DSC ANALYSIS OF POST-YIELD DEFORMED PBT
Effects of thermal history

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The effect of the deformation temperature on the energy stored in post-yield deformed poly(butylene terephthalate) PBT, was studied by means of DSC tests. Deformed specimens were rapidly cooled after unloading, in order to avoid the energy relaxation processes occurring before the DSC measurements. Cooling revealed to have a significant contribution on the whole stored energy, as shown by DSC tests conducted on undeformed PBT specimens conditioned at various temperatures. This work is aimed at separating the effects due to cooling and those ascribed to deformation on the energy storage and release processes, permitting to better understand previous findings on post-yield compressed PBT.

Introduction

In previous papers [1, 2] the energy stored in post-yield deformed semicrystalline poly(butylene terephthalate) (PBT) was measured by differential scanning calorimetry (DSC) tests, following an approach widely employed on amorphous and semicrystalline polymers [3–11] and well covered in books and review articles [12–15]. Our investigation focused on the effects of strain, strain rate and deformation temperature on the stored energy and the results can be summarized as follows: *i*) for a fixed deformation temperature the stored energy increases with strain; *ii*) for a given deformation at room temperature the stored energy increases with strain rate; *iii*) for a fixed strain rate stored energy decreases as the deformation temperature increases.

DSC measurements are a powerful methodologies not just for the evaluation of the stored energy amount, but also for the investigation of the energy release process of post-yield deformed polymers. On the basis of this analysis it was possible to compare the energy release with the strain recovery process. This comparison was performed with varying the ageing time [3, 4, 12, 13] and temperature [6, 7, 12, 13, 16]. This latter effect was studied by thermal scansions performed within the approach of so-called thermally stimulated recovery (TSR) methodology. As a result, a common nature for the two processes was evidenced. In addition, DSC experiments have the important capability, with respect to other methods such as deformational calorimetry, to reveal changes in the crystallinity content and structure, as for example in the case of the strain induced crystallization in highly stretched materials [17–20].

A thermodynamic approach to the investigation of large deformations in polymers was often applied by means of deformational calorimetry, which furnished relevant information on the heat dissipated during the deformational processes [15, 21–25] and permitted to evaluate the amount of energy stored in the material [3, 4, 26–30]. For the evaluation of stored energy this technique is believed to convey more precise results with respect to alternative methods [15]. In fact, although a generally good agreement between the various techniques is found, methods such as DSC measurements and heat of dissolution calorimetry provide lower values for the stored energy [15]. The reasons of the lower energies measured have to be addressed to the specimens physical ageing and the relaxation of internal energy during the time elapsed between deformation and measurement; on the contrary, this problem does not arise with deformation calorimetry, since stored energy is measured during the experiment. Godovskii reported these differences for plastically compressed polystyrene (PS) [15]. The effect of the relaxation time was studied by Müller and co-workers, in dissolution calorimetry experiments on poly(vinyl chloride) (PVC), revealing that this difference can be rather high (around 75%) in the case of a 12 h aging at room temperature [26, 31]. Further, by

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means of DSC experiments Oleyinik and co-workers studied how the ageing time affects the energy release process, revealing that, in addition to the loss in the measured stored energy, the onset temperature for the energy release process shifts to higher values as the relaxation time increases [3, 4, 12, 13].

These considerations highlight the non-negligible effect of the specimen thermal history after deformation when the energy storage is evaluated by DSC. Thus, in a previous paper [1], when adopting this investigation technique, we tried to have maximum information on the stored energy in our samples by cooling them in liquid nitrogen at the end of the loading-unloading cycle, in order to hinder the relaxation process. Since no information is available about the effect of the cooling stage on the stored energy, in the present work this effect is investigated and the previous results re-examined and discussed, with particular reference to those concerned with specimens deformed at various deformation temperatures.

Experimental

DSC analyses were conducted on undeformed specimens subjected to various thermal histories. Specimen geometry and DSC test parameters were chosen consistently with the testing conditions reported in our previous paper [1] for the deformed specimens.

Cubic specimens (5.5×5.5×5.5 mm) were machined from injection moulded PBT rectangular test bars (127×12×6 mm) kindly supplied by Radici Novacips SpA (Villa d'Ogna, Bergamo, Italy). All specimens were treated for 3 h at 190°C under vacuum and slowly cooled down in the oven in order to release thermal stresses and uniform the effect of the previous thermal history.

DSC measurements were performed by a Mettler DSC-30 calorimeter on about 15 mg of material obtained from a central part of the cubic specimens at a heating rate of 10°C min^{-1} in a nitrogen flux of about 100 mL min^{-1}. From DSC measurements the glass transition temperature, T_g, the melting point, T_m and the crystallinity degree, X_c, of the material were determined; for the undeformed material the following results were obtained: $T_g \approx 47°C$, $T_m \approx 220°C$ and $X_c \approx 38\%$. The crystallinity percentage was assessed by integrating the normalized area under the endothermal peak and rationing the heat involved to the reference value of 100% crystalline polymer, corresponding to 145 J g^{-1} [32].

Specimens were then placed in an oven and conditioned for at least 30 min at various temperatures (T_{COND}=35, 45, 60, 80, 100°C) and subsequently quenched in liquid nitrogen. All the specimens were tested by DSC after an average time

of 2–3 min after quenching. Further, in order to deepen the effects of the quenching stage, two sets of additional DSC tests were conducted: *i*) on cubic specimens subjected to different quenching conditions; *ii*) on specimens with different geometry subjected to quenching in liquid nitrogen. In all these experiments the specimens were firstly conditioned at T_{COND}=100°C. In the former set of experiments, the specimens after conditioning were cooled in water at 5°C and in air at room temperature. The other tests were conducted on specimens with different surface to volume ratios, S/V: so, beside the usually employed cubic specimens ($S/V \sim 1.1$), also 35×10×1 mm ($S/V \sim 2.2$) and 2.6×2.6×1 mm ($S/V \sim 3.5$) specimens were conditioned, quenched and tested by DSC.

Results and discussion

Effect of thermal history

DSC analysis of the specimens quenched from various conditioning temperatures provided the curves reported in Fig. 1. A comparison between the traces of the specimen quenched from room temperature and those quenched from higher temperatures reveals the presence of an exothermal anomaly in the curves referred to the specimens treated above room temperature, that becomes more pronounced as the conditioning temperature increases. The anomalous trend closely reminds the exothermal plateau described for the deformed PBT specimens in our previous papers [1–2]. Consistently to our approach on deformed materials, the presence of the exothermal signal is interpreted as the release of a portion of energy stored within the material as a consequence of the thermal treatment. This thermal history effect can be more conveniently represented
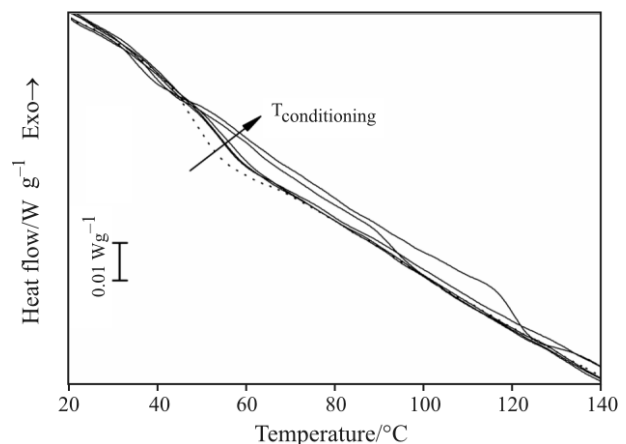

Fig. 1 DSC traces for PBT cubic specimens rapidly cooled in liquid nitrogen from room temperature (dotted line) and from higher conditioning temperatures (solid line; T_{COND}=35, 45, 60, 80 and 100°C)

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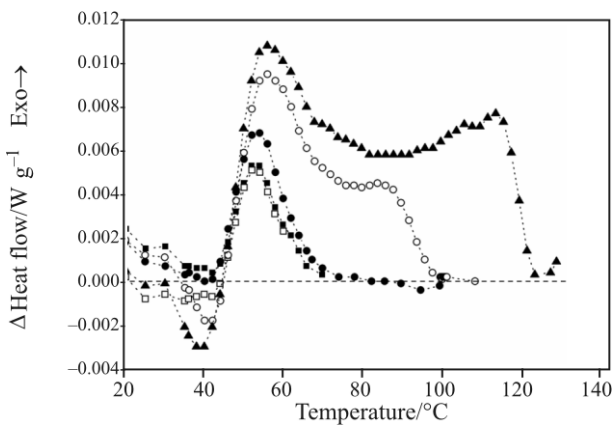**Fig. 2** Differential heat flow, Δ(Heat flow), as a function of temperature for PBT cubic specimens conditioned at T_{COND} and rapidly cooled in liquid nitrogen: $T_{COND}=\blacksquare - 35°C$, $\square - 45°C$, $\bullet - 60°C$, $\circ - 80°C$ and $\blacktriangle - 100°C$

in terms of a specific differential heat flow, Δ(Heat flow), as shown in Fig. 2. The differential heat flow is calculated as the heat flow difference between the traces of the specimen treated above room temperature and the trace for the specimen quenched from room temperature, considered as a baseline. This representation permits to evidence how for all the conditioning temperatures the heat release process onsets at the same temperature of about 45°C, i.e. close to the material's T_g and displays a maximum at about 50–60°C. As the conditioning temperature increases both the signal intensity and its extent on the temperature scale become larger. This latter effect of the conditioning temperature can be described as follows: for T_{COND} values up to T_g the exothermal signal extends up to 65°C; for higher conditioning temperatures, it extends up to about 10–15°C above T_{COND}. In addition, for specimens conditioned at 80 and 100°C an evident pre-T_g endothermic signal is present. This peak is thought to be related to the sub-T_g heat flow transition found in quenched materials and described elsewhere [33]; however, here it will be regarded only as a minor side effect and not further investigated.

The obtained results suggest that part of the stored energy measured in specimens deformed at various temperatures (from 35 to 100°C) could be partially due to the specimen thermal history.

To understand the relevance of this energetic contribution with respect to the whole energy stored in deformed materials, the DSC traces measured on just conditioned specimens and on deformed specimens were compared in terms of differential heat flow for corresponding values of the conditioning and deformation temperature; the DSC traces of deformed

materials were measured on PBT specimens compressed at $\varepsilon_0=30\%$ and $V_{load}=1$ mm min^{-1}. Figures 3a and b report these comparisons for $T_{COND}=T_{DEF}=45°C$ and $T_{COND}=T_{DEF}=100°C$, respectively. It is important to underline that in the determination of the differential heat flow for both the conditioned undeformed and deformed specimens the same baseline was adopted. It is interesting to observe that for a temperature close to T_g, the effect of the thermal history plays a minor role in comparison to that played by the deformation; a comparison of the curves for $T_{COND}=T_{DEF}=35°C$ leads to similar conclusions. By contrast, in the case of $T_{COND}=T_{DEF}=100°C$, the two exothermal signals show comparable intensities. Such a relevant effect of the thermal history can be observed also for $T_{COND}=T_{DEF}=80°C$, while only a slight effect is found for $T_{COND}=T_{DEF}=60°C$. Thus, the thermal history effects can be thought as significant only in the case of deformation temperatures well above T_g. From the results of Fig. 3b, the DSC exothermal response of the specimen deformed at 100°C can thus be interpreted
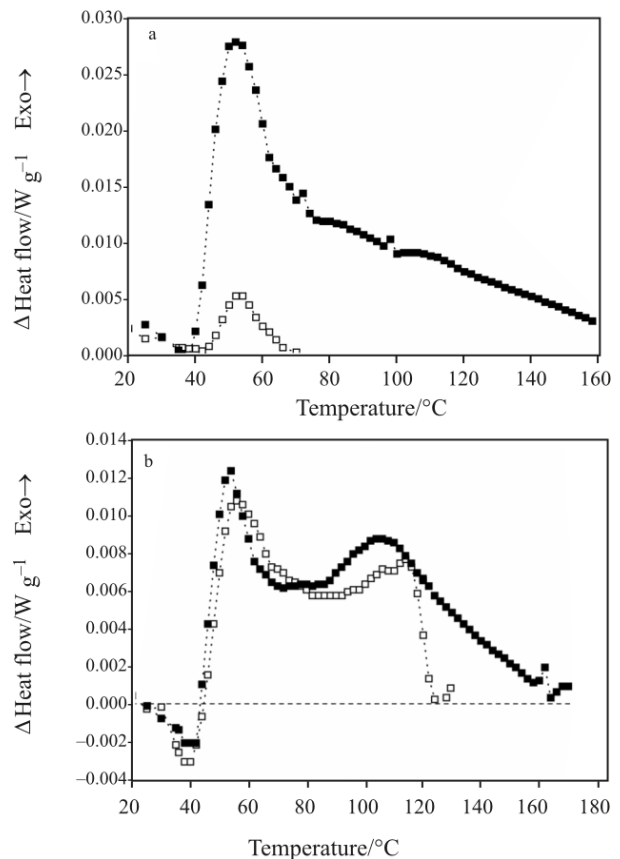

Fig. 3 Differential heat flow, Δ(Heat flow), measured in DSC tests on $\blacksquare$ – specimens deformed at $\varepsilon_0=30\%$ and $\square$ – undeformed specimens for corresponding values of conditioning and deformation temperatures, after quenching in liquid nitrogen: a – $T_{COND}=T_{DEF}=45°C$ and b – $T_{COND}=T_{DEF}=100°C$

as due to the specimen thermal history for temperatures up to 110°C, while the deformational contribution appears only at higher temperatures. An evidence of this fact can be seen also in the results presented in a previous paper [2], in which specimens deformed at T_{DEF}=100°C at various strain levels were subjected to DSC tests and revealed that the effect of the strain level on DSC thermograms is mainly restricted to a temperature region ranging from 110°C up to the temperatures involved in recrystallization and melting processes.

The energy stored in conditioned specimens could be tentatively ascribed to the presence of locally strained regions within the bulk, generated by the thermal stresses due to differential cooling between the core and the surface of the specimens. For increasing conditioning temperatures larger energy amounts are stored, because of the higher levels of thermal stresses settled within the specimen by the rapid cooling. The more pronounced effect found at conditioning temperatures well above T_g can be interpreted as a consequence of the higher thermal expansion coefficient at these temperatures: higher stresses are in fact generated due to the larger strain difference between the cooled surface and the still warmer specimen's inner core.

To better understand the nature of the stored energy in conditioned undeformed samples, further experiments were performed on specimens treated at 100°C and subjected to rapid cooling in different media (i.e. liquid nitrogen, water and air) and on specimens with various geometries conditioned at 100°C and rapidly quenched in liquid nitrogen. The results of DSC analysis, reported in terms of differential heat flow, are represented in Figs 4 and 5, respectively. The shape of the curves and the temperature range covered by the exothermal effect are quite similar but
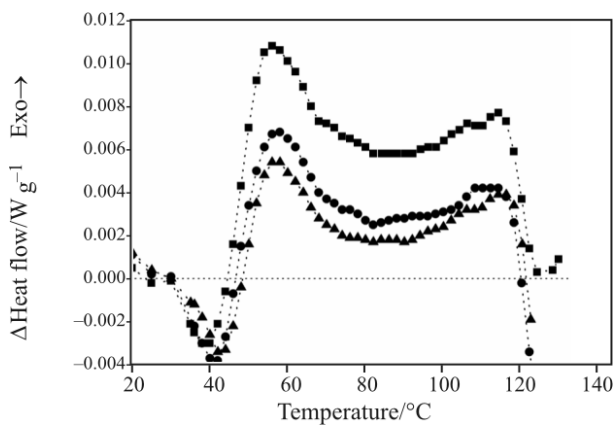
the intensity of the signals becomes more pronounced as the efficacy of the quenching medium improves (Fig. 4) and as the surface to volume ratio of the specimen decreases (Fig. 5). This suggests that the excess energy is stored during the cooling stage and that thermal stresses, whose effects are smaller for larger surface to volume ratio, can be reasonably thought as the main cause of the stored energy. It is not excluded that part of this stored energy can be due to additional thermal stresses that arise in the regions of the amorphous/crystalline interface as a consequence of the different thermal expansion coefficients of the two phases. It is not easy to evaluate this contribution in specimens having different geometries, due to the different cooling conditions that take place at various distances from the specimen outer surfaces, producing maximum and minimum effects at the samples extremities and in the centre, respectively. However, such a contribution to the total stored energy is expected to become less important as the surface to volume ratio becomes larger. Thus, our results suggest that possible thermal stresses at amorphous/crystalline interface have not a relevant role, at least within the surface to volume ratio range here explored.

These results are of some relevance from a methodological point of view. In fact, the data reported in Fig. 4 show that the effect of thermal treatment is present on DSC traces also when specimens are slowly cooled in air at room temperature. Therefore, when the effect of temperature on deformed specimens is studied by DSC tests, the effect of the sample cooling on the resulting traces can not be avoided. A possible way to overcome this problem is to adopt as baseline the DSC trace of an undeformed specimen, conditioned at
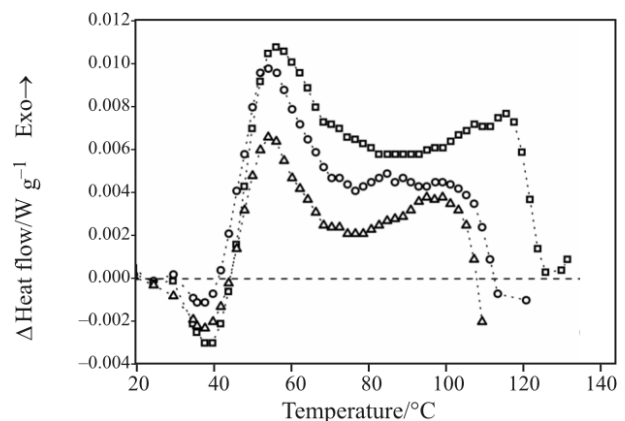

Fig. 4 Differential heat flow, Δ(Heat flow), measured in DSC tests on cubic specimens quenched from T_{COND}=100°C and rapidly cooled in various media ■ – liquid nitrogen; ● – water (at T=5°C) and ▲ – air (at room temperature)

Fig. 5 Differential heat flow, Δ(Heat flow), measured in DSC tests on specimens with different geometries (i.e., shape and surface to volume ratio, S/V) quenched from T_{COND}=100°C; quenching was performed by immersion in liquid nitrogen, for: □ – cubic specimen, S/V~1.1 mm^{-1}; ○ – tensile bar, S/V~2.25 mm^{-1}; △ – cubic specimen, S/V~3.5 mm^{-1}
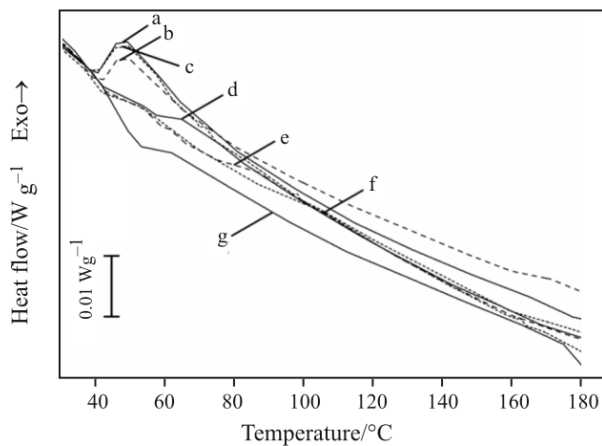
Fig. 6 DSC traces for PBT cubic specimens compressed at ε_0=30%, at V_{load}=1 mm min^{-1} and at various deformation temperatures, T_{DEF}=a – 25, b – 35, c – 45, d – 60°C, e – 80, f – 100°C and g – of an undeformed specimen

the deformation temperature and cooled in the same conditions as the deformed one.

The results presented so far indicate that the energy stored in a sample deformed at a given temperature can be reasonably ascribed to two distinct processes, one related to the specimen thermal history and the other to its deformation. An evaluation of this latter term can be obtained by a simple subtraction of the thermal history contribution from the net exothermal signal, or, alternatively by comparing the DSC traces of deformed and undeformed specimens provided that they were both subjected to the same thermal history. Moreover, since the energetic term due to thermal history is seen to be also dependent on external factors, such as the quenching conditions and the specimen geometry, the total stored energy measured in a DSC test on a deformed specimen is inevitably affected by the geometry and the nature of the experimental setup. Thus, the subtraction of the thermal history term could help in leading to an intrinsic evaluation of the deformational stored energy.

Effect of deformation conditions

The effect of the deformation conditions on energy storage was widely investigated by the authors in other papers [1, 2, 9, 10], where attention was focused on the effects of the deformation temperature and strain rate in semicrystalline polymers for deformations both below and above the glass transition temperature of the amorphous regions. Our findings were compared with the behaviour described by others for amorphous polymers (Oleinik *et al*. on PS [12] and epoxy systems EAN [3, 4]; Nanzai *et al*. on epoxy systems [7]). Even if for both semicrystalline and amorphous polymers it was seen that lower energy was stored as the deformation
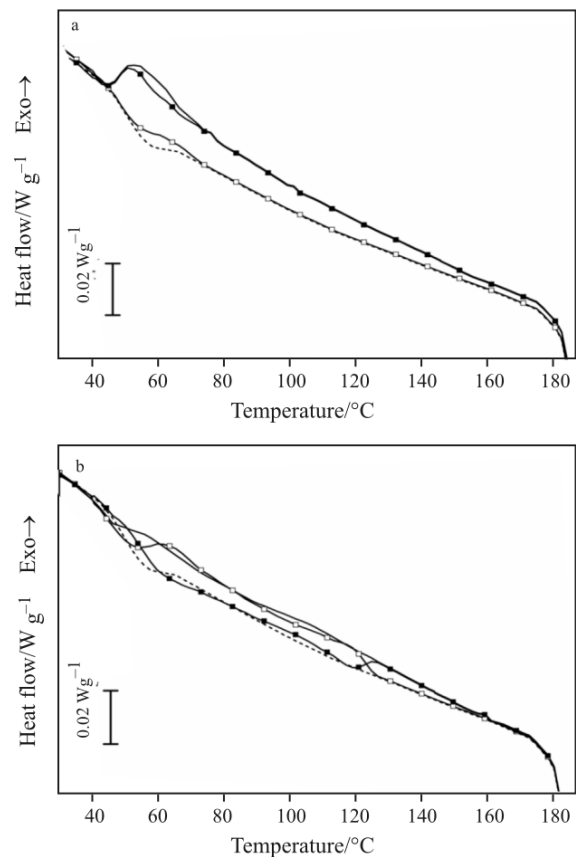

Fig. 7 DSC traces of —— – deformed and --- – undeformed specimens and decomposition of the total exothermal signal in the □ – conditioning and ■ – deformational components for PBT cubic specimens compressed at ε_0=30%, at V_{load}=1 mm min^{-1} and at a – T_{DEF}=45 and b – T_{DEF}=100°C

temperature increased, some differences were found in their energy storage and release behaviour. The results obtained for semicrystalline PBT compressed at various temperatures are reported in Fig. 6. The deformation was applied for a strain level ε_0=30% at a loading rate V_{load}=1 mm min^{-1}. First, for what concern the stored energy, it was seen that semicrystalline materials present partial energy storage also for deformation above T_g, whereas for these deformation temperatures no energy is stored in amorphous polymers. The peculiar behaviour displayed by semicrystalline polymers was ascribed to a mobility gradient within the interphase between the crystalline domains and the amorphous regions of the polymer [34]. A second difference concerns the energy release process: in amorphous polymers the exothermal process starts from temperatures close to the deformation temperature; conversely, our investigations on PBT revealed that for all the deformation temperatures the energy release process always starts from a temperature close to the material's T_g. These results

have to be reconsidered in the light of the findings presented in the previous section of the present paper.

In fact, only when DSC traces of the conditioned specimens are subtracted from the traces measured on deformed specimens for corresponding values of conditioning and deformation temperatures it is possible to truly evaluate the part of the exothermal signal related only to the release of deformational stored energy. As an example of how the total signal can be subdivided in the two energy contributions, Figs 7a and b refer to the cases of deformation temperatures T_{DEF}=45 and 100°C, respectively. It is possible to see that for a deformation close to T_g the exothermal signal due to deformation is practically coincident with that of the total stored energy, also after the subtraction of the conditioning component; on the other hand, Fig. 7b evidences the significant difference between the total stored energy and its pure deformational contribution and that in this case the thermal history effect cannot be neglected.

The resulting traces representing the purely deformational energy contribution are reported in Fig. 8. The curves show that the onset temperature of the energy release process clearly depends on the deformation temperature. For deformation temperatures up to T_g no significant difference is found for the onset temperature and the release of deformational energy initiates at temperatures in the narrow interval between the deformation temperature and the glass transition temperature. On the other hand, for specimens deformed above T_g the release of deformational energy begins at temperatures close to the deformation temperature. The insert of Fig. 8 compares these onset

temperatures for the total energy release process and for the part related only to the deformational contribution. It comes out that for temperatures below T_g both processes present the same onset temperature of about 40°C. For deformation temperatures above T_g, different onset temperatures characterize the two phenomena. The total energy release process starts at temperature somewhat higher than 40°C while the onset temperature for the deformational energy release increases with T_{DEF}. Isolation of the deformational term of the stored energy permits thus to underline a closer similarity for the energy release process of amorphous and semicrystalline polymers.

The resulting traces are particularly interesting in solving a controversy found in our studies on energy storage and strain recovery of semicrystalline materials. It was reported that the release of stored energy in a deformed polymer is closely related to the strain recovery process [3, 7, 12, 13, 35] and these processes are both starting at a temperature close to the deformation temperature [36–45]. Therefore, in our case if the comparison would have been made on the basis of the total deformation energy release process we would have admitted that there is a portion of stored energy which is released without the recovery taking place. Conversely, isolation of the pure deformational term of the total stored energy reveals that both deformational energy release and strain recovery processes begins at the same temperature, supporting the hypothesis that they are intimately related. The knowledge of the thermal history effects permits to isolate the pure deformational term. The energy stored in the undeformed conditioned specimens was evaluated by integration of the area between the DSC curves of thermally conditioned specimens and the baseline. This energy contribution, $\Delta U_{ST,COND}$, can
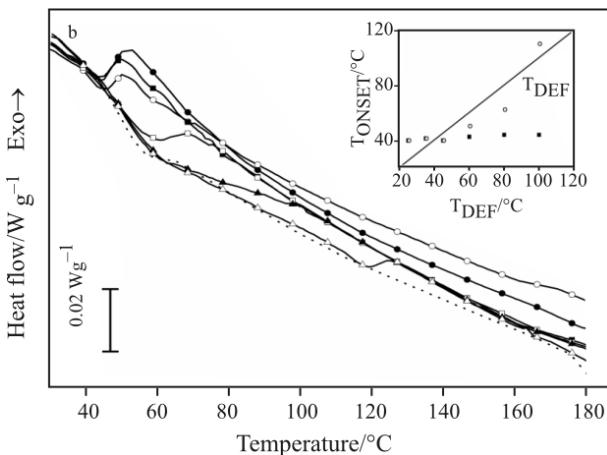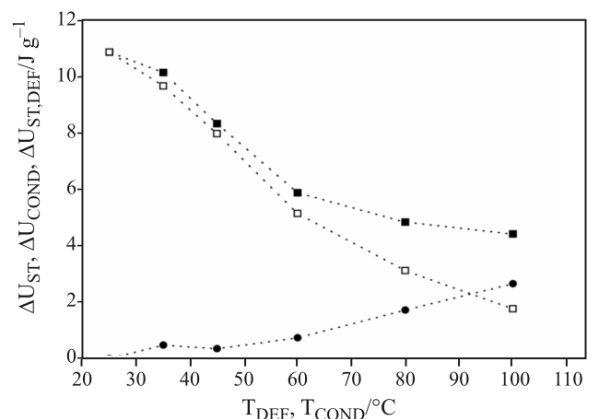

Fig. 8 DSC traces relative to the deformational stored energy for specimens deformed at various deformation temperatures ● – 25, ○ – 35°C, ■ – 45, □ – 60, ▲ – 80, △ – 100°C and of ··· – an undeformed specimen. Insert: onset temperatures of the ■ – total and ○ – deformational energy release process as a function of the deformation temperature

Fig. 9 Total stored energy, ■ – ΔU_{ST} (previously measured for PBT cubic specimens compressed at ε_0=30% [1] and at V_{load}=1 mm min^{-1}) and repartition in the components due to ● – conditioning, $\Delta U_{ST,COND}$ and □ – deformation, $\Delta U_{ST,DEF}$, for corresponding values of the conditioning and deformation temperature (T_{COND} and T_{DEF})

Table 1 Effects of deformation temperature, T_{DEF} and loading rate, V_{load}, on the total stored energy, ΔU_{ST} and on the deformational component of the stored energy, $\Delta U_{ST,DEF}$, as measured in DSC tests on PBT cubic specimens compressed at $\varepsilon_0=30\%$

V_{load}/mm min^{-1}	$T_{DEF}=25°C$	$T_{DEF}=45°C$		$T_{DEF}=100°C$	
	$\Delta U_{ST}=\Delta U_{ST,DEF}$/J g^{-1}	ΔU_{ST}/J g^{-1}	$\Delta U_{ST,DEF}$/J g^{-1}	ΔU_{ST}/J g^{-1}	$\Delta U_{ST,DEF}$/J g^{-1}
10	13.6	9.1	8.7	5.2	2.5
1	10.9	8.3	8.0	4.4	1.8
0.05	7.1	8.3	7.9	3.0	0.4

be subtracted, for corresponding values of conditioning and deformation temperatures, from the total stored energy, ΔU_{ST}, to obtain the deformational stored energy, $\Delta U_{ST,DEF}$. It is worthwhile to remark that these energy terms refer to the energy stored in the sample at the beginning of DSC experiments and not to the energy stored in the sample after unloading, since some portion of energy could be lost in the meanwhile. These energy terms are reported in Fig. 9 as a function of deformation (and conditioning) temperature.

It is possible to see that $\Delta U_{ST,COND}$ increases with conditioning temperature, at a rate faster for temperatures higher than T_g. Conversely, $\Delta U_{ST,DEF}$ displays a decreasing trend with the deformation temperature, similarly to that found for the total stored energy, from which it only slightly differs for temperatures up to about 60°C, whereas significant differences are observed for higher temperatures. It is noteworthy that at the highest investigated temperatures the two subcomponents have closely comparable values.

The effects of deformation temperature and strain rate on the terms ΔU_{ST} and $\Delta U_{ST,DEF}$ are summarized in Table 1. At all temperatures both the total stored energy and its deformational component increase with strain rate. It is interesting to note that the

specimen deformed above T_g at the lowest strain rate shows an almost complete absence of stored energy.

In our previous paper [1] a repartition of the mechanical work for a loading-unloading post-yield deformation cycle was proposed. Accordingly to the first law of thermodynamics, considering that part of the work was dissipated and part is stored in the deformed material, the knowledge of the mechanical work, W and of the total stored energy, ΔU_{ST}, allowed us to calculate the dissipated energy, Q, as [3, 5, 12, 14, 15, 27–29]:

$$Q=W-\Delta U_{ST} \qquad (1)$$

More precisely, in our work the term Q includes also the portion of energy released during the time elapsed after unloading and prior to DSC scanning.

On the basis of the results reported in the present paper, it appears that a more appropriate repartition has to be done considering the term $\Delta U_{ST,DEF}$ instead of ΔU_{ST}, as stored energy. The quantities resulting from this revised energy repartition are represented in Fig. 10 in the case of a compression at $\varepsilon_0=30\%$ at a $V_{load}=1$ mm min^{-1}. With respect to the previous results referring to the total stored energy, a trend more markedly decreasing with temperature can be observed. It appears that for deformation temperatures up to T_g,
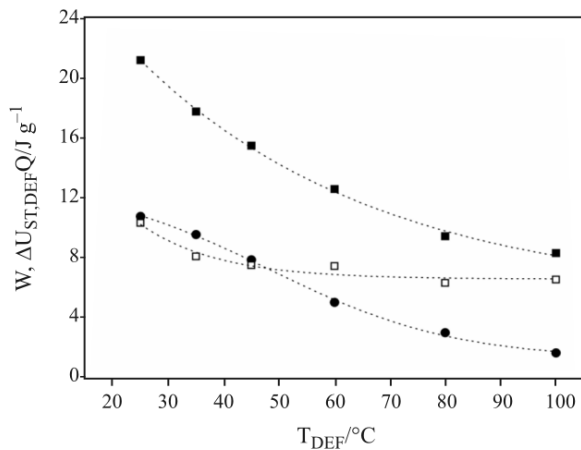

Fig. 10 ■ – Total deformation work, W (previously measured for PBT cubic specimens compressed at $\varepsilon_0=30\%$ and at $V_{load}=1$ mm min^{-1} [1]) and repartition in the components of ● – deformational stored energy, $\Delta U_{ST,DEF}$ and □ – dissipated energy, Q as function of deformation temperature, T_{DEF}
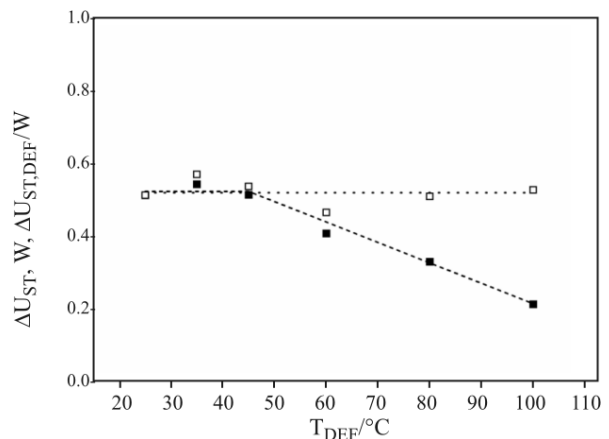

Fig. 11 Stored energy to work of deformation ratio measured in DSC tests on PBT cubic specimens compressed at $\varepsilon_0=30\%$ and at $V_{load}=1$ mm min^{-1} as evaluated on: □ – total stored energy, ΔU_{ST}; ■ – deformational stored energy, $\Delta U_{ST,DEF}$

the two terms, $\Delta U_{ST,DEF}$ and Q, assume similar values. As the deformation temperature rises above T_g a marked divergence between the two terms is found, being the dissipative term Q higher than $\Delta U_{ST,DEF}$. In Fig. 11 the ratio between the deformational stored energy and the mechanical work of deformation, $\Delta U_{ST,DEF}/W$, is represented for various deformation temperatures, together with the ratio $\Delta U_{ST}/W$. For deformation temperatures up to T_g it clearly appears that the ratio $\Delta U_{ST,DEF}/W$ follows a trend similar to that displayed by the ratio $\Delta U_{ST}/W$ assuming a value somewhat higher than 0.5. For higher deformation temperatures the ratio $\Delta U_{ST,DEF}/W$ almost linearly decreases with T_{DEF}. These results, together with those reported in Fig. 8, suggest that different deformation mechanisms are taking place in the temperature intervals below and above T_g.

Conclusions

The effect of the thermal history on the energetic state of semicrystalline PBT specimens conditioned at various temperatures and subjected to rapid cooling was studied by DSC analysis. It is shown that a certain amount of energy is stored within the material as a consequence of the specimens cooling. As the conditioning temperature increases a larger portion of energy is stored and its release takes place over a larger temperature interval.

A comparison with the DSC traces of the specimen deformed at various temperatures permits to establish that the energy released from a deformed specimen can be divided in two terms: *i*) a thermal component due to the material cooling, that becomes significant only in the case of deformation temperatures well above T_g; *ii*) a purely deformational component, which onsets at a temperature close to the deformation temperature. The subtraction of the thermal component from the total exothermal signal permits to quantify this latter component. The general trend described in our previous paper for the total stored energy is confirmed also for its deformational component, which is seen to decrease with temperature and increase with strain rate. Nevertheless, the isolation of a pure deformational energy component permits to more correctly account for the effects of the deformation temperature on the ratio between stored energy to total work of deformation: a constant value of about 0.5 is found for deformation temperatures up to T_g, while a larger dissipative behaviour is observed as the temperature further increases.

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