Macromol. Symp. **2004**, *205,* 171—180

Spectroscopic Imaging Techniques for Characterization of Polymer Morphologies: A Combination of Infrared and Electron Microscopy

Andreas Gupper,[1] *Peter Wilhelm,**[1] *G. Kothleitner,*[1] *K.-J. Eichhorn,*[2] *G. Pompe*[2]

[1] Research Institute for Electron Microscopy, Graz University of Technology and Centre for Electron Microscopy Graz, Steyrergasse 17, A-8010 Graz, Austria
E-mail: peter.wilhelm@felmi-zfe.at
[2] Institute of Polymer Research Dresden, Hohe Strasse 6, 01068 Dresden, Germany

Summary: The morphological characterization of polymer blends consisting of polyamide and poly(tetrafluoroethylene) using FT-IR spectroscopy and electron microscopy is described. To enhance the lateral resolution – one of the main limits in infrared spectroscopy – a combination with scanning electron microscopy and analytical electron microscopic methods of a transmission electron microscope was made. The possibilities of electron energy loss spectroscopy and energy filtered transmission electron microscopy (EFTEM) in the area of polymer characterization are outlined.

Keywords: analytical electron microscopy; infrared spectroscopy; morphology

Introduction

The design of high tech materials is amongst the most strongly developing areas in materials science. The number of high-end materials is continuously growing and their fields of application are nearly unlimited. Additionally, modern applications ask for materials properties that cannot be obtained without special processing, for instance stabilising or coating, and / or a careful selection of feedstock materials. Generally, industry tends towards better and controlled quality throughout the production process. The basis for these needs in materials science is an excellent analytical understanding that supports development on one hand, and on the other hand leads research away from a simple trial and error approach to a more sophisticated experimental design and planning. Simply controlling and adjusting macroscopic properties allows a certain amount of tuning final properties but is not sufficient for fundamental improvements. Less pragmatic and less industrial approaches however, show that product improvement is only achievable by having a thorough understanding of the underlying microscopic properties. Only a controlled microstructure can

© 2004 WILEY-VCH Verlag GmbH & KGaA, Weinheim
DOI: 10.1002/masy.200450116

give rise to a controlled macrostructure, which ultimately is responsible for the final material properties. Therefore, in the analytical chain microscopic characterization methods play a fundamental role. The whole potential of new materials systems, whether they might be manufactured of a single compound or be a composite, can only be evaluated, if the microscopic details down to the molecular or atomic level are fully understood. This is absolutely mandatory, if the development of new products should be successful and in sync with today's demands.

In this work the combination of two well established techniques has been worked out on hand of a commercial polymer blend. The chemical richness of infrared spectroscopy and the excellent lateral resolution of electron microscopy were used to characterise the morphologies of polyamide / poly(tetrafluoroethylene) blends that have been treated by electron irradiation in order to enhance mechanical stability and gliding properties.

Infrared spectroscopy is a widespread and highly appreciated technique due to the richness of chemical information that can be obtained from FT-IR spectra. In last years the coupling of an FT-IR spectrometer to a microscope further increased the number of successful applications based on the extended variety of problems that could be addressed with a higher lateral resolution. Nevertheless, in modern high performance materials also a resolution in the range of several micrometers is sometimes not enough for accurate materials description. Therefore, the combination with electron microscopes was searched, which provides much more detailed morphological information and nowadays also chemical information of areas very much confined in space. With scanning electron microscopy morphological details can be quickly identified and the analytical electron microscopic techniques in a transmission electron microscope (TEM) EELS (electron energy loss spectrometry) and EFTEM (energy filtered transmission electron microscopy) can reveal chemical information down to molecular or atomic level, which in combination with vibrational spectroscopy can deliver a nearly complete picture of the ongoing processes during materials processing and manufacturing.

The materials system under investigation is a combination of polyamide and poly(tetrafluoroethylene). Such polymer composites are of commercial interest: the unique gliding properties and the low coefficient of friction of poly(tetrafluoroethylene) result, paired

© 2004 WILEY-VCH Verlag GmbH & KGaA, Weinheim

with the mechnical stability provided of a polyamide matrix, in work pieces that can be employed e.g. as bearings in automobile industry, as gear wheels, or for mobile parts in electronic devices, such as printers of fax machines, where external lubricants can soil the paper.

In the past the two polymer phases have not been linked and mechanical as well as gliding properties were not satisfactory in all regards. By activating poly(tetrafluoroethylene) by electron irradiation these two phases should be linked to improve materials properties. In this work here the dependence of polymer morphology in respect to irradiation dose will be described.

Experimental Section

The chemical composition of the blend material is known from processing. For the here presented results a 50 / 50 weight-percent PA / PTFE blend was used. Activation of PTFE for reaction with PA was obtained by electron irradiation in inert atmosphere. Electron dose varied between 0 and 2000 kGy depending on the degree of activation. More detailed information about sample preparation, basic processing and materials processing are described elsewhere.[1,2]

Infrared spectra and mappings were recorded with a Bruker Hyperion system that consists of an Equinox 55 step scan FT-IR spectrometer coupled to an IR Hyperion microscope. For signal detection a highly sensitive MCT detector is employed. The accessible spectral range covers the region from 4000 to 600 cm^{-1}. Bruker's OPUS software was used for data handling. All spectra were acquired in transmission mode from 5 micrometer thin sections that have been prepared with an ultamicrotome using diamond knifes and working at low temperatures (about -80°C) to prevent smearing.

Scanning electron microscopic images were recorded on a Leo Gemini DSM 982 system equipped with a FEG (Schottky) cathode. Sections of the material were prepared and polished before they were carbon coated (to reduce charging effects). In some pictures tiny white spots originating from silicon carbide, which are an artefact of sample preparation, are visible and have been identified by energy dispersive X-ray spectrometry (EDXS).

For TEM images a Philips CM20 microscope equipped with a Gatan imaging filter (GIF) was employed. Samples were prepared with a cryo-ultramicrotome. For TEM investigations sample thickness had to be reduced to a value of 50 nanometers.

© 2004 WILEY-VCH Verlag GmbH & KGaA, Weinheim

Results and Discussion

Infrared Spectroscopy

The possibilities of infrared spectroscopy cover chemical phase identification and with sufficiently large particle sizes also determination of phase distribution in polymer blends. Materials without any previous activation by electron irradiation proved to have PTFE particles incorporated into the PA matrix, which are in the order of several micrometers and can be resolved using FT-IR spectroscopy. With a mapping approach and measuring the sample in transmission mode the distribution of PTFE clusters can be described. Figure 1 represents the PTFE distribution in a non activated blend material. It shows the integrated band area between 1174 and 1122 $cm^{-1}$of the $\nu(CF_2)$ band of poly(tetrafluoroethylene) at 1156 cm^{-1}. The imaging approach, which provides a higher spatial resolution at much lower acquisition times has recently been described for a similar system but was not applied in this case.[3,4]

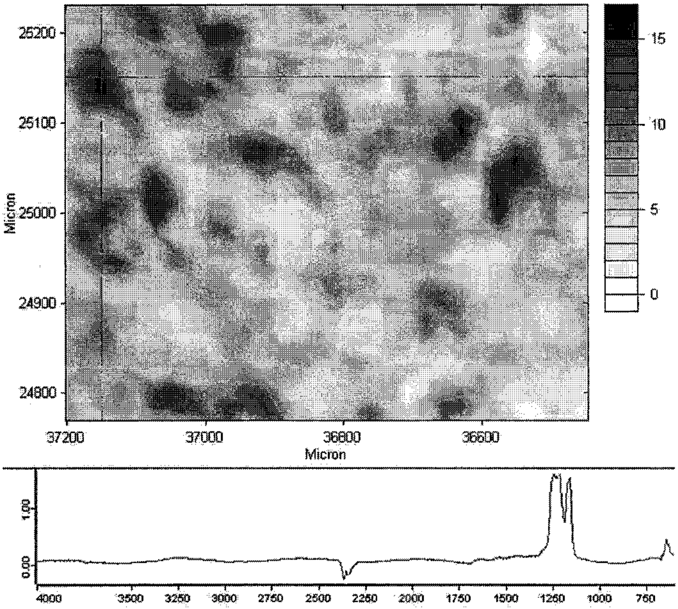


Figure 1. PTFE distribution map of a non-activated PA / PTFE blend. The $\nu(CF_2)$ band in the region from 1174 – 1122 cm^{-1} has been integrated. High intensities of PTFE appear black whereas PA rich areas are white. The location where the spectrum below the map has been acquired is indicated by the cross-hair.

© 2004 WILEY-VCH Verlag GmbH & KGaA, Weinheim

In a second step also samples with higher electron irradiation doses were investigated by infrared spectroscopy. None of them allowed the creation of spatial distribution maps similar to the one in figure 1. All spectra showed a nearly equal content of PA and PTFE with only minor fluctuations of band intensities from the expected mean value. Although, it was not possible to resolve the morphology due to the small particle size (details can be found in the SEM section) some changes in the spectra due to the formation of new bonds between PTFE and PA have been expected.

Unfortunately, it turned out that the number of such bonds – especially amide bonds in the neighbourhood of CF_2 groups – is not large enough to be detected. The bulk material covers the slightly shifted bands and currently work is under progress to remove the unchanged bulk material by solvent extraction. We expect that with a less intensive matrix the detection of this small number of bonds building the interface between the two polymers should become possible.

Scanning Electron Microscopy

The higher lateral resolution of electron microscopic imaging techniques was employed to characterise the PTFE particle size in the different blend materials.

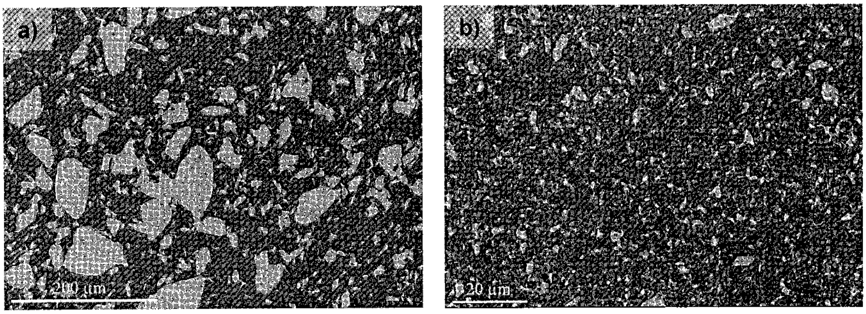


Figure 2. SEM images of a) an untreated sample and b) a specimen with PTFE activation (500 kGy).

Figures 2 a and b shows the decrease of PTFE particle sizes in higher activated materials. In these images the brighter areas represent PTFE particles. This has been proved by EDXS, where a

© 2004 WILEY-VCH Verlag GmbH & KGaA, Weinheim

signal of fluorine could be found in brighter regions, which is unambiguously correlated with the presence of PTFE [3]. In darker areas no fluorine but nitrogen was found, which resembles the PA phase. Again, the small bright spots are an artefact of sample preparation, which arise from silicon carbide that was used for polishing.

In figure 2a an overview of the sample without activation and chemical linkage is shown. The size is in the order of several micrometers, which is also in concordance with the FT-IR results reported above. Bigger particles with a diameter of more than 400 micrometers have also been observed but the figure below is representative for the distribution of PTFE particles in this special specimen. When the PTFE material is activated with higher doses of electron irradiation a remarkable decrease or particle size is expected and is also observed. Figure 2b contains morphological information of a sample irradiated with 500 kGy and verifies the assumption made before. Although there are still some particles with diameters larger than one micrometer the medium values lies below this threshold. Additionally to the particle size decrease porosity gets higher implying also troubles with sample preparation for accurate scanning electron microscopic pictures. Islands are formed within the specimen surface, which are carbon coated but not sufficiently connected to the rest of the sample. Thus, charging effects are pronounced and image acquisition becomes more difficult. A sample with an electron dose of 2000 kGy has been investigated but the extreme height-differences over an area necessary for a meaningful image made an acquisition of a sharp image impossible. Nevertheless, it could be recognised that particle size further decreased and is in line with the expectations.

Transmission Electron Microscopy:

Grace to its superior lateral resolution and chemical sensitivity, TEM and EELS were involved for the further characterization of our materials. Sample preparation was challenging for the TEM specimens used here. With an ultramicrotome 50 nanometer thin sections were cut using a diamond knife while working at low temperatures (-80 °C). This thickness is required to allow electrons passing the sample and prevent them of being multiply scattered, low temperatures should avoid the smearing of sample features. Experiments were only performed on the specimens with a 500 kGy electron dose (not to be confused with the electron dose in the TEM, which has a completely different meaning). A zero loss filtered image (15 eV slit centred on the

© 2004 WILEY-VCH Verlag GmbH & KGaA, Weinheim

elastic signal) of a PTFE cluster in that material is shown in figure 3. For untreated polymers the high spatial resolution was not required and higher activated materials were unfortunately not stable enough under the conditions of the transmission electron microscope. Already after short electron exposure time destruction of the polymer could be observed, making it impossible to focus and acquire an image. When moving the electron beam over the sample, PTFE particles of several nanometers could be seen, however a representative study was impossible due to the short observation periods. The values for the mean PTFE particle size in the examined sample determined with TEM are in good agreement with the SEM results.

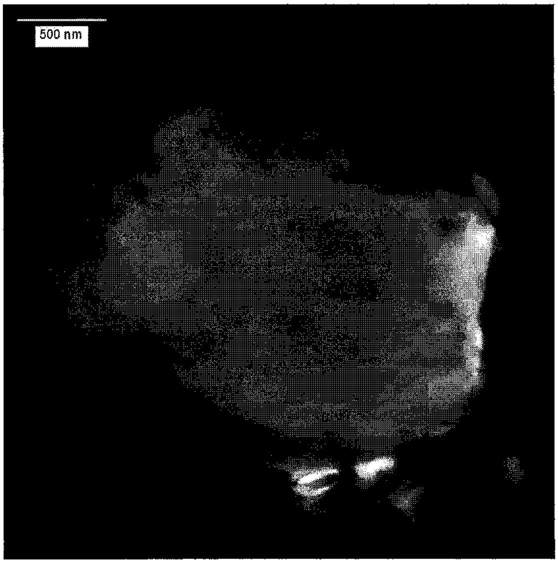


Figure 3. Zero loss filtered TEM image of a PTFE cluster in the PA matrix. Grey zones represent PTFE, black ones indicate PA and bright white areas are due to holes in the sample.

Chemical identification of the polymer phases is accessible via EELS spectra, which can be obtained from spots in the range of some nanometers.

Figure 4 displays the C*K* and F*K* edges (the latter one appears only in the PTFE spectrum) of the PA and PTFE phases. Spectral features are markedly different in particular at the beginning of the edge (ELNES) that it seems appropriate to differentiate between the two materials based on this spectrometric information (fingerprinting).

© 2004 WILEY-VCH Verlag GmbH & KGaA, Weinheim

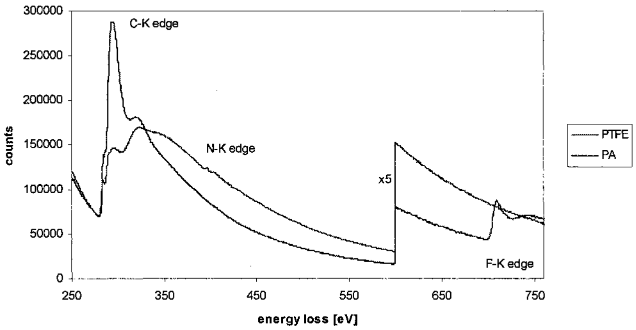
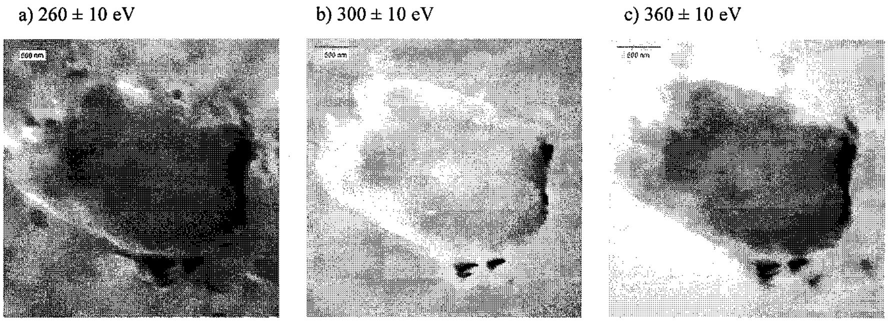


Figure 4. Electron energy loss spectra of the grey and black zones in figure 3 covering the energy loss range from 250 to 750 eV.

In figure 5 a-c energy filtered images are shown that contain only information from electrons of specific energy. They are formed with an energy selecting slit positioned at 260 ± 10 eV (a), 300 ± 10 eV (b), and 360 ± 10 eV (c), respectively. Comparing these pictures with the EELS data it can be seen that differences in brightness in the same region of the image are caused by the changing intensities in the EELS spectra.


a) 260 ± 10 eV

b) 300 ± 10 eV

c) 360 ± 10 eV

Figure 5. Energy filtered images of the area shown in figure 3. The three images comprise information from electrons of a) 260 ± 10 eV, b) 300 ± 10 eV, and c) 360 ± 10 eV energy only.

In a very similar approach the distribution of fluorine (F*K* edge at 685 eV) over the investigated area can directly be visualised by acquiring background images (625 ± 15 eV and 667 ± 15 eV)

© 2004 WILEY-VCH Verlag GmbH & KGaA, Weinheim

and calculating a background under the FK edge, which is subtracted from the image acquired at the F*K* edge energy.[5] In dark zones of figure 6, which represent areas of low edge intensity, no fluorine is present. There, the net signal intensity of the background is nearly identical to that of the background underneath the edge, and hence resembles the matrix. In figure 6 bright areas denote the presence of fluorine in the PTFE phase. Furthermore, in the bright PTFE particle some black zones can be found. These could be due to the interpenetration of the two polymers. It is an indication of improved polymer miscibility due to a better compatibility induced by the formed copolymers occurring after PTFE activation by electron irradiation.

Figure 6. Elemental distribution map of fluorine in the PA/PTFE (500 kGy) compound obtained by the 3 window methode.[5]

Conclusions

Infrared spectroscopy contains a lot of spectral information that is very valuable to follow chemical changes. Although in this case we could not find any changes due to the extremely low concentration of newly formed bonds between PA and PTFE and in presence of bulk PA and

© 2004 WILEY-VCH Verlag GmbH & KGaA, Weinheim

PTFE the possibilities of FT-IR spectroscopy may not be underestimated. With the new approach of FT-IR imaging and especially of ATR imaging also the lateral resolution of the instruments became much better and reduces one limitation of the technique.

The combination of vibrational spectroscopy and electron microscopy turned out to be an excellent choice, when the chemical composition is known from IR or Raman spectroscopy and the morphological details can be revealed with the high lateral resolution of an electron microscope. Also the analytical features available on scanning and transmission electron microscopes turned out to be applicable and very useful in polymer science.

Acknowledegement

The authors would like to thank Dr. Lehmann from the Institute of Polymer Research Dresden, Germany for providing the samples.

[1] L. Häußler, G. Pompe, D. Lehmann, U. Lappan, *Macromolecular Symposia* **164**, 411 (2001)
[2] B. Hupfer, D. Lehmann, G. Reinhardt, U. Lappan, U. Geißler, K. Lunkwitz, K. Kunze, *Kunststoffe* **91**, 96 (2001)
[3] A. Gupper, P. Wilhelm, M. Schmied, S.G. Kazarian, K.L.A. Chan, J. Reußner, *Applied Spectroscopy* **56**, 1515 (2002)
[4] A. Gupper, P. Wilhelm, M Schmied, E. Ingolic, *Macromolecular Symposia* **184**, 275 (2002)
[5] F. Hofer, W. Grogger, G. Kothleitner, P. Warbichler, *Ultramicroscopy* **67**, 83 (1997)

© 2004 WILEY-VCH Verlag GmbH & KGaA, Weinheim