



## INTRODUCTION

Multilayer plastic foils are important packaging materials which are used to extend the shelf life of food products and drinks. Fourier transform infrared (FT-IR) spectroscopic imaging using attenuated total internal reflection (ATR) can be used for the identification and localisation of different layers in multilayer foils. A new type of ATR crystal was used in combination with a linear array detector through which large sample areas (400\*400µm<sup>2</sup>) could be imaged with a pixel size of 1.6 µm. The method was tested on laminated plastic packing materials containing 5 to 12 layers. The results of the identification of the different materials using ATR FT-IR were compared with Differential Scanning Calorimetry (DSC) and the layer thickness of the individual layers measured by ATR FT-IR was compared with polarised light microscopy (LM) and Scanning Electron Microscopy (SEM).

## METHODOLOGY

FT-IR spectral data were collected on a Perkin Elmer Spectrum 100 FT-IR spectrometer interfaced to a Spectrum Spotlight 300 FT-IR microscope equipped with a 16x1 pixel linear Mercury Cadmium Telluride (MCT) detector. A new ATR accessory was used consisting of a 0.6 mm radius germanium hemispherical internal reflection element (IRE). The ATR accessory is mounted on the X,Y stage of the FT-IR microscope. A variable pressure mechanism using a force lever ensures contact between sample and crystal. The crystal is scanned laterally by the IR beam leaving the crystal on the sample. Images were obtained with a pixel size of 1.6 µm. For both sample and background, 16 interferograms with a spectral resolution of 8 cm<sup>-1</sup> were co-added and Fourier transformed. The position of the crystal on the sample was determined using visible light (the FT-IR microscope is equipped with a LED and CCD camera). The Perkin Elmer Spotlight (v.1.4.1) and Hyperview (v 3.0) software were used for spectral processing. Images were corrected for atmospheric influences using the Spotlight software. The Hyperview software was used for principal component analysis (PCA). The principal components were obtained after the following processing steps: conversion to absorption, 1<sup>st</sup> derivative, subtraction of average, additional CO<sub>2</sub> suppression, cropping the spectral range to 3600 - 730 cm<sup>-1</sup>.

Multilayer foil samples were embedded in a transparent two component polymer matrix (epoxy). The matrix needs to harden overnight and can be cut by a microtome with glass knives to obtain a flat surface which can be imaged by the ATR FT-IR microscope.

## RESULTS

The foil in the first example (foil I) is composed of a core layer of ethylene vinylalcohol copolymer (EVOH). Adhered to the EVOH layer are two layers of polyamide (PA, Nylon 6). These layers are surrounded by 2 layers of polyethylene (PE). The most significant chemical features detected in the ATR FT-IR spectral image of the five-layered foil sample are shown in figure 1. The average (co-added) FT-IR spectra within the different layers are shown in figure 2. These spectra were used to identify the different components. A good match was obtained with the FT-IR spectra of PE, PA and EVOH in the spectral library. This is in agreement with the analysis using DSC by which the following compounds could be identified: PE, PA Nylon 6 and EVOH. An overlay of the FT-IR score images after thresholding and the visible image obtained using the FT-IR microscope is shown in figure 3. There is a good correspondence between the visible and FT-IR images. The layer thicknesses of the individual layers analysed from the ATR FT-IR images is in good agreement with those measurements from SEM and LM images (see table 1).

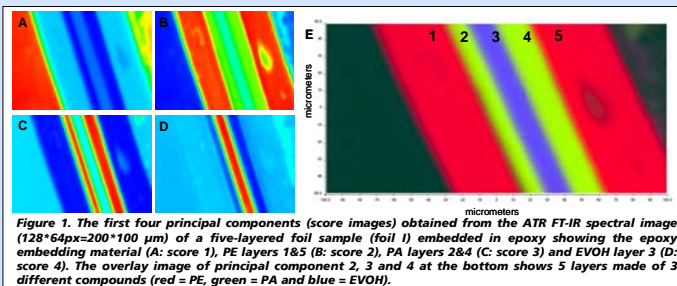


Figure 1. The first four principal components (score images) obtained from the ATR FT-IR spectral image (128\*64px\*200\*100 µm) of a five-layered foil sample (foil I) embedded in epoxy showing the epoxy embedding material (A: score 1), PE layers 1&5 (B: score 2), PA layers 2&4 (C: score 3) and EVOH layer 3 (D: score 4). The overlay image of principal component 2, 3 and 4 at the bottom shows 5 layers made of 3 different compounds (red = PE, green = PA and blue = EVOH).

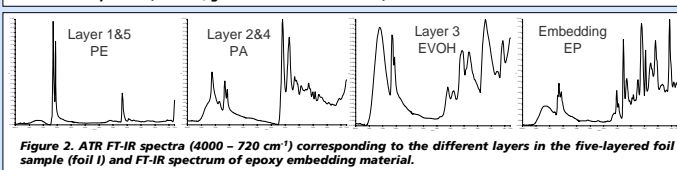


Figure 2. ATR FT-IR spectra (4000 - 720 cm<sup>-1</sup>) corresponding to the different layers in the five-layered foil sample (foil I) and FT-IR spectrum of epoxy embedding material.

layer	Width, µm (±2)			compound
	ATR FT-IR	LM	SEM	
1	34	33	34	PE
2	9	11	13	PA
3	12	13	12	EVOH
4	14	15	13	PA
5	35	35	32	PE
total	104	107	104	

Table 1. Composition and layer thickness of a five-layered foil sample (foil I) analysed from ATR FT-IR, LM and SEM images.

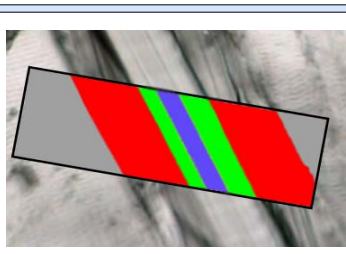


Figure 3. Correlating ATR FT-IR with visible imaging for the five-layered foil sample (foil I): overlay of visible image with areas of compounds identified in the ATR FT-IR images (red = PE, green = PA, blue = EVOH and grey = epoxy (EP) embedding material).

The performance of ATR FT-IR microscopy was tested by imaging a twelve-layered foil sample (foil II) containing layers down to 4 µm. An overlay of the FT-IR score images after thresholding and the visible image obtained using the FT-IR microscope is shown in figure 4. The foil sample contains EVOH (layer 8) sandwiched between 2 layers of PA (layer 7&9), 2 layers of EVA (layer 6&10) used as adhesive layer and 2 layers of PE (layer 5&11). The foil sample contains a circular inclusion composed of PA. Polarised LM and SEM images obtained from different locations of the foil sample are shown in figure 6. SEM was not able to visualise all layers in the foil sample. The thin layers in the polarised LM images are difficult to distinguish.

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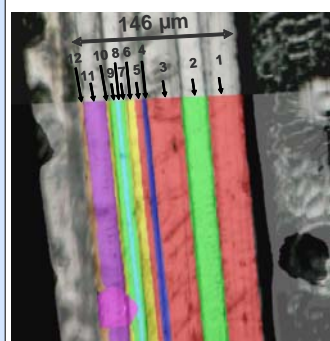


Figure 4. Correlating ATR FT-IR with visible imaging for a twelve-layered foil sample (foil II): visible image with overlay of areas of compounds identified in the ATR FT-IR image. Image size: 300 µm \* 300 µm.

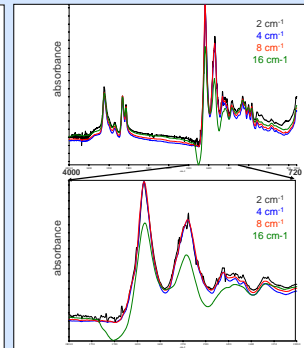


Figure 5. Spectrum (co-added) of the PA layer in the twelve-layered foil sample at a spectral resolution of 2, 4, 8 and 16 cm<sup>-1</sup> (top: 4000-720cm<sup>-1</sup>, bottom: 1800 - 1300 cm<sup>-1</sup>).

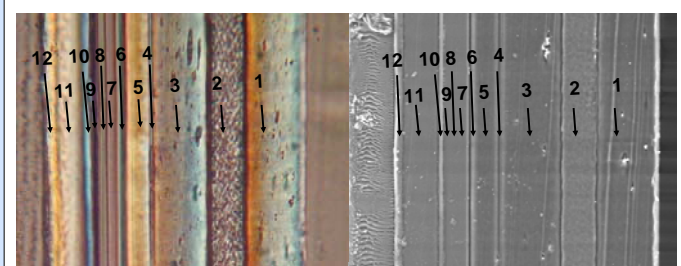


Figure 6. Polarised LM image (left) and SEM image (right) of a twelve-layered foil sample (foil II) embedded in epoxy. Image size: 195 µm \* 150 µm.

layer	Width, µm (±2)			compound
	ATR FT-IR	LM	SEM	
1	32	34	35	PE
2	22	24	22	PA
3	31	30	36	PE
4	4	3	35	PE*
5	7	12	16	PE
6	7	5	16	EVA
7	4	6	6	PA
8	5	5	15	EVOH
9	4	5	6	PA
10	4	4	3	EVA
11	19	14	21	PE*
12	5	4	5	PE*
Total	147	150	154	

Table 2. Composition and layer thickness of a twelve-layered foil sample (foil II) analysed from ATR FT-IR, LM and SEM images (PE\* = PE containing additives).

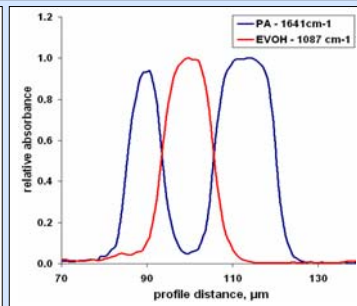


Figure 7. Absorbance profile of PA (1641 cm<sup>-1</sup>) and EVOH (1087 cm<sup>-1</sup>) across the centre of the five-layered foil sample (foil I: layer 2, 3 and 4).

The spatial resolution was determined by analysing the ATR FT-IR spectral images using an edge response test. The pixel size of these images is 1.56 µm. Absorption profiles based on the peak areas of the stretching vibration (amide I) at 1641 cm<sup>-1</sup> of PA and C-O stretching vibration of EVOH at 1087 cm<sup>-1</sup> across the PA and EVOH layers of the five-layered foil sample (foil I) are shown in figure 7. The resolution was calculated as the full-width-at-half maximum (FWHM) of the fitted first derivative of the absorbance profile (edge response). The spatial resolution measured between 1000 and 1200 cm<sup>-1</sup> and 1600 and 1800 cm<sup>-1</sup> is 3.9 ± 0.5 µm and 3.5 ± 0.4 µm, respectively.

## CONCLUSION

ATR FT-IR imaging can be used for the identification and localisation of different layers in multilayer plastic packing material. It has been demonstrated that individual layers with a thickness of about 3 µm could be identified in multilayer foils with a total thickness ranging from 100 to 150 µm. This will give more in-depth information about the layer composition and structure which can be used to predict the functional performance of the packaging material. A good correspondence was found between visible and FT-IR images. The layer thickness of the individual layers analysed from FT-IR images are in good agreement with those analysed using polarised LM and SEM images and the chemical compositions of the layers with the results of the characterisation of the total foil sample by DSC. The new type of ATR crystal enables imaging of large areas (400 µm \* 400 µm) with a spatial resolution of about 4 µm (measured at wavenumbers ranging from 1000 to 1730 cm<sup>-1</sup>) which is about a factor 2 better than can be obtained using transmission FT-IR imaging. An additional advantage of ATR is the ease of sample preparation (no fragile thin slices needed).

[1] G. van Dalen, P.C.M. Heussen, R. den Adel and R.B.J. Hoeve, Attenuated total internal reflection infrared microscopy of multilayer plastic packaging foils, Applied Spectroscopy, tentatively scheduled for publication in the June 2007 issue [61(6)] of Applied Spectroscopy.