechanisms initiated by the abstraction of H atoms from the polymer (RH) by O atoms to produce free radical sites (R•) as detected by EPR spectroscopy [17]. Reaction of the free radicals with O₂ form alkoxy radicals (RO•) which undergo dissociation by Reaction (1); combine with radicals via Reaction (2); or abstract a hydrogen atom, Reaction (3) [16,18].



Rearrangement of peroxy free radicals (RO₂•), formed from the reaction of R• with O₂, result in stable functional moieties, such as, ketones, aldehydes and vinyl groups [16]. Subsequent reactions of the aldehydes may lead to the formation of acids, esters or carbonates [16]. Aldehydes would appear at a binding energy of ca. 287 eV [13] and may be present in this study. The carbonate/anhydride moieties are often the highest oxidized form of bound carbon before CO₂ is released as observed in the molecular beam-surface scattering experiments involving atomic oxygen and PS [19]. The release of CO₂ and cleavage of the polymer chain are often indicators of the formation of a weak boundary layer which was detected by washing the O atom treated PS samples, resulting in an oxygen concentration decrease of 5 ± 1 at % O compared to a 4.9 at % O decrease with VUV photo-oxidation [4]. Weight loss measurements due to the release of CO₂ during the reaction of O atoms with PS have been previously reported [20–24].

The addition of O atoms across the unsaturated phenyl groups form phenols [18], and react with unsaturated sp² C bonds to produce a triplet biradical that undergo ring closure to form epoxide, rearrange to make carbonyl compounds, or decompose into free radicals producing the ether linkage [25] as reported in Table 1. Reaction with the phenyl groups result in the observed decrease of the energy loss $\pi \rightarrow \pi^*$ transition with treatment time (Figure 3, Table 1).

The lack of surface roughness changes indicate that the incorporation of the polar oxygenated functional groups on the surface of PS were responsible for the ca. 50% decrease in water contact angle (Figure 2), compared to a ca. 25% decrease using VUV photo-oxidation [4], and hence an increase in hydrophilicity. Higher levels of oxidation were achieved with the downstream MW plasma discharge of the Ar/O₂ mixture treatment (23.6 ± 0.9 at % O) than with VUV photo-oxidation (ca. 20 at % O) [4]. Also, less carbonate-like, O–(C=O)–O; and anhydride, O=C–O–C=O, moieties were observed in Table 1 (3.3%) than using VUV photo-oxidation (4.3%), although the amount of weak boundary layer washed away were within experimental error.

5. Conclusions

The downstream MW discharge of an Ar/O₂ mixture was a good controlled method for studying the reaction of oxygen atoms with the surface of PS in the absence of radiation to produce saturation levels of 23.6 ± 0.9 at % O. XPS analysis showed the initial formation of C–O and carbonyl groups and with increasing treatment time, ester, carbonate-like, and anhydride groups are formed. Advancing water contact angle and AFM measurements showed that the increase in hydrophilicity is mainly due to surface oxidation and not changes in topography. A weak boundary layer was formed during treatment which, when washed with water, decreased the O saturation level down to 18.6 ± 1 at % O.

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Conflicts of Interest: The authors declare no conflict of interest.

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