

Rapid Ablative Laser Technique (ICP-MS) for Monitoring Material Homogeneity in Polypropylene

*AE Pillay¹, S Vukusic^{1,2}, S Stephen¹, A Abd-Elhameed¹

¹ Department of Chemistry, ² Department of Chemical Engineering, The Petroleum Institute, PO Box 2533, Abu Dhabi, UAE.

*Correspondence to: AE Pillay, apillay@pi.ac.ae

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Abstract

Efficient mixing of additives in polymer material is essential for uniform distribution. This paper explores the capability of using a high-resolution ICP-MS (Inductively Coupled Plasma – Mass Spectrometry) laser ablation technique to assess the uniformity of distribution of selected metal dopants in polypropylene samples. This study simulates the distribution of residual metal catalysts in polymer material and could provide an insight into investigating the bulk dispersion of catalytic residues. Ablative laser technology is relatively unexplored for this purpose, and is one of the few contemporary instrumental methods available for consummate evaluation of material homogeneity. Polypropylene samples were especially loaded with appropriate levels of metal oxides [ZnO, TiO₂, Mg(OH)₂] to achieve ppm levels on distribution in the bulk material. The study subsequently examined the distribution of the metal dopant in the solid phase - both spatially and depth-wise - using a 100 µm-diameter laser beam coupled to an ICP-MS instrument. The laser (213 nm) was programmed to ablate a total depth of 25 µm at each point at 5-µm intervals. Prior to each run, the instrument underwent appropriate calibration and correction for background. The study did not necessitate standardization, and signal intensities were compared with surface metals and those occurring internally. Spectra were generated to observe fluctuations in characteristic metal intensity with penetration depth. In some cases, wide variations were observed by more than two orders of magnitude. The experimentally determined results indicated that metal intensity consistently showed a steady decline with depth, suggesting that most of the spike was concentrated on the surface. In some cases 'hotspots' were observed at certain points, where the dopant accumulated, indicating imperfect mixing of the additive. Uneven levels of surface metals are particularly significant, as these metals would play a major role in abrading and subsequently migrating into the surrounding environment. Irregular distribution of sub-surface metals is equally important as it could provide useful information of dispersion in the bulk of the polymer material. Our work would be of definite interest to environmental science and materials research, and could be useful in modeling studies.

Keywords: Polypropylene; laser ablation; depth-profiling; ICP-MS.

Introduction

Synthetic polymers, like polypropylene, are currently used in a wide number of commodity products (from ice cream boxes to carpet fibres); and applications in engineering and biotechnology [1–6]. Uneven distribution of minor metals in polymeric material – originating from certain additives - could possibly affect the bio-stability and biocompatibility of biomedical implants, stents and other such devices [2], [5]. Therefore, superior mixing capability is vital to ensure optimum material homogeneity. Unusually high levels of embedded surface metals could affect studies such as tissue engineering and biospecific adhesion of cells to polymeric surfaces. Performance of cellular bioadhesion and polymer films for semiconductor applications would be unsatisfactory if surfaces accumulated elevated levels of superficial metals due to inferior mixing capability. Furthermore, some types of polymers are designed to encapsulate fluids such as oral pharmaceutical mixtures and liquid petroleum products. There is a general need to know the distribution of surface metals on such polymeric materials [2] as they could migrate into such fluids and create unwanted effects.

Our group has developed an ultrasensitive technique for assessing the distribution of bulk metals in polymer matrices; and pinpointing areas on the surface to study spatial dispersion of metals. The technique uses laser ablation linked to an ICP-MS instrument. It is semi-quantitative [7–9], and capable of high-resolution detection over a wide range of elemental levels. Polymers are usually mixed and synthesized with catalysts and additives containing

minor metal components and impurities. Some of these metals migrate to the surface, while others remain embedded deep in the polymeric product. It is thus, unlikely to obtain polymeric material completely devoid of unwanted metallic residues, and ablative laser technology has the ability to study homogeneity of such distributions in the polymer matrix. The aim of this paper, therefore, is to explore the potential of our method for rapidly evaluating material homogeneity (spatially and depth-wise) using suitable polymer samples.

Methods

Sample preparation

A single polypropylene homopolymer (HE445FB) was used as base material to prepare the compounded materials. The compounded materials were made with a Prism TSE 24 (Thermo Fisher Scientific, Newington NH, USA) twin-screw extrusion machine with extrusion conditions of 230°C, and were then dried and pelletized. A Ferromatic Milacron FM60 (Malterdingen, Germany) injection molding machine was used to prepare 20 plaques of each material with dimensions of 60 x 60 x 2 mm. Three different mineral fillers (dopants) were used individually in samples (titanium & zinc oxide; and magnesium hydroxide). TiO₂ was supplied by Ishihara Sangyo Kaisha (Osaka, Japan); ZnO by Elementis Pigments (Stoke-on-Trent, UK); and Mg (OH)₂ by Merck (Darmstadt, Germany). Samples were loaded with the appropriate metal oxides to attain ppm distributions in the bulk material.

ICP-MS

Samples were investigated with a Perkin Elmer SCIEX DRC-e ICP-MS fitted with a New Wave UP-213 laser ablation system. The polymer plaques were cut to fit into a special sample holder with dimensions 5 cm x 5 cm. No serious pre-treatment was necessary prior to irradiation. Samples were subjected to 213-nm laser irradiation at different points on the sample. The level of the beam energy was 30%, with a fluence of approximately 3 J/cm² and beam diameter of 100 μm. The laser was programmed to ablate a depth of 5 μm at each point and repeatedly scanned the surface, recording measurements after each ablation to a total depth of 25 μm. The process is rapid and a depth of 25 μm can be attained in a few minutes. Control samples containing no dopant were irradiated under identical conditions. As expected, no traces of dopant were detected in the controls.

Instrumental performance

Characteristic intensities originating from the metals of interest were measured; and valid considerations were given to potential interferences and matrix effects. Prior to each run, the instrument underwent calibration and correction for background [8], [10]. The study was largely semi-quantitative in the absence of standardization, and for purposes of comparison, all measurements were conducted under identical experimental conditions. Signal intensities were compared with surface metals and those occurring in the bulk of the sample; and appropriate spectra were produced to observe variations in characteristic metal intensity spatially and with penetration depth.

Validating the analytical performance of the laser technique was conducted on an available certified standard (NIST, Certificate 613). A point to note is that repeatability studies with the laser could be affected by accumulation of debris in the crater formed by the laser. This effect is not particularly marked, but its extent has not been established and wider studies are needed to determine exactly how pronounced it is. In addition, imperfect beam spots due to slight perturbations in focusing could lead to significant scatter in the results [7]. In our case we examined the performance of the instrument for different isotopes by taking replicate measurements (n = 3) for equivalent counting times at random points on the standard. Relative standard deviations of less than 5% were attained (Table 1) indicating that the operational performance of the instrument was acceptable.

Table 1: Measurements (counts/sec) of reproducibility in a NIST 613 standard.

Measurement	⁵⁹ Co	⁸⁵ Rb	⁸⁸ Sr	¹³⁸ Ba	¹⁴⁰ Ce	²³⁸ U
1	503	718	3688	1618	1023	1805
2	511	736	3672	1624	1141	1814
3	491	735	3587	1620	1036	1792
Mean + RSD	502 ± 1.6%	730 ± 1.1%	3649 ± 1.2%	1621 ± 0.15%	1067 ± 4.95%	1804 ± 0.50%

Results and Discussion

Surface characterization and spatial distribution

Characterizing polymer surfaces in terms of metal distribution is particularly important to obtain knowledge of the completeness of mixing; and the level of metallic residues. Poor mixing could result in slight variations in density in the solid sample, which could affect the purpose for which the polymer is intended - for example, monitoring gas permeability through the bulk material. Thus, employing dopants is a facile way of ascertaining the homogeneity of mixing. Uneven distribution of dopant on the surface could be a reflection of uneven blending. As previously stated, such non-uniformity in the integrity of the polymer could create unwanted problems, especially if they are used for highly sensitive purposes, such as tissue engineering and implants in biomedicine.

Apart from evaluating homogeneity, characterization of surfaces is useful to locate 'hotspots' or areas of unusually high metal intensity. In this respect, the metal residue itself could play an intricate role in its distribution. As the polymer solidifies, some metals with greater mobility and affinity for the matrix could find themselves bound within the matrix. Others with fewer predilections to remain ingrained could migrate to the surface and accumulate at certain points. This is significant from the perspective of surface purity, and the possibility of contamination could be marked if extraneous ingrained metals migrate into the environment associated with the polymer – especially if it is used as a hyperpure thin film or to encapsulate solutions, such as jet-oil and body fluids. The location of such metal components, therefore, depends not only on the competency of mixing but also on the potential of some metals with the capacity to migrate. A point to note is that ablative laser technology possesses the capability of pinpointing microspheres in polymer material that are 'relatively' clean. Since it is not possible for the matrix to be completely devoid of metal impurities (such as catalytic residues), the laser could be useful for locating minute areas depleted of metal content, which could be subsequently exoriated from the polymer surface and used for making thin films and other sensitive devices.

Typical distribution patterns are presented in Figures 1 and 2, which portray slightly different trends in metal distribution (for Ti and Mg, respectively) across the polymer surface, underscoring the point that modeling such surface distributions in a polymer matrix could be complex. The plot for Mg passes through a minimum; whereas the Ti distribution delineates a distinct upward trend. The typical distribution for the Zn sample (Figure 3) reflects a downward trend, indicating that none of these metals follows a definite pattern making it difficult to predict their spatial dispersion. The reason for such variations in surface dispersion is not clear, and could potentially be attributed to the nature of the dopant and perhaps matrix effects when the material is impregnated with additives. Other factors such as the shear profiles [11] and behavior of the dopant in the molten phase could also play a role in determining the trends depicted in Figures 1-3. It must be stressed that these trends could be dependent on several parameters, so the feasibility of accurately modeling such distributions would rely on a number of variables.

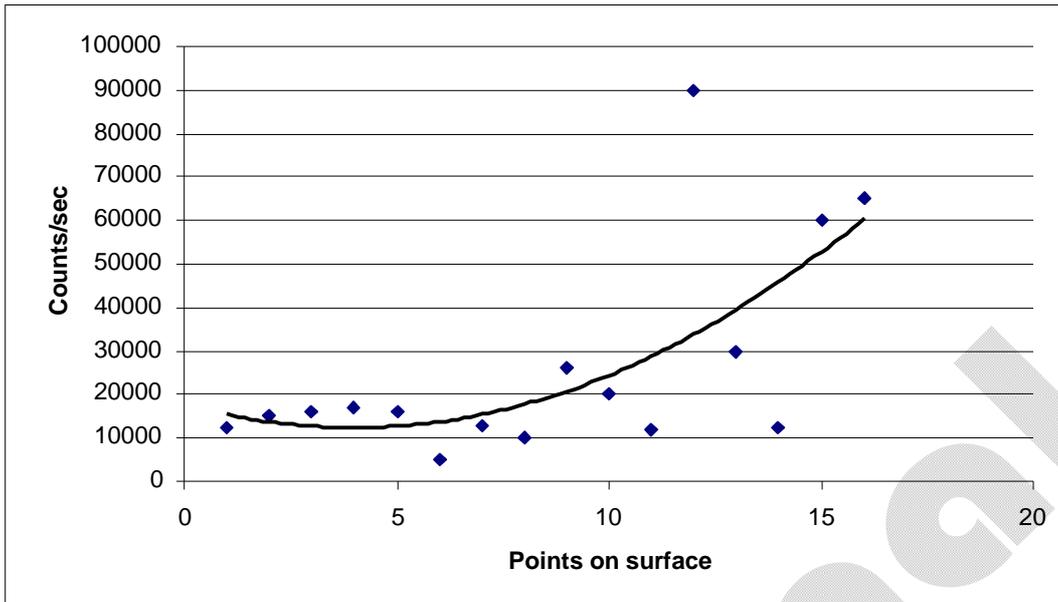


Figure 1: Spatial plot (surface plot) of Ti sample.

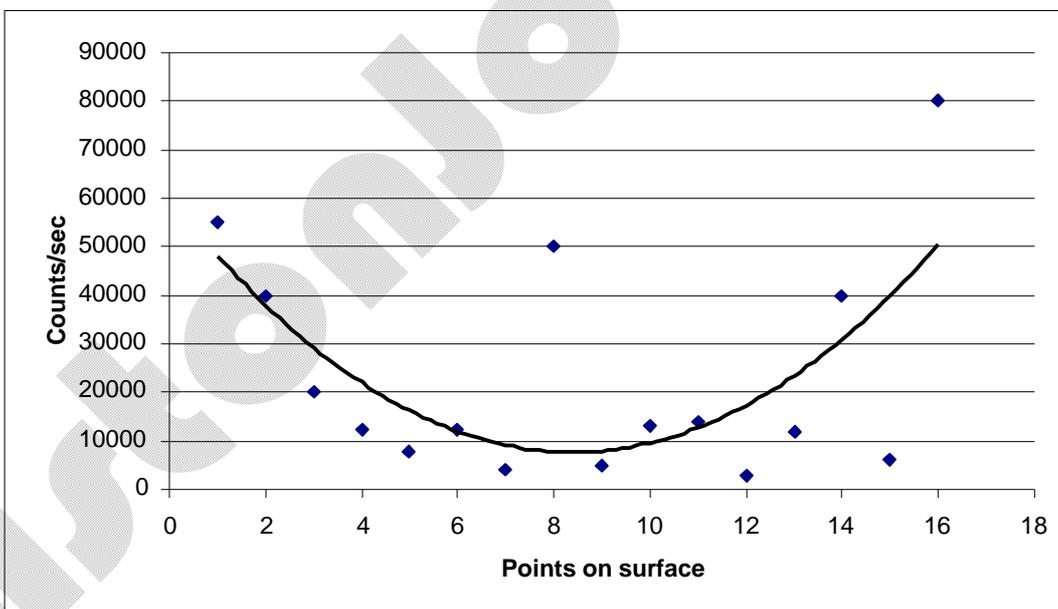


Figure 2: Spatial plot (surface plot) of Mg sample.

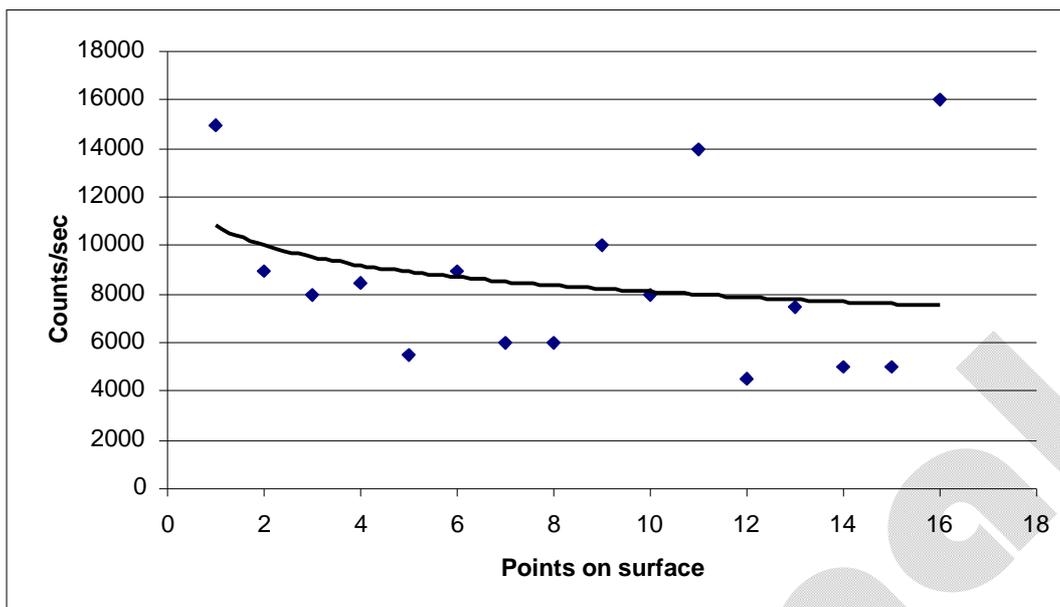


Figure 3: Spatial plot (surface plot) of Zn sample.

Depth profiling

Depth profiling is a special process to investigate metal distribution beneath the surface. Very few contemporary instrumental methods have the capability to study metal intensity with depth. X-ray methods are useful, but lack the ability to control depth penetration. Nuclear particle irradiation is equally useful, but such techniques require nuclear accelerators, and tend to be limited to only a few microns below the surface. The competence, therefore, of the laser approach to delve to discrete depths below the surface of a sample is attractive for homogeneity studies in bulk materials.

To determine whether depth distribution follows a specific trend, single spots on each sample were randomly selected and their depth-profiles modeled. Typical plots appear in Figures 4-6. All three figures portray a distinct downward trend. A notable feature of Figure 4 (Zn sample) is the marked difference in intensity between the high and low points (about a factor of 4). Figures 5 and 6 (Ti and Mg samples, respectively) depict a more gradual decrease in metal intensity. These declining depth features suggest that surface intensities tend to be more pronounced; and ostensibly, it seems easier for depth-profiling trends to be modeled on a mathematical basis. Once again, such definite trends could arise from the mixing process and could be linked to shear profiles in the mold of the injection molding [11]. Clearly, the tail ends of the plots in Figures 4-6 pinpoint areas of diminished metal content, and demonstrate the superior property of the laser in locating micro-regions of depleted metal content in the polymer. It is suggestive from all three plots that depth distribution of metals is conducive to mathematical treatment, but whether or not these features could ultimately be correlated with parameters associated with behavior of the dopant in the molten phase, matrix effects or the crystalline nature of the additive remain to be investigated.

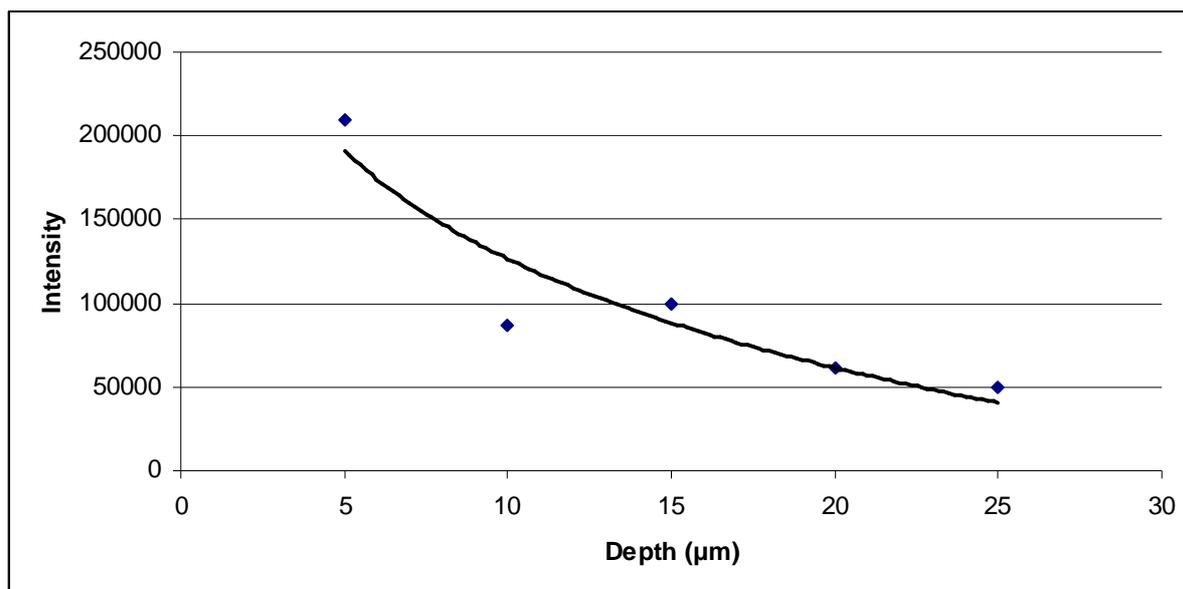


Figure 4: Plot showing Zn depth-distribution in polymer sample.

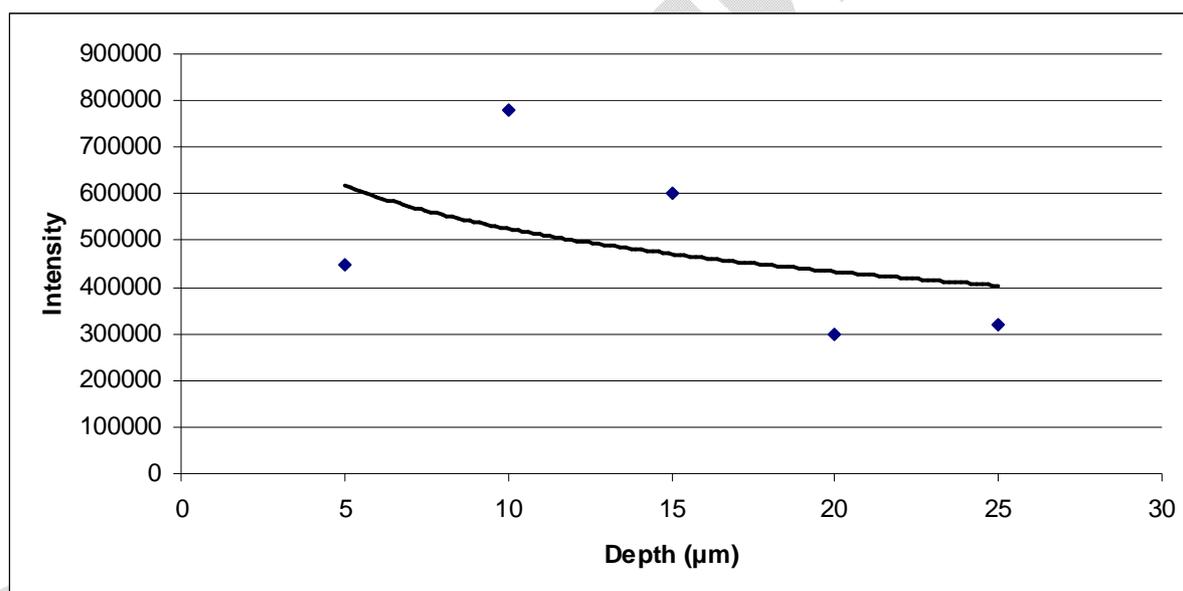


Figure 5: Plot depicting Ti depth-distribution in polymer sample.

'Hotspots'

Figure 7 is a typical depth-profiling spectrum of a fragment of the Zn sample showing 'hot-spots' with progressive depth below the surface. The tall peaks in the spectrum represent these 'hotspots' (or abnormally high metal intensities at certain points), which probably reflect areas in the polymer matrix where the metal accumulated.

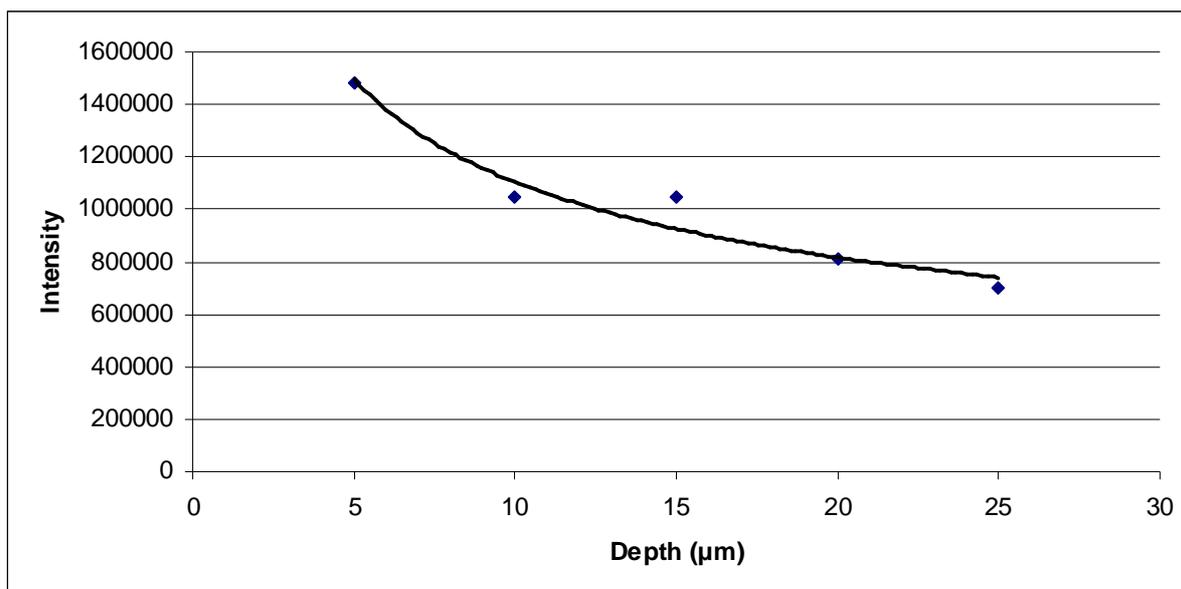


Figure 6: Plot of Mg depth-distribution in polymer sample.

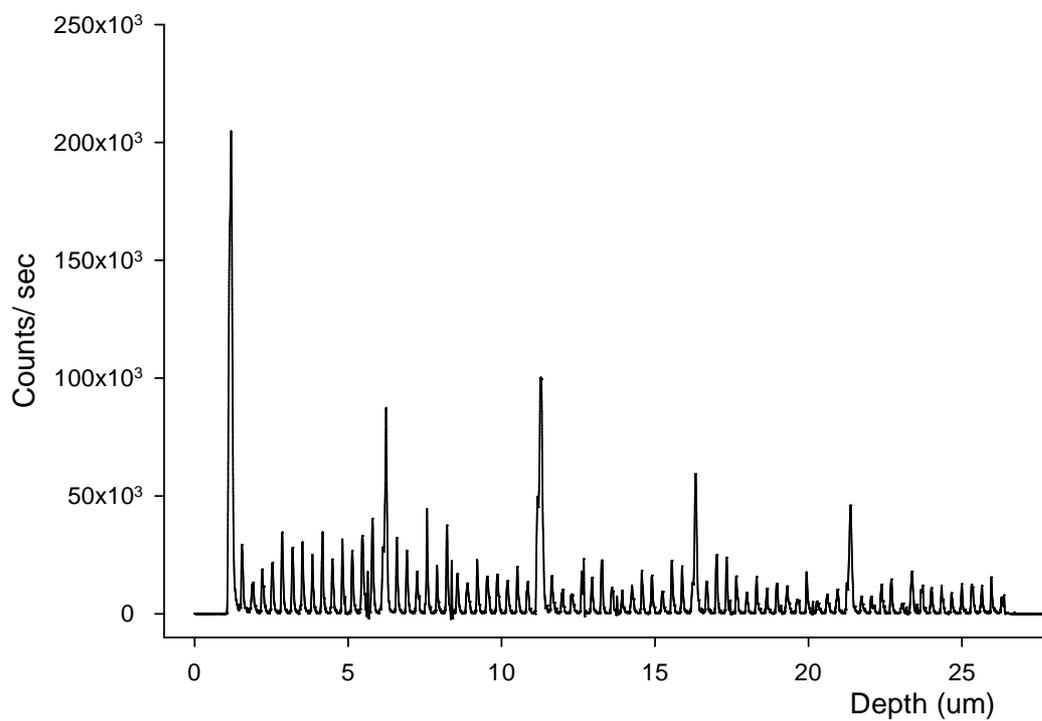


Figure 7: Depth-profiling spectrum of zinc sample showing 'hot-spots'.

It is not clear at this stage why the metal additives would conglomerate at these points; but these 'hotspots' provide distinct evidence that the mixing process is imperfect and could be related to some of the factors described above. A point to note is that peaks between the lofty ones (in Fig 7) are much lower in intensity, and eventually taper off to considerable diminished levels producing differences in intensities by factors of roughly 100, at certain points. A notable feature of the study is that high and low metal intensities differ appreciably in all cases. The overall data highlight two important points: (i) that the dopant is unevenly distributed in the matrix; and (ii) to accurately model these distributions, other factors such as migration of the dopant in the molten phase, physical properties of the dopant and matrix and molding effects [11], have to be taken into account. In general, the investigation demonstrated that ablative laser technology is well suited to studying material homogeneity in polymers, and could be applied on a routine basis for quality control.

Conclusions

High-resolution laser technology has the capability of delineating spatial and depth distribution of embedded metals in polymer matrices. It appears that such distributions would depend on several variables such as the nature of the metal, its affinity for the matrix, the matrix itself and the additives used. It is not clear at this stage whether such distributions could be treated mathematically and modeled. In the case of spatial distributions, we observed varying trends in metal content, indicating that applying modeling statistics to such distributions would be complex. However, depth-distributions seemed to follow a general declining trend, suggesting that it might be easier to model such trends. It would definitely be useful to implement laser technology more widely for modeling purposes and this particular aspect could be a suitable extension to our study. It would also be useful to investigate the impact of a range of base polymers on spatial and depth distributions of metal additives. It would be ideal to find a suitable base polymer that could suppress the mobility of metals to the surface. This 'suppression' or embodiment of the metals and metal residues within the core of the base polymer would be highly beneficial, for the obvious reason that there would be little or no migration of these metals into the medium surrounded by the polymer.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

AEP developed the project and supervised preparation of the manuscript; SV assisted with preparation of the manuscript, sample collection and data analysis; SS operated the ICP-MS and helped with spectral analysis; AAE assisted with sample handling and measurement of specific sample parameters.

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