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Polarized FT-IR Photoacoustic Spectroscopy on Polymer Fibers

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Summary: The orientation of macromolecular chains in two melt-spun polymer fibers (segmented polyurethane elastomer and melt-modified polyolefine fibers) was studied by photoacoustic spectroscopy (PAS) with polarized light in the mid-infrared range. The PAS orientation functions calculated from the photoacoustic signal intensities of orientation sensitive bands describe the orientation of the different chain segments with respect to the fiber axis. Thus, the orientation of hard and soft segments in the unstressed polyurethane fiber is different and both are similiar to that of the corresponding injection molded bars. With increased spinning velocity an improved orientation of the polyolefine chains along the fiber axis, but only in the amorphous regions of the polymer, were detected.
Only a slight reduction of orientation was measured as a result of the subsequent chemical crosslinking in the polyolefines.

Keywords: molecular orientation; polarized FT-IR photoacoustic spectroscopy; polyolefin fibers; polyurethane fibers

Introduction

In addition to Raman spectroscopy photoacoustic spectroscopy (PAS) with linearly polarized IR light it is also able to characterize the orientation of macromolecular chains in polymer materials. Without any further sample preparation it is possible to investigate the polymeric products as received from extrusion or injection molding. As in polarized Fourier Transform infrared transmission spectroscopy [1,2] the polarizer is set parallel and perpendicular to a preferred sample direction given by the processing regime. From the corresponding photoacoustic signal intensities of orientation sensitive bands dichroic ratios can be obtained.

Using the so-called PAS orientation functions calculated from the dichroic ratios it is possible to get orientation data for the different polymer segments in dependence on processing conditions, e.g. temperature, drawing or deformation processes in a testing machine. The method was tested successfully to determine orientation effects in blends of polypropylene with polyethylenes [3] or

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with thermoplastic polyurethanes [4]. In the present study we characterize for the first time the orientation of macromolecular chains in melt-spun fibers with polarized FT-IR PAS. We investigate a commercial unstretched segmented polyurethane elastomer fiber and melt-modified polyolefine fibers processed with different spinning velocities. The aim was to demonstrate that polarized FT-IR PAS is able to detect and to quantify orientation effects also in polymer fibers.

Experimental

Polarized FT-IR PAS

PAS Measurements

The polarized FTIR-PAS measurements were performed on an IFS 66v/S (BRUKER) with the photoacoustic cell MTEC 200 (AMES, IOWA). The fibers were wound around a special, notched sample holder with the fiber axis aligned exactly in one direction. Then the holder was placed precisely in a defined position with respect to the fiber direction in the PAS cell. The cell was purged with Helium for at least one hour before measuring. The polarized PA spectra were recorded by rotating the KRS - 5 wire grid polarizer (SPECAC) between 0° (II) and 90° (⊥) with respect to the fiber bundle. Carbon black was used as background (measured also with the polarizer at 0° and 90°).

The mirror velocity was 0,139 cm/s (2.2 kHz). To get a good signal-to-noise ratio 2000 scans/spectrum were co-added at a resolution of 8 cm^{-1}. Further details are described in our previous paper [4].

Determination of the "photoacoustic" dichroic ratios and orientation function

The applied procedures for the evaluation of the polarized PA spectra of the fibers and data handling were in principle the same as already described in detail for extruded strands, granules and bars in our previous paper [4].

Assuming an uniaxial chain alignment along the fiber axis, the photoacoustic orientation function f_{PAS} was calculated from the dichroic ratios obtained from the PA spectra with perpendicular and parallel position of the polarizer. Based on Fraser's function for the " perpendicular" bands ($f_{PAS} \equiv f\perp$, when the dipole transition moment is located perpendicular to polymer chain axis) equation (1) and for the "parallel" ones ($f_{PAS} \equiv f\,II$, when the dipole transition moment is located parallel to the polymer chain axis) equation (2) were applied:

$$f_\perp = -2(R-1)/(R+2) \qquad (1)$$

$$f_{II} = (R-1)/(R+2) \qquad (2)$$

The dichroic ratio is defined as $R = A_{II} / A_\perp$, and A_{II} and $A_\perp$ are in our experiments the absorbance-like photoacoustic signal intensities in the spectra with polarizer parallel (II) and perpendicular (⊥) to the fiber axis.

It is known that a relation between the photoacoustic signal-intensity and absorbance is given, if the samples are optically opaque and thermally thick as we assumed for our samples. Of course, only bands of medium and weak intensity were analysed to exclude saturation effects and nonlinearities [3,4] .

Materials

Melt-spun polyurethane fibers

A commercial segmented polyurethane elastomer fiber (elastan yarn, 77 dtex, SPANTEL™ , Kuraray Co.,Ltd., Okayama/Japan) was used. Such fibers have high water resistance and high stretch recovery [5] . The fiber diameter was about 20 µm.

The polymer melting point is in the range of T_M=230-290°C. The segmented polyurethane consists of the following typical structure units: polyester glycol soft segment (***SS***) + butandiol chain extender ($\boldsymbol{R_1}$) + diphenylmethane-4,4-diisocyanate (MDI) based hard segments ($\boldsymbol{R_2}$). Therefore, the following schematic polymeric structures have to be considered when discussing the PA spectra:

$[-O - \boldsymbol{R_1} - O - CO - HN - \boldsymbol{R_2} - NH - CO]_n - [O - (\boldsymbol{SS}) - O-]_m$ with

$(\boldsymbol{SS})$ based on $HO - [(CH_2)_2 - O - OC - (CH_2)_4 - CO - O]_x - (CH_2)_2 - OH$

(MW of $(\boldsymbol{SS})$ ~ 2000 g/mol).

Melt-spun modified polyolefine fibers

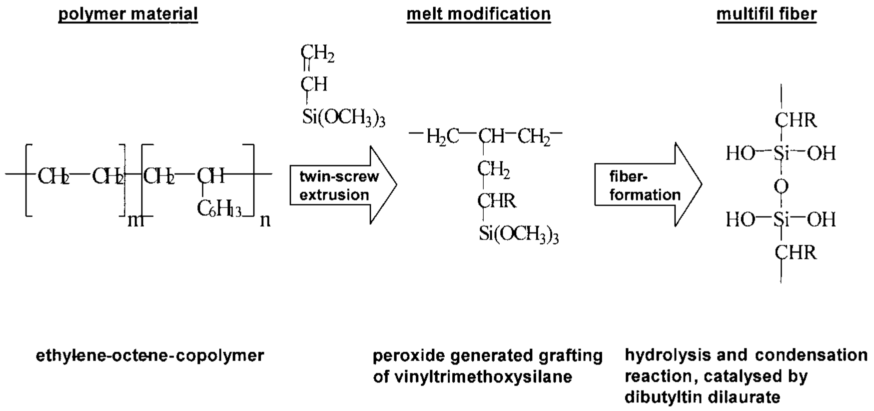
These fibers are based on commercial ethylene–octene copolymers (ENGAGE® , DuPont Dow

Elastomers). The initial material used in the applied extrusion-melt spinning process was a 50/50 blend of EN8200/EN8400 (T_M ~ 60°C, M_n~20000 g/mol, M_w~60000g/mol). The octene content was determined by NMR spectroscopy to be 14 mol%. The diameter of the fibers produced at our institute using this process was about 300 µm.

The aim of the work of Beyreuther, Hoffmann et al. [6,7] was the improvement of thermal and mechanical properties of these elastomeric fibers via chemical modification by direct connection of reactive extrusion and melt spinning.

Chemistry, equipment and technology of this new type of reactive processing were described in detail by these authors. Scheme 1 shows the chemistry of the two performed modification reactions on the polyolefine main chains during the different processing steps (peroxide initiated silane grafting, crosslinking after hydrolysis).

Scheme 1. Chemistry and technology during the production of the modified melt-spun polyolefine fibers according to Hoffmann et al. [6]



Results and Discussion

Orientation of hard and soft segments in the polyurethane fibers

From WAXS experiments [5] it is known that at room temperature the unstretched polyurethane fiber samples which were also used in our PAS experiments have an amorphous unoriented soft segment matrix and strongly disordered, partially weak crystalline sections of hard segments, which are only slightly oriented. Fig. 1 shows the PA spectra of the fiber sample measured with light polarized both parallel (II) and perpendicular ($\perp$) to the fiber axis. The different dichroic behavior of characteristic bands is clearly seen even though the photoacoustic signal intensities are very low. The most important vibration modes of the segmented polyurethane structure (with their II (π) or $\perp$(σ) character) could be assigned to the spectra [2] :

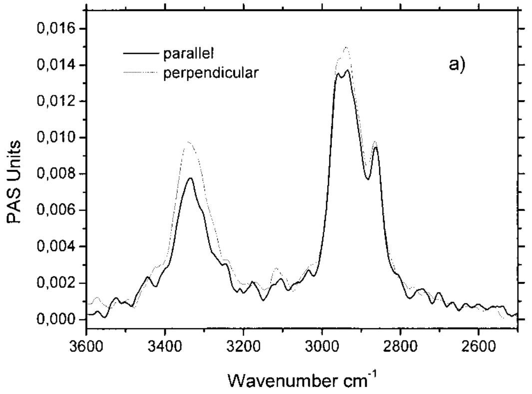
3340 cm^{-1} $\nu(NH)_{urethane}$ $\perp$, 2940 and 2860 cm^{-1} ν_{as} , ν_s (CH_2), 1741 cm^{-1} $\nu(C{=}O)_{ester}$ $\perp$, 1715 cm^{-1} $\nu(C{=}O)_{urethane}$ $\perp$, 1316 cm^{-1} $\nu(C\text{-}N)_{urethane}$ II , 1081 cm^{-1} $\nu(C\text{-}O\text{-}C)_{urethane+ester}$ II. As expected the hard and soft segments show different orientations. The corresponding photoacoustic dichroic ratios and orientation functions are given in Table 1.

Table 1. Dichroic ratios R and orientation function f_{PAS} of hard and soft segments

band	R	f_{PAS}	segment character
3340 cm^{-1}	0,73	0,2	hard
1715/1741 cm^{-1}	0,85	0,1	hard + soft
1316 cm^{-1}	1,21	0,1	hard + soft
1081 cm^{-1}	0,99	0	soft

The results of the polarized PAS are in good agreement to the WAXS results:

The hard segments in this common unstretched elastomeric polyurethane fiber are better oriented than the soft segments which show nearly no orientation. Nevertheless, the overall orientation is not very high. It is very similar to the orientation of 50% elongated injection-molded thermoplastic polyurethane bars (also determined by polarized FTIR-PAS [4]), but low in comparison to stretched polyurethane films [2] .



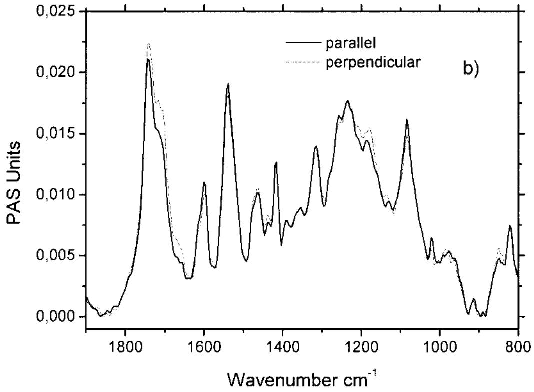


Figure 1. Polarized PA spectra of the polyurethane fibers,
a) in the range 3600 – 2500 cm^{-1} , b) in the range 1900 – 800 cm^{-1}

Orientation of polymer chains in the polyolefine fibers

Due to the described reactive processing and chemical crosslinking the mechanical properties of the modified polyolefine fibers have been improved remarkably with increasing spinning velocity v and draw down ratio λ [6] . As desired an increased yield stress and ultimate tensile strength were obtained, as well as a decreased elongation at break. At the same time better thermal properties were measured, for example a shift of the flow initiation point from 70°C to 180°C. From WAXS, DSC and birefringence measurements can be concluded that the degree of crystallinity and orientation in the crystalline regions of the modified polyolefines remain relatively constant [7] . Surprisingly, no dependence on spinning velocity/draw down ratio was detected using these methods. Therefore, it was assumed that especially the improvement of mechanical properties with increasing spinning velocity should be connected with a better orientation of the polyolefine chains, but in the amorphous regions of the fibers.

The PA spectra of non-crosslinked polyolefine fibers melt-spun at v = 500 m/min show differences between parallel and perpendicular polarization with respect to the fiber axis in the whole mid-infrared region (Fig. 2). The sample was a fiber bundle carefully aligned in the PAS cell as described above.

As reference and for validation of the polarized PAS we used the same fibers, but fully shredded. The obtained small pieces were randomly placed on the sample holder without preferred direction and measured with parallel and perpendicular polarized light. If the method works well no preferred orientation should be detectable in the polarized spectra.

In fact, this behavior was exactly found in the spectra (Fig. 3): There is no difference between parallel and perpendicular polarization.

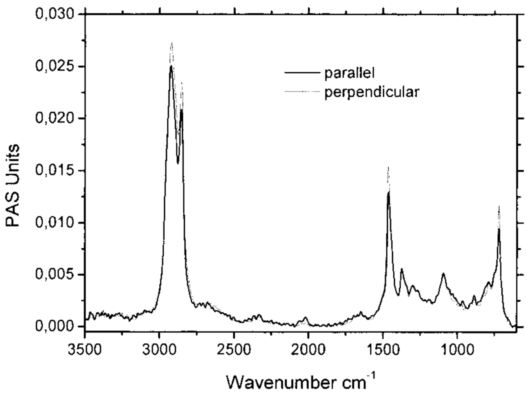


Figure 2. Polarized PA spectra of the polyolefine fibers (non-crosslinked, v = 500 m/min), fiber bundle carefully aligned in the PAS cell

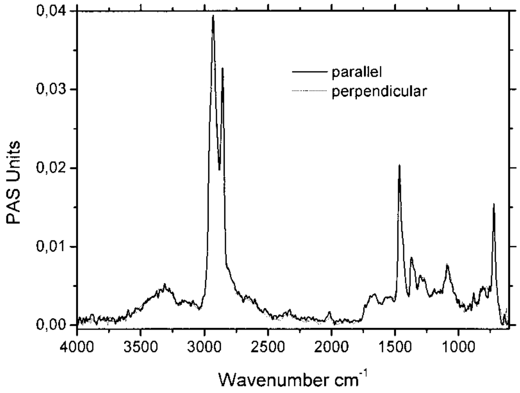


Figure 3. Polarized PA spectra of the polyolefine fibers (non-crosslinked, v = 500 m/min), fully shredded pieces randomly placed on the sample holder

From the chemical point of view the polyolefine copolymers used for the fiber production are very similar to polyethylenes (low octene content). Characteristic polyethylene bands were assigned to the PA spectra, some of them should come from vibrations of chain segments mainly in the amorphous regions (**a**) [8,9] : 2931 cm^{-1} ν_{as} (CH_2) $\perp$, 2856 cm^{-1} ν_s (CH_2) $\perp$, 1468 cm^{-1} $\delta(CH_2)$ $\perp$, 1372/1303 cm^{-1} $\omega(CH_2)$ II, **a** and $\delta(CH_3)_{\text{in side chain}}$, 1088 cm^{-1} $\nu(CC)$ **a**, 721 $cm^{-1}\rho(CH_2)$, $\perp$, **a** (but also from crystalline phases if existing). It is well-known that a band at 730 cm^{-1} in the IR transmission spectrum of polyethylene comes definitely from the crystalline phase. Therefore, the spectrum of a common semi-crystalline polyethylene is dominated by the typical band dublett at 730/720 cm^{-1} . But in the polarized PA spectra of our non-crosslinked and crosslinked fibers only a single non-splitted band arises at 721 cm^{-1} (Fig. 4).

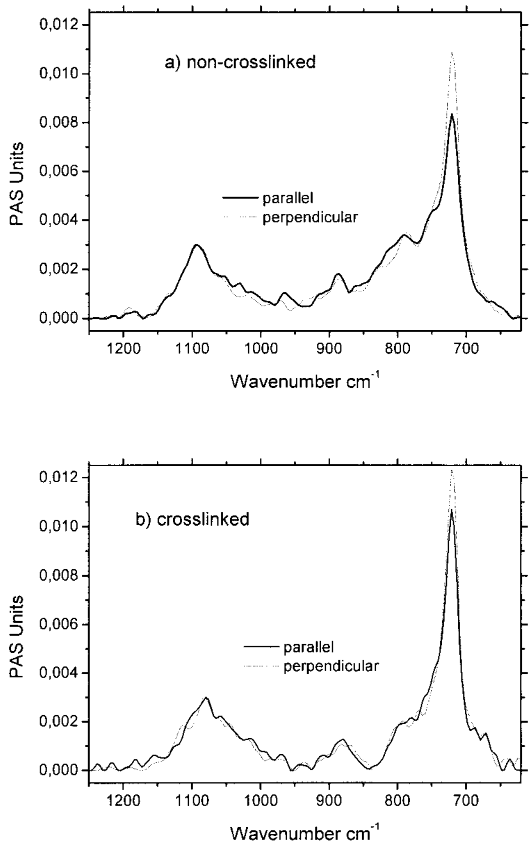


Figure 4. Polarized PA spectra of the (a) non-crosslinked and (b) crosslinked polyolefine fibers showing the band at 721 cm^{-1} (v = 500 m/min)

It should mostly be representative for polyethylene main chains in the amorphous phase. An increased spinning velocity results in an increase of deformation and stress. In addition to an increase of orientation a deformation-induced crystallization could be possible. We checked it by calculating of the structural absorbance $A_0 = (A_{\parallel} + 2A_{\perp})/3$ [1]). No significant differences were found for the band at 721 cm^{-1} when the spinning velocity was increased. Therefore, the changes of this band in the polarized PA spectra with increasing spinning velocity should only come from changes in the orientation of the polymer chains in the amorphous phase. The calculated dichroic ratios and orientation functions are presented in Figures 5 and 6.

It can clearly be seen that the orientation of the polymer chains along the fiber axis in the amorphous regions of the fibers has improved with increasing spinning velocity. From our point of view these results are important for a better understanding of the improved mechanical properties of the fibers, and confirm our assumption that the orientation in the amorphous phase plays a crucial role. Chemical crosslinking and network formation disturb the order of the polymer chains. Thus, a lower orientation is found for the crosslinked fibers.

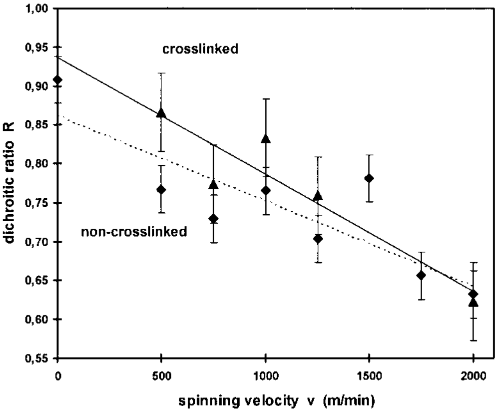


Figure 5. Dichroic ratios R (band at 721 cm^{-1}) of the non-crosslinked (Λ) and crosslinked (7) polyolefine fibers as function of spinning velocity v

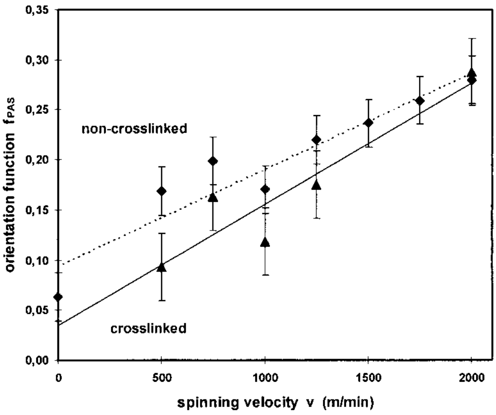


Figure 6. Orientation function f_{PAS} (band at 721 cm^{-1}) of the non-crosslinked (Λ) and crosslinked (7) polyolefine fibers as function of spinning velocity v

Conclusions

Polarized FT-IR Photoacoustic Spectroscopy is proved to be a tool to characterize orientation phenomena in polymer fibers in dependence on processing parameters without disturbance of fiber structure caused by sample preparation. Using this method it was possible to determine the different orientations of the hard and soft segments in an elastomeric polyurethane fiber. Furthermore, we found that the orientation of polymer chains in the amorphous regions of modified polyolefine fibers was enhanced with increasing spinning velocity. This should play an important role to explain the improved mechanical properties of the fibers.

Acknowledgement

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