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Solvent-free silver-nanoparticle surface-assisted laser desorption/ionization imaging mass spectrometry of the Irganox 1010 coated on polystyrene

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ABSTRACT

Imaging mass spectrometry (IMS) of the antioxidant Irganox 1010 coated on a polystyrene (PS) was conducted using solvent-free silver-nanoparticle surface-assisted laser desorption/ionization (Ag-NP SALDI). The lateral resolution and probing depth of Ag-NP SALDI-IMS, which are important factors in determining the surface sensitivity, were investigated. Direct Ag vapor deposition produced a 10-nm-thick homogenous layer of Ag-NPs on the Irganox 1010/PS thin film. Ag adduct ions of Irganox 1010 and PS repeating structures, and Ag cluster ions appeared in the mass spectrum, which showed that Ag-NPs on the sample surface enhanced the ionization efficiency by functioning as cationization agents. At the lateral resolution of this method (20 μm), complementary grid patterns (55 lines per inch) of Irganox 1010 on the PS were observed. The probing depth was investigated with Irganox 1010 layers of different thicknesses, the detection of silver adduct ions of PS indicated Ag-NP SALDI could ionize the PS layer beyond the Irganox 1010 layer. The probing depth was 50–100 nm for 10-nm-thick Ag-NP SALDI.

1. Introduction

Over the last decade, matrix-assisted laser desorption/ionization imaging mass spectrometry (MALDI-IMS) [1,2] has been widely applied to biological studies. MALDI-MS is considered to be a powerful tool for synthetic polymer and additive analyses [3–5]; however, MALDI-IMS in industrial applications is still limited, even though the number of reports is increasing [6–14]. For IMS in industrial applications, the surface sensitivity and lateral resolution are crucial for understanding segregation, defects, and degradation on the surface. Solvent-free sample preparation, which was first developed for polymer analysis [15–18], can be applied to surface analysis without changing the surface composition. Some solvent-free matrix applications have been used in IMS, including sublimation [19], dry-coating [20], and the total solvent-free method [21]. These methods can be used to carefully control the sizes of the matrix crystals, and can produce crystal layers that are 1–10 μm thick, which will improve IMS results. For surface sensitive analysis using MALDI-MS, Wesdemiotis et al. developed a technique called surface layer MALDI-MS, which was used to probe the surface concentration of a polymer blend with a depth resolution of <2 nm [22]. Fouquet et al. applied surface layer MALDI to depth profiling by combining the measurement with a beam etching technique [23], which gave a depth resolution of <40 nm.

Another ionization technique used for IMS is surface-assisted laser/desorption ionization (SALDI) [24–34]. Kawasaki et al. described a solvent-free procedure for platinum vapor deposition SALDI-IMS [32]. They applied this technique to small molecules on printed paper or thin-layer chromatography plates. In this study, we investigated the lateral resolution and probing depth using solvent-free Ag-NP SALDI-IMS assuming it would analyze the additive on the polymer layer. We constructed a thin film with two layers by coating the antioxidant Irganox 1010 on a polystyrene (PS) surface. The maximum depth of analyte ionization with Ag-NP SALDI-IMS was defined as the probing depth. Ag-NPs were homogenously distributed by vacuum deposition to form a 10-nm-thick layer. In solvent-free MALDI, direct contact between the analyte and a matrix with smallest possible remaining crystallinity, and sufficient absorption of the matrix at the laser wavelength are

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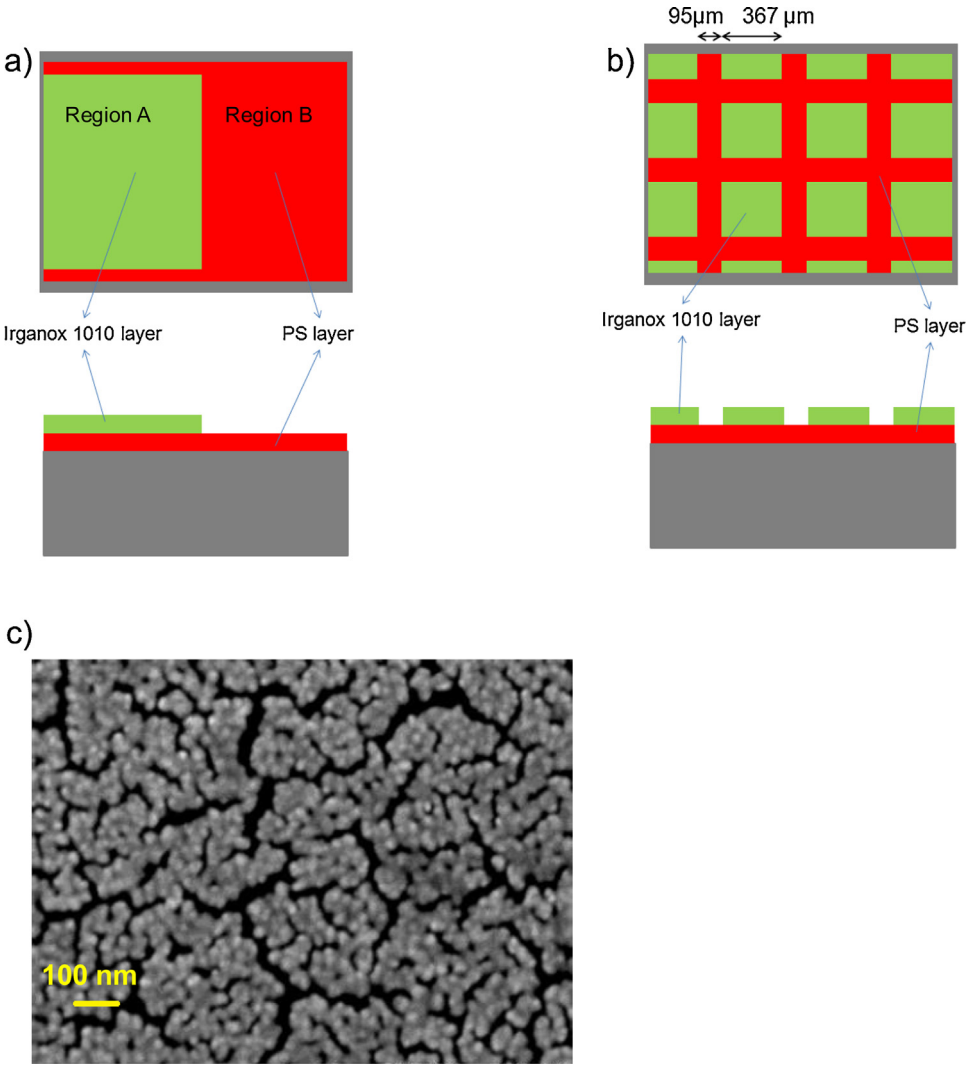

Fig. 1. Diagram of two types of two-layered thin film: a) Irganox/PS and b) Irganox-grid/PS. c) Scanning electron microscopy of Ag-NP vacuum-deposited on the surface of a sample. The gray particles are Ag-NPs.

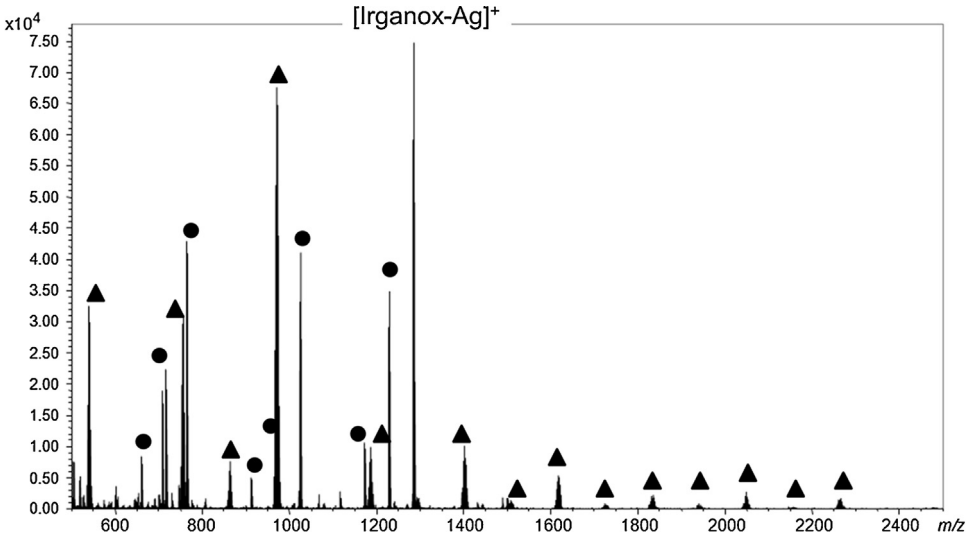

Fig. 2. Mass spectra of Ag/Irganox–150 nm/PS with Irganox layer (Region A in Fig. 1a). The silver adduct ions of Irganox 1010 and its related ions (solid circle) and silver cluster ions (solid triangle) were observed.