



Non-Newtonian Fluid Mechanics (Part - III)

Mechanical Engineering Department, Shahrood University of Technology

> By M. Norouzi April 2021

Viscoelastic Fluids



Viscoelasticity is the property of materials that exhibit both viscosity and elastic characteristics when undergoing deformation. Many materials of practical interest (such as polymer melts, polymer and soap solutions, some biological fluids) exhibit viscoelastic behavior; they have some ability to store and recover shear energy.

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Viscoelastic fluids exhibit the following specification:

- 1. Relaxation and retardation time constants (relaxation spectra)
- 2. Memory effect
- 3. The first and second normal stress differences
- 4. Nonlinear viscometric functions
- 5. Unsteady elongational viscosity

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Rheological Tests

There are some standard tests for viscoelastic fluids which are useful to measure the different material modulus and rheological properties. They usually performed at constant or variable temperature (for some classes of materials, they should down at constant or variable, magnetic or electric fields). The results of these tests are useful to know the rheological behaviors of material in different conditions and the main of them are:

- 1. Stress Relaxation
- 2. Creep
- 3. Recoil
- 4. Frequency Sweep and Amplitude Sweep
- 5. Viscometric Tests
- 6. Steady and Unsteady Elongational Tests





In stress relaxation test, a suddenly step strain is applied on a sample of material and the response of stress is measured.





Observations of real materials (viscoelastic solids and fluids) shows that the stress is decreased rapidly in initial time and finally approaches to the limiting value.

The required time in which the stress is approach to the limiting value is known as the relaxation time.

For ideal Newtonian fluids, this time constant is zero and for ideal Hookean solids, it is approach to infinity.



Stress Relaxation Test





Time of applied deformation in seconds





Fluid type	Temperature (K) T	e Relaxation time (s) λ	Zero-shear viscosity (Pa-s) η_0	Rigidity η _o /λ (Pa)
Water	293	$\sim 10^{-12}$	0.001	109
Mineral oil	303	7×10^{-10}	0.5	7×10^{8}
Poly-dimethysiloxane	{ 303	10^{-6}	0.3	3×10^{5}
	1 398	1.7×10^{-4}	100	6×10^{5}
Low-density polyethylene	§ 388	10	2×10^{5}	2×10^{4}
	1513	0.1	3000	3×10^{4}
High-density polyethylene	§ 453	0.07	2000	3×10^{4}
	\ 493	0.05	1000	2×10^{4}
High-impact polystyrene	§ 443	7	2×10^{5}	3×10^{4}
	1483	3	1×10^{5}	3×10^{4}
0.5% Hydroxyethyl- cellulose in water	300	0.1	1.3	13
2% Polyisobutylene solution in Primol oil	300	100	1000	10
Glass	300	>10 ⁵	>10 ¹⁸	\sim 5 × 10 ¹⁰

TABLE 1.8. Viscoelastic fluid properties

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Basic Elements of Linear Models







 $\tau = \eta \dot{\gamma}$

Isaac Newton (1642-1726)

$$\begin{array}{c}
G \\
\bullet & & \\
 & \\
 & \tau = G\gamma
\end{array}$$



RobHook (1635-1703)



Maxwell Model





James Clerk Maxwell (1831-1879)

A Maxwell material is a viscoelastic material having the properties both of elasticity and viscosity. It is named for James Clerk Maxwell who proposed the model in 1867. It is also known as a Maxwell fluid. The Maxwell model can be represented by a purely viscous damper and a purely elastic spring connected in series.



Maxwell Model



Derivation the equation

From the elements of Maxwell model, we have:

$$\begin{cases} \gamma = \gamma_1 + \gamma_2 \\ \tau = \tau_1 = \tau_2 \end{cases} \& \begin{cases} \tau_1 = G\gamma_1 \\ \tau_2 = \eta \dot{\gamma}_2 \end{cases}$$
(1)

Therefore,

$$\gamma = \gamma_1 + \gamma_2 \xrightarrow{\text{Time derivation}} \dot{\gamma} = \dot{\gamma}_1 + \dot{\gamma}_2$$
 (2)

From Eq. (1), it is simply concluded that,

$$\begin{cases} \dot{\gamma}_1 = \dot{\tau} / G \\ \dot{\gamma}_2 = \tau / \eta \end{cases}$$
(3)

By substituting Eq. (3) into the Eq. (2), we have

$$\dot{\gamma} = \dot{\tau} / G + \tau / \eta \longrightarrow \tau + \frac{\eta}{G} \dot{\tau} = \eta \dot{\gamma}$$
 (4)

It is important to mention that, the term η/G has the dimension of time so it could be considered as a time constant (λ). Finally, the Maxwell constitutive equation is obtained as follows:

$$\tau + \lambda \dot{\tau} = \eta \dot{\gamma} \tag{5}$$

where λ is the relaxation time constant of Maxwell model.

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Response of Maxwell model to the stress relaxation test:

As mentioned before, in the stress relaxation test, a step strain is applied on the sample and the stress is measured. Therefore, the shear strain of this test can be expressed as:

$$\gamma = \gamma_0 H(t) = \begin{cases} 0 & t < 0 \\ \gamma_0 & t \ge 0 \end{cases}$$
Therefore,

$$\dot{\gamma} = 0 \quad for \ t \ge 0 \qquad (7)$$
By substituting Eq. (7) into the Eq. (5), we have

$$\tau + \lambda \dot{\tau} = 0 \qquad (8)$$
The solution of above equation is

$$\tau = \tau_0 e^{-t/\lambda} \qquad (9) \qquad \text{Time}$$

The above result has a good agreement for response of viscoelastic materials and Maxwell equation is usually used to model the effect of relaxation time.





In creep test, we supposed that the material is subjected to a one-step stress history and the response of shear deformation is measured.





Creep Test





Response of fluid-like material



For some cases, it is impossible to tell which type of behavior is occurred.

In these cases, a knowledge of the material microstructure is useful.



Kelvin-Voigt Model





Kelvin-Voigt (KV)

William Thomson (1824-1907) Woldemar Voigt (1850-1919)

 $\tau = G\left(\gamma + \frac{\eta}{G}\dot{\gamma}\right)$

Woldemar Voigt (1850 - 1919)

William Thomson

1st Baron of Kelvin (1824 - 1907)

The Kelvin-Voigt model, also called as Voigt model and Mayer model, can be represented by a purely viscous damper and purely elastic spring connected in parallel. It is a useful equation to model both creep and recoil tests.



Kelvin-Voigt Model



Derivation the equation:

From the elements of Kelvin-Voigt model, we have:

$$\begin{cases} \gamma = \gamma_1 = \gamma_2 \\ \tau = \tau_1 + \tau_2 \end{cases} & \begin{cases} \tau_1 = G\gamma_1 \\ \tau_2 = \eta \dot{\gamma}_2 \end{cases}$$
(10)

Based on Eq. (10), we can conclude that

 $\tau = \tau_1 + \tau_2 \rightarrow \tau = G\gamma_1 + \eta \dot{\gamma}_2 \qquad (11)$

Eq. (11), can be written as

$$\tau = G\left(\gamma + \xi \dot{\gamma}\right) \tag{12}$$

where ξ is a time constant ($\xi = \eta/G$) which is known as the Retardation Time. The Retardation time is the delayed response to an applied force or stress and can be described as "delay of the elasticity".

The above result has a good agreement for response of Solid-like materials in creep test.

 $\gamma(t) = \gamma_0 e^{-t/\xi} + \frac{\tau_0}{G} \left(1 - e^{-t/\xi} \right)$

$\tau = \tau_0 H(t) = \begin{cases} 0 & t < 0 \\ \tau_0 & t \ge 0 \end{cases}$

Response of Kelvin-Voigt model to the creep test:

By substituting Eq. (13) into the Eq. (12), we have

$$\tau_0 = G\left(\gamma + \xi \dot{\gamma}\right) \longrightarrow \xi \dot{\gamma} + \gamma = \frac{\tau_0}{G} \tag{14}$$

measured. Therefore, the shear stress of this test can be expressed as:

By considering the initial value of $\gamma(0) = \gamma_0$, the so of Eq. (14) is:

$$\tau_0 = G\left(\gamma + \xi \dot{\gamma}\right) \longrightarrow \xi \dot{\gamma} + \gamma = \frac{\tau_0}{G} \tag{(4)}$$

(14)
$$(14)$$
 (14) $(1$

(14)
(14)

$$\gamma_0$$

(15)
 τ_0/G
 τ_0/G
 τ_0/G
 τ_0/G
 τ_0/G
 τ_0







(13)

As mentioned before, in the creep test, a step stress is applied on the sample and the shear strain is







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Recoil Test: During the creep test, if we would free the material at time $t=t_1$ (the stress suddenly becomes to zero), then the elastic element would retard the material back until the deformation becomes zero. This experiment is known as the recoil test.

Response of Kelvin-Voigt model to the Recoil Test:

In recoil test, the stress suddenly becomes zero at $t=t_1$. Therefore, from the Eq. (12), we have:

$$\gamma + \xi \dot{\gamma} = 0 \tag{16}$$

By considering $\gamma(t = t_1) = \gamma_1$, the solution of above equation, is:

$$\gamma = \gamma_1 e^{-(t-t_1)/\xi} \quad \text{for } t \ge t_1 \tag{17}$$

This response indicates that ξ has the role of retardation time constant in Kelvin-Voigt model.







Response Functions: Let $R(\gamma,t)$ be the stress relaxation function and $C(\tau,t)$ be the creep function. Here, $R(\gamma,t)$ is in form of shear stress and $C(\tau,t)$ is in form of shear strain. It is important to mention that the relation between shear stress and shear strain is in form of odd function, so we have:

$$R(\gamma, t) = G(t)\gamma + O(\gamma^3), \qquad (18)$$

and

$$C(\tau, t) = J(t)\tau + O(\tau^{3}), \qquad (19)$$

The coefficients of linear terms are the linear stress relaxation modulus, G(t), and the linear creep compliance, J(t). The values of these functions at t=0 are denoted G_g and J_g (g for glass) and the value at $t \to \infty$ are G_e and J_e (e for equilibrium). Immediately after application of a step stress or strain, the response is independent whether it is the stress or the strain which is to be held constant in the future. Hence, at t=0, $\tau = G_g \gamma$ and $\gamma = J_g \tau$ so $G_g J_g = 1$. If the stress and strain approach to limiting value, it is irreverent which one was held absolutely constant for positive times. Therefore, we have $G_e J_e = 1$. G and J are only reciprocal for these two cases and they are roughly reciprocal for other times. It is also possible to prove that for any applied strain and stress; the following relationships are established:

$$\tau(t) = \int_{-\infty}^{t} G(t - t') d(\gamma(t'))$$
(20)
$$\gamma(t) = \int_{-\infty}^{t} J(t - t') d(\tau(t'))$$
(21)







Viscoelastic Spectra

The Maxwell element cannot describe creep and the Voigt element cannot describe stress relaxation. The Maxwell does describe stress relaxation and the Voigt does describe creep, but as exponential functions of time. Most observed creep and relaxation processes in polymers progress more gradually. The components of the complex modulus for the Maxwell element, and those of the complex compliance for the Voigt element, depend on frequency. These elements may be considered as building blocks for useful models. Therefore, polymeric materials are characterized by a broad range of relaxation and retardation times.

It is important to mention that there are some discrete and continuous approaches to estimate the viscoelastic spectrums.



Burgers Model







J. M. Burgers (1895-1981)

The Burgers model is usually defined based on the parallel connection of two Maxwell elements. It is a four constant linear viscoelastic model which brings two individual relaxation times, a constant viscosity and a retardation time.



Burgers Model



Derivation the Burgers equation:

From the schematic shape of Burgers equation in previous slide and Eq. (5), we can express the following relationships for any branches.

For branch No. 1: $\tau_1 + \lambda_1 \dot{\tau}_1 = \eta_1 \dot{\gamma}_1$ (22a) For branch No. 2: $\tau_2 + \lambda_2 \dot{\tau}_2 = \eta_2 \dot{\gamma}_2$ (22b)

where $\lambda_1 = \eta_1 / G_1$ and $\lambda_2 = \eta_2 / G_2$. It is important to remember that the branches are parallel so: $\tau = \tau_1 + \tau_2$ and $\gamma = \gamma_1 = \gamma_2$.

By summing Eq. (22a) and (22b), we have:

$$\tau_1 + \tau_2 + \lambda_1 \tau_1 + \lambda_2 \tau_2 = \eta_1 \dot{\gamma} + \eta_2 \dot{\gamma} \longrightarrow \tau + \lambda_1 \tau_1 + \lambda_2 \tau_2 = (\eta_1 + \eta_2) \dot{\gamma}$$
(23)

By time derivation of Eqns. (22a) and (22b), it is concluded that,

$$\dot{\tau}_1 + \lambda_1 \ddot{\tau}_1 = \eta_1 \ddot{\gamma} \xrightarrow{\times \lambda_2} \lambda_2 \dot{\tau}_1 + \lambda_1 \lambda_2 \ddot{\tau}_1 = \eta_1 \lambda_2 \ddot{\gamma}$$
(24a)

$$\dot{\tau}_2 + \lambda_2 \ddot{\tau}_2 = \eta_2 \ddot{\gamma} \xrightarrow{\times \lambda_1} \lambda_1 \dot{\tau}_2 + \lambda_1 \lambda_2 \ddot{\tau}_2 = \eta_2 \lambda_1 \ddot{\gamma}$$
(24b)

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By summing Eq. (24a) and (24b), we have:

$$\lambda_{2}\dot{\tau}_{1} + \lambda_{1}\dot{\tau}_{2} + \lambda_{1}\lambda_{2}\left(\ddot{\tau}_{1} + \ddot{\tau}_{2}\right) = \left(\eta_{1}\lambda_{2} + \eta_{2}\lambda_{1}\right)\ddot{\gamma}$$

$$\longrightarrow \qquad \lambda_{2}\dot{\tau}_{1} + \lambda_{1}\dot{\tau}_{2} + \lambda_{1}\lambda_{2}\ddot{\tau} = \left(\eta_{1}\lambda_{2} + \eta_{2}\lambda_{1}\right)\ddot{\gamma}$$

$$(25)$$

Finally, by adding Eq. (23) and (25), the Burgers Equation is obtained as follows:

$$\tau + (\lambda_1 + \lambda_2)\dot{\tau}_1 + (\lambda_1 + \lambda_2)\dot{\tau}_2 + \lambda_1\lambda_2\ddot{\tau} = (\eta_1 + \eta_2)\dot{\gamma} + (\eta_1\lambda_2 + \eta_2\lambda_1)\ddot{\gamma}$$

$$\longrightarrow \tau + (\lambda_1 + \lambda_2)\dot{\tau} + \lambda_1\lambda_2\ddot{\tau} = (\eta_1 + \eta_2)\left(\dot{\gamma} + \frac{\eta_1\lambda_2 + \eta_2\lambda_1}{\eta_1 + \eta_2}\ddot{\gamma}\right)$$
(26)

The Burgers equation can be also expressed as:

$$\tau + \alpha_1 \dot{\tau} + \alpha_2 \ddot{\tau} = \eta (\dot{\gamma} + \beta \ddot{\gamma}) \tag{27}$$

where
$$\alpha_1 = \lambda_1 + \lambda_2$$
, $\alpha_2 = \lambda_1 \lambda_2$, $\eta = \eta_1 + \eta_2$ and $\beta = \frac{\eta_1 \lambda_2 + \eta_2 \lambda_1}{\eta_1 + \eta_2}$





Response of Burgers model to the stress relaxation test:

Based on Eqns. (6) and (7), the following differential equation can be expressed from Eq. (26):

$$\tau + \left(\lambda_1 + \lambda_2\right)\dot{\tau} + \lambda_1\lambda_2\ddot{\tau} = 0 \tag{28}$$

The detail of solution of above equation is:

$$\lambda_{1}\lambda_{2}\ddot{\tau} + (\lambda_{1} + \lambda_{2})\dot{\tau} + \tau = 0$$

$$\lambda_{1}\lambda_{2}r^{2} + (\lambda_{1} + \lambda_{2})r + 1 = 0, \qquad \Delta = (\lambda_{1} + \lambda_{2})^{2} - 4\lambda_{1}\lambda_{2} = (\lambda_{1} - \lambda_{2})^{2}$$

$$r_{1,2} = \frac{-(\lambda_{1} + \lambda_{2})\pm\sqrt{(\lambda_{1} - \lambda_{2})^{2}}}{2\lambda_{1}\lambda_{2}} \longrightarrow \begin{cases} r_{1} = -1/\lambda_{1} \\ r_{2} = -1/\lambda_{2} \end{cases}$$

$$\tau = \tau_{0,1}e^{-t/\lambda_{1}} + \tau_{0,2}e^{-t/\lambda_{2}} \xrightarrow{+\gamma_{0}} G(t) = G_{0,1}e^{-t/\lambda_{1}} + G_{0,2}e^{-t/\lambda_{2}} \qquad (29)$$

The above relationship indicates that the Burgers model brings two relaxation times.





The Jeffreys Model is usually defined based on parallel connection of Maxwell and viscous elements. It could be considered as an especial case of Burgers model (Eq. (26)) by substituting $\lambda_2 = 0$:

$$\tau + \lambda \dot{\tau} = \eta \left(\dot{\gamma} + \xi \ddot{\gamma} \right) \tag{30}$$

The Jeffreys equation is a three constant model which brings a relaxation time (λ), a retardation time (ξ) and a viscosity (η). This equation is usually used to model dilute polymeric solutions in which a little polymeric additive is solved in a Newtonian solvent.

Equation (30) is also derived by considering some details in Burgers equation including: $\eta_p = \eta_1$, $G_p = G_1$, $\eta_s = \eta_2$, $\lambda = \lambda_1 = \eta_p / G_p$, $\eta = \eta_p + \eta_s$ and $\xi = \lambda \eta_s / \eta$. Here, λ and η_p are the relaxation time and viscosity of polymeric additives, η_s is the viscosity of Newtonian solvent and η is the viscosity of solution.

The Oldroyd-B model is a well-known quasilinear model which is considered as the generalization of Jeffreys model for large deformations (fluid flow).







Discrete Relaxation Spectra





The generalized (multi-modes) Maxwell model is defined as the parallel connection of some Maxwell elements. Therefore, the Burgers equation is a two-modes generalized Maxwell model. Due to the linear form of this model, the superposition principle is valid and similar to Eq. (29), we can conclude the following relationships for the generalized Maxwell model:

$$\tau = \sum_{i=1}^{n} \tau_{0,i} e^{-t/\lambda_i} \qquad \& \qquad G(t) = G_e + \sum_{i=1}^{n} G_i e^{-t/\lambda_i}$$
(31)

The above equation is suitable to model the discrete relaxation spectra of viscoelastic materials.







The generalized Kelvin-Voigt model

A group of Kelvin-Voigt elements in series represents the generalized Kelvin-Voigt model. It can specify a discrete spectrum of retardation times, each time ξ_i being associated with a spectral compliance magnitude J_i . Applying the superposition principle on Eq. (15) and considering $\gamma_0 = 0$, we can derive the following response to the creep test:

$$\gamma(t) = \sum_{i=1}^{n} \frac{\tau_0}{G_i} \left(1 - e^{-t/\xi_i} \right) \qquad \& \qquad J(t) = \sum_{i=1}^{n} J_i \left(1 - e^{-t/\xi_i} \right)$$
(32)





The Continuous Relaxation Spectrum:

If the number of elements in the generalized Maxwell model is increased without limit, the result is a continuous spectrum in which each infinitesimal contribution to rigidity $Fd\lambda$ is associated with relaxation times lying in the range between λ and $\lambda + d\lambda$. Actually, experience has shown that a logarithmic time scale is far more convenient; accordingly, the continuous relaxation spectrum is defined as $Hd(Ln\lambda)$, the contribution to rigidity associated with relaxation times whose logarithms lie in the range between $Ln\lambda$ and $Ln\lambda + d(Ln\lambda)$, a measure of the population of relaxation mechanisms with relaxation times in this interval. (Evidently, $H=F\lambda$). For the continuous spectrum, equation (31) becomes

$$G(t) = G_e + \int_{-\infty}^{\infty} H(\lambda) e^{-t/\lambda} d(\mathrm{Ln}\lambda)$$
(33)

The constant G_e is added to allow for a discrete contribution to the spectrum with $\tau = \infty$, for viscoelastic solids; for viscoelastic liquids (uncross-linked polymers), of course, $G_e=0$.







The characteristic zones of the viscoelastic time scale are clearly apparent in H: the glassy zone to the left of the principal maximum, the transition zone where H drops steeply, the terminal zone where it approaches zero, and a region to the right of the transition zone in examples III, IV, and VII where H is relatively flat (the plateau) or passes through a minimum.



The Continuous Retardation Spectrum:

In an entirely analogous manner, if the generalized Kelvin-Voigt model is made infinite in extent, it represents a continuous spectrum of retardation times, L, alternatively defined by the continuous analog of equation (32):

$$J(t) = J_g + \int_{-\infty}^{\infty} L(\xi) \left(1 - e^{-t/\xi}\right) d(\ln\xi) + t / \eta_0$$
(34)

In this case an instantaneous compliance J_g must be added to allow for the possibility of a discrete contribution with $\xi = 0$ (It can be down via canceling a damper inside the model). Although J_g may be inaccessible experimentally, its presence must be inferred or else instantaneous deformation would require infinite stress. A term t/η_0 must be added if one of the springs has zero rigidity, as must be the case for an uncross-linked polymer), etc.







At long times, L, like H, should vanish when an uncross-linked viscoelastic liquid polymer reaches the state of steady flow. This condition is observed for Examples I, II, and III. For Example IV, there are compliance mechanisms persisting beyond the longest times for which data are available. The plateau or minimum in the spectrum H corresponds very roughly to a maximum in the spectrum L.

Some Points on Linear Viscoelastic Models



By parallel and series connections of different damper and spring elements, we can derive the different linear constitutive equations. It is possible to show that the general form of these equations is:

$$\tau + \alpha_1 \dot{\tau} + \alpha_2 \ddot{\tau} + \alpha_3 \ddot{\tau} + \dots + \alpha_n \frac{d^n \tau}{dt^n} = \eta \left(\dot{\gamma} + \beta_1 \ddot{\gamma} + \beta_2 \ddot{\gamma} + \dots + \beta_m \frac{d^{m+1} \gamma}{dt^{m+1}} \right)$$
(35)

The above linear equation brings a constant viscosity and, *n* and *m* discrete relaxation and retardation times, respectively. They are appropriate for small deformations while their results are not usually correct for large deformations and fluid flow. These models are widely used in solid mechanics and polymer Engineering for the problems in which the size of deformations is small. They are also useful for interoperating the results of some standard rheological tests such as stress relaxation, creep, recoil, frequency sweep and amplitude sweep tests. The linear equations cannot model the nonlinear viscometric functions (viscosity and, the first and second normal stress differences coefficients) and extensional viscosity. Therefore, there are not suitable to model the flow of viscoelastic fluids. Some nonlinear and quasilinear constitutive equations for flow of viscoelastic liquids are derived base on generalization of linear models.

