

# Time-resolved X-ray scattering studies of creep in oriented UHMWPE films

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Received 21 February 2005; received in revised form 7 July 2005; accepted 13 July 2005

## Abstract

The change in the crystalline structure of oriented melt-crystallised and gel-cast UHMWPE (Stamylan) films of various draw ratios during creep upon constant load has been followed in real time using synchrotron X-ray diffraction techniques at the synchrotron radiation source ANKA (Angstroemquelle Karlsruhe) at Forschungszentrum Karlsruhe (Germany). The shift of (002) Bragg reflections with time of loading and change in their halfwidth are observed for all the samples investigated. The analysis of the data shows a difference in the behaviour of loaded gel-cast and melt-crystallised films. The longitudinal crystallite sizes in the former grow with time, while in the latter they become smaller. Besides, the splitting of a (002) profile in WAXS patterns of melt-crystallised samples (including unstressed samples) was revealed. Several possible causes of this splitting are suggested. One of them is the co-existence of strained crystallites in monoclinic and orthorhombic crystalline modifications.

The observed phenomena is discussed in terms of coherent disposition of crystallites in microfibrils, one-dimensional diffraction on taut-tie molecules, probable pulling-out of the molecules from crystallites upon creep and inhomogeneity of stress distributions.

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**Keywords:** Creep; Oriented gel-cast and melt-crystallized UHMWPE films; Synchrotron WAXS patterns

## 1. Introduction

Despite the outstanding short-term properties of ultra-high molecular weight polyethylene (UHMWPE) films and fibres (tensile strength and Young modulus), its long-term properties (creep, in particular) are low, which dramatically restricts their application. In order to search for a proper route for improving creep characteristics, the creep mechanism has been intensively studied by many authors. It was widely accepted that creep deformation is controlled by both deformation of the molecular network and intra-crystalline slip. This conclusion was mainly drawn on the basis of the data activation analysis [1–5]. However, with the help of a unique laser interferometric technique (Doppler creep rate meter) it was shown that interfibrillar slip occurring in a 'stick-slip' mode contributed to total creep deformation of gel-cast UHMWPE films at a great extent [6,7]. The strong influence of intermicro- and intermacro-fibrillar structure on the creep process has been observed. Recently, the

distribution of axial molecular stresses and their change during creep of gel-spun UHMWPE fibres were intensively studied using Raman spectroscopy [8]. The bimodal axial molecular stress distribution was revealed, the bimodal character being reinforced with a load, which was attributed either to slip at the interfaces or to crystal plasticity.

The question arises as to what is a true role of the crystalline regions in a creep process. May they operate as 'microclamps' (physical knots) for the load-bearing taut tie-molecules passing through crystalline and disordered regions or are they partially destroyed with time of loading?

The aim of this work was to follow after the change in a crystalline structure in loaded oriented UHMWPE films in real-time creep experiments using a synchrotron X-ray source for monitoring a change in WAXS pattern with time of loading. The advantage of the use of synchrotron radiation is in its very high intensity, which is higher than that of the most powerful impulsive X-ray tube by a factor of 3–5. This allows one to perform wide-angle diffraction on a single fibre or a thread film, while in routine experiments the bundle of samples should be put in an X-ray pathway to provide sufficient WAXS intensity. It is especially undesirable in the experiments with stressed samples because of possible misorientation of separate fibres and non-uniformity of a stress distribution.

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## 2. Experimental

The samples investigated were gel-cast and melt-crystallised drawn films produced from UHMWPE (Stamylan) of  $M_w = 2 \times 10^6$  Da kindly supplied by DSM, The Netherlands. The initial unoriented films were especially prepared by different methods aiming at production of the samples of different morphology. As it was established in our early publications [6,9], the drawn gel-cast films have a small amount of interfibrillar tie-molecules (which, in our opinion, results in easy creep), while the melt-crystallised films have many interfibrillar ties suppressing their drawability. It was of importance to follow the behaviour of the crystallites in the loaded drawn films of such diverse morphologies.

The gel-films were cast from 1.5% UHMWPE solution in xylene and dried in air. The resulting xerogel films were cut in  $1 \pm 0.1$  mm wide strips and drawn to various draw ratios (DR = 25, 60 and 110) using multi-stage zone drawing technique. Their thickness and width reduced with drawing down to 0.012 and 1.09 mm for a sample of DR = 25–0.006 and 0.75 mm for a sample of DR = 60 and to 0.002 and 0.6 mm for a sample of DR = 111, respectively. The melt-crystallised films were obtained by compressing at 170 °C and 150 GPa with a subsequent quenching in icy acetone (–95 °C). Then they were also cut in 1 mm wide strips but could be drawn only up to draw ratio DR = 4–5. The thicknesses of the samples were about 0.044 mm and width about 0.9 mm.

Creep experiments were carried out in a dead load mode at  $T_{\text{room}}$  on the drawn UHMWPE films. The load was chosen in such a way to apply a stress on each sample equal to 50% of its tensile strength. A real-time wide-angle X-ray scattering was performed during the creep. The X-ray source was PX-beamline at ANKA (Angstroemquelle Karlsruhe GmbH, Germany). This has an X-ray mirror and a double-crystal Si(111) monochromator giving intense X-rays in a range 3.1–0.6 Å. The flux is  $10^{12}$  photon/s in the  $0.2 \times 0.3$  mm<sup>2</sup> focused spot. A focal point is at the centre of the experimental work space, near the detector plane. The divergence of the beamline is small. It is 0.03° in vertical and 0.2° in horizontal direction.

A wavelength of  $0.750 \pm 0.003$  Å and a sample-to-detector distance of 39.5 mm were chosen for the experiments in order to register (002) reflections on the CCD camera. A pinhole collimator of 500 μm was placed just before the specimen. Wide-angle X-ray diffraction was performed on a single film during its deformation under dead load in a home-made set-up as shown schematically in Fig. 1. Exposure times for WAXS were 300 s. The variation in size of the sample was recorded simultaneously with a video camera. The X-ray patterns were then processed by FIT2D program, and X-ray profiles obtained were fitted by the PEAKFIT. The full width at half-maximum (fwhm) was used to evaluate the longitudinal crystallite sizes  $D_{002}$  by the Sherrer method.

## 3. Results and discussion

For a reasonable comparison of properties of the samples of various draw ratios with different tensile strength, all the

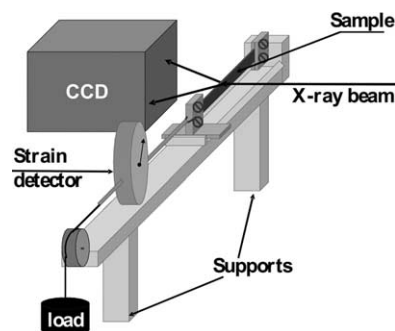


Fig. 1. Schematic set-up for a WAXS scattering study of creep process.

samples investigated were exposed to the action of 50% of their own tensile stress. So that the applied stresses were 610, 1350 and 1670 MPa for gel-cast films of DR = 25, 60 and 111, respectively, while for melt-crystallised film the stress was as small as 128 MPa. The creep curves are shown in Fig. 2. A gel-cast film of DR = 111 exhibits the lowest creep-rate and deformation-to-break, while the highest creep rate is for a gel-cast sample of the low draw ratio (DR = 25). However, creep resistance of a melt-crystallised film with even lower draw ratio (DR = 4) is higher than that of the little drawn gel-cast film. The reason of this discrepancy was discussed in our earliest publications [9,10]. It was established that a large amount of interfibrillar tie-molecules in melt-crystallised films hinders interfibrillar slip and increases creep resistivity.

The WAXS patterns were taken from a single film. First they were recorded from unstressed samples, a small stress being applied to remove the gaps in a loading set-up. Then the WAXS patterns were recorded with exposure times of 300 s. The duration of creep experiments was in the range 1–5 h. A number of patterns were processed for each sample investigated. As an example, a series of successive diffraction patterns from gel-cast film of DR = 60 is given in Fig. 3.

The Bragg diffraction angle  $\theta_m$  of the (002) reflection, its intensity and fwhm are inferred from an analysis of peak profiles.

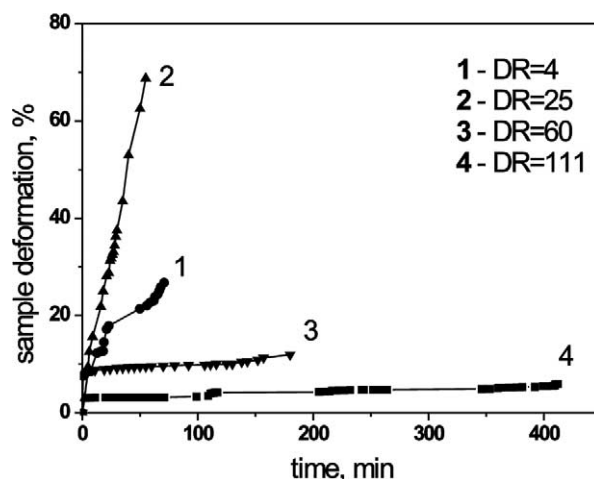


Fig. 2. Creep curves of drawn melt-crystallized and gel-cast films.

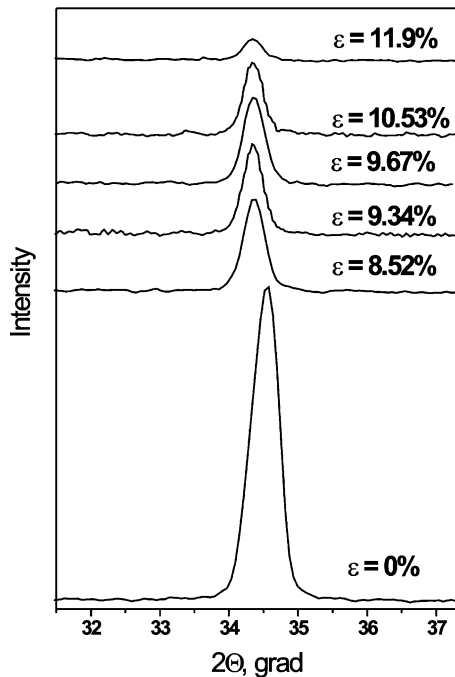


Fig. 3. Integrated WAXS intensity profiles from WAXS patterns recorded in real time during dead-load creep of a drawn gel-cast UHMWPE (Stamylan) film with draw ratio 60.

### 3.1. Gel-cast samples

It is found that in the WAXS patterns of the loaded samples (except a sample of DR=111), the angle position of the (002) reflection shifts with time to a lower value of  $\theta_m$ , as compared to its position in diffraction patterns of unstressed samples. It evidences an extension of a crystalline unit cell in the direction of molecular axis during the creep process. A shift ( $\Delta\theta_m$ ) monotonically grows with time of creep despite the practically constant stress.

Using the value of the shift, a relative lattice deformation ( $\Delta d/d$ ) in  $c$  direction can be calculated in accordance with an equation derived from the Bragg law ( $\Delta d/d = -\Delta\theta_m \cot\theta_m$ ). Maximum shift observed in a WAXS pattern of the sample of DR=25 at the end of creep experiment ( $\varepsilon_{\text{samp}} = 68.75\%$ ) was  $0.12^\circ$ , which corresponds to  $\Delta d/d = \varepsilon_{\text{cr}} = 0.0066$ . For the sample of DR=60 ( $\varepsilon_{\text{samp}} = 11.9\%$ ) the maximum value of crystalline lattice deformation is slightly less (0.0048). If we assume that the average stress applied to a sample ( $\sigma$ ) is equal to that applied of the crystallites one can then calculate an apparent longitudinal Young modulus of crystalline lattice ( $E$ ) using the Hook law ( $E = \sigma/\varepsilon_{\text{cr}}$ ). The calculated values for the samples of DR=25 and 60 appeared to be quite different. The apparent Young modulus of crystallites in the sample of DR=60 is approximately 300 GPa, while that in the sample of DR=25 is only about 100 GPa. The former is close to the theoretical estimates of C–C bond modulus [11] but larger than the values typically inferred from X-ray data [12]. The latter is unreasonably low. It suggests a high inhomogeneity of stress distribution in this less oriented sample. It can be caused by a broad crystal size distribution and by the existence of the

disordered regions containing tie-molecules of different length. The crystalline framework should be then loaded significantly higher than the sample. At the same time the stress distribution in the highly oriented sample (DR=60) is obviously almost uniform.

We carried out an additional experiment on this sample increasing the initially applied load in a stepwise manner. The relative deformation of crystalline lattice inferred from the X-ray data is plotted versus applied stress in Fig. 4. It is apparent that increasing stress above 50% of the tensile stress does not result in a noticeable increase of crystalline lattice deformation. It leads to an implausibly high estimate of the apparent modulus. This phenomenon was recently also observed upon loading similar samples and was explained by pulling out the taut tie-molecules from crystallites [13,14]. We suggest that in our case the same events occur. When a stress applied to a sample reaches a certain level, the overstressed taut tie-molecules begin to pull out of the crystals. The portion of a crystallite, which does not contain such molecules, appeared to be less loaded than the sample and less deformed. The value of the apparent modulus of crystallites then increases.

Thus, one can conclude that crystallites even in the almost perfectly structured material providing more or less homogeneous stress distribution across the molecules may only serve as the ‘micro-clamps’ and resist to creep up to a certain limit of applied stress. When the applied stress exceeds 50% of its tensile strength the crystallites begin to deteriorate.

One should also emphasize that the scattered intensity of the (002) peak decreases with time of loading, which can be caused by the increasing amount of crystalline defects. However, it makes it difficult to draw a definite conclusion as regards possible types of defects without an analysis of a profile of a (004) reflection. Unfortunately, a geometric confinement did not allow us to register the higher orders of the (002) peak.

The behaviour of an ultimately drawn gel-cast sample differs from the samples described above. The crystalline unit cell appeared to be slightly compressed in it. A gradual shift to larger Bragg angles is observed with time. The maximum shift at the end of the creep process was equal to  $0.03^\circ$  ( $\Delta d/d = 0.0008$ ).

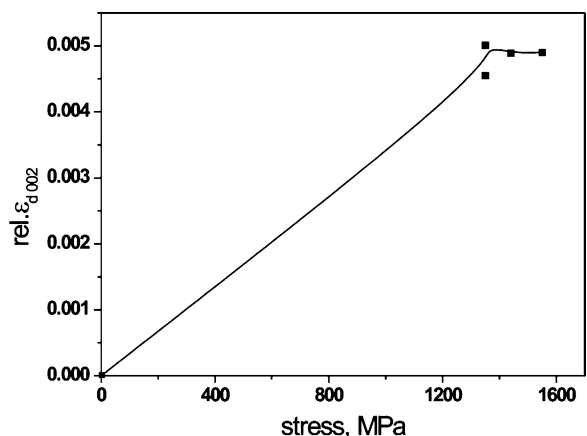


Fig. 4. Dependence of relative deformation of 002-spacing in gel-cast UHMWPE film of 60 draw ratio on applied stress.

At first sight the operation of the compressive forces in the drawn sample seems implausible. However, the compressive forces can be generated because of fracture of strained microfibrils leading to formation of kink bands. This often occurs in highly drawn material under load [9,10,15]. In such a highly drawn (maybe even 'overdrawn') sample (DR=111) the kink band formation should be very extensive. Creep at room temperature may intensify this process in such a way that almost all the sample volume will be involved in it.

Let us consider now the other changes in the WAXS patterns during creep. It was found that the X-ray profile of (002) reflections changes with time of loading. However, as distinct from a number of observations [13,14,16], a halfwidth of the meridional peaks reduced in all the gel-cast samples investigated.

We used the values of fwhm derived from PEAKFIT fitting to calculate of the apparent longitudinal crystallite sizes ( $D_{002}$ ). This approach is widely used in the literature, though, for correct estimation a series of (00*l*) reflections is necessary to distinguish profile broadening caused by crystal size from that caused by distortion effect. As mentioned above, geometrical limitations did not allow us to record the other (00*l*) reflections. So that the values of crystallites length determined from (002) X-ray profiles are not very accurate and should be used rather for comparison purposes in one and the same experiment.

The calculated values of  $D_{002}$  in unstressed gel-cast samples appeared to be sufficiently small (about 100 Å). However, a significant growth of the apparent crystallite sizes was observed during creep. The change in a crystal length under load in gel-cast samples is shown in Fig. 5. For the sake of simplicity, the apparent  $D_{002}$  sizes in the unstressed samples are assigned to 100%. A significant growth of crystallites in the samples of DR=60 and 111 with creep deformation is evident. The crystallites in the film of DR=25 at first grow fast but then their increasing becomes slower and at the last stage of creep the longitudinal crystal sizes becomes even smaller than those, which were reached at the previous stage.

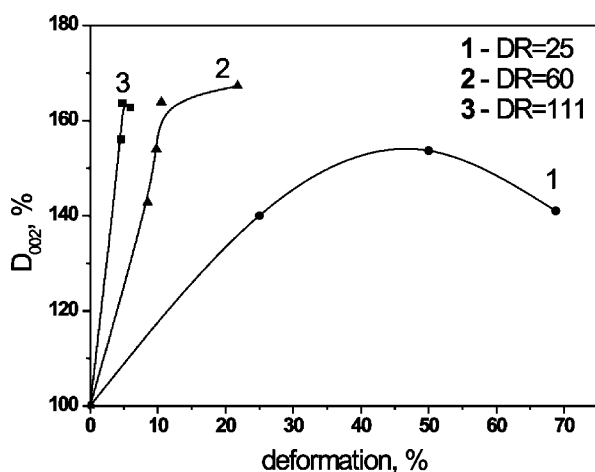


Fig. 5. Change in the longitudinal crystallites sizes (in % to original unloaded samples) during creep of gel-cast UHMWPE films of draw ratio 25(1), 60 (2) and 111(3).

The question arises as to why the crystallites in such highly oriented samples are so small, and how can they grow to such a great extent when the content of the disordered regions in them does not exceed 20–30%. Let us remind that the sizes of crystallites are actually the sizes of the three-dimensional regions of coherent scattering. The length of a crystalline region in microfibrils of highly oriented samples can be very large. However, if any very small disordered zone (containing small defects, such as kinks, twisted segments of tie-molecules, taut tie-molecules not three-dimensionally ordered, etc.) would be located in it, the diffraction from the neighbouring crystalline portions would not be coherent and they would be taken as two distinct crystallites [17–19]. At the same time, such small defects do not disturb the mechanical continuity and do not dramatically influence the mechanical properties. This explains a great scatter in crystal length (from 50 to 700 Å) cited in literature for various stiff and strong gel-spun UHMWPE fibres [20–23]. The sizes of three-dimensional coherent regions depend on the method of production of such fibers.

We suggest that this is the case we encountered. The coherence in the neighbouring crystallites in microfibrils of gel-cast oriented films we investigate is probably loosened because of inclusion of some small defect zones in crystalline regions of microfibrils. A slight axial misorientation of crystallites in microfibrils may lead to the same effect. During creep the defects located in disordered zones may migrate through the crystallites and annihilate at the molecular ends, the twisted segments may untwist, the neighbouring crystallites may rotate and put in a coherent position. All of that provides the coherence between neighbouring crystallites in microfibrils and leads to an increase in longitudinal sizes of coherent regions. A reduction of the crystallite length is only observed in the last stage of creep in the sample of DR=25, which evidences a possible deterioration of coherent regions with time.

The growth of the size of coherent regions is registered in presented work probably because the experiments are carried out not on the fibres but on the films with a developed texture, as inferred from the high ratio of intensity (110) and (200) peaks. In accordance to theoretical estimates the intensity (110) and (200) reflections has to be in the ratio 3.77 in non-textured material [24]. However, the intensity of (110) reflection in the diffraction pattern of the film of DR=60 was higher than the intensity of (200) peak by a factor of 16, while in the diffraction patterns of the films with DR=25 and 111 the ratio of these intensities was about 8.

### 3.2. Melt-crystallised samples

A diffraction pattern of the drawn melt-crystallised sample with DR=4 differs from those of the drawn gel-cast films. The (002) diffraction peak shows well pronounced splitting into two peaks already in the unstressed state. A complicated shape of the (002) profile is preserved during the whole time of a creep experiment (Fig. 6). The WAXS image of the (002) reflection is given in Fig. 7(a). A profile of the (002) reflection is



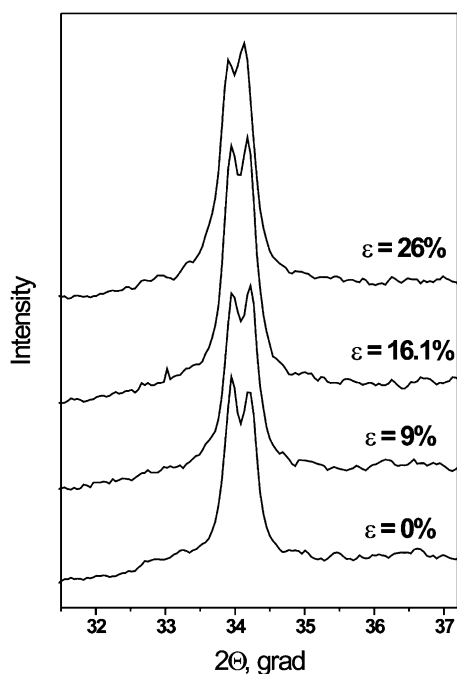


Fig. 6. Integrated WAXS intensity profiles from WAXS patterns recorded in real time during dead-load creep of a melt-crystallized UHMWPE (Stamylan) film with draw ratio 4.

presented in Fig. 7(b). The thin lines indicate the best fit using Pearson function. We designate the peak closest to the primary beam as peak 1 and the more remote peak as peak 2.

We suggest that it is the high degree of monochromatization of the primary synchrotron beam provided by the use of a double crystal monochromator, and high intensity of synchrotron X-ray source enabling to investigate a single thin film, which allowed to reveal this phenomena. It was not earlier revealed in oriented UHMWPE samples. It could be masked in the diffraction patterns recorded with the help of conventional diffractometers because of possible overlapping reflections from layered or thick samples, which are used for providing the detected level of scattered intensity. No literature references to this observation are available elsewhere.

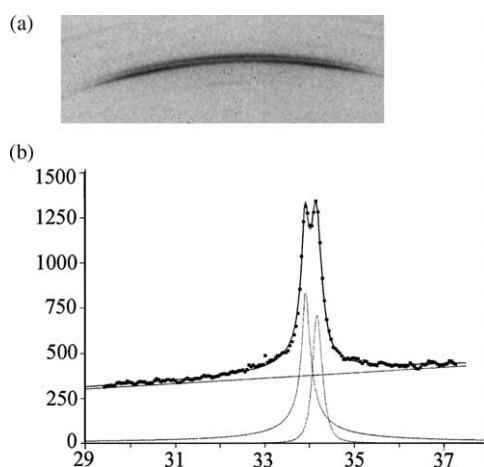


Fig. 7. X-ray diffraction pattern of a melt-crystallized drawn sample (a) and an example of fitting its profile (b).

The diffraction angle of peak 2 (already as in the unstressed sample) is slightly less than the standard one characteristic for orthorhombic PE unit cell. It allows one to suggest that the orthorhombic crystallites in an initial film are somewhat strained a little. It may actually occur if we take into account a high content of the entanglements typical of melt-crystallized UHMWPE, which put obstacles on the way of drawing. With time of loading the (002) reflection continues to shift towards smaller angles. The relative deformation of crystalline lattice in the direction of molecular axis inferred from X-ray data is less than that in gel-cast samples with DR = 25 and 60 and equal to 0.002. However, it is higher than the value of crystalline deformation, which could be expected taking into account the small stress applied to the sample investigated. One should assume inhomogeneous stress distribution inside the sample.

The origin of peak 1 is still open to question. Careful examination of the diffraction pattern (Fig. 7(a)) reveals two maxima of intensity located on each side of the meridian of the WAXS pattern (coincident with drawing direction) at an angle of about  $10^\circ$ . Since the angle between basal and lateral planes of the monoclinic unit cell is  $105^\circ$ , it is reasonable to propose that these reflections originate from the crystallites in monoclinic modifications. The angular distribution of the crystallites is probably broad so that the intensity of the (002) reflection on the meridian is sufficiently high (peak 2). It is worthy of note that the area of peak 1 and peak 2 profiles are in a ratio 80:20, which means that PE in the melt-crystallized drawn film is predominantly in the monoclinic modification. As known, the monoclinic phase is only stable under stress. So that one should assume that such a significant portion of a volume is subjected to internal stresses. It slightly decreases during creep and at the end of the creep experiment the ratio becomes equal to 70:30. This change can be attributed to possible scissions of load-bearing molecules and/or microfibrils in a loaded sample, which results in kink formation and a partial release of the internal stresses. Attributing peak 2 to the monoclinic modification appears justified. However, in this case on the equator of the WAXS pattern the (010) reflection of the monoclinic phase should appear together with the (110) reflection of the orthorhombic modification. Unfortunately, long exposure time chosen for reliable detection of the (002) profile resulted in 'over-exposure' of equatorial reflections, which made it difficult to resolve separate reflections.

It is possible to explain the appearance of peak 1 in another way. As known, in the diffraction pattern of unoriented PE material the (002) profile is overlapped by the other ones disposed on each side of it. Their diffraction angles  $\theta_m$  in WAXS pattern obtained at synchrotron radiation with wave length of  $0.75 \text{ \AA}$  should be equal to  $33.64^\circ$  (I) and  $35.23^\circ$  (II). One may assume that the observed peak 1 located at the angle  $33.95^\circ$  is the reflection I originating from a still not re-arranged material. However, there is no hint of the existence of reflection II at  $35.23^\circ$ . Besides, it is difficult to imagine that there is still such a big amount of non-fibrillar material in the sample of DR = 4.

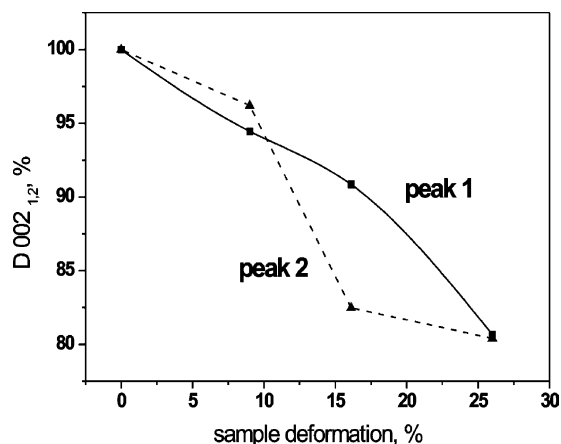


Fig. 8. Change in the longitudinal crystallites size (in % to original unloaded samples) during creep of melt-crystallized film with DR=4 calculated for both peaks from fitted profiles.

Finally, one could assume the existence of a family of microfibrils tilted to the axis of drawing, which contain the strained orthorhombic crystallites. Suffice it to remind four-point SAXS patterns from unstressed oriented melt-crystallised samples, which evidences the tilt of crystallites maintained obviously by strained interfibrillar molecules [9,10]. Much more work is needed to elucidate this question.

One should add that both peaks in the melt-crystallised film under load become broader which are in accordance with the observations on gel-crystallised drawn fibres [13,14,16]. The values of  $D_{002}$  calculated from the broadening of both peaks decrease with increase of creep deformation (Fig. 8). On one side the observed reduction implies that the crystallite deteriorate during creep of melt-crystallised samples. On the other side it can be attributed to a tilt of crystallites via intracrystalline slip (and the reduction of their apparent sizes) occurring under the action of interfibrillar tie-molecules bringing the external stress to fibrillar crystallites more effectively, than in the case of gel-cast samples.

#### 4. Conclusions

A real-time diffraction scattering study of creep at room temperature in oriented films of UHMWPE of various draw ratios and different methods of production shows that the behavior of crystalline regions dramatically depends on film morphology, which controls the stress distribution in crystallites.

In the not ultimately drawn gel-cast films (DR=25) in which the difference in length of tie molecules is still large enough, the inhomogeneity of stress distribution over sample volume is high and the crystallites appear to be subjected to tensile stress higher than the stress applied to a sample. This is suggested by the low apparent Young modulus of deformation of crystalline lattice in the direction of molecular axis calculated from the shift of the (002) reflection to smaller Bragg's angle. The crystal deformation increases with time of loading.

In the gel-cast film of DR=60 the stress distribution is more homogeneous. The majority of molecular segments not incorporated in crystalline regions has obviously the trans-zigzag conformation and the crystallites are subjected to a tensile strength comparable to that applied to the sample. The value of Young modulus of crystallites inferred from X-ray data coincides with the theoretical estimates. The apparent growth of the modulus with the increasing stress over 50% of the tensile stress is attributed to pulling out tie-molecules from the crystalline lattice. This allows to conclude that the crystallites cannot play a role of 'micro-clamps' when the applied stress exceeds this value.

Creep of ultimately drawn ('overdrawn', to be exact) gel-cast samples leads to slight compression of crystallites because the deterioration of the sample under tensile load results in formation of kink bands and development of compressive forces.

The growth of the apparent longitudinal crystallite sizes in gel-cast films with time of loading is attributed to the appearance of coherence in diffraction from neighbouring crystallites, caused by the elimination of defects from small disordered zones between them.

A well pronounced texture is discovered in gel-cast films.

As distinct from gel-cast films the sizes of the regions of coherent scattering in melt-crystallised samples decrease during creep. A complicated morphology is deduced from the observed splitting of 002 reflection. A different possible cause of this phenomena could be the co-existence of monoclinic and orthorhombic crystallites, the remnants of not re-arranged initial structure and/or crossed microfibrils.

#### Acknowledgements

E.M. Ivan'kova is grateful to Russian Science Support Foundation for financial support. G. Buth (PX-beamline, Forschungszentrum Karlsruhe GmbH, Institute for Synchrotron Radiation) is acknowledged for technical assistance.

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