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# TEMPERATURE-MODULATED DIFFERENTIAL SCANNING CALORIMETRY

## IX. Some comments on the rigid amorphous fraction in semi-crystalline poly(ethylene terephthalate)

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## Abstract

The increment of heat capacity at the glass transition for semi-crystalline poly(ethylene terephthalate) (PET) observed by temperature-modulated differential scanning calorimetry (TMDSC) shows significant deviations from a simple crystalline/amorphous two-phase model. Introduction of a rigid amorphous fraction, which is non-crystalline but which also does not participate in the normal glass transition, allows a much better description of the transition behaviour in semi-crystalline PET. Certain questions arise such as what is the rigid amorphous fraction and over what temperature range do these rigid amorphous segments devitrify? These TMDSC results show that the rigid amorphous component may be treated as an interphase between amorphous and crystalline phases. This interphase does not exhibit a separate glass transition temperature at temperatures above the normal $T_g$. The suggestion is made that the glass transition of the rigid amorphous component occurs continually between the glass transition temperature of the amorphous phase and up to about 135°C for this particular sample of PET.

**Keywords:** crystallinity, heat capacity, PET, TMDSC

## Introduction

As the level of crystallinity increases in a semi-crystalline polymer, the increment of heat capacity over the glass transition, $\Delta C_p$, decreases. Assuming that a simple additivity rule applies to the two-phase model (amorphous and crystalline phases only), the decrease of $\Delta C_p$ should be directly proportional to the increase in crystallinity. This is not always observed to be the case. However, in practice, DSC experiments frequently are not conducted with sufficient care and accuracy to distinguish this discrepancy [1–4]. The amorphous fraction ($\chi_a$) is seen to be smaller than the non-crystalline fraction ($1-\chi_c$). Wunderlich *et al.* [1, 2] introduced a third fraction, which is non-crystalline, but which also does not participate in the main glass transition. They refer to this fraction as rigid amorphous ($\chi_r$). It is further defined by Eq. (1).

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$$\chi_r = 1 - \chi_c - \chi_a \tag{1}$$

The following questions arise. Where is the missing heat capacity? What is the detailed nature of this rigid amorphous fraction? When do the chain segments in this rigid amorphous fraction vitrify/devitrify?

In this short communication, the differential of heat capacity with respect to temperature ($dC_p/dT$) signal from temperature-modulated differential scanning calorimetry (TMDSC) has been used to study the above questions. This signal has previously been shown [5] to be sensitive to the existence and amount of interfacial materials in multi-component polymer systems.

## Experimental

The amorphous PET used in this study was obtained from ICI. $M_n$ and $M_w$ values were 9200 and 18400, respectively. They were determined using gel permeation chromatography calibrated with polystyrene standards.

Prior to all the calorimetry experiments, the PET was dried in vacuum at 80°C for 24 h.

Samples for the melt crystallization experiments were preconditioned in the DSC cell by cooling from the melt state to 0°C at rates of 5 and 30°C $\mathrm{min}^{-1}$. The samples were first held at 300°C for 10 min to ensure complete melting.

A TA Instruments 2920 TMDSC and their DSC were used for these thermal property measurements. Both temperature and base line were calibrated as for conventional DSC. The TMDSC (and DSC) heating rate was 3°C $\mathrm{min}^{-1}$. The modulation amplitude and period were ±1.0°C and 60 s, respectively. Sample mass was between 7 and 9 mg and the experiments were performed under a nitrogen flow of 35 mL $\mathrm{min}^{-1}$. In these experiments, because we were only interested in the increment of heat capacity, $\Delta C_p$ value was calibrated according to the method shown in literature [6].

## Results and discussion

Figure 1 shows the heat flow *vs.* temperature plots for the dried as supplied amorphous PET and the PET samples which were cooled from 300 to 0°C at 5 and 30°C $\mathrm{min}^{-1}$, respectively. For the amorphous PET sample, the crystallinity was found by experiment to be equal to zero when calculated according to the method suggested by Wunderlich [1]. The value of the increment of heat capacity was found to be 0.35 J $\mathrm{g}^{-1}$ °$\mathrm{C}^{-1}$.

Comparing the amorphous sample and the PET sample cooled from the melt at 30°C $\mathrm{min}^{-1}$, it can be seen the amorphous PET shows a two-peak crystal-

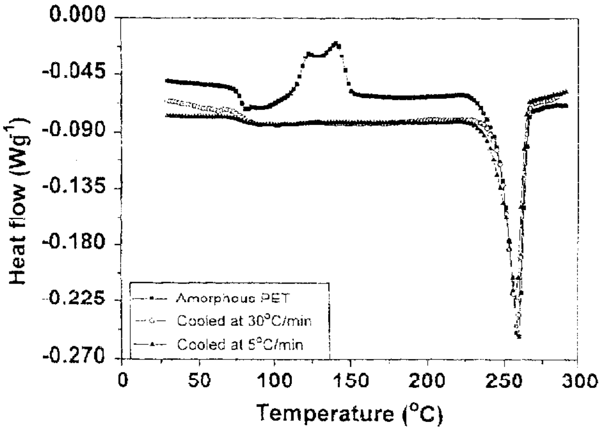

**Fig. 1** Heat flow *vs.* temperature for the amorphous PET and the PET samples cooled at 5 and 30°C min$^{-1}$

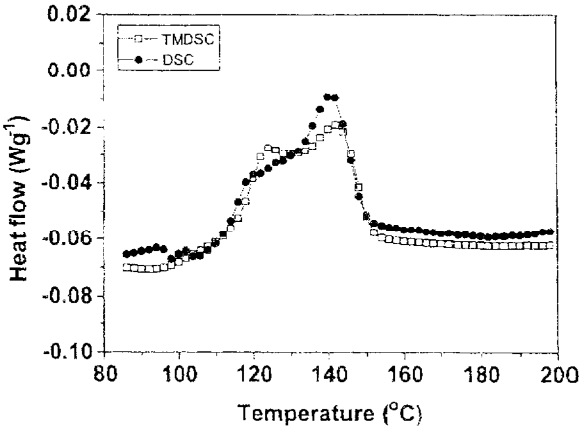

**Fig. 2** Comparison for the recrystallization heat flow *vs.* temperature signals obtained from TMDSC and DSC

lization exotherm at around 130°C. This result has been repeated several times and was found on every occasion. Figure 2 gives a comparison for the results from TMDSC and DSC. For the PET sample, the nature of this two-peak crystallization exotherm does not result from the modulation process.

Figure 3 shows the differential of heat capacity, $dC_p/dT$, which was obtained directly from TMDSC, *vs.* temperature signal for PET samples with different thermal histories. It can be seen that the $dC_p/dT$ *vs.* temperature data for the amorphous PET was distinctly lower than that for other two PET samples be-

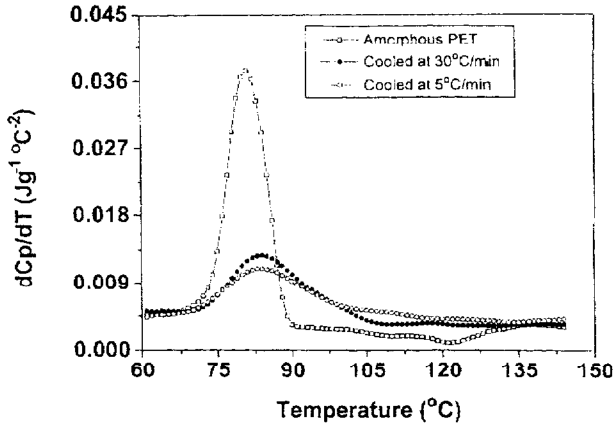

Fig. 3 d$C_p$/d$T$ *vs.* temperature signals for the PET sample with different thermal histories

tween the glass transition of the amorphous phase and 135°C. What is its physical meaning of this observation?

From the calculations of $\Delta C_p$ and crystallinity, there is not a one-to-one correspondence between crystallinity and the increase in heat capacity in the glass transition interval [1]. Such a deviation may be caused by molecular segments whose mobility is restricted, despite being at least partially located in the amorphous phase. When the morphology of semi-crystalline polymers is described by the two-phase model, it can be imagined that the transitions related to amorphous and crystalline phases will be separated. When the morphology exhibits an interphase, the transitions in such a system will not be separated. This point has been proved [5, 7, 8] in amorphous polymer–polymer blends. Here we give another example for such a situation. Figure 4 shows the change of d$C_p$/d$T$ signals *vs.* temperature for a poly(methyl methacrylate) core-poly(vinyl acetate) shell latex particle film [9, 10] and the physical blend of these core and shell materials. These core–shell latex particles are believed [10, 11] to have a three-phase morphology: the shell, an interphase between core and shell phases and the core phase. Between 50 and 100°C, the d$C_p$/d$T$ value for core–shell latex film is distinctly larger than that for the physical blend. This difference, we believe [10, 11], results from the interphase between core and shell phases.

Comparing Fig. 3 with Fig. 4, the behaviour of d$C_p$/d$T$ *vs.* temperature signal between 90 and 135°C for the PET cooled at 5 or 30°C min$^{-1}$ is similar to that between 50 and 100°C for the core–shell latex film. It is possible that the change of d$C_p$/d$T$ *vs.* temperature signal between 90 and 135°C for the PET cooled at 5 or 30°C min$^{-1}$ results, similarly, from an interphase between amorphous and crystalline phases. It can be judged from the following experiments, whether or not

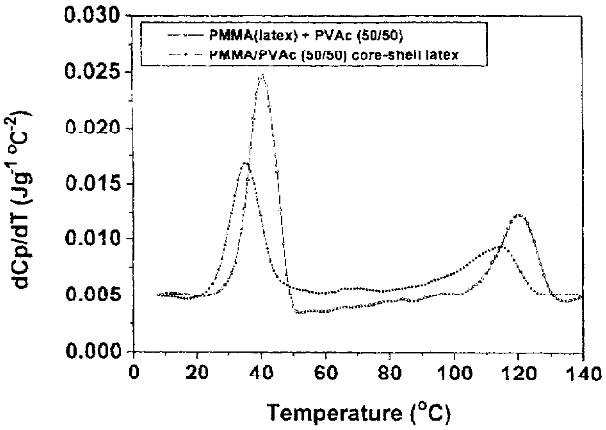

**Fig. 4** $dC_p/dT$ *vs.* temperature signals for a core–shell latex particle film and the physical blend of core and shell materials

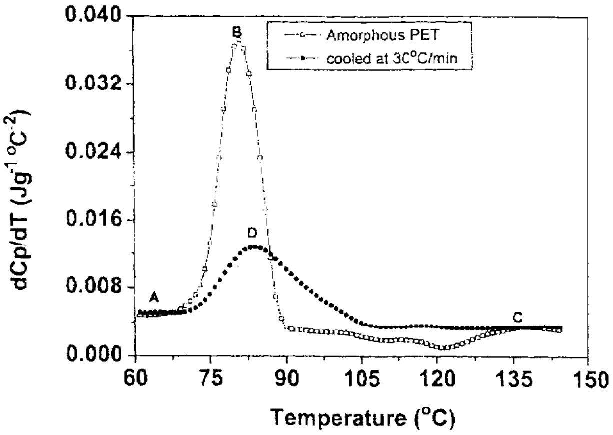

**Fig. 5** $dC_p/dT$ *vs.* temperature signals for the amorphous PET and the PET cooled at 30°C $\mathrm{min}^{-1}$

the change of the $dC_p/dT$ *vs.* temperature signal between 90 and 135°C for the PET cooled at 5 or 30°C $\mathrm{min}^{-1}$ results from interphasial zones between the amorphous and crystalline phases. Choosing different cooling rates to make samples with different degrees of crystallinity or rigid amorphous fraction, the values of $dC_p/dT$ *vs.* temperature signal between 90 and 135°C would decrease as the weight fraction of amorphous phase increases. Indeed, the values of the $dC_p/dT$ *vs.* temperature signal between 90 and 135°C decrease for the PET cooled at 30°C $\mathrm{min}^{-1}$ compared to PET cooled at 5°C $\mathrm{min}^{-1}$.

For the PET sample cooled at 30°C $\mathrm{min}^{-1}$, the heat of fusion was about 46 J $\mathrm{g}^{-1}$. The calculation was conducted based on the integration of the heat flow signal.

This makes the crystallinity about 38%, when 120 J $g^{-1}$ [11] is taken as the heat of fusion for a 100% crystalline PET sample. Based on the $dC_p/dT$ *vs.* temperature signals shown in Fig. 5 for the amorphous PET and the PET cooled at 30°C $min^{-1}$, the difference of the area of curve ABC and ADC divided by 0.35 J $g^{-1}$ $°C^{-1}$ would be equal to the degree of crystallinity, i.e.,

$$\delta C_p/0.35 = \int_{68}^{135} (\text{curve ABC} - \text{curve ADC})dT/0.35$$

This procedure yields a value of 0.37. For the PET sample cooled at 5°C $min^{-1}$, the crystallinity changes little compared with the PET cooled at 30°C $min^{-1}$. Only the rigid amorphous fraction increases (Fig. 3).

For the above calculation, the limits of the integration were considered to be the start point of the glass transition and the point at which the value of $dC_p/dT$ is the same for both amorphous and semi-crystalline PET. As far as the base-line is concerned, it is not important for the difference of integration. Here, the value 0 for $dC_p/dT$ was chosen as the base-line in the integration. The 0.37 value is within experimental error the same as 0.38.

So, we suggest that a three-phase model does adequately represent the observed behaviour, at least for this semi-crystalline polymer. This model has an amorphous phase, an interphase and a crystalline phase.

## Conclusions

The rigid amorphous component can be regarded as an interphase between amorphous and crystalline phases. This rigid amorphous fraction does not exhibit a separate glass transition temperature, but the glass transition of the rigid amorphous component occurs continually between the glass transition temperature of the amorphous phase up to about 135°C for this sample.

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