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Short communication

Quenching of polymer inside aluminum DSC pans: Origin of an apparent artifact

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ABSTRACT

To obtain amorphous polymer samples for thermal analysis by differential scanning calorimetry (DSC), a typical procedure involves quenching the sample, which is encapsulated inside an aluminum DSC pan and lid, into liquid nitrogen or liquid nitrogen-cooled glass beads. We demonstrate that this procedure can cause an artifact endotherm in the subsequent DSC scan of the polymer. The artifact is not related to the polymer sample itself, but is possibly due to phase change of surface moisture introduced during the process of transferring into the DSC cell. A procedure to eliminate the artifact is discussed.

In polymer thermal analysis, it is often desirable to obtain an amorphous film, so as to measure the amorphous solid state heat capacity below T_g, to measure the heat capacity step at the glass transition (T_g) of the fully amorphous state, or to study the cold-crystallization kinetics above T_g. A typical procedure involves quenching the polymer sample, which is encapsulated inside an aluminum differential scanning calorimetry (DSC) pan and lid, into liquid nitrogen (LN_2). Since a hot DSC pan and lid cause the immediate evaporation of LN_2, with formation of an insulating layer of nitrogen gas, an improvement in heat transfer was suggested [1–3] whereby the DSC pan containing the sample was quenched into LN_2-cooled glass beads.

This quenching procedure was applied to poly(butylene terephthalate), PBT, a relatively well-known thermoplastic semicrystalline polymer and a type of polyester [4,5]. The glass transition temperature, T_g, of PBT is reported to range from 295 to 354 K [1,2,6–9]. For quenched amorphous PBT, an apparent "lower T_g" was observed between 225 and 255 K from DSC measurements [1]. The quenched amorphous PBT was obtained by quenching molten PBT, sealed in an aluminum DSC pan and lid, either into liquid nitrogen (LN_2) or into LN_2-cooled glass beads [1,2]. Then the aluminum DSC pan containing the polymer was transferred immediately into the DSC cell and kept at a temperature lower than 255 K [1,2]. Recently, Pyda et al. [2] reported that the "lower T_g" was actually an irreversible endotherm, and was not caused by a glass transition relaxation of either the mobile or the rigid amorphous PBT fractions. In the present work, we report that the apparent "lower T_g" [1] is not caused by any transition of the PBT itself. A possible origin of this artifact may be phase change of condensed moisture on the surface of the pans.

PBT was obtained from Scientific Polymer Products (#962) in pellet form. Nylon-6 (resin grade #8082) was obtained from Honeywell in pellet form. Both PBT and Nylon-6 pellets were first compression-molded from the melt (533 K) and cooled to room temperature to obtain film samples. The films were encapsulated into an aluminum DSC pan and lid using a hand operated mechanical press, and then heated to the polymer melting point in a Mettler hot stage. The DSC pan containing the molten polymer was quenched into LN_2 and transferred rapidly into the DSC cell and kept at 223 K for DSC measurements. Similar experiments were conducted using quenching into LN_2-cooled glass beads. For comparison, an empty, quenched aluminum pan and lid were subjected to the same mechanical pressing history and the same thermal history. They were quenched into LN_2 from 533 K (or, in one case from room temperature) and then transferred quickly into DSC cell and kept at 223 K prior to scanning.

DSC studies were carried out using a TA Instruments DSC (TA Q100). The reference was an empty aluminum pan and lid with mass matched to that of the sample pan and lid. The reference pan and lid received no thermal treatment. Indium was employed for the temperature and heat flow calibration. The heat capacity was evaluated with respect to sapphire standard. Dry nitrogen gas was purged into the DSC cell with a flow rate of 50 mL/min. All DSC measurements were performed at a heating rate of 5 K/min.

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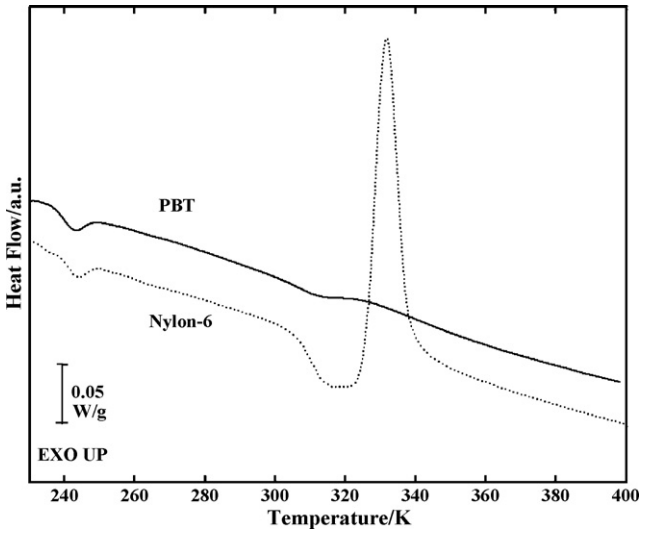

Fig. 1. Heat flow vs. temperature at 5 K/min of quenched PBT (solid line) and quenched Nylon-6 (dotted line). The samples were encapsulated in aluminum DSC pan and lid, and then quenched into liquid nitrogen. Curves are displaced vertically for clarity. An artifact from the quenching appears at about 243 K.

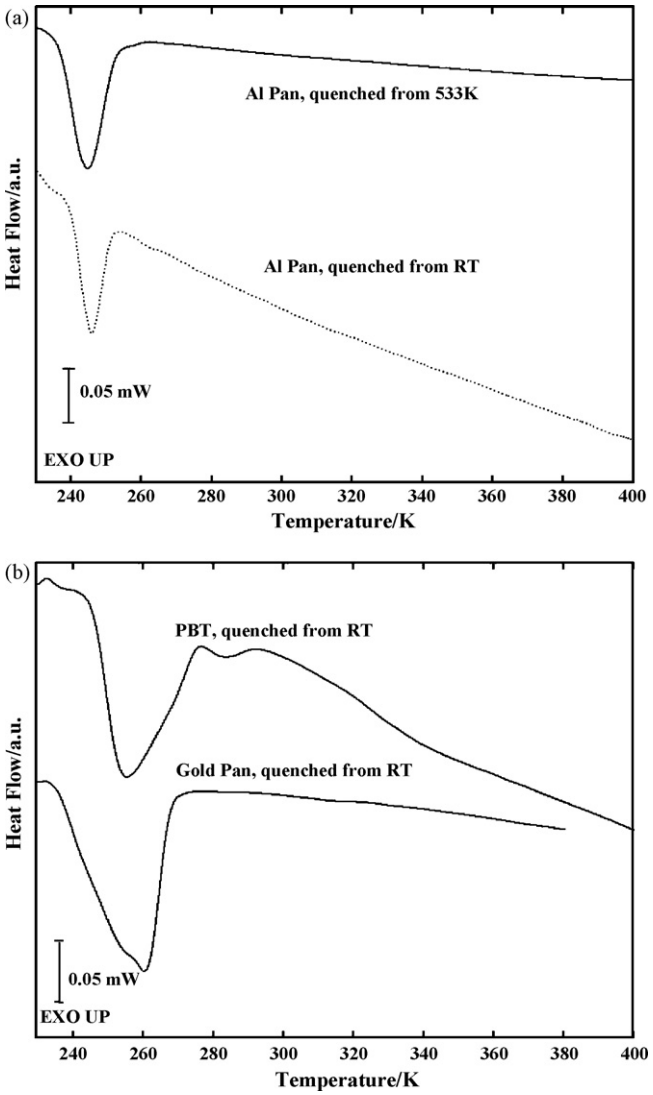

Fig. 2. (a) Heat flow vs. temperature at 5 K/min of aluminum pan and lid quenched into liquid nitrogen, either from 533 K (solid line) or from room temperature (RT, dotted line). (b) PBT without encapsulation in any pan (upper curve), and empty gold pan (lower curve). Curves are displaced vertically for clarity in both parts of the figure. Differences in the masses of the pans and lids account for the difference in the slopes of the heat flow curves.

Endotherms are presented with downward deflection in our scans.

Fig. 1 shows the DSC curves for quenched PBT and Nylon-6, both encapsulated in Al DSC pan and lid, from 230 to 400 K. The glass transition of Nylon-6 is observed at about 308 K and immediately above T_g, the sample starts to crystallize, as indicated by the large and distinct exothermic peak. The glass transition of PBT is observed at about 312 K and it, too, started to crystallize immediately after the glass transition but the exothermic peak is broad and flat. In addition, in both samples, a lower endothermic peak is observed at about 243 K. This peak was considered as a "lower glass transition" in previous studies of PBT [1]. However, recently Pyda et al. [2] used temperature-modulated DSC (TMDSC) to separate the reversing and non-reversing components in the vicinity of the "lower T_g". They suggest the feature should be interpreted as a non-reversing endothermic peak of PBT which was difficult to reproduce, but in any case should not be considered as the major glass transition of PBT [2].

DSC curves are shown in Fig. 2a for empty aluminum pan and lid, quenched either from 533 K (solid curve) or from room temperature (dotted curve). An endothermic peak was observed for empty aluminum pans and lids, at a temperature very close to the position of the lower endothermic peak seen in the scans of quenched PBT and Nylon-6 (see Fig. 1). Aluminum pans from both TA Instruments and PerkinElmer showed the same effect when they were quenched. We conclude that the endothermic peak is not related to the relaxation of the polymer samples.

To investigate the origin of this artifact, we performed additional studies using a gold pan. A DSC curve is shown in Fig. 2b for a gold pan without a lid (lower curve) quenched from room temperature into liquid nitrogen. An endothermic peak was observed for the gold pan, at a temperature a little higher than the position of the lower endothermic peak seen in the scans of aluminum pans and lids (see Fig. 2a). This test indicates the artifact is not related specially to the selection of aluminum pans and lids.

The artifact is also not related to the use of metal pan and lid. Shown in the upper curve of Fig. 2b is a PBT sample cut from film, not encapsulated inside any pan, and quenched from room temperature into liquid nitrogen before transfer to the DSC cell. This sample scan shows that the large endothermic peak appears even in the absence of the aluminum, and occurs at a temperature very close to the position of the lower endothermic peak seen in the scans of aluminum pans and lids (see Fig. 2a). The common element among all these samples is the transfer from the liquid nitrogen, through air, into the DSC cell. Although this takes only a few seconds, still it is possible that moisture can condense onto the sample during this time.

As noted, this artifact that can be misinterpreted as coming from the polymer sample encapsulated inside the DSC pan and lid. Since the procedure for quenching molten polymers is an often-used approach, we present below a strategy for removing the endothermic "artifact" from the DSC traces.

Fig. 3 shows the DSC curves of quenched PBT and Nylon-6, encapsulated in Al DSC pan and lid, and a quenched empty aluminum pan and lid, after annealing at 273 K for one minute. The endothermic peak below 273 K is no longer observed in any of the annealed samples. This indicates that the endothermic peak: (1) is not caused by polymer itself; (2) results from an irreversible process and can be removed by annealing. The annealing we used, a

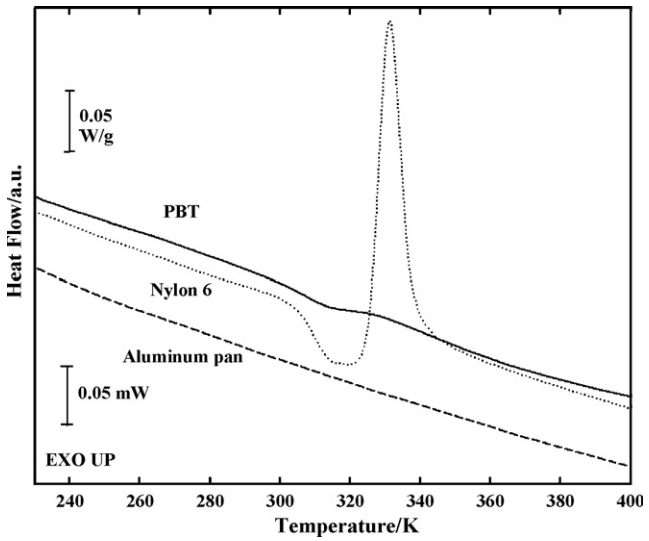

Fig. 3. Heat flow vs. temperature after annealing, for PBT encapsulated in Al pan and lid (solid line), Nylon-6 encapsulated in Al pan and lid (dotted line), and empty aluminum pan and lid (dashed line). The vertical axis scaling is in units of W/g, for PBT and Nylon-6 (normalized for sample mass), or mW, for the aluminum pan and lid. Curves are displaced vertically for clarity.

1-min anneal at 273 K, was sufficient to remove the spurious peak. We also performed slow cooling experiments from 533 to 223 K at cooling rates of 10 and 5 K/min. In these types of experiments with aluminum pans, no endothermic peak was observed below 273 K. In cases where the annealing treatment cannot be used, it may be necessary to place the DSC instrument into an inert atmosphere glove box to prevent moisture condensation.

To obtain the fully amorphous polymers such as PBT and Nylon-6 which have glass transitions just above room temperature, the rapid cooling method (quenching) is typically used. And, for DSC measurements, normally the polymer is rapidly cooled while it is encapsulated within the aluminum DSC pan. In the present work, we show that the endothermic peak observed at about 243 K is an artifact, not due to the polymer relaxation, and can be removed by annealing at room temperature.

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