ELASTO-ELASTIC AND VISCO-PLASTIC PROPERTIES OF THERMOSETTING PLASTICS

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I. F. KANAVETS and L. G. BATALOVA

ELASTO-ELASTIC AND VISCO-PLASTIC PROPERTIES OF THERMOSETTING PLASTICS

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Changes in the mechanical properties of thermosetting plastics under the influence of temperature and long-acting loads have been insufficiently studied. The closest connection between the structure of a material and its mechanical properties, on the basis of modern concepts concerning high polymers and of the work of P. A. Rebinder, is established from measurements of the kinetics of development of pure shear deformation after the application of a prescribed constant stress, and of the kinetics of deformation decay after unloading (1).

The investigations were carried out on the most important types of plastics manufactured on the basis of phenol-formaldehyde and aniline-formaldehyde resins of the resol and novolac types. The specimens for the experiments were prepared by hot molding under conditions ensuring the degree of curing of the resin required for technical products. Measurements of the elasto-elastic and visco-flow properties of the cured plastics were performed on an apparatus constructed for this purpose, allowing measurement of the shear deformation developing under the action of a constant force in the regions of elasto-elastic and plastic flow, in degrees of angle of rotation, with an accuracy up to 0.2°.

Measurements were made on cylindrical specimens 10 mm in diameter and 100 mm long in the working part, at stresses ranging from 50 to 425 kg/cm^2, temperatures from 20 to 180°, and times from 1 to 500 hours.

The time-constant magnitude of the torque was set by a load suspended from a pulley of radius 100 mm. Stress relaxation in the materials and the limiting shear stress P_k were measured with a pendulum dynamometer from the decrease in the angle of deflection of the pendulum with time. The elastic modulus, viscosity coefficient, and relaxation time were calculated by the method described in the works of P. A. Rebinder (1).

As a result of the measurements carried out it was established:

1. Thermosetting plastics at normal temperature, under the influence of a constant, long-acting load at stresses above the yield point P_k, in addition to elastic and elasto-elastic deformation, also undergo residual deformations. Irreversible deformation is also observed after heating the specimen

at a temperature of 90° for 15 hours.

2. On different types of materials at normal temperature, loading causes an elastic deformation 2-3 times greater than the elasto-elastic deformation (Fig. 1). Upon unloading of the specimen, elastic recovery is also 2-3 times greater than elasto-elastic recovery. The elastic and elasto-elastic deformations during loading are greater than during unloading; the elasto-elastic modulus is 2-3 times greater than the elastic modulus.

Upon unloading and upon subsequent loadings, the elastic modulus and the elasto-elastic modulus are greater than under the initial loading (Tables 1 and 2).

The magnitude of the elastic deformation increases with increasing stress in proportion to the applied stress up to 300-350 kg/cm^2, while the elastic component, in addition, also increases with increasing duration of action of the force.

The moduli G_1 and G_2, under loading up to 325 kg/cm^2 and at normal temperature, remain practically invariant. Depending on the grade of the material, the magnitude of the shear modulus lies within the range from 16 to 22,000 kg/cm^2, and the modulus of elasticity within the range from 50,000 to 79,000 kg/cm^2. A certain decrease in the moduli when the stress is increased from 325 kg/cm^2 to 425 kg/cm^2, and then an increase under repeated loads (see Tables 1 and 2), is explained not by the formation of new chemical bonds under loading, but by the destruction of the rare "cross-linking" between individual aggregates of molecules and by the more frequently entangled polymer chains entering into action under repeated loads.

Table 1

Change in the elastic-elastic and visco-plastic properties of press material K-18-2 as a function of temperature

	20	60	80	100	120	140	160	180
Temperature, °C	20	60	80	100	120	140	160	180
G, kg/cm^2	22140	14300	10000	7000	4900	3850	1920	1635
$\eta_1 \cdot 10^{-13}$, poise	640	450	160	60	25	10	5.88	8.62
$\tau_1 \cdot 10^{-10}$, sec	289	31.4	16	8.58	5.1	2.59	3.03	5.28
G_2, kg/cm^2	59700	25000	17200	10550	5000	2000	792	400

	20	60	80	100	120	140	160	180
$\eta_2 \cdot 10^{-11}$, poise	2400	180	75	25	6.86	1.3	2.79	4.71
$\tau_2 \cdot 10^{-7}$, sec	402	72	43.7	23.7	13.7	6.5	35	118

Table 2

Change in the shear modulus and modulus of elasticity of press material K-18-2 as a function of temperature (during unloading)

	20	60	80	100	120	140	160	180
Temperature, °C	20	60	80	100	120	140	160	180
G_1, kg/cm^2	87000	85000	23000	15000	9230	9250	6100	7310
G_2, kg/cm^2	180000	62000	43000	29200	22000	16000	11480	9800

3. The duration of action of the force reduces the magnitude of the deformation of elastic recovery in the following way: after 30 sec (on material grade K-18-2), the elastic deformation under loading is greater than under unloading by 10%; after 20 hours—by 25%, and after 500 hours—by 50%. This also indicates partial rupture of the bonds (the rare "cross-linking" of individual chains). The elastic deformation under loading, however, with increasing time of action of the load, exceeds the deformation under unloading by approximately 45-60%. The end of the development of elastic deformation and the transition to a straight line (the tangent of whose angle of inclination serves to determine the viscosity) at normal temperatures and at stresses above the yield point are observed, depending on the grade of the material, after 100 to 300 hours and more.

To obtain invariant values of viscosity and relaxation periods, the duration of the experiment must be greater than the indicated time for the development of elastic deformation and the transition to a straight line. When the stress is increased above the yield point up to destruction of the material, over a shorter experimental time there is observed a certain (within a factor of two) increase in viscosity and relaxation periods. Therefore, machine tests carried out with low, practically attainable loading rates do not give invariant indices of viscosity and relaxation periods. Pe

relaxation periods τ_1 and τ_2 in thermosetting plastics are measured in tens of years (see Table 1 and Fig. 3).

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

4. Elastic and recoverable deformation increase as the experimental temperature is raised (Fig. 1); moreover, below the heat-resistance temperature (T_c) the recoverable deformation remains smaller than the elastic deformation, while at temperatures above T_c it increases sharply in comparison with the elastic deformation. This indicates the absence of frequent "cross-linking" of polymer molecules throughout the entire volume of the material.

5. The applied stress decreases with time not to zero, but to a certain limit P_k of the order of 200-250 kg/cm^2, which determines the limiting shear stress and is a measure of the branching of the polymer chains and of the structural network in phenoplasts. In repeated experiments the value of P_k increases from 250 to 350 kg/cm^2 (Fig. 1). The limiting shear stress decreases with increasing temperature according to the same law:

$$P_k = Ae^{-\frac{U}{kT}}$$

(A is a constant, U is the bond energy), according to which the viscosity coefficient decreases with increasing temperature.

Fig. 1. Increase in elastic (1) and recoverable (2) deformation under loading as a function of temperature, and also after removal of the load—elastic (3) and recoverable recovery (4); 5—decrease of the limiting shear stress with increasing temperature. In repeated experiments P_k is above 250 kg/cm^2.

6. The limiting shear stress P_k, the modulus of elasticity, and the modulus of recoverable deformation, in semilogarithmic coordinates as functions of the reciprocal absolute temperature, are expressed by two intersecting straight lines (Fig. 2). The break point falls in the region of the heat-resistance temperature (about 137°). The bond energy, determined from the tangent of the angle of inclination of the straight lines in the region up to 130°, lies in the range from 3300 to 3830 cal/mol of bonds. This indicates the predominance of the hydrogen type of intermolecular bonds. Above 130° the angle of inclination of the straight lines to the abscissa axis is greater (Fig. 2). The activation energy, determined from the angle of inclination of the straight lines, varies from 8900 to 17650 cal/mol of bonds. Such a magnitude of activation energy is observed in the curing processes of phenol-formaldehyde resins in molding powders ([2]).

Fig. 3. Change in the modulus of resilience G_1, the modulus of elasticity G_2, the viscosity coefficient η_1 and relaxation time τ_1 of viscous flow, and the viscosity coefficient η_2 and relaxation time τ_2 in the region of elastic flow, as a function of temperature

Figure 3: Fig. 3. Change in the modulus of resilience G_1, the modulus of elasticity G_2, the viscosity coefficient η_1 and relaxation time τ_1 of viscous flow, and the viscosity coefficient η_2 and relaxation time τ_2 in the region of elastic flow, as a function of temperature

Fig. 2. Change in the shear modulus of elasticity G_1 and the recoverable modulus G_2 of material grade K-18-2, and of the limiting shear stress P_k, as functions of the reciprocal absolute temperature: a, b—G_1 and G_2 under loading; c, d—G_1, G_2 during unloading.

Consequently, under the action of shear deformations in technical materials manufactured on the basis of phenol-cresol- and aniline-formaldehyde resins, ···

aldehyde resins the further chemical curing process proceeds only at temperatures above 130°. These experiments also confirm the fact that the holding time, established from the external appearance of phenoplastic products, does not ensure that the reaction proceeds to completion. Further, after the reaction has gone to completion, shear deformations (in repeated experiments) overcome only the resistance of hydrogen bonds. This is indicated by the parallel course of the two upper straight lines (Fig. 2), for which the bond energy lies within 3300–3800 cal/mol of bonds.

7. The fact that at normal temperature the elastic deformation is greater than the resilient deformation, while the modulus of resilience is smaller than the modulus of elasticity, indicates the loose structure of plastics, which is sparsely "crosslinked" by hydrogen bonds. Under the influence of load the sparse network is destroyed; therefore, under repeated loads and with increasing deformation, a more frequent interlacing of branched polymer chains is overcome, which explains the absence of complete reversibility under repeated loads, and not only the high viscosity of elastic flow.

Fig. 3. Change in the modulus of resilience G_1, the modulus of elasticity G_2, the viscosity coefficient η_1 and relaxation time τ_1 of viscous flow, and the viscosity coefficient η_2 and relaxation time τ_2 in the region of elastic flow, as a function of temperature

Some authors evaluate this effect as hardening of the material under repeated loads ([3]). The "crosslinking" of polymer chains into aggregates in phenol-formaldehyde molding materials does not extend through the entire thickness of the material, owing to which it is possible, and is indeed observed, for elastic deformation to develop to a large magnitude compared with resilient deformation at temperatures above T_c and stresses above the elastic limit (Fig. 1).

8. The decrease in the modulus of resilience G_1, the modulus of elasticity G_2, and the viscosities of plastic η_1 and elastic flow η_2 (relaxation periods τ_1 and τ_2) with increasing temperature is observed only up to the heat-resistance temperature. At temperatures above T_c, an increase in η_1 and (τ_1) is observed, while η_2 (and τ_2) increase still more markedly than η_1 and τ_1 (Fig. 3). This is explained by a chemical reaction proceeding in thermosetting molding materials under the influence of temperatures above 130° and shear deformations. Shear deformations partially destroy the loose structure of the resins and thereby remove steric obstacles to entry into the reaction

unreacted products. As a result of such a reaction, "cross-linking" of polymer segments in the chains predominates and, to a lesser extent, "cross-linking" of individual aggregates with one another takes place; this explains the predominant increase in the relaxation period of elastic flow τ_2 as compared with the period of plastic flow τ_1 at temperatures above 130° (Fig. 3).

For these reasons, articles made of thermosetting plastics are stronger in the case when a greater destruction of the loose structure of the resins in the stream is achieved during the forming of the articles than in the case when the articles are formed almost in the absence of flow of the material.

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Note: Figure translations are in progress. See original paper for figures.