

## **Oxidation of EPDM: oxidation depth measurements and effects on material properties**

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<b>Summary</b>		
<p>Polymers are known to be susceptible to heterogeneous oxidation when they are exposed to harsh environments, e.g. relatively high dose rates of ionizing radiation in oxygen containing atmosphere. Exposure to such environments could cause a formation of oxidation profile in the vicinity of the surface, where degree of oxidation is decreased as moved towards the bulk. This kind of situation is not usually desirable after artificial ageing and verification of homogeneous oxidation needs to be confirmed.</p> <p>In this study three different analysis techniques, including Time of Flight Secondary Ion Mass Spectroscopy analysis (ToF SIMS), Fourier Transmission Infrared Spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC), were used to detect oxidation in artificially aged EPDM samples. ToF SIMS seemed to be most promising method in detection of early oxidation even though it requires carefulness in sample preparation. Since the good resolution of the instrument, uneven sample surface finish can result in erroneous measurement results. FTIR seemed to be promising method in detection of oxidation products at the surface of studied samples but its use is strictly limited to samples that do not contain carbon black as filler material. It was observed that DSC is also capable to detect oxidation related changes in the studied samples but its resolution is very limited when formation of linear oxidation profile towards the bulk is required.</p>		
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## Preface

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This work was conducted as part of the project “Condition Monitoring, Thermal and Radiation Degradation of Polymers inside NPP Containments (COMRADE)” executed within the SAFIR 2018 research program in cooperation with SP Technical Research Institute of Sweden. The purpose of this study was to use different analysis techniques in oxidation profile measurements on artificially aged EPDM samples and estimate their applicability for this purpose. Finnish State Nuclear Waste Management Fund (VYR), VTT Technical Research Centre of Finland Ltd, Energiforsk and Swedish Radiation Safety Authority (SSM) are acknowledged for funding this work.

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## 1. Introduction

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Oxidation can be considered as one major mechanism governing polymer degradation at ambient as well as elevated temperatures and under ionizing radiation. Molecular oxygen is known to diffuse within the polymer and radicalize by ionizing radiation. The formed peroxy radical can react with the surrounding structures causing chain scission or formation of hydro-peroxides that is further decomposed and producing additional radicals. Thus it can be thought that during irradiation in air atmosphere, two reactions compete with each other: transportation and consumption of oxygen. The oxygen transportation follows Fick's law and also the Arrhenius equation i.e the diffusion increases upon temperature increase. These two reactions define whether the irradiated sample will oxidate homogenously (i.e. oxygen diffusion is uniform) or will the irradiation induced oxidation concentrate on the vicinity of the surface. Homogenous distribution of oxygen is known to cause additional degradation for the material [Reynolds et al. 1995].

In this study, the focus is on evaluating applicability of different techniques on measuring the oxidation profile created in EPDM samples during accelerated ageing. These techniques include Time of Flight Secondary Ion Mass Spectroscopy analysis (ToF SIMS) Fourier Transform Infrared Spectroscopy (FTIR) and differential scanning calorimetry (DSC). Obtaining uniform oxygen diffusion is required when polymer components are artificially aged to correspond to the degraded/aged condition that they will reach after normal service conditions (low dose rate and temperature). Proper use of these different analytical techniques that could be used in oxidation profile measurements is required in order to distinguish homogenous vs. heterogenous diffusion of oxygen from each other when polymeric samples are analysed after accelerated ageing treatments.

## 2. Goal

The goal for this study is to verify different techniques that could be used in oxidation profile measurements and analyse how the surface oxidation will relate to the overall mechanical properties on the studied EPDM materials.

## 3. Methods

The studied materials included sulphur and peroxide cured EPDM rubber manufactured by James Walker Ltd. The samples for tensile testing were stamped out of two millimeter sheet supplied by the manufacturer. For the surface oxidation measurements five millimetre sheet was used since it was presumed to be a sufficient thickness for a formation of an oxidation gradient. The thicker sheets also made the sample preparation easier. For FTIR analysis an EPDM blend without carbon black was prepared which was also in form of five millimetre sheet. Peroxide cured EPDM was used in DSC analyses. Sample materials were aged to different conditions after which testing was performed. On the thicker samples the concentration of oxygen on the surface and in the bulk material was compared by using three different methods (DSC), (ToF SIMS) (FTIR).

### 3.1 Ageing

The samples were artificially aged to the different conditions as described in Table 1. Irradiation ageing at near room temperature (1) and thermal ageing (2) were conducted to both sample qualities. Simultaneous irradiation ageing and thermal ageing (3) was conducted on sulphur cured samples and the ageing of peroxide cured EPDM was conducted sequentially instead of simultaneous treatment (4).

The irradiation treatments were conducted at ROZA irradiation facility in ÚJV Řež, Czech Republic. The heat treatments were conducted at SP laboratory located in Borås, Sweden. The irradiations chamber was well-type where the gamma ray source ( $^{60}\text{Co}$ ) were located in the middle of and the samples were lowered around it. Simultaneous elevated temperature was obtained by placing part of the samples into specially built thermoboxes. During the irradiation treatments, a constant dose rate of 0,39 kGy/h were applied. Ageing parameters (absorbed dose and temperature) are similar to those present at nuclear power plant during loss of coolant accident (LOCA).

Table 1. Ageing environments for the studied samples.

Ageing environment	Temperature/°C	Mean absorbed dose/kGy	Total net treatment time/h
1	28,6±1,0	228±23	525
2	125,0±1,0	0	508
3	125,7±1,3	228±23	525
4	28,6±1,0/125,0±1,0	228±23/0	525/508

### 3.2 Tensile testing

Tensile testing was conducted for the samples in order to see the overall degradation induced in the samples after the exposures to each ageing condition. The tensile testing was

done according to ISO 37 standard. Tensile testing sample dimension was according to standard type 1A. The tensile testing machine was equipped with optical elongation gauge. Tensile testing results provided information on the amount of degradation induced in the material after exposure to each ageing environment. Surface degradation can yield in very small scale surface defects that act as an initiation sites for macro scale cracks.

### 3.3 ToF SIMS analysis

During the ToF-SIMS analysis the material is bombarded by a pulsed ion beam and secondary ionized molecular fragments are emitted from the surface and analyzed in the detector. Each incoming ion pulse causes emission of particles from an area of a diameter down to 0,1 $\mu\text{m}$ . From each target area a complete high resolution mass spectrum is obtained. Thus, ToF-SIMS can give a two dimensional image with high lateral resolution based on any selected ion mass. The analysed samples were cut from the five millimeter sheet that were aged according to Table 1, forming thus two cross section samples. The two cross section samples were placed in the ToF SIMS sample chamber in way that the oxidised surfaces were tightly pushed together and the ion beam was first introduced to bulk material from which it proceeded towards the surface of the first cross section sample. The interface here is the plane between the two cross section samples and after surpassing the interface, the ion beam moves from the surface towards the bulk of the second cross section sample. This way the oxygen content could be analysed from the bulk to surface and vice versa. As a result two  $\text{O}^-$ -intensity spectra and an image of oxygen concentration along the sample cross section is created.

The ToF-SIMS analysis was conducted with a TOFSIMS IV instrument (IONTOF GmbH, Germany) using 25 keV  $\text{Bi}_3^+$  as primary ions. High mass resolution images of 500 $\times$ 500  $\mu\text{m}^2$  with 256 $\times$ 256 pixels were acquired in bunched mode with a pulsed current of 0.10 pA. High resolution images of 200 $\times$ 200  $\mu\text{m}^2$  with 256 $\times$ 256 pixels were acquired using burst alignment mode with a pulsed current of 0.05 pA. The primary ion density dose (PIDD) was kept below  $1 \times 10^{-12}$  to ensure a native sample surface. The resulting spectra and images were analyzed with SurfaceLab 6 (IONTOF GmbH, Germany). The pulsed current is advantageous for polymers analysis since it is possible to analyze the material without coating the surface to avoid electrical charging.

### 3.4 FTIR analysis

FTIR device allows detection of the oxidation products, such as carboxylic acid, ketones and esters, on the surface with depth of nanometer scale. Most rubber materials contain high loads of carbon black filler and this causes total absorption of the infrared light used by the technique. Thus FTIR is tested on two EPDM qualities which have identical composition except other EPDM grade contains carbon black while in the other material carbon black has been replaced by clay. Based on the results applicability of FTIR to analyse carbon black containing EPDM grades can not be evaluated. Five millimetre thick samples without carbon black were analyzed on the surface and in the center of the cross section of the samples. A Thermo Electron FTIR Spectrophotometer equipped with an ATR (Attenuated Total Reflection) attachment, allowing analyses directly on the material surface, was used.

### 3.5 DSC analysis

DSC analyses were performed on cylindrical shaped samples having a five millimetre diameter cut from the middle of the five millimetre sheet. These cylindrical samples were then cut to smaller, some hundred  $\mu\text{m}$  thin slices, with a microtom. These small slices were analysed with DSC thus creating an oxidation profile from the surface layer deeper into the bulk material. The used procedure was the measurement of oxidation induction time (OIT) which provides information on the oxidative state of the studied sample. OIT was measured by using differential scanning calorimeter. The OIT measurement procedure comprehend

from three stages where in the first one sample was heated in nitrogen environment up to 225°C and this temperature was held constant during the whole measurement. At the second stage the nitrogen atmosphere was replaced with oxygen and during the third stage exothermic peaks characteristic to different decomposition reactions induced by oxidation were measured.

## 4. Results and discussion

### 4.1 Tensile testing

The results from tensile testing are shown in Table 2. The largest increase in tensile strength and modulus was seen after simultaneous exposure to gamma radiation and heat. Also the largest decrease in elongation at break was after exposure to this environment. Increase in tensile strength and modulus is indicative to additional crosslinking [Lay, 2013]. Sequential exposure to heat and gamma radiation yielded slightly increased degradation than exposure to heat only. The tensile strength values after exposure to environments 2 and 3 are quite similar but above the reference value. The modulus values at these environments are also higher than the reference value. Exposure to gamma radiation only did not yield in significant changes in tensile strength and only small increase in modulus value. However, a clear decrease in elongation at break is observed which is along with the common assumption that elongation at break is sensitive property when degradation of polymer materials is considered. Based on the tensile testing results, thermo-oxidative ageing seems to have greater influence to material degradation on sulphur cured EPDM than irradiation induced ageing. The opposite observation was done with peroxide cured samples, indicating the effect of vulcanizing agent to the ageing behaviour.

*Table 2. Tensile test results for sulphur (S) and peroxide cured (P) samples after different ageing environments. Standard deviation marked in brackets.*

Ageing environment and curing agent	Tensile strength/MPa	Elongation at break/%	Modulus (at 100% strain)/MPa
REF (S)	9,4 (1,15)	433 (113)	2,9
REF (P)	13,0	182	5,2
1 (S)	9,3 (0,80)	281 (40)	3,8
1 (P)	11,5 (1,04)	126 (8)	8,5
2 (S)	11,3 (0,30)	188 (9)	6,1
2 (P)	14,6 (1,14)	178 (11)	6,7
3 (S)	11,4 (0,58)	136 (10)	8,3
4 (P)	12,3 (0,98)	117 (3)	9,8

### 4.2 ToF SIMS analysis

The principle how the ToF SIMS analyses were performed is shown in Figure 1. The pulsed ion beam is introduced first to the bulk material of the cross section surface (shown as D in the middle picture in Figure 1) from which it begins to progress towards the direction of the interface. Since two cross section surfaces were analysed at once (not seen in Figure 1), the

vicinity of the interface in the graphs may be located either at the distance 0  $\mu\text{m}$  or at ca. 400  $\mu\text{m}$  depending on the direction of the ion beam. In Figure 1 (in the middle) one of these cross section samples is seen with the interface pointed by an arrow. The  $\text{O}^-$  signal intensity (i.e. the oxygen content) is recorded as a function of distance from the interface (shown on left in Figure 1). Also a graphic two dimensional illustration on the analysed oxygen content on the cross section surface can be produced with this method (shown right in Figure 1). Even though the surface of the reference sample seems to be quite rough, oxygen (green colour in the image) can be detected in higher quantities in the vicinity of the surface than in the bulk. From the reference sample it can be analysed that the oxidation layer is approximately 220  $\mu\text{m}$  thick. The high intensity variation detected from the bulk analyses are considered to be caused by the uneven surface.

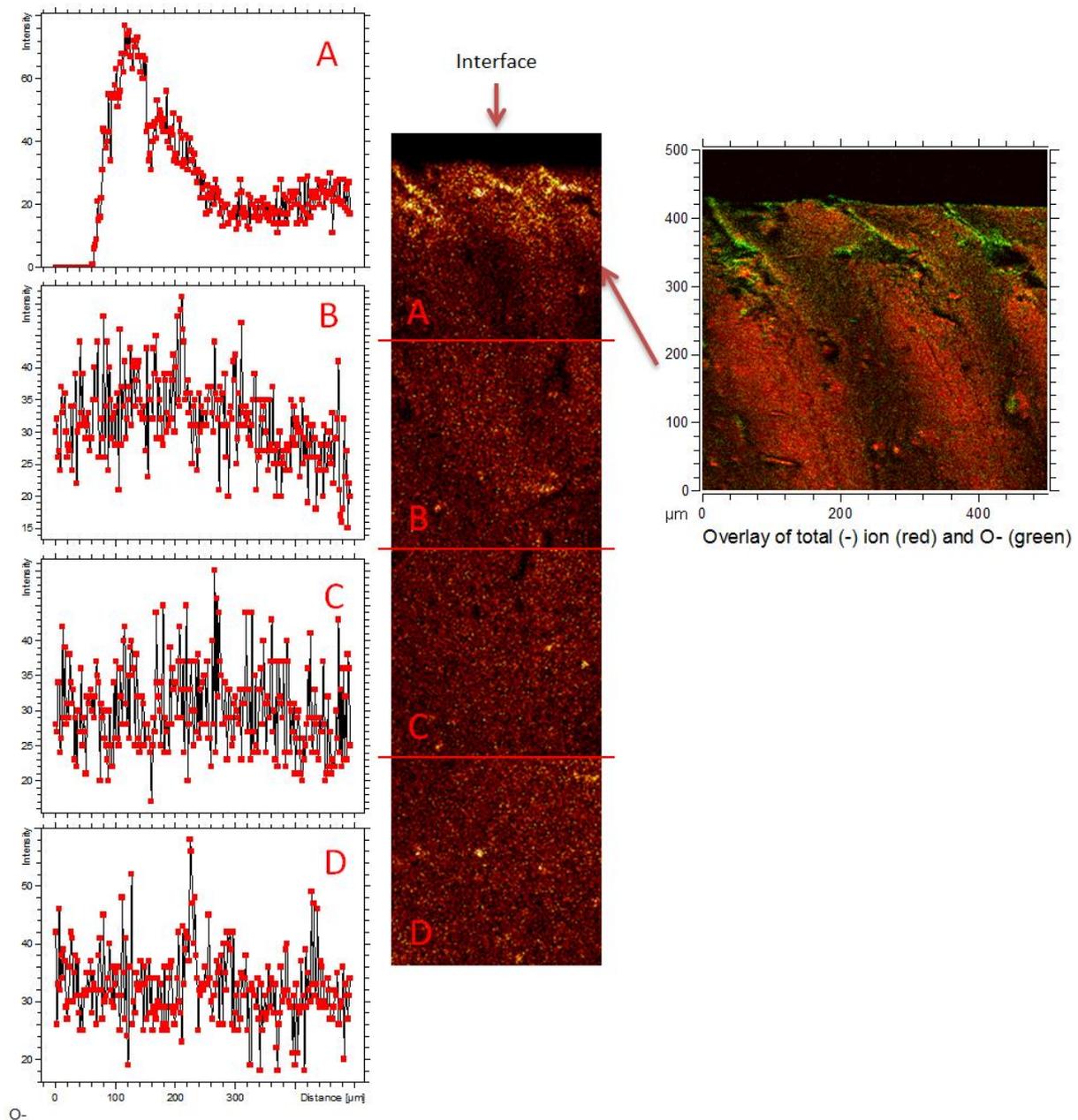


Figure 1: ToF SIMS analysis result on the EPDM reference sample. To the left oxygen intensity measurement spectra as function of distance from the surface. Corresponding images on the surface are pointed out with letters A, B, C and D. Oxygen is visualized with green colour in the overlay imaging to the right.

The repetitive measurement for the reference sample is shown in Figure 2. Again, the thickness of the oxidized surface layer can be evaluated to be 220  $\mu\text{m}$ . In case of the reference sample, good repeatability is achieved.

Figures 3 and 4 show the results obtained from samples exposed to ageing environment 1. From the first analysis round the oxidized layer thickness is calculated to be 140 and 160  $\mu\text{m}$  and from the repeated measurement 340  $\mu\text{m}$ . The repeated measurement with the second sample yielded in approximately double as high oxidized layer thickness.

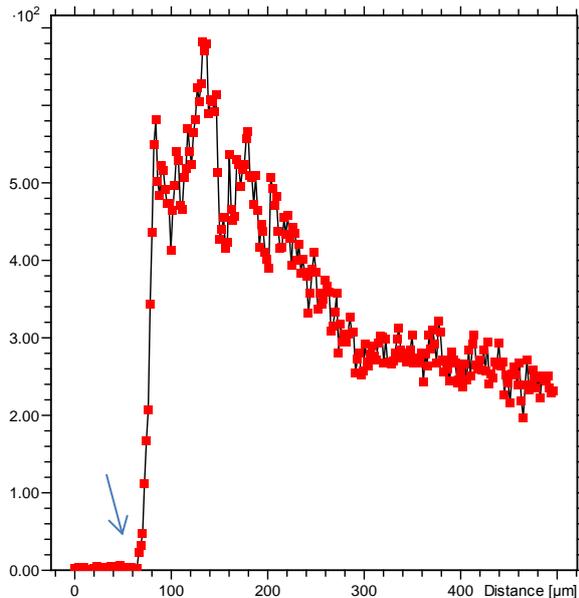
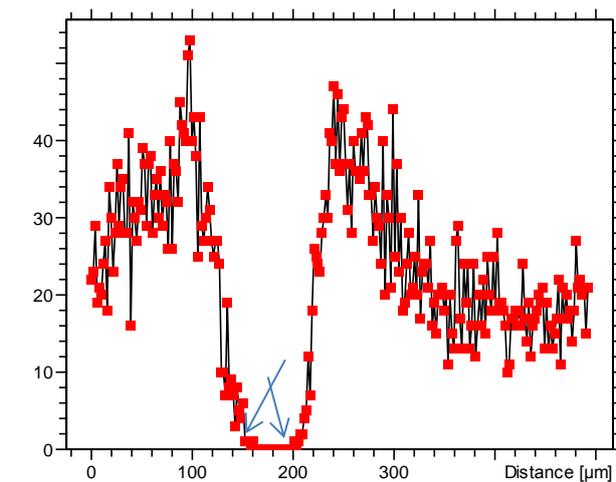


Figure 2: O<sup>-</sup> signal intensity as function of distance from the interface (shown with an arrow) for second reference measurement.



O-

Figure 3: O<sup>-</sup> signal intensity as function of distance from the interface (shown with arrows) after exposure to 228 kGy of gamma radiation.

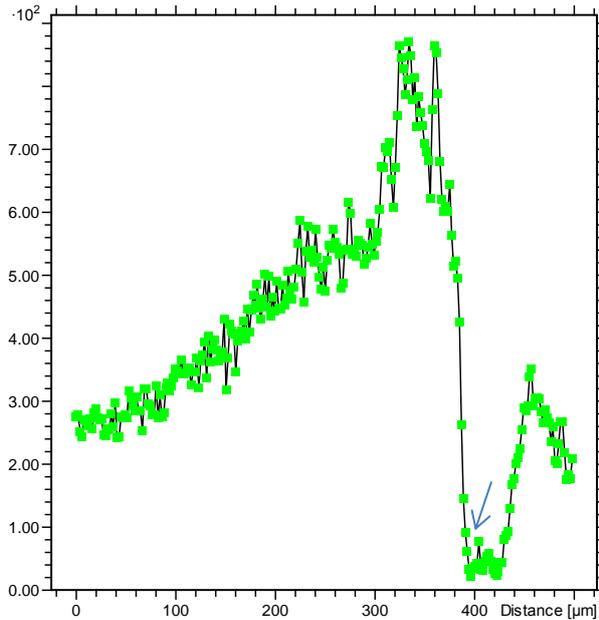


Figure 4: Repeated measurement result of  $O^-$  signal intensity as function of distance from the interface (shown with an arrow) after exposure to 228 kGy of gamma radiation.

The oxidation profile for the thermally only aged sample is shown in Figure 5. The bulk level intensity was achieved approximately 520  $\mu\text{m}$  from the interface. The intensity level of the bulk material can be seen in Figure 6, which is continuation from Figure 5. In Figure 6 as the distance in x-axis grows, more closer the interface is. In the case of this thermally only aged sample, the other cross section sample did not yield in clear intensity levels within the bulk material so no oxidized layer thickness could be determined.

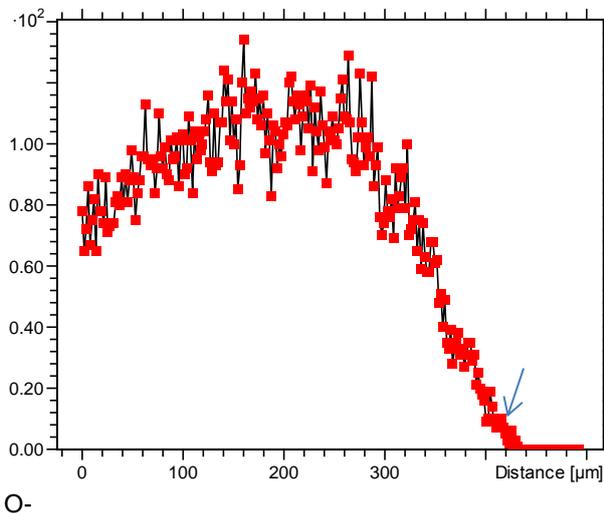
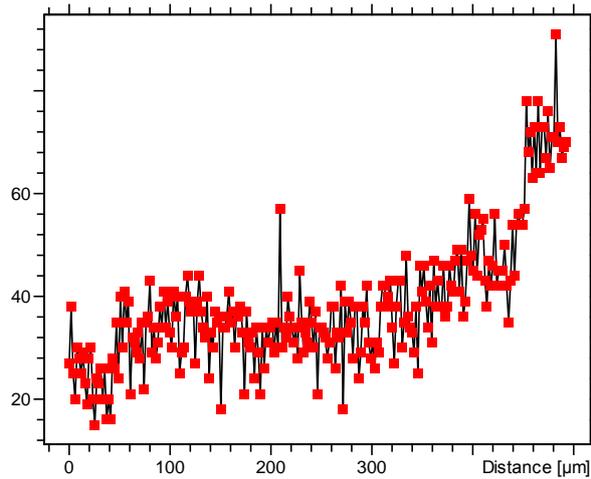


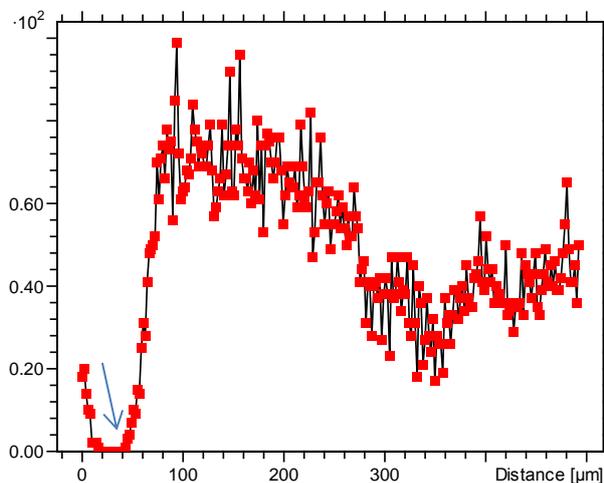
Figure 5:  $O^-$  signal intensity as function of distance from the interface (shown with an arrow) after exposure to 125°C.



O-

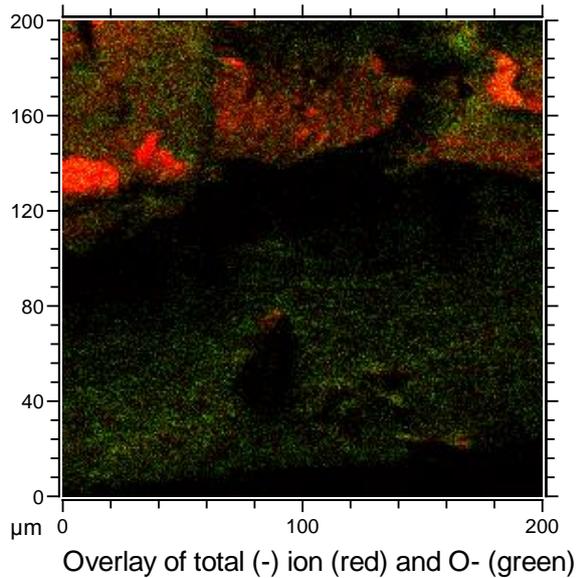
*Figure 6:  $O^-$  signal intensity in the bulk material after exposure to 125°C. Above 400  $\mu\text{m}$  the higher intensity is due to the oxidation layer (continuation from the previous figure).*

In Figure 7 the spectrum for sample that was exposed to gamma radiation and thermal ageing is displayed. The oxidation layer thickness is estimated to be ca. 240  $\mu\text{m}$ . Here again, the other cross section surface displayed uneven surface characteristics, as can be seen in Figure 8, when compared to the opposing even cross section surface shown in Figure 9. From Figure 8 it can be seen that the other cross section sample has a flaw which separates the oxidazide surface layer from the less oxidized bulk material.

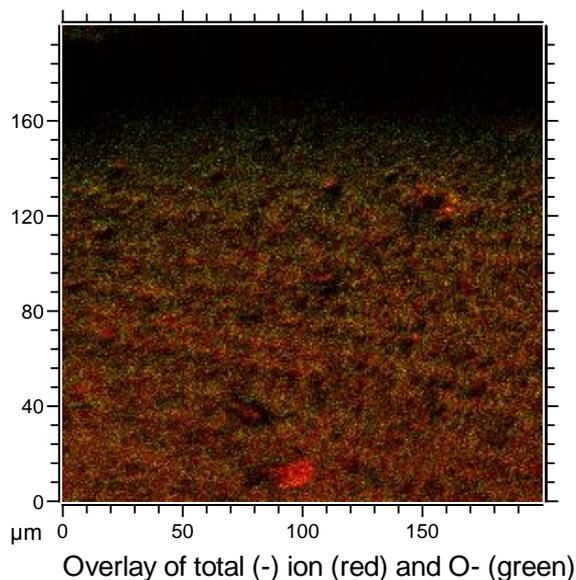


O-

*Figure 7:  $O^-$  signal intensity as function of distance from the interface (shown with an arrow) after exposure to 228 kGy and 125°C.*



*Figure 8: Two dimension oxidation graph obtained with sample irradiated and exposed to thermal ageing with uneven cross section surface (opposite surface to the one shown in next figure). Interface is on the bottom of the figure.*



*Figure 9: Two dimension oxidation graph obtained with sample irradiated and exposed to thermal ageing with even cross section surface (opposite surface to the one in previous figure). Interface is on the top of the figure. The cross section surface is clearly less rough than the opposing surface shown in previous figure.*

The O<sup>-</sup> - signal was normalized to the CH-signal in order to compare the amount of oxygen in different samples since the signal itself is not quantitative. The comparison between CH-intensity measurements indicate that when thermal ageing only is applied, the CH-intensity is clearly higher than in other samples, as shown in Figure 10. This would indicate that the thermo-oxidative ageing would be greater than radiation induced ageing. This observation is in aligne with the tensile test results.

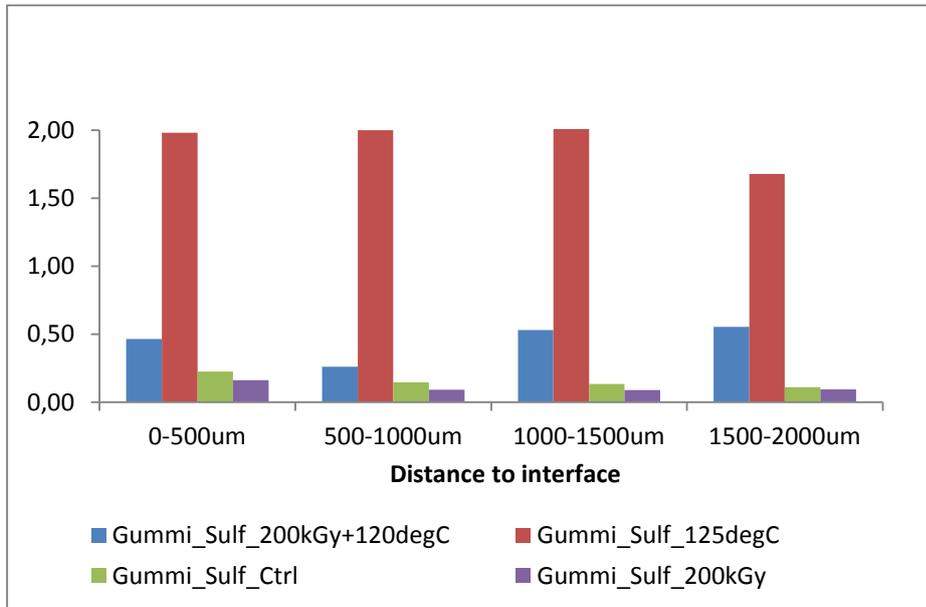


Figure 10: Ion intensity of O- normalized to CH- (y-axis) vs distance to interface (x-axis) after exposure to different ageing environments. Green bar indicates reference sample, purple ageing condition 1, red ageing condition 2 and blue ageing condition 3.

Based on the results ToF-SIMS can clearly detect the oxidation occurring in the vicinity of surfaces of the aged samples. The carbon black filler did not disturb the analyses. Based on these results alone no clear correlation to the material condition (i.e. material properties measured in tensile testing) could be drawn. The obtained oxidation profile thicknesses seemed to vary when repetition measurements were conducted. During repetition measurement the analysis spot changes which would indicate that material is oxidised quite heterogeneously or the material itself would be heterogenous (at least at the analysis range ca. 0,1µm). Also the effect of uneven cross section surfaces contribute to the measured intensities. However, improvements in sample preparation to obtain cross section surfaces and increasing the number of analysed samples is considered to yield more reliable evaluation of the oxidation profiles.

When the obtained results are compared to the tensile testing results, no direct correlation between mechanical properties and oxidation profile thickness could be seen i.e. the largest oxidation layer thickness did not yield in largest decrease in mechanical properties.

### 4.3 FTIR analysis

The oxidation products of interest included carboxylic acid, ketones and esters on the polymer chain. These carbonyl groups have absorption bands at wavelengths in the range of 1712, 1720 and 1735  $\text{cm}^{-1}$ , respectively.

A difference between the surface and the bulk material was observed on the reference material, as shown in Figure 11. Based on the differences in the two spectra, it was suspected that a coating or release agent may have been applied on the surface and/or an additive may have migrated to the surface. No relevant match to the spectrum achieved on the rubber material surface was found in the reference databases. Di-methylbenzyl Diphenylamine was the closest match and this chemical is used as catalyst in for example epoxy systems. More data on the ingredients of this specific EDPM blend would be required for more detailed interpretation of result.

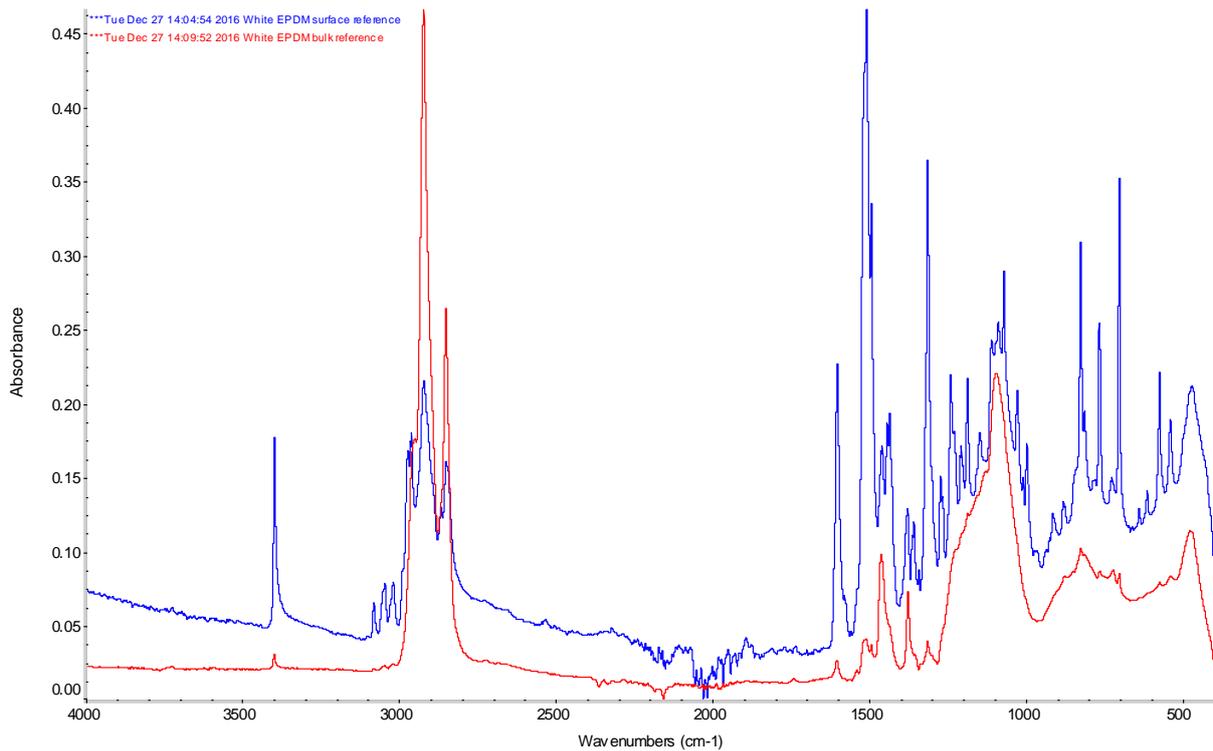


Figure 11: Comparison of the surface (blue spectrum) and the bulk (red spectrum) of the reference sample shows a difference in absorbance between the bulk and the surface.

In Figure 12 bulk spectra recorded from the aged and reference samples are compared. From the comparison it can be seen that the bulk material does not change significantly upon irradiation or ageing, which is along with the results obtained with ToF SIMS. All samples except for the sample which was only aged at 125°C showed a small absorption band at 1600 and 3400  $\text{cm}^{-1}$ . These absorption bands are also present on the spectra from the surface and probably origin from the sample preparation.

In Figure 13 the recorded surface spectra for reference and surface samples are shown. It seems that ageing conducted at elevated temperature has effect on the absorption bands between 500-1500  $\text{cm}^{-1}$  since they seem to disappear and the spectra becomes more similar to the bulk material. For the irradiated only sample the spectrum at these wavenumbers does not differ that much from the reference. The explanation is probably that a substance on the surface evaporates or decomposes at the elevated temperature. Another interesting observation is that only thermally aged sample shows a broad absorption band between ca. 3550-3000  $\text{cm}^{-1}$ . This is thought to be related to formation of OH-groups.

The comparison measurement between carbon black containing samples and samples that contained clay instead of carbon black was also conducted. The resulted spectrum with carbon black samples did not contain any peaks since all infrared light is absorbed by the sample. Thus the method is not applicable EPDM containing carbon black.

According to the results no oxidation products were found in the surface or bulk material. However, changes in absorption bands were observed due to the ageing treatments. More detailed analysis of these findings would require data on the ingredients of the studied EPDM blend. FTIR method seems to be sensitive to detect different compounds from surfaces and also bulk, when sample preparation is conducted with care. It is also known that quite high concentrations of oxidation products are required to be detected by FTR spectroscopy.

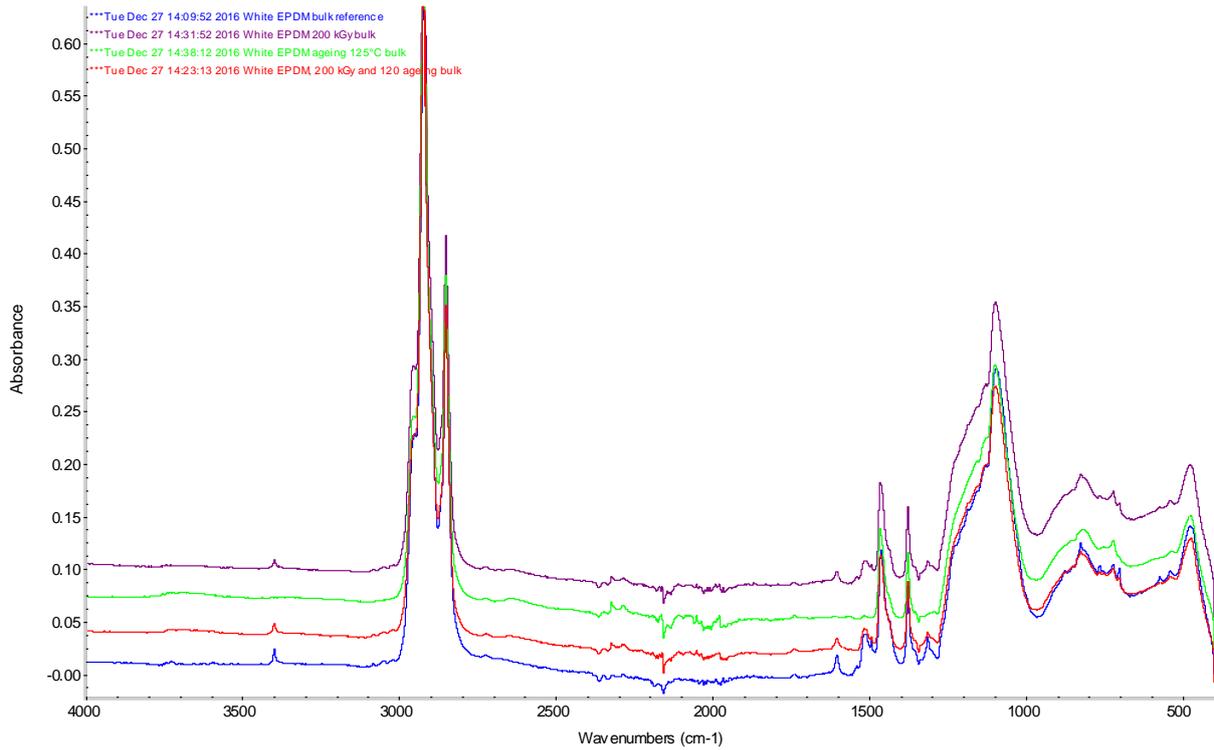


Figure 12: Spectra from the bulk material in samples before and after ageing.

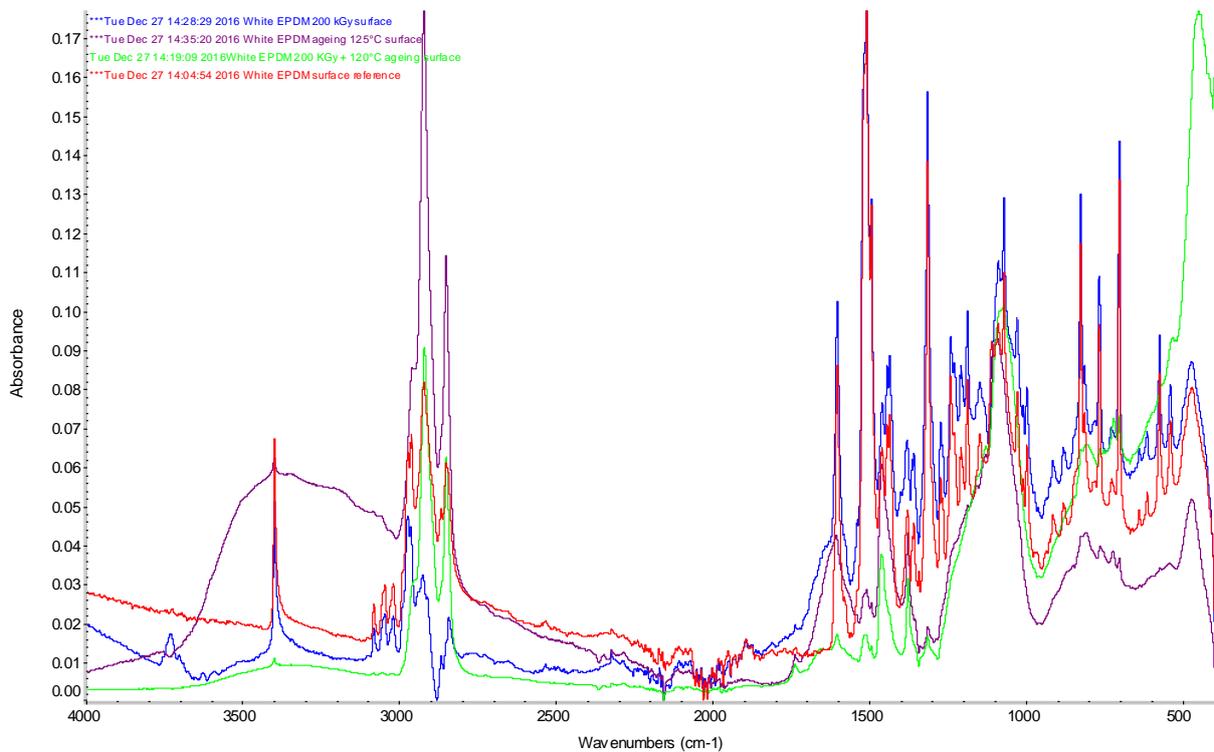


Figure 13: Spectra from the sample surfaces before and after ageing.

When the results were compared to the mechanical testing results shown in Table 2, no clear correlation with absorption bands and mechanical properties could be drawn.

#### 4.4 DSC analysis

The results for the reference sample oxidation profile measurements are shown in Figures 14 and 15. The sample preparation became more challenging than expected. In Figure 14 the sample thickness was 240  $\mu\text{m}$  and in Figure 15, 700  $\mu\text{m}$ . The formed thermograms show exothermic peaks with different magnitudes at the corresponding induction times. Differences in the exothermic peaks hint that there are some differences in the compositions between the surface and bulk samples. In order to evaluate these difference in detail, the ingredients of the blend would be required. The OIT defined for the surface sample is about half the size than in the case of the bulk sample which indicates that more oxidation has occurred in the surface layers. During the sample preparation it was noted that repeatability in order to obtain samples of same sizes was challenging as well as preparing thin (i.e. < 200  $\mu\text{m}$ ) samples. Thus DSC analysis has a limited resolution when oxidation profile formation is considered, especially when compared to ToF SIMS analysis.

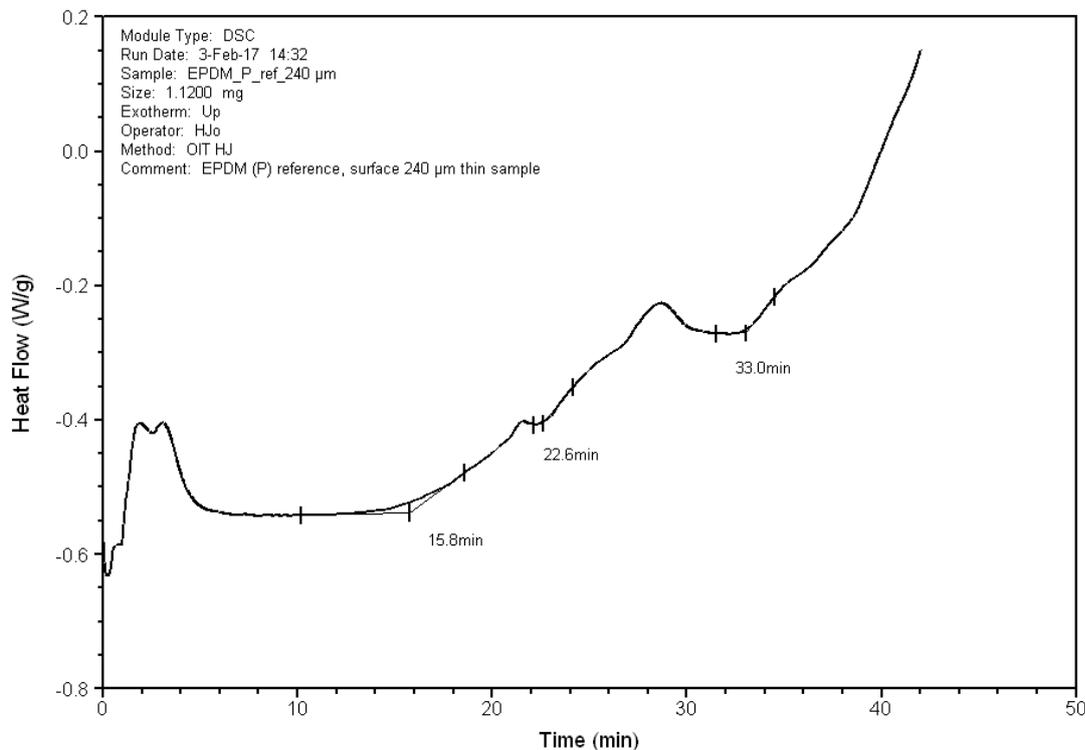


Figure 14: DSC thermogram for 240  $\mu\text{m}$  thick sample prepared from the surface of reference sample.

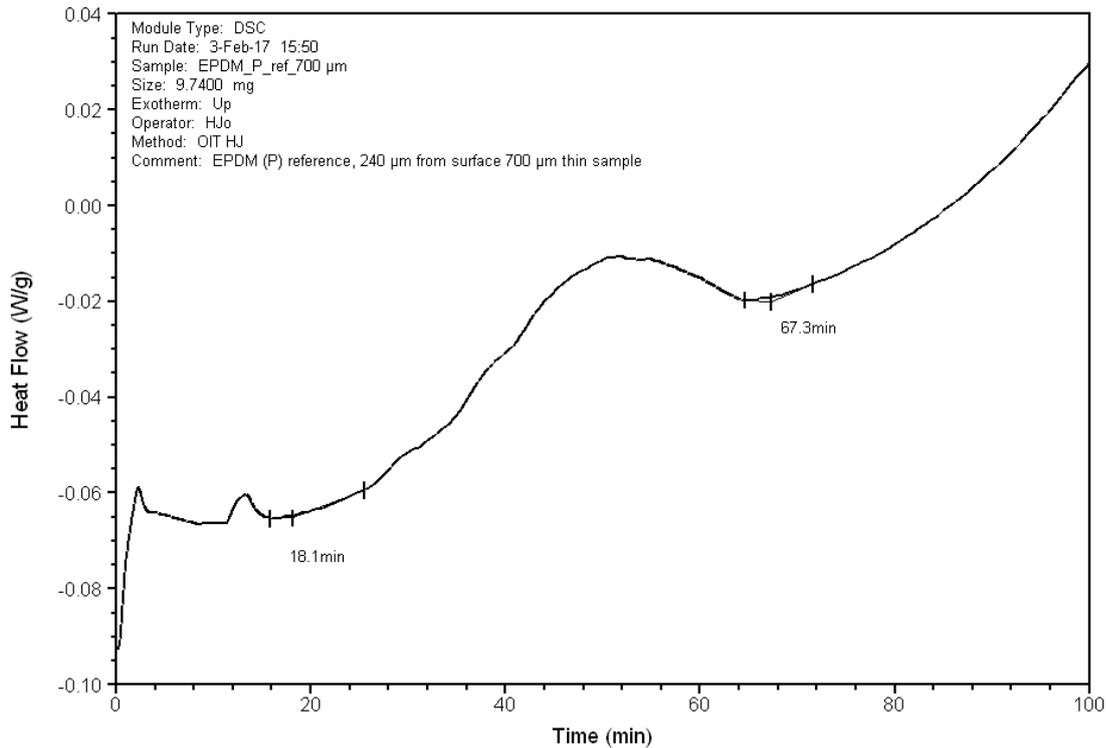


Figure 15: DSC thermogram for 700 μm thick sample prepared from 240 μm beneath the surface of reference sample.

In Figures 16 (from surface up to 270 μm deep) and 17 (from 270 μm to 690 μm) DSC thermogram for samples that had been aged 125°C are shown. The two recorded spectra seem to be very similar to each other. Also the calculated OITs are close to each other. This would indicate that similar oxidation conditions are present up to 690 μm from surface.

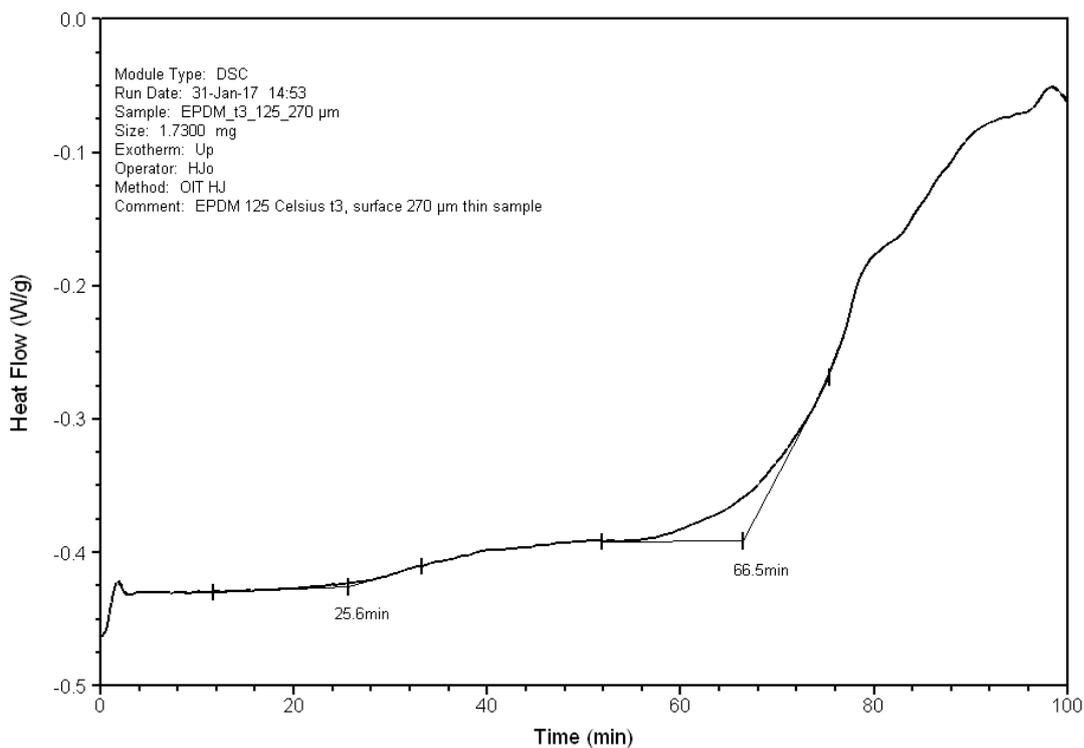


Figure 16: DSC thermogram for 270 μm thick sample prepared from the surface of sample aged at 125°C.

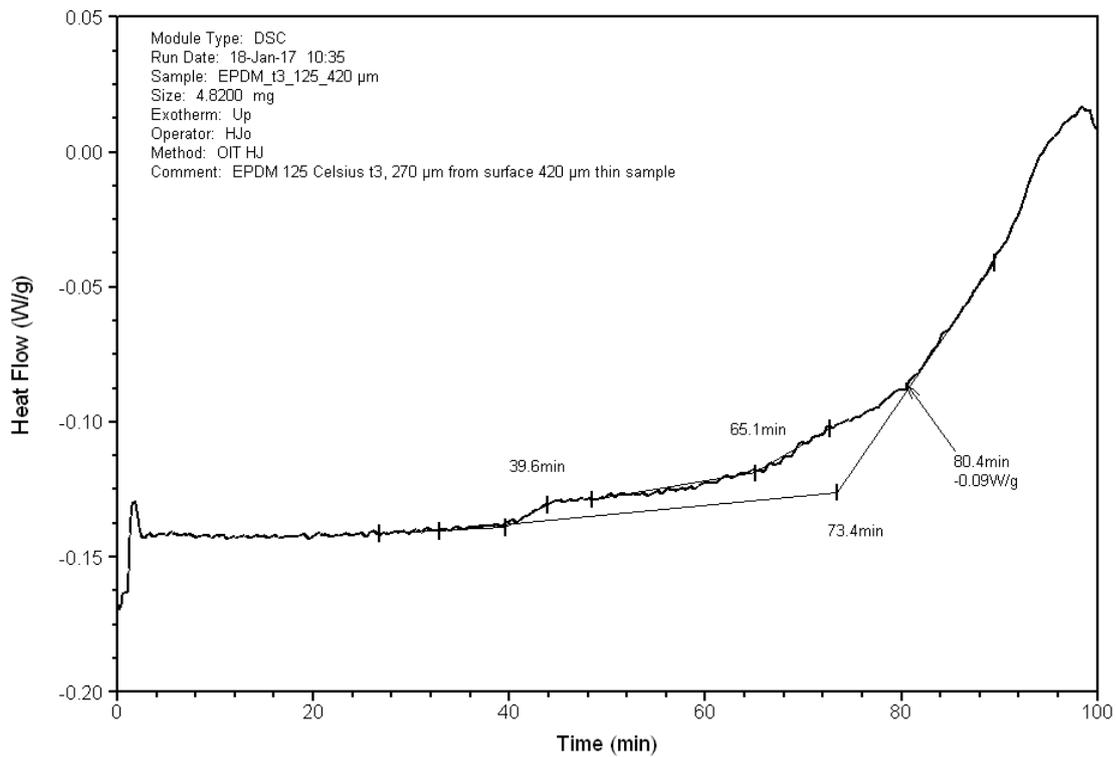


Figure 17: DSC thermograph for 420 μm thick sample prepared from 240 μm beneath the surface of the sample aged at 125°C.

Figures 18 and 19 show the two thermograms measured for samples irradiated with dose of 228 kGy. The surface sample (200 μm thick) in Figure 18 has clearly different thermogram than the sample analysed beneath it (200-610 μm). OITs differ by a factor of five.

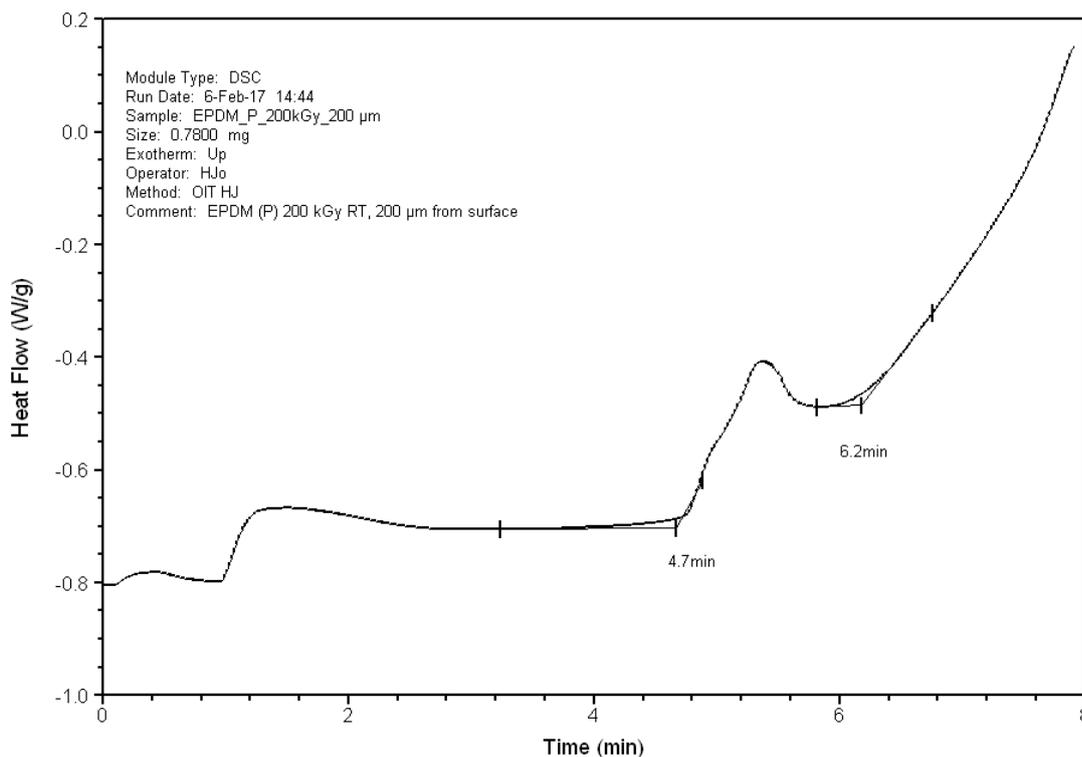


Figure 18: DSC thermograph for 200 μm thick sample prepared from the surface of sample irradiated with total dose of 228 kGy.

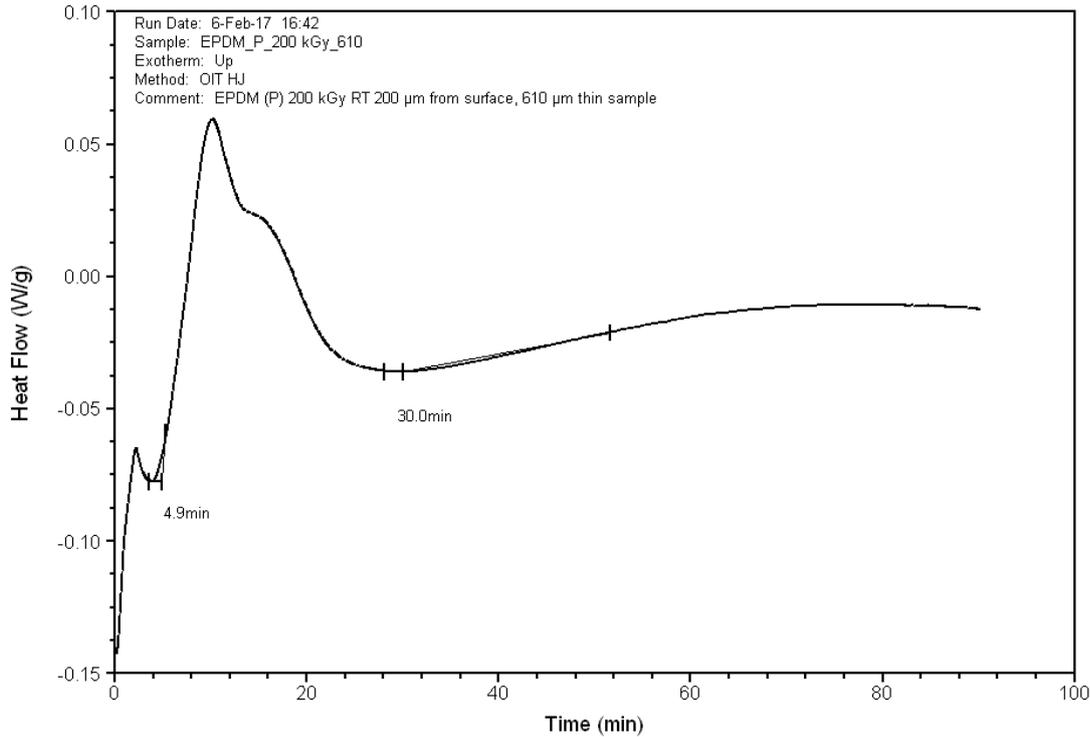


Figure 19: DSC thermograph for 410 μm thick sample prepared from 200 μm beneath the surface of the sample irradiated with total dose of 228 kGy.

In Figures 20-22 DSC thermograms for samples irradiated and thermally aged are shown. The measured spectra are similar in shape and the OITs are also similar independent from the sample distance from the surface. This is the reason why third sample was analysed deeper in the material. It seems that in this ageing condition samples are aged similarly up to distance of 1450 μm.

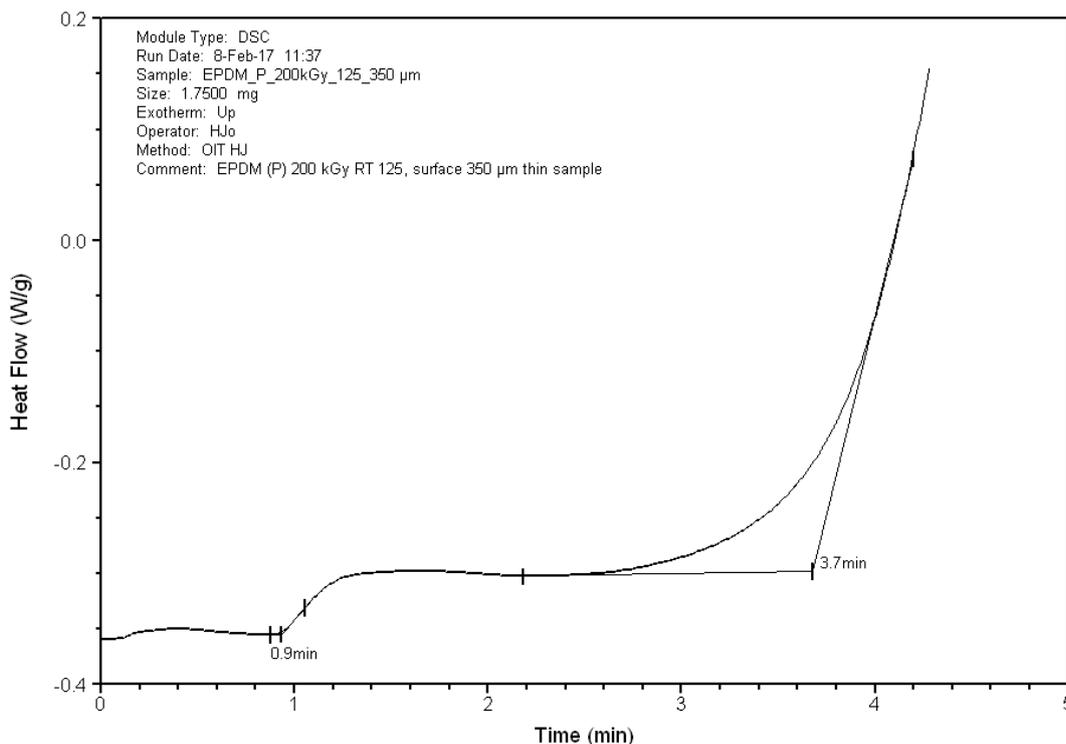


Figure 20: DSC thermograph for 350 μm thick sample prepared from the surface of sample irradiated with total dose of 228 kGy and thermally aged at 125°C.

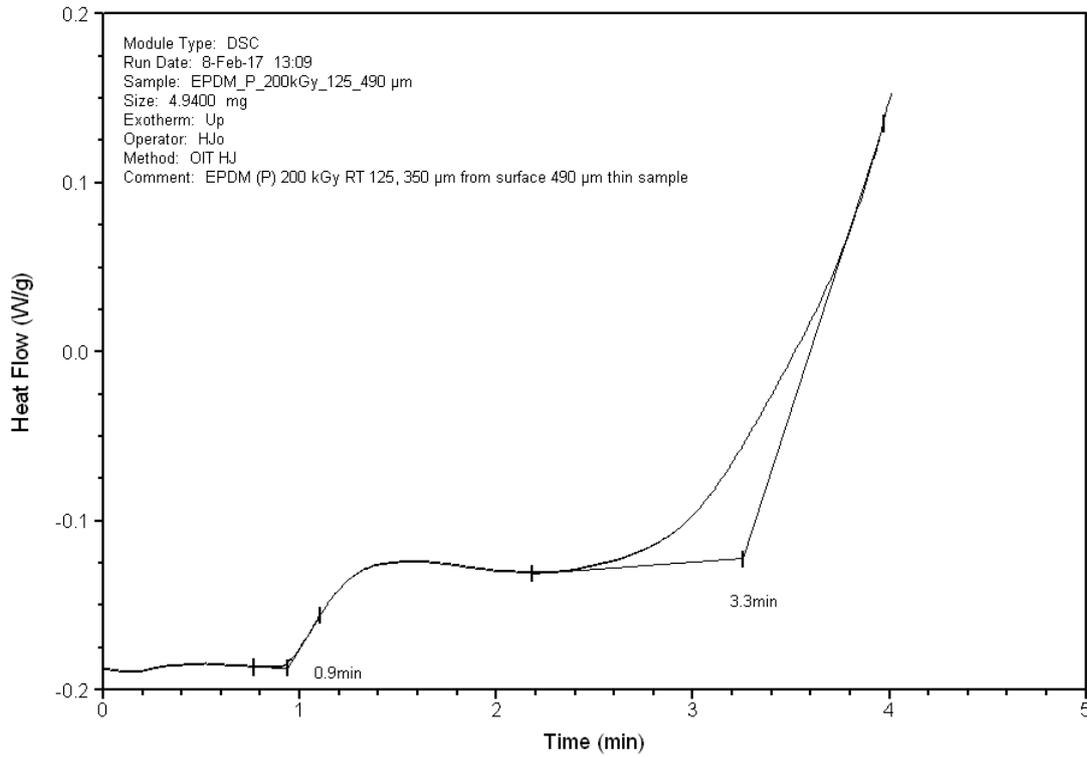


Figure 21: DSC thermograph for 490 μm thick sample prepared from 350 μm beneath the surface of the sample irradiated with total dose of 228 kGy and thermally aged at 125°C.

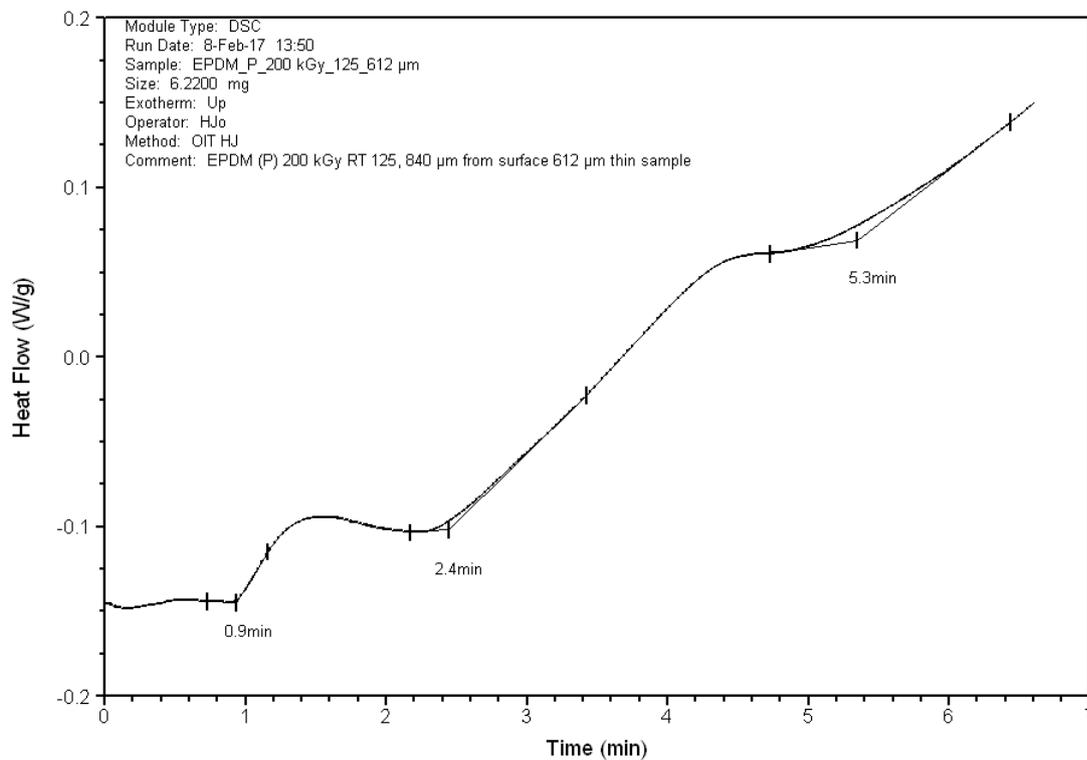


Figure 22: DSC thermograph for 612 μm thick sample prepared from 840 μm beneath the surface of the sample irradiated with total dose of 228 kGy and thermally aged at 125°C.

When the results obtained with DSC were compared to tensile results, it can be seen that similar trend between decreasing OIT and tensile properties could be seen with samples gone through irradiation treatment. The thermally only aged sample seemed to have similar OIT and mechanical properties than reference sample. When oxidation profile thicknesses of the two samples that received the 228 kGy dose of gamma radiation were considered, they seemed to be clearly different in thickness. However, the elongation at break value had decreased almost the same amount with both samples so no clear correlation between oxidation depth and mechanical properties could be drawn.

## 5. Conclusions

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Three different techniques ToF SIMS, FTIR and DSC were tested for analysis of oxidation behaviour of artificially aged EPDM samples. The samples were analysed from the surface towards bulk and the differences in oxidation were recorded. From the three different techniques ToF SIMS seemed to be most promising one in detection of oxidation. ToF SIMS showed good resolution but it was sensitive to unevenity of the surface. Thus more careful or advanced sample preparation is required in order to obtain sufficiently even surface for the analysis. The use of FTIR was shown to be very limited in case of EPDM since it was not applicable for samples that contained carbon black. However, if the used filler material did not absorb the used infrared beam, information on the oxidation products/change in composition of substances in the vicinity of the surface could be detected. DSC seemed also detect oxidation in the studied samples but the resolution was considered to be clearly below what ToF SIMS is capable. Although no clear correlation between material mechanical properties and formation of oxidation profile could be drawn with sulphur cured EPDM samples, it seems that thermo-oxidative ageing is more detrimental than radiation induced ageing. For the peroxide cured EPDM samples, plane thermal ageing did not yield in significant degradation and the radiation ageing was considered to be more detrimental for this material.

## References

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