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Investigations on Multilayer Films: Electron Microscopy and Infrared Spectroscopy – Possibilities and Limitations

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Summary: The study of multilayer films has become an important issue, since every year improved materials are produced. They have to be optimally designed in order to enable the maintenance of aroma, taste and nutritional value of the goods. This is primarily achieved by the use of special laminated films, additives and oxygen barriers. In addition, ecological and economical factors force the industry forwards to create more environmental-friendly and cheaper films. In this study, two multilayer packaging films differing in the layer and barrier composition are examined with light microscopy (LM), transmission electron microscopy (TEM) and Fourier transformed infrared (FTIR) microspectroscopy: LM gives the number and the thickness of the layers, but there is no information about the chemical composition and the coatings. FTIR and Raman Spectroscopy enable the chemical characterization of the identified layers, but the lateral resolution is restricted in the μm range. TEM visualizes the important characteristics (coatings, filler particles) and enables the detection of inorganic fillers (EELS, EDX), but the organic components cannot be analyzed. Therefore, the use of complementary techniques is crucial in order to achieve a complete analysis of multilayer foils.

Special attention was paid on the preparation procedure, since ultrathin sections are an important prerequisite for TEM observation and there is little known about the "perfect" preparation of multilayer films.

Keywords: FTIR imaging; microtomy; multilayer

Introduction

Multilayer films are composed of several layers, which vary in thickness, width and coatings. Each layer performs a different function: layers based on polyolefines (i.e. polypropylene, polyethylene, polyamide) convince due to their excellent flexibility and stability, whereas layers of EVOH, PVDC, aluminium or special polyamides provide impermeability and sealing ability.[1]

The final application of multilayered materials is mainly in the area of packaging. Every year, improved multilayer films are demanded to enlarge the range of material application. The desired properties of the final product depend on the composition of the different layers.[2] Most multilayer films use aluminium as a barrier layer. Although aluminium has proved to be an important ally in the fight against waste, energy consumption and environmental damage compared to other materials, there is still a tremendous amount of energy needed for its production. An alternative to aluminium is found in the area of special polyamides or coated polyethylene terephthalates (PET).

In the study of multilayer materials, FTIR spectroscopy is used to identify the different layers, whereas the important characteristics of the structure are examined by TEM, which has generally been proved to be a

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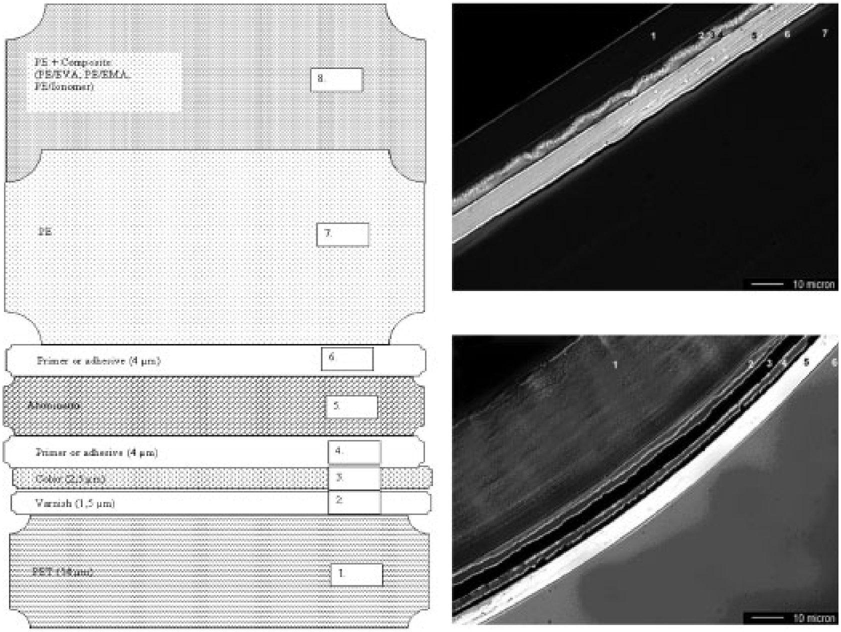

Figure 1.
Schematic representation of the multilayered architecture of the investigated sample (MLF1) and white light micrograph.

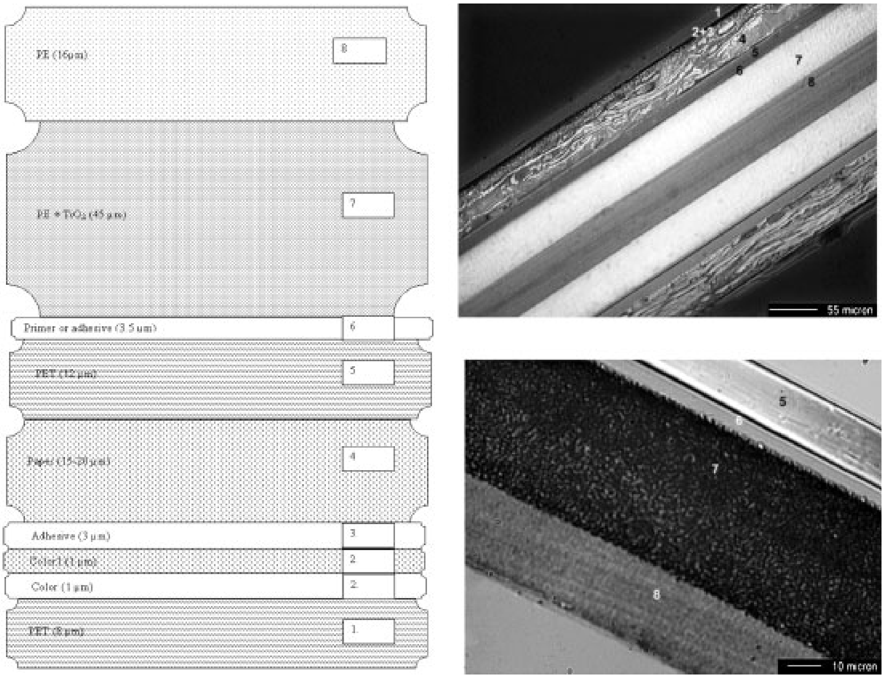

Figure 2.
Schematic representation of the multilayered architecture of the investigated sample (MLF2) and white light micrograph.

promising tool revealing the finest details of internal material structure.[3]

Transmission studies with FTIR spectroscopy require flat semithin cross-sections (2–20 μm thick), whereas specimen preparation for TEM, which is an essential requirement, is a difficult venture. Normally, a series of ultra-thin sections of an equal thickness are produced with an ultramicrotome. However, in the case of multilayer films microtomy encounters its limits. The main problems result from the fact that it is almost impossible to ‘‘ideally’’ cut several adjoined layers of different composition simultaneously, since each layer requires its own cutting requirements. Therefore, even if the ideal embedding material is used and the knife is accurately adjusted for one layer, the other layers are sliced too thickly, might break, curl or peel away. As a consequence, it is almost impossible to view all layers at once.

With FTIR-imaging the problems become a bit more complicated. In order to achieve clear chemical images, the neighbouring layers should consist of components with different characteristic vibrations. Moreover, since the spatial resolution with imaging is

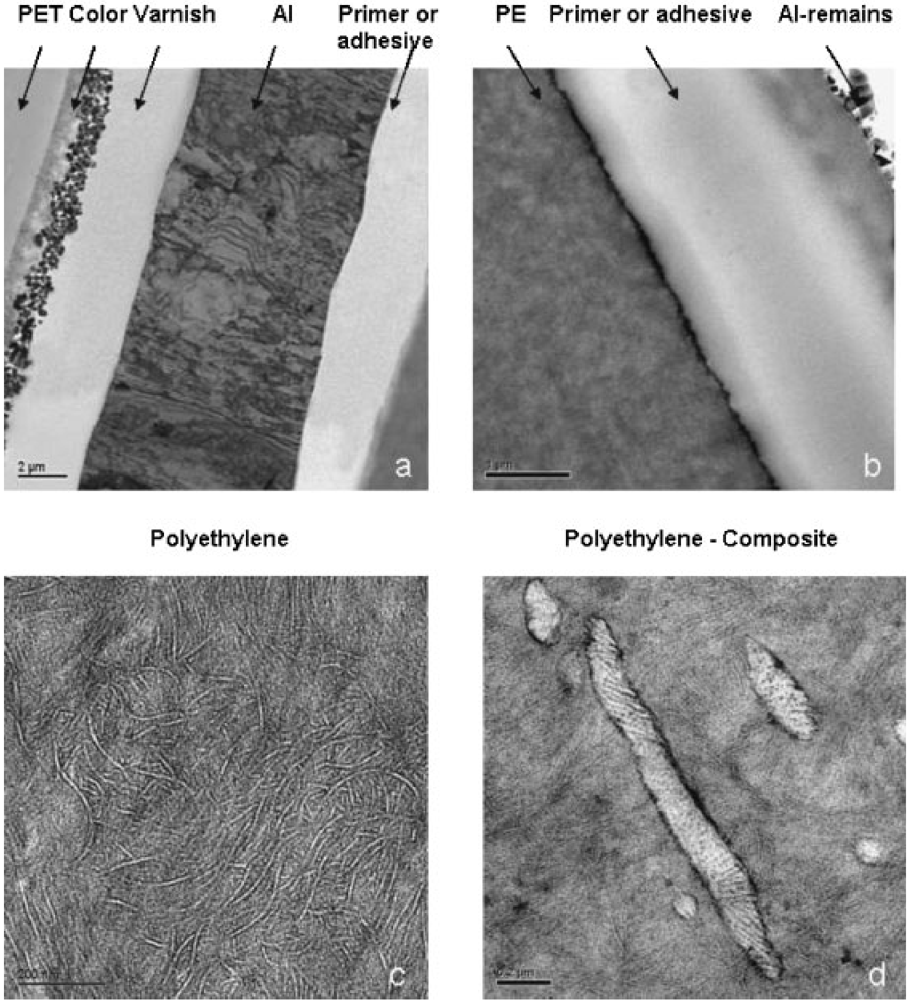

Figure 3.
Transmission electron micrographs from the sample MLF1: a – cryo-ultrathin section (Al-layer present); b – ultrathin section (Al-layer corroded due to RuO_4-staining); c and d – ultrathin sections after RuO_4-staining.

bound to the characteristic wavelength, used to create the chemical image, very thin layers (5 μm and below) are quite difficult to represent and/or identify, even by using the ATR-imaging technique.

Experimental Part

Two different multilayer packaging films (MLF) were tested, varying in thickness and (barrier) layer composition: MLF 1 with aluminium as barrier layer, MLF 2 without aluminium.

Stripes were embedded in two component epoxy embedding resin Epofix®, which was cured for 8 hours at 50 °C. The hardened samples were trimmed and the multilayer materials were cut with an Ultracut E Leica ultramicrotome, using a 45 ° Diatome diamond knife at an angle of 6 °. In cases of difficulties (i.e. detaching or curling foils), the samples were cut with a Leica FCS cryo-ultramicrotome, using a 35 ° diamond knife.

Surface sections and semithin sections were observed by light microscopy (Zeiss Axioplan).

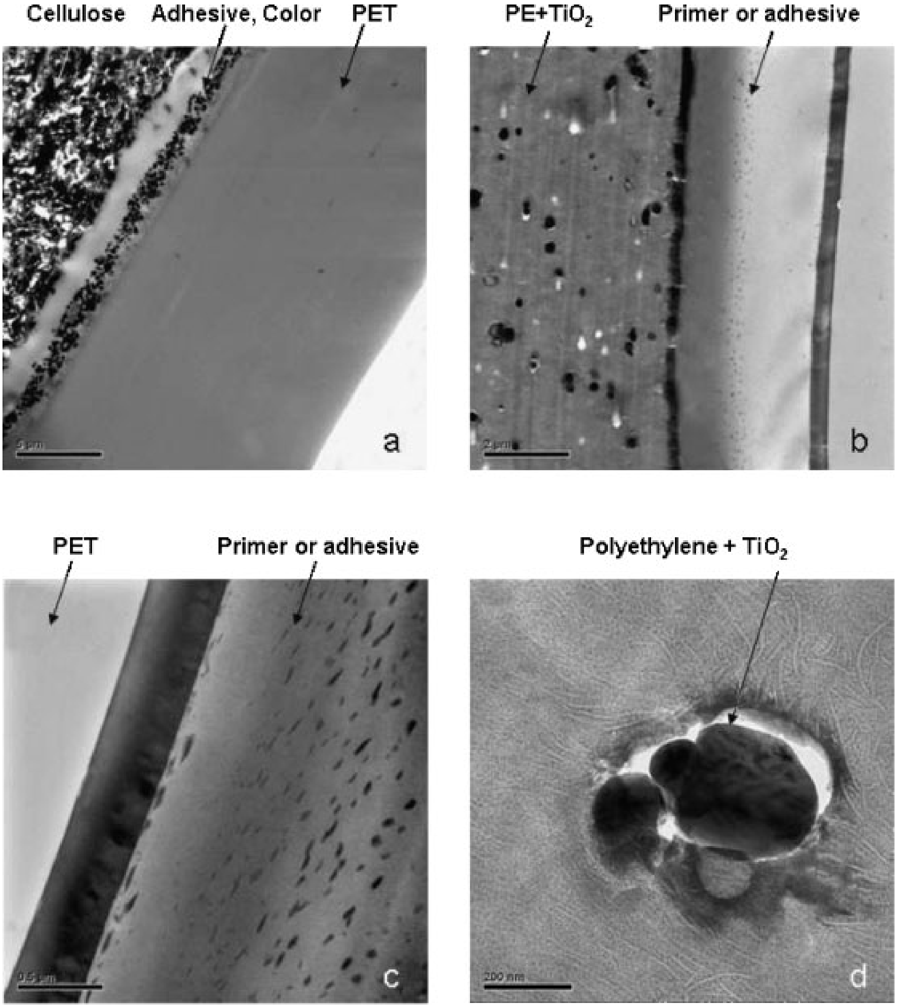

Figure 4.
Transmission electron micrographs from the sample MLF2: a–d – ultrathin sections after RuO_4-staining.

Ultrathin sections were observed with TEM using a FEI Tecnai G^2 electron micro-scope with Gatan Bioscan camera (Model 792).

Semithin sections were analyzed by means of FTIR transmission- or ATR- imaging. The experiments were carried out using an Equinox 55 scientific FTIR spectrometer, coupled to a Bruker Hyperion 3000 FTIR microscope. A cassegrainian x15 mirror objective was used for the transmission experiments and a x20 ATR- objective with Ge-crystal was used for the ATR-imaging experiments. The imaging detector was a 64×64 FPA MCT detector, cooled with liquid nitrogen. Thus, the investigated sample area was $270 \times 270\ \mu m^2$ in transmission and $50 \times 50\ \mu m^2$ in ATR mode. Images were collected with typically 16fold accumulation and 4 cm^{-1} spectral resolution in the 4000–900 cm^{-1} spectral range; measuring time per image including background was about 30 minutes. Data evaluation was carried out by using the OPUS® 6.0 software package (Bruker).

Raman spectra were obtained using a Renishaw Ramascope 2000 system, coupled to a Leica DMLM scientific microscope. The used objective was Olympus NPlan 50x NA = 0.75, dispersive grating with 1800 lines/mm, corresponding to a spectral resolution of 4 cm^{-1}. A He-Ne laser (633 nm) with 17 mW output power was used. Typical accumulation time of the spectra was 3×10 seconds.

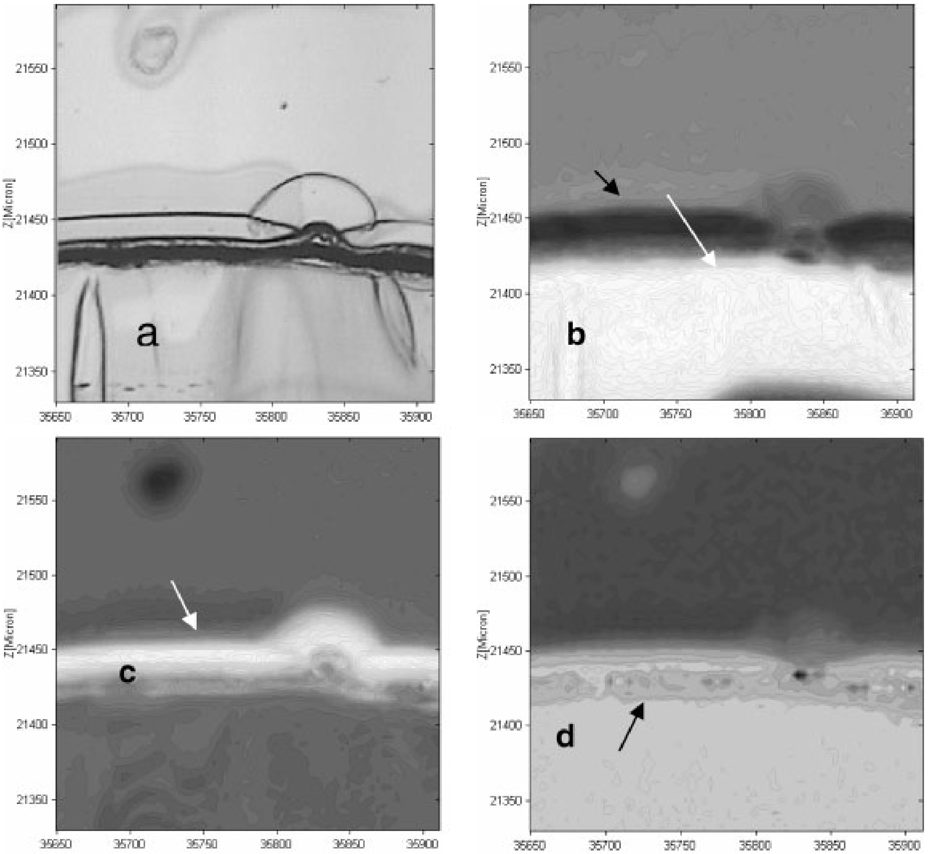

Figure 5.

MLF 1 – transmission FTIR images of a semi-thin crosssection, field of view $270 \times 270\ \mu m^2$, axes scaling in μm, relevant layers indicated with arrows from left to right: a - white light micrograph, b - PE distribution ($\nu_{C\text{-}H}$ 3000–2750 cm^{-1}) (white arrow) and Al (black arrow), c - PET ($\nu_{C=O}$ 1735 cm^{-1}), d - varnish ($\nu_{C=C}$ 1601 cm^{-1}).

Results and Discussion

Light microscopy gives the number and the thickness of the layers, but there is no information about the chemical composition and the coatings. Both multilayer foils consist of 8 layers (Figure 1).

TEM visualizes the important characteristics (coatings, filler particles) and enables the detection of inorganic fillers (EELS, EDX), but the organic components cannot be identified. In addition to the cutting problems and the detached from the adjacent epoxy-embedding, the samples

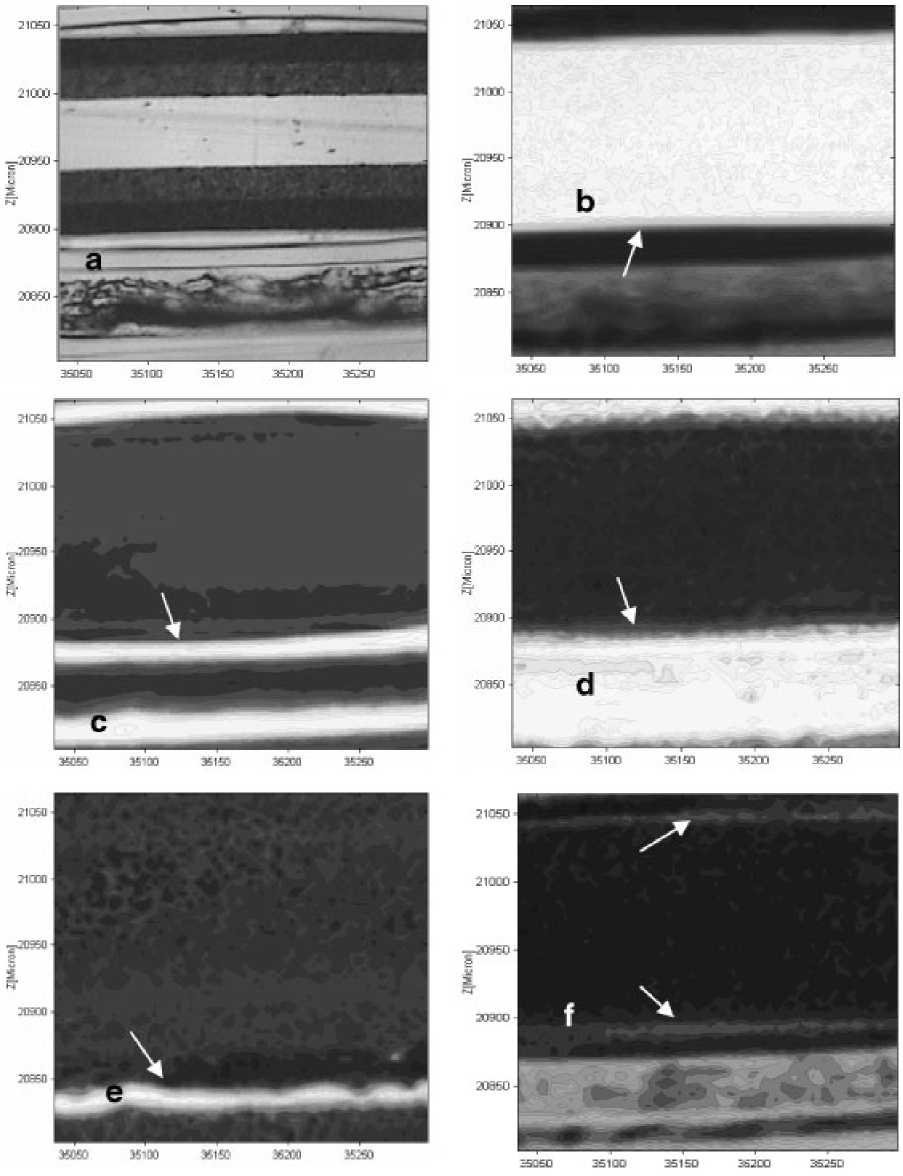

Figure 6.
MLF 1– transmission FTIR images of a semi-thin crosssection, field of view 270 × 270 μm^2, axes scaling in μm^2, relevant layers indicated with arrows from left to right: a – light micrograph, b - PE and PE + TiO_2 ($\nu_{C\text{–}H}$ 3000–2750 cm^{-1}), c - PET ($\nu_{C=O}$ 1735 cm^{-1}), d - cellulose ($\nu_{O\text{–}H}$ 3400 cm^{-1}), e - SiO_x ($\nu_{O\text{–}H}$ 3550 cm^{-1}), f - varnish ($\nu_{C=C}$ 1601 cm^{-1}).

have to be stained with RuO_4 in order to visualize their ultrastructure in TEM. In the case of MLF 1 the aluminium is destroyed. Samples with aluminium are therefore cut unstained with the cryo-ultramicrotome (Figure 3 and 4).

FTIR and Raman microspectroscopy enable the chemical characterization of the identified layers, but the lateral resolution is restricted (5–10 μm for FTIR and 1–2 μm for Raman). Most of the layers in the samples could be resolved in transmission imaging mode, as it is shown in Figure 5 and 6. The overall image quality is sufficiently high, as well as the quality of the extracted spectra, which were used for the materials' identification. It is noted here, that the FTIR imaging is an appropriate tool for layers identification and/or representation, requiring however good quality micrographs, which serve as a help and reference. In this case TEM possesses an unrivalled spatial resolution and serves as a reference for the determination of layers thicknesses

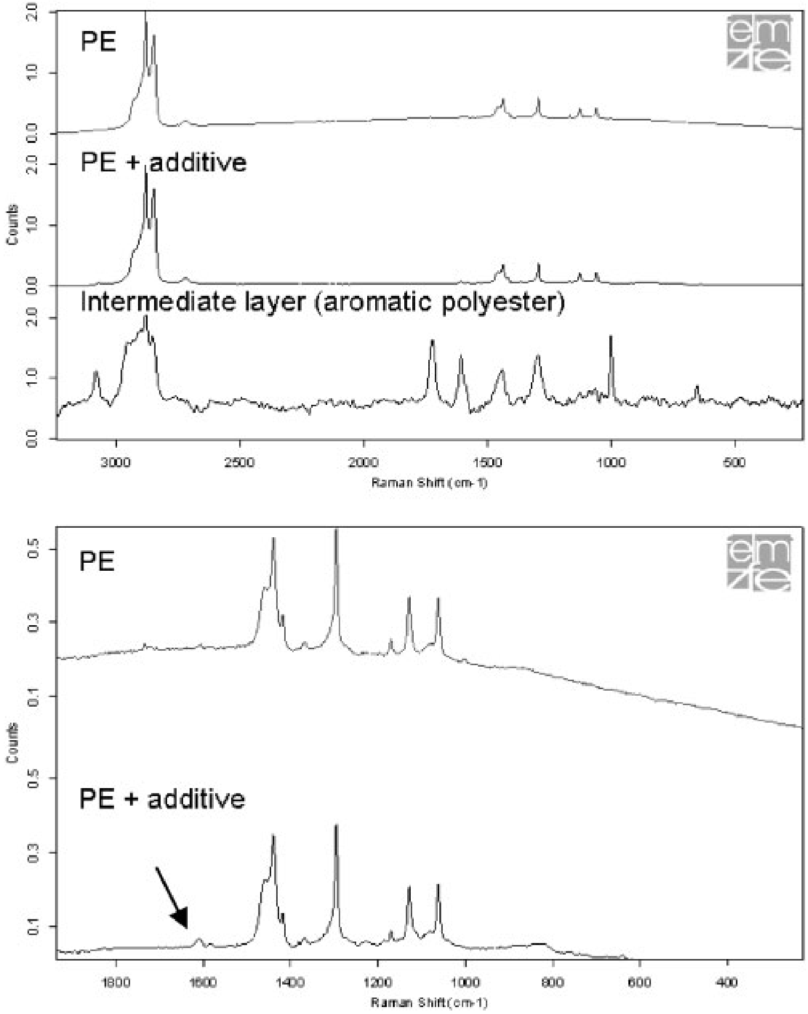

Figure 7.

MLF1: Raman spectra, showing the difference between the two PE-layers note the weak band at 1600 cm^{-1} in the zoomed spectral region on the lower figure, indicated with an arrow; and the identification of the intermediate layers 4 and 6.

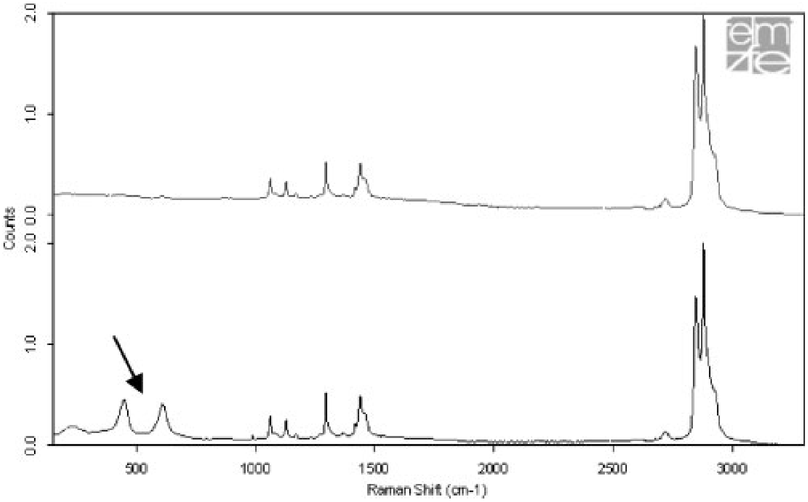

Figure 8.
MLF2: Raman spectra from the PE-layers, proving the presence of rutile (TiO_2); in the lower spectrum there are Raman bands at 612, 449 and 240 cm^{-1} (indicated with arrow).

or the location of certain layer. The latter is quite useful when components with similar spectral features are present in the sample next to each other, like in the case of MLF1 – PET and aromatic polyester as neighbouring layers.

Raman microspectroscopy was useful for the identification of the composite PE material in MLF1 – small band at 1608 cm^{-1}, obviously an additive and/or maleic anhydride grafting – Figure 7. It was already shown by TEM, that in one of the PE-layers of MLF2 a TiO_2 phase was present; this turned out to be the rutile modification – Figure 8.

Since the thinner layers in MLF1 and 2 couldn't be clearly distinguished in the transmission FTIR images, ATR imaging experiments were carried out. The results (Figure 9) show clearly two distinctive layers

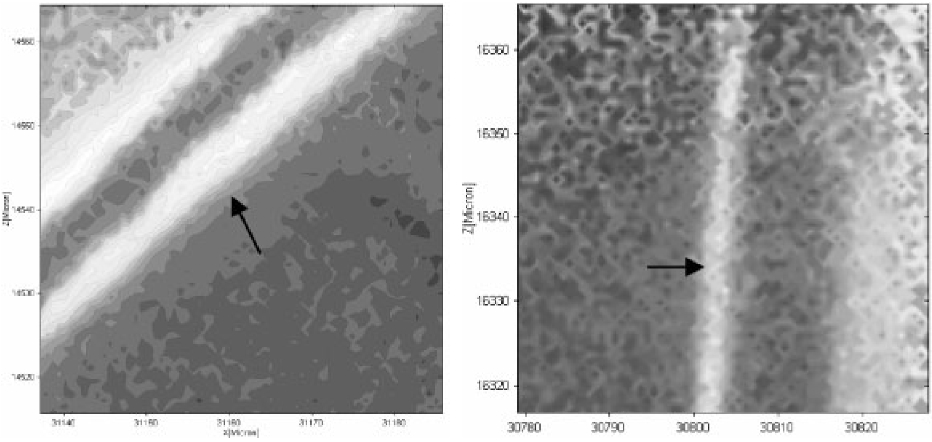

Figure 9.
FTIR-ATR images from the sample MLF1 and MLF2, field of view 50 × 50 μm^2, axes scaling in μm. The relevant layers (layer numbered with 6, cf. Figure 1 and 2) are marked with arrows.

for MLF1 with the Al in-between. The thinner layer consists of aromatic polyester and/or polyurethane (cf. Figure 3 – ‘‘Varnish’’) and is about 5 μm thick; the thicker layer in the figure summarizes two layers (cf. Figure 3 – ‘‘Varnish’’ and ‘‘Color’’) and its thickness is about 9 μm, according to the ATR data. In the ATR-image of MLF2 there is a thin layer of around 3.5 μm thickness; next to the PET layer (cf. Figure 4 ‘‘Primer or adhesive’’). This is in good agreement with the TEM data.

In conclusion, we were able to show that the investigation and characterization of multilayered materials is quite complicated with respect to the visualization and identification. White light microscopy is an uncomplicated approach, giving enough preliminary information about the layered architecture of the sample. However, TEM is superior and the information thereof is much more detailed and, therefore, helps within the further investigation steps. The spatial resolution of the vibrational spectroscopic methods in their classical form is the limiting factor in that case. The theoretical achievable spatial resolution with ATR-imaging is about 1–2 μm. This would be the case with an ‘‘ideal’’ sample e.g. perfect contact between the crystal and the sample and high spectra heterogeneity in terms of distinctive bands in the low wavelengths region (3000 cm^{-1} and above). Thus, layers with thickness as low as 3 μm, could successfully be resolved with ATR-FTIR imaging. The thinnest layers in Figure 1–3 are too thin and/or possess no distinctive spectral features with respect to their environment, making their identification with imaging spectroscopy an impossible task. The attempt to use Raman microscopy for that purpose did not bring any results because of strong fluorescence. It is however possible that at other excitation wavelengths or even by using FT- Rman spectroscopy the Raman spectra could become strong enough and/or the fluorescence could drop down, however we did not try that because of lack of instrumentation.

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