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Work, heat and stored energy in compressive plastic deformation of glassy polymers

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Abstract

For a number of organic glassy polymers with different chemical structures and immiscible blends, the mechanical work expended for deformation, the plastic deformation heat and the internal energy stored in deformed samples (stored energy of cold work) have been measured using different experimental techniques.

A comparison of the measured quantities is made and suggestions concerning their nature are discussed. It is found that the fraction of expended mechanical work transformed into stored internal energy upon deformation is very high for all studied systems. This reflects the non-isostructural character of inelastic deformation in glassy polymers. A two-stage deformation mechanism is introduced and the experimental results are analyzed in a framework of the suggested mechanism.

Keywords: DC; Deformation; DSC; Glassy polymer; Mechanism; Polymer

1. Introduction

The balance of work W expended for deformation of a solid sample and the fractions of W transformed into deformation heat Q and the internal energy ΔU stored in the deformed sample, provide important information about the mechanism of the deformation process itself and about specific features of the response of

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different types of solids to an external mechanical load. This has been reviewed extensively for crystalline metals [1–3]. A number of measurements for solid organic polymers have been made [4–8] and the results discussed [9–12].

In many polymers, complications arising in the analysis of inelastic deformation processes in polymers mostly depend on their amorphous structure. Translationally irregular macromolecules are not crystallizable and, on cooling below their glass transition temperatures T_g, form disordered (glassy) solids. Very often, organic polymers may crystallize partially (semi-crystalline polymers) and their amorphous phase (below T_g) exists in the glassy state as well. The disordered structure of glasses does not permit application of the elegant model of plastic deformation in crystals to describe the mechanical behavior of glasses.

Compared to crystals, the deformation of disordered solids is poorly understood and the proposed models are quite controversial.

Measurements and analyses of W, Q and ΔU of the inelastic deformation of glassy and polymer blends performed over the last few years have revealed new features of their mechanical behavior and new deformation mechanisms [10–12]. In the case of polymer glasses, measurements of quantities characterizing the thermodynamics of their inelastic deformation are even more important than for crystalline solids, because they provide not only the unknown physical characteristics of the investigated materials, but also important additional information about the mechanisms of deformation in such solids.

In this paper, we present our W, Q and ΔU data measured for several organic polymers and materials, compare them with other data in the literature, and analyze them in the framework of their macromolecular nature, the structure of the studied materials and previously suggested mechanisms of deformation.

2. Materials, experimental procedures, and results

During recent years, we have performed mechanical and calorimetric measurements on different groups of polymers, namely

(1) conventional linear, commercial high molecular weight glassy polymers, such as polystyrene (PS), polycarbonate (PC), polymethylmethacrylate (PMMA), poly-(benzo phenon)-imid (PI), amorphous polyethelenetherephtalate (a-PET), and polyphenyleneoxide (PPO);

(2) semi-crystalline polymers, such as PET, and polybuthelenetherephtalate (PBT);

(3) crosslinked polymers, such as cured networks based on bifunctional epoxy oligomers, and *meta*-phenelenediamine (EAN). By changing the ratio between epoxy and amine in non-cured mixtures, networks with different concentrations of chemical crosslinks after cure have been prepared [13] and then deformed in the glassy state;

(4) polymer blends, such as ABS, PC/PET, PC/PBT, PC/ABS. (The blends were kindly provided by the Plastic's Institute Moscow.)

For all the samples, we have measured the stress–strain curves (uniaxial compression, loading and unloading with the same cross-head speed of 10^{-1}–

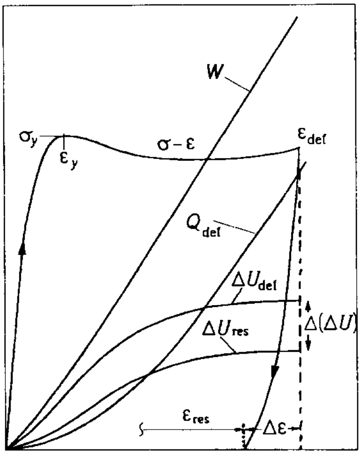

Fig. 1. Quantities characterizing the isothermal deformation process in solid polymers: deformation work W, deformation heat Q_{def}, internal energy stored by sample upon straining ΔU_{def}, internal energy stored by deformed, but unloaded sample ΔU_{res}, the difference $\Delta(\Delta U) = \Delta U_{def} - \Delta U_{res}$, residual strain ε_{res}, the strain released upon sample unloading $\Delta\varepsilon$, and a stress–strain curve $\sigma-\varepsilon$ typical for glassy polymers.

10^{-2} min^{-1}) at room temperature (RT) using an Instron 1122 mechanical tester and a home-made deformation calorimeter (see below). From the stress–strain curves, the mechanical work W (used for sample deformation) was received as a function of macroscopic strain

$$W = \int_0^{\varepsilon_{def}} \sigma \, d\varepsilon - \int_{\varepsilon_{def}}^{\varepsilon_{res}} \sigma \, d\varepsilon \tag{1}$$

The first term is the work expended during sample loading and the second is the work released during sample unloading. All other quantities are defined in Fig. 1.

Deformation calorimetric (DC) measurements were made with a home-made instrument, based on a commercial (Calvet-type) isothermal calorimeter DAK-1 (produced by Experimental Plant of Scientific Instruments of the USSR Academy of Sciences, Chernogolovka, Moscow region) equipped with a home-made loading cell.

Differential scanning calorimetric (DSC) measurements were made using a DSC-990 (Du Pont Instrument) and a DSC-7 (Perkin-Elmer), by heating the deformed, but unloaded samples at a constant rate.

Typical stress–strain and DC curves from (glassy) sample loading and unloading, and DSC curves of undeformed and deformed (with residual strain ε_{res}) samples are shown in Figs. 1, 2 and 3, respectively.

Changes in deformation work W, deformation heat Q_{def} and internal energy ΔU stored by the deformed sample are also shown in Fig. 1. The values of W for compressive deformation of different glassy polymers and blends are shown in Fig. 4.

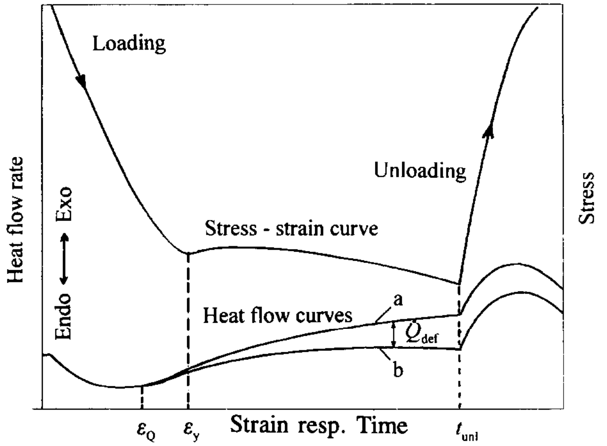

Fig. 2. Typical experimental deformation calorimetric curves for an isothermal deformation process of glassy polymers in active uniaxial compressive loading mode at constant strain rate (ε is proportional to time): curve a, with sample; curve b, same procedure, but without sample.

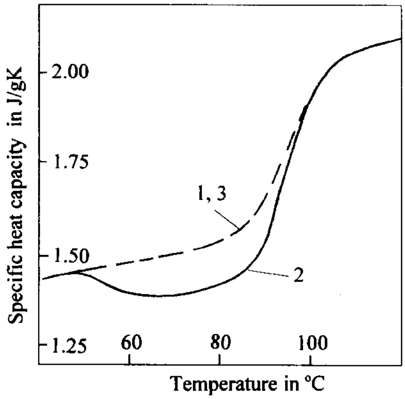

Fig. 3. DSC curves: (1) undeformed; (2) deformed in uniaxial compression mode (ε_{res}, 20%; T_{def}, room temperature); (3) compressed with hydrostatic pressure (p, 1 GPa; T_{def}, 23°C). Samples of PS: mass, 5–10 mg; heating rate, 20 K min^{-1}.

Typical experimental DC curves are shown in Fig. 2. This indicates how $\dot{Q}_{def}$ was measured and calculated from our experiments. Curves a and b in Fig. 2 depict the heat flow rate appearing upon deformation of the loading cell in compression mode, with and without polymer sample respectively. From the difference between curves a and b, the value of the experimental heat of deformation $\dot{Q}_{exp}$ can be calculated for any value of ε_{def} at the respective time. To receive the true $\dot{Q}_{def}$ values, all measured $\dot{Q}_{exp}$ values were corrected for the calorimeter inertia using the equation [14]

$$\dot{Q}_{def} = \dot{Q}_{exp} + \tau \, d\dot{Q}_{exp}/dt \tag{2}$$

where τ is the time constant of the calorimeter (5 min in our case).

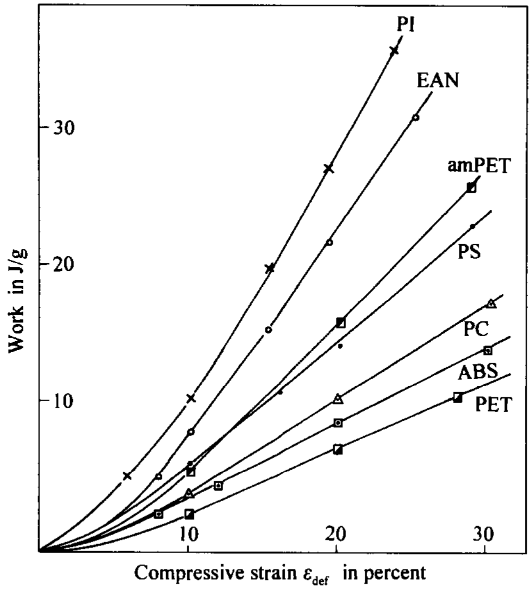

Fig. 4. Work W per mass unit expended for uniaxial compressive deformation of different glassy polymers and blends at room temperature.

Unfortunately we could not completely compensate for the heat appearing due to the deformation of the loading device itself (without polymer sample) because of its massive design, which is necessary for application of the high mechanical forces required to reach macroscopic yielding for the samples used (cylinders, $d = 2-3$ mm, $h = 3-4$ mm). Therefore, curve b in Fig. 2 should be taken as the zero-line for all our DC measurements.

Furthermore, from Fig. 2 one may see that at low deformation the heat flow is negative in our experiments and curves a and b practically coincide. Hence, the measured endotherm at low deformations appears to be due to the deformation of the pure loading cell and the heat of polymer deformation at this deformation interval is comparatively small.

The deformation of the loading cell is evidently elastic because exactly the same amount of heat (but of the opposite sign) disappears from it during its unloading (Fig. 2).

Measurements in this region of the pure elastic (Hookean) deformation heat of the studied polymers should be performed with another loading cell. Values of the Hookean part of the deformation heat are known for many polymers [9] and might be estimated for isothermal deformation conditions from the equation

$$Q_h = \alpha T V_0 E \varepsilon \qquad (3)$$

where α is the linear thermal expansion coefficient, ε the strain, E the modulus and V_0 the sample volume.

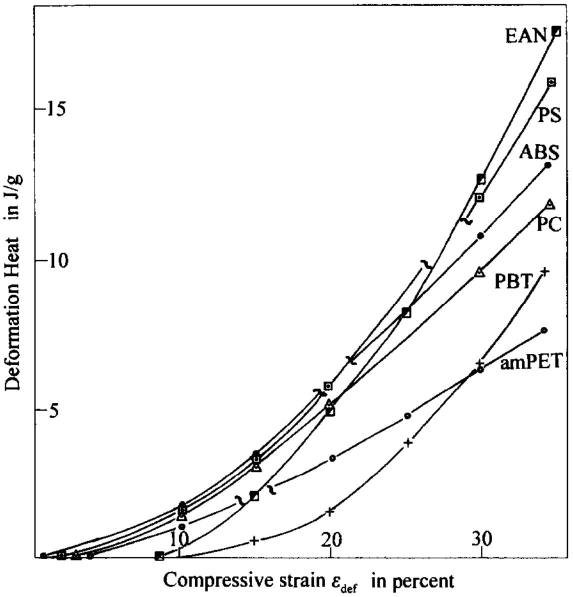

Fig. 5. Heat Q_{def} per mass unit produced on uniaxial compressive deformation of different glassy polymers and blends at room temperature.

Measurements of Q_h [9] for glassy PS and PET have shown that Q_h is about 0.6–0.7 J g^{-1} for $\varepsilon = 3\%$ at room temperature, which is much lower than the maximum ΔU stored in these polymers when deformed plastically. At small strains only, Q_h is not comparable with the plastic heat and might be neglected further. Therefore, for our conditions the heat Q_{def}, in reality, characterizes only the inelastic deformation of the studied polymers. The change in Q_{def} with macroscopic strain ε_{def} for several polymers and blends is shown in Fig. 5.

From the measured W and Q_{def}, the internal energy stored in deformed samples might be calculated from the First Law of Thermodynamics

$$\Delta U = W + Q_{def} \tag{4}$$

In all our cases, Q_{def} was negative (exothermic deformation heat). The values of ΔU_{def} and ΔU_{res} (DC measurements) for different polymers and blends are shown in Fig. 6. ΔU_{def} is the energy stored by the polymer during its loading. ΔU_{res} is the remaining stored energy after unloading the sample. It was found in all cases that $\Delta U_{def} > 0$ when $\varepsilon_{def} > 0$, and $\Delta U_{res} > 0$ when $\varepsilon_{res} > 0$, whereas at $\varepsilon_{res} = 0$ $\Delta U_{res} = 0$.

Fig. 1 also indicates the definition of $\Delta\varepsilon$, the strain which releases from the deformed sample during its unloading.

Fig. 3 depicts typical DSC traces of plastically deformed samples of glassy polymers immediately after their unloading. A typical feature of such DSC traces is the existence of exothermic C_p anomalies in the deformed samples with remaining strain ε_{res}.

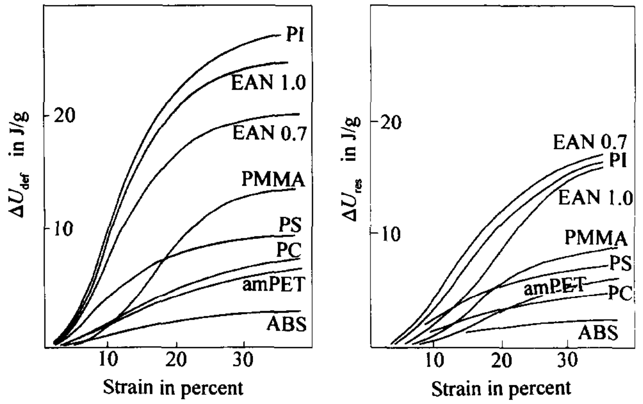

Fig. 6. Stored energy per mass unit in loaded (ΔU_{def}) and unloaded (ΔU_{res}) polymer glasses and blends, deformed isothermally by uniaxial compression at room temperature.

It has been pointed out [6,13,15,16] that this anomaly appears to be due to the release of ΔU_{res} upon heating the plastically deformed samples.

From Fig. 3, it follows that ΔU_{res} is mainly stored in the region below T_g, i.e. in the glassy state of the deformed polymer. The amount of stored energy released in the T_g interval and above is markedly lower than that in the glassy state.

Some of the stored energy released in the T_g interval and slightly above may be due to the energy differences between the conformational states of macromolecules in the deformed and undeformed samples. However, the amount of the energy should depend on ε_{def} and should be small at strains below 100% due to the very small increase in the concentration of the extended conformers before this region of deformation, and also to the small difference between the energies of the extended and non-extended conformers.

During isothermal polymer aging, the stored deformation energy relaxes with time. This behavior of deformed polymers is shown in Fig. 7 for EAN polymer at different aging temperatures.

We have also measured the ε_{res} recovery during heating of deformed samples [13,15,16]. A typical curve is shown in Fig. 8. Usually, glassy polymers deformed by compression completely recover their size and shape on heating slightly above T_g. Only semi-crystalline polymers do not show complete size-recovery at T_g [17], not on heating up to the fusion temperature T_m. This is due to true plastic deformation in the polymer crystallites.

The main feature of an ε_{res} recovery process is the appearance of part of the total size-recovery in the glassy state of a polymer, if the sample has been deformed below T_g. This never happens with samples deformed above T_g and then cooled down below T_g under conditions of constant srain [10,15]. Even though samples strained above T_g have the same amount of residual strain (after unloading samples below T_g) as the samples deformed in the glassy state, they never show any size recovery below T_g (curve 1, Fig. 8) [10,12,13,18].

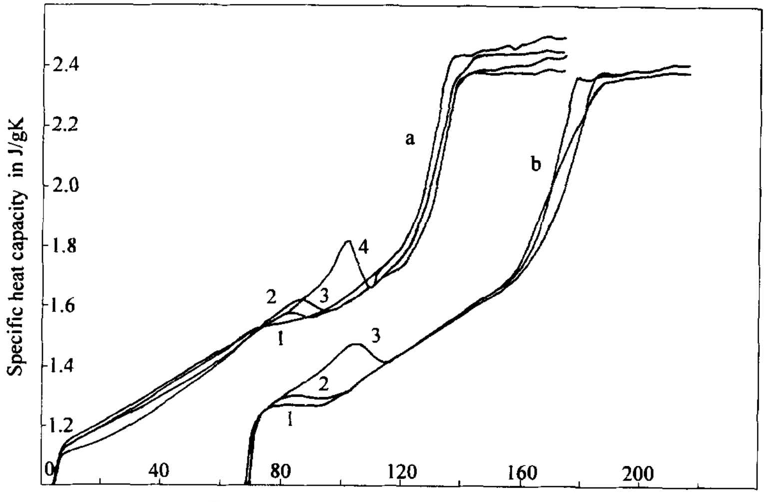

Fig. 7. Relaxation of C_p anomaly during storage of glassy EAN after deformation. Curves (a): $\varepsilon_{res} = 20\%$, $T_{def} = 25°C$, storage time of unloaded sample at 57°C: (1) 5 min; (2) 10 min; (3) 30 min; and (4) 42 h. Curves (b) $\varepsilon_{res} = 22\%$, $T_{def} = 25°C$, storage time of unloaded sample at T_{def}: (1) 10 min; (2) 20 min; and (3) 25 h. Sample masses: 5-10 mg; heating rate, 10 K min^{-1}.

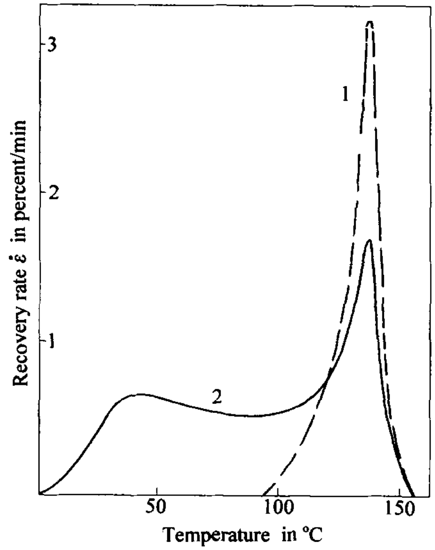

Fig. 8. The rate of recovery $\dot{\varepsilon}_{res}$ as a function of temperature upon heating of a typical example of EAN ($T_g = 145°C$). Curve (1): $\varepsilon_{res} = 17\%$, $T_{def} = 160°C$; deformed sample was cooled to room temperature at constant strain and then unloaded. Curve (2): $\varepsilon_{res} = 20\%$, $T_{def} = 27°C$. Heating rate 20 K min^{-1}.

Comparison of Figs. 3 and 8 shows (see also Refs. [10,12,15,18]) that the major part of ΔU_{res} should be related to the fraction of the $\varepsilon_{\mathrm{res}}$ annealing heat which disappears from the sample during heating below T_g.

We conclude that the structural changes responsible for high-level energy storage in plastically deformed glassy polymers are characteristic of the glassy state of the material and should be considered in the framework of the glass structure.

3. Discussion

Interpretation of most of the presented results will be made in the framework of a deformation mechanism that has been discussed in detail in Ref. [10]. Here we will introduce the mechanism only briefly, so that the reader will understand the following discussion.

3.1. *Inelastic deformation mechanism for glassy polymers*

It is well known that the deformation of polymers in a rubbery state involves changes in the size and shape of macromolecular coils, due to the appearance of a higher concentration of extended conformers in them. Because extended conformers also appear in macromolecules upon deformation of polymers in the glassy state, the idea of stress-aided conformational rearrangements in glassy polymers has been elaborated extensively [19–21]. However, such a mechanism does not account for the excited metastable structural state in polymer glasses that appears on straining, and manifests itself through its high-level energy storage.

Deformation calorimetry measurements clearly show that the excited state appears as the first response of the glassy sample to external mechanical force and it should be accounted for in every deformation model. Moreover, it was found that conformational rearrangements in macromolecules of polymer glass upon straining at low deformation temperatures T_{def}, compared with T_g, appear only when the excited structural state becomes well developed [10,12,18]. In other words, conformational rearrangements in macromolecules of the glassy polymer at low T_{def} never appear directly as stress-aided transformations, but are a result of some transformations of the structure in the energy-rich state of the polymer.

Analysis of all the experimental data led to the conclusion that conformational changes in coils may only take place in the micro-volumes of the glassy bulk, in which the local stored energy $\Delta U_{\mathrm{def}}^{\mathrm{loc}}$ is sufficiently high [10].

It was found (see Ref. [10] for details) that the high energy state in deformed polymer glasses is the result of the nucleation of very localized small-scale shear events, the so-called PST, plastic shear transformations [10,22]. Each PST contains some shear strain and excessive energy. The summation over all these local strains and energies gives a substantial fraction of the total sample strain and practically the total energy stored in the deformed sample. The structure and the thermodynamic and kinetic properties of PSTs in deformed glassy polymers were discussed in greater detail elsewhere [10]. Here we only emphasize that the nucleation of PSTs is not connected with conventional conformational changes in the polymer and does not produce any serious volume changes in the glass.

This first stage of the inelastic deformation of glassy polymers is the nucleation of PSTs, which develop in the sample upon straining up to steady macroscopic plastic flow. However, the nucleation of the PSTs is not the only process operating in a glass during straining. The other process becomes very important when the concentration of PSTs in the polymer becomes high enough.

This second process is the disappearance of PSTs. In this stage of deformation, the PSTs carrying the highest local energy and strain, undergo spontaneous structural rearrangements into new conformers in the polymer chains. Due to this event, the local stored energy $\Delta U^{\mathrm{loc}}_{\mathrm{PST}}$ is dissipated, but the strain $\varepsilon^{\mathrm{loc}}_{\mathrm{PST}}$ is accumulated by the new, extended conformers. In the physical sense, this means the disappearance of energy-reach PSTs from a system which is, from the kinetic point of view, a kind of termination.

The rate of the second process increases with PST concentration, i.e. with macroscopic strain up to the moment when a system reaches the condition of steady plastic flow. In this view, the steady plastic flow of the polymer glass is the process when the rates of PST nucleation and termination become equal. The proposed mechanism is shown schematically in Fig. 9. Path 1 depicts the PST nucleation process and path 2 is the PST termination. Path 3 represents the conventional rubber-like deformation process when macromolecular coils become extended due to direct stress-aided conformational changes in them. It was found [10] that transformations represented by path 3, unlike the rubbery deformation, do not take place directly in polymer glass, but only through PSTs carrying the highest energy $\Delta U^{\mathrm{loc}}_{\mathrm{PST}}$.

For our analysis here, the important part of the mechanism is the plastic dissipation (path 3), the termination stage of the total deformation process, because it determines, as we will see later, the heat of inelastic deformation Q_{def} of glassy

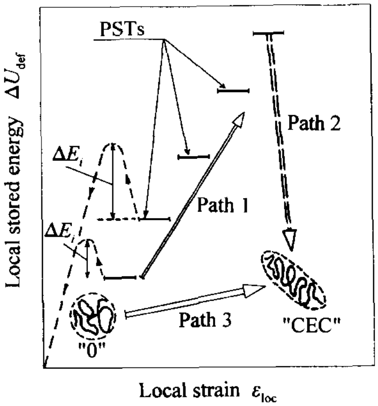

Fig. 9. Plastic deformation mechanism for glassy polymers: "0" and "CEC" are initial and deformed (conformationally excited) macromolecular coils: ΔE_i, activation energy of ith PST recovery.

samples. The first process, PST nucleation, is an endothermic process (an increase in the internal energy of the polymer) and the second stage is an exothermic process, realized through structural rearrangement of the type, high-energy PST → new extended local conformation in chain, during which release of stored local energy occurs.

We do not yet know the mechanism of the transformation. The rearrangement probably takes place due to the accumulation of a great part of the local strain energy $\Delta U^{\mathrm{loc}}_{\mathrm{PST}}$ by internal rotational degrees of freedom of the macromolecules. In contrast to the dissipation of stored energy through crack or void formation [11], we will call this PST → new conformer transformation plastic dissipation.

The presence of high-intensity plastic dissipation upon straining should bring the sample to saturation with respect to the stored deformation energy ΔU_{def} and ΔU_{res}, which is in fact the case in most of the investigated materials [6,10,11,18,23] (see also Fig. 6).

In the framework of the suggested deformation mechanism we will now discuss the main features of deformation work, deformation heat release and internal energy storage in glassy polymers upon their plastic deformation.

3.2. *Work expended for deformation*

The values of the work W for the studied systems are shown in Fig. 4. At small strains, W increases proportionally to ε^2, as it should for the Hookean strain region [24]

$$W = E\varepsilon^2/2 = \sigma^2/2E \tag{5}$$

and then changes practically linearly. Polymers of higher modulus and yield stress generally show higher W.

However, a comparison of the absolute values of W for different polymers is only possible at the same relative temperatures $T_{\mathrm{def}}/T_{\mathrm{g}}$. Normalization of W for T_{g} has also shown that W is higher for polymers with higher modulus.

From the shape of glassy polymer stress–strain curves, it is evident that the total deformation work W might be subdivided into two parts: W_{y}, the work expended for a sample deformed up to the macroscopic yield point ε_{y}, and W_{f}, the work expended during macroscopic plastic flow of a sample, i.e. for $\varepsilon_{\mathrm{def}} > \varepsilon_{\mathrm{y}}$. W_{y} should be proportional to E or to the product $E\sigma_{\mathrm{y}}$, and W_{f} to the plastic flow stress σ_{f}.

The data for W_{y} and W_{f} as a function of E and σ_{f} respectively are shown in Figs. 10 and 11. In reality, W_{y} increases more than linearly with the compressive modulus, which means that the chosen simplest correlation is not complete. Some other factors should be taken into account, e.g. $(W_{20\%} - W_{\mathrm{y}})$ is really proportional to σ_{f}; however, $(W_{40\%} - W_{\mathrm{y}})$ deviates little from linearity, probably because of strain hardening of the sample.

It is interesting that semi-crystalline polymers with glassy amorphous phases (PET, PBT) and blends also obey this simple correlation. The results mean that the expended deformation work is not directly sensitive to the morphology or to fine

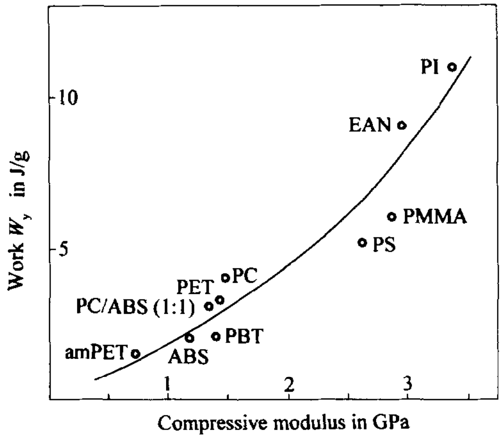

Fig. 10. The work W_y per mass unit expended to reach the yield point ε_y during uniaxial compressive deformation of different polymers and blends at room temperature as a function of compression modulus.

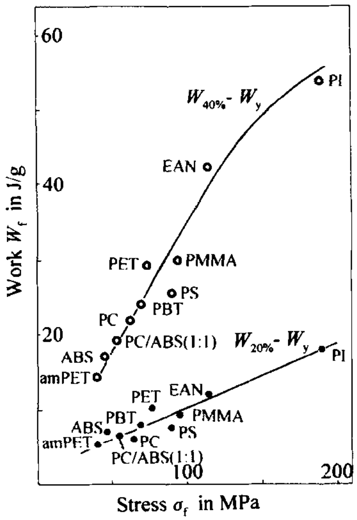

Fig. 11. The work W_f per mass unit expended for plastic flow during compression of the studied systems as a function of flow stress σ_f. $W_f = W_e - W_y$, where W_e is $W_{20\%}$ resp. $W_{40\%}$, the total deformation work expended for the given polymer at a strain level of 20% resp. 40% and W_y, the work to reach the yield point.

details of the polymer and blend structure. It is sensitive only to the modulus and yield or flow stress values.

3.3. The heat of plastic deformation

The change of Q_{def} with compressive strain is shown in Fig. 5. There are several important features in the behavior of Q_{def}:

Table 1
Parameters, characterizing the appearance of Q_{def} in glassy polymers upon straining (uniaxial compression, room temperature)

Polymer	ABS	PC	PS	PMMA	EAN	PI
$\varepsilon_Q/\varepsilon_y$	0.25	0.35	0.6	0.65	0.9–1.0	≈1.0

(1) The start of heat release upon loading takes place at quite different strains (ε_Q) for different polymers. The normalization of ε_Q in relation to ε_y gives a set of parameters for different polymers characterizing the moment when Q_{def} starts to increase upon straining (Table 1).

(2) At higher strains ($\varepsilon_{\mathrm{def}} > 25\%$), Q_{def} becomes parallel to W for most cases which means that the stored deformation energy, ΔU_{def} and ΔU_{res}, reaches saturation upon deformation for many polymers.

(3) Usually Q_{def} begins releasing earlier if the rate $\mathrm{d}Q/\mathrm{d}\varepsilon$ is lower, as can be seen in Fig. 5. The polymers for which $\varepsilon_Q/\varepsilon_y$ is high show quite a high rate of heat production.

The main question arising here is associated with the nature of Q_{def}. The deformation heat in a crystal's plasticity appears to be due to dissipation of energy by moving dislocations. We do not believe that this kind of dissipation plays an important role in glassy media because large-scale motions (gliding) of elementary strain carriers cannot exist in completely disordered structures. In glasses, it seems that each step of PST "moving" is the process of PST nucleation.

Within this framework, the origin of Q_{def} in glasses, including polymers, should be completely different from that in crystals. We suggested earlier [10,11] that the origin of Q_{def} upon inelastic straining of glassy polymers is the dissipation process shown as path 2 in Fig. 9. Indeed, the only exothermic process in the whole deformation scheme is the plastic dissipation. The stage of PST nucleation is endothermic because it brings a deformed polymer to a metastable state with a higher than initial internal energy level.

If the assumption about the nature of Q_{def} in polymer glasses is true, ε_Q is a reflection of the moment when the plastic dissipation starts to operate in a given sample upon straining. It is evident that if the parameter $\varepsilon_Q/\varepsilon_y$ is smaller than unity, the plastic dissipation starts locally in a sample before macroscopic yielding is reached in the entire sample. In other words, small values of $\varepsilon_Q/\varepsilon_y < 1$ are the manifestation of local yielding and, therefore, of the spatially heterogeneous character of yielding in the solid polymer.

The influence of an early appearance of plastic dissipation on the level of ΔU, stored in different polymers upon their straining, will be discussed later.

Here we only emphasize that a theoretical model describing the transformation of excited PST into new local conformers in macromolecules is now quite desirable. The model should help in understanding the mechanism of plastic dissipation, the process reflecting the ability of polymer materials to show high toughness [11].

3.4. Internal energy changes in deformed glassy polymers

The very specific feature of the plastic deformation of polymer glasses is the extremely high amount of energy stored in them. For metals [1-3], only several percent of W is transferred into stored energy. The largest part of the total W for metals is dissipated into deformation heat.

The situation is completely different for glassy polymers. For PI, PMMA, PS and EAN, the portion ΔU_{def} of W is close to 100% at strains $\varepsilon_{\mathrm{def}} < \varepsilon_{\mathrm{y}}$, and reaches 30%-50% at $\varepsilon_{\mathrm{def}} = 40\%$ [10,11]. Even for ABS, where the ratio of $\Delta U_{\mathrm{def}}/W$ is the lowest throughout all studied systems, still 20% of W is stored in the sample at $\varepsilon_{\mathrm{def}} = 40\%$.

These results show that the inelastic deformation of glassy polymers is a very non-isostructural process, in contrast to the deformation of crystalline metals. The corresponding structural transformations responsible for the energy change begin from very small (practically Hookean) strains. This means that many of the macroscopic properties of inelastically deformed glassy polymers should be related not to the initial (prior to straining) polymer structure, but to the new quite excited structure. For example, crazing, cracking, orientation phenomena, fatigue and some other properties of solid polymers under stress should be correlated with the structure of the deformed polymers that are saturated by PSTs.

One should distinguish at least three different quantities of the internal energy stored by glassy polymers: ΔU_{def}, ΔU_{res} and $\Delta(\Delta U)$. All are shown in Fig. 1. ΔU_{def} is the excess of internal energy in the sample during its straining, i.e. when the applied stress $\sigma > 0$. ΔU_{res} is the energy stored by the deformed, but after deformation, completely unloaded sample, where $\sigma = 0$. And

$$\Delta(\Delta U) = \Delta U_{\mathrm{def}} - \Delta U_{\mathrm{res}} \tag{6}$$

is the energy released by the deformed sample during its unloading.

Measurements of ΔU_{def} can only be performed by deformation calorimetry (one-step method [1,2]). ΔU_{res} can be measured, for example, by DSC [8,16,23,25] and by precise measurements of the dissolution heat of the strained sample [23]. In two-step methods (DSC, heat of dissolution measurements), the losses of stored energy ΔU_{res} during the elapsed time between the time of unloading and the start of measurements should be taken into account.

Fig. 7 shows the change in the DSC traces of deformed EAN (1:1) polymer after different times of isothermal storage in the unloaded state. It is clear that the endothermic C_p anomaly relaxes during storage time. As the area of the anomaly is proportional to ΔU_{res} (strictly speaking ΔH_{res} in the case of DSC measurements), it can be seen that ΔU_{res} decreases with storage of the deformed sample. Fig. 12 shows the change in magnitude of the stored enthalpy as a function of time elapsed between the moments of unloading the sample and starting the DSC run. The shortest time we could reach in this experiment was 10 min. From Fig. 12 one can see that ΔH_{res} from the first possible measurements is about 10 ± 1 J g^{-1} and is substantially smaller than the ΔU_{res} of EAN measured by DC (which is about 15 J g^{-1}, see Fig. 6). About one third of ΔU_{res} is lost during the first 10 min after

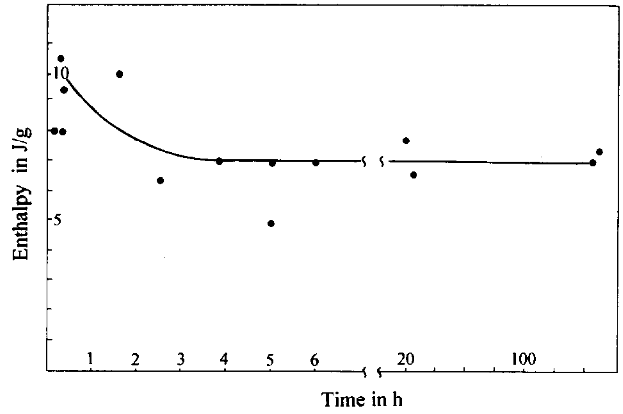

Fig. 12. Enthalpy change ΔH per mass unit versus storage time of deformed samples of EAN: $\varepsilon_{\text{res}} = 20\%$; T_{def} = room temperature; storage temperature = room temperature; heating rate = 10 K min^{-1}.

unloading the sample at RT. The relaxation of ΔU_{res} is faster at higher storage temperatures (Fig. 7). About two to three hours after the time of unloading, ΔU_{res} seems to come close to saturation, but in reality the relaxation continues slowly.

From these results, it becomes clear why the experimental results for ΔU_{res} from different methods (DC, DSC and heat of dissolution) are different [23]. Markedly low values of ΔU_{res} were received from dissolution heat measurements [23]. However, this now seems appropriate because the relaxation rate of ΔU_{res} should be higher in the presence of solvent vapors (toluene in our case [23]) prior to complete dissolution of the sample.

From DSC data and the measurements of ε_{res} recovery [10], it is evident that ΔU_{def} and ΔU_{res} increase with T_{def} decrease. This deformation behavior of glassy polymers, together with the fact that ΔU_{res} release (see Figs. 3 and 7) and ε_{res} recovery (Fig. 8) of the deformed samples upon heating [10] during DSC measurements always starts at temperatures close to the temperature of sample unloading after plastic straining (usually a little above because of the discussed ΔU_{res} relaxation during sample storage), resulted in the conclusion [10,18] that all PSTs nucleated by applied stress exist in the stressed samples, but that a fraction of them disappears upon unloading. This happens due to the change in the activation energy of the PST recovery process to the undeformed unexcited state in the presence of external stress. Upon external stress removal, all PSTs with activation energy below $\Delta E_{\text{act}}^{\text{rec}} < \approx kT_{\text{def}}$ (where k is the Boltzmann constant) are released from the sample. Only PSTs with $\Delta E_{\text{act}}^{\text{rec}} > \approx kT_{\text{def}}$ stay in the sample and recover comparatively slowly. This relaxation process is seen in Figs. 7 and 12. Recovery of the first type is comparatively fast and occurs during unloading. This is the reason why the processes of ε_{def} and ΔU_{res} relaxation (recovery) always start close to the unloading temperatures upon heating.

In Fig. 7, there is another interesting feature of the C_p endothermic anomaly relaxation behavior, namely the exothermic overshoot appearing after longer storage times of the sample in question. There is a lot of discussion in the literature about the origin of this overshoot (see Ref. [25], for example and references therein). We shall not discuss this question in detail here. We would like to emphasize only that the amount of overshoot is directly related to the plastic deformation of the glassy sample and to the process of its residual strain recovery.

The overshoot only appears with recovery of the highest energy PSTs, not with that of the low energy ones. It was shown earlier [10] that the higher the energy $\Delta U^{\mathrm{loc}}_{\mathrm{PST}}$, the higher the activation barrier $\Delta E^{\mathrm{loc}}_{\mathrm{act}}$ of its recovery and the higher the thermal fluctuation there has to be in a given volume of deformed sample to overcome this barrier. This is, probably, the reason why the overshoot increases with the storage time of a deformed sample.

The levels of stored energy ΔU_{def} and ΔU_{res} are very different for chemically different glassy polymers (Fig. 6). Why is this so?

We have failed to correlate this difference with the rigidity of the macromolecules, the differences in modules and T_g of the studied polymers. However, the above formulated suggestion concerning the origin of Q_{def} for polymer glasses gives, we believe, the answer to this question.

Indeed, the deformation process behind the yield point ε_y becomes steady-state for many glassy polymers [26,27]. And ΔU_{def} and ΔU_{res} also show real saturation for many cases (see Fig. 6). Our assumption here is the following: the saturation of ΔU_{def} is related to the steady-state character of the deformation process. Steady ΔU_{def} is reached in a sample when the rates of PST nucleation and PST disappearance by plastic dissipation become equal. The more intense the PST termination process, the lower the amount of the excessive energy that might be accumulated by a polymer upon straining.

The effectivity of the dissipation process manifests itself through the kinetics of the Q_{def} production. If plastic dissipation starts very early (small ε_Q and $\varepsilon_Q/\varepsilon_y$), the dissipation rate is high from the beginning of the deformation process and the highest energy PSTs are able to arise at low external stresses and strains.

The ability of the polymer to nucleate the high energy PST at low external stress indicates that the structure of the polymeric glass in question is quite suitable for the PST nucleation process and, as a result, for a fairly effective plastic dissipation.

We do not yet know what kind of glass structure is favorable for the nucleation of PSTs. However, a simple model can be formulated: the earlier (by stress and strain) the termination process starts, the faster the steady ΔU_{def} will be reached and the lower the level of ΔU_{def} should be in the deformed polymer.

The moment when plastic dissipation starts might be defined by the dissipation parameter $\mathrm{DP} = \varepsilon_Q/\varepsilon_y$ [10,11] (Table 1). Comparison of ΔU_{def} for different polymers (Fig. 6) and DP values (Table 1) shows that the following assumption is valid: the lower the DP, the smaller the ΔU_{def} at saturation.

ABS and PC start their plastic dissipation way before they reach their macroscopic ε_y, and ΔU_{def} at saturation is quite low. But, in both types of EAN and PI for instance, plastic dissipation starts only together with the macroscopic yielding, and their ΔU_{def} values at saturation are the highest. This result is quite important because it seems to support two suggestions, introduced earlier, namely those concerning the origin of the deformation heat in glassy polymers and the level of the stored energy of cold work, which is defined by the steady energy state which the polymer reaches during deformation. One argument supporting these suggestions is the very good correlation of DP with the stored energy ΔU_{def}.

Early production of Q_{def} indicates that local plastic flow in polymer glasses starts at quite low (compared to ε_y) macroscopic strains, which means that plastic deformation occurs very heterogeneously in a sample. One can imagine that in ABS, known as a phase-separated blend, plastic deformation and yielding take place spatially very heterogeneously. However, it is not clear why the heterogeneity is fairly pronounced in PC, which is structually uniform, as is generally accepted. The heterogeneous character of stress and strain distribution upon plastic deformation of glassy PC might present a new interesting question in the study of glassy polymers. An answer to this question may bring a deeper understanding of the process under discussion.

4. Conclusions

Calorimetric measurements performed for a number of polymeric systems with different chemical natures and structures have shown that a very important feature of their deformation behavior is its non-isostructural character, which manifests itself by the high internal energy level of the deformed samples. But a really deep analysis of all the results obtained has not yet been carried out. However, even the first approach has revealed several features that are quite important for an understanding of the plasticity of glassy polymers and for future development of the problem.

It is evident that many new, previously unknown details of glassy polymer plastic deformation have been revealed by calorimetric measurements. And we are absolutely sure that further calorimetric studies will bring more important, new information.

The results presented, in our view, as well as showing all the existing physical models of glassy polymers plasticity, indicate that they are not complete. New models of the deformation have to take into account the transition of polymeric glasses into an excited structural state upon straining and the behavior of the state under stress.

Relaxation phenomena in deformed polymers have also to be accounted for in this situation. Very probably the processes of PST nucleation exist in non-polymeric glasses as well as, for instance, in metallic glasses. Checking this might bring new information about their deformation behavior.

However, future calorimetric measurements would not help in one weak point: they cannot give a direct answer to the question about the nature of the structural rearrangements which take place in polymer glasses upon straining. An analysis by more direct structural methods is very desirable and of high importance.

There is no doubt that a high level of energy storage exists in such systems. In other words, new excited structures should be present in polymer glasses and an appropriate method should be found to detect and characterize them. Unfortunately, such research has not yet been initiated, according to the polymer literature.

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