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NON-ISOTHERMAL CRYSTALLIZATION OF UHMWPE

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Abstract

Processing of Ultra High Molecular Weight Polyethylene (UHMWPE) parts involves non-isothermal cooling leading to crystallinity variations, which cause variations in the mechanical properties. Study of non-isothermal crystallization kinetics of UHMWPE forms the basis for process modelling. The crystallization of UHMWPE was studied at seven different cooling rates. The crystallization onset and peak temperatures were linearly related to the cooling rate. The crystallization of UHMWPE was concluded to be a nucleation dominated process with small contribution from growth of nuclei. Differences in ultimate crystallinity (~11%) were produced due to different cooling rates. A significant portion of the change in ultimate crystallinity occurred at lower cooling rates (<6°C min^{-1}). At higher cooling rates (6–22°C min^{-1}) the change in ultimate crystallinity was insignificant.

Keywords: non-isothermal crystallization, UHMWPE

Introduction

Polymer processing involves application of heat and pressure to the polymer in a specific cycle. The properties of the final product depend on the processing cycle used. During a typical processing cycle the polymer is melted, shaped and then cooled. The cooling rate determines the crystallinity of the polymer, which in turn determines the mechanical properties of the polymer. Variations in cooling rate can cause non-uniform temperature distribution leading to non-uniform crystallinity distributions within the part. The non-uniform crystallinity distribution leads to part with varying stiffness and strength since the mechanical properties of the semi-crystalline polymer are crystallinity dependent. Hence, it is important to study and analyze the relationship between time, temperature, cooling rate and crystallinity for developing predictive process models for polymers.

Chew *et al.* [1] studied the isothermal and non-isothermal crystallization kinetics of High Density Polyethylene (HDPE). Although crystallization kinetics of Low Density Polyethylene (LDPE) and HDPE has been widely studied, crys-

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tallization kinetics of UHMWPE has not received the same attention. UHMWPE has significantly higher molecular mass (~10^6) than either LDPE (~10^3) or HDPE (~10^5). Effect of molecular mass on crystallization of polymers has been studied by researchers. Barrales *et al.* [2] studied the effect of molecular mass on rate of crystallization of polyethylene fractions at high undercoolings. They found that the crystallization rate was slightly dependent on molecular mass for high molecular mass fractions (>10^5). However, the ultimate crystallinity was significantly affected by molecular mass and it reduced from 85% for the lowest molecular mass fraction ($1.8\cdot10^3$) to 35% for the highest molecular mass fraction ($1.55\cdot10^6$). Fatou *et al.* [3] studied the influence of molecular mass on regime crystallization in polyethylene and found profound effect of molecular mass on regime crystallization. They showed that for very high molecular mass, crystallization is nucleation dominated as the nucleation rate is much greater than the growth rate. Zhu *et al.* [4] studied the effect of molecular mass on melting and crystallization of UHMWPE. However, the study was conducted for one cooling rate and did not include any kinetics modeling. In the current study non-isothermal crystallization kinetics of UHMWPE at different cooling rates has been studied.

Experiments

UHMWPE powder manufactured by Hoechst Celanese (GUR 415) was used in the study. The bulk density of the powder was 400 kg m^{-3} and the number average molecular mass was $7.3\cdot10^6$. The number average powder particle size obtained using laser diffraction (Malvern MF15) was 200.2 μm.

Differential Scanning Calorimetry (DSC)

Calibration

Differential Scanning Calorimetry (DSC) experiments were conducted using a TA Instruments DSC model 2920. The DSC was calibrated with 12.6 mg of Indium standard using heating rates of 22, 20, 15, 10, 5, 3 and 1°C min^{-1}. The melting point onset for Indium was taken as 156.5985°C and the heat of fusion was taken as 28.42 J g^{-1} [5].

Janeschitz-Kriegl *et al.* [6, 7] described a method to calibrate a DSC for the temperature lag between the sample and furnace. The energy balance for the DSC is governed by the following equation

$$(m_p c_p + m_s c_s)\frac{dT_s}{dt} + m_s h_s \frac{d\xi}{dt} = hA(T_s - T_f) \tag{1}$$

where T_s is the temperature of the sample, T_f is the furnace temperature, h is the heat transfer coefficient between the top of the furnace and the bottom of the pan,

A is the area of contact, m_p, c_p, m_s and c_s are the mass and specific heat of the pan and the sample respectively, h_s is the latent heat of fusion and ξ is fraction of phase transformation.

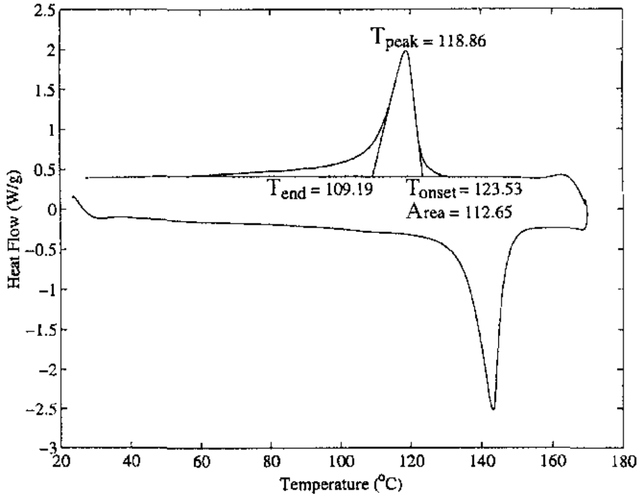

Fig. 1 Typical DSC scan showing heat flow, baseline and onset and peak crystallization temperatures

The product of the heat transfer coefficient h and the area of contact between the pan and the furnace A, can be calculated from the exponential decay of the heat flow curves for pure metals. Using the calculated values for hA the temperature lag between the furnace and the pan can be calculated using

$$\Delta T = T_s - T_f = -\dot{T}_f\left(\frac{1}{\alpha} + \frac{m_s}{hA}p(t)\right) \qquad (2)$$

where $\dot{T}_f p(t)$ is the DSC signal (W g^{-1}) and $\alpha = hA/(m_p c_p + m_s c_s)$. The recorded DSC temperatures were corrected for the temperature lag between the pan and furnace according to the above equation.

Experiments

A refrigerated cooling accessory using compressed nitrogen gas at a flow rate of 150 ml and a pressure of 138 kPa was used for cooling. Nitrogen was also used as purge gas with a flow rate of 25 ml s^{-1}. The highest available scanning rate of 5 points s^{-1} was used during the measurements as suggested by Porter and Wang [8]. They concluded that a small sample size and a high scanning rate are suited for accurate melting temperature measurement. Pascaud *et al.* [9] have shown that samples of identical mass have to be tested for comparison purposes. The samples used in this study were between 4 and 5 mg crimped in aluminium pans.

An empty aluminium pan was used as reference. The samples were equilibrated at a temperature of 25°C and then heated to 170°C at a rate of 10°C min^{-1} where they were soaked at 170°C for 5 min to ensure complete melting to the samples. The samples were then cooled to the room temperature at 22, 20, 15, 10, 5, 3 and 1°C min^{-1} respectively. For ensuring repeatability, each of the above tests was conducted three times.

The crystallinities χ of the samples were calculated using the following formula

$$\chi = \frac{\Delta h}{\Delta h_{100}} 100 \tag{3}$$

where Δh is heat of crystallization of the sample and Δh_{100} is the heat of crystallization for a 100% crystalline sample taken as 288 J g^{-1} [10]. Area under the heat flow curve using a baseline from 52 to 135°C (Fig. 1) [11–13] was used to calculate the heat of crystallization Δh (112.65 J g^{-1}). Using the inflection point on the peak, a tangent to the heat flow curve was drawn. The intersection of the tangent and the baseline was taken as the extrapolated onset temperature (T_{onset}= 123.53°C), the peak of heat flow was taken as the peak crystallization temperature (T_{peak}=118.86°C) and the extrapolated onset temperature at the end of heat flow as the end of crystallization (T_{end}=109.19°C).

Results and discussion

The polymer powder was heated from room temperature to 170°C at a rate of 10°C min^{-1}. During heating the onset of melting was observed at 135.25±0.17°C,

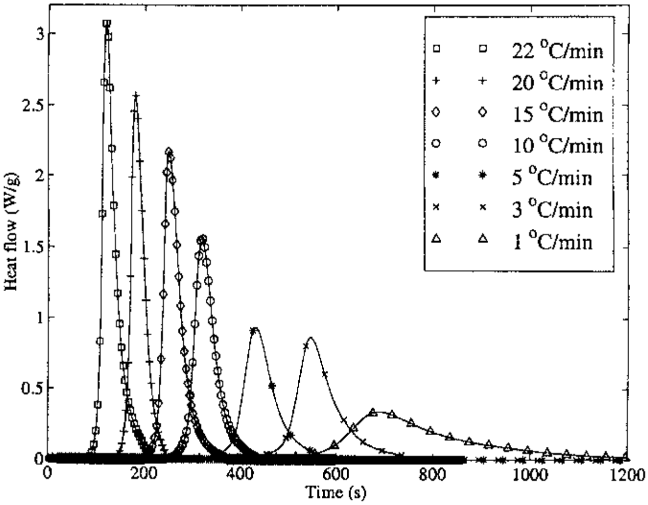

Fig. 2 DSC curves showing differences in crystallization characteristics due to cooling rate

the mean temperature at the peak heat flow was osberved at 144.44±0.34°C. The average crystallinity of the virgin powder was measured as 56.4±2.4%.

Figure 2 shows crystallization curves from DSC measurements at different cooling rates. The crystallization curves showed broader base and shorter peaks for lower cooling rates compared to higher cooling rates. The peak heat flow changed from 3.08 to 0.29 W g^{-1} when the cooling rate was reduced from 22 to 1°C min^{-1}. The total time for crystallization is much shorter for the fastest cooling rate of 22°C min^{-1} than for the slow cooling rate of 1°C min^{-1}.

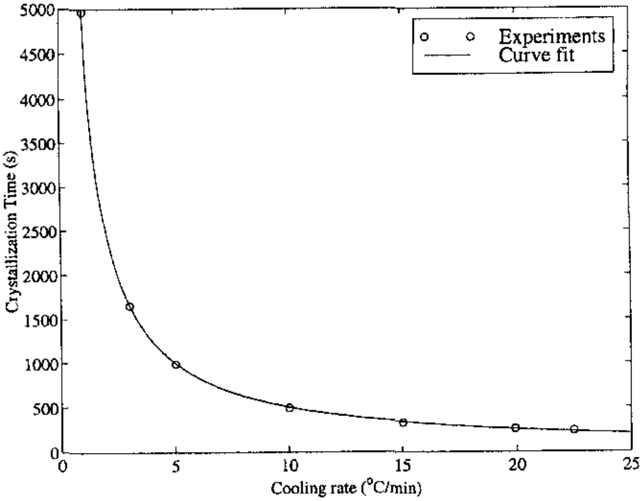

Fig. 3 Crystallization time for different cooling rates

Figure 3 shows the total time required for crystallization at different cooling rates. The total crystallization time was obtained as the difference between the extrapolated end and the extrapolated start time of crystallization. The experimentally measured values follow a nonlinear relation

$$t=4.897\cdot 10^{3}CR^{-0.984} \tag{4}$$

where t is the total time for crystallization in s and CR is the cooling rate in °C min^{-1}. Increase in the cooling rate reduces the crystallization time. The time for crystallization at the fastest cooling rate (22°C min^{-1}) is just ~238 s which is almost 20 times less than the time for crystallization (~4900 s) at the lowest cooling rate (1°C min^{-1}). The lesser crystallization times means less time for reorganization of the polymer chains at the higher cooling rates than at the lower cooling rates.

Figure 4 shows the crystallization scans as functions of temperature. The curves show significant variations during the later part of crystallization. The peak and onset temperatures during crystallization also change. The peak and

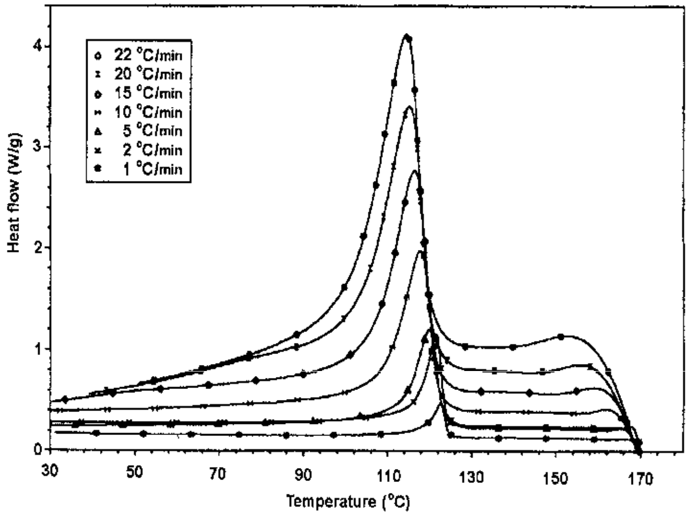

Fig. 4 Effect of cooling rate on the crystallization curves

onset temperatures referred here are measured during the cooling scans hence the onset temperature is higher than the peak temperature. An empirical linear relation between the cooling rate *CR* (°C min^{-1}) and the crystallization onset temperature T_{onset} (°C), peak temperature T_{peak} (°C) and end temperature T_{end} (°C) can be obtained (Fig. 5).

$$T_{\text{onset}} = 124.09 - 0.09CR \tag{5}$$

$$T_{\text{peak}} = 121.94 - 0.24CR \tag{6}$$

$$T_{\text{end}} = 115.91 - 0.62CR \tag{7}$$

The higher cooling rate leads to lower onset and peak temperatures implying higher undercoolings. The higher undercoolings are necessary since the time available for crystallization decreases as the cooling rate increases. The crystallization end temperature T_{end} would be proportional to the minimum crystal size. The reduction in peak crystallization temperature indicates that the maximum lamellar thickness reduces with increased cooling rate. A reduction in peak crystallization temperature would be expected since the initial lamellar thickness l_g is inversely proportional to undercooling ΔT and can be written as [14]

$$l_g \cong \frac{a_1}{\Delta T} + a_2 \tag{8}$$

where a_1 and a_2 are constants.

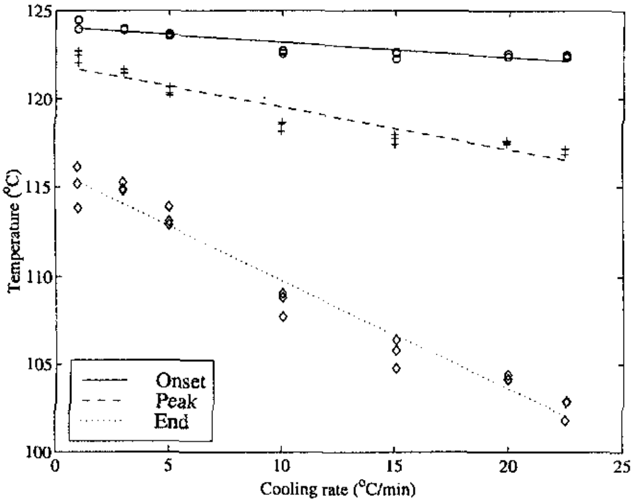

Fig. 5 Effect of cooling rate on melting onset and peak temperatures

The extremely high molecular mass of the samples hinders crystal growth. The crystallization of the sample would be expected to be nucleation dominated [3]. The nucleation-dominated crystallization would be expected to produce lamellae close to their initial size with very little increase in their thickness. The temperature difference $dT=T_{\text{onset}}-T_{\text{peak}}$ is proportional to the lamellar size distribution within the material.

$$dT = 8.19 + 0.53CR \tag{9}$$

Value of dT increases with an increase in cooling rate indicating that an increase in the cooling rate increases the lamellar thickness variation to a certain extent as shown in Fig. 6. The higher cooling rate provides little time for the lamellae to grow thus increasing the lamellar size distribution.

Figure 7 shows relative crystallinity of UHMWPE with measured values. The crystallization was faster for higher cooling rates than for lower cooling rates. The increase in the cooling rate implies lower crystallization temperatures. The lower crystallization temperatures require smaller lamellae for stability leading to an increase in the nucleation. The fast crystallization rates observed provide further evidence of a nucleation-dominated process.

From the measured values of crystallinity, half times of crystallization can be calculated which correspond to time required for completion of half the crystallization. The half times show a steady reduction with increase in the cooling rate (Fig. 8). The half times $t_{1/2}$ for the experimental data and the cooling rate CR follow a simple empirical relation.

$$t_{1/2} = 569.6CR^{-1.09} \tag{10}$$

The crystallization half times are inversely proportional to the crystallization rates. The crystallization rates thus increase with increase in the cooling rate. The increase in the crystallization rates with and increase in the cooling rate would be expected. The extremely high molecular mass of UHMWPE would imply that the crystallization is nucleation dominated. There can be two different types of nucleation one is isothermal and the other non-isothermal (Ziabicki [15–16] and Wasiak [17]). The non-isothermal nucleation rate is proportional to

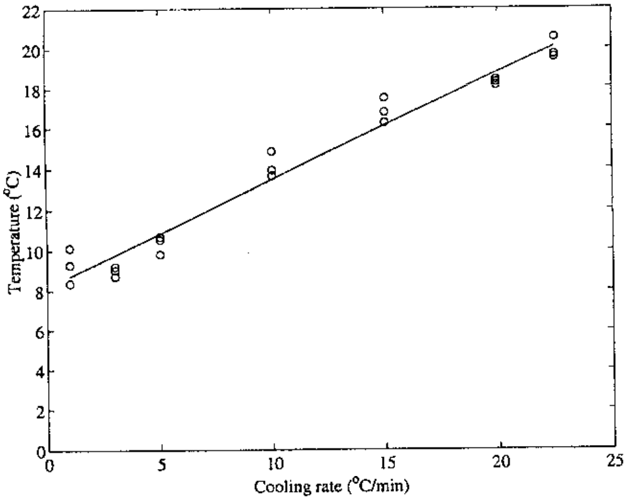

Fig. 6 Effect of cooling rate on $dT=T_{end}-T_{peak}$

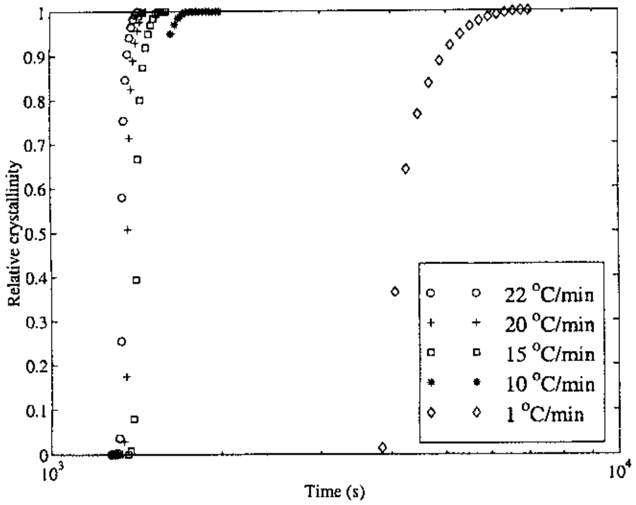

Fig. 7 Crystallization kinetics for different cooling rates

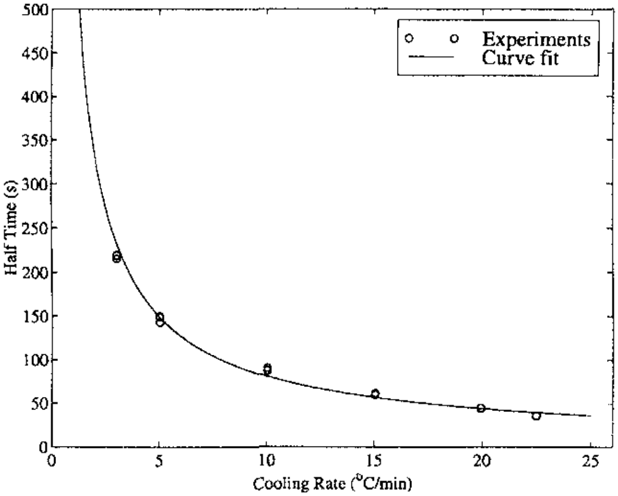

Fig. 8 Crystallization half time variation due to cooling rate

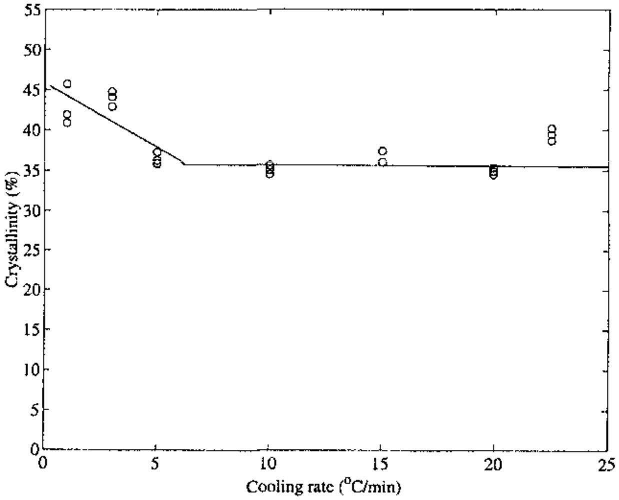

Fig. 9 Effect of cooling rate on ultimate crystallinity

the cooling rate and thus would increase with and increase in the cooling rate. The increased nucleation rate would increase the crystallization rate of the polymer.

The ultimate crystallinity was measured as 42.5±1.6%. The crystallinities observed for different varieties of polyethylene range from around 30 to 80% [2]. An increase in the molecular mass reduces the ultimate crystallization. The ultimate crystallinities for different cooling rates are plotted in Fig. 9. A bilinear curve fit can be used to approximate the measured ultimate crystallinity (χ_{ultimate}) values.

$$\chi_{\text{ultimate}} = 45.8 - 1.61\,CR \quad \text{for } CR < 6.38\ ^{\circ}\text{C min}^{-1} \text{ and} \tag{11}$$

$$\chi_{\text{ultimate}} = 35.6 - 0.01\,CR \quad \text{for } CR > 6.38\ ^{\circ}\text{C min}^{-1} \tag{12}$$

During the slow cooling rates (<6.38°C min^{-1}), the ultimate crystallinity changes significantly (1.6% for every 1°C min^{-1} change) with cooling rate changes than during faster cooling rates (>6.38°C min^{-1}). Nucleation rate is maximum near the polymer melting temperature and reduces fast as the temperature is reduced. If the cooling rate is too fast for all the nucleation sites to form stable nuclei then the number of nuclei formed will reduce dramatically. Since the nucleation rate is the determining factor in crystallization ultimate crystallinity reduces with an increase in the cooling rate. However, at cooling rates >6.4°C min^{-1}, the temperature of the polymer reduces to well below melting allowing very short time for nucleation. Hence, the crystallinity does not change significantly at cooling rates >6.4°C min^{-1}.

The ultimate crystallinity surprisingly increases at the highest cooling rate (22°C min^{-1}). The possible reasons for the increase could be many. The actual experiments were conducted by setting the cooling rate on the DSC controller at 25°C min^{-1}, but the average calculated cooling rate measured temperature and time values came out to 22°C min^{-1}. The cooling rate was very non-uniform, possibly introducing some non-linear effects. All of these factors meant that the experiments at 22°C min^{-1} were not well controlled, leading to greater uncertainties in the results.

Conclusions

Non-isothermal crystallization of UHMWPE was studied at seven different cooling rates. A linear relation between the cooling rate and the peak and onset temperatures of crystallization was observed. Increase in the cooling rate from 1 to 22°C min^{-1} was observed to cause a proportional decrease in the peak temperature from 122 to 114°C and the onset temperatures from 114 to 100°C. A slower cooling rate was concluded to produce lamellae of smaller thickness variation than a faster cooling rate. Increase in the cooling rate was observed to increase the undercooling leading to smaller nuclei. The cooling rate had a significant effect on the crystallization rate as well as crystallization kinetics, however the changes in ultimate crystallinity were comparatively smaller. Increase in the cooling rate from 1°C min^{-1} to around 6.4°C min^{-1} changed the ultimate crystallinity from around 43 to 35%. Further increase in the cooling rate to a maximum of 22°C min^{-1} had a negligible effect on the ultimate crystallinity.

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