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Stress stabilization of the orthorhombic and hexagonal phases of UHM PE gel-spun fibres

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In highly oriented polymers, stress can stabilize fibres against melting by favouring the low entropy fibrillar state against the high entropy melt. In this work we have investigated the thermal stability of gel-spun ultra-high modulus polyethylene subjected to tensile stress. The Daresbury X-ray synchrotron radiation source and optical microscopy have been utilized to follow dynamically the transformation, melting and recrystallization of fibres, under optimum conditions of controlled stress. The orthorhombic phase is stable up to 164°C, after which the crystals transform into a hexagonal phase which can be stable up to temperatures as high as 179°C. Whilst this is the greatest thermal stability reported for the orthorhombic phase, the question of the ultimate stability is still unanswered and is presently limited by the effectiveness of the stress transfer to the fibrils.

Introduction

Application of high pressures normally promotes stability of the solid phase. It has long been recognized that this is the case for semicrystalline polymer systems, where crystallization at high temperatures and pressures reveals novel morphological features. For example, in bulk polyethylene, the application of pressure can stabilize the normal orthorhombic (o) crystals, and enable a stable two-dimensional hexagonal (h) crystal structure, with an anomalously high longitudinal mobility of the polymer chains[1]. It is thought that this high chain mobility in h phase is responsible for chain folding reorganization towards thicker or even chain-extended crystals[2].

In highly oriented polymers, stress can play a similar role to pressure; by energetically favouring the low entropy fibrillar crystal state it can stabilize fibres against melting of the o phase and enable observation of a stable h phase. Based on observations of birefringence, Odell et al.[3] reported an increase in melting temperature of constrained interlocking melt-produced shish-kebabs from 136 to 160°C. Smook and Pennings[4] reported similar observations on ultra-high molecular weight polyethylene (UHM PE) fibrils prepared by the surface growth technique with enhancement of the melting point up to 180°C. Using gel-spun fibres, Van Aerle and co-workers[5,6] combined such observations with X-ray studies to reveal the stability of the o phase, the o–h transition and melting of the h phase. These workers report the o–h transition at 152°C, and melting of the h phase above 175°C.

It is our belief that the ultimate stability of oriented material depends largely upon the effectiveness of the constraints applied to the fibrous material. In the present

work we set out to establish the best possible constraints upon the sample against contraction and melting. We observe birefringence, stress in the fibrils and, using the Daresbury Synchroton Radiation Source (DSRS), we dynamically record the X-ray scattering and hence identify the transformation, melting and recrystallization of the material. Here we will show the attainment of o–h transition at temperature as high as 164°C, at atmospheric pressure.

Achievement of the most effective constraints presents two principal requirements. First, the sample must be embedded in a matrix material which can support a high shear and compressive stress at elevated temperature. We found a u.v. curing low viscosity cyanoacrylate adhesive to be most effective. Second, the stress must be effectively transferred from the polymer/matrix interface into the interior of the polymer. This is best achieved by maximizing the surface area, in practice utilizing very fine fibrils. We used Allied Chemicals Spectrum 900, a highly oriented gel-spun fibre with an average fibrillar diameter of around 60 μm.

Experimental and results

Birefringence. Figure 1 shows the birefringence of the fibrils observed in the hot-stage polarizing microscope as a function of temperature. The fibrils placed in between cover slips are embedded within cured cyanoacrylate. As can be seen, the birefringence falls only slightly up to around 170°C; the final traces of birefringence are observable beyond 179°C. When a sample that has been almost completely melted, as assessed by birefringence, is cooled to recrystallize the material, then we see recrystallization of oriented material, presumably nucleated by the remaining fibrillar cores.

Stress. In the present work we studied stress dependence upon temperature in the constrained fibres. Here fibres are immersed within cyanoacrylate except for

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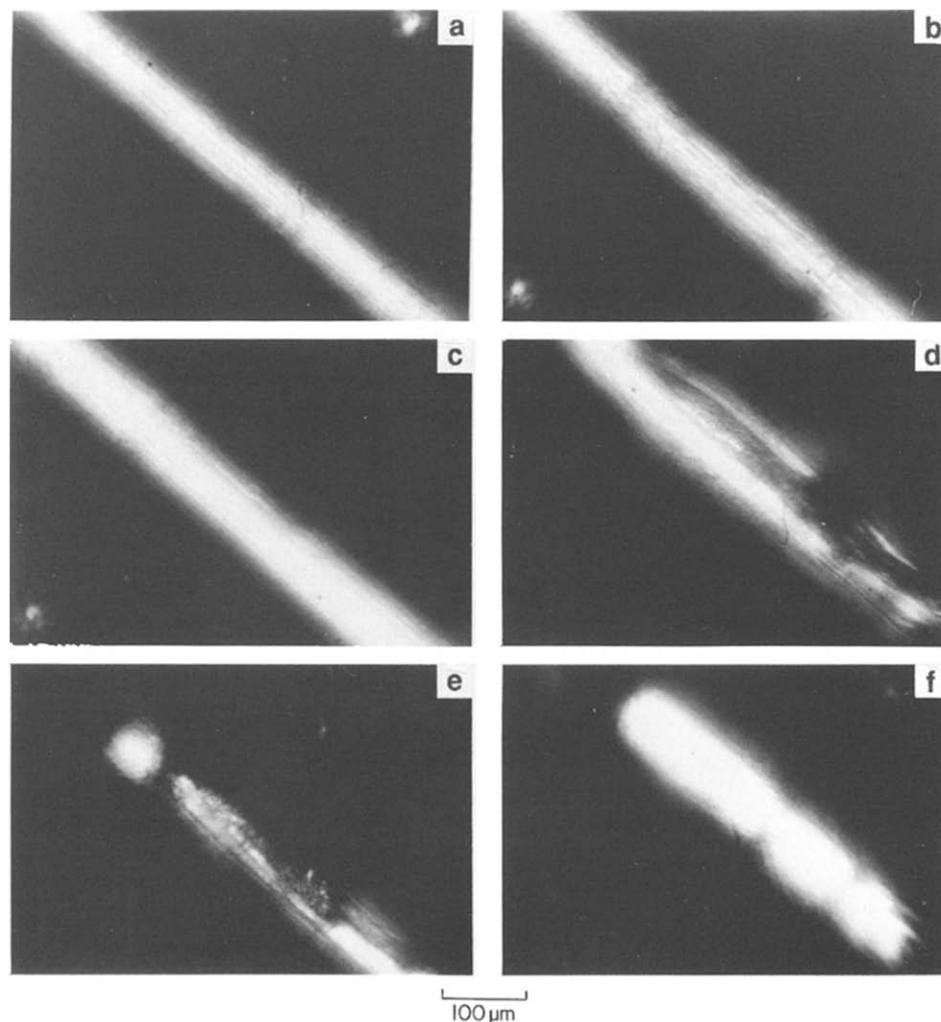
Figure 1 Polarizing microscope observations of a constrained fibril during heating: (a) 40°C; (b) 147°C; (c) 166°C; (d) 170.5°C; (e) 179°C; (f) after recrystallization at 120°C

a small region (about 1 mm long) in the centre, and are kept under stress by clamping their ends and maintaining length. Any relaxation of stress within these fibres could be measured to a precision of 1 MPa. On heating to 140°C within a well calibrated and insulated chamber, no significant change in stress is observed (*Figure 2*). A gradual increase in stress is measured on heating above 140°C and below 164°C. A sharp decrease in stress to zero (within the experimental limitations) occurs just above 164°C. A decrease in the stress corresponds to relaxation within the fibre. While cooling from 170°C down to 130°C the stress in the fibre remains almost zero. Once the temperature falls below 130°C, down to 90°C a continuous increase in stress from 0 to 190 MPa is measured. Below 90°C the load remains nearly constant. This increase in load on cooling corresponds to contraction of the fibre when the constraints are released.

X-ray observations — stability of o and h phases. To reveal the molecular changes within the fibre, and to know the corresponding variation in stress with temperature in the constrained fibres, we used time-resolved wide-angle X-ray scattering (WAXS) facilities at DSRS. A two-dimensional detector is used for the fast collection of the data. This is one of the experimental necessities to be discussed later. *Figure 3a* shows (1 1 0) and (2 0 0) o reflections at 162°C of a well oriented,
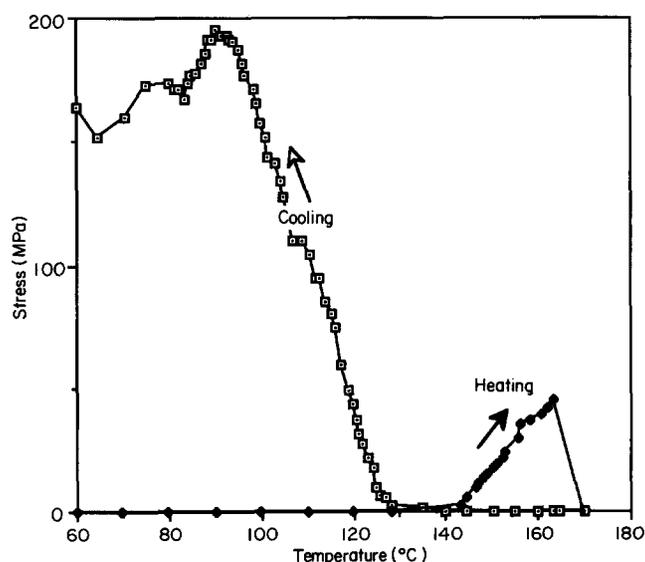
Figure 2 Stress *versus* temperature for constrained fibrils during heating up to 170°C and subsequent cooling

gel-spun, well constrained fibre immersed within the cyanoacrylate. On raising temperature by only 2°C appearance of the {1 0 0} h reflection is seen (*Figure 3b*). It should be noted that as the {1 0 0} h reflection strengthens, the (1 1 0) and (2 0 0) o reflections weaken. On leaving at
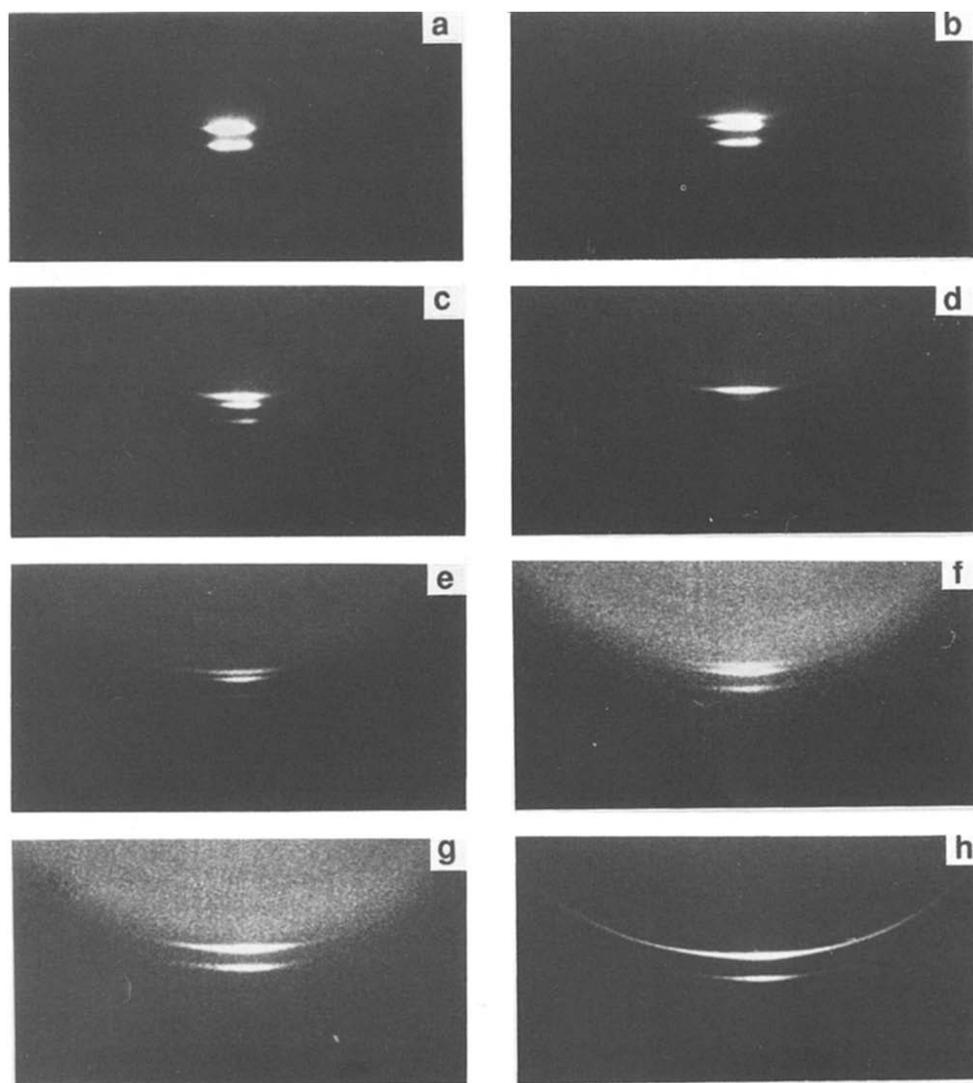
Figure 3 X-ray diffraction patterns of constrained fibrils during heating: (a) 162°C; (b)–(d) 164°C; and cooling: (e) 157°C; (f) 152°C; (g) 135°C; (h) 86°C

164°C for a longer time (*Figure 3c*) it is observed that while the {1 0 0} h reflection increases in intensity and (1 1 0), (2 0 0) o reflections diminish in intensity, scattering from the amorphous region in the form of a halo occurs. *Figure 3d* shows the presence of the h phase together with scattering from the amorphous region at the background of these reflections. *Figure 3d* also shows that on leaving the sample within the h phase for a longer time, loss in orientation occurs. On heating the sample further, 4–6°C above o–h transition temperature, the sample breaks. But on cooling below 164°C, at 157°C (*Figure 3e*), the reappearance of (1 1 0) and (2 0 0) o reflections is seen along with the weakening of {1 0 0} reflection of the h phase. No change in intensity of the amorphous region is seen. This indicates that on cooling, the first order phase transition from h to o phase in the fibres occurs, while the amorphous region does not crystallize. On leaving for longer times at 157°C (*Figure 3f*) the intensity of h {1 0 0} reflection decreases continuously whereas intensity of o (1 1 0) and (2 0 0) reflections increases. *Figure 3g* shows the presence of (1 1 0) and (2 0 0) o reflections together with amorphous scattering at 135°C, whereas the {1 0 0} reflection from the h phase completely disappears. Partial orientation in the fibre is maintained. When the fibre is cooled further below 130°C, intensity from the amorphous region starts disappearing whereas

the intensity of (1 1 0) and (2 0 0) o reflections increases continuously. This further crystallization is seen as the appearance of an arc and the complete disappearance of scattering from the amorphous region at 86°C (*Figure 3h*).

Discussion

The role of stress in stabilizing the o phase is clear. The stress energetically favours the low entropy chain-extended fibrils against the high entropy contracted melt, analogous to the role of pressure, which energetically favours the high density crystalline phase. It is clear from comparison of *Figures 2* and *3* that once the stress begins to drop, the o phase is no longer stable. In the present work, due to the high quality of constraints, we have managed to maintain a high stress beyond 160°C, and this has enabled stabilization of the o phase, as revealed by *Figure 3c*, up to the unprecedented temperature of 164°C.

Beyond 164°C the crystals do not melt but transform into the h phase, together with a drop in stress to levels that were too low to be recorded (< 1 MPa). Even though externally applied stresses are very low in the h phase they are still essential for stability; if constraints are removed then the h phase melts immediately. The reduction in stress is partly related to a progressive
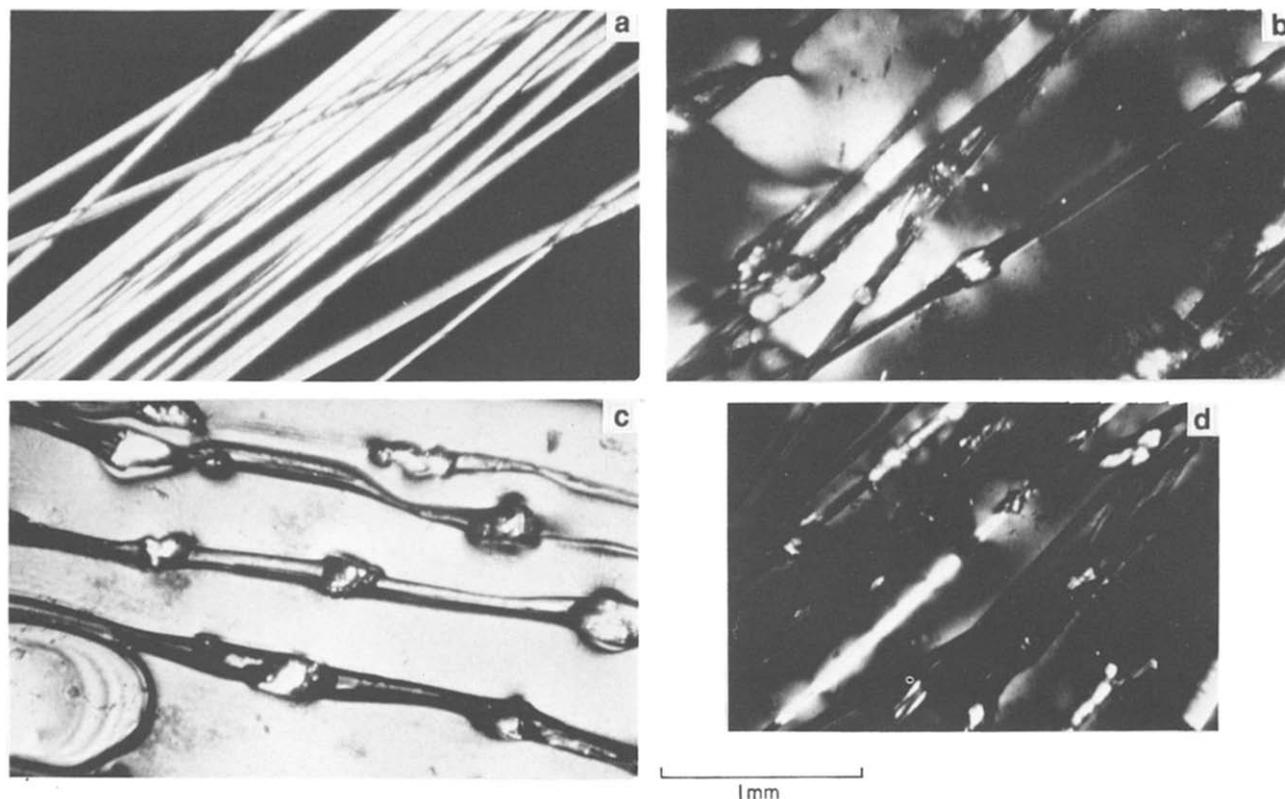
Figure 4 (a) Low magnification polarizing microscope observation of constrained fibrils at room temperature; (b) after heat-treatment up to 175°C; (c) bright field view after heat treatment to 175°C; (d) polarizing micrograph at 179°C

decrease in crystallinity (to around 15% as assessed by integrated X-ray intensity in *Figure 3e*). It may also be related to the often reported high chain mobility of the h phase[1,2]. Nevertheless, it is curious that the low entropy h phase appears stable with such a small applied external stress.

We would expect that the partially molten h fibril would consist of very fine crystal cores within a melt matrix, perhaps more than 3000 Å apart[7]. As the material is recrystallized on cooling, the h cores retransform to o (*Figure 3g*) with only o phase present at 157°C. These observations are in close agreement with observations of the h–o transition under pressure[8]. Below 130°C, molten matrix material recrystallizes onto these nuclei (*Figure 1f*). Although by birefringence the crystallized material is overall oriented by the nuclei, it is clear from *Figure 3h* that the orientation is much weaker. We believe this is due to recrystallization into a twisting *c* axis overgrowth shish-kebab, which can occur when the nuclei are widely spaced[7]. Recrystallization of the melt material below 130°C leads to recovery of the stress (*Figure 2*).

In the light of this composite view of an h fibre at high temperature, it is possible that the stresses on the h cores are much greater than the externally applied stresses. This could be due in part to their reduced volume fraction, but also to the fact that contraction of h cores would require shearing through the very viscous UHM PE melt, which could generate high stresses that would not be seen externally.

It is worth noting that the results recently reported by Van Aerle *et al.*[6] are based upon partially stretched material, where the chains are not fully extended. It is likely that the h phase in such material would be much less stable, since it can relax its stress internally by chain

mobility without contraction through the melt. The chain mobility within the h phase in the partially drawn material (relative to the fibre having full chain extension) will be much more prominent, as the thermodynamic driving force will favour full chain extension.

The present stability of the o phase at 164°C is the greatest reported. But the question of the ultimate stability of the o phase is still unanswered. Constraints, even in this experiment, are limited by the adhesion, mechanical and thermal stability of the matrix. *Figure 4* shows a low magnification view at room temperature before treatment (*Figure 4a*) and after heat treatment (*Figures 4b–d*) of the same sample as shown in *Figure 1*.

On heating the constrained fibres above 150°C we observe a progressive process of retraction and loss of birefringence of parts of the fibrils. As the fibrils attempt to contract, so stress is transferred to the cyanoacrylate matrix, showing as stress birefringence (*Figure 4b*). Retraction is always accompanied by a breakdown of the matrix material, the original fibre channels rupturing sideways as shown in *Figure 4c* (bright field optical micrograph). In other parts of the material, where the performance of the matrix is better, the fibres can remain locally constrained and highly birefringent up to temperatures as high as 179°C (*Figure 4d*).

Conclusions

Although we have demonstrated greatly enhanced stability of the o phase with stress, our findings suggest that the principal limitation to stability is still the quality of constraint. We speculate that etching of these fibres, to improve matrix adhesion, and use of better matrices like ceramics, which can withstand high temperatures without any loss in constraint efficiency, may further

enhance the stability of the o phase and hence the melting temperature of UHM PE fibres. Potential applications of high-temperature high-modulus polyolefins do not require any illustration.

References

1 Bassett, D. C., Block, S. and Piermarini, G. J. *J. Appl. Phys.* 1974, **45**, 4146
2 Hikosaka, M. *Polymer* 1990, **31**, 458
3 Odell, J. A., Grubb, D. T. and Keller, A. *Polymer* 1978, **19**, 617
4 Smook, J. and Pennings, A. J. *Colloid Polym. Sci.* 1984, **262**, 712
5 Van Aerle, N. A. J. M. and Lemstra, P. J. *Polym. J.* 1988, **20**, 131
6 Van Aerle, N. A. J. M., Lemstra, P. J. and Braam, A. W. M. *Polym. Commun.* 1989, **30**, 7
7 Bashir, Z. and Odell, J. A. *J. Mater. Sci.* in press
8 Rastogi, S., Hikosaka, M., Kawabata, H. and Keller, A. *Macromolecules* 1991, **24**, 6384