

LINEAR VISCOELASTICITY

Crispulo Gallegos and Francisco J. Martínez Boza

*Complex Fluid Engineering Laboratory. Departamento de Ingeniería Química.
University of Huelva. 21071 Huelva, Spain*

Keywords: linear viscoelasticity, superposition principle, stress relaxation, creep, oscillatory shear, relaxation spectrum

Contents

1. Introduction
2. The Boltzmann superposition principle
3. Derivative models for the relaxation modulus
4. Relaxation spectrum
5. Small strain material functions
 - 5.1. Stress relaxation
 - 5.2. Creep
 - 5.3. Small Amplitude Oscillatory Shear
6. Calculations of the linear relaxation and retardation spectra from experimental linear viscoelasticity functions
 - 6.1. Calculation of the Linear Relaxation and Retardation Spectra from $G(t)$ and $J(t)$
 - 6.1.1. Transform Inversion Methods
 - 6.1.2. The Method of Ferry and Williams
 - 6.2. Calculation of Relaxation and Retardation Spectra from Harmonic Responses
 - 6.2.1. Transform Inversion Methods
 - 6.2.2. The Method of Ferry and Williams
 - 6.3. Least Squares Method
 - 6.4. Regularization Method
 - 6.4.1. Calculation of $H(\lambda)$ from $G'(\omega)$
 - 6.4.2. Calculation of $H(\lambda)$ from $G''(\omega)$
 - 6.4.3. Calculation of $L(\tau)$ from $J(t)$
- Glossary
- Bibliography
- Biographical Sketches

Summary

Viscoelastic materials possess both viscous and elastic properties in varying degrees. For a viscoelastic material, internal stresses are a function not only of the instantaneous deformation, but also depend on the whole past history of deformation. For real materials, the most recent past history has much more influence. Linear viscoelasticity is the simplest response of a viscoelastic material. If a material is submitted to deformations or stresses small enough so that its rheological functions do not depend on the value of the deformation or stress, the material response is said to be in the linear viscoelasticity range. This chapter reviews the Boltzmann superposition principle, the constitutive equations for linear viscoelasticity (mainly in simple shear), the use of

mechanical models analogies to describe the linear viscoelasticity behavior of real materials, the description of experimental tests in shear necessary to obtain the different small strain material functions, and the methods to calculate the linear relaxation and retardation spectra of viscoelastic materials.

1. Introduction

As can be deduced from its name, viscoelastic materials possess both viscous and elastic properties in varying degrees. For a viscoelastic material, internal stresses are a function not only of the instantaneous deformation, but also depend on the whole past history of deformation. For real materials, the most recent past history has much more influence. This is the reason why these materials may be described as having fading memory. Linear viscoelasticity is the simplest response of a viscoelastic material. When a material is deformed, thermodynamic forces immediately begin to operate to restore the minimum-energy state. Movement from the rest state represents a storage of energy. This type of energy is the origin of elasticity on many different materials, i.e. polymer solutions, polymer melts, concentrated suspensions, concentrated emulsions, asphalts, lubricating greases, etc. If a material is submitted to deformations or stresses small enough so that its rheological functions do not depend on the value of the deformation or stress, the material response is said to be in the linear viscoelasticity range.

2. The Boltzmann Superposition Principle

Consider the function $\gamma(t)$ as representative of some cause (shear strain) acting on a given material, and the shear stress, $\sigma(t)$, the effect resulting from this cause. A variation in shear strain, occurring at time t_1 will produce a corresponding effect at some time later, t , which can be expressed as:

$$\sigma(t) = G(t - t_1)\delta\gamma(t_1) \quad (1)$$

$G(t - t_1)$ is an influence function, also known as relaxation function, or relaxation modulus (with a physical significance that will be discussed later on), which is a property of the material and relates cause and effect. It is a function of the time delay between cause and effect. This influence function is a decreasing function of $(t - t_1)$, representing a “fading memory”, and is independent of the strain amplitude (Dealy, J.M. and Wissbrun, K.F., 1995).

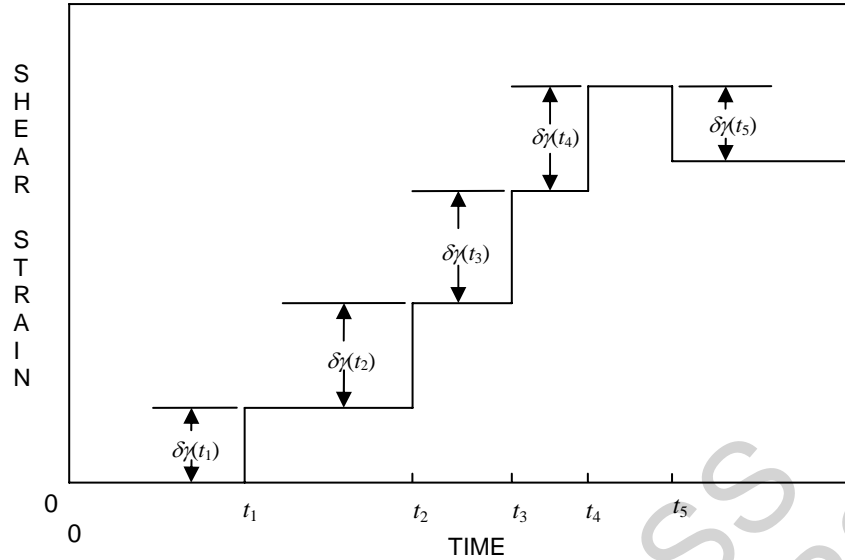


Figure 1. Series of strain increments applied on a given material (adapted from Dealy, J.M. and Wissbrun, K.F. (1995) “Melt rheology and its role in plastic processing”. Chapman & Hall, London (UK).

To calculate the stress resulting from a strain introduced at time t_2 , it is assumed that the incremental response of the material to this second strain is independent of the one previously introduced:

$$\sigma(t) = G(t - t_1)\delta\gamma(t_1) + G(t - t_2)\delta\gamma(t_2) \quad (2)$$

A series of N changes in the shear strain, each occurring at a different time (see Figure 1), will all contribute cumulatively to the stress at some later time. Thus:

$$\sigma(t) = \sum_{i=1}^N G(t - t_i)\delta\gamma(t_i) \quad (3)$$

If the change in strain occurs continuously, the sum may be replaced by an integral:

$$\sigma(t) = \int_{-\infty}^t G(t - t')d\gamma(t') \quad (4)$$

which can also be written as:

$$\sigma(t) = \int_{-\infty}^t G(t - t')\dot{\gamma}(t')dt' \quad (5)$$

The lower limit implies that all the strains that have occurred in the past will contribute to the effect at the present time, t . However, for a material with a fading memory, there will be a time prior to which all the strains which have previously occurred will have a

negligible contribution. Thus, an experiment generally starts at some time ($t = 0$) when the material is free of stresses. In this case:

$$\sigma(t) = \int_0^t G(t-t') d\gamma(t') \quad (6)$$

All these linear constitutive equations are only appropriate to describe the behavior of materials submitted to shear deformations. However, they can be generalized for any type of deformation that can be applied on the material. Thus, if the shear strain is replaced by the strain tensor, and the shear stress by the stress tensor, different forms of the Boltzmann superposition principle are obtained:

$$\sigma_{ij}(t) = \int_{-\infty}^t G(t-t') d\gamma_{ij}(t') \quad (7)$$

or

$$\sigma_{ij}(t) = \int_{-\infty}^t G(t-t') \dot{\gamma}_{ij}(t') dt' \quad (8)$$

3. Derivative Models for the Relaxation Modulus

As can be deduced from the previous description, the linear response of a given material to any type of deformation can be predicted if the relaxation modulus has been experimentally obtained. However, it is previously necessary to correlate the evolution of the linear relaxation modulus with time.

A classical approach to the description of the linear viscoelastic behavior of real materials which exhibit combined viscous and elastic properties is based upon an analogy with the response of combinations of certain mechanical elements (a spring for elasticity, and a dashpot for viscosity). Such models are, of course, idealized and purely hypothetical, and are useful for representing the behavior of real materials only to the extent that the observed response of the real material can be approximated by that of the model.

The simplest models are the Maxwell model, which can be constructed as a combination of one spring and one dashpot in series (see Figure 2), and the Voigt or Kelvin model (see Figure 3), which is represented by one spring and one dashpot in parallel.

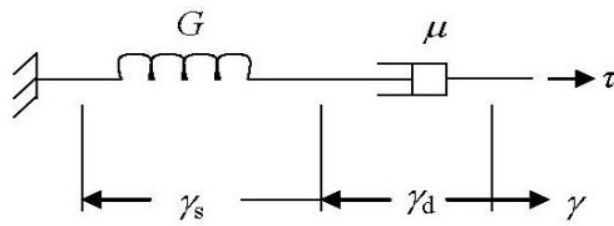


Figure 2. Mechanical analog of the Maxwell model

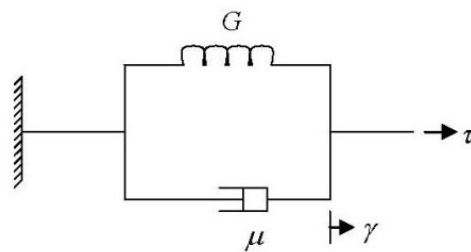


Figure 3. Mechanical analog of the Kelvin-Voigt model

For the Maxwell model, the resulting equation that describes the time dependence of the shear linear relaxation modulus is as follows:

$$G(t) = G_0 [\exp(-t / \lambda)] \tag{9}$$

and the linear constitutive equation:

$$\sigma_{ij}(t) = \int_{-\infty}^t G_0 \{ \exp[-(t-t') / \lambda] \} \dot{\gamma}_{ij}(t') dt' \tag{10}$$

It can be deduced that this model predicts an initial purely elastic response of the material, and a further exponential decay with time, reaching 37% of its initial value at a time equal to λ . The material property λ is a characteristic time constant of the material, and its called the relaxation time.

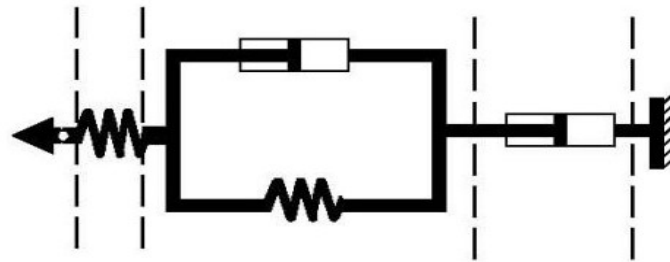


Figure 4. Mechanical analog of the Burgers model

There are a large number of models that can be formulated by combining different numbers of springs and dashpots together in diverse ways, aiming to simulate the evolution of the linear relaxation modulus of real materials. Thus, the Burgers model is a combination of a Maxwell element and a Voigt element in series (see Figure 4). However, one of the most useful for viscoelastic fluids is the generalized Maxwell model (see Figure 5), which, in essence, assumes that, instead of a single relaxation time, the fluid has a response characteristic of a whole series, or distribution, of relaxation times.

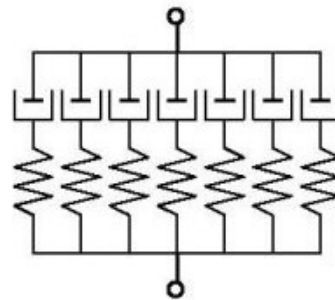


Figure 5. Mechanical analog of the generalized Maxwell model

This model can be made to fit data for many real materials if a suitable distribution of relaxation times is used. Thus, between 5 and 10 Maxwell's elements are usually sufficient to fit experimental data reasonably well. Such a set of values is called a “discrete spectrum” of relaxation times of the material. In this case, the shear relaxation modulus is represented by the following equation:

$$G(t) = \sum_{i=1}^N G_i [\exp(-t / \lambda_i)] \quad (11)$$

whilst the linear constitutive equation can be written as:

$$\sigma_{ij}(t) = \int_{-\infty}^t \sum G_k \{ \exp[-(t-t') / \lambda_k] \} \dot{\gamma}_{ij}(t') dt' \quad (12)$$

4. Relaxation Spectrum

Another approach to the quantification of the linear relaxation modulus is the use of a continuous relaxation spectrum $H(\lambda)$. Using it provides a continuous function of relaxation time, λ , rather than a discrete set. Thus, $G(t)$ can be represented in terms of a continuous function, $F(\lambda)$, as follows:

$$G(t) = \int_0^{\infty} F(\lambda) [\exp(-t/\lambda)] d\lambda \quad (13)$$

where $F(\lambda)d\lambda$ is the relaxation modulus corresponding to a relaxation time comprised between λ and $\lambda + d\lambda$.

An alternative distribution function, $H(\lambda)$, may be used in place of $F(\lambda)$, defined as:

$$H(\lambda) = \lambda F(\lambda) \quad (14)$$

and

$$H d \ln(\lambda) = F d \lambda \quad (15)$$

The relaxation modulus is now defined as:

$$G(t) = \int_{-\infty}^{\infty} H(\lambda) [\exp(-t/\lambda)] d(\ln \lambda) \quad (16)$$

There are several methods to determine the linear relaxation spectrum of viscoelastic materials from experimental data of different linear viscoelasticity functions. Consequently, it is necessary to establish the usual experimental tests for the material linear viscoelasticity characterization, and to define the corresponding linear viscoelasticity functions that are derived from those tests.

5. Small Strain Material Functions

A number of small strain experiments are used in rheology. Some of the more common techniques are stress relaxation, creep, and sinusoidal oscillations. In the linear viscoelastic region, all small strain experiments must be related to one another through $G(t)$, or through $H(\lambda)$. Different experimental methods are used because they may be more convenient or better suited for a particular material or because they provide data over a particular time range. Furthermore, it is often not easy to transform results from one type of linear viscoelastic experiment to another, and, consequently, several functions are often measured.

-
-
-

TO ACCESS ALL THE 25 PAGES OF THIS CHAPTER,
Visit: <http://www.eolss.net/Eolss-sampleAllChapter.aspx>

Bibliography

Barnes, H.A., Hutton, J.F. and Walters, K. (1989) "An introduction to rheology". Elsevier, Amsterdam (Holland). [A very popular introductory text on Rheology].

Barnes, H.A. (2000) "A handbook of elementary Rheology". Institute of Non-Newtonian Fluid Mechanics-University of Wales, Aberystwyth (Wales, UK). [General and relevant text book for a chapter on linear viscoelasticity].

Dealy, J.M. and Wissbrun, K.F. (1995) "Melt rheology and its role in plastic processing". Chapman & Hall, London (UK). [General and relevant text book for a chapter on linear viscoelasticity].

Ferry, J.D. (1980) "Viscoelastic properties of polymers". John Wiley & Sons, New York (USA). [General and relevant text book for a chapter on linear viscoelasticity].

Macosko, C. W. (1994) "Rheology principles, measurements and applications", VCH Publishers, New York (USA). [General and relevant text book for a chapter on linear viscoelasticity]

Madiedo, J.M. and Gallegos, C. (1997) "Rheological characterization of oil-in-water emulsions by means of relaxation and retardation spectra". *Recent Res. Devel. In Oil Chemistry*, **1**, 79-90. [Basic review on main calculation methods of relaxation and retardation spectra].

Mezger, T. (2006) "The Rheology handbook", Vincentz Network, Hannover (Germany). [An engineering textbook on rheology with detailed advice for experimental rheology].

Moreno, R. (2005) "Reología de suspensiones cerámicas". CSIC, Madrid (Spain). [A basic text book concerning rheology and physico-chemical properties of ceramic suspensions]

Riande, E. (2004) "Reología de polímeros fundidos y disoluciones" in *Ciencia y Tecnología de Materiales Poliméricos, Vol. 1*, eds. L. Garrido, L.M. Ibarra, and C. Marco, Instituto de Ciencia y Tecnología de Polímeros-CSIC, Madrid (Spain). [A chapter on linear viscoelasticity of polymers included in a general text book on polymer science and technology].

Tanner, R.I. (1985). "Engineering Rheology" Clarendon Press, Oxford (UK). [General and relevant text book for a chapter on linear viscoelasticity].

Tshoegl, N.W. (1989) "The phenomenological theory of linear viscoelastic behavior". Springer Verlag, Berlin (Germany). [General and relevant text book for a chapter on linear viscoelasticity].

Biographical Sketches

Crispulo Gallegos is Professor of Chemical Engineering and Chair at the University of Huelva (Spain). He received his PhD from the University of Seville in 1982. From 1985-1997 he was Professor of Chemical Engineering at the University of Seville (Spain). He has also been Visiting Professor at several universities, including the University of Cambridge (UK) and Université Laval (Canada). His research interests lie in rheology, microstructure and processing of complex fluids. Professor Gallegos is the author of more than 200 papers in scientific journals and books, and author of more than 200 contributions to international and national conferences. He is co-inventor in 8 patents. He is member of the Editorial Boards of different scientific journals. Dr. Gallegos has been Scientific Coordinator of the Food Technology Area of the National Agency for Evaluation and Prospective of the Spanish Ministry

for Science and Technology (2001-2004). Since 2009, he is President of the European Society of Rheology.

Francisco J. Martínez Boza is Professor of Chemical Engineering at the University of Huelva (Spain). He received his PhD from the University of Seville in 1996. From 1996-2001 he was Assistant Professor at the University of Huelva. His research interests lie in high-pressure rheology and processing of complex materials such as bituminous mixtures, synthetic binders, heavy fuels, lubricants, etc. Researcher in more than 25 public and private research projects, he is author of more than 35 papers in scientific journals and books, more than 40 contributions to national and international conferences, and co-inventor in 4 patents. Prof. Martínez is a member of the “Real Sociedad Española de Física y Química” and the Spanish Group of Rheology. He was a member of the Organizing Committee of the meeting “Eurorheo 2002-Joint Meeting of British, Italian, Portuguese, and Spanish Rheologists”, and co-editor of the book “Progress in Rheology: Theory and Applications”.

UNESCO - EOLSS
SAMPLE CHAPTERS