

Processing of Ultrahigh Molecular Weight Polyethylene

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Synopsis

The extent of recrystallization of nascent UHMWPE powder is easily measured by calorimetry. Melting and recrystallization of nascent UHMWPE at 140°C can be suppressed by compression molding. Crystals of UHMWPE prepared from dilute solution show a peak melting temperature of 140°C and exhibit crystallinity up to 75.5% depending on crystallization temperature. Large changes in crystallinity result from drawing single crystal mats or compression-molded films.

INTRODUCTION

Reports on the calorimetric melting behavior of ultrahigh molecular weight polyethylene (UHMWPE)¹⁻³ have shown that nascent crystallized powder has a higher melting point and crystallinity than material recrystallized from the melt. Moreover, the melting peak temperature and crystallinity of the powder were increased to 147°C and almost 80%, respectively, following prolonged annealing at 134°C.⁴ It was suggested⁵ that the nascent powder was composed of extended chain crystals, while melt-crystallized polyethylene had the usual folded chain morphology. Heating above 134°C, produced a conversion from nascent to melt crystallized morphology. For example, heating at 140°C precipitated a rapid and continual recrystallization of nascent polyethylene to folded crystals. This conversion was observed to be reproducible and was easily detected by subsequent calorimetric analysis.^{3,4} Recently, we have observed that the melting behavior of UHMWPE is very sensitive to experimental variables during processing. In this paper, we examine the effects of compression molding, crystallization from dilute solution, and drawing.

EXPERIMENTAL

Materials

Commercial-grade ultrahigh molecular weight polyethylene (UHMWPE) was obtained from Hercules (Hercules 1900) as a fine white powder which had been recovered directly from a slurry process with a hydrocarbon diluent.⁶ Reagent xylene, "Baker analyzed" from J. T. Baker Chemical Co., was used

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without further purification. Antioxidant, 2,6-di-*t*-butyl-*p*-cresol was 99 + %, Gold Label, from Aldrich Chemical Co.

Calorimetry

Samples were weighed with either a Mettler balance (Model #H78AR) or a Cahn electrobalance (Model #7500). Melting and recrystallization were studied in a differential scanning calorimeter (Perkin-Elmer DSC-4) calibrated with an Indium standard. Samples were heated from 50°C at a heating rate of 10°C/min to 170°C and cooled at a rate of 10°C/min to 50°C. In order to normalize the melting behavior, samples were always subjected to repeated melting and cooling cycles, and the areas of melting peaks normalized for remelted samples. The areas of melting and recrystallization peaks were either measured with a planimeter (LASICO, Model L-30) or measured and printed out directly using an on-line computer (IBM PC).

Compression Molding

Samples were prepared by placing 5 g of UHMWPE powder on the bottom platen of a press (Duke Hydraulic Hot Press) which had been preheated to 130°C and applying a specific force up to 1.33×10^6 N. The sample was kept under pressure for 4 h at 140°C, whereupon the heater was turned off and the sample cooled in place gradually to room temperature. Then, the pressure was released, the film removed, and its dimensions determined. Film thickness was measured with a micrometer.

Crystallization from Dilute Solution

Solutions of 0.05 and 2 wt% UHMWPE powder were prepared by heating in boiling xylene containing 2 wt% (based on the polymer) antioxidant for 24 h. The hot solution was then transferred to a cylindrical filter thermostated at specified temperatures in a water bath. Within 0.5 h, clouds of polymer crystals appeared in the solutions. Suspensions were filtered directly in the bath at elevated temperature to produce single crystal mats. These were removed from the filter and dried in a vacuum oven.

Drawing

Compression-molded films and single crystal mats were cut into samples 50 mm long and 10 mm wide and drawn in a Instron (Model #1122) in an environmental chamber set at 140°C at a crosshead speed of 2 mm/min to various draw ratios. The length of the sample subject to drawing approximated 15 mm. Some samples were drawn two or three times in order to achieve the higher draw ratios. The draw ratio was calculated from the ratio of weight per unit length for undrawn and drawn samples.⁷

Scanning Electron Microscopy (SEM)

Dried suspensions and filtered mats of UHMWPE crystallized from dilute solution, drawn mats, and drawn compression-molded films were mounted on

a base plate and the surface made conductive by the deposition of a layer of gold and palladium in a vacuum chamber. Scanning electron micrographs were taken at several magnifications up to $20,000\times$ with a Cambridge Stereoscan microscope (Model S4-10).

RESULTS

Compression Molding

Compression-molded films of UHMWPE varied in thickness from 1.702 to 0.635 mm, in the center of each film, corresponding to pressures of 1.01×10^5 to 1.72×10^7 Pa, respectively. Also, each film varied in thickness from center to edge, with the edge being slightly less than 50% as thick as the center. Following compression molding at 140°C , resultant films produced varied amounts of low and high melting peaks that depended on pressure and sample location. For all samples, regardless of external molding pressure from 0 to 1.72×10^7 Pa, and except for a 10 mm rim around the edge of each film, a single high temperature melting peak at about 145°C was observed with a crystallinity of about 77% [Fig. 1(a)]. Calorimetric measurements of samples taken from the edges of compression-molded films showed two peaks at 130°C and 141°C [Fig. 1(b)]. The relative areas of the two peaks depended reproducibly on molding pressure. However, occasional variability was observed, which seemed to correlate with distance from the film edge. In general, the amount of low melting material from such samples increased with external molding pressure and the crystallinity decreased.

Crystallization from Dilute Solution

Single crystal mats, prepared by filtering suspensions of UHMWPE precipitated from dilute xylene solution, showed single high melting calorimetric endotherms at 140°C with crystallinity dependent on crystallization temperature. For crystallization at 90°C , the calorimetric crystallinity was 75.5% (Fig. 2); at 80°C , 74.1% and at 70°C , 71.8%, respectively. If the solutions were cooled to room temperature, the crystals collected showed a crystallinity of 72.7%. Studies of these crystals in the scanning electron microscope revealed their lamellar nature.

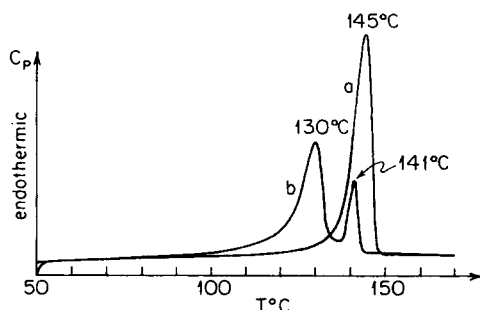


Fig. 1. Melting of UHMWPE film compression-molded from powder at 140°C and 5.04×10^6 Pa for 4 h: (a) center of film; (b) edge of film.

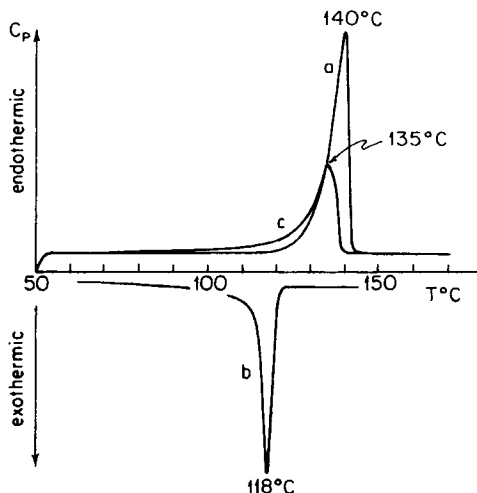


Fig. 2. Melting (a), recrystallization (b), and remelting (c) of UHMWPE single crystal mat crystallized from 0.05% solution in xylene at 90°C for 0.5 h.

Drawing

The melting behavior of compression-molded UHMWPE was examined following drawing at several temperatures. The most extensive studies involved samples compression molded at 140°C at 1.72×10^7 Pa and at 1.21×10^7 Pa which were drawn to draw ratios up to 24 at 140°C. Before drawing, a single melting peak was shown at 145°C corresponding to a crystallinity of approximately 77%. Following drawing, a more complex, multiple, melting pattern was often shown (Fig. 3), and the crystallinity varied with draw ratio. At a draw ratio of 4.65, the crystallinity had dropped to 58%, but increased fairly uniformly to 78% at a draw ratio of 24. On drawing, films develop a fibrous appearance in the scanning electron microscope.

Following drawing at 140°C of a single crystal mat crystallized at 90°C, the calorimetric recrystallization exotherm was extremely sharp (Fig. 4). At a low draw ratio (3.4), a multiple melting peak resulted, and the crystallinity was reduced to 37%. This increased to about 45% on increasing the draw ratio up to 7 for this sample or up to 23, for a sample prepared from more concentrated

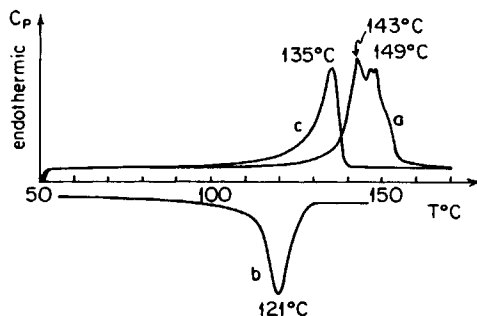


Fig. 3. Melting (a), recrystallization (b), and remelting (c) of UHMWPE film which had been molded at 140°C and 1.72×10^7 Pa for 4 h and then drawn at 140°C to a draw ratio of 24.

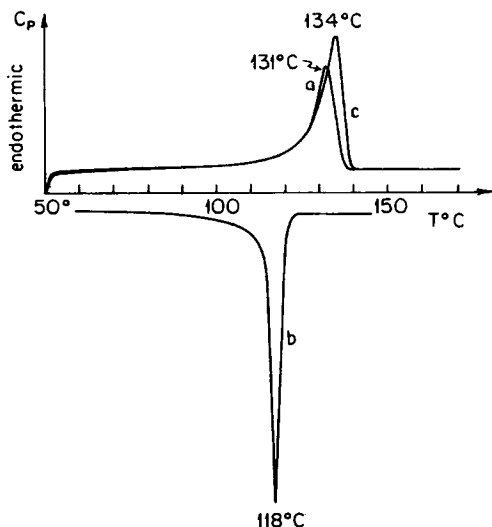


Fig. 4. Melting (a), recrystallization (b), and remelting (c) of UHMWPE single crystal mat crystallized from 0.05% solution in xylene at 90°C for 0.5 h and then drawn at 140°C to a draw ratio of 4.53.

solution. After drawing, single crystal mats appear fibrous in scanning electron micrographs.

DISCUSSION

It should be emphasized that the term “nascent” refers only to the “as-received” powdered polyethylene from the polymerization reactor, implying a unique morphology, resulting from the near simultaneity of polymerization and crystallization. The effect of pressure during compression molding on the recrystallization of nascent crystals of UHMWPE is shown by the appearance of the calorimetric trace on subsequent melting in DSC. Since samples compression molded at 140°C while constrained between heated platens show a single high melting peak, independent of external applied pressure, we concluded that the partial melting of nascent crystals was suppressed in the mold. It has been reported⁸ that the recrystallization of molten linear polyethylene was suppressed in constrained environments. The conversion of nascent crystals of 80% crystallinity to folded crystals of 50% crystallinity is accompanied by a large decrease in density. The density of the perfect crystal is 1000 kg/m³, and the density of amorphous polyethylene is 865 kg/m³.⁹ Therefore, preventing free expansion while heating to 140°C could suppress melting. Even when no external molding pressure was applied, considerable pressure was developed by constraining the powder between heated platens.

However, a surprising observation is the apparent increase in the amount of melting of nascent crystals in the film edge by *increasing* the external pressure. It is possible that the edge of the film is increasingly distorted by increasing platen pressure and expands into the region between the platens, producing a thin film at reduced local pressure. Moreover, with increased

platen pressure and contact, improved heat transfer facilitates the thermally induced transition.

Crystals of UHMWPE crystallized from hot xylene solutions and filtered at specific crystallization temperatures showed a lamellar habit and the expected dependence of crystallinity on temperature. With increasing crystallization temperature, thicker crystals were produced¹⁰ and the percentage of polymer in chain folds decreases. As a result, the overall density and crystallinity increase with crystallization temperature. Solutions allowed to cool to room temperature or to 70°C, crystallize during cooling at a range of temperatures above 70°C and so exhibit similar crystallinities. It was observed that following crystallization from dilute xylene solution of either dissolved UHMWPE powder or molded films, resultant mats show the same melting behavior. However, the peak melting points of crystalline mats are lower (140°C) than for nascent powder (145°C).^{1,4} As pointed out,⁴ crystals prepared from dilute solution contain folded molecules, unlike the extended chain packing of nascent polymers. Also, during crystallization from solution, extensive molecular fractionation occurs,^{11,12} as the most perfect molecules crystallize first. For crystallization at 90°C for 0.5 h and hot filtration, resultant crystal mats consist of the most linear molecules of very high molecular weight. As a result of such fractionation, the recrystallization exotherm of the molten mat [Fig. 2(b)] is much sharper than usual for nascent crystals.

The drawing of compression-molded UHMWPE at 140°C induced considerable damage to the crystalline texture, producing very large decreases in crystallinity and local variations in structure.¹³ However, at increasing draw ratios, the extended chain morphology was enhanced and the crystallinity increased from 58 to 78%. The variations in structure induced by drawing produce the complex melting pattern (Fig. 3). Indeed, the most highly oriented and perfect material showed a melting peak at 149°C.

Similarly, drawing single crystal mats at 140°C induced fibrillation and caused substantial damage. The generation of extended chain regions provided nuclei for rapid and sharp recrystallization exotherms. Since the crystal mats had already undergone molecular fractionation during high temperature crystallization and hot filtration from dilute solution, the subsequent recrystallization exotherm [Fig. 4(b)] is extremely sharp. However, the extensive damage produced variable morphologies often shown by multiple melting peaks and reduced crystallinity.^{7,14} It was reported that drawing to very high draw ratios (up to 200) considerably enhanced the crystallinity, and it was concluded that the crystalline/amorphous two-phase texture was destroyed and reorganized into a single phase, highly oriented crystalline morphology.¹³

CONCLUSIONS

Films of UHMWPE powder, compression-molded at 140°C, retain the calorimetric behavior characteristic of the nascent state to a degree dependent on molding pressure and sample location, as the recrystallization of nascent crystals can be suppressed in the mold. Crystals of UHMWPE prepared from dilute xylene solutions produced a single melting endotherm peaking at 140°C and increase in calorimetric crystallinity from 71.8 to 75.5% depending on crystallization temperature. Molecular weight fractionation during crystallization from solution at 90°C produces sharp recrystallization exotherms.

Drawing of compression-molded or single crystal mats of UHMWPE produced large changes in crystallinity. For compression-molded UHMWPE, the crystallinity decreased at low draw ratios but increased on further drawing to 78% at a draw ratio of 24, as the extended chain morphology was probably enhanced. Variations in structure resulting from drawing yielded an endotherm showing multiple melting, with a high temperature peak at 149°C. Drawing single crystal mats at 140°C induced fibrillation with extended chain regions, providing nuclei for recrystallization over an extremely narrow temperature range.

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References

1. H. D. Chanzy, E. Bonjour, and R. H. Marchessault, *Colloid Polym. Sci.*, **252**, 8 (1974).
2. Lin Shangan, Lu Yun, Wang Haihua, Chang Qixing, Liang Kuiming, Xiu Jiarui, Luo Huayou, and Liao Kairong, *Chem. J. Chinese Univ.*, **1**, 97 (1980).
3. Liang Kuiming, Tan Xixun, Lu Yun, and Lin Shangan, *Chem. J. Chinese Univ.*, **6**, 275 (1985).
4. Xi-you Wang and R. Salovey, *J. Appl. Polym. Sci.*, **34**, 593 (1987).
5. T. Georgiadis and R. St. John Manley, *Polymer*, **13**, 567 (1972).
6. Dr. T. S. Dziemianowicz, Research Engineer, Himont Research and Development Center, Wilmington, DE, private communication.
7. K. Furuhashi, T. Yokokawa, and K. Miyasaka, *J. Polym. Sci., Polym. Phys. Ed.*, **22**, 133 (1984).
8. D. C. Bassett, *Principles of Polymer Morphology*, Cambridge University Press, Cambridge, 1981, p. 129.
9. R. J. Young, *Introduction to Polymers*, Chapman and Hall, London, 1981, 1983, p. 209.
10. Ref. 8, p. 39.
11. J. J. Point, M. Ch. Colet, and M. Dosiere, *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 357 (1986).
12. A. J. McHugh, E. P. Vrahopoulou, and B. J. Edwards, *J. Polym. Sci., Polym. Phys. Ed.*, **25**, 953 (1987).
13. P. F. Van Hutten, C. E. Koning, and A. J. Pennings, *J. Mater. Sci.*, **20**, 1556 (1985).
14. K. Furuhashi, T. Yokokawa, C. Seoul, and K. Miyasaka, *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 59 (1986).

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