

# X-ray spectromicroscopy of branched polyolefin blends

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## INTRODUCTION

It is generally difficult to determine the phase diagram of polyolefin blends directly by measuring the composition of phase separated domains. The constituent materials differ only in the amount and/or length of sidechains and provide little spectroscopic differences and limited contrast in traditional microscopies [1-3]. Indirect methods to determine the phase diagram involve a large number of samples and elaborate contrast enhancement methods. Here, we explore the utility of Near Edge X-ray Absorption Fine Structure (NEXAFS) microscopy to determine polyolefin phase diagrams directly by determining the composition of phases in a limited number of samples. We have used the scanning transmission X-ray microscope (STXM) at beamline 7.0 to investigate thermally annealed blends of an ethylene-butene copolymer (EBC with 3.7 mol % butene) and of an ethylene-octene copolymer (EOC with 3.33 mol % octene). Despite the very similar chemical structure of these copolymers (they differ only in the length of the side chain, i.e. ethyl versus hexyl groups) NEXAFS microscopy can be used to a) directly visualize the morphology without staining or etching, and b) determine the composition of the phases in such blends.

## EXPERIMENTAL

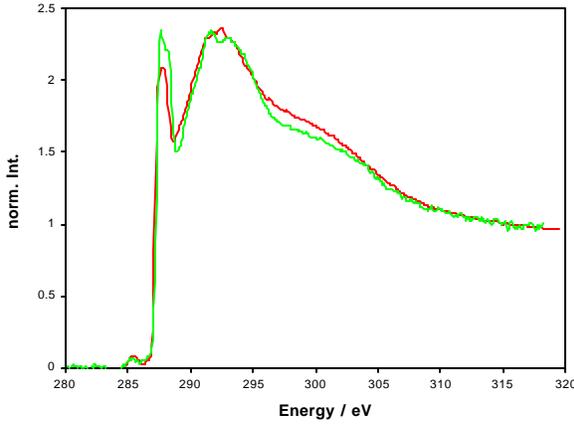
0.1 % m/m solutions of EBC and EOC (experimental polymer made with single site catalyst technology) in xylene were mixed in two different ratios (samples A1-4: 33%, samples C1-4 67% EOC). Subsequently, methanol was added to precipitate the polymer. The precipitate was collected by filtering and dried. The samples were vacuum-annealed at 180°C (samples A1, C1), 160°C (samples A2, C2), 140°C (samples A3, C3) and 120°C (samples A4, C4), respectively, quenched to -7°C and cryo-microtomed to about 100-200 nm in thickness.

The data were acquired at beamline 7.0.1. C1s-NEXAFS reference spectra of the pure components were derived from line-spectra (i.e. the same line scan at many photon energies). Image sequences of up to 80 images of small areas (typically 10  $\mu\text{m}$  x 10  $\mu\text{m}$ ) as well as small series of large images (typically 6 images, 60  $\mu\text{m}$  x 60  $\mu\text{m}$ ) were also recorded.

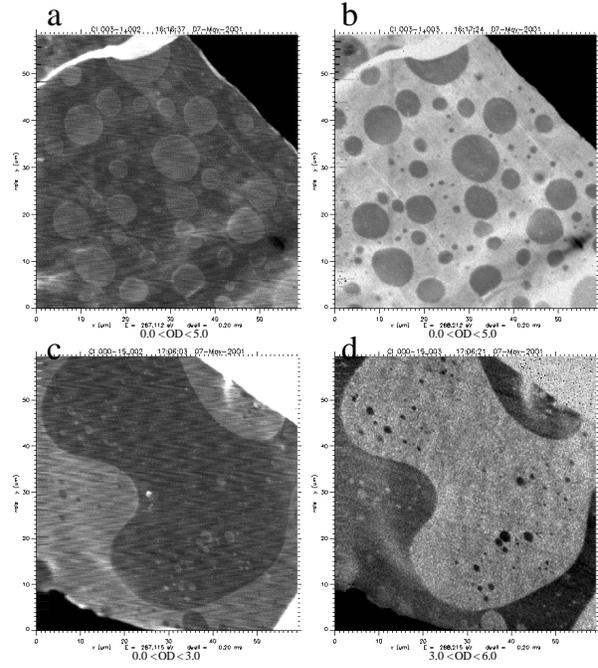
## RESULTS AND DISCUSSION

The C1s-NEXAFS spectra of the two components are shown in Fig. 1. The most noticeable difference between both spectra is found in the 287-288eV energy region. EBC shows two closely spaced peaks (typical for linear polyethylene or polyolefins with few or short side-chains), EOC shows only one broad signal (typical for polyolefins with many or long side-chains). These signals are interpreted as  $\sigma^*(\text{C-H})$  resonances [4]. Their spectral variations primarily reflect different intermolecular distances rather than different degrees of crystallinity. These spectra were used as reference spectra during the “stack fit” procedure [5] to determine the component maps.

Fig. 2 shows typical optical density (OD) images of two of the samples. The domains of the two phases can be clearly distinguished. Because EBC shows a higher absorption coefficient at 288.2eV than EOC (see Fig. 1), regions with high EBC concentration appear bright in Fig. 2b



**Fig. 1:** C1s-NEXAFS reference spectra of the components: Red: ethylene-octene copolymer, green: ethylene-butene copolymer, both normalized to an edge jump of unity between 283eV and 315eV.



**Fig. 2:** Typical STXM optical density (OD) images of samples A3 (33% ethylene-octene copolymer): a), b) and C3 (67% ethylene-octene copolymer): c), d). Images a) and c) are taken at 287.1eV. Here domains, which are rich in the ethylene-octene copolymer appear bright. Images b) and d) are taken at 288.2eV and ethylene-butene rich domains appear bright in this case.

and 2d. At 287.1eV the opposite is the case and EOC rich regions appear bright. As expected from the ratio of the components in the mixed solutions, EBC forms the matrix- or majority-phase in sample A3 (a,b) and EOC in sample C3 (c,d).

After the images of an images sequence are aligned to correct for lateral shifts, the spectrum of each pixel in the stack area can be fitted by a linear combination of the reference spectra ( $R_{oct}(E)$  and  $R_{but}(E)$ ) and a constant, which is energy-independent (*constant*):

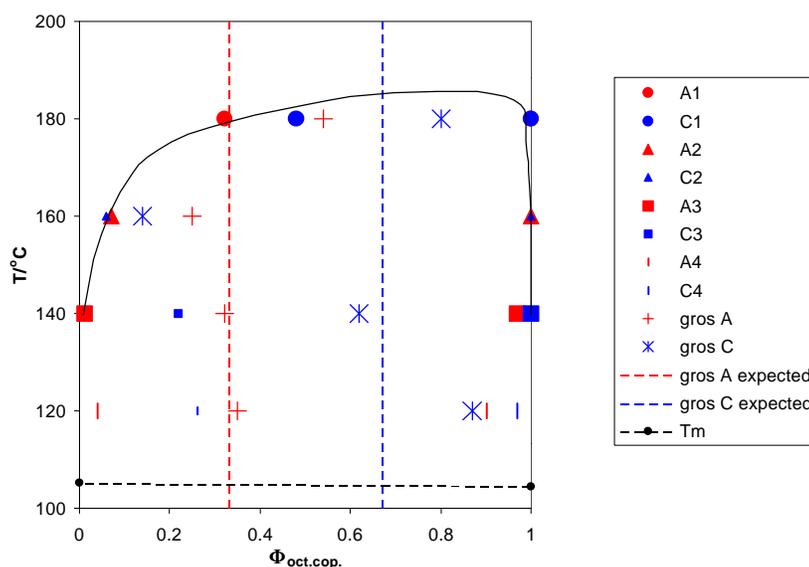
$$OD(E, x, y) = t_{oct}(x,y)*R_{oct}(E) + t_{but}(x,y)*R_{but}(E) + constant(x,y)$$

Thereby matrices of the effective thickness of the components  $t_{oct}(x,y)$  and  $t_{but}(x,y)$  and of the constant are determined and can be represented by component maps.

From these maps, regions in the matrix and in the minority phase were chosen carefully to not include inclusions of the other phase. Averaging over all pixels of these regions yields the effective thicknesses  $t$ . Since the sample contained only the two polymers, the composition  $\Phi_{oct}$  (here the mass-fraction of EOC) can be calculated:

$$\Phi_{oct} = \frac{t_{oct}}{t_{oct} + t_{but}}$$

Thus, two composition values, one for the matrix and one for the minority phase, are derived for each sample. Fig. 3 shows these results for the different annealing temperatures. If we assume that the thermodynamical equilibrium was reached during the annealing and that the quenching conserved the composition of the melt, this diagram can be interpreted as a phase diagram. Although we presently estimate large errors (10-15%), an upper critical solution temperature behavior and a broad two-phase region is clearly visible.



**Fig. 3:** Proposed phase diagram for the system poly(ethylene-ran-butene) – poly(ethylene-ran-octene). Small symbols were used, if the estimated reliability of the data was low. The gross amounts of the components from area weighted averages of the compositions and the gross amount expected from the preparation are indicated also.

In summary, we used NEXAFS-microscopy to determine the morphology and the composition of a specific polyolefin blend. The differences in the NEXAFS spectra of short- and long-branch copolymers provide sufficient image contrast, especially in the 287-288eV energy region, to image the morphology without further sample preparation (staining, etching). The polymers investigated show phase separation at all annealing temperatures. The matrix phase is always formed by the component that had the higher concentration in the solution and in the case of the EBC rich samples the gross sample composition is close to the solution composition. This indicates an almost quantitative precipitation by methanol. The phase diagram can be determined by quantitative evaluation of image sequences.

## REFERENCES

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