Supplementary Information

Identifying and mapping chemical bonding within Phenolic Resin using Secondary Electron Hyperspectral Imaging.

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1. Additional background

1.A - Background of the interpretation of Secondary electrons

The primary electron beam interacts with atoms within the material by causing electrons to be emitted. These emissions are as a result of a range of physical interactions (2). Figure SI1 shows the interaction volume of a primary electron beam and a range of association emission.

Elastic interactions are those which change the path of the incident electrons in the primary electron beam probe whilst having a negligible effect on their kinetic energy. Inelastic interactions in contrast are those which result in a loss of kinetic energy of the incident electrons (3). High energy electrons that are emitted by an elastic interaction of an incident electron, with the nucleus of the material samples' atoms, are designated as back scattered electrons (BSE). The energy of BSEs is comparable to that of the beam probe's incident electrons. Electrons emitted from the sample at lower energy are categorised as SE. SEs typically display energy voltage of less than 50 eV. Secondary electrons (SE) result from inelastic scattering and are the consequence of either collisions within the electron cloud or by interaction with loosely bound electrons in the material's structure.

The electron beam probe will only interact within a finite interaction volume due to the effect of inelastic interactions. This volume is depended on the primary beam energy. The greater the primary beam energy is the greater volume of sample interaction. This incident beam interaction volume is repersented in figure SI1 with a characteristic 'waterdrop' shape.

SEs are the sample emissions that are associated with SEM images (4). SEs may be emitted from the materials at relatively low kinetic energies, < 10 eV, as a result of potential interaction with electron clouds. The low kinetic energy places a significant limit on the actual escape depth of SEs emitted from a sample, which can often be <10 nm, as a consequence SE derived images are inherently surface specific. To interpret the images generated by an SEM it is essential to understand how the SE contrast is captured. Selection of an appropriate detector by the user is also dependent on this knowledge.



Figure SI 1 – Diagram shows the relative escape depths of SEs and BSEs and their interaction paths prior to detection. Image adapted from (5) with permission from Elsevier. "Schematic of the electrons emitted from a range, R, below the surface of the sample. SE1 is generated from impacted electrons (IE) right after incidence, SE1 have spatially localised information (s1). Then, IE spread to interaction volume with a size of range R."

There are a number of different ways that SEs are detected in an SEM (See SI 1), the majority of SEs detected originate as a result of inelastic interactions between the probe incident electrons and the sample (4), in addition to collisions between BSEs and the SEM chamber components after emission from the target sample surface. (This process is depicted in figure SI 1) These different sources of SEs are termed *SE1*, *SE2* and *SE3* retrospectively. SEs from each of these difference sources exhibit dissimilar signals types for both resolution and contrast. When undertaking SEM analysis of a polymer's topographical nanostructure, it is essential to configure the apparatus with a detector which can isolate *SE1* from *SE2* and *SE3*. Despite both *SE1* and *SE2* emissions providing topographical contrast due to their angular distribution and their short escape depth (as shown in Fig2). *SE1* emission differs from that of *SE2* as a result of their interaction paths, *SE2s* emissions are generated from BSEs when they pass through the surface, when exiting the sample, unlike *SE1* which are generated

from impacted electrons directly after beam incidence. *SE1* emissions are therefore possess spatially localised information and are suitable for processing into high resolution surface images.



Figure SI 2 –Diagram showing the topographic effect on SEM contrast of *SE1* and *SE2* emissions. Figure amended from "Yougui Liao, Practical Electron Microscopy and Database, (2006), www.globalsino.com/EM/"

1. B- Electron Detectors within an SEM.

Both SE and BSE emissions can each be exploited to extract complementary sets of information from a target sample within an SEM. Modern SEMs are configured to utilise detectors which have the ability to distinguish between these two types of emissions and are capable of filtering either SEs or BSEs from an intermixed sample image signal. As previously highlighted the ability to research surface effects in polymers at the nanoscale level relies primarily on the capture of target images built from *SE1s* emissions. The most common detector used in SE imaging is the Everhart-Thornley detector (ETD). ETDs mix *SE1, SE2* and *SE3* emissions, this provides limited resolution with SE images being hard to interpret in respect to their specific SE emissions. Alternatively, the other commonly used SE detector is the Through-lens detector (TLD). The TLD supresses SE2 and S3 to collect mainly SE1 emission (6). By virtue of collecting *SE1* emissions the TLD can

provide high resolution surface images, suited perfectly for the use of chemically mapping the nanoscale surface of polymers. The TLD used for this study is depicted in figure SI 3. This TLD step up utilises electrostatic deflectors to enable the detection of SEs when set to a high-resolution immersion mode where target samples are immersed in a magnetic field and the TLD is positioned above the objective lens of the electron column (8).



Figure SI 3. Schematics of TLD arrangements in SEMs manufactured by FEI Co. XL-30 design TLD. Adapted from (8) with permission from Elsevier.

Configuration of TLD detectors varies according to both manufactures and actual SEM models. Figure SI 3 illustrates a FEI XL-30 design which is a widely used SEM having a TLD integrated into the incident electron probe consisting of a scintillator detector and a 'deflector' electrode (8). The deflector is installed as a guide to drive SEs towards the detector and is set to a bias of -60V. This bias can be adjusted to collect *SE1* emissions from energy ranges of interest. Additionally, the SEM's pole-piece incorporates a positively biased electrode whose purpose is to help attract SEs within the specimen chamber towards the detector. TLDs predominantly detect *SE1s* which provide the highest spatial resolution information as they are emitted by the target sample through direct interaction with the primary electron beam.

<u>1.C – Information contained in secondary electron spectroscopy (SES)</u>

Electrons emitted from a target sample through probe electron/material interactions within the SES can be detected and displayed by way of spectra constructed according to their measured energy ranges. From the resultant spectra, conclusions can be drawn regarding the samples chemical composition and structure. SES is not a recent development for material characterisation, SES has been investigated since 1947 (9). Over the last few decades, SES has only recently started to flourish through innovations in instrumentation, signal processing and imaging proficiency (10,11,12,13).

The process of developing SE spectra wholly relies on the probe electron – material interactions. SES measures electron emission energies post inelastic sample collisions. SES benefits from employing a low KeV (between 0.5-2 keV) primary electron beam which makes it possible for the SES to collect the spectra of beam sensitive materials. Although, SEs are produced throughout the primary beam interaction depth, only SEs emitted within the SE escape depth can be detected, as SEs emitted at a greater depth will be absorbed by the bulk of the sample material. The SE shallow escape depth raises the issue of surface contamination affecting the spectra results, a problem faced by other surface analysis techniques. However, SES has been shown to have operational characteristics that allow it to overcome substantial surface contamination to produce accurate spectra that are reproducible and reveal characteristics of the underlying material (10, 13). In contrast EELS provides an average measurement over the material samples thickness and does not allow for high resolution surface characterisation. For polymers which require a tailored surface, such as polymer derived biomaterials, the SES form of detailed surface analysis is considered to be an essential perspective due to the fact that established cells react to a biomaterial's surface on the nanoscale level.

Although, SES, EELS and XPS all have strengths as material characterisation methods, the singular ability of SES to support the secondary electron hyperspectral imaging (SEHI) technique is considered particularly advantageous for the analysis of a range of material types. As distinctive SE energy spectra have been collected for many decades (9,12,13) it is often wrongly assumed that SE images show only topographical contrast. However, with recent progress in SE spectra analysis and energy-filtering detection, advances in capability now enable the capture of spectral images from selected distinct SE energy ranges, which studies have shown to carry chemical and functional information [11, 14, 19]. Both SE and BSE emitted at low primary beam energy ranges contain chemical information. Lower energy SEs contains information about valence bands and higher energy SEs (*SE2*) have been associated to the atomic number of the elements from which they are emitted (13). BSE imaging has demonstrated a capacity to provide chemical contrast images of materials where topographical features are negligible however, SEHI can provide comparable images of materials at significantly enhanced image resolutions (14). Standard SEM images are compiled from all surface emitted SEs without discrimination of their energy ranges. In contrast, SEHI compiles a series of images based on the specific energy ranges of emitted SEs. SEHI software processes this captured series of energy range images to construct an inclusive SE spectrum for the material.

Figure SI 12 (graphical abstract) displays the process by which information contained in the SEHI spectrum provides the basis for mapping chemical changes within the surface of materials. This capability is predicted to provide new opportunities for researchers to characterise novel polymer materials. The value of the SEHI characterisation technique has successfully been demonstrated in range of applications, varying between the analysis of molecular orientation within organic electronic devices, semi-crystalline polymers chemical mapping and exposing variations in nanostructures that form natural materials (11, 15). SEHI can be summarised as a technique that is responsive to surfaces and is capable on beam sensitive materials of resolving chemical, compositional and structural differences at the nanoscale level. It is proposed that an effective microanalysis tool for nanostructured polymers, results from the integration of the capabilities of a low voltage SEM and those of secondary electron microscopy.

1.D - Modelling secondary electron spectroscopy (SES)

SE emissions captured in electron microscopes has been the subject of an increasing number of studies, using a modelling approach that simulates the production of secondary electron emission from sample materials. Many of these studies have adopted the Monte Carlo approach to simulation modelling. Within a Monte Carlo simulation a statistical probability is assigned to every event, with the probability figure based on first principles and available experimental results. Multiple events are simulated until the process yields a statistically relevant result. Monte Carlo simulation, based on a conductive polymer using experimental data, has revealed that a material's local crystallinity and electron affinity directly influence the SE energy spectrum (16,17).

In addition to polymer analysis, further insightful work has been directed at carbon species analysis. The characteristic SE spectra of sp3 hybridised, sp2 hybridised, or hydrocarbon contamination moieties captured using a combination of experimental studies and Monte Carlo based simulation has been published (18, 19). This result has enabled carbon based contamination and deposition induced by the electron beam within a SEM to be identified and mitigated. Through applied modelling simulations, significant advances in the appreciation of time dependence both in secondary electron emission (20) and in the charge dynamics of insulators (21) have been made.

2. Additional Results

2. A - Selecting the Region of Interest (ROI) for Phenolic Resin.

Figure SI 4 shows an example of the process used to select ROIs of phenolic resin samples for SES and SEHI analysis. After having been subject to flexural testing, spectra were collected from the centre of a cross-section area of P382 resin exposed as result of flexural testing (figure SI4 A). The red boxes within the figure show how by increasing the magnification the user can select the length scale of sample area they wish to analyse. The ability to perform multi-length scale analysis is one of the key advantages of using SES and SEHI. The material system is described in detail in Hamad et al (1).

Figure SI 4 – A diagram showing the process of selecting a ROI within Phenolic resin prior to SES and SEHI analysis. Red boxed inserts show the process of enhancing magnification to allow the user to analyse a length scale of interest.

2.B - Secondary electron spectroscopy (SES) analysis of long cure phenolic resin.

Previous work has validated SES's ability to isolate chemical bonding and functional groups in a range of materials (22). However, this is the first time such analysis has been conducted on phenolic resin. To corroborate the SES results described in the main manuscript an additional phenolic sample was included as a control sample. This control is a phenolic resin sample produced by the application of a long cure cycle, with the same F:P molar ratio as that of the Phenolic 382 used in this publication. The only difference between the two materials is that the control sample's long cure cycle does not employ a fast acting acid catalyst and consequently cures over a longer period of time and produces a void free material.

A comparison between phenolic 382 and a long cured phenolic resin (LCP) has previously been conducted in Hamad et al 2019 (1) study, there it was concluded that although a P832 cure time was substantially shorter than LCP, its flexural strength properties were significantly reduced, 88 MPa and 47 MPa respectively (1). Fourier Transform Infrared Spectroscopy (FTIR) measurements captured in this study showed that there was a reduction in ether bridges formation within phenolic resin cured using a fast action catalyst when compared to that of phenolic resin cured without such an acid catalyst. The paper stated that the more acidic the catalyst, the more the phenol is protonated and therefore the less nucleophilic it is (1). As a result, it is less likely that it will follow the crosslinking mechanism which forms ether bridges. Figure SI 5 displays a spectra comparison of the LCP control sample and the three areas of P382. Here, we observe the results are consistent with those given in the Hamad et al publication. The LCP control sample shows a greater molecular order peak emission (1.4 - 2.3 eV) and increased CH vibrations emissions (2.3 - 4.3 eV) compared to that of the PR832 sample areas. This result is expected as both an increase in crystallinity and methylene bridges (CHx related) in the LCP sample would indeed create a material with greater flexural strength. A point of interest in the SES data is that the LCP does show more emissions are related to methylene bridge (CH) than ether bridge (CO) formation. This finding is predicted by the chemical crosslinking analysis described above and supports the proposition that an increasing ratio of acid catalyst inclusion would favour methylene bridge formation. When comparing CO functional group emission between LCP and areas of PR382 it is also noticeable that CO bonding is slightly less in LCP. This is also an expected result as even though ether bridges are still present in LCP they are not the anticipated prevailing method of crosslinking within this material.

Figure SI 5 - Secondary electron spectra with accompanying SEM images for LCP (long cure) and PR382 Area 1, 2 and 3 highlighting SE regions identified as associated with functional group emissions. Area 1 & 2 HFW = 30 μ m whereas Area 3 HFW = 25 μ m.

2.C - Secondary electron spectroscopy (SES) energy calibration.

Prior to SE spectra capture it is good practise is to collect test spectra from known sample materials for the purpose of energy range calibration and assessment of the SEM environment conditions for SE collection. By virtue of SES high surface sensitivity it has been shown that surface contamination, often in the form of amorphous carbon, can produce emissions that are captured by SES and distort the resulting target materials spectra. The amorphous carbon can be present within the chamber of the SEM as a consequence of previous use prior to imaging or it can form on the surface of a test material as a product of the e-beam probe. Essential requirements for a control sample are to calibrate the SE energy ranges and also to have the ability through their SE spectra to highlight contamination indicators. For these purposes the authors recommend the use of highly oriented pyrolytic graphite (HOPG) as the energy calibration sample of choice. HOPG is a molecular ordered form of synthetic graphite (23). HOPG offers a calibration spectra, for collection accuracy, by observing background emission

peaks within a materials spectrum. Figure SI 6 gives an example of this calibration process by comparing the spectra of PR382 to that of the calibration HOPG material. With SEHI being shown to be effective in monitoring beam damage (19) the technique can therefore be utilised to avoid beam damage through an appropriate choice of frame integration and short dwell times. This study also evaluated SES's ability to characterise contributions of sp2-like or sp3-like bond types and amorphous hydrogenated carbon on HOPG surfaces (20). In such circumstances, we use HOPG to avoid contamination by regularly plasma cleaning the chamber and then monitoring sp2 amorphous carbon build up within the HOPG spectra after prolonged exposure (19).

Figure SI 6 - Secondary electron spectra with accompanying SEM images for PR382 and HOPG. Spectra emission normalised to MW peak SE emission range. Spectra highlights SE regions associated with functional group emissions.

2. D - Observing the drying process of Carbon paint using SES.

In this investigation a dynamic experimental approach was designed to demonstrate the capabilities of SES to identify functional group changes over time within a material whilst within an SEM. The material selected for this experiment was a Carbon paint known as "Conductive graphite paint with isopropanol base" (Agar Scientific). Carbon paint is commonly used to attach a material of interest to an aluminium stub prior to SEM imaging. After the material of interest is positioned on the stub, Carbon paint is applied and the user waits for it to dry/set to bind the material to the stub. As the Carbon paint dries, the paint's isopropanol base evaporates. In this study, carbon paint alone was applied to an aluminium stub and spectra were collected at regular time points as the carbon paint dried. The purpose behind the experiment was twofold; firstly, to analyse how long it takes for the paint to dry, which is useful information to SEM users in general, and secondarily as the paint dries and the isopropanol evaporates off the surface, to monitor the prevalence of functional groups (CO, OH and CH) which are predicted to gradually decrease over time as a consequence. Figure SI 7 displays SES spectra captured during this experiment which corroborate the experimental results with the predicted results. OH and CO functional groups were observed to greatly diminish as the carbon paint dried by the evaporation of isopropanol. After 30 minutes from commencement of the experiment the dried carbon paint, now purely graphite flakes, as expected provided spectra that was markedly similar to that of the HOPG spectra shown in figure SI 6.

Figure SI 7 - Secondary electron for Graphite flakes in an Isopropanol base taken at different time points. Spectra emission was normalised to MW peak SE emission range. Spectra highlights SE regions associated with functional group emissions.

2. E - CH / CO / OH Mapping of Phenolic Void remnants.

Figure SI 8 displays component analysis of PR382. In this instance non-negative matrix factorisation (nnmf) isolated three major components between 2 – 6 eV; firstly a component around 3.2 eV, highlighted in the text as CH vibrations, a second component peak at 4.5 eV related to CO bonding and lastly a component peak around 5.5 eV related to OH groups. The images displayed in figure SI1 reflect the spatial variation in components 1, 2 and 3 in response to void like macrostructures. These images provide further support for the view that CO bonding is apparent with greater emission. within the void sites than when compared to either CH or OH.

Figure SI 8 - Non negative matrix factorisation (nnmf) multivariate analysis of PR382. Isolating three components: component 1 is associated with CH Vibrations, component 2 is associated with CO bonding and component 3 is associated with OH groups. Each spectrum includes an inset of the resulting void images from nnmf component analysis (HFW = 3 µm).

2. F - Nanoindentation

Figure SI 9 shows the measured modulus obtained through nanoindentation mapping with a KLA Tencor NanoG200. Using a diamond Berkovich tip at a load of 0.02 mN, corresponding to an average depth of approximately 150 nm, the map was collected with an indent spacing of 0.9 µm. Care must be taken when considering the values reported: the absolute values have been calculated through a proprietary method which has been shown to produce variable data. Furthermore, this dataset is collected with a relatively low load, owing to the requirement to space the indents in close proximity to one another. The capacity of the mapping method to accurately collect data at such loads has not been tested. Finally, the specimen is known to contain scratches throughout the surface. Considering these caveats, the data can be used speculatively to compare the relative modulus from pixel to pixel. In this respect, the variability shown arises from a combination of surface effects and fundamental material behavioural change from the presence of ether bridges.

Figure SI 9 – Nanoindentation mapping of Phenolic Resin P382. Nanoindentation modulus measured through nanoindentation mapping with a KLA Tencor NanoG200. Using a diamond Berkovich tip at a load of 0.02 mN, corresponding to an average depth of approximately 150 nm, the map was collected with an indent spacing of 0.9 μm.

3. More detailed methodology background

3.A Selection of suitable component analysis method

An example data set that analysed phenolic resin was used to highlight the selection of the component analysis methodology. In this instance a 5 component analysis was selected for review. Component Analysis is used to determine the spectrum distribution of components in the material. In Fig SI 10, the spectrum plot of five (5) components is shown. Two methods are utilised to compare their performances in the component analysis. Firstly, the Principal Component Analysis (PCA) that aims to reduce the dimensionality of the data (stack of hyperspectral SEHI image) in an interpretable (components) way. It achieves this by preserving the information of the data within the components and clustering positive and negative correlated components together. PCA assumes that the components are a linear combination of features and therefore, concentrates these features within the first component of the data as shown in Fig SI 11. Additionally, we notice large variance axes in the first component, while areas of low variance axes are treated as noise with little information in subsequent components especially in components 3 and 4. The orthogonality assumption of PCA implies that spectrum is only concentrated in the first component of the analysis. On the other hand, the Non-Negative Matrix Factorization (NNMF) method preserves the spatial information of extracted components that corresponds to the structural differences in the components, hence retaining the global structure of the material. It achieves this by allowing only additive (positive) correlated combinations this enables an intuitive representation of the data since each component form a part of the data (see Fig SI10).

Figure - SI 10 FIVE COMPONENT ANALYSIS USING THE NON-NEGATIVE FACTORIZATION METHOD

Figure SI 11 - FIVE COMPONENT ANALYSIS USING THE PRINCIPAL COMPONENTS ANALYSIS METHOD

The above analysis shows that the NNMF performs better when dealing with SEHI image stacks due to its ability to efficiently extract features that are only positively correlated which ensures that both spatial and structural information are retained. Additionally, this non-negativity nature of NNMF improves result interpretation and precision.

4. Graphical Abstract

Figure SI S12 displays the graphical abstract for this publication.

"Secondary Electron Hyperspectral Imaging (SEHI) is an innovative SEM-based analysis tool allowing spatially-resolved chemical analysis beyond elemental composition."

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