

Analysis of Thermal Properties of Polymeric Biomaterials. I. Ultrahigh-Molecular-Weight Polyethylene

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ABSTRACT: The effects of sample size and heating and cooling rates on thermal transitions of ultrahigh-molecular-weight polyethylene (UHMWPE) were investigated. The thermal parameters were studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). While heating rates and sample size had strong effects on thermal properties, the influences of cooling rates were minor. For DSC, broad melting transitions were obtained at faster heating and/or slower cooling rates and larger sample sizes. Higher melting temperatures were obtained when heating rates and sample size were increased. Slower cooling rates also produced higher melting and crystallization temperatures. Faster cooling rates yielded lower heats of fusion during melting and also lower heats of crystallization. The dependence of peak melting and crystallization temperatures on the heating and cooling rates are illustrated by two empirical formulas. For TGA, it is found that faster heating rates and larger sample sizes produced higher decomposition temperatures. This detailed analysis may explain the large variations in the reported data on thermal properties and crystallinity of UHMWPE and provide solutions to the current clinical problems associated with polymeric biomaterials. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1353–1361, 1998

Key words: ultrahigh-molecular-weight polyethylene; thermal properties; differential scanning calorimetry, thermogravimetric analysis; biomedical

INTRODUCTION

Ultrahigh-molecular-weight polyethylene (UHMWPE) is clinically used in total joint replacement as load-bearing articulating components. Although short-term use of the polymer is very successful, its long-term performance has been a concern for many years. For implants made of UHMWPE, changes in properties (chemical and physical) arise mainly from the following two aspects: (1) manufacturing and gamma irradiation sterilization processes before implantation; (2) chemical attack and mechanical loading during implantation.^{1,2} In addition to chemical and mechanical properties, the thermal behavior and

crystallinity of retrieved UHMWPE implants differ significantly from nonimplanted polymer.^{3,4} It has been shown that these properties are affected by gamma irradiation, which is currently used to sterilize UHMWPE implants.^{5–8} Furthermore, the properties of the radiation-sterilized UHMWPE materials change with time; this is defined as post-irradiation aging.^{6,9,10} Postirradiation aging effects are believed to be due to latent free radicals after irradiation and slow oxidation of polyethylene in an oxygen-containing environment.^{11,12}

It is generally agreed that long-term performance (wear, creep, fracture, and fatigue) of UHMWPE plays a key role in the success of total hip and knee arthroplasties. Many factors contribute directly or indirectly to the failure of polyethylene components during implantation, including thermal properties (for example, melting and oxida-

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tion temperatures) and crystallinity. As a result, many publications dealing with thermal properties of UHMWPE have appeared in the literature over the past several years.³⁻¹⁵ Thermal properties are mainly studied by differential scanning calorimetry (DSC) analysis because of its simplicity, high reproducibility, small sample size, and fast sample turnover. DSC has also been utilized to determine the crystallinity of UHMWPE by comparing the measured heat of fusion to that of fully crystallized polyethylene, which is a known value.¹⁶ Yet, a close examination of the DSC data published on UHMWPE indicates a large variation in the reported values. The calculated crystallinity, for example, can be as low as 30% to as high as 88%, and the measured melting points can have a more than 10°C difference, even if the material types, fabrication methods, and irradiation conditions identical.^{4,6-9,13-15}

Recently, an attempt was made by Pascaud et al.¹⁵ to address some of the discrepancies in the literature. Their DSC study on UHMWPE compared melting temperature and degree of crystallinity and found that these two parameters are dependent on sample size, although theoretically the melting point and crystallinity percent should be independent of sample size. When the sample size was increased (from 4.4 to 27.1 mg), they found that peak melting temperatures and heats of fusion first dropped, then increased. The study concluded that no definite trend was found between thermal parameters and sample size.

Thermal behaviors of polymers are important and closely related to processing conditions and end performance. For polymeric biomaterials like UHMWPE, which are mainly used as load-bearing orthopedic implants, melting transitions are important as they define the lower limits of melt-processing and upper limits of use. Furthermore, any increases in melting temperatures may suggest formation of crosslinking and/or increases in crystallinity. Alternately, decreases in melting points may result from the chain scission and/or decreases in crystallinity. These changes will, in turn, alter the mechanical performance of the polymers. This is particularly important if such changes occur during the service life of the polymer implants.

As an important analytical tool, thermogravimetric analysis (TGA) is widely used in polymer research to determine the weight-change profile of a material subject to heating. From TGA studies, thermal decomposition temperature, ratio of components in a mixing system, and heat resistance

of a polymer can be evaluated. The thermal decomposition temperatures are important as they determine the upper limits of melt-processing of polymers. Therefore, it is relevant to evaluate how the thermal decomposition temperature is related to the performance of polymeric biomaterials. Surprisingly, very little information is available on analysis of polymeric biomaterials by this method.

Despite the questions raised concerning long-term performance of UHMWPE, there is currently no literature describing systematic studies relating DSC and TGA experimental conditions, such as sample size and heating and cooling rates, to the melting, crystallization, decomposition temperatures, and heat of fusion or crystallinity of the polymer. Although the work by Pascaud et al. was a good step towards comparing data in the literature, only sample size effects were examined with no definitive conclusions. As a result, the present study was directed towards evaluating thermal properties of UHMWPE using DSC and TGA methods. This article is the first in a series of thermal analysis of polymeric materials. Emphasis was placed on the effects of sample size as well as heating and cooling rates on the melting, crystallization, and thermal decomposition temperatures and the heat of fusion of UHMWPE.

EXPERIMENTAL

Materials

A commercial medical grade UHMWPE (GUR405) in the form of fine powder was obtained from Hoechst-Celanese Co., Corpus Christi, Texas. The virgin polymer has a molecular weight of about 6 million. The melting temperature of the unprocessed polymer, as determined by DSC using a sample size of 5 mg and a heating rate of 10°C/min under nitrogen purge, is 145°C. In this study, virgin powder polymer was melted and compression-molded into sheets using a square metal frame (15 × 15 cm) placed between two stainless steel plates at a temperature of 180°C and pressure of 7 MPa for 20 min in a Carver Laboratory Press under an ambient laboratory environment. After being subject to compression-molding treatment, the melting temperature of UHMWPE dropped to 132°C.

Differential Scanning Calorimetry

A Perkin-Elmer Pyris 1 DSC analyzer with a computer data system (Pyris Series) was used.

The instrument was first calibrated using a high purity grade indium standard, and then recalibrated every week during the experiment with no observable instrument deviation. Rectangular polymer samples weighing 1, 5, 10, and 20 mg (nominal $\pm 5\%$ variation) were cut from compression-molded sheets using a razor blade such that each sample was a single piece of polymer sheet. The samples were prepared in such a way that surface area and volume were proportionally increased as sample weight was increased. Then, the sample was placed in a two-part aluminum pan, compacted, and scanned under nitrogen purge. For each DSC experiment, the first cycle entailed heating and cooling the sample at $10^\circ\text{C}/\text{min}$ over the experimental temperature range to erase the previous thermal history. The samples were then subjected to repeated cycles and the data were collected. Each cycle involved heating from 25 to 180°C , then cooling immediately from 180 to 25°C at different heating and cooling rates. Heating and cooling rates ranged from 1 to $80^\circ\text{C}/\text{min}$.

Thermogravimetric Analysis

TGA experiments were performed on UHMWPE samples using a Perkin–Elmer TGA-7 analyzer. The instrument was calibrated using a magnetic calibration reference material according to the manufacturer's recommendation. Rectangular polymer samples were prepared in the same way as described for the DSC experiments. Each TGA experiment was performed under nitrogen purge. For the purpose of this study, four sample sizes of 5, 10, 20, and 30 mg (nominal $\pm 5\%$ variation) and five heating rates of 5, 10, 20, 40, and $80^\circ\text{C}/\text{min}$ were used.

RESULTS AND DISCUSSION

DSC Results

DSC thermograms were used to study the following two events: melting (endothermic) and crystallization (exothermic). For every single DSC experiment, the following four thermal parameters were collected: peak melting temperature (T_{mp}), heat of fusion (ΔH_m), peak crystallization temperature (T_{cp}), and heat of crystallization (ΔH_c). Based on ΔH_m values, the present crystallinity of the polymer could then be evaluated. The effects of sample size as well as heating and cooling rates

on these parameters are discussed in the following sections.

Dependence of T_{mp} and T_{cp} on Heating and Cooling Rates

Figure 1 shows a typical DSC thermogram for a 5-mg sample scanned at different heating rates with the cooling rate kept at $10^\circ\text{C}/\text{min}$. This graph clearly indicates the strong dependence of melting transitions of UHMWPE on heating rates, which is due to heat lag effects and related to kinetics. With increasing heating rates, melting transitions broadened and melting points extended to higher temperatures. However, the increased heating rates did not affect the crystallization behavior as all cooling curves exhibited exactly the same shapes, indicating excellent reproducibility of the DSC method. Figure 2 displays the DSC thermogram for a 5-mg sample scanned at different cooling rates with the heating rate kept at $10^\circ\text{C}/\text{min}$. This graph clearly indicates the dependence of thermal transitions (both melting and crystallization) of UHMWPE on cooling rates. Melting transitions broadened slightly and peak melting points extended to higher temperatures with decreasing cooling rates, although the changes were less significant than those associated with heating rates (Fig. 1). Alternately, crystallization transitions became more intense and broadened, and the peak crystallization temperatures decreased as cooling rates were increased.

Figures 1 and 2 explicitly show that both heating and cooling rates affect the melting transitions of UHMWPE, but that heating rates have a more significant impact. Quantitatively, the peak melting temperatures can change by more than 10°C as the heating rates are increased from 1 to $80^\circ\text{C}/\text{min}$. From a polymer physics viewpoint, these phenomenon are closely related to polymer chain mobility, in addition to heat lag effects. As most polymers have varying chain lengths with variable relaxation times, a longer average relaxation time will be needed for a polymer to respond to heat applied at faster rates (higher heating rates), effectively yielding a broad melting peak and moving the melting points to higher temperatures. Similarly, faster cooling rates would result in a less perfect crystallization, suggesting lower melting and crystallization temperatures.

The relationship between melting temperatures of UHMWPE and heating and cooling rates can be mathematically described. Assuming that melting temperatures are functions of both heat-

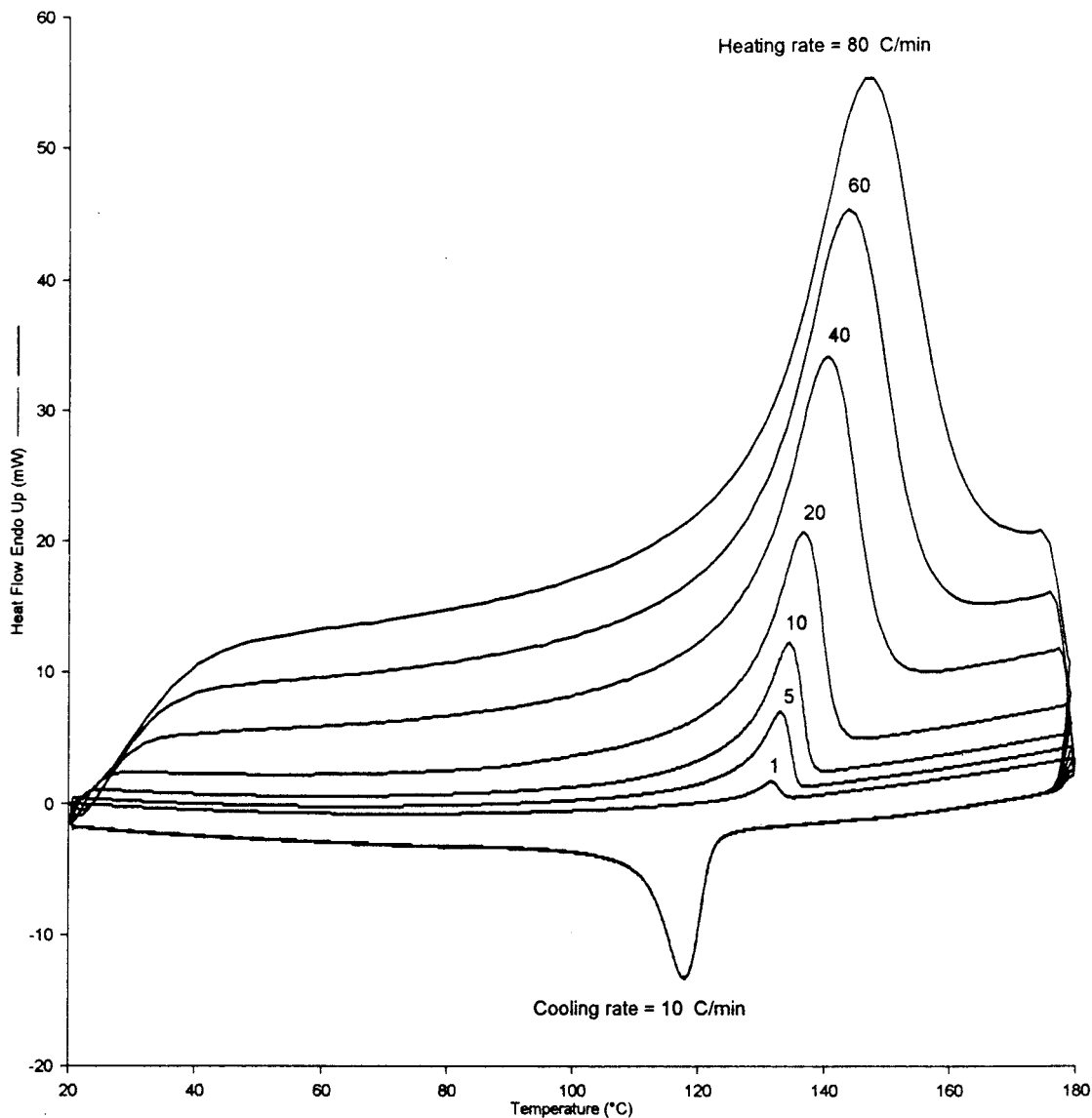


Figure 1 DSC thermogram of UHMWPE. Heating rates ranged from 1 to 80°C/min while the cooling rate was kept constant at 10°C/min. Sample size = 5 mg.

ing and cooling rates for a constant sample size, we have

$$T_m = f(T_{HR}, T_{CR}) \quad (1)$$

where T_m is the melting temperature, and T_{HR} and T_{CR} are the heating and cooling rates, respectively. A complex function like eq. (1) needs at least 4 constants to be solved, and, typically, T_m is not a simple function of T_{HR} and T_{CR} alone. Therefore, the effects of heating and cooling rates on T_m are treated separately. First, one may consider only the influence from heating rates while keeping cooling rates at a fixed value. By plotting

the experimentally determined values of peak melting temperature (T_{mp}) against T_{HR} , the relationship between T_{mp} and T_{HR} is best described by eq. (2) for constant cooling rates and sample sizes, as follows:

$$T_{mp} = T_{mo} + K_m \sqrt{T_{HR}} \quad (2)$$

where T_{mo} is the melting temperature at infinitely small heating rates and K_m is a constant.

In eq. (2), T_{mo} and K_m are constants to be determined. Equation (2) indicates that the peak melting temperature increases with the square root of

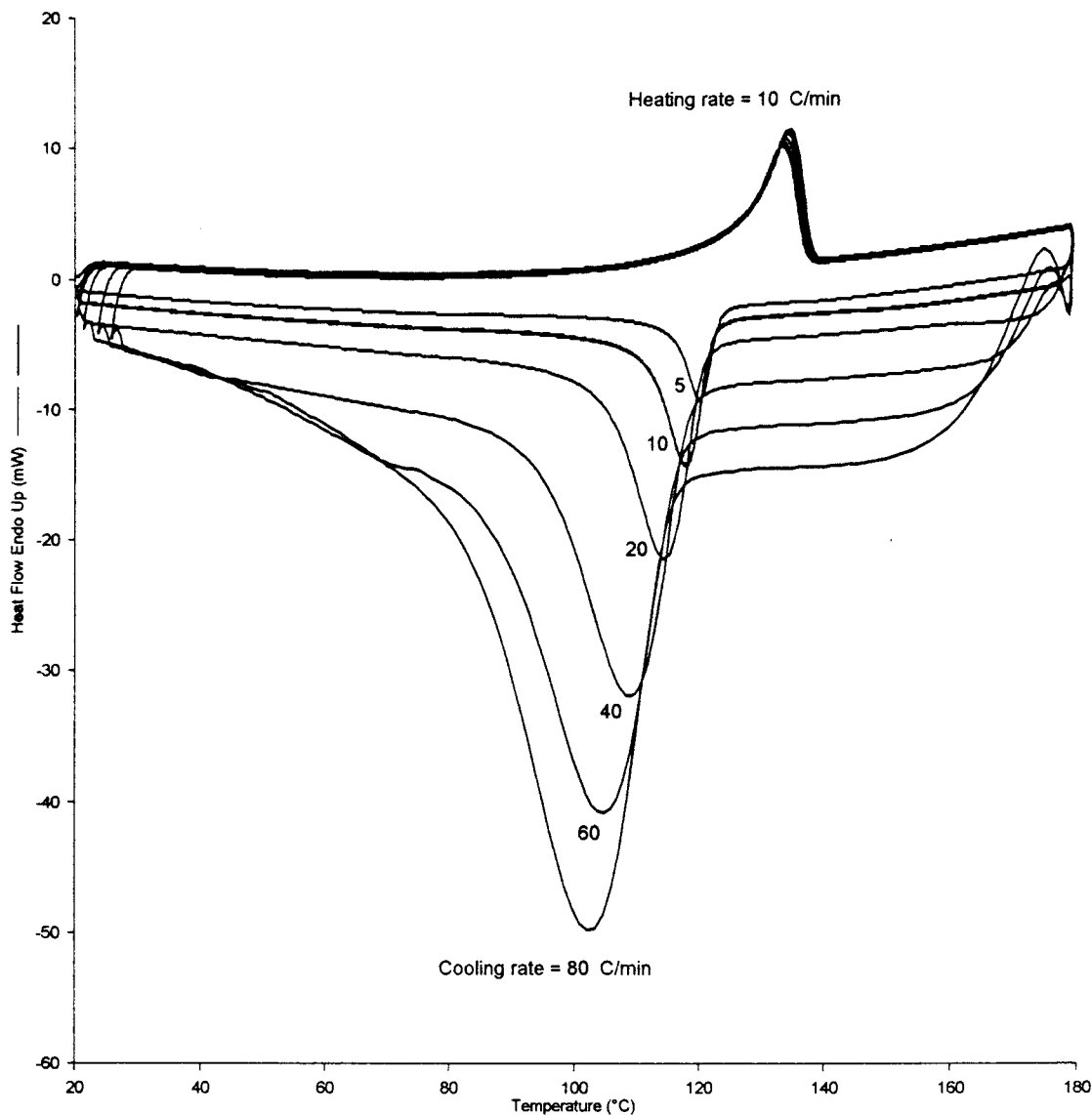


Figure 2 DSC thermogram of UHMWPE. Cooling rates ranged from 5 to 80°C/min while heating rates were kept constant at 10°C/min. Sample size = 5 mg.

increasing heating rates. Based on the experimental data for T_{mp} at different values of T_{HR} for $T_{CR} = 5^\circ\text{C}$ and a sample size of 5 mg, T_{mo} and K_m were determined using a curve fit analysis, and eq. (2) is rewritten as

$$T_{mp} = 129.7 + 1.5\sqrt{T_{HR}} \quad (3)$$

From eq. (3), we expect a peak melting point of nearly 130°C when heating rates are approaching zero, which is the ideal condition mathematically. Alternately, melting points will be much higher as heating rates are increased. This is likely to

occur because the heating rates of crystals exceed their melting rates, resulting in superheating.

A similar analysis of the effects of heating and cooling rates on peak crystallization temperature (T_{cp}) and heat of crystallization (ΔH_c) indicates that heating rates seldom affect the crystallization behavior of UHMWPE (Fig. 1). Understandably, at a temperature of 180°C, UHMWPE is in the melted state, regardless of previous heating rates. Therefore, crystallization temperatures and heats of crystallization should only be influenced by cooling rates when the polymer is cooled from temperatures above melting. Quantitatively, when the cooling rates changed from 5 to 80°C/

min, a difference of approximately 10°C in crystallization temperatures was observed.

Similar to the analysis of melting temperatures, we can mathematically describe the change of crystallization temperatures with cooling rates. It was found through analysis of the experimental results that the dependence of peak crystallization temperatures (T_{cp}) on the cooling rates (T_{CR}) is best illustrated by eq. (4) for constant heating rates and sample size, as follows:

$$T_{cp} = T_{co} - T_{\infty}e^{-(K_c/T_{CR})} \quad (4)$$

where T_{co} is the peak crystallization temperature at infinitely slow cooling rates and T_{∞} is defined as $T_{co} - T_{cp}$ when cooling rates are extremely high.

In eq. (4), T_{co} , T_{∞} , and K_c are experimentally determined constants. Based on the experimental data for $T_{HR} = 10^\circ\text{C}$ and a sample size of 5 mg, the above constants were calculated using iteration methods, and eq. (4) is rewritten as

$$T_{cp} = 123.3 - 17.2e^{-(11.8/T_{CR})} \quad (5)$$

Equation (5) indicates that the peak crystallization temperature should increase with decreasing cooling rates even though a broad crystallization peak was observed at faster cooling rates. The peak crystallization temperatures approach a constant when the crystallization rates approach zero, which is a near equilibrium and a mathematically ideal condition. According to the above equation, the peak temperature at equilibrium should be about 123°C. Alternately, when cooling rates get extremely high, peak crystallization temperatures approach a constant value of approximately 106°C. Thus, the peak crystallization temperatures are delimited between 106 and 123°C. Equation (5) can also be better understood if one realizes that when cooling rates are faster than the crystallization rates, the polyethylene will not crystallize and essentially supercools as an amorphous glassy polymer. In such extreme cases, melting and crystallization temperatures cannot be detected.

Sample Size

Sample size and shape also play important roles in the thermal characterization of polymeric materials. Small and thin samples yield better qualitative results because of enhanced resolution due to good heat transfer throughout the sample, whereas larger samples yield more precise quanti-

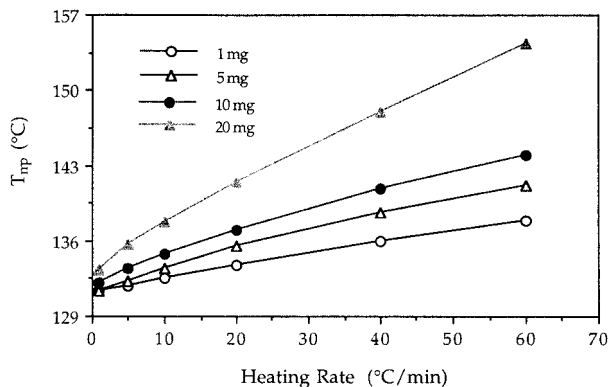


Figure 3 Effects of heating rates and sample size on peak melting temperature (T_{mp}) of UHMWPE.

tative measurements to a limit of sample size. In this study, effects of sample size on thermal transitions of UHMWPE were examined. The dependence of peak melting temperatures (T_{mp}) on sample size is illustrated in Figure 3. The influences of heating rates on T_{mp} are also described in this graph. Clearly, sample size and heating rates strongly affect the T_{mp} of UHMWPE.

Unlike previously published results,¹⁵ we observed that melting temperatures increased with increasing sample size. Thus, sample size and heating rates have the same effect on melting behavior of UHMWPE. Quantitatively, when the sample sizes were increased from 5 to 20 mg, increases in melting temperatures from less than 5°C at a heating rate of 1°C/min to greater than 15°C at a heating rate of 60°C/min were recorded. Although the authors¹⁵ did not report the shape of their samples, we predict that the varying sample shapes might be the primary reason for unpredictable melting behavior trends of UHMWPE from their study.

Dependence of ΔH_m and ΔH_c on Experimental Conditions

Figure 4 summarizes the dependence of heats of fusion (ΔH_m) on heating rates and sample size. It is clear from this graph that ΔH_m is strongly affected by both heating rates and sample size. As the sample weight increased, ΔH_m increased proportionally. This result is contrary to the data published by Pascaud et al.¹⁵ Figure 4 shows that slower heating rates (<20°C/min) had significantly more influence on the ΔH_m than faster heating rates (>20°C/min). Slower cooling rates may yield a higher ΔH_m as longer relaxation times are allowed, thus producing more perfect

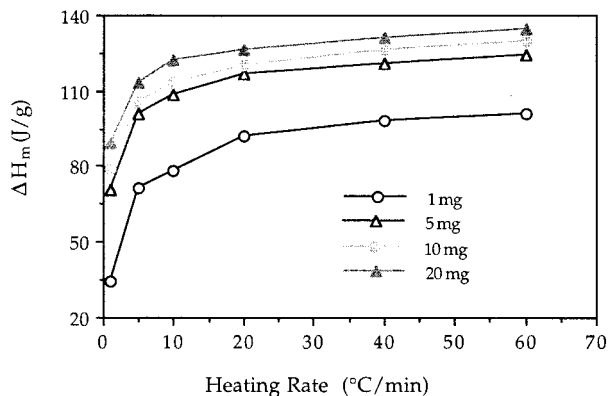


Figure 4 Effects of heating rates and sample size on heat of fusion (ΔH_m) of UHMWPE.

crystals compared to faster cooling rates. This suggests that for the UHMWPE materials, comparing crystallinity derived from experimental ΔH_m is meaningful only when identical experimental conditions are employed. Furthermore, the thermal history of the sample must be reported. Otherwise, the comparison of data from published sources will give varying results and possibly misleading conclusions. This is particularly important when correlating thermal properties and crystallinity to the failure mechanisms of UHMWPE orthopedic implants.

Unlike ΔH_m , heats of crystallization (ΔH_c) are relatively independent of heating rates. However, the experimental data revealed that cooling rates strongly influenced ΔH_c as faster cooling rates yielded low ΔH_c values. Quantitatively, ΔH_c decreased approximately from 130 to 110 J/g when the cooling rates were increased from 5 to 60°C/min. These results indicate clearly that a faster cooling rate results in a less perfect crystallization, as can be expected. It also suggests a higher energy system for a faster cooling rate, which will gradually approach equilibrium with time by lowering the system energy. Small differences between ΔH_c and ΔH_m were observed in this DSC study, although they should be theoretically equivalent when heating rates are identical to cooling rates.

Prediction of Crystal Size and Distribution

Figures 1 and 2 show that the width of the melting peaks depends on heating and cooling rates. Thus, the crystal distribution and size of UHMWPE predicted according to peak width will be significantly affected by the DSC experimental conditions. It is seen from Figure 1 that faster heating

rates resulted in a broader peak width even when the polyethylene was crystallized at the same cooling rate. In such cases, it is generally assumed that the same crystals, crystal size, and/or crystal distribution would be expected for the polymer. Therefore, to predict and/or compare crystal size and distribution, identical heating and cooling rates must be used. As expected, slower cooling rates yielded a slightly widened peak of the melting transitions (Fig. 2), which may indicate a more perfect crystallization during cooling. However, the effects of cooling rates are minor in comparison to heating rate effects.

TGA Results

TGA was used to study the weight change profiles of UHMWPE subject to heating under a nitrogen environment. Effects of sample size and heating rates on weight loss of the polymer were examined. Figure 5 illustrates typical TGA thermograms. The graph clearly illustrates the strong influence of heating rates on the thermal decomposition behavior of UHMWPE. In general, doubling the heating rate increased thermal decomposition temperatures by 20°C while maintaining the curve shape. This is again due to heat lag. From TGA results, the onset thermal decomposition temperature (T_d) was calculated, and effects of sample size and heating rates on T_d are displayed in Figure 6. It is clear from this figure that the T_d increased with increasing sample size and heating rates. Thus, the effects of heating rates and sample size on thermal properties are similar whether the DSC or TGA method is used. Quantitatively, UHMWPE starts to decompose at a temperature well above 400°C in the nitrogen environment, and to completely decompose the polymer, the temperature must exceed 500°C. When heating rates were increased from 5 to 80°C/min, an increase of about 60°C in thermal decomposition temperatures was observed. When sample sizes were increased from 5 to 30 mg, an approximate increase of 15 to 40°C in thermal decomposition temperatures was measured. These results suggest that a very high T_d would be expected when very high heating rates and/or large sample sizes are used.

CONCLUSIONS

An intensive, quantitative study was conducted on thermal properties of UHMWPE, a polymer

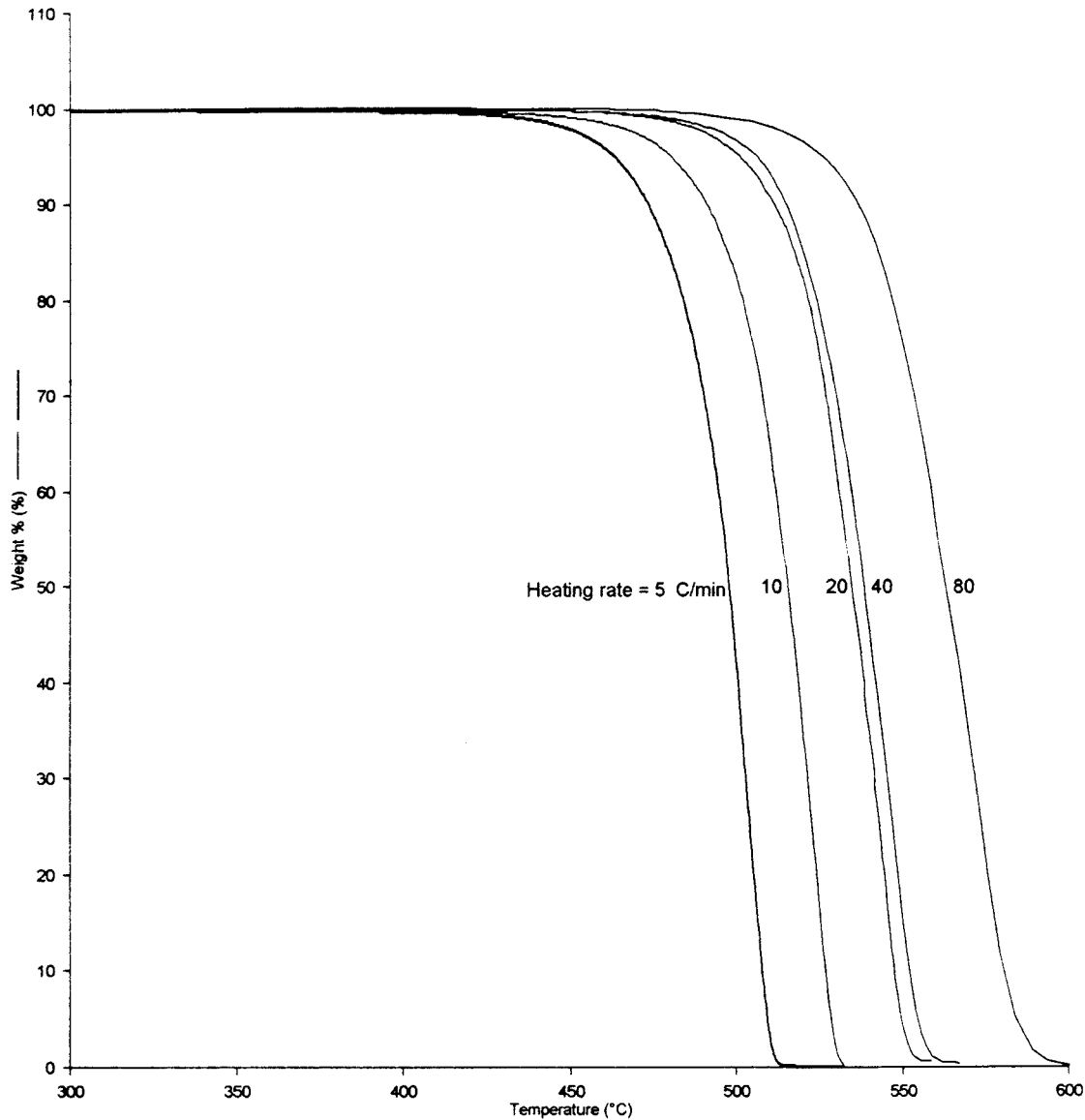


Figure 5 TGA thermogram of UHMWPE at heating rates ranging from 5 to 80°C/min. Sample size = 10 mg.

widely used as medical implants. DSC and TGA results shows that sample size and heating and cooling rates significantly affected the thermal behaviors of the polymer. Faster heating rates yielded more intense and broad thermal transitions with high transition temperatures. Larger sample size and faster heating and slower cooling rates resulted in high melting temperatures. The heats of fusion (therefore, crystallization) increased with increasing heating rates and sample size. The dependence of peak melting and crystallization temperatures on heating and cooling rates was mathematically described

using two empirical formulas provided in this study. Faster heating rates and larger sample sizes yielded high thermal decomposition temperatures. The overall results suggest that the experimental conditions should be well-defined in determining thermal properties and crystallinity of UHMWPE using DSC and TGA tools as these methods are widely utilized to evaluate UHMWPE biomaterials. Because UHMWPE is widely used as orthopedic implants in total joint reconstruction, the conclusions reached in this study may explain the large variations of thermal data reported in the literature and provide

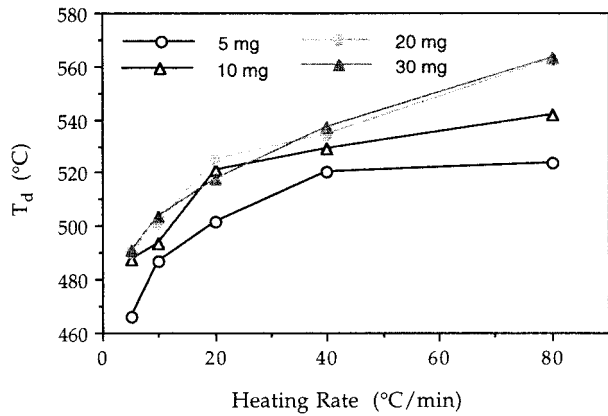


Figure 6 Effects of heating rates and sample size on onset thermal decomposition temperature (T_d) of UHMWPE.

solutions to current clinical problems associated with UHMWPE biomaterials.

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