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FT-IR studies on the mechanical response of the crystalline fraction in ultrastrong polyethylene tapes

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Abstract: FT-IR spectra of UHMW-PE tapes with different moduli have been studied in dependence of mechanical deformation and stress. Small spectral variations have been revealed in the difference spectra. Band shifts of the 730/720 cm^{-1} doublet have been observed under stress relaxation and upon stretching. A clear correlation between the shift of crystalline bands and the Young's modulus could be determined. Polarized measurements demonstrated variations in the mechanical response of nearly perfectly oriented and non-oriented crystallites. Crosslinking was performed by blending the polyethylene with 10% polysilane and UV-irradiation of the drawn material. The band shift increases as the linkage between oriented crystal blocks is improved with higher draw ratios and chemical crosslinking.

Key words: Ultrahigh molecular weight polyethylene; strain induced IR band shifts; stress distribution in PE fibres; gel spinning; polysilanes

Introduction

Fibers and tapes with exceptional moduli and tensile strength can be prepared from ultrahigh molecular weight polyethylene (UHMW-PE) by the so-called gel spinning/drawing process [1–4]. Drawing above the α-transition temperature converts chain folded lamella crystals into uniaxially oriented fibers with highly extended chains. The values obtained for the Young's modulus and tensile strength are in the range of 150–200 GPa and 2–5 GPa [5–7], respectively. Thus, the theoretical maximum strength of a single extended polyethylene chain is approached, whose modulus has been estimated to be about 300 GPa associated with a tensile strength of approximately 20 GPa [8–9]. The properties of the actual fibers are less good because of the limited molecular weight and the imperfections in the supermolecular structure.

Ultradrawn UHMW-PE fibers are usually not fully crystalline [10–13]. The degree of crystallinity approaches values close to 100% only in the case of draw ratios of $\lambda > 100$ [12, 14] and, also in this case, formation of an apparent amorphous fraction is observed below the melting point upon raising the temperature above room temperature [14]. With respect to the latter observation, two other effects appear to be important: i) Shrinkage of ultradrawn UHMW-PE fibers upon unconstrained heating below melting is larger than expected from the shrinkage of the lattice along the *c*-axis [13, 15]. Correspondingly, extra proportional formation of a retractive stress is observed upon heating a UHMW-PE fiber with constrained elongation [13]. ii) The deformation of ultradrawn UHMW-PE results as a combination of plastic flow and of a reversible, nearly stress-linear contribution [16].

Recently, we reported on solid-state ^{2}H-NMR investigations [17] which demonstrated a constrained, but practically nonoriented amorphous fraction and an almost perfectly oriented crystalline fraction. However, spin-lattice relaxation time-sensitive ^{2}H-NMR experiments indicated considerable mobility for part of the highly oriented chain segments with a smooth transition from nonmobile to mobile PE segments, which is also accompanied by a small but significant increase in the width of the orientational distribution. This was explained by a model in which defects are not homogeneously distributed over the crystal, but are concentrated in clusters of varying size and with locally different mobility of the conformational defects. Evidence for such a nonrandom defect distribution has also been obtained by transmission electron microscopy studies [18] which showed preferential penetration and oxidation by the staining agent within small streaks perpendicular to the fiber axis of the microfibrils. This complicated microstructure of polyethylene originates from the solid-state drawing process. Transformation of folded-chain crystals to perfect chain extended structures cannot be achieved because chain ends, folds, trapped entanglements and jogs become enclosed within the oriented fibrillar crystals. The defects cannot be expelled from the crystal phase, but are concentrated in small inclusions. Thus, also within the crystals, the UHMW-PE chains are not fully extended. This is consistent with recent neutron-scattering data [19], demonstrating a root-mean-square deviation of chain segments in the range of 6–13 units in the a-direction, and of 10–20 units in the b-direction of the orthorhombic unit cell.

Due to the subtle and difficult to visualize variations in crystal morphology of chain-extended fibers, it is not yet possible to clearly correlate the fiber properties, preparation conditions, and the fiber structure. Moreover, detailed insight requires data about the stress/strain contributions of the different fiber components and the mechanical linkage between high modulus crystallites which cannot be determined separately by conventional mechanical testing techniques.

Vibrational spectroscopy was shown to be a powerful technique for monitoring changes in the molecular structure caused by mechanical loading [20]. Various stretching effects, i.e., conformation and orientational changes as well as intra- and intermolecular force variations can be observed with high precision and high time resolution. Under mechanical loading, band shifts were observed for highly oriented semicrystalline polymers [21, 22] as well as for isotropic polymer glasses [23, 24]. Recently, also Raman experiments have been reported on UHMW-PE fibers, relating mechanical properties with the special fiber morphology [25–27]. In this paper, we describe an approach to monitor both stretching behavior and mechanical response of different components of the UHMW-PE fibers by mechanical FT-IR experiments.

Experimental

Preparation of ultradrawn UHMW-PE tapes

Polyethylene gels were prepared from a 1.5% solution of UHMW-PE (Hizex 240 M, $M_w = 1.5 \cdot 10^6$) in xylene as described by Lemstra [28]. The dried gels were compressed and annealed at 60 °C under vacuum at a pressure of 20 MPa to remove voids. Subsequently, they were cut into tapes which were drawn at 125 °C to draw ratios of $\lambda = 10$ to $\lambda = 100$. Draw ratios were established by means of ink marks brought on the tapes before drawing. UHMW-PE/polydi-*n*-pentylsilane blends were prepared by crystallizing both components simultaneously. Ultradrawn tapes were prepared according to the same procedure as mentioned above. Chemical crosslinking was initiated by UV-irradiation in a nitrogen atmosphere.

FT-IR-spectroscopy:

IR experiments were performed using a FTS-60 Digilab spectrometer. A gold-wire grid polarizer (KRS-5) was used to observe polarized spectra and to determine the dichroic ratios. UHMW-PE tapes were cut into strips of 50×5 mm^2 and had a thickness of 3–5 μm. Micromechanical experiments were carried out with a micrometer precision-stretching device, which could be mounted inside the measuring compartment of the spectrometer. A spindle with counterrotating threads was used to achieve stretching simultaneously in both directions, ensuring that the investigated center part of the sample was not moved with respect to the IR beam. Spectra were recorded with a resolution of 2 cm^{-1}. Spectral subtraction techniques and modern FT-IR spectrometer allow the evaluation of band shifts as small as 0.01 cm^{-1} [29]. Lorentz fits were used for calculation of the frequency changes [30]. Subtraction coefficients were set to 1, when the fibers were strained by $\varepsilon = 1 - 6\%$ at ambient temperature, neglecting an insignificant decrease in the sample thickness. Spectra of UHMW-PE tapes of different drawn ratios λ were normalized to the strong 1260 cm^{-1} band of small polydimethylsiloxane impurities.

Results and discussion

Figure 1 shows how the IR bands of the PE segments, which are not all-trans planar, change upon drawing. The assignments of IR-bands of amorphous or disordered polyethylene segments are well known [31]. At least four PE bands can be clearly distinguished in the region from 1410–1200 cm^{-1}: 1378 cm^{-1} (CH_3-deformation), 1368 cm^{-1} (CH_2-wagging in a GTG′ segment), 1353 cm^{-1} (CH_2-wagging in GG segment), and 1303 cm^{-1} (CH_2-wagging in a GTG′ segment). The band at 1260 cm^{-1}, which is marked as internal standard (IS), belongs to small amounts of polydimethylsiloxane, PDMS, and is not affected

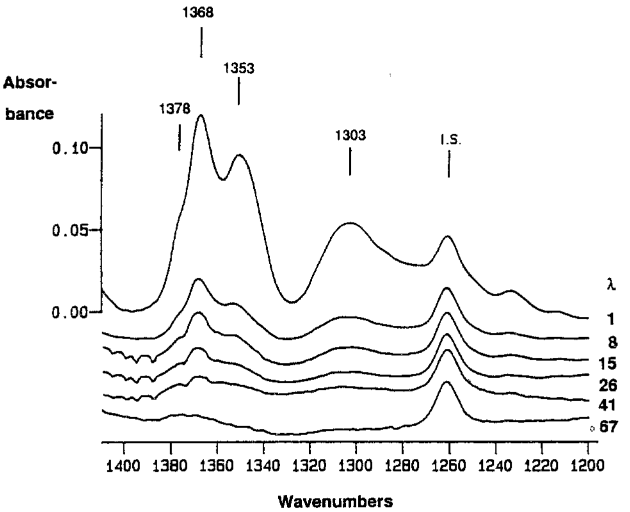

Fig. 1. FT-IR spectra of UHMW-PE tapes of increasing draw ratios between 1400 and 1200 cm^{-1}. The decreasing bands are characteristic for disordered chain segments. IS: internal standard band at 1262 cm^{-1} (PDMS)

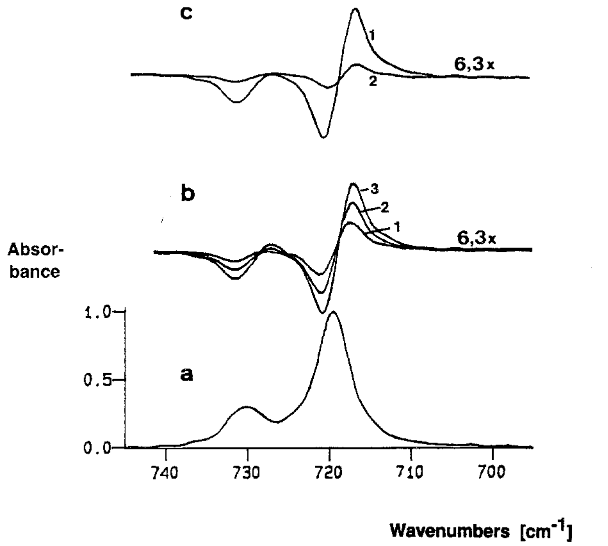

Fig. 2. Stress/strain response of the CH_2 rocking band of oriented crystallites of a $\lambda = 20$ drawn UHMW-PE tape as observed with the polarizer perpendicular to the fiber axis. a) Absorbance spectrum. b) Strain effect in the difference spectra 1 $\varepsilon = 1.6\%$, $\Delta\nu = 0.12\ cm^{-1}$; 2) $\varepsilon = 3.2\%$, $\Delta\nu = 0.22\ cm^{-1}$; 3) $\varepsilon = 6\%$, $\Delta\nu = 0.31\ cm^{-1}$. c) Stress relaxation after 6% elongation: 1) frequency shift directly after stress application; 2) after 60 h stress relaxation

by the drawing procedure. (During the gel preparation, the PE tapes had been contaminated by traces of silicon-grease which are insignificant for the mechanical properties.)

Changes in the concentration of the different segmental structures which occur upon drawing the gel-films can be registered by monitoring the signal intensities of the bands listed above [32,33]. The PDMS band was used for the precise intensity calibration of the weak bands of the conformational defects. As shown in Fig. 1, all bands for the disordered PE segments decrease with increasing draw ratio. This is explained by extension and orientation of the chain segments which are originally not in an all-trans conformation, i.e., transformation of amorphous to crystalline material, unfolding, and elimination of crystal defects.

The 750–690 cm^{-1} region was chosen to investigate the effect of mechanical deformation on the "crystalline" bands (Figs. 2–5). Especially suitable for this purpose is the doublet at 730/720 cm^{-1} which arises from out-of-phase and in-phase CH_2-rocking vibrations in the PE unit cell. Transition moments of the 730 and 720 cm^{-1} vibrations are parallel to the *a*-axis and the *b*-axis, respectively. The asymmetry in the intensity of the doublet shown in Figs. 2–4 is caused by the preferential orientation of the *a*-axis perpendicular to the surface of the drawn film [12, 34].

For a draw ratio $\lambda = 20$, the strong UHMW-PE tapes could be strained at ambient temperature up to $\varepsilon = 6\%$. Two different experiments have been performed to study the strain/stress response of the crystalline IR bands: i) tapes of a particular draw ratio were compared in dependence of a strain ε; ii) stress relaxation was observed at constant ε. For stress relaxation as well as for the strain experiments, the series of spectra were recorded without moving the analyzed area of the sample with respect to the IR beam. Thus, it was ensured that the difference spectra are not misrepresented by small inhomogeneities of the UHMW-PE tapes.

i) Changes of the 730/720 cm^{-1} doublet, which result from uniaxial stretching of the highly oriented UHMW-PE fiber are shown in Fig. 2b. The figure shows a series of difference spectra $(Abs_\varepsilon(\nu) - Abs_{\varepsilon=0}(\nu))$ for varying elongation ε in the range of the elastic deformation. A mere band shift is indicated for the 720 cm^{-1} band by the derivative-like shape of the difference spectrum. In contrast, frequency and intensity changes are observed for the 730 cm^{-1} band. The shift of the 730 cm^{-1} band is larger than that of the 720 cm^{-1}

band. The effects above are completely reversible when the stress is released.

ii) The effect upon stress relaxation at a strain of $\varepsilon = 6\%$ $(Abs_{\varepsilon=6}(\nu) - Abs_{\varepsilon=0}(\nu))$ is demonstrated in Fig. 2c for a tape drawn to $\lambda = 20$. Figure 2c gives the spectral variation for the oriented crystalline fraction (polarization perpendicular to the fiber axis). After 60 h, the stress-induced band shift decreased practically totally.

The dichroic ratio of the crystalline bands determined by polarizing FT-IR-measurements reaches a maximum at a draw ratio of about 10, and demonstrates a high orientation already directly after the necking, as was also observed for linear PE of lower molecular weight [35]. Only a very small fraction of crystallites is not aligned. Stress response of this fraction can be observed by polarized experiments. Figure 3b represents strain-dependent infrared spectra which were recorded with the polarizer directed parallel to the fiber axis. Only small changes in the signal intensity were observed in this case. Thus, chains which did not become oriented parallel to the fiber axis do practically not respond to the strain. Figure 3c demonstrates complete recovery of the 730/720 cm^{-1} band for the nonoriented crystallites upon stress relaxation at a strain of 6%.

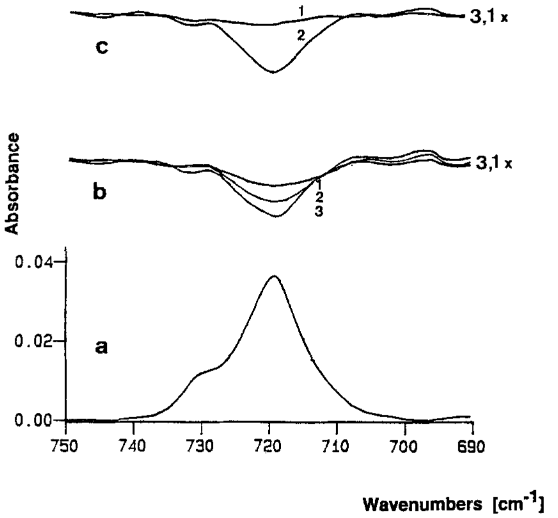

Fig. 3. Stress/strain response of the CH_2 rocking band of nonoriented crystallites of a $\lambda = 60$ drawn UHMW-PE tape as observed with the polarizer parallel to the fiber axis. a) Absorbance spectrum. b) Strain effect in the difference spectra: 1) $\varepsilon = 1.6\%$; 2) $\varepsilon = 3.2\%$, 3) $\varepsilon = 6\%$. c) Stress relaxation after 6% elongation: 1) frequency shift directly after stress application; 2) after 60 h stress relaxation

Clearly, the effects demonstrated in Figs. 2 and 3 are correlated with the stress/strain response on the molecular scale: the band shift appears to be a stress-sensitive parameter. As mentioned above, similar effects have been observed before in vibrational spectra of stressed, oriented semicrystalline polymers, as well as for isotropic polymeric glasses [21–24, 36].

So far, the data demonstrated that the stress response of crystalline domains can be observed directly by an increasing band shift effect. Consequently, it should be possible to utilize the band shift effect for mechanical testing of highly oriented PE fibers and to correlate the stress response of the crystalline fiber component to macroscopic properties. As pointed out above, dichroism experiments show that the orientation of the crystallites in the PE fibers approaches uniformity already at relatively small draw ratios ($\lambda = 10$). Also, x-ray diffraction [12] and ^{2}H-NMR experiments [17], which are more sensitive to variations of small orientational distributions, indicated nearly perfect orientation already at $\lambda < 20$. Thus, the improvement of the mechanical strength at higher draw ratios cannot be explained by further orientation of the crystallites.

However, the mechanical properties are not only determined by chain orientation, but also by chain extension and an even stress/strain distribution between different fiber components. If the strain contribution of the fibrillar crystals can be observed by the band shift of the 730/720 cm^{-1} vibration, it must be possible to observe differences in the spectra for tapes with different draw ratios, i.e., different Young's moduli in the stress/strain response of the chains in the fibrillar crystals.

Figure 4 shows the band shift for a series of tapes with varying λ at constant strain $\varepsilon = 1.2\%$. In order to eliminate the influence of the sample thickness variation in the course of the drawing procedure, all spectra were normalized with respect to the internal standard band (1260 cm^{-1}). The band shift, i.e., the stress response of the crystalline fraction, increases with increasing λ, resp. modulus of the fiber. A clear correlation between the frequency shift and the Young's modulus is shown in Fig. 5, which demonstrates an increasing strain of the fibrillar crystallites when fibers of higher modulus are strained. Thus, the band shift indicates

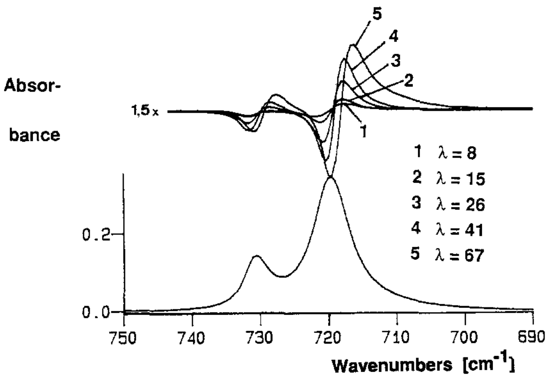

Fig. 4. Frequency shift of the 720 cm^{-1} band for fibers with different draw ratios (modulus) at constant strain: $\varepsilon = 1.2\%$; 1) $\lambda = 8$, $\Delta\nu = 0.04$ cm^{-1}; 2) $\lambda = 15$, $\Delta\nu = 0.08$ cm^{-1}; 3) $\lambda = 26$, $\Delta\nu = 0.25$ cm^{-1}; 4) $\lambda = 41$, $\Delta\nu = 0.56$ cm^{-1}; 5) $\lambda = 67$, $\Delta\nu = 1.6$ cm^{-1}

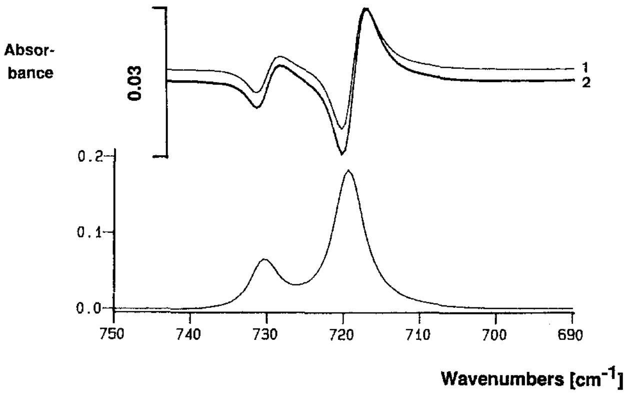

Fig. 6. Frequency shift of the 720 cm^{-1} band of UV-irradiated drawn UHMW-PE blends with 10% polysilanes upon $\varepsilon = 1.2\%$ strain, $\lambda = 30$, T = 25 °C; 1) before UV-irradiation; 2) after 20 h UV-irradiation $\lambda = 254$ nm

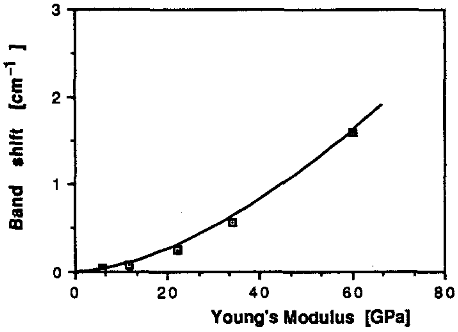

Fig. 5. Correlation of the 720 cm^{-1} bandshift with Young's modulus.

improvement of the linkages between the nearly perfectly oriented crystallites.

A more even stress/strain distribution between the different fiber components should also result when the ties between the microfibrillar crystallites can be improved by crosslinks. The better the linkage between extended chains belonging to different extended chain crystallites, the higher moduli can be expected. As is described elsewhere in more detail [37], UHMW-PE gels containing 10% of UV-sensitive polysilanes were drawn to tapes and, subsequently, irradiated by low-energy UV-irradiation (366 nm). Polysilane and polyethylene do not form mixed crystals, but the polysilane becomes incorporated between the fibrillar PE-crystals as an ultrathin layer by the simultaneous crystallization and the subsequent drawing process. UV-decomposition of the polysilane resulted in generation of radicals which yield interfibrillar crosslinks without attacking the load bearing C — C backbone.

Figure 6 shows the crosslinking effect on the shift of the 720/730 cm^{-1} band $(Abs_{\varepsilon=1.2}(\nu) - Abs_{\varepsilon=0}(\nu))$. In order to ensure reproducibility of the IR experiments on the blends, the UV-treatment was performed on the sample as mounted in the mechanical stretching device. The peak-to-peak intensity, i.e., the value of the band shift increases by more than 15%. This proves that extended chain crystallites participate in the deformation process more efficiently.

Conclusion

FT-IR measurements can be employed to gain information on the molecular stress/strain response of gel-drawn UHMW-PE. In addition to monitoring stress/strain dependent variations of the conformation-sensitive CH$_2$-wagging vibrations, which indicate changes of disordered (non-crystalline) chain segments, also the strain contribution of particular fiber components can be observed by highly reproducible bandshifts. The 730/720 cm^{-1} rocking vibration was shown to indicate the strain contribution of the chain extended fibrillar crystallites: the increase of the band shift, which is observed when a macroscopic strain ε is applied, is reversible upon stress relaxation. At constant macroscopic strain ε, the band shift is correlated to the modulus of the fiber. Nonoriented crystallites are little affected by the macroscopic deformation.

Concerning the properties of the fibers it can be summarized: the stress/strain distribution between different fiber components determines the fiber strength to a large extent. The value of the modulus depends on the chain extension and the linkage between the oriented fiber crystallites. Ultradrawing results in improvement of the morphology with regard to both aspects. Improvement of the linkages between fibrillar crystallites can be achieved also by introduction of chemical crosslinks between those crystallites. As an application of this approach, radical intercrystalline crosslinking was performed by addition and UV-irradiation of a polysilane. In agreement with the considerations mentioned above, the increased strain sensitivity of the 730/720 cm^{-1} band-shift implies an increase of the Young's modulus.

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