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Data Interpretation

Correction of melting peaks of different PE grades accounting for heat transfer in DSC samples

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Abstract

In this work, the effect of heat transfer on the apparent melting behavior of linear low-density polyethylene (LLDPE) and recycled high-density polyethylene (rHDPE) was studied. Experimental melting temperature distributions (MTD) were shown to be significantly affected by the heating rate of the scan and the sample mass. The sample mass dependence of the MTD is attributed to thermal inertia of differential scanning calorimetry (DSC) samples. On the other hand, the heating rate dependence of MTD is in apparent contrast with the thermodynamic nature of the melting process. The existence of temperature gradients, responsible for heat transfer in DSC samples, was explained by adimensional analysis and evaluation of the Biot and Deborah numbers. A previously introduced equation was used to model melting behavior of the polymers. The parameters from non-linear regression were shown to be dependent on the product between the scanning rate and the square of sample mass. Regression parameters were extrapolated at infinite Deborah number. The MTD obtained at infinite Deborah number was considered the real MTD of the polymer, and was coupled with a heat transfer model to calculate the actual temperature of the sample. The local rate of heating, multiplied by the true MTD, provided the local rate of melting. The average rate of melting was compared with the experimental DSC signal. The very close agreement of the experimental and numerical prediction results evidence that the observed differences between melting curves obtained at different heating rates and sample mass can be attributed to thermal gradients in the DSC sample.

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1. Introduction

Differential scanning calorimetry (DSC) is a widely used technique used for the evaluation of the enthalpy and temperature of melting of semicrystalline polymers. To obtain accurate measurements, calorimetric measurements should be made under very slow heating rates, to ensure thermodynamic reversibility of the process [1]. Nevertheless, if the melting or crystallization behavior of the material needs to be characterized at higher heating or cooling rates, such as those typically involved in polymer processing, DSC experiments are performed at higher scanning rates (5–50 K/min), which may be responsible for experimental errors, mainly due to two distinct effects:

- The thermal resistance between the sample holder and the oven [2,3]. This effect is scanning

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rate dependent and can be corrected through instrument calibration [2,4].

- Thermal gradients within the DSC sample [1,2,5]. This effect depends on scanning rate, sample mass and thermal diffusivity [4], and cannot be corrected through instrument calibration. This arises from the much higher thermal diffusivities of calibration standards (i.e. indium and zinc), compared with that of polymers [6].

Different approximate methods have been proposed to account for the effect of thermal gradients within the DSC sample [1,4]. Other proposed methods are based on the solution of non-steady-state conduction equations accounting for heat transfer in the sample [3,7–9]. These approaches, however, do not account for the presence of phase transitions during the DSC scan, which strongly affect heat transfer [10]. Further, most of the reported works only deal with numerical prediction, without comparison with experimental data or validation of the numerical method. This is mainly due to the lack of adequate analytical techniques to measure the temperature of the DSC sample. Only recently, a high-speed infrared camera was used to measure the temperature on the top surface of samples in temperature modulated DSC (TMDSC) [8,11,12], in a temperature range far above the melting temperature range. Accordingly, the heat transfer model used for comparison with experimental data does not incorporate enthalpy terms accounting for phase transitions.

The melting process is not significantly affected by kinetics, as is the case of crystallization [13–17], because for melting no nucleation is needed. In a previously reported study, the melting behavior of linear low-density polyethylene (LLDPE) was shown to be dependent on the scanning rate [18]. In the absence of kinetic-related phenomena, this observation was attributed to the non-uniform temperature in the sample, and to the existence of temperature differences between the programmed DSC oven temperature and the actual sample temperature [19], ultimately leading to inaccurate measurements.

Recently, some authors studied the melting behavior of different polymers by means of conventional heat flux DSC or TMDSC, introducing the hypothesis of superheating during polymer crystal melting [20–23]. According to this kinetic approach, melting of polymer crystals follows the melting temperature distribution (MTD) with a retardation time, mainly depending on the scanning rate and the melting kinetic of each crystallite. In deriving the kinetic expression for melting of different polymers, temperature gradients in the polymer sample were neglected, and a uniform temperature in the DSC sample was assumed.

In other cases, the heating rate dependence of melting curves was attributed to the occurrence of melting, re-crystallization and re-melting effects taking place at high temperatures, when thickening of crystalline lamellae can take place. Such phenomena usually involve different effects on the melting endotherms derived from DSC analysis, including

- shifting to higher temperatures for slower heating rates, as a consequence of the increasing crystallization rate [24–26];
- multiple melting endotherms associated with the alternating effects of melting and crystallization [26].

In this work, the melting behavior of LLDPE and recycled high-density polyethylene (rHDPE) was studied at different scanning rates and sample masses. Experimental melting curves were compared with a previously introduced thermodynamical model [18]. The equivalence of sample mass and scanning rate on the shape of MTD was assessed by plotting the parameters from non-linear regression as a function of the product of the scanning rate by the square sample thickness. The existence of a single master curve accounting for the simultaneous effect of scanning rate and sample mass indicates that the observed differences between the MTD obtained at different scanning rates can be entirely attributed to heat transfer effects for the polymer under investigation. On the other hand, no kinetic effect during melting was observed, for the system under investigation, in the time scales which are typical of a continuous heating scan. The true MTD of different PE grades was obtained by extrapolating experimental MTD at infinite Deborah number. In previously reported works [1,27,28], the extrapolated zero heating rate distribution was regarded as the true melting temperature of various calibration standards. In order to account for the heating rate and sample mass dependence of melting curves for LLDPE and rHDPE, the true MTD was coupled with a heat transfer model based on an enthalpy method, to evaluate the temperature in the sample as a function of time and heating rate.

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