PERIODIC SHEAR DEFORMATION OF A CURING EPOXY COMPOSITION*

L. A. Faitel'son, V. D. Kiseleva, and V. I. Alksne

The curing of an epoxy resin with amines is investigated in relation to the changes in the viscoelastic shear characteristics. The effect of the shear deformation amplitude on the curing kinetics is considered.

In the course of the curing process viscofluid soluble thermosetting resins become hard and insoluble. The kinetics of this process have chiefly been investigated by physicochemical methods – dilatometry [1-5], infrared spectroscopy [6-9], calorimetry [10]. Numerous investigations have been devoted to the time and temperature dependences of the mechanical characteristics of cured thermosets, i.e., the end product. The changes in the mechanical characteristics accompanying the reaction between the functional groups of the resin and the hardener have received only a limited amount of attention. In these instances only individual stages of the reaction have been studied – either the initial period preceding gelling or the end stage. This is because of experimental difficulties that prevent the entire curing process, which is characterized by a broad range of variation of the numerical values of the mechanical characteristics, from being covered. The initial period is important in relation to the choice of the necessary material processing conditions and the parameters of the processing equipment and determines the length of time during which the material remains in a state suitable for processing.

Extensive information on the state of the material throughout the curing process can be obtained by mechanical spectrometry (the frequency dependence of the viscoelastic characteristics). In [6, 11-14] methods were developed for determining the dynamic modulus of elasticity and the loss tangent from the change in the frequency of the natural torsional or flexural vibrations of a thread impregnated with the investigated hardening composition. The impregnated thread is composite specimen. Estimating the stiffness of the thread as a homogeneous material is not entirely correct, and the results of the above-mentioned studies express the relative change of stiffness and permit only a qualitative estimation of the changes in the mechanical characteristics. In [15] the initial period of curing of a polyester resin was investigated in relation to the change in the components of the complex modulus on the frequency interval 0.01-0.1 Hz.

Our object was to establish the frequency dependence of the modulus in the linear region of deformation and the effect of finite-amplitude deformations on the curing kinetics.

We investigated a composition consisting of Epoxy epoxy resin with 10% dibutyl phthalate (DBP) as plasticizer and 10% polyethylenepolyamine (PEPA) as hardener. The test temperature was 19-23°C. The large area of contact between the specimen and the metal parts of the working unit of the instrument together with the thinness of the specimen (1.0-1.5 mm) made it possible to neglect exothermic effects in the curing reaction.

In order to determine the viscoelastic characteristics we employed a Weissenberg rheogoniometer [16] and a rheometer based on the VR-2 rotary viscometer [17]. The upper half of the rheometer working


Fig. 1. Construction of the working unit of the instruments (a) and equivalent impedance diagram: 1) electrodynamic vibrator; 2) transducer; 3) diaphragm; 4,5) working unit; 6) connecting rod; 7) velocity transducer; $K_M$ is the elasticity of the suspension; $Z_n$ is the impedance of the apparatus; $Z_0$ is the impedance of the specimen; $Z_1$ is the impedance of the electrodynamic vibrator; $V_1$ and $V_2$ are velocity meters (transducers 2 and 7).

unit (cone) was suspended from cruciform leaf springs, permitting only angular displacements, and driven by an electrodynamic vibrator; the lower half (plate) was fixed. The instrument is so designed that the working unit with the cured composition can easily be removed and cleaned. This eliminates the restrictions imposed, for example, by the Weissenberg rheogoniometer with respect to the permissible duration of cure [15].

Another advantage as compared with existing instruments [18] is the possibility of an almost instantaneous change of amplitude. The construction of the working unit of the rheometer is shown in Fig. 1 together with the equivalent impedance diagram. Vibrations are transmitted from the electrodynamic vibrator to the cone through a transducer and connecting rod. A second inductive transducer measures the velocity amplitude at the point of attachment of the rod to the cone. The transducer signals are transmitted to a phase-sensitive voltmeter–vectorimeter and oscillograph. The electrodynamic vibrator is supplied by a low-frequency audiofrequency oscillator across an amplifier. The viscoelastic characteristics of the composition (complex shear modulus and its components) were determined by measuring the mechanical impedance of the specimen [19, 20].

It follows from Fig. 1b that $Z_u = -\frac{K_M}{\omega} \frac{V^*}{V_1}$, where $K_M$ is the stiffness of the elastic elements; $\omega$ is the angular frequency. Denoting $\frac{V^*}{V_1} = \frac{1}{\omega} \frac{U_{*V}}{U_{*V}^*}$, we obtain $Z_u = -\frac{K_M}{\omega} \frac{U_{*V}^*}{U_{*V} U_{*V}^*}$ is the complex ratio of the disturbing force to the rate of displacement of the connecting rod at its point of attachment to the cone.

The phase-sensitive voltmeter–vectorimeter gives the signal components: $U_{*V} = U_{F} + j V_{F}$; $U_{*V}^* = U_{F} - j V_{F}$. Expressing the complex ratio $U_{*V}/U_{*V}^*$ in terms of the ratio of the components and substituting in the expression for the impedance, we obtain

$$Z_u = \frac{K_M \omega}{\omega} \left( \frac{U_{*V} V_{F} - U_{*V}^* V_{F}}{U_{*V}^2 + V_{F}^2} \right), \quad X_u = -\frac{K_M \omega}{\omega} \left( \frac{U_{*V} V_{F} + U_{*V}^* V_{F}}{U_{*V}^2 + V_{F}^2} \right).$$

The instrument constant $K_M \omega = 3.2 \times 10^7$ dyn/cm was determined by calibration. The mechanical impedance of the specimen is equal to the difference between the mechanical impedance of the apparatus with the specimen and the mechanical impedance of the apparatus alone, i.e., $Z_0 = Z_n - Z_0; \quad R_0 = R_n - R_0; \quad X_0 = X_n - X_0$.

The complex shear modulus and its components were calculated from the relations [21] $G^* = \frac{\omega}{c} Z_0; \quad G' = -\frac{\omega}{c} X_0; \quad G'' = G'.

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