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Thermodynamics of the pre-yield deformation behavior of glassy polymers: measurements with new deformation calorimeter

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The paper is dedicated to the honor of Dr. Günther Höhne whose skill and knowledge define the success of the work

Abstract

New deformation calorimeter was designed and built. The calorimeter is capable of measuring the differential heat flow between two cells containing a sample and a dummy. Deformation is performed in either compression or tension mode and ensures the equal forces applied to the sample and dummy in every moment during loading and unloading. The sensitivity of the calorimeter is <1 μW, and the time constant is about 3–4 min. High sensitivity of the instrument allows the measurement of very small deformation heats appearing at low strains (pre-yield strain region). Such data did not exist in polymer literature. Cylindrical samples with 4 mm diameter and 6 mm length were made of glassy polymers, such as polystyrene, (poly)methylmethacrylate, (poly)carbonate and cured epoxy-aromatic amine networks. Samples were deformed at room temperature by uniaxial compression up to strains 8–15% (which is slightly above upper yield point for polymers studied) with the loading rate 1 MPa/min. The same measurements with Cu single crystal were performed for comparison. The work and heat of deformation were measured and the internal energy stored in the deformed samples was calculated with the use of first law of thermodynamics. Total strain, work, heat and stored energy of deformation were split for the elastic (Hookean) and inelastic parts. It was found that in inelastic process all studied glassy polymers store internal energy which does not recover even after unloading of the samples. The parameter $\mathrm{d}U_{\mathrm{in}}/\mathrm{d}W_{\mathrm{in}}$, giving the fraction of the inelastic deformation work W_{in} stored as the internal energy was measured as a function of strain. For annealed samples this parameter is close to 100% for small inelastic strains and decreases to 60% as deformation approaching to yield point. This supports the earlier formulated idea [Polym. Sci. 35 (11) (1993) 1819] that high level of energy storage is the characteristic feature of inelastic response of glassy substances. In contrast, the Cu single crystal does not show any energy storage during elastic and plastic deformation processes. Within experimental accuracy, all deformation work for Cu single crystal is converted to heat. Different deformation behavior of crystal and polymer glasses reflects the differences in deformation mechanisms for both types of the solids. Some details of the inelastic response mechanism for glassy solids based on measured results are discussed.

Keywords: Plastic deformation; Glassy polymers; Deformation heat; Deformation work; Stored energy of deformation; Deformation calorimetry

1. Introduction

Thermodynamic characterization of inelastic deformation of crystalline and amorphous solids have

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issued important information about mechanisms of elastic, anelastic and plastic response of matter [1–5]. Recently, the measurement of deformation work W, deformation heat Q and especially stored deformation energy ΔU for glassy polymers have compelled to formulate new mechanism of plastic deformation in such solids [4,6–10].

For the analysis of energy changes in the deformed samples several calorimetric methods can be used, e.g. the structural recovery of the deformed samples in differential scanning calorimeters (DSC) [5,11,12] or measuring of the difference in dissolving heat for deformed and undeformed samples [13,14]. Deformation calorimetry (DC) is, however, the unique method for direct measurement of the deformation heat and energy stored in the samples while it is deformed. The idea of DC is the measurement of heat Q exchanged of the sample and external work W of deformation simultaneously. If there are no other forms of energy involved, the stored energy ΔU (the change of internal energy of sample on its deformation) can be calculated from the first law of thermodynamics:

$$\Delta U = W + Q \tag{1}$$

For uniaxial compression Q usually has a negative sign (heat is released from the sample), while W is positive. Since for many solids the difference between absolute values of Q and W in the pre-yield strain region does not exceed 5%, both these quantities should be measured with high enough accuracy to get reliable values for ΔU.

The Tian–Calvet-type calorimeter [15,16] is usually used to measure small heat flow rates, such as the heat released during deformation of glassy polymers. Although rather sensitive, this calorimeter generally has a very large time constant (up to 20 min), which is comparable to the time scale of the deformation experiment. Therefore, only the integral value of the heat can be evaluated from the measured heat flow rate because of unavoidable ‘‘smearing’’ of the signal due to the slow heat exchange (thermal lag). To overcome such deficiency, the stepwise loading of the sample with time periods for thermal relaxation between the steps is sometimes used [15]. However, we tried to avoid such loading regime because of the complicated deformation kinetics and stress relaxation taking place in polymers between the loading steps.

Instead, we performed a permanent deformation of the sample with on-line measurement of heat flow rate. For correction of the thermal lag a special mathematical ‘‘desmearing’’ procedure was used [16].

The corrected (desmeared) heat flow rate dQ_0/dt can be calculated from the measured signal dQ_m/dt as a solution of the convolution integral equation:

$$\frac{dQ_m}{dt}(t) = \int \frac{dQ_0(\tau)}{dt} \Phi(t-\tau)\, d\tau \tag{2}$$

where $\Phi(t)$ is the ‘‘apparatus’’ (or Green’s) function of the calorimeter, defined as the normalized response to the δ pulse thermal loading.

In addition to the heat from the specimen, the measured signal usually contains some amount of heat produced by other loaded parts of the DC, such as specimen holders or other force transferring elements (Thomson heat):

$$\frac{dQ_{Th}}{dt} = -T\alpha V \frac{d\sigma}{dt} \tag{3}$$

where σ is the local varying stress, α the linear coefficient of thermal expansion and V the volume of the respective parts of the calorimeter.

It is known that for precise DC measurements a very stable and uniform temperature field ($<10^{-4}$ K) within sensitive parts of calorimeter is the main condition for a stable baseline and reliable measurements of long lasting and week signals. If the DC measurements are performed at room temperatures, very good thermal insulation of the cell against ambient is, therefore, required. This demand is often difficult to fulfill if the compression loading deformation mode is used (uniaxial or plane strain compression), since massive rods should be used to transfer force from the external loading machine to the sample. As a result, DC measurements were up to now restricted to temperatures not to far above ambient (maximum 60 °C) and never at low temperatures.

However, the measuring of the energy balance is potentially a very powerful tool for the study of inelastic deformation in solids. However, for most existing today deformation calorimeters, the measurement of deformation heat is still a complicated procedure leading often to not very accurate results. Only few studies have been done so far with sufficiently good accuracy. It is especially true for pre-yield deformation region of polymer solids because all measured deformation heat is quite small.

To meet these experimental difficulties, we have designed, built and tested a new deformation calorimeter, capable to measure very small deformation heats in a wider temperature range. The calorimeter makes use of the hydraulic loading elements and can generally be assembled from standard mechanical and electronic equipment. In this paper, we will introduce new deformation calorimeter and will show results of the room temperature DC measurements of the deformation work (*W*), deformation heat (*Q*) and stored deformation energy (*U*) in the pre-yield strain region for several glassy polymer, such as polystyrene (PS), polycarbonate (PC), polymethylmethacrylate (PMMA) and cured epoxy-aromatic amine network (EAAN), and for single crystal of Cu for comparison.

2. Experimental

2.1. Deformation calorimeter

We used a special Calvet-type differential calorimeter from *Barberi* (France) with two sides open sensitive tubes as a heat sensitive part of the device. Two sensitive cells with a diameter 10 and 100 mm length each separated one from another by 20 mm are connected with thermopiles (*Barberi* system) to measure the differential heat flow between the cells with a sensitivity of 85 mV/W. The apparatus scheme is shown in Fig. 1. The time constant of such a calorimeter is usually about 3–4 min, depending on which sample holder is used (Fig. 2).

The sample (2 in Fig. 1) and an invar dummy of the same size (3) are fixed between pairs of sample holders (4–7) within the working and reference cells of the calorimeter, respectively. The reason for using a dummy on a reference side is to compensate for the Thomson heat from the deformation mechanics and the holders. The use of hydraulic force transfer ensures that the force applied to the sample and that to the dummy are equal in every moment. The dummy, made of invar alloy, has a very low thermal expansion coefficient and, thus, a very low Thomson heat of deformation. As a result, only the deformation heat of the sample itself is left in the measured differential heat flow rate. All other heats cancel each other out to the greatest extent.

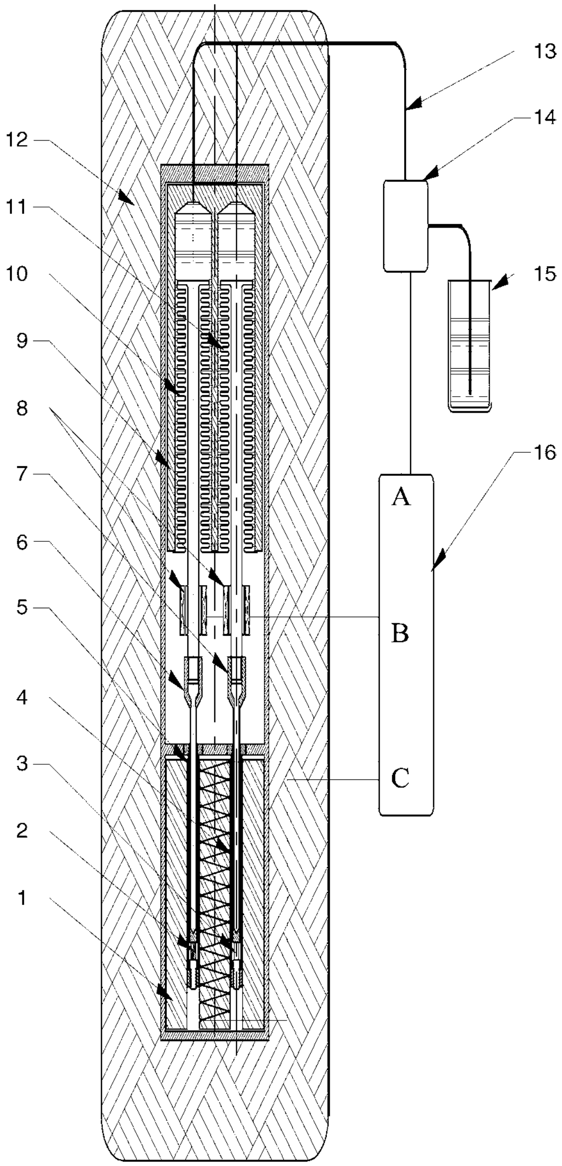

Fig. 1. The scheme of differential deformation calorimeter with hydraulic loading system: 1: Calvet-type differential calorimeter, 2: sample, 3: dummy, 4–7: sample holders, 8: displacement sensor, 9: hydraulic block, 10, 11: bellows, 12: thermal insulation, 13: PVC tube, 14: hydraulic pump, 15: oil tank, 16: recorder, recording: (A) force; (B) strain; (C) heat flux.

Two deformation modes, uniaxial compression and tension of samples can be performed with different constructed holders. Although the compressive deformation, compared to the uniaxial tensile mode, usually

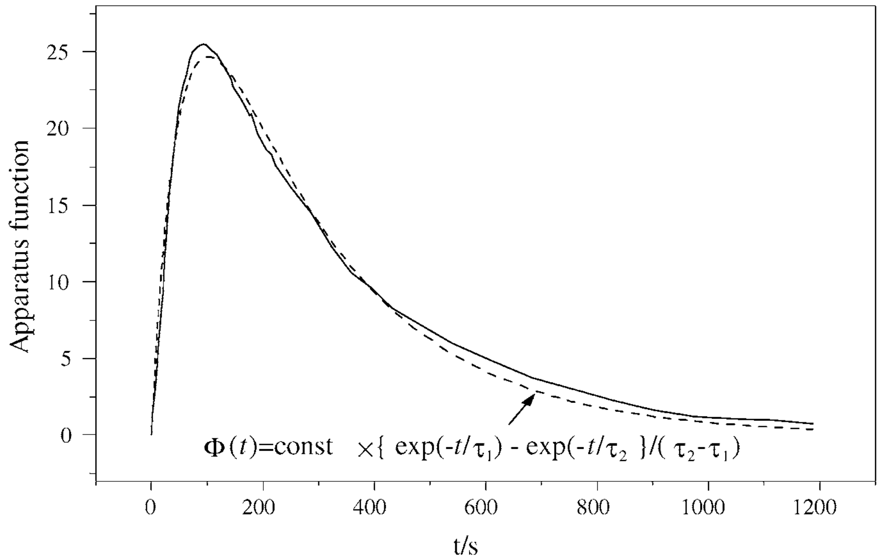

Fig. 2. The apparatus function (solid line) of the calorimeter with holders for the compression loading deformation mode and polymer sample, and the theoretical curve (dashed line) for the Calvet–Tian calorimeter [16].

requires samples with larger cross-section (to avoid sample bending) and therefore larger force, we preferred to use this scheme because of more uniform strain distribution in a sample, the non-brittle response of most common glassy polymers and a larger gage volume of the sample. The relatively high maximum force (2500 N) of our device makes the compressive mode possible. Polymer samples for these experiments were usually small cylinders of 4 mm diameter and 6 mm length.

Sample holders (5, 6) are connected to the hydraulic unit (9), which contains two sets of working bellows (10, 11) filled with thin silicon oil. Both calorimetric and hydraulic units are placed into a well insulated thermostat (12). The bellows are connected to one another (to ensure exact the same pressure) and to the hydraulic pump outside the thermostat via a very thin (0.018 in.) PVC tube (13). Both pipes and the pump are the standard equipment used for high pressure liquid chromatography (HPLC) measurements. The maximum oil pressure in the instrument reaches 70 bar (7 MPa), leading to maximum force of 2.5 kN on each of two sets of sample holders.

Using the bellows results in a well damped, smooth and reliable operation of the deformation mechanics in a rather wide temperature range, but decreases the stiffness of loading system to a value of 15.7 N/mm. Since this is much lower than the stiffness of the sample itself, a linear raise of the force at constant pumping rate was ensured. In deformation calorimetric experiments the constant force rate mode ($\mathrm{d}F/\mathrm{d}t = \mathrm{const}$) is an advantage since the remaining Thomson heat flux (from clamps and holders as well as from the sample) is constant (see Eq. (3)) in this mode and can be easily subtracted from the measured signal as a baseline.

The disadvantage of the constant force rate mode is the instability of the sample on raising the force above the yield point. Only the pre-yield strain region of the most of polymers can be studied in this way. The stiffness of the loading system can be lowered further, if necessary, by including air bubbles somewhere in the hydraulic system. This does not change the linear response of the system to the increasing pressure.

The standard HPLC pump (Jasco Inc., Japan) was used to generate pressure. The pump is capable of working either in constant pressure or in constant flow mode at rates from 0.001 to 20 ml/min. This results in sample deformation in the calorimeter at either constant force (creep) or at constant force rate. In both cases the sample strain can be separately measured with the displacement sensor (8) with an accuracy of 0.001 mm.

The apparatus function (the thermal pulse response) of the calorimeter with a compression mode loaded sample is shown in Fig. 2. The shape of the curve is quite close to the theoretical curve (dashed line) derived for a Calvet–Tian type calorimeter [16]:

$$F(t) = \mathrm{const}\frac{\exp(-t/\tau_1) - \exp(-t/\tau_2)}{\tau_2 - \tau_1} \quad (4)$$

Long and short-term time constants of the calorimeter with polymer sample, dummy and compression loading system installed are $\tau_2 = 245$ s and $\tau_1 = 52$ s, respectively. Due to the rather big difference of the two time constants, the lower one can be ignored. In this case the integral Eq. (2) can be transformed to a differential equation [14]:

$$\frac{\mathrm{d}Q_0}{\mathrm{d}t}(t) = \frac{\mathrm{d}Q_\mathrm{m}}{\mathrm{d}t}(t) + \tau_2\frac{\mathrm{d}}{\mathrm{d}t}\frac{\mathrm{d}Q_\mathrm{m}}{\mathrm{d}t} \quad (5)$$

and a simplified desmearing procedure for correction of the measured heat flux signal $\mathrm{d}Q_\mathrm{m}/\mathrm{d}t$ was actually applied. In this procedure, however, the short-term time constant $\tau_1 = 52$ s was not compensated for, and it characterizes the resulting time resolution of the measuring system. The heat flow rate resolution threshold is about 1 μW under optimal isothermal conditions.

As it was mentioned above, the whole deformation calorimeter can be placed into a proper thermostat. The temperature range is limited by solidification and boiling temperatures of the hydraulic liquid used. Since the only unavoidable interconnections between the calorimeter and ambient is the thin PVC pressure pipe and some electric wires, the insulation of the thermostat can be made very effective. Because of the high demands on thermal stability and isothermal conditions a rather long time of equilibration (12 h) is needed between mounting the sample and starting the measurement.

2.2. Samples

The experiments were performed in compression at constant engineering stress rate mode ($\mathrm{d}\sigma/\mathrm{d}t = 1$ MPa/min) on the series of standard, commercially available, glassy polymers with already known deformation behavior, to show the performance of the device and compare with other literature values. We have tested atactic polystyrene (PS-115 M grade, $M_\mathrm{w} = 2 \times 10^5$, $M_\mathrm{w}/M_\mathrm{n} = 7.5$, T_g (DSC) = 97 °C), atactic polymethylmethacrylate (PMMA–SD 35 grade, $M_\mathrm{w} = 10^5$, $M_\mathrm{w}/M_\mathrm{n} = 6$, T_g (DSC) = 110 °C), polycarbonate (PC–Macrolon 2100, T_g (DSC) = 147 °C), and a cross-linked epoxy-amine network polymer (EAAN: T_g (DSC) = 144 °C) [17]. The cylinder shaped specimens (4 mm diameter, 6 mm length) were machine-made from the bulk material and annealed for 20 min in a dry air atmosphere at temperatures: $T = T_\mathrm{g} + 10^0$. Afterwards the specimens were either slowly cooled in the closed oven down to room temperature (cooling rate ca. 2 °C/min) or quenched into ice water. All calorimetric measurements were performed at room temperature.

3. Results

The measured heat flux functions (logarithmic scale) together with the respective stress and strain curves for constant stress rate loading regime with the rate 1 MPa/min are given in Fig. 3. The slow loading assures a correct measurement of the heat flow involved, since the thermal lag and the smearing is small in this time scale, as the apparatus function (Fig. 2) is narrow compared to the measured curve.

During the elastic phase of deformation (Hookean strain region) only the Thomson heat was detected for all of the tested polymers as a small constant heat flow of 0.2–0.7 $\mu\mathrm{W/mm}^3$ in accordance with Eq. (3). The measured Thomson heat flow is generally somewhat smaller for the quenched samples than for the annealed ones. That caused by the lower thermal expansion coefficient of the annealed polymer glasses. The small but nevertheless significant difference for the quenched and annealed samples shows the high precision of the new calorimeter.

From Eq. (1) the internal energy u_el (per unit of sample volume) for the elastic region of deformation at constant stress rate $\mathrm{d}\sigma/\mathrm{d}t = c$ can be calculated as:

$$\frac{\mathrm{d}u_\mathrm{el}}{\mathrm{d}t} = \frac{\mathrm{d}w_\mathrm{el}}{\mathrm{d}t} + \frac{\mathrm{d}q_\mathrm{el}}{\mathrm{d}t} \quad (6)$$

using Hook's law $\sigma = E_\mathrm{el}e_\mathrm{el}$ for calculation of w_el and Eq. (3) for q_el:

$$\frac{\mathrm{d}w_\mathrm{el}}{\mathrm{d}t} = \sigma\frac{\mathrm{d}\varepsilon_\mathrm{el}}{\mathrm{d}t} = \frac{\sigma}{E_\mathrm{el}}\frac{\mathrm{d}\sigma}{\mathrm{d}t} = \frac{c^2}{E_\mathrm{el}}t \quad (7)$$

$$\frac{\mathrm{d}q_\mathrm{el}}{\mathrm{d}t} = -T\alpha\frac{\mathrm{d}\sigma}{\mathrm{d}t} = -c\alpha T \quad (8)$$

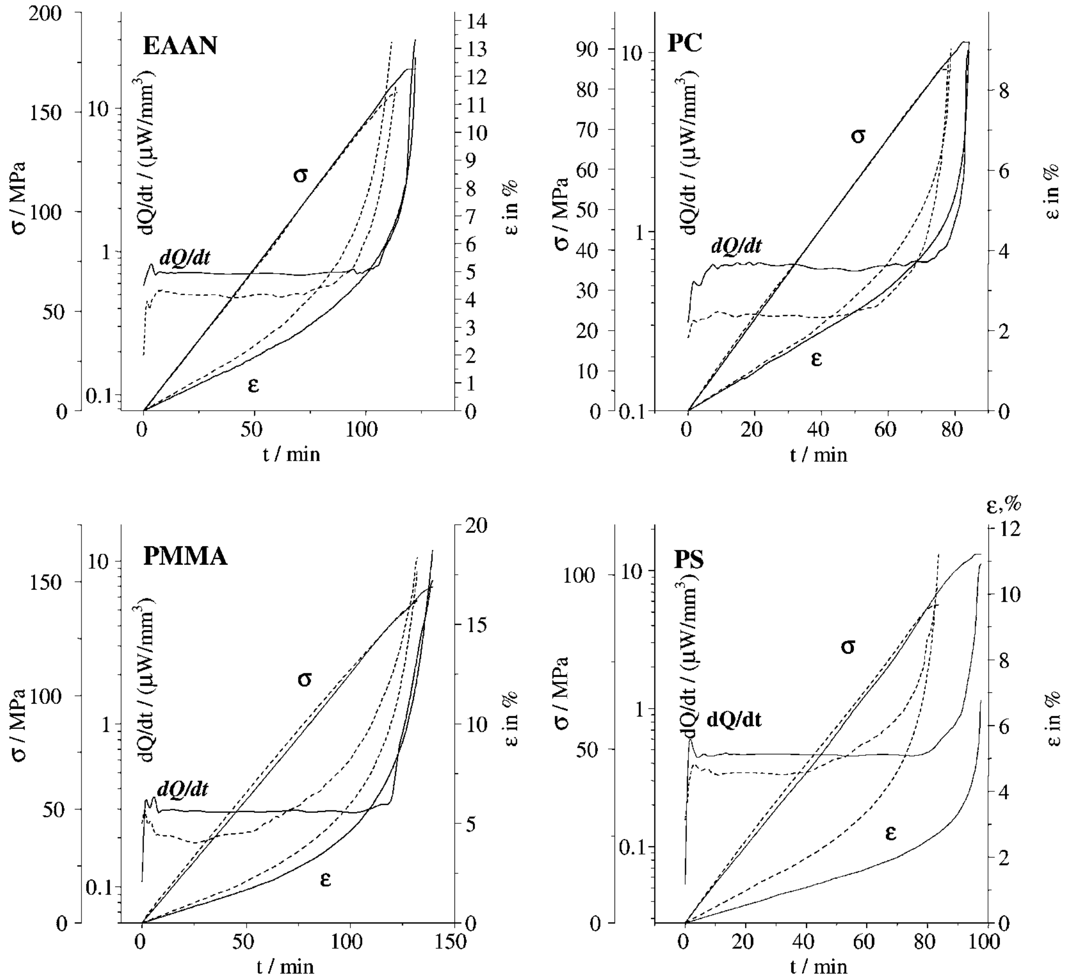

Fig. 3. Heat flow rate, stress and strain vs. time curves for different polymers deformed in compression mode at a constant (engineering) stress rate of 1 MPa/min. Annealed samples (solid lines), quenched samples (dashed lines).

where w_{el} is the external elastic work, q_{el} the Thomson heat (per unit of sample volume), and E_{el} the elastic compression modulus of the sample material. As long as the strain is elastic, the stored internal energy ΔU_{el} is completely released on unloading.

The loading beyond the elastic (Hookean) region results in a softening of the material and consequently in a considerable raise of the strain rate (Fig. 3). Since our main interest is the study of inelastic deformation, it is useful to split the full strain to the inelastic and elastic parts as described in Section 4. Because the applied force increases linearly, the elastic (Hookean) component of the total strain increases linearly too and can be determined by extrapolation from the initial elastic region of deformation. The difference between the measured and this extrapolated elastic strain yields the inelastic component of the strain:

$$\varepsilon_{in} = \varepsilon - \varepsilon_{el} = \varepsilon - \frac{\sigma}{E_{el}} \qquad (9)$$

Furthermore, the external work rate can easily be separated into elastic and inelastic parts, by splitting the elastic and inelastic components of the strain which is an extensive variable:

$$\frac{dw_{in}}{dt} = \sigma\frac{d\varepsilon}{dt} - \sigma\frac{d\varepsilon_{el}}{dt} = \frac{dw}{dt} - \frac{dw_{el}}{dt} = \frac{dw}{dt} - \frac{c^2}{E_{el}}t \qquad (10)$$

In a similar way, we can subtract the Thomson (elastic) heat flux (Eq. (8)) from the measured one to obtain the fraction which is connected with inelastic deformation of the sample. The sum of the inelastic work rate $\mathrm{d}w_{\mathrm{in}}/\mathrm{d}t$ and the inelastic heat flux $\mathrm{d}q_{\mathrm{in}}/\mathrm{d}t$ yield the inelastic stored energy (under applied stress):

$$\frac{\mathrm{d}u_{\mathrm{in}}}{\mathrm{d}t}=\frac{\mathrm{d}w_{\mathrm{in}}}{\mathrm{d}t}+\frac{\mathrm{d}q_{\mathrm{in}}}{\mathrm{d}t} \tag{11}$$

Eq. (11) can obviously be obtained from the general energy flow balance by the subtraction of Eq. (6).

Only during inelastic deformation the irreversible internal energy ΔU_{in}, which remains in the sample even after unloading, can be produced [4–7]. This actually means that certain structural changes must take place during inelastic deformation of polymers which are bound up with an increase of internal energy in the deformed material. It might be, therefore,

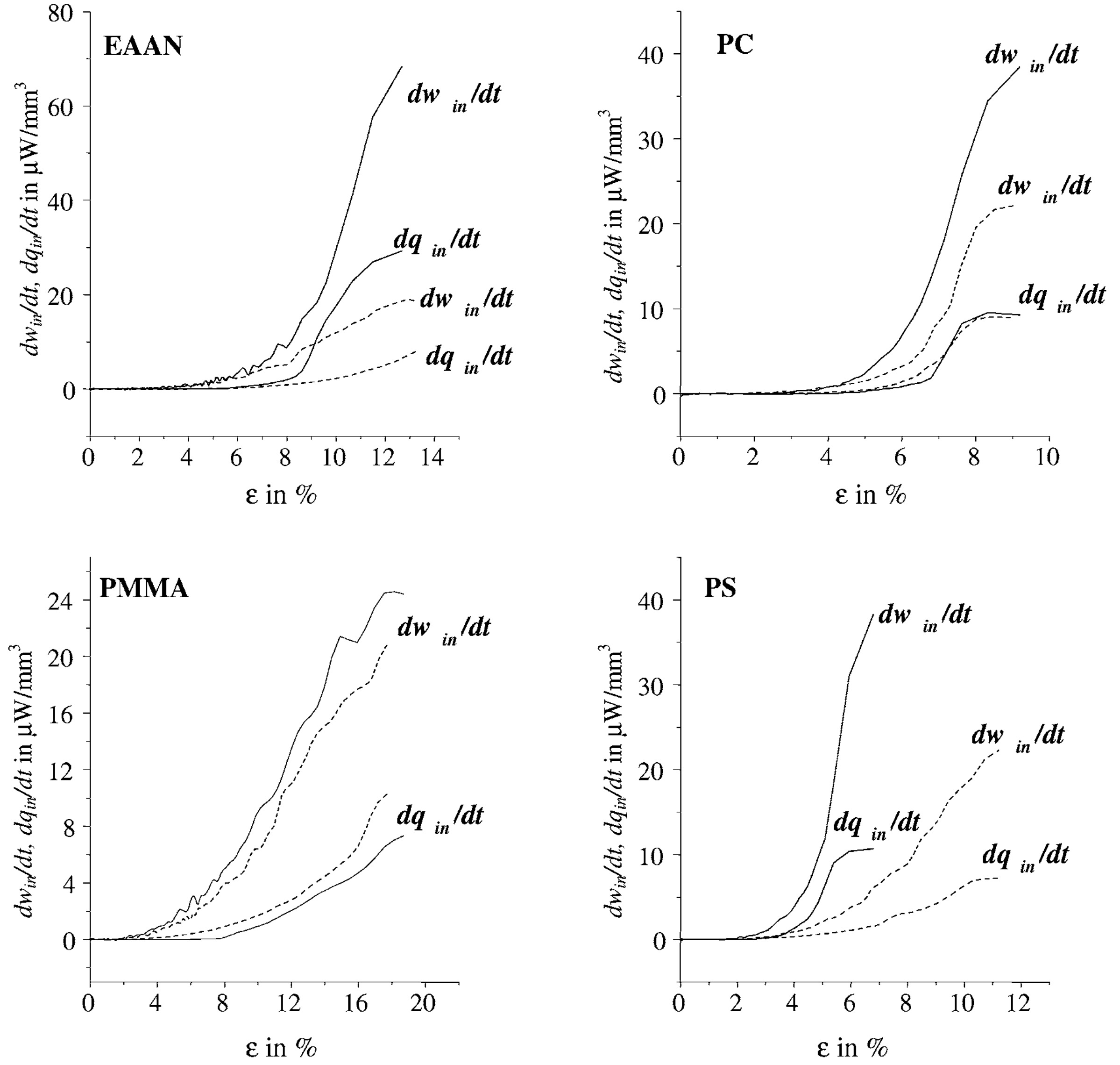

Fig. 4. Inelastic deformation heat flow rate and inelastic deformation external work rate vs. full compressive strain for different polymers. Annealed samples (solid lines), quenched samples (dashed lines).

interesting to monitor the inelastic portion of the internal energy (Eq. (11)). Unlike the elastic deformation, there are always relaxation processes involved in inelastic response of solids which need time. The current state of deformed sample is no equilibrium state and the variable $\varepsilon_{\rm in}$, unlike $\varepsilon_{\rm el}$, depends in every moment on the stress prehistory. It should be born in mind that all our results are obtained in constant stress rate mode, and all quantities in the energy balance of inelastic deformation (Eq. (11)) are measured with the sample being under external stress in a non-equilibrium state.

The dependence of inelastic heat flux and inelastic work rate versus sample total strain ε during pre-yield deformation stage calculated with Eqs. (10) and (11) are shown in Fig. 4. It is interesting to note that the thermal effects are considerably different for annealed and quenched glassy polymers. For small inelastic strain (in the beginning of that region) annealed samples does not show any thermal effect, only (elastic) Thomson heat is observed there while softening occurs. This means that for an annealed sample in the beginning of loading the inelastic work of deformation is totally stored as internal energy. Later, with further deformation of the annealed samples, additional heat flow appears and increases faster then is the case with quenched samples. The difference between quenched and annealed polymers is more distinct for PMMA and polystyrene, which are more brittle materials than the others.

The parameter $\mathrm{d}U_{\rm in}/\mathrm{d}W_{\rm in}$ gives the fraction of the inelastic work stored as internal energy of inelastic strain. For annealed samples this parameter is close to 100% for small inelastic strain and decreases to about 60% as approaching to yield point (Fig. 5a). In case of quenched material, for all studied polymers except EAAN still very large fraction, but not 100%, of inelastic external work is stored during pre-yield deformation stage (50–80%, Fig. 5b). Note that results on Fig. 5 are obtained in the presence of external load, on unloading the stored energy decreases somewhat due to the internal relaxation processes.

High level of stored energy is the characteristic feature of inelastic response of the disordered solids (glasses) [4–11]. The deformation behavior of metallic crystals differs distinctly in this point. For a copper single crystal all the external work is released from the sample as a deformation heat at the beginning of the inelastic deformation region (Fig. 6). Hence, there is practically no energy storage during this phase of pre-yield inelastic deformation of Cu crystal. This result is consistent with the data of [1,2].

From Fig. 3 follows that there is an almost exponential increase of the inelastic strain and an even faster raise of the heat flow rate when the stress is approaching the yield stress $\sigma_{\rm y}$. In other words, the fraction of heat released per unit of inelastic strain tends to increase at higher strains. The quantity of the internal energy stored per unit of inelastic strain, $\chi(\varepsilon)$, using Eqs. (10) and (11), reads:

$$\chi(\varepsilon) = \frac{\mathrm{d}u_{\rm in}}{\mathrm{d}\varepsilon_{\rm in}} = \sigma + \frac{\mathrm{d}qe}{\mathrm{d}\varepsilon_{\rm in}} \qquad (12)$$

This quantity is plotted in Fig. 7. For all tested polymers $\chi(\varepsilon)$ behaves in a similar way: first it increases, then a

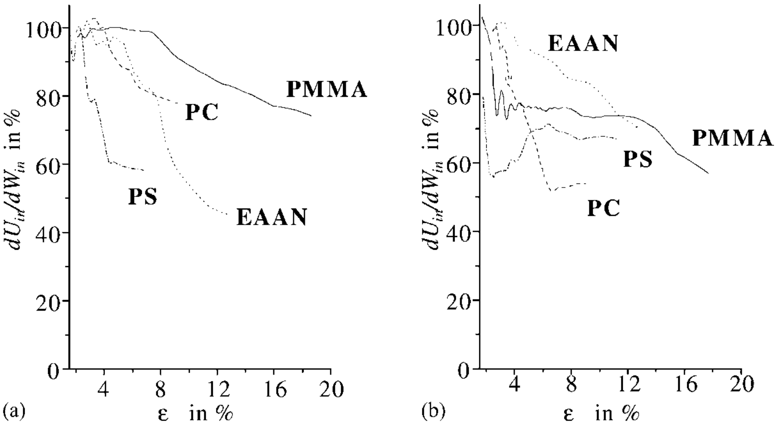

Fig. 5. The ratio $\mathrm{d}U_{\rm in}/\mathrm{d}W_{\rm in}$ in the process of deformation for studied polymers, (a): annealed samples, (b): quenched samples.

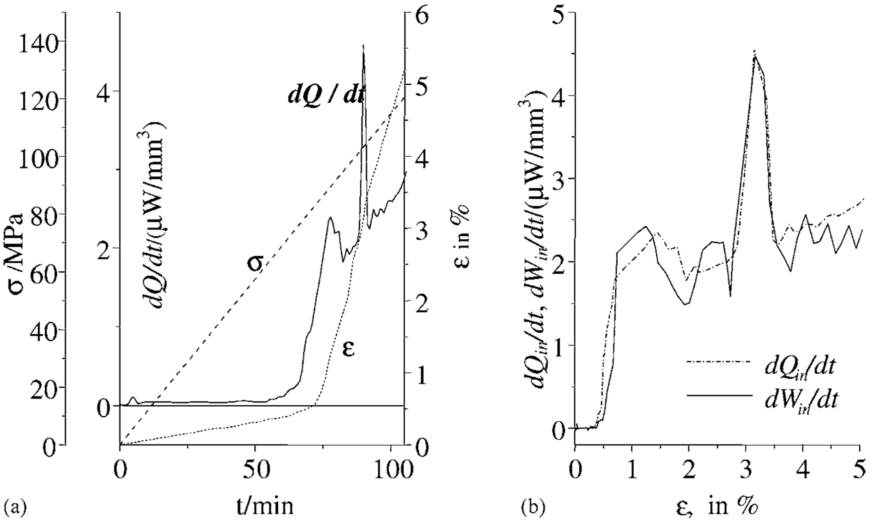

Fig. 6. Deformation of a copper single crystal in uniaxial compression mode along the (1 1 2) slip system at constant stress rate: (a)—heat flow rate, stress and strain vs. time, (b)—inelastic part of heat flow rate and work rate vs. full ($\varepsilon_{\mathrm{def}}$) engineering strain.

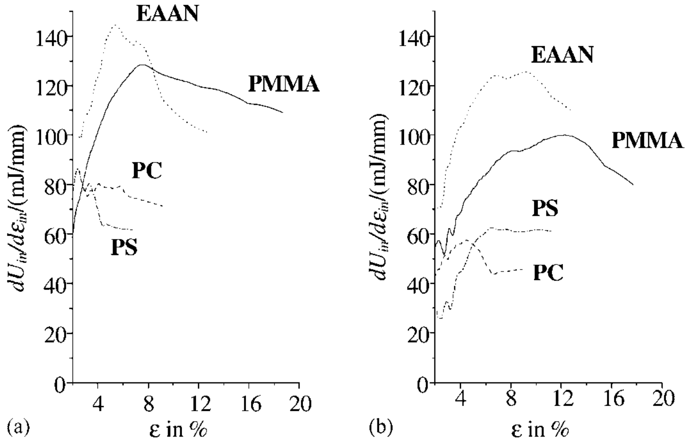

Fig. 7. The value of internal energy stored per unit of inelastic strain $\varepsilon_{\mathrm{an}}$, $\chi(\varepsilon_{\mathrm{an}}) = \mathrm{d}U_{\mathrm{in}}/\mathrm{d}\varepsilon_{\mathrm{in}}$, as a function of full strain ε for different polymers, (a): annealed samples; (b): quenched samples.

broad maximum, occurs, followed by an decrease when the deformation approaches the yield point. Again, for the annealed samples this quantity is somewhat higher than for the quenched ones.

4. Discussion

Although the accumulation of inelastic strain looks very similar for glasses and crystals, the heat release drastically differs. For the compression of annealed polymer glasses, the inelastic part of strain in pre-yield regime causes no heat release. Mechanical work done is stored by a sample as an internal energy ΔU. For the comparison we have performed the same DC measurements for the annealed Cu single crystal (the same deformation conditions). It was found that Cu single crystal shows exactly opposite to glassy polymers behavior (Fig. 6). Practically all inelastic work of the deformed Cu crystal is transformed to deformation heat. There is no any energy storage in this case. Other metallic crystals show the same behavior also [1,2]. Such difference in the deformation work transformation suggest a principally different mechanisms of inelastic deformation for these two classes of solids, glasses and crystals, respectively [4,10].

The reported results agree well with experimental data previously obtained using several experimental techniques to investigate the evolution of polymer glass structure on deformation. DSC measurements on plastically deformed samples (containing the residual strains upon unloading) of glassy polymers [4,5], for instance, show a considerable raise of internal energy in the deformed state. The main part of this excess internal energy is stored in that component of the residual strain which recovers already below T_g (usually from T_{def} up to T_g) [4]. Such residual strain recovery (so called "low temperature recovery" [3,4,17]) is related to anelastic strain component [18]. In the deformation calorimeter experiments it should, therefore, appear at small strains, in the beginning of the inelastic response of a sample. From Fig. 7 it is clear that the function (stored energy per unit of anelastic strain) reaches its maximum already at rather small strains (annealed samples: 3% for polystyrene and PC, 8% for PMMA and EAAN). Yield strains ε_y for these samples, at the used deformation regime, are 8 and 12% correspondingly. It means that the subsequent decrease of χ at higher strains (Fig. 7) is certainly related to the processes of deformation softening and yielding.

Within the framework of the deformation mechanism proposed and analysed in [4,6–9] and developed further in [9] the decrease of the quantity χ is caused by transition of sample to the steady plastic deformation regime. In the framework of deformation mechanism of [4,6–9], the increase of ΔU caused by nucleation of "shear transformations" (ST), regions of concentrated inelastic local shear strains in a glassy solid [10,19]. When the concentration of STs is small (small strains) these STs are not interacting yet. However, at the yield region, when the concentration of ST becomes high, the interaction of different STs appear. STs merge and the local strains in merged STs is growing. Each act of merging release the energy stored in separated STs (the merged STs has lower local ΔU compared to the sum of energies of the non-merged STs), resulting in the decrease of sample ΔU as seen in Fig. 7 (ΔU decrease after the broad maximum). The strain level ε_χ where the maximum of χ is observed, as well as the maximum value $\chi(\varepsilon_\chi)$ itself, depends on the intensity of the energy relaxation processes in question.

Hence, the dissipation parameter, introduced elsewhere [8] as the value reflecting internal brittleness of polymer glass (the effectivity of accumulated ΔU dissipation in deformation process), can be defined more accurately as the ratio of ε_χ and the strain level of the yield point ε_y:

$$\eta = \frac{\varepsilon_\chi}{\varepsilon_y} \qquad (13)$$

The difference of heat effects for the annealed and quenched samples can also be explained within this model. In the beginning of inelastic deformation of polymer glasses, the annealed samples does not produces additional heat because of only a poor interaction of STs. This could be caused by a smaller initial concentration of ST in the annealed glassy samples, compared to that of the quenched ones.

Several other interesting effects are seen in the present DC data. Consider, for example, the differences in work and heat components of energy balance for different polymers (Fig. 4). For PC and PMMA, quenching leads to a minor decreasing of the work (dW/dt) and increasing of the amount of heat (dQ/dt). As a result, the internal energy decreases (compare Fig. 7a and b). For EAAN and polystyrene, quenching seriously decreases both work and heat fluxes, but the internal energy practically does not change. Such features of deformation of different polymer glasses are related to some quantitative difference in deformation kinetics. The decrease of heat flow rate shows that the interaction of the STs becomes slower and dissipation of ΔU becomes worse. At the same time ST nucleation becomes easier due to the decrease of sample modulus, resulting in the reduction of the dW/dt upon quench.

However, the results presented here as well as those reported earlier on the deformation behavior of polymers [4–11] require more research to come to a better understanding. The new sensitive deformation calorimeter seems to be a powerful tool for future studies on polymer solids, which will be done in future.

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