Characterization of polyester coatings by FTIR-ATR, confocal Raman microscopy and MALDI-TOF MS

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INTRODUCTION

Polymeric coatings are complex formulations that can contain different components such as cross-linking agents, resins, lubricants, pigments, solvents, etc. To evaluate the safety of the coatings it is necessary to identify the potential migrants. In the last years, polyester-based coatings are being used as an alternative to epoxy resins due to the uncertainties about its potential adverse effects.
In this work, several analytical techniques were used in order to characterize the type of coating on the inside of the cans. The cans used in this study were provided by an industrial partner, which were not in previous contact with food.
In order to investigate the potential migrants, the samples were extracted and analyzed by MALDI-TOF MS. Data published in the scientific literature were used to create a homemade database of possible monomer combinations and tentatively identify some of them used in manufacturing.

EXPERIMENTAL

Identification of the type of coating

Can sample

The type of polymeric coating was identified using an ATR (attenuated total reflectance)-FTIR spectrometer equipped with a diamond optical crystal and by confocal Raman microscopy. The spectra identification was performed by comparing recorded spectra with several commercial spectral libraries.

Identification of potential migrants

Extraction with acetonitrile for 24h at 70ºC

Concentration under nitrogen stream until dryness

+0.05 mL of ACN

MALDI-TOF MS analyses were performed with a smartbeam-I laser in the positive-ion reflector mode. Trans-2-[3-(4-tertbutylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used as MALDI matrix, sodium trifluoroacetate as the cationization agent and tetrahydrofuran as dissolvent.

RESULTS AND DISCUSSION

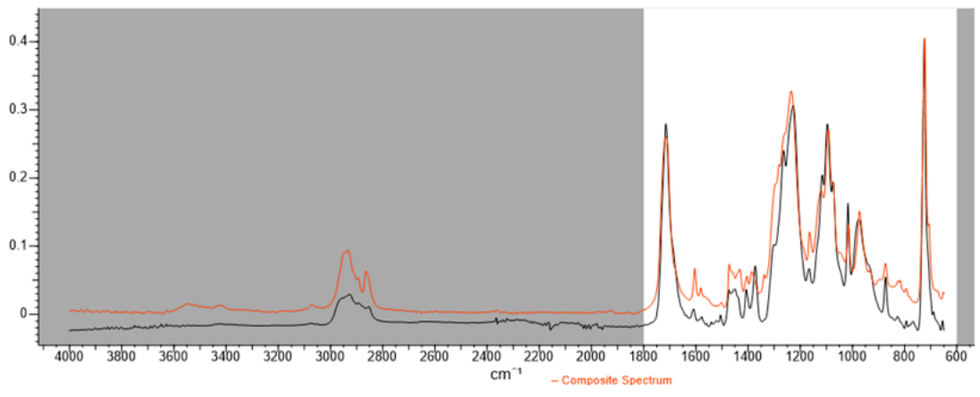

Figure 1. IR spectrum of the internal side of one sample (dark) compared to the IR of the Spectral Library (red)

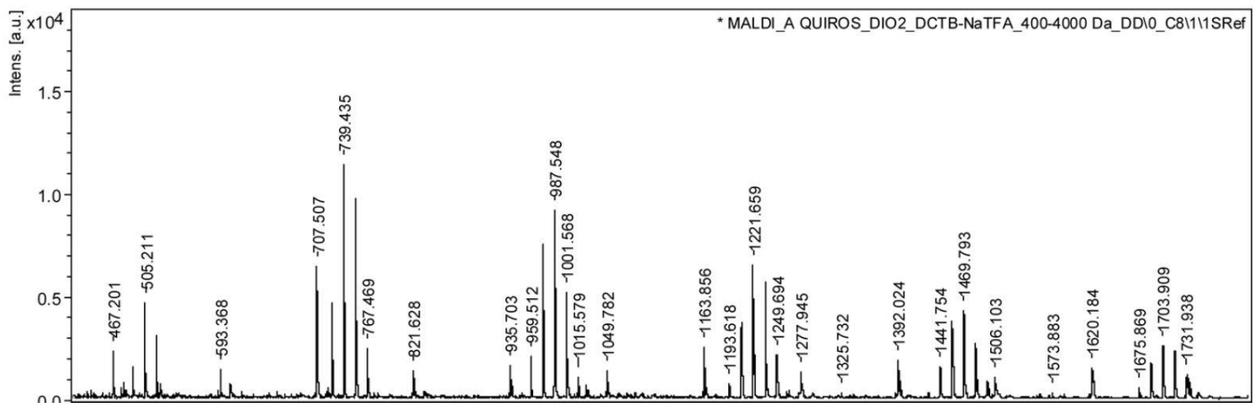

Figure 3. MALDI mass spectrum of the acetonitrile extract of one sample

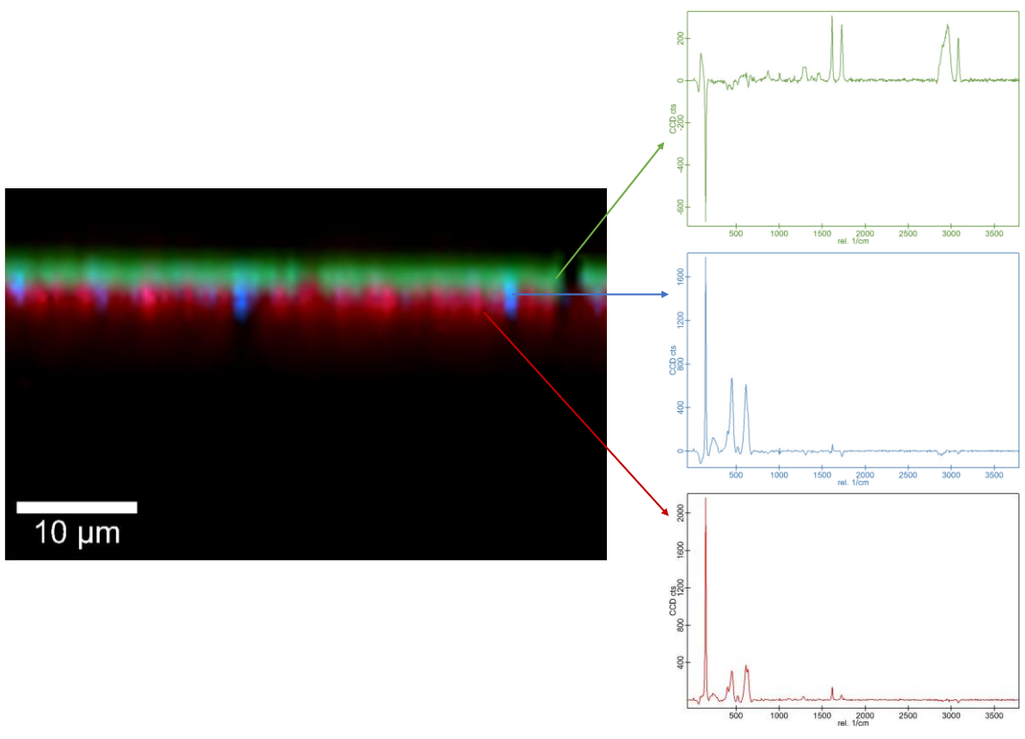

Figure 2: Raman spectra and corresponding color-coded Raman imagen of the internal side of one sample. Green: PET; blue: titanium oxide; red: polyester

- All of the samples have in common that they contain an internal polyester type coating (Figure 1).
- This identification could be confirmed by confocal Raman microscopy. In addition, this technique allows to see that the layer in contact with the food was the corresponding to the PET (Figure 2).
- Observing the mass spectra obtained with MALDI-TOF MS, all of the samples presented series of signals that appeared at intervals of 234.1 Da, which corresponds to a phthalic/isophthalic/terephthalic acid (PA) with neopentyl glycol (NPG).
- Adjacent mass groups were observed separated by 14 Da apart from each other. Exchanging neopentyl glycol with 1,6-hexanediol (HD) increases the mass by 14 Da, while exchanging neopentyl glycol with 1,3-butanediol, 1,4-butanediol (BD) or 2-methyl-1,3-propanediol (MBO) reduces the mass by 14 Da. So, it was possible to tentatively identify the adduct of the cyclic oligomer 2PA+2NPG with sodium (491.2), the adduct of the cyclic oligomer 2PA+NPG+HD with sodium (505.2) and the adduct of the cyclic oligomer 2PA+2HD with sodium (519.2).
- In addition, another series of signals appeared at intervals of 114.1 Da were identified in this sample, which were assigned to the adduct of caprolactone cyclic oligomers with sodium.

Acknowledgement

The study was financially supported by the Ministerio de Ciencia, Innovación y Universidades, by Fondo Europeo de Desarrollo Regional (FEDER), and by Agencia Estatal de Investigación Ref.No. PGC2018-094518-B-I00 “MIGRACOATING” (MICIU/FEDER, UE). Antía Lestido is grateful for her grant “Programa de axudas á etapa predoutoral” da Xunta de Galicia (Consellería de Cultura, Educación e Ordenación Universitaria).