APPLICATION OF FT-RAMAN SPECTROSCOPY FOR ANALYSIS OF PHTHALATE ESTERS IN PVC PLASTICS

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Introduction

Polyvinyl chloride, PVC, is a common polymer used extensively for a wide range of industrial and household products. To achieve the proper material characteristics (e.g. softness, ductility), plasticizers such as phthalates are usually added to the otherwise hard and brittle PVC, sometimes in very large (>20 w%) concentrations. Phthalates are not chemically bonded to PVC and will with time escape by evaporation or extraction by contact with liquids. There is serious concern that fat-soluble phthalates such as DEPH in vinyl kitchen foil, medical devices, cable insulation, and sheathing may harm the reproductive organs of e.g. infants exposed [1].

PVC is readily distinguished from other common polymers (e.g. polyethylene, polypropylene, polystyrene) by use of Raman spectroscopy. For comprehensive reviews of general application of Raman spectroscopy on polymers, e.g. Everall [2] and Hendra [3] may be consulted.

In this project we tried to use Raman spectroscopy to detect traces of phthalates (Fig. 1) in PVC products. As the Raman literature is quite sparse on phthalates, we measured a range of commonly used phthalates for reference purposes. Nyquist [4] has reported only parts of the spectra of 21 phthalate esters, and the Sadtler 4701 Raman database of Basic Monomers & Polymers [5] contains only 11. The measurements that we have performed will be reported elsewhere [6] and include: dibutyl, diethyl, dipentyl, diheptyl, di(2-ethylhexyl), dinonyl, diisodecyl, ditridecyl, butyl benzyl, bis-(2-methoxyethyl) and other phthalates.

By far the most commonly used phthalate plasticizer in PVC is di(2-ethylhexyl) phthalate, DEHP (also referred to as diisooctyl phthalate, DOP) and several products containing this phthalate have been studied.

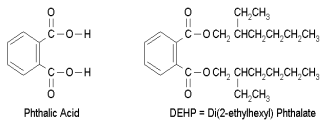

Figure 1: Phthalates are diesters of phthalic acid, often symmetric like DEHP.

Spectrometry

Spectra were obtained using a Bruker FRA-106 Fourier-Transform Raman instrument with a 1064 nm laser and a liquid N_2 cooled Ge-diode detector.

All spectra were measured at approx. 23ºC with no particular specimen preparation for solids, while liquids were measured in small test glass tubes.

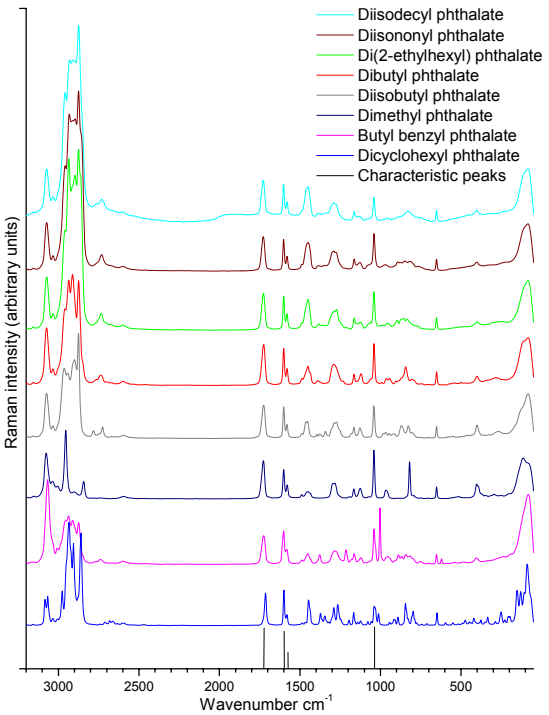

Figure 2: Raman spectra of several pure phthalates. At the bottom is shown the most characteristic, common peak positions of the phthalate ester group.

Pure Phthalates

In Figure 2 the Raman spectra of eight phthalates are shown. Common to all the Raman spectra of the measured phthalate esters are four characteristic peaks, found at 1040, 1581, 1601 and 1726 cm^{-1}. The relative intensities of these peaks vary slightly for different phthalates but provide nevertheless an identifiable "fingerprint" of the phthalate ester group as a whole. We therefore foresee an easy way to identify the presence of phthalates in many consumer products.

PVC samples

In Figure 3 the Raman spectra of four PVC consumer products and two reference spectra are shown. The presences of DEHP in the PVC products C, D and E have been established by chemical analysis and the Raman spectra of these three samples clearly display peaks that can be recognized as due to PVC and DEHP, respectively. The Raman spectrum of the product C consists almost exclusively of peaks which can be found in spectra A and B, whereas products D and E display some peaks, which must be ascribed to the other substances present in the sample (for D perhaps a carbonate filler).

The product F is an example of a sample of unknown chemical composition, and the resemblance of the Raman spectrum to the aforementioned (product C, D and E) lead us to suspect that it is a PVC product containing quite large amounts of DEHP.

Sample G is a PVC product softened with a non-phthalate plasticizer (polyadipates), a fact that is clearly obvious from the Raman spectrum.

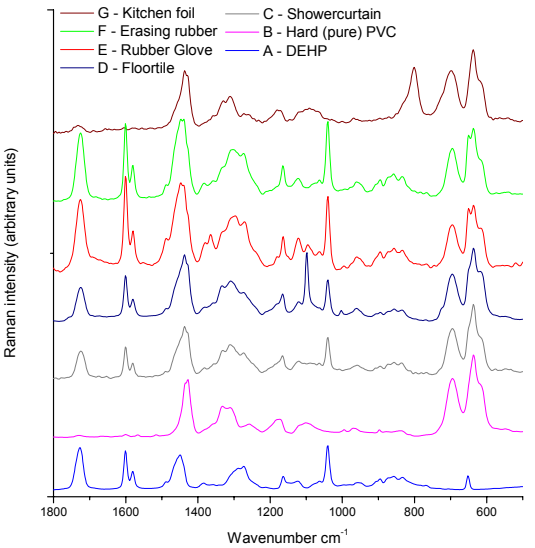

Figure 3 : Examples of FT-Raman spectra of PVC sample products/references. A: DEHP, B: Hard PVC from workshop, C: Shower curtain, uncoloured and opaque, D: floor tile, white, E: Rubber glove, red and smooth, F: Pencil erasing rubber, uncoloured and opaque, F: Kitchen foil (wrap) declared with zero phthalate content.

Conclusion

FT-Raman spectroscopy seems to be a suitable and easy technique for analysing PVC samples – with respect to identifying the base-polymer (PVC) as well as for identifying certain used plasticizers. We estimate this method to be very viable for the screening of large amounts of e.g. consumer products for possible phthalate ester contents.

Acknowledgement

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References

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