SILENT DISCHARGE TREATMENT OF BIAXIALLY ORIENTED POLYPROPYLENE

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Non-equilibrium plasmas can be used to modify the surface chemical and topographical properties of polymers. Biaxially oriented polypropylene has been silent discharge treated and then analysed by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The former shows that the level of surface oxidation introduced by plasma modification rises with treatment time, whereas AFM reveals the formation of globular features comprising of low molecular weight oxidised carbon species.

1. Introduction

Non-equilibrium electrical discharges are widely used to modify the surface properties of polymers. For example inert gas plasmas have been used to etch polymers [1], CF_4 plasmas can be employed to fluorinate polymers [2-3], and oxygen plasma treatment can increase polymer wettability via surface oxidation [4]. In order to completely understand the effect of plasma treatment on the surface properties of the polymers, both the chemical and physical changes caused by the plasma need to be investigated. The chemical properties of plasma treated polymers have been extensively examined by surface sensitive analytical techniques such as X-ray photoelectron spectroscopy (XPS) [5-7] and static secondary ion mass spectrometry (SSIMS) [8]. However the study into the physical effects of the plasma (i.e. surface topography and morphological changes) have been mainly restricted to a few scanning electron microscopy (SEM) studies [9-10]. The relatively recent invention of the atomic force microscope (AFM) overcomes the limitations of the SEM [11]. The AFM can image non-conducting samples down to nanometer scale resolution without the need for any additional sample preparation (thus no need to coat the sample). Both the

chemical and physical effects of the silent discharge treatment of biaxially oriented polypropylene have been investigated by using XPS and AFM techniques respectively.

2. Experimental

Silent discharge treatments were performed using a home-built parallel plate dielectric barrier discharge reactor operating at 3 kHz, 11 kV, with an electrode gap of 3.00 ± 0.05 mm, [12]. Small strips of biaxially oriented polypropylene film (ICI) were washed in a 50/50 mixture of isopropyl alcohol and cyclohexane prior to treatment. Samples were then silent discharge treated for a variety of times ranging from 30 s to 300 s.

XPS measurements were performed on a Kratos ES300 electron spectrometer equipped with a MgKα source (1253.6 eV) and a hemispherical analyser. Photo-emitted electrons were collected at a take-off angle of 30° from the substrate normal, with electron detection in the fixed retardation (FRR, 22:1) mode. XPS spectra were accumulated on an interfaced IBM PC computer. Instrumentally determined sensitivity factors for unit stoichiometry of C(1s):O(1s) were taken as equalling 1.00:0.62.

A Digital Instruments Nanoscope III atomic force microscope operating in the Tapping Mode was used for studying the topography of each sample.

3. Results

3.1 X-ray Photoelectron Spectroscopy

XPS was used in order to determine the O/C ratio of the silent discharge treated surfaces. The variation in the O/C ratios obtained, as a function of treatment time is shown in Fig. 1(a). C(1s) XPS spectra were peak fitted with Gaussian peaks of equal full width at half maximum (FWHM), using a Marquardt minimisation computer program. Energies distinctive of different types of oxidised carbon moieties were referenced to the hydrocarbon peak (-$\underline{C}_xH_y$-) at 285.0 eV, carbon adjacent to a carboxylate group (>$\underline{C}$-CO_2-) at 285.7 eV, carbon singly bonded to one oxygen atom (>$\underline{C}$-O-) at 286.6 eV, carbon singly bonded to two oxygen atoms or carbon doubly bonded to one oxygen atom (>$\underline{C}$=O / -O-$\underline{C}$-O-) at 287.9 eV, carboxylate groups (-O-$\underline{C}$=O) at 289.0 eV, and carbonate carbons (-O-$\underline{C}$O-O-) at 290.4 eV. The peak fitted spectra are shown in Fig. 1(b).

The C(1s) spectrum of clean polypropylene consists of a single peak at 285.0 eV which corresponds to $\underline{C}_xH_y$ groups belonging to -CH, $-CH_2$ and $-CH_3$ functionalities contained in the polymer. Oxidised carbon species at higher binding energies are evident in the C(1s) spectrum following silent discharge treatment. The intensity of the high binding energy shoulder increases with longer treatment times, which is consistent with the observed trend in the O/C ratio as shown in Fig. 2. At short treatment times, the $\underline{C}$-O group is the most prominent oxygenated functionality.

With longer exposure times (i.e. from 120 to 300 s), the highly oxidised carbon species become more prominent; this suggests that carbon atoms which have already undergone oxidation are being further oxidised.

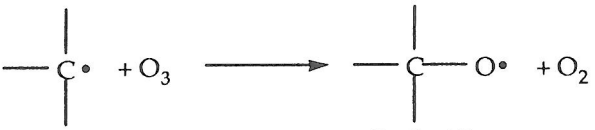
3.2 Atomic Force Microscopy

AFM images were taken of untreated polypropylene and silent discharge treated polypropylene, Fig. 2. The AFM image of untreated polypropylene reveal a fibrillar structure with polymer fibrils oriented in two directions reflecting the biaxial nature of the film. Silent discharge treatment of the polymer causes a significant amount of surface roughening in conjunction with the apearance of globular species.

4. Discussion

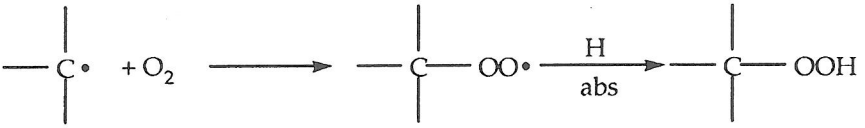
The silent discharge reactor was invented over a hundred years ago [13], and both the chemistry and physics of the silent discharge have been widely studied. It is well established that a silent discharge reactor operating in air produces a variety of reactive species including ozone and ultraviolet radiation (UV) [14,15]. Ozonation of a polymer surface can produce oxygenated carbon functionalities [16]. For instance, hydrogen abstraction from the polymer chain by ozone attack can initiate oxidation:

This carbon radical centre can then react with another ozone molecule to form an oxidised free radical:

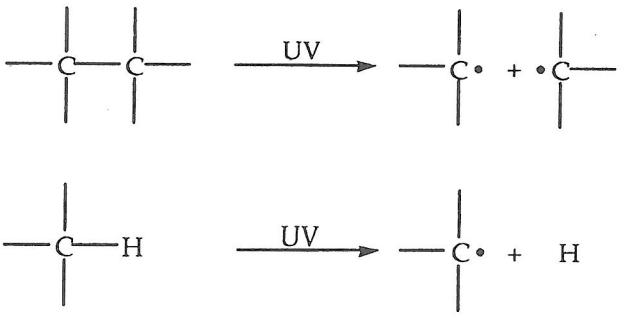


Radical I

Alternatively the primary carbon radical can react with molecular oxygen creating a hydroperoxide group [16]:



Although ozonolysis can explain a great deal about the effect of the silent discharge on a polymer surface, it cannot completely account for the observed behaviour. In order to fully explain the chemistry of the silent discharge we have to consider the effect of the UV radiation component upon the polymer surface. Oxidation and cleavage of polymer chains can also be initiated by the UV irradiation [17]:



These radicals can then go on to react with molecular oxygen or ozone in order to generate the oxygenated carbon centres.

Although atomic oxygen is generated in the silent discharge reactor, it quickly either recombines to form molecular oxygen or reacts with molecular oxygen to form ozone [15]. Therefore the concentration of atomic oxygen is never high enough to significantly effect the surface chemistry of the polypropylene.

There is a clear difference between the AFM images of untreated and silent discharge treated polypropylene. The formation of these globular features can be attributed to either low molecular weight oxidised material (LMWOM) [9,18] or local surface melting [18]. LMWOM is generated by the dual action of chain oxidation and chain cleavage, as mentioned earlier. The globular features could be due to the conglomeration of the LMWOM caused by the difference in surface energies between the LMWOM and the untreated polymer. Alternatively, the globular features can be accounted for in terms of local surface melting, during the silent discharge treatment [19]. Washing of the silent discharge treated polypropylene sample in a 50/50 mixture of common solvents (isopropyl alcohol and cyclohexane), removes the globular features, thereby indicating that the droplets are soluble. This supports the hypothesis that the globules consist of LMWOM, since high molecular weight species tend not to be soluble.

5. Conclusions

Atmospheric non-equilibrium silent discharge treatment of biaxially oriented polypropylene causes the polymer surface to become oxidised. This can be accounted for in terms of the dual action of ozone and UV radiation contained within the silent

discharge plasma upon the polymer surface. Silent discharge treatment also produces globular type features on the polymer surface which can be attributed to low molecular weight oxidised carbon material.

6. References

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7. Figures

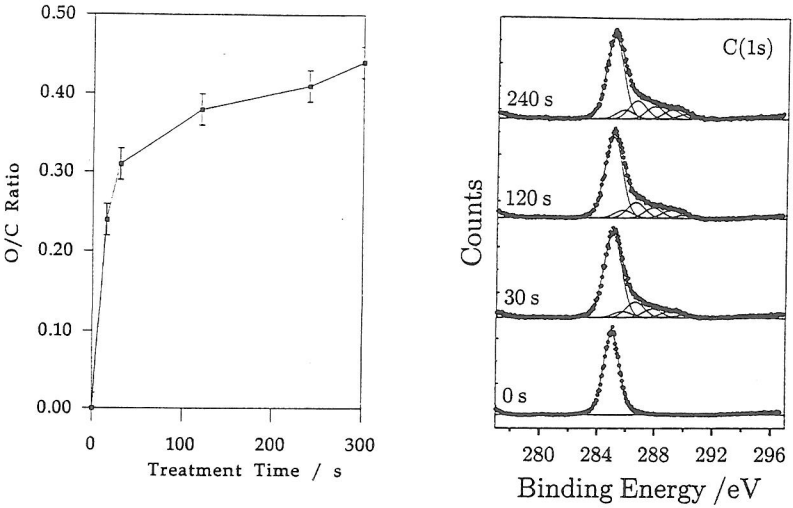

Fig. 1: XPS data, (a) the variation of O/C ratio and (b) peak fitted C(1s) XPS spectra (times are treatment times) for silent discharge treated polypropylene.

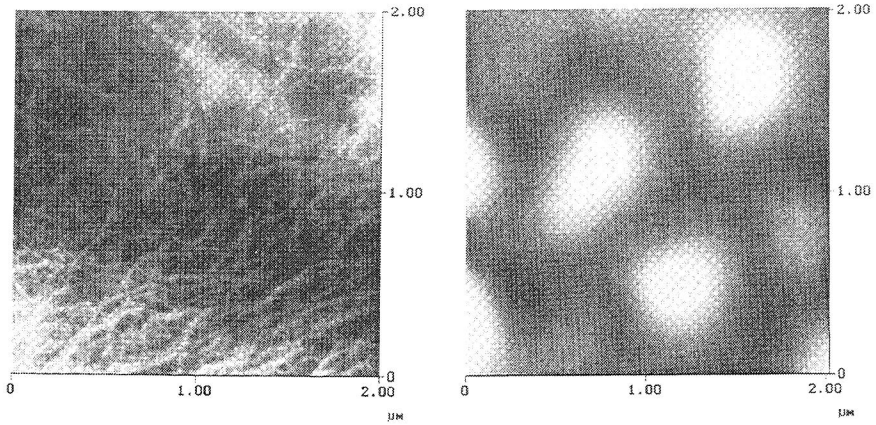

Fig. 2: AFM images of (a) untreated and (b) 30 seconds silent discharge treated polypropylene.