APPLICATION NOTE | Multilayer Polymer Film Identification

Multilayer laminate film consists both polymeric and inorganic layers that are widely used in a variety of industries. They can be found in adhesives, various packaging, coatings and many others. To both polymer film manufacturers and end users, it is important that the quality and chemical composition of the polymer films meet specification. To date, there are not many available analytical techniques to identify the chemical composition, defects and inclusions on polymer films without extraction. Here we report the use of ToF-SIMS for multiple layer film cross section analysis which provides rich chemistry information on both polymeric and inorganic layers with sub-µm spatial resolution.

In this study, an industrial multilayer film with limited chemical information was used. The identification and spatial distribution of polymer and inorganic layers were exanimated by imaging the corresponding characteristic peaks.

The film was sandwiched between two pieces of polystyrene with cyanoacrylate adhesive. The cross section was prepared using Leica® EM UC7 with cryo-attachment at a temperature of -40ºC using a 45º cryo-diamond knife.

SIMSs spectra and images were obtained using a Bi+ ion sources operated at 25 kV. Charge compensation was accomplished with a low energy electron beam. Both high mass resolution spectra and high spatial resolution images were acquired. Figure 1 shows both positive and negative ion mass spectra obtained from a multilayer polymer film cross section. Several characteristic ions of polyethylene terephthalate (PET) were identified including $C_7H_4O^+$ (*m/z* 104), $C_9H_9O_2^+$ (*m/z* 149), $C_7H_4O_2^-$ (*m/z* 120) and $C_7H_5O_2^-$ (*m/z* 121). When acquiring high spatial resolution mass spectral images, these PET fragments were then chosen to illustrate the layout of the film structure.

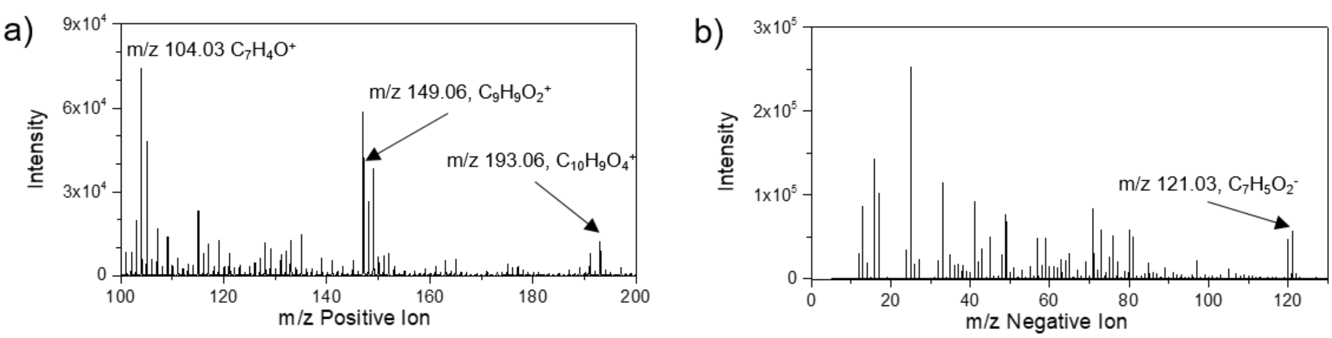

Figure 1 a) Positive ion and b) negative ion mass spectra obtained from multilayer polymer film cross section area.

To examine the distribution of PET and other layers in the cross-section of the film, PET fragments ions $C_7H_4O^+$ at *m/z* 104 and other predominated ions including $C_4H_7^+$ at *m/z* 55 and $C_3H_8N^+$ at *m/z* 58 in the spectrum were imaged. Figure 2 displays the individual and overlaid images of these three ions. $C_7H_4O^+$ showed predominantly high ion intensity in three thick layers, suggesting the polymer in these layers was PET. The long chain alkyl fragment showed higher ion intensity in two thinner layers, which were in between PET layers. The image of $C_3H_8N^+$ showed the location of the cyanoacrylate adhesive. The overlaid image of these three ions indicated a film structure with five polymer layers.

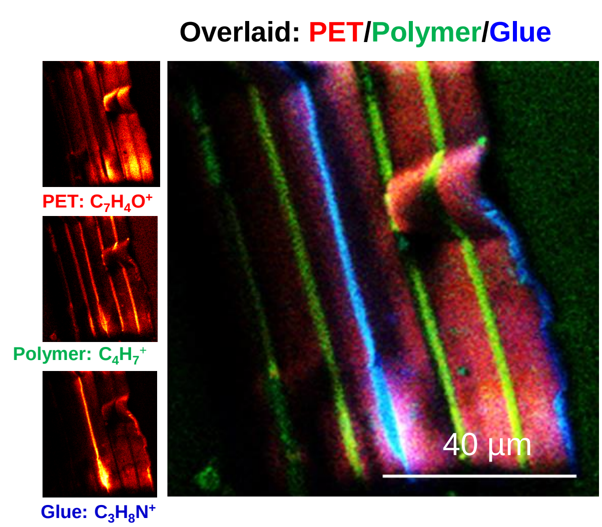

Figure 2 Positive ion high lateral resolution images of $C_7H_4O^+$ at *m/z* 104 (in red), $C_4H_7^+$ at *m/z* 55 (in green) and $C_3H_8N^+$ at *m/z* 58 (in blue), as well as the overlaid image of these three ions.

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The negative ion image of $C_7H_5O_2^-$ at *m/z* 121 further confirmed that the polymer of the three thick layers was PET (Figure 3). The thinner layers between PET layers were most likely a type of adhesive for the purpose of lamination. From positive ion ToF SIMS spectrum and image, we knew that the lamination layer comprised a long chain alkyl group. In the negative ion image, these layers were predominately attributed with CNO^- at *m/z* 42 and with an ion at *m/z* 121 (Figure 4). CNO^- is indicative of imide bond or carbamate bond. The ion at *m/z* 121 could be assigned either to $C_7H_5O_2^-$ or $C_7H_7NO^-$. The latter can originate from the rigid segment of aromatic diisocyanates from polyurethane (PU). Together with the long chain alkyl fragment $C_4H_7^+$ observed from the positive ion image, chemical composition of the adhesive was tentatively assigned to be polyurethane.

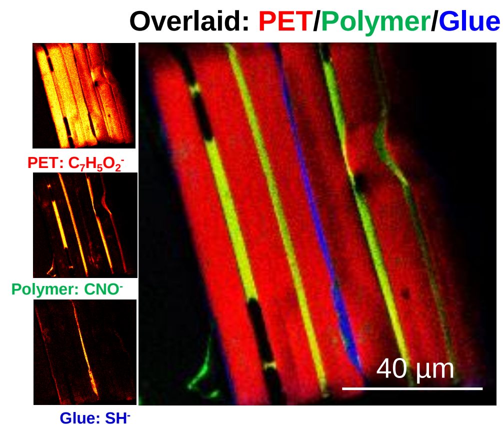

Figure 3. Negative ion high lateral resolution images of $C_7H_5O_2^-$ at *m/z* 121 (in red), CNO^- at *m/z* 42 (in green) and SH^- at *m/z* 33 (in blue), as well as the overlaid image of these three ions.

Many packaging materials, especially for high value foods, contain layers of aluminum foil as it is an effective barrier against moisture, air, odors and UV light. The multilayer film analyzed in this study also contains metal layers. From the high mass resolution spectrum Al^+ at *m/z* 27 was observed. However, the mass interference of $C_2H_3^+$ makes it difficult to map the aluminum distribution in a high lateral resolution image. The problem was solved by gently sputtering the cross section area with bismuth direct current beam with 14 nA current, which was rastered over 200 µm × 200 µm with 128 pixels x 128 pixels for 5 frames. The sputtering process would not alter the layer structure but the organic chemical information was significantly reduced. Figure 4 shows the overlaid image of PET in red, PU in green and aluminum in blue. It clearly showed that there were three aluminum layers.

Figure 9 shows the multilayer diagram derived from ToF-SIMS analysis. The multilayer film contains three layers of PET and three layers of aluminum laminated with two layers of Polyurethane adhesive. The work demonstrates the capability of ToF-SIMS for determining the chemical composition and spatial distribution of multilayer polymer film.

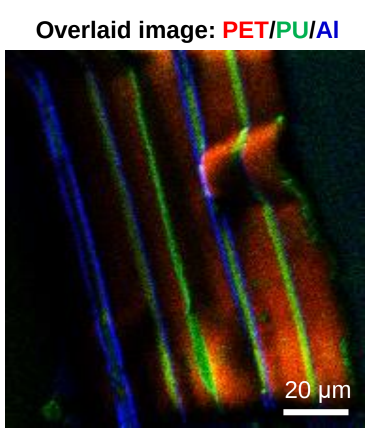

Figure 4. Overlaid image of $C_7H_4O^+$ at *m/z* 104 (in red), $C_4H_7^+$ at *m/z* 55 (in green) and Al^+ at *m/z* 27 (in blue).

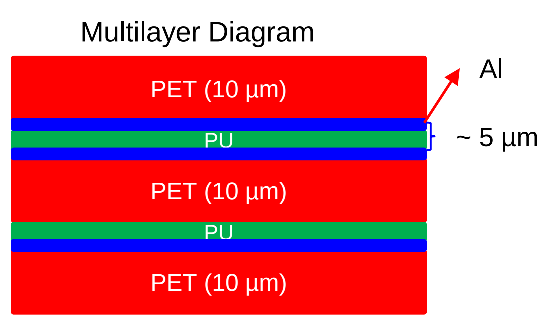

Figure 5. Diagram of the multilayer film deduced from ToF-SIMS analysis.

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