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Thermal calorimetry of polymer simple shear deformation and its applications

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Abstract

The application of deformation calorimetry to the study of polymer structure and properties has appeared to be rather successful. However, up until now, most of the theories and experiments have dealt with mainly uniaxial stretching. Nevertheless, study of the simple shear deformation mode is valuable both for theory and applications. The theoretical thermodynamic description of simple shear deformation for polymer rubbers and glasses is presented. The application of the results obtained to the investigation of adhesion and fibre/matrix interphase phenomena for, respectively, polymer adhesive interlayers and composite materials is considered.

Keywords: Deformation; Polymer; Shear

1. Introduction

Solid state deformation is usually described in the framework of pure mechanical parameters. However, any deformation is a thermodynamic process, characterized by full-scale changes in thermodynamic potentials (mechanical, free internal ener-

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gies, etc.). For an experimentalist, this requires the simultaneous measurement of both the mechanical and heat effects accompanying the deformation processes. This thermal analysis of the deformation processes contains important information about the molecular structure of a solid. Most of the thermodynamic experiments were performed in the uniaxial extension–contraction deformation mode only; in addition, the thermodynamic description is best developed for this case. Unfortunately, the simple shear deformation mode has, up until now, been beyond the scope of researchers. Nevertheless, because of its unique feature concerning a priori zero-volume changes in the course of deformation, simple shear study may contribute substantially to the understanding of the thermoelasticity of network and solids. Moreover, this is valid for many practical cases, for example, while studying adhesion in substrate/polymer adhesive systems and the fibre/matrix interface in composite materials.

It is the purpose of the present study to give theoretical consideration to the simple shear deformations of polymer rubber and glassy interlayers and their applications in adhesion and composite interface study.

2. Polymer networks

2.1. Equations of state

The thermoelastic behaviour of polymer networks (as well as polymer glasses) is described by relationships derived with the aid of an appropriate analysis of the equation of the state. A number of theories have been developed to describe the network elastic behaviour, the affine deformation and phantom network models being the two limiting cases [1].

This phantom-like idealization does not take into account the intermolecular interaction and may be valid only for highly swollen networks. The intermolecular interaction is accounted for in the model of trapped entanglements [2]. Furthermore, a “constrained-junction” model has been developed [3], based on the Ronca–Allegra idea that, in the first approximation, all intermolecular interactions are concentrated at the junctions [4]. The Flory–Erman theory and its modifications (for example, Refs. [5]–[7]), unites the two extreme cases providing the transition from an affine to a non-affine strain deformation and, thus, a quantitative interpretation of the real network elastic behaviour. The validity of this model was also confirmed in deuterium nuclear magnetic resonance experiments [8]. Another important approach to describe rubber elasticity are slip-link models [9] and their developments (for example, Refs. [10] and [11]). Modern rubber elasticity theories also account for the influence of the molecular weight distribution of the network chains [12], the existence of network defects, such as weak inhomogeneities in the cross-link density [13], polydispersity (in the framework of the mechanical random central force network model [14]), the network swelling behaviour (for example, Ref. [15]), etc. Unfortunately, most of the modern rubber elasticity theories were developed for the simple extension deformation mode, with only a few exceptions concerning tension (for example, Refs. [16] and [17]), pure shear [18], torsion [19–21] and simple shear [22].

The global mechanical properties of the network for various modes of deformation are reasonably well accounted for by the universal approach of van-der-Waals-conformation gas networks with weak interactions [23–25]. This approach uses the well-known analogy between an ideal gas expansion and rubber deformation and allows the intermolecular interaction to be taken into account by introducing a "global interaction parameter". Briefly, an unfilled van der Waals network is characterized by three parameters: the maximum strain λ_m, the mean molecular weight of the stretching invariant unit M_u, and the empirical parameter a, which characterizes the global intermolecular interaction. The modified theory [26,27] accounts for the contribution of the loading by introducing the parameters, characterizing filler cluster distribution and filler-to-filler and filler-to-matrix interaction. From the physical point of view, this approach takes into account the local "liquid" network properties as well as the cooperative character of interchain intractions. It appears to be rather successful for explaining stress-strain dependences in the range of both minute and small deformations and in the non-Gaussian area [28] for all deformation modes.

2.2. Thermoelasticity

It would be very attractive to analyse some of the latest equations of state for the rubber elasticity in the framework of the chosen approach; however, as mentioned above, at present we do not have a more informative equation of state for the simple shear deformation mode than the expression from the classical theory of elasticity for Gaussian networks under the action of the tangential component of the shearing force. Theoretical and experimental description of the rubber thermoelasticity were obtained by theoretical and experimental study of the temperature dependence of the elastic deformation-force/torque patterns [29–31] (let us call this the "classical approach") or by thermodynamic analysis of the rubber equation of state in the framework of van-der-Waals' [23–27] and Godovsky's [21,32] models and direct measurements of the mechanical work and heat during deformation (we can define this as a "thermodynamic approach"). In the last case the difference between van dar Waals and Godovsky's approaches is in the way of taking into account the intermolecular interaction. In the first, this interaction is included in the initial equation of the state, while in the second it is accounted for by the introduction of a temperature-dependent volume change during the deformation. From the above consideration, it is clear that both approaches have to be in good correlation, and the expression of the first can be easily treated in the framework of the second, and vice versa [27].

Because the thermodynamic approach provides direct relationships between deformation parameters and deformation energetic effects, it is preferable for the thermoelasticity study. The predicted theoretical dependences may be easily and directly verified with the aid of the stretching calorimeter technique [25,32] (the direct measurement of the energetic effects are an added advantage of the thermodynamic approach). Most impressive and informative results were obtained by application of the above approach to thermoelastic analyses of the simple extension deformation mode [21,23–27,32]. For example, in Godovsky's approach [21,32] the initial equation of state from the classical rubber elasticity theory [1] is analysed

$$f/A = K(\lambda + \lambda^{-2}) \tag{1}$$

where f is a retraction force, acting within the specimen with cross-sectional area A, λ is the stretching ratio, and K is the topological parameter. The thermodynamic analysis of Eq. [1] taking into account the volume–temperature dependence, resulted in the expressions [21] for deformation dependences of specific (per mass of sample m) values of mechanical work (W/m), and the isobaric–isothermal heat effect $(Q/m)_{P,T}$ in uniaxial extension (or compression) (Fig. 1(a)). The following physical ideas are implicit in these expressions.

(i) The volume change accompanying extension, $\mathrm{d}V$, is the responsible for the contribution of intermolecular effects to $(Q/m)_{P,T}$ and $(U/m)_{P,T}$.

(ii) Contributions of intra- and intermolecular interactions to $(Q/m)_{P,T}$ and internal energy, $U = Q + W$, $(U/m)_{P,T}$ can be separated mathematically.

(iii) As a result of competition between intra- and intermolecular effects, the dependence of $(Q/m)_{P,T}$ on λ (or $\varepsilon = \lambda - 1$) must exhibit the so-called "inversion point", at which initial endothermic effects change into exothermic ones. It is to be emphasized that such inversion may be observed in polymer networks in principle only in extension as far as, in general, $\alpha > 0$ and $|\beta| = 1.5 \times 10^{-3}\mathrm{K}^{-1}$, and the internal rotation in flexible-chain polymers is hindered. (Here $\alpha = -\mathrm{d}\ln(\rho/\mathrm{d}T)$ is the bulk thermal expansion coefficient, ρ is the density, and $\beta = \mathrm{d}\ln(\langle h_0^2\rangle/\mathrm{d}T)$ is the temperature coefficient of the mean square, end-to-end dimensions of unperturbed macromolecules).

In the thermoelastic behaviour of polymer networks in torsion, the corresponding volume change, δV_{tor}, varies as the square of relevant deformation parameter, Ψ (here Ψ ($= \phi l$) is the torsion parameter, l is the length of a cylindrical sample, and ϕ is the angle of twist), whereas in the case of uniaxial extension, the volume change accompanying extension, δV_{ext}, is proportional to λ, so that $\delta V_{\mathrm{tor}} \ll \delta V_{\mathrm{ext}}$ [20]. Thermodynamic analyses of the torsion were carried out using both the "classical" [20] and "thermodynamic" [21] approaches. A comparison of the thermoelastic behaviour for simple extension and torsion deformation modes [33] leads to the following characteristic features of the thermoelasticity of polymer networks in torsion.

(i) The absence of "thermoelastic inversion" phenomena.

(ii) The independence of the ratio of the energetic component to the total torque on the torsion parameter, Ψ.

It was shown elsewhere [21,27,34], that the volume changes in the course of the deformation are crucial in the treatment of both the elastic and thermoelastic behaviour of polymer networks. So, it would be interesting to compare the thermoelastic behaviour in simple uniaxial extension, torsion and simple shear deformation modes, which are characterized, respectively, by meaningful, very small, and zero volume changes.

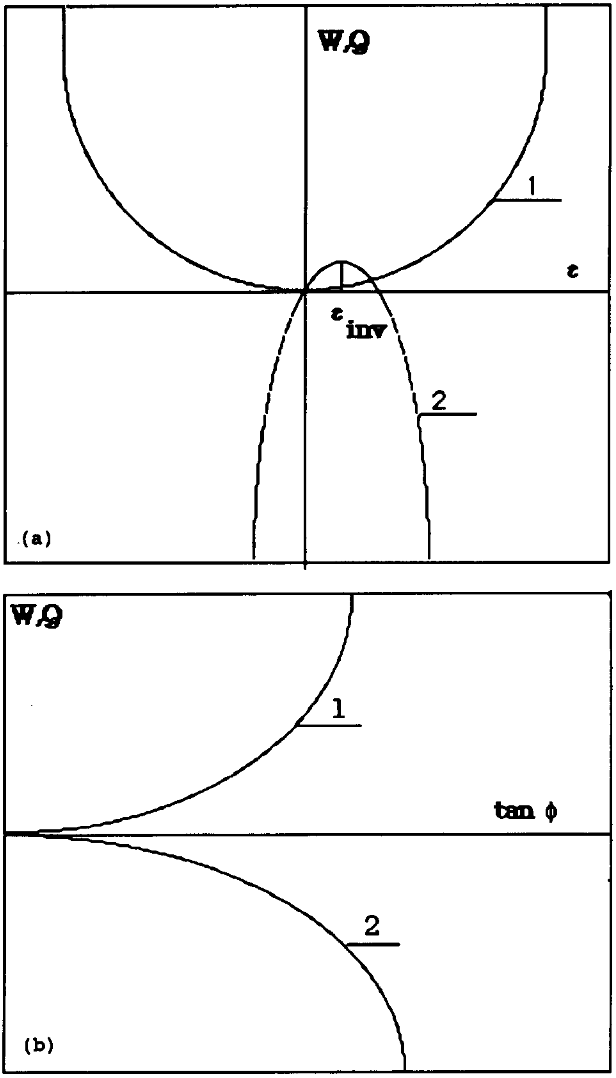

Fig. 1. Energetic effects of deformation of polymer networks (schematic). (a) Uniaxial stretching (at $\beta < 0$). (b) Isobaric–isothermal simple shear. Curves 1, mechanical work; curves 2, heat; $\varepsilon_i = \lambda_i - 1$, the inversion point.

The thermoelastic analyses of the equilibrium extension and compression should also be mentioned [27].

2.3. Simple shear thermoelasticity

As already mentioned, the early experimental results of Meyer and van der Wyk established the absence of thermoelastic inversion phenomena for simple shear deformation [1]. This experimental observation was supported by theoretical analysis, carried out in accordance with the "classical approach" [22]. It was shown that for simple shear, the ratio $f_{e_{xy}}/f_{xy}$ obeys the equation

$$f_{e_{xy}}/f_{xy} = -(T/m)(\partial M/\partial T)_{P,l_0,\phi} + \alpha T \tag{2}$$

$$(\partial f_{xy}/\partial T)_{P,l_0,\phi} = M(\beta - \alpha) \tag{3}$$

where f_{xy} is the total tangential component of the shearing force and $f_{e_{xy}}$ the corresponding energetic contribution, and ϕ is the angle of the slope of the lateral face of the sample, l_0, subjected to shear stress.

These expressions bear resemblance to the respective expressions for the torsion case. One can explain this fact by the similar character of the volume changes during simple shear and torsion deformation [33].

The above approach, however, does not take into consideration the normal component of the shearing force; nor were the equations relating directly the energetics of the deformation to the shear deformation parameter ϕ derived.

In our previous work [33] we tried to derive a theoretical description for the simple-shear thermoelastic deformation for polymer networks. It would be very attractive to analyse some of the latest equations of states for rubber elasticity in the framework of the chosen approach: however, at present the only equation of state for the simple shear deformation mode is that obtained from the classical theory of elasticity for Gaussian networks under the action of the tangential component of the shearing force

$$G = t_{xy}/\tan\phi \tag{4}$$

where G is the shear modulus, t_{xy} is the tangential stress, and ϕ is defined above.

Starting from the equation of state (4), using the ideal gas-classical Gaussian networks analogy and the analogy from Maxwell's thermodynamics transformation, we arrived at expressions for the energetic effects under isothermal conditions of simple shear (Fig. 1(b))

$$(W/m) = (G/2\rho)\tan^2\phi \tag{5}$$

$$(Q/m)_{V,T} = -(G/2\rho)(1-\beta T)\tan^2\phi \tag{6}$$

$$(U/W)_{V,T} = \beta T \tag{7}$$

The set of equations, (5)–(7), is only valid for a purely entropic intramolecular origin of the restoring force, the idea of which was accepted in the classical "gas-like" theory of rubber elasticity. In accordance with the applied "thermodynamic approach", the contribution of the intermolecular effects was accounted for by a "liquid-like" rubber thermal expansion, i.e. $V = V(T)$, which leads to the following expression for heat and internal energy of the isothermal–isobaric simple shear deformation

$$(Q_{xy}/m)_{P,T} = -(G/2\rho)(1 + \alpha T - \beta T)\tan^2\phi \tag{8}$$

$$(U_{xy}/W)_{P,T} = -\alpha T + \beta T \tag{9}$$

The expressions (5), (8) and (9) describe the simple shear thermoelasticity at fairly small deformations when the tangential component of the total shear stress dominates. The contribution of the normal component to simple shear energetic effects was also accounted for. As a result, general thermodynamic equations for polymer networks in the isobaric–isothermal regime of simple shear, accounting for the contributions of both the tangential and normal components of the shear stress, were obtained [33]

$$(W_{XX}/m)_{P,T} = (G/2\rho)(l_0/b)D(\phi) \tag{10}$$

$$(Q_{XX}/m)_{P,T} = (G/2\rho)(l_0/b)(1 + \alpha T - \beta T)D(\phi) \tag{11}$$

where

$$D(\phi) = (1/4) \tan \phi(1 + \tan^2 \phi)^{3/2} - (1/8)\{(1 + \tan^2 \phi)^{1/2} + \ln[\tan \phi + (1 + \tan^2 \phi)^{1/2}]\} \tag{12}$$

where b is the specimen width (along the shearing force direction). The validity of the developed description was proved in thermoelastic experiments with natural rubber samples in both simple shear and uniaxial stretching deformation regimes [33].

Compared to Eqs. (5)–(9), Eqs. (10) and (11) reveal the following features.

(i) The energetic effects depend on samples dimensions, i.e. b.

(ii) The energetic effects increase with the deformation parameter $\tan \phi$, not as a square parabola, $\tan^2 \phi$, but as a more complex function, $D(\phi)$ (or as a cubic parabola, $\tan^3 \phi$, in the range of intermediate deformations).

From the above analyses one can see that the thermoelastic behaviour of real polymer networks in simple shear is fundamentally different from that in simple extension where competition between intramolecular and intermolecular interactions leads to a "heat inversion" phenomenon. However, there is a rather close similarity to equations describing the torsion case, e.g. as in the shear case, the ratio $(Q/W)_{\delta V}$ does not depend on the deformation parameter and, hence, thermoelastic inversion will not occur (Fig. 1(b)).

Having compared Eqs. (5)–(7) and (6)–(9) one can readily obtain Eqs. (13) and (14) to characterize the heat effects and internal energy originating from the volume changes

$$(Q/W)_{\delta_V} = (Q/W)_{P,T,l_0,\phi} - (Q/W)_{V,T,l_0,\phi} = -\alpha T \tag{13}$$

$$(U/W)_{\delta_V} = (U/W)_{P,T,l_0,\phi} - (U/W)_{V,T,l_0,\phi} = -\alpha T \tag{14}$$

The last relationship is a natural result of the idea accepted here concerning the description of the real network properties by introducing the $V = V(T)$ dependence. A more detailed discussion of Eqs. (13) and (14) is given elsewhere [33].

Further analysis of Eqs. (5)–(12) makes it possible, in principle, to separate contributions from intramolecular and intermolecular interactions, containing terms with αT and βT, respectively. For example, a salient feature of the simple shear regime as compared to uniaxial extension [21,32], biaxial extension [35] or equilibrium extension and compression [27], is the independence of the contribution from intermolecular interactions to the deformation parameter.

3. Polymer glasses

As with polymer networks, a thermodynamic theory for the deformation behaviour of polymeric glasses in simple shear regimes is so far lacking. The most straightforward approach to a theoretical description of the thermoelastic properties of polymers is also based on the "thermodynamic approach" i.e. on the analysis of appropriate equations of state.

3.1. Equations of state and thermoelasticity

Most of the thermoelastic experiments with polymer glasses have been carried out in the simple extension deformation mode [21,36]. The experimental data at fairly small deformations are reasonably well accounted for by the classical theory of thermoelasticity for the solid [37]. Thermoelasticity inversion phenomena (the salient feature of the simple extension deformation mode for polymer networks) are not observed in this case; rather, the heat deformation dependence has a linear pattern (Fig. 2(a)). The special deformation behaviour in polymer glasses for simple extension, torsion [38], compression [39] and, also, simple shear [40,41] regimes is concerned with irreversible plastic deformation phenomena starting at very small deformations ($\varepsilon \approx 0.7\%-1\%$). A brief review of modern plastic flow theories is contained in Ref. [42]. It was shown that the free volume change in the course of deformation is also an important aspect of glass thermoelasticity. The conclusion was confirmed in experiments on the release of "physical ageing" at different deformation modes [43].

Thermoelasticity theories for polymer glasses and networks can be united in the framework of a phenomenological model, using a classical network model to interpret the deformation behaviour of glasses [36]. Suggesting that quasi-static plastic extension of a glass occurs without producing defects, introducing the strain-dependent modulus and using a "network" equation of state for the simple extension [1,21], the authors derived the expression for the total strain energy which contains two separate terms, namely, "energy" and "network" (conformation) terms. The energy term contribution dominates at small and intermediate deformations, while large strain deformation is governed by the conformation term. The results of thermoelastic measurements for the simple extension mode were in good accordance with the proposed model, both in "pre-necking" and "post-necking" (plastic) areas.

Summarizing, we may conclude that at present there is neither a thermodynamic theory, nor sufficient experimental data concerning the thermoelasticity of simple shear for polymer glasses.

3.2. Simple shear thermoelasticity

Expressions describing the energetic effects in the course of simple shear deformation for polymer glasses were obtained [42] using the "thermodynamic approach".

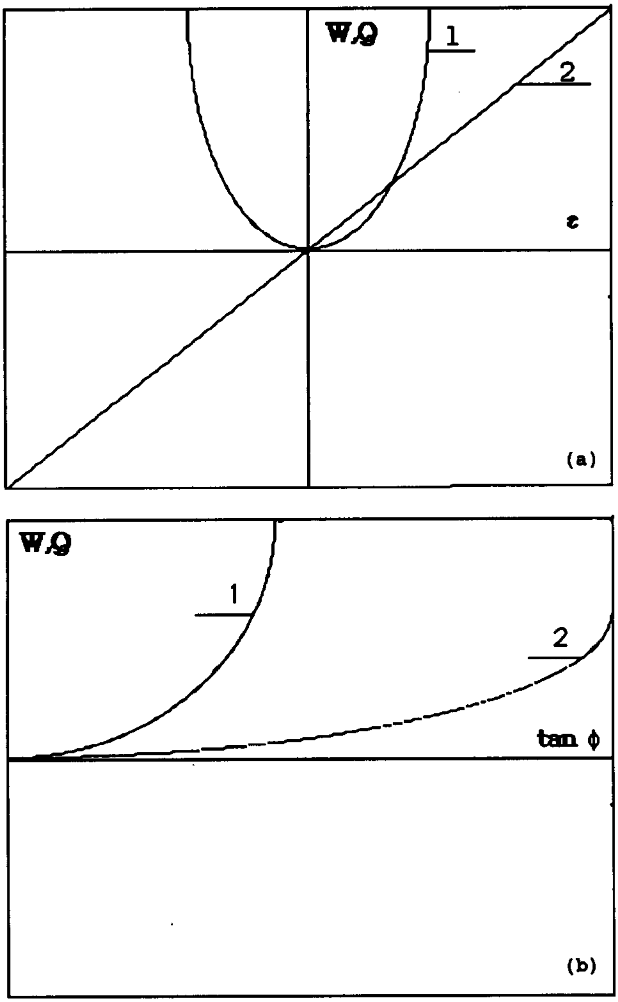

Fig. 2. Energetic effects of deformation of polymer glasses (schematic). (a) Uniaxial stretching (at $\alpha_l > 0$). (b) Isobaric–isothermal simple shear. Curves 1, mechanical work; curves 2, heat.

Having started from the classical equation of state of a solid subjected to the action of a shearing stress σ

$$\sigma = G(1+\alpha_l T)\tan\phi \tag{15}$$

where G is the shear modulus and α_l is the linear thermal expansion coefficient, and using the same algebra as in the case of polymer networks, we arrived at the scaling form expressions for the isothermal–isobaric conditions under the action of tangential and normal components of the shearing stress

$$(W/m) = (G/2\rho)Y(\phi) \tag{16}$$

$$(Q/m)_{P,T} = (W/m)_{P,T}\alpha_1 T \qquad (17)$$

$$(U/W)_{P,T} = 1 + \alpha_1 T \qquad (18)$$

where $Y(\phi) = \tan^2 \phi$ for the tangential component and $Y(\phi) = (l_0/2b)D(\phi)$ for the normal component of the shear stress (Fig. 2(b)). It follows from Eq. (18) that for the simple shear of polymer glasses, there is no thermoelastic inversion, as in the network case. Because $\alpha_1 < 10^{-4}$ K^{-1} for the majority of polymeric glasses [42], the heat effects accompanying simple isothermal shear should not be large, Eq. (17). The theory was verified in deformation calorimeter experiments with polystyrene samples [42].

The above theory is only valid for reversible (elastic) deformation. To extend the theory to plastic deformation, it is possible to apply the phenomenological model [36], introducing the conformation "network" term $U = (1/2)\ G \tan^2 \phi$ and the strain-dependent shear modulus $G = G(\tan \phi)$

$$G(\tan \phi) = Go \exp\{-[\tan \phi - 1]/[(\tan \phi)_y - 1]\} \qquad (19)$$

in the same way as was done for the simple extension modulus [36] (here $(\tan \phi)_y$ is the deformation "quasi"-yielding point). We are planning to develop these ideas in the future.

4. Adhesion

An interesting application of the above thermodynamic description of simple shear deformation, which up to now was beyond the scope of researchers, is a thermodynamic study of the adhesion properties of polymer interlayers, from both the fundamental and applied points of view.

4.1. Adhesion theories and methods

There are many physical and chemical concepts of adhesion mechanism [44–46]; however, until now, there has been no unified adhesion theory [47]. Naturally, an absence of a unified approach to the explanation of adhesion phenomena hinders the introduction of a universal parameter characterizing the adhesive strength (AS) of an adhesive joint (AJ). Further complications are concerned with the existence of different microdefects in the interfacial zone and, also, with the irreversibility of the failure process (which, itself, is in contradiction with the general definition of adhesion as a reversible phenomenon [46]). Moreover, most technical adhesion experiments (shearing, peeling at different angles, normal detachment, ply separation, torsion [48], pull-out scratch [49], etc., mechanical tests) are carried out under thermodynamically non-equilibrium conditions, the same being true for the new atomic force microscope technique [50], which determines the adhesion of the particles (in spite of the low debonding rate of the method). Meanwhile, these non-equilibrium adhesion evaluations are incorrect in principle [46]. Blister adhesion tests [51], which do not deal with the mechanical separation of an adhesion layer from the substrate should also be mentioned, although the injection of liquid at the interface can change this.

It is worth noting that for all deformation modes of testing the adhesion, one must also consider the influence of the so-called "deformation component of adhesive strength" which depends mostly on the bulk viscoelastic properties of the adhesive itself [47,52].

Equilibrium thermodynamic methods based on study of the interfacial tension seem to be more correct [46,53,54]. However, in this case too, the contact angle of wetting depends on the viscoelastic properties of the adhesives [55] (another disadvantage of the method is the necessity of eliminating the dissolution of the substrate and any adsorption from the liquid or gaseous phase [56]). Moreover, there is no strict connection between AS and wetting angle [46].

The group of AJ non-destructive test methods is also characterized by the dependence of the obtained AS estimates on the volumetric and surface properties of adhesives [44,57].

Following from the analysis, it is important to take into account the contribution of the adhesive viscoelastic properties to the integral energy characteristics of the AJ deformation process.

4.2. *Thermodynamics of the shear deformation of adhesive joints*

One can expect that simultaneous measurement of the mechanical and heat effects involved in the deformation and failure of adhesive joints will contribute to a solution of this problem. For example, let us consider the AJ shear deformation. In the standard scheme of the AJ shear test (Fig. 3), obviously, the stage of irreversible adhesion or cohesion failure is preceded by the stage of reversible shear deformation of the adhesive, which is responsible for the appearance of the AS deformation component. For a thermodynamic description of the shearing rubber AJ deformation, one can try to apply expressions (5) and (8)–(12). The fact, that for simple shear deformation the concomitant mechanical work and heat have different signs, suggests that the viscoelastic contribution of an adhesive can be separated.

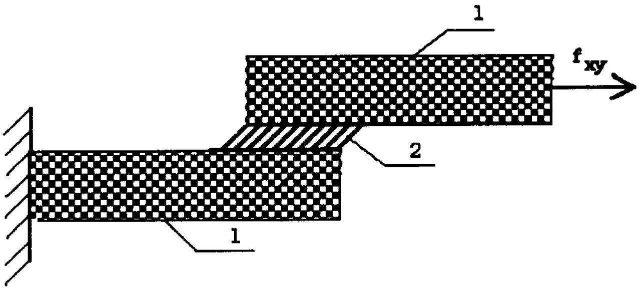

Fig. 3. Standard scheme of the shearing adhesion test: 1, substrate; 2, adhesive interlayer.

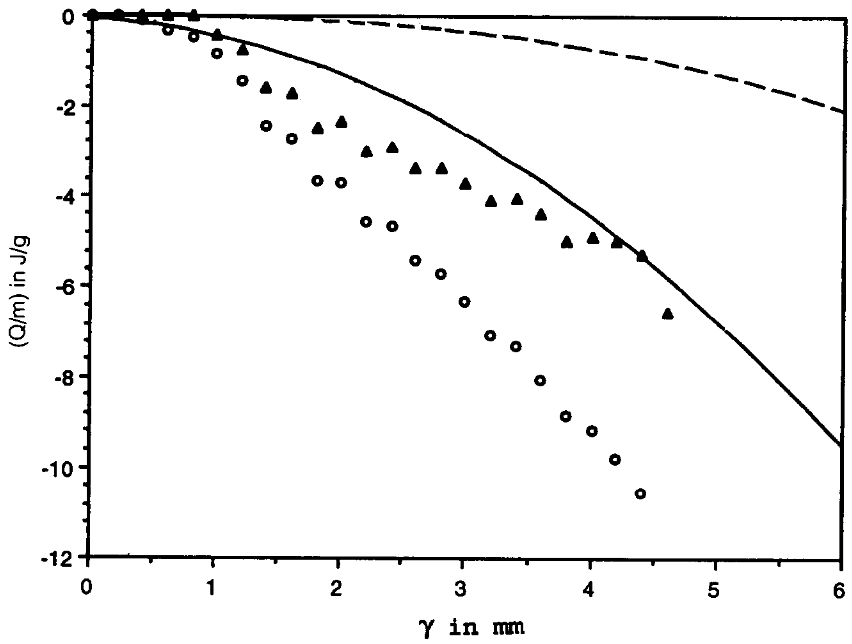

Fig. 4. Deformation dependence of the reduced heat 0, open circle of the "metal–adhesive interlayer–metal" adhesive joint: ——, calculated curve; ○, experimental curve; – – –, normal component contribution; ▲, adhesive joint failure.

Experiments of this type have been performed [33,48] for "metal–uncured rubber adhesive–metal" systems. A solution of uncured butyl rubber with additives in polar solvents served as the adhesive layer. The AJ deformation energetics was studied in the deformation microcalorimeter (using the method of continuous and step-by-step shear with different shear rates).

The dependence of the reduced mechanical work W/m on the squared deformation parameters $\tan^2 \phi = (\gamma/l_0)^2$ was linear over practically the whole range of shears up to the AJ complete failure (at $\gamma = 4$–7 mm). This testifies to the physical structurization of the uncured adhesive layer and the applicability of expressions (8) and (9) (which characterize the behaviour of the polymer networks), for the description of the thermodynamics of shear.

The calculated curves for the reduced heat $(Q/m)_{\mathrm{calc}}(\gamma)$ (Fig. 4, solid line) are close to the parabolic dependence predicted by Eq. (9). (In Eq. (9), for the adhesive layer being studied, we assumed $\alpha = 5 \times 10^{-3}$ K^{-1} and $\beta = 1 \times 10^{-3}$ K^{-1}; here α was determined from the Simha–Boyer relation [48], while β was determined by the least-squares fit of the experimental values of the reduced work W/m.) The obtained experimental dependence $(Q/m)_{\mathrm{exp}}(\gamma)$ (Fig. 4, circles), up to the values $\gamma_{\mathrm{lim}} \approx 1$ mm, shows a rather good agreement with the calculated dependences; however, at $\gamma > \gamma_{\mathrm{lim}}$ the experimental curve deviates from the calculated one towards higher exoeffect values. Such deviation cannot be connected with the effects of the limited extensibility of networks (which are similar to the effects which occur in the case of uniaxial extension of the networks, for the description of which Mooney–Rivlin-type [1] potentials have been introduced, because there is no chemical network in uncured rubber. However, accounting for the considerable (at large γ values) contribution of the normal component of shear to the thermal effects of deformation (for the current thickness of the adhesive layer, $l_0 = 0.05$ mm) does not allow the experimental curve to be described as well (broken line). It must be assumed that the exothermic processes of failure of the metal–adhesive-interlayer–metal AJ, which take place simultaneously with the adhesive shear deformation process, bear the responsibility for the deviation of the experimental deformation dependences of heat from the calculated ones. Then the $(Q/m)_{\mathrm{adh}}(\gamma)$ dependence, due to AJ failure, at the initial stage of the failure can be determined graphically by subtracting the $(Q/m)_{\mathrm{exp}}(\gamma)$ curve from the $(Q/m)_{\mathrm{calc}}(\gamma)$ curve (Fig. 4, triangles), where γ_{lim} is the thermodynamic criterion for the onset of the AJ failure process.

It is pertinent to underline that we failed to determine either the viscoelastic contribution or the γ_{lim} value from the deformation dependence of the reduced work alone, which did not reveal any inflection over the whole range of γ. This observation can be explained by the similar (parabolic) character of the above dependence for the irreversible process of adhesive failure and reversible shear process.

5. Fibre/matrix interphase in polymer composite materials

It is well known that the level of fibre/matrix adhesion influences strongly the ultimate mechanical properties of fibre-reinforced polymer composite materials. There have been some attempts to explain this influence, although only the interphase concept, i.e. a three-dimensional region between bulk fibre and matrix, has been successful. The interphase includes the two-dimensional contact area between fibre and matrix (the interface): interface penetration fibres and matrix has also been demonstrated [58]. It is now widely accepted that the fibre/matrix interface is one of the most important factors controlling both the mechanical properties of the composite and its enviromental stability [59].

5.1. Methods for observing interfacial phenomena

The mechanical properties of the interface are characterized mainly by the interfacial shear strength, σ, between the fibre and the surrounding matrix [60]. The methods for evaluating interface properties can be divided into the so-called "direct" and indirect approaches. Indirect methods include 3-point bending of a single-fibre specimen (SFS) with a small aspect ratio, interfacial crack propagation in SFS under a compressive load, and methods based on dynamic mechanical, ultrasonic wave, and acoustic and photoelastic analyses [58,61]. Laser Raman spectroscopic techniques for both isotropic and anisotropic fibre are described elsewhere [62,63]. The fibre wettability method [64] allows the fibre surface energy to be evaluated; however, it does not consider the fibre/matrix interaction. In fact, indirect methods can only be used for comparative analysis.

The group of "direct" methods includes the single-fibre (SF) fragmentation test, SF microindentation and pull-out tests, and microbonding. Briefly, fragmentation tests are carried out with SFs embedded in the matrix. Under the loading, either in tension or compression [65], the SF fails, the failure process being developed until some critical SF saturation length. It is worth noting [66] that the interface properties are not measured directly in this test either; rather, a shear-lag analysis, based on the fibre fragmentation length distribution, is carried out on the SF fragments. In the microindentation test, a probe pushes a fibre out from a supporting matrix, and the pushing force and path are registered. The idea of the pull-out technique for evaluation of the fibre/matrix interaction is to pull out an embedded fibre from the solidified thermoset or thermoplastic resin block in the direction perpendicular to it. A steadily increasing force is applied to the free end of the fibre with simultaneous monitoring of the load and displacement of the process. The three-fibre pull-out technique is a modification of this method [67]. Microbonding is, in fact, a variation of the pull-out technique. The difference being that the fibre is a polymer microdroplet with a hemispherical form embedded in a small amount of polymer; the movement of the microdroplet during the test is limited by a microvice plate. Summarizing the features of these techniques, the following main disadvantages are apparent [58]: the presence of a meniscus on the fibre, the variation of both the microdroplet size and the points of contact (for microbonding), the necessity of using matrices with a strain limit at least three times that of the fibre, the contradiction between the sophisticated statistical technique to characterize the fibre fragment length distribution and the oversimplifying of the interphase stress-state representation (for SF fragmentation), frequent fibre crushing during the test (microindentation), the drawbacks in the treatment of the results and also fibre failure during the pull-out technique. (Note that bundles of fibre can be used to overcome the last disadvantages [60]).

It is commonly accepted for all these techniques that the shearing forces on the interface fibre/matrix are those responsible for the failure processes. So, one can apply the developed thermodynamic description of polymer simple-shear deformation to analyse fibre/matrix interaction in composites, in accordance with ideas first discussed in Ref. [68].

5.2. Pull-out test

Let us consider the pull-out test (Fig. 5) as being the most developed and reliable technique [69]. The debonding process during pull-out consists of two stages: debonding (the formation of an interfacial crack) and overcoming the fibre/matrix friction (which is due to shrinkage of the cured resin or due to the thermal mismatch effect during cooling [70]).

From a typical experimental curve of the pull-out test (Fig. 6) one can determine the force F (stress σ) required to overcome the fibre–matrix interaction τ

$$F = 2\pi r l \sigma \tag{20}$$

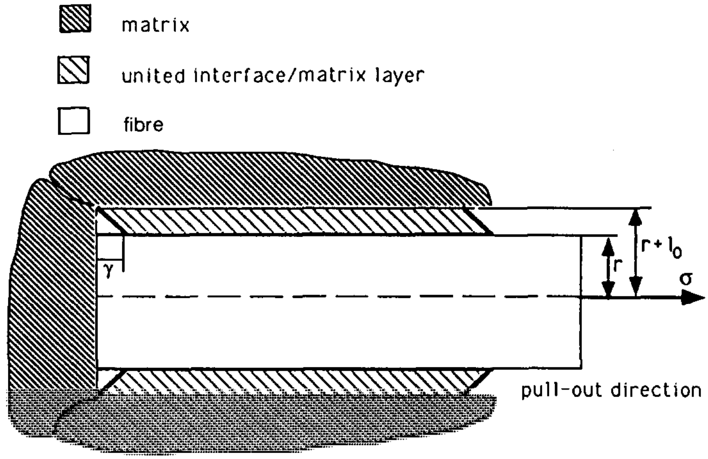

Fig. 5. Scheme of the pull-out test: γ, shear parameter; r, fibre radius; l_0, thickness of the united interface/matrix layer; σ, pull-out strength.

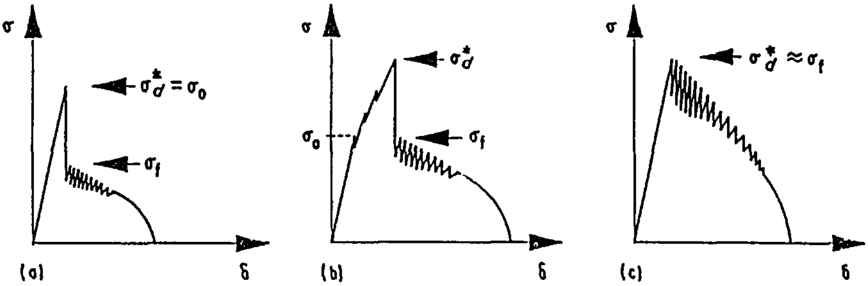

Fig. 6. Schematic representation of applied stress σ versus displacement during single-fibre pull-out test [69] for: (a) totally unstable ($L \leq l_{\max}$); (b) partially stable ($L > l_{\max}$); and (c) totally stable ($l_{\max} \approx 0$) debond process. L is the total fibre length, σ_0 is the frictionless debond stress, σ_d is the maximum debond stress, σ_f is the frictional pull-out stress, and $l_{\max}$ is the maximum bond length.

where σ is the interfacial shear stress and r and l are, respectively, the fibre radius and embedded length. To prevent fibres breaking during the test, the tensile stress in pull-out sould be less than the fibre ultimate tensile stress σ_{fu}, that is, taking into account Eq. (20), the maximum embedded fibre length $l_{\max}$ should be less than $\sigma_{fu}r/2\tau$ [60].

Eq. (20), obtained assuming uniform shear stress, is the simplest mechanical equation of the pull-out process. However, for an elastic matrix the tensile forces are no longer uniform, instead a hyperbolic distrubution of the load along the embedded fibre is found [71]. Moreover, it does not represent the deformation dependence of the force (strength); rather, it deals with ultimate values only. Obviously, to describe the deformation energetics of a pull-out test one needs to analyse an appropriate equation of state, in the same manner as performed for polymer networks and glasses.

5.2.1. *Equations of state*

There are several theoretical approaches to describe the pull-out process that can be separated in accordance with the shear debonding criterion used, i.e. the maximum shear stress approach (based on the "shear-lag" model) and the energetic approach [69]. The recently developed improved Zhou–Kim–Mai model for fibre pull-out and interfacial debonding [72] unites these two approaches, also accounting for the dependence of debond stress on debond length. However, it is possible to divide the existing theories into those based on the models of catastrophic and two-step debonding [71]. It should be noted that normal stresses (caused, for example, by shrinkage processes) also contribute to fibre/matrix interface mechanics. Banbaji's generalized theory [71] attempts to introduce normal stresses into the equation of the state for the pull-out test. One can use Banbaji's theoretical constitutive state equations for a thermodynamic analyses of the pull-out process.

However, the fibre/matrix system is rather complex, so that all the known theories are based on some simplifications. For example, the same elastic properties for the fibre and matrix are assumed in the Banbaji and Greszczuk–Lawrence models [58,71], the increase in the interfacial fracture toughness with the debond length was not accounted for in Gao–Mai–Cotterell's and Hsueh's models [69] (which means that crack propagation does not occur exactly along the fibre direction, the failure occurring instead within the interface). Nor was the effect of the fibre radius relative to that of the matrix examined in the two last models (in spite of the experimental finding of this effect [73]). The most detailed Zhou–Kim–Mai model still requires some simplifications, namely, that the fibre has a precisely cylindrical shape, and that both matrix and fibre are perfectly elastic and isotropic; another assumption concerns the fibre/matrix interface which is assumed to be either perfectly bonded or totally debonded. One must bear in mind the contribution of the matrix plastic flow around the fibre [59] (this yielding process is most important for short-length fibres [74]), the effect of the interface stiffness on its thickness and moduli [66,72], and also the influence of the slipping.

In addition the problems concerning the theoretical treatment of the pull-out experiments, there are problems associated with the properties of the interphase materials, which are seldom measured accurately [69]. The nature of the interphase itself is one of the most crucial questions. Some authors [66] consider three sets of material properties to model the interphase, namely, the soft, stiff and no interface cases. In other's opinion [69], the interphase is softer than the bulk material. However, the presence of the fibre significantly increases the modulus close to the fibre interphase. The interphase thickness is also unclear. Different authors take it to be from $0.001D_f$ to $0.05D_f$ for different composite systems [66], where D_f is the fibre diameter.

5.2.2. *Thermodynamics of interphase shear deformation*

Let us consider the most simple case of the debonding (the first part of the pull-out process followed by friction) as a result of single-fibre pull-out from the matrix (Fig. 5). As mentioned, it is not clear to what extent an interphase penetrates into both the matrix and the fibre; its properties and their changes within the matrix are still unknown. Thus, for thermodynamic analyses one has to use some simplified model. Let us separate the "united" matrix/interface layer involved in the simple shear deformation. This layer itself is assumed to be purely elastic, and the stress distribution along the fibre is considered to be uniform. Also, the fibre is supposed to be much stiffer in comparison with the above "united" layer, so that all the shear deformation is a result of the displacement of this uniform layer. Normal stresses are not considered. Poisson contraction is ignored and the yielding is excluded. Let us first consider the glassy united layer.

Having used the thermodynamic relations (2) and (3), where m is now the mass of the united layer with thickness l_0, $m = \pi l_0 l(2r + l_0)$, we arrive at the simplest thermodynamic description of the isobaric–isothermic pull-out process

$$W = [G\pi l(2r + l_0)/2l_0]\gamma^2 \tag{21}$$

$$Q_{p,T} = W\alpha_1 T \tag{22}$$

where r is the fiber radius, γ the current displacement and G the united layer shear modulus.

The same analysis for the rubber united-matrix/interface layer leads to the results

$$W = [G\pi l(2r + l_0)/2l_0]\gamma^2 \tag{23}$$

$$Q_{p,T,l_0} = -W(1 + \alpha_v T - \beta T) \tag{24}$$

Here G is determined from the original stress-displacement curves, while l_0 can be chosen by the least-squares fit of the experimental W values. (It is important to note that in this way one can obtain additional information concerning the interphase thickness.) To account for cases of large deformation one can introduce to Eqs. (21)–(24) the D (ϕ) function, Eq. (12), instead of the square term. However, the deformation is still considered elastic.

The interesting observation here is the different signs of the thermoelastic effects for the supposed rubber and glassy united layers, which may provide additional information about their nature. The thermoelastic contribution of the fibres can be separated by means of routine uniaxial extension measurements.

(It should be noted that thermoelastic analysis for the friction process was also carried out, for both simple linear and non-linear models [70]. However, the friction does not deal directly with the sample shear deformation mode, which is now receiving attention.)

6. Conclusions

The modern polymer elasticity and thermoelasticity theories are briefly considered and a short review of the existing tests for evaluation of the adhesive strength of AJ and fibre/matrix interactions in composite materials is presented. The theoretical thermodynamic treatment of simple shear deformation for both polymer networks and glasses is reported. A comparison with the usual uniaxial stretching deformation mode is carried out. The outstanding feature of the simple shear