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A study of the chemical and morphological alterations of PS and PC surfaces induced by excimer laser treatments

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The effect of laser irradiation on polystyrene (PS) and bisphenol-A polycarbonate (PC) has been studied by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), optical microscopy and surface profilometry. The dependence of the surface chemical and morphological properties on wavelength and fluence has been investigated.

On both materials no apparent chemical modification was induced by irradiation at 350 nm, there is no evidence of non-linear effects. Morphological alterations were induced in the PS subsurface, due to thermal shock effects. The irradiation of both polymers at 248 and 193 nm did not result in photoassisted oxidation. In the case of PS, etching is evident at 193 nm. Irradiation of PC at 248 nm induces oxygen depletion and photo-Fries rearrangements, whereas at 193 nm oxygen depletion and etching are predominant. In both polymers etching yields peculiar surface morphologies, namely the formation of debris and cone-like structures.

1. Introduction

In a previous work, we studied the effect of excimer laser treatments (193 and 248 nm) on polyethylene (PE), polypropylene (PP) and polytetrafluoroethylene (PTFE) [1]. The main results were smoothing of the polymeric materials' surface and change of their surface tension, both irradiating at 193 nm and 248 nm.

Most of the excimer laser work on polymers had dealt with ablative photodecomposition phenomena [2–4]. Polymers such as poly(ethyleneterephthalate) (PET), polymethylmethacrylate (PMMA) and polyimide (PI) have been studied.

An X-ray photoelectron spectroscopy (XPS) study of the effect of irradiating PMMA and poly(α-methylstyrene) (PMeS) with 193 nm lasers has been reported by Burrell *et al.* [5]. At fluence levels comparable to ours they did not find any evidence of compositional changes for both of the polymers they studied. In XPS and SEM studies carried out by Lazare *et al.* on 193 nm irradiated PET, oxygen depletion and roughening of the surface were observed [6]. The development of well-defined conical structures on polyimide (PI) and PET surfaces, after excimer laser treatments, has been attributed to the shielding effect of particulate impurities [7, 8].

For the present work, we chose to study polystyrene (PS) and polycarbonate (PC). PS, unlike PMeS, is a relatively insensitive negative resist [10] and it has been shown to undergo crosslinking under irradiation. Its photooxidation behaviour has been studied extensively and it has been shown that it leads to the formation of C–OH, C=O and COOH groups through a hydroperoxide mechanism [11]. PC also undergoes chemical modifications under UV irradiation, both formation of inter-chain bonds [12] and photo-Fries rearrangement have been reported [13].

We have investigated the modifications in surface composition and morphology induced when operating at different wavelengths (193, 248, 350 nm), doses and fluences. Our experiments have been performed in air to understand whether photooxidation phenomena occur as a consequence of laser irradiation.

2. Experimental procedure

Commercial polystyrene (Edistir 20100, Montedipe SpA, Mantova, Italy) and Bisphenol-A polycarbonate (Makrolon, Mobay Corp., Pittsburgh) were compression moulded to yield 0.4 mm thick sheets. No attempt was made to extract any of the various additives (antioxidants, UV stabilizers, etc.) present in the commercial polymers.

The surface modifications were induced by the output of a Lambda-Physik EMG 102 (Gottingen, FRG) excimer laser at 193 nm (ArF), 248 nm (KrF) and 350 nm (XeF). The determination of single pulse energy was made by measuring the average power of the laser at 5 Hz operation frequency. The irradiation area was accounted for and a conversion to a single pulse fluence (in mJ cm^{-2}) was performed. The typical energy per pulse varied with the wavelength but was normally below 100 mJ, while the irradiated area was approximately 1 cm^2. The pulse frequency was kept at 1 Hz or at 5 Hz in the case of longer exposures, in

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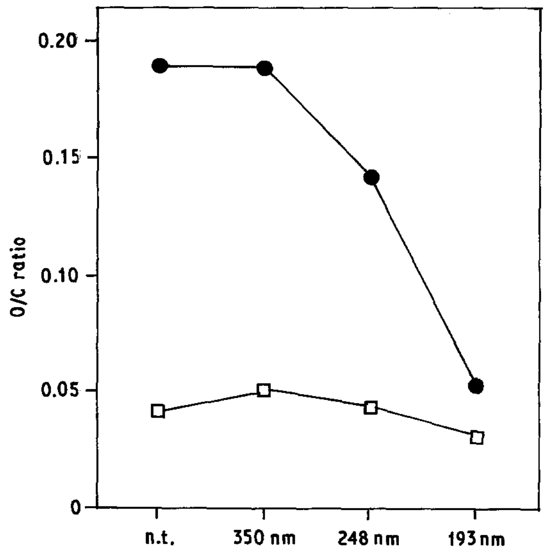

Figure 1 XPS O/C ratios as a consequence of excimer laser treatments of PS (□), PC (●).

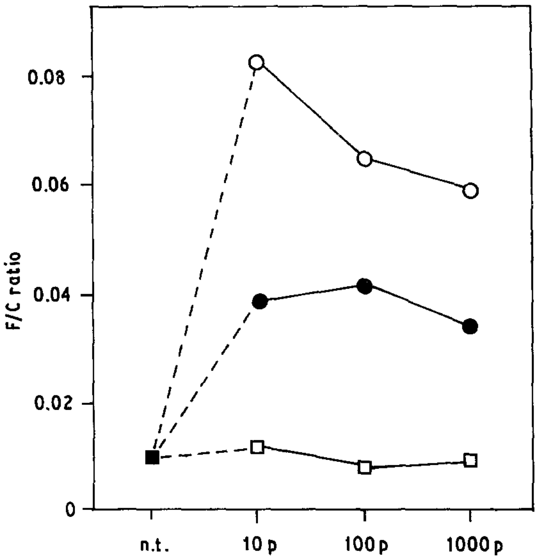

Figure 2 XPS F/C ratios as a consequence of excimer laser treatments of PC (tagging experiments) for untreated, (■), 350 nm (□), 248 nm (○), 193 nm (●).

order to minimize cumulative heating. The single pulse had a FWHM of about 15 nsec.

XPS spectra were measured *ex situ* on a PHI (Eden Prairie, Minnesota) model 548 XPS-AES spectrometer, using the Mg$K\alpha$ radiation (1253.6 eV) from a 400 W source. The analysis chamber pressure was maintained near 2×10^{-7} Pa, without baking. Signal averaging to improve the signal-to-noise ratio was performed connecting the spectrometer to a PDP 11/50 computer. Further data processing (smoothing, background subtraction, integration, deconvolution) was carried out using in-house software on a Sperry 1100/72 mainframe computer. The contamination C 1s peak was used as a reference and set to 284.6 eV. Surface compositions were calculated from the spectra using the appropriate sensitivity factors [9]. Tagging experiments were performed using trifluoroacetic anhydride, a reagent leading to mixed anhydride and esters respectively when reacted with COOH and OH groups, according to the procedure suggested by Lazare *et al.* [6].

SEM micrographs were obtained using a Cambridge Instruments (Cambridge, UK) model Stereoscan 604 microscope and the surface was coated with gold to avoid charging problems. Optical micrographs have been obtained using a Leitz Orthoplan (Wetzlar, FRG) microscope. A Tencor Alphastep (Mountain View, California) 100 profilometer was used to measure the depth of laser etching.

3. Results

3.1. XPS

To understand the effect of the wavelength on the surface composition, PS and PC were irradiated at 350 nm, 248 nm and 193 nm with nearly constant fluence and amount of energy introduced into the polymer. In Fig. 1 the XPS O/C ratios before and after the treatment are plotted.

In the case of PS, some oxygen is present on the untreated specimen, due to the preparation by compression moulding [14, 15]. As a consequence of excimer laser irradiation, the amount of oxygen at the sample surface is always similar to that in the untreated sample and shows some decrease with the irradiation wavelength, suggesting that no photo-assisted oxidation occurred. In the case of PC, the treatment at 350 nm does not affect significantly the surface composition, suggesting that multiphoton phenomena are not important. Irradiations at 248 and 193 nm decrease strongly the O/C ratio, ruling out again photooxidation.

To better characterize the PC surface after excimer laser treatments, we treated the specimens with trifluoroacetic anhydride. The latter has been shown to react with surface OH and COOH groups and consequently the measured fluorine concentration is an indication of the concentration of the above mentioned oxygenated functions.

In Fig. 2, the result of tagging experiments is displayed on laser treated PC surfaces. The introduction of some fluorine on the untreated sample is probably due to reactions of the fluorinated anhydride with phenolic end-groups or with oxygen containing contaminants present on the sample surface. The F/C ratios after irradiation at 350 nm are similar to that of the untreated specimen suggesting that no photochemically induced reaction occurred. On the contrary those obtained after irradiation at 248 and 193 nm are significantly higher, suggesting an increase in the number of C—OH and COOH groups.

To understand these trends, it is necessary to consider the possible reactions induced by irradiation in the presence of oxygen. An alternative is chain scission, leading to either crosslinking or formation of monomers/oligomers. The other is rearrangement, PC is known to undergo photo-Fries rearrangements, with the formation of C—OH groups on the aromatic ring [12, 13].

After 248 nm irradiation, a strong increase in F/C ratio coexisted with a decrease in the O/C ratio. The occurrence of photo-Fries rearrangements might in this case be supported. In fact, for each photo-Fries rearrangement two new C—OH groups are formed. Chain scission would not account for the high C/F

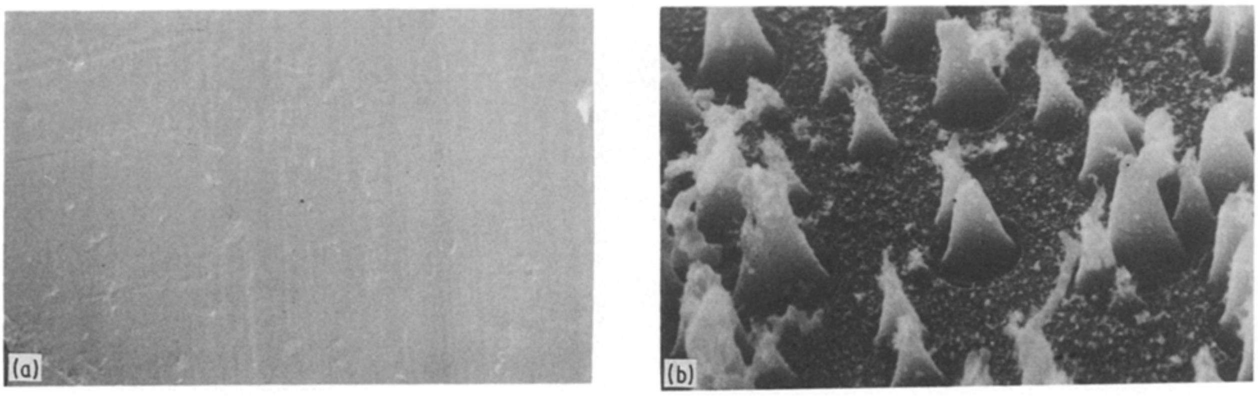

Figure 3 SEM micrographs of (a) untreated PS; (b) PS treated with 100 pulses at 193 nm.

ratio, since a phenolic end-group would be the most that formed at each event. At higher total energy values, a decrease in the F/C ratio has been observed, suggesting that, after a higher number of pulses, chain scission partially overcomes photo-Fries rearrangements. At 193 nm the F/C ratio is quite a lot lower than at 248 nm, only marginally higher than in the untreated specimen and, within the experimental error, insensitive to the number of pulses. In this case, chain scission might be considered the main photodegradation phenomenon.

3.2. SEM

An SEM micrograph of untreated PS is shown in Fig. 3a. The irradiation at 350 and 248 nm does not induce significant alterations of the surface morphology. On the contrary, as shown in Fig. 3b, after treatment at 193 nm some remarkable cone shaped structures appear.

The surface morphology of PS, as evidenced by SEM micrographs, is insensitive to 350 nm irradiation, but in the subsurface a diffuse crazing occurred. Figs 4a and b show optical micrographs of PS untreated and treated at 350 nm. The crazes reach an approximate depth of 150 μm. All of the energy introduced into the polymer at 350 nm is probably transformed into thermal energy in a very short time, producing a thermal shock sufficient to induce craze formation. As expected, the density of the crazes depends on the fluence and not on the total energy. No craze formation has been observed after irradiation at 248 nm, suggesting that not all the photochemical energy is converted into heat.

The cone shaped microstructures of Fig. 3b originate from etching of PS at 193 nm. It has been shown [7] that microparticulate impurities shield the underlying polymer from the laser radiation producing the cone shaped structure. Debris is present around and on top of the cones. Most likely the latter are originated by the redeposition of heavy oligomers. Variable fluence experiments showed that by increasing the fluence a diminished debris formation is formed, due to the fact that the average molecular weight of the fragments is lower.

Using a surface profilometer a rough estimate of etch rates was made. Irradiation of PS at 248 nm did not induce significant etching (< 1 nm/pulse), while a 100 μm/pulse etch rate was found for 193 nm irradiation, confirming SEM evidence.

In Fig. 5a an SEM micrograph of untreated PC is shown. In Figs 5b and c the effects of 248 and 193 nm irradiation are displayed. At 350 nm no modification of the surface morphology is evident. No crazing has been observed for PC after 350 nm irradiation, due, probably, to a better resistance of PC to thermal shocks.

The ashing observed after 248 nm irradiation is clear evidence of photochemical events. Variable fluence experiments confirmed this assignment, in fact at very low fluence (17.5 mJ cm $^{-2}$) only some bubbles appeared on the sample surface, suggesting microfusion. An increase of the furnace to 35 mJ/pulse induced some ashing (threshold for the onset of photochemical modifications), and at higher fluence, 49 mJ cm^{-2}, (Fig. 4b) ashing became very substantial.

When the 193 nm radiation is applied, etching

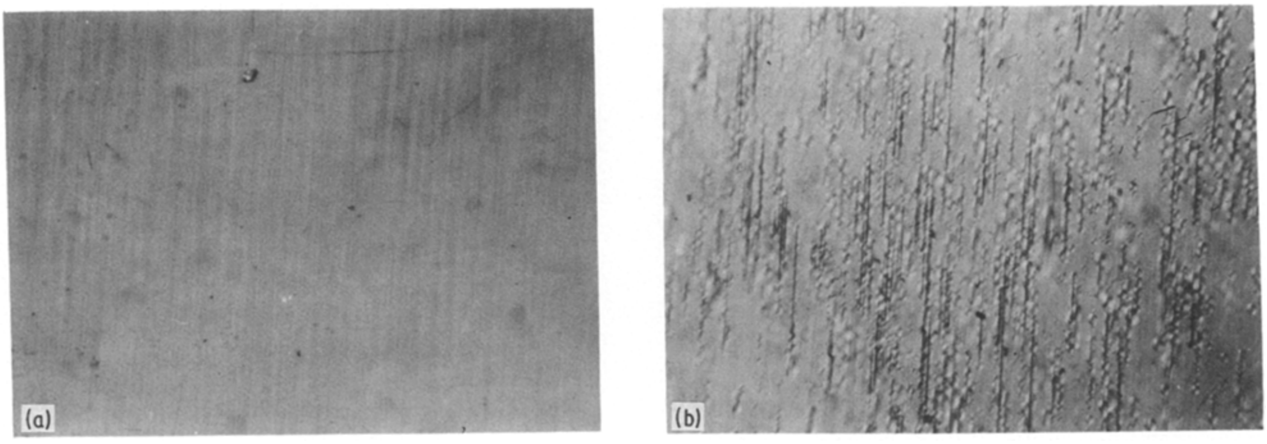

Figure 4 Transmission optical microscopy micrographs of (a) untreated PS; (b) PS treated with 100 pulses at 350 nm.

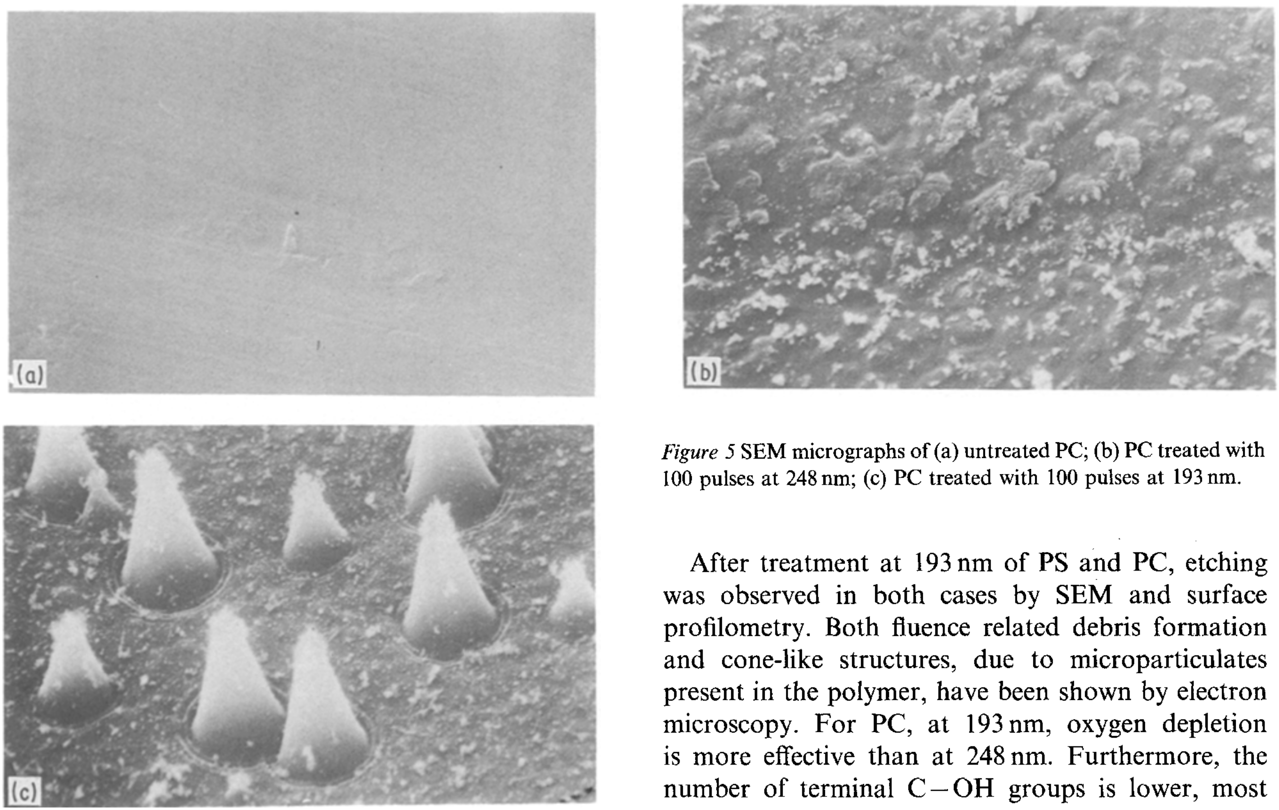

Figure 5 SEM micrographs of (a) untreated PC; (b) PC treated with 100 pulses at 248 nm; (c) PC treated with 100 pulses at 193 nm.

is clearly the dominant phenomenon. The evidence collected for PC at 193 nm parallels that found for PS, as shown in Fig. 5c. Again etching of the polymer leads to cone shaped structures. Lowering the fluence induced, as verified for PS, the formation of increased amount of debris, due to a lower photochemical efficiency.

Very low etch rates (< 4 nm/pulse) were observed by surface profiling as a consequence of 248 nm laser irradiation of PC, confirming XPS and SEM evidence, while etch rates around 70 nm/pulse have been found after 193 nm irradiation.

4. Discussion and conclusions

By combining XPS and SEM techniques, complemented by optical microscopy and surface profilometry, it has been possible to achieve some insight into the effect of laser radiation on PS and PC. It is worth noting that for both polymers, irrespective of the wavelength, the irradiation in the presence of oxygen does not induce photooxidation.

Irradiation at 350 nm does not induce chemical modifications in both PS and PC. Most of the photochemical energy is transformed into heat. In PS the resulting thermal and pressure shocks induce microcrazing.

In the case of PS, the 248 nm irradiation induces a very low etch rate, maybe some crosslinking takes place. In the case of PC, simultaneous oxygen depletion and formation of oxygen-containing end group is observed, as shown by the variation of XPS O/C and F/C ratios. The occurrence of photo-Fries rearrangements can partially account for this evidence, since it does not alter the total amount of oxygen, but only transforms two non-terminal oxygens in C–OH groups.

After treatment at 193 nm of PS and PC, etching was observed in both cases by SEM and surface profilometry. Both fluence related debris formation and cone-like structures, due to microparticulates present in the polymer, have been shown by electron microscopy. For PC, at 193 nm, oxygen depletion is more effective than at 248 nm. Furthermore, the number of terminal C–OH groups is lower, most likely because etching prevails over photo-Fries rearrangement.

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References

1. V. MALATESTA, F. GARBASSI, and E. OCCHIELLO, in Proceedings of The International Conference on Lasers '86, Orlando, Florida, November 3–7, 1986 (Society for Optical and Quantum Electronics, Mclean, Va, USA).
2. J. T. C. YEH, *J. Vac. Sci. Technol.*, **84**, (1986) 653 and refs therein.
3. R. SRINIVASAN, B. BRAREN, D. E. SEEGER and R. W. DREYFUS, *Macromolecules*, **19** (1986) 916 and refs therein.
4. V. SRINIVASAN, M. A. SMRTIC and S. V. TABU, *J. Appl. Phys.* **59** (1986) 3861.
5. M. C. BURRELL, Y. S. LIU and H. S. COLE, *J. Vac. Sci. Technol.* **A4** (1986) 2459.
6. S. LAZARE and R. SRINIVASAN, *J. Phys. Chem.* **90** (1986) 2124.
7. P. E. DYER, S. D. JENKINS and J. SIDHU, *Appl. Phys. Lett.* **49** (1986) 453.
8. J. E. ANDREW, P. E. DYER, D. FORSTER and P. H. KEY, *Appl. Phys. Lett.* **43** (1983) 717.
9. "Handbook of X-Ray Photoelectron Spectroscopy", Perkin Elmer Physical Electronics Division, Eden Prairie, 1979.
10. T. M. HALL, A. WAGNER and L. F. THOMPSON, *J. Appl. Phys.* **53** (1982) 3997.
11. J. F. RABEK and J. SANTRA, *Macromolecules* **19** (1986) 1679 and refs therein.
12. J. D. WEBB and A. W. CZANDERNA, *ibid.* **19** (1986) 2810 and refs therein.
13. A. GUPTA, A. REMBAUM and J. MOACANIN, *ibid.* **11** (1978) 1285.
14. D. J. CARLSSON and D. M. WILES, *ibid.* **2** (1969) 587.
15. *Idem, ibid.* **4** (1971) 173.

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