Plasticity of Semicrystalline Polyethylenes Viewed Through the Prism of Thermodynamics

Eduard Oleinik,[1] Olga Salamatina,[1] Sergey Rudnev,[1] Zbigniew Bartczak,[2] Andrzej Galeski[2]

[1]*N.N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow 119991, Russia*
[2]*Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz 90-363, Poland*

ABSTRACT: Thermodynamic characteristics such as mechanical work W_{def} and heat Q_{def} of plastic deformation were measured at room temperature for several non-oriented linear high and ultrahigh molecular mass polyethylenes (PEs). The characteristics were registered simultaneously at room temperature active uniaxial compressive loading in the strain interval $\varepsilon_{def} = 0$–50% and rate 4×10^{-2} min^{-1}. An isothermal Calvet-type deformation calorimeter was used for the measurements. Changes of the internal energy ΔU_{def} stored by deformed samples were calculated from W_{def} and Q_{def} according the first law of thermodynamics. It appears that all thermodynamic quantities linearly depends on degree of crystallinity $\chi = 0.5$–0.9 (DSC) at conditions of the study. Such behavior of W_{def}, Q_{def}, and ΔU_{def} had permitted an extrapolation of measured quantities to crystallinities $\chi = 0.0$ (pure amorphous phase) and $\chi = 1.0$ (pure crystalline phase) and determination of deformation thermodynamic characteristics for each of them. Both phases participate into W_{def}. It appears that the work W_{def}^{cr}, necessary to deform PE crystallites is considerably higher than W_{def}^{am}, the work necessary to deform the amorphous phase. At $\varepsilon_{def} \leq 30\%$ W_{def}^{cr} is 3–4 times higher than W_{def}^{am} and about two times higher at higher strains. From W_{def}^{am} and W_{def}^{cr} stress–strain curves for both phases of PE were withdrawn. Deformation heat of the amorphous phase Q_{def}^{am} is orders of magnitude lower than Q_{def}^{cr}. It reflects the entropic nature of deformation of rubbery amorphous phase of PEs at low ε_{def}. The Q_{def}^{cr} originates from a friction during glide of dislocations trough crystallites. Interesting behavior shows the stored energy of cold work $\Delta U_{def} = f(\chi)$. At strains $\varepsilon_{def} \leq 30\%$, the stored energy ΔU_{def}^{am} is a little lower than ΔU_{def}^{cr}. However, ΔU_{def}^{am} becomes higher than ΔU_{def}^{cr} at $\varepsilon_{def} > 30\%$. The ratio $\Delta U_{def}/W_{def} = f(\varepsilon_{def})$ was constructed also. The ratio gives the fraction of W_{def}, which is transformed into the stored energy of cold work ΔU_{def} at loading. Behavior of several materials: glassy polymers, PE, and crystalline metals were compared in terms of the ratio. At elastic process, the ratio $\Delta U_{def}/W_{def}$ tends to unity for all the materials. Whole W_{def} in this case is converted into ΔU_{def}. With ε_{def} growth dissipative processes appear and deformation heat is evolved. The ratio tends to $\Delta U_{def}/W_{def} < 1$. Comparison of three mentioned above materials show, that critical stage of their deformation kinetics is nucleation of the inelastic strain carriers (dislocations in crystals, for example). Initiation is completed very early (at $\varepsilon_{def} \leq \varepsilon_y$, the yield strain) for crystalline metals and about 92–98% of the expended W_{def} becomes converted into deformation heat at $\varepsilon_{def} \geq \varepsilon_y$. Plasticity proceeds differently in glassy polymers. Initiation stage continues in glasses for a high strain ε_{def} level, usually higher than ε_y. The curve $\Delta U_{def}/W_{def} = f(\varepsilon_{def})$ for PEs is located between curves characteristic for metals and glassy polymers. Initiation of PE plasticity becomes completed at $\varepsilon_{def} \approx 10$–20%. At $\varepsilon_{def} > 30\%$ the ratio does not depends on ε_{def} and stay constant on the level 0.35–0.55 for different PEs. The nature of such saturation is not understood yet. Thermally stimulated recovery of residual strains ε_{res} stored in deformed and unloaded PEs at different ε_{def} was measured also. The rate recovery curves $d\varepsilon_{res}/dT$ show two separate peaks, one with maximum at T_m and the other with maximum much below T_m. Integration of both gives amount of ε_{res} accumulated in amorphous phase and crystallites of PE at different applied strains. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: polyethylene; plastic deformation; thermodynamics

INTRODUCTION

Polyethylene is the polymer for whose plasticity, structure and structural transformations occurring during deformation are well documented.[1–4] Isotropic semicrystalline linear PEs consists of two phases at least, crystalline and amorphous. In this work we will base our interpretation on the two-phase structure of the semicrystalline PE. Degree of crystallinity of PEs is varied broadly and depends on the history of the sample. Both phases are strongly mixed, entangled, and interpenetrated. Therefore, both phases participate in a sample macro-deformation simultaneously and jointly. Such complex structure of PE produces strong deformation coupling between both phases and make the process highly constrained.

Under normal conditions linear PE is crystallized into a spherulitic morphology[1–3] with lamelar type

TABLE I
Investigated PEs and Their Characteristics

PE sample code	M_w	M_w/M_n	χ^a	$T_m{}^a$ (°C)	E^b (GPa)	$\sigma_y{}^c$ (MPa)	$\varepsilon_y{}^c$ (%)
PE-1	5.0×10^5	13.0	0.606	140.5	0.40	18.0	5.0
PE-2	1.5×10^5	–	0.520	132.5	0.30	20.0	7.7
PE-3	1.5×10^5	–	0.850	145.0	0.60	30.0	5.6
PE-4	$\approx 10^6$	–	0.710	134.5	0.43	25.0	15.5
PE-5	0.8×10^5	4.4	0.756	137.5	0.50	31.0	9.0
PE-6	4.8×10^5	12.2	0.608	138.0	0.45	35.0	13.0

[a] DSC measurements at heating rate 10°/min.
[b] E is the compressive modulus; $T_{\mathrm{def}} = T_{\mathrm{room.}}$
[c] σ_y and ε_y—engineering yield stress and strain.

crystallites in it. Crystallites undergo plastic deformation of crystallographic type under the action of external force through dislocation mechanisms. It is established now that cold plasticity of crystallites controls deformation kinetics of an entire PE sample.

The amorphous phase of material consists of highly entangled chains forming a continuous molecular network surrounding crystallites. Inter-crystalline phase contains tie-molecules, cilia, loops, which transmit stresses between both phases.[5,6]

At T_{room} an amorphous phase is liquid and shows a rubbery behavior (T_g of PE is below $-100°C^7$) and is the softest component of material with high molecular mobility. The amorphous phase becomes stretched and more "rigid" mechanically at later deformation stages.[8] The principal mode of a PE amorphous phase deformation is an interlaminar shear.

Studies of a deformation thermodynamics had helped to discover many new features in plastic behavior of materials, crystalline metals,[9] glassy polymers,[10] and silicate glasses.[11] In polymer field thermodynamic studies of deformation in glassy polymers[10,12,13] were especially successful because they broke up to big extend traditional view on deformation behavior of chain glasses.

There are only few papers devoted to deformation thermodynamic study of PE.[14,15] These studies had discovered several interesting features of deformation response of PE. However, the deformation thermodynamic picture was not completed and well understood. Authors could not separate fractions of deformation thermodynamic parameters belonging to crystalline and amorphous phases.

In this study, we attempt to make next steps in the deformation thermodynamic study of PE inelastic deformation. Good data about thermodynamics of elastic processes in PEs one may find in Ref. 14. Our measurements of the thermodynamics of plasticity for high MM linear PEs with different crystallinities presented in this paper had permitted us to separate mechanical and thermodynamic behavior of both phases.

EXPERIMENTAL

Studied six PEs and their characteristics are shown in Table I. All studied PE samples except of PE-4 were commercial products of BASF, Germany. PE-4 was the high molecular mass medium-density polyethylene supplied by DSM, the Netherlands. Molecular masses M_w and M_w/M_n numbers were provided by suppliers. Degrees of crystallinity χ and melting temperatures T_m were measured using the differential scanning calorimeter "DSC-910" (DuPont Instruments), indium calibrated. Scan rate was 10°C/min. Sample masses for the measurements were 5–7 mg. The unit volume fusion heat Δh_f of PE crystals was chosen as 293 J/cm^3.[16]

Deformation thermodynamic characteristics were measured on a custom build Calvet-type isothermal calorimeter.[17–19] The calorimeter measures simultaneously the deformation heat Q_{def} and stress–strain ($\sigma-\varepsilon$) curves. Area under $\sigma-\varepsilon$ curves is the work W_{def} expended for sample deformation. Technical details of the measurements and precautions necessary to diminish potential heat leak out of calorimeter can be found in Refs. 17–20. Changes in the internal energy ΔU_{def} (so called the stored energy of cold work[9]) of samples were calculated from the first low of thermodynamics.

All measurements were performed at T_{room} and uniaxial compression deformation mode. Strain interval was $\varepsilon_{\mathrm{def}} = 0–50\%$ and strain rate 4×10^{-2} min^{-1}. Samples for such measurements were cylinders $\varnothing = 2–4$ mm and height $h = 3–6$ mm. Cylinders were machined from larger rods received from producers. Machining rate was slow. Remains cut out of rods had shown DSC-traces the same as received samples. Mechanical characteristics of PEs received under these conditions are shown in Table I. Stress–strain diagrams for all studied PEs are shown in Figure 1.

DATA DESCRIPTION AND INTERPRETATION

Variations of W_{def} with χ are shown in the Figure 2. In the $\chi = 0.5–0.9$ range W_{def} yields straight lines

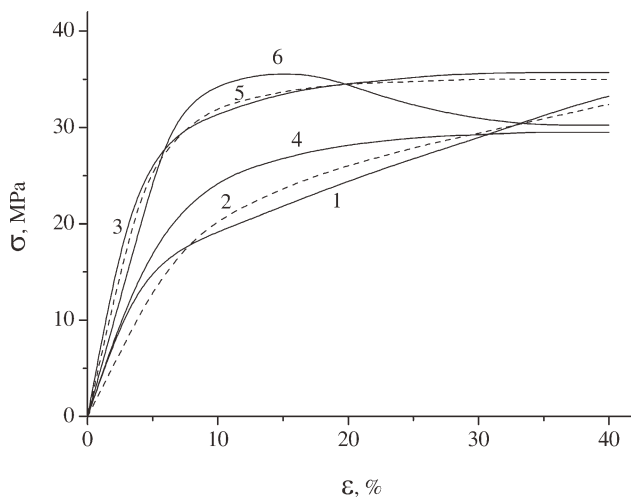**Figure 1** Stress–strain curves for studied PEs registered at T_{room}; uniaxial compression at the strain rate 4×10^{-2} min^{-1}; samples as they shown in Table I: PE-1 (1), PE-2 (2), PE-3 (3), PE-4 (4), PE-5 (5), PE-6 (6); σ and ε are engineering values.

growing from a lower to higher crystallinity for any strain level.

Deviations of W_{def} values out of straight lines are small at low strains and are increased at higher strains. Such behavior reflects, probably, some structural transformations and decomposition in material, breaking of lamella, for example, at strain increase. Extrapolation of lines to zero and 100% crystallinities gives values of W_{def}, which should be expended to deform plastically PE crystallites, W_{def}^{cr}, and pure amorphous phase, W_{def}^{am}, up to $\varepsilon_{def} = 40\%$.

Figure 2 clearly shows that W_{def}^{cr} ($\chi = 1.0$) is higher than W_{def}^{am} ($\chi = 0.0$) for all ε_{def}. This is not surprising because an amorphous phase of PEs is rubbery, mechanically soft at T_{room}. Straight lines of Figure 2 show that both, crystallites and amorphous phase of PEs introduce their fractions into total W_{def} additively. The total W_{def} for any PE under study cab be calculated from the data of Figure 2 if degree of crystallinity is known.

It is interesting to compare W_{def} for two types of solid polymeric structures, PE lamellar crystals (W_{def}^{cr}) and isotropic glassy polymers, W_{def}^{g}. For PE the W_{def}^{cr} is about 11 J/g at $\varepsilon_{def} = 30\%$, and reaches $\approx$16.5 J/g for $\varepsilon_{def} = 40\%$ (Fig. 2). At the same time, the W_{def}^{g} reaches about 25 J/g for Polystyrene (PS) and 18 J/g for Polycarbonate (PC)[12,13,19,21] at the similar straining conditions. For Polyimid (PI) and an aromatic amine cured the diglycidyl ether of resorcinol Epoxy the W_{def}^{g} is about 40 J/g ($\varepsilon_{def} = 30\%$).[13,19,21] The comparison shows that resistances to plastic deformation of PE crystals and bulk PC are close. However, the PC is one of the softest polymer through other polymer glasses. Glassy polymers with higher module, PI and the mentioned above

cured Epoxy, show considerably higher W_{def}^{g}, that is, the higher deformation resistance. It means that the resistivity of polymer glasses to plastic deformation is, in general, higher, than resistivity of PE lamella crystals. It is known from literature, that the most difficult stage of plastic process in solids is the generation of plasticity carriers.

Higher resistivity of polymer glasses to plastic deformation in comparison to lamellar crystals, it seems, occurs due to more difficult generation of plastic strain carriers in a disordered glass. If it is true, such feature of glassy polymer's plasticity may appears by two ways: ether due to more difficult generation of one individual plastic strain carrier, or to necessity to generate higher than in crystal critical concentration of such carriers. The critical concentration of plastic carriers is necessary to start the macroscopic plastic flow in a material. To answer this question deeper investigation of plastic processes in polymeric solids is necessary.

Figure 3 represents experimental data for $Q_{def} = f(\chi)$ for PEs studied. Again, Q_{def} depends on χ linearly and extrapolation gives Q_{def}^{cr} and Q_{def}^{am} for both phases of PE. Difference between the curves of $Q_{def} = f(\chi)$ and curves $W_{def} = f(\chi)$ (Fig. 2) is related only to the behavior of the amorphous phase. Values of the Q_{def}^{am} are close to zero (are quite small) for all studied strains. Low level of Q_{def}^{am} reflects the entropic character of deformation of an amorphous component of PE.

Uncoiling of PE chains through enrichment of them by *trans*-conformers should not produce the deformation heat. It is well known that extended *trans*-conformers in PE have lower energy than *gauche*-conformers.[22] Therefore, an appearance of trans-conformers in amorphous chains at PE deformation can create only the energy release during sample straining. However, experiments unequivocally show that
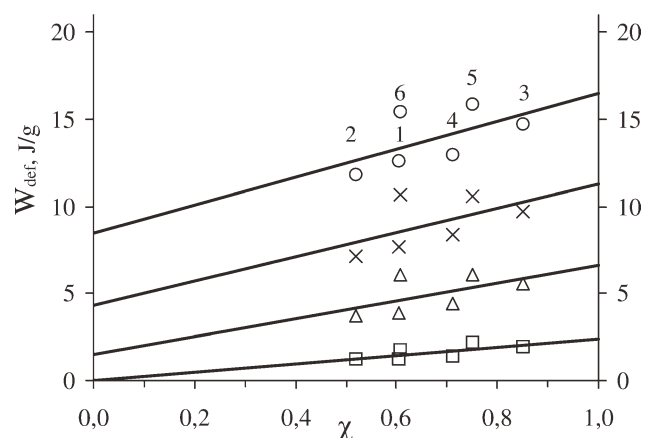

Figure 2 W_{def} as a function of crystallinity χ at different strains [$\varepsilon_{def} = 10(\square)$, $20(\triangle)$, $30(\times)$, and 40% ($\bigcirc$)] for different PEs: PE-1 (1), PE-2 (2), PE-3 (3), PE-4 (4), PE-5 (5), PE-6 (6).
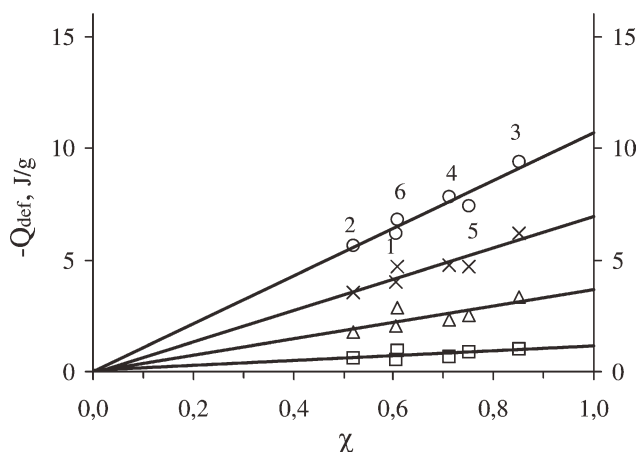
Figure 3 $-Q_{def}$ as a function of χ at different strains [ε_{def} = 10($\square$), 20($\triangle$), 30($\times$), and 40% ($\bigcirc$)] for different PEs: PE-1 (1), PE-2 (2), PE-3 (3), PE-4 (4), PE-5 (5), PE-6 (6); in thermodynamics it is accepted,[9,20] that the heat of a process is counted as positive when it's go into sample; the plastic deformation heat $-Q_{def}$ shown in this figure has a sign minus because it always evolves out of a sample.

energy ΔU_{def} of the amorphous phase of PE is increased with accumulated strain.

The data show that amount of plastic deformation heat Q_{def} of semicrystalline PEs is defined mainly by plastic deformation of crystallites. Let us now to compare amount of $-Q_{def}^{cr}$, plastic deformation heat of PE lamellar crystals with $-W_{def}^{g}$ for glassy polymers. At ε_{def} = 30%, values of $-Q_{def}^{cr} \approx 7$ J/g for PE, which is close to that for PC.[18,19] For PS and cured Epoxy $-Q_{def}^{g} \approx 12$–13 J/g. The comparison shows that an efficiency of plastic dissipation in both materials is close in spite of differences in dissipation mechanisms in them. In crystals the heat of plastic deformation originates mainly from the "friction" of dislocations at their glide over planes of crystalline lattice. In glasses, classic dislocations and any dislocation-like glide cannot exist due to their translational irregularity. Absence of the translational motions of plastic carriers in glass makes "frictional" dissipation in them inoperative. The heat at deformation of glassy polymer appears due to termination of plastic carriers,[10,12,21] because each carrier evolves its extra-energy at termination. The termination is a relaxation process when a carrier looses local strain and energy accumulated in it. The structure of a carrier becomes transformed into its original (pre-deformed) form.[10,12]

Now we will consider the stored energy of cold work ΔU_{def} accumulated by PEs during their deformation. Data on $\Delta U_{def} = f(\chi)$ are shown in Figure 4. Again, linear growth of ΔU_{def} with PE crystallinity occurs and the extrapolation of straight lines to χ = 0.0 and 1.0 is possible. The energy ΔU_{def}^{am} stored by an amorphous phase is smaller than ΔU_{def}^{cr} at $\varepsilon_{def} \leq$ 30%. At higher strains ΔU_{def}^{am} exceeds ΔU_{def}^{cr}. Both

phases carry energy excess in a deformed state. However, when amorphous chains become more extended and stretched ΔU_{def}^{am} becomes higher in it. This result may be correlated with computer modeling data.[8] Computed average stress in amorphous phase of PE becomes higher than in crystalline phase. However, it occurs at much higher strain level.

Comparison of values ΔU_{def}^{cr} with the deformation energy stored in glassy polymers ΔU_{def}^{g} demonstrates that ΔU_{def}^{cr} is about twice lower at ε_{def} = 30% than values measured for PS and PC.[10,19,21] The stored energy of cold work ΔU_{def} always exists in plastically deformed solids.[3,9,13,23–25] Such energy excess reflects an appearance in a bulk of material under loading some local structures (configurations) with a higher level of potential energy. In crystals such structures are dislocations.[9,23] However, classic dislocations, if they exist in a glass, can't glide due to structural disorder in it. Unfortunately, we do not know yet the real structure of the excited sites in deformed glasses (including glassy polymers). We only know that such structures always carry locally some amount of inelastic strain together with energy excess.[3,7,13] Therefore, considering macroscopic plastic deformation of glassy polymers we will call these local structures the " inelastic (or plastic) strain carriers." It was found[13,21] that such structures carry mainly the shear strains, but small voluminal component may exist also (the density changes of the plastically deformed glassy polymers are usually quite small). The carriers appear at loading polymer glasses, first of all, in the deformation regime of anelastisity[7] (delayed elasticity).[21] Such "strain carriers" play somehow a role of dislocations in crystals: they produce and accumulate locally new plastic strains during sample loading. The mechanism of such production of strain is not clear yet.
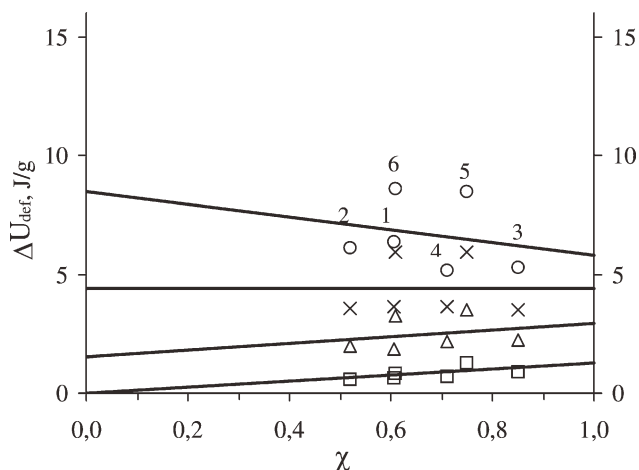

Figure 4 ΔU_{def} as a function of χ at different strains [ε_{def} = 10($\square$), 20($\triangle$), 30($\times$), and 40% ($\bigcirc$)] for different PEs: PE-1 (1), PE-2 (2), PE-3 (3), PE-4 (4), PE-5 (5), PE-6 (6).
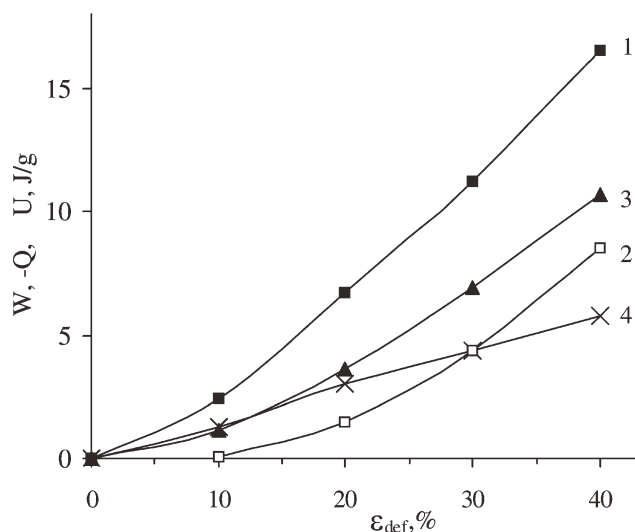
Figure 5 W_{def}^{cr} (1), $W_{def}^{am} = \Delta U_{def}^{am}$ (2), $-Q_{def}^{cr}$ (3), and ΔU_{def}^{cr} (4) for studied PEs as a function of ε_{def}.

Lower level of ΔU_{def}^{cr} in PEs in comparison with ΔU_{def}^{g} may occur due to two reasons: or due to lower concentration of dislocations necessary to create the macroscopic plastic flow in PE crystallites in comparison with such concentration of plastic carriers in glass, or due to lower (in average) energy necessary to generate one dislocation in crystal in comparison with generation of one individual plastic strain carrier[10,12,13,21] in glassy polymer.

The quantitative thermodynamic parameters characterizing plastic deformation each of coexisting phases of semicrystalline PEs as functions of ε_{def} are shown in Figure 5.

From the Figure 5 one may see that the highest resistance (the highest W_{def}^{cr}) to plastic deformation always shows the crystalline phase. Whole work expended to deformation of an amorphous phase W_{def}^{am} becomes transformed into the stored energy, but not to heat (see Fig. 3). Only crystallites are responsible for an appearance of plastic deformation heat Q_{def} at PE loading. The energy ΔU_{def}^{cr} is a little higher than ΔU_{def}^{am} at applied strain $\varepsilon_{def} < 30\%$, and becomes lower at $\varepsilon_{def} > 30\%$.

Neither ΔU_{def}^{cr}, nor ΔU_{def}^{am} show saturation up to $\varepsilon_{def} = 30\%$. It seems that ΔU_{def}^{cr} demonstrates some tendency to saturation at $\varepsilon_{def} > 30\%$. If it is true the saturation reflects tendency of crystals to reach constant concentration of dislocations. Absence of the stored energy saturation shows that concentration of dislocations in PE crystallites is continue to grow and dislocation termination rate is not high enough yet to levels off ΔU_{def}^{cr}. An amorphous phase has no tendency for saturation at all, and such behavior reflects non-plastic character of deformation in the phase.

Deformation thermodynamic data allow also to compare deformation behavior of amorphous phase

of PE with the behavior of non-crystalline rubbery polymers, such as natural rubber, ethylene–propylene, and ethylene–octene–propylene copolymers. For these rubbery polymers deformed at room temperature it was experimentally demonstrated that $W_{def} < 0.05$ J/g at strains 40–50%, and values of $\Delta U_{def} \approx 0.02$–0.05 J/g.[14,15,24] The results show that the deformation work W_{def}^{am} and the energy ΔU_{def}^{am} of PE at least an order of magnitude higher ($W_{def}^{am} = \Delta U_{def}^{am} \approx 4.5$–8.0 J/g at $\varepsilon_{def} = 40$–50%; see Fig. 5 also) than in non-crystalline rubbery polymers.[14,15] The comparison unequivocally demonstrates that rubbery phase of PE behaves differently. Similar conclusion had appeared also earlier.[24] Cause for such difference may be deformation constrains existing in PE due to its complex structure. Such constrains do not exist in non-crystalline rubbery polymers. The amorphous phase in PE covers each lamellar crystallite by thin layer of the network of entangled chains. PE phases cannot be involved into sample deformation separately. Because of differences in rigidity and deformability of phases mechanical constrains may play an important role in deformation process.[1–3] Thermodynamic results show that constrains in PE start to operate from quite small applied strains.

Knowledge of W_{def}^{am} and W_{def}^{cr} permits to reconstruct stress–strain curves separately for crystalline and amorphous phases of PEs. These stresses (σ^{cr} and σ^{am}) are derivatives of corresponding works $dW_{def}^{cr}/d\varepsilon_{def}$ and $dW_{def}^{am}/d\varepsilon_{def}$.[10] The reconstructed stress–strain curves are shown in Figure 6.

The curve for σ^{am}-ε_{def} is always located below the curve σ^{cr}-ε_{def} At $\varepsilon_{def} = 12$–34% the σ^{am} grows little faster than σ^{cr}. However, any tendency to curve's crossing does not exist. It's interesting to mention that ΔU_{def}^{am} becomes higher than ΔU_{def}^{cr} at strain $\varepsilon_{def} = 30\%$ (Fig. 5). But such energy ΔU_{def}^{am} increase does
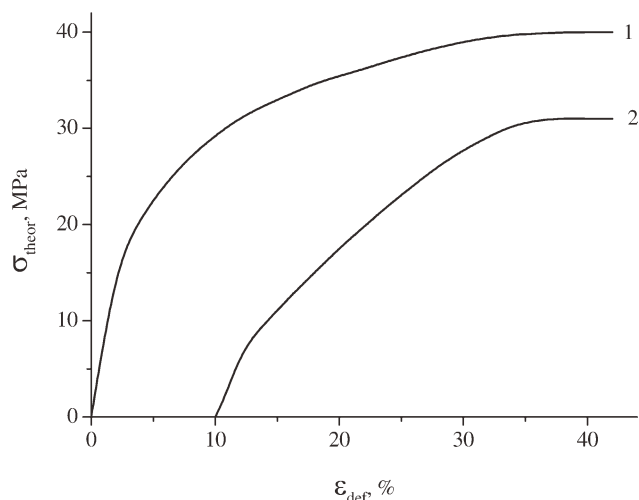

Figure 6 Stress–strain curves for crystalline σ^{cr} (1) and amorphous σ^{am} (2) phases of PEs. Curves were received from W_{def}^{cr} and W_{def}^{am} data of Figure 5.

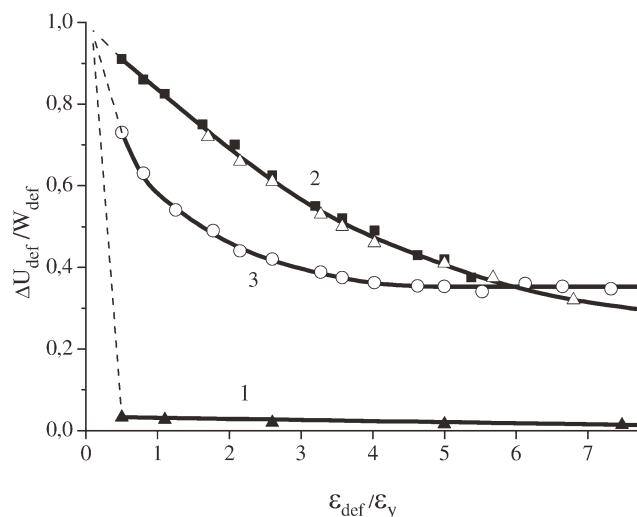**Figure 7** Comparison of the ratio $\Delta U_{def}/W_{def}$ for different materials at $T_{def} = T_{room}$: 1—crystalline metal (▲)[25]; 2—glassy polymers (PS—△, PMMA—■); PE-3 (○) (all studied PE show qualitatively similar curves with level of saturation $\Delta U_{def}/W_{def} = 0.35$–$0.55$); ε_y—yield strain.

not produce yet high level of stresses and the experimental relation $\sigma^{am} < \sigma^{cr}$ for PE is valid in all studied in this work strain region. At strains $\varepsilon_{def} > 33\%$ it appears that σ^{am} becomes constant. We can't explain yet this result.

Similar stress–strain curves for both phases were calculated in computer modeling of PE deformation.[8] Main features of stress–strain curves in Figure 6 looks the same with theoretically computed curves[9] at strain interval $\varepsilon_{def} \leq 40\%$. However, differences appear at higher strain level. Calculated curves show, that σ^{am} becomes higher than σ^{cr} at strains $\varepsilon_{def} > 1.3$–1.4 (log strain). Future thermodynamic studies of PEs at higher strains are, probably, necessary.

Another quantity characterizing plastic deformation of any solid is the ratio $\Delta U_{def}/W_{def} = f(\varepsilon_{def})$. The ratio demonstrates which fraction of the expended W_{def} is transformed into stored energy ΔU_{def} at given strain. Value of the ratio is changed with applied strain. The ratio is often used in studies of plasticity mechanisms in crystalline metals and glassy polymers.[9,12,13,19,21] Data presented in Figure 7 show behavior of the ratio $\Delta U_{def}/W_{def}$ as a function of ε_{def} for three materials: crystalline metals,[9,23] glassy polymers,[13,19,21] and semicrystalline PE (this work).

As an abscissa we used here is the strain normalized for the yield strain, that is, the value $\varepsilon_{def}/\varepsilon_y$. The normalization allows to plot materials with different ε_y in a single demonstration frame. Data of Figure 7 demonstrate that at low strains all materials give $\Delta U_{def}/W_{def} \approx 1$ (dashed line of curve 1 show only a trend of the ratio to go to unity, because we

were not able to find experimental data on ΔU_{def} and W_{def} for metals in this strain range). It is not surprising because at linear elastic strain range dissipation is absent. All linear elastic work W_{def}^{el} is completely transformed into the elastic energy ΔU_{def}^{el}. After sample unloading the elastic energy ΔU_{def}^{el} is transformed into heat of elastic deformation Q_{def}^{el} completely.

Dissipation during deformation appears at strains ε_{def} when anelastic (delayed elastic) regime becomes operational. The dissipation becomes even stronger when plastic regime occurs. Balance between ΔU_{def} and Q_{def} in anelastic and plastic regimes, that is, a balance between structural changes and dissipative processes at material's straining depends on deformation mechanisms operating in given solid. Let us consider crystalline metals first (curve 1 in Fig. 7). At room temperature straining and low strains ($\varepsilon_{def}/\varepsilon_y = 1$), soon after linear-elastic range plastic processes start and about 92–98% of W_{def} of metals becomes transformed into plastic deformation heat Q_{def}.[9,23] Such behavior continues up to high strains also, and very low amount of ΔU_{def}^{pl} is stored in crystals. Causes leading to such behavior of crystalline metals are not understood now.[25] An absence of the stored energy ΔU_{def} growth with ε_{def} points out, probably, on the absence of increase in concentration of mobile dislocations in metallic crystals.

The situation is completely different in glassy polymers. The curve 2 (Fig. 7) represents the ratio $\Delta U_{def}/W_{def}$ for PMMA and PS.[13,21] This type of behavior is typical for many glassy polymers.[13,19,21] At linear-elastic regime $\Delta U_{def}/W_{def} \to 1$. Then dissipation grows up at inelastic deformation regimes. However, the dissipation does not accelerate very fast. In glassy polymers the ratio stay close to 0.5
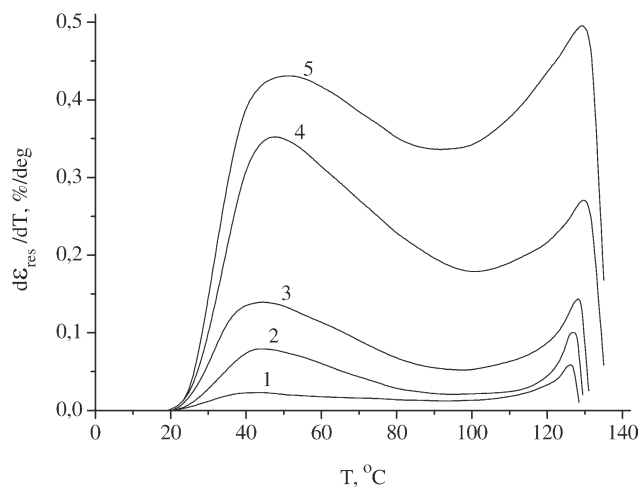

Figure 8 Curves of thermally simulated recovery rate of ε_{res} for PE-4 sample deformed to $\varepsilon_{res} = 2.6$ (1), 4.8 (2), 11.8 (3), 31.7 (4), and 53.8% (5); $T_{def} = T_{room}$, strain rate 4×10^{-2} min^{-1}, $dT/dt = 10°C/min$.

even at $\varepsilon_{def} = 40\%$. About the half of entire W_{def} is still transformed into ΔU_{def}. It means that generation of plastic strain carriers in glass still continues even at strains higher than ε_y. Such thermodynamic features of plastic deformation of glassy polymers reflect serious difference in plasticity mechanisms operating in them and metallic crystals. However, plastic behavior of some metallic glasses reminds the behavior of polymer glasses from the energy storage point of view. Metallic glass also store the energy excess at plastic deformation.[26]

The $\Delta U_{def}/W_{def}$ ratio for PE (curve 3, Fig. 7) deviates from the behavior of both, crystalline metals and glassy polymers. All studied PEs show similar curves. The initial decay of the $\Delta U_{def}/W_{def}$ with ε_{def} is slower than in metals but faster than in glassy polymers. The most interesting and unclear yet feature of PE plastic deformation is related to the constant ratio $\Delta U_{def}/W_{def}$ at $\varepsilon_{def} >15$–25%. The ratio constancy demonstrates that rates of ΔU_{def} growth and decay are close. The situation is similar to the steady deformation. However, we can't introduce now any deformation mechanism explaining such feature of PE plasticity. And we do not know other materials, which behave in similar manner.

Finally, we would like to consider a thermally stimulated recovery of residual strain ε_{res} accumulated by PE samples during their room temperature loading. After unloading of plastically deformed PE samples they always contain some ε_{res}. A deformed sample needs to be heated to remove ε_{res}. All ε_{res} disappear at sample heating above T_m, when crystallites loose all ε_{pl}^{cr}, the plastic strain accumulated in them. It happens due to melting of crystallites.

The ε_{res} recovery rate curve shows how and at which temperatures different components of ε_{res} relax out of samples. In Figure 8 typical thermally stimulated ε_{res} recovery rate curves[21] are shown for sample PE-4 containing different amounts of ε_{res}. Several important features of the recovery curves should be emphasized:

- For all PEs, recovery is the two-stage process, at least; we believe that the high temperature peak is related to the recovery of plastic strain in crystallites.
- The low temperature recovery process is related, in our view, to the recovery of ε_{res} in both, crystalline and amorphous phases of PE; locally excited structures carrying local plastic residual strains occur in crystalline and amorphous phases.
- Excessive energy, structure and strain disappear during a deformed sample heating at temperature intervals, where thermal energy becomes sufficient to "erase" given excited structure from a polymer bulk; in other words, the ther-

mal energy should be sufficient for overlapping the barrier of recovery.

CONCLUSIONS

1. Thermodynamic quantities characterizing plastic deformation of linear, high MM PEs were measured. At first time, the quantities characterizing plastic deformation of crystallites and deformation behavior of the amorphous phase were separated from experimental data.
2. Quantities W_{def}, Q_{def}, and ΔU_{def} linearly depend on crystallinity degree. The linearity permits to withdraw thermodynamic characteristics separately for crystals and amorphous phase.
3. Stress–strain curves for the amorphous and crystalline phases at PE loading were withdrawn from W_{def}^{am} and W_{def}^{cr} data.
4. Comparison of values of deformation thermodynamic quantities for PE crystals and glassy polymers is done. It is shown that it is more difficult to deform glassy polymers plastically than lamellar crystals of PE.
5. Comparison of W_{def} and ΔU_{def} for the amorphous phase of PE and non-crystalline natural rubber and ethylene–propylene rubbery copolymers were performed. The comparison shows that much higher amount of work W_{def} is necessary to deform the amorphous phase of PE than amorphous non-crystalline rubbers. And also, the amorphous phase of PE stores much higher amount of the energy ΔU_{def} than mentioned rubbers. These data probably points out on deformation constrains existing in PE, but not in non-crystalline rubbers.
6. Changes of the ratio $\Delta U_{def}/W_{def}$ with strain ε_{def} for studied PEs were constructed. The comparison of the ratio for three different materials: crystalline metals, glassy polymers and PE had done. Results show that generation of strain carriers is the critical step in kinetics of plastic deformation of all these materials. However, the development of plasticity is appeared differently in all materials under comparison. In metals the initiation stage ends at small strains and after that the expended W_{def} is transformed into Q_{def} nearly completely, for 92–98%.[9,23] The situation is completely different for glassy polymers. Carrier's generation stage in glassy polymers continues up to high strains, considerably higher ε_y and the ratio stays high, $\Delta U_{def}/W_{def} = 0.4$–0.5, up to deformations $\varepsilon_{def} = 40\%$. The result shows that the generation of strain carriers proceeds in glassy polymers at strains higher than yield strain. For PE the behavior of $\Delta U_{def}/W_{def}$ ratio is

located between crystalline metals and glassy polymers.

7. Thermally stimulated recovery of ε_{res} in deformed PEs shows that ε_{res} is always recovered in two stage process, at least. Part of ε_{res} is recovered below T_m and this part belongs to the strain recovery, we believe, in both, crystallites and rubbery phases. Part of ε_{res} recovered at T_m belongs to the recovery of crystals

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