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Modelling the uptake of suspended materials and salts in nearshore waters by plastics using nuclear microscopy and depth profiling analytical tools



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ABSTRACT

Plastic debris becomes a persistent contaminant in aquatic systems. The adherence of abiotic and biotic materials to plastics may potentiate structural changes and their degradation. How the major and minor elements present in sea water interact with polymers is largely unknown.

Nuclear microprobe clusters PIXE and RBS techniques, which offer unique possibilities to characterize the materials deposited on the surface of plastics rejected to the aquatic environment. In particular, these techniques enable to examine the penetration of elements in deposits into the plastic structure. Food packaging polymers, high-density polyethylene (HDPE) and polyethylene terephthalate (PET) exposed to turbid water of the Tagus estuary were studied. The deposition mosaic contained clastic, biota and saline components. A major finding was the diffusion of the ion Cl⁻ in the polymer matrix. This was possible by examining elemental profiles taken in transversal sections of the polymers. The depth structure of deposits was estimated using RBS and PIXE data applying the programs OMDAQ2007 and WiNDF, which illustrate the capabilities of these analytical tools in the micro-scale analysis of deposits. The results obtained pointed out for a multilayer depth structure which can decode the complex arrangement of cellular and sediment materials deposited on the polymer's surface. In addition, it was possible to identify sources of uncertainties in simulating the interface and the changeable polymer matrix in sub-surface layers.

1. Introduction

Increasing amounts of floating plastic debris in rivers, estuaries and sea is a preoccupying environmental and toxicological issue [1]. Over time, plastics break down into smaller pieces due to weathering, such as sunlight exposure, oxidation, waves action, currents, and grazing forming particles with less than 5 mm, the so called microplastics [2,3]. It is currently consensual that the adherence of biota and inorganic suspended particles, as well as soluble materials to plastics eventually interacts with polymers. Besides the concentration of these constituents in the plastic particles, it favours their structural changes, degradation and fragmentation [4–6]. However, how abiotic (earth crust materials and saline compounds) and biotic materials in water interact with the polymers and promote their ageing process is still an open question.

Recent studies point out for a possible sorption of those materials by the polymer, which may be dependent on the plastic chemical nature [7,8]. Other possible process involves adherence of clastic materials to plastics increasing oxidized moieties [9] that in turn facilitate the adhesion of microorganisms. These synergistic events persist through time leading to a relatively steady film covering the plastic material, which may favour the weathering of the surface of the polymer [5,6].

Measurements of chemical elements deposited on plastics at a microscale are virtually lacking. Especially, how major constituents of seawater, e.g., the elements Cl, Na, S, Ca, K and Br, interact with polymers is largely unknown.

Microbeam capabilities offer unique possibilities to characterize the complex deposits on the surface of daily use plastics, which are rejected to the marine environment. Nuclear microscopy, which mainly clusters

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PIXE and RBS techniques together with ion beam analytical tools, such as OMDAQ2007 [10,11] and WiNDF [12,13], enable us to characterize the depth structure of the deposits and assess the depth distribution of elements in the deposit and inside the polymer matrix [14–17]. This will help reconstructing a 3-dimentional picture of the deposits and characterize polymer matrix changes. The objective of this study is thus to examine the elemental composition of deposits in plastics exposed to a turbid estuarine environment and to learn about the depth penetration of key elements into the plastics.

2. Materials and methods

Food packaging polymers, such as high-density polyethylene (HDPE) and polyethylene terephthalate (PET) were exposed to turbid water of the Tagus estuary for 30 days. Pieces of these polymers of

approximately of $2.5 \times 5 \text{ cm}^2$ suspended in the upper of the water column were used. After exposure, samples retrieved from the site were air dried. Pieces of approximately 0.5 cm^2 , representative of high and low deposition areas, were cut for further nuclear microscopy analysis. For precise and clean cuts a surgical blade was used. Pristine HDPE and PET samples were used as controls.

The polymer materials were analysed at the nuclear microprobe facility of IST/CTN [18,19]. A proton beam of 2.0 MeV and 100 pA current focused to a $3 \times 3 \mu m^2$ spot size was used. PIXE and RBS analysis were carried out simultaneously to assess the micro-distribution maps of elements on the surface (surface analysis) and in cross sections (transversal analysis) of the HDPE and PET samples. Elemental profiles were also obtained in selected regions of transversal sections. Acquisition of data was performed using OMDAQ (Oxford Microbeams Ltd, UK) [20].



Fig. 1. Deposition mosaic in PET and HDPE exposed to turbid waters. Low (A) and high (B) deposit regions on PET containing marine organisms and sediments. (A) isolated cell (Ca map) -surrounded by sediment material (Si, Fe maps) and saline deposits (Cl map); the red dashed lines delineate the cell contour depicted in the Ca map. (B) Complex layered arrangement of sediment materials, saline deposits and cells likely observed in (A). High-loaded sediment area in a PET sample (C) and low-loaded deposit area in HDPE (D), showing identical pattern for the elemental composition of sediment materials (e.g., Si, Fe, K); the Cl distribution, mostly associated to sea salt showed a different pattern (as in A and B panels). Content gradient is represented by a colour dynamic scale: high content – red, low content – blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The polymer samples were mounted on a sample stage with a goniometer that enabled the positioning of the samples to produce elemental mapping of the surface deposits and of the transversal sections of the polymers. Prior to analysis the polymer samples were carbon coated to avoid charge build up.

The analysis of PIXE and RBS data obtained in surface mapping and transversal profiles was carried out using software analytical tools: (i) OMDAQ 2007 (Oxford Microbeams Ltd, UK), which includes RBS spectra simulation and fitting module to estimate the sample matrix composition while providing beam charge normalization together with an interface for GUPIXWIN [21,22] for quantitative elemental PIXE data [10,11]; (ii) WiNDF V9.3.42 [12] to define a high-resolution depth profile structure of the deposit and changes of the polymer matrix interface. WiNDF combines RBS and PIXE data for multi-layered structured samples in which elemental PIXE yield is calculated from the found RBS solution and compared with elemental PIXE spectra intensity in order to find a consistent sample depth profile solution [12]. In both OMDAQ2007 and WiNDF approaches the depth profile is represented by finite layers with constant concentrations [14].

3. Results and discussion

3.1. Elemental and morphological characterization of the polymer's deposits

In both HDPE and PET the deposition mosaic consisted of abiotic and biotic components. The deposits showed saline compounds, sediment-like materials and a large diversity of organisms dispersed in a non-homogeneous manner and arranged in a complex layered distribution, as can be depicted in Fig. 1. Biota can be easily identified through the Ca map, as calcium carbonate is the building block for the cell walls, shells and skeletons of many marine organisms [23]. Moreover the geometry of the forms looks like cell walls. Marine organisms are intertwined with sediment materials that can be inferred by Si, Fe and K maps, and saline deposits such as Cl (see Fig. 1-A and B) even when cells are isolated in regions with very low deposit (Fig. 1-A). This distribution pattern suggests an association of biota with sediment materials that may stabilize the adhesion to the polymer substrate. Sediment materials consisted of a variety of grain sizes, probably a mixture of silt, clay or other constituents (as inferred by Si, Ti, Fe, K and Ca maps) and salt particles (e.g., Cl) (Fig. 1-C). These elemental signatures are also present in regions of the plastics with very low deposits (Fig. 1-D). However, the distribution of Cl followed a pattern different from the other elements in the sediment material. This was also evident in panels A and B of Fig. 1, where Cl particles that populate the deposit regions showed well defined boundaries likely crystals of sea salt and were not correlated with major sediment grains or cells.

3.2. Elemental distribution profiles of the polymer cross section

The polymer matrices and deposits were also inspected by transversal analysis. By rotating the samples of 90°, the cross section of the polymer could be scanned and line profiles produced in regions of interest. These line profiles were taken in both pristine (control) and exposed samples. In the latest, high-loaded regions, low-loaded regions



Fig. 2. Images of surface analysis of pristine PET (A) and HDPE (D), transversal scans of the respective cross section (B and E), and elemental profiles for the line scans indicated by the red line on transversal maps (C and F). The content gradient in elemental maps is represented by a dynamic scale: high content – white, low content – black. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. Elemental profiles in PET (A) and HDPE (B) samples with deposit. The origin of the depth scale was set for the 90^{0} aligned edge of the polymer using the C signal (major element in the polymer matrix). The peaks at the left (negative values of the depth scale) correspond to elements detected in the deposit. The homogeneous distribution of Ti and the granular inclusions of Ca in the HDPE matrix can be depicted. A diffusion of Cl in both PET and HDPE matrices can be clearly denoted. The PET graph (A) only shows the aligned edge of the polymer cross section. The HDPE graph (B) shows the entire cross section of the polymer, thus the deposit on the opposite surface (depth > 320 mm) is also partially visualized.

and virtually clean regions of the plastic sample were examined. The number of counts for each element in the PIXE and RBS spectra was plotted in function of depth. Only one edge was analysed at a time, due to the system geometry.

3.2.1. HDPE and PET polymers characterization

The results obtained for the pristine polymers, showed that PET is a very uniform material (Fig. 2A, B and C). The HDPE polymer used in the study contained Ti homogeneously distributed in the C matrix and Ca in grain-like structures (Fig. 2D and E). These features can be clearly inferred in surface and transversal analysis and in elemental profiles (Fig. 2C and F).

3.2.2. Elemental profiles of polymer's cross-sections with deposits

In Fig. 3 cross section analyses of PET and HDPE samples of a highload deposit region are displayed. The selected cases illustrate the profiles of elements detected in the PIXE and RBS spectra in the polymer's cross section. The plastic surface was set visually by the user using the C signal from RBS spectra to define the edge of the polymer. This boundary was taken as the zero depth. The elemental distributions showed that deposits can be easily identified by well-defined peaks of several elements (e.g., Si, K, Ca, Ti, Fe) in front of the substrate edge. The elemental profiles of polymer's cross-sections enabled to have an estimation of the deposit thickness. A Gaussian fit of the peaks of individual elements provided a consistent estimation of the width of the deposit in each sample. For the line scans plotted in Fig. 3, the deposit widths were of $9-15\,\mu$ m in PET and $14-18\,\mu$ m in HDPE. However, the calculated deposit width is just indicative and comparison between samples not straightforward.

The observations suggest relevant Cl diffusion in the polymer matrix in both PET and HDPE (see Fig. 3 A and B). However, the Cl diffusion into the plastic was largely nonhomogeneous. In some regions a relevant diffusion occurred whereas others are devoid of Cl, as illustrated by the images of the transversal sections of both polymers in Fig. 4. There was no evidence of diffusion for any other element detected.

This procedure had limitations in what concerns assessing penetration profiles at the deposit-polymer interface. The major limitations were imposed by the lateral resolution of the beam and the demarcation of the polymer boundary defined visually by the user.

Nevertheless, the surface and transversal characterization of the polymers enabled us (i) to associate elemental composition with sediment deposits and identify biological colonization of the plastic surface, (ii) to evaluate the magnitude of the thickness of the deposits, and (iii) to establish elemental profiles which permitted to identify the nonhomogeneous diffusion of Cl in both polymer matrices.

3.3. Evaluation of depth structure of deposits

The cross-section analyses of the polymers did not provide information about the structure of the deposits, despite important information about the elemental composition of those deposits and the spreading of Cl inside the polymer's matrix. Besides, the manipulation of the sample may create artefacts as particles of the deposit can be dragged or splashed to the cross section during cut. Also, transversal analysis of thin plastics (< 100 μ m) will be demanding.

Therefore, it is important to translate the results obtained in transversal analysis to surface analysis. This is possible by using RBS data of surface analysis and the ion beam tools OMDAQ 2007 and WiNDF programmes that enable to estimate the structural composition of the deposit and to examine the deposit-polymer interface and the changes of the polymer matrix. The rationale of using RBS data of surface analysis is the better depth resolution achieved with RBS in comparison to the transversal profiles, which are limited by the beam lateral resolution.

The approach was applied to spectra collected in two types of deposits on PET and HDPE, such as biological and sediment materials. These spectra correspond to point analysis from details identified in surface analysis maps, i.e., tiny areas equivalent to the beam dimensions (approximately $3 \times 3 \,\mu\text{m}^2$).

3.3.1. Pristine HDPE and PET matrix estimation

The polymer matrix was first estimated using the RBS spectra of pristine polymers and included in OMDAQ2007 and WiNDF analysis of deposits as a substrate layer. The HDPE matrix estimation using both OMDAQ2007 and WiNDF produced the same result (C 99% + (Ca + Ti) 1%; thickness > 300 μ m), whereas the PET matrix was marginally different when OMDAQ2007 results (C 67% + O 33%; thickness > 100 μ m) were compared to WiNDF results (C 77% + O 23%; thickness > 100 μ m). The OMDAQ2007 result of the RBS fit was consistent with the PET stoichiometry (C₁₀H₈O₄).

3.3.2. Examining the depth structure of polymer's deposits with OMDAQ2007

A three-layer structure was initially assumed for the two types of deposits: (i) the thin carbon coating used to avoid charge build up during irradiation; (ii) the deposit layer based on major elements that can be detected in both RBS and PIXE spectra; and (iii) the fixed substrate layer, the polymer matrix.

After the user initial guess, improvements were obtained by adjusting elemental composition in each layer and RBS detector resolution. The fit results obtained for a detail of a cell adherent to HDPE, corresponding to the cell wall and a sediment deposit on PET are



Fig. 4. Nonhomogeneous Cl distribution in scans of transversal sections of PET, $530 \times 530 \,\mu\text{m}^2$ (A) and HDPE, $2010 \times 2010 \,\mu\text{m}^2$ (B). Other elements, such as K and Fe were apparently confined to the deposit on the polymer surface. The arrows in the Cl maps indicate the 90^o aligned edge of the polymer. Content gradient is represented by a colour dynamic scale: high content – red, low content – blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

displayed in Fig. 5. Regarding the cell detail (Fig. 5-A) the first layer reproduced the thin C film at the surface (C 100%; thickness = $0.08 \,\mu$ m) and the second layer was consistent with biological material composition and thickness (C 19% + O 67% + Ca 13% + Zn 0.2%; thickness = $22.8 \,\mu$ m). The substrate layer was the simulated HDPE matrix as referred above.

Likely, for the sediment region, the first layer reproduced the thin C film at the surface (C 100%; thickness = $0.05 \,\mu$ m), the second layer was consistent with sedimentary material composition (C 53% + O 37% + Ca 9.2% + Fe 0.8%; thickness = $23.3 \,\mu$ m), and the third layer corresponded to the PET matrix (Fig. 5-B). However, OMDAQ2007 did not reproduce the shape of the resonance very well or the shape of the barriers of heavier elements in the spectra (Fig. 5-B). The results obtained point out that a more complex matrix structure may be required, which has to be defined manually when using OMDAQ2007. If this multilayer structure has PIXE detectable common elements in each layer, it implies that the GUPIXWIN capability of calculating elemental concentrations using PIXE spectra can only be performed in a single layer, as total multilayer quantitative analysis is only possible if layers do not share the same element(s).

3.3.3. Examining the depth structure of polymer deposits with WiNDF

The WiNDF can estimate a multilayer composition and thickness that best describe the sample with the best possible accuracy departing from an initial guess defined by the user (e.g., OMDAQ2007 best fit). The deposit thickness, number of layers and matrix composition was then estimated by adjusting detector resolution, RBS and PIXE charge and combining relevant elements in both RBS and PIXE spectra. Thus, elemental concentrations can only be calculated for the elements that are detected both by PIXE and RBS. The WiNDF generates a single solution consistent with the RBS depth profile as fit parameter and PIXE elemental yields.

The WiNDF results obtained for the RBS spectra analysed previously with OMDAQ2007 (Fig. 5) are displayed in Figs. 6–9.

3.3.3.1. Depth structure of a cell detail. The WiNDF simulation of the RBS spectra of the cell detail on HDPE provided an interesting solution for the depth structure described by four layers, which is meaningful in terms of cellular morphology. The quality of the fit was evident and the agreement between the experimental PIXE yields and those calculated for the sample structure fitted was also very good (Fig. 6A and B). Apart the first thin C coating layer (as obtained in OMDAQ2007 approach), the second layer composition (C 16% + O 68% + Ca 16%) reproduced the atomic percentages in calcium carbonate (CaCO₃) a major constituent of the cell wall of many marine organisms, and the third layer, showed a composition closer to an intracellular milieu, less Ca, more C and O (C 26% + O 66% + Ca 9%). The fourth layer was noteworthy as it reveals a mixed composition of the cell wall and the polymer (C 0.2% + O 2.2% + Cl 0.4% + Ca 34% + substrate 63%). This mixed composition is compatible with the required cell adhesion to the substrate (the 5th layer - HDPE) and may reflect the biodegradation of the polymer surface carried out by enzymatic hydrolysis of specific polymer bonds [5,6,24]. The layer structure and the relative elemental composition of each layer can be represented by plotting the fitted depth profile derived from the RBS data with the linear depth scale as in Fig. 7.

3.3.3.2. Depth structure of a sediment material. The results obtained with WiNDF for the sediment material, evidenced the high complexity of the deposit that could be already guessed from the unsatisfactory OMDAQ2007 result. The simulation delivered a depth structure of 8 layers with different thicknesses and composition, compatible with a mixture of organic matter and earth crust materials [25]. This structure reproduced the spectra shape accurately. The calculated PIXE yields for Si, Cl, K, Ca and Fe showed also a remarkable agreement with the experimental data (see Fig. 8A and B). The depth structure evidenced a larger organic contribution at the deposit surface (higher C atomic percentage in the first three layers) and more oxidized Fe, Ca and Si earth crust materials [25] deeper in the deposit. Interestingly, Cl was





Fig. 5. OMDAQ2007 results of 2.0 MeV ¹H⁺ RBS spectra from a cell wall detail on HDPE (A) and from sediment material on PET (B). The calculated partial signals of the elements are shown. RBS spectra goodness of fit is given by chi2 value and depicted in the plotted line of residuals (box below the spectra).

also present at deeper layers, suggesting proximity of the substrate that may favour its diffusion into the polymer matrix (Fig. 9). The Cl⁻ ions, a major ion in seawater, may have an important role in plastic degradation that is still not fully elucidated [26]. However, due to the low yield of the elements of interest relative to matrix it was not possible to model the diffusion of Cl or any other element into the matrix. To assess matrix changes the element yield should overcome the uncertainty of the fit of the upper layers and the matrix. Beam straggling in upper layer of the deposit and attenuation of the incoming energetic particles by the materials in the deposit also limit the analysis capacity in the evaluation of polymer-deposit interaction and matrix changes.

3.4. Future work

There are plenty of room to improve both OMDAQ2007 and WiNDF



Fig. 6. WiNDF results for the same spectra in Fig. 5 A. The plot includes the RBS spectra raw data and full simulation of the cell wall. The calculated partial signals of the elements are shown (A). The PIXE results are plotted as a bar graph. Experimental PIXE yields are compared to the calculated yields for the layer structure obtained in the RBS simulation (B).



Fig. 7. Plot of the fitted depth profile (see Fig. 6) derived from the RBS data with the linear depth scale. The origin of the depth scale was set at the deposit surface. The layers L1 to L4 are indicated. L4 evidenced a mix composition of cellular and polymer (substrate) materials.

depth structure assessment. A common issue will be the acquisition of spectral data with greater statistical power. This would help improving the estimation of diffusion of elements into the polymer matrix. The examination of deposits in a temporal scale perspective would also shed light on the adhesion process of materials to plastics and on the diffusion of ions present in seawater, such as Cl⁻. The WiNDF capabilities account for roughness, voids and different layer edge configurations [12], which would be interesting to explore in the search of solutions that would describe more accurately the spectral data of deposits. However, WiNDF is a time consuming approach and convergence to an appropriate solution is not always obtained. On the other hand the OMDAQ2007 analyses are carried out in a friendly user interface, are fast and quantitative results are not only limited to the elements present in RBS and PIXE spectra. The evaluation of multilayer depth structures is also possible, although the final solution may be only qualitative.



Fig. 8. WiNDF results for the same spectra in Fig. 5 B. The plot includes the RBS spectra raw data and full simulation of the sediment region. The calculated partial signals of the elements are shown (A). The PIXE results are plotted as a bar graph. Experimental PIXE yields are compared to the calculated yields for the layer structure obtained in the RBS simulation (B).



Fig. 9. Plot of the fitted depth profile (see Fig. 8) derived from the RBS data with the linear depth scale. The origin of the depth scale was set at the deposit surface. The multi-layered arrangement of the sediment deposits can be well depicted.

4. Conclusions

To our knowledge, the reported results were the first measurements on the micro-distribution of chemical elements present in the deposits of floating plastics.

Major findings were the diffusion of the ion Cl⁻ in the polymer matrix and the determination of the depth structure of biotic and sediment deposits on PET and HDPE polymers. The absorption of elements such as Cl by the polymer and the deposition of sediment materials may have consequences in plastic degradation speed, transference of metals and contaminants and in their toxicity to aquatic life.

Combining both transversal and surface analysis can be a good exploratory strategy to assess matrix penetration profiles and depth structure of abiotic and biotic deposits on plastic materials. Although assessing the polymer-deposit interaction and matrix changes was not straightforward, the depth structure of the deposit can be well defined as long as the RBS spectra can be well modelled. In these cases, submicrometre depth resolution can be achieved.

The results of the present study evidence that nuclear microscopy in combination with the OMDAQ2007 and WiNDF analytical tools offer unique possibilities to study plastic degradation and plastic chemical transfer with minimal sample manipulation.

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