Melting behaviour of gelspun/drawn polyolefins

MELTING BEHAVIOUR OF GELSPUN/DRAWN POLYOLEFINS

C.W.M. Bastiaansen[1] and P.J. Lemstra[2*]

1) DSM Research and Patents, P.O. Box 18, 6160 MD Geleen, The Netherlands
2) Eindhoven University of Technology, Department of Polymer Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Abstract: The melting behaviour of gelspun/drawn UHMW-PE and UHMW-PP fibres was investigated. Unconstrained UHMW-PE and UHMW-PP fibres melt at 142°C and 170°C, respectively. Upon constraining, by holding the fibres at a fixed length or by embedding the fibres in a matrix, an increase in the melting temperature of both fibres is observed. In the case of UHMW-PE fibres a solid-solid phase transition in polyethylene at 155°C from the orthorombic to the hexagonal crystal structure occurs. Above 155°C, the fibres can not sustain any load. This solid-solid phase transition at 155°C sets an upper limit to both the maximum curing and continuous use temperature of PE-fibre reinforced composites. In gelspun/drawn UHMW-PP, such a detrimental solid-solid phase transition is absent, and therefore the increase in melting temperature can be utilized effectively. For example, heating of UHMW-PP fibres for 30 minutes at 200°C does hardly affect the room temperature Young's modulus and tensile strength if the fibre is constrained during heating.

INTRODUCTION

In the past decade a large effort has been made to bridge the gap between the strength and stiffness of polyolefins crystallized from an isotropic melt or solution and the theoretical strength and stiffness of linear, infinitely long, chain-extended polyolefin structures (Ref. 1-3). The prime objective of these efforts was to exploit the intrinsic high strength and modulus of polyolefines by generating chain-extension/alignment. Recently processes have been developed for the production of high-strength and high-modulus polyolefin fibres such as melt-spinning/drawing and solution (gel)-spinning/drawing (Ref. 4,5). In the gelspinning process a semi-dilute solution of an Ultra-High-Molecular-Weight polyolefin is spun and after quenching/crystallization drawn in

the solid state to extend and align the macromolecules. UHMW-PE fibres are currently produced with a Young's modulus and tensile strength of respectively 100-150 GPa and 3-4 GPa. In the case of UHMW-PP the maximum achievable Young's modulus and tensile strength found were respectively 40 GPa and 1.5 GPa (Ref. 6,7).
The melting behaviour of drawn polyolefin fibres is rather complex (Ref. 8). Various melting endotherms can be observed which are difficult to interpret (Ref. 9). Previous studies on the melting behaviour of gelspun/drawn polyethylene indicated that the various melting endotherms originated from the sample preparation methods used (Ref. 12,13). An additional comparative study was performed on the melting behaviour of both UHMW-PE and UHMW-PP gelspun/drawn structures. Special attention is devoted in this study to the influence of constraining on the melting behaviour of these fibres in view of their possible application in composites.

EXPERIMENTAL

UHMW-PE fibres were supplied by Dyneema Vof, a joint venture of DSM and Toyobo. The multifilament fibre possessed a Young's modulus of 110 GPa and a tensile strength of 3.2 GPa.
The UHMW-PP grade used in this study ($M_w \sim 2 * 10^3$ kg mol^{-1}) was supplied by Himont (USA). UHMW-PP fibres were spun/drawn possessing a Young's modulus of 35 GPa and a tensile strength of 1.5 GPa.
The Young's modulus and tensile strength of the fibres at room temperature were measured using a Zwick tensile tester at a strain rate of 0.01 s^{-1}. Corona discharge was employed to improve adhesion of the PE and PP fibres to the epoxy matrix.
Shrinkage measurements were performed in an thermostatically controlled oven. A standard heating rate of 5°C/min was used. In these measurements the fibres were allowed to shrink freely, and the change in length of the fibres was measured.
Retractive force measurements were performed in an oven equipped with a load cell. During the measurements the fibres were held at a fixed length, and a standard heating rate of 5°C/min was used.

DSC-curves were recorded on a Perkin-Elmer DSC-2. A standard heating rate of 5°C/min was used. To investigate the influence of constraining on the melting behaviour of fibres, different sample preparation methods were used:

a. Unconstrained melting
   In unconstrained DSC-experiments, chopped fibres, length 1-2 mm, were used, and a few droplets of silicon-oil were added to the DSC-pans to improve heat contact and to allow friction-free shrinkage upon melting.

b. Constrained melting
   Corona-treated fibres were embedded in epoxy and/or polyester resins to constrain the fibres. Prior to the DSC-measurements the epoxy resin was cured for 12 hours at 120°C. In the case of UHMW-PE a few DSC-experiments were performed on chain-extended fibres wound tightly around a thin wire to which the ends of the fibre were knotted.

Annealing experiments on UHMW-PP fibres were performed in a thermostatically controlled silicon-oil bath. During the annealing experiments the fibres were held at a fixed length. After annealing, the fibres were washed with acetone to remove residual traces of silicon-oil. High temperature WAXS patterns were recorded of fibres held at a fixed length using a Statton camera. Ni-filtered Cu-Kα radiation was used and generated at 40 kV/25 mA. The sample to film distance was 40 mm.

RESULTS AND DISCUSSION

A. UNCONSTRAINED MELTING OF PE AND PP FIBRES

In Figure 1a and 1b shrinkage measurements are shown of respectively UHMW-PE and UHMW-PP fibres. In these measurements the shrinkage is defined as the relative change in sample length, $\Delta l/l_0 * 100\%$, l_0 being the initial sample length at room temperature. As can be inferred from these figures, the UHMW-PE and UHMW-PP fibres melt and shrink approximately 96% in a narrow temperature range around respectively 142°C and 170°C. The high values for the total shrinkage indicate that the UHMW-PE and UHMW-PP fibres indeed consist of highly extended macromolecules (Ref. 9) which recoil upon melting.

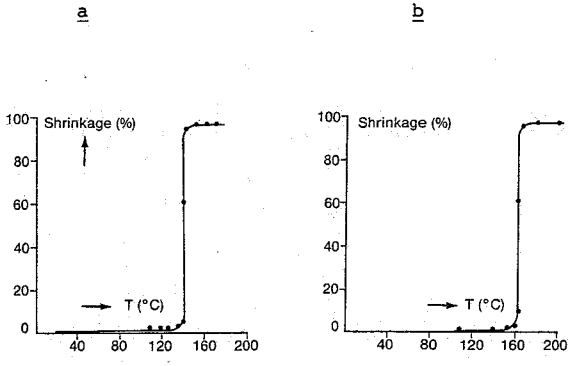

Figure 1. Shrinkage measurements of:
a. UHMW-PE fibres
b. UHMW-PP fibres

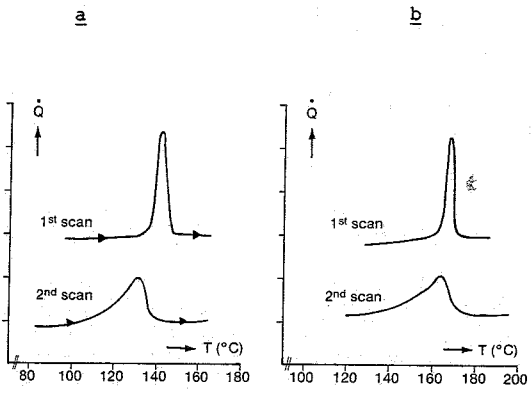

Figure 2. DSC experiments of unconstrained fibres
a. UHMW-PE fibres
b. UHMW-PP fibres

In Figure 2a and 2b DSC-measurements are shown of chopped UHMW-PE and UHMW-PP fibres suspended in silicon-oil. In the first scan single melting endotherms are observed at respectively 142°C and 171°C, (peak values), which is close to the melting temperatures estimated from the shrinkage measurements. The melting temperature, heat of fusion and crystallinity of both the UHMW-PE and UHMW-PP fibres are listed in Table 1.

	T_{m_1} (°C)	ΔH_1 (J/g)	cryst. (%)	T_{m_2} (°C)	ΔH_2 (J/g)	cryst. (%)
PE	142	239	81	133	122	42
PP	171	122	73	163	65	38

Table 1. Melting temperature, heat of fusion and crystallinity of unconstrained UHMW-PE and UHMW-PP fibres

The crystallinity was calculated assuming a heat of fusion of crystalline polyethylene and polypropylene of respectively 293 kJ/kg and 165 kJ/kg. Upon quenching and re-scanning, again single melting endotherms are observed (Figures 2a and 2b). The melting temperature, heat of fusion and crystallinity of both fibres have decreased indicating that the original chain-extended morphology of the fibres is completely lost after the first scan in the DSC experiments.

B. CONSTRAINED MELTING OF UHMW-PE FIBRES

In Figure 3 retractive force measurements of UHMW-PE fibres held at a fixed length are shown. As can be inferred from this figure, stress builds up in the fibre during heating to a maximum of approximately 50 MPa and the fibre fractures at 152°C. The temperature at which the fibres fracture is relatively high (compare with figure 1a and 2a), which indicates that the constraining during the retractive force measurements influences the melting behaviour of the UHMW-PE fibres. In a previous study (Ref. 9) on the melting behaviour of UHMW-PE fibres, several melting endotherms could be observed during heating in the DSC, Figure 4.

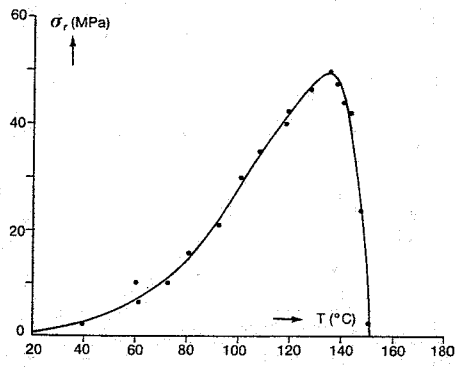

Figure 3. Retractive force measurements of UHMW-PE fibres

In these experiments, UHMW-PE fibres were wound tightly around a wire with knotted ends. However, if constrained properly, only one endotherm is observed (Ref. 12,13). Figure 5 shows the melting behaviour of UHMW-PE fibres embedded in an epoxy matrix. Compared to figure 2a, the melting endotherm shifts to 155°C. Upong melting and rescanning, several melting endotherms are observed indicative of some memory of the original chain-extended morphology of the UHMW-PE fibres.

The endotherm at 155°C in the first scan of UHMW-PE fibres embedded in a matrix material is commonly associated with a solid-solid phase transition from an orthorombic to a hexagonal crystal structure (Ref. 8,9,11,12). Characteristic for this hexagonal or rotator phase of polyethylene is the high mobility of macromolecules within the crystal lattice (Ref. 10). In retractive force measurements this increase in mobility allows macromolecules to slip past each other and recoil, thus causing the failure of the fibres.

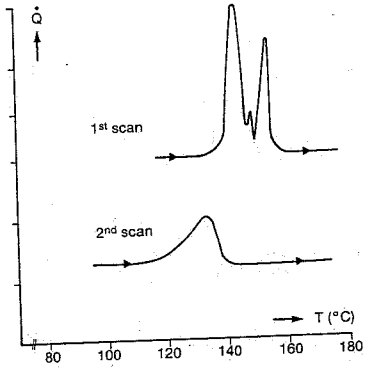

Figure 4. DSC-experiments of UHMW-PE fibres wound around a thin wire

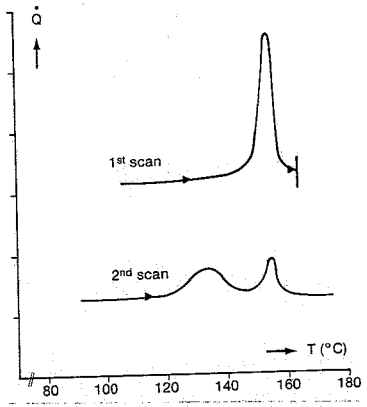

Figure 5. DSC-experiments of constrained UHMW-PE fibres

The hexagonal phase observed in embedded UHMW-PE fibres at temperatures above 155°C should yield a melting endotherm upon heating to higher temperatures. These melting endotherms are indeed experimentally observed, but a large scatter in peak temperatures depending on the embedding matrix causes problems to define a proper melting temperature. In Figure 6 shrinkage and retractive force measurements on an unidirectional UHMW-PE reinforced composite material are shown (matrix material: epoxy resin, fibre to epoxy ratio = 1:1). From this figure it is clear that during both fabrication and practical use the temperature of the composite material should never exceed 155°C since this will result in fracture, shrinkage and loss in Young's modulus and tensile strength of the composite.

C. CONSTRAINED MELTING OF UHMW-PP FIBRES

In Figure 7 retractive force measurements are shown of UHMW-PP fibres. These measurements show that UHMW-PP fibres, if held at a fixed length, fracture at temperatures well above 200°C.

In DSC-experiments on UHMW-PP fibres embedded in a suitable matrix material, the first significant melting endotherm appears at approximately 220°C. These experiments show that there is a substantial gap between the melting temperature of UHMW-PP fibres which are allowed to shrink freely and the melting temperature of UHMW-PP fibres held at a fixed length (compare figure 8 and figure 2b). After quenching and re-scanning a single melting endotherm is observed indicating that the UHMW-PP melt was completely randomized in the first scan after heating to 260°C.

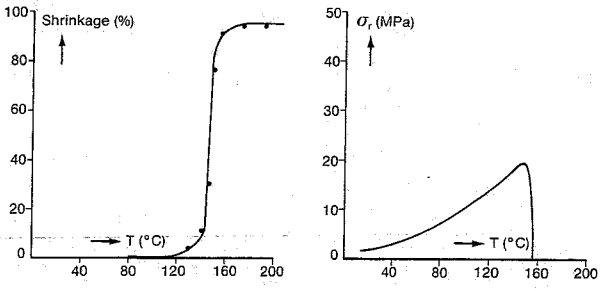

Figure 6. Shrinkage and retractive force measurements of an unidirectional UHMW-PE fibre reinforced composite

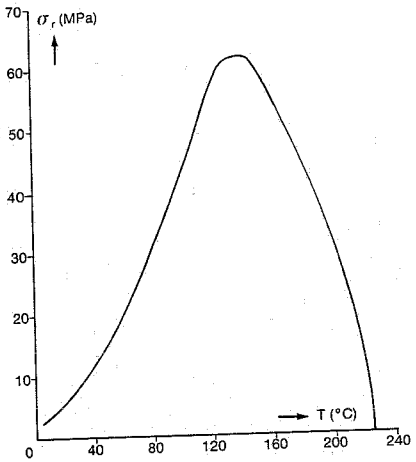

Figure 7. Retractive force measurements of UHMW-PP fibres

In Figure 9 high temperature WAXS patterns are shown of UHMW-PP fibres. As can be seen in this figure the reflections are sharp indicating that there is a high level of molecular orientation in the fibres. If the UHMW-PP fibres are held at a fixed length during the WAXS experiments a decrease in intensity of the reflections is not observed even after heating for 2 hours at 210°C.

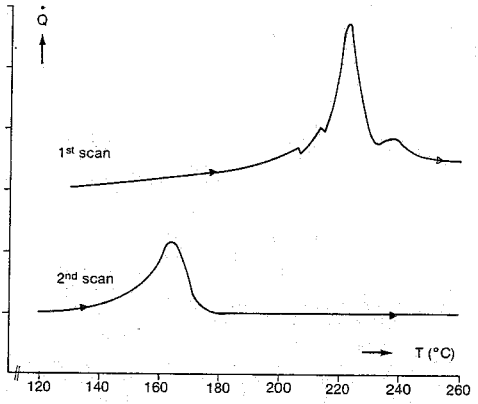

Figure 8. DSC-experiments of constrained UHMW-PP fibres

a b

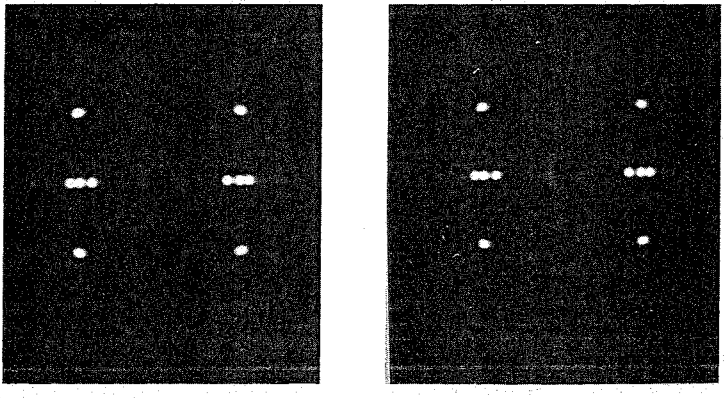

Figure 9. High temperature WAXS patterns of contrained UHMW-PP fibres: a) 180°C; b) 210°C

T (°C)	t (min)	$E_{23°C}$ (GPa)	$\sigma t_{23°C}$ (GPa)
-	-	35	1.3
180	10	33-36	1.2-1.4
180	30	34-36	1.1-1.3
200	10	35-37	1.3-1.4
200	30	34-37	1.3-1.4

Table 2. Young's modulus and tensile strength at room temperature of constrained UHMW-PP fibres as a function of annealing time and temperature

In Table 2 the Young's modulus and tensile strength at room temperature of UHMW-PP fibres are listed as a function of annealing-time and temperature. The UHMW-PP fibres were held at a fixed length during these experiments. As can be seen in Table 2, the UHMW-PP fibres retain their Young's modulus and tensile strength even after heating for 30 minutes at 200°C. These experimental observations show that UHMW-PP fibre composites can be fabricated and cured at temperatures up to at least 200°C, without any loss in properties, if the fibre is held at a fixed length during processing/curing.

CONCLUSIONS

The melting behaviour of gelspun/drawn UHMW-PE and UHMW-PP fibres can be influenced strongly by imposing constraints. In the case of UHMW-PE fibres, the maximum continuous use temperature is limited due to the orthorombic-hexagonal solid-solid state transition at 155°C. Above this temperature the chain mobility in the hexagonal phase causes macroscopic failure of the fibre upon annealing and/or stress. In the case of UHMW-PP fibres, effective constraining can be utilized to increase the melting temperature, and consequently the curing and use temperature range is increased significantly.

REFERENCES

1. Capaccio, G., Crompton, T.A., Ward, I.M., Polymer, 17 664 (1976)
2. Zwijnenburg, A., Pennings, A.J., Colloid and Polymer Science, 254, 868 (1976)
3. Southern, J.M., Porter, R.S., J. Appl. Pol. Sci., 14, 2305 (1970)
4. Capaccio, G., Gibson, A.G., Ward, I.M., Ultra-High Modulus Polymers (Eds. A. Ciferri and I.M. Ward), Appl. Sci. Pub., London, Chpt. 1.
5. Lemstra, P.J., Kirschbaum, R., Ohta, T., Yasuda, H., Developments in oriented polymers-2, Editor I.M. Ward, Elsevier Applied Science, 1987
6. Matsuo, M. et al., Polymer Journal, 18, 759 (1986)
7. Peguy, A., R. st-John Manly Polymer Com., 25, 39 (1984)
8. Clements, J., Ward, I.M., Polymer, 23, 935 (1982)
9. Smook, J., Ph.. thesis, University of Groningen, The Netherlands, 1984
10. Bassett, P.C., Liquid Crystalline Polyethylene in Polyethylenes 1933-83, Conference issue, Ed. The Plastics and Rubber Institute, London, 1983
11. Van Aerle, N., Lemstra, P.J., to be published
12. Lemstra, P.J., Kirschbaum, R., Polymer Special issue Specialty Polymers, 26, 1372 (1985)
13. Kanamoto, T., Hoshiba, T., Yoshimara, T., Tanaka, K., Takeda, M., Reports on Progress in Polymer Physics in Japan, 28, 227 (1985)