

Polymer characterisation by spectroscopic imaging: infrared and electron microscopy: a good match

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Introduction

Polymer materials, used in all branches of modern industry, are becoming more and more complex (polymer blends, laminates and polymer compounds, functional polymers). Product improvement is achievable only by having a thorough understanding of the underlying microscopic properties. Only a controlled microstructure can give rise to a controlled macrostructure, which is mainly responsible for the final material properties. Therefore, characterisation methods with micro- and nano-scale resolution play a fundamental role in the understanding and development of new materials and their quality control in industrial laboratories.

Modern microscopy techniques provide high-resolution morphological images, down to the nanometre scale. At the Austrian Centre for Electron Microscopy and Nanoanalysis in Graz (Centre for Electron Microscopy Graz and Research Institute for Electron Microscopy of the Graz University of Technology) work is focused on materials' characterisation at micro- and nano-scale levels. Its equipment includes electron microscopy (SEM, ESEM, TEM) with various analytical capabilities (EDXS, WDXS, EELS, EFTEM) and preparation methods (cryo-ultramicrotomy, FIB) and both FT-IR and Raman micro-spectroscopy.

The applicability of electron microscopy to polymers is often considerably restricted because of poor contrast. FT-IR

spectroscopy has proven analytical power for investigating microscopic areas. The availability of FPA (focal plane array) detectors has opened up an even wider field of imaging applications (e.g. examination of multi-component systems), enabling improved spatial resolution, since masking apertures are no longer needed with these systems.¹ So, for polymer investigations, the complementary combination of electron microscopy and vibrational micro-spectroscopy is of particular importance; both methods benefit from each other's advantages.

PTFE/PA polymer blend

In this article we report on a reactive poly(tetrafluoroethylene)/polyamide 6 (PTFE/PA) blend,² which represents an ideal material for comparative imaging studies, giving higher contrast in electron microscopy (due to its high fluorine content) as well as strong and distinct infrared absorption spectra. It is known that upon conventional mixing of common PTFE micro-powder and PA in an extruder at about 280°C, relatively large PTFE particles occur in the final product because of the immiscibility of the polymers. However, by irradiation with electrons in air, reactive groups are produced on the PTFE powder. As a result of the reaction of these functionalised particles with the molten PA in the extruder block, copolymers are formed, which improve the compatibility of both

components. At the same time a decrease in PTFE particle size proportional to the irradiation dose can be observed in the blend. So, a PTFE/PA compound with better properties is produced, which can be applied as wear resistant, maintenance-free slide bearing material. Comparative analytical studies on a similar but non-reactive polymer blend system including IR and Raman imaging, SEM and micro-thermal analysis have been reported recently.³

IR chemical imaging and resolution problem

Whenever the question comes down to "what chemical species are in my sample, how much of each is present and—most importantly—where are they located?" chemical imaging can provide the solution. Chemical (or spectral) imaging combines molecular spectroscopy (IR, Raman, NIR etc.) and digital imaging to depict sample morphology, composition and structure visually. Such images can be obtained by mapping (sequential scanning of a certain area in two dimensions, using a single-element detector) or simultaneous recording of a certain area by using an array of detector elements such as that in a FPA or, for Raman, a CCD. In both cases, whether single-point mapping or FPA imaging, for each pixel constituting the sampled area (or volume element, strictly speaking) a full IR spectrum is acquired.

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IR imaging using FPA detectors has considerable advantages over conventional mapping experiments:

1. Mapping is time consuming, which can lead to loss of stability and higher manpower costs.
2. Spatial resolution is limited severely by diffraction at apertures. FPA imaging provides better resolution and better reproducibility of the data, requiring no microscope stage/sample movement.
3. Kinetic experiments can be followed much more readily with FPA imaging.

High computing power, which is needed for imaging (fast readout and processing, data storage) does not cause any significant problems when using state-of-the-art PCs, and FT-IR measurements can be performed with commercial spectrometers operating in rapid scan mode now, rather than in step scan mode, for FPA detectors with array sizes of up to 128×128 pixels.

Lateral spatial resolution is a critical point when planning and interpreting imaging experiments.⁴ The resolution of an optical instrument is defined as the minimum distance between two objects at which they can still be separated. One criterion for judging this separation is the "Rayleigh criterion" (r), which is equivalent to "26.4% contrast". According to this criterion, resolution depends on the radiation wavelength (λ) and the numerical aperture (NA) of the objective. The latter is determined by the angular aperture (2θ) and the refractive index (n) of the medium between the objective and the sample (air or ATR crystal).

$$r = \frac{1.22\lambda}{2NA}; NA = n \sin \theta$$

Theoretically, two points should have a distance of at least $2r$, in order to recognise them as distinct objects. In practice resolution is further deteriorated due to optical aberrations, but may be improved by:

1. Using characteristic absorption bands at higher wavenumbers (shorter wavelength), i.e. C–H and O–H stretching vibrations, however, they are generally not very specific.

2. Increasing the NA by using a higher refractive index material (ATR crystal) in the case of an internal reflection spectroscopy measurement.

For evaluation of PTFE distribution, we use its absorption band at around 1200 cm^{-1} . The $15\times$ Cassegrainian objective of our microscope has a NA in air of 0.6, so a spatial resolution of $17 \mu\text{m}$ can be expected to discriminate individual PTFE clusters. By using the ATR objective (magnification $20\times$, Ge crystal with $n = 4$) the nominal spatial resolution could be improved to approximately $4 \mu\text{m}$.

Experimental details

Polymer blend

PTFE TF 2025 (Dyneon GmbH, Germany) was irradiated at the Institute of Polymer Research Dresden at ambient temperature in air with a dose of 500 kGy . Then the micro-powder was thermally treated at 200°C h^{-1} in air. After this treatment, its molecular weight is lower and reactive groups (i.e. COOH) are formed. Polyamide PA6 SH 3 (Leuna GmbH, Germany) was used as the blend matrix material. The compounds (50/50 wt.-% PTFE/PA, $\sim 30/70$ vol.-% PTFE/PA) were processed in a twin-screw extruder at a mass temperature of about 280°C (which is lower than the PTFE melting temperature of about 320°C). At this temperature most of the crystallites in the PTFE phase were not molten during the processing.

Microscopic methods

Scanning electron microscopic images were recorded on a Leo Gemini DSM 982 system [Leo (Zeiss) Elektronenmikroskopie GmbH, Oberkochen, Germany] equipped with a Field Emission Gun, FEG, (Schottky) cathode. PTFE phases were identified by energy dispersive X-ray spectrometry (EDXS). FT-IR spectra and images were acquired on a Bruker Hyperion 3000 microscope (Bruker Optik GmbH, Ettlingen, Germany), equipped with a $15\times$ Cassegrainian objective (for transmission experiments) and a $20\times$ ATR objective (Ge crystal). With 64×64 detector elements of the FPA, an area of $270 \times 270 \mu\text{m}^2$ in transmission

mode and $50 \times 50 \mu\text{m}^2$ in ATR mode can be recorded. The microscope was connected to a Bruker Equinox 55 spectrometer. For TEM images, a Philips CM20 microscope (FEI Company, Eindhoven, Netherlands) with a Gatan imaging filter (GIF) was used (Gatan Inc., Pleasanton, USA). The GIF spectrometer (model 678) was operated in diffraction coupled EELS mode; a two-dimensional CCD camera with a YAG scintillator was used as detector, having 1024^2 pixels

Results

Figure 1(a) shows a SEM micrograph of the blend material ($5 \mu\text{m}$ thick section, as used for IR experiments, area: $270 \times 270 \mu\text{m}^2$). PTFE cluster size varies over a wide range; the smallest less than $1 \mu\text{m}$ across; the largest with approximately $100 \mu\text{m}$ in one dimension (see right part of the image). The material is porous, with some holes, one of them very large (see, for example, the left part of the image). In Figure 1(b) the same sample area is presented as an IR FPA transmission image. Spatial resolution is as expected. The large PTFE cluster and the hole are well approximated. Small PTFE clusters of $8\text{--}10 \mu\text{m}$ size can be distinguished with their dimensions well comparable to those in the SEM micrograph.

An IR ATR image is presented in Figure 2(a) (area: $50 \times 50 \mu\text{m}^2$). Some small clusters, approximately $4\text{--}5 \mu\text{m}$, can be seen. With ATR experiments the sample has to be in contact with the ATR crystal, and the measurement is very surface specific, typically probing depths less than $1 \mu\text{m}$. Some broadening of the regions within the image could be caused, not only by diffraction effects, but also arise from compressing soft samples. Figures 2(b) and 2(c) show the IR ATR spectra of a PTFE-rich and a PA-rich region, respectively.

Transmission electron microscopy and EELS

Due to its superior spatial resolution, TEM (transmission electron microscopy) and EELS (electron energy loss spectroscopy) and EFTEM were used for further characterisation of the PA–PTFE blends.⁵ With

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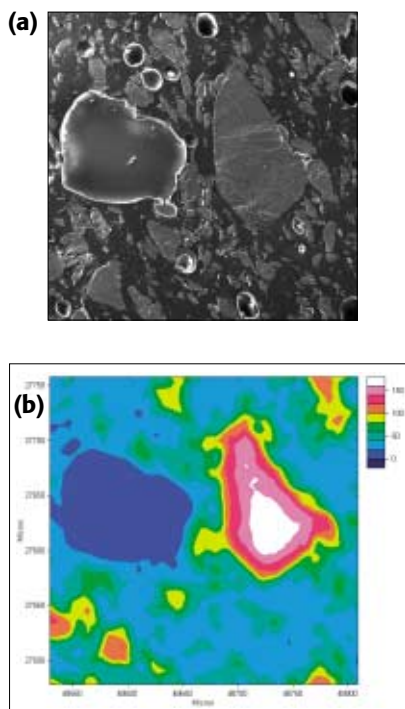


Figure 1. (a) SEM micrograph of a PA-PTFE blend section (area: $270 \times 270 \mu\text{m}^2$). (b) IR FPA image obtained in transmission mode of the same sample area as in (a). PTFE absorption band was integrated between 1185 and 1130 cm^{-1} . Small PTFE clusters of $8\text{--}10 \mu\text{m}$ in diameter can be distinguished.

an ultra-microtome, 50 nm thin sections were cut using a diamond knife at low temperatures to avoid smearing of the sample. Figure 3(a) displays the C–K and F–K edges (the latter appearing only in the PTFE spectrum) of the PA and PTFE phases. Spectral features are markedly different, in particular at the beginning of the C–K edge at 284 eV (ELNES: energy loss near edge structure), enabling a differentiation between the two materials. Energy-filtered images show the distribution of fluorine [Figure 3(b)], calculated from the F–K edge at 685 eV after background subtraction by the “3 window method”. Within the very small PTFE particle, some black zones can be found. These could be due to the interpenetration of the two polymers, which is a further indication of improved phase miscibility due to PTFE activation.

Conclusions

Infrared imaging has considerable advantages over conventional mapping experiments, namely short measuring times

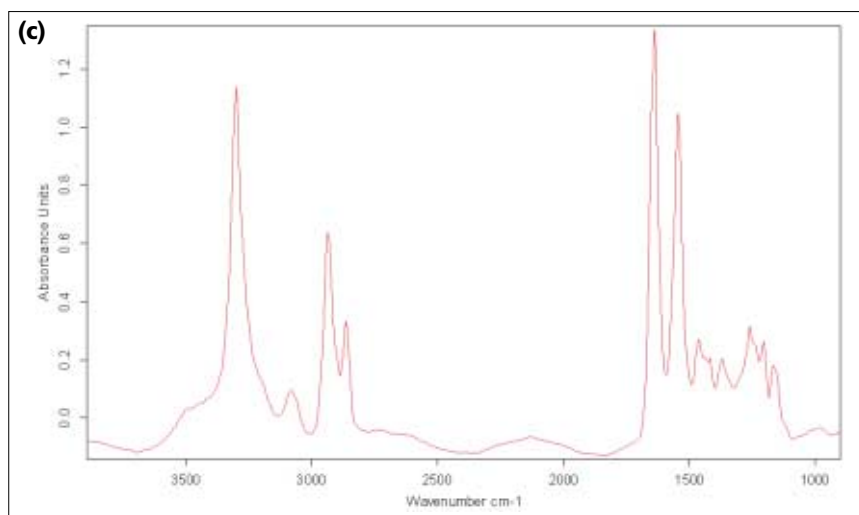
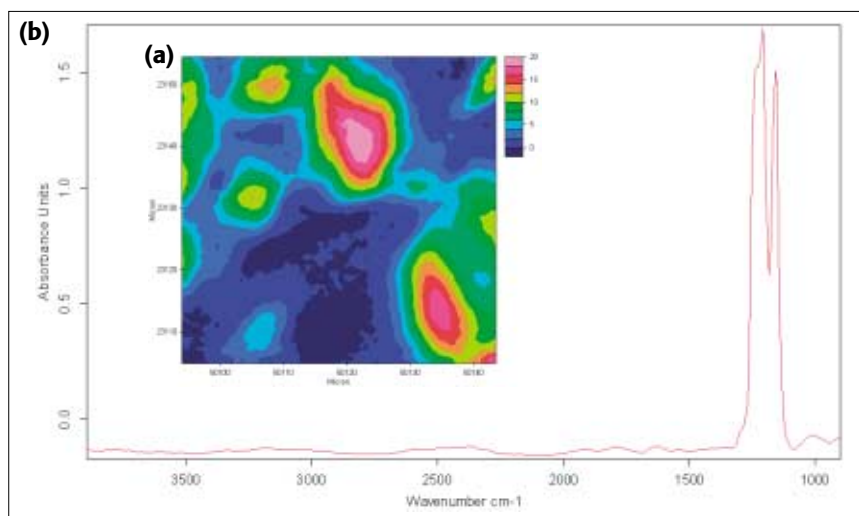


Figure 2. (a) IR ATR image of a PA-PTFE blend (area: $50 \times 50 \mu\text{m}^2$) with some small PTFE clusters ($4\text{--}5 \mu\text{m}$, left part of the area); PTFE band integration as in Figure 1 (b). (b) IR ATR spectrum of a PTFE rich area. (c) IR ATR spectrum of a PA rich area.

and improved spatial resolution. As with other microscopic techniques, the output of the measurements is readily comprehensible to non-spectroscopists. Transmission experiments are straightforward, generally with reliable results and reasonable resolution (features below $10 \mu\text{m}$ can be detected). ATR experiments cannot be performed contactless, therefore attention should be paid to possible deformation of soft samples; although, spatial resolution can be extended further by using this technique, and no sectioning of the sample is necessary. Useful complementary information will most likely be obtained also from other microscopic techniques (e.g. light, Raman and electron microscopy, X-ray and electron spectroscopy, micro-thermal analysis),

depending on the system under investigation. The combination of vibrational spectroscopy and electron microscopy turned out to be an excellent choice here for, evaluating chemical composition from IR spectra and morphological details with high lateral resolution from electron microscopy.

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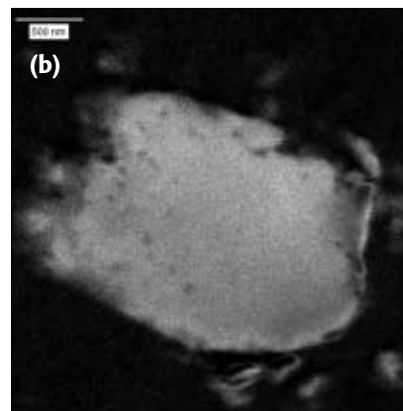
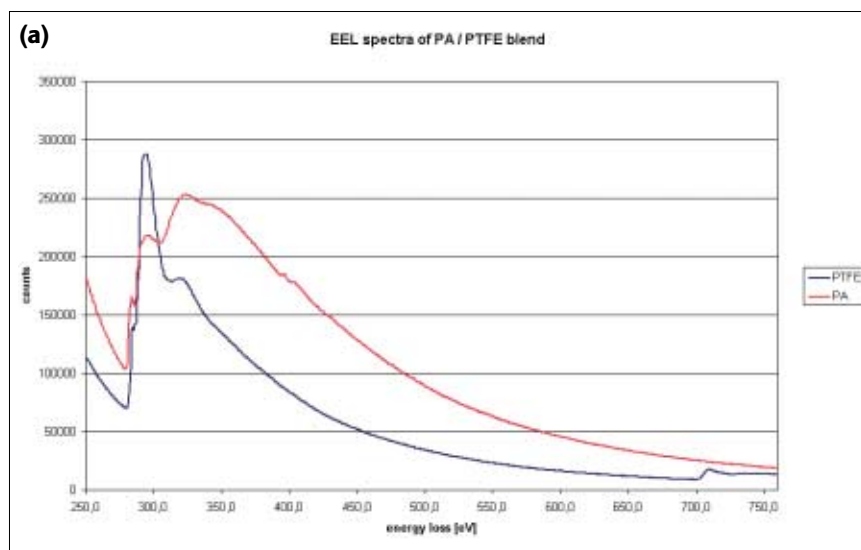


Figure 3. (a) EELS spectra of PA and PTFE phases. (b) Fluorine elemental distribution map.

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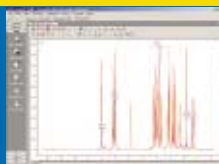


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