Poly(ethylene terephthalate) surface modification by deep UV (172 nm) irradiation

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Abstract

The prospects of obtaining desired surface-mediated characteristics while retaining bulk-mediated physical properties and avoiding potential environmental issues with wet chemical technology lends considerable appeal to photochemical approaches. We investigated the response of poly(ethylene terephthalate) to 172 nm UV from a xenon excimer lamp in the absence of oxygen, using XPS, ToF/SIMS, and AFM. The main effects are increasing loss of a C=O moiety and carboxylic acid production without effect on topography up to a total fluence of 16 J/cm². Above this level no further change in surface chemistry was evident, but surfaces became rougher, suggesting the onset of etching.

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1. Introduction

Improved value in use of major commercial polymers will come chiefly from enhanced surface or interface properties: adhesion, increased (or decreased) permeability, antisoil, and antimicrobial functionality. Poly(ethylene terephthalate) (PET) is an especially attractive target because of its wide use in textiles and packaging, though all applications

are highly cost sensitive so that wet chemical (fiber finishes) or extrusion coatings (films) dominate. An alternative, potentially attractive approach would take advantage of the ability of UV light to drive radical processes to transform surface chemistry.

There are few reported studies of the effect of deep (<250 nm) UV on PET. No effect was found by XPS for excimer laser irradiation in air at 248 nm of biaxially oriented film at 12 mJ/cm² (below the ablation threshold) [1]. For 193 nm irradiation in nitrogen, a loss of oxygen-containing species is evident by XPS even at 10 mJ/cm² [2]. C–O was affected more than C=O. Even though the fluence in both excimer laser studies was below the ablation threshold, thermal effects were not absent, since the polymer

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was amorphized in both cases. Irradiation with 185 nm Hg vapor light in vacuum led to reduced surface oxygen as seen by XPS, but increased uptake of derivatizing reagents for carboxyl functionality [3]. In contrast, repeating the experiment with a filter that excluded 185 nm emission and passed only the 254 nm component resulted in little or no effect [3], consistent with the 248 nm observations. Irradiation in nitrogen at 222 nm (KrCl excimer lamp) resulted in a modest increase in surface oxygen species as seen by XPS, but only after 500 J/cm² [4]. At this fluence level, the question of a possible role for residual oxygen in the treatment cell atmosphere is hard to avoid.

Nonetheless, the effect of UV wavelength at these low fluences suggests that interesting (and perhaps useful) photochemistry may be taking place. Advances in UV sources, surface characterization and computational modeling motivate us to revisit the investigation of the effect of deep UV radiation on PET.

2. Experimental

2.1. Excimer laser exposures

It seemed appropriate to connect the present work with the previous studies by carrying out a few excimer laser exposures. The PET used was 12 μ m thick commercial production Mylar[®] LB 48 film (Dupont). We used a Lambda LPX 325i having either an ArF (193 nm) or KrF (248 nm) fill, with the beam spread by a cylindrical lens to obtain the desired fluence as a single shot. About 1 cm-wide strips of the film were rinsed with HPLC grade isopropanol and end-mounted in 35 mm slide holders. The irradiations were accomplished in a homemade chamber continuously swept by boil-off from liquid nitrogen.

2.2. Excimer lamp exposures

The rest of the UV-irradiations were accomplished with a dielectric barrier discharge (DBD) excimer lamp of our own construction; a detailed review of such lamps may be found in [5]. The annular configuration consists of an inner quartz tube to carry cooling water, an annular space for the active gas, and a

43 mm diameter outer Suprasil[®] quartz tube, 50 cm in length. The lamp was operated at atmospheric pressure filled with undiluted xenon gas (Spectra Gas Laser Grade) to produce 172 nm UV. The lamp is enclosed within a coaxial polycarbonate cylinder, sealed at the ends and continuously swept by boil-off from liquid nitrogen. The material to be treated was attached to the inner surface of the enclosure, providing a constant distance to the lamp of about 7 cm. The irradiance at the sample position was measured with an International Light Model 1400A photometer with a SED-185 detector head. The spectral energy distribution of the lamp and the detector response curve do not overlap perfectly, necessitating a correction factor of 2 to the meter reading to obtain the UV dose. Average irradiance received at sample position is about 50 mW/cm². Multiple samples were acquired at UV dose levels of 4, 8, 16, and 32 J/cm². In each case, a piece of polyethylene (PE) film was treated along with the PET. If subsequent XPS showed other than trace oxygen pick-up by the PE, the run was discarded.

2.3. Surface analysis

Samples for surface analysis were rinsed with isopropanol (Fisher, HPLC grade) and then deionized water (>18 M Ω) prior to introduction, with the exception of one set of samples exposed to 32 J/cm². XPS analysis of the 172 nm treated material was carried out with a Specs “PHOIBOS” system, using a Mg anode (1253.6 eV) operated at 15 kV and 200 W. To better reveal the surface functional group population, a complete set of samples was derivatized with silver trifluoroacetate [3] by overnight (18 h) exposure to a 10^{−2} M solution of AgOCOCF₃ in acetone and then washed repeatedly with acetone. XPS of the laser-irradiated materials employed a VG ESCALab, also with a Mg anode.

Time of flight secondary ion mass spectrometry (ToF/SIMS) provides a more sensitive surface analysis [6] and is especially effective for polymers [7]. We used a PHI “TRIFT II CE” instrument to raster a 200 μ m $\times$ 200 μ m surface area with 15 keV gallium ion beam at 600 pA current with extraction voltage set at 7200 V. Data acquisition time was set for 5 min and sample surface received an ion dose of 2.4E + 11 ion/cm². Surface topography was characterized by atomic

Fig. 1. Comparison of the C 1s region of untreated PET film (upper curve at 288.5 eV) to 248 nm irradiated (middle) and 193 nm irradiated (lowest).

force microscopy (AFM) using a digital instruments “NanoScope[®] IV” scanning probe microscope in intermittent contact (“tapping”) mode. The scan rate was set at 0.5 Hz to scan over multiple $2\ \mu\text{m} \times 2\ \mu\text{m}$ sampling areas. Second-order flattening was applied to the data before surface roughness analysis.

3. Results and discussion

3.1. XPS

The interpretation of PET core level spectral lines is well established [8,9]. The average intensity ratio of C

Fig. 2. Effect of 172 nm UV on surface oxygen content as determined by XPS. The dashed line is only a guide for the eye.

Fig. 3. Effect of 172 nm UV on relative C=O content of surface carbon as determined by XPS. The dashed line is only a guide for the eye.

1s and O 1s peaks from three untreated PET samples is 10.00/4.24, which is close to the nominal value 10/4. Fig. 1 shows data from the C 1s region of the untreated and two laser-treated materials. All spectra were shifted so that the aliphatic carbon peaks appears at 284.6 eV and normalized so that peak has the same

height over background. They were not smoothed. The difference between the untreated material and that irradiated at 248 nm is small indeed, less than the noise in the previously reported [1] spectra. Further, that material received only 12 mJ/cm² of 248 nm light, versus 17 mJ/cm² here. In contrast, it is evident 12 mJ/

Fig. 4. Effect of 172 nm UV on $I_{C-O}/I_{C\text{aromatic}}$ as determined by XPS. The dashed line is only a guide for the eye.

Fig. 5. Relationship between relative surface oxygen content and relative carbonyl content. The solid line is a model calculation assuming that oxygen content changes only via carbonyl content change.

cm^2 at 193 nm leads to significant loss of both oxygen-related carbon species.

Fig. 2 presents the effect of 172 nm UV irradiation on the surface oxygen to total carbon ratio for three equivalent samples. The ratio decreases with increasing UV dose upto about 16 J/cm^2 , and then levels-off

at about one-sixth less than its original value. For films receiving 32 J/cm^2 , the decrease of O/C ratio relative to that of untreated material was 8–10% greater for films analyzed as-treated, compared to films rinsed before analysis. The unwashed film was also somewhat tacky to touch.

Fig. 6. Relative surface silver content as a function of UV dose.

Fig. 7. ToF/SIMS positive ion spectra of: (a) untreated PET; (b) PET subject to 16 J/cm^2 of 172 nm UV.

Fitting the individual carbon peak components—carbonyl, ethoxy, and aliphatic—gives further insight. In untreated material, the measured average intensity ratio was 0.82/1.13/3.00, in reasonable agreement with the nominal value 1/1/3 and with previous studies of high purity PET (0.96/1.12/3.00) [10]. Fig. 3 shows that the loss of carbonyl carbon is

similar to the decrease of total oxygen/carbon ratio, in contrast with the constancy of ethoxy carbon (Fig. 4). In fact oxygen loss closely tracks carbonyl carbon loss (Fig. 5).

The silver trifluoroacetate derivatization provides yet another view [3]. Silver trifluoroacetate reacts with PET surface carboxylic acid groups to

Scheme 1. Generation of characteristic mass fragments of PET.

Fig. 8. Topographic images of: (a) untreated; (b) 16 J/cm^2 irradiated; (c) 32 J/cm^2 irradiated PET films.

Fig. 8. (Continued).

yield surface bound silver carboxylate salts according to:

Fig. 6 shows that Ag/C ratio increases with UV dose upto about 16 J/cm^2 , suggesting that formation of carboxylic acid end groups accompanies the other changes. Since, the derivatization reaction proceeds only for surface-exposed acid groups, while the XPS signal originates from at least the top few nanometers, the Ag/C ratio likely understates the surface acid group concentration.

3.2. ToF/SIMS

ToF/SIMS provides the most sensitive currently available view of polymer surface chemistry [6,7]; PET has been extensively investigated [11]. As shown in Fig. 7a, $m/z = 104, 105, 148, 149, 193$ are characteristic peaks of PET. Their formation can be summarized in Scheme 1 [11]. Upon ion bombardment, the weakest bond disassociates and may form a carboxy and alkyl radical pair. The active carboxy radical can extract hydrogen from neighboring molecules to form end carboxylic group. Further ion bombardment

may cleave another weak C–O bond and form the characteristic 193 mass peak. Subsequent fragmentation leads to 149 and 105 mass peaks. Alternatively, the carboxy radical may not have time to extract hydrogen before being lift off surface so that 148 and 104 mass peaks form with one proton short. The mass peaks that appear in the UV-modified PET sample are similar to the original PET sample except for the difference in the relative intensity (Fig. 7b). In the UV-modified PET sample, the intensity ratios of high mass fragment m/z 149 (or $m/z = 105$) to low mass fragment m/z 148 (or $m/z = 104$) are much higher (two to three-fold) than the original PET. It may be attributed to pre-existing polymer end groups in favor of producing 149 m/z and 105 m/z peaks instead of their radical counterparts. In addition, peak intensity at $m/z = 165$ also increases dramatically for the UV-treated material, perhaps originating from decarbonylation products.

3.3. AFM

Topographical analysis was carried out with AFM comparing UV-treated and untreated PET samples. Fig. 8 shows topographic images of untreated, 16 J/

cm² irradiated and 32 J/cm² irradiated films. The root-mean-square (RMS) surface roughness for samples that received 16 J/cm² or less was between 1 and 2 nm, but increased to above 4 nm for samples subjected to 32 J/cm². Together with the XPS data showing that 32 J/cm² dose samples have similar oxygen/carbon ratio, carbonyl/carbon ratio and Ag/carbon ratio to those of 16 J/cm² dose samples, it suggests that further irradiation beyond 16 J/cm² may lead to low molecular weight species that can be rinsed away with isopropanol. This is also consistent with the slightly lower oxygen/carbon ratio of 32 J/cm² UV-irradiated PET surface prior to isopropanol rinsing, which has an oxygen/carbon ratio of about 8% less than that of the isopropanol rinsed sample. The observed cone structures in UV-etched 32 J/cm² sample have diameter ranging from tens of nanometers to a few hundred nanometers, in good agreement with PET spherulites dimension [12,13]. This suggests that crystalline PET may be more resistant to degradation by deep UV light than amorphous material.

4. Conclusion

The effect of 172 nm Xe excimer lamp irradiation on PET in the absence of oxygen upto 16 J/cm² is dominated by carbonyl elimination and acid group formation, in contrast with the effect of irradiation at other deep UV wavelengths seen here and in previous studies. Further work is needed to definitively elucidate the relationship if any, carbonyl elimination and acid group formation. At UV dose levels higher than

16 J/cm², differential etching roughens semi-crystalline PET surface.

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References

- [1] D.S. Dunn, A.J. Ouderkirk, *Macromolecules* 23 (1990) 770.
- [2] M. Chtaib, E.M. Roberfroid, Y. Novis, J.J. Pireaux, R. Caudano, P. Lutgen, G. Feyder, *J. Vac. Sci. Technol. A* 7 (1989) 3233.
- [3] S. Lazare, R. Srinivasan, *J. Phys. Chem.* 90 (1986) 2124.
- [4] D. Praschak, T. Bahners, E. Schollmeyer, *Appl. Phys. A* 66 (1998) 69.
- [5] U. Kogelschatz, H. Esrom, J.-Y. Zhang, I.W. Boyd, *Appl. Surf. Sci.* 168 (2000) 29.
- [6] A. Benninghoven, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 1023.
- [7] K. Wien, *Nucl. Inst. Meth. Phys. Res. B* 131 (1997) 38.
- [8] D. Clark, *CRC Crit. Rev. Solid State Mater. Sci.* 8 (1978) 1.
- [9] D.W. Dwight, J.E. McGrath, J.P. Wightman, *J. Polym. Sci., Appl. Polym. Symp.* 34 (1978) 35.
- [10] G. Beamson, D. Briggs, *High resolution XPS of organic polymers*, The Scienta ESCA300 Database, Wiley, England, 1992, p. 174.
- [11] G.J. Leggett, J.C. Vickerman, D. Briggs, M.J. Hearn, *J. Chem. Soc., Faraday Trans.* 88 (1992) 297.
- [12] G.E. Sweet, J.P. Bell, *J. Polym. Sci., Phys. Ed.* 16 (1978) 1935.
- [13] M.W. Gurnick, DuPont Tejin Films, Private communication.