JOURNAL OF MATERIALS SCIENCE 22 (1987) 1450–1456

Surface effect of flame treatments on polypropylene

Part 2 *SIMS (FABMS) and FTIR-PAS studies*

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Static secondary ion mass spectroscopy (fast atom bombardment mass spectroscopy), (SIMS (FABMS)) and Fourier transform infrared–photo-acoustic spectroscopy (FTIR–PAS) studies have been performed on samples of polypropylene subjected to different numbers of flame treatments. SIMS spectra allowed us to identify unambiguously the site of oxidation in the methyl pendant groups, because of the striking decrease in the intensity of the methyl fragment in positive-ion spectra. The behaviour of the surface concentrations of hydroxyl, formyl and carboxyl groups as a function of the number of flame treatments has also been observed, leading us to an hypothesis supporting the effectiveness of hydroxyl groups in promoting paint adhesion. FTIR–PAS spectra did not show evident changes on passing from untreated to flame-treated samples. This negative evidence is also important: it implies a limited depth of oxidation. In the light of previous XPS results and FTIR–PAS characteristics (thickness of the observed layer and sensitivity) we suggest a depth of oxidation of some 10 to 20 nm.

1. Introduction

In Part 1 of this work we presented paint adhesion, surface tension and XPS studies on flame-treated polypropylene [1]. We found that the behaviour of surface tension and paint adhesion is that displayed in Fig. 1. XPS studies allowed us to observe the formation of various kinds of polar groups, hydroxyl, carbonyl and carboxyl. With the increase in the number of treatments we suggested an increase in the depth of oxidation and further oxidation of hydroxyl and carbonyl groups to carboxyl moieties.

With the aim of substantiating those observations, particularly on a qualitative level, we undertook ulterior studies using secondary ion mass spectroscopy (fast atom bombardment mass spectroscopy) and vibrational techniques. Compared to XPS, secondary ion mass spectroscopy (SIMS) has a shallower depth of analysis. The observed fragments are produced in the first one or two layers of the material, as compared to the 3 to 5 nm examined by XPS. It allows a mass spectrum of the surface to be obtained and the fragmentation affords quite sophisticated qualitative information [1–3].

Vibrational techniques can also be very informative. We chose Fourier transform infrared–photoacoustic spectroscopy (FTIR–PAS) spectroscopy [4–6] because it does not require any sample handing, such as contacting with an internal reflection element (IRE). As with other vibrational techniques, such as IRS–IR is cannot be considered a true surface technique. The thermal diffusion length, in our case some 10 μm, is a good estimate of the thickness of the analysed layer.

2. Experimental techniques

Plaques (20 cm × 7 cm × 0.3 cm) of a high-impact polypropylene were injection moulded at 250° C by Plastinjector GBF 90 injection machine. The flame treatment was performed by placing the plaque on a conveyor-belt under a linear burner supplied by Samia SpA. A propane–air mixture was used to obtain the flame. The temperatures in the flame were 1200 and 1040° C, at 2 and 4 cm for the burner, respectively.

The flame equipment allowed the use of different speeds for passing the specimen under the flame; the range was 1 to 30 m min^{-1}. The distances from the burner were varied in the range 1 to 6 cm. The polypropylene samples were studied as thick sheet (1 cm × 1 cm) mounted on to stainless steel sample holders using double-sided adhesive tape.

The equipment used to obtain static SIMS spectra is a VG SIMSLAB instrument. The essential components consist of an ion/atom gun designed in UMIST laboratories and described in detail elsewhere [7], a secondary ion energy analyser after the design of

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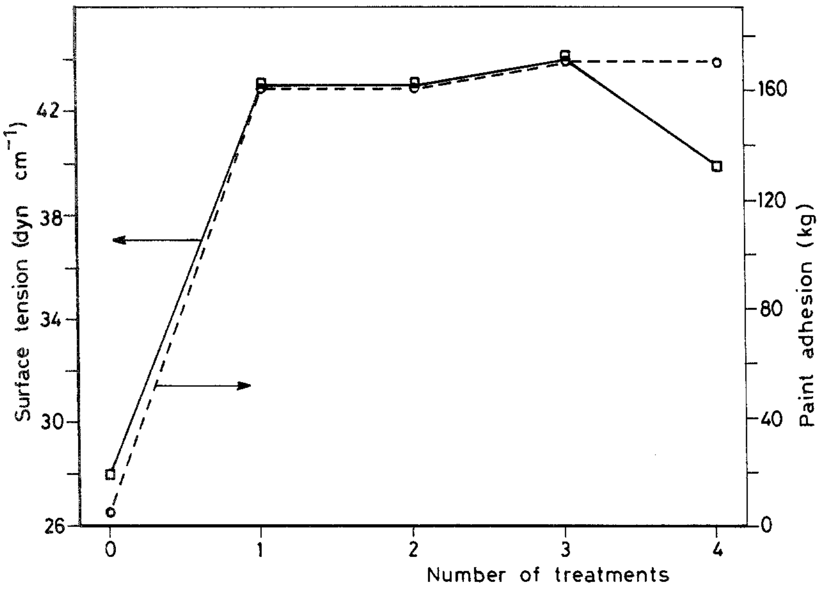


Figure 1 Paint adhesion (– – –) and surface tension (——) as a function of the number of flame treatments.

Wittnoack *et al.* [8] and a quadrupole mass spectrometer (VG MM12-12, 0-1200 Daltons).

A precision specimen manipulator allows movement in *x*, *y* and *z* directions along with 180° rotation about the *z*-axis. A railway system and vacuum lock allow fast transfer of specimen from atmosphere to UHV in approximately 3 min. The base pressure in the system is 10^{-8} Pa, but normal chamber working pressure during operation of the ion/atom gun is in the region of 10^{-5} Pa argon. The ion/atom gun provides a mass filtered beam of argon ions or atoms (0.5 to 2 keV energy) which strikes the sample at 30° incident to the surface plane and is focused into an area of 0.3 cm^2. An electron flood gun (VG LEG 31, 500 eV energy, 0.1 nA to 10 μA cm^{-2} current density) is available for stabilization of the surface potential when sample charging occurs.

Static SIMS spectra were acquired using 2 keV argon atoms with a flux density of 3×10^9 atom cm^{-2} sec^{-1} measured in the manner described previously [7]. A PDP 11 based computer system was used to ramp the mass spectrometer and simultaneously collect the secondary ion signal from the pulse counting equipment. With a combined setting up and spectral acquisition time of 600 sec the total dose for positive and negative ion spectra was approximately 2×10^{12} atoms cm^{-2} per sample. This falls well within the established regime for static SIMS spectra of "undamaged" polymer surfaces [9].

SIMS is not a directly quantitative technique, since the sputter yields for the different fragments are not known a priori [10]. We chose to plot the normalized intensities of some of the peaks against the number of flame treatments. The normalization of intensities has been obtained using as internal standards the peaks at 41 Daltons (positive ions spectrum) and at 25 Daltons (negative ions spectrum). These peaks, relative to the hydrocarbon fragmentation of the polymer, should be the most reproducible.

FTIR–PAS spectra where obtained at the Bruker Demo Centre in Karlsruhe.

2.1. SIMS (FABMS)

FABMS has been chosen since it does not induce charging problems. It has been shown that in polymeric materials FABMS is definitely more dependable than static SIMS [7]. We examined samples subjected to 0, 1, 2, 4 flame treatments.

The positive and negative ions spectrum of untreated polypropylene are displayed in Fig. 2. As previously reported [11] the positive ions spectrum (top) reflects essentially the hydrocarbon fragmentation. The peak at 15 Daltons is relative to the methyl cation, those at 27 and 29 Daltons to fragments with two carbon atoms ($C_2H_3^+$ and $C_2H_5^+$). Fragments with three carbon atoms produce peaks at 39, 41 and 43 Daltons. Four carbon atoms correspond to peaks at 53, 55, 57 and five carbon atoms to peaks at 65, 69, 71 Daltons. It should be noted that the 69 peak is typical of polymers with methyl pendant groups such as polypropylene and polymethacrylates. It has been attributed [8] to the dimethylcyclopropyl cation, particularly stable because of resonance and induction effects [12].

The negative ions spectrum (Fig. 2, bottom) is again dominated by the hydrocarbon fragmentation. The peaks at 12, 13, 14 Daltons are relative to C^-, CH^-, CH_2^- fragments. At 24, 25, 26 Daltons there are peaks due to C_2^-, C_2H^-, $C_2H_2^-$. The fragments with three carbon atoms give peaks from 36 Daltons onwards, those with four carbon atoms from 48 onwards. Traces of peaks relative to fragments with five carbon atoms appear from 60 Daltons.

Limited amounts of oxygen appear at 16 and 17 Daltons (O^- and OH^-). In the positive ions spectrum some H_2O^+ gives the small peak at 18 Daltons. The presence of a limited number of oxidized functions or plain printed polypropylene is well known [13]. The injection moulding itself is able to produce some oxidation at the surface.

In Fig. 3 the positive (top) and negative (bottom) ions spectra relative to the sample treated once are shown. In the positive ions spectrum the hydrocarbon fragmentation is still the dominant feature. It should in any case be noted that the intensity of the 15 Daltons peak, the methyl cation, underwent a considerable decrease with respect to the untreated sample. At the same time the 18 Daltons peak (H_2O^+)

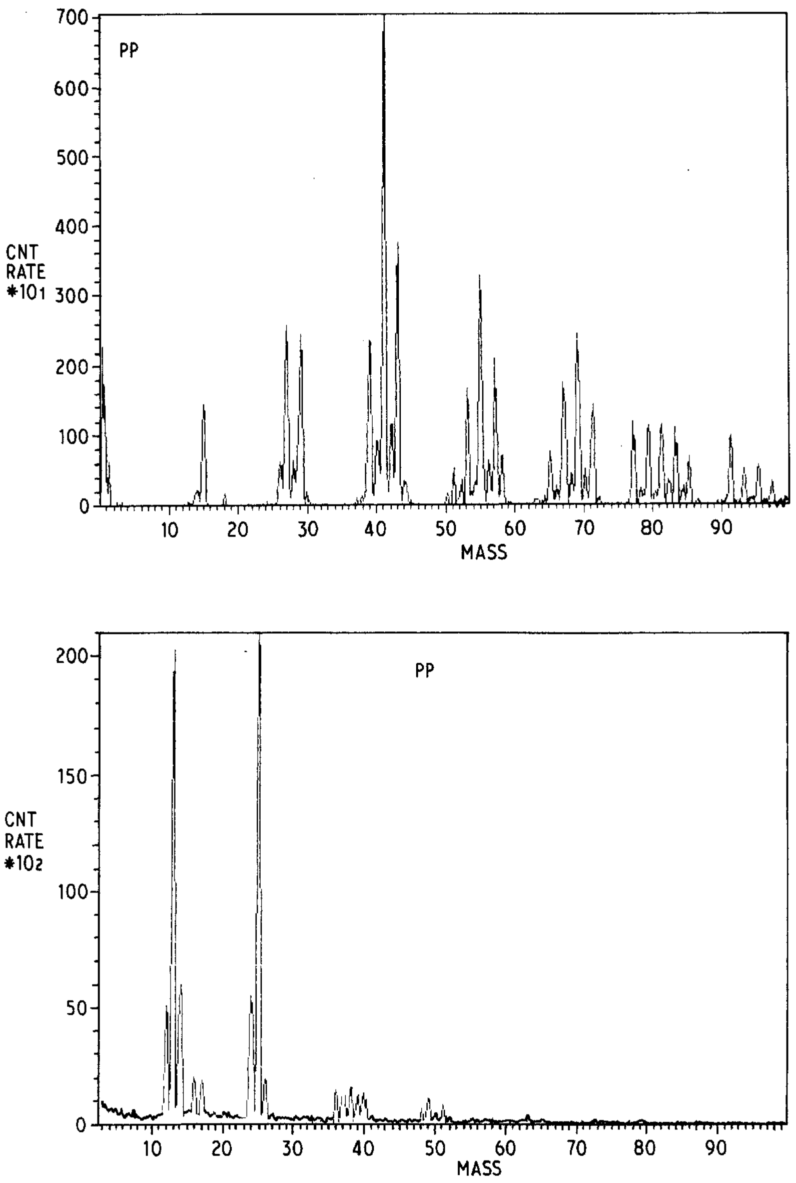


Figure 2 Positive (top) and negative (bottom) ion FABMS spectra of untreated polypropylene.

strongly increases, and a new peak is formed at 31 Daltons (CH_2OH^+). These features testify both the beginning of the oxidation at the surface and a possible involvement of methyl groups in the oxidation phenomena. A collateral event is the appearance of peaks at 58 and 42 Daltons. These fragments suggest the diffusion of nitrogen-containing additives to the surface as a consequence of the flame treatment.

In the negative ions spectrum (Fig. 3, bottom) it is immediately evident that the amount of oxygen present at the surface has increased as a consequence of the flame treatment, as expected. Peaks at 16, 17, 32, 33 Daltons are assigned to oxygen (respectively O^-, OH^-,O_2^-, O_2H^-). Apart from the presence of peaks due to fragmentation of the polymer, it is possible to observe the formation of oxygen containing functions. The peak at 41 Daltons is attributed to C_2OH^-, corresponding to hydroxyl or formyl functions. Barely visible are peaks at 57 and 59 Daltons, due to carboxyl functions ($C_2O_2H^-$ and $C_2O_2H_3^-$).

Various inorganic anions are also present, for example chlorides (35 and 37 Daltons). These fragments probably originate from inorganic anions either present as surface contamination or diffused to the surface as a consequene of the treatment. The spectra relative to the sample treated twice just confirm the observations on the sample treated once. Both the decrease of the methyl peak and the increase of the peaks due to oxygen containing functions are confirmed.

Similar conclusions can be reached observing the spectra relative to the sample four times flame treated. It should be noted that the amount of hydroxyl groups does not seem to increase with the fourth treatment nor does the intensity of the methyl peak decrease, while there is some increase in the intensity of the peaks ascribable to carboxyl groups.

SIMS (FABMS) results extremely interesting in the qualitative analysis of the chemical phenomena consequent to the flame treatment of polypropylene. Its distinguishing features are the possibility of observing unambiguously the fragments corresponding to different oxidized functions and its astounding sensitivity which allowed us, for example, to monitor the presence of carboxyl groups in the samples treated once and twice. This task had proved impossible by XPS [1].

2.2. FTIR–PAS

We also undertook vibrational studies on our samples. In Fig. 4 the spectra relative to the untreated sample (top) and the sample treated four times (bottom) are

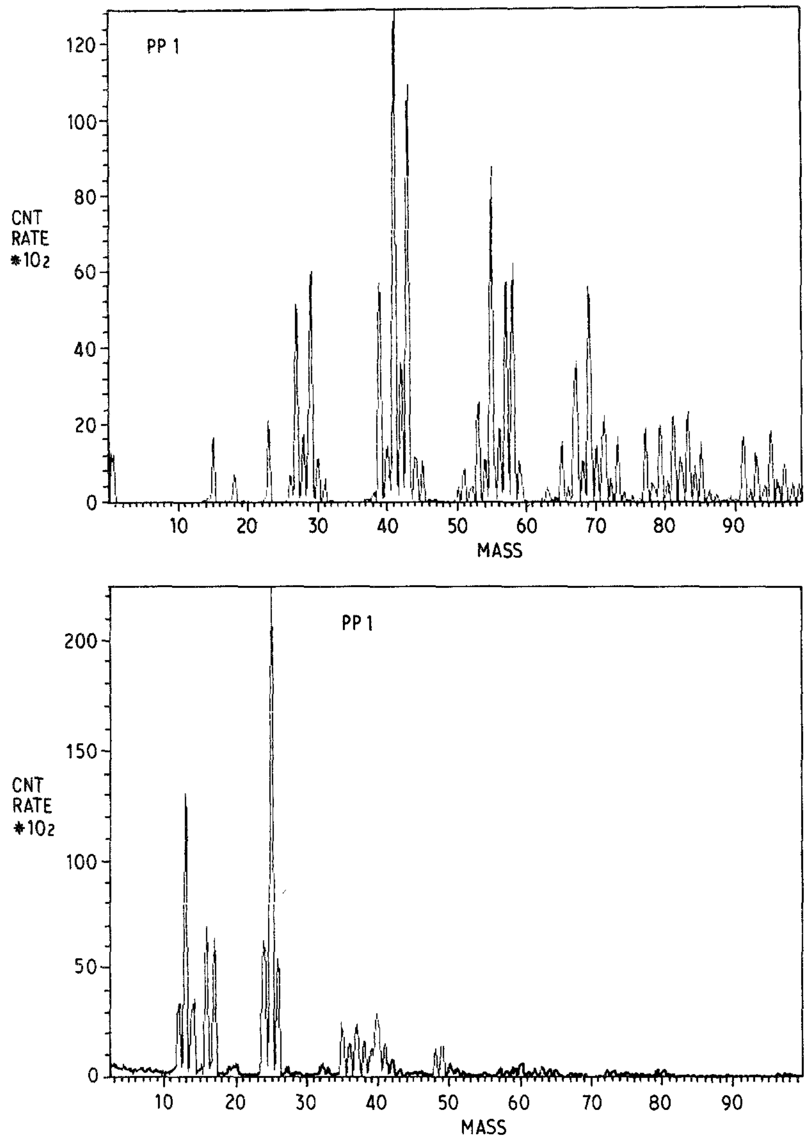


Figure 3 Positive (top) and negative (bottom) ion FABMS spectra of polypropylene flame treated once.

Figure 4 FTIR–PAS spectra of untreated polypropylene (top) and polypropylene flame treated four times (bottom).

displayed. The sample treated four times should be the most oxidized, as demonstrated by XPS measurements [1], but comparing the two spectra in Fig. 4 it is not possible to note significant variations. There is no evidence of a significant modification of the bands typical of the polymer and no bands due to oxygen containing groups, for example carbonyl or carboxyl groups appear. The distortions in Fig. 4 are caused by an imperfect elimination of the water and carbon dioxide signals originating from the photoacoustic cell (the transport gas was air). This experiment suggests that the modification induced by the treatment is restricted to the first few tens of nanometres. The bulk of the polymer is unaffected by the treatment. With our experimental parameters the thermal diffusion length can be estimated in some 10 μm. The thickness of the observed layer can be assumed equal to the thermal diffusion length. Using FTIR–ATR, Ohta and Iwamoto [14] have shown that the technique is able to detect a 2 nm thick layer on top of a different polymer. Even remembering that FTIR–PAS is less sensitive and that the concentration of polar groups is limited, some 10 to 20% [1], a modification involving more than 10 to 20 nm, should have been detectable.

This result is interesting from a technological point of view, since mechanical properties, for example,

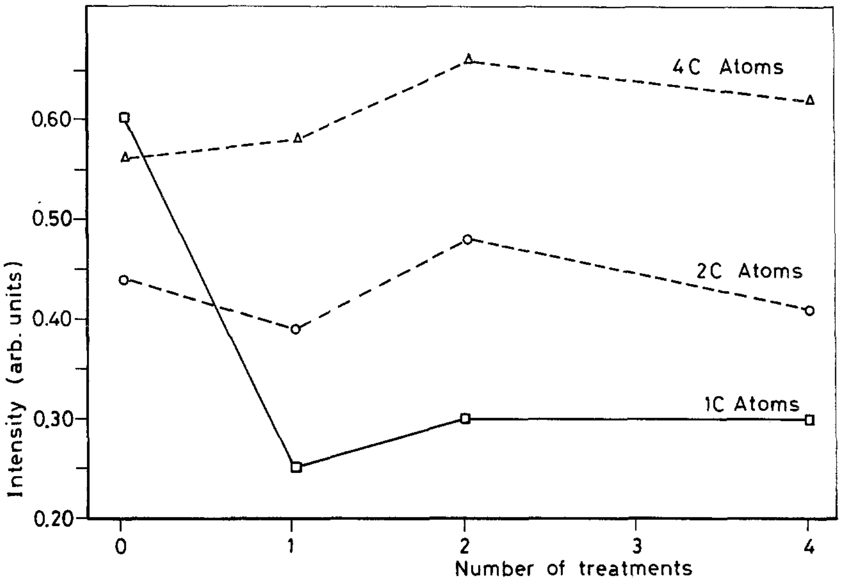


Figure 5 The intensities of positive ion peaks corresponding to hydrocarbon fragments with one, two and four carbon atoms plotted against the number of flame treatments.

depend on bulk characteristics of the polymer. In our case the flame treatment does not alter the bulk of the material.

3. Discussion

The observation of the behaviour of the normalized intensities of FABMS peaks with the number of flame treatments affords much interesting information. The intensities of the positive ions due to hydrocarbon fragmentation show different trends as a function of the number of treatments. The peaks relative to fragments with one, two and four carbon atoms have the behaviour displayed in Fig. 5. The methyl peak (15 Daltons) shows a dramatic decrease with the first flame treatment, about 50% of the original intensity. On the other hand, the peaks relative to fragments with two and four carbon atoms remain quite constant in intensity (the variations are less than 10% and can be ascribed to experimental uncertainties).

It is also interesting to consider the behaviour of fragments corresponding to oxidized functions. SIMS does not allow direct estimates of functional group concentrations, but the total amount of oxygen-containing functions present in the first one or two layers does not seem to change drastically whether we consider the sample treated once, twice or four times. The main evidence we extract is that the intensities of peaks relative to different oxygen-containing functions show different trends with the number of flame treatments.

The behaviour of the positive ions peaks 31 (CH_2OH^+) and 18 (H_2O^+) are displayed in Fig. 6. The CH_2OH^+ fragment shows an increase up to two flame treatments, to decrease after four treatments. On the other hand, the H_2O^+ peak increases again with the fourth treatment. To explain these trends it should be remembered that the CH_2OH^+ fragment is originated by hydroxyl groups essentially, while H_2O^+ can be produced by hydroxyl and perhaps also by carboxyl functions or can come from water adsorbed at the surface, the adsorption is favoured by the presence of polar groups.

Fig. 7 shows the behaviour of the negative ions peaks at 41 and 59 Daltons. The 41 peaks is due to a C_2OH^- fragment, coming from hydroxyl or formyl moieties. The 59 peak has been attributed to $C_2O_2H_3^-$ and its origin lies in carboxyl groups. The 41 peak increases up to two flame treatments, to remain constant after four treatments, the 59 peak keeps increasing also with the fourth treatment.

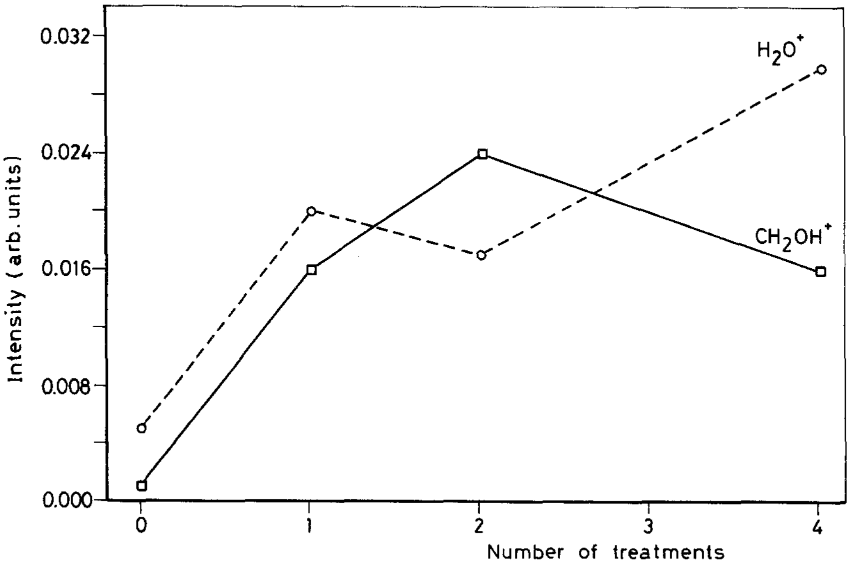


Figure 6 The intensities of CH_2OH^+ and H_2O^+ fragments plotted against the number of flame treatments.

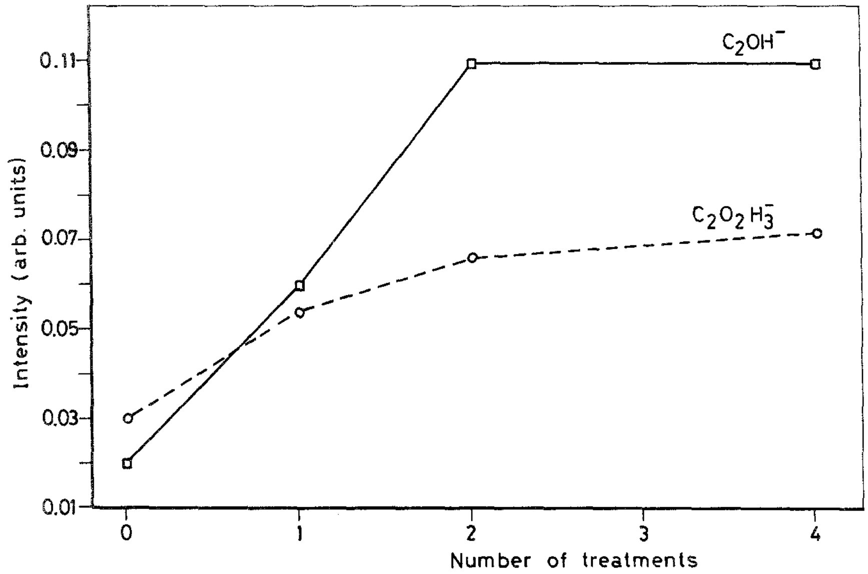
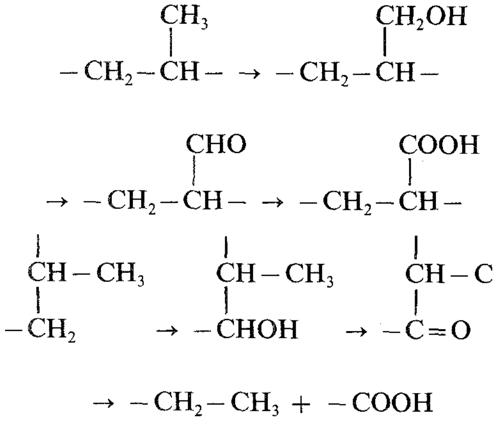


Figure 7 The intensities of C_2OH^- and $C_2O_2H_3^-$ fragments plotted against the number of flame treatments.

Some conclusions can be drawn from this evidence. First of all it is possible to locate the site of the oxidative attack. Two routes are conceivable:



$$\mathrm{-CH_2-\overset{CH_3}{\overset{|}{CH}}-} \rightarrow \mathrm{-CH_2-\overset{CH_2OH}{\overset{|}{CH}}-}$$

$$\rightarrow \mathrm{-CH_2-\overset{CHO}{\overset{|}{CH}}-} \rightarrow \mathrm{-CH_2-\overset{COOH}{\overset{|}{CH}}-}$$

$$\begin{array}{l} | \\ \mathrm{CH-CH_3} \\ | \\ \mathrm{-CH_2} \end{array} \rightarrow \begin{array}{l} | \\ \mathrm{CH-CH_3} \\ | \\ \mathrm{-CHOH} \end{array} \rightarrow \begin{array}{l} | \\ \mathrm{CH-CH_3} \\ | \\ \mathrm{-C=O} \end{array}$$

$$\rightarrow \mathrm{-CH_2-CH_3} + \mathrm{-COOH}$$

The first route involves an attack on the methyl pendant groups with successive formation of hydroxyl, formyl, carboxyl functions. The second route involves an attack on skeleton methylene groups, to give secondary hydroxyl groups and then a ketone function. To account for the formation of carboxyl groups it is necessary to postulate a breakage of the polymeric chain. Our evidence does not agree with this second mechanism. In fact the alteration in the intensity of the methyl fragments and the contemporary indifference to the number of flame treatments of the fragments with more than one carbon atom is in agreement with the first mechanism, implying essentially a limited decrease in the number of "free" methyl groups. The second mechanism would not justify a strong change in the methyl intensity and would require a change in the intensity of fragments for example with two carbon atoms. Furthermore the formation of CH_2OH^+ fragments is typical of primary alcohols and not of secondary alcohols.

It is then intriguing to try to relate the behaviour of peaks corresponding to different oxidized functions to the relevant surface tension and paint adhesion values (Fig. 1). CH_2OH^+ and C_2OH^- show an analogous trend. Both continue to increase up to the second treatment to show then either a diminution or a constant trend. On the other hand, H_2O^+, OH^- and $C_2O_2H_3^-$ display a monotonous increase with the number of treatments.

These trends (Figs 6 and 7) are consistent with a step-by-step oxidation. First of all hydroxyl functions are formed, the oxidation proceeds then with subsequent formation of formyl and carboxyl groups. The simultaneous decrease in hydroxyl groups and increase in carboxyl functions can be explained as a consequence of the oxidation of hydroxyl groups to carboxyl groups with the iteration of flame treatments.

The surface tension does not change strikingly on passing from one to two and four flame treatments, confirming that the total amount of oxygen-containing functions is relatively constant, whichever the number of flame treatments. We also observed that the surface tension is slightly sensitive to the transformation of hydroxyl and formyl groups to carboxyl groups, as demonstrated by the small decrease after the fourth treatment (Fig. 1). Probably this effect is a consequence of the strong tendency of carboxyl groups to give hydrogen bonds with other polar groups present in the material, as already suggested [1].

Paint adhesion remains more or less constant with the increase in the number of flame treatments, whatever the number of treatments. Two hypotheses can be presented to explain this behaviour. (1) Hydroxyl, formyl and carboxyl functions are all similarly effective in promoting adhesion. (2) The number of oxidized functions necessary to give adhesion is relatively low and a sufficient amount is already formed with the first treatment. The partial alteration in quantity of the different oxidized functions with further flame treatments is insufficient to alter paint adhesion (Fig. 1). Since paint adhesion very probably involves a chemical reaction, usually the quality of the oxidized functions participating in a reaction is far from indifferent. We think then that the second hypothesis can offer a better explanation of the experimental observations.

With the first treatment hydroxyl groups are predominantly formed, so they should be considered the main promoters of paint adhesion. In this respect it should be remembered that the role of C–OH groups in polyolefin printability has been emphasized recently by Briggs *et al.* [15, 16].

4. Conclusions

SIMS, contact angle [1], XPS [1] and FTIR–PAS experiments were performed on our samples and a comprehensive view of the effects of the flame treatment at different depths was obtained. At the surface, in the first one or two layers, the amount of oxidized functions does not change macroscopically, increasing the number of flame treatments, as testified by SIMS and contact-angle measurements. The quality of oxidized groups somewhat changes, with a partial transformation of hydroxyl functions (considered the main promoters of paint adhesion) in carboxyl groups.

At intermediate depth observed by XPS (3 to 5 nm) the effects of oxidation are still clearly visible [1]. The number of polar groups shows a constant increase with the number of flame treatments, the depth of oxidation is then a function of the number of treatments.

FTIR–PAS spectra show that the flame treatment does not result in an observable oxidation in the first 10 μm, even after four flame treatments. We suggest a depth of oxidation of some 10 to 20 nm, taking into account FTIR–PAS sensitivity.

Acknowledgements

We wish to thank Dr Morterra (University of Turin) for the recording of FTIR–PAS spectra, and Bruker for FTIR–PAS instrument time.

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Received 2 June
and accepted 18 August 1986