

Rheo-optical Fourier-transform NIR spectroscopy of polyamide 11

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In order to optimise the end-use properties of semicrystalline polymers such as polyamide 11 (PA 11) in structures of interest for the petroleum industry, the modelisation of their behaviour under mechanical load is a prerequisite. One way to perform this, consists in describing the local material behaviour by using a constitutive stress-strain equation and in calculating the structural behaviour with a finite element model. To evaluate these local deformations on a structural scale simultaneous near-infrared (NIR) spectroscopic and mechanical measurements have been performed in rheo-optical experiments. From the corresponding data, conclusions have been drawn in terms of the orientational behaviour of the polymer in elongation-recovery tests up to 60% strain at 27 °C and 60 °C. Apart from the changes observed as a function of temperature, significant spectroscopic differences could be detected for the absorption bands characteristic of aliphatic sequences and the NH-functionalities, respectively, of the investigated polymer.

The mechanical properties of polymeric materials are of considerable importance to their engineering applications. Apart from the chemical structure and the thermal history, molecular orientation has a major influence on the end-use properties of a polymer. To modelise the behav-

our of a semicrystalline polymer such as PA 11 under mechanical load, detailed experimental data on the transient structural changes during deformation and recovery of this polymer are required. Rheo-optical infrared spectroscopy is one of the few techniques available, to provide data on crystallization, orientation and conformational changes of a polymer during mechanical treatment [1-3]. Basically, for such measurements, polarization spectroscopy in the mid- and near-infrared region is combined with a mechanical stress-strain test and allows the correlation of the micro- and

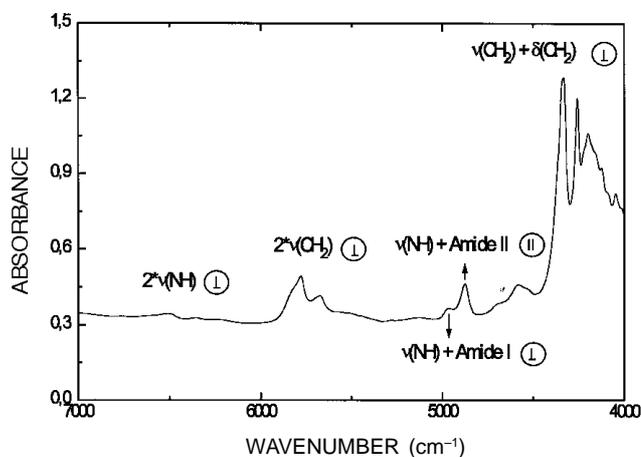


Figure 1. NIR-spectrum of a polyamide 11 film (c.a. 500 μm) with assignment and polarization properties of selected absorption bands.

macroscopic structural changes derived from the data on the same sample by different techniques. Due to the thin film samples ($< 20 \mu\text{m}$) required for MIR-measurements, NIR-spectroscopy is increasingly utilized for this technique with polymer test samples of several hundred micrometers thickness. In view of the established band assignments and polarization properties of the NIR-spectrum of PA 11 (Fig. 1), however, an equivalent information content can be expected from rheo-optical FTNIR-spectroscopy.

Experimental

The experimental principle of rheo-optical FTIR-spectroscopy is outlined in figure 2. The film specimen to be tested is uniaxially drawn and recovered in a miniaturized, variable-temperature stretching machine which fits into the sample compartment of the spectrometer. During the mechanical treatment interferograms are acquired in about 6 s-intervals with light polarized alternately parallel and perpendicular to the stretching direction. Upon completion of the experiment, the interferograms are transformed to the corresponding spectra for further processing of the data. The construction of the electromechanical apparatus utilized for the deformation experiments has been described in detail elsewhere [1-3]. In this stretching machine polymer test samples with varying gauge dimensions (length: 5 – 10 mm, width: 4 – 25 mm, thickness: up to 1000 μm) can be uniaxially drawn at variable elongation rates (linear or exponential) at temperatures between 25 and 200 $^{\circ}\text{C}$ ($\pm 0.5 \text{ }^{\circ}\text{C}$). The specimen to be tested is held between two clamps which are moved by a stepper motor by means of a spindle drive and which are attached to force and displacement transducers, respectively. The polarization plane of the incident radiation is alternately adjusted parallel and perpendicular to the

stretching direction by a pneumatically rotatable wire-grid polarizer which is controlled by a computer.

The thermal pretreatment of the samples and the mechanical and spectroscopic parameters of the rheo-optical experiments are summarized below:

Experimental temperature: 27 $^{\circ}\text{C}/60 \text{ }^{\circ}\text{C}$
 Maximum strain: 60%
 strain rate: $\dot{\epsilon} = 0.001 \text{ s}^{-1}$
 sample length: 20 mm
 sample width: 4 mm
 sample thickness: 530 and 540 μm
 thermal treatment: drying in vacuum for 3 days at 80 $^{\circ}\text{C}$
 number of scans per spectrum: 50
 spectral resolution: 4 cm^{-1}

The NIR-spectroscopic part of the work was performed on a BRUKER IFS 88 FTIR-/FTNIR-spectrometer equipped with a tungsten halogen source, a quartz beamsplitter and a liquid- N_2 cooled InSb detector.

Differential scanning calorimetric measurements of different PA 11 test specimens revealed a crystallinity of approximately 21% ($\pm 2\%$).

The extremely large number of polarization spectra collected during the rheo-optical FTNIR experiment necessitated the development of a specific evaluation software [4]. The data presented below have been derived in terms of the orientation function f of absorption bands whose transition moment directions have been assumed to be perpendicular to the local polymer chain axis [1-3]

$$f = -2 \frac{R-1}{R+2} \quad (1)$$

by a procedure appropriately correlating the successively measured integral absorbance values A_{\parallel} and A_{\perp} . The dichroic ratio R is defined as $R = A_{\parallel} / A_{\perp}$. For perfect parallel chain alignment f becomes unity, for perpendicular alignment $f = -\frac{1}{2}$, and for random orientation $f = 0$.

Results and discussion

Figures 3 and 4 show the stress-strain diagrams obtained at 27 $^{\circ}\text{C}$ and 60 $^{\circ}\text{C}$ up to 60% elongation and subsequent recovery to zero stress of PA 11 samples of 540 μm and 530 μm thickness. At 27 $^{\circ}\text{C}$, a drastic increase of stress in the Hooke-region (0 – 5% strain) followed by a further increase of the stress level between 20% and 40% strain beyond the first yield point (about 10% strain) can be observed. A second, more diffuse, yield point occurs between 30% and 40% strain and levels off in a plateau region up to 60% strain. Upon recovery to zero stress, a permanent deformation of more than 35% strain is retained. In the stress-strain test performed at 60 $^{\circ}\text{C}$ a drastic reduction of the stress level is observed throughout the whole elongation range up to 60% and the permanent deformation upon recovery is reduced to below 30% strain.

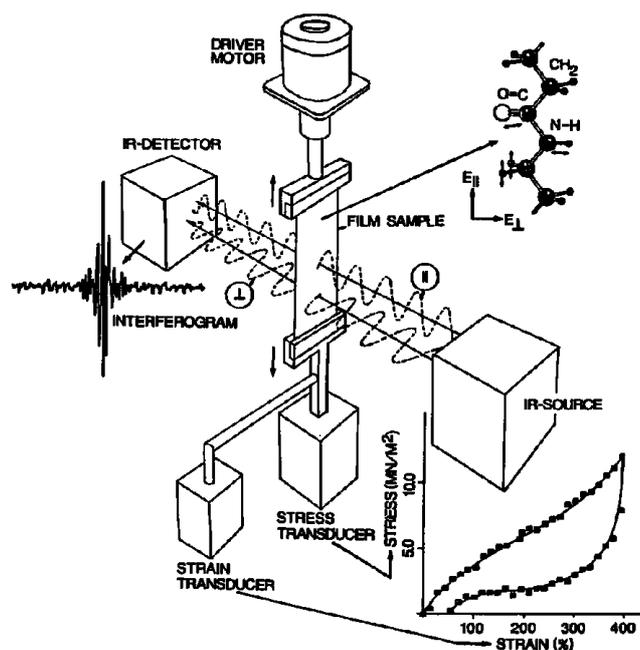


Figure 2. Experimental principle of rheo-optical FTIR- and FTNIR-spectroscopy.

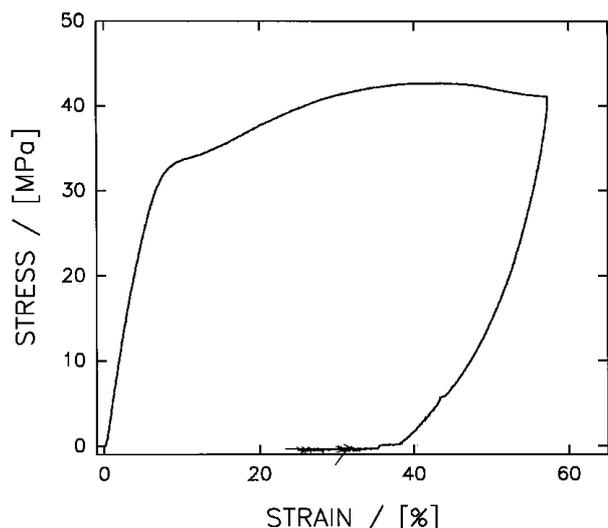


Figure 3. Stress-strain diagram of PA 11 film (540 μm) at 27°C.

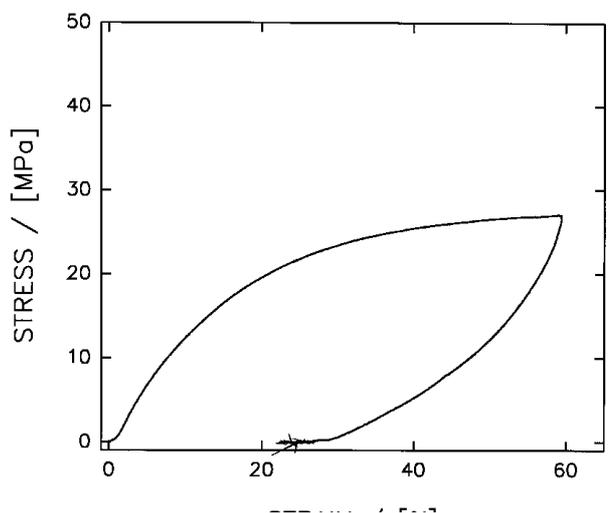


Figure 4. Stress-strain diagram of PA 11 film (530 μm) at 60°C.

For the characterization of the segment-specific orientation of the PA 11 during elongation and recovery, the absorption bands at 4343 cm^{-1} ($\nu(\text{CH}_2) + \delta(\text{CH}_2)$) and 6510 cm^{-1} ($2 \times \nu(\text{NH})$) (see Fig. 1) have been selected to represent the aliphatic sequence and the NH-group of the amide functionality, respectively (identical results have been obtained with other aliphatic- and amide-specific absorption bands). The figures 5 and 6 show the corresponding orientation function/ strain-plots for these absorption bands with reference to the mechanical treatment at 27 °C and 60 °C, respectively.

For these two types of segments, the following orientational behaviour could be differentiated:

1. The aliphatic chain segments show an increase of their order parameter throughout the elongation procedure and a slight decrease during recovery (Figs. 5 and 6). Basically, this behaviour is indicative of the expected aliphatic chain alignment during elongation and some desorientation with a large permanent deformation

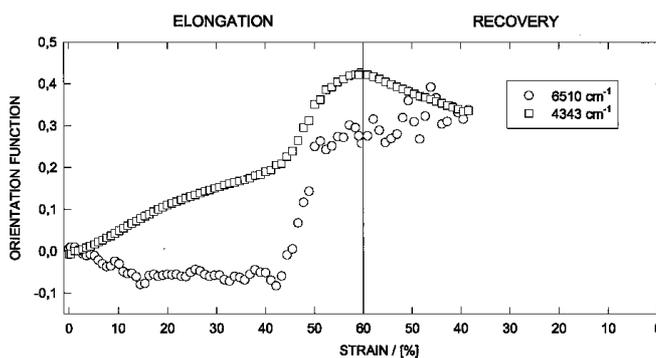


Figure 5. Orientation function/strain-plots for the 4343 cm^{-1} and 6510 cm^{-1} absorption bands corresponding to the mechanical treatment at 27 °C.

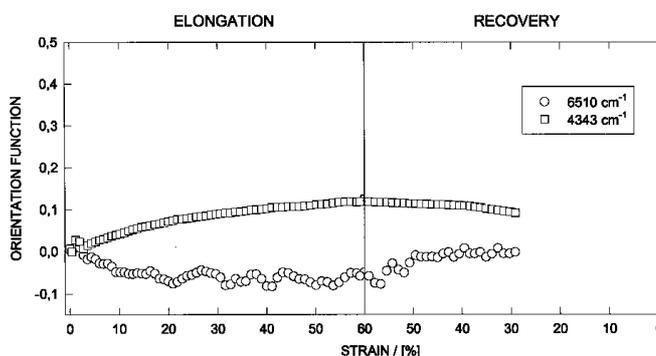


Figure 6. Orientation function/strain-plots for the 4343 cm^{-1} and 6510 cm^{-1} absorption bands corresponding to the mechanical treatment at 60 °C.

(depending on the temperature of the mechanical test) during recovery. At 27 °C, a strong increase of the orientation function is observed in the region of the second diffuse yield point around 40% strain. In the 60 °C experiment only a general reduction of the orientational effects but no steep increase is observed during elongation. This phenomenon can readily be explained by the exclusive neck formation around 40% strain at the lower drawing temperature accompanied by the strong increase in aliphatic chain alignment. At maximum strain of 60%, the orientation functions derived for the aliphatic segments are about 0.4 (27 °C) and 0.1 (60 °C). The orientation function values correspond to average inclination angles of the aliphatic segments with the drawing direction of about 39° and 50°, respectively.

2. The absorption band representing the NH-amide functionality, however, shows a completely different behaviour. Because a transverse orientation of the local chain axis is difficult to imagine, the slightly negative orientation functions up to about 40% strain (for both temperatures) (Figs. 5 and 6) have to be explained in terms of a distortion of the transition moment from the direction perpendicular to the polymer chain. This can be readily envisaged for the hydrogen-bonded NH-groups during the deformation process when polymer chains glide past each other. While the orientation function remains under zero

throughout the mechanical treatment at 60 °C, a steep increase towards positive values (up to $f = 0.3$) is observed between 40% and 60% strain for the 27 °C experiment. The neck formation accompanied by strong local deformational forces leads to a disruption of the strained hydrogen bonds and a subsequent undistorted reorganization in the highly positively aligned polymer chains. Such effects have, to our knowledge, so far never been reported for thermoplastic polyamides.

Conclusion

The deformation of PA 11 at ambient temperature is accompanied by a shoulder-neck formation at about 40% strain

which leads to a disruption of overstressed hydrogen bonds and a subsequent undistorted reorganization in the highly oriented polymer. At elevated temperature, the temperature-induced loosening of the hydrogen bonds effects much lower deformational forces which are also accompanied by lower orientational effects. Additionally, no indications for a necking procedure can be derived from the spectroscopic data.

References

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