Experimental Testing of Lateral and Depth Resolution in Imaging Methods

Peter Wilhelm, Boril Chernev, Peter Pölt*

Summary: A polymer laminate and a PA-PTFE blend were studied by various imaging methods (FT-IR, Raman, ESEM). Different lateral and depth resolution of the methods were used to gain complementary information on the structure of the materials. Radiation damage caused by the electron beam during ESEM investigation was studied by Raman global imaging.

Keywords: electron microscopy; FT-IR microscopy; heterogeneous polymers; imaging; Raman microscopy

Introduction

Polymer blends and laminates are very important materials in the modern industry. Because market and economy as well as ecology make higher demands on new products, their micro-morphology and interface chemistry has to be well known in order to achieve the desired properties.

The thickness of individual layers in laminates can be tested by several microscopic methods (light, electron, infrared, Raman etc.), thus allowing a mutual testing of the limitations of the individual methods,[1] especially those recently introduced (namely vibrational micro-spectroscopy[2,3]). The lateral resolution of infrared imaging can be improved by using an ATR objective with a high refractive Germanium crystal. However, in some cases individual layers cannot be discriminated accurately, because the corresponding IR spectra are too similar or characteristic spectral features too weak.

While lateral resolution can be estimated by applying the Rayleigh criterion (considering wavelength and numerical aperture[4]), depth resolution varies considerably with the applied imaging method in each case. With transmission experiments it depends on the sample thickness (IR transmission) or the penetration depth of the evanescent wave (ATR), respectively. With reflection methods (Raman, SEM), however, the situation can be more complicated.

Methods

Semi-thin cross-sections (about 5 μm thick) were prepared from the polymer materials by means of an ultra-microtome Ultracut E (Reichert-Jung), supplied with a 45° diamond knife. FT-IR images were recorded in transmission mode using a Bruker Hyperion 3000 infrared microscope with x15 Cassegrainian objective. The microscope was coupled to a Bruker Equinox 55 scientific FT-IR spectrometer. The detector was a Bruker focal plane array (FPA) MCT detector with liquid nitrogen cooling. Spectral resolution was 4 cm^{-1}, 32 images were accumulated.

For Raman microscopy a dispersive Renishaw 2000 system was used. A HeNe laser (633 nm) with a maximal output power of 17 mW was the exciting laser light source. Rayleigh scattering was removed by a set of holographic Notch filters and the signal detected by a two-dimensional, Peltier cooled charge-coupled device (CCD)

Austrian Centre for Electron Microscopy and Nanoanalysis, Institute for Electron Microscopy, Graz University of Technology, Steyrergasse 17, A-8010 Graz, Austria
Fax: +43 (0) 316 811596
E-mail: peter.wilhelm@tugraz.at

camera. Raman images were acquired in global imaging mode. Dielectrical band pass filters with a resolution of approximately 20 cm^{-1} were used for selection of specific spectral regions.

The SEM images were recorded by an ESEM (Environmental Scanning Electron Microscope) FEI Quanta 600 FEG with both secondary (SE) and backscattered (BSE) electrons. The former give mainly topography, the latter phase contrast. In the case of BS-electrons higher mean atomic number of a phase gives higher brightness in the image. In contrast to the high vacuum mode in the ESEM mode (pressure around 1 torr) a coating of an electrically non-conductive sample to avoid charging is not necessary. The electrons at the specimen surface are neutralized by positive ions generated by collisions of electrons with the gas molecules (air). Thus the specimen surface is not modified, but care has to be taken to avoid specimen damage caused by the electron irradiation.

Polymer Laminate

A polymer laminate film (for packaging) was composed of nine layers (Table 1).

Table 1.
Individual layers of the polymer laminate (EVA: ethylene vinyl acetate; LLDPE-MAH: maleic anhydride grafted linear low-density polyethylene; COPA: co-polyamide).

EVA	45 μm
LLDPE-MAH	5 μm
COPA	32 μm
LLDPE-MAH	5 μm
EVA	66 μm
LLDPE-MAH	5 μm
COPA	32 μm
LLDPE-MAH	5 μm
EVA	45 μm

The EVA and COPA layers could be resolved quite well by FT-IR transmission imaging (Figure 1).

FT-IR ATR images showed an intermediate region between COPA and EVA of about 5 μm (Figure 2). However, a clear identification of that layer as MAH modified LLDPE was not possible due to the low MAH content. The corresponding carbonyl absorption bands should appear at 1790 and 1740 cm^{-1}, but did not show in the ATR spectra.

A simple line scan with Raman microscopy, on the other hand, clearly showed the LLDPE-MAH layer as a ca. 5 μm broad

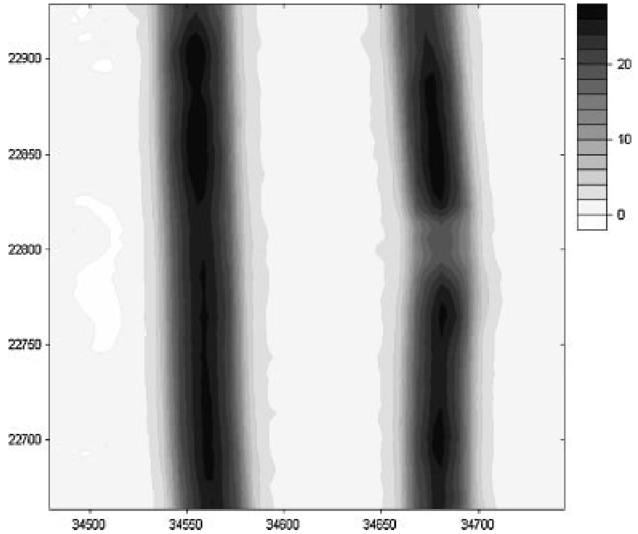

Figure 1.
FT-IR transmission image of the polymer laminate. Amide I band of COPA was integrated (intensity values represented in dark colour). Image area: 266 μm * 266 μm.

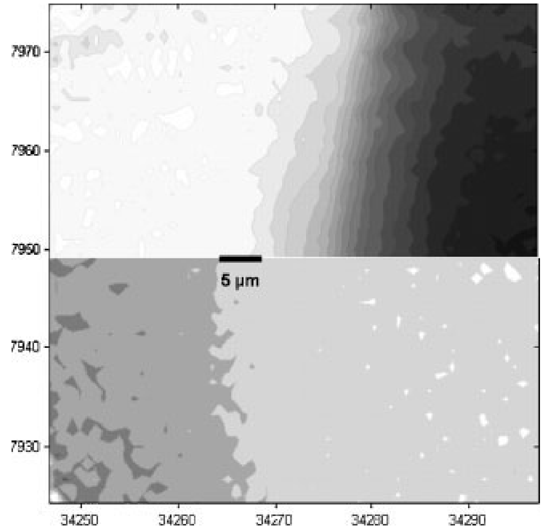

Figure 2.

FT-IR ATR image of the polymer laminate (right: COPA layer; left: EVA layer). The amide I band of COPA (upper half of the image) and the ester band of EVA (lower half) were integrated (intensity values represented in dark colour). Image area: 50 µm * 50 µm. A 5 µm intermediate region (assumed LLDPE-MAH layer is indicated.

plateau with the evaluation of three different Raman lines (Figure 3).

Polymer Blend

A polymer blend composed of 80 % PA (polyamide), 18 % PTFE (polytetrafluoro'-ethylene) and 2 % silicone oil was investigated by Raman global imaging. The material was intended to be used for friction bearings, and hence size and distribution of the PTFE clusters was an important feature. For Raman imaging we used the 733 cm^{-1} line of PTFE as described recently.[1]

Comparative images were obtained from that blend by environmental scanning electron microscopy (ESEM). Because of

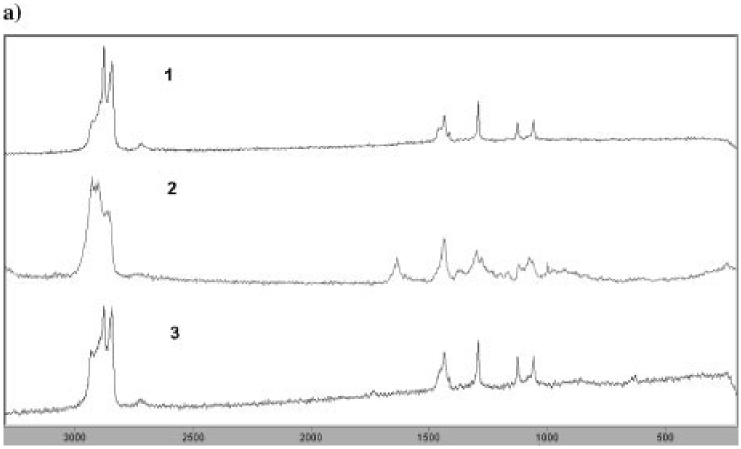

Figure 3.

a. Raman spectra of the individual layers; 1:LLDPE-MAH, 2: COPA, 3: EVA (abscissa: wave numbers in cm^{-1}, ordinate: intensity in arbitrary units). b. Raman line scan of polymer laminate using three different Raman lines (abscissa: position in µm, ordinate: intensity in arbitrary units).

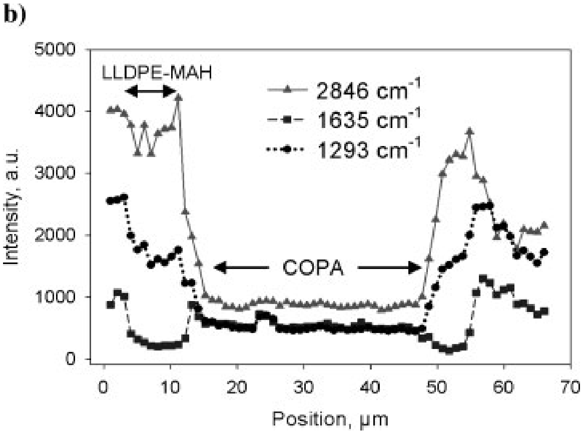

Figure 3.
(*Continued*)

the ESEM advantages (no coating of electrically non-conductive samples necessary) it was possible to image the same area first in ESEM, then in the Raman microscope, and afterwards to repeat that cycle again. In both methods penetration depth is several micrometers (depending on exciting beam energy and interaction of photons or electrons with matter). That phenomenon might account for some differences in the initial images (Figure 4, upper images).

During the second observation in the ESEM (Figure 4, lower images) some additional PTFE clusters (obviously somewhat below the surface) became visible (especially in the right half of the back-scattered electron image), and clusters at the surface appear very bright (charging by electrons).

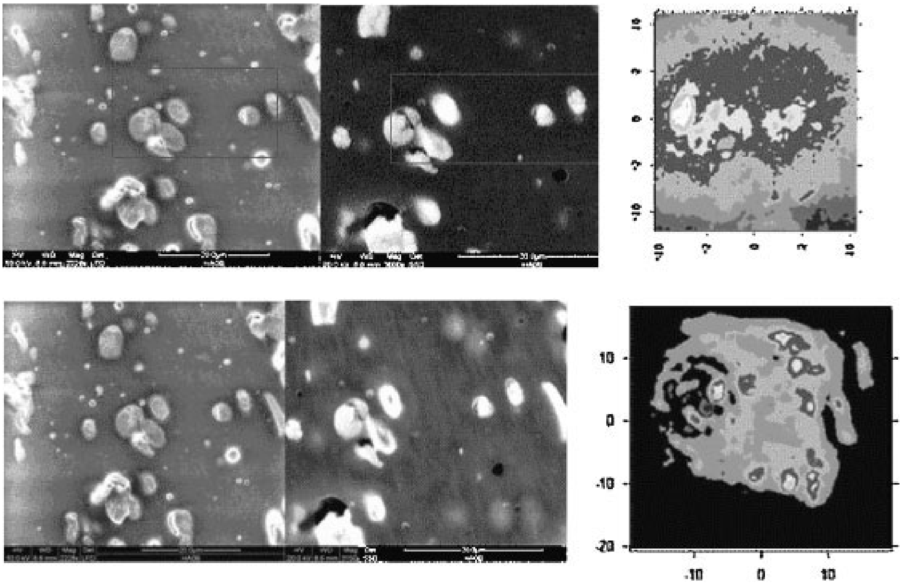

Figure 4.
ESEM (left) and Raman (right) images of the same area (ca. 20 µm * 10 µm). ESEM images show both secondary electron images (left) and back-scattered electron images (right).

A subsequent Raman image revealed that the clusters originally at the surface were destroyed by the ESEM electron beam, and new clusters became visible (obviously due to a certain destruction of the PA surface).

Conclusions

FT-IR Imaging has considerable advantages over conventional mapping experiments, whenever size and distribution in a multicomponent environment has to be evaluated: above all short measuring times (several minutes) and better spatial resolution. The output is readily comprehensible to non-spectroscopists (comparable to other microscopic techniques). Transmission experiments are straightforward, generally with reliable results and reasonable resolution.

ATR imaging further enhances lateral resolution (mainly by using high refractive index crystals), but weak spectral features may be hard to detect. In such cases complementary information by other methods, e.g. Raman microscopy, can be very helpful. Comparison of different imaging methods can tell us about structures at and slightly below the surface of the material studied (exploiting their varying depth resolutions). Radiation damage can be checked by complementary imaging methods.

Acknowledgements: Polymer samples were kindly provided by NAPIAG Kunststoffverarbeitung, Zeltweg, Austria, and IB Steiner, Spielberg, Austria. The authors gratefully financial support by the UniINFRASTRUKTUR Offensive des RFT, Vienna, Austria.

[1] A. Gupper, P. Wilhelm, M. Schmied, S. G. Kazarian, K. L. A. Chan, J. Reußner, *Appl. Spectrosc.* **2002**, *56*, 1515.
[2] J. L. Koenig, "*Microspectroscopic Imaging of Polymers*", ACS Professional Reference Book **1998**.
[3] J. M. Chalmers, N. J. Everall, M. D. Schaeberle, I. W. Levin, E. N. Lewis, L. H. Kidder, J. Wilson, R. Crocombe, *Vibr. Spectrosc.* **2002**, *30*, 43.
[4] K. L. A. Chan, S. G. Kazarian, *Appl. Spectrosc.* **2003**, *57*, 381.