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Post-yield compressed semicrystalline poly(butylene terephthalate): energy storage and release

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Abstract

Post yield deformation of semicrystalline poly(butylene terephthalate) (PBT) is studied by differential scanning calorimetry (DSC) measurements on compressed specimens after unloading. In particular, the effects of strain level, loading-unloading rate, and deformation temperature are analyzed. DSC traces indicate that a remarkable fraction of the mechanical work of deformation (in the range from 25 up to 62%) is stored in the material after unloading. Final strain dependence of stored energy values for specimens deformed up to 40% follows the general S-shaped trend observed for many amorphous and semicrystalline polymers. The ratio of the stored energy to the mechanical work of deformation ($\Delta U_{ST}/W$) is decreasing as the final deformation level increases. For a given final strain level, the amount of energy stored in specimens deformed under T_g increases as either loading or unloading rates increase: in particular, both ΔU_{ST} and $\Delta U_{ST}/W$ values are linearly increasing with the logarithm of loading rate. On the other hand, energy storage for specimens deformed at T_g results to be practically independent from the loading rate. Moreover, as the deformation temperature increases from 25 to 100 °C, ΔU_{ST} values markedly decrease, while the ratio $\Delta U_{ST}/W$ is almost constant around an average value of about 51%.

Keywords: Energy storage; Deformation; Poly(butylene terephthalate)

1. Introduction

Deformation of solid materials requires energy to be accomplished. In general, the mechanical work of deformation is in part required for the elastic deformation (reversible), in part stored in the material as internal energy (non-elastic reversible component), and in part dissipated during the deformational process (viscous or irreversible component) [1]. After the pioneer works conducted in the 1960s and 1970s by Müller and co-workers [2,3] and Godovsky [1] on the thermodynamics of cold drawing of glassy and semicrystalline polymers, it was clear that a considerable fraction of the mechanical work can be stored in a polymeric material. In fact, more recent studies conducted on several glassy and semicrystalline polymers and blends [4–7] showed that 45–85% of the mechanical work of deformation can be converted into internal energy and stored in the material after unloading. In contrast, 90–98% of the mechanical work is generally dissipated in stretching various common metals [8].

The energy stored in a deformed polymer causes an increase of its internal energy that a number of researchers measured by various methods such as deformation calorimetry, dissolution calorimetry and/or differential scanning calorimetry (DSC) [1–7,9–27]. Godovsky [1] compared some literature data of the energy stored in polystyrene samples compressed up to various levels of plastic deformation. The data obtained by independent methods agreed quite well and the agreement among DSC data of various author was also satisfactory. Somewhat lower energy values measured by DSC and heat of solution methods could be attributed to the time delay between deformation and measurements, since relaxation of internal energy begins from the time the deformed sample is unloaded. In deformation calorimetry, this factor is excluded since the dissipated energy, Q, is measured directly as the heat generated during deformation [1–7, 17–19] while the stored internal energy, ΔU_{ST}, is evaluated

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from the first law of thermodynamics, $\Delta U_{ST} = W - Q$, where the mechanical work W expended for the sample deformation is estimated by integration of the registered stress–strain curves. On the other hand, ΔU_{ST} stored in a highly deformed polymer may be determined by DSC analysis by testing a specimen before and after the imposition of a given deformation. The DSC traces of deformed polymers usually reveal anomalies in the heat capacity such as endothermic peaks or plateaus. The area under these is closely related to the stored energy and generally interpreted as a release of enthalpic energy created during the deformation process [1–7,9–19,21–27]. Its amount is usually quantified by evaluating the area enclosed by the heat capacities curves of the deformed and undeformed samples. Most of the published experimental data have been obtained on glassy polymers [1,9–23] and only few investigations have been focused on semicrystalline polymers [1–7,23–27]. Moreover most of the data concerning the thermodynamics of plastic deformation of glassy and semicrystalline polymers have been obtained on uniaxial extension rather than uniaxial compression [1]. Generally speaking, during uniaxial compression of polymeric materials, a steady increase of internal energy for deformation levels up to 30% is observed. However, when the values of compressive deformation reach 35–40% the stored energy approaches a constant level [4–7,9–12, 14–19,21,26]. Moreover, it is important to note that the energy release process in a highly deformed polymer is generally accompanied by dimensional changes that tend to revert the sample geometry to its undeformed state (strain recovery) [9,10,15,17,18,20–22,24–37]. For glassy polymers deformed below glass transition temperature, several studies [9,10,15,22,28–31,34,36] have shown that the strain recovery reaches completion in a short time by bringing the polymer to or above its glass transition temperature (T_g). This total recovery occurs even at large deformations (up to more than 50%) and it concerns also the microstructural state since the polymer recovers its initial properties [5,38, 39]. On the other hand, for highly deformed semicrystalline polymers the strain recovery has been proven to be not complete even at temperatures well above T_g [26,27].

The actual means by which this energy is stored during yielding and subsequent deformation is not yet fully understood [21]. Robertson [40], Argon [41], and Boyce et al. [42] suggest that the stored energy could be a consequence of distorting or rotating chain segments under the action of shear components of stress ('liquid-like' approach). On the other hand, Bowden [43], Oleynik [15, 17–19], Perez [44], and G'Sell [13,45] ascribe the process to inhomogeneous and localized shear transitions or shear defects rather like dislocations in crystals ('crystal-like approach'). Some constitutive models have been also recently proposed to describe the enthalpy recovery in both amorphous and semicrystalline polymers [42,46,47].

The amount of energy internally stored for a given deformation level seems to be affected by the loading conditions, such as strain rate [1,14] and deformation temperature [1,12,15,25,27], but the available literature data are quite scarce. Since most of mechanical properties of polymers are strongly dependent on time and temperature, it is therefore of general interest to study how parameters like strain rate and deformation temperature may affect their energy storage ability. Aim of this study is hence to investigate the effect of the deformation level, the strain rate, and the deformation temperature on the energy storage process in post-yield compressed semicrystalline poly(butylene terephthalate) (PBT).

2. Experimental

2.1. Specimens preparation

Cubic specimens ($5.5 \times 5.5 \times 5.5$ mm^3) were machined from injection moulded PBT rectangular test bars ($127 \times 12 \times 6$ mm^3) 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 thermal history.

2.2. Specimen deformation

An electromechanical testing machine (Instron, model 4502) was used to perform loading–unloading cycles in uniaxial compression under displacement control. A clip-on extensometer (Instron, model 2620) was fixed to the compression plates whose surfaces were accurately oil-lubricated in order to minimize end-friction. All tests have been performed in a thermostatic chamber (Instron, model 3119) permitting a temperature control within ±1 °C. Specimens were subjected to a loading ramp up to various final strain levels, ε_0, in the range from 5 to 40%, and at various cross-head speeds, V_{load}, in the range between 0.05 mm/min (i.e. strain rate 1.52×10^{-4} s^{-1}) and 10 mm/min (i.e. strain rate 3.03×10^{-2} s^{-1}). The unloading stage was conducted at two cross-head speeds, V_{unload}, i.e. 500 mm/min (fast unloading), and 0.05 mm/min (slow unloading). After the compression cycle, specimens were rapidly cooled and stored in liquid nitrogen, and analyzed by DSC within 6 min after unloading.

2.3. Differential scanning calorimetry (DSC)

DSC measurements were performed by a Mettler DSC-30 calorimeter in order to determine the glass transition temperature, T_g, the melting point, T_m, and the crystallinity degree, X_c, of the material. Measurements were performed on about 15 mg of material (obtained from a central part of the cubic specimens) at a heating rate of 10 °C/min in a nitrogen flux of about 100 mL/min. For the undeformed material the following results were obtained: $T_g \approx 47$ °C,

$T_m \approx 230$ °C, and $X_c \approx 38\%$. The crystallinity percentage was assessed by integrating the normalized area under the endothermal peak and ratioing the heat involved to the reference value of the 100% crystalline polymer, corresponding to 145 J/g [48]. DSC measurements were also performed, under the conditions reported above, on samples deformed at various strain levels (ε_0), loading rates (strain rate $(d\varepsilon/dt)_{load}$ or cross head speed V_{load}), unloading cross-head speeds (V_{unload}), and deformation temperatures (T_{def}) in order to evaluate the energy stored in the material and released during heating.

3. Results and discussion

3.1. Stored energy

Fig. 1 reports a typical stress–strain curve obtained in a loading–unloading compression cycle on PBT specimen. After unloading from a given final strain, ε_0, a residual deformation, ε_{res0}, is reached. Fig. 2(a) shows DSC traces of specimens deformed under $T_g(T_{def} = 25$ °C) at various deformation levels. The endothermal peak associated with the melting process of the crystalline regions is substantially not affected by the deformational process (Fig. 2(a)). This is consistent with the investigation of Godovsky [1] who did not observe changes in melting temperature (T_m) and crystallinity content (X_c) of semicrystalline PBT cold drawn in tension up to a natural draw ratio of 5.2. The same author reported a marked increase of both T_m and X_c for other polymers, like HDPE, LDPE, and iPP. A magnification of Fig. 2(a) clearly shows that a broad exothermal peak (or plateau) becomes more and more pronounced on the DSC traces as the strain level increases (Fig. 2(b)). This peak ranges from temperatures somewhat higher than the deformation temperature up to a level close to the recrystallization and melting processes, being particularly intense at temperatures near T_g (47 °C). The area under such exothermal peak, ΔU_{ST}, represents the energy stored in the deformed material and released during heating in the DSC chamber [1–7,9–19,21–27]. This phenomenon has been widely observed and studied on highly deformed glassy polymers [1,9–23], where the exothermal peak, interpreted as an evidence of the relaxation process connected to the deformation recovery, usually extends from the deformation temperature up to glass transition. The wider extent of the energy release process for semicrystalline polymers, already reported for PET [25] and PBT [27], has been attributed to the mobility gradient due to the interphase between the crystalline domains and the amorphous regions [25–27,49]: as a consequence, the relaxation process for semicrystalline polymers spreads up to temperatures well above T_g even if it can be still attributed to a release of internal energy stored in amorphous regions [1].

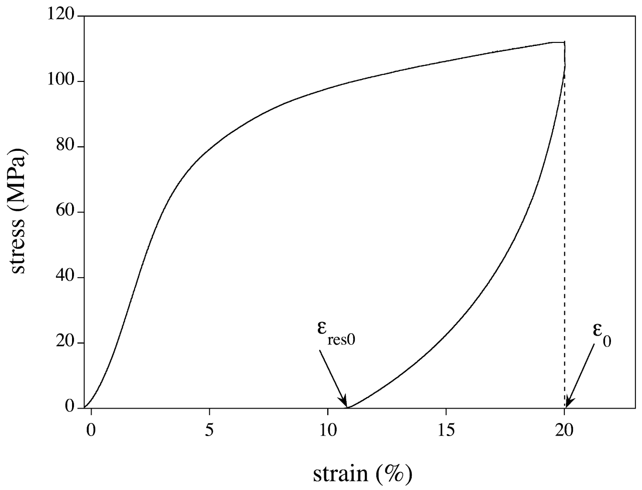

Fig. 1. Typical stress–strain curve obtained at $V_{load} = V_{unload} = 0.05$ mm/min for a PBT specimen deformed at $T_{def} = 25$ °C.

The energy released during sample heating, ΔU_{ST}, was evaluated by measuring the area enclosed between the DSC traces of deformed and undeformed specimens within the temperature limits corresponding to the onset of the peak to about 180 °C, and the results obtained for samples loaded and unloaded at different rates at room temperature are reported in Fig. 3 as a function of the final applied strain. The energy stored as a function of the final strain follows the general S-shaped trend observed for many amorphous and semicrystalline polymers [6,7,9–12,14–19,21,26]. In fact, most curves display an initial steady increase up to approximately 30% deformation and then a tendency to level off. Moreover, the internal energy values observed at the lowest strain rate are quantitatively in excellent agreement with the data reported by Oleinik and co-workers [6] obtained by a different approach (deformational calorimetry) on semicrystalline PBT after loading and unloading compression cycles at comparable rates. Fig. 3 also provides indications about the effects of the loading and unloading rates on the ability of the material to store energy when deformed, that can be summarized as follows: (i) the higher the loading rate, the higher the energy stored in the material; (ii) the higher the unloading rate, the higher the energy stored in the material. Moreover, it is interesting to observe that loading rate is more important than unloading rate in determining the amount of energy the material can store. As clearly evidenced in Fig. 4, for sample deformed under T_g, the energy ΔU_{ST} is a linear function of the logarithm of the strain rate (or deformation velocity) of the loading stage. This result is consistent with the deformational calorimetry data reported by Godovsky [1], who evaluated a linear dependence of the mechanical work, the dissipated energy and the stored energy, on the logarithm of the drawing velocity for uniaxially drawn semicrystalline polymers (LDPE, HDPE, iPP, PA-6). On Fig. 4 it is also possible to observe that the stored energy is almost independent from the deformation rate when the deformation temperature is raised up to the glass transition temperature. The strain rate dependence of the internal

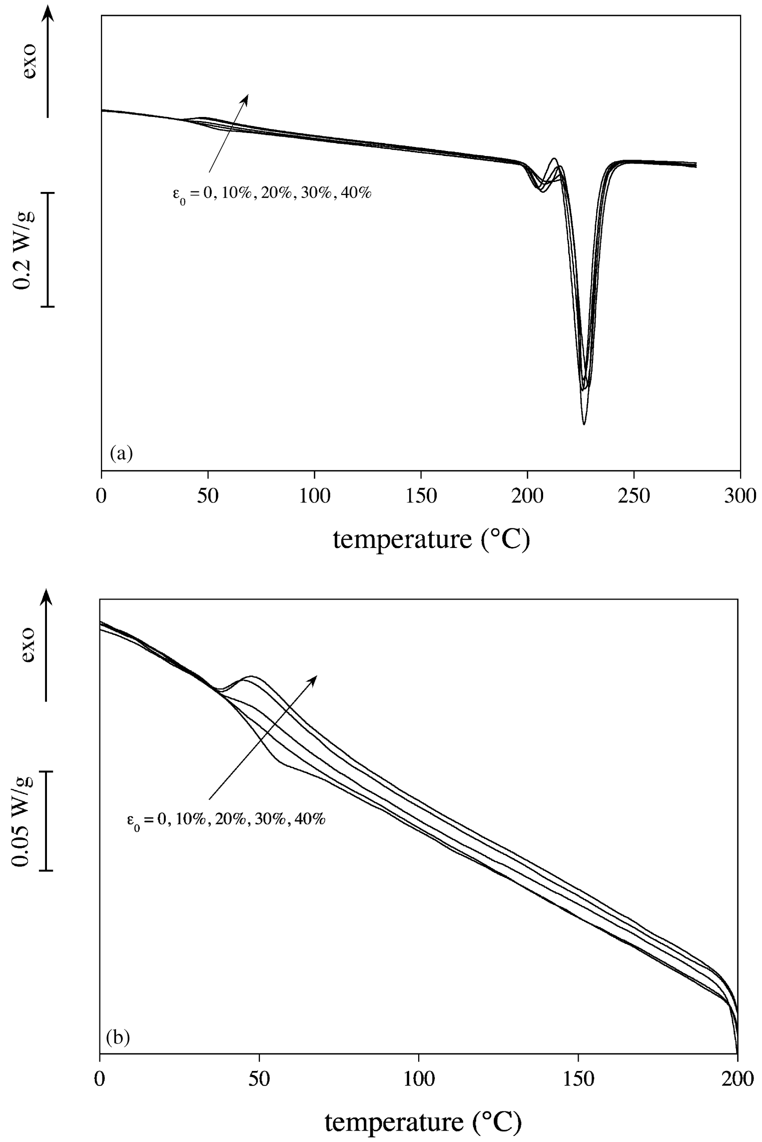

Fig. 2. (a) DSC traces of PBT samples deformed at $T_{def} = 25$ °C up to various final strains at $V_{load} = 10$ mm/min and $V_{unload} = 500$ mm/min. (b) magnification of Fig. 1(a).

energy released during DSC scan is strongly influenced by the deformation level. In fact, as evidenced in Fig. 5, the slope of the lines representing ΔU_{ST} values as a function of the logarithm of loading rate increases as the final strain level increases. According to a 'crystal like' approach to plasticity in glassy polymers [13,15,17–19,43–45], at temperatures below the glass transition, plastic strain nucleates as thermo-mechanically activated shear induced defects, called shear micro domains (SMD), in the presence of pre-existing quasi point defects. These are points of fluctuation in the value of local free volume of the amorphous matrix, predisposed for the easy nucleation of defects in a way that resembles the nucleation of dislocations in metals. In this framework, our results indicate that the nucleation of SMDs, responsible of the energy internally stored in a polymer deformed under T_g, is enhanced as the deformation rate increases. This effect is clearly evident at elevated strain levels (higher than 30%) and practically negligible at low strain levels.

More detailed information regarding the deformation temperature dependence of the stored energy are reported in Fig. 6. For a given strain rate and level of final deformation, the energy stored in the material decreases as the deformation temperature increases. It is interesting to note that, differently from glassy polymers, a certain amount of deformation energy is stored even if the material is deformed at temperatures much higher than its T_g. Moreover, the temperature at which the exothermal peak reaches a relative maximum, T_{max}, shifts toward higher values as the deformation temperature increases. Interestingly enough, the exothermal peak shifts to higher temperatures only if specimens are deformed at temperatures higher than T_g.

Results of Figs. 4–6 show that rate (of deformation) and

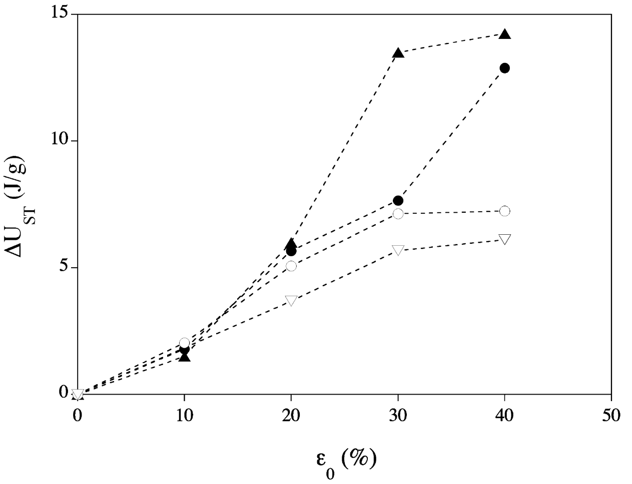

Fig. 3. Energy released during DSC scans, ΔU_{ST}, vs. final strain, ε_0, for samples deformed at $T_{def} = 25$ °C under various loading–unloading conditions: (▲) $V_{load} = 10$ mm/min, $V_{unload} = 500$ mm/min; (●) $V_{load} = 10$ mm/min, $V_{unload} = 0.05$ mm/min; (○) $V_{load} = 0.05$ mm/min, $V_{unload} = 500$ mm/min; (▽) $V_{load} = 0.05$ mm/min, $V_{unload} = 0.05$ mm/min.

temperature (of deformation) have opposite effects on the stored energy: high deformation rates induce higher stored energy values; conversely, high deformation temperatures lead to lower stored energy values. All this observations are suggesting that the mechanism by which energy is stored in the material is influenced by the viscoelastic nature of the polymer under investigation. Nevertheless, the data obtained in this work are not sufficient to assess if a time-temperature superposition occurs between the investigated variables (deformation time and temperature).

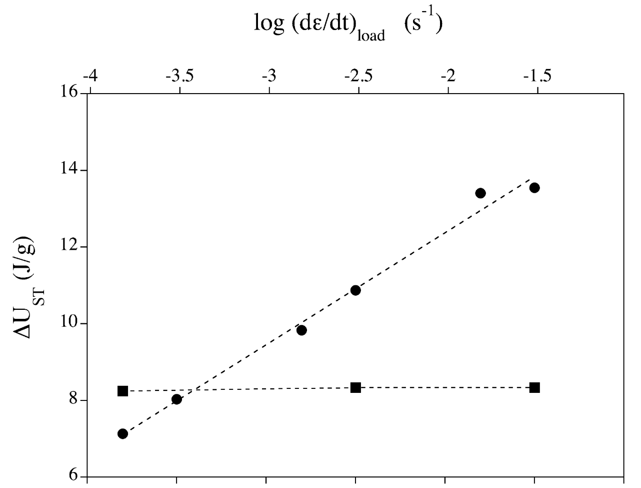

Fig. 4. Effect of the loading rate on the energy released during DSC scans, ΔU_{ST}, for specimens deformed up to $\varepsilon_0 = 30\%$ with $V_{unload} = 500$ mm/min at: $T_{def} =$ (●) 25 °C and $T_{def} =$ (■) $= 45$ °C.

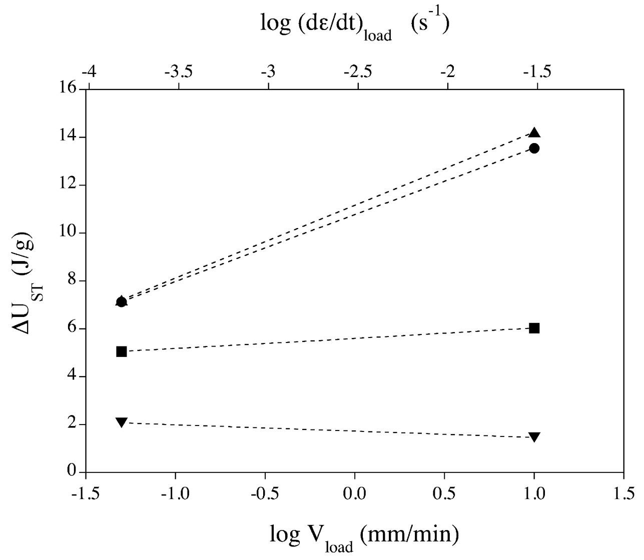

Fig. 5. Effect of the loading rate on the energy released during DSC scans, ΔU_{ST}, for specimens deformed at $T_{def} = 25$ °C and $V_{unload} = 500$ mm/min. Final strains are: (▼) $\varepsilon_0 = 10\%$; (■) $\varepsilon_0 = 20\%$; (●) $\varepsilon_0 = 30\%$; (▲) $\varepsilon_0 = 40\%$.

3.2. Mechanical work of deformation and dissipated energy

The stress–strain curves recorded during the loading–unloading cycle allows one to determine the mechanical work of deformation, W, that is the work spent for changing shape and dimensions of the body being deformed. In particular, [18]:

$$W = \int_0^{\varepsilon_0} \sigma(\varepsilon)\mathrm{d}\varepsilon - \int_{\varepsilon_{res0}}^{\varepsilon_0} \sigma(\varepsilon)\mathrm{d}\varepsilon \qquad (1)$$

where the first term corresponds to the work spent during the loading phase, and the second refers to the work released during the unloading. As reported in Fig. 7, the mechanical work strongly depends on the final strain level reached: as

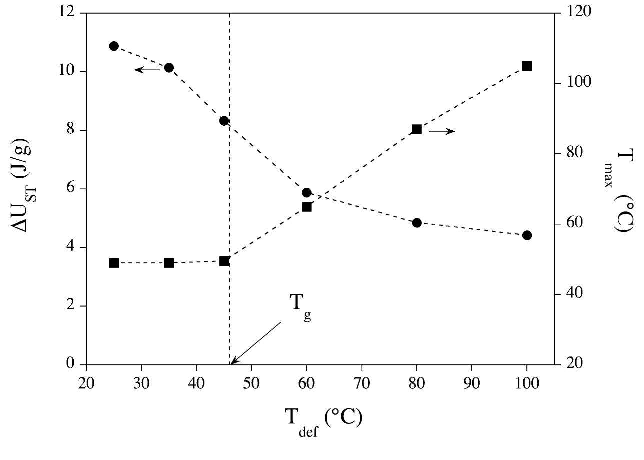

Fig. 6. Effect of the deformation temperature T_{def} on the energy released during DSC scans ΔU_{ST} (●) and on the temperature of relative maximum of the exothermal peak T_{max} (■) for samples deformed up to $\varepsilon_0 = 30\%$ at $V_{load} = 1$ mm/min and $V_{unload} = 500$ mm/min.

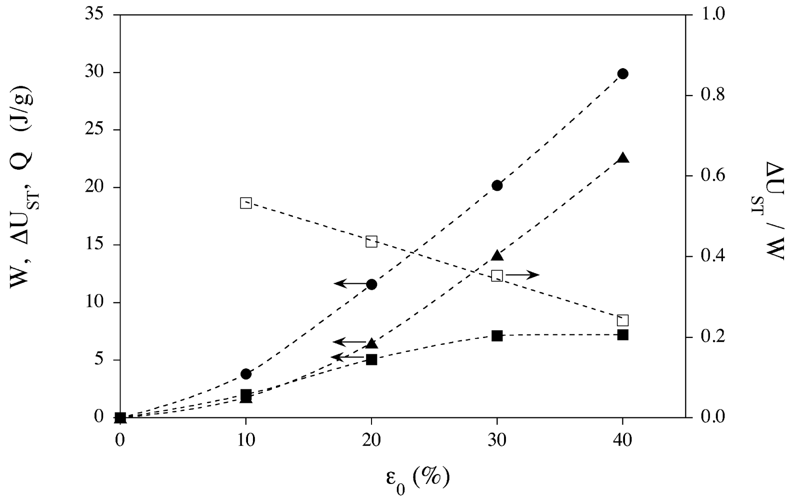

Fig. 7. Effect of the final strain level ε_0 on W (●), ΔU_{ST} (■), Q (▲), and the ratio $\Delta U_{ST}/W$ (□) for samples deformed at $T_{def} = 25$ °C, $V_{load} = 0.05$ mm/min and $V_{unload} = 500$ mm/min.

expected, for low strain levels W is proportional to ε_0^2, while in the post-yield region it almost linearly depends on ε_0. Normally, in post-yield deformation of glassy and semicrystalline polymers, part of the mechanical work of deformation is dissipated (Q) while another part is stored in the deformed material (ΔU_{ST}). Since the first law of thermodynamics is valid for all deformations, whether reversible or irreversible, its application to post-yield deformation allows one to calculate the energy dissipated in a loading–unloading cycle, as [1,2,4–7,14–19,21]:

$$Q = W - \Delta U_{ST} \tag{2}$$

The typical dependence of the quantities ΔU_{ST} and Q on the final strain is reported on Fig. 7. It is interesting to note that the observed trend agrees with the data obtained by numerous authors by deformational calorimetry on glassy and semicrystalline polymers deformed under similar conditions [1,4–7,18,21]. The ratio of the stored energy to the mechanical work of deformation ($\Delta U_{ST}/W$) is also reported on Fig. 7. This ratio is clearly decreasing as the strain level increases in good accordance with the data reported by Li and co-workers [10,11] on glassy polymers. More recently, Shenogin et al. [50] measured the fraction of the inelastic deformation work stored as internal energy in many different amorphous polymers, such as polystyrene, poly(methyl methacrylate), polycarbonate and a cured epoxy, in the pre-yield region by a new deformational calorimeter. They found that the parameter $\Delta U_{ST}/W$ is close to 100% for small inelastic strain and decreases to 60% as deformation approaches to yield.

The strain rate dependence of the measured quantities W and ΔU_{ST}, and of the derived quantity Q, is showed in Fig. 8. It can be noted that both W and ΔU_{ST} are increasing with loading rate while the dissipated energy Q is decreasing. In the same graph, the effect of strain rate on the ratio $\Delta U_{ST}/W$ is also reported. It is interesting to observe that this ratio is linearly increasing with the logarithm of the loading rate thus indicating that the molecular mechanism of energy storage is effectively more active as the strain rate increases.

On the other hand, as reported in Fig. 9, values of W, ΔU_{ST}, and Q, evaluated at a loading speed of 1 mm/min, are markedly decreasing with deformation temperature thus evidencing an opposite effect with respect to strain rate. This behavior is suggesting that the mechanism by which energy is internally stored in the material is influenced by the viscoelastic nature of the polymer under investigation. Interestingly enough, the ratio $\Delta U_{ST}/W$ is practically independent from the deformation temperature oscillating around an average value of about 51%.

4. Conclusions

Semicrystalline PBT specimens were compressed and

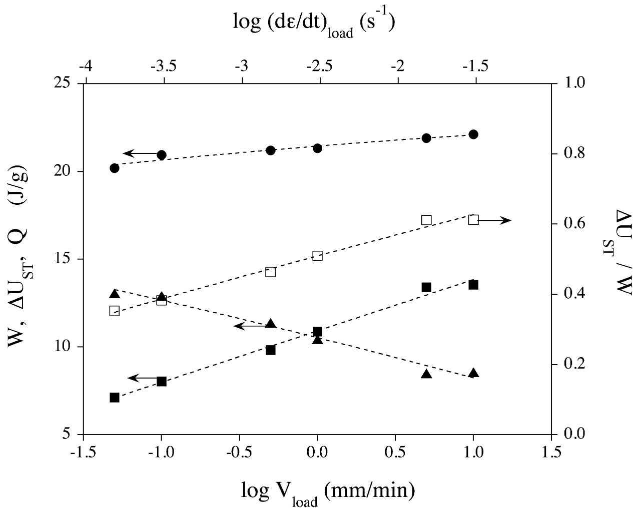

Fig. 8. Effect of loading rate on W (●), ΔU_{ST} (■), Q (▲), and the ratio $\Delta U_{ST}/W$ (□) for samples deformed up to $\varepsilon_0 = 30\%$ at $T_{def} = 25$ °C and $V_{unload} = 500$ mm/min.

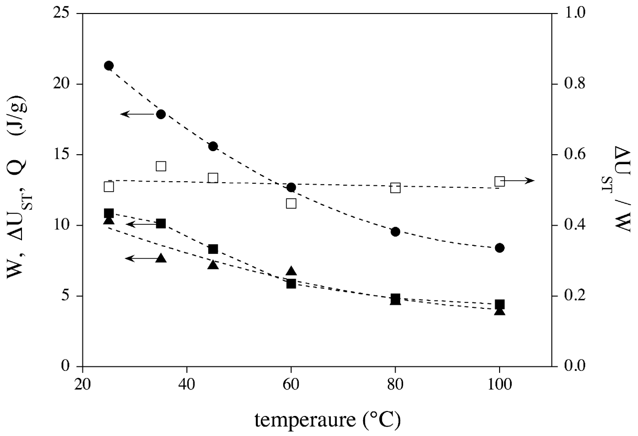

Fig. 9. Effect of the deformation temperature T_{def} on W (●), ΔU_{ST} (■), Q (▲), and the ratio $\Delta U_{ST}/W$ (□) for samples deformed up to $\varepsilon_0 = 30\%$ at $V_{load} = 1$ mm/min and $V_{unload} = 500$ mm/min.

unloaded at various loading–unloading rates and temperatures up to many different strain levels. DSC traces indicated that a remarkable fraction of the mechanical work of deformation (in the range from 25 up to 62%) was stored in the material after unloading. During DSC measurements the release of energy (ΔU_{ST}) stored in the material ranged from temperatures somewhat higher than the deformation temperature up to a level close to the recrystallization and melting processes, being particularly intense at temperatures near T_g.

Final strain dependence of stored energy values for specimens deformed up to 40% followed the general S-shaped trend observed for many amorphous and semicrystalline polymers. The ratio of the stored energy to the mechanical work of deformation ($\Delta U_{ST}/W$) was decreasing as the final deformation level increased.

For a given final strain level, the amount of energy stored in specimens deformed under T_g increased as either loading or unloading rates increased: in particular, both ΔU_{ST} and $\Delta U_{ST}/W$ values were linearly increasing with the logarithm of loading rate. On the other hand, energy storage for specimens deformed at T_g resulted to be practically independent from the loading rate.

Moreover, as the deformation temperature increased from 25 to 100 °C, ΔU_{ST} values markedly decreased while the ratio $\Delta U_{ST}/W$ resulted almost independent, oscillating around an average value of about 51%. All these observations are suggesting that the mechanism by which energy is internally stored in the material is influenced by the viscoelastic nature of the polymer under investigation.

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