A ToF-SIMS Investigation of a Buried Polymer-Polymer Interface Exposed by Ultra-Low-Angle Microtomy.

Steven J. Hinder^{1*}, Chris Lowe², James T. Maxted² and John F. Watts¹

¹ The Surface Analysis Laboratory, School of Engineering, University of Surrey, Guildford, Surrey GU2 7XH, UK.

² Becker Industrial Coatings Ltd, Goodlass Road, Speke, Liverpool L24 9HJ, UK.

Abstract :

The interfacial region of a model, multilayer coating system on an aluminium substrate has been investigated by high resolution time-of-flight secondary ion mass spectrometry (ToF-SIMS). Employing ultra-low-angle microtomy (ULAM), the interface between a poly(vinylidene difluoride) (PVdF) based topcoat and a poly(urethane) (PU) based primer ‘buried’ over 20µm below the PVdF topcoat’s air/coating surface was exposed. Imaging ToF-SIMS and subsequent post-processing extraction of mass spectra of the ULAM exposed interface region and the PVdF topcoat and PU primer bulks indicates that the material composition of the polymer-polymer interface region is substantially different to that of the bulk PVdF and PU coatings. Analysis of the negative ion mass spectra obtained from the PVdF/PU interface reveals the presence of a methacrylate based component or additive at the interface region. Reviewing the topcoat and primer coating formulations reveals the PVdF topcoat formulation contains methyl methacrylate (MMA)/ethyl acrylate (EA) acrylic co-polymer components. Negative ion ToF-SIMS analysis of an acrylic co-polymer confirms it is these components that are observed at the PVdF/PU interface. Post-processing extraction of ToF-SIMS images based on the major ions of the

MMA/EA co-polymers reveals these components are observed in high concentration at the extremities of the PVdF coating i.e. at the polymer-polymer interface but are also observed to be distributed evenly throughout the bulk of the PVdF topcoat. These findings confirms that a fraction of the MMA/EA acrylic co-polymers in the formulation segregate to the topcoat-primer interface where they enhance the adhesive properties exhibited by the PVdF topcoat towards the underlying PU primer substrate.

Keywords :

Time-of-Flight Secondary Ion Mass Spectrometry; Buried Interface; Ultra-low-angle Microtomy; Multilayer Coatings; Imaging SIMS.

Running Headline :

A ToF-SIMS Investigation of a Buried Polymer-Polymer Interface.

Introduction :

The requirement to understand interface related phenomena such as structure, adhesion and chemistry is critical in the evaluation of the effectiveness of the commercial formulations employed today to produce polymeric coatings and paints for metal substrates. In many of the commercial polymeric coatings system available a multilayer system must be adopted, typically a primer to ensure a strong adhesion to the metal substrate exists and a topcoat to provide the desired surface properties such as resistance to weathering and for aesthetic purposes. Fundamental to the success of such a multilayer coating system is the polymer-polymer intercoat adhesion that occurs between the topcoat/primer interfaces. However, the techniques available to investigate the interface chemistry, when coatings or paints are applied at the thickness levels employed commercially, are extremely limited.

Much of the work reported to date concerning the investigation of buried interfaces on a variety of materials systems has principally relied upon direct examination of the interface by a variety of spectroscopic techniques. Wang and Wang used soft X-ray emission spectroscopy to analyse the interface between manganese thin films and a Si substrate¹ whilst Yang *et al* employed X-ray standing wave spectroscopy to examine an Fe/Cr interface.² The analysis of buried polymeric interface have also been reported, Kugler *et al* used X-ray photoelectron spectroscopy to investigate a poly(*p*-phenylene-vinylene) on indium-tin-oxide interface³ while sum frequency generation spectroscopy has been used by both Harp *et al* and Chen *et al* to examine polymer/polymer interfaces.⁴⁻⁵ Typically, such spectroscopic techniques are restricted

to the examination of interfaces at best a few hundred nanometres below the sample surface. Leadley and Watts, however, used a different approach to probe the metal-polymer interface. Very thin (ca. 2nm) polymer films were cast onto metal substrates and high resolution XPS was used to monitor changes in the C1s spectrum, as a result of specific interactions at the interface.⁶⁻⁷ This approach is very successful for the study of the interface chemistry relating to model systems on metal substrates, but is limited in its ability to determine interphase characteristics of real surfaces. In the 'real-world' of commercial polymeric paints and coatings however, the need is often to investigate an interface buried tens or hundreds of microns below the paint/coating's air/coating surface. In this case, direct examination of an interface by spectroscopic means is not possible and alternative methods of gaining access to the 'buried' interface must be sought.

To investigate buried interfaces in metallic and inorganic material systems a number of mechanical techniques are available that remove material in a well-defined and geometric manner. Techniques such as ball cratering⁸⁻⁹ and angle lapping⁹⁻¹¹ remove material from a specimen by means of polishing or abrading mechanisms. These result in the production of shallow craters or tapers through the sample material and across the interface of interest. However, although Cohen and Castle¹² demonstrated the applicability of using cryo-stage ball cratering for the Auger electron spectroscopy investigation of metal/polymer interfaces, such abrading/polishing techniques cannot generally be applied to organic materials. When techniques such as ball cratering and angle lapping are applied to organic material systems such as

polymeric coatings and paints the resulting crater or taper surface generally suffers from smearing of the polymeric material, resulting in a loss of resolution and the possibility that the material removal mechanism induces chemical or physical change.

The ULAM sample tapering technique is an extension of the angle lapping procedure particularly suited to the production of tapers through organic material systems. In a previous paper the ULAM technique was described in some detail and the morphology and topology of the PVdF topcoat and PU primer surfaces resulting from the ULAM tapering procedure¹³ were characterised. Additionally, it was demonstrated that the ULAM procedure is particularly suited to exposing polymer/polymer interfaces as the resulting taper does not exhibit sample smearing,¹³ enabling the retention of depth resolution for subsequent analyses. X-ray photoelectron spectroscopy (XPS) analysis at high spatial resolution of changes in elemental concentration across a PVdF/PU interface exposed by ULAM has been demonstrated by Hinder *et al* with a theoretical depth resolution of 13nm.¹⁴ Additionally, XPS compositional depth profiling, using a ULAM taper, of a polyamide coating to which an organosilane had been added has been demonstrated by Guicheney *et al.*¹⁵ However, the depth resolution attainable by XPS on a ULAM taper is limited by the X-ray spot size achievable, currently 12-15µm. Thus, although XPS provides quantitative data about a ULAM exposed interface, it is not able to achieve the level of chemical specificity available from the high resolution spectral data obtainable on today's high resolution ToF-SIMS instruments.

In the work described in this paper, the ULAM technique is employed to impart an ultra-low-angle taper through a PVdF topcoat and PU primer multilayer, polymeric coating system thus exposing the PVdF/PU interface buried over 20 μ m below the PVdF topcoat's air/coating surface. High resolution imaging ToF-SIMS and post-processing of the mass spectra and ion image extraction from raw, imaging SIMS data enables characterisation of the interface region and the individual coating's bulk characteristics. Analysis of the spatial distribution of components within the multilayer coating system employed is also demonstrated.

Experimental :

Materials and Methods

The PVdF topcoat/PU primer, multilayer coating samples on Al substrate, employed here for buried interface analysis, were prepared at Becker Industrial Coatings Ltd. The polymeric topcoat is a typical PVdF based commercial formulation. This is based on a polyvinylidene fluoride resin blended with acrylic co-polymers. The fluoropolymer provides high durability performance and chemical resistance. The acrylics enhance the film forming properties, rheology and gloss control and pigment dispersion. In addition, it is accepted within the coatings industry that these acrylic copolymers contribute to the adhesive properties of the PVdF topcoat towards primers. The PVdF formulation used in the study was pigmented with mainly blue and white pigments. The term PVdF topcoat used throughout this paper refers to the topcoat formulation based on a blend of a PVdF resin with acrylic co-polymers and other minor additives. The primer coating is a polyurethane commercial formulation. The polyurethane formulation is based on a mixture of a blocked hexamethylene diisocyanate and an aromatic polyester resin, which contains a yellow anticorrosive pigment.

The samples were provided as cured coatings on Al panels (~16 cm × 10 cm × 0.5 mm). To prepare specimens for ULAM processing samples ~1 cm² were cut from the panel using an industrial guillotine. To ensure that any burrs or asperities formed at the rear of the sample by the guillotining process were removed, the rear of each specimen was polished using a silicon-carbide abrasive paper (Struers, Glasgow,

UK). At all times great care was taken to ensure the procedures used to cut the specimen from the sample panel and to prepare the specimen for ULAM processing resulted in the specimen remaining flat.

Ultra-low-angle Microtomy

A schematic of the ULAM apparatus as employed in the production of ultra-low-angle tapers is presented in Figure 1. The ULAM processing of samples was carried out on a Microm HM355S motorised rotary microtome (Optech Scientific Instruments, Thame, UK) equipped with a standard specimen clamp and a tungsten carbide knife. The ultra-low-angle sectioning blocks ($\sim 3.5 \times 3.5 \times 0.7$ cm) were manufactured in-house from high-quality steel. The ultra-low-angle sectioning blocks have one 3.5×3.5 cm² tapered face raised by a defined amount (in μm) relative to the parallel edge of the tapered face. A detailed description of the ULAM procedure can be found elsewhere.¹³ The ultra-low-angle tapers through the PVdF/PU coatings employed here were produced using a ultra-low-angle sectioning block possessing a 25 μm rise, giving a nominal taper angle of $\sim 0.04^\circ$. Such a taper angle provides a theoretical analysed depth of ~ 360 nm in the 500×500 μm^2 ToF-SIMS images presented in Figure 4 and Figure 6.

Surface Analysis by ToF-SIMS

Imaging ToF-SIMS analyses of the ULAM taper sections were carried out on an ION-TOF GmbH (Munster, Germany) ToF-SIMS IV-200. The instrument is equipped with a reflectron analyser and microchannel plate detector with 20kV post-

acceleration capability. An Au_3^+ ion source was employed as such sources provide superior secondary ion yields over that available from the more conventional Ga^+ source used in imaging SIMS. It is also noted that the spot size of an Au_3^+ beam ($\sim 1\ \mu\text{m}$ in the pulsed mode) and thus the resolution, is not as good as that available from a Ga^+ source. However, the spatial resolution offered by the Au_3^+ source was sufficient for the SIMS images presented in this manuscript. The primary ion dose was within the static limit at $1.2 \times 10^{11}\ \text{ions}/\text{cm}^2$. ToF-SIMS image data was acquired over a $500 \times 500\ \mu\text{m}^2$ area at a resolution of 256×256 pixels. A 25 keV primary ion beam delivering 0.03 pA of current was employed. Imaging data was acquired at 1 cycle per pixel with a total of 126 scans. A cycle time of 200 μs was employed. Charge compensation was achieved using a pulsed electron flood source. Data acquisition and post-processing analyses were performed using the IonSpec Version 4.5.0.0 & IonImage Version 3.0.0.61 software products.

Mass spectra acquisition for the MMA/EA acrylic co-polymer component employed in the PVdF topcoat formulation was carried out on a VG Scientific (East Grinstead, UK) Reflectron ToF-SIMS spectrometer. This instrument is equipped with a MIG 300PB pulsed liquid gallium ion source and a two-stage reflectron time-of-flight analyser. Static SIMS conditions (ion dose $< 10^{13}\ \text{ions}/\text{cm}^2$) were employed with a 16 keV beam, delivering 2 nA of current. The region of the surface analysed was a $500\ \mu\text{m}$ wide square rastered area.

Preparation of the MMA/EA resin for ToF-SIMS analysis.

The MMA/EA acrylic co-polymer in ethyl diglycolacetate solvent was available in liquid form. A drop of the MMA/EA solution was placed onto aluminium foil and spread using a glass rod to create a thin polymer layer. The aluminium foil/resin sample was placed into a pre-heated oven at 160°C for 10min to remove the solvent. The aluminium foil/resin sample was then cut to provide specimens $\sim 1 \text{ cm}^2$. These specimens were mounted on SIMS stubs for analysis.

Results and Discussion :

ULAM has been employed to expose the interfacial region of a model PVdF topcoat/PU primer multilayer coating system on Al substrate. The ULAM exposed interface is buried some 20-25 μm below the air/coating surface of the PVdF topcoat. The coating formulations employed here (which themselves are based on commercial formulations) are known to exhibit a strong adhesion between the PVdF topcoat and the PU primer. A schematic depicting the apparatus employed in the ULAM tapering of specimens is presented in Figure 1. The concept underlying the formation of ultra-low-angle tapers through polymeric materials by ULAM is very simple; a specimen is mounted on a sectioning block possessing an ultra-low-angle taper on one of its faces, this specimen is then presented to the microtome knife such that sectioning of the polymeric material by the microtome knife imparts a geometrically well-defined ultra-low-angle taper through the specimen. Inset in Figure 1 is a digitally recorded optical image of a PVdF/PU coating on Al substrate that has been sectioned by ULAM such that the interface between the two coatings has been exposed. The ultra-low-angle taper (as indicated by the arrow in the inset in Figure 1) cuts the blue PVdF topcoat's air/coating surface, passes through the bulk of the PVdF topcoat, exposes the interfacial region of the PVdF/PU coatings and terminates in the bulk of the yellow PU primer. The image inset in Figure 1 demonstrates that ULAM can be employed to expose a 'buried' interface, making that interface available for subsequent examination.

In Figure 2 four high resolution ToF-SIMS images incorporating a PVdF/PU interface region exposed by ULAM tapering are presented. Each of the images in Figure 2 is $500 \times 500 \mu\text{m}^2$ in size and was acquired at a resolution of 256×256 pixels. In Figures 2a and 2b the ToF-SIMS images reveal the outline of the PU regions of the ULAM taper whilst the images presented in Figures 2c and 2d reveal the shape of the PVdF regions of the ULAM taper. Figure 2a is a positive ion image of the ion at a nominal mass of $149m/z$ which we attribute to the $\text{C}_8\text{H}_5\text{O}_3^+$ fragment originating from a phthalate species¹⁶ in the polyester/polyurethane base resin employed in the PU coating formulation. The similar image in Figure 2b is a negative ion image of the same region for the nominal mass $26m/z$ which we have attributed to the CN^- fragment of the PU primer coating formulation. The ToF-SIMS images presented in Figures 2c and 2d are complementary to those of Figures 2a and 2b respectively. Figure 2c is a positive ion image of the ion at a nominal mass of $59m/z$ which is attributed to the $\text{C}_3\text{H}_4\text{F}^+$ fragment¹⁶ resulting from fragmentation of the PVdF polymer component of the PVdF topcoat. Figure 2d is a negative ion image of mass $19m/z$ readily attributed to the high-intensity F^- ion that dominates PVdF mass spectra.¹⁶ The images presented in Figure 2 reveal that the PVdF/PU interface region, as exposed by ULAM tapering, is somewhat heterogeneous with an interface region composed of a series of ‘island’ like structures. Analysis of the images in Figure 2 suggests the ‘islands’ observed at the PVdF/PU interface originate from the underlying PU primer coating. That is, the ‘islands’ are observed with contrast in Figures 2a and 2b which are associated with the PU primer but the same regions are observed to exhibit no contrast (black regions) in Figures 2c and 2d, the images

associated with the PVdF topcoat. It may be suggested that the ‘island’ like features observed at the PVdF/PU interface region in Figure 2 are due to an unevenness in the surface of the underlying PU primer. As the ULAM induced taper results in the thinning of the PVdF topcoat as the taper progresses towards the PVdF/PU interface, the unevenness in the surface of the underlying PU primer results in small features that exhibit increased height at the PU surface being exposed by ULAM tapering and thus being observed as ‘islands’ within the PVdF topcoat as it thins towards the interface region. A silica matting agent of 2 microns average particle size is incorporated into the PU primer to deliberately roughen the surface and enhance mechanical adhesion. The images in Figure 2 may well attest to this. However, it is clear that the high-resolution ToF-SIMS images presented in Figure 2, do enable the regions associated with the PVdF bulk, the PU bulk and the PVdF/PU interface to be defined along the ULAM taper.

Analysis of the images presented in Figure 2 and additional, related ToF-SIMS images suggests that the PVdF/PU interface region of the sample is substantially different in terms of material composition to that of the PVdF and PU bulk coatings. ToF-SIMS mass spectra were retrospectively extracted from raw ToF-SIMS image data (the areas used to perform these mass spectra extractions are indicated in Figure 2c). Extracted negative ion mass spectra for the mass range 0-200 m/z of the PU bulk, PVdF/PU interface and PVdF bulk regions of a ULAM tapered specimen are presented in Figure 3. In Figure 3a the negative ion mass spectra extracted from the PU bulk region of the ULAM taper is presented. It is observed in Figure 3a that the

negative ion mass spectra of the PU bulk is characterised by prominent fragment ions at 25, 41, 42, 49, 66, 100 and 121 m/z . The ions observed at 49 m/z (C_4H^-) and 121 m/z ($C_7H_5O_2^-$) are attributed to fragments from the base polyester/polyurethane resin component of the PU primer formulation. This resin is polymerised from both aromatic (in the form of phthalic acid) and aliphatic monomers polyester components. The ions at 41 m/z (CHN_2^-) and 66 m/z ($C_3H_2N_2^-$) are attributed to the nitrogen containing hexamethylene diisocyanate cross-linker in the PU primer formulation.¹⁷ The peak at 42 m/z is attributed to the OCN^- ion, such a fragment might arise from fragmentation of one or more of the components or additives included in the PU primer formulation. It has not yet been possible to attribute the ion at 100 m/z to a specific fragment or assign its origin to a component or additive of the PU formulation.

In contrast to the PU primer mass spectra in Figure 3a, the negative ion mass spectra extracted from the PVdF bulk region of the specimen presented in Figure 3c exhibits only five prominent peaks, these are observed at 19, 25, 39, 49 and 85 m/z . The ions at 19 and 39 m/z are attributed to the F^- and F_2H^- fragments respectively and arise from fragmentation of the base PVdF resin component of the PVdF topcoat formulation.¹⁶ The peak at 85 m/z is attributed to the $C_4H_5O_2^-$ fragment of an acrylic co-polymer component of the PVdF topcoat formulation. It has not yet been possible to attribute the fragment or assign the PVdF topcoat formulation component or additive that gives rise to the ion observed at 49 m/z in Figure 3c. The ion observed with strong intensity in both Figures 3a and 3c at 25 m/z is attributed to the C_2H^- fragment, a common

fragment observed in high intensity in most negative ion mass spectra acquired from organic materials. The negative ion mass spectra retrospectively extracted from a region at the PVdF/PU interface and presented in Figure 3b is substantially different to the mass spectra observed in Figures 3a and 3c for the PU and PVdF coating bulks. Although the mass spectra in Figure 3b contains peaks consistent with both the PVdF topcoat (F^- at $19m/z$ and F_2H^- at $39m/z$) and the PU primer (OCN^- at $42m/z$ and $C_6H_4O_2^-$ at $121m/z$) the spectra also contains high intensity peaks at 31, 55, 71, 85, 87, 141 and $185m/z$. This mass spectral data confirms that the regions of the ULAM taper associated with the PVdF/PU interface possess a material composition different to that of the PVdF and PU coating bulks. Consideration of the high intensity peaks observed in Figure 3b (not attributable to the PVdF or PU coatings) and ion matching utilising a SIMS mass spectral database¹⁶ suggests the PVdF/PU interface region of the ULAM tapered sample is rich in a methacrylate containing material.

Reviewing the PVdF topcoat and PU primer formulations adopted for use in the production of the model coating system employed in the work described here reveals that only the PVdF topcoat formulation contains any acrylic components or additives. Investigation of the material composition of the acrylic components and additives used in the PVdF topcoat formulation indicates that only the acrylic copolymers used contain significant proportions of methacrylate. One of the acrylic co-polymers employed is composed of 70.3% MMA, ~28% EA and ~1% butyl methacrylate.¹⁸ A sample of this acrylic co-polymer was obtained and a negative ion ToF-SIMS mass spectrum for the mass range $30-200m/z$ of the acrylic co-polymer is presented in

Figure 4. It is observed that the high intensity peaks that characterise the acrylic co-polymer in the mass spectra presented in Figure 4 are the same as those observed in Figure 3b for the PVdF/PU interface region. The high intensity peaks diagnostic of the acrylic co-polymers (and observed in both Figure 3b & Figure 4) are attributed to specific fragments¹⁹ and assigned to acrylic co-polymers components in Table 1. This analysis indicates that the PVdF/PU interface region is rich in the acrylic co-polymers and confirms that a fraction of the acrylic co-polymers segregates to the PVdF/PU interface, possibly during the stoving process. Such segregation of coating formulation components and additives towards the coating surface is a well documented phenomenon.²⁰⁻²² Indeed, some coating additives such as flow and levelling agents are added to coating formulations with the express intent of having them segregate to the coatings surface where they modify the properties exhibited by the coatings surfaces.²³⁻²⁵

Table 1.

Ion mass / Da	Fragment	Component/Additive
31	CH_3O^-	MMA
55	$\text{C}_3\text{H}_3\text{O}^-$	MMA
71	$\text{C}_3\text{H}_3\text{O}_2^-$	EA
85	$\text{C}_4\text{H}_5\text{O}_2^-$	MMA
87	$\text{C}_4\text{H}_7\text{O}_2^-$	MMA/EA
141	$\text{C}_8\text{H}_{13}\text{O}_2^-$	MMA
185	$\text{C}_9\text{H}_{13}\text{O}_4^-$	MMA/EA

MMA = methyl methacrylate.

EA = ethyl acrylate.

Having determined that a fraction of the acrylic co-polymers component of the PVdF formulation segregates to the interface of the PVdF topcoat, the negative ions'

diagnostic of the acrylic co-polymers contained in the raw, high resolution, imaging ToF-SIMS data can be examined in more detail. The negative ion ToF-SIMS mass spectra, post-processing extracted from the negative ion image data reveals that the ions characteristic of the acrylic co-polymers typically exhibits peaks containing two components (except the ion at a nominal mass of $141m/z$ that contained four contributing components). The high resolution, negative ion, ToF-SIMS mass spectra for the mass range $30.95\text{--}31.15m/z$ is presented in Figure 5. It is observed in Figure 5 that the peak with a nominal mass of $31m/z$ contains two contributing components, a less intense component at lower mass ($31.01m/z$) and a more intense component at higher mass ($31.03m/z$). The lower intensity component at $31.01m/z$ is attributed to the CF^- ion originating from fragmentation of the base PVdF resin and the more intense component at $31.03m/z$ from the CH_3O^- fragment of the acrylic co-polymers. Negative ion ToF-SIMS images were retrospectively extracted for each of the ions diagnostic of the acrylic co-polymers (see Figure 4). In the case of each nominal mass, all component peaks that contributed to that nominal mass were selected for ion image extraction and an ion image produced and inspected.

In Figure 6 high resolution, negative ion ToF-SIMS images of the 31, 55, 71, 85, 87 and $141m/z$ ions diagnostic of the acrylic co-polymers (see Table 1) are presented. Each of the images in Figure 6 is $500 \times 500 \mu m^2$ in size and was acquired at a resolution of 256×256 pixels. It is observed in all the ion images presented in Figure 6 that areas rich in the acrylic co-polymers exhibit high image intensity and that these areas are consistent with the PVdF/PU interface region. Although all six of the

images presented in Figure 6 exhibit high intensity regions at the PVdF/PU interface and lower intensity regions associated with the PVdF bulk, the levels of contrast observed are variable and depend upon the intensity exhibited by the acrylic co-polymers ion and on the contribution ions from the PU bulk region make to image formation. The ion image in Figure 6d (nominal $85m/z$) provides the most striking contrast of all the images presented in Figure 6. It is observed in Figure 6d that the PU bulk region of the ion image provides little or no contrast to the image (upper region of image which is principally black) indicating that the origin of the $C_4H_5O_2^-$ fragment at $85m/z$ is confined to the PVdF topcoat containing regions of the ion image. It is further observed in Figure 6d that the $C_4H_5O_2^-$ fragment at $85m/z$ is observed within the PVdF bulk region of the ion image (lower region of the image, principally red in colour) indicating that the acrylic co-polymers are distributed throughout the bulk of the PVdF topcoat in an even manner. However, at the PVdF/PU interface region of Figure 6d (effectively the air/coating PU surface and the coating/substrate PVdF surface) it is observed that the $C_4H_5O_2^-$ fragment at $85m/z$ (and the ions associated with the other images presented in Figure 6) exhibit a high intensity in this region indicating a greater concentration of the acrylic co-polymers at the PVdF/PU interface than in the PVdF topcoat bulk. Such an increase in the concentration of the acrylic co-polymers at the PVdF/PU interface is further evidence of the segregation of a fraction of the MMA and EA co-polymers to the base of the PVdF topcoat and thus to the PVdF/PU interface. Analysis of the ion images in Figure 6 suggest the MMA and EA acrylic co-polymers are distributed throughout the PVdF bulk in an even manner enabling the acrylic co-polymer to perform its primary

functions, that of enhancing the mechanical, rheological and dispersive properties of the PVdF topcoat. However, the ion images presented in Figure 6 also confirm that a significant fraction of the acrylic co-polymers segregate to the base of the PVdF topcoat, increasing the concentration of the MMA and EA containing acrylic co-polymers at the PVdF/PU interface, here they perform their secondary function, that of enhancing the adhesive properties of the PVdF topcoat towards the PU primer substrate.

Conclusions :

We have demonstrated that the ULAM sample tapering technique in combination with high mass resolution, high spatial resolution imaging ToF-SIMS can be used to investigate ‘buried’ polymer-polymer interfaces. In the work reported here the polymer-polymer interface analysed by ToF-SIMS was buried over 20 μm below the PVdF topcoat’s air/coating surface. Possibly more significantly, we have demonstrated that ULAM in combination with a high spatial resolution analysis technique (ToF-SIMS in this case) enables materials localised towards, or in greater concentration, at ‘buried’ interfaces to be characterised and observed. In the work described here we have revealed how lesser components of a coating formulation, MMA and EA based acrylic co-polymers, are distributed within a coating and also demonstrated how the spatial distribution of these components within the coating are directly related to the specific functions the components are added to the formulation to perform. That is, we have demonstrated that the MMA and EA based acrylic co-

polymers are distributed evenly within the PVdF topcoat bulk (where they enhance various physical properties of the coating) but in addition that a significant fraction of the acrylic co-polymers segregate to the PVdF topcoat base, and thus the PVdF/PU interface region, where they are found in greater concentration than in the PVdF coating bulk. Here the acrylic copolymers enhance the adhesive properties of the PVdF topcoat towards the PU primer.

Acknowledgements ;

Grateful thanks are extended to ION-TOF GmbH and Dr Birgit Hagenhoff and her colleagues at Tascon GmbH for the provision of ToF-SIMS facilities. The authors acknowledge the financial support of the EPSRC (Grant no. GR/N65745).

References :

1. Wang J, Wang T. *Mater. Sci. Eng. B*. 2000; **72**: 156.
2. Yang S-H, Mun BS, Mannella N, Kim S-K, Kortright JB, Underwood J, Salmassi F, Arenholz E, Young A, Hussain Z, Van Hove MA, Fadley CS. *J. Phys.: Cond. Matt.* 2002; **14**: L407.
3. Kugler T, Andersson A, Logdlund, Holmes AB, Li X, Salaneck WR. *Synth. Met.*, 1999; **100**: 163.
4. Harp GP, Gautam KS, Dhinojwala A. *J. Am. Chem. Soc.* 2002; **124**: 7908.
5. Chen C, Wang J, Even MA, Chen Z. *Macromolecules*. 2002; **35**: 8093.
6. Leadley SR, Watts JF. *J. Adhes.*. 1997; **60**: 175.
7. Leadley SR, Watts JF. *J. Electron Spectrosc. Relat. Phenom.* 1997; **85**: 107.
8. Walls JM, Hall DD, Sykes DE. *Surf. Int. Anal.* 1979; **1**: 204.
9. Walls JM. *Thin Solid Films*. 1981; **80**: 213.
10. Tarng ML, Fisher DG. *J. Vac. Sci. Technol.* 1978; **15**: 50.
11. Lea C, Seah MP. *Thin Solid Films*. 1981; **75**: 67.
12. Cohen JM, Castle JE. *Inst. Phys. Conf. Ser.* No 93. Chapter 5 1988; **1**: 275.
13. Hinder SJ, Watts JF, Maxted JT. Submitted for publication to the *J. Mater. Sci.*, February 2004.
14. Hinder SJ, Watts JF, Lowe C. Accepted for publication in *Surf. Int. Anal.* August 2004.
15. Guicheney M, Watts JF, Abel M-L, Brown AM, Audenaert M, Amouroux N. Accepted for publication in *Surf. Int. Anal.* August 2004.

16. In *The Wiley Static SIMS Library* (Version 2), vol. 2. Vickerman JC, Briggs D, Henderson A (eds). John Wiley: Chichester, 1999; Organic Materials - Homo Polymers.
17. Coullerez G, Léonard D, Lundmark S, Mathieu HJ. *Surf. Int. Anal.* 2000; **29**: 431.
18. Lazzari M, Chiantore O. *Polymer*, 2000; **41**: 6447.
19. Hearn MJ, Briggs D. *Surf. Int. Anal.* 1988; **11**: 198.
20. Perruchot C, Abel M-L, Watts JF, Lowe C, Maxted JT, White RG. *Surf. Int. Anal.* 2002; **34**: 570.
21. Perruchot C, Watts JF, Lowe C, Beamson G. *Int. J. Adhes. Adhes.* 2003; **23**: 101.
22. Horgnies M, Darque-Ceretti E, Combarieu R. *Prog. Org. Coat.*, 2003; **47**: 154.
23. Leadley SR, Watts JF, Blomfield CJ, Lowe C. *Surf. Int. Anal.* 1998; **26**: 444.
24. 1Perruchot C, Watts JF, Lowe C, White RG, Cumpson PJ. *Surf. Int. Anal.* 2002; **33**: 869.
25. Watts JF, Abel M-L, Perruchot C, Lowe C, Maxted JT, White RG. *J. Electron Spectrosc. Relat. Phenom.* 2001; **121**: 233.

Figure 1. Schematic depicting the concept of ultra-low-angle microtomy used to impart a ultra-low-angle taper through a multilayer polymeric coating system. Inset is a digitally recorded optical image of a PVdF/PU multilayer coating interface exposed by ultra-low-angle microtomy.

Figure 2. Imaging ToF-SIMS images ($500 \times 500 \mu\text{m}^2$) of a) positive ion image of $149m/z$ showing PU region of sample, b) negative ion image of $66m/z$ showing PU region of sample, c) positive ion image of $59m/z$ showing PVdF region of sample, d) negative ion image of $19m/z$ showing PVdF region of sample. The white squares inserted into figure c indicate the regions from which the mass spectra presented in Figure 3 for the PVdF topcoat bulk (1), PU primer bulk (2) and the PVdF/PU interface (3) were extracted.

Figure 3. Negative ion mass spectra, retrospectively extracted from an imaging ToF-SIMS PVdF/PU interface image as in Figure 2. The mass spectra are from; a) the PU primer region, b) the PVdF/PU interface region and c) the PVdF topcoat region of the specimen.

Figure 4. A negative ion ToF-SIMS mass spectra of the pristine acrylic co-polymer component of the PVdF topcoat formulation in the mass range 30-200 m/z .

Figure 5. High resolution negative ion ToF-SIMS mass spectra for 31 m/z showing that two components contribute to this nominal mass.

Figure 6. Imaging ToF-SIMS negative ion images $500 \times 500 \mu\text{m}^2$ acquired at a resolution of 256×256 pixels showing the segregation of the acrylic co-polymers to the PVdF/PU interface. a) 31 m/z , b) 55 m/z , c) 71 m/z , d) 85 m/z , e) 87 m/z and f) 141 m/z ion images.