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A ToF-SIMS/MVA approach to identify phase segregation in blends of incompatible but extremely similar resins

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Abstract

This work presents a data analysis extension to a well-established methodology for the assessment of organic coatings using imaging time-of-flight secondary ion mass spectrometry (ToF-SIMS). Such an approach produced results that can be analysed using a multivariate analysis (MVA) procedure that performs the simultaneous processing of spatially and chemically related datasets. The coatings consist of two commercial resins that yield extremely similar spectra and there are no peaks of sufficient intensity that are uniquely diagnostic of either material to provide an unambiguous identification of each. In order to resolve the problem, in addition to microtome-based sample preparation steps of tapers for the analysis through sample thickness, standard samples in cured and uncured conditions are introduced and measured in the same fashion as the specimens under investigation. The resulting ToF-SIMS imaging datasets have been processed using non-negative matrix factorisation (NMF), which enabled identification of phase separation in the cured coatings.

Introduction

There are many areas of scientific and technological endeavour where it is advantageous to use blends or mixtures of polymeric materials. In some instances blends are formed as a result of complete miscibility of the two or more polymeric phases, but in many cases this is not the case and phase separation of the component materials occurs following the mixing procedures¹. If the polymers are easily identifiable (such as PMMA and PVC) segregation can be identified by standard chemical analysis methods (such as FT-IRS), microbeam methods (such as energy dispersive X-Ray analysis in a scanning electron microscope) or surface specific chemical analysis methods such as X-ray photoelectron spectroscopy or time-of-flight secondary ion mass spectrometry (ToF-SIMS)²⁻⁷. ToF-SIMS is one of the most suitable analytical techniques for this purpose as it provides surface mass spectra with molecular specificity at an extremely good detection limit. However, ToF-SIMS becomes difficult to apply with a high degree of certainty should the polymers comprising the blend be extremely similar in chemical composition but still possess a tendency to phase segregate. The work described in this paper deals with such a case. A paint has been formulated of two fully pigmented, but extremely similar, commercial polyester resins, both of which are crosslinked with the same curing agent (hexamethoxy methyl melamine – HMMM).

The coatings investigated in this work are approximately 20 μm in thickness and rather than prepared as cross-sections of the paints on their substrates a novel taper-sectioning method has been employed. Hinder et al^{8,9} introduced this methodology over a decade ago which is now a very well established way of investigating buried polymer/polymer and polymer/metal interfaces in organic coatings: the exposure of cross-sections by creating tapers using ultra-low-angle microtomy (ULAM). In contrast to the more usual ToF-SIMS approach of dual-beam depth profiling, one of the advantages of using ULAM is the larger extent of possible depths of analysis. ToF-SIMS analysis of ULAM exposed cross-sections are usually done in imaging mode^{10,11} and in some cases the areas

comprising all interfaces of interest will be larger than the maximum primary ion beam raster size, which demands the use of large area methodologies such as stage rastering, resulting in several large datasets if more than one taper is analysed. One way to go about dealing with several similar large imaging ToF-SIMS datasets is the application of multivariate analysis (MVA) to a matrix that contains the intensities of a set of peaks for every pixel of each image arranged in rows. This is known in the literature as “row-wise matrix augmentation” and has been done before with ToF-SIMS data ¹². “Column-wise augmentation” is also possible when more than one independent detector acquire data for the same set of samples (or pixels) ^{13,14}.

Another practice for MVA is the insertion of rows containing measurements of well-known standard samples that may be part of the samples under investigation. This has proven to be useful as it sets directions of variance within the dataset, which means that, when these are analysed together with mixed systems, MVA methods that seek to “un-mix” signals will be aided by the purity of the data of such standard samples and potentially enable their relative quantification ^{15,16}.

This paper proposes a methodology for row-wise matrix augmentation (referred to in this paper as “map stitching”) in combination with standards samples for the study of four large area datasets of exposed interfaces in a mixed organic system. The organic systems under consideration are blends of two fully formulated and pigmented paint systems based upon similar commercial polyester resins.

Experimental

Sample preparation

The polyester resin films were prepared by Becker Industrial Coil Coatings. A resin mixture containing the commercial polyester resins and HMMM cross-linking agent, together with

1
2
3 usual pigmentation and additives was stirred together and applied onto chromium (VI) pre-
4 treated Al and Zn substrates using a spiral bar coater. The coated panels were then cured at
5 232°C for 45 seconds (Zn substrate) and 237°C for 35 seconds (Al substrate) in a hot air
6 oven. The final coating thicknesses of the films were within the range 20 – 22 µm. The
7 formulation description of all the specimens are detailed in Table 1. The preparation onto
8 different substrates was done as part of a previous internal investigation that sought to
9 understand the influence of the substrate on the formation of blends. The study concluded
10 that there is no chemical influence by the substrate.
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19 Ultra-low angle microtomy (ULAM) was employed to expose the interfacial regions
20 “buried” around 20-25 µm below the true top surface of the coating, making it available for
21 subsequent analysis with ToF-SIMS. Specimens of the coatings were cut down by use of an
22 industrial guillotine from the ~20 cm x 10 cm Zn and Al panel to ~1 cm² squares. Following a
23 well-established methodology described by Hinder et al ^{8,9}, the squares were then
24 microtomed at an angle of 2° using the Microme HM355S motorized rotary microtome
25 (Optech Scientific Instruments, Thame, UK) fitted with a tungsten carbide knife. For the
26 current work on these specific coatings, the angle chosen was bigger than the usual so that
27 both the top surface/primer and primer/substrate interfaces could be revealed in a single
28 taper (see Figure 1). The resulting sample is tilted by 2° in the chamber before analysis to
29 ensure the surface is normal to the extraction optics of the time-of-flight mass spectrometer,
30 making it suitable for ToF-SIMS analysis. As mentioned in the Introduction, the two polyester
31 resins that compose the blend yield extremely similar secondary ions spectra, which makes
32 difficult their spatial identification in a ToF-SIMS imaging dataset. Therefore, in order to aid in
33 the spatial differentiation of the two incompatible resins forming the blend, standard pure
34 samples of both polyester resins (in the cured and uncured conditions) were prepared on
35 zinc substrates, following a similar application procedure used for the mixed polyester
36 coating films. The results of such standard samples were then processed by MVA, together
37 with data from the mixed systems, as a single matrix. The use of standard samples to
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achieve relative quantification of ToF-SIMS data through MVA has shown to be effective before^{15,16}.

Figure 1: Schematic of sample preparation using ULAM. Two main interfaces are exposed on the obtained tapers.

Table 1: Details of coatings A to D and standard samples S1 to S4.

COATING	A	B	C	D	S1	S2	S3	S4
POLYESTER 1	50%	50%	50%	50%	100 % (cured)	100 % (uncured)	0 %	0 %
POLYESTER 2	50%	50%	50%	50%	0 %	0 %	100 % (cured)	100 % (uncured)
SUBSTRATE	Al	Zn	Zn	Al	Zn	Zn	Zn	Zn
PIGMENTS	No	No	Yes	Yes	No	No	No	No

ToF-SIMS analyses

ToF-SIMS analyses were carried out on a TOF.SIMS 5 equipment from IONTOF GmbH (Münster, Germany) using a 23 keV Bi_3^+ primary ion beam delivering 0.3 pA in the high current bunched mode with 100 μs cycle time. Positively charged secondary ions were analysed. For the pure standard samples, the beam was rastered over $500 \times 500 \mu\text{m}^2$ regions producing secondary ions images of 128×128 pixels. This is consistent with the spot size of the Bi_3^+ beam in the high-current bunched mode (ca. $3.5 \mu\text{m}$) which is used to achieve high spectral resolution, at a resolution, $m/\Delta m$ on $^{29}\text{Si}^+$ peak, of ca. 8000. The whole area comprising both interfaces was too irregular (both in terms of charging and topography) to be analysed using an automated stage raster. Instead, six patches of $500 \times 500 \mu\text{m}^2$ (128×128 pixels) each were measured with charge compensation optimisation prior to each measurement, resulting in a total analysed area of $1 \times 1.5 \text{ mm}^2$ per sample. Each patch was scanned 50 times so that the total dose per patch was kept under the static limit of 10^{13} ions/ cm^2 . In order to ensure homogeneous charging, all samples were mounted on glass slides and a low energy, 20 eV, electron flood was used to neutralise charge build-up on the sample surface. All datasets were stitched together subsequently as described in next section.

Data analysis

The data analysis consisted of four main steps: peak area picking and exporting; importing data into analysis software; multivariate analysis and production of results.

Peak picking and exporting

The spectra of each standard sample and all large area patches were calibrated using the same calibration points. A peak list containing 669 peaks was then created using the

SurfaceLab software (IONTOF GmbH) from automated peak search routines on the pure spectra of the two polyester resins. Data cubes containing the maps of the areas of all selected peaks were then exported for each 500 x 500 μm^2 scan (see schematic in Figure 2). The export format chosen was the binary .BIF6.

Loading data into analysis software

The BIF6 files were loaded into the *simsMVA* Matlab app (<http://mvatools.com>) using the stitch function which creates a single matrix containing all (stitched) patches and the standard sample images, for all the samples described in Table 1. The first row of Figure 2 shows a schematic with the stitching procedure and the resulting map for the peak at 149 u ($\text{C}_8\text{H}_5\text{O}_3^+$). The dataset with the stitched maps could then be processed as a single matrix, which is a detail of great importance for the spatial differentiation of the two resins as it will be shown in the Results Section. The entire dataset of 24 patches plus 4 standard samples has a total of **393,216 pixels x 669 peaks**.

Figure 2: Schematic of the data stitching procedure followed by multivariate analysis.

Multivariate analysis

Once loaded into *simsMVA*, the images can be further processed. Before the determination of an optimal workflow, several tests were done. The tests involved different ways of data normalisation; different data pre-processing other than Poisson scaling; the use of a variety of NMF algorithms such as multiplicative update rules or alternating least squares; removal the standard samples from the dataset (or only some of them) and playing with different levels of pixel subsampling. The chosen data analysis workflow was:

- I. Prior to any MVA, two pre-processing steps are performed: normalisation of all maps intensities by total counts per pixel and Poisson scaling of the peak intensities.
- II. Selection of a subset of pixels using low discrepancy subsampling as proposed in ¹⁷. The computer used was a *Dell Optiplex 9020* PC with a core i5 processor and 32 GB of RAM. Such amount of memory could easily handle the 393,216 x 669 elements of the dataset but the use of training sets enables the analysis to be done in any conventional PC and it has shown to be effective for multivariate analysis of ToF-SIMS imaging data, in which neighbour pixels are highly correlated ¹⁷⁻¹⁹. Furthermore, with reduced subsets the total processing time is conveniently reduced to a few seconds for the dataset presented in this paper.
- III. Determination of number of NMF components by contrast analysis: NMF is performed several times for the subsampled dataset with varying number of components. For each result, obtained with **k components**, the contrast G_k of matrix **W** was calculated accordingly to the definition by Silva et. al ²⁰:

$$G_k = \frac{1}{k} \sum_{i=1}^k std(w_i)$$

Where w_i are the columns of matrix $\mathbf{W}$, as shown in Figure 2. The highest k that still presents a significant increment in contrast G_k is considered the ideal number of components that contains relevant information of the dataset.

IV. NMF of the subsampled dataset. For the application of NMF to ToF-SIMS images, the subsampled data is unfolded into a Matrix $\mathbf{A}_s$ containing samples (pixels) in rows and variables (spectral channels) in columns. The method then finds an approximate factorisation $\mathbf{A}_s \approx \mathbf{W}_s \mathbf{H}_s$ into non-negative factors $\mathbf{W}_s$ and $\mathbf{H}_s$. $\mathbf{H}_s$ is interpreted as the characteristic spectra of components and $\mathbf{W}_s$ is interpreted as the “concentration” distribution of the components over the samples. The number of components is defined by the inner dimension of the product $\mathbf{W}_s \mathbf{H}_s$. The second and third rows of Figure 2 show a schematic of the dataset unfolding and factorisation.

V. Calculation of the full matrix $\mathbf{W}$ using the original unfolded dataset $\mathbf{A}$ and the pseudo inverse of matrix $\mathbf{H}_s$: $\mathbf{W} = \mathbf{A} * \mathbf{H}_s / (\mathbf{H}_s^T * \mathbf{H}_s)$.

For the dataset presented in this paper, a subset of 10 % of the total number of pixels was used for all calculations and NMF was achieved using a multiplicative update rule-based algorithm that minimises the Kullback-Leibler divergence^{21,22}.

Results

The contrast analysis results for up to 20 NMF components are present in Figure 3. It shows that contrast stops increasing after 6 components, which means that the addition of extra components are either incorporating noise or overfitting the data. Therefore, 6 components

were chosen and Figures 4 and 5 present the final NMF results of the stitched dataset. Optimal factorisation was achieved after 500 iterations.

Figure 3: Contrast analysis for NMF results of the stitched dataset.

Figure 4: NMF results. First row: identification of tapers accordingly to Table 1 and reconstruction error. Second and third row: Intensity maps of components 1 to 6.

The map on the top of Figure 4 presents the distribution of the approximation error (total counts of the matrix subtraction $\mathbf{A} - \mathbf{WH}$). The other maps are the folded intensities of each component (columns of matrix $\mathbf{W}$). The image on the left-hand side of Figure 5 is an overlay of the intensities of all components (matrix $\mathbf{W}$) with one colour attributed to each component. The labels A-D and S₁-S₄ correspond to the different samples as described in Figure 2 and Table 1. The intensity a component determines the opacity of its colour across the pixels. The plots on the right-hand side of Figure 5 are the characteristic spectra of each component (matrix $\mathbf{H}$). The results demonstrate the ability of NMF analysis in the identification and visualisation of the interfacial layers across the bulk surfaces of both the pigmented and the un-pigmented coating specimens under comparison. In the overlay maps it is possible to observe that component 1 (in red) is very intense at the cured top surface of the coatings across the samples set. This is consistent with the images representative of the cured standard surfaces S₁ and S₃. The spatial distributions shown by the intensity maps of components 3 and 6 (green and pink, respectively) discriminates the immiscible polyester resins 1 and 2 across the bulk of all four coating specimens. They are also identified accordingly at the uncured standard surfaces S₂ and S₄. This enables prompt phase identification and also brings insights into the interfacial chemistry across the bulk. Component 2 (in yellow) is attributed to inorganic ions mostly formed from pigments dispersed in the resin layers of coatings C and D, where it can be seen that the pigmentation seems to have agglomerated at the interfacial region between polyesters 1 and 2. The presence of component 2 in some regions of the top surface of all samples is attributed to sodium and potassium contamination. Component 4 corresponds to the Al substrates of coatings A & D. Component 5 corresponds to the Zn substrates of Coatings B and C.

Figure 5: Phase identification and morphology characterisation using NMF analysis. The image on the left-hand side is an overlay of all components (matrix **W**) with one colour attributed to each component. The intensity of each component determines the opacity of its colour across the pixels. The plots on the right-hand side are the characteristic spectra of each component (matrix **H**).

Discussion

Effect of curing

In the NMF results, the surface of the cured reference samples matches the top surface of all coatings while the uncured standard samples are the ones that enable differentiation of the two polyesters across the layers within the ULAM tapers. A straightforward conclusion for this would be that the cross-linked polyesters become indistinguishable by ToF-SIMS and the layers buried underneath it are not completely cured hence why they show similarities to the uncured standard samples. However, one cannot discard the possibility of something else being on top of all surfaces that undergo curing (oven contamination, surface segregation of minor components, etc...). ToF-SIMS is highly surface sensitive and in this case all that is being measured at the top surfaces is whatever is covering them, leaving only the uncured standard samples with distinguishable features. One way to find out whether this is only a surface effect of cured resins is to cut the top surface of the standard samples and investigate their bulk with ToF-SIMS, which is planned as future work. Another approach that can be taken is the acquisition of dual-beam ToF-SIMS depth profiles of the standard samples. However, the results presented in this paper show that, for the coatings, the “top surface” regions are of some 250 μm thick, which may make depth profiling inviable.

Immiscibility of polyesters

It is clearly shown in the results that the two immiscible polyester resins are well separated across the bulk of the four specimens and the multivariate analysis enabled the identification of interfacial phases without prior knowledge of the system. Two different morphologies were identified and differentiated by NMF analysis across the bulk of the un-pigmented coating specimens (*A* and *B*). In both coatings *A* and *B*, polyester 2 is concentrated at the top coat interface. However, coating *B* presents discrete globular structures throughout the bulk towards the Zn interface, while in coating *A* polyester 2 forms a less concentrated, irregular web-like shape. The pigmented coatings (*C* and *D*) presented similar behaviour but polyester 2 is now concentrated at both interfaces, with smaller globules formed across the bulk. There are two factors that may have influenced those observed differences, the first

being the presence of pigments that seem to follow the distribution of polyester 2 (even around the globules). The second possible factor is the curing process: regardless of the pigments, the phase distribution of polyesters 1 and 2 seems to represent “snapshots” of different stages of their separation (or mixing), with coating A showing an initial stage where both resins are still disputing space and coating D showing a final layers structure. This may mean that the curing process needs more control if a more reproducible manufacture procedure is desired. In addition it is clear that the substrate type (aluminium or hot dipped galvanised steel - HDGS) has a secondary role to play in the phase separation of the polyester blend. Comparing the unpigmented blends (A and B of Figures 4 and 5) it is clear that the extent of phase separation is not the same, the dispersed phase (polyester 2) having a significantly large size in the case of the HDGS substrate. Turning now to the pigmented system a similar occurrence is revealed, in this case of the HDGS substrate a fine dispersion of polyester 2 is evident in the middle (polyester 1) layer in addition to the two adjacent layers of polyester 2 either side of the inner layer. In the case of the aluminium substrate only the three layer “sandwich” structure is observed with little, if any, phase separation of polyester 2 in the well define layer of polyester 1. The reason for this is unclear but it is thought to be unlikely the specific interaction between substrate and resin, which would occur over very short distances. More likely is that the difference in thermal mass of the two substrates is responsible. Zinc and low carbon steel have values of thermal conductivity significantly below that of aluminium (about one half and one quarter respectively) thus the coatings deposited on aluminium benefit from a higher input of thermal energy to aid phase segregation thus the fine phase distribution on these substrates is better developed than the coarser distributions on the HDGS substrate. As phase separation develops so, eventually, a three-layer structure develops. A full investigation of the chemistry involved in these processes and the influence of pigmentation is intended to be discussed in a future paper.

Further applications of the methodology

The methodology can be applied to any set of measurements that may benefit from the simultaneous processing of all datasets and the addition of standard samples. In fact, an ongoing piece of research seeks to use the very same approach in order to achieve relative quantification of pure materials in a series of large area ToF-SIMS measurements of lithium-based corrosion protective coating ¹⁶.

Another application was on a project for the understanding of the interface between polyurethanes coatings and steel substrates, where the “stitching” approach was taken in order to analyse, as a single matrix, data from depth profiles of a coating obtained with two different etching beams: C_{60}^{+} and Ar_{1200}^{+} ²³. One promising application that is on its early stages is part of a project that seeks to detect metabolized drugs on fingerprints using imaging mass spectrometry ²⁴. Several large area maps of fingerprints were acquired and initial tests were done using the maps stitching approach with the addition of measurements of reference drugs.

Conclusion & Future work

The proposed methodology successfully identified the spatial distribution of two very similar polyester resins across tapers of 4 different coatings. Some secondary ion peaks will show higher or lower intensity for one of the polyesters but still all characteristic peaks are present in the standard spectra of each resin. For this reason, it is very difficult to obtain single ion differentiation of the two polyesters and an approach that takes into account the multivariate aspect of the data is much more effective. As future work it is intended to investigate the effects of pigmentation and the details of the chemistry that happens along the coatings production, especially the cross-linking process.

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Graphical abstract:

For table of contents only.

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