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Flame Treatment of Polypropylene:

A Study by Electron and Ion Spectroscopies

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Abstract

The effects of flame treatment on the surface characteristics of four injection moulded, automotive grade, polypropylene samples, pigmented with carbon black, have been studied. The changes in wettability have been monitored by water contact angle and Dyne inks, whilst XPS has been used to establish the changes in oxygen surface concentration as a function of flame treatment. As expected carbon pigmented and carbon plus talc filled samples showed a significant increase in oxygen concentration and surface wettability with increasing flame treatment. For the glass filled sample this effect was not so pronounced. Inspection of the XPS valence band shows initial attack in the flame treatment process to be at the pendant methyl group of the poly(propylene) molecular architecture. XPS in conjunction with cluster ion bombardment shows the depth of surface treatment to range from ca. 7 nm at one pass of flame treatment to some 15 nm following seven passes. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) shows the segregation of characteristic additives during the injection moulding process which are subsequently greatly reduced during the flame treatment. As treatment level increases oxygen increases from mono-atomic to diatomic attachment. This work extends the understanding of the flame treatment of moulded polyolefines and establishes that the beneficial properties conferred are the result of the conjoint effect of the oxygenation of the bulk polymer along with the removal of surface segregated processing aids.

Introduction

Flame treatment improves the adhesion qualities of polymers prior to the application of coatings and adhesives. With flame treated surfaces, bond strength and durability is greatly improved. The attraction of using flame treatment as opposed to corona discharge or plasma treatment rests with the ease with which non uniform shapes can be treated (by robotically controlled burners) and the perceived longevity of the treatment conferred in the flaming process. Indeed flame treatment generally provides better stability than corona treatment [1]. However, it is generally believed that the low pressure plasma treating process may provide surfaces with greater stability than chemical etching, corona, flame, or other common polymeric treatment processes. An advantage of plasma treatment is that it is largely independent of the shape of the object to be treated, although it can only be used as a batch process. In the case of flame treatment of irregularly shaped objects allowance must be made for the risk of accumulation of heat in regions where surface orientation changes abruptly.

The process is typically used in place of adhesion promoters and as flame treatment is comparatively economical, the overall cost of a production process is reduced. Eliminating primers from a production process has the added benefit of eliminating the associated solvent emissions making the overall production process significantly more environmentally friendly. Flame treatment technology is used widely throughout industry, one prominent example is the use of flame treatment within the automotive industry is for the surface adhesion improvement of polypropylene mouldings (eg car bumpers and other components) prior to painting. The exact nature of the chemical modifications brought about by the process have been studied by several workers for polyolefine film, such as Briggs *et al* [2], Strobel, *et al* [3], Sutherland *et al* [4] as well as Abel *et al.* for extruded PVC [5]. Comparison of the data for these two classes of material show that in the case of the polyolefines, where the work was all carried out on blown or biaxially oriented film, the mechanism of treatment involved the oxidation of the surface, a feature which could readily be followed using a surface chemical analysis method such as X-ray photoelectron spectroscopy. Films of this type generally do not include processing aids such as antioxidants and lubricants. In the work of Abel *et al* [5], however, the mechanism was less clear as it was found that such processing aids present in the polymer segregated to the surface and the flame treatment process involved removal of anti-oxidants and UV stabilisers from the surface. One parameter that has not been fully investigated in polymer flame treatment is the depth of the treatment zone, although it is generally accepted that the longevity of the flame treatment process is associated with the depth of this zone. Briggs *et al* speculated that this might be some 4 - 9 nm in depth [3]. The advent of argon cluster ion bombardment in conjunction with XPS has the potential to allow this parameter to be explored in detail to establish treatment/depth relationships.

As indicated above flame treatment is widely used in the automotive industry for the treatment of complex parts such as bumpers and dashboards prior to painting, bonding or coating. In this work a series of automotive grade, filled, polypropylene compounds were investigated. In the use of robotic flame procedures it is inevitable that some overlapping of one pass with a previous or subsequent one occurs as shown in Figure 1. With this in mind a study of multiple passes through the flame treatment station has been undertaken. The nature of multiple treatment passes can be of critical importance as, although good wetting is a requirement for good adhesion, it is no guarantee of a strong adhesive joint or a well adhering coating. By increasing the number of passes of flame-treatment, the oxygen incorporation can increase, but it may also lead to the formation of an over-treated surface layer than can then act as a weak boundary layer once adhesive or paint is applied. The overall aim of the work presented in this paper is to establish relationships that exist in terms of process parameters, surface chemistry and quality assurance experimental observables such as water contact angle.

A range of automotive polypropylenes have been processed by flame treatment and wettability investigated by water contact angle and Dyne ink measurements and changes in surface chemistry monitored by XPS. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) has been used to gain additional information regarding the oxygenation process and to elucidate the nature and fate of the major processing aids.

Experimental

Materials

For this research four different automotive grade polypropylene (PP) materials were provided by SABIC Europe, all were pigmented with carbon black and filled with talc or glass fibres as described in Table 1.

Each of these polymers is used in current vehicle production and all are flame treated in industry prior to bonding or painting. The samples were supplied as injection moulded plaques (150mm x 240mm x 3mm) that had been carefully wrapped in aluminium foil immediately following manufacture.

During manufacture of such polymer parts there are many additives included in the formulation aimed at providing a benefit to the end user, or assisting in the manufacturing process. These can include anti-static agents, UV protectors, release agents, anti-oxidants and many more [6]. Standard antioxidant and mould release additive package is present in the compositions in this study. No further details relating to the exact formulation have been provided by SABIC.

Flame Treatment

The flame treatment was carried out using a commercial flamer head manufactured by The Aerogen Company Ltd. These are widely used throughout industry for surface treatment and have been used for in-house investigations on thin film prior to this investigation on thicker material. The burner was an Aerogen AT-530 8" mounted above a conveyor belt on which the samples are placed in a metal tray. The burner was supplied with natural gas and dust filtered compressed air which was mixed in a venturi located upstream (5 metres) of the burner to ensure a premixed laminar flame. An oxygen meter ensured accurate determination of the equivalence ratio by measuring the excess oxygen in the post combustion gases.

Using this equipment the parameters which could be varied were conveyor belt speed (dwell time of sample in flame), burner to specimen distance, equivalence ratio, excess oxygen value, air pressure differential, air pressure, fuel gas flow rate. The equivalence ratio, Ø, is defined as:

$$\emptyset = (m_{fuel}/m_{oxidiser})/(m_{fuel}/m_{oxidiser})_{stoich}$$

There are a number of experimental variables within the flame treatment procedure and rather than investigate a large matrix of experimental parameters, optimum conditions were established using Dyne ink results of ca. 50 mJ m^{-2}. After a short exploratory investigation, and with advice from the manufacturers of the burner on the basis of their extensive experience of setting up flame treatment installations, the conditions described in Table 2 were adopted and an equivalence ratio of 0.93 was used, i.e. the flame was slightly (1.77%) oxygen rich as indicated by the in-line meter. In practice, a single pass of the sample under the flame gave rise to a dwell time of ca. 0.01 seconds.

The dwell time for flame treatment is the length of time the flame is in contact with a point of the surface being treatment, for some materials this can be changed without many consequences such as metals or ceramics. Polymers, however, will start to melt if this is increased too much in one pass. In industrial practice it is not uncommon for overlap to occur as shown in Figure 1. For this reason single (in one direction) and multiple flame treatment passes were employed, in the case of multiple passes a ninety seconds delay was allowed between each pass.

Surface Analysis

The analysis of the samples was carried out using a VG Scientific ESCALAB MkII fitted with a Thermo Scientific Alpha 110 analyser and a Thermo Scientific XR3 digital X-ray source. The Al Kα (1486.6 eV) source was used for all analyses. The survey, core level and valence band spectra were recorded with pass energies of 200, 20 and 70eV respectively. All spectra exhibited electrostatic charging so the methylene carbon peak was set at 285.0 eV before interpretation of the data was carried out. Quantification was carried out using Avantage *v.4.3* software provided by the instrument manufacturer and contained the analyser transmission function correction values. A degradation test was performed prior to the investigation, alongside the optimisation study, and showed that X-ray induced degradation does occur, which was shown by a loss of oxygen in a treated sample but it was not deemed to be substantial enough in the time frame for the analysis to affect the results. Confirmatory studies were also undertaken with a Thermo Scientific ESCALAB 250Xi equipped with a X-ray monochromator, to allow the valence band region of the spectrum to be recorded at improved resolution and intensity, and an argon cluster ion source (Thermo Scientific MAGCIS) was also used on this system to enable depth profiles to be obtained of the flame treated PP. The source was operated with small clusters (ca. 1000) at a primary beam energy of 6 keV.

ToF-SIMS was performed on a TOF.SIMS^5 system from ION-TOF GmbH, using 10kV Bi_3^+ ions ensuring that data were recorded well within the static SIMS limit of 10^{13} ions cm^{-2} $analysis^{-1}$, the beam was pulsed at 10 kHz, operated in the high current bunched mode for high spectra resolution (> 10^4 at m/z = 29 u) and was rastered over an area of 500 x 500 μm^2. ToF-SIMS spectra were acquired in both positive and negative ion modes over a mass range of m/z = 1-600 u. ToF-SIMS was carried out to provide an indication of the level of oxygenation achieved on the PP samples and also to establish the presence or otherwise of processing aids on the untreated surface and their subsequent displacement during the flame treatment process. The assignment of the peaks is based on comparison of the experimentally recorded mass (following mass calibration), M_{meas}, with that of the theoretical (exact) mass of the candidate fragment ion, M_{ext}. The accuracy of this assignment is expressed as a parameter, Δ, in parts per million where:

$$\Delta = ([M_{meas} - M_{ext}]/M_{ext}) \times 10^6$$

An assignment was assumed to be correct when $\Delta \leq 50$ ppm. Values of Δ are provided within the spectra included in this paper.

Dyne[a] inks, from 32 to 56 dyne cm^{-1}, were used immediately after treatment to give an indication of the surface energy and ensure that treatment had taken place successfully. This is a method used throughout industry to provide an approximate estimation of surface wettability by the use of a series of fluids which possess increasing surface tensions, as discussed by Rance [7].

The water contact angle data was also obtained using a Krüss Easydrop apparatus, with the static sessile drop method using a drop volume of 5µl. This was carried out within two hours of treatment, to give a comparison of surface wettability as a function of process variables. The samples used for water contact angle measurements were cut to measure 100 x 15 mm before being flame treated. A total of 11 measurements were taken at regular intervals along the centreline of each sample and mean values are recorded, standard deviations were calculated and are included with the data set. They are around 2 ° for most samples. The time between treatment and analysis of the samples was minimised to ensure a reliable result. This was limited by the location of the treatment apparatus and analysis equipment however and the longest duration from treatment to analysis was no more than 8 hours. An ageing investigation was also conducted alongside the main analysis for 8 weeks in a dust free environment in dry laboratory air and the samples were found to have no significant reduction in surface energy or C/O ratio.

Results and Discussion

Untreated Injection Moulded Polypropylene

XPS survey spectra for the as received, untreated PP samples for the four sample types are shown in Figure 2. Table 3 presents the surface chemical compositions derived from the high resolution XPS data together with the water contact angle and the wettability inferred by the use of Dyne Inks, immediately after treatment.

Flame Treated Polypropylene

Following flame treatment with 1, 3 or 7 passes the analysis protocol used on the untreated surfaces was repeated. The XPS survey spectra of PP Sample A following flame treatment are shown in Figure 3. The associated quantitative surface chemical analyses and contact angles, together with Dyne Ink assessment, for all four sample types of PP are presented in Table 4

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[a] Dyne cm^{-1} is the CGS unit of surface tension. In the SI system units of mN m^{-1} are used, which are numerically equal to those in dyne cm^{-1}.

Surface Composition of Injection Moulded PP and the Effect of Flame Treatment

The as-received surfaces will be considered first before moving on to the effect of flame treatment. Two of the materials investigated, Sample A and D, present the expected XPS results, in that the only features present in the survey spectrum are those related to carbon, dominated by the C1s peak at 285.0 eV but also the C*KLL* Auger transition at 1200 eV and a weak signal from valence band features in the region 0 – 20 eV. The other two sample types show small amounts of oxygen and sulphur in the surface analyses. These samples also show a slightly higher water contact angle at 103° - 104°, compared with 98° – 99° for the purely hydrocarbon surfaces. The source of the sulphur signal is not clear, although in the untreated Sample B and C it is centred at 164 eV (Figure 4(a)) typical of an organic sulphur consisting compound, presumably associated with the talc filler as sulphur is only consistently present in samples that are talc filled. On flame treatment a significant proportion of the sulphur is oxidised as shown in the peak fitted spectrum of Figure 4(b), with a major component of the S2p now being centred at 168 eV. The higher binding energy component could possibly be attributed to an inorganic sulphate, exposed on flame treatment. This alternative possibility is not considered likely as there is no charge balancing cation present in the spectrum.

Tables 3 and 4 provide a very clear story in terms of the modification that occurs to the PP surface on single or indeed multiple passes of flame treatment. Firstly, as expected, there is a general increase in oxygen at the surface with increasing number of passes. This is to be expected as with each pass there will be an energised interaction of the polypropylene with the free radicals and so forth in the active region of the flame. This will lead to more oxygen being incorporated at the surface. This can be seen by the increase in the O/C ratio across the sample set with an increasing numbers of passes. The only sample that does not follow this trend being Sample C but the significant level of oxygen in the as received analysis points to extraneous material being present at the surface which may be removed in the early stages of flame treatment. Thus the overall flame treatment process may be a combination of processing aid removal and surface oxidation.

Another important consideration is the possibility of pendant group scission/modification occurring during the flame treatment process. This can be assessed by inspection of the XPS valence band as described by Briggs *et al* as the shape of the valence band gives an indication of the overall molecular structure [3]. The valence band region of the XPS spectrum of PP contains a molecular orbital structure associated with C2p (5 – 12 eV), C2s (12 – 22 eV) and O2p (5 – 12 eV) electrons and the core like O2s orbital at 26 eV. The intense peak at 15 eV associated with the untreated PP is ascribed to the pendant methyl group as proposed by Briggs *et al* [3].

Figure 45 shows the valence band XPS spectra for Sample B. The intensity of the characteristic peak at 15 eV, attributed to the methyl pendant group, reduces with increasing number of passes and appears the lowest after seven passes of the flame. It implies that there is a reduction in the presence of the methyl pendant group consistent with its removal in the early stage of treatment. This, along with the increase in the peak at 26eV which is for O2s and the reduction in the peaks at 11eV and 17eV, attributed to the CH_2 backbone structure, could show the degradation of the methyl group on flame treatment, either by direct chain scission or oxygenation, following the spectral analysis of Briggs *et al* [3] and Pireaux *et al* [8]. Foerch *et al* [9] extended these analyses identifying the peaks at 11 eV and 17 eV as the σ bonding and σ* anti-bonding orbitals.

Depth of Flame Treatment

The data of 3 and 4 show quite conclusively that there is a correlation between the amount of oxygen incorporated into the sample surface and the extent of exposure to the flame. In order to investigate the depth to which such treatment extends a newly established technique for depth profiling of polymers, in conjunction with XPS, was utilised. A method widely used in materials characterisation is compositional depth profiling at nanometre depth resolution, achieved by sputtering the sample with elemental ions (typically Ar^+) combined with surface analysis by electron (XPS or AES) or ion spectroscopies (SIMS). This has been routinely carried out on metals and inorganic materials since the 1970s. As the ion energy is rather high, gross damage of organic, polymeric and biological samples occurs, making it totally impractical to obtain compositional depth profiles of these important technological and scientific materials. Research work starting twenty years ago indicated that profiling of organics was possible providing the sputtering projectile was not a single ion but a cluster of atoms with a single charge (meaning the energy associated with each atom of the cluster was correspondingly lower). A relatively recent review [10], concludes that cluster ions based on Buckminster Fullerene (C_{60}) are likely to be the most promising for profiling of polymers. A C_{60}^+ source is not, however, the panacea for all organic profiling requirements and is beset by several insurmountable problems; small cluster size, a tendency for the source to deposit carbon and a selectivity for organics than can be profiled. The solution, pioneered by Matsuo *et al.* and published by Ninomiya, *et al.* [11] is to use very large (ca. 2500) argon clusters, and it is this approach that has been used to estimate the depth of analysis as a function of the number of passes during the flame treatment process. Freshly flame treated samples were prepared for this part of the work and the results of depth profiling of Sample A flame treated with 1, 3 and 7 passes are shown in Figure 6. The etch rate was estimated using the data for an Irganox™ 1010/3114 standard

[12] obtained on the same system and under the same conditions, in conjunction with Cumpson's work on relative etch rates [13], which yields an estimated polypropylene etch rate of 0.173 nm s^{-1}.

Figure 6 shows that the oxygen concentration reduces as a function of depth, and although the initial oxygen concentrations increase with the extent of flame treatment all decay to a plateau value approaching zero over the same depth. The reduction in oxygen concentration is of an exponential-like shape as one would expect from a diffusion controlled process, the minimum oxygen concentration varies depending on the level of flame treatment from 15 nm for a single pass to some 30 nm for the seven pass sample. Taking the mid-point of the oxygen concentration profile as a measure of treatment depth these data can be approximated to a depth of treatment of 7 nm and 15 nm respectively.

ToF-SIMS Investigation of the Oxygenation Process

The XPS data of Table 4 clearly shows the incorporation of oxygen into the sample surfaces following flame treatment. In order to examine the chemical aspects of such incorporation, ToF-SIMS was carried out on Sample A to provide an indication of incorporation mechanism. Figure 7 shows nominal mass 69 u data following a series of flame treatment passes. The fidelity of the assigments is established by the low values of the Δ parameter (described in the Surface Analysis section), for the candidate ions.

The initial oxygenation of the polypropylene consists mostly of a single oxygen atom being incorporated into the PP backbone at the surface, as indicated by the presence of the $C_4H_3O^+$ fragment after a single pass. Then, with subsequent passes the oxygenation process becomes more intense with the gradual appearance of a diatomic fragment $C_3HO_2^+$ in the spectrum.

It is informative to compare this behaviour with that of Sample C, a specimen which showed a significant presence of surface oxygen by XPS. The regions from the m/z = 57 u part of the ToF-SIMS spectra (one of the spectral regions diagnostic of polypropylene [14]) are shown in Figure 8, and it is clear that although a single pass of flame treatment does indeed increase the level of oxygenation at the surface, as indicated by the intensity of the $C_3H_5O^+$ ion, there is a significant level of chemically incorporated oxygen in the untreated surface. The spectra of Figure 8 are comparable in terms of treatment level to the lower two spectra in Figure 7. This taken together with the XPS data indicates that although some of the oxygen at the sample surface, all initially ascribed to the presence of fillers such as talc and glass, has been correctly attributed, the other source of oxygen is either the oxidation of the PP backbone or the presence of oxygen containing additives. The increase of the oxygen containing ion would seem to indicate the former possibility although the same ion is known to occur in additives such as Irganox^{TM} 1010 (See Table 5). One can speculate, therefore, that in the case of the talc filled PP specimens (Samples B & C) there is segregation of processing aids or additives to the surface, a sulphur containing species is also oxidised on flame treatment. Whether this occurs at a concentration which is sufficient to influence the oxygen concentration as measured by XPS is open to conjecture.

In order to establish the presence or otherwise of surface segregated processing and other aids the ToF-SIMS spectra of as received Samples A was examined for fragment ions associated with known additives, paying particular attention to the ions known to be associated with Irganox^{TM} 1010 and ethylene bis-stearamide. These are two very widely used additives for which the ToF-SIMS spectra are well documented with major ions listed in Table 5. Sample A was chosen as it has no apparent O1s signal so if oxygen containing additives are detected they are at a surface concentration below the XPS detection limit. ToF-SIMS, with its superior detection limit should resolve this uncertainty.

Examination of the regions of the spectrum characteristic of common additives shows that both ethylene bis-stearamide and Irganox 1010 are identified at the surface of the as-received Sample A Figures 9 and 10 (lower), all characteristic ions being present. The same spectral region of the flame treated specimen, Figures 9 and 10 (upper), show that the characteristic peaks are no longer present as the dominant features, but that fragment ions consistent with the oxidation of PP now predominate. This is reinforced by the lower mass component at m/z = 57 u where the peak assigned to C_3H_5O increases significantly on flame treatment.

The two additives identified have specific purposes in the formulation; ethylene bis-stearamide is a lubricant and Irganox^{TM} 1010 is an anti-oxidant. The fact that such molecules segregate to the material surface during the injection moulding process is not unexpected and has been observed in previous unpublished work (carried out as part of an extension of the flame treatment of PVC described in [5]). Thus the flame treatment process when applied to such PP samples is rather more complex than first envisaged with an initial step involving the removal, or at least the significant reduction, of the additives identified above and a secondary stage involving the oxidation of the PP molecular structure. As the extent of flame treatment is increased, by the use of multiple passes, the oxidation increases, both in terms of the extent that is achieved at the surface (as demonstrated by the data of Table 4 and Figure 5), and the depth to which the oxygenation is achieved as illustrated by the depth profiles of Figure 6. The XPS measurements correlate well with measurements of wettability (both water contact angle and Dyne inks), this reinforces the view, along with the ToF-SIMS data of Figure 7, that the degree of oxygenation at the surface is increasing along with the concomitant increase in depth.

Conclusions

By surface flame treatment of polypropylene compounds for automotive applications the surface free energy (i.e. wettability) was raised to a level which is sufficient for applying adhesive or paint. XPS studies showed that the level of oxygen incorporation at the surface increases the most after first pass of the flame, with the extent of flame treatment (i.e. number of passes) it can further increase. XPS in conjunction with argon cluster ion sputter profiling indicated that the extent of oxygen also increases with depth as a function of level of treatment. The depth of flame treatment varied from 7 – 15 nm for the treatment levels investigated in this study. Valence band XPS showed that the pendant methyl groups are preferentially attacked during flame treatment.

The segregation of processing additives, specifically Irganox 1010 and ethylene bis-stearamide, was identified by ToF-SIMS on the as received plaques. Their presence was shown to be significantly reduced with a single pass of the flame treatment procedure. The presence of such molecules at the free surface as a result of the injection moulding process is anticipated, as the phenomenon has been well documented in the past. However very little work has been carried out on the effects of flame treatment on materials produced in this manner, most studies having been conducted on blown, biaxially oriented film which will not contain such processing aids. Thus, for injection moulded components, it is envisaged that in the very early stage of flame treatment the mechanism is one of removal of extraneous surface. In addition the XPS data is reinforced by ToF-SIMS and the presence of di-oxygen fragments ions allows the mechanism of high levels of oxygenation to be deduced.

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Tables

Table 1. SABIC Europe designated PP automotive grades for injection moulding, used in the current work. All samples are pigmented with carbon black.

DESIGNATION	POLYMER DESCRIPTION	TYPICAL USE
Sample A: SABIC®PP 108MF10	Super high impact polypropylene copolymer	Bumpers
Sample B: SABIC®PP Compound 19T1040	40 % talc-filled polypropylene homopolymer	Under the hood (fan shrouds)
Sample C: SABIC®PP Compound 19T1020	20 % talc-filled polypropylene homopolymer	Under the hood (fan shrouds)
Sample D: STAMAX 20YK270E	20 % long glass filled polypropylene copolymer	Various (e.g. instrument panel carriers)

Table 2. Flame treatment process variables showing optimum values adopted in this study.

Parameter	Range	Optimum
Conveyor speed (mm s^{-1})	85 – 1000	1000
Excess oxygen reading (%)	0 – 6.9	1.77
Burner to substrate gap (mm)	18 – 200	100
Air pressure differential (mm H_2O)	0 – 240	115
Air pressure reading (mbar)	0 – 2000	44
Methane flow rate (l min^{-1})	32 – 56	N/A

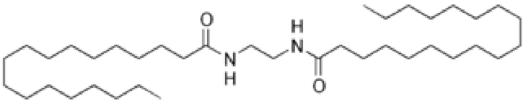
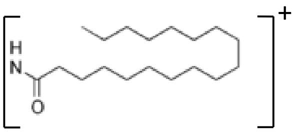
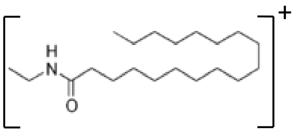
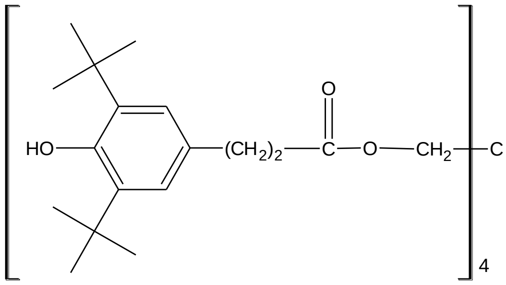
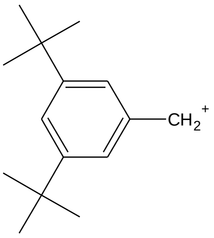
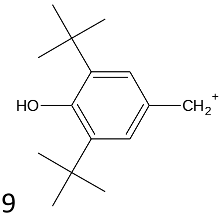
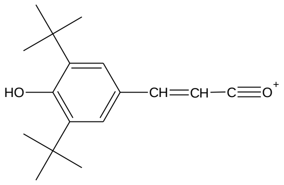
Table 3. Quantitative XPS data for the as-received polypropylene samples together with contact angle and Dyne Ink values.

	Surface Concentration/at %					
	Carbon	Oxygen	Sulphur	O/C ratio	Water Contact Angle (°)	Dyne Ink Level (mN^{-1})
A	100.0	0	0	0.00	98 ± 1.1	30
B	96.8	2.9	0.3	0.03	104 ± 1.9	<30
C	98.5	1.1	0.4	0.01	103 ± 1.8	<30
D	100.0	0	0	0.00	99 ± 1.8	32

Table 4. Quantitative XPS data, together with contact angle and Dyne ink results, for Samples A, B, C and D following single and multiple passes through the flame treatment process.

	Surface Composition/at %						
Specimen	C	O	S	N	O/C ratio	Contact angle (°)	Dyne ink level (mNm^{-1})
Sample A							
Untreated	100.0	0.0	0.0	0.0	0.0	98 ± 1.1	30
1 pass	89.6	10.0	0.4	0.0	0.11	70 ± 1.6	52
2 passes	89.3	10.7	0.0	0.0	0.12	66 ± 4.2	56
3 passes	85.1	14.9	0.0	0.0	0.18	62 ± 3.2	56
5 passes	83.9	16.1	0.0	0.0	0.19	N/A	N/A
7 passes	83.1	16.9	0.0	0.0	0.20	N/A	N/A
Sample B							
Untreated	96.8	2.9	0.3	0.0	0.03	104 ± 1.9	<30
1 pass	88.2	11.8	0.0	0.0	0.13	65 ± 2.2	56
2 passes	82.4	14.8	1.2	0.8	0.18	67 ± 2.1	52
3passes	78.9	17.6	2.4	1.1	0.22	63 ± 1.8	52
Sample C							
Untreated	98.5	1.1	0.4	0.0	0.01	103 ± 1.8	<30
1 pass	84.6	15.0	0.4	0.0	0.18	70 ± 2.1	52
2 passes	90.9	7.4	1.7	0.0	0.08	72 ± 4.2	52
3 passes	81.3	15.7	1.7	1.3	0.19	65 ± 2.3	56
Sample D							
Untreated	100.0	0.0	0.0	0.0	0.0	99 ± 1.8	32
1 pass	93.8	6.2	0.0	0.0	0.07	72 ± 3.3	56
2 passes	91.6	8.4	0.0	0.0	0.09	73 ± 2.3	56
3 passes	91.2	8.8	0.0	0.0	0.10	67 ± 2.7	56

Table 5. Major additives in the PP samples considered in this work and characteristic positive fragment ions.

Additive	Chemical structure	Characteristic peaks (m/z)
Ethylene bis-stearamide		282  310 
Irganox™ 1010		57 $C_3H_5O^+$  203  219 259 

Figures

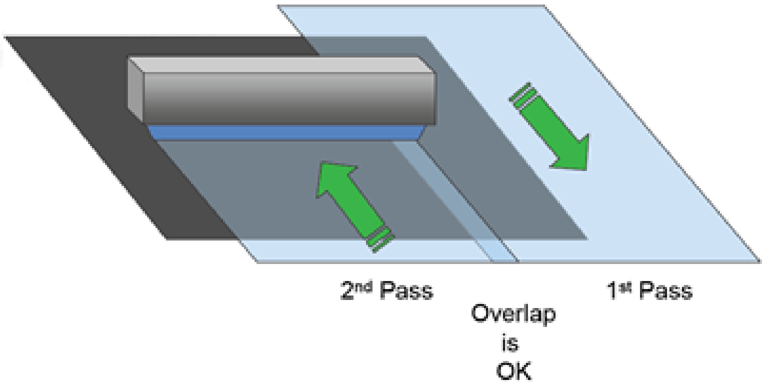


Figure 1. Schematic showing the mode of operation for two flame passes over a substrate surface.

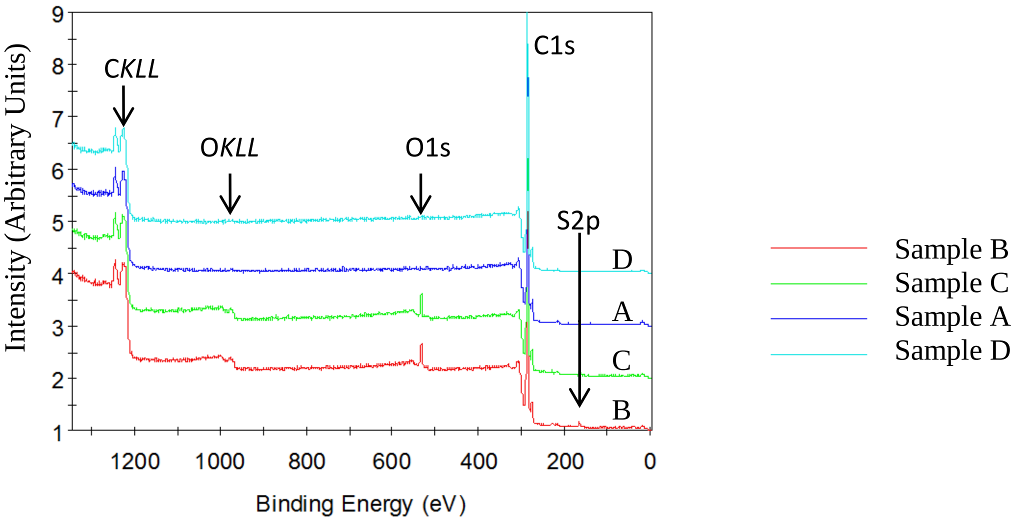


Figure 2. Survey spectra for untreated PP samples.

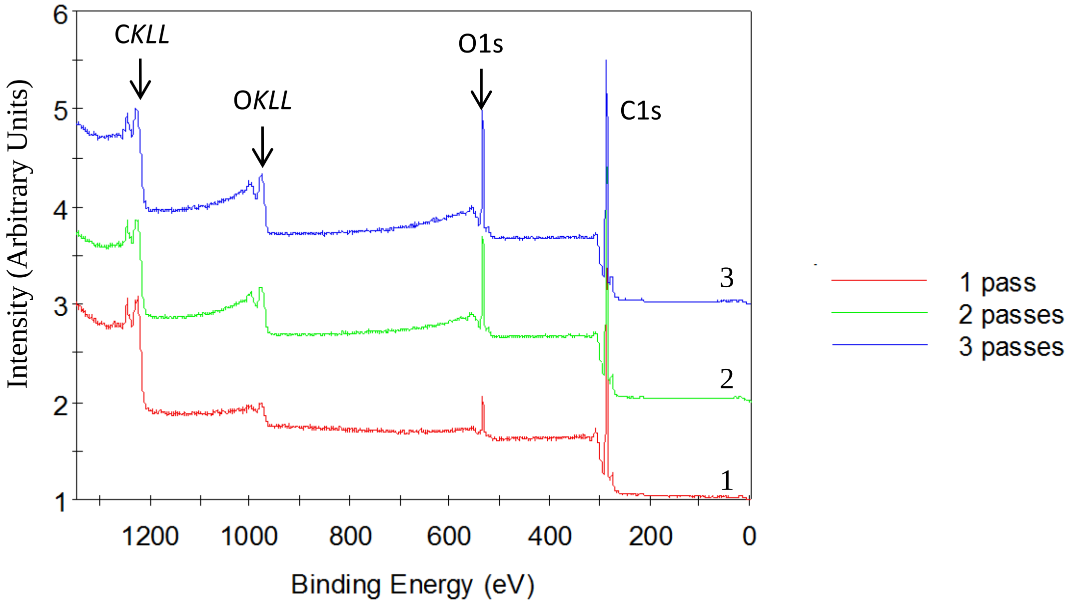
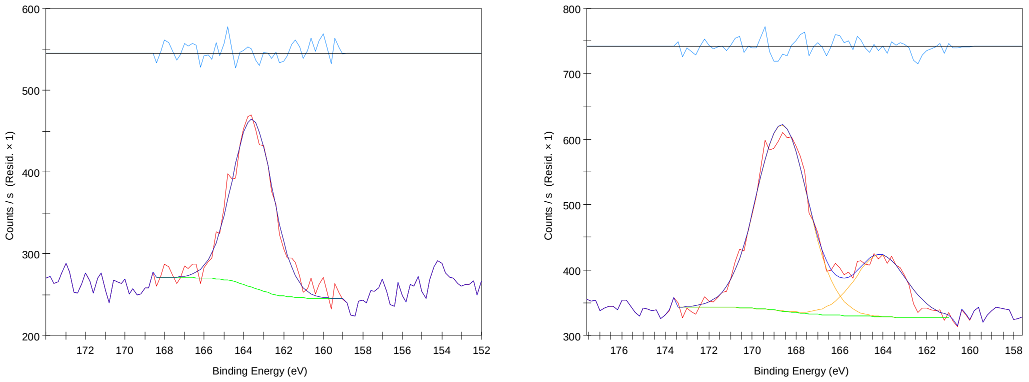


Figure 3. XPS survey spectra of flame treated polypropylene Sample A as a function flame treatment dwell time.


(a)

(b)

Figure 4. Sulphur 2p XPS spectra of Sample C, (a) untreated showing a single components at 164 eV and, (b) showing a much reduced intensity at 164 eV and a new, more intense, component at 168 eV.

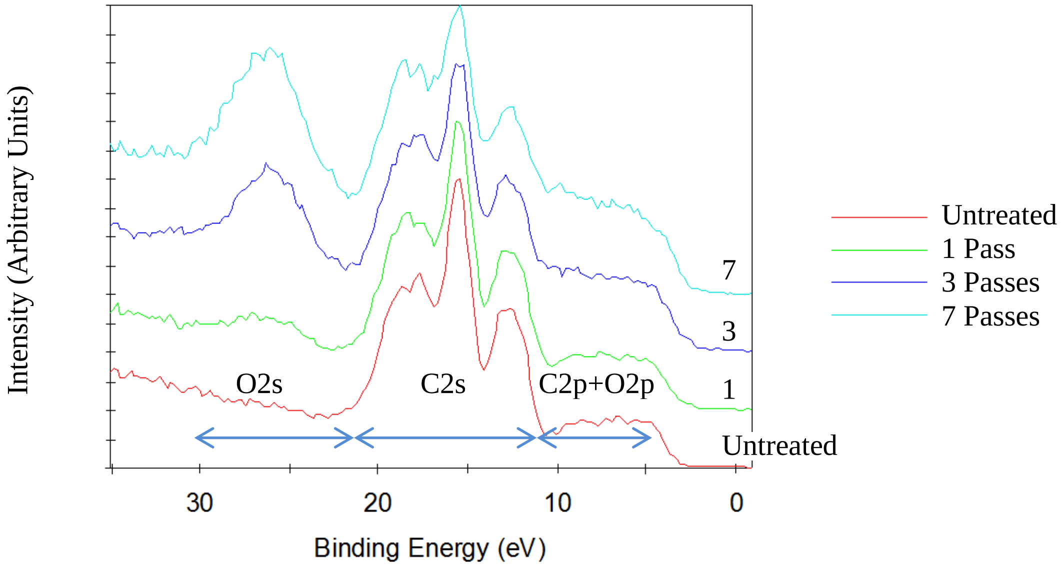


Figure 5. Valence band spectra acquired using a monochromated AlKα source for Sample B following flame treatment. From bottom to top: untreated, treated with 1 pass, treated with 3 passes and treated with 7 passes.

Figure 4

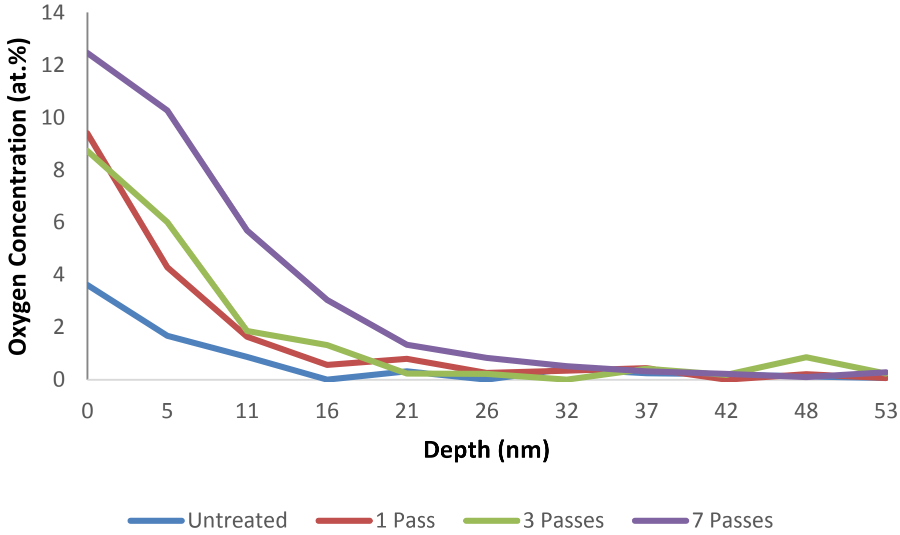


Figure 6. XPS cluster ion depth profile showing oxygen content in treated Sample A as a function of the number of passes.

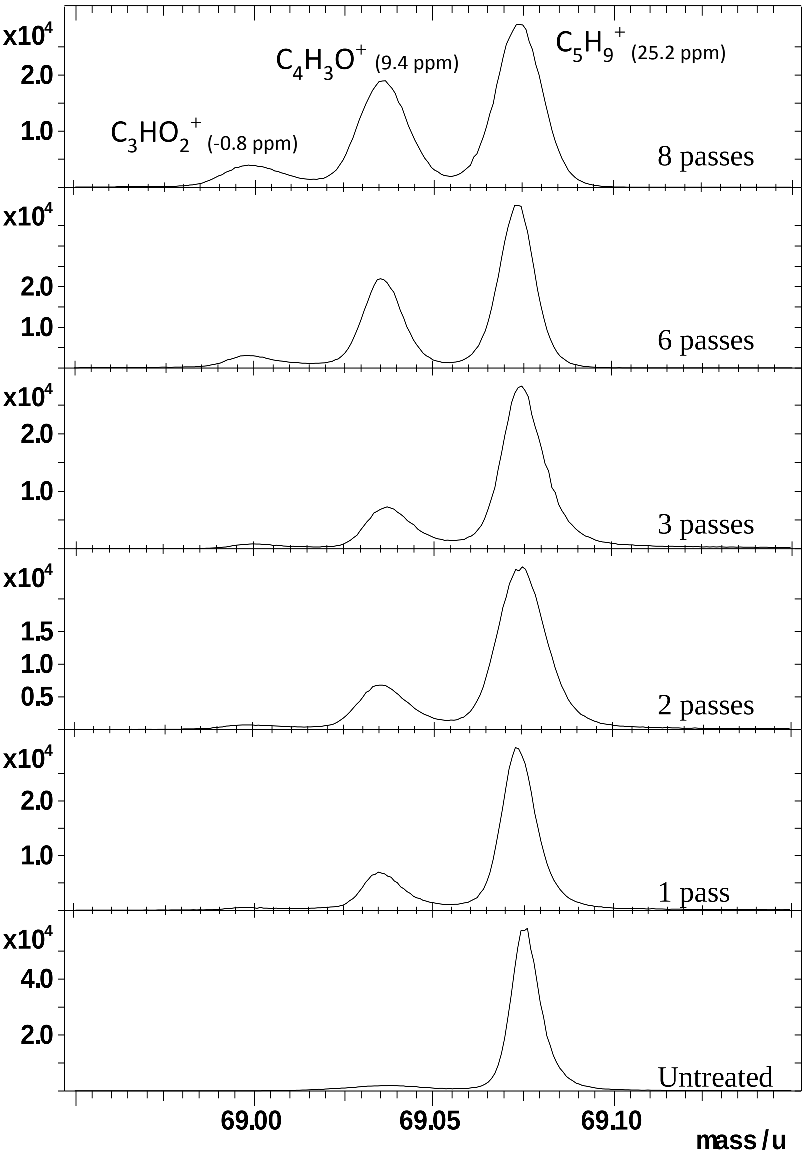


Figure 7. Positive ToF-SIMS spectra at nominal mass m/z = 69 u of multiple treatments of Sample A.

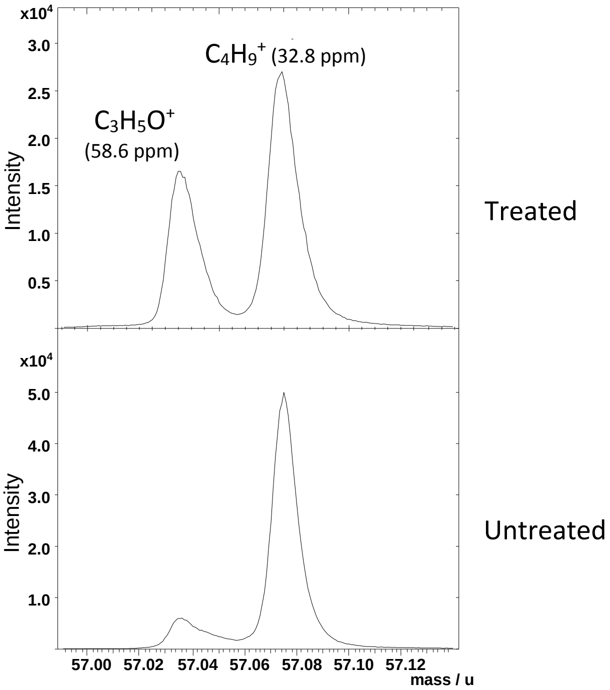


Figure 8. Positive ToF-SIMS spectra at nominal m/z = 57 u for Sample C in the untreated and treated (one pass) conditions.

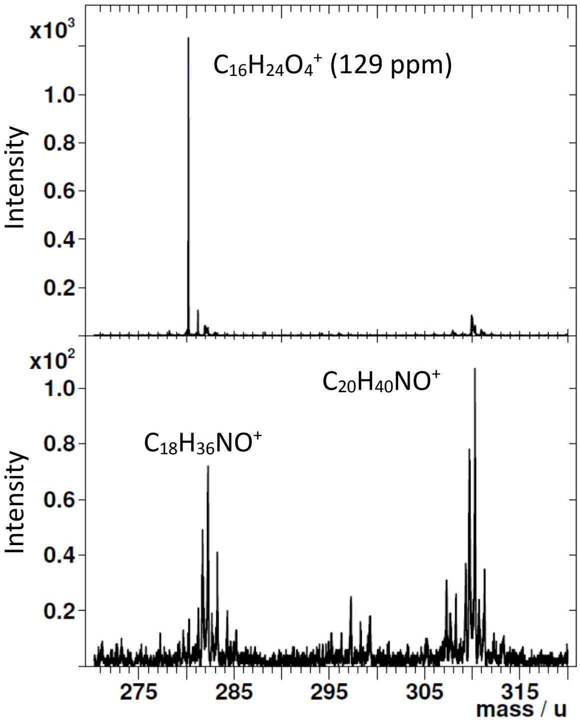


Figure 9. ToF-SIMS showing ethylene bis-stearamide characteristic peaks, observed on Sample A (lower spectrum), much reduced following flame treatment (upper spectrum).

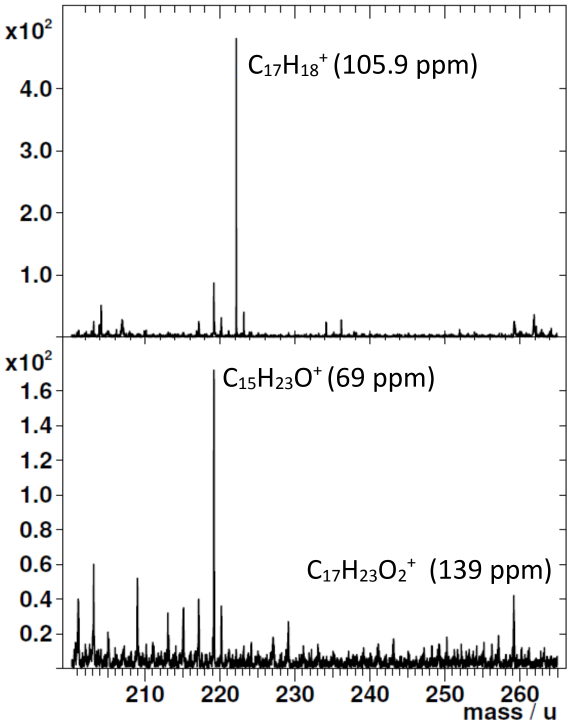


Figure 10. Irganox™ 1010 characteristic peaks observed on Sample A (lower spectrum), much reduced on flame treatment (upper spectrum).