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## Effect of flame treatment on formulated polyvinylchloride surface: A study using ARXPS

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### ABSTRACT

Industrial PVC samples have been flame treated in order to improve their surface properties for adhesion. Using a novel procedure to avoid X-ray damage, as-received and treated PVC were analysed by angle resolved X-ray photoelectron spectroscopy (ARXPS) to assess the effect of the flame treatment. An increase of wettability was obtained and tested using dyne inks showing that the flame treatment has an effect on the surface. In terms of chemistry, it was found that a reduction of the covalent chlorine to chloride is observed while a decrease of carbon and increase of oxygen concentrations are the other main effects. ARXPS shows that the chloride species appear to segregate to deeper layers than the immediate surface intimating that the difference in wettability may have been obtained by eliminating already pre-existent surface contamination.

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### 1. Introduction

Polyvinylchloride (PVC) is a widely used commodity polymer and its specific application is the use in the manufacture of window frames. Sometimes, it is desirable to give the frame the appearance of wood for decorative purposes. Until recently, the surface of PVC window frames has been rendered compatible with adhesives by applying a chlorine based primer to the material. However, recent European regulations on volatile organic compounds (VOCs) have made this method obsolete. It is therefore necessary to use another method in order to treat the surface of the PVC to enhance wettability and increase surface energy. Various treatments are available such as corona or plasma but they tend to be short lived which is rather inconvenient when the process has to be used for manufacture and external decorative layers cannot be stuck/applied straight away. A more flexible approach needs to be used with a long lived treatment such as flame treatment which has been shown to be stable for up to several weeks [1]. Although this treatment has been available for many years, it needs proper assessment for PVC, as it has been used mostly on polyolefins to date.

One of the most widely adapted methods for the examination of the surfaces and surface treatments is X-ray photoelectron

spectroscopy (XPS) but one of the difficulties of XPS of PVC is that it degrades readily under exposure to X-rays. However recent improvements of XPS acquisition methods make such analysis now possible by reducing the time necessary to analyse PVC to a few seconds (using a snap shot analysis procedure). In this work we describe the use of flame treatment on PVC window frames profiles. Various parameters, such as distance to the flame or speed at which the surface was treated, have been investigated in order to increase wettability for the subsequent use of adhesives. In order to understand the effect of the flame treatment, in terms of surface chemistry modification and as a function of depth, angle resolved XPS (ARXPS) was used and we report here the preliminary results obtained.

### 2. Experimental

#### 2.1. Flame treatment

Plasticised PVC originally sourced from VEKA plc was flame treated using a commercial flame treatment system. Samples were taken from real window profiles and treated using variety of combination of process. As such, the samples dealt with within this piece of work contain pure PVC as well as a variety of other components and additives in their formulation. These may include, to name but a few, fillers, stabilisers (UV and heat), impact modifiers and plasticizers. Five samples were treated, numbered from 1 to 4 according

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**Table 1**  
Summary of parameters used for flame treatment.

Sample	Gas flow (l min <sup>-1</sup> )	Output (Btu h <sup>-1</sup> in. <sup>-1</sup> )	Air flow (l min <sup>-1</sup> )	Oxygen (%)	Burner gap (mm)	Conveyer speed (m min <sup>-1</sup> )
1	8.15	5100	265	1.90	75	40
2	6.30	4000	200	1.90	75	30
3	6.30	4000	200	1.80	60	30
4	10.10	6300	328	1.70	60	40
4 (film)	10.10	6300	328	1.70	60	40

to the variation of the treatment parameters with the fifth sample (described as 4 with film) treated in the same conditions as sample 4 but immediately after removing the protection film usually present on PVC profiles just prior to adhesive deposition. No film was present on the other, carefully wrapped, samples and they were kept away from contamination by handling and transport in aluminium foil. Table 1 summarizes the treatments applied to the PVC samples in terms of the process parameters used such as conveyer speed, oxygen amount or distance between the sample and the burner (burner gap). The sample treatment was performed by The Aerogen Company Limited. Changes in surface energy were assessed using a series of “dyne inks ranging in surface tensions from 32 to 56+ N m<sup>-1</sup>. The process was used to provide a facile and immediate assessment of modifications brought about by the flame treatment process.

## 2.2. XPS analysis

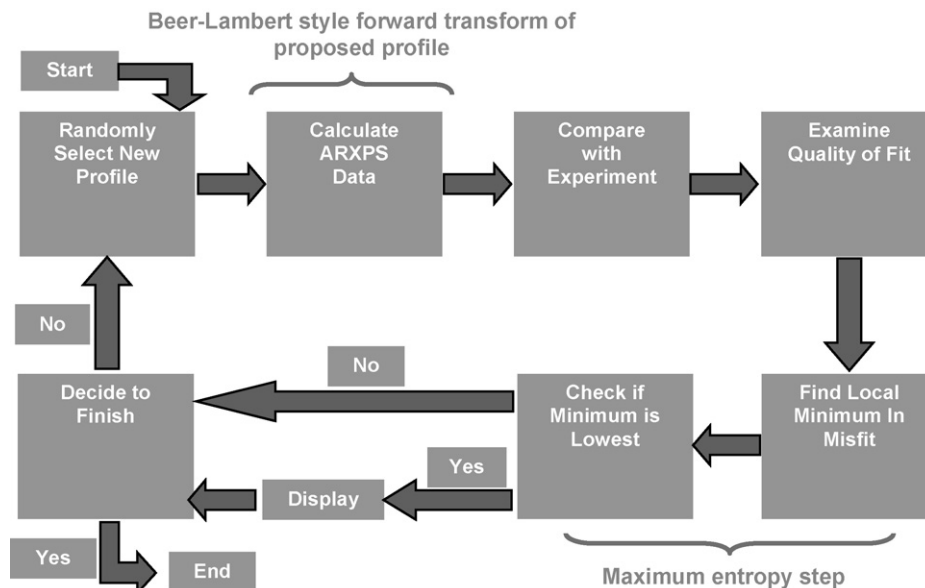
XPS analyses were achieved using a Thermo Scientific Theta Probe spectrometer with monochromated Al K $\alpha$  radiation with a 400  $\mu$ m spot size and a 100 W power. Spectral processing was carried out using the manufacturer's computer software, Avantage v2.66. The pass energy was set up at 300 eV for the survey spectra and 200 eV for the high resolution spectra of the core level regions of interest: C 1s, O 1s, Pb 4f, Si 2p, Ca 2p, and Na 1s. Such high pass energies are used because data recording has been performed using the “snap-shot” capability of the instrument (see below). Parallel angle resolved XPS was performed using 16 angles from 21.875° to 78.125°. Snap shot analysis was used on the samples in order to minimize sample damage under X-ray exposure reducing the analysis time from a few minutes per high resolution window to a few seconds. In this mode, the whole of the energy range required is

dispersed over the detector so the energy setting of the analyser remains constant throughout the acquisition. The energy range is set to be equal to the required range for the spectrum and electrons from the whole energy range are collected simultaneously. The time penalties associated with over-scanning, stepping and settling are therefore eliminated. Besides the X-rays are scanned over a relatively large area and data summed up avoiding further possible damage to the sample.

The treatment of angle resolved data follows the standard forward transform approach used by many authors over the last three decades and critically assessed by Cumpson [2,3]. This forms the basis of the software included in the Avantage v2.66 datasystem which also includes an element of maximum entropy based on the Skilling-Jeaynes criteria described for angular resolved XPS by Smith and Livesey [4]. The approach implemented in the software is described by the flow diagram of Fig. 1. It is well known that the noise present in the spectra used for any angular resolved reconstruction of a depth profile is a critical parameter. Care was taken to ensure that counting statistics were more than adequate to provide a good quality depth profile as established in our previous work [5].

## 3. Results

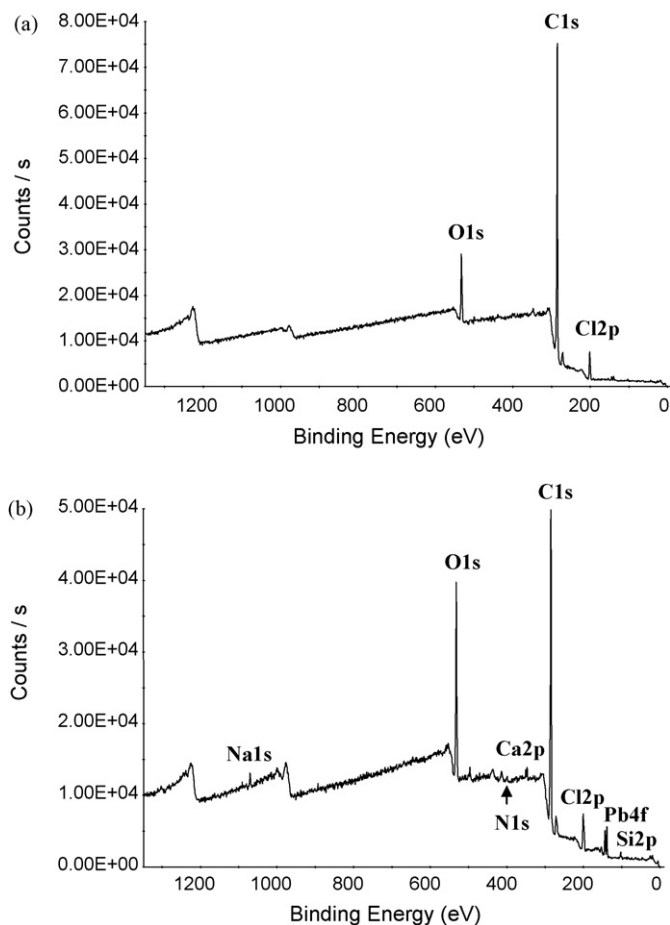
PVC samples were flame treated using a range of various parameters (see Table 1). Table 2 shows the results obtained with the dyne inks. Sample 4 exhibits the highest surface energy as the surface treatments were improved each time the parameters were modified. Ideally each parameter should have been studied in isolation to report their effect correctly but this was not possible both in terms of time available and material (substrate) resources. It is anticipated that the surface treatment should increase the surface energy and this is indicated by the increase of the dyne ink level used to



**Fig. 1.** Flow diagram indicating the approach implemented in the software for ARXPS data treatment.

**Table 2**  
Dyne ink levels obtained for samples examined in this work.

Sample	Dyne ink level
1	44
2	44
3	48
4	>56
4 (film)	>56



**Fig. 2.** Comparison of survey spectra for as-received PVC (a) and sample 4 (b) (all angles collapsed).

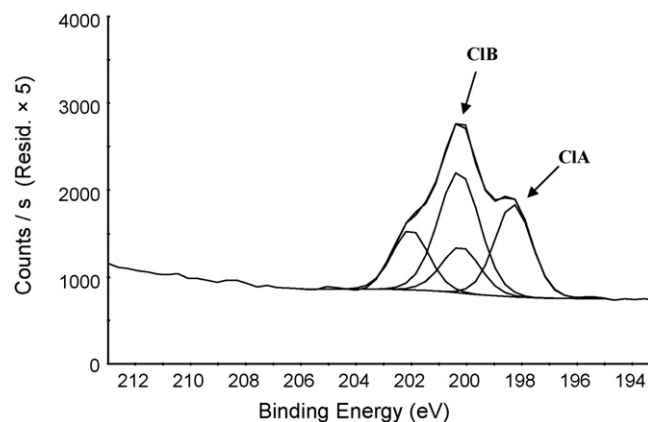
characterise the surface at the factory. It is also important to note that sample 4 covered with a protection film also experiences an increase in surface energy.

Fig. 2 shows a comparison of the survey spectra recorded for as-received PVC and sample 4. The spectra indicate the presence of carbon, oxygen, chlorine and a minor element lead, and following treatment sodium, silicon, calcium as well as nitrogen and potassium at trace levels (not all shown as the signals are very small);

**Table 3**  
Surface composition of samples (all angles collapsed).

Sample	C	O	Cl	Pb	Na	Si	Ca	N
PVC as-received	86.0	10.7	3.1	0.1	–	–	–	–
1	69.3	22.5	3.7	0.6	0.6	1.6	0.6	1.3
2	66.1	24.9	4.1	0.5	1.0	1.2	1.3	1.1
3	79.2	15.4	2.3	0.7	0.3	0.7	0.9	0.5
4	74.5	20.0	2.8	0.5	0.5	0.9	–	0.8
4 (film)	70.8	21.3	5.6	–	–	0.1	0.6	1.6

(–) Below detection limit or trace level.



**Fig. 3.** Peak-fitted Cl 2p signal for sample 2 indicating the two chlorine species present after flame treatment.

most of the unlabelled peaks corresponds to either secondary peaks from lead or sodium). Lead originates from salts (phthalate or stearate) used as heat stabilisers within the compound whereas calcium (in the absence of zinc) may be assigned to fillers [6,7]. Nitrogen may be from additives too. The main differences between the two spectra are seen in the variation of the carbon and oxygen concentrations, the former decreases while the latter increases. Table 3 shows the data obtained for the as-received and treated samples. For this particular table, data are reported as “collapsed” data that is the summation of data for all available angles. The concentration of most elements increases but for carbon, which is showing a marked decrease instead. All samples exhibit an increase in oxygen concentration as well as variations of chlorine concentration. Notwithstanding the differences in concentrations of the elements, the most striking difference is observed for the chlorine signal. Fig. 3 shows the peak-fitted signal of Cl 2p for sample 2 which divides in two different types. If peak-fitting is performed taking into account the spin orbit splitting, two components are found for the main component Cl 2p<sub>3/2</sub> at binding energies of 200.3 and 198.3 eV which may be assigned to a covalent and ionic species, respectively, although sample 4 with film exhibits only one type of chlorine assignable to a covalent species. Further observation of the high resolution signals indicates that the carbon signal is modified as well as the chlorine signal (positions of peak-fitted peaks are given in Table 4). Peak-fitting of the signal indicates four components. The first component is assigned to CC, CH; the second to an ester component, the third and fourth to carbon carboxylate and carboxylic acid groups. In addition, one may have superimposed on these signals carbon bound to nitrogen or silicon. The main difference between untreated and treated PVC is the decrease in the CC, CH and ester component of the carbon apart for sample 3 and sample 4 with film respectively.

To understand the hierarchy of the chemical layers, chemical profiles were created. In addition and to help the preparation of the profiles curves graphs were produced as seen in Fig. 4 where one can evaluate the variation of the elements concentration as

**Table 4**  
Components obtained for peak-fitted signal of C 1s and Cl 2p (eV/(at.%)).

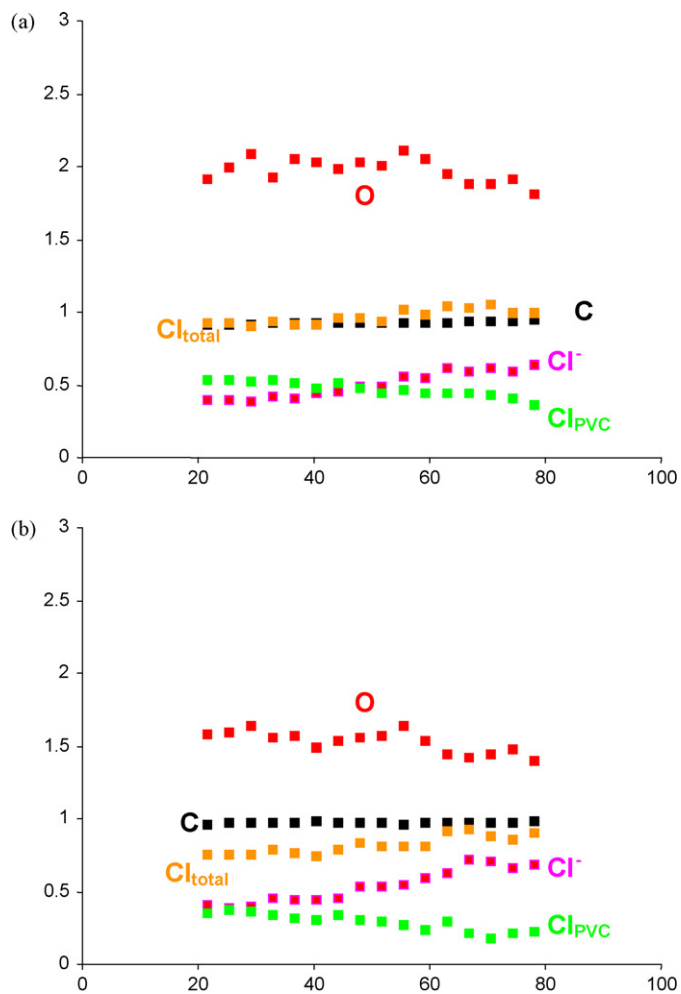
Carbon fit		Components (binding energy/surface composition)			
Sample	1	2	3	4	
PVC as-received	285.0 (55.1)	285.9 (22.2)	287.1 (6.5)	289.4 (2.2)	
1	285.0 (45.3)	286.1 (14.0)	287.3 (5.3)	289.1 (4.6)	
2	285.0 (44.6)	286.3 (12.0)	287.6 (5.1)	289.1 (4.3)	
3	285.0 (55.7)	285.9 (15.6)	287.3 (4.1)	289.2 (3.9)	
4	285.0 (47.2)	286.0 (17.2)	287.3 (6.1)	289.2 (4.1)	
4 (film)	285.0 (31.0)	286.0 (22.2)	287.3 (12.1)	289.3 (5.6)	

Chlorine fit		Components (binding energy/surface composition) <sup>a</sup>	
Sample	1	2	
PVC as-received	N/A	198.9 (3.2)	
1	198.3 (1.4)	200.4 (2.2)	
2	198.3 (1.7)	200.3 (2.4)	
3	198.3 (1.5)	200.4 (0.9)	
4	198.3 (1.4)	200.5 (1.4)	
4 (film)	N/A	200.5 (5.6)	

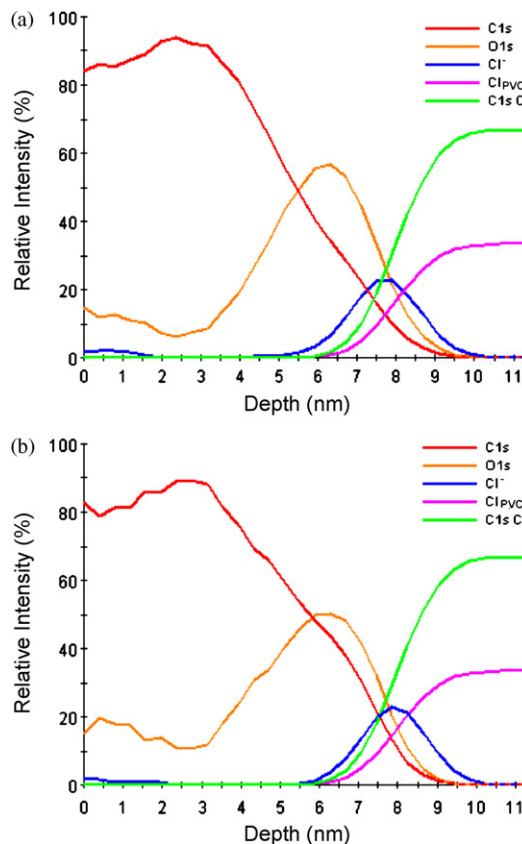
<sup>a</sup> Binding energy provided for Cl 2p<sub>3/2</sub>, intensity for chlorine species.

a function of the take off angle of the electrons examined. Those curves were created for the two most interesting samples created in this work, i.e. samples 3 and 4. The highest value angles correspond to the surface sensitive angles on the right hand side of the



**Fig. 4.** Relative concentrations of elements as a function of take off angle for sample 4 (a) and sample 3 (b) respectively. Concentrations were divided by corresponding element concentration for the untreated PVC although Cl<sup>-</sup> and Cl<sub>PVC</sub> are divided by the total amount of chlorine.

graph. They indicate that the amount of chlorine and carbon are similar for sample 4 compared to PVC but the amount of oxygen is twice as much. For sample 3 the amount of oxygen is not as high relatively and when the carbon is similar, chlorine shows a difference with a marked decrease, particularly for the bulk sensitive angles. These curves also indicate clearly that the chloride component of the chlorine signal (Cl<sup>-</sup>) is more pronounced towards the surface sensitive angles than the covalent chlorine, which is consistent with the flame treatment (Cl<sub>PVC</sub> corresponds to the covalent chlorine, i.e. bound to the PVC skeleton). Profiles resulting from these assump-



**Fig. 5.** Reconstructed profiles of element concentrations for sample 3 (a) and sample 4 (b). C 1s corresponds to other carbon functionalities than those bonded to chlorine.

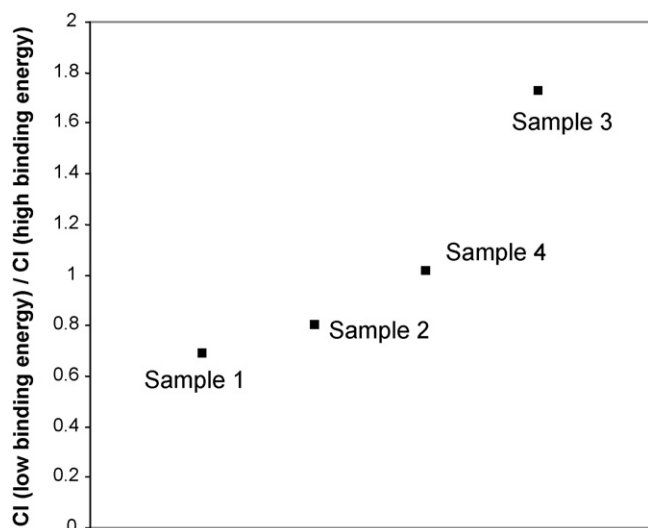


Fig. 6. Angle integrated ratio of Cl (low binding energy) to Cl (high binding energy).

tions and XPS angle resolved data are shown for samples 3 and 4 in Fig. 5.

#### 4. Discussion

The chlorine signal exhibits two components that may be assigned to covalent chlorine and chloride. Only in the case of the sample initially covered with a protection film is the chloride component not visible. One of the possible explanations is that the flame treatment has induced the transformation of some of the covalent chlorine into chloride which is a reduction of the chlorine species. The flame contains two regions, one reducing and another oxidising with the oxidising region being present predominantly outside or at the bottom of the flame and the reducing part in the inner region or top (for flame treatment the flame is upside down compared to a Bunsen burner). According to what region in which the sample finds itself, the effect will be totally different. If the sample is oxidised, it is anticipated that the carbon will exhibit increased corresponding chemistry, i.e. alcohol, ester, acidic or carboxylic functionalities. However the sample may also have undergone reduction which explains the transformation of covalent chlorine into chloride ions. This is probably an indication that the sample was exposed to the reducing part of the flame. If one examines the ratio of the chloride to the covalent chlorine one can also see that the distribution ratio of the two species varies according to the actual treatment of the PVC sample and that the ratio is the highest for the samples where the sample was closest to the burner for samples 3 and 4. To illustrate this, Fig. 6 shows the ratio of  $\text{Cl}^-$  to  $\text{Cl}_{\text{PVC}}$  for samples in order of treatment or for samples 1 to 4. Sample 4 with film prior to treatment makes an exception to this explanation and this seems to imply that extraneous material was deposited from the protection film onto the surface of this sample presumably preventing any effect from the flame on the covalent chlorine.

If flame treatment was to impart oxidation to the surface, an increase of the carbon bearing oxygen would be seen as for the treatment of polypropylene [8]; therefore one would anticipate similar results for PVC. As shown above, variations of the chemistry are obtained upon treatment of the PVC by flame. A decrease in unfunctionalised carbon is accompanied by increase of oxygen, lead and calcium, the two latter being characteristic of components present in the formulation of the PVC. The only component indicating an increase in the carbon signal is the fourth carbon (carboxylate

or carboxylic functionality). If oxidation of the material was seen, one would expect to see a decrease of CC, CH to the benefit of other more oxygen like bearing carbons. This is not the case here and the small reduction in carbon 2 and 3 seems to be consistent with a reduction of the surface. However, as indicated above the fourth component increases which is not consistent with reduction but rather with oxidation. Another explanation is possible: the results may indicate that other more labile components may have been segregating to the PVC surface prior or after the flame treatment, in particular components with CC, CH or ester functionalities. Besides, carbon bound to oxygen species may have been removed then replaced by new functionalities on the polymer where the chlorine is transformed into chloride rendering the obtained results seemingly similar in terms of oxygen related functionalities. Also, other components than pure PVC are present within the system and as additives have indeed been shown to segregate to the surface [9], it may be difficult to separate the effect of the flame on the functionalisation of the polymer matrix or on elimination of low molecular weight present on the surface of the material under study. The increase of oxygen is not totally explained by the small increase in the carbon related signal (carbon 4) but may simply originate from additives bearing oxygen such as fillers, in particular calcium carbonate which, in turn, may indicate a slight damage of the material by overheating.

Fig. 5 shows the profiles obtained. These profiles have to be considered with caution, however, as the sample is not pure PVC and that they should not be considered beyond approximately 8 nm because of the uncertainty related to the poor signal to noise ratio associated with deeper depth signals. The signals decrease exponentially and less confidence is given to data returned below such depth. They are however consistent with indications given in Fig. 4 that the chloride species are found above the covalent chlorine species in terms of depth of treatment. As indicated in the profile they do not dominate the extreme surface (a small amount seems to be present however) of the sample but rather are found below the surface at a depth of a few nanometres. Intuitively the concentration of chloride ions should be more intense closer to the surface and then decrease in some fashion (abruptly or not), the observation here is totally different and may be evidence for diffusion of the ions further within the structure subsequent to their formation. Alternatively the effect of the flame is not felt at the outside surface but deeper within the sample. This with variation of the chemistry as described above seems to imply that the increase in wettability is more connected with some "cleaning effect" of the surface rather than a dramatic effect on the chemistry. However, it seems quite likely that the profiles are slightly overestimated in depth or would benefit (as would the authors) from knowing the real hierarchy of layers present on this commercial PVC better as the raw data clearly indicate that a small amount of chloride is present at the extreme surface. Another interesting aspect of the profiles indicates that the oxygen is depleted towards the extreme surface of most of the samples, this together with the fact that the oxygen profile and the chloride species do not coincide shows that the increase in oxygen seen in the collapsed angle data are not necessarily related. The variation in oxygen signal may be related to variation/diffusion of oxygen containing species rather than a result of the flame treatment or to the exposure of oxygen containing species such as additives/fillers.

#### 5. Conclusions

Industrial PVC window profile samples have been exposed to flame treatment in order to improve their wettability and surface energy. Their surface chemistry has been assessed using XPS and ARXPS. The findings are the following:

- The surface chemistry changes with a decrease in unfunctionalised, CC, CH type of carbon, an increase in oxygen and of other elements related to additives present within the formulated PVC.
- The chlorine signal changes from covalent chlorine to a mixture of covalent chlorine and chloride ions species unless a sample is initially covered with a protection film.
- ARXPS data indicate that the chloride ions species are mostly buried at a depth of a few nanometres with the covalent species buried further down.
- A “cleaning effect” of labile components readily segregating to the PVC surface may account for some of the observed variations of the surface chemistry.

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