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# THERMODYNAMIC EFFECTS IN THE TESTS ON DYNAMIC ELONGATION OF POLYMER COMPOSITES

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A method and results of dynamic tensile tests applied to an orthotropic polymer composite are described. Its mechanical properties are dependent on both the temperature and the strain rates. On the basis of experiments, the increments of the potentials of internal energy, free energy, enthalpy and free enthalpy are determined. The results are planned to, be used to formulate an energy strength criterion for a fibrous composite.

## 1. INTRODUCTION

In the study of mechanical properties of composites it appears important to work out a test method which could be applied in a complex stress state and which would take into account the influences of the deformation rates and the temperature fields. Thus the material properties will be tested in the conditions similar to those encountered under the actual conditions of a particular structure. Up to now neither a unification nor a normalization of the test methods for composites have been worked out [1–4]. Various test devices and specimens are in current use which makes it difficult to compare different results and to verify the hypotheses put forward.

Polymer composites belong to a class of visco-elastic materials being particularly sensitive to the duration of loading and even small changes in temperatures. Few papers [5–9] have been devoted to the problem of behaviour of plastics and composites under variable strain rates and temperature. The data available from the dynamic tests performed on polymer composites and the influences of strain rates and temperature on their mechanical parameters show the demand for further investigations accounting for a sufficiently broad interval of strain rates and temperature. No publications are also known on the experimental determination of thermodynamic potentials.

## 2. Aim and method of the tests

A layered polymer composite made of epoxy resin Epidian 53 with the hardener ZI and reinforced by the glass fabric STR-58 was tested. The specimens had the form of plates and tubes. Content of glass (by weight) in the composite was 50 percent. To investigate the thermodynamic effects in the dynamic tensile tests, tubular testpieces were used. The axis of orthotropy was inclined to the loading direction at the angles $\varphi = 0°$ and $\varphi = 45°$. Preparation of the specimens and their dimensions were described in [10].

In order to determine the thermodynamic potentials it is necessary to know the basic thermal properties of the material such as its thermal expansion coefficient, thermal conductivity and the specific heat capacity.

Linear thermal expansion of the composite was measured on a stand for investigating the linear expansion by the interference method. The measurement results are shown in Fig. 1. Since the properties of the studied composite were identical in its plane (the fabric had the same number of fibres in the warp and in the weft), the measurements were taken in the orthotropy directions *1* and *3* (*3* denotes a direction perpendicular to the surface of the fabric).

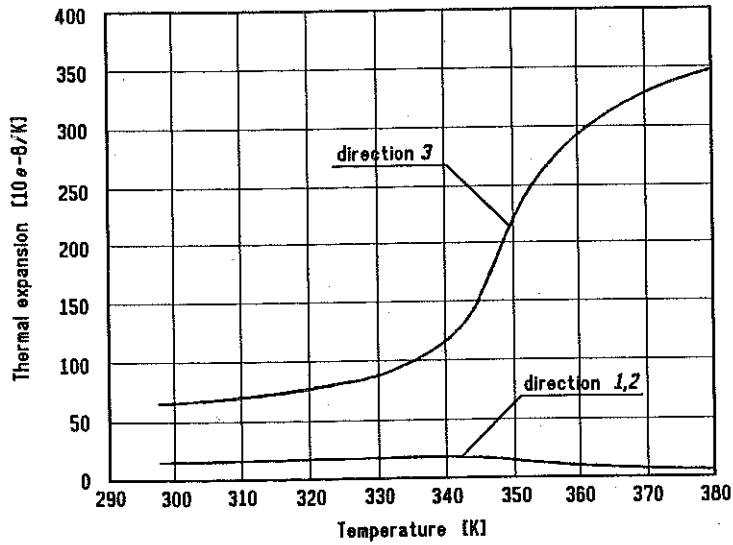


FIG. 1. Thermal linear expansion coefficient $\alpha$ in the principal directions of orthotropy vs. temperature.

Thermal conductivity was measured on a stand by means of a protective thermal plate. The results for thermal conductivity in the directions *1* and *3* are presented in Fig. 2.

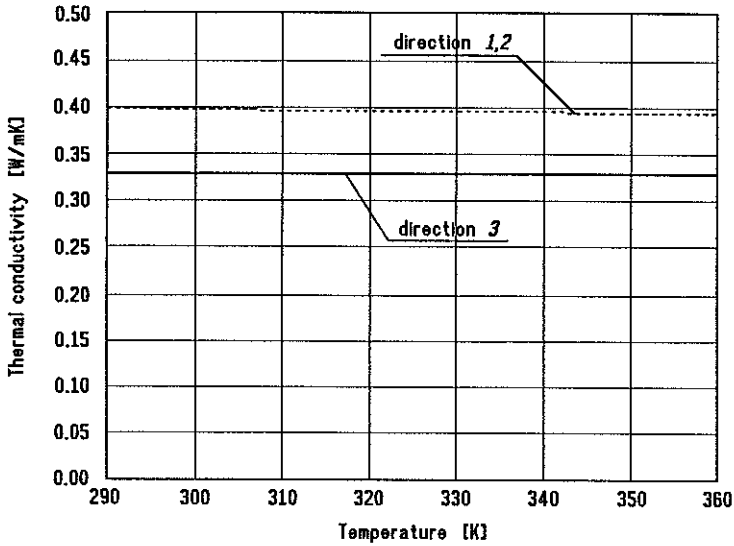


FIG. 2. Thermal conductivity $\lambda$ vs. temperature.

Specific heat capacity of the composite was measured directly by means of a differential scanning microcalorimeter DSC-7. Suitable results are plotted in Fig. 3.

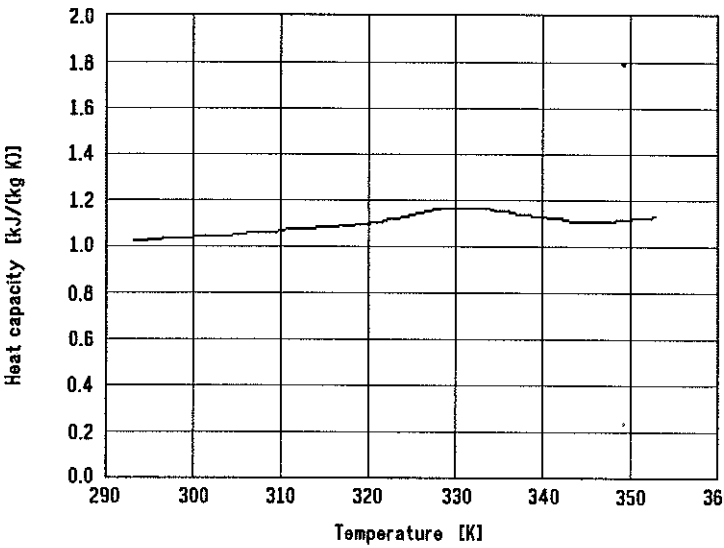


FIG. 3. Specific heat capacity $c_\sigma$ vs. temperature.

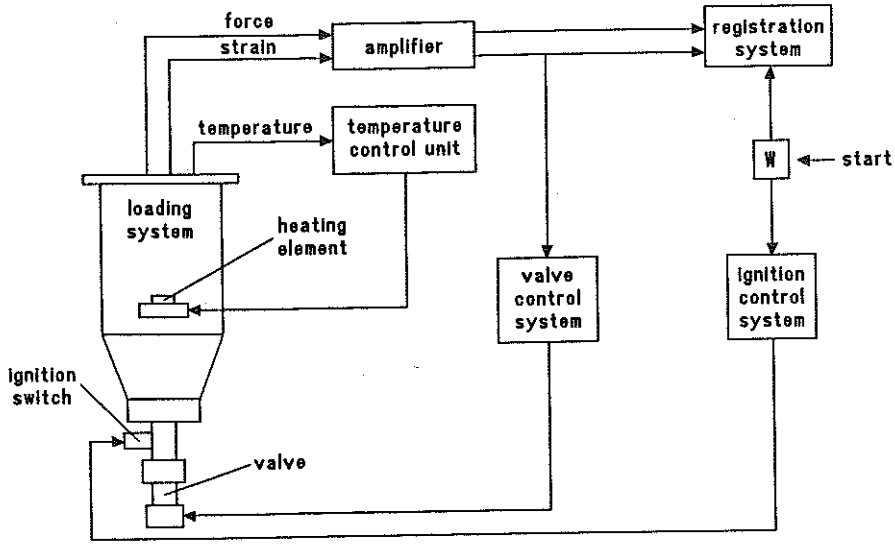


FIG. 4. Block diagram of a device for dynamic tests.

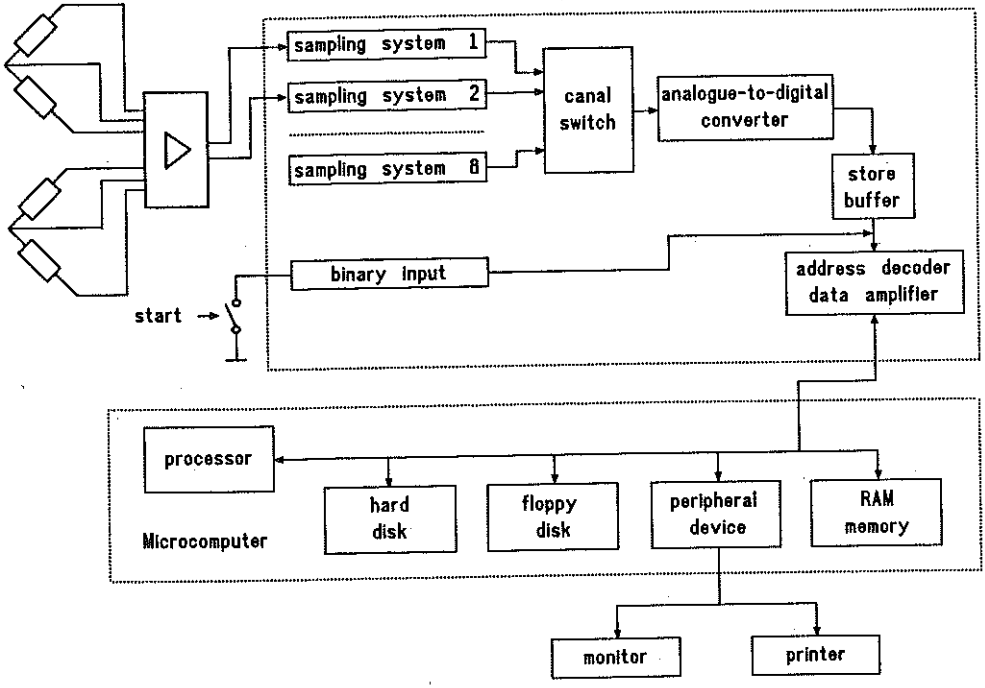


FIG. 5. Outline of the measuring and registration system.

To examine the specimens in broad ranges of strain rates and temperature, a special device was prepared. Its block diagram is shown in Fig. 4. The loading system was described in [9], the scheme of the measuring and registering system is presented in Fig. 5. The system consists of converters for the loading and deformations, a signal amplifier, a module of an analogue-to-digital converter LC-020 and a microcomputer. A detailed description of the stand was given in [10]. The strain rates are variable in the interval $0.00001 < \varepsilon' < 20\ [s^{-1}]$, the maximum load can reach $P = 30\,kN$ and the temperature vary between 293 and 370° K.

## 3. Analysis of the test results

Results of the dynamic tensile tests were registered in the computer memory in the form of changes of elongation and loading during the test (Fig. 6a). The diagrams $P = P(t)$ and $\varepsilon = \varepsilon(t)$ were used to determine the strain rates $\dot{\varepsilon}$, the the relationships $\sigma = \sigma(t)$, tensile strength $R_m$ and the fracture strain $\varepsilon_n$. From the relationship $\sigma = \sigma(\varepsilon)$ shown in Fig. 6b the initial longitudinal Young's moduli were determined as the slopes of the tangents to the curves $\sigma = \sigma(\varepsilon)$ at the origin of the coordinate axes. A nonlinear model of viscoelastic material was assumed to model the behaviour of the composite. The obtained values were processed statistically. The determined mean values and the assessed confidence intervals of particular parameters were used to prepare the diagrams $E = E(\dot{\varepsilon})$, $R_m = R_m(\dot{\varepsilon})$, $\varepsilon_n = \varepsilon_n(\dot{\varepsilon})$ for the specimens with $\varphi = 0°$ and $\varphi = 45°$; they are plotted in Figs. 7, 8 and 9, respectively.

The glass fibre used in the composite had $R_m = 1032\,MPa$ and $E = 64660\,MPa$. The glass fibres were found to remain elastic up to rupture and no permanenet strains were observed.

The hardened resin matrix of the composite was considerably weaker. Its mechanical parameters were: $R_m = 42\,MPa$ and $E = 2270\,MPa$. As a viscoelastic material, it changed its properties when the temperature and the strain rates were varied. An increase in the strain rate produced an increase in the strength $R_m$ and Young's modulus $E$ and reduction of the fracture strain $\varepsilon_n$. Elevated temperature caused rapid decreases in both the strength and the modulus and an increase in the fracture strain.

The deformation and fracture mechanisms of the composite consisting of hardened resin reinforced by glass fibres depend considerably on the phe-

nomena that take place both in the resin and on the fibre-resin interface. Certain changes in these mechanisms are connected with appearance of new stress distributions in the structure of the composite [11]. The reasons for this may be different, e.g. temperature, strain rate and the volumetric constant of fibres. Changes in these parameters influence the behaviour of the matrix.

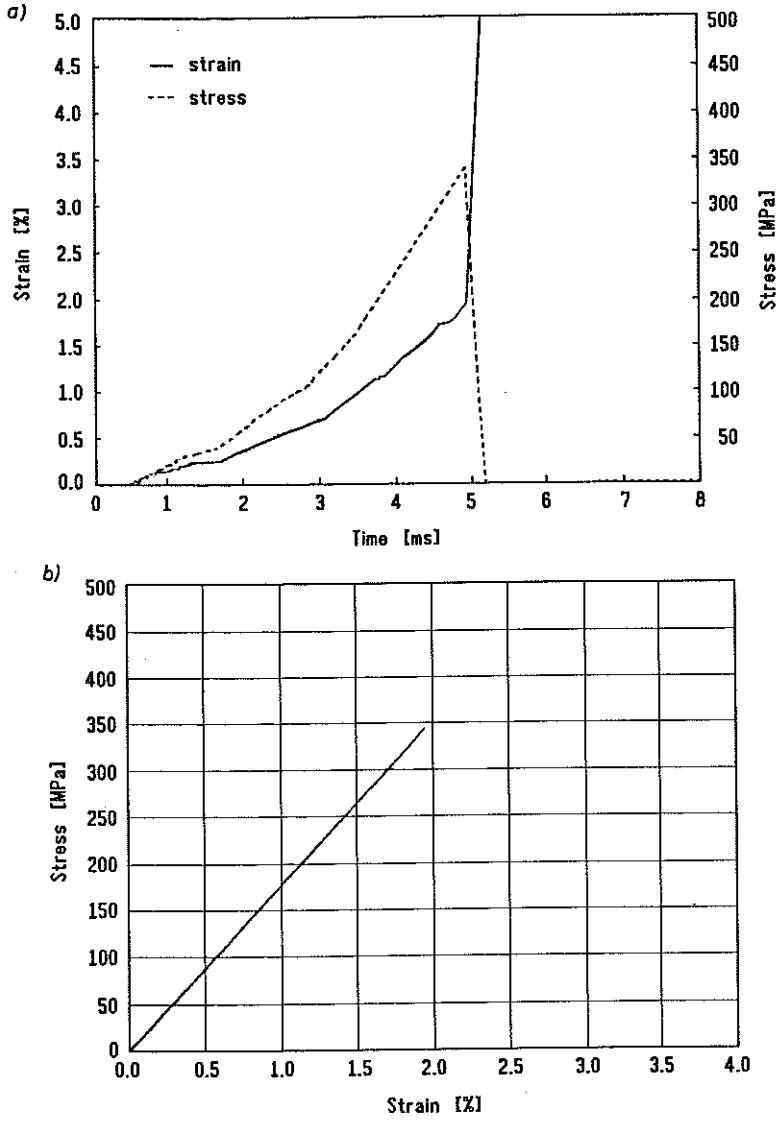


FIG. 6. Strain and stress variations during the test (a) and the corresponding tensile curve (b); $T = 293\,\mathrm{K}$.

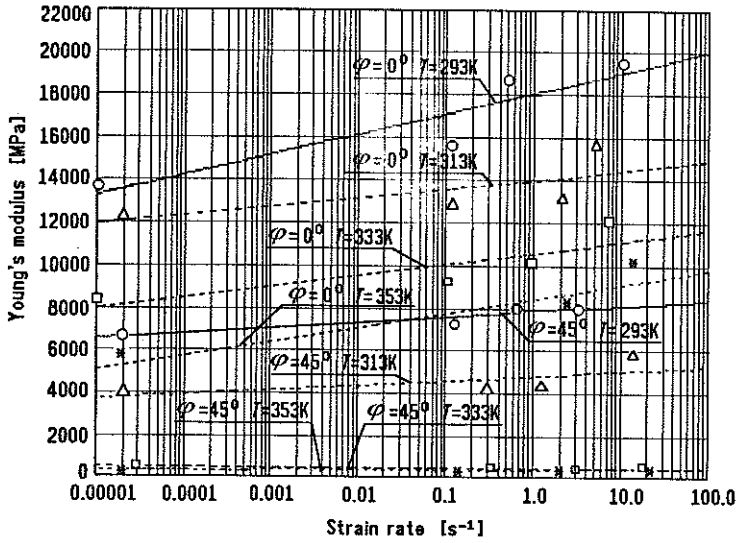


FIG. 7. Relationship $E = E(\dot{\varepsilon})$ for various $T$.

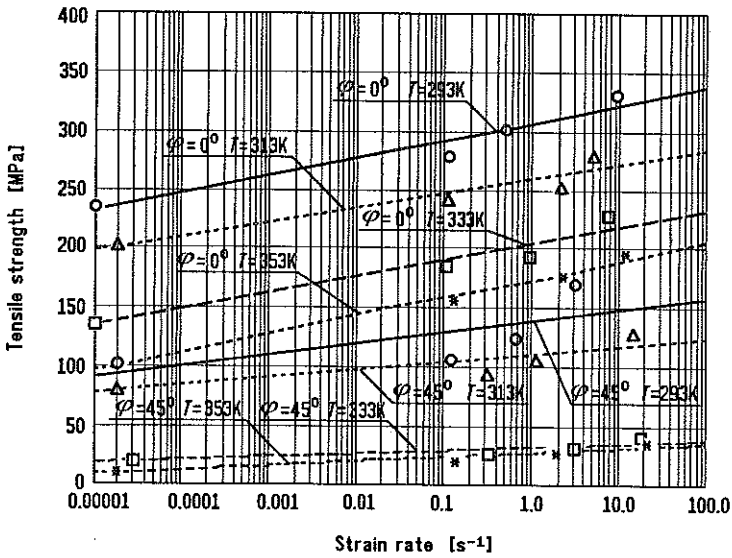


FIG. 8. Relationship $R_m = R_m(\dot{\varepsilon})$ for various $T$.

During the analysis of the influence of temperature on the mechanical properties of the composite it appears important to know the glass transition temperature $T_g$ for the particular polymer. $T_g$ characterises the point of transition from the glassy to the plastic state.

Increase in temperature of the composite causes certain changes in the

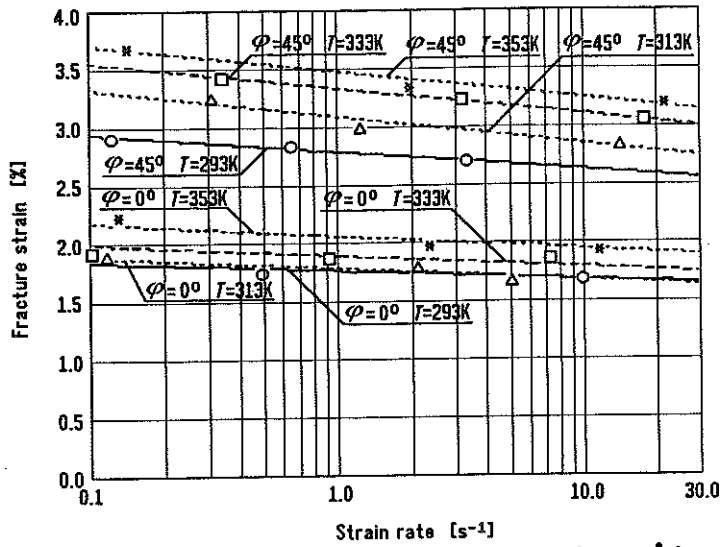


FIG. 9. Relationship between the fracture strains $\varepsilon_n$ and strain rate $\dot{\varepsilon}$ for various $T$.

interaction between the fibre and the matrix due to a phase change of the latter. That is why the fracture mechanisms of composites consisting of brittle fibres and a semibrittle matrix will be different from those formed in the composite made of brittle fibres and a plastic matrix ($T > T_g$). In the former case fracture consists in a critical number of ruptures occurring in the fibres, in the latter the fracture is a result of rupture of one or several fibres, or a result of pulling out of some fibres.

The temperature changes, apart from the varying properties of the matrix, produce also shearing stresses at the fibre-matrix interfaces. They are found to grow in proportion to the increasing temperature. The reason is a difference in the linear thermal expansion coefficients of the matrix $\alpha_0$ and of the glass fibre $\alpha_w$. Those shearing stresses produce, in turn, some stresses that act in the direction of the fibres.

When only few fibres rupture under small strain rates, the relaxation processes cause a decreasing stress concentration at the neighbouring fibres [11] and no conditions are generated for further propagation of ruptures (accumulation of defects). As the strain rates increase, the matrix becomes more brittle and the rupture of the weakest link initiates a macrofracture whose propagation is a real reason for the destruction of the whole specimen. At further increase in the strain rate and the corresponding brittleness, the fibres can start to separate from the matrix.

The relationships shown in Figs. 7–9 indicate an influence of the discussed

factors (strain rate, temperature and a manner of reinforcement) on longitudinal Young's modulus, tensile strength $R_m$ and the fracture strains $\varepsilon_n$, respectively.

When the orthotropy axis 1 coincides with the principal direction (Fig. 7), the changes in the properties of a matrix (caused by the temperature and strain rates) determine in a unique manner the character of those changes for the whole composite.

When the loading direction is inclined to the orthotropy axis 1 (in the test the angle was equal to 45°), no uniqueness mentioned above can be observed to exist. Young's modulus vs. strain rate and temperature curves are shown in Fig. 7. Increasing strain rates lead to an increase in the modulus $E$ at temperatures lower than the glass transition temperature $T_g$ (changes of positions of fibres in the matrix are hindered). Above $T_g$ the strain rates do not practically affect the value of the modulus (small Young's modulus of the matrix, possibility of changes in positions of fibres in the plastic matrix). Temperature increase (Fig. 7) causes a rapid reduction of the modulus $E$.

The tensile strength $R_m$ increases together with the increasing strain rate. Above $T_g$ this increase is found to be slower. Increase in temperature of the composite (Fig. 8) leads to a considerably lower strength $R_m$. Increase in the strain rates is associated with a decrease of the fracture strains $\varepsilon_n$ (Fig. 9); the latter increase with growing temperature (Fig. 9).

## 4. An attempt to determine the thermodynamic potentials

The increments of thermodynamic potential occurring under external actions can be determined provided the physical reasons (intensive magnitudes) [2] are known. Information on these magnitudes was supplied by the experimental investigations. These increments were found at limit states of fracture of specimens and referred to a state assumed to be a natural one (Fig. 10), i.e. for $T = 293\,\mathrm{K}$, $\sigma_{ij} = 0$, $\varepsilon_{ij} = 0$. The limit state was reached in two stages. First, energy of thermal type was supplied and, secondly, energy of work type was provided (heat and work done are the means of transmitting energy and not its form [13]).

The specimen was placed in the loading system in such a way that it could freely deform under temperature changes. Then $\sigma_{ij} = \text{idem}$. No internal stresses were accounted for that were generated by the difference in the linear expansion coefficients of the matrix and the fabric. Thus the first

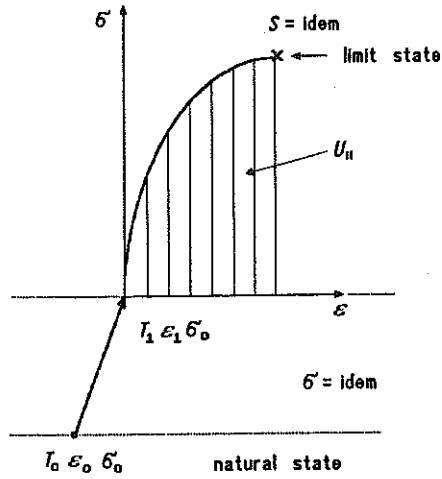


FIG. 10. Changes in the state parameters during the tests.

stage corresponds to a transition at constant stress.

Employing the relationship [11]

$$\left(\frac{\partial G}{\partial T}\right)_{\sigma_{ij}} = -S\,, \tag{4.1}$$

where $G$ – free enthalpy, $T$ – temperature, $\sigma_{ij}$ – stress tensor, $S$ – entropy, and knowing the function $S = S(T)$, we can determine the increment of the free enthalpy at the first stage. A change in the entropy $S$ of the specimen heated from the temperature $T_0$ to $T_1$ under the condition $\sigma_{ij} = \text{idem}$ can be calculated from the formula [14]

$$S = \int_{T_0}^{T_1} \frac{c_\sigma dT}{T} = c_\sigma \ln \frac{T_1}{T_0} = c_\sigma \ln\left(1 + \frac{\theta}{T_0}\right), \tag{4.2}$$

where $c_\sigma$ stands for specific heat capacity at constant stress (calculated as the mean value in the temperature interval $T_0 \div T_1$), $\theta = T_1 - T_0$ denotes the temperature excess.

The free enthalpy increment is then expressed as

$$G_{\mathrm{I}} = -\int_0^{\theta} c_\sigma \ln\left(1 + \frac{\theta}{T_0}\right) d\theta\,. \tag{4.3}$$

Expanding $\ln(1+\theta/T_0)$ into an infinite series, preserving two first terms and integrating (the integration constants in Eqs. (4.2) and (4.3) vanish since for

the assumed natural state $S = 0$ and $G = 0$), we finally obtain

$$G_{\mathrm{I}} = -c_\sigma \left( \frac{\theta^2}{2T_0} + \frac{\theta^3}{6T_0} \right). \tag{4.4}$$

Knowing the relationships between the potentials [14], we can calculate the increments of the remaining potentials at the first stage:

$$F_{\mathrm{I}} = G_{\mathrm{I}} + \sigma_{ij}\varepsilon_{ij}\,, \qquad U_{\mathrm{I}} = F_{\mathrm{I}} + ST_1\,, \qquad H_{\mathrm{I}} = G_{\mathrm{I}} + ST_1\,. \tag{4.5}$$

At the second stage the energy of the work type was supplied over a time shorter than that characteristic for the thermal conductivity of the specimen, i.e.

$$t_\lambda = \frac{\varrho c_\sigma \delta^2}{4\lambda}\,, \tag{4.6}$$

where $\varrho$ – density, $c_\sigma$ – heat capacity at constant stress, $\delta$ – thickness of the specimen and $\lambda$ – coefficient of thermal conductivity.

For the examined composite $t_\lambda = 2.9\,\mathrm{s}$ to the second stage is, from the thermodynamic point of view, an adiabatic process. In what follows a reversible process is assumed to take place and a state of thermodynamic balance, which in fact cannot be realized in actual processes. A reversible adiabatic process continues with no change of entropy, $\Delta S = 0$. This circumstance enables us to assume that the diagram of the parameters of the states $\sigma_{ij}$, $\varepsilon_{ij}$ (Fig. 6b) is represented by the relationships $\sigma = \sigma(\varepsilon)$ under $S = \mathrm{idem}$.

Next, making use of the relation

$$\left( \frac{\partial U}{\partial \varepsilon_{ij}} \right)_S = \sigma_{ij}\,, \tag{4.7}$$

where $U$ – internal energy, $\varepsilon_{ij}$ – strain tensor, and conducting graphical integration, we can determine the value of the internal energy $U$ fed into the system at the second stage. The increments of the remaining thermodynamic potentials can be found from the following formulae:

$$F_{\mathrm{II}} = U_{\mathrm{II}} - ST_1\,, \qquad H_{\mathrm{II}} = U_{\mathrm{II}} - \sigma_{ij}\varepsilon_{ij}\,, \qquad G_{\mathrm{II}} = H_{\mathrm{II}} - ST_1\,. \tag{4.8}$$

The potential increments in the limit state are obviously sums of the increments from both the stages,

$$U = U_{\mathrm{I}} + U_{\mathrm{II}}\,, \quad F = F_{\mathrm{I}} + F_{\mathrm{II}}\,, \quad H = H_{\mathrm{I}} + H_{\mathrm{II}}\,, \quad G = G_{\mathrm{I}} + G_{\mathrm{II}}\,. \tag{4.9}$$

Following the above procedure, the increments of the thermodynamic potentials for the specimens $\varphi = 0°$ and $\varphi = 45°$ were determined for various rates of processes. Some of the results are presented in Figs. 11–14. For a complete set of results the reader is referred to [10]. A general conclusion can be drawn that the rates of processes affect the increments of the thermodynamic potentials negligibly.

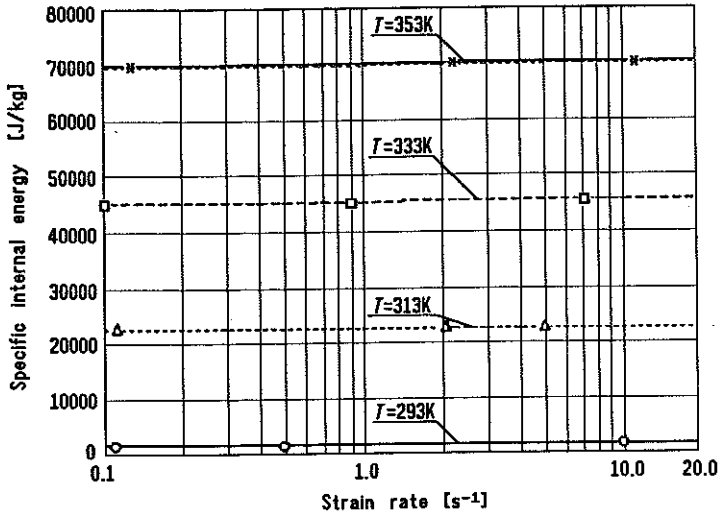


FIG. 11. Specific internal energy $U$ (corresponding to the fracture of a specimen) as a function of the strain rate $\dot{\varepsilon}$ for the testpieces $\varphi = 0°$.

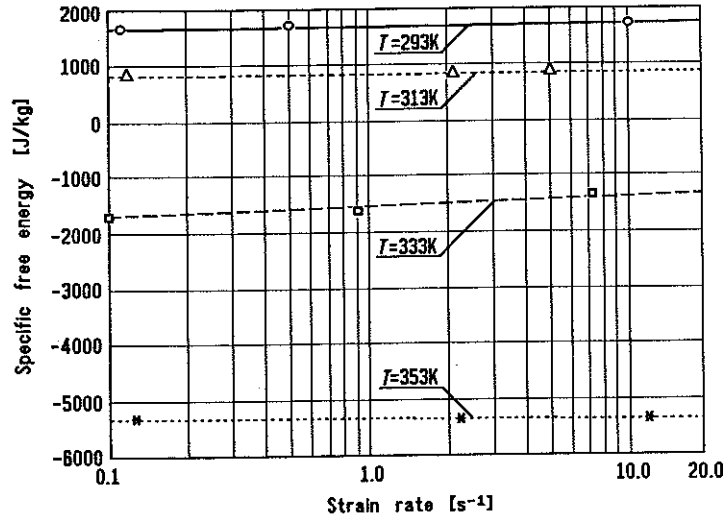


FIG. 12. Specific free energy $F$ (corresponding to the fracture of a specimen) as a function of the strain rate $\dot{\varepsilon}$ for the testpieces $\varphi = 0°$.

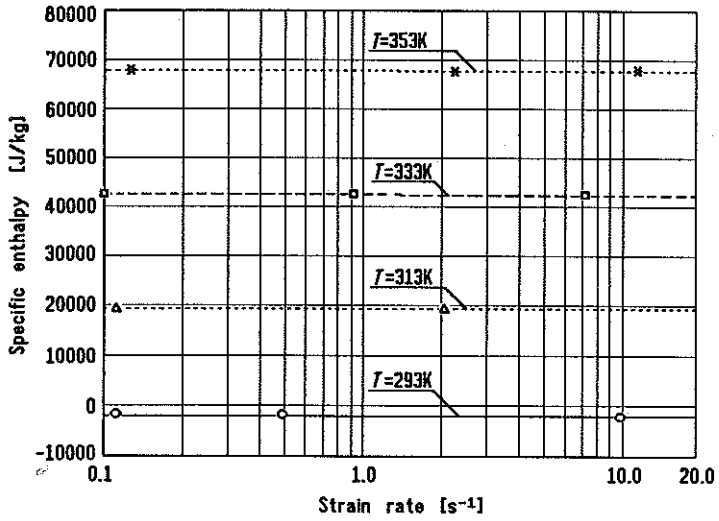


FIG. 13. Specific enthalpy $H$ (corresponding to the fracture of a specimen) as a function of the strain rate $\dot{\varepsilon}$ for the testpieces $\varphi = 0°$.

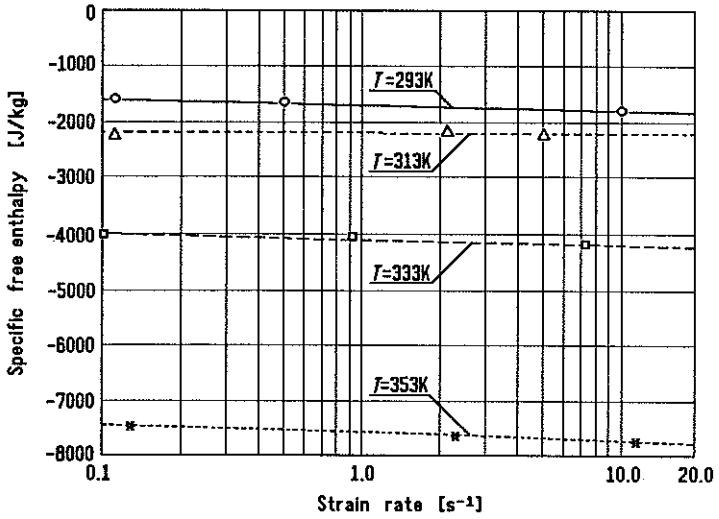


FIG. 14. Specific free enthalpy $G$ (corresponding to the fracture of a specimen) as a function of the strain rates $\dot{\varepsilon}$ for the testpieces $\varphi = 0°$.

The relevance of the selected thermodynamic potentials was stressed in [12] and a concept was put forward that it is the increments of free energy or, alternatively, of free enthalpy that can be treated as a measure of strength.

The determined increments of the potentials of internal energy, free energy, enthalpy and free enthalpy are equivalent and can constitute a basis for the assessment of strength of the examined polymer composite.

## 5. Conclusions

1. The test results confirm the validity of the assumed method for investigation of the thermodynamic effects with the use of the described stand. Various materials can be successfully studied in this way.

2. The influence of temperature and the strain rates in the examined composites is found to be pronounced so far as Young's modulus and the tensile strength are concerned, while it remains negligible when referred to the fracture strain.

3. The main problem in the thermodynamics of materials is the determination of an admissible thermodynamic process. The presented results of tests (Figs. 11–14) supply the limiting values for processes occurring in the considered composites.

4. The increments of thermodynamic potentials depend only slightly on the strain rates, but significantly on the temperature.

5. The determined increments of thermodynamic potentials or limiting points can be used to assess the strength of the studied composites.

## References

1. Х.И.Анискевич, А.А.Малмейстер, Ю.О.Янсон, *Методика испытаний трубчатых образцов из полимерных материалов при сложном напряженном состоянии в условях температурного воздействия*, Механика композитных материалов, 1, 1984.

2. A.Broniewski, A.Iwasiewicz, J.Карко and M.Płaczek, *Test methods and assessment of properties of plastics* [in Polish], WNT, 1970.

3. W.Szczepiński, *Experimental methods in solid machanics* [in Polish], PWN, Warszawa 1984.

4. Ю.С.Уржумцев, В.П.Маиборода, *Технические средства и методы определения прочностных характеристик конструкций из полимероб*, Машиностроение, Москва 1984.

5. П.М.Хачатрян, Э.Б.Слободник, Ю.В.Зеленев, А.Б.Айвазов, *Динамические свойства полимерных композиций в широких температурно-частотных диапазонах*, Механика композитных материалов, 1, 1986.

6. Ю.В.Суворова, А.М.Думанский, В.С.Добрынин, Г.П.Машинская, В.В.Гладышев, *Разрушение органопластика в зависимости от скорости нагружения и температуры*, Механика композитных материалов, 3, 1984.

7. J.ZAWADZKI and E.SWIĄTEK, *Influence of temperature, strain rate and stress concentration on the short-term strength of PCW* [in Polish], Prace Naukowe Inst. Mat. i Mech. Techn. Pol. Wrocł., Wrocław 1973.

8. Ю.П.ЗЕЗИН, Ю.И.КОЗЫРЕВ, Н.И.МАЛИНИН, Ю.Я.БАРТ, М.А.ТУНДА, *Влияние температуры и скорости нагружения на свойства полимерных материалов*, Механика композитных материалов, 2, 1985.

9. S.OCHELSKI, *Dynamic strength of polymer composites* [in Polish], Engng. Trans., **38**, 1, 1990.

10. R.GIELETA, *Thermodynamic effects in the dynamic stretching of polymer composites* [in Polish], Doctoral thesis WAT, Warszawa 1992.

11. Ю.В.СУВОРОВА, Т.Г.СОРИНА, Г.М.ГУНЯЕВ, *Скоростные зависимости прочности углепластиков*, Механика композитных материалов, 4, 1990.

12. J.ZAWADZKI, *Problems of strength and fatigue of polymers as structural materials* [in Polish], PWN, Warszawa 1978.

13. K.GUMIŃSKI, *Thermodynamics* [in Polish], PWN, Warszawa 1972.

14. E.TYRKIEL, *Thermodynamics for the material engineering* [in Polish], Wydawn. Politechniki Warszawskiej, Warszawa 1978.

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