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Rapid communication

Study of polymers and their blends using TOF-SIMS ion imaging

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ABSTRACT

Time of flight mass spectrometry (TOF-SIMS) was used to see the feasibility of viewing polymer directionality initially of simple polymers like polyethylene (PE) and then graduating to relatively more complex polymer composites involving poly-urethene (PU) and Carbon Nano Tube (CNT) admixture with different mixture concentrations using the Bi ion source. Based on the ion images obtained, it is suggested that directional characteristics of polyethylene, or polyurethane were not visible. However, CNT clusters were identifiable in the pure form of the material and so was CNT inside the admixture. Change in cluster shape inside the admixture at different concentrations indicated the extent of change in strength in the polymer mixture to expect. It was possible to correlate such information with the polymer tensile strength and hardness data measured separately by traditional methods. Similar analysis of high resolution TOF-SIMS ion imaging of other polymer blends are likely to fetch important information on why certain compositions are stronger or why certain compositions do not have the desired or expected properties.

It has been reported for a while that some polymers show visible but broad X-Ray diffraction (XRD) peaks, suggesting some semblance of periodicity and directionality issues [1–3]. However, such directionality should be possible only in reasonably simple polymers, which are reasonably linear in character. There is no direct method to experimentally observe such directionality, even with electron microscopy techniques. So an academic query is up to what extent is it possible to Determine Polymer Orientation using Ion Imaging Mode of time of flight secondary ion mass spectrometry (TOF-SIMS) and under what experimental conditions. In ion imaging, the area under study is broken up into small grids called pixels of the same size for ease of data collection and analysis. TOF-SIMS mass fragment data is collected from each such pixels and analyzed, in terms of their different ion fragment distributions. Thereafter, it might be to possible to experiment on what extent is it possible to visualize the orientation of more complex polymers using such techniques. The advantage in TOF-SIMS as compared to electron microscopy techniques is that the ion distribution can be counted pixel wise over the measurement area, up to ppm impurity levels, thereby giving unique information content on the dispersion or localization issues with different ions of interest, while in electron microscopy, even using EDAX, composition issues are not identifiable, especially if the impurity content in question is less than 1%. In organics – polymers, electron microscopy can give only elemental information, while in TOF-SIMS, with smaller pixel sizes, extraction of more reliable ion fragment related information is available. Some representative earlier work on polymers involving TOF-SIMS are also found in literature [4–6]. If analysis of polymer composites by TOF-SIMS is possible, using ion imaging, it might be possible to improve the properties of different polymer blends and better understand the relation of strength variation with the blending ratios. This was the motivation for the present experimentation and associated discussions. With the above issues in mind, initially the analysis of TOF-SIMS ion images for relatively simple polyethylene (PE) $[CH_2{-}CH_2]_n$ was considered as it is one of the simplest polymers possible and in thin planer sheet form, it is expected to have some form of directional orientation, if at all such phenomena are to be visible in any polymer. Moreover, literature reports suggest that PE does show directionality properties in XRD patterns [1]. Thereafter, TOF-SIMS data was collected from a more complicated carbon nano tube based sheet (CNT) and poly – urethane (PU) polymer sheet $[C_{17}O_4N_2H_{16}]_n$, and after that, a polymer mixture involving different ratios of carbon nano tube (CNT) and poly – urethane were considered and the related results are also discussed below. The polymer mixture of CNT and poly – urethane was chosen because it is a little more complicated and estimation of strength issues in a planar 2-D form in such blends is not possible apriori. A successful analysis may also help in better understanding other observations from other experimental techniques regarding its hardness and other materials property related issues.

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Polyethylene (PE) samples in planer form were prepared by dispersing commercially sourced 99% pure polyethylene granules from M/S Reliance Industries India in toluene as a solvent – dispersing agent and then dried to get a smooth planer shape. The polymer mixture of (CNT) and poly – urethane, with different ratios of the two polymers with CNT concentrations of 0% (pure polyurethane), 1%, 5%, 10% and 100% (pure CNT) were considered with samples prepared in sheet form by dispersing the two polymers in di-methyl formamide (DMF) and then drying the mixture. Details of the preparation process and raw material issues are available elsewhere [1].

TOF-SIMS measurements were done on these samples for their ion content analysis at room temperature using an Ion-TOF-V-100 instrument with a Bi^+ ion source operated at 25 keV for detection by collecting mass spectra data. Such mass spectral data collection was done for 5.5 min in each case. The rastered area and signal detection was done from 100 μm × 100 μm region in each case as that is closely the optimized detection spot size dimension for getting good ion counts, including that for impurities during data collection – imaging. High current bunched mode (HCBM) was used. Such issues have been discussed in the paper by Todd et al. [7,8]. The pixel size was chosen as 2048 × 2048 over this 100 μm × 100 μm region, with one shot per pixel in random mode to reduce charging effects. Bi^+ was chosen as it has a much higher current than the Bi^{3+}. The Bi^+ ion current was about 1 pA. Such pixel size of about 50 nm was chosen to try and increase information content spatially. As stated, samples for analysis were made into very thin sheets and were in contact with metal plates and thus with the sample holder to reduce charging effects further. Appropriate charge neutralization mechanisms were used and optimized with the operating software to avoid charging of the samples during data collection.

The work was started with room temperature mass spectra of polyethylene (PE) having a general formula of $(CH_2{-}CH_2)_n$; related mass calibration was done by considering the ion peaks of H^+, HH^+, C^+, CH_3^+, $C_2H_3^+$, $C_2H_5^+$, $C_3H_3^+$, $C_3H_5^+$, $C_4H_7^+$, $C_4H_8^+$, $C_5H_9^+$. Though, representative standard mass spectra for PE and PU is available in literature [9], such standard mass spectra had been taken using a Ga^+ ion liquid metal ion source, which was popular earlier, while the present spectra has been taken using a Bi^+, using the time of flight (TOF) technique. Due to the difference in their individual mass, the resultant ion solid interaction at the polymer surface is different and the relative ion intensity peak ratios are thus also different. Moreover, such ion mass spectra and related imaging can also be done using other secondary ion mass spectrometry techniques, eg. as reported for analysis of brain tumor cell analysis using Cameca IMS series SIMS instruments [10]. However, the former is a destructive process while TOF based techniques are pseudo nondestructive and also have a better mass resolution. Some groups have used their own lab built TOF instruments for such ion

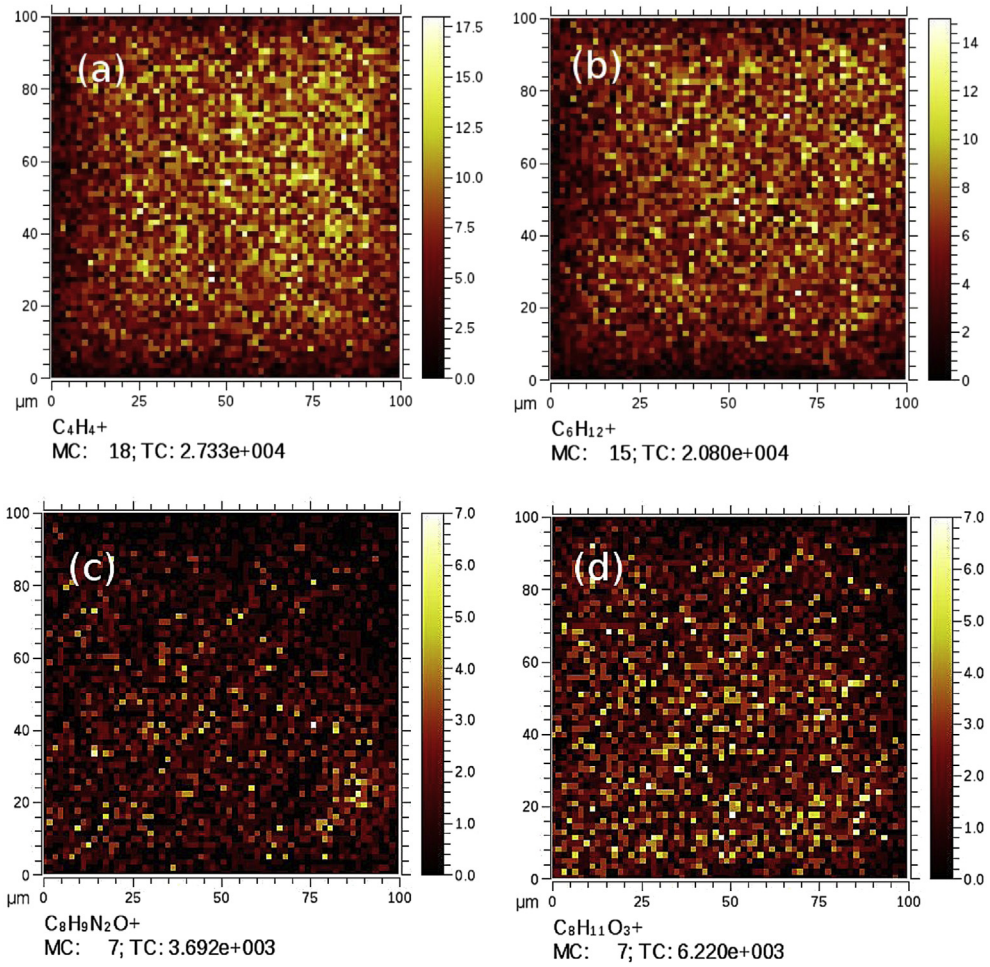

Fig. 1. The two representative ion images from polyethylene (PE) for (a)$C_4H_4^+$ and (b) $C_6H_{12}^+$ with no visible contrast suggesting lack of directionality. Ion images from positive ion fragments from polyurethane (PU) sheets, dispersed with di-methyl formamide (DMF) eg. from ion fragments like (c) $C_8H_9N_2O^+$, and (d) $C_8H_{11}O_3^+$ also suggest lack of directionality – orientation.