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A methodology to investigate heterogeneous oxidation of thermally aged cross-linked polyethylene by ToF-SIMS

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Artificial ageing of polymeric insulation jackets is routinely performed in order to assess end-of-life material characteristics. Practical constraints including high temperatures/short times ageing treatments lead to strong influence of diffusion-limited oxidation (DLO) resulting in unreliable life-time predictions. This study proposes a new experimental approach to the investigation of cable insulation ageing, exploiting analytical techniques capable of resolving chemistry at the length scale relevant for DLO (nano-microscale). When studying the potential effects of DLO using time of flight secondary ion mass spectrometry (ToF-SIMS) sample preparation becomes crucial. This paper presents the development of a methodology to generate suitable specimens to investigate the DLO effect using ToF-SIMS. A reference polymeric material has been thermally aged in various DLO conditions. Cross sections of aged samples were generated using three different methods. In order to assess the most suitable approach for this study, cross-section topography were scanned using a profilometer and the surface chemistry was investigated using ToF-SIMS together with multivariate analysis methods.

KEYWORDS

DLO, heterogeneous oxidation, MVA, polymer ageing, ToF-SIMS, XLPE

1 | INTRODUCTION

Many control systems and materials used in second- and third-generation nuclear power plants (NPPs) were engineered and tested foreseeing an average operational lifetime of 40 years.[1] Currently, a considerable number of NPPs are reaching this operational lifetime threshold and should in principle cease their activity. However, given the high and continuous demand of energy and the delays in fourth-generation commercial reactor deployment, the possibility to extend the NPPs lifetime is now under evaluation, with extensions up to 60 years (in Europe) or even up to 80 years (in the United States), raising operational safety concerns. Therefore, potential effects of ageing over core plant structures need to be properly assessed and managed. One of the critical components for a safe operation of NPPs is the electrical cabling system.[2] There are typically around 1500 km cables in a NPP, used for diagnostics, control, and power transmission. Numerous studies have shown that upon ageing, the physical and electrical properties of the insulators composing these cables are degrading, raising concerns about a potentially critical component of the NPP operation. Evaluating and extrapolating the loss of function of these cables upon ageing beyond 40 to 60 years have been the object of many studies, which revealed the complexity of the mechanisms at play.

Accelerated artificial ageing, by means of thermo-oxidation, of cable polymeric insulation jackets was and is routinely performed in order to predict material performance decay.[3,4] Practical operative constraints including high temperature/short time artificial ageing treatments lead to strong influence of diffusion-limited oxidation (DLO) mechanisms that cannot be accounted for assuming a simple "Arrhenius-like" behaviour of volume-averaged mechanical and chemical properties resulting in unreliable life-time predictions when extrapolating material properties for long service times.[5,6] DLO occurs when the oxygen consumption rate exceeds the oxygen diffusion rate. Oxygen is primarily consumed at the surface limiting the supply of oxygen to the interior of the polymer resulting in heterogeneous, graded oxidation.

When studying heterogeneous oxidation at the microscale level, sample preparation becomes crucial. Several factors such as time, complexity, resources, and potential outcome are involved, and most of the times a compromise is required. This work presents the development of a methodology to prepare suitable specimens to investigate the effect of DLO on reference materials using time of flight secondary ion mass spectrometry (ToF-SIMS), to apply it subsequently to commercial cables used in NPPs.

An equivalent to the most used cable jacket insulator material in NPPs, cross-linked polyethylene (XLPE), has been thermally aged in various nonequilibrium DLO conditions.[7–10] A methodology to produce cross sections of XLPE in order to study the ageing effects with depth was developed, and the generated specimens were studied using a chemical analysis technique capable to resolve chemistry at the microscale such as ToF-SIMS. Additionally, to achieve a better understanding of the high amount of information present in ToF-SIMS mass spectra, a data analysis method related to multivariate analysis was proposed to obtain information about the spatial distribution of oxidized compounds.[11,12]

2 | EXPERIMENTAL

2.1 | Sample preparation

XLPE was produced at the University of Bologna and provided in the form of sheets. XLPE sheets were cut to a practical size (approximately 10 × 20 mm) with a thickness of 2 mm. Samples were thermally aged in air using a Memmert oven at 175°C for specific times up to 1000 hours. After ageing, cross sections were prepared in order to have access to in-depth polymer chemical information using several cutting methods as described below.

To avoid edge effects due to the diffusion of oxygen from different faces during the ageing treatment, only the central part of each specimen was used for this study. A considerable amount of XLPE was removed from each side and discarded resulting in specimens of approximately 5 × 10 × 2 mm. Given the large amount of specimens required for this work, several approaches were used searching to develop the most efficient methodology to achieve suitable cross sections for DLO-related studies. Three different approaches were adopted to obtain a cross section from each specimen. The initial approach consisted in a manual cut using a scalpel obtaining thick cross sections (∼1 mm). This procedure provides a rapid and straightforward cross-section preparation and easier sample handling. The second approach adopted was to use a rotatory ultramicrotome (Leica EM UC7). Ultramicrotome provides full control of thickness allowing the production of cross sections in the nanometre range; however, sample handling becomes significantly more complex and polymer deformation becomes an issue on highly aged samples. The last approach was to use a rotatory cryomicrotome (Leica CM1800 Cryostat). In this case, samples are embedded in a commercial water-soluble freezing tissue (Leica Biosystems) at low temperature to hold the sample and minimize sample deformation while cutting. The cutting is performed at −24°C and can also have a precise control of the thickness. After producing the cross sections, three washing cycles with deionized water at 40°C were performed in a vial with a stirring magnet to dissolve the possible remains of the embedding freezing tissue. Once cross sections were ready to analyse, they were mounted in a bar using double sided copper tape and transferred to load lock for pumping down before analysis.

2.2 | ToF-SIMS analysis

ToF-SIMS analysis was carried out using a ToF-SIMS IV system from IONTOF GmbH (Muenster, Germany). At least 5 mass spectra (both positive and negative polarity) were acquired on each specimen using a 25-keV Bi_3^+ primary ion beam operated in the high-current bunched mode. Given the high surface sensitivity of this technique, the top surface was sputtered for 60 seconds using an Ar_n^+ cluster ions source (Ar_{1300}^+) to eliminate any potential surface contamination before the measurements and as part of the freezing tissue removal procedure. The primary ion dose was kept below the static limit (10^{13} ions/cm^2). Due to the insulating properties of the specimens, a low-energy electron flood gun was used to eliminate charge build up on the surface during analysis. The raster area was 300 × 300 μm^2 for analysis and 800 × 800 μm^2 for Ar sputtering avoiding any potential edge effect.

2.3 | Data processing

ToF-SIMS mass spectra were preprocessed using the SurfaceLab software V6 (IONTOF GmbH). All mass spectra were calibrated using a unique mass list with a large number of masses to have reliable peak assignments. A peak list was created with more than 200 peak areas, and all assignments had a deviation below 100 ppm. The peak list was made of a combination of ion fragments from unaged and aged XLPE. Inorganic ion fragments as well as saturated peaks were excluded from the peak list, since the first ones would interfere in the variance and composition of the components hindering a potential semiquantitative analysis of the heterogeneous oxidation and the last ones would result in the generation of extra components describing the nonlinear intensity variation of saturated peaks.[13]

The large and complex ToF-SIMS data sets were processed using simsMVA software (http://mvatools.com).[14] Images of selected peaks were exported as BIF6 files and loaded into the imaging mode of simsMVA. For each specimen, three images were loaded and stitched forming a unique image of dimensions 300 × 900 μm^2. The stitched data were normalized by total ion intensity, Poisson scaled, and mean centred [only for principal component analysis (PCA)]. PCA was then performed to obtain information of the number of components describing the data. This information was taken into account for the non-negative matrix factorization (NMF) analysis.[15] These data analysis methods are known for decreasing significantly the dimensionality of the data resulting in faster processing times and easier extraction of information.

3 | RESULTS AND DISCUSSION

The complexity of sample preparation increased with the ageing time applied. When XLPE is thermally aged, chemical and mechanical properties change[16] decreasing the polymer resistance to deformation and complicating the production of flat and undamaged cross sections. Any approach delivering suitable cross sections from a sample of a certain ageing time was also valid for samples aged for lower times. Therefore, this paper will focus on the results from samples with long ageing treatment. In order to compare the three approaches, this work will present the results of XLPE aged for 100 hours because it was not possible to produce undamaged cross sections from XLPE aged for times over 100 hours using an ultramicrotome, since the highly aged polymer showed significant deformation while cutting towards the outer part of the sample, where the DLO effect is more pronounced.

Figure 1 shows ToF-SIMS mass spectra from three specimens aged at 175°C for 100 hours and produced with the approaches described in Section 2.1. Each spectrum shows the same peak corresponding to a characteristic XLPE fragment ($C_4H_6^+$) at nominal mass 54. It can be seen that the mass resolution at this peak is considerably different in each spectrum. Spectrum acquired from cross sections produced using a scalpel had the lowest mass resolution (3600) at nominal mass 54, followed by the specimens produced using an ultramicrotome (4600). The best peak mass resolution was achieved on cross sections generated using a cryomicrotome with values over 6500 at that nominal mass. Figure 2 shows ToF-SIMS total count images acquired on the same cross sections. Figure 2A shows a 300 × 300 μm^2 image of the specimen produced using a scalpel. It can be seen an uneven distribution of counts in one direction. This decrease in counts is usually related to a continuous relative increase or decrease of the specimen thickness in a certain direction, which might have been induced by the manual cutting since the cutting angle is not accurately controlled.

Time of flight mass spectrometer measures the time that an ion takes to travel a known distance to determine its mass-to-charge ratio. Specimen height variation will make ions coming from different regions of a scanned area to travel slightly different paths resulting in

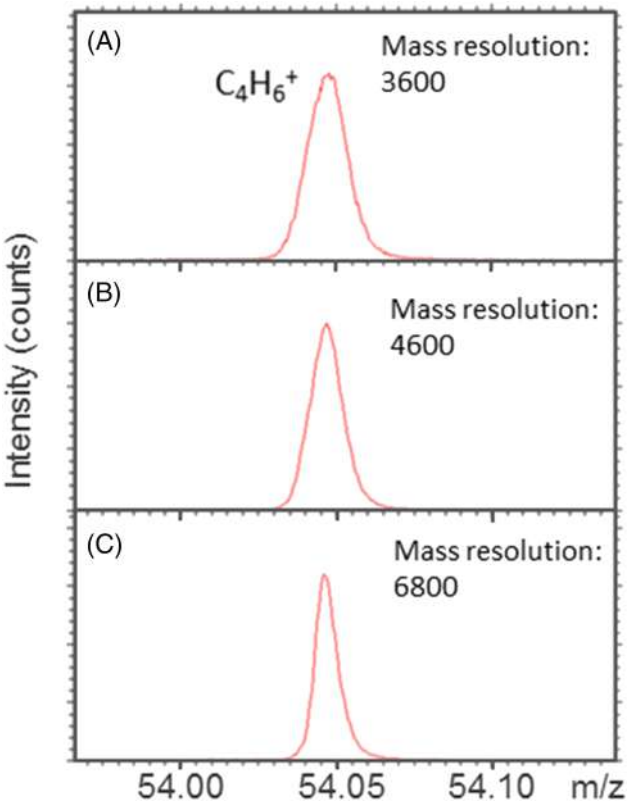

FIGURE 1 Time of flight secondary ion mass spectrometry spectra (positive polarity) from three specimens produced using a scalpel (A), an ultramicrotome (B), and a cryomicrotome (C). Each spectrum shows the same peak corresponding to a characteristic cross-linked polyethylene fragment ($C_4H_6^+$) at nominal mass 54

different flight times. Depending on how large the height variation is, the ions can either reach the detector with a slight flight time difference broadening the peaks and thus decreasing the mass resolution (Figure 1A) or not reaching the detector at all (Figure 2A). Figure 2B shows a 100 × 100 μm^2 image of the same specimen with low counts towards the edges and poor spatial resolution. Reducing the area of analysis might decrease the effect due to the height variation but could cause other negative effects related to charging build up on the top surface. Specimen thickness and raster area are two important parameters when analysing insulators with ToF-SIMS since differential charging might increase with thickness and with the reduction of the raster area having a negative impact in data quality.[17] Sample thickness enhances the insulating properties of the polymer hindering charging dissipation, and a small beam raster pattern increases the chances of scanning adjacent pixels in a short period of time not allowing enough time for accumulated charge to dissipate. Figure 2C shows an image of the specimen produced using an ultramicrotome. Overall, thinner cross sections (~60 μm) and control of the cutting angle seem to have contributed to a mass resolution improvement and a better image definition. However, well-defined features containing lower counts are distinguished, which might be related to surface roughness induced by the cut. Figure 2D shows an image of a cross section of approximately 60 μm in thickness produced using a

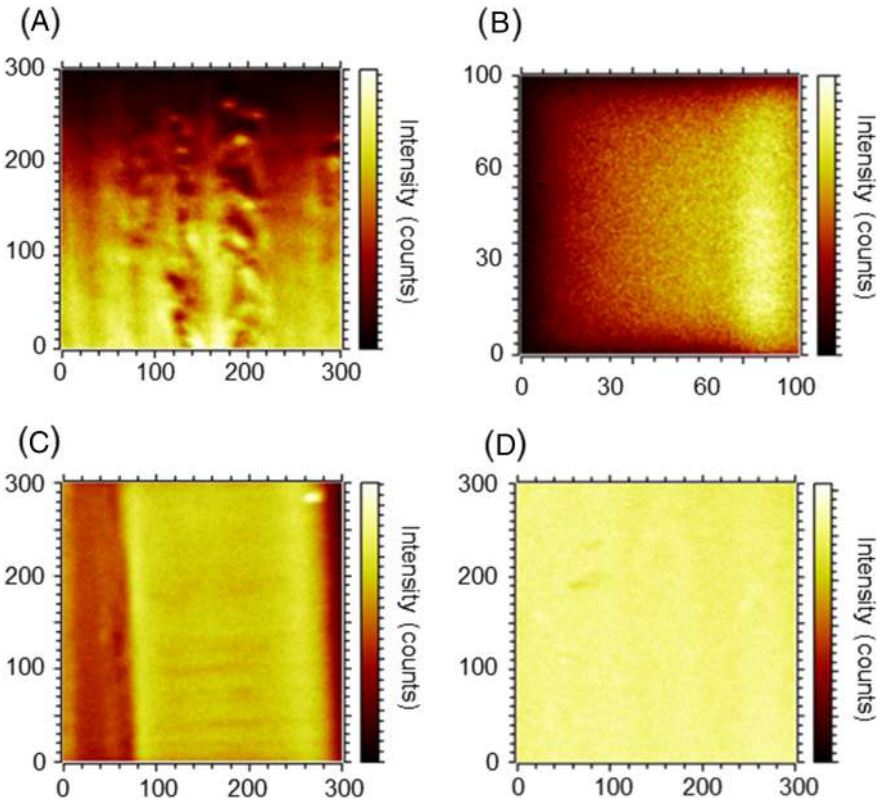

FIGURE 2 Total count time of flight secondary ion mass spectrometry images from three specimens produced using a scalpel (A-B), an ultramicrotome (C), and a cryomicrotome (D). Specimen thickness was of approximately 1 mm for (A-B) and 60 μm for (C-D)

cryomicrotome. In this case, a homogenous count distribution over the entire analysis area is seen without appreciable signs of charging or significant roughness. This surface homogeneity together with the high mass resolution achieved suggests that cryomicrotome is the best approach to produce suitable cross sections for this study.

A crucial factor of the successful preparation of suitable cross sections using a cryomicrotome was the embedding freezing tissue. The embedding tissue together with the low temperature provided sample support reducing significantly potential deformation while cutting. However, because the freezing tissue contains oxygen, it needed to be totally removed from the cross-section surface to avoid interferences with the heterogenous oxidation studies. Washing cycles with deionized water as well as argon cluster sputtering were performed to eliminate the water soluble embedding freezing tissue from the surface. Mass spectra from different sample sets were acquired and processed to assess the degree of freezing tissue removed from the specimen surface. Figure 3 shows a plot with a vertical axis representing the combination of intensities of some XLPE characteristic fragments ($C_4H_7^+$, $C_5H_9^+$, $C_5H_7^+$, and $C_7H_{11}^+$) and a horizontal axis representing a combination of intensities of some characteristic oxygen-containing fragments from the embedding tissue (CH_3O^+, $C_2H_3O^+$, $C_2H_4O^+$, $C_2H_5O^+$, $C_2H_6O^+$, $C_3H_5O^+$, and $C_3H_6O^+$). Before washing, the plot shows a significant surface contamination on specimens produced with the cryomicrotome due to the embedding tissue. The subsequent washing procedure removed a significant amount of the tissue, but it did not achieve a strong reproducibility based on the dispersion observed on the measurements acquired on washed specimens. In contrast, the washing procedure followed by argon cluster sputtering appeared to be highly reproducible and the intensity of oxygen-containing fragments was lower than for the pristine XLPE, indicating not only a complete removal of the freezing tissue but also the elimination of adventitious contamination commonly found in most surfaces.

However, when using sputtering methods in polymers, there is always concern regarding polymer damage induced by the sputter ion beam itself. To investigate any possible damage due to the sputter source, the combination of intensities of some characteristic XLPE fragments ($C_4H_7^+$, $C_5H_9^+$, $C_5H_7^+$, and $C_7H_{11}^+$) was plotted for each argon sputter scan (4.4 s/scan) in pristine XLPE as shown in Figure 4. The intensity of these fragments showed a sharp increase due to the removal of adventitious contamination during the first seconds of sputtering and stayed constant for the rest of the experiment (96.8 s). This proved that the 60-second sputter cleaning used to remove the freezing tissue was not damaging the polymer confirming to be a suitable cleaning method for this study.

In order to have a better understanding of the effects of specimen preparation on the ToF-SIMS characterization, a profilometer (Alpha-Step IQ) was used to obtain topographic information of the samples produced by the three approaches. Several measurements of 2-mm distance were performed in each specimen. The first analysis carried out was the assessment of the specimen flatness. The difference in height within a specimen was obtained from the first and last points of each scan, and the cutting angle was calculated. Cross sections produced using a scalpel showed to have an average difference in height of ~80 μm within the 2-mm scan length and a cutting angle of 0.039° ± 0.012° explaining the uneven distribution of counts

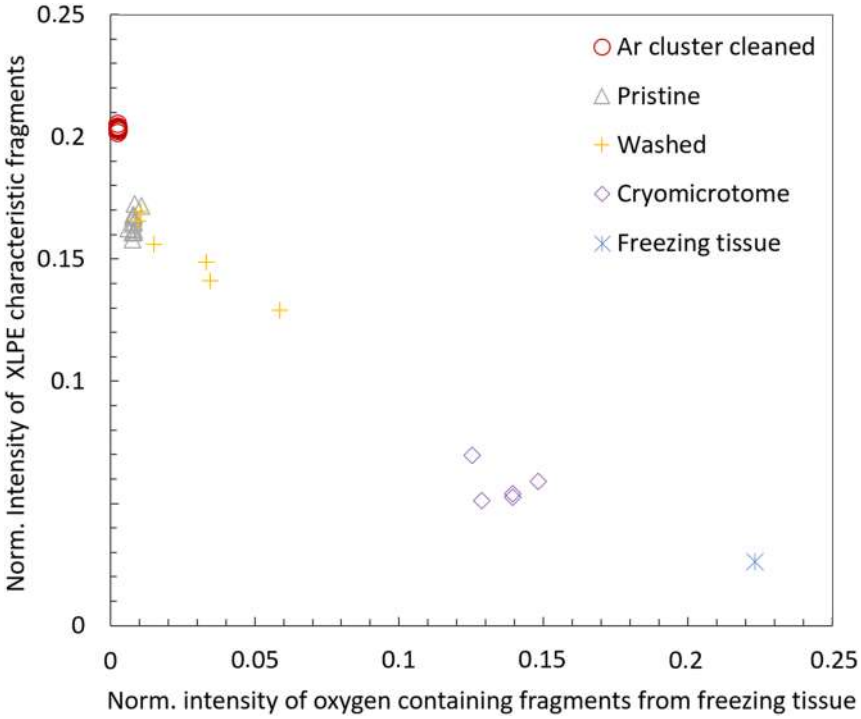

FIGURE 3 A plot showing the normalized intensities of cross-linked polyethylene (XLPE) characteristic fragments ($C_4H_7^+$, $C_5H_9^+$, $C_5H_7^+$, and $C_7H_{11}^+$) against normalized intensity of some characteristic oxygen-containing fragments (CH_3O^+, $C_2H_3O^+$, $C_2H_4O^+$, $C_2H_5O^+$, $C_2H_6O^+$, $C_3H_5O^+$, and $C_3H_6O^+$) from the embedding tissue of five different samples

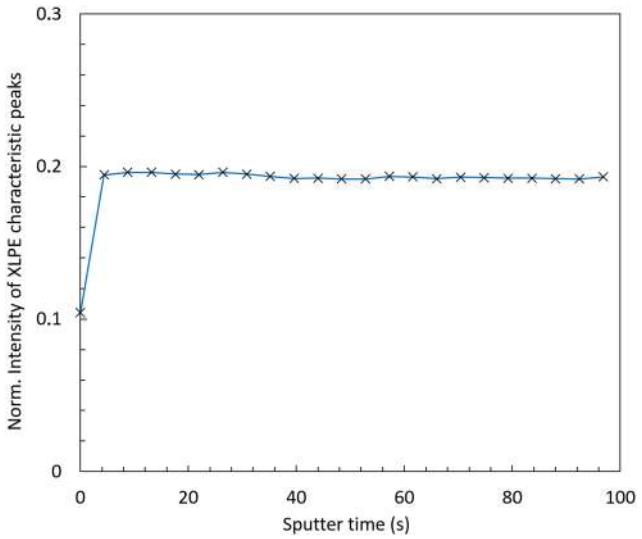

FIGURE 4 Time of flight secondary ion mass spectrometry depth profile showing the combination of intensities of cross-linked polyethylene (XLPE) characteristic peaks ($C_4H_7^+$, $C_5H_9^+$, $C_5H_7^+$, and $C_7H_{11}^+$)

shown in Figure 2A and the low mass resolution. Cross sections produced with ultramicrotome and cryomicrotome had an average difference in height of approximately 1 and 0.5 μm within the scan length and a cutting angle of 0.004° ± 0.002° and 0.0015° ± 0.0007°, respectively. The second analysis performed was the assessment of the surface roughness. The surface profile was obtained setting a constant cut-off of 80 μm for all the specimens. Figure 5 shows three graphs illustrating also the surface profile of the three different specimens. While the surface of the specimens cut with a scalpel presented a moderate low roughness (average Ra of 0.16 ± 0.04 μm), the smallest surface roughness was observed in the specimens cut with the cryomicrotome, with an average Ra of 0.06 ± 0.01 μm (Figures 5A and 5C, respectively). Specimens produced with the ultramicrotome showed the largest average Ra (0.41 ± 0.02 μm) with localized regions of ~6 μm of height difference (Figure 5B), which could be the reason of the well-defined features containing lower counts shown in Figure 2C. This localized roughness could be attributed to the polymer deformation during cross-section generation.

Taking into account all the results presented above, cryomicrotome followed by three washing cycles and Ar sputtering was the approach adopted for the preparation of cross sections to study the heterogeneous oxidation of thermally aged XLPE. NMF analysis was performed on ToF-SIMS images acquired from unaged and aged specimens (175°C for 300 h). Based on PCA results, two NMF components were considered. The first one represented the untreated XLPE, containing CxHy type of fragments, while the second one comprised also oxygen-containing fragments describing the XLPE oxidation. The relative intensity of this component is visualized in Figure 6 with a range of colours being cyan the lower intensity and yellow the highest. The left side of the cross-section image shows the outer part of the polymer, whereas the right side shows the most inner part (bulk). The NMF component spatial distribution over the cross section shows a clear heterogeneous oxidation with its highest degree concentrated along the surface. The results obtained indicate that ToF-SIMS technique is able to provide robust data about the heterogeneous oxidation of polymeric insulation jackets, provided that a suitable sample preparation protocol is followed to produce high-quality surfaces.

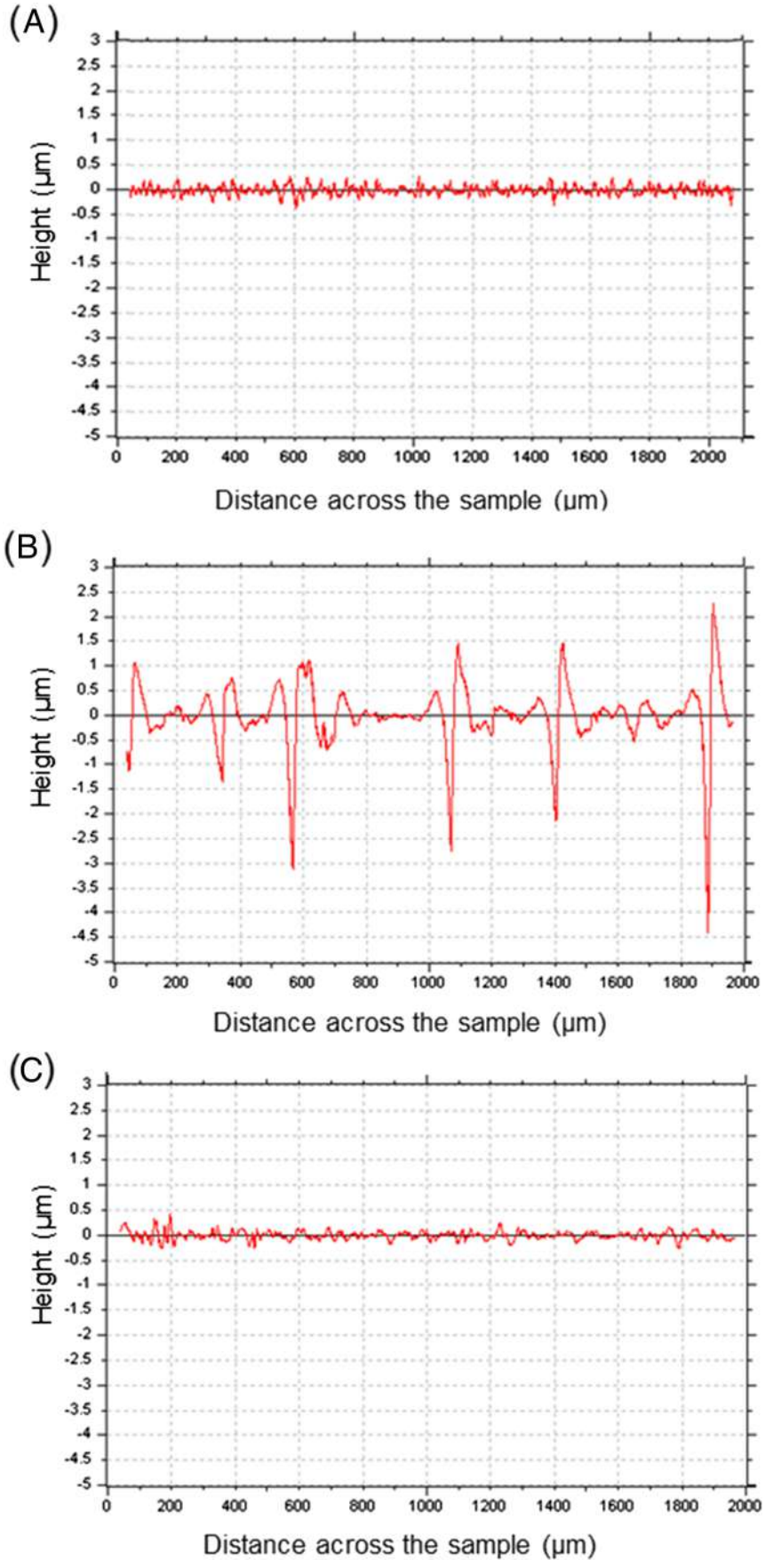

FIGURE 5 Three graphs showing the surface roughness of three specimens generated using a scalpel (A), an ultramicrotome (B), and a cryomicrotome (C)

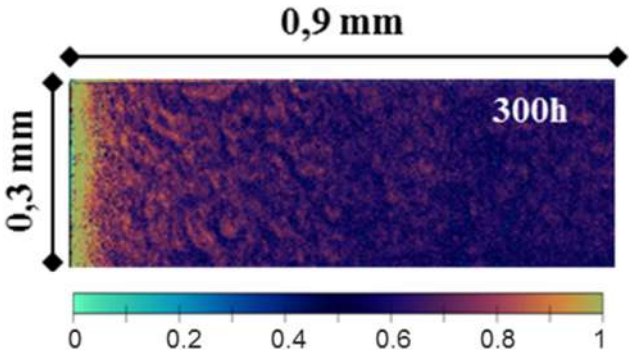

FIGURE 6 Cross-section image showing the spatial distribution of the nonnegative matrix factorization component representing the cross-linked polyethylene oxidation on a specimen aged at 175°C for 300 hours. The change of colour is the signature of the diffusion-limited oxidation effect

4 | CONCLUSIONS

This work reported the successful development of a suitable methodology to expose the cross section of aged XLPE to study the effect of DLO at microscale level. Cryomicrotome showed to be the most appropriate cutting instrument obtaining the lowest degree of roughness and best cutting angle control, which is crucial for ToF-SIMS analysis. Moreover, the combination of the washing procedure with the argon cluster sputtering showed to be an effective approach to remove the embedding tissue, producing clean and undamaged cross-section surfaces. ToF-SIMS analysis together with multivariate analysis was able to show the distribution in depth of the heterogeneous oxidation induced by the DLO effect during the thermal treatment.

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REFERENCES

1. International Atomic Energy Agency. Management of life cycle and ageing at nuclear power plants: improved I & C maintenance: report prepared within the framework of the technical working group on nuclear power plant control and instrumentation. International Atomic Energy Agency; 2004.
2. *Assessment and management of ageing of major nuclear power plant components important to safety: in-containment instrumentation and control cables volume* I; 2000.
3. Duckworth RC, Kidder MK, Aytug T, Fifield LS, Glass W III, Davis S. Mechanical and chemical properties of harvested Hypalon cable jacket subjected to accelerated thermal aging. *Nucl Technol*. 2018;1-8.
4. Cinquin J, Colin X, Fayolle B, et al. Thermo-oxidation behaviour of organic matrix composite materials at high temperatures TL - 3. *Adv Aircr Spacecr Sci*. 2016;3(VN-re(2)):171-195.
5. Celina M, Gillen KT, Assink RA. Accelerated aging and lifetime prediction: review of non-Arrhenius behaviour due to two competing processes TL-90. *Polym Degrad Stab*. 2005;90(VN-r(3)):395-404.
6. Celina MC. Review of polymer oxidation and its relationship with materials performance and lifetime prediction TL-98. *Polym Degrad Stab*. 2013;98(VN-r(12)):2419-2429.
7. Onr. *ENSREG topical peer review on ageing management—United Kingdom National Assessment Report*.
8. *Spanish National Assessment Report on Ageing Management of the Spanish Nuclear Power Plants Topical Peer Review 2017*.
9. *Report by the Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety (BMUB) on topical peer review ageing management of nuclear power plants and research reactors*; 2017. http://www.bmub.bund.de
10. *Safety assessment of nuclear facilities in France ageing management*; 2017.
11. Lee JLS, Gilmore IS, Fletcher IW, Seah MP. Multivariate image analysis strategies for ToF-SIMS images with topography. *Surf Interface Anal*. 2009;41(8):653-665.
12. Trindade GF, Abel M-L, Lowe C, Tshulu R, Watts JF. A time-of-flight secondary ion mass spectrometry/multivariate analysis (ToF-SIMS/MVA) approach to identify phase segregation in blends of incompatible but extremely similar resins. *Anal Chem*. 2018;90(6):3936-3941.
13. Graham DJ, Castner DG. Multivariate analysis of ToF-SIMS data from multicomponent systems: the why, when, and how. *Biointerphases*. 2012;7(1):49.
14. Trindade GF, Abel M-L, Watts JF. simsMVA: a tool for multivariate analysis of ToF-SIMS datasets. *Chemom Intel Lab Syst*. 2018;182:180-187.
15. Trindade GF, Abel M-L, Watts JF. Non-negative matrix factorisation of large mass spectrometry datasets. *Chemom Intel Lab Syst*. 2017;163:76-85.
16. Boukezzi L, Boubakeur A, Laurent C, Lallouani M. Observations on structural changes under thermal ageing of cross-linked polyethylene used as power cables insulation. *Iran Polym J*. 2008;17:611-624.
17. Cushman C, Zakel J, Fisher L, Banerjee J, Lunt BM, Smith NJ, Linford MR. Sample charging in ToF-SIMS: how it affects the data that are collected and how to reduce it. Vac Technol Coat. March 2018, 23-28.

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