Non-Newtonian Fluid Mechanics

(Part - IV)

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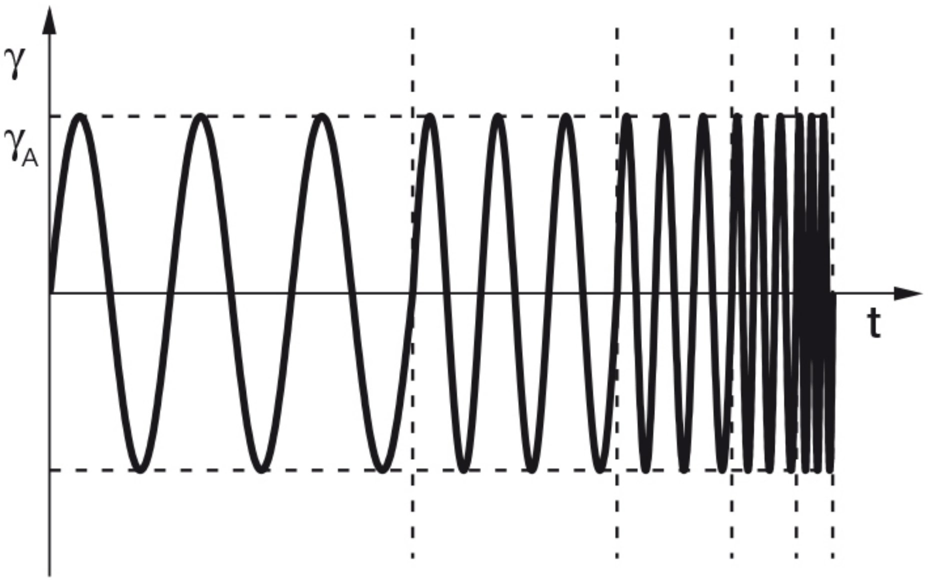
Oscillatory Test

Oscillatory Test: In an oscillatory measurement, the material is subjected to a sinusoidal stress or strain and the strain or stress response is measured. The rheological material behavior can be measured as a function of time, temperature, strain or stress amplitude and frequency. The results obtained provide information about the sample structural properties such as MW, molar mass distribution (MWD), concentration, crosslinking density for polymers or particle/domain size, shape, interface properties, etc. for multiphase fluids. This information is important in product development (formulation) to predict product performance and processing behavior of new or modified materials.

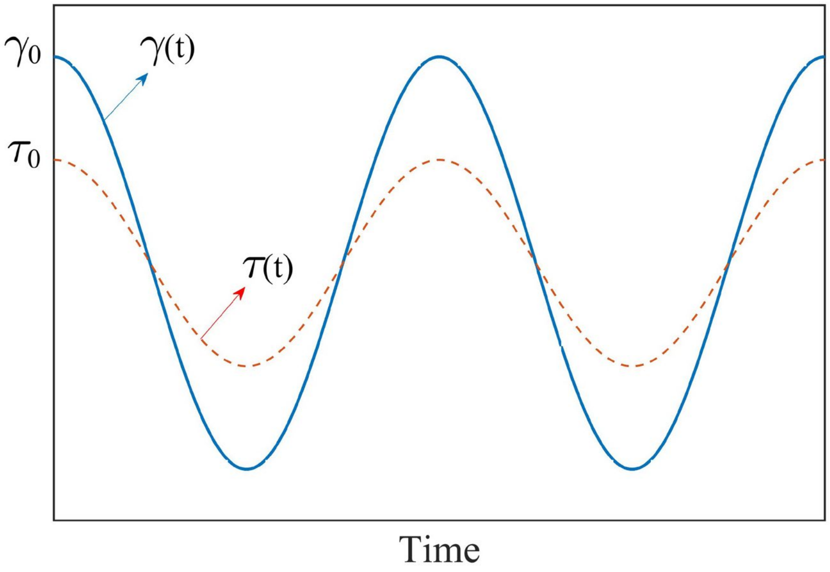
Preset of a frequency sweep, here with controlled shear strain and an increase or decrease in frequency in five steps. The strain amplitude γ_A is kept constant over all five measuring points.



Oscillatory Test

For analysis of this test, it is supposed that the material is under the periodic shear stress of $\tau = \tau_0 \cos \omega t$ and the shear strain is measured via rheometer.

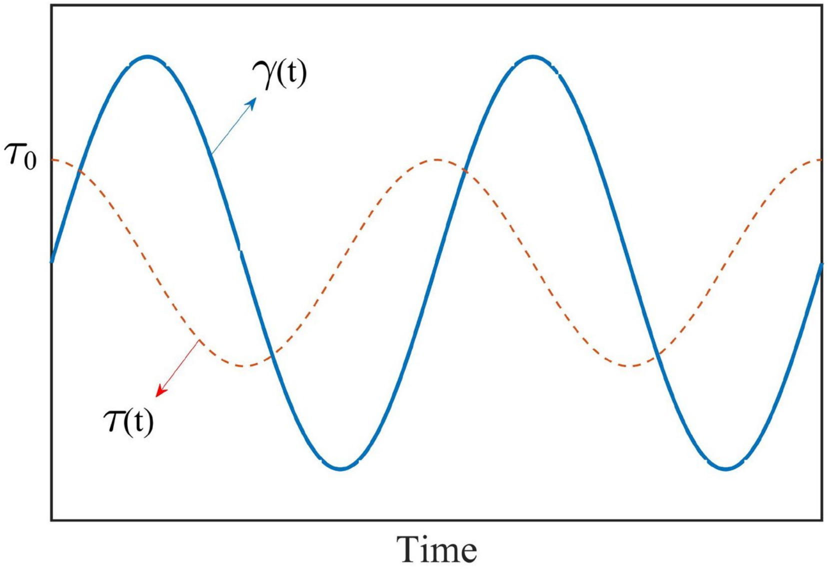
Ideal Hookean Solids



$$\tau = G\gamma, \quad \tau_0 \cos \omega t = G\gamma$$

$$\gamma = \frac{\tau_0}{G} \cos \omega t = \gamma_0 \cos \omega t$$

Ideal Newtonian Fluids



$$\tau = \eta \dot{\gamma}, \quad \tau_0 \cos \omega t = \eta \dot{\gamma}$$

$$\gamma = \frac{\tau_0}{\eta\omega} \sin \omega t \rightarrow \gamma = \frac{\tau_0}{\eta\omega} \cos(\omega t - \frac{\pi}{2})$$

Oscillatory Test

The strain response of viscoelastic materials to this test is: $\gamma = \gamma_0 \cos(\omega t - \delta),\ 0 \le \delta \le \pi/2$. The term δ is the phase lag and it is equal to zero and $\pi/2$ for ideal solids and liquids, respectively. For viscoelastic fluids, it is in the range of $0 \le \delta \le \pi/2$ and could be considered as the contribution of solid-like and fluid-like behaviors.

Using the complex numbers is a useful tool to interpret the results of oscillatory measurement. For this purpose, the complex stress (τ^*) and strain (γ^*) are defined and their relation with real part of them are as follows:

$$\tau = \tau_0 \cos \omega t = \mathrm{Re}\left\{\tau_0 e^{i\omega t}\right\} = \mathrm{Re}\left\{\tau^*\right\} \tag{1a}$$

$$\gamma = \gamma_0 \cos(\omega t - \delta) = \mathrm{Re}\left\{\gamma_0 e^{i(\omega t - \delta)}\right\} = \mathrm{Re}\left\{\gamma^*\right\} \tag{1b}$$

The complex shear modulus and complex viscosity are defined as:

$$G^* = \frac{\tau^*}{\gamma^*} = G' + iG'' \tag{2a}$$

$$\eta^* = \frac{\tau^*}{\dot{\gamma}^*} = \eta' + i\eta'' \tag{2b}$$

where G' and G'' are known as storage modulus and loss modulus, respectively.

Oscillatory Test

Now, we continue with complex shear modulus which is more common to interpret the results of this test. By substituting Eq. (1) into the Eq. (2a), we have:

$$G^* = \frac{\tau^*}{\gamma^*} = \frac{\tau_0 e^{i\omega t}}{\gamma_0 e^{i(\omega t - \delta)}} = \frac{\tau_0}{\gamma_0} e^{i\delta} \tag{3}$$

Therefore,

$$G' = \frac{\tau_0}{\gamma_0} \cos\delta \tag{4a}$$

$$G'' = \frac{\tau_0}{\gamma_0} \sin\delta \tag{4b}$$

The following relations are existed between the modulus:

$$\tan\delta = \frac{G''}{G'},$$

$$\eta' = \frac{G''}{\omega}, \quad \eta'' = \frac{G'}{\omega} \quad \& \quad \left|\eta^*\right| = \frac{\left|G^*\right|}{\omega} \tag{5}$$

Oscillatory Test

The results of Maxwell model for oscillatory test:

By beginning from Maxwell model, we have:

$$\tau + \lambda\dot{\tau} = \eta\dot{\gamma} \xrightarrow{\tau=\tau_0 \cos\omega t} \tau_0 \cos\omega t - \lambda\omega\tau_0 \sin\omega t = \eta\dot{\gamma}, \qquad (6)$$

By dividing Eq. (6) to $-\lambda\omega\tau_0$, it is concluded that

$$\sin\omega t - \frac{1}{\lambda\omega}\cos\omega t = \frac{-\eta}{\lambda\tau_0\omega}\dot{\gamma}, \qquad (7)$$

By supposing $\tan\theta = \dfrac{1}{\lambda\omega}$, we have:

$$\sin\omega t - \tan\theta\cos\omega t = \frac{-\eta}{\lambda\tau_0\omega}\dot{\gamma},$$

$$\sin\omega t - \frac{\sin\theta}{\cos\theta}\cos\omega t = \frac{\sin\omega t\cos\theta - \sin\theta\cos\omega t}{\cos\theta} = \frac{\sin(\omega t - \theta)}{\cos\theta} = \frac{-\eta}{\lambda\tau_0\omega}\dot{\gamma}, \qquad (8)$$

$$\sin(\omega t - \theta) = \frac{-\eta\cos\theta}{\lambda\tau_0\omega}\dot{\gamma}$$

Oscillatory Test

By integration from Eq. (8):

$$\frac{-1}{\omega}\cos(\omega t-\theta)=\frac{-\eta\cos\theta}{\lambda\tau_0\omega}\gamma,$$

$$\gamma=\frac{\lambda\tau_0}{\eta\cos\theta}\cos(\omega t-\theta) \qquad (9)$$

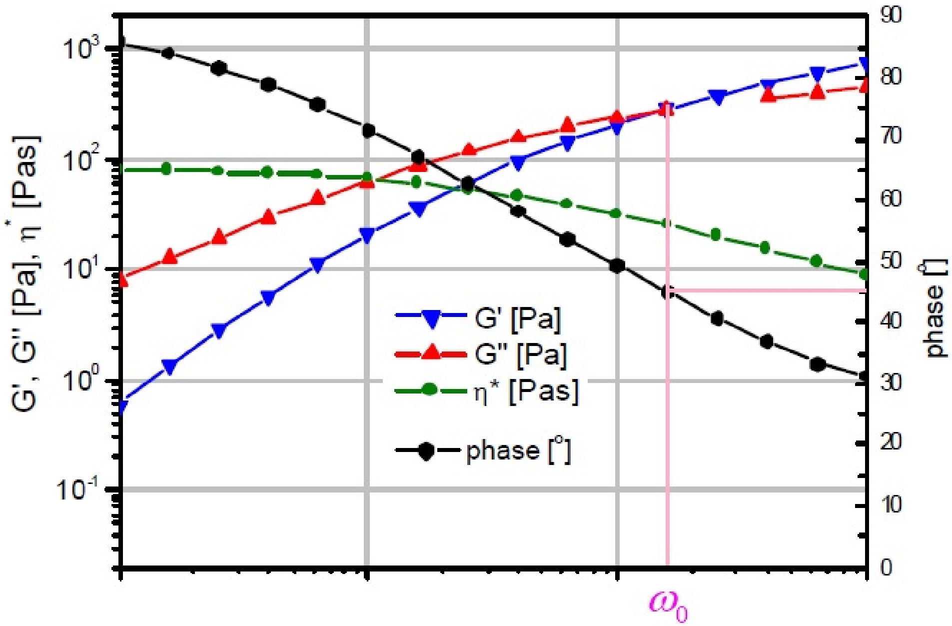
Comparison Eqns. (1b) and (9) resulted that

$$\gamma=\gamma_0\cos(\omega t-\delta)$$

$$\gamma_0=\frac{\lambda\tau_0}{\eta\cos\theta},\qquad \theta=\delta \qquad (10)$$

As mentioned before, $\tan\theta=\dfrac{1}{\lambda\omega}$, so:

$$\tan\delta=\frac{1}{\lambda\omega} \qquad (11)$$



Frequency dependence of a high viscosity silicone oil (silicone putty).

Using the frequency sweep test, the data of G' and G'' is measured for different frequencies. Based on Eq. (5), we have $\tan\delta=G''/G'$. Therefore, using Eq. (11), at the intersection point of the curves of G' and G'', we have: $\lambda=1/\omega_0$ (Here, ω_0 is the frequency at the intersection point). It is a usual method to estimate the relaxation time.

Oscillatory Test

Substituting Eq. (10) into the (4), we have:

$$G' = \frac{\tau_0}{\dfrac{\lambda \tau_0}{\eta \cos\delta}} \cos\delta = \frac{\eta}{\lambda} \cos^2\delta \qquad (12a)$$

$$G'' = \frac{\tau_0}{\dfrac{\lambda \tau_0}{\eta \cos\delta}} \sin\delta = \frac{\eta}{\lambda} \cos\delta \sin\delta \qquad (12b)$$

From Eq. (11), we have:

$$\cos\delta = \frac{\lambda\omega}{\sqrt{1+\lambda^2\omega^2}}, \quad \sin\delta = \frac{1}{\sqrt{1+\lambda^2\omega^2}} \qquad (13)$$

Finally, by substituting Eq. (13) into the Eq. (12), the response of Maxwell model to frequency sweep test is obtained as follows:

$$G' = \frac{\lambda\eta\omega^2}{1+\lambda^2\omega^2} \qquad (14a)$$

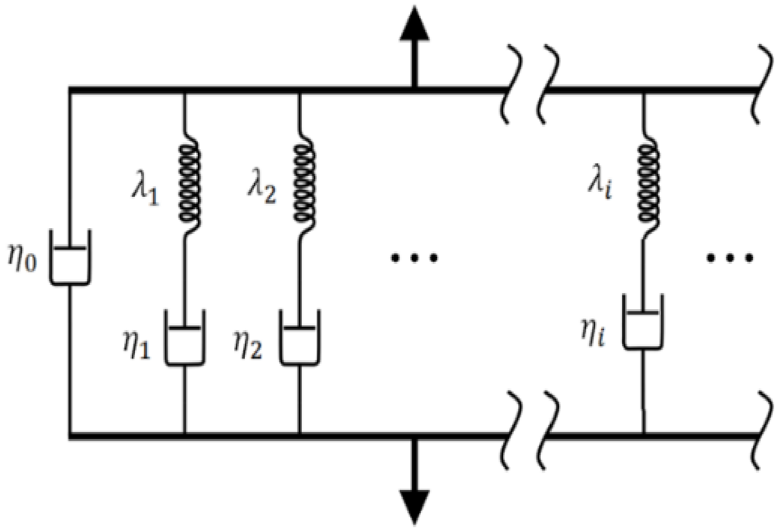
$$G'' = \frac{\eta\omega}{1+\lambda^2\omega^2} \qquad (14b)$$

Oscillatory Test

It is possible to obtain the coefficients of Maxwell model (η and λ) by curve fitting the Eq. (14) on the experimental data of storage and loss modulus. For example, they could be estimated via minimizing the root-mean-square error (RMSE) between the model and experimental data:

$$f(\lambda,\eta)=\sqrt{\sum_{j=1}^{m}(G'_{Data}-G'_{Model})^2+(G''_{Data}-G''_{Model})^2} \quad (15)$$

where m is number of data points. As mentioned before, the generalized Maxwell model is useful to estimate the discrete relaxation spectrum. Using superposition principle for results of Eqn. (14), the response of generalized (multi-mode) Maxwell model can be expressed as:



$$G'=\sum_{i=1}^{n}\frac{\lambda_i\eta_i\omega^2}{1+\lambda_i^2\omega^2}, \qquad G''=\eta_0\omega+\sum_{i=1}^{n}\frac{\eta_i\omega}{1+\lambda_i^2\omega^2} \quad (16)$$

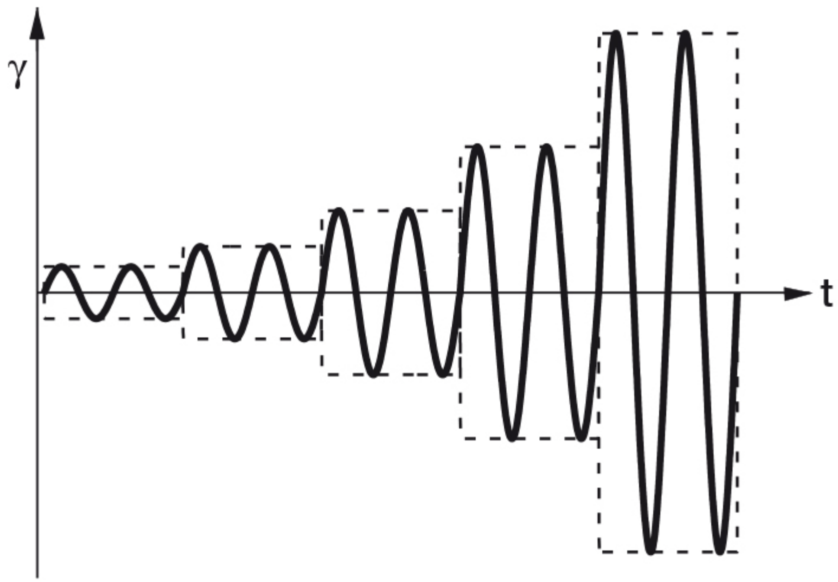
$$\eta=\sum_{i=0}^{n}\eta_i, \qquad \bar{\lambda}=\left(\sum_{i=0}^{n}\eta_i\lambda_i\right)\Big/\left(\sum_{i=0}^{n}\eta_i\right) \quad (17)$$

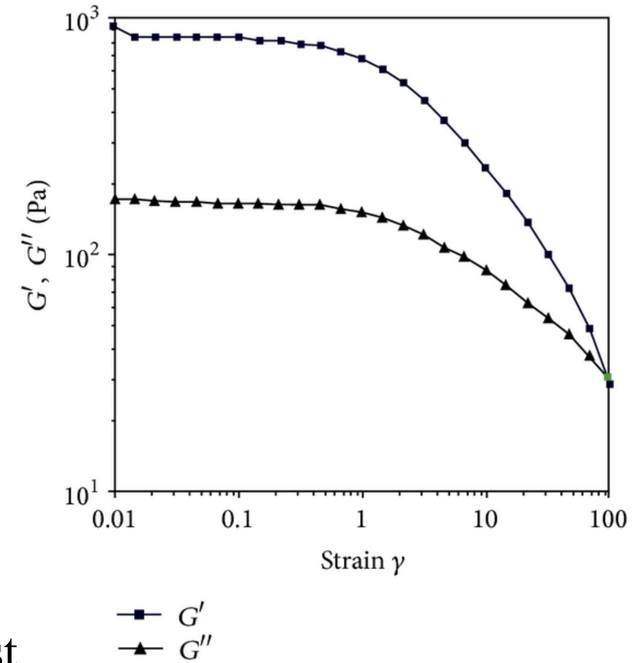
where η is viscosity at zero shear rate, $\bar{\lambda}$ is average relaxation time and, η_i and λ_i are the viscosity and relaxation times of each Maxwell elements, respectively. Here, a viscous element (η_0) is parallelized to model for better fitting on experimental data of polymeric liquids.

Oscillatory Test

Some tips about oscillatory test

1. Determining an appropriate value for percentage of strain before doing the frequency sweep test is so important to obtain the linear data. For this purpose, it is better to do an amplitude sweep test at a constant low frequency (for example: $\omega = 1Hz$) and determine a bound of strain in which the storage and loss modulus is constant. You can use any value of strain percentage in this bound but to assurance to capture the linear data during the frequency sweep test, it is better to select a value at the middle of this bound.





Amplitude Sweep Test

Oscillatory Test

2. The concept of an entanglement network (or the restraint of each molecule in an effective tube) is associated with a terminal relaxation time which is much longer than it would be in the absence of such topological restraints and increases rapidly with molecular weight. By contrast, the shorter relaxation times are governed by the same monomeric friction coefficient that characterizes rates of translatory motion of short segments in the absence of entanglements. As a result, the terminal zone of the storage modulus (for example) is displaced toward lower frequencies to an extent which increases with increasing molecular weight, while between the terminal zone and the transition zone there appears a plateau region where G' changes only slightly with frequency.
3. The storage modulus and loss modulus are changed with ω^2 and ω in terminal zone, respectively.
4. The storage modulus is a monotonic function of frequency and any drop in this graph especially at large frequencies is an error that could be attributed to the inertia effect of measuring system.
5. It is possible to estimate the yield stress via sweep frequency test! For this purpose, the graph of the lag phase versus the stress should be plotted. The yield stress can be considered as an average value of stress in which the phase angle is increased drastically from zero to 90 degree.
6. The frequency sweep provides a characteristic fingerprint of the material. At higher frequency, G' shows a plateau value referred to as plateau modulus. The plateau value relates to the average molecular weight between entanglements M_e. At low frequency, the loss modulus is a measure of the materials viscosity (G''/ω) and the ratio G'/G''^2 of the elasticity.

Oscillatory Test

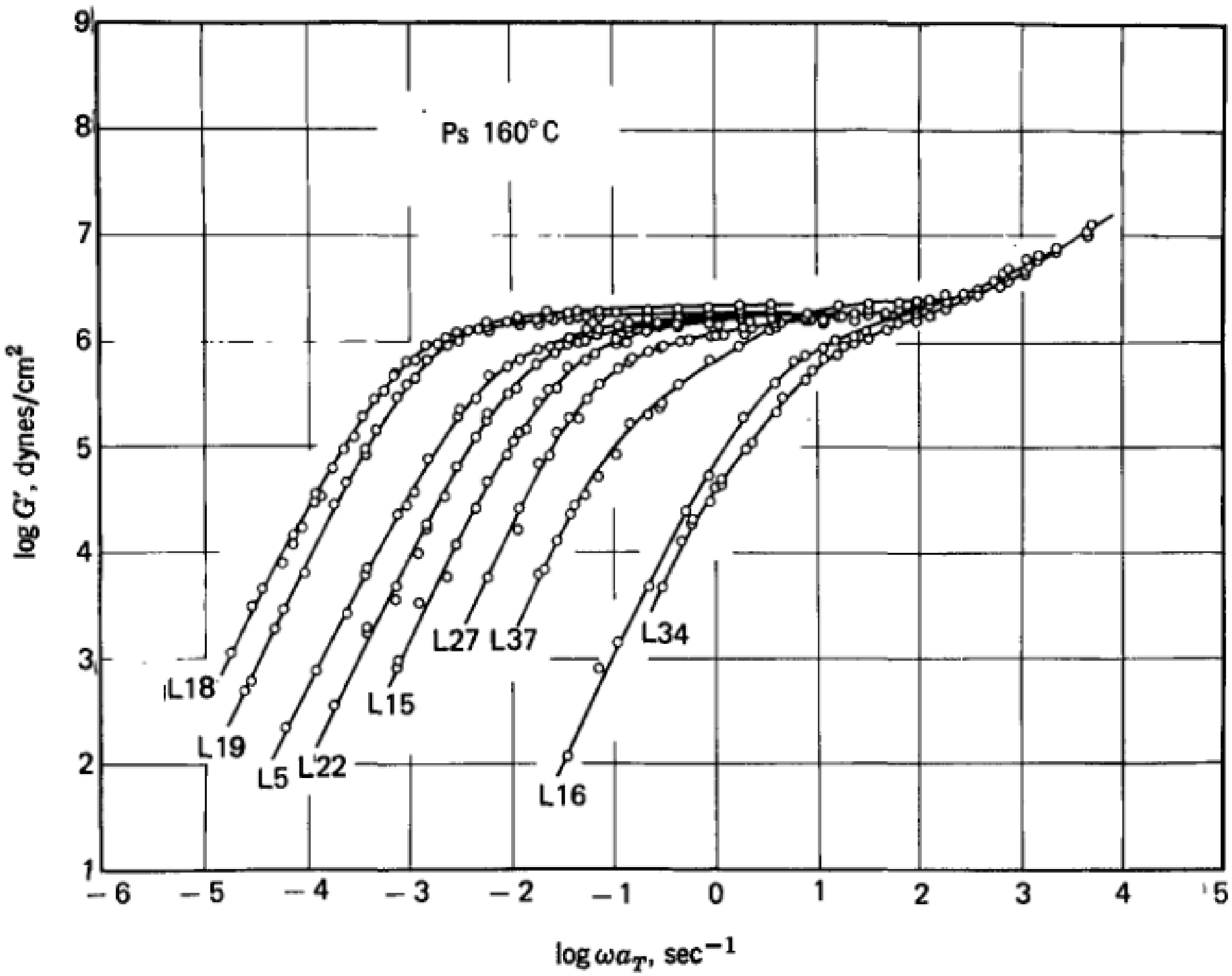
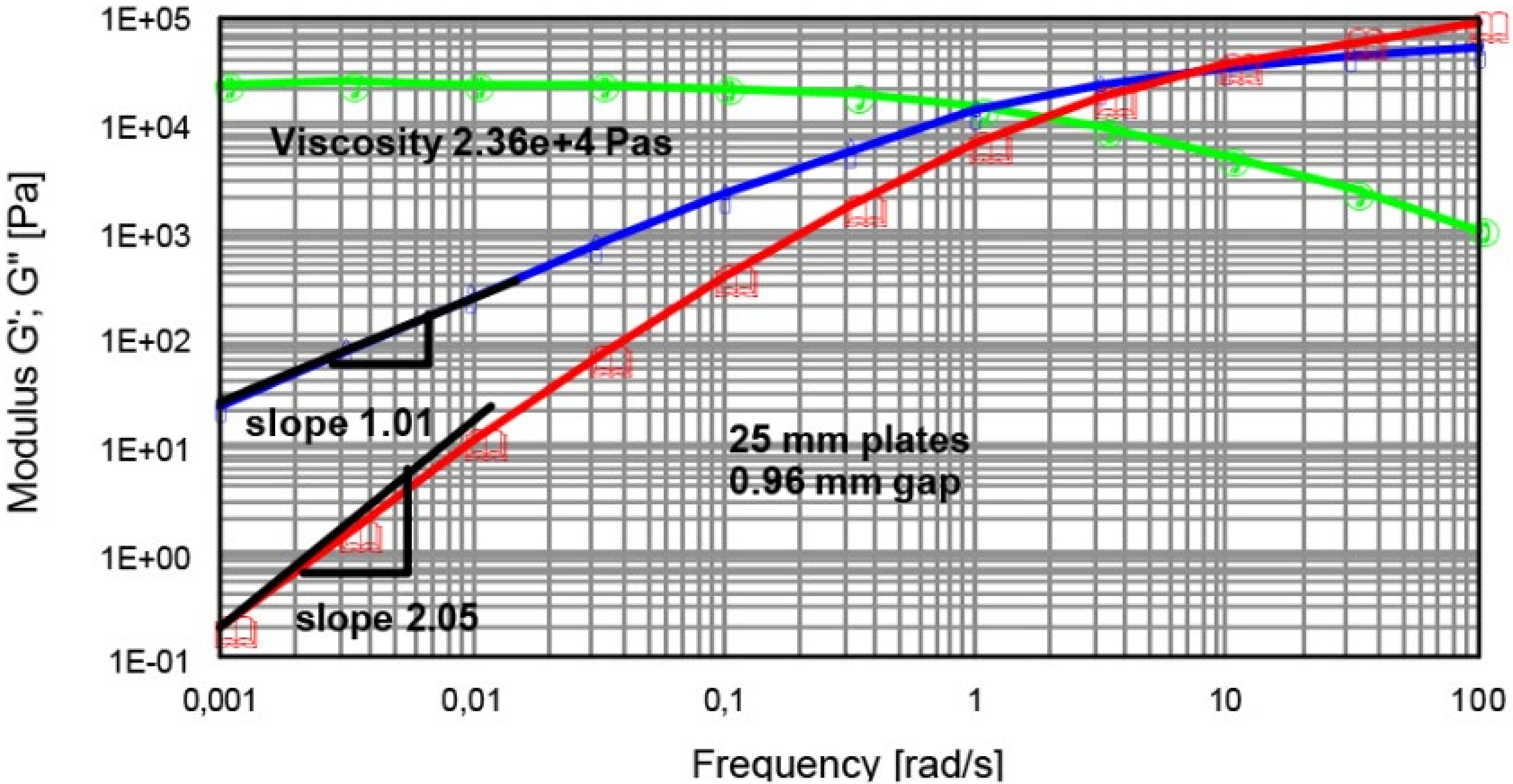


FIG. 13-2. Storage modulus of narrow-distribution polystyrenes,[3] plotted logarithmically against frequency reduced to 160°C. Viscosity-average molecular weights from left to right, $\times 10^{-4}$: 58, 51, 35, 27.5, 21.5, 16.7, 11.3, 5.9, 4.7. (Onogi, Masuda, and Kitagawa.[3])

Oscillatory Test



A Summary on Responses of Basic Models

Maxwell Model

$$J(t) = J_i + t/\eta_i$$

$$G(t) = G_i e^{-t/\tau_i}$$

$$G'(\omega) = G_i \omega^2 \tau_i^2 (1 + \omega^2 \tau_i^2)$$

$$G''(\omega) = G_i \omega \tau_i/(1 + \omega^2 \tau_i^2)$$

$$\eta'(\omega) = \eta_i/(1 + \omega^2 \tau_i^2)$$

$$J'(\omega) = J_i$$

$$J''(\omega) = J_i/\omega \tau_i = 1/\omega \eta_i$$

$$\tan \delta = 1/\omega \tau_i$$

Kelvin-Voigt Model

$$J(t) = J_i(1 - e^{-t/\tau_i})$$

$$G(t) = G_i$$

$$G'(\omega) = G_i$$

$$G''(\omega) = G_i \omega \tau_i = \omega \eta_i$$

$$\eta'(\omega) = \eta_i$$

$$J'(\omega) = J_i/(1 + \omega^2 \tau_i^2)$$

$$J''(\omega) = J_i \omega \tau_i/(1 + \omega^2 \tau_i^2)$$

$$\tan \delta = \omega \tau_i$$

where τ_i is the relaxation and retardation time constants of Maxwell and Kelvin-Voigt model, respectively. J^* is the complex compliance and defined as $J^* = \gamma^* / \tau^* = 1/G^* = J' - iJ''$.


It will be all worth it in the END