Raman microprobe analysis and ageing in dielectrics

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Abstract. Subsurface voids in samples of electrically stressed low density polyethylene (LDPE) were analysed using confocal Raman microprobe spectroscopy (CRMS). An optical depth profiling technique was used to probe a void along the optic axis whilst a burst void was analysed at various lateral positions. Spectra from the voided samples showed signatures with similar features to those found in previous studies of electrical trees in polyethylene, including the presence of the D and G bands of disordered sp² carbon. Results and spectra were then compared to the depth profiles and spectra from block and thin film samples of polyethylene and polystyrene which indicated that the established theory behind CRMS is oversimplified and that the detected signal is largely influenced by the optical properties of the material in question. Overall the study showed that despite some spatial resolution limitations of the technique, depth profiling is a useful tool in the analysis of aged polymers and dielectrics as it can show the variations in chemical composition with respect to position along the lateral and optic axis, a property especially relevant to electrical trees.

1. Introduction
The topic of ageing in dielectric materials has attracted much research and study [1] due to its applications in high voltage insulation. The process of ageing occurs when the material is exposed to intense electric fields. These ageing processes span from the quantum level to complete macroscopic failure. Defects within a material are formed and evolve through partial discharge (PD) activity to form electrical tree like structures.

In recent studies [2, 3] confocal Raman microprobe spectroscopy (CRMS) has begun to reveal the chemical processes involved in electrical treeing and ageing in dielectric materials. This technique is thought to have the potential to provide spectroscopic data with a spatial resolution of the order of ~1 µm along both the lateral and optic axes [4] and, since excitation involves visible photons, the technique is also capable of interrogating the interior of transparent dielectrics, for example polyethylene and polystyrene.

Raman studies of electrical trees in polymers have, however, cast doubt upon these assertions [3] and, if the potential of this approach is to be realised, the true spatial origin of the detected Raman photons must be determined. This paper describes a new approach to this problem and combines optical depth profiling with studies of Raman excitation in a range of materials and sample geometries, including a chemical analysis within voids that have experienced PD activity.

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2. Materials and Methods

Two samples of low density polyethylene (LDPE) (~700 µm thick) were prepared by heating and pressing a blend of PE and the blowing agent azodicarbonamide into a mould. Heating the samples causes the blowing agent to decompose, hence leaving voids within the sample. One of the samples (Sample 1) has experienced partial discharge within it but has not broken down, leaving a number of closed subsurface voids. In the second sample (Sample 2) of LDPE extensive partial discharges within the material induced a breakdown, causing a void to burst. For comparison to the LDPE samples, block samples (~5 mm) were made of polyethylene (PE) and polystyrene (PS) by heating and compressing a mould of the sample. Thin films (~70 µm) of PS were also prepared in the same way.

Samples were analysed using a Renishaw Raman RM1000 microscope using a Renishaw NIR 780TF CW diode laser, wavelength 785 nm and output power of 25 mW, and a x50 objective lens. The spectrometer was set up in confocal mode, with a slit width of 15 µm and a CCD area of 5 pixels (image height) x 574 pixels (spectrometer range), which acts as a virtual confocal pinhole. All spectra of the LDPE samples consist of extended scans between 3500 cm\(^{-1}\) and 100 cm\(^{-1}\) and were built up of 25 accumulations of 10 s each. In order to minimise sample damage, all spectra were obtained with the laser power set to 25%. The spectra obtained from the PE and PS samples used for comparison were taken over a smaller static range around the main peaks and built up of 10 accumulations of 10s.

3. Results

Initially reference spectra were obtained from the focal surface of the block samples of PE and PS and the main peaks in the spectra identified. The magnitude of these peaks was then recorded as a function of vertical stage position (relative to the focal surface of the sample) hence producing depth profiles of the samples in question. This technique of ‘optical sectioning’ [5] was also applied to the thin film sample of PS and the depth profiles in figures 1 and 2 were obtained. From these depth profiles in figure 1, we can see that for the samples tested the Raman signal extends both above and below the sample surface. Also once a maximum intensity has been reached the signal declines at varying rates. The signal decline for PE is much steeper than for PS, an effect associated with the optical clarity of each material as this decline is caused by scattering effects within the sample. For the PS film in figure 2, the signal drops off very rapidly due to the lower surface of the sample. The width of the depth profile for the film is however close to half the physical thickness of the sample, which, as Everall discussed in 2000 [6], is due to refraction effects at the upper surface. It is apparent however from figure 2 that it is possible to use CRMS in the analysis of thin films and, hence, the technique can be extended to layered samples, voids and electrical trees in polymeric dielectrics.

![Figure 1. Raman depth profiles of block samples of PE (○) and PS (●)](image)

![Figure 2. Raman depth profiles of a thin film sample of PS](image)
A void in Sample 1 was probed and analysed using the same optical sectioning technique mentioned above. Spectra shown in figure 3 were gathered at various stage positions ranging from the focal point being at the sample surface to it being deep inside the void. From figure 3 we can see that, at the surface of the sample and for ~100 µm below the surface, the spectrum for PE is obtained. Below this point there is no PE present in the spectra, indicating the presence of a void. Beneath the surface of the sample there is a rise in the spectra at the lower wave numbers. This rise is associated with fluorescence effects and, although chemical data cannot be extracted from this it, indicates ageing [7]. As predicted in figure 1, the signal for PE is slightly greater beneath the surface at a stage height of -65 µm than at the sample surface. It is worth pointing out that there is an additional feature present in all of the spectra at about 550 cm\(^{-1}\), which is not present in scans of pure PE but seems to be present throughout the sample including inside the void. Only by further chemical analysis will the exact nature and origin of this feature be determined.

Figure 4 shows the spectra gained by focusing on the surface of Sample 2 at various lateral positions (indicated on figure 5) of a failed void instead of depth profiling a complete void. From this data we can see that region A gives a typical PE spectrum as the laser is focused in a region of undamaged PE. Region B is in the centre of the burst void where there was no sample and so the spectra gained from this region shows nothing other than vestigial PE, peaks associated with material remote from the focal point. In the spectra at low wave numbers, gained from the edge of the void (region C) a PE signal is recognisable but with an increase in background signal as with the spectra in figure 3. Again we take this to indicate fluorescence and hence ageing. Finally in region D, which corresponds to the discoloured region at the edge of the burst void, a large amount of fluorescence and the D and G bands of carbon are present indicating the presence of sp\(^2\) bonded carbon [3]. The signature for region D is characteristic of electrical trees grown in PE. (Note all spectra have been offset from each other by equal amounts along the y axis in order to improve clarity).

**Figure 3.** Raman spectra at various stage positions for void in sample 1

**Figure 4.** Raman spectra for various lateral positions on failed void in sample 2
4. Discussion

CRMS is an adaptation of established confocal imaging theory which claims that all light from out of focus planes from a transparent/translucent material is excluded from the final image by using a small aperture or ‘pin hole’ at the back focal plane of the objective lens. This means that when focused above a sample no data should be attainable and, if the sample is uniform, the data gathered from below the surface should also be uniform. In contrast to this our data shows that it is possible to get a Raman signal when focused above the sample and, with increasing focal depth, the signal attenuates at a rate associated with the clarity of the sample. The results show that detected Raman photons do not come from the focal point alone and that the detected signal is influenced by the optical properties of the sample in question, thus making the exact spatial resolution difficult to determine. Despite these limitations with respect to spatial resolution, depth profiling nevertheless can provide data that demonstrated variations in chemical composition with position in a subsurface void. Potential approaches for improving the spatial resolution CRMS could include the application of beam scattering theory to in confocal geometries which would enable a more complete understanding of the effects of refraction and diffraction on the system. Once the spatial resolution of CRMS can be properly determined, the full potential of its application in the study of subsurface featured in dielectrics can be realized.

Finally, previous Raman studies of electrical trees in PE have yielded the 3 following signatures [2, 3, 8]; pure PE in the regions in-between tree branches, fluorescence in the regions close to the tree channels and the D and G bands of disordered sp² carbon in the centre of mature, conducting tree channels. As can be seen from the results presented above, the same three spectral signatures as those found in electrical trees were obtained by a lateral examination of voided samples that have experienced partial discharge activity.

5. Conclusions

In brief, samples of LDPE containing sub surface voids have been examined using CRMS using a depth profiling technique. These results were compared to depth profiles of block and film samples of PE and PS and it was found that the concept of confocal microscopy is not as simple as generally thought and is subjected to inaccuracies in spatial resolution as the Raman photons which contribute to the detected signal emanate from both above and below the focal surface. CRMS has provided
data which demonstrates variations in chemical composition with position within voids and revealed that, within a void which has experienced a partial discharge activity, the same signatures as those found in electrical trees are seen. Therefore, despite its limitations, CRMS is a useful tool in the determination of chemical variations beneath the surface of a sample and would be an effective tool in the analysis of ageing and breakdown in dielectric materials.

6. References
1. L. A. Dissado, J.C.F., *Electrical Degradation and Breakdown in Polymers*, ed. G.C. Stevens. 1992, London, UK: Peter Perigrinus.
2. Vaughan, A.S., et al., *On the structure and chemistry of electrical trees in polyethylene*. Journal of Physics D-Applied Physics, 2006. 39(5): p. 962-978.
3. Vaughan, A.S., S.J. Dodd, and S.J. Sutton, *A Raman microprobe study of electrical treeing in polyethylene*. Journal of Materials Science, 2004. 39(1): p. 181-191.
4. Tabaksblat, R., R.J. Meier, and B.J. Kip, *CONFOCAL RAMAN MICROSCOPY - THEORY AND APPLICATION TO THIN POLYMER SAMPLES*. Applied Spectroscopy, 1992. 46(1): p. 60-68.
5. Everall, N.J., *Modeling and measuring the effect of refraction on the depth resolution of confocal Raman microscopy*. Applied Spectroscopy, 2000. 54(6): p. 773-782.
6. Everall, N.J., *Confocal Raman microscopy: Why the depth resolution and spatial accuracy can be much worse than you think*. Applied Spectroscopy, 2000. 54(10): p. 1515-1520.
7. Sayers, P.W., et al. *Investigation of the structural changes in LDPE and XLPE induced by high electrical stress*. in Eighth International Conference on Dielectric Materials, Measurements and Applications. 2000. Edinburgh, UK: Iee.
8. Liu, X.S., A.S. Vaughan, and G. Chen, *A Raman spectroscopic study of bulk and surface ageing phenomena in polyethylene*. 2003 Annual Report Conference on Electrical Insulation and Dielectric Phenomena, 2003: p. 145-148.

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