

Melting Behavior of Ultra-High Modulus and Molecular Weight Polyethylene (UHMWPE) Fibers

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SYNOPSIS

Superheating and double-melting endotherms are the characteristic melting behaviors of gel-spun ultra-high modulus and molecular weight polyethylene (UHMWPE) fibers in differential thermal analysis (DTA). A mostly orthorhombic structure with very little amorphous content is indicated by wide angle x-ray scattering (WAXS) data. The melting temperatures are elevated and believed to result from superheating and incomplete chain relaxation in the highly oriented and crystalline structure. The melting behavior of the fibers is shown to be strongly affected by changes in polymorphic transformations and in intercrystalline disordered domains. Compression in the direction perpendicular to fiber axis causes significant increases in the 110 and 200 dimensions of the orthorhombic structure. Such lateral compression increases monoclinic forms and perhaps amorphous content, and decreases the degree of transformation to hexagonal phase. Superheating, which is related to the intercrystalline stress, can be reduced by the presence of interacting solvents such as trichlorobenzene. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Crystalline structures of polymers are highly influenced by their molecular weights and processing methods. Melt processing of high-density polyethylene produces a partially crystalline structure with folded-chain crystallites imbedded in a less ordered polymer matrix.¹ When the molecular weight of the polymer is too high for melt processing, other spinning and drawing processing methods must be employed. The high molecular weight coupled with novel processes can produce polymer structures and properties that are significantly different from those of the melt-processed solids. Ultra-high modulus and molecular weight polyethylene (UHMWPE) is one such example. Gel-spun UHMWPE fibers have been reported to have a highly oriented and extended-chain crystalline structure with limited disordered domains in the interfibrillar and intercrystalline regions.^{2,3} The fibrillated fiber structure consists of macrofibrils and microfibrils.⁴ In the microfibrils, the long crystal blocks are connected by short dis-

ordered domains.⁵ These disordered domains are thought to contain physical entanglements, taut tie molecules (TTM), chain ends, and other imperfections.

The unique crystalline structure of UHMWPE fibers can be illustrated by their melting behavior. The equilibrium melting temperature of melt-crystallized polyethylene is 141.6°C.¹ Melting of free-grown⁶ and gel-spun⁷ UHMWPE fibers, on the other hand, has shown three melting peaks at 141°, 150.5°, and 159.5°C. The 141°C endotherm was thought to result from melting of the unconstrained fibrillar crystals and lamellar crystals overgrown from the shish-kebab fibrils. Upon being heated to temperatures between 149° and 152°C, the orthorhombic crystalline structure melts and goes through solid-state phase transformation to hexagonal crystals that melt at 159.5°C.⁷⁻⁹

Thermal analysis is an effective way to depict the processing-related structural features in polymers. In the case of highly crystalline and oriented polymers, such as UHMWPE fibers, the detection of thermal transitions can be significantly affected by sample preparation and experimental conditions. This article presents data to illustrate how the melting behavior of the gel-spun UHMWPE fibers can

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be altered if lateral compression is employed to enhance sample packing and heat transfer. In addition, the effects of free annealing and solvent interaction on thermal behavior are also included.

EXPERIMENTAL

The ultra-high molecular weight and modulus polyethylene (UHMWPE) fibers studied were Spectra 1000 filaments from Allied Signal, Inc. Differential thermal analysis (DTA) was performed on a Mettler TA 2000M system. Unless otherwise specified, all DTA scans of the UHMWPE fibers were performed in nitrogen from 30°C to 200°C at a 5°C/m heating rate. Al₂O₃ was used as the reference. The conversion of peak area to heat (J/g) was calibrated using indium as a standard at the corresponding heating rates. About 3.5 to 4 mg of fibers were wound into small loops and placed at the bottom of a sample pan. The reported values for melting temperature (T_m) and heat of fusion (H_f) were averages of triplicated DTA runs.

The melt from the first DTA was cooled to 30°C before another DTA scan was run on the same sample. The effects of heating rates were studied by

varying the rates from 5°C/min to 29.9°C/min. When pressure was applied, the fiber loops were compressed laterally into a pellet at 13,000 psi for the designated lengths of time. Free annealing of fibers was done in the DTA by heating the fibers at 5°C/min to the selected annealing temperature. The specimen was held at the annealing temperature for 10 min before resumption heating to 200°C. The effects of solvent interaction on the melting behavior of UHMWPE fibers were evaluated with reagent grade trichlorobenzene. The solvent was delivered over the fibers in the DTA sample pan using a microsyringe. The DTA was run in the same manner as described above.

Wide angle x-ray scattering measurements (WAXS) were performed on randomly oriented UHMWPE filaments according to a previously reported method.¹⁰ A DIAN-XRD 800 diffractometer, which is equipped with a graphite monochromator to give 50 kV Cu K α radiation at 15 mA, was used. WAXS scans were performed from 10° to 50° at a rate of 1.6°/min. The crystallite dimensions and interplanar spacing (d) were calculated following methods described before.¹¹

RESULTS AND DISCUSSION

Melting of gel-spun UHMWPE fibers in DTA begins at around 128°C and appears as a doublet (Fig. 1). The low-temperature (LT_m) endotherm observed at about 150°C is the main melting peak. It is followed by a smaller peak at about 160°C, or the high temperature (HT_m) endotherm. The total heat of melting is 247.3 J/g. Following cooling to 30°C, the second DTA thermogram shows a melting singlet at nearly 141°C with a reduced endotherm of 161.0 J/g.

The equilibrium melting temperature of unconstrained fibrillar polyethylene crystals is 141.6°C.¹² Absence of this melting endotherm from the DTA scan of the original UHMWPE fibers suggests a fibrillar structure with interfibrillar stress and constraint. The much elevated LT_m (150°C) is believed to result from superheating of the highly crystalline matrix containing large and extended-chain crystals. The reported solid-state orthorhombic-hexagonal phase transformation occurs following partial melting at this temperature range. The HT_m endotherm is from melting of the hexagonal crystalline structure and possibly from randomization of chains to the gauche state in the melt.⁶

The second DTA scan shows a melting endotherm that is close to the equilibrium melting temperature

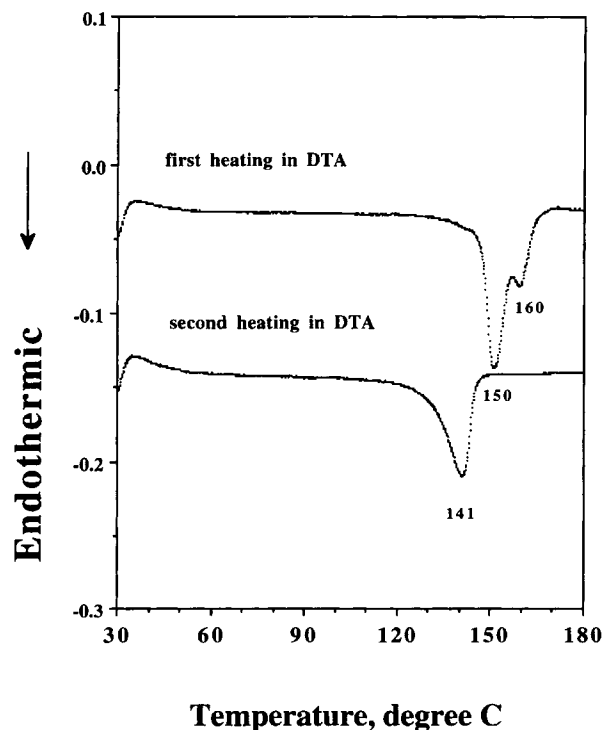


Figure 1 DTA thermograms of UHMWPE fibers during two consecutive runs.

of the polyethylene crystals. The singlet indicates that either an unconstrained fibrillar or a lamellar crystalline structure was formed from cooling the first DTA melt. The solid-state transformation and the subsequent melting around 158° to 160°C during first DTA heating are characteristics of the original fiber structure. Such transformation during heating is a result of the gel-spinning and drawing processes and is not observed from the second DTA scan.

DTA Heating Rates

The peak temperatures of both the LT_m and HT_m endotherms were elevated and the heat of fusion was lowered slightly with increasing DTA heating rates (Fig. 2). Extrapolation to the 0°C/m heating rate gives the temperature and heat of fusion values at which the rates of heat supply and the heat transfer from crystal surface to interior are equal. If a heat of fusion value of 293 J/g is used for the equilibrium crystals of polyethylene,¹² the extrapolated heat of fusion at 0°C/m heating rate, or 251.8 J/g, corresponds to 86% crystallinity.

In theory, the melting temperature extrapolated to the zero heating rate should be free of the effects of superheating. However, the extrapolated melting

temperature (148.8°C) is still higher than the melting temperature of equilibrium crystals (141.6°C). This observation suggests that superheating only partially explains the elevated melting temperature.

Melting of unstrained UHMWPE fibers is said to be initiated at the defect-crystal interfaces.⁷ Considering the constrained fibrillar structure, one possible source of additional elevation of melting temperature is the limited chain relaxation near these interfaces. The relaxation-limiting factors of UHMWPE fibers in the intercrystalline and interfibrillar regions include the entangled chains and the TTM among crystals, the constraint on the rotational isomeric states, or the reduced randomization of chains into the gauche conformation, and the high viscosity of the molten chains. The elevation of the melting temperature beyond that which can be explained by superheating suggests that chain relaxation in the disordered domains may not be complete in the first melting cycle. Persistence of melt orientation was observed under a polarizing microscope. Therefore, the crystalline structure from cooling the first melt is believed to be fibrillar due to incomplete chain relaxation. The single endotherm during second DTA is from melting of unstrained fibrillar crystals.

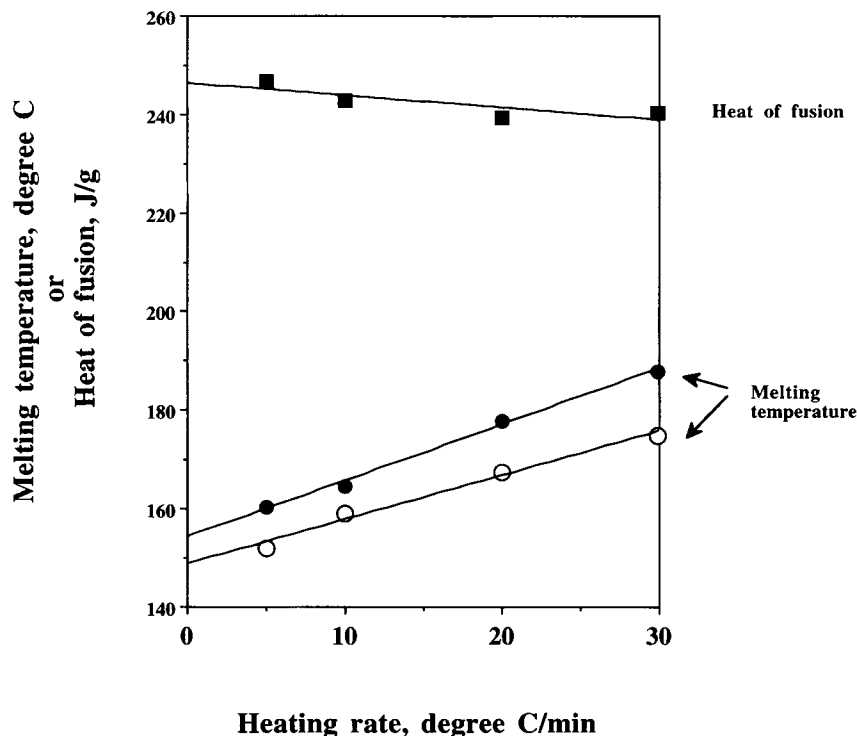


Figure 2 Effects of DTA heating rate on the melting temperatures and heat of fusion of UHMWPE fibers: ○: LT_m ; ●: HT_m ; ■: H_f .

Lateral Compression

The DTA thermograms of UHMWPE fibers compressed for varying lengths of time under 13,000 psi are shown in Figure 3. Although neither the LT_m nor HT_m temperature was affected, the HT_m melting endotherm was reduced incrementally with increasing compression time. The melting enthalpy was lowered from 247 to 232 J/g upon 1-min compression and was further reduced to 228.4 J/g after 1 additional min. The melting enthalpy was not affected by further compression. After 10 min of compression, the HT_m melting peak became nearly indistinguishable from the main melting (LT_m) peak. The disappearance of the HT_m peak with longer compression times indicates significant reduction or elimination of crystal transformation to the hexagonal phase. Widening of peak width also suggests size reduction of original crystals.

WAXS of UHMWPE fibers show three distinctly identified peaks at 2θ s of 19.70° , 21.84° , and 24.18° (Fig. 4). A shoulder at 23.22° and several small peaks at 30.48° , 36.66° , 41.2° and 44.34° are also observed. The amorphous halo which ranges from 15° to 25° is very weak. The WAXS data indicate

a mostly orthorhombic structure with very little amorphous content in the UHMWPE fibers. With increasing lengths of compression perpendicular to the fiber axis, the three main peaks increase in their intensities, with largest increase in the 19.70° peak. New peaks at 23.22° , 25.04° , and 35.09° are also detected.

After 1 min of compression, the 19.70° peak nearly doubled from 11.27 to 20.37 nm (Table I). The calculated hkl reflections of the monoclinic structure are at 2θ s of 19.5° and 35.4° .¹³ Because the amorphous background also centers around 20° , peak enlargement at 19.70° could be due to increases in amorphous content as well as monoclinic form. Detection of the new peak at 35.09° indicates the existence of the monoclinic crystalline form. This observation is consistent with other reports that indicate that the orthorhombic structure of polyethylene is transformed into the monoclinic structure when stress is applied in the direction perpendicular to the molecular axis.¹⁴⁻¹⁷

Longer compression (10 min) causes slight increases in the 110 and 200 dimensions of the orthorhombic structure. However, such crystal enlargement in the orthorhombic structure do not ap-

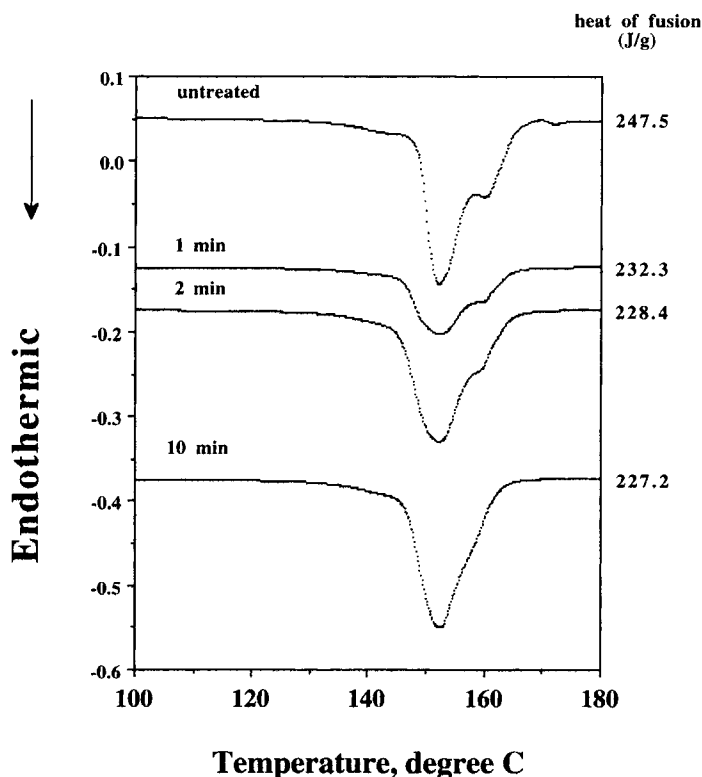


Figure 3 DTA thermograms of UHMWPE fibers compressed at various lengths of time.

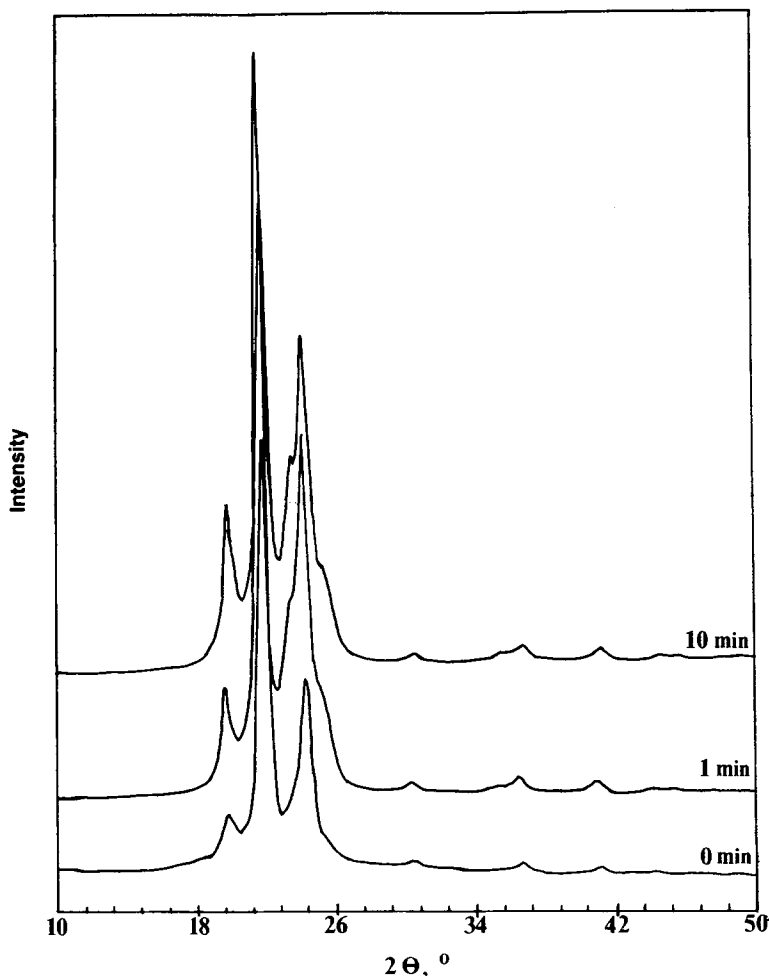


Figure 4 WAXS patterns of UHMWPE fibers compressed at various lengths of time.

pear to affect the intensity nor the position of the LT_m peak. In fact, the increase in monoclinic forms and perhaps amorphous content appear to be sufficient to prevent the transformation from orthorhombic to hexagonal phase.

Annealing

The effects of annealing on the melting behavior of UHMWPE fibers are shown in Figure 4. The fibers were annealed for 10 min at 120, 140, 144, 150, and 155°C. Annealing at 120°C did not affect the melting behavior as expected because this is below the pre-melting temperature (128°C). Annealing at 140 and 144°C produced small endotherms of 38.8 and 38.1 J/g, respectively, near the annealing temperatures. The HT_m endotherms remain at the same temperature, but become more distinctly separated by annealing. It appears that prolonged annealing be-

tween 140 and 144°C, i.e., at a temperature just above the equilibrium melting temperature, allows relaxation of strained inter-crystalline chains.

Annealing at 150°C causes complete separation of the double endotherms. An endotherm of 176.6 J/g at 152.8°C was detected during annealing. Another one of 31.1 J/g was detected at 160°C after resuming the DTA heating. Heating at 150°C for an extended period allows for the same melting and solid-state crystalline transformation that was observed previously at around 151°C. Both the total heat of melting and the peak height from melting the hexagonal crystalline phase decreased with increasing annealing temperatures from 140° to 150°C. The reduced transformation to the hexagonal phase on fibers annealed at the 140° to 150°C temperature range suggests more thorough melting at crystallite surfaces without the transformed recrystallization.

Table I. Wide Angle X-Ray Scattering (WAXS) or UHMWPE Fibers

	Bragg Angle (2θ), Degree	hkl		Crystallite Size, nm	d Spacing, nm
		Monoclinic	Orthorhombic		
Untreated	19.70	010		11.27	0.451
	21.84		110	20.45	0.407
	24.18		200	14.63	0.368
Compressed for 1 min	19.75	010		20.37	0.455
	21.68		110	20.44	0.410
	24.02		200	15.45	0.370
	23.22	200		*	*
	25.04	210		*	*
	25.04	210		*	*
Compressed for 10 min	19.75	010		20.37	0.455
	21.68		110	24.09	0.410
	24.02		200	17.83	0.370
	23.22	200		12.37	0.383
	25.04	210		9.63	0.356

* Observed, but too small to be calculated.

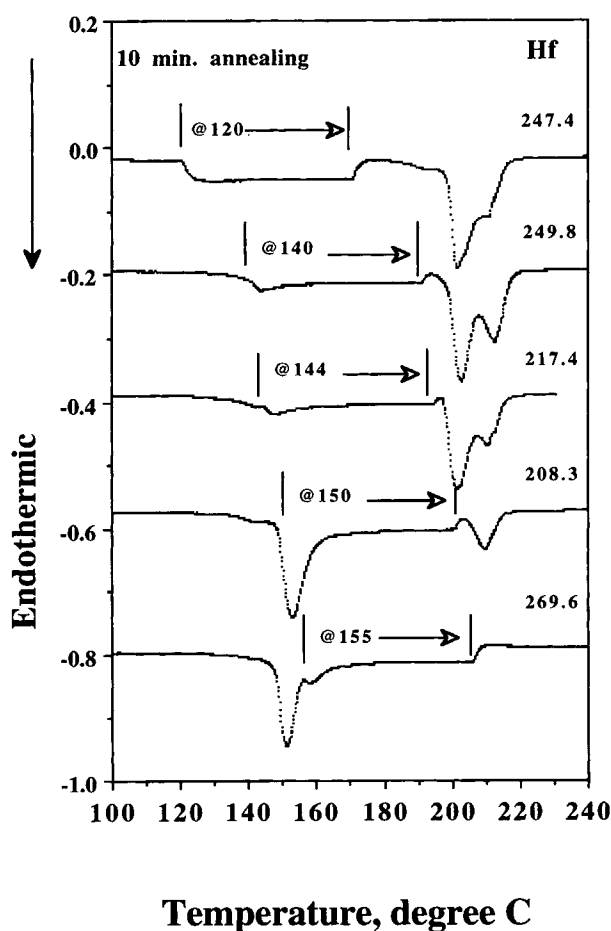


Figure 5 DTA thermograms of UHMWPE fibers annealed during heating.

Following the annealing runs, the specimens were cooled to 30°C and rerun under the same DTA conditions. All fibers have similar melting temperatures near 141°C. The heat of fusion values were lowered to about 162 J/g for those annealed at 144°C and 150°C. The reduced heat of fusion suggests that interfibrillar and intercrystalline stress is reduced by annealing at temperatures between the melting temperatures of interfibrillar (~ 141°C) and orthorhombic crystals (~ 151°C). Previously, annealing at temperatures between 149°C and 152°C has been reported to increase the relaxation of the TTM¹⁸ and lowers the tensile modulus without changing tensile strength.¹⁹

Solvent Effects

DTA of the UHMWPE fibers was run with 59.1% (wt) trichlorobenzene (TCB) added. Figure 6 shows the first and second heating thermograms of UHMWPE with TCB. A shoulder at 128°C and two distinct melting peaks at 141.2°C and 158°C were observed. The existence of small crystals is indicated by the shoulder. Superheating was not observed, but the solid-state phase transformation remained. Because TCB is a solvent for polyethylene, it can increase chain mobility in the intercrystalline regions in the fibers. The interfibrillar or intercrystalline stress responsible for superheating was apparently eliminated by the solvent-induced chain mobility. The second DTA thermogram was similar to the

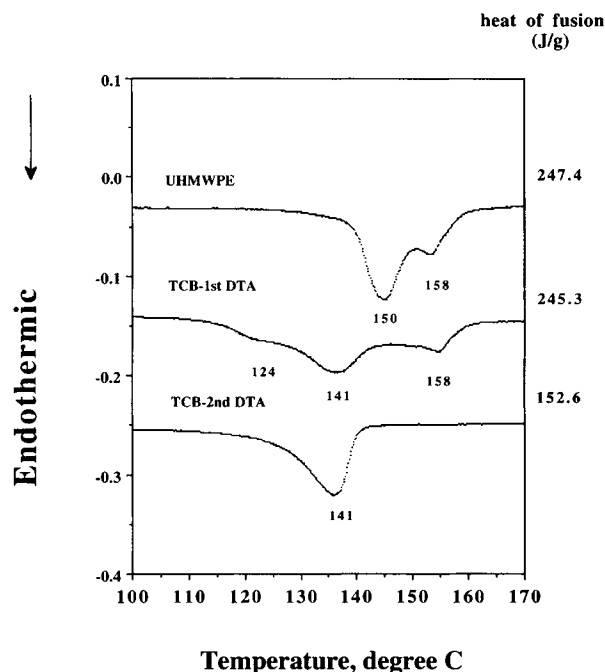


Figure 6 DTA thermograms of UHMWPE fibers with 59.1% trichlorobenzene (TCB) added.

second DTA of the fibers without TCB. That melting of the orthorhombic crystalline structure occurs without superheating and that melting enthalpy remains the same indicate that the solvent does not interfere with the crystalline domains in the fibers.

SUMMARY

The LT_m peak at 151°C and the HT_m peak at 160°C are characteristics of the unique structure of the gel-spun UHMWPE fibers. The melting enthalpy extrapolated at $0^\circ\text{C}/\text{m}$ heating rate, or 251.8 J/g , corresponds to about 86% crystallinity. Superheating and incomplete relaxation of the chains in the molten state are evident during the first melting cycle in DTA. Superheating becomes more pronounced with increasing heating rates while intercrystalline chain relaxation decreases. The less complete relaxation appears to facilitate orthorhombic-hexagonal phase transformation during DTA heating.

Results of this study show that changes in the melting behavior of the gel-spun UHMWPE fibers can be effective indicators of structural changes in the crystalline phases as well as in the intercrystalline areas. Lateral compression increases the crys-

talline dimensions of the orthorhombic structure, but diminishes orthorhombic-hexagonal transformation. Reduction of such phase transformation during heating is due to the increased monoclinic phase and perhaps amorphous content of the fibers. Annealing near the equilibrium melting temperature of polyethylene ($140\text{--}144^\circ\text{C}$) helps to identify the melting of the unconstrained fibrillar or lamellar crystals in the fiber that was not observed under normal DTA heating conditions. Annealing at temperatures between the melting temperatures of unstrained fibrillar crystals ($\sim 141^\circ\text{C}$) and orthorhombic crystals ($\sim 151^\circ\text{C}$) reduces interfibrillar and intercrystalline stress.

Superheating of UHMWPE fibers in DTA is not observed with the addition of trichlorobenzene. This interactive solvent promotes intercrystalline chain mobility and reduces interfibrillar and intercrystalline stress, thus preventing superheating. The solvent also appears not to affect the crystalline structure or linkages responsible for solid-state transformation. The use of an interacting solvent, such as TCB, in DTA may be useful for discerning the interfibrillar and intercrystalline stress in UHMWPE fibers.

REFERENCES

1. A. Peterlin, *Polym. Eng. Sci.*, **18**(6), 466 (1978).
2. A. E. Zachariades and T. Kanamoto, *High Modulus Polymers with Stiff and Flexible Chains*, Zachariades and Porter, Eds., Marcel Dekker, Inc., New York, 1987.
3. D. J. Dijkstra and A. J. Pennings, *Polym. Bull.*, **19**, 73 (1988).
4. A. J. Smook and A. J. Pennings, *Colloid Polym. Sci.*, **262**, 712 (1984).
5. A. Zwijnenburg, P. F. van Hutten, A. J. Pennings, and H. D. Chanzy, *Colloid Polym. Sci.*, **256**, 729 (1978).
6. A. J. Pennings and A. Zwijnenburg, *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 1011 (1979).
7. W. Hoogsteen, G. ten Brinke, and A. J. Pennings, *Colloid Polym. Sci.*, **266**, 1003 (1988).
8. G. Ewen, E. W. Fischer, W. Piesczek, G. Strobl, *J. Chem. Phys.*, **61**, 5265 (1988).
9. D. H. Bonsor and D. Bloor, *J. Mater. Sci.*, **12**, 1552 (1977).
10. D. A. Timm and Y.-L. Hsieh, *J. Polym. Sci., Polym. Phys. Ed.*, **31**, 1873 (1993).
11. Y.-L. Hsieh and S. Mo, *J. Appl. Polym. Sci.*, **33**, 1479 (1987).

12. B. Wunderlich and G. Czornyj, *Macromolecules*, **10**, 906 (1977).
13. C.-P. Lafrance, M. Pezolet, and R. E. Prud'homme, *Macromolecules*, **24**, 4948 (1991).
14. H. Kiho, A. Peterlin, and P. H. Geil, *J. Appl. Phys.*, **35**, 1599 (1964).
15. M. Bevis and E. B. Crellin, *Polymer*, **12**, 666 (1971).
16. T. Yemni and R. L. McCullough, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 1385 (1973).
17. Y. Takahashi, T. Ishida, and M. Furusaka, *J. Polym. Sci., Polym. Phys. Ed.*, **26**, 2267 (1988).
18. D. J. Dijkstra and A. J. Pennings, *Polym. Bull.*, **17**, 507 (1987).
19. D. J. Dijkstra and A. J. Pennings, *Polym. Bull.*, **19**, 481 (1988).

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