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Analysis of Polyadipate Ester Content in PVC Plastics by Means of FT-Raman Spectroscopy

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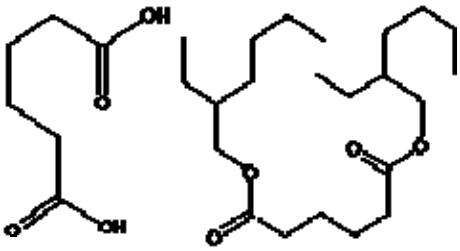
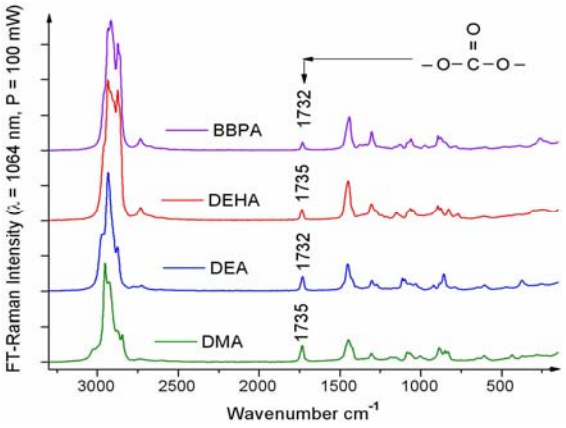
Plasticizers are needed in flexible PVC (PolyVinylChloride) products. There is serious concern that commonly used phthalate esters may harm life reproduction systems [1]. To avoid the problems, instead adipate di-esters (AEs) of C8 to C10 alcohols are used as higher prized alternatives [2]; e.g. di-2-ethylhexyl adipate or DEHA [103-23-1], also known as Adimoll® or di-octyl adipate, DOA, see Fig. 1. A widely used plasticizer in food (cling) films is DEHA, often in combination with polymers, epoxidized soya-bean oil, etcetera. DEHA also occurs in children toys [1]. We have previously shown that the presence of phthalate esters in PVC can be rapidly analyzed by Fourier transform (FT-) Raman spectroscopy excited with a 1064 nm laser [3]. Here in this project we report a similar study. The aim was to find out whether FT-Raman spectroscopy can be used to determine the presence of adipate esters (AEs) as plasticizers in commercial flexible PVC products, and if the kind of ester and how much of the AEs is present in soft PVCs. We applied FT-Raman spectroscopy to a range of AE plasticizers in pure form contained in small glass tubes as well as in samples of poly vinyl chloride. We report reference spectra of 10 AEs (given in the Table); among those dimethyladipate (DMA, [627-93-0]), diethyladipate (DEA, [141-28-6]), DEHA, and bis(1-butylpentyl)adipate (BBPA, [77916-77-9]).



<--Fig. 1. Adipic acid and Di-2-ethyl-hexyladipate *(DHEA).*



-->Fig.2. Spectra.

Results and Conclusion.

It was demonstrated that the presence of AEs in a PVC product is detectable by FT-Raman spectroscopy in plastic test samples made by mixing PVC and e.g. DEHA (Adimoll®). The spectra indicated the AE content could be found, qualitatively as well as quantitatively. Thus by use of proper reference samples, quantitative determination of the AEs content was possible from a single Raman

measurement. It was however found that AEs as a group cannot be identified by characteristic FT-Raman spectroscopy bands, because other aliphatic dicarboxylic esters have similar bands, e.g. at around 1733 cm^{-1}, ascribed to the C=O stretching vibration of the ester group, -(C=O)-O-C- (Fig. 2).

Table. Studied Neat Adipate Esters: Name, CAS-number, number of C-atoms and source.

Diisobutyl adipate, iso-butyl, [141-04-8], C14, Sigma-Aldrich
Diisodecyl adipate, iso-decyl, [27178-16-1], C26, Sigma-Aldrich
Diamyl adipate, iso-amyl, C16, (own product)
Diisopropyl adipate, iso-propyl, [6938-94-9], C12, (own product)
Diisononyl adipate, iso-nonyl, [33703-08-1], C24, BASF
Bis (1-butylpentyl) adipate, BBPA, [77916-77-9], C24, Sigma-Aldrich
Di-2-ethylhexyl adipate, DEHA, [103-23-1], C22, Bayer (Lanxess)
Diethyl adipate, DEA, [141-28-6], C10, Sigma-Aldrich
Dimethyl adipate, DMA, [627-93-0], C8, Sigma-Aldrich
Di-1-hexyl adipate, 1-hexyl, C18, (own product)

Experimental.

Spectra were obtained with a Bruker IFS 66 Fourier-Transform spectrometer with a FRA-106 Raman attachment. The exciting source was a 1064 nm near-infrared Nd-YAG laser with a nominal power of 100 mW. The scattered light was filtered and collected on a liquid N_2 cooled germanium-diode detector giving a resolution of approx. 2 cm^{-1} between individual pixels. Raman spectra were collected over the range from 3500 cm^{-1} (Stokes spectra) to -1000 cm^{-1} (anti-Stokes spectra) at approximately 23 ºC with no particular specimen preparation. All mentioned adipate esters (see Table) were liquids at 23 ºC. The esters were obtained commercially or made in our laboratory by means of mixtures of adipic acid and the corresponding alcohol (1-hexyl, isoamyl, isopropyl). The plastics samples, home made and commercially bought, were just placed in the beam. Further details will be described elsewhere [4].

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