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RAMAN MICROPROBE ANALYSIS OF ELECTRICAL TREEING IN SILICONE RUBBER

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Abstract: Previous papers have identified Raman microprobe analysis as a useful tool in the chemical analysis of electrical trees and have successfully applied the technique to trees grown in polyethylene. This paper comprises a detailed spectroscopic study of electrical trees grown in silicone rubber. A selection of trees of varying fractal dimensions were exposed using cryogenic microtomy and then the individual tree channels were subjected to surface specific Raman microprobe analysis. It was found that although some trees show that few chemical changes have occurred, some trees (including some where complete breakdown has occurred) show evidence of the presence of silica and carbon, the latter possibly originating from the side groups of the polymer chain. After this, some of the samples were then analyzed using scanning electron microscopy (SEM) to provide an alternative method of analysis and to reinforce the conclusions made. Results are discussed in comparison to previously published results from a similar analysis on trees in polyethylene.

1 INTRODUCTION

The subject of electrical treeing in polymeric materials is a technologically important phenomenon due to its application in high voltage insulation materials. The formation of electrical trees in polymers can lead to catastrophic electrical breakdown and failure of the material in its ability to act as an insulator. The process of electrical treeing occurs in three stages, the first of which is inception - the formation of a micro void in the polymer at a region of high electrical stress [1]. Secondly this micro void develops into a fractal structure composed of fine channels which develop through partial discharge activity; this is the growth stage of the electrical tree. Finally when the tree channels create a continuous conducting path between the two electrodes, breakdown occurs. The trees that occur can be described as either branched or bushed depending on their fractal dimension D_f. Branched trees have fewer channels and grow more rapidly (and at lower inception voltages) than bushed trees and occurs when $1<D_f<2$ conversely bushed trees occur at $2<D_f<3$ [2, 3]. Studies based on measurements of PD activity and optical observations have shown that it is not only their internal structure and colouration that differs between the two types of tree but the electrical activity that produced them as well [4-6]. Branched trees are more conducting in nature and, as the walls of the tree channels are sufficiently conducting to prevent discharges from within the tree, the electrical activity is confined to the growth tips. Bushed trees however are thought of as non-conducting and electrical activity occurs throughout the entire tree [6-8].

In order to understand how electrical trees are formed we need to understand how low density regions/voids can be produced in solids with the application of an electric field. The development and growth of electrical trees involves the chemical conversion of polymers into volatile fragments due to the transfer of energy from the electric field [9] and is determined by the partial discharge activity within the trees and is affected by many factors such as morphology [10], chemical composition [11], mechanical stress [7] and so on. The final form of the tree structure which develops (i.e. if it is conducting/non conducting) is determined by the degree of influence of these factors but the exact process of electrical treeing remains unclear.

Two papers by Vaughan *et al* (2004 and 2006) [12, 13] investigated the structure and chemical changes involved in electrical treeing in polyethylene with the application of confocal Raman microprobe analysis (CRMA). Raman spectra obtained from a conducting tree in these studies showed that an electrical tree structure can be interpreted to contain 3 separate elements that vary from different spatial positions within the tree. Firstly throughout the tree (both in the tips of the tree channels and in the surrounding bulk material), the spectra for PE can be seen. Secondly in the main body of the tree the presence of fluorescence was identified which is usually linked to the degradation of a material. Finally when analysing the tree channels the D and G bands of sp^2 hybridised carbon can be seen. This suggests that the tree channels can be thought to be surrounded by a conducting carbon shell with non conducting PE tips.

This study aims to extend this work further by performing a similar analysis on trees grown in silicone rubber. This will enable us to see if similar trends can be found in the spectra when the chemical structure of the polymer is markedly different to PE. In this initial study, samples of breakdown channels and tree branches in silicone rubber samples will be examined using CRMA and SEM in order to compare the results to those obtained by Vaughan *et al* such that an improved understanding of the chemical processes involved in electrical treeing can be found.

2 EXPERIMENTAL

2.1 Materials

The samples in this study were all made from the Dow Corning Sylgard 184 Silicone Elastomer kit. This kit contains the base compound and a curing agent. In order to make the samples the 2 compounds were mixed at a ratio of 10:1, degassed and cured in a mould at 100 °C as per the kits instructions. Samples were then cut to size (6x10x15 mm and used to grow electrical trees.

2.2 Method

Electrical trees were grown in the silicone rubber samples by inserting a hypodermic needle (tip radius approx $10\ \mu$m) into the sample such that there is a 2 mm gap between the needle tip and a planar earthed electrode. A voltage of 12 kV rms (AC 50 Hz) was applied until a tree formed at the needle tip or a complete breakdown occurred. Samples containing an electrical tree / breakdown channel were then cut open using an RMC MT-7 ultra microtome equipped with a CR-21 cryo-system set at -120 °C in order to provide a surface containing open segments of the tree/ breakdown channel.

Samples were then characterised at various positions around the tree/breakdown channels using a Lecia microscope coupled to a Renishaw Raman RM1000 system using a Renishaw NIR 780TF semiconductor diode laser (wavelength 780 nm) of power 25 mW. The spectrometer was set up in line with Renishaw's recommendations for confocal operation of the spectrometer. All spectra were obtained using an extended scan between 3500 cm^{-1} and 100 cm^{-1} and were built up of 25 accumulative scans of 10 s and were processed using SigmaPlot 10. After initial Raman characterisation the above microtomed surfaces were sputter coated with gold and the tree structures examined by scanning electron microsocopy (SEM).

3 RESULTS AND DISSCUSSION

Figure 1 shows an optical micrograph of a breakdown channel in a sample. The approximate positions that were analysed via RMS are marked and the resulting spectra can be found in figure 2 which show a number of spectra within the breakdown channel and in the surrounding area respectively. From these spectra we can see that as with the results obtained by Vaughan *et al* [12, 13] there are 3 components to the breakdown channel. Firstly in all the spectra the typical peaks relating to silicone rubber can be seen between 200 and 900 cm^{-1} and in all cases these peaks are superimposed on varying degrees of fluorescence. This suggests that as with the PE there is some material degradation in the areas surrounding the breakdown channel. This fluorescence appears to be greatest inside the breakdown channel and then is dramatically reduced as the results are obtained from greater distances away from the channel. This suggests that in the case where breakdown occurs in silicone rubber, there is a large amount of material degradation, but that this degradation is localised and restricted to the region The presence of carbon in the breakdown channel suggests that the breakdown process of silicone rubber involves the breakdown of the bonds between the polymer backbone, consisting of silicone and oxygen, and the side groups of the polymer chain that contain carbon. The presence of carbon found in aged PE samples in previous work [13] suggests chain scission of the polymer backbone itself, if this was the case with silicone rubber however, it would be expected that results showed a large amount of SiO_2. The results given here however show little or no evidence of this and so, casts doubt upon the exact processes that are involved in electrical ageing. Future work will investigate this topic further and other methods such as FTIR will be applied in order to confirm or deny the presence of SiO_2 in electrically aged silicone rubber, and hence, enable a deeper understanding of the chemical processes involved in electrical treeing.

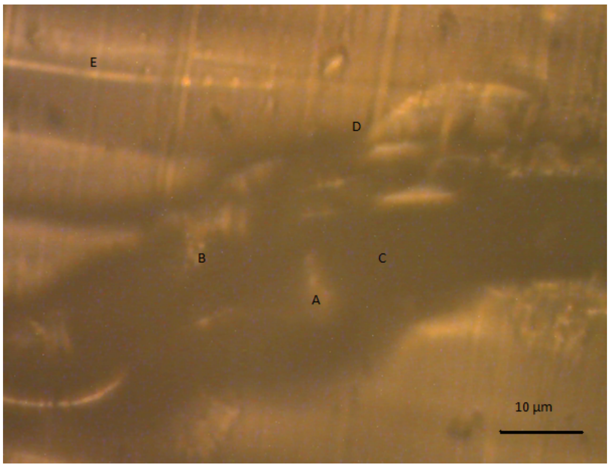


Figure 1: Optical Micrograph showing the relative positions analysed on an electrical breakdown channel in silicone rubber

Figure 4 shows another optical micrograph of an electrical tree found in a sample of silicone rubber. Once again the surface of this sample has been

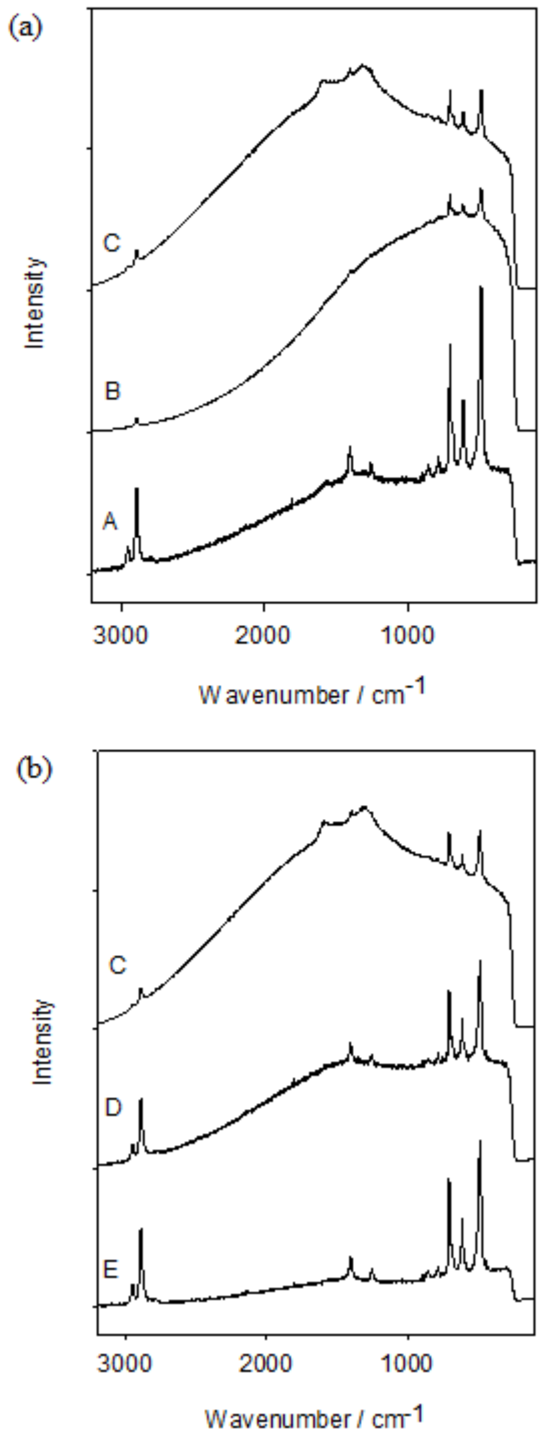


Figure 2: Raman spectra of positions (a) A, B and C and (b) C, D and E of the breakdown channel in silicone rubber

microtomed down in order to expose segments of the tree channel. It is worth noting that under reflected light this tree appears black in colouration, leading to the possibility of it being a conducting tree. As well as this it is also worth mentioning the simplicity and small scale of the tree, this is because the method for growing trees in silicone rubber has not yet been fully established and as a result the trees tested were very small in size (approximately 125 µm) and contain very few branches. It is thought that by reducing the radius of curvature of the needle electrode (and therefore increasing the field at this point) and by increasing the applied voltage, larger more complex trees will be formed.

The areas marked in figure 4 were sampled via RMS and the corresponding spectra can be found in figure 5. Figure 5a shows various scans from inside the tree channels and from this we can see that although there are some similar features to those found in figure 2 they are by no means as dominant as with the breakdown sample. Once again the peaks relating to silicone rubber can clearly be seen in all spectra and, unlike before,

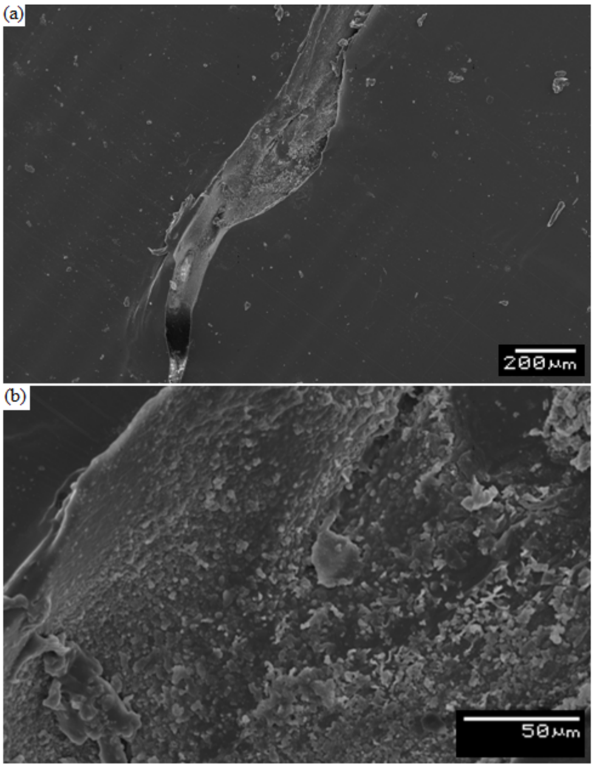


Figure 3: SEM images showing (a) section of breakdown channel analysed via Raman microscopy and (b) a close up of the central portion of the breakdown channel

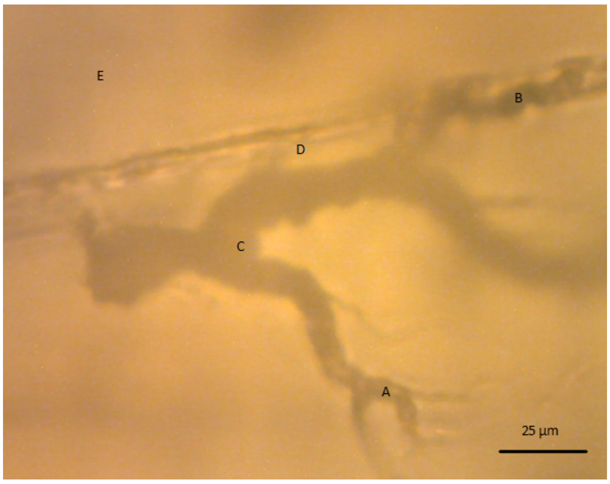


Figure 4: Optical micrograph showing the relative positions analysed on an electrical tree grown in silicone rubber

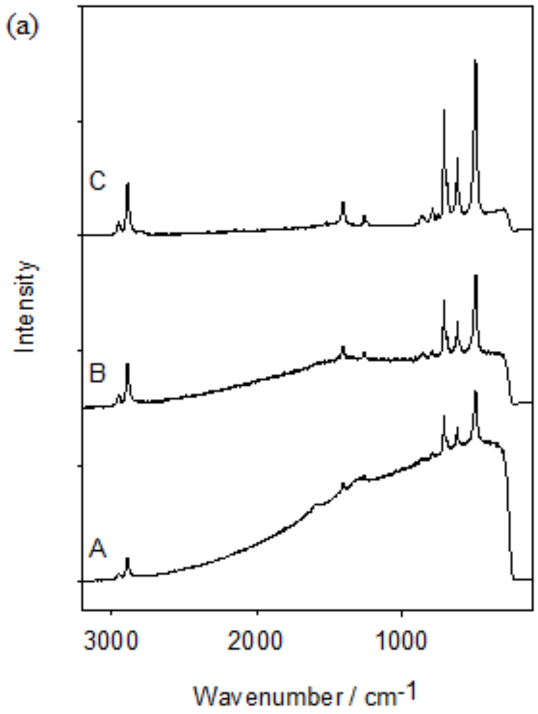
they are now the dominant feature in the spectra. At positions A and B there is the presence of fluorescence but again its intensity and contribution to the spectra are not as large as those obtained from the breakdown channel. Inside the tree channel there is a feint presence of carbon, but this is by no means the dominant feature and the chemical matrix is largely unchanged. In figure 2 the D and G bands dominated the spectrum, but in the spectra for the tree channel the bands are only slightly visible meaning that there appears to be only a small amount of carbon on some sections of the walls of the tree channel instead of a thick shell as found in the breakdown channel. Figure 5 b shows various scans from the surrounding area of the tree all of which show spectra very similar to the original matrix. This shows that although the tree itself may be slightly fluorescent the immediate surrounding area is not. This may however change if a similar analysis is performed on a 'bushier' tree.

As with the results obtained by Vaughan *et al* the results from these two samples show three key elements even if the relative proportions are different in silicone rubber [12,13]. The presence of the original matrix is clear in all spectra, which (as with the PE) is superimposed on a background of fluorescence when focused upon the tree/breakdown channels. In both the tree and the breakdown channels there also appears to be varying degrees of carbon which is consistent with that of conducting trees in PE. One difference is that there appears to be little or no fluorescence in the surrounding matrix as was shown by Vaughan *et al* [13]. The reasons for this is unclear but as the tree examined contained only a few branches could be due to the material degradation being localised to the tree channels. Alternatively the lack of fluorescence could be due to the lack of tree channels below the surface at the points of analysis as there was with the PE samples tested by Vaughan *et al* [13].

Figure 6 shows a typical SEM micrograph of the tree channel analysed in figures 4 and 5. As with the breakdown channel there is little evidence of any morphology of the sample. From this image we can see that the tree channel breeches the surface at several intersections but with this sample it proved difficult to draw any conclusive opinions about the SEM images as was done with the breakdown channel and further testing is needed on different types of trees in silicone rubber.

4 CONCLUSION

From the above results we can draw the following conclusions:



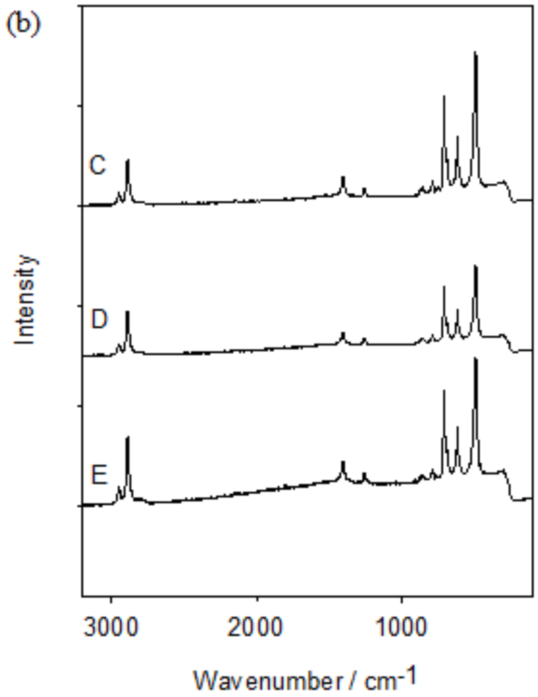


Figure 5: Raman spectra of positions (a) A, B and C and (b) C, D and E in an electrical tree in silicone rubber

- As proposed in previous chapters, CRMA is indeed an effective tool in the analysis of electrical trees and enables us to chemically characterise the internal structure of tree channels grown in silicone rubber that have been exposed to the surface via microtomy. This method however is still not without flaws and care is needed not to create physical damage to the electrical trees caused by the localised heating effect of the laser.

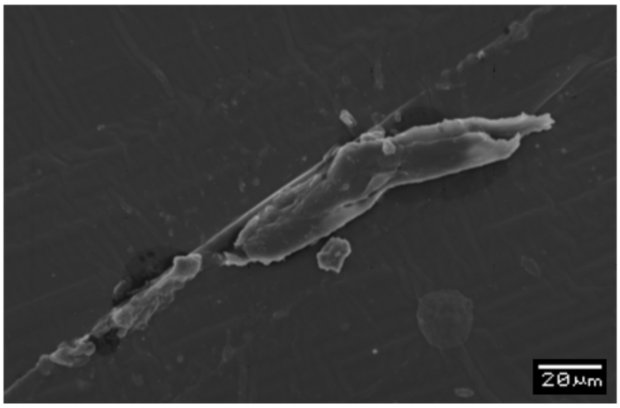


Figure 6: SEM image of an area of tree channel analysed via Raman microscopy

- Previous work using CRMA to analyse electrical trees in PE showed that there were 3 key features (polymer, fluorescence and carbon) to the spectra obtained in conducting electrical trees. By contrast non conducting trees show increased fluorescence but do not show any carbon [12, 13]. The results obtained from the breakdown channel show the same 3 features as those found in conducting trees in PE. The results obtained from the tree channels in silicone rubber show some evidence of fluorescence and carbon but not to the same extent as trees in PE or the breakdown channel. This means that it is likely that a similar process is involved in electrical treeing in both PE and silicone rubber.

- SEM imaging of the breakdown channel is also in agreement with previously published work on conducing trees in PE and a nodular shell, likely to be related to carbon, lines the walls of the breakdown channel. Results from the tree channel were inconclusive.

In summary the results obtained provide a good preliminary step in being able to understand the process of electrical treeing in silicone rubber and show similar spectra to those found in work previously published. Future work in this study will aim to develop an experimental protocol for the formation and analysis of electrical trees. Analysis will then be extended to include a wider range of electrical trees grown in silicone rubber to include trees of a ‘bushier’ structure and to compare the differences between conducting and non conducting trees. As well as this, a more in depth analysis of the relation between tree structure and fluorescence will be performed. This method will also be applied to a variety of electrical trees grown in another organic polymer such as polystyrene in order to create another comparison. Once a more in depth analysis has been achieved then a more conclusive understanding of electrical trees in different polymers and the processes involved in their production can be achieved.

5 ACKNOWLEDGMENTS

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