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X-ray photoelectron spectroscopy studies of polymer surfaces

Part 3 *Flame treatment of polyethylene*

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X-ray photoelectron spectroscopy showed that a normal flame treatment caused a high level of oxidation in low-density polyethylene. 0.02% of the antioxidant 2,6-ditert-buty-*p*-cresol did not reduce the degree of oxidation or the level of adhesion in contrast to the extrusion of low-density polyethylene. It is estimated that the depth of oxidation is between 40 and 90 Å which is much less than for a moderate chromic acid treatment or with extrusion. There were no significant changes in the XP-spectra or adhesion levels of flame treated samples after 12 months.

1. Introduction

To achieve satisfactory adhesion with polyethylene it is normally necessary to carry out a pre-treatment. However, there is much controversy as to whether the pre-treatments are effective by increasing the surface energy or by eliminating weak boundary layers [1–8]. In Part 1, the effect of chromic acid on polyolefins was studied [7]. In Part 2, another surface treatment was examined [8]; this method involved melting polyethylene onto aluminium followed by dissolution of the metal [6]. In the present paper, the flame treatment of polyethylene is examined using X-ray photoelectron spectroscopy.

The two most widely used pre-treatments for polyolefins are the corona discharge and flame method. The corona discharge treatment is almost always used for the pre-treatment of polyolefin films whereas the flame treatment is usually used for thicker sections, e.g. to improve the printing on bottles. Although the flame treatment has been widely used for about 25 years [9], little has been published on the changes caused by the treatment to the polymer surfaces. The reason for the paucity of information on the chemistry of the treated surfaces is that until fairly recently no technique was available that was sufficiently sensitive to detect any change in the surface chemistry. However, X-ray photoelectron spectroscopy (XPS) is not only sufficiently sensitive to detect such changes but can provide quantitative information on oxidation levels.

In the present communication, XPS and adhesion data are presented for the flame treatment of low-density polyethylene (LD PE); in particular the effects of gas flow rates, an antioxidant and "ageing" are examined.

2. Experimental details

2.1. XPS measurements

XPS data were obtained using an AEI ES200B electron spectrometer employing MgK_α exciting radiation (1253.6 eV). The electron analyser was operated in the fixed retarding ratio (FRR) mode. Samples were examined in the form of rectangles (20 mm x 6 mm) cut from untouched sheet and mounted with double-sided Sellotape

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onto the probe tip. The working pressure in the spectrometer chamber was 10^{-8} Torr.

Binding energies are corrected to Cls = 285.0 eV for the untreated polyethylenes. The instrument was calibrated so that the $Au4f_{\frac{7}{2}}$ peak had BE = 84.0 eV relative to the Fermi level. Binding energies are considered to be accurate to ±0.2 eV.

Deconvolutions were carried out using a Du Pont 310 Curve Analyser with Gaussian functions.

2.2. Materials

"Alkathene" 47 is a low-density polyethylene with a melt flow index of 2 and is a product of I.C.I. Ltd. "Alkathene" 11 is the same polymer as "Alkathene" 47 but contains 200 ppm (0.02%) of "Topanol" OC antioxidant (2,6-ditertiary butyl-*p*-cresol). Blown films of both polymers (thickness 0.125 mm) were used. "Araldite" AV100 and HV100 are products of Ciba-Geigy Ltd.

2.3. Treatment and bonding

The apparatus used was a laboratory bottle flaming rig at Plastics Division, I.C.I. Ltd, Welwyn Garden City. It consists of a rotating spindle with a spigot to which a bottle of diameter 50 mm can be attached, and a burner which can be brought close to the bottle. The distance between the burner nozzles and the bottle was 50 mm. The burner itself was 150 mm wide with 94 jets. The flame used was a natural gas–air mixture and the flow of each gas could be adjusted.

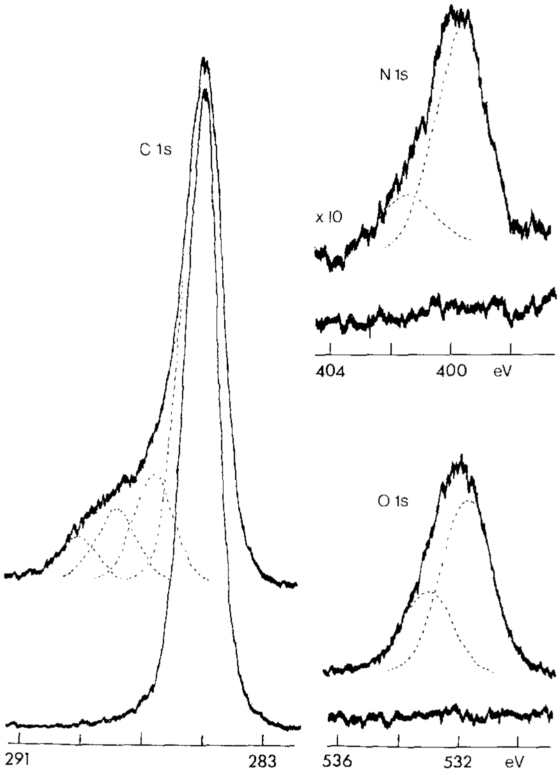

Figure 1 Core level spectra (on the binding energy scale) from Alkathene 11 before treatment (lower trace) and after flame treatment (4× "normal" treatment). Count rate = 3×10^3 counts sec^{-1} (high resolution spectra).

A piece of polyethylene film was affixed to a bottle by means of double-sided tape and the bottle was then rotated at 290 r.p.m. The film was then treated; the normal treatment was for 1.2 sec with flow rates for natural gas and air of 37 and 150 cm^3 sec^{-1}, respectively. The film was then removed and re-affixed so that the other side could be treated. During these operations, the films were only handled by their edges. After treatment, the edges were cut off, and the films handled only with clean tweezers. The films were stored in the dark prior to testing.

Composite lap joints were made of aluminium (127 mm x 25.4 mm x 3 mm) –epoxide adhesive–polyethylene film (0.125 mm)–epoxide adhesive–aluminium (127 mm x 25.4 mm x 3 mm) with a resultant 25.4 mm x 25.4 mm overlap [6]. The epoxide adhesive system was "Araldite" AV100 plus "Araldite" HV100 used in the ratio of 1:1, the adhesive was cured for 3 h at 60° C. The lap joints were tested at 6.25 mm min^{-1}, the values quoted being the mean of ten results.

3. Results

For both film formulations flame treatments were carried out with four different sets of conditions. In each of these the air : gas ratio is approximately the same at 4.1 to 4.4. For the "normal" setting the flow rates are 37 and 150 cm^3 sec^{-1} for gas and air, respectively. For the "high" and "low" settings these figures are 74/317 and 18.5/75, respectively. In each case the film spends 1.2 sec in the flame. Samples were also treated for four times this period (4 x "normal").

XPS examination of control (untreated) samples indicated very low levels of oxidation. Treated samples gave intense Ols signals and sometimes weaker Nls signals. Peak areas have been converted into relative atomic concentrations using relative elemental sensitivity factors determined with the same instrument from pure organic materials sublimed *in situ*. These factors are O:C = 1.55 and N:C = 1.30 from the ls signals. The XPS data and the corresponding adhesion results are shown in Table I.

TABLE I XPS and joint strength data for polyethylenes which have been flame treated

Polymer	Treatment time (sec)	Natural gas flow ($cm^3\ sec^{-1}$)	Air flow ($cm^3\ sec^{-1}$)	O:C (at.%)	N:C (at.%)	Lap shear‡ strength ($MN\,m^{-2}$)	Standard deviation σ sample
Alkathene 47*	0	0	0	0.25	0	0.55	0.07
Alkathene 47	1.2	37	150	16.9	0.94	6.6	0.6
Alkathene 47	4.8	37	150	31.0	3.2	7.2	0.7
Alkathene 47	1.2	74	317	15.3	2.2	6.8	0.7
Alkathene 47	1.2	18.5	75	6.8	0	5.1	0.6
Alkathene 11†	0	0	0	< 0.25	0	0.36	0.04
Alkathene 11	1.2	37	150	20.5	1.5	5.6	0.5
Alkathene 11	4.8	37	150	33.4	3.2	7.2	0.4
Alkathene 11	1.2	74	317	13.7	2.5	6.4	0.3
Alkathene 11	1.2	18.5	75	5.1	0	5.7	0.4

* Contains no additives.

† Contains 0.02% 2,6-ditert-butyl-*p*-cresol.

‡ With the treated polymers the failure was always a mixture of apparent interfacial and material.

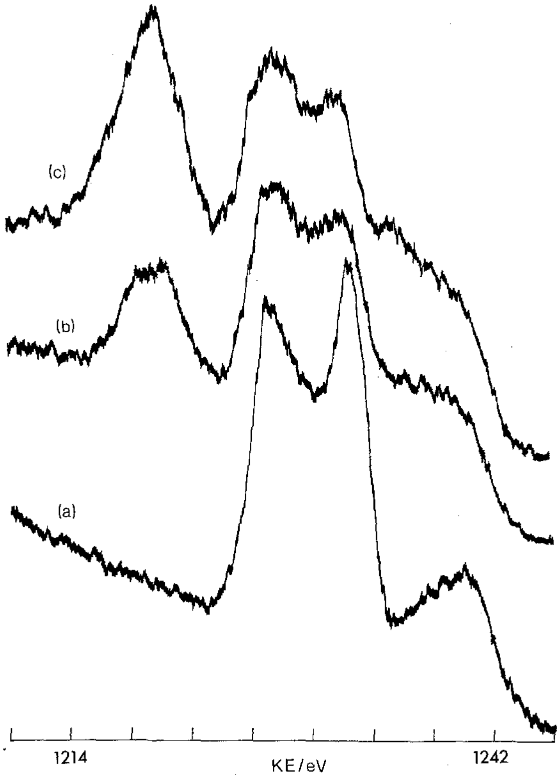

Figure 2 Valence band spectra from Alkathene 11 (a) untreated, (b) after "normal" flame treatment, (c) after 4× "normal" flame treatment. Count rate = 10^3 counts sec^{-1} (low resolution spectra).

Typical spectra from polyethylene surfaces before and after flame treatment are shown in Fig. 1. A simple deconvolution of the Cls spectrum for the most oxidized surface gives three peaks to higher binding energy (BE) of the primary (hydrocarbon) peak. As discussed previously [7, 10] these can be identified as carbon singly bound to oxygen (e.g. *C*–OH, *C*–O–C, $-\overset{O}{\overset{\|}{C}}-O-C$ and possibly *C*–OOH), carbonyl (*C*=O) and carboxyl (–*C*OOH, –*C*OOR) with increasing BE. The broad Ols signal at 532 eV is not particularly informative since all the oxygen functions noted above give BEs near 532 eV except $O-\overset{|}{C}=O$ which has a BE some 1.5 eV higher. The Nls signal is also broad and distinctly asymmetric on the high BE side. The major contributor to this peak has a BE of 399.7 eV which is consistent with either $-NH_2$ or –CN groups [11, 12]. The minor contributor has a BE too low for directly oxidized nitrogen functions but not inconsistent with $-\overset{O}{\overset{\|}{C}}-NH_2$ or $-\overset{O}{\overset{\|}{C}}-NH-$ [13].

Valence band spectra of flame-treated samples (Fig. 2) are in general similar to those shown in Part 1 for low-density polyethylene oxidized by chromic acid [7]. The peak which appears at ~ 1220 eV (KE) is due to 02s electrons. The Ols:02s ratio, which can be used to assess the depth of oxidation, is in all cases significantly greater than the value obtained for homogeneous samples (~ 10)*. The approximate values obtained range from 16 to 20 and follow a trend which increases as the overall level of oxidation decreases.

Angular variation spectra were also obtained for the least oxidized sample. Any difference between the (01s:C1s) intensity ratio for electron

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* In Part 1 the quoted values for the 01s:02s ratio are strictly a factor of 2 too high. This arose because the 02s peak, being very broad, was run on a compressed scale such that the measured area was half the true area.

take-off samples of 10° or 75° (with respect to the surface) was within the experimental error.

Film samples for two of the treatment levels ("normal" and four times "normal" for Alkathene 11) were re-examined more than 12 months after the first investigation. In both cases only minor spectral changes were observed and no significant deterioration in the adhesion levels had occurred. These spectral differences are probably not significant compared with the likely overall variability of surface composition.

4. Discussion

The degree of oxidation of low density polyethylene with a normal flame treatment was similar to that observed with a severe chromic acid treatment [7]. Because failure of the polyethylene usually occurred in the adhesion tests, it was not possible to relate the degree of oxidation with the adhesion levels. Such a correlation has been shown to exist with a range of chromic acid treatments [14] and it is likely that poor adhesion after flame treatment will be associated with a low level of oxidation.

Optimization of surface treatment via the air/gas ratio and time in the flame has been examined [15]. Although we have not examined samples displaying a wide range of oxidation levels, it is clear that variation of these parameters brings about distinct changes in the surface chemistry, especially in the relative populations of oxygen and nitrogen functions (see Table I). Whether or not these relatively subtle variations are important from the adhesion viewpoint requires more study; it is worth noting, however, that these results indicate that the other important variables, i.e. the position of the surface relative to distinct regions of the flame [15] could be fruitfully investigated by XPS.

The combustion of hydrocarbons is a highly complex process [16, 17] and many excited species are present in the flame including free radicals, ions, atoms and electrons. In view of the marked variation in surface chemistry brought about by changes in gas composition (especially the number of nitrogen functions) it seems likely that these species do take part directly in the modification process. The possibilities include excited states of O, NO, OH, NH and CN. It is also probable that ionization events (via ions, metastables, electrons or photons) lead to production of chain radicals which react with oxygen via well recognized mechanisms to produce –OH, –C=O, –COOH etc. By a combination of these mechanisms the species observed by XPS can be broadly explained.

The depth of treatment can be assessed from the 01s:02s intensity ratios and angular variation data. As discussed previously [7] this assessment depends on a knowledge of inelastic electron mean-free paths (IMFP) in polymeric materials. Following the recent discussion by Clark and Thomas on this matter [18] we take $\lambda(\text{Cls}) \sim 14$ Å and $\lambda(02\text{s}) \sim 30$ Å*. 01s:02s ratios significantly greater than ~ 10 imply an inhomogeneous oxygen distribution within the 02s sampling depth ($3\lambda \sim 90$ Å). The lack of angular dependence of the 01s:Cls ratio, on the other hand, implies homogeneity within the Cls sampling depth (~ 42 Å). Thus the polymer surface is modified to a depth, d, such that $40\text{ Å} < d < 90\text{ Å}$.

Although there have been reports in the literature on the effect of flame treatment (see [15]) there is, in fact, no hard evidence to back up speculation. In view of the above finding this is not surprising. This level of oxidation at the surface is confined to such a thin layer that previous methods of investigation would have failed to detect it. Of the various means of oxidizing LDPE we have studied, the depth of oxidation is much greater for melt extrustion [10] and chromic acid treatment [7] than for flame or electrical discharge treatment. This is in accord with the ability of internal reflection infra-red (ATR or MIR) spectroscopy to detect surface chemical changes with the first two methods but not with the last two. Very recently it has been shown that MIR can just detect the effects of electrical discharge treatment of LDPE (at commercially applied levels) whilst XPS can comment in detail on this treatment at very low levels [19]. Techniques similar to those discussed above show that the treatment depth is greater than for flame treatment [20, 21].

The efficiency of flame treatment as an oxidizing agent can be easily assessed by comparing the valence band spectra in Fig. 2 with those from chromic acid etching of the same LDPE presented in Part 1 [7]. The degree of oxidation is given by the ratio of the 02s peak intensity to the average intensity of the polyethylene valence band. This ratio is only ca. 30% lower for LDPE

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* Appropriate to excitation by MgK_α radiation.

flame treated under normal conditions (1.2 sec exposure, Fig. 2b) than for LDPE chromic acid etched for 30 min at 70° C (Fig. 3c in [7]) – a relatively severe treatment by commercial standards [23]. Both resulting surfaces give similar levels of adhesion with an epoxide adhesive.

As the data in Table I show, we detected no significant difference between the surfaces of LDPE with or without antioxidant (200 ppm level) after flame treatment under any of the conditions used. This is in marked contrast to our data for thermal oxidation of similar polymers during melt extrusion [10]. This level of antioxidant caused a significant reduction in the degree of surface oxidation; at the 2000 ppm level oxidation was completely inhibited. We also detected lower oxidation levels for antioxidant containing polymers extruded at 300° C compared with 280° C. We tentatively attributed this to increased volatilization of the antioxidant from the surface at the higher temperature. Extending this argument to the present system is not unreasonable since surface temperatures will increase sharply during passage through the treatment zone. The polymer surface is positioned in the oxidizing region of the flame about 5 mm from the tip of the visible inner cone. The flame temperature at this point is of the order of 2000 K [16]. An alternative possibility is that the surface antioxidant is destroyed by some oxidative mechanism.

Adequately flame-treated LDPE film is known not to suffer from serious deterioration in adhesion if adequately protected [22, 23] and if mobile additives are not present [15]. This is borne out by the present investigation which found no significant loss of adhesion after storage for more than 12 months and no significant difference in the XP-spectra emerged over the same timescale.

5. Conclusions

(1) A normal flame treatment of LD polyethylenes causes a level of oxidation similar to a severe chromic acid treatment.

(2) 0.02% of the antioxidant, 2.6-ditert-butyl-*p*-cresol did not reduce the degree of oxidation or the level of adhesion.

(3) The depth of oxidation was between 40 and 90 Å, i.e. much less than observed with a moderate chromic acid treatment or after extrusion.

(4) There were no significant changes in the XP-spectra or adhesion levels of flame treated samples after 12 months.

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