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The detection of radicals in strained, high-modulus polyethylene fibres

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It is shown that loading ultra-high molecular weight polyethylene (UHMW-PE) fibres up to about 50% of their theoretical strength causes bond scission to occur as corroborated from the number of radicals monitored. In addition, a creep test on UHMW-PE fibres also showed an ongoing production of radicals in the polymer. Although precise quantification of the radical concentration is difficult, a first estimate shows that there is a significant number (of the order of 4×10^{13} spins) compared with the total number of polymer chains (10^{14}) that run through the cross-section of the PE rope employed in the experiments.

(Keywords: UHMW-PE fibres; radicals; electron spin resonance)

INTRODUCTION

The subtleties in the molecular structure of polymeric materials appear to reach a level of complexity which has thus far prevented full and detailed comprehension at the molecular level. Polymeric structures that are generally believed to be more simple, such as ultra-high molecular weight (UHMW) ultra-oriented polyethylene fibres (PE), might be considered as appropriate starting materials for further increasing our knowledge in this specific field. The experimental moduli[1,2] of these fibres approach the theoretical modulus[3], while the strain to failure is typically four to five times lower than that expected from theoretical calculations[4].

Most published works aimed at describing the macroscopic mechanical properties from a more microscopic point of view have not gone beyond applying Tagayanaki-type models[5–7]. For a true link between the molecular structure and morphology, it is necessary to employ experimental methods allowing for the direct probing of these molecular aspects. In this context, various groups have applied Raman spectroscopy and/or X-ray diffraction to study these high-modulus PE fibres under strain[8–13]. These studies have revealed that the PE fibres exhibit a bimodal strain distribution upon straining, this being evident from the splitting of the Raman C–C stretching bands. Since a similar splitting was observed from wide-angle X-ray scattering data, it was concluded that the bimodal strain distribution is present at the crystalline block level.

Furthermore, it was shown from the Raman spectroscopic data that the relative band area of the highly shifted Raman band exhibited the same time dependence as the stress in a creep test[9,11]. This suggests a relation between the release of strain in blocks of polymer chains, as monitored by the Raman experiment, and macroscopic creep. This strain release could be caused either by chain slippage or by chain failure, where chain failure would most definitely account for the sudden relaxation on the time scale of the Raman experiments. Reasoning from experiments on UHMW ultra-oriented PE fibres with methyl side groups on the main chain of polyethylene, Bastiaansen[14] has concluded that the fracture mechanism in UHMW-PE fibres is predominantly controlled by chain scission. Ohta *et al.*[15] argued, also based on methyl-branched UHMW-PE fibres, that the creep mechanism is dominated by chain slippage in the crystalline part of the material.

With electron paramagnetic resonance (e.p.r.), radicals resulting from chain scission can be detected. In the present contribution we report on e.p.r. measurements on strained UHMW-PE fibres, including a first study of the effect of stress relaxation (creep) on bond scission as monitored by the production of radicals.

EXPERIMENTAL

E.p.r. is a very sensitive technique, with a typical detection limit of 10^{10} spins for a resonance line with a peak-to-peak linewidth of 1 Gauss (0.1 mT). However, since the quantity of radicals created per unit volume of loaded chain is relatively small, it is necessary to monitor ropes or bundles rather than single filaments, in order to maximize the probability of detecting radicals in an e.p.r. cavity. The maximum diameter of a rope which can be fed through a standard commercial e.p.r. cavity is about

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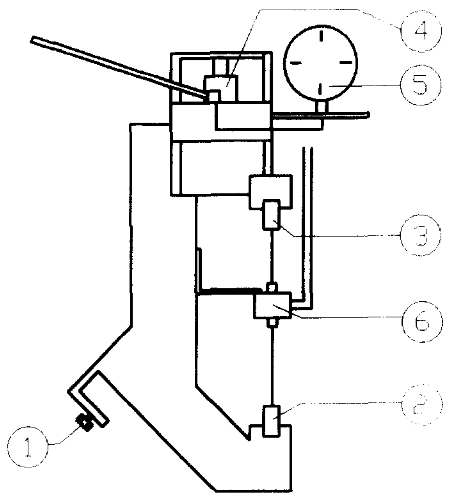


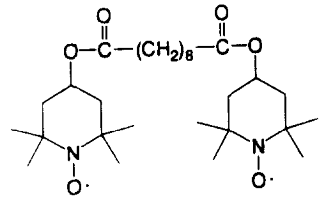
Figure 1 Schematic drawing of the straining rig: 1, bolts to fix the rig on the magnet yoke; 2, fixed clamping device; 3, moveable clamping device; 4, automobile jack; 5, pressure gauge; 6, e.p.r. resonator

9 mm, which, taking account of the number of chains per cm^2 in crystalline PE, is equivalent to about 5×10^{14} chains. In addition, UHMW-PE fibres such as the Dyneema SK-60 fibre studied here have a very high modulus and yield strength. To perform *in situ* measurements under stress in an e.p.r. cavity, a straining device was developed. Because of the nature of the e.p.r. experiment care must be taken to avoid any magnetic material in the construction. An obvious choice is stainless steel, which is both strong and non-magnetic. To reduce weight wherever possible, stainless steel was replaced by aluminium. In this way the total weight of the constructed apparatus could be kept as low as 100 kg. This limited weight made it possible to mount the straining device on the magnet with the aid of a simple lifting device.

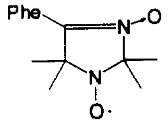
Figure 1 presents a schematic drawing of the straining rig. The device fits on the yoke of a Varian E-12 magnet and is secured with two bolts (1). The lower cable clamping device (2) is fixed while the upper one (3) can move upwards. This movement was accomplished with a commercially available automobile jack (4). The jack was operated manually and the force applied on the fibres was monitored with a pressure gauge (5). In order to align the fibres in the centre of the resonator (6), its position could be adjusted with respect to the straining rig.

With this set-up it was possible to load the fibres with a maximum force of 50 000 N. The largest attainable strain was 150 mm on an initial length of 600 mm. This set-up allowed for constant strain experiments. Constant stress experiments could be carried out by adjusting the force manually during the experiment.

As is known, radicals can react readily with oxygen from the air, giving rise to peroxy radicals, which then are only a derivative of the primary radicals initially formed. Although low temperature measurements would lead to stabilization of formed radicals, it influences the mechanical properties of the fibre. Therefore, the measurements were carried out at room temperature. To prevent the primary radicals reacting with oxygen from the air, the resonator was flushed during measurements with a gentle stream of nitrogen gas. Since the primary radicals decay rapidly in air at room temperature, they were trapped by a spin trap (a nitroxy-radical compound). Thus the registered decrease of the e.p.r. signal of the spin trap is taken as a measure of the radicals formed in the PE fibre. Two different nitroxides were tried as dopant molecules. One is the oxidized Tinuvin 770 species which has the molecular structure



The second nitroxide is called nitroxide II for convenience and has the structure[16]



The PE fibre was doped with the nitroxide by soaking the fibre in a 1 wt% solution of the spin label in dichloromethane for 1 h.

E.p.r. spectra were recorded on a Bruker EPR spectrometer at the University of Nijmegen. The scan time for one spectrum was about 1.5 min. The theoretical maximum attainable strength for our 4 mm diameter cable was around 17 000 N, of which we obtained some 10 000 N. The theoretical maximum is calculated here as the strength based on the strength of individual, finite length monofilaments. Since the cable is not an ideal composition of monofilaments, this maximum strength was not attained; this was in full quantitative agreement with the results of independent tests on standard straining equipment at DSM. This indicates that the doping procedure employed does not have any serious effect on the mechanical properties of the fibre.

In the present set of experiments no attempts were undertaken to remove dissolved oxygen from the polymer. However, all e.p.r. spectra recorded did not reveal any sign of peroxy radicals. Furthermore, the presence of peroxy radicals would imply a reduced decrease of the e.p.r. signal of the nitroxy spin trap. Therefore the absolute absence of dissolved oxygen could only lead to an even larger number of chain scissions, making this process even more important than already concluded on the basis of the nitroxy radical decay data presented below.

RESULTS

Both the oxidized Tinuvin 770 doped fibre as well as the nitroxide II doped fibre showed an e.p.r. spectrum. However, after briefly washing the fibres with dichloromethane there was no e.p.r. signal left on the oxidized Tinuvin 770 doped fibre, whereas the spectrum was retained for the nitroxide II doped fibre. From this

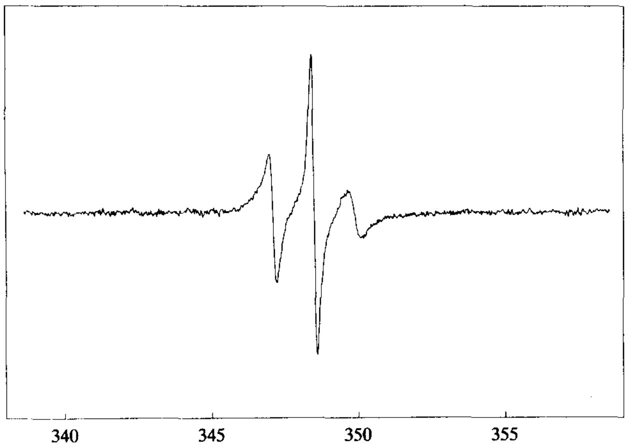


Figure 2 A typical e.p.r. spectrum of the nitroxide II spin label absorbed in Dyneema SK-60 fibres

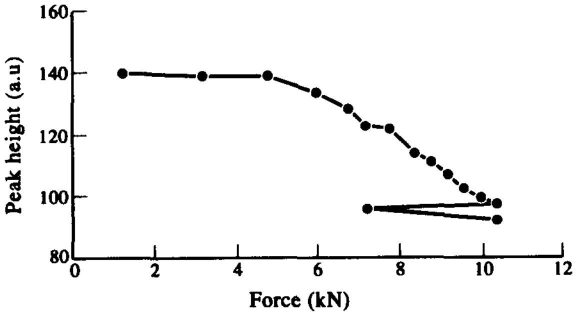


Figure 3 Peak height of the central line of the nitroxide triplet spectrum as a function of the applied force

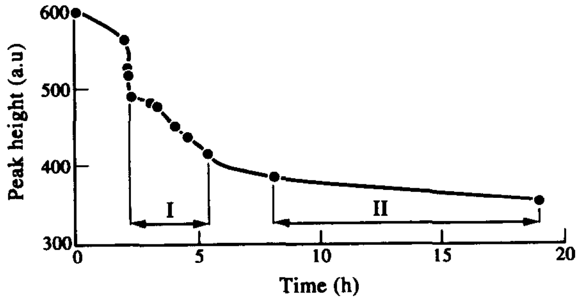


Figure 4 Peak height of the central line of the nitroxide triplet spectrum as a function of time: I, region of constant force; II, region of constant strain

Table 1 Results of creep experiment

Applied force (N)	Time (h)	Peak height, central line
4800		648
6000		642
0		608
6000		642
0		609
6000		625
0		614
6000	0.0	603
8000	2.0	564
9000	2.13	526
9000	2.17	518
9000	2.21	489
9000	2.36	489
9000	3.06	483
9000	3.36	477
9000	4.11	451
9000	4.56	437
9000	5.41	414
8000[a]	8.08	385
6500[b]	19.05	352

[a] As the maximum strain limit of the straining rig had been reached, the force could not be increased again to 9000 N

[b] After leaving the set-up under constant strain overnight, the force had decreased to 6500 N

experiment we concluded that a relatively large nitroxide species like oxidized Tinuvin 770 is unable to diffuse into the PE fibre. Consequently, we continued the experiments making exclusive use the nitroxide II spin label. From these observations we obviously cannot be sure that the nitroxide II spin label has diffused right through to the centre of the filaments. As a result, the number of radicals detected in the experiments (the results of which are presented below) are a lower bound to the total number of chain scissions. This implies that the actual number of chain scissions might be even larger than detected from the experiments presented in this paper, which further emphasizes the importance of chain scission in the current context.

In the first experiment in which stress was actually applied, the force was increased stepwise until 10 400 N. During this experiment an e.p.r. spectrum was observed; *Figure 2* gives a typical example. It may be noted that the e.p.r. signal lineshape cannot be identified with the shape originating from a free NO radical. Apparently there is an interaction between the spin label and the polymer. Furthermore, the lineshape of the first e.p.r. line at $g = 2.0152$ was subject to change during loading, whereas the second line at $g = 2.0070$ did not show any variation in this respect. Therefore determination of the spin trap concentration was based on the peak heights of this second, most intense peak.

In *Figure 3* the intensities (peak heights) are plotted for the loading experiment just described. It is observed that the concentration of nitroxy radicals decreases with increased applied force. At a force of 10 400 N the decrease of the spin label amounts to 30%. When reducing the force to 7200 N the e.p.r. signal intensity remained almost constant. Upon applying the load again to 10 400 N a further decrease of the signal was found, accompanied by breaking of the filaments. The total reduction in the number of nitroxy radical spins during this experiment was calculated as 38%.

The results of the second experiment have been collected in *Table 1* and are depicted in *Figure 4*. From the data in *Table 1* it was inferred that the cycle of applying a force of 6000 N and releasing it to zero has a small effect (~5%) on the nitroxy radical concentration. The reduction of the signal intensity when going from 6000 N load down to zero load at every cycle was attributed to a change in the orientation (geometry effect) of the fibre in the cavity upon loading.

The experiment on this sample was continued by increasing the load to 9000 N. This load was kept constant by manual adjustment for about 5 h. The nitroxy radical concentration decreased by 30% during this time interval. The sample was subsequently left overnight at constant strain. A further reduction of the number of nitroxy radicals was observed. The total drop in nitroxy radicals over the time span of the experiment was >40%.

The part of the experiment in which the load was kept constant over a 5 h period is essentially a creep experiment (region I in *Figure 4*). Because the load was not adjusted overnight the last part of this experiment can be characterized as a constant strain experiment (region II in *Figure 4*). Both types of experiment demonstrated a decrease in nitroxy radical concentration and thus an increase in polymer chain bond scission in the UHMW-PE.

SUMMARY AND CONCLUDING REMARKS

The absolute spin concentration of the nitroxy doped UHMW-PE at zero stress was estimated to be about 1×10^{14} spins per cm sample length, using a reference sample of known spin concentration (weak pitch, $(1.0 \pm 0.1) \times 10^{13}$ spins per cm sample length). The absolute spin concentration was determined by using a double resonator cavity, TE104. A 40% decrease in nitroxy radical concentration then corresponds to 4×10^{13} radicals formed in the PE due to mechanically applied force. Since the cross-section of a 4 mm diameter PE crystal has about 10^{14} polymer chains, the 4 mm diameter rope has at most this number of polymer chains going through its cross-section. Therefore the number of radicals per chain is equal to 0.4 radicals per cm chain length. Thus the level of nitroxy radical decay, which is a measure for strain-induced radicals in the polyethylene, is non-negligible and one simply cannot neglect the possible importance of chain scission in both the final polymer fracture as well as in the mechanism of the creep process. On the other hand, the e.p.r. data by themselves do not exclude that part of the molecular mechanism of creep caused by chain slippage.

In conclusion, we have shown that loading UHMW-PE fibres up to about 50% of their theoretical strength causes bond scission to occur as corroborated from the number of radicals monitored. In addition, a creep test on UHMP-PE fibres also showed an ongoing production of radicals in the polymer. Although precise quantification of the radical concentration is difficult, a first estimate leads to a significant number (of the order of 4×10^{13} spins) compared with the total number of polymer chains (10^{14}) that run through the cross-section of the PE rope employed in the experiments.

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REFERENCES

1 Wang, L.-H., Porter, R. S. and Kanamoto, T. *Polym. Commun.* 1990, **31**, 457
2 Porter, R. S., Kanamoto, T. and Zachariades, A. E. *Polymer* 1993, **35**, 4979
3 Meier, R. J. *Macromolecules* 1993, **26**, 4376
4 Boudreaux, D. S. *J. Polym. Sci., Polym. Phys. Edn* 1973, **11**, 1285
5 Rossignol, J. M., Sequela, R. and Rietsch, F. *Polymer* 1990, **31**, 1449
6 Sweeney, J. and Ward, I. M. *J. Mater. Sci.* 1990, **25**, 697
7 Wong, W. F. and Young, R. J. *J. Mater. Sci.* 1994, **29**, 520
8 Prasad, K. and Grubb, D. T. *J. Polym. Sci., Polym Phys. Edn* 1989, **27**, 381
9 Van Eijk, M. C. P., Leblans, P. J. R., Meier, R. J. and Kip, B. J. *J. Mater. Sci. Lett.* 1990, **9**, 1263
10 Kip, B. J., Van Eijk, M. C. P. and Meier, R. J. *J. Polym. Sci. Part B: Polym. Phys. Edn* 1991, **29**, 99; see also *Chemtracts-Macromol. Chem.* 1991, **2**, 282, condensation by D. Prevorsek
11 Moonen, J. A. H. M., Roovers, W. A. C., Meier, R. J. and Kip, B. J. *J. Polym Sci., Polym. Phys. Edn* 1992, **30**, 361
12 Wong, W. F. and Young, R. J. *J. Mater. Sci.* 1994, **29**, 510
13 Meier, R. J. and Kip, B. J. *Microbeam Anal.* 1994, **3**, 61
14 Bastiaansen, C. W. M. *Thesis*, Eindhoven University of Technology, 1991, pp. 93–94
15 Ohta, Y., Sugiyama, H. and Yasada, H. *J. Polym. Sci., Polym. Phys. Edn* 1994, **32**, 261
16 Volodarsky, L. B., Kutikova, G. A., Sagdeev, R. Z. and Molin, Yu. N. *Tetrahedron Lett.* 1968, **9**, 1065