



Fig. 3. Relative flexural strength and flexural modulus versus relative degree of cure of an ambient-temperature-cured unsaturated polyester-styrene copolymer.

Differential thermal analysis determinations were found to be much simpler to perform than the flexural properties determination, in respect of both the time of the determination and the sample preparation. (The casting of resin bars was necessary for the flexural determinations. Any shape casting is suitable as a sample for DTA, since these samples are powdered.) Since the degree of cure data, as determined by DTA, was found to be more consistent in fitting a smooth curve than the flexural values, and since the DTA data have been found to be more reproducible than the flexural data, it would also seem that the DTA determinations are more precise (if not more accurate) than the flexural property determinations.

This investigation is continuing, and results in greater detail will be submitted for publication at a later date.

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Received July 25, 1961

Stress Relaxation in Molten Polymers

As a result of extensive experimental work on stress relaxation of molten polymers of the linear and branched type (with few or no crosslinks), our attention was drawn to the following phenomenon which was shown more or less clearly in all the instances of the investigation.

The relaxation times tend to be independent on the initial value \mathcal{T}_{ss} of the stress (namely, of the shear stress following cessation of the steady-state flow). This occurs particularly at the higher values of \mathcal{T}_{ss} , and is better verified when the values attained by the relaxation stresses \mathcal{T} are low.

The phenomenon will be called here *relaxation isochronism*. It was thought to be a consequence of the nonlinearity (non-Hookeanity) of the elasticity of molten polymers. Indeed, when the strains γ are extremely large, as they are in the case of stress relaxation following cessation of a steady-state viscous flow at high steady-state stresses, a linear (Hookean) stress-strain relationship cannot be assumed.

It can be shown that a stress-strain *asymptotic* relationship is a sufficient condition for "isochronic" relaxation; "asymptotic" means that as the stress \mathcal{T} increases toward infinity the corresponding strain γ tends toward an asymptotic value γ_m .

The general differential equation of the stress relaxation, $\dot{\mathcal{T}} = -\eta d\gamma/dt$, was integrated, with the aim of obtaining the stress-time equation $\mathcal{T} = f(t)$ which is valid within the whole range of the investigated values of the initial stress, and which is in agreement with the actual stress-time relationships experimentally found.

This integration was done under the assumption that the internal friction η which is effective in the stress relaxation phenomena (not to be confused with the measured melt viscosity of the bulk polymer) is a constant, namely, that it depends only on the structure and temperature of the polymer, and not on the stress or the time.

Furthermore, some different nonlinear stress-strain relationships have been assumed, as: Asymptotic-exponential:

$$\gamma = \gamma_m \left[1 - \exp \left\{ -\frac{\mathcal{T}}{\mathcal{T}_k} \right\} \right] \quad (1)$$

Asymptotic-hyperbolic:

$$\gamma = \gamma_m \mathcal{T} / (\mathcal{T} + \mathcal{T}_k) \quad (2)$$

Nonasymptotic logarithmic:

$$\gamma = \gamma_c [\ln(\mathcal{T} + \mathcal{T}_k) / \mathcal{T}_k] \quad (3)$$

Here γ_m , γ_c , and \mathcal{T}_k are constants characterizing the elastic features of any given polymer sample at a given temperature. Such constants are defined and calculated from the experimental data of the stress relaxation.

The stress-time relationships resulting from such integrations fulfill more or less strictly the condition of relaxation isochronism.

Models consisting of linear elastic elements coupled with nonlinear ones, characterized by eqs. (1)-(3), can be defined, giving stress-time relationships which are in agreement with the experimentally recorded ones, within the limits of experimental accuracy.

Details of the calculations and applications to experimental instances will be given in subsequent work.

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Received August 1, 1961