Polymer melting: thermal resistance effects in a DSC

Ge Wang and Ian R. Harrison *

Polymer Science Program, Department of Materials Science and Engineering, The Pennsylvania State University, 325 Steidle Building, University Park, PA 16802 (USA)

(Received 23 November 1992; accepted 1 November 1993)

Abstract

Thermal lag has long been recognized as a problem in differential scanning calorimetry (DSC) and a correction procedure that assumes constant thermal resistance is often adopted for application as needed. Using various special sandwiched samples composed of high purity indium and polyethylene films, we have found that thermal resistance varies significantly with location within a polymer sample. Indium foil located near the sample surface melts earlier and most of it melts quickly, compared to indium located in the middle of the sample. Experimental data were analyzed using Gray's theory and excellent agreement was achieved when allowing for heat capacity differences for different locations within the sample. This work provides a more comprehensive understanding of the melting process, and is essential to decoupling instrumental and sample effects.

INTRODUCTION

Differential scanning calorimetry (DSC) has been widely used to study thermal transitions of polymeric materials. Quantitative and qualitative information such as glass transition temperatures, melting temperatures and heats of fusion can be conveniently obtained from DSC thermal curves. However, if quantitative measurements of true peak shape and fine details of the melting process are desired, information is more difficult to acquire.

It is well known that DSC thermal curves are affected by sample size, packing and thermal history [1–5]. Size and packing effects arise primarily because of the low thermal conductivities of polymers which cause temperature gradients within DSC samples. When the temperature of a sample pan is increased, only material that is in direct contact with the pan can change temperature responsively. Material further away from the pan surface, in the interior of the sample, will not be able to respond to change at the same rate; this behavior results in a complicated overall thermal response. Even for low molecular weight, pure materials, the melting peak is not a spike, but rather a peak with finite width and a particular shape.

---

* Corresponding author.

Accurate melting temperatures are therefore difficult to determine, especially for semi-crystalline polymers whose crystalline components can have different melting temperatures, perhaps as a result of differences in lamellar thickness.

In order to compensate for thermal lag, a line is drawn from the unknown's peak maximum to the baseline; the slope of this line is the same as the slope of the leading edge from a reference material's melting peak [6–8]. This method is severely limited as it requires matching thermal conductivity and sample geometry for reference and sample. More importantly, the method is flawed because it assumes a constant thermal resistance throughout the sample. In fact, we will show that thermal resistances for different locations within a DSC sample are not the same.

As part of a larger effort to decouple "instrumental" broadening and "sample" effects, we have investigated the influence of sample size on polymer melting using a unique sample structure. This study revealed a considerable amount of detailed information about the melting process within typical DSC samples. In addition, we were able to calculate thermal resistance differences between a sample's surface and its midpoint.

EXPERIMENTAL PROCEDURE

High density polyethylene (HDPE) blown film with a thickness of ≈0.08 mm was punched into circular pieces using a paper hole punch. The circular film had a diameter corresponding to the inner diameter of our DSC aluminum pans. The average weight of one circular layer of PE film was ≈2 mg. Thin indium foil (thickness, 0.02–0.03 mm; purity, 99.999%) was prepared by pressing 0.1 mm indium foil between clean glass slides separated by a razor blade edge. The indium foil samples had a circular shape whose area was ≈3 mm². Samples with various sandwich structures were made by carefully stacking indium boil and polyethylene films into DSC aluminum pans in different sequences. Three sample configurations represented by In/kPE/In/kPE, kPE/In/kPE and In/kPE are shown in Fig. 1; k is the number of PE films used and stacking sequence is read from left to right.
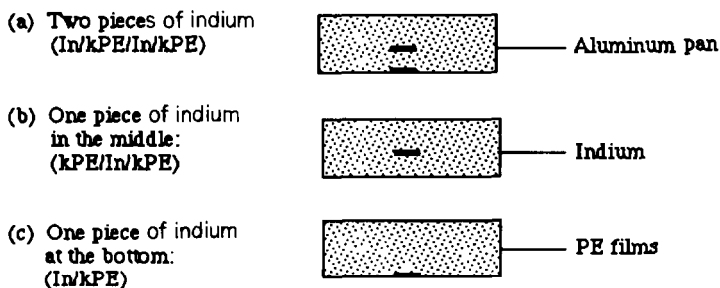

(a) Two pieces of indium (In/kPE/In/kPE) — Aluminum pan

(b) One piece of indium in the middle: (kPE/In/kPE) — Indium

(c) One piece of indium at the bottom: (In/kPE) — PE films

Fig. 1. Sample configurations.

A Perkin-Elmer 7500 DSC instrument was used for all DSC runs. The instrument was previously calibrated at 10°C min^{-1} against a normal indium sample (≈ 5 mg). Argon was used as the purge gas. In all cases, only the indium portion of the melting curve is shown.

THEORETICAL BACKGROUND

When a sample is very small, thermal resistances R for different locations within the sample are practically identical. One can reasonably assume that sample temperature T_s is uniform and equal to that of the container. Based on energy conservation and Newton's law governing the rate of heat flow, Gray derived equations describing the shape of a DSC peak for this type of small sample [9].

The first half of the peak has a leading edge which is a straight line whose slope is governed by thermal resistance and heating rate (see Fig. 2). The peak tail for the second half of the peak is a curve which decays exponentially from peak maximum to baseline. The first and second half-peaks are described by eqn. (1) and (2), respectively

$$\frac{dq}{dt} = \frac{1}{R}\frac{dT}{dt}t \tag{1}$$

$$\frac{dq}{dt} = \left(\frac{dq}{dt}\right)_{max} \exp\left(\frac{-t}{RC_s}\right) \tag{2}$$

where t is time, dq/dt is heat flow rate, dT/dt is heating rate and C_s is the heat capacity of the sample.
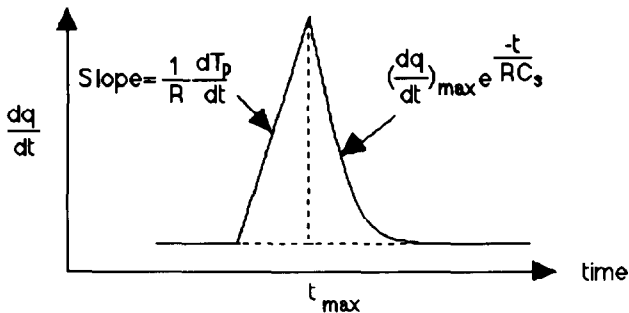

Fig. 2. DSC curve for a sharp transition.

RESULTS AND DISCUSSION

Our initial interest lay in determining the melting point as a function of location within a sample. DSC thermal curves of three samples with In/kPE/In/kPE configurations are shown in Fig. 3. All three thermal curves have the same onset temperature which is the melting point of a
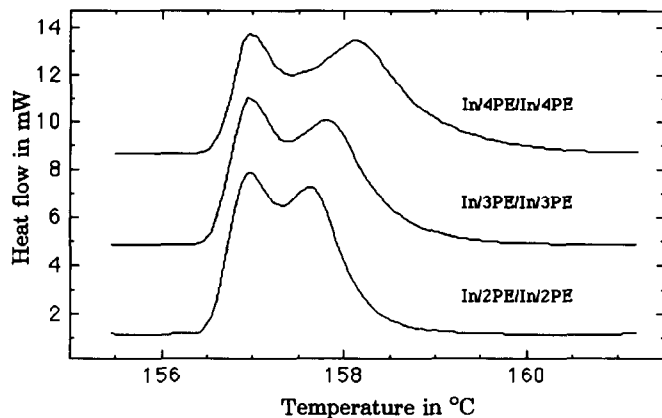
Fig. 3. DSC curve of samples having In/kPE/In/kPE configurations.

"normal" indium. All show two overlapped peaks due to melting of the two indium films located at different positions within the DSC pan. The first, low temperature peak corresponds to melting of the indium located at the bottom of the sample. This indium foil is in direct contact with the highly conductive Al pan and melts first. The second, higher temperaure peak corresponds to melting of indium foil in the middle of the sample. The apparently higher temperature for this middle indium is the result of thermal lag brought about by the PE films which have relatively low thermal conductivities.

Because the two indium foils were approximately the same size, we expect that the two melting peaks would have nearly the same peak height and shape, and that the only difference would be that the second melting peak was shifted to higher temperatures. However, although the peak temperature of the second peak does shift to higher temperatures as expected, the two peaks do not seem to have the same shape. The second peak appears to be somewhat shorter and broader than the first. As the number of separating PE films increases, so does the amount of broadening of the second peak and its peak maximum shifts to higher temperatures.

Broadening of the second peak can be explained by reference to eqns. (1) and (2). One of the important assumptions used in deriving these equations was that sample temperature is uniform throughout the whole sample, as it would be for very small samples. Clearly, the total sample used in this test (indium and PE films) does not fit this criterion and the temperature gradient across such a sample cannot be ignored. However, the two pieces of indium foil are indeed small and do not significantly interfere with each other's temperature profile. Therefore, the individual indium melting transitions can be considered as two separate "sharp" transitions, and can be analyzed separately using Gray's equations.
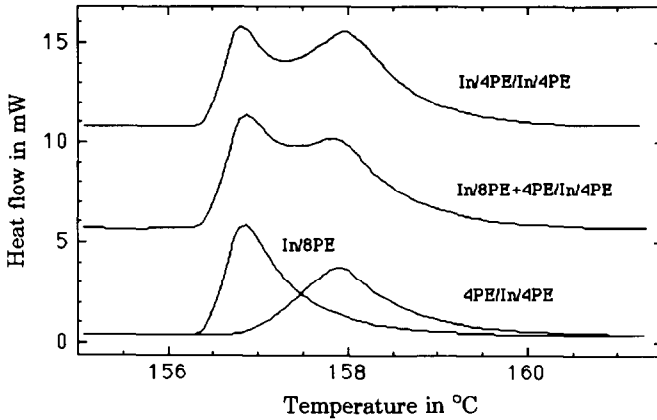
Fig. 4. DSC curves of two separate samples having In/8PE and 4PE/In/4PE configurations (bottom); co-added DSC curves (middle); and DSC thermogram of a sample having In/4PE/In/4PE configuration (top).

In order to analyze the double-foil melting peaks, two samples with In/8PE and 4PE/In/4PE configurations were tested, and their individual DSC curves are shown overlaid at the bottom of Fig. 4. The melting peaks from these two samples should closely simulate the first and second melting peaks observed in a combined sample having an In/4PE/In/4PE configuration. From the separate individual melting peaks we clearly see that the slope of the first melting peak is greater than that of the second. In addition, the onset of melting for indium in the middle of the sample is shifted to higher temperatures. Furthermore, the peak tail for the first peak is longer than that of the second higher temperature peak. Adding these two separate peaks together results in the overlapped peak shown in the middle of Fig. 4 which is very similar to the curve at the top of Fig. 4, obtained by testing a sample containing two indium foils. Although the co-added thermogram and the original double-foil thermogram are similar, certain differences exist which will be discussed in a subsequent paper.

According to eqn. (1), the smaller the value of R, the greater the leading edge slope. For indium located at the bottom of the sample pan, its thermal resistance R_1 is close to the minimum thermal resistance R_0. Thus, the onset slope of the melting peak for this indium is larger. For indium in the middle of the sample, its thermal resistance R_2 is larger than R_1; thermal resistance depends on the length and thermal conductivity of the path through which heat is transferred. Thus, the slope of the second peak is smaller than that of the first peak and the initial half-peak of the second peak appears broader.

In order to derive more detailed information about the melting process in the double-foil samples described above, additional runs were made with
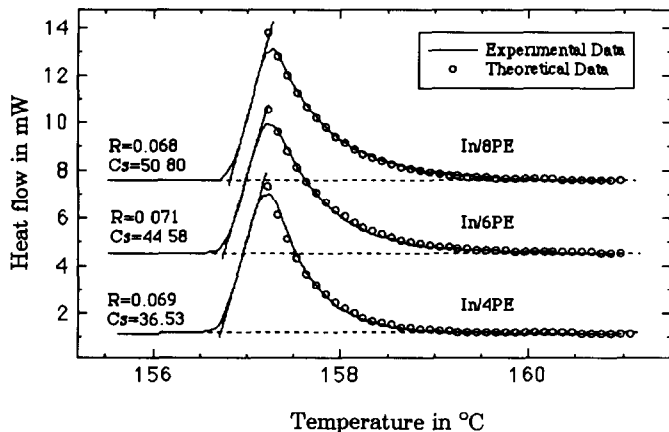
Fig. 5. Indium melting peaks for three samples with different numbers of PE films on top of the indium.

individual indium foils either in contact with the sample pan or in the middle of a stack of PE films. Figure 5 shows DSC melting peaks for three samples having In/kPE-type configurations. Equations (1) and (2) were used to fit experimental data. Thermal resistance was calculated from the leading slope of the peaks and heat capacities were derived from the peak tail using eqn. (2). As can be seen, the fit is surprisingly good. From Fig. 5, we see that as the number of PE films increases from four to eight, the R value is essentially constant and lies between 0.068 and 0.071. Because the path between the heater and the indium sample remains approximately the same for all three samples, their thermal resistance should indeed be similar.

In contrast, the calculated heat capacity C_s has a much stronger dependence on the number of PE films. In the original derivation of eqn. (2), C_s is the total heat capacity of sample material plus sample pan. Intuitively, heat capacity should therefore increase with the number of PE films used, as is observed. The calculated heat capacity increase for every two PE films is ≈ 9 mJ $°C^{-1}$; experimentally we observe ≈ 7 mJ $°C^{-1}$ which is in reasonably good agreement with the calculated value.

DSC curves for three samples with kPE/In/kPE configurations are shown in Fig. 6. In these samples, the distance between heater and indium foil increases with the number of PE films. Therefore, we anticipate an increase in R value as the number of PE films increases; this is manifested as a decrease in the initial slope of the peaks. The average increase in R value caused by two layers of PE film is $\approx 0.06°C$ mW^{-1}. Onset melting temperatures also increase by $\approx 0.3°C$ with every two PE films. However, C_s values are almost the same for all three centrally located indium samples, irrespective of the number of PE films, and are much smaller than the C_s
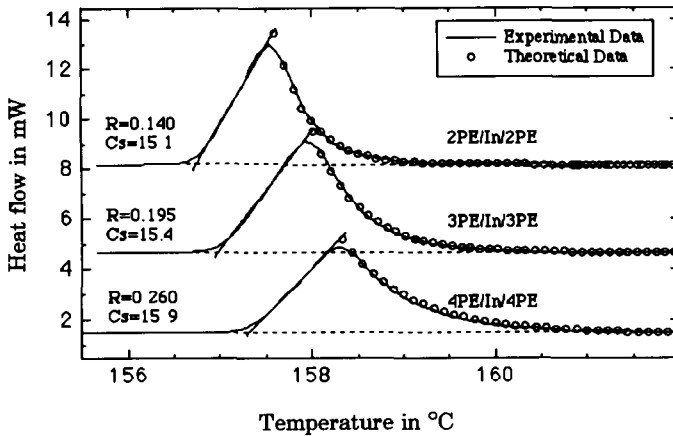
Fig. 6. Indium melting peaks for three samples with different numbers of PE films below and above the indium.

values shown by indium foils in contact with the pan (Fig. 5). When centered indium foil begins to melt, the container and much of the material around the indium has already been brought to a temperature which is a little higher than the melting point of indium. Only a small part of the middle layer of the sample needs to be heated, and it is this small part of the total sample that contributes to the observed heat capacity. The effective sample size for different indium locations is shown schematically in Fig. 7.

Finally, samples with In/2PE/In/2PE/In/2PE/In/2PE/In configuration were tested and a typical DSC thermogram is shown in Fig. 8. A single indium sample with In/8PE configuration is also shown as a reference. These multiple-foil samples are models for the behavior expected from a thick polymer sample composed of identical crystallites with identical sharp melting points. Peak width at half height is considerably broader for the multiple-foil sample compared with the individual foil reference. Clearly even a sharply melting material will have an apparently broad melting peak
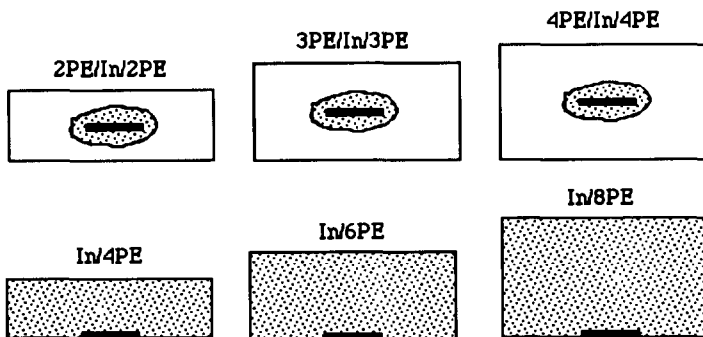

Fig. 7. Schematic representation of effective sample size shown as shaded area for two different sample configurations with different numbers of PE films.
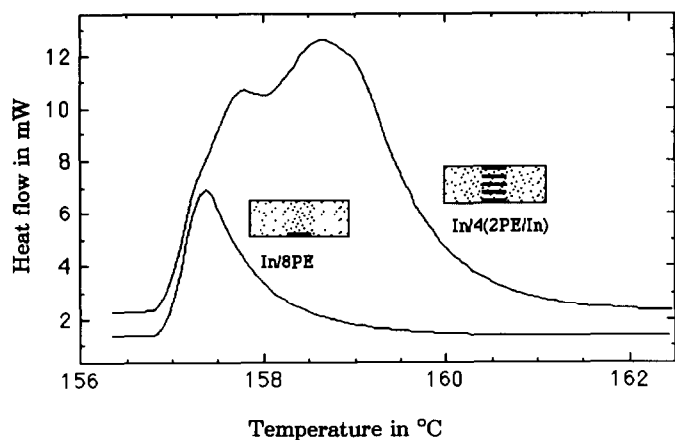
Fig. 8. DSC curves for a sample containing 5 indium foils.

if the components are not in good contact with the pan, and will experience different degrees of thermal resistance and heat capacity effects.

CONCLUSIONS

Using a number of special sandwiched samples consisting of high purity indium and HDPE films, we have been able to reveal detailed information regarding the melting transition in DSC samples. Variation in thermal resistance is quite significant and is a function of location within the sample. Indium foil located near the sample surface melts earlier and most of it melts relatively quickly compared to indium located in the middle to the sample. Differences in indium peak shape and position are observed in samples containing two indium foils. This effect is more obvious as sample size or k increases. These observations clearly suggest that it is not appropriate to use the leading edge of a reference melting peak positioned through a sample maximum to correct for thermal lag.

Peak shape equations based on energy conservation and Newton's law have been successfully used to fit experimental data, provided that heat capacity differences for different locations within the sample are taken into consideration.

The melting behavior of thin indium foils at different locations within a polymer sample closely simulates the situation where identical, sharply melting polymer crystallites are distributed within an amorphous polymer matrix. Therefore a broad melting peak can simply reflect a distribution of crystal locations within a sample and is not necessarily an indication of a distribution of thicknesses of the lamellas. This work provides a more comprehensive understanding of the melting process in a sample pan, and is essentially to our ultimate goal of decoupling instrumental and sample effects.

ACKNOWLEDGMENTS

REFERENCES

1 I.R. Harrison and W.D. Varnell, J. Therm. Anal., 25 (1982) 391.
2 B. Ke, J. Polym. Sci. Part A, 1 (1963) 1453.
3 J. Runt and I.R. Harrison, in R.A. Fava (Ed.), Methods of Experimental Physics, Vol. 16, Part B, Academic Press, New York, 1980, p. 287.
4 E. Pella and M. Nebuloni, J. Therm. Anal., 3 (1971) 229.
5 W.P. Brennan, B. Miller and J.C. Whitwell, in R.S. Porter and J.F. Johnson (Eds.), Proc. Am. Chem. Soc. Symp. Anal. Calorimetry, Chicago, Illinois, September 13–18, 1970, p. 441.
6 Thermal Analysis Newsletter, No. 5, Perkin-Elmer Corporation, Norwalk, CT.
7 G.L. Driscoll, I.N. Duling and F. Magnotta, in R.S. Porter and J.F. Johnson (Eds.), Proc. Am. Chem. Soc. Symp. Anal. Calorimetry, San Francisco, California, April 2–5, 1968, p. 271.
8 A. Wlochowicz and M. Eder, Polymer, 25 (1984) 1268.
9 A.P. Gray, in R.S. Porter and J.F. Johnson (Eds.), Proc. Am. Chem. Soc. Symp. Anal. Calorimetry, San Francisco, California, April 2–5, 1968, p. 209.