Journal of Thermal Analysis, Vol. 38 (1992) 1271-1281

HEAT AND STORED ENERGY OF PLASTIC DEFORMATION OF SOLID POLYMERS AND HETEROGENEOUS BLENDS

O. B. Salamatina, S. N. Rudnev, V. V. Voenniy and E. F. Oleynik

INSTITUTE OF CHEMICAL PHYSICS, ACADEMY OF SCIENCES OF RUSSIA,
MOSCOW, RUSSIA

Measurements of the mechanical work (A), the heat of deformation (Q) and differences between these quantities, i.e. the internal energy (ΔU) stored in samples were performed under the unidirectional compression loading conditions by using constant temperature deformation calorimetry. It is shown for several glassy (PS, PC, PI-BD, PET, epoxy-amine network, ABS) semi crystalline (PBT, PET) polymers and blends (PC: ABS, PC: PBT), that 45–85% of the mechanical work of deformation is converted to internal energy stored in deformed samples ΔU is quite high as compared with metals.

Keywords: energy storege, polymers

Introduction

Measurement of the heat effects under the deformation of solids is a powerful method for studies of the mechanical response. The transformation of the mechanical work into heat and dissipation of this work and the stored energy gives important information about the structural mechanism of the deformation microprocess.

The energy and entropy changes were quantitatively analyzed in detail for the highly elastic deformation of rubber [1, 2]. Less systematic information was obtained in the case of glassy and semi-crystalline polymers [3].

In recent years detailed investigations of the thermodynamic aspects of a plastic deformation of glassy and semi-crystalline polymers and blends, have been performed in the Institute of Chemical Physics, USSR Academy of Sciences [4–8].

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Experimental

The experimental method mainly used in this work was the method of deformation calorimetry [6, 7]. In the commercial Calvet-type differential calorimeter was placed a loading cell where a sample could be loaded by tension or compression. In the experiments the stress-strain curve (i.e. mechanical work A_ε of deformation), as well as the heat Q_ε dissipated in the process were measured simultaneously. The difference between the two values $\Delta U_\varepsilon = A_\varepsilon - Q_\varepsilon$ gives the internal energy stored in the deformed sample.

The strain was calculated as

$$\varepsilon(t) = [V \cdot t - F(t) \cdot Z]/h_0$$

where $\varepsilon(t)$ is the strain at time (t), V is the loading rate (mm/min), $F(t)$ is the loading force, h_0 is the sample length, Z is an empirical parameter determined by the deformation properties of the metal parts of the loading cell. It was found by the comparison of the strain-strêss curves obtained in the loading machine INSTRON–1122 and in the loading cell of our calorimeter at the same T_{def} and the same loading rate.

To receive the real Q_ε we have to correct the experimental $Q_\varepsilon^{\mathrm{exp}}$ values by using Tian's equation:

$$Q_\varepsilon(t) = A \int_0^t \dot{Q}\,\mathrm{d}t + B\tau(\dot{Q}) = A\,Q^{\mathrm{exp}}(t) + B\tau\dot{Q}(t)$$

where $Q_\varepsilon(t)$ is the total heat dissipated till the moment t, $\dot{Q}(t)$ is the rate of heat dissipation at t (this value is directly measured by the calorimeter), τ is the time constant of the calorimeter system. A and B are constants and can be calculated by calibration.

The heat obtained directly using the calorimeter is the sum of the deformation heat of the stressed sample and the deformation heat of the deformed loading cell.

To obtain the real deformation heat of the stressed sample a second loading (without the sample) was made. The second loading was made so that the curve of stress ($F(t)$) in the second run was the same as the curve $F(t)$ in the first run (Fig. 1). So we obtained $Q'(t)$, where $Q'(t)$ is the heat of deformed metal parts of the loading cell.

The real heat (the heat of the stressed sample only) is equal to:

$$Q^s(t) = Q_\varepsilon(t) - Q'(t)$$

The precision of the determination of the heat is 2-3 % at a calorimeter sensitivity of 10^{-7} W.

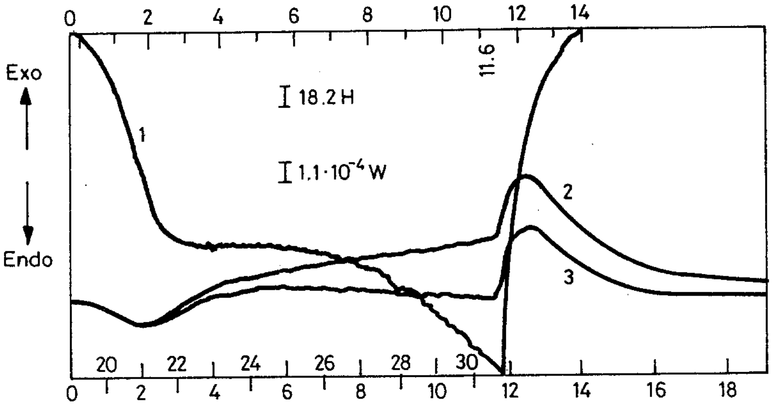

Fig. 1 Curves measured with the deformation calorimeter: 1. force-time curve. 2. heat flux in the first run. 3. heat flux in the second run

The following commercial linear amorphous polymers were studied: polycarbonate (PC), atactic polystyrene (α–PS), polyethylene-terephthalate (α–PET), polyimide based on benzophenon tetracarboxylic acid dianhydride and 4,4'-diaminodiphenyl ether (PI–BD), epoxy-aromatic amine network (EAN), prepared

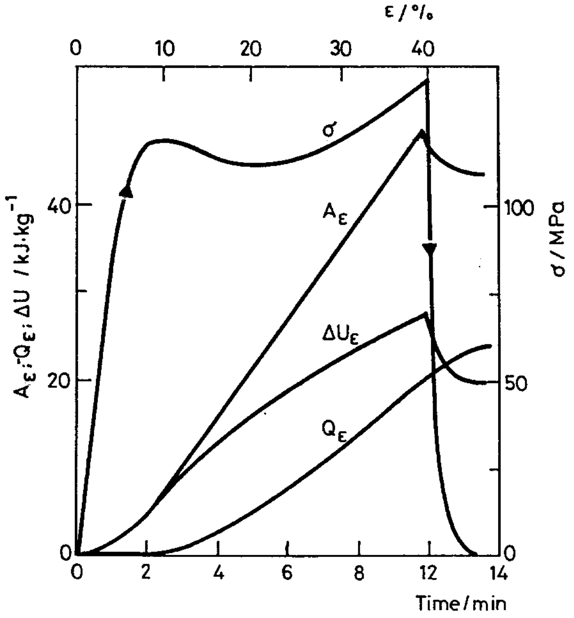

Fig. 2 Kinetic curves for σ, A_ε, Q_ε, ΔU_ε. Polymer: EAN (NH/V = 1). $(d\varepsilon/dt)_{load} = (d\varepsilon/dt)_{unload} = 3\cdot10^{-2}\ \mathrm{min}^{-1}$. Unidirectional compression. $T_{def} = 298$ K

Table 1 The values of deformation work, heat and stored deformation energy for T_{def} = 298 K and ε = 40% (uniaxial compression)

Polymer	T_g K	$E_{25°}$ GPa	A_ε	Q_ε kJ· kg^{-1}	ΔU_ε	$Q_\varepsilon/A_\varepsilon$	$\Delta U_\varepsilon/A_\varepsilon$	ΔU_{irr} kJ· kg^{-1}	$\Delta(\Delta U)$	$\frac{\Delta U_{irr}}{A_\varepsilon}$	$\frac{\Delta(\Delta U)}{A_\varepsilon}$
EAN 1 (NH/V=1)	417	2.9	51	23	28	0.45	0.55	16	12	0.31	0.24
EAN 2 (NH/V=0.7)	346	3.0	42	21	21	0.50	0.50	16	5	0.38	0.12
PI–BD	543	3.3	62	32	30	0.52	0.48	14	16	0.23	0.25
PS	368	2.6	29	20	9	0.69	0.31	6	3	0.21	0.10
PC	423	1.5	26	18	8	0.69	0.31	5.5	2.5	0.21	0.10
a–PET	340	0.7	16	9	7	0.56	0.44	5.5	1.5	0.34	0.10
PET(cr.)	340	1.3	34	17	17	0.50	0.50	14	3	0.41	0.09
PBT(cr.)	340	1.3	24	13	11	0.54	0.46	9	2	0.38	0.08
PC+ABS(1:1)	—	1.4	23	17	6	0.74	0.26	4	2	0.17	0.09
ABS	371	1.2	20	17	3	0.85	0.15	1	2	0.05	0.10

by curing the diglycidyl ether of resorcinol (DGER) with metaphenylenediamine (m-PhDA) at different ratio of the reagents (NH/V=1, =0.7).

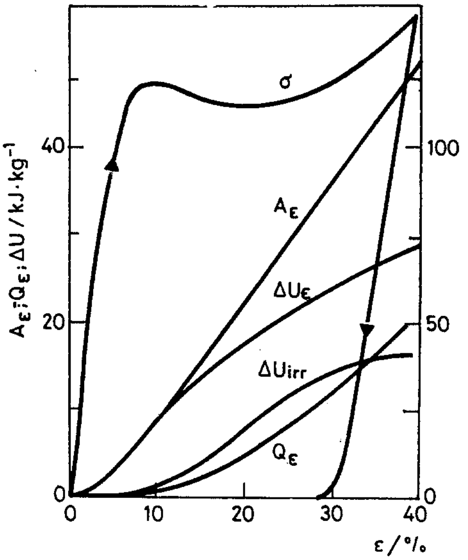

Fig. 3 Changes of σ, A_ε, Q_ε, ΔU_ε and ΔU_{irr} with deformation ε along of stress-strain curve. Polymer: EAN (NH/V = 1). Other experimental conditions are the same as for Fig. 1

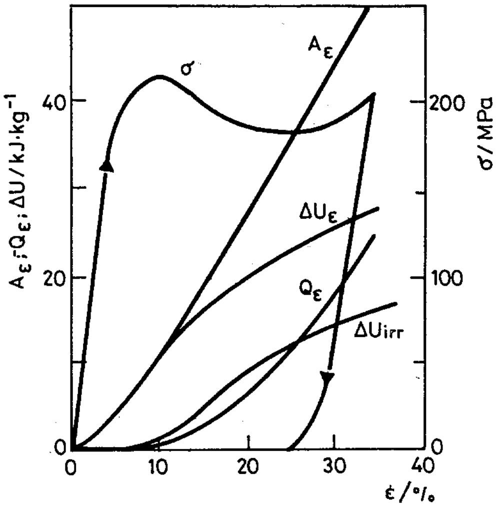

Fig. 4 The same as for Fig. 3. Polymer: PI–BD

Semi-crystalline PET (k = 50%) and polybuthyleneterephthalate (PBT, k = 60%) and polymer blends: ABS, PC-ABS, PC-PBT were also investigated.

Cylindrical samples (d = 2 mm, h_o = 3 mm) were used for uniaxial compression loading with constant crosshead speed ($d\varepsilon/dt = 10^{-1}$–$10^{-2}$ min^{-1}) at room temperature T_{def} = 298 K. Before deformation and calorimetric measurements all samples were annealed in an atmosphere of dry air at $T = T_g + 10$ K for twenty minutes and then were cooled to room temperature at a rate of 50 deg/min. this procedure permitted to standardize the thermal prehistory of samples.

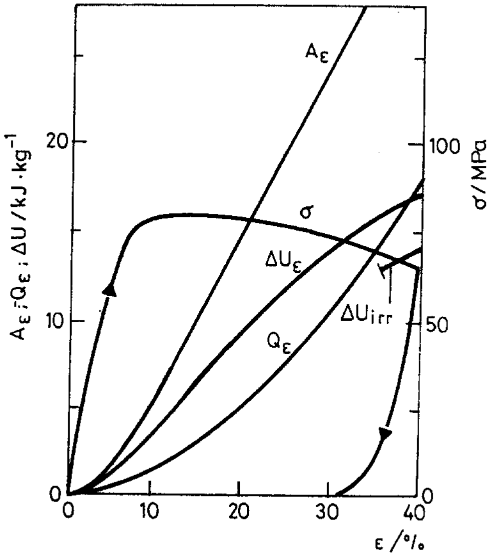

Fig. 5 The same as for Fig. 3. Polymer: PET (cr.)

All data showing A_ε, corrected Q_ε and ΔU_ε values for all the investigated polymers are shown in Figs 2–9 and in Table 1. Values of A and Q have usually different signs because Q in the nonlinear deformation of polymeric glasses is usually positive (i. e. inelastic deformation is an exothermic process). However, for the better comparison of the results in Figs 2–9 all A, Q and ΔU values are shown in the same sector of coordinate system.

One should realize the differences between values measured in loaded and unloaded samples. The values measured for the loaded samples along stress-strain curves (i.e. the values received in direct loading up to a chosen deformation ε) are A_ε, Q_ε and ΔU_ε, but the values for completely unloaded samples are A_{irr}, Q_{irr}, ΔU_{irr}. It is seen from Figs 3–9 that ΔU_ε is always larger than ΔU_{irr}, i.e. the sample deformed to given ε stores more energy under load than after its unloading.

The stored energy of the deformed sample was also determined by the following calorimetric methods:

a) as the difference between the heats of dissolution of the deformed and undeformed samples;

b) as the area of a C_p-anomaly on the DSC-curve of the deformed sample [7].

Discussion

The main parameter in deformation kinetics to which all other values should be referred is A_ε – the mechanical work supplied to a sample to deform it up to a desirable deformation ε. We shall discuss here only the inelastic deformation region because all measured values of Q_ε become experimentally well measurable and reproducible starting only from macroscopic yield strains ε_y. For all our cases ε_y was 5–10% but Hooke's law is obeyed only up to $\varepsilon = 1.52\%$ in our conditions.

The values of A_ε (for $\varepsilon = 40\%$) are quite different (Table 1) for all investigated polymers and vary from 62 J/g (PI) to 16 J/g (α–PET). This simply reflects the difference between the mechanical properties of the investigated polymers. The polymers with a comparatively high elastic modulus (E_{25}) have the larges values of A_ε, however, differences of A_ε in this group (PI, EAN) definitely come from the "plastic" part of their stress-strain curves, i.e. from the curve part after the upper yield point. For example, PI shows some strain hardening (presumably, orientational one) and EANs do not.

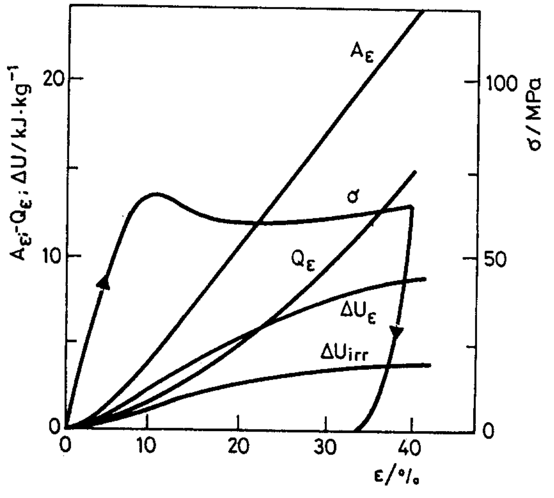

Fig. 6 The same as for Fig. 3. Polymer: α–PET

Possibly the differences in A_ε also depend on the relation between T_{def} and T_g. For example EAN with ratio NH/V = 0.7 has the lowest T_g and A_ε in this group.

However, this conclusion does not work through all the systems. PC has the same T_g as EAN (NH/V = 1) but the E_{25} and A_ε for PC are smaller. PS has lower T_g than PC, however, higher E_{25} and this immediately is reflected in the higher A_ε value. At the same time PS shows smaller value of A_ε in comparison with EAN (NH/V = 1) while both have close E_{25} valuse.

ABC-plastic with the same T_g as PS has an E_{25} value smaller than PS and an A_ε about 30% lower than PS.

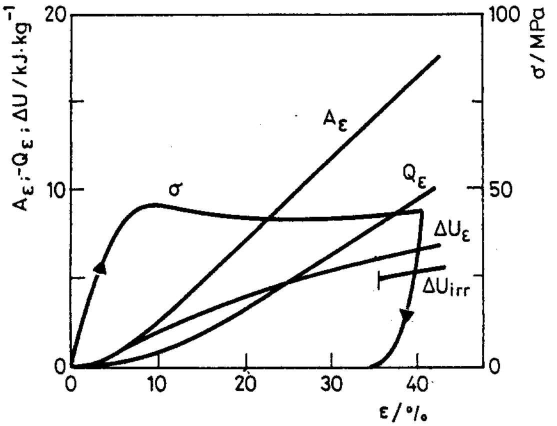

Fig. 7 The same as for Fig. 3. Polymer: PC

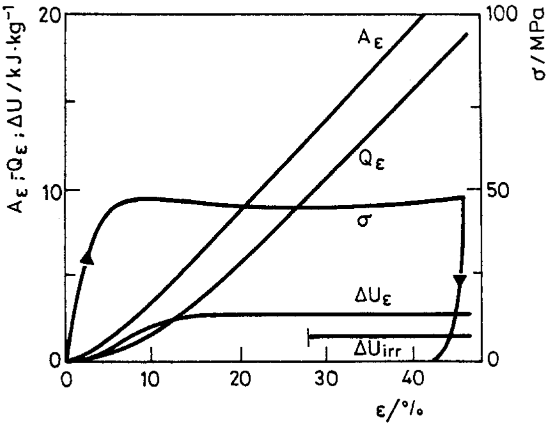

Fig. 8 The same as for Fig. 3. Polymer: ABS

The major part of A_ε is converted during a plastic deformation process to an exothermic heat Q_ε. The amount of Q_ε (for $\varepsilon = 40\%$) varies for the investigated systems from 45% to 85% of A_ε (Table 1). However, this is not true for lower strains. Up to strains of 15–30% the major part of A_ε is converted to stored energy ΔU_ε. This situation is quite typical for all the investigated polymers and blends and clearly reflects some changes in the deformation process after the cross-point of the ΔU_ε and Q_ε curves (Figs 2–9). The portion of internal energy U_ε stored in the deformed polymer is from 15 to 50% of A_ε (ε = 40%) for all the systems (Table 1).

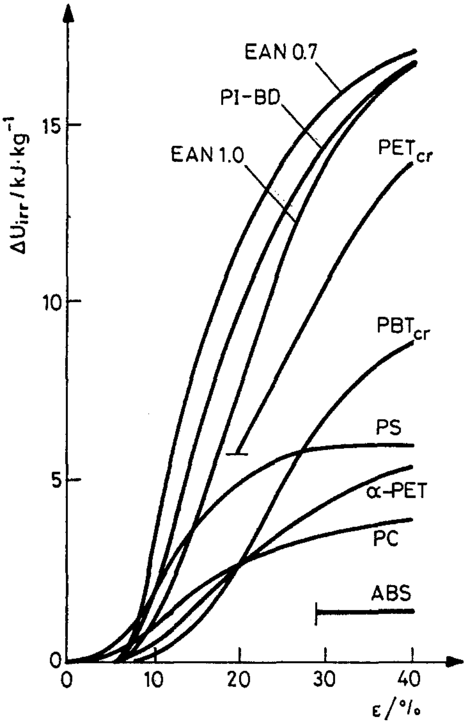

Fig. 9 ΔU_{irr} for all the investigated polymeric systems. All experimental conditions are the same as for Figs 2–8

It is well known that for metals the portion of A_ε dissipated to heat is even larger and usually close to 90% of A_ε [9].

These facts at least mean that the processes of plasticity in polymeric glasses are mechanically more activated than in crystalline metals. This large amount of stored energy is undoubtedly the reflection of some structural changes appearing in glassy samples during deformation. It is an important current problem connected with glassy polymers to elucidate the structure of deformation defects.

Data about an internal energy storage in deformed polymeric glasses are shown in Fig. 9. These glasses have also some amount of ε_{irr}-deformation which is not recovered at T_{def} during the long period of time allowed after unloading [4-

7]. For all cases $\Delta U_\varepsilon > \Delta U_{irr}$. This means that a part of total stored internal energy $\Delta(\Delta U)$ may exist only in a loaded sample and immediately disappears on unloading at T_{def}. these processes exist for all strains and ΔU_ε converts to ΔU_{irr} during unloading. The difference $\Delta(\Delta U) = \Delta U_\varepsilon - \Delta U_{irr}$ is converted to exothermic heat. A small part of deformation disappears from the sample together with $\Delta(\Delta U)$ [4]. All the results for the investigated heterogeneous blends reasonably correspond to the data received for the their individual components. The data for A_ε, Q_ε, U_ε and their changes for blends PC–ABS and PC–PBT of different composition are shown in Table 1.

It is interesting to analyze the data for semi-crystalline polymers (PET, PBT) and compare the differences between glassy and semi-crystalline PET.

Amorphous and crystalline PET have different $A_{\varepsilon=40\%}$ which obviously reflect the differences in stress-strain curves (Figs 6, 7). The presence of crystallites makes the yield stress higher.

The normalized values $Q_\varepsilon/A_\varepsilon$ and $\Delta U_\varepsilon/A_\varepsilon$ are close to each other The same is true for $\Delta(\Delta U)_\varepsilon/A_\varepsilon$. This shows that the plasticity in crystalline and amorphous regions of PET has approximately the same thermodynamic characteristics of deformation. This conclusion has a support in [8] where it was found that crystalline and glassy regions of PET ($k = 50\%$) bring equal portions into plastic deformation of the polymer at $T_{def} < T_g$.

The comparison of all the data for PBT and PET brings us to the conclusion that the same is probably valid for PBT. All normalized values of ΔU_ε, $\Delta(\Delta U)_\varepsilon$, Q_ε are close to those of PET. This possibly means that the differences in chemical structure of PET and PBT do not play an important role in elementary plastic events.

There are several other features of plasticity which raise some questions. The largest portion of A_ε is converted to Q_ε for ABS. At the same time this plastic has the lowest value of $\Delta U_{irr}/A_\varepsilon$, however, the ratio $\Delta(\Delta U)_\varepsilon/A_\varepsilon$ is normal. It is evident that these ratios are the smallest for blends. EAN 1 and PI-BD show high values of $\Delta(\Delta U)_\varepsilon/A_\varepsilon$.

Formal analysis of the data shows that all the quantities: A_ε, Q_ε, ΔU_ε, ΔU_{irr} and $\Delta(\Delta U)$ even normalized in respect to A_ε are quite different for polymers of different chemical nature. It is clearly seen also from Fig. 9.

The understanding of the correlation between the quantities mentioned above and the chemical nature of the polymer is an important current problem of polymer plasticity. However, the existing results do not show any simple correlation with the nature and flexibility of the investigated polymers and additional efforts should be made to clarify this problem.

References

1 Yu. K. Godovsky, Polymer, 22 (1981) 75.
2 C. Price, Proc. Roy. Soc., 1976, Ser.A, v. 351, p. 331.
3 G. W. Adams and R. Y. Ferris, Polymer 30 (1989) 1824.
4 E. F. Oleynik, Progr. Colloid Polymer Sci, 80 (1989) 140.
5 E. F. Oleynik, Polymer 19 (1987) 105.
6 V. V. Voenniy, Diplom Work, Moscow Phys-Tech. Inst., (USSR), 1990.
7 O. B. Salamatina, S. I. Nazarenko, S. N. Rudnev and E. F. Oleynik, Mech. Compoz. Mater, (USSR), 6 (1988) 979.
8 S. S. Sheiko, O. B. Salamatina, S. N. Rudnev and E. F. Oleynik, Visokomolec. Soed. (USSR), A32 (1989) 1551.
9 H. Quinney and G. Taylor, Proc. Roy. Soc. Lond., A163 (1937) 157.

Zusammenfassung — Mittels Konstanttemperatur-Deformationskalorimetrie wurden bei gerichteter Kompressionsbelastung Messungen der mechanischen Arbeit (*A*), der Deformations-wärme (*Q*) und der Differenz beider Größen, d.h. der in den Proben enthaltenen inneren Energie (ΔU) durchgeführt. Für einige amorphe Polymere (PS, PC, PI-BD, PET, Epoxy-Amine-Netzwerk, ABS), halbkristalline Polymere (PBT, PET) und Gemische (PC:ABS, PC:PBT) wurde gezeigt, daß 45-85 % der mechanischen Deformationsarbeit in den Proben als innere Energie gespeichert wird.