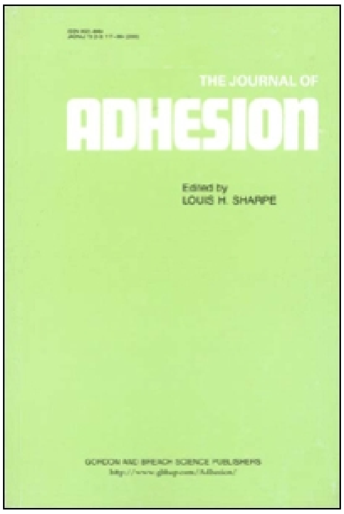

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Flame Treatment and Surface Characterisation of Rubber-Modified Polypropylene

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The flame treatment of a rubber-modified polypropylene has been studied using XPS, contact angle measurement, SEM, vapour-phase derivatisation, and a composite butt adhesion test. Optimum air-to-gas ratio and the distance from the inner cone tip to the polymer surface were found to be ~11:1 and ~0.5 cm, respectively. The lack of correspondence between contact angle and surface oxygen concentration was proposed to be due to the reorientation/migration of surface functional groups that had been incorporated during flame treatment. SEM shows changes in surface topography induced by intense flame treatment. Trifluoroacetic anhydride (TFAA) was found to derivatise —OH groups selectively by using model polymers. About 30% of the incorporated oxygen on flame-treated polypropylene surfaces was found to be present as —OH. Under most flame conditions studied, the interfacial adhesion with an epoxy adhesive or a polyurethane paint was found in excess of the polymer's cohesive strength. The results obtained are compared with those from a propylene homopolymer and an ethylene/propylene copolymer.

KEY WORDS flame treatment; rubber-modified polypropylene; adhesion; XPS; vapour-phase derivatisation; hydroxyl groups; contact angle; surface preparation; functional group migration/orientation; trifluoroacetic anhydride.

1. INTRODUCTION

For a variety of applications for polypropylene (PP), good adhesion properties are required. However, the adhesion of PP to other materials is normally poor due to its low surface free energy and the lack of functionality on its surface. To achieve good adhesion, some kind of surface treatment is necessary. For thicker articles, particularly for blow moulded plastic bottles or vehicle bumpers, flame treatment is usually used.

Effects of flame treatment on a propylene homopolymer and an ethylene/propylene copolymer were reported in two previous papers.[1–2] Mild flame treatment was found to be effective in promoting the adhesion of a polyurethane paint to PP. Surface oxygen concentration of PP was increased after flame treatment. Vapour-phase derivatisation with trifluoroacetic anhydride (TFAA) suggested that up to 20% and 30% of the oxygen introduced on the surfaces is present as hydroxyl groups for PP homopolymer and an ethylene-propylene copolymer, respectively.

The present work is a further study on flame treatment of a rubber-modified polypropylene. The surface effects resulting from flame treatment were studied using XPS and contact angle measurement. The relationship between surface oxygen concentration and contact angle was discussed. Vapour-phase derivatisation with TFAA was evaluated using model polymers with known amounts of functional groups, and was subsequently employed to examine the concentrations of hydroxyl groups on flame-treated polypropylene surfaces. Adhesion levels with both an epoxy adhesive and a polyurethane paint were assessed using a composite tensile butt test.

2. EXPERIMENTAL

A polypropylene blended with 20–30% EPDM (ethylene propylene diene terpolymer), Procom D1631 5F76 (ICI) was converted into 100μm film free from slip or antistatic agents by Venus Packaging. A two-pack polyurethane paint, M615-122 + M210-763 (ICI), was mixed and air sprayed onto both sides of the polypropylene surfaces. The paint was cured for 30 min at 90°C, 10 min after spraying. The thickness of the dry paint film was ~30μm. The epoxy adhesive used for the adhesion test, as described in a previous paper,[1] was AV100 + HV100 (Ciba-Geigy). Details of flame treatment were also included in our previous paper.[1] A piece of polymer film backed by an aluminum plate was passed through the flame using a chain conveyor system. A mixture of air and natural gas was used as the fuel gas. The polymer film was treated in a single pass through the flame, and the flame contact time (the time needed for a single point on the polymer surface to pass through the flame) was kept constant at 0.04 seconds.

Purified grades of liquids, water (triple distilled) and diiodomethane (~99%, Aldrich), were used for contact angle measurement. Their surface tensions were measured using a Krüss K10T tensiometer, and found to be 72.8 and 50.3 mN/m, agreeing well with literature values, *i.e.* 72.8 and 50.8 mN/m, respectively.[3] Details of contact angle measurement can be found in a previous paper.[2] Advancing or receding contact angle was measured 10 sec after the advancing or receding of a drop with a diameter of 2~4 mm.

A VG ESCALAB MKI spectrometer was used to record XPS spectra, and vapour-phase derivatisation with trifluoroacetic anhydride (TFAA, 99+%, Aldrich) was used to facilitate the XPS analysis of—OH groups on the surface. Details of XPS analysis and vapour-phase derivatisation using a vacuum frame is also found in an earlier paper.[2]

Poly(vinyl alcohol) (PVA) (M.W.~14,000, Aldrich), poly(acrylic acid) (PAA) (M.W. ~250,000, Aldrich), and poly(vinyl methyl ketone) (PVMK) (Aldrich) were used as model polymers. They were prepared by dipping a piece of poly(ethylene terephthalate) (PET) (Melinex grade O, ICI), first cleaned with trichloroethylene in ultrasonic bath, in their respective solutions, *i.e.* 10% PVA aqueous solution, 4% PAA aqueous solution, and 4% PVMK solution in dimethylformamide. The films were then dried and kept in a desiccator. XPS analysis confirmed complete coverage of the surface of the PET substrate.

3. RESULTS AND DISCUSSION

3.1 Flame Treatment Parameters

Flame treatment parameters, including air-to-gas ratio, flame intensity, and the distance from the inner cone tip to the polymer surface, were examined for their effects as previously done in our studies of propylene/ethylene copolymer.[2] Effects of varying each of the parameters on surface oxygen concentration and contact angle were examined. Flame contact time was maintained at 0.04 sec throughout the study.

Effects of varying the air-to-gas ratio (8.6:1–15.1:1) were studied by varying air flow rate while keeping gas flow rate at 2.6 l/min and the distance at 1.0 cm. It was found that the air-to-gas ratio was less critical for the rubber-modified polypropylene studied here than for the homopolymer or the propylene/ethylene copolymer. Maximum oxidation as measured by XPS and minimum water advancing contact angle were obtained in the range of ~11:1.

Flame intensity was studied by varying the total flow rate (16.9–67.8 l/min) while keeping the air-to-gas ratio constant at 11.8:1 and the distance at 1.0 cm. Surface oxygen concentration increased approximately linearly with total flow rate. Water advancing contact angle rapidly decreased initially with total flow rate. However, a slight increase in water advancing contact angle with flame intensity was found at high total flow rates (>~40 l/min), which is not in a close correspondence with the XPS results.

Effects of varying the distance (0–6.0 cm) between the flame's inner cone tip and the polymer surface were investigated while keeping the air-to-gas ratio at 11.8:1 and the total flow rate at 33.9 l/min. Maximum surface oxygen concentrations and minimum water advancing contact angle were obtained at a distance of ~0.5 cm, after which surface oxygen concentration was found to decrease and contact angle was found to increase with the distance.

3.2 Relationship Between Surface Oxygen Concentration and Contact Angles

Advancing contact angles of water and diiodomethane are plotted against surface oxygen concentration in Figures 1 and 2 for the results obtained in the studies of flame parameters.

It has been shown by Figure 1 that, initially, the water advancing contact angle decreases rapidly with surface oxygen concentration. However, at high oxygen concentrations (>~5 atomic%), the water advancing contact angle has been shown to level off or perhaps even increase slightly. Diiodomethane advancing contact angle is much less dependent on oxygen concentration (Figure 2) although there may be a slight decrease initially. This indicates that the dispersion part of the surface free energy, γ_s^d, for the least wettable patches on the surface, remains relatively constant under various flame conditions.[2]

Significant water and diiodomethane contact angle hystereses were found. They are plotted against surface oxygen concentration in Figure 3. Water contact angle hysteresis increases approximately linearly with oxygen concentration, while diiodomethane contact angle hysteresis is much less dependent on oxygen concentration.

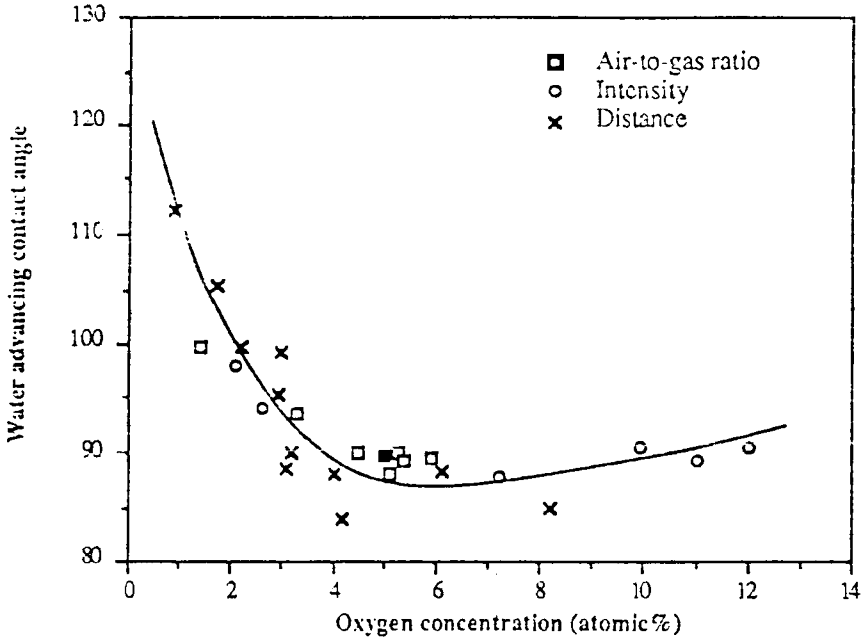


FIGURE 1 Correlation between water advancing contact angle and surface oxygen concentration.

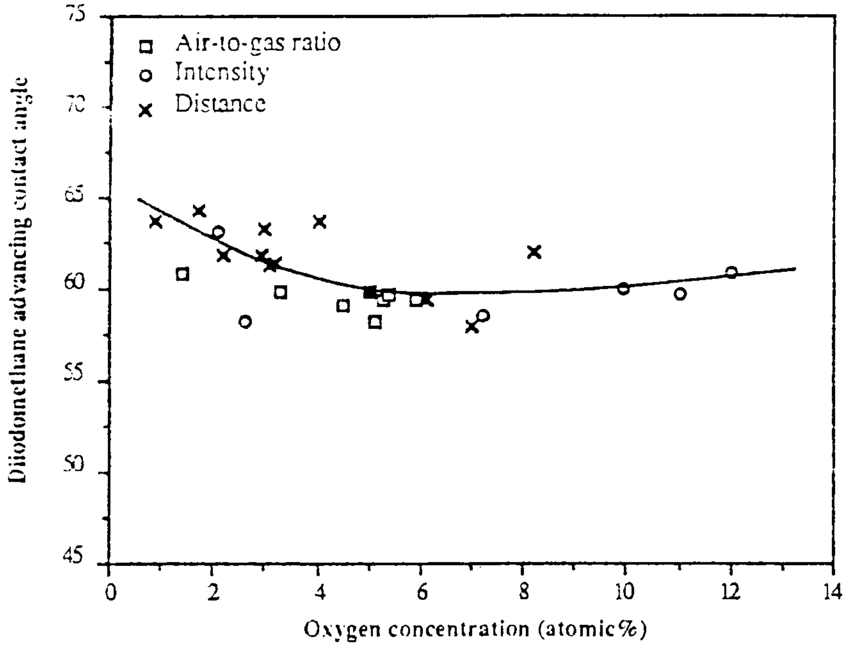


FIGURE 2 Correlation between diiodomethane advancing contact angle and surface oxygen concentration.

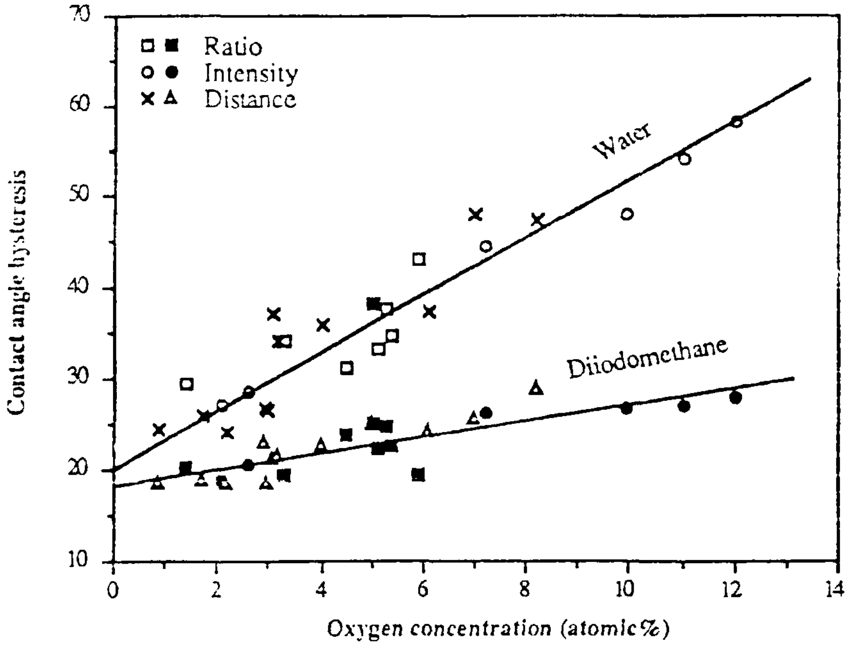


FIGURE 3 Correlation between contact angle hysteresis and oxygen concentration.

More oxygen-containing functional groups on the surface would result in a more polar surface and thus a stronger interaction between the polymer surface and a polar liquid. Therefore, water advancing contact angle would be expected to decrease with surface oxygen concentration. This is not the case, and a variety of possibilities were investigated to explain this non-correspondence.

Surface topography Scanning electron microscopy (SEM) was used to examine the surface topography before and after the flame treatment at various flame conditions (Figure 4). Significant increase in surface roughness was observed after flame treatment except at very low flame intensities. Figure 4d shows evidence of melting of the polymer on the surface treated with very intense flames. If surface roughness is the only reason for the non-correspondence between water advancing contact angle and oxygen concentration at high flame intensities, contact angle hysteresis of diiodomethane would be expected to increase in a similar way as water contact angle hysteresis. This was not observed (Figure 3). Therefore, surface roughness may make small, but not major, contribution to the non-correspondence.

Surface chemistry The non-correspondence could be explained if the type of functional groups present on the surface changed with flame intensity in such a way as to produce oxygen-containing groups at a high flame intensity, which were less polar than those produced at a low flame intensity, on the surface. Although high-energy resolved XPS spectra were complex, no significant changes in functionality were found.

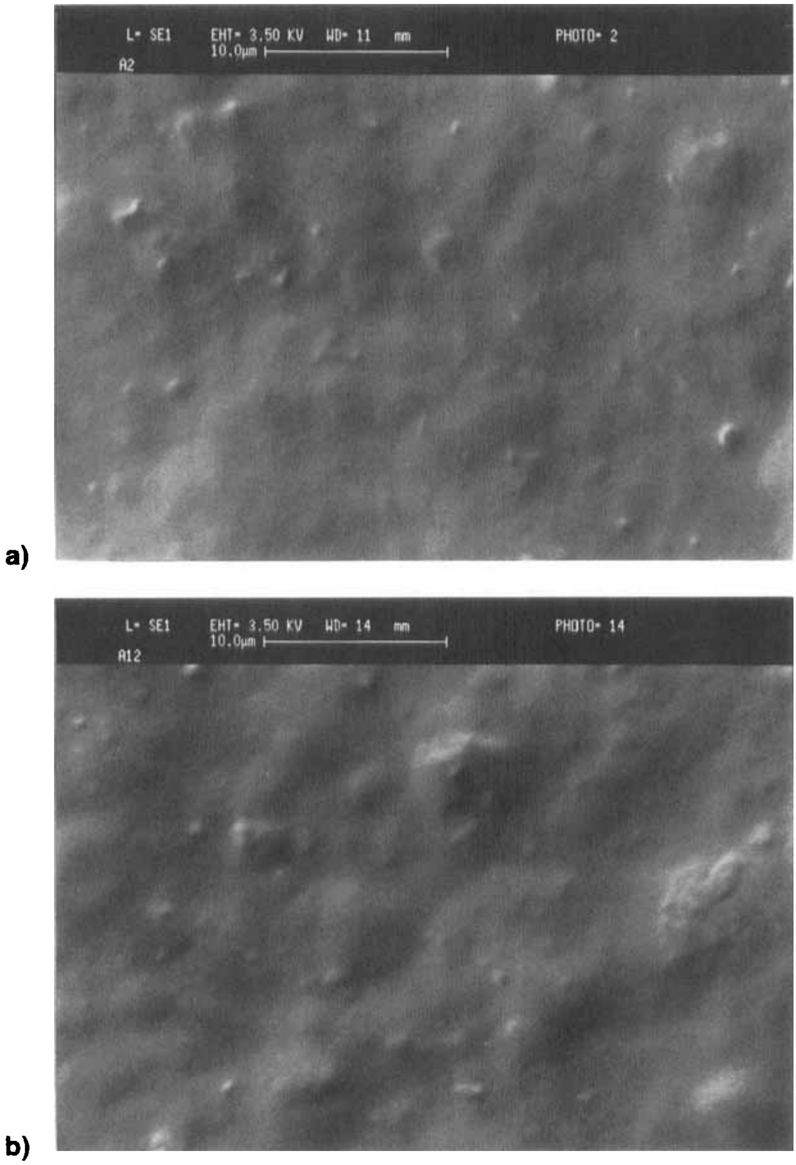
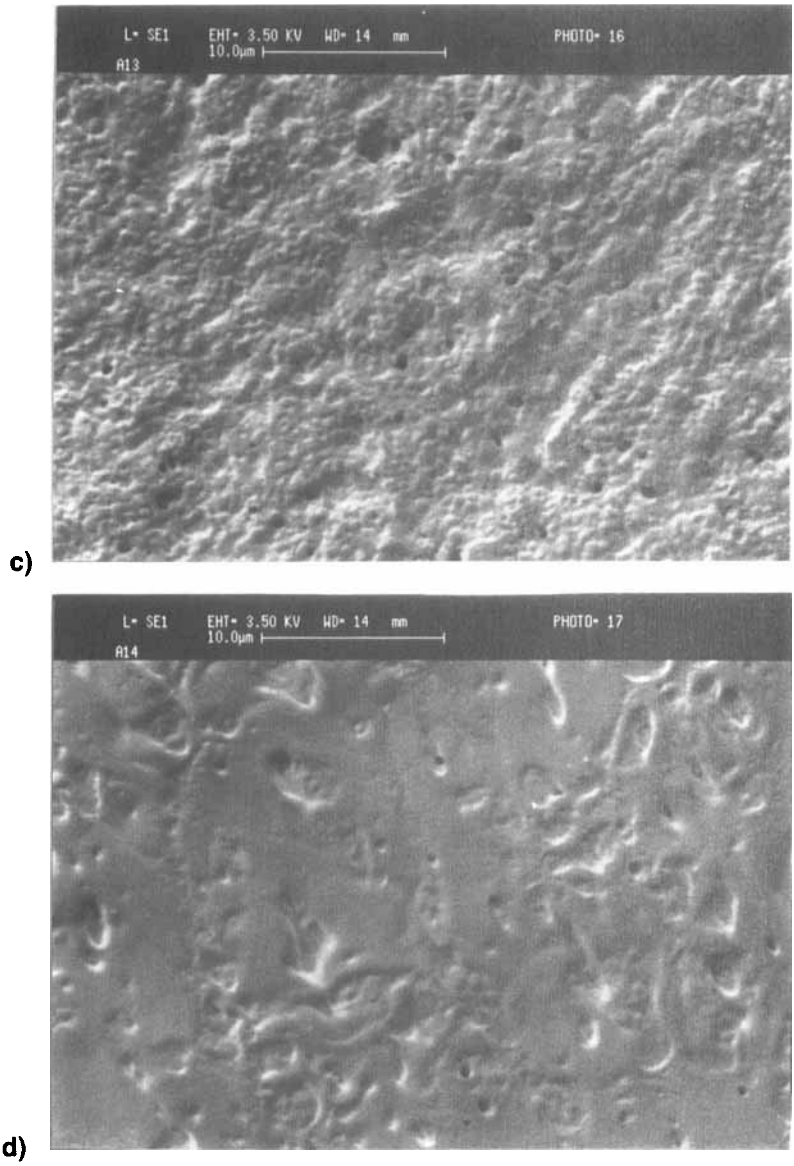
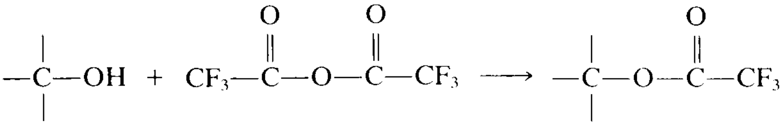


FIGURE 4 SEM micrographs of rubber-modified polypropylene before and after flame treatment: a) untreated; and treated at total flow rate b) 16.9 l/min, c) 33.9 l/min, d) 67.8 l/min. Flame treated conditons: air-to-gas ratio 11.8:1, the distance 1.0 cm, flame contact time 0.04 sec.



Vapour-phase derivatisation with trifluoroacetic anhydride (TFAA) was used to investigate further possible changes in surface chemistry. The derivatisation reaction can be written as,



$$-\overset{|}{\underset{|}{C}}-OH + CF_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CF_3 \longrightarrow -\overset{|}{\underset{|}{C}}-O-\overset{\overset{O}{\|}}{C}-CF_3$$

To evaluate the reactivities of TFAA, some model polymers with known amounts of functional groups were used, *i.e.* PVA, PAA, and PVMK for —OH, —C(=O)OH, and C=O, respectively. By reacting TFAA with PVA using a vacuum frame, limiting fluorine incorporation was obtained within a reaction time of ~2 hrs. No significant increase in fluorine incorporation occurred by further prolonging the reaction time. The reactivities of TFAA towards other model polymers were also examined. Results are listed in Table I.

Compared with the reaction with PVA, reaction of TFAA with PAA or PVMK can normally be ignored, suggesting that TFAA is reasonably selective towards hydroxyl groups in a carbon-oxygen system. This is in agreement with the results of Chilkoti *et al.*[5]

Polypropylene surfaces treated under various flame conditions were also derivatised with TFAA using a vacuum frame. Fluorine concentrations detected by XPS were then converted into the atomic percentages of oxygen present as —OH groups.[6] Hydroxyl group concentration is plotted against oxygen concentration in Figure 5.

A good linear relationship is shown by Figure 5, indicating that about 30% of the oxygen incorporated onto the polymer surface by flame treatment is present as hydroxyl groups. A comparable percentage was found for a propylene/ethylene copolymer, while a lower percentage (~20%) was found for a propylene homopolymer.[2]

Surface heterogeneity For a smooth but heterogeneous surface with patches greater than 0.1μm, the advancing contact angle is representative of the least wettable part of the surface and the receding contact angle of the most wettable part of the surface.[4] An increase in the hysteresis of water contact angle would, therefore, be expected if the difference in polar contribution to the surface free energy of least wettable and most wettable parts of the surface increased with the intensity of flame treatment. While the increase in hysteresis can be adequately accounted for by surface heterogeneity, the increase in advancing contact angle can

TABLE I
Elemental compositions of model polymers derivatised by TFAA for 2 hrs using a vacuum frame

Polymer	Functional group	Elemental compositions (atomic%) C	O	F
PVA	$-\overset{\vert}{\underset{\vert}{C}}-OH$	51.3	23.3	25.4
PAA	$-\overset{\overset{O}{\Vert}}{C}-OH$	65.2	31.2	3.6
PVMK	$-\overset{\overset{O}{\Vert}}{C}-$	78.9	17.2	3.9

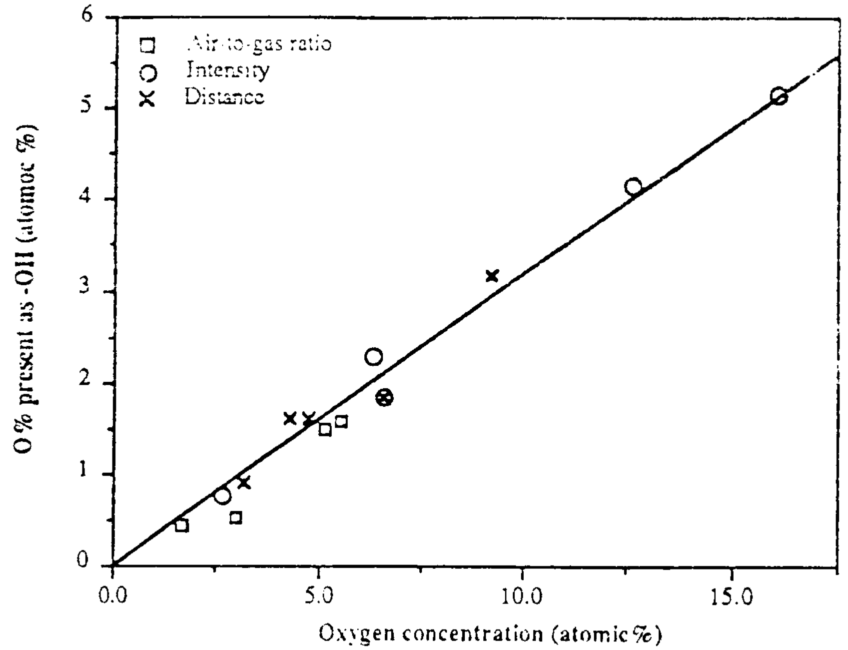


FIGURE 5 Correlation between —OH concentration and oxygen concentration introduced by flame treatments under various flame conditions.

not. There is some evidence for surface melting during intense flame treatment (Figure 4d). Under these conditions, there is clearly sufficient mobility in the polymer chains for oxygen-containing groups to reorientate or migrate away from the surface. Such reorientation or migration would be expected to have a large effect on water contact angle, which is determined principally by interactions in the outer atom layer, but to have a less effect on oxygen concentration as measured by XPS which samples deeper (~10nm) into the polymer.

Variation in composition as a function of depth was studied using different take-off angles (90° and 30°). Results have shown an enrichment in oxygen concentration at the near surface treated with mild flames (total flow rate 33.9 l/min). However, a depletion in oxygen concentration at the near surface was found on surfaces treated with intense flames (67.8 l/min). This supports the idea that there exists a very thin (<2nm) layer with reduced oxygen concentration at the surface of the samples treated by intense flames.

3.3 Adhesion Levels with Epoxy Adhesive and Polyurethane Paint

Adhesion levels of the polymer surfaces, treated under selected flame conditions, with both epoxy adhesive and polyurethane paint were assessed using a composite butt test.[1] Results are listed in Table II.

Untreated polypropylene showed poor adhesion to epoxy adhesive or polyurethane paint. Without first wiping the polymer surface with a suitable organic sol-

TABLE II
Adhesion levels of flame-treated rubber-modified polypropylene surfaces under selected flame conditions

	Adhesion level (MPa)			
Flame conditions	with epoxy adhesive		with PU paint	
Untreated	1.7	I	2.6	I
Air-to-gas ratio				
8.6:1	11.7	M	8.9	C
9.7:1	11.6	M	9.7	M
11.8:1	11.7	M	11.7	M
14.0:1	11.8	M	9.0	C
15.1:1	8.9	C	3.0	I
Total flow rate (l/min)				
16.9	22	I	9.1	C
25.4	11.6	M	11.8	M
33.9	11.7	M	11.7	M
50.8	11.5	M	11.8	M
67.8	11.6	M	12.1	M
Distance (cm)				
0.25	10.6	M	11.6	M
1.0	11.7	M	11.7	M
2.0	8.4	C	10.3	M
4.0	6.5	C	9.3	C
6.0	3.9	I	5.7	I

vent (*e.g.* trichloroethylene), the polyurethane paint was observed to dewet shortly after the spraying. Table II shows that high adhesion levels have been achieved by flame treatment. For most of the samples, adhesion failures were found cohesive within polypropylene, indicating that the interfacial adhesion exceeded the cohesive strength of the polymer itself.

4. CONCLUSIONS

Effects of flame treatment of a rubber-modified polypropylene have been studied using XPS, contact angle measurement, SEM, vapour-phase derivatisation, and an adhesion test. Optimum flame conditions for this particular polymer were found to be: air-to-gas ratio 10:1–13:1, and the distance between the flame's inner cone tip and the polymer surface 0.5 cm.

Contact angles of water and diiodomethane were correlated to surface oxygen concentration. An initial rapid decrease in water advancing contact angle with surface oxygen concentration was found. However, at higher oxygen concentrations (>~5 atomic%), water advancing contact angle was found to level off. This lack of correspondence was attributed to the reorientation/migration of functional groups away from the surface, and possibly to a lesser extent to surface roughness. The melting of the polymer on the surface, as demonstrated by SEM, made the reorientation/migration of functional groups possible. Diiodomethane advancing contact angle was found relatively constant, indicating that the dispersion part of the surface free energy, γ_s^d, for the least wettable patches on the surface, did not vary significantly with oxygen concentration.

The selectivity of TFAA towards hydroxyl groups has been proved by vapour-phase derivatisation using model polymers with known amounts of functional groups. By derivatisation with TFAA, about 30% of the oxygen generated by flame treatment has been shown to be present as —OH groups. Since TFAA has also been found to react with epoxide groups,[7] further derivatisation is in progress to study the possibility of their existence on flame-treated surfaces. High adhesion levels with both epoxy adhesive and polyurethane paint were found, with complete adhesion failure being within the polypropylene film for most of the samples.

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