On the Long-Term Strength of Specimens Made of Phenol-Formaldehyde Press Powders

M. NATOV and S. VASILEVA, *Higher Institute of Chemical Engineering, Kv. Durvenitsa, 1156 Sofia, Bulgaria,* and G. KOTSEV, *Institute of Metal Research and Technology, Bulgarian Academy of Science, Kv. Geo Milev, 1574 Sofia, Bulgaria*

Synopsis

The study of the long-term strength (LTS) of polyethylene, poly(vinyl chloride), and poly-oximethylene shows that the $\ln \tau - \sigma$ relation for specimens, undergoing tension, is S-shaped. Structure changes during the process of deformation may occur in these polymers. However, the structure of spatial-grid polymers (solidifying phenol–formaldehyde resins, for instance) does not prove to be stress-sensitive and experiments show that the $\ln \tau - \sigma$ relation can be described with sufficient accuracy by employing an equation of the form $\tau = \tau_0 \exp[(U - \gamma\sigma)/(RT + \alpha\sigma^n)]$.

INTRODUCTION

As is known application of polymers in mechanical elements or parts requires evaluation of the long-term strength (LTS) of the material. However, it is established for a wide range of stresses that mechanical properties depend on time for quite a number of materials, i.e., fracture occurs after a definite period of time.[1-3] Yet, the "safe stress," below which strength does not depend on time, needs further elucidation. Approaches developed recently assume that break of chemical and intermolecular bonds in polymers occurs due to mechanical stresses. Hence, fracture can be described by employing Arrhenius' equation which gives an account of the kinetics of chemical processes

$$V = k \exp(-U/RT) \tag{1}$$

where V is the rate of the chemical process, k a preexponential factor, U the activation energy; R the universal gas constant, and T temperature.

The reciprocal value of the velocity of fracture gives the long-term strength. Since researchers most often assume that stress affects the activation energy of the process, a number of them[4-11] propose to employ a modification of Arrhenius' equation where the activation energy decreases linearly with stress. However, if frequency of the oscillation of polymer kinetic units changes due to stresses, the thermal energy RT should be apparently affected as well. This effect can be taken into account by introducing an additional term in the denominator of the power index of eq. (1).

It has been established[12-14] that polymer spectra change significantly under stress. Furthermore, relaxation parameters vary as well when polymer speci-

mens undergo preliminary loading. Henceforth, we use the following LTS–stress relation

$$\tau = \tau_0 \exp[U/(RT + \alpha\sigma^n)] \qquad (2)$$

where τ is the long-term strength, δ the applied stress; τ_0 the limit LTS, U the activation energy of fracture, T temperature, R the universal gas constant, and α and n constant quantities.

We tested specimens made of various materials; nonsaturated polyester resin, polyoximethylene, and poly(vinyl chloride),[15] and established complete coincidence between experiments (at room temperature) and values calculated by following eq. (2).

Since stresses in general affect not only the activation energy but also the apparent thermal energy to which the activation energy is compared, the LTS can be given by

$$\tau = \tau_0 \exp[(U - \gamma\sigma)/(RT + \alpha\sigma^n)] \qquad (3)$$

where γ is a constant quantity which can differ significantly from the structure-sensitive quantities in the previous equation.[7-9]

A number of researchers[7-9] introduce the LTS by employing equations where stress is in the numerator of the power index of the modified Arrhenius equation. Hence, any difference between LTS calculations and experimental evidence can be explained regarding the structure changes under stresses. Gul et al.,[7] Zhurkov and Narzulaev,[8] and Bartenev and Kartaschov,[9] for instance, have accounted for effects of structure changes by introducing into the equations structure-sensitive coefficients, the latter depending on the stress value. Structure changes occurring during the experimental study of LTS can be avoided by testing polymer specimens with appropriate structure which is not sensitive to mechanical impacts; we test specimens of solidifying phenol–formaldehyde press powders which obey the above requirements.

MATERIAL AND METHODS OF INVESTIGATION

We use RSB-050 press powder, without ammonium (OVH.KHM 93-66), with the following characteristics: (a) density 1.34 g/cm^3; (b) water absorption 0.10 g/dm^2 in 24 h; (c) thermal resistance (according to Martens) 119°C; (d) shock resistance 5.1 kJ/m^2; (e) bending strength 86 MPa; (f) tension strength 57.0 MPa.

Specimens were made by material pressing at 160°C (the pressure value was 25 MPa) and consecutive annealing at 110°C for 168 h. Conditions of preparation were chosen to obtain maximum strength and minimum deformability, i.e., maximum spatial lacing of the material. Specimen dimensions and time of pressing are given in Table I.

The long-term strength under any constant stress is determined by calculating the mean LTS of 30 specimens and is measured in seconds. This quantity of specimens provides confidence estimation of the real LTS within a range of 0.30–0.37 with mean squared (standard) deviation within ranges of 0.5–0.9 and confidence level equal to 0.95. Specimens are caught in grips by which load is applied.

TABLE 1

Specimen dimensions mm			Time of preliminary	Pressing time—
Length	Width	Thickness	pressing—min.	min.
40	6	2	1^{20}	4
60	9	3	1^{40}	5^{30}

The experimental technique consists of the following:

—Low tension stress is applied by means of weights and specimens are tested in a special cabinet and at constant temperature, 20 °C (the stress does not exceed 55 MPa in this case). Loading time till fracture is measured by hand, using a chronometer.

—LTS under high stresses (over 55 MPa) is determined by using a special loading device.[16] The fixed (upper) grip is connected to an electronic counter which measures the loading time till fracture with an accuracy of 10^{-7} s. The lower grip catches the device movable unit, which is loaded and driven electrodynamically, thus applying stress of the "rectangular cycle," which rapidly increases to a definite value and remains constant. Stress pulsations are avoided as a result.

RESULTS AND DISCUSSION

We analyze at first the LTS–stress relation obtained by testing specimens at room temperature (the specimen cross section is 6×2 mm^2). Figure 1 shows the $\ln \tau - \sigma$ curve which is S-shaped; the dashed line represents scatter of data and dots are experimental points. The curve is drawn after eq. (3), where $\ln \tau_0 = -4.30$, $U = 80,900$ J/mol, $n = 25$, $\alpha = 5 \times 10^{-191}$ J/Pa^{25} mol, $\gamma = 8.06 \times 10^{-4}$ J/Pa mol. Let us divide the curve into three regions: upper, middle, and lower ones. The middle straight line represents the region where the visual record of LTS is superimposed on data obtained by using the high-stress device. Since the chemical and supermolecular structure of the specimens do not change during our experiments, the curve character is not due to variation of structure-sensitive parameters, as it is in equations which assume that stresses affect the activation energy only. Moreover, if stresses affect the energy factor in the Arrhenius equation via the apparent thermal energy, then the relation character is easily comprehensible, i.e.:

—The lower part represents LTS under high stresses, when the value of the power index denominator is determined by the large $\alpha \sigma^n$ member.

—The upper part represents LTS when $\alpha \sigma^n$ is negligible with respect to RT.

—The middle part represents the case when both members $(U - \gamma \sigma)$ and $(RT + \alpha \sigma^n)$ affect fracture.

Since the scale factor affects the strength index of polymer materials, we investigate the LTS of specimens with various cross sections. Figure 2 shows that when specimens with cross sections of 12 and 27 mm^2, respectively, are tensed, the ranges of data scattering differ from one another. Statistics shows that LTS under high stresses is not affected by the specimen dimensions, but
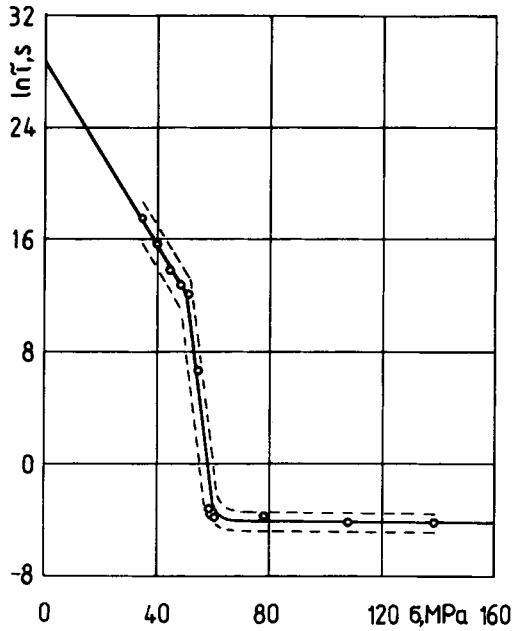
Fig. 1. LTS–stress relation for tensed specimens of phenol–formaldehyde press powders: (---, ○) interval of data spread and mean values; (—) $\ln \tau = \ln \tau_0 + (U - \gamma\sigma)/RT + \alpha\delta^n$) curve.
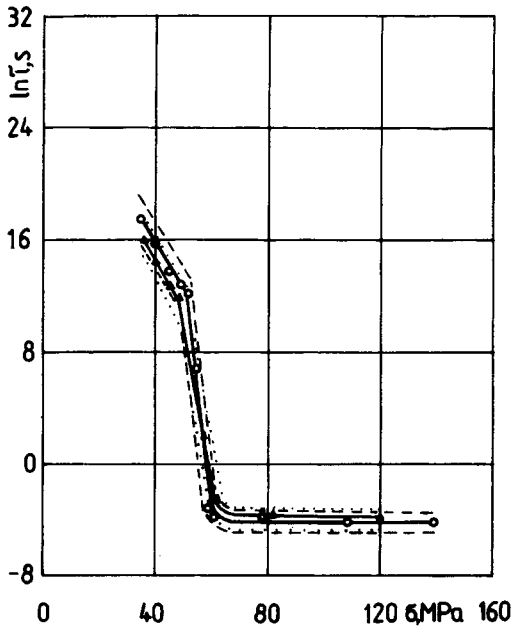

Fig. 2. LTS–stress relation for tensed specimens of phenol–formaldehyde press powders with various cross sections: (---, ○) interval of data spread and mean values; the specimen cross section is 12 mm²; (⋯ , ▲) interval of data spread and mean values; the specimen cross section is 27 mm².

depends on the latter when low stresses are applied. For now it is difficult to explain the effect of specimen dimensions on the LTS.

CONCLUSIONS

1. The LTS of specimens made of phenol–formaldehyde press powders is investigated for a wide range of stresses. It is established that the $\ln \tau - \sigma$ relation is nonlinear and S-shaped.

2. Specimen LTS can be determined with sufficient accuracy if a supposition is made that stresses affect not only the activation energy, but the Arrhenius' energy factor as well via the apparent thermal energy.

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