Anomalous Heat Capacity of High-Density Polyethylene Melts at High Temperature

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ABSTRACT: The first measurements of heat capacity of high-density polyethylene have been obtained for melts in the high-temperature region of 180–260°C. A heat-flow twin calorimeter was used. Abrupt transitions are noticed at 212 and 228°C, analogous to transitions seen earlier with rheological and surface tension measurements. Possible explanations for these phenomena are offered. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 466–469, 2012

Key words: polyethylene; HDPE melts; heat capacity at high temperature; transitions

INTRODUCTION

Polyethylene (PE), the most widely used and produced polymeric material, is still not fully understood, decades after its commercial introduction. Despite its relatively simple chemical structure (chains of CH_2 groups in linear and branched conformations), melts of PE in both the pure and blended states have been reported to have various anomalies in their macroscopic properties which impact their industrial processing as well as end use. For example, with the linear chains of high-density polyethylene (HDPE), the rheological properties[1,2] appear to undergo two transitions at temperatures well above the crystalline melting point ($T_m = 137$–$140°C$). These two transitions ($T_1 = 210°C$ and $T_2 = 230°C$) lie within the range of industrial melt processing, so their existence is relevant to many processing operations as well as to molecular explanations. Yet, the existence of T_1 and T_2 remains controversial because they have not been widely studied and there is no molecular explanation found as yet. There is some thermodynamic evidence for their existence from differential scanning calorimetry[3]; however, the scanning technique is not convincing to everybody. We have therefore embarked on measurements of the heat capacity C_P at constant pressure (one atmosphere) but with a simple direct calorimetric method in a further search for T_1 and T_2.

An additional purpose for this investigation is to provide experimental values of C_P for HDPE in the liquid state. Earlier measurements were made on HDPE in the solid (crystalline) state and no values have been available for melts, despite this being the condition for industrial operations such as extrusion, molding, and others.

EXPERIMENTAL

Materials

In work on the rheology of HDPE reported previously,[1,2] commercial samples were provided by six industrial manufacturers. It is assumed that the samples used Ziegler–Natta catalysis, so that the samples could have contained trace amounts of catalyst (Ti, Al) which would not affect C_P for the bulk polymers. As rheological tests were very similar among the six samples, only one was selected for the new calorimetric study – namely, the HDPE from Quantum Chemical. This sample had a weight-averaged molecular weight of $M_w = 85,149$ (mistakenly reported in Ref. 3 as 785,149). The number-averaged molecular weight was $M_n = 17,347$. The Quantum sample, like the others, contained sufficient antioxidant to prevent oxidative degradation during melt processing and during the C_P experiments reported here.

Apparatus

A twin heat-flow calorimeter (Setaram, C.80, Lyon, France) (Fig. 1) has been used for our studies. This

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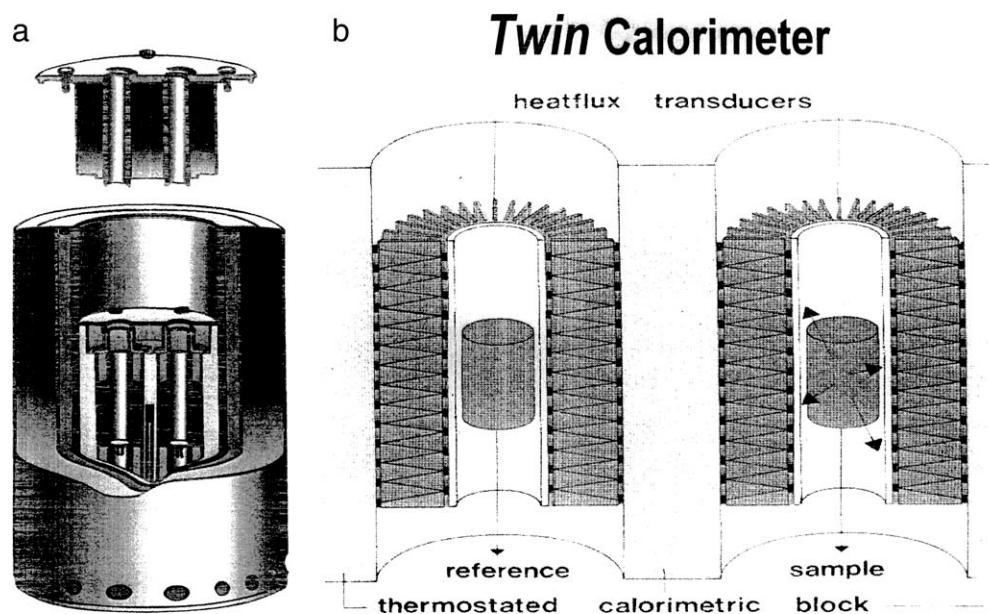*Correspondence to:* M. C. Williams (mike.williams@ualberta.ca).

Figure 1 Block diagrams of heat-flow twin calorimeter. (a) Cutaway of interior, with test and reference cells loaded. (b) Cross-section, showing test sample discharging heat and reference cell discharging none.

calorimeter is more precise than others not only because of its numerous thermopile detectors around the cells (2) but also because of its bigger size of the cells (about 10 mL volume) compared to a few milligrams for a differential scanning calorimeter (DSC). The calorimeter has been calibrated with sapphires from National Institute of Science and Technology (NIST). The C_P values of sapphire have been measured by NIST over a wide range of temperature and are used generally for calorimeter calibration. Details of the calibration method are given elsewhere.[4,5] This calorimeter has two cells, sample and reference. The idea of using the reference cell is to cancel the effect of cell differences during the heating process. However, there could be still a small difference between two cells. We had to run blank/blank (keeping both cells empty) tests at exactly the same conditions as for the heat capacity measurements and subtract the blank/blank signal from the heat capacity signal for each measurement. In this process, the signal of the calorimeter is only from the HDPE sample.

Procedure

The Quantum HDPE sample was placed inside the sample cell and it was flushed with helium gas to remove any oxygen present in the cell before closing it. This eliminated any oxidation of the sample. The presence of helium gas also increased the thermal conductivity in the cells (sample and reference). The heat capacity measurements at a specified temperature with the C. 80 instrument requires that one perform two runs under identical conditions: one

blank/blank where both cells are empty, one with sample measurement, the sample under study is placed in the measurement cell, and reference cell kept empty. After thermal equilibration, the temperature is increased by 2°C intervals at a precisely known rate and the calorimetric signal recorded. In the second test the "reference" run, the cells (both empty) are subjected to the same experimental procedure. Subtracting the signal of the reference run from that of the sample condition allows one to correct for the very slight mass difference between the sample and reference cells. The average C_P over the scanned temperature range (ΔT) is obtained by integrating the corrected calorimetric signal (Q) in the appropriate manner. Then, $C_P = Q/\Delta Tm$, where m is sample mass. Actual experimental temperatures are within 0.08°C of the reported temperatures, and uncertainties in reported heat capacities are estimated to be 0.9%, where the middle temperature of ΔT was taken for the measured heat capacity temperature. The details of the heat capacity measurement method were given elsewhere.[4,5] The precision of our HDPE data is ±5%.

RESULTS

The heat capacities for quantum HPDE at 1 atm on a mass basis over the high-temperature range 180–250°C relevant to melt processing are given in Figure 2. There are no other published data in this range, to our knowledge. The Polymer Handbook[6] contains a graph of $C_P(T)$ (their Fig. 2 in "Results" section) but no data are displayed and the smoothed curve
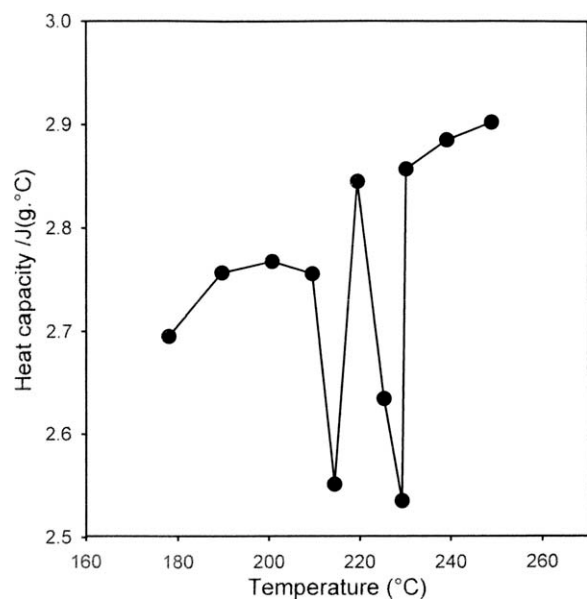
Figure 2 Heat capacity (specific heat) of a sample of HPDE as a function of temperature. The transitions in the melt state occur at $T_1 = 212°C$ and $T_2 = 228°C$. Sample obtained from Quantum Chemical Company.

terminates at about 160°C. They cite a study[7] that was carried only to about 150°C.

In Figure 2, the data points are connected by a line intended only to guide the reader's eye and not represent a continuous function $C_P(T)$.

DISCUSSION

The overall trend of the data in Figure 2, over the interval 180–250°C, is that $C_P(T)$ increases with temperature monotonically in a nearly linear fashion, as might have been expected. However, this trend is interrupted by sharp downward excursions which seem to mark the two transition temperatures, $T_1 = 212°C$ and $T_2 = 228°C$. Thus, the new calorimetry verifies the earlier rheometry findings and similar findings with surface tension and density measurements.[8] The existence of T_1 and T_2 now appears to be incontrovertible.

Explanations for the two high-temperature transitions are not certain. One explanation assigns a previously unsuspected degree of structural order to the melt medium. This would parallel the order in liquid crystal polymers (LCP), which are also known to display high-temperature transitions from one type of meso-structure to another and ultimately to the amorphous condition. However, the nature of structural order in LCP is known to be of long range, which is very difficult to exist in stationary HDPE melts. Existence of structural order in HDPE melts was also suggested by NMR data of Bremner and Rudin,[9] and Kamel and Charlesby[10] suggested

substantial molecular order in the range 140–204°C. In addition, Kolnaar and Keller[11–13] reported an abrupt drop in pressure at 150°C during the capillary extrusion of HDPE, interpreted as because of a structural transition in the melt ordering at that temperature. Furthermore, the rheological measurements of the first normal stress function (N_1) reveal peculiarities[14] that are seen only with LCP melts and solutions of nematic character. Melt short range ordering in linear HDPE or in linear segments of linear-low-density PE (LLDPE) could also be the reason for the reported immiscibility of PE blends as discussed elsewhere.[15] That is, blends of HDPE with other PE (e.g., low-density PE and LLDPE) appear not to form miscible melts despite their chemical similarities which might predict mutual solubility. Instead, the viscosity of such blends resembles that of emulsions. This sort of behavior seems consistent with HDPE having structure which can be ruptured in the blending process, to form particles that are dispersed in a medium of the other PE having different structure or none.

CONCLUSIONS

a. The heat capacity of HDPE melts at temperatures of processing operations is much different than normally believed, with negative excursions from an increasing $C_P(T)$ at $T_1 = 212°C$ and $T_2 = 228°C$. These excursions can be as much as 0.25 J g^{-1} °C^{-1} (T_1) and 0.32 J g^{-1} °C^{-1} (T_2), which can be significant in heat-balance equations for processing.

b. Values of T_1 and T_2 measured for C_P agree with measurements made by rheology, surface tension, density, and DSC.

c. Explanations for these transitions await further research, but are believed to be related to structural order in HDPE melts. The nature of this order was not investigated.

References

1. Hussein, I. A.; Williams, M. C. Macromol Rapid Commun 1998, 19, 323.
2. Hussein, I. A.; Williams, M. C. J Appl Polym Sci 2004, 91, 1309.
3. Hussein, I. A.; Williams, M. C. Macromolecules 2003, 33, 520.
4. Maham, Y.; Hepler, L. G.; Mather, A. E.; Hakin, A. W; Marriott, R. A. J Chem Soc Faraday Trans 1997, 93, 1747.

5. Handa, Y. P.; Hawkins, R. E.; Murphy, J. J. J Chem Thermodyn 1984, 16, 623.

6. Brandrup, J.; Immergut, E. H., Eds. Polymer Handbook, 2nd ed.; Wiley: New York, 1975, Section III, p. 216.

7. Wunderlich, B.; Dole, M. J Polym Sci 1957, 23, 201.

8. Chan, C. V.; Elliot, J. A. W.; Williams, M. C. J Appl Polym Sci 2003, 90, 4061.

9. Bremner, T. J.; Rudin, A. J Polym Sci Polym Phys Ed 1992, 30, 1247.

10. Kamel, I.; Charlesby, A. J Polym Sci Polym Phys Ed 1981, 19, 803.

11. Kolnaar, J. W. H.; Keller, A. Polymer 1994, 35, 3863.

12. Kolnaar, J. W. H.; Keller, A. Polymer 1995, 36, 821.

13. Kolnaar, J. W. H.; Keller, A. J NonNewtonian Fluid Mech 1997, 69, 71.

14. Hussein, I. A.; Williams, M. C. J NonNewtonian Fluid Mech 1999, 86, 105.

15. Hussein, I. A.; Williams, M. C. Rheol Acta 2004, 43, 602.