A ToF-SIMS investigation of a buried polymer/polymer interface exposed by ultra-low-angle microtomy

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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’ >20 µm 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 of 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 that 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 that 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 that 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 confirm 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. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: time-of-flight secondary ion mass spectrometry; buried interface; ultra-low-angle microtomy; multilayer Coatings; imaging SIMS

INTRODUCTION

The requirement to understand interface-related phenomena such as structure, adhesion and chemistry is critical in 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 available a multilayer system must be adopted, typically a primer to ensure that 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 relied principally 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 an Si substrate, whereas Yang et al. employed x-ray standing-wave spectroscopy to examine an Fe/Cr interface. Analysis of the buried polymeric interface has been reported, Kugler et al. used x-ray photoelectron spectroscopy to investigate a poly(p-phenylene–vinylene) on indium–tin–oxide interface and sum frequency generation spectroscopy has been used by both Harp et al. and Chen et al. to examine polymer/polymer interfaces. Typically, such spectroscopic techniques are restricted to the examination of interfaces at a few hundred nanometres below the sample surface. Leadley and Watts, however, used a different approach to probe the metal/polymer interface. Very thin (~2 nm) polymer films were cast onto metal substrates and high-resolution XPS was used to monitor changes in the C 1s spectrum as a result of specific interactions at the interface. 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 cratering8–11 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 AES investigation of metal/polymer interfaces, such abrading/polishing techniques cannot be applied generally 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 ultra-low-angle microtomy (ULAM) sample tapering technique is an extension of the angle lapping procedure that is 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 morphological and topological of the poly(vinylidene difluoride) (PVdF) topcoat and polyurethane (PU) primer surfaces resulting from the ULAM tapering procedure3 were characterized. Additionally, it was demonstrated that the ULAM procedure is particularly suited to exposing polymer/polymer interfaces because the resulting taper does not exhibit sample smearing, 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. at a theoretical depth resolution of 13 nm.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 Guichenuy et al.15 However, the depth resolution attainable by XPS on a ULAM taper is limited by the x-ray spot size achievable, which is currently 12–15 µm. 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 time-of-flight secondary ion mass spectrometry (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 >20 µm 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 enable characterization 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 PVdF 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 contributes 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 PU commercial formulation. The PU formulation is based on a mixture of a blocked hexamethylene disocyanate and an aromatic polyester resin that contains a yellow anticorrosive pigment.

The samples were provided as cured coatings on Al panels (~16 cm x 10 cm x 0.5 mm). To prepare specimens for ULAM processing, samples of ~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 silicon carbide abrasive paper (Struers, Glasgow, UK). At all times great care was taken to ensure that 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 Fig. 1. The ULAM processing of samples was carried out on a Microm HM355S motorized rotary microtome (Optech Scientific Instruments, Thame, UK) equipped with a standard specimen clamp and a tungsten carbide knife. The ultra-low-angle sectioning blocks (~3.5 x 3.5 x 0.7 cm) were manufactured in-house from high-quality steel. The ultra-low-angle sectioning blocks have one 3.5 x 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 an ultra-low-angle sectioning block possessing a 25 µm rise, giving a nominal taper angle of ~0.04°. Such a taper angle provides a theoretical analysed
were acquired over a 500 µm wide square rastered area. The region of the surface analysed was presented in Fig. 3 and Plate 2.

**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 instrument equipped with a reflectron analyser and microchannel plate detector with 20 kV post-acceleration capability. An Au⁵⁺ ion source was employed because 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 Au⁵⁺ beam (~1 µm in the pulsed mode) and thus the resolution are not as good as those available from a Ga⁺ source. However, the spatial resolution offered by the Au⁵⁺ source was sufficient for the SIMS images presented in this manuscript. The primary ion dose was within the static limit at 1.2 x 10¹¹ ions cm⁻². The ToF-SIMS image data were acquired over a 500 x 500 µm² area at a resolution of 256 x 256 pixels. A 25 keV primary ion beam delivering 0.03 pA of current was employed. Imaging data were acquired at one 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 and IonImage Version 3.0.0.61 software products.

Mass spectra acquisition for the methyl methacrylate–ethyl acrylate (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 ToF analyser. Static SIMS conditions (ion dose <10¹⁵ ions cm⁻²) were employed, with a 16 keV beam delivering 2 nA of current. The region of the surface analysed was a 500 µm 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 then cut to provide specimens of ~1 cm². These specimens were mounted on SIMS stubs for analysis.

**RESULTS AND DISCUSSION**

Ultra-low-angle microtomy 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 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 Fig. 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. The inset in Fig. 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 Fig.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 Fig. 1 demonstrates that ULAM can be employed to expose a ‘buried’ interface, making that interface available for subsequent examination.

In Plate 1 four high-resolution ToF-SIMS images incorporating a PVdF/PU interface region exposed by ULAM tapering are presented. Each of the images in Plate 1 is 500 x 500 µm² in size and was acquired at a resolution of 256 x 256 pixels. In Plates 1(a) and 1(b) the ToF-SIMS images are 360 nm in the 500 x 500 µm² ToF-SIMS images presented in Fig. 3 and Plate 2.
reveal the outline of the PU regions of the ULAM taper, whereas the images presented in Plates 1(c) and 1(d) reveal the shape of the PVdF regions of the ULAM taper. Plate 1(a) is a positive ion image of the ion at a nominal mass of 149 m/z, which we attribute to the C₆H₂O₃⁺ fragment originating from a phthalate species in the polyester/polyurethane base resin employed in the PU coating formulation. The similar image in Plate 1(b) is a negative ion image of the same region for the nominal mass 26 m/z, which we have attributed to the CN⁻ fragment of the PVdF topcoat formulation. The ToF-SIMS images presented in Plates 1(c) and 1(d) are complementary to those of Plates 1(a) and 1(b), respectively. Plate 1(c) is a positive ion image of the ion at a nominal mass of 59 m/z, which is attributed to the C₄H₇F⁺ fragment resulting from fragmentation of the PVdF polymer component of the PVdF topcoat. Plate 1(d) is a negative ion image of mass 19 m/z readily attributed to the high-intensity F⁻ ion that dominates PVdF mass spectra. The images presented in Plate 1 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 Plate 1 suggests that the ‘islands’ observed at the PVdF/PU interface originate from the underlying PU primer coating, i.e. the ‘islands’ that are observed with contrast in Plates 1(a) and 1(b) are associated with the PU primer but the same regions are observed to exhibit no contrast (black regions) in Plates 1(c) and 1(d), the images associated with the PVdF topcoat. It may be suggested that the ‘island’-like features observed at the PVdF/PU interface region in Plate 1 are due to an unevenness in the surface of the underlying PU primer. Because the ULAM-induced taper results in 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 average particle size is incorporated into the PU primer to roughen the surface and enhance mechanical adhesion. The images in Plate 1 may well attest to this. However, it is clear that the high-resolution ToF-SIMS images presented in Plate 1 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 Plate 1 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 extracted retrospectively from raw ToF-SIMS image data (the areas used to perform these mass spectra extractions are indicated in Plate 1(c)). 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 Fig. 2. In Fig. 2(a) the negative ion mass spectra extracted from the PU bulk region of the ULAM taper is presented. It is observed in Fig. 2(a) that the negative ion mass spectrum of the PU bulk is characterized by prominent fragment ions at 25, 41, 42, 49, 66, 100 and 121 m/z. The ions observed at 49 m/z (C₇H₁₄O₃⁻) and 121 m/z (C₆H₁₀N₂⁻) are attributed to fragments from the base polyester/polyurethane resin component of the PU primer formulation. This resin is polymerized from both aromatic (in the form of phthalic acid) and aliphatic monomer polyester components. The ions at 41 m/z (CH₃N⁺) and 66 m/z (C₆H₉N₂⁻) are attributed to the nitrogen-containing hexamethylene disocyanate cross-linker in the PU primer formulation. 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 been possible yet 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 Fig. 2(a), the negative ion mass spectrum extracted from the PVdF bulk region of the specimen presented in Fig. 2(c) exhibits only five prominent peaks, observed at 19, 25, 39, 49 and 85 m/z. The ions at 19 and 39 m/z are attributed to the F⁻ and F₂H⁻ fragments, respectively, and arise from fragmentation of the base PVdF resin component of the PVdF topcoat formulation. The peak at 85 m/z is attributed to the C₆H₂O₃⁻ fragment of an acrylic co-polymer component of the PVdF topcoat formulation. It has not been possible yet 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 Fig. 2(c). The ion observed with strong intensity in both Figs 2(a) and 2(c) at 25 m/z is attributed to the C₄H₅O₂⁻ fragment, a common fragment observed in high intensity in most negative ion mass spectra acquired from organic materials. The negative ion mass spectrum retrospectively extracted from a region at the PVdF/PU interface and presented in Fig. 2(b) is substantially different to the mass spectra observed in Figs 2(a) and 2(c) for the PU and PVdF coating bulks. Although the mass spectrum in Fig. 2(b) contains peaks consistent with both the PVdF topcoat (F⁻ at 19 m/z and F₂H⁻ at 39 m/z) and the PU primer (OCN⁻ at 42 m/z and C₆H₁₀N₂⁻ at 121 m/z), the spectrum also contains high-intensity peaks at 31, 55, 71, 85, 87, 141 and 185 m/z. These mass spectral data confirm 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 Fig. 2(b) (not attributable to the PVdF or PU coatings) and ion matching utilizing a SIMS mass spectral database suggests that 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.
Plate 1. Positive and negative ToF-SIMS images (500 × 500 µm²): (a) positive ion image of 149 m/z showing PU region of sample; (b) negative ion image of 66 m/z showing PU region of sample; (c) positive ion image of 59 m/z showing PVdF region of sample; (d) negative ion image of 19 m/z showing PVdF region of sample. The white squares in (c) indicate the regions from which the mass spectra presented in Fig. 2 for the PVdF topcoat bulk (1), PU primer bulk (2) and PVdF/PU interface (3) were extracted.

Plate 2. The ToF-SIMS negative ion images (500 × 500 µm²) acquired at a resolution of 256 × 256 pixels, showing 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; (f) 141 m/z ion images.
Figure 2. Negative ion mass spectra extracted retrospectively from a ToF-SIMS PVdF/PU interface image as in Plate 1. The mass spectra are from the PU primer region (a) the PVdF/PU interface region (b) and the PVdF topcoat region (c) of the specimen.

Sample of this acrylic co-polymer was obtained and a negative ion ToF-SIMS mass spectrum for the mass range 30–200 m/z of the acrylic co-polymer is presented in Fig. 3. It is observed that the high-intensity peaks that characterize the acrylic co-polymer in the mass spectrum presented in Fig. 3 are the same as those observed in Fig. 2(b) for the PVdF/PU interface region. The high-intensity peaks diagnostic of the acrylic co-polymers (and observed in Figs 2(b) and 3) are attributed to specific fragments 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. 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.

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 spectrum,
Figure 3. Negative ion ToF-SIMS mass spectrum of the pristine acrylic co-polymer component of the PVdF topcoat formulation in the mass range 30–200 m/z.

Table 1. PVdF topcoat, acrylic co-polymer fragment and component assignments

<table>
<thead>
<tr>
<th>Ion mass (Da)</th>
<th>Fragment</th>
<th>Component/additive(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>CH(_2)O(^-)</td>
<td>MMA</td>
</tr>
<tr>
<td>55</td>
<td>C(_3)H(_3)O(^-)</td>
<td>MMA</td>
</tr>
<tr>
<td>71</td>
<td>C(_3)H(_2)O(^2-)</td>
<td>EA</td>
</tr>
<tr>
<td>85</td>
<td>C(_4)H(_5)O(^2-)</td>
<td>MMA</td>
</tr>
<tr>
<td>87</td>
<td>C(_4)H(_7)O(^2-)</td>
<td>MMA–EA</td>
</tr>
<tr>
<td>141</td>
<td>C(_8)H(_13)O(^2-)</td>
<td>MMA</td>
</tr>
<tr>
<td>185</td>
<td>C(_9)H(_13)O(^4-)</td>
<td>MMA–EA</td>
</tr>
</tbody>
</table>

\(^a\) MMA = methyl methacrylate. EA = ethyl acrylate.

Figure 4. High-resolution negative ion ToF-SIMS mass spectrum for 31 m/z, showing that two components contribute to this nominal mass.

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 141 m/z, which contained four contributing components). The high-resolution, negative ion ToF-SIMS mass spectrum for the mass range 30.95–31.15 m/z is presented in Fig. 4. It is observed in Fig. 4 that the peak with a nominal mass of 31 m/z contains two contributing components, a less-intense component at lower mass (31.01 m/z) and a more-intense component at higher mass (31.03 m/z). The lower intensity component at 31.01 m/z is attributed to the CF\(^-\) ion originating from fragmentation of the base PVdF resin, and the more-intense component at 31.03 m/z is from the CH\(_3\)O\(^-\) fragment of the acrylic co-polymers. Negative ion ToF-SIMS images were extracted retrospectively for each of the ions diagnostic of the acrylic co-polymers (see Fig. 3). 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 was produced and inspected.

In Plate 2 high-resolution negative ion ToF-SIMS images of the 31, 55, 71, 85, 87 and 141 m/z ions diagnostic of the
acrylic co-polymers (see Table 1) are presented. Each of the images in Plate 2 is 500 × 500 µm² in size and was acquired at a resolution of 256 × 256 pixels. It is observed in all the ion images presented in Plate 2 that areas rich in the acrylic co-polymers exhibit high image intensity and these areas are consistent with the PVdF/PU interface region. Although all six of the images presented in Plate 2 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-polymer ions and on the contribution that ions from the PU bulk region make to image formation. The ion image in Plate 2(d) (nominal 85 m/z) provides the most striking contrast of all the images presented in Plate 2. It is observed in Plate 2(d) 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 C₅H₁₀O₂⁻ fragment at 85 m/z is confined to the PVdF topcoat containing regions of the ion image. It is further observed in Plate 2(d) that the C₅H₁₀O₂⁻ fragment at 85 m/z is observed within the PVdF bulk region of the ion image (lower region of the image, principally lighter 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 Plate 2(d) (effectively the air/coating PU surface and the coating/substrate PVdF surface) it is observed that the C₅H₁₀O₂⁻ fragment at 85 m/z (and the ions associated with the other images presented in Plate 2) 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 Plate 2 suggests that 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 of enhancing the mechanical, rheological and dispersive properties of the PVdF topcoat. However, the ion images presented in Plate 2 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 and performing 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 >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 localized towards, (or in greater concentration at) ‘buried’ interfaces to be characterized and observed. In the work described here we have revealed how lesser components of a coating formulation, i.e. MMA- and EA-based acrylic co-polymers, are distributed within a coating and we have demonstrated also how the spatial distribution of these components within the coating is directly related to the specific functions that these components perform. Thus, 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.

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REFERENCES