ToF-SIMS Depth Profiling of a Complex Polymeric Coating Employing a C₆₀ Sputter Source.

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Abstract :

A complex poly(vinylidene difluoride) (PVdF)/poly(methyl methacrylate) (PMMA) based coil coating formulation has been investigated using time-of-flight SIMS (ToF-SIMS). Employing a Bi₃⁺ analysis source and a Buckminsterfullerene (C₆₀) sputter source, depth profiles were obtained through the polymeric materials in the outer few nanometres of the PVdF topcoat. These investigations demonstrate that the PVdF coating's air/coating interface is composed principally of the flow agent included in the formulation. Elemental depth profiles obtained in the negative ion mode demonstrate variation in the carbon, oxygen and fluorine concentrations within the coating with respect to depth. All 3 elemental depth profiles suggest that the PVdF coating bulk possesses a constant material composition. The oxygen depth profile reveals the presence of a very thin oxygen rich sub-surface layer in the PVdF coating, observed within the first second of the sputter/etch profile. Retrospectively extracted mass spectra (from the elemental depth profile raw data set) of the PVdF coating sub-surface and bulk layers indicates this oxygen rich sub-surface layer results from segregation of the acrylic co-polymers in the formulation towards the PVdF coating air/coating interface. Molecular depth profiles obtained in both the positive and

negative secondary ion modes provide supporting evidence to that of the elemental depth profiles. The molecular depth profiles confirm the presence of a sub-surface layer rich in the acrylic co-polymers indicating segregation of the co-polymers towards the PVdF topcoats air-coating surface. The molecular depth profiles also confirm that the PVdF component of the topcoat is distributed throughout the coating but is present at a lower concentration at the air-coating interface and in the sub-surface regions of the coating, than in the coating bulk.

Keywords :

Time-of-Flight Secondary Ion Mass Spectrometry; Depth Profiling; C₆₀; Coil Coatings; Polymer

Running Headline :

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Introduction :

The capability to perform SIMS depth profiling analysis of organic molecular solids and polymeric materials has long been desired. If such depth profiling were to enable both elemental and molecular depth profiles to be obtained then this would greatly enhance the range of applications of the technique. However, although metallic and inorganic materials are commonly investigated by SIMS depth profiling techniques, ion induced damage of organic sample surfaces typically leads to a loss of molecular specificity within the depth profile layers. Now however, with the availability of cluster ion based primary ion sources the possibility for depth profiling organic or polymeric materials exists.

The use of the SF_5^+ cluster ion sources as a depth profiling sputter/etch tool was first demonstrated by Gillen *et al* when analysing boron implanted silicon and Ni/Cr multilayer samples ⁽¹⁾. Fuoco *et al* then demonstrated that SF_5^+ cluster ions could be employed to sputter through polymeric materials by depth profiling through a PMMA thin film on silicon ⁽²⁾. Norrman *et al* also employed SF_5^+ sputter depth profiling to investigate PMMA and poly(vinyl chloride) films spin coated onto Si wafer ⁽³⁾. Later, Mahoney *et al* used SF_5^+ depth profiling to investigate poly(d-*L*-lactic acid) (PLLA) doped with 4-acetamidophenol ⁽⁴⁾ and PLLA doped/blended with a poly(ethylene oxide) based triblock co-polymer ⁽⁵⁾.

More recently, with the advent of the Buckminsterfullerene (C_{60}) cluster ion source, the depth profiling of organic/polymeric materials has made great advances. Much of the early development and characterisation of the C_{60} source was undertaken at the laboratories of Vickerman in the UK ^(6,7), Winograd in the USA ^(8,9) and by commercial manufacturers of ToF-SIMS instruments and components ⁽⁹⁻¹¹⁾. Winograd has applied the C_{60} ion source to the investigation of a variety of materials and systems for both static SIMS and SIMS imaging analysis, such investigations include SIMS imaging of lipids in picolitre vials ⁽¹³⁾ and the characterisation of solid-phase combinatorial libraries ⁽¹⁴⁾. However, much of the work of Winograd and his colleagues with the C_{60} ion source is founded on its use as a sputter/etch tool for depth profiling analyses. Winograd has demonstrated C_{60} depth profiling of polycrystalline metals ⁽¹⁵⁾, Langmuir-Blodgett films ^(16,17), peptides in a trehalose matrix ⁽¹⁸⁾ and using ice as the matrix for histamine ^(19,20).

The use of the C_{60} ion source as a sputter/etch source for the depth profiling of polymeric materials has also been reported, although to date the numbers of such reports is very limited. Weibel *et al* employed a C_{60} source to investigate poly(ethylene terephthalate) and poly(styrene) polymers ⁽⁷⁾ while Szakal *et al* investigated a model PMMA polymeric system ⁽²¹⁾. Of course the use of a C_{60} source as a sputter/etch tool is not restricted to ToF-SIMS analysis and Sanada *et al* have demonstrated the use of a C_{60} source for sputter/etching in the XPS depth profiling analysis of poly(tetrafluoroethylene) and SiO_2/Si samples ⁽²²⁾. To date, most of the C_{60}

sputter/etch depth profiling studies on polymeric materials have relied upon well characterised, simple, model, homopolymer systems.

In this paper we investigate the application of the C₆₀ sputter/etch source to the depth profiling of a complex polymeric coating formulation based on PVdF (see Figure 1a for polymeric structure), acrylic co-polymers (see Figures 1b and 1c for polymeric structures) and a range of other minor additives. The coating is a typical PVdF based commercial formulation in which the main resin is blended with acrylic co-polymers. The fluoropolymer confers high durability performance and chemical resistance upon the coating. The acrylics enhance the film forming, rheology, gloss control and pigment dispersion properties of the coating. Additionally, it is accepted within the coatings industry that the inclusion of acrylic copolymers as flow agents in the formulations contributes towards the adhesive properties exhibited by the PVdF topcoat towards primer coatings by improving substrate wetting. This is achieved by them segregating to the primer/topcoat interface as shown in a recent study, using ToF-SIMS, by Hinder *et al* ⁽²³⁾. The PVdF formulation used in these studies was pigmented with mainly blue and white pigments. Elemental, negative molecular ion and positive molecular ion depth profiles are all demonstrated. Such studies enable layers of differing molecular composition to be characterised within a single coating.

Experimental :

Materials and Methods

The PVdF topcoat/polyurethane (PU) primer, multilayer coating samples on an Al substrate were prepared at Becker Industrial Coatings Ltd. The term PVdF topcoat used throughout this paper refers to the topcoat formulation based on a blend of a PVdF resin (see Figure 1a for polymeric structure) with acrylic co-polymers (see Figures 1b and 1c for polymeric structures) and a number of other minor additives including flow agent and pigments. The PVdF topcoat was applied onto pre-primed Al substrate and ‘cured’ at a peak metal temperature (PMT) of 249°C. The samples were thus provided as ‘cured’ coatings on Al panels (~16 cm × 10 cm × 0.5 mm) and 1 × 1 cm² specimens for ToF-SIMS analysis were cut using a guillotine. The PU primer coating is ~5 µm thick whilst the PVdF topcoat is ~24 µm thick. Thus the overall thickness of the primer/topcoat system on the Al substrate is ~29 µm.

Surface Analysis by ToF-SIMS

ToF-SIMS analyses were carried out on an ION-TOF GmbH (Münster, Germany) TOF.SIMS 5 system. The instrument is equipped with a reflectron type analyser and microchannel plate detector with 20kV post-acceleration capability. A Bi liquid metal ion source (LMIS) was employed for mass data acquisition. Mass data was acquired using the Bi₃⁺ cluster ion. Such cluster ions provide superior secondary ion yields to those available from the more conventional Ga⁺ source. Mass data acquisition was

performed by raster scanning over a $73 \times 73 \mu\text{m}^2$ area. A 25 keV Bi_3^+ primary ion beam delivering 0.2 pA of current was used. A cycle time of 100 μs was employed for mass data acquisition. A C_{60} ion source was employed as the sputter/etch tool. The area analysed by the LMIS was at the centre of the sputter/etch crater formed using the rastered C_{60} beam. The Buckminsterfullerene ions are produced by electron impact ionisation of a C_{60} vapour. The C_{60} source produces both singly and doubly charged C_{60} ions, only the C_{60}^+ ion was used for sputter/etching in the depth profiling experiments described here. The C_{60}^+ sputter/etch area was $300 \times 300 \mu\text{m}^2$. A 10 kV, 15 nA C_{60}^+ primary ion beam with a fluence of 1.4×10^{14} ions cm^{-2} was employed⁽²⁴⁾. A sputter/etch interval of 0.01 s was used for all of the depth profile studies described here. The depth profiling analyses were performed in the ‘non-interlaced’ mode, that is, repeat cycles of mass data acquisition by the Bi LMIS, sputter/etch by the C_{60} source, followed by charge compensation using a low energy electron flood gun were employed. Estimation of the C_{60} sputter etch rate for the PVdF based coating employed here (obtained using a surface profilometer), suggests an etch rate of $\sim 3 \text{ nm s}^{-1}$ for the $300 \times 300 \mu\text{m}^2$ etch area used here.

Results and Discussion :

In Figure 2a a negative ion ToF-SIMS mass spectrum acquired at the air/coating surface of a PVdF based topcoat is presented. It is a well established fact that in a coating formulation such as the one employed here i.e. one in which an additive designed to segregate to the coating surface is included, the coatings surface chemistry will be dominated by the surface segregated material to a thickness of typically 1 nm ^(25,26). In the PVdF topcoat formulation employed here an acrylic flow agent additive is included. This flow agent is designed to segregate to the coating surface, to lower the free energy of the coating surface and thus to enhance the wetting of the substrate and the coatings appearance. In Figure 2b a negative ion mass spectrum acquired from the pure flow agent (drop cast onto aluminium foil from acetone solution) is presented. It is observed that the mass spectra in Figures 2a & 2b are very similar with the peaks at m/z 41, 71, 81, 87 127, 129 and 171 being characteristic of the acrylic flow agent. Assignment of ion formula and structure for the m/z 41, 71, 81, 127, 129 and 171 ions are given in Table 1. However, no assignment or structure has been made for the ion peak observed at m/z 87. This is because the exact formulation of the commercially available flow agent employed is unknown (for reasons of commercial confidentiality). It is highly likely that the ion at m/z 87 arises as the result of additional materials included in the flow agent formulation and thus it is observed in the mass spectra in both Figures 2a and 2b. It is also observed that the mass spectrum in Figure 2a (the PVdF topcoats air/coating surface) contains some additional peaks to those in Figure 2b at m/z 19, 39 and 85. The peaks at m/z 19 and 39 are assigned to the F^- and F_2H^- ions respectively and

indicate that although outermost surface of the coating is predominantly acrylic flow agent some mixing with the PVdF resin has taken place. The peak observed in Figure 2a at m/z 85 is believed to originate from the acrylic copolymers included in the topcoats formulation (see Figure 4 and Table 2). These results suggest that the PVdF topcoat air/coating interface is composed primarily of the flow agent. This is as anticipated and in keeping with the work of Leadley *et al* and Perruchot *et al*, both of whom demonstrated that a coil coatings surface chemistry is dominated by the flow agent added to the coatings formulation ^(25,26).

In Figure 3 a negative ion elemental depth profile from a PVdF topcoat air/coating surface a short distance into the PVdF coating is presented. Changes in the intensity (and thus concentration) of C, O and F have been followed with respect to sputter time and thus depth into the PVdF topcoat. Although one must be aware of the phenomenon of the surface transient in the initial stages of depth profiling and therefore must be cautious when discussing data from early in the depth profile, it is observed in Figure 3 that the C depth profile exhibits an intensity maximum at or close to the coating surface (0-0.2 s of etching). The C intensity then gradually decreases with depth until the C intensity reaches a stable value in the bulk of the PVdF topcoat (after ~3 s of etching).

The shape of the O depth profile in Figure 3 is similar to that of the C depth profile, however, the O depth profile exhibits an intensity maximum after ~0.4 s of etching and like the C depth profile the intensity of the O depth profile is then seen to

decrease with depth, with a stable intensity being reached after ~3-4 s of etching. This similarity in the shape of the depth profiles for C and O in Figure 3 suggests that the surface and sub-surface regions of the PVdF topcoat are rich in C/O containing materials, when compared to the PVdF topcoat bulk (the region beyond 3 s of etching in Figure 3).

The shape of the F depth profile in Figure 3 is substantially different than the depth profiles observed for C and O. It is observed that the F depth profile in Figure 3 exhibits an intensity minimum at the topcoat surface (0 s of etching), the F intensity then increases steadily with depth in the sub-surface region of the coating (0-2 s of etching). The intensity of the F depth profile continues to increase during the next second of etching but at a lesser rate before reaching a stable intensity (beyond 3 s of etching) in the PVdF topcoat bulk. That the F intensity is at a minimum at the PVdF topcoat's air/coating surface is consistent with the interpretation of the data in Figure 2a which showed that the PVdF topcoat's air/coating surface is dominated by the flow agent, although a small quantity of fluorinated materials are also observed at the air/coating surface. In the sub-surface region of the PVdF topcoat the intensity of the F depth profile is increasing with depth while the C and O depth profiles are decreasing with depth. This suggests segregation of C/O containing materials in the coating formulation towards the PVdF topcoat's air/coating surface.

No assessment was made of the floor of the sputter/etch crater after acquiring the depth profile data. However, given that the total analysis depth of the depth profile

data reported here is within the top 20-30 nm of the coating, ion etch damage and the surface roughness of the etch crate floor are expected to be minimal. Thus it is anticipated that the depth profiles presented here will have suffered little or no loss in ion intensity due to ion induced damage of the etch crater floor. Additionally, although the coating studied is pigmented, the presence of pigment particles presented no problems in the depth profile experiments reported here. No attempt was made to acquire depth profiles in regions of the coating away from pigments. Indeed, it is anticipated that the pigment particles are well dispersed throughout the coating bulk. Furthermore, it is not really feasible, using the changes in material composition observed in the coating employed here, to determine the depth resolution of a C60 source when depth profiling a PVdF based coating. However, Shard *et al* using organic delta-layers of aluminium hydroxyquinolate in Irganox 1010 have estimated that the depth resolution of a C60 source when depth profiling a polymeric system is $<10\text{ nm}^{(27)}$.

The stability of the intensity of the C, O and F depth profiles (beyond 3 s of etching) in Figure 3 suggests that the PVdF topcoat bulk possesses a homogenous material composition. The homogeneity of the coating bulk composition contrasts sharply with the sub-surface region of the PVdF topcoat which shows considerable variation in material composition due to materials in the formulation segregating towards the PVdF air/coating surface. Inspection of a series of mass selected images retrospectively extracted from the raw depth profile data, from a depth consistent with the coating bulk, reveals that the bulk material is homogenous in nature. No phase

segregated domains were observed in the images inspected and the images indicate that within the coating bulk the different components of the coating are evenly dispersed. These results are further evidence that the coating bulk possesses a homogenous material composition.

Analysis of the elemental depth profiles in Figure 3 establishes that the sub-surface and bulk regions of the PVdF topcoat possess differing material compositions. In Figure 4 negative ion mass spectra, retrospectively extracted from the raw data sets of the elemental depth profiles in Figure 3, are presented. The mass spectrum in Figure 4a was extracted from the oxygen rich sub-surface layer at ~0.4 s of etching (see Figure 3), while the mass spectrum in Figure 4b was extracted from the bulk region of the PVdF topcoat at ~6 s of etching (see Figure 3). Both of the mass spectra in Figure 4 contain large peaks at m/z 19 (F⁻) and m/z 39 (F₂H⁻). The observation of the peaks at m/z 19 and 39 in Figure 4a and 4b indicates that the PVdF resin is present in both the sub-surface and bulk regions of the PVdF topcoat. There are a number of peaks in Figure 4a that display a much greater intensity than those observed in Figure 4b, namely the peaks at m/z 55, 71, 85, 139, 141 and 185. (see Table 2 for peak assignments). Assignment of ion formula and structure for the m/z 55, 71, 85, 139, 141 and 185 ions are given in Table 2. These peaks are attributed to the fragmentation of the PMMA/ poly(ethyl acrylate) (EA) based co-polymers included in the PVdF topcoat formulation ⁽²⁸⁾. It is interesting to note that these ions are the same as those observed by Hinder *et al* when investigating the segregation of acrylic copolymers to the PVdF topcoat/PU primer interface ⁽²³⁾. In Figure 4b only the peaks at m/z 19, 31

and 39 (F^- , CF^- and F_2H^- respectively) can be assigned unequivocally to the PVdF component of the formulation in the coating bulk. Unfortunately, the majority of $\text{C}_x\text{H}_y\text{F}_z$ peaks diagnostic of PVdF occur in the positive SIMS mass spectrum. It is likely the additional high intensity peaks observed in Figure 2b at m/z 72, 73, 103 and 121 originate from additives included in the coating formulation. However the coating bulk is a complex mixture of components and any attempt to assign these peaks formulas or structures would be highly speculative and so has not been attempted.

Insets in Figures 4a and 4b are negative ion mass spectra for the mass range m/z 30.9-31.2 for the sub-surface (Figure 4a) and bulk (Figure 4b) regions of the PVdF topcoat. It is observed in the insets in Figure 4 that the peak with a nominal mass of m/z 31 contains two contributing components, a lower mass component at m/z 30.99 and a higher mass component at m/z 31.02. The lower mass component at m/z 30.99 is attributed to the CF^- ion ($\Delta m = -23$ ppm) originating from fragmentation of the base PVdF resin and the higher mass component at m/z 31.02 is assigned to the CH_3O^- fragment ($\Delta m = 126$ ppm) originating from fragmentation of the acrylic co-polymers. It is observed in the inset in Figure 4a that the peak at higher mass, CH_3O^- , is the more intense of the two peaks, while in the inset in Figure 4b this fragment is the lower intensity peak. Conversely, in the inset in Figure 4a the lower mass peak, CF^- , is the lower intensity peak while in the inset in Figure 4b it is the high intensity peak. These results confirm that there are compositional differences between the sub-surface and bulk layers of the PVdF topcoat and indicate that the sub-surface region

of the PVdF topcoat is rich in the PMMA/EA co-polymers. These results also suggest that it is the acrylic co-polymers in the formulation that are segregating towards the PVdF topcoats air/coating surface. However, the acrylic copolymers are unable to reach the air/coating surface of the PVdF topcoat because of the presence of the lower free-energy acrylic flow agent in the formulation. Thus the surface segregating acrylic copolymers appear to form an acrylic rich sub-surface layer within the PVdF topcoat. It should be noted that in this case the flow agent used has a much higher carbon content, when compared to the acrylic copolymers. This scenario is not always the case as some flow agents contain less carbon than oxygen.

To further investigate the probable segregation of acrylic co-polymers to the sub-surface region of the PVdF topcoat, negative ion molecular depth profiles were obtained. It has previously been demonstrated that the use of a C_{60} source for sputter/etching allows chemical and molecular specificity to be maintained when etching through a number of different polymeric materials ⁽²¹⁾. In Figures 5a and 5b negative ion depth profiles for the molecular fragments, CF^- , CH_3O^- , F_2H^- and $C_4H_5O_2^-$ are presented. In addition, for comparative purposes, a molecular depth profile obtained for the $C_8H_{17}O^-$ fragment ion, diagnostic of the acrylic flow agent included in the topcoat formulation (see Table 1), is also included in Figures 5a and 4b. When presenting ToF-SIMS depth profiles it is common practise to use a logarithmic scale due to the large dynamic range of the intensity data and this convention has been followed for Figures 3 and 5a. In Figure 5b the depth profile data from Figure 5a is alternatively presented employing a linear scale, both to emphasise

differences in the shapes of the depth profiles and to demonstrate variations in depth profile intensities. It is observed in Figure 5a that the molecular ions attributed to the acrylic co-polymers, CH_3O^- and $\text{C}_4\text{H}_5\text{O}_2^-$, possess depth profile shapes very similar to those observed for C and O depth profiles in Figure 3 with intensity maximums at 0.4 ± 0.1 seconds of etching. Furthermore, the depth profile for the CF^- molecular ion from the PVdF component is identical in shape to that observed for the fluorine depth profile in Figure 3. The F_2H^- depth profile in Figure 5a is also similar in shape to the F depth profile in Figure 3 showing increasing fluorine intensity with depth in the surface and sub-surface regions of the topcoat followed by a region of more stable fluorine intensity within the PVdF topcoat bulk. The SIMS depth profile for the $\text{C}_8\text{H}_{17}\text{O}^-$ flow agent fragment is most intense at the coating surface. The intensity of the $\text{C}_8\text{H}_{17}\text{O}^-$ depth profile is then seen to decrease rapidly with etch time and thus depth in Figure 5. The $\text{C}_8\text{H}_{17}\text{O}^-$ ion is then only observed with a minimal intensity in that part of the $\text{C}_8\text{H}_{17}\text{O}^-$ depth profile obtained in the coating bulk (after 2 s of etching). The molecular depth profiles in Figure 5 provide further evidence for the formation of an acrylic rich layer within the sub-surface region of the PVdF topcoat, resulting from segregation of the acrylic co-polymer towards the topcoat air/coating surface.

Given the low surface free energy of the PVdF it may be expected that this component would actually be the one to preferentially segregate to the air/coating surface. However the makeup of the surface reflects the processes that occur during application and “cure”. That is the liquid is applied, the flow agent segregates to the

surface containing predominantly solvent. This helps with substrate wetting and equalises surface free energies to give a smooth coating surface. As the paint is heated, the solvents evaporate through the flow agent and the PVdF starts to dissolve in the solvents that remain. The low molecular weight PVdF will dissolve first and will segregate to the surfaces. However the viscosity will be increasing at the same time, inhibiting this process. At peak metal temperature, during the short cure cycle, a full interpenetrating network will have been formed between the PVdF and the acrylic resins but the mobility of the PVdF will be negligible. Thus any concentration gradients that have been set up will be made permanent by the quench immediately after the oven exit. The acrylic co-resin is already in solution when the paint is cold and although it cannot compete with the flow agent for the surface, it will still segregate to just under the flow agent setting up a double layer which becomes more dispersed as more PVdF dissolves and migrates towards the surface.

The acquisition of depth profiles of organic materials such as polymeric coatings is clearly not restricted to negative ion profiles although these are often more useful from a diagnostic point of view. In Figure 6 a series of positive ion molecular depth profiles obtained from a PVdF air/coating surface are presented. For PVdF the use of the positive ion mass spectrum provides the benefit of making available a greater number of molecular fragments, typically of the form $C_xH_yF_z^+$, than are available in the negative ion SIMS mass spectrum. In Figure 6 the depth profile data is presented using a linear scale to emphasise the variation in the depth profile intensities. In Figure 6 depth profiles obtained for the $C_3HF_4^+$ ion at m/z 113 and the $C_3H_2F_5^+$ ion at

m/z 133 (originating from the PVdF component) are presented. It is observed in Figure 6 that the $C_3HF_4^+$ and $C_3H_2F_5^+$ depth profiles possess shapes very similar to those observed in Figure 3 for the fluorine depth profile and in Figure 5 for the CF ion depth profile. These positive ion molecular depth profiles for fragments originating from PVdF again demonstrate that there is a depletion of PVdF in the surface and sub-surface regions of the coating, when compared to the PVdF topcoat bulk. The $C_3HF_4^+$ and $C_3H_2F_5^+$ depth profiles in Figure 6 again reveal that a stable intensity of fluorinated fragments originating from PVdF is obtained after ~3-4 s of etching, indicating the bulk region of the PVdF topcoat has been reached at this point. The depth profiles obtained for the $C_2H_5O^+$ fragment at m/z 45 and the methacryloyl ion $C_4H_5O^+$ at m/z 69 (diagnostic of the acrylic co-polymers) ⁽²⁹⁾, are again very similar in shape to the elemental oxygen depth profile in Figure 3 and the CH_3O^- and $C_4H_5O_2^-$ molecular depth profiles in Figure 5. The shape of the $C_2H_5O^+$ and $C_4H_5O^+$ depth profiles in Figure 6 are yet further evidence for the presence of a sub-surface segregation layer rich in the acrylic co-polymer components of the PVdF topcoat formulation. In addition, for comparative purposes, a molecular depth profile obtained from the $C_8H_{17}^+$ fragment ion, diagnostic of the acrylic flow agent included in the topcoat formulation, is also included in Figures 6. The SIMS depth profile for the $C_8H_{17}^+$ flow agent fragment is most intense at the coating surface. The intensity of the $C_8H_{17}^+$ depth profile is then seen to decrease rapidly with etch time and thus depth in Figure 6. The $C_8H_{17}^+$ ion is then only observed with a minimal intensity in that part of the $C_8H_{17}^+$ depth profile in Figure 6 obtained from the coating bulk (after 2 s of etching).

The elemental, negative ion and positive ion molecular depth profiles and the mass spectra extracted from different regions within the PVdF topcoat all point to the PVdF topcoats surface region being composed of 3 distinct layers. The outer air/coating surface principally contains the flow agent included in the PVdF topcoat formulation, in this case an acrylic flow agent (see Figure 2). Typically, flow agent layers are 0.5-1.5 nm thick ⁽³⁰⁾ depending on the flow agent employed and its concentration. Below this outermost flow agent layer is a sub-surface layer rich in the acrylic co-polymer included in the PVdF topcoat formulation. This acrylic rich sub-surface layer is formed by the segregation of a substantial fraction of the acrylic co-polymers towards the PVdF topcoats air/coating surface. The finally layer is the PVdF topcoat bulk which exhibits a stable PVdF/acrylic copolymer material composition.

The elemental and molecular depth profile data presented in Figures 3, 5 and 6 owe much to the properties of the C₆₀ source. The original design of this source as a primary ion source capable of producing primary ion pulses with nanosecond time widths is beneficial to the depth profiler. That is, when the C₆₀ source is employed as a sputter/etch tool, sputter/etch intervals in the millisecond time range are readily available. Such short sputter/etch intervals are typically not available when using dynamic SIMS, and in this work a surface segregated layer is identified within the first one second of sputter/etch time (equivalent to a thickness of around one nanometre). The ability to obtain elemental and molecular depth profiles of cured

polymeric coatings, made possible in this case by the unique capabilities of the C₆₀ sputter/etch source, will be of great importance to the coatings industry and the coating formulator in particular as it will enable a greater understanding of coatings related issues such as intercoat adhesion and weathering.

Conclusions :

We have demonstrated the use of a bismuth cluster ion analysis source and a C₆₀ sputter/etch source in combination to obtain elemental and molecular depth profiles from a complex PVdF based topcoat formulation. The elemental depth profiles obtained revealed the presence of a very thin oxygen rich layer in the sub-surface region of the coating. Additionally, the elemental depth profile showed that the surface and sub-surface regions of the coating were depleted in fluorine when compared to the bulk of the coating. Mass spectra of the sub-surface and bulk layers of the PVdF topcoat (extracted from elemental depth profile data set), negative ion molecular depth profiles and positive ion molecular depth profiles all provided evidence that the sub-surface layer of the PVdF topcoat is rich in the acrylic co-polymers included in the PVdF topcoats formulation. These results indicate the segregation of the acrylic co-polymers towards the air/coating surface of the PVdF topcoat. Overall these results suggest the surface region of the PVdF topcoat is composed of three distinct layers; a thin flow agent layer at the outer surface, an acrylic co-polymer rich sub-surface layer and the topcoat bulk which possesses a stable material composition.

The 3 layers can be explained by the processes that take place during the application and “cure” of the PVdF. The fact that there is an acrylic rich layer just under the flow aid could help with scratch and abrasion resistance. However, it could also mean that the initial drop in gloss retention on exposure to the environment is rapid but the decline is arrested once the bulk of the PVdF is exposed.

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Figure 1. Polymeric structures of (a) poly(vinylidene difluoride), (b) poly(methyl methacrylate) and (c) an acrylate. For structure (c) R1 is C₂H₅ for the copolymers and C₈H₁₇ for the flow agent included in the topcoat formulation.

Figure 2. ToF-SIMS negative ion mass spectra of (a) PVdF topcoat air/coating surface and (b) acrylic flow agent.

Figure 3. Elemental depth profiles of carbon (C), oxygen (O) and fluorine (F) obtained from a PVdF topcoat air/coating surface.

Figure 4. ToF-SIMS negative ion mass spectra extracted from the raw depth profile data in Figure 2. a) Spectra extracted from the acrylic rich sub-surface layer, b) spectra extracted from the coating bulk. Insets show region of m/z 30.9-31.2 from each spectrum (component at m/z 30.99 is CF⁻, whilst that at m/z 31.02 is CH₃O⁻).

Figure 5. Negative mode, molecular ion depth profiles of the PVdF topcoat air/coating surface. The CF^- and F_2H^- ions (in red) originate from the PVdF resin while the CH_3O^- and $\text{C}_4\text{H}_5\text{O}_2^-$ fragments (in blue) originate from the acrylic copolymers. The $\text{C}_8\text{H}_{17}\text{O}^-$ ion (in green) originates from the acrylic flow agent included in the coating formulation. (a) Depth profiles using a logarithmic scale, (b) Same depth profiles using a linear scale.

Figure 6. Positive mode, molecular ion depth profiles of the PVdF topcoat air/coating surface. The C_3HF_4^+ and $\text{C}_3\text{H}_2\text{F}_5^+$ fragment ions (in red) originate from the PVdF resin while the $\text{C}_2\text{H}_5\text{O}^+$ and $\text{C}_4\text{H}_5\text{O}^+$ fragment ions (in blue) originate from the acrylic co-polymers. The $\text{C}_8\text{H}_{17}^+$ fragment ion (in green) originates from the acrylic flow agent included in the coating formulation.

Ion mass / m/z	Ion Formula	Ion Structure
41	$C_2H_1O^-$	$HC\equiv C-O^-$
71	$C_3H_3O_2^-$
81	$C_5H_5O^-$
127	$C_8H_{15}O^-$
129	$C_8H_{17}O^-$
171	$C_{10}H_{19}O_2^-$

Table 1. PVdF topcoat, acrylic flow agent fragment ion assignment.

Ion mass / <i>m/z</i>	Ion Formula	Ion Structure
55	C ₃ H ₃ O ⁻	H ₂ C=C=CH-O ⁻
71	C ₃ H ₃ O ₂ ⁻
85	C ₄ H ₅ O ₂ ⁻
139	C ₅ H ₉ O ₂ ⁻
141	C ₈ H ₁₃ O ₂ ⁻
185	C ₉ H ₁₃ O ₄ ⁻

Table 2. PVdF topcoat, sub-surface region fragment ion assignment.