TIME-DEPENDENT BEHAVIOR OF SOLID POLYMERS

I. Emri and M. Gergesova

Center for Experimental Mechanics, University of Ljubljana, Ljubljana, Slovenia, and Institute for Sustainable Innovative Technologies, Ljubljana, Slovenia

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Summary

The mechanical properties of solid polymeric materials quite generally depend on time, i.e., on whether they are deformed rapidly or slowly. The time dependence is often remarkably large. The complete description of the mechanical properties of a polymeric material commonly requires that they be traced through 10, 15, or even 20 decades of time. The class of polymeric materials referred to as thermorheologically and/or piezorheologically simple materials allows use of the superposition of the effects of time and temperature and/or time and pressure in such materials as a convenient means for extending the experimental time scale.

The chapter reviews the experimental techniques and the mathematical formalism needed for the characterization and modeling of the time-dependent mechanical material functions, discusses limitations of the existing theories (models), and presents some latest developments in the mathematical modeling of viscoelastic material functions.

1. Introduction

Solid polymers and their macro- and nano-composites exhibit time-dependent mechanical properties that can profoundly affect the functionality and durability of polymer products. The degree of change in the mechanical properties of polymeric materials over time depends on many factors. (Time-dependent changes of the material's mechanical properties caused by chemical processes will not be discussed in this chapter.) These are primarily the temperature, pressure, humidity, and stress conditions to which the material is subjected during its manufacture and during its application. Therefore, processing parameters, like pressure and temperature, play an important role in determining the quality of parts made by injection molding, compression molding, extrusion, etc. Unsuitable processing conditions may cause parts to warp or crack. These phenomena can occur in manufactured articles even in the absence of any mechanical loading, in particular, in the presence of high-modulus fillers. Explosions (detonations) represent special cases entailing extremely high temperatures and pressures.

The mechanical behavior of polymeric materials is generally characterized in terms of their time-dependent properties in shear or in simple tension. The time dependence of their bulk properties is almost universally neglected. The effect of temperature on the shear and tensile properties of polymeric materials has been fairly well understood since about the forties of the last century. By contrast, little effort went into the determination of their time-dependent bulk properties and – after initial years of activity – research on the effect of pressure lay effectively dormant. This was probably due mainly to the

difficulty of making precise measurements at rather small volume deformations. The materials used in current applications simply did not appear to require a deeper understanding of the time dependence of their bulk properties and of the effect of pressure on their time-dependent shear properties to warrant exerting the exacting effort required. This situation has now changed. The demand for sustainable development (Sustainable development aims at preserving, for the benefit of future generations, the environment and the natural resources culled from it without lowering currently excepted standards of living.) requires optimization of the functional and mechanical properties of new multi-component systems such as composite and hybrid materials, structural elements, and entire structures. Optimization of material use requires a much deeper understanding of the effect that temperature and pressure exert on the time dependence of the bulk as well as the shear properties of the constituents of these materials than is currently available.

Since about the 1980s there have been some highly significant changes in what needs to and what can be achieved in characterizing materials with time-dependent properties, notably polymeric materials. On the one hand there has been a tremendous increase in the use and variety of polymer-based materials such as multicomponent materials (e.g., macro- and nano-composites and hybrid materials), multiphase (multidispersion) materials (e.g., block and graft copolymers, and polyblends), as well as semi-crystalline engineering materials, all of which require new or improved methods of characterization. On the other hand, there have been notable advances in the availability and sophistication of state-of-the-art sensors, and of methods of data acquisition and manipulation. Characterization of solid polymeric materials in an efficient and easily applied manner is now possible.

1.1. Time Dependence

Why should we be concerned about time-dependence? Simply put: the mechanical properties (and many other physical properties: dielectric, optical, etc.) of *ALL* materials are time-dependent, i.e., they vary with time in response to an applied load or deformation. This phenomenon is simply a consequence of the Second Law of Thermodynamics according to which a portion of the imparted energy of deformation is always dissipated as heat by viscous forces even while the rest may be stored elastically. The dissipation is neither instantaneous nor infinitely slow and is therefore a *rate process*. It is this that renders the physical properties time-dependent. Time-dependent behavior may be virtually *purely elastic* (no dissipation) to virtually *purely viscous* (instantaneous dissipation), or it may be anything in-between. The behavior of polymeric materials typically falls between the extremes and is therefore *viscoelastic*. The behavior may be expressed suitably by the *Deborah number*, De, the ratio of the material time scale, ξ_{mat}, on which molecular rearrangements take place, to the experimental time scale, t_{exp},

$$De = \xi_{mat}/t_{exp} .$$ (1)

For a purely elastic material, $De = \infty$, for a purely viscous one, $De = 0$, and for a viscoelastic material, $De \cong 1$. Viscoelastic behavior is thus characterized by material functions of time – or, equivalently, of frequency – in addition to certain material constants.

1.2. Rheodictic and Arrheodictic Behavior

An important fundamental distinction exists in polymeric materials between *rheodictic* (from the Greek "rheos", a flow, and "deiktikos", to be able to show) and *arrheodictic* behavior. The first refers to a material that is capable of displaying *steady-state flow*, i.e., can deform (in theory) indefinitely. Typically, uncross-linked polymers and polymer melts are rheodictic materials. Conversely, an arrheodictic material is one that cannot exhibit steady-state flow. Cross-linked rubbers are typically arrheodictic materials. In these the cross-links between the polymer chains prohibit indefinite deformation.

1.3. Time-Dependent Response

A mathematical expression embodying the manner in which a material responds to an applied excitation is called a *response function*. Response functions fall into two main groups. Those that are strain-induced, i.e., arise from the imposition of a strain or a rate of strain display relaxation behavior because the stress that they evoke relaxes with time. Those that are stress-induced, i.e., arise from the imposition of a stress or a rate of stress display retardation behavior because the strain they produce is retarded, i.e., it reaches its final value only after an appropriate time. The response to an excitation is linear when it obeys two conditions. These are: first, that an increase in the excitation increases the response by the same factor. This is stress-strain linearity. Second, a sequence of excitations imposed at different times must act independently. This is time dependence linearity. It is also referred to as time-shift invariance because, if it is obeyed, a shift in the excitation along the time (or frequency) scale shifts the response on the same scale by the identical amount without changing it in any other manner.

Of the time-dependent linear viscoelastic response functions we consider primarily those that arise in response to the imposition of a unit step function, $h(t)$ or in response the imposition of a unit slope function, $p(t)$, of time. (The unit step function restricts to positive values the values of the function it multiplies. The function $a \cdot h(t)$ represents a step of height a imposed at $t = 0$. The slope function, $p(t) = t \cdot h(t)$, restricts to positive values the simple proportionality to t. The function $a \cdot p(t)$ is a straight line of slope $a = \tan \alpha$. The imposition of a slope excitation is also called a start-up experiment.) The former, i.e., $G(t)$, $J(t)$, $E(t)$, $D(t)$, $K(t)$, $B(t)$, $\mu(t)$, etc., are referred to as step responses while the latter, i.e., $\eta(t)$, $\phi(t)$, $\xi(t)$, $\beta(t)$, $\zeta(t)$, etc., may be referred to as slope responses. Both are also referred to as transient responses, although this term is sometimes reserved for the step responses.

When polymers are exposed to an external load their responses typically consist of an essential time-dependent part, the viscoelastic function, and a time-independent part, the viscoelastic constant or constants. The latter may, or may not, be absent, depending on the particular response function under consideration. Since both the viscoelastic functions and the viscoelastic constants represent properties of the material whose mechanical properties they describe, they are material functions and/or material constants.

We note that, just as any elastic material constant can be expressed in terms of any two others, any linear viscoelastic transient response function can be expressed in terms of two other transient functions in the same group, and any dynamic response function can likewise be expressed in terms of two other dynamic functions taken from the same group. Converting a dynamic into a transient function is another matter. As we shall demonstrate, all these tasks are most easily carried out with the help of line spectra. Section 3 shows how this can be done.

1.3.1. Viscoelastic Functions

The viscoelastic functions are distributions of *relaxation times* (more correctly, distributions of moduli on relaxation time) in response to the imposition of a strain excitation, or distributions of *retardation times* (more correctly, distributions of compliances on retardation time) if the behavior is prompted by the imposition of a stress. In accordance with general practice, we denote both the relaxation and the retardation time by the common symbol, λ. (In the literature it is more common to use symbol τ instead of λ to denote the relaxation and the retardation times, however we have reserved τ to denote shear stresses) The context almost always makes it clear just which meaning is implied. The distributions of response times are commonly referred to as *spectral functions* or simply as *spectra*.

1.3.2. Viscoelastic Constants

In shear, the viscoelastic constants are G_e, G_g on the one hand, and J_e, J_g and J_e^0, ϕ_f on the other. The subscripts "e" and "g" signify, respectively, the equilibrium and the glassy (i.e., instantaneous) shear modulus or shear compliance. In a rheodictic material J_e^0 is the steady-state shear compliance while ϕ_f is the steady-state shear fluidity, the reciprocal of the steady-state shear viscosity, η_f, the subscript "f" referring to the steady-state. In bulk, we have K_e, K_g and B_e, B_g the equilibrium and the glassy bulk modulus and bulk compliance, respectively. There is no steady-state bulk compliance or steady-state bulk fluidity because a rheodictic material cannot show steady-state flow in a bulk deformation. The same observation applies to the time-dependent Poisson's ratio.

Analogous symbols denote the corresponding viscoelastic constants for the derived response functions. Thus, for example, E_e is the equilibrium tensile modulus, υ_g is the glassy Poisson's ratio, and ζ_f is the steady-state elongational viscosity.

2. Rheological Models

It is important to realize that force is a secondary (derived) physical quantity which was in the past introduced intuitively. In addition to forces generated by the gravitational potentials we have forces resulting from the interaction of matter. Refraining to the linear theory we may intuitively define three "types" of forces: i) forces proportional to the displacement, $F = k_1 \cdot x$; ii) forces proportional to the velocity, $F = k_2 \cdot \dot{x}$; and iii) forces proportional to the acceleration, $F = k_3 \cdot \ddot{x}$. It is easy to see that the last equation represents the second Newton's Law, when $k_3 = m$. In the linear theory of viscoelasticity we usually neglect the inertial effects; therefore, we will limit our discussion to the first two rheological elements. They are commonly represented as Hookean spring and Newtonian dashpot, shown in Figure 1. We have replaced the force, F, with the stress, σ, and let $k_1 = E$, and $k_2 = \eta$, where E and η are the Young's (Thomas Young, 1775-1829, English physicist and physician) modulus and the Newtonian viscosity, respectively. Equivalently we need to replace the displacement, x, with the strain, ε, and the velocity, $\dot{x}$, with the strain-rate, $\dot{\varepsilon}$.

$$\sigma(t) = E \cdot \varepsilon(t) \qquad\qquad \sigma(t) = \eta \cdot \dot{\varepsilon}(t)$$
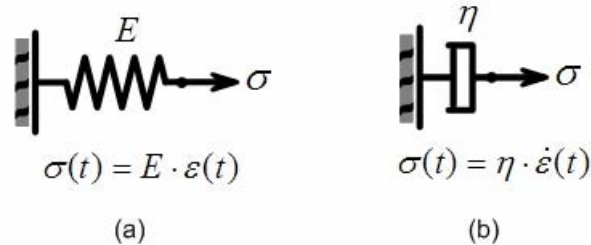
(a)   (b)

Figure 1. Basic rheological elements: a) Hookean spring, and b) Newtonian dashpot

By doing this we find for the Hookean spring,

$$\sigma(t) = E \cdot \varepsilon(t), \tag{2}$$

and for the Newtonian dashpot

$$\sigma(t) = \eta \cdot \dot{\varepsilon}(t). \tag{3}$$

We combine basic rheological elements to model more complex behavior. When elements are placed in parallel then both elements are exposed to the same strain, and stresses may be added, whereas when they are placed in series then both elements are exposed to the same stress and the strains should be added.

2.1. The Maxwell and Voigt Models

Combining the two basic elements in series and/or in parallel we can construct different complex rheological models. Among those, Maxwell and Voigt models are the simplest; this is why we often call them rheological units. They are shown in Figure 2.
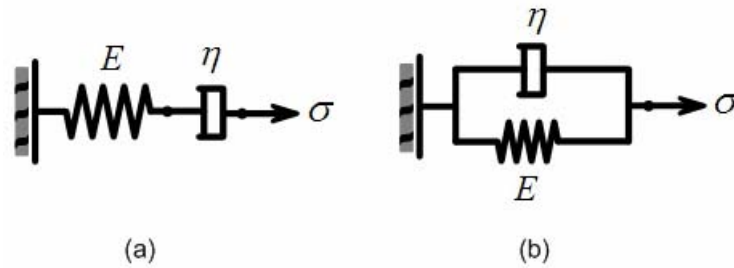
Figure 2. Basic rheological models: a) Maxwell model, and b) Voigt model

The Maxwell Model

A series of combination of a spring and a dashpot is called a Maxwell model, Figure 2a. Since the same stress acts through both elements of the model, and the strains are additive, we have

$$\dot{\varepsilon}(t) = \frac{\dot{\sigma}(t)}{E} + \frac{\sigma(t)}{\eta}. \tag{4}$$

This expression, which interrelates the stress, the strain, and the rate of strain, is the constitutive equation for the Maxwell unit. Note that it contains time derivatives, so that a simple constant of proportionally between stress and strain – must be broadened to account for this more complicated behavior. One may define several different modules appropriate for various types of loading (excitations). The relaxation moduli, $G(t)$ and $E(t)$, and the creep compliance, $J(t)$ and $D(t)$, mentioned earlier are just two examples. It is usually not difficult to obtain these various moduli from the governing constitutive equation by solving it as an ordinary differential equation subject to the appropriate boundary conditions. In a stress relaxation test, for instance, one has $\varepsilon(t) = \varepsilon_0 h(t)$, and $\dot{\varepsilon}(t) = 0$ for $t > 0$. In this case Eq. (4) becomes,

$$\frac{1}{E}\frac{d\sigma}{dt} = -\frac{\sigma}{\eta}, \tag{5}$$

and after integration,

$$\sigma(t) = \varepsilon_0 E \exp(-t/\lambda_{\mathrm{M}}) = \sigma_0 \exp(-t/\lambda_{\mathrm{M}}). \tag{6}$$

Here we introduced a characteristic parameter, $\lambda_{\mathrm{M}} = \eta/E$, with units of time, termed the relaxation time. For $t = \lambda_{\mathrm{M}}$ we find,

$$\sigma(t = \lambda_{\mathrm{M}}) = \sigma_0 \exp(-1) = E/\mathrm{e} = 0.369\sigma_0, \tag{7}$$

where "e" is the base of the Napierian logarithms. The response to a step strain is shown in Figure 3a.

The relaxation modulus, $E(t)$, may be obtained from Eq. (6), noting that the initial stress is just needed to stretch the spring to a strain, ε_0. Thus,

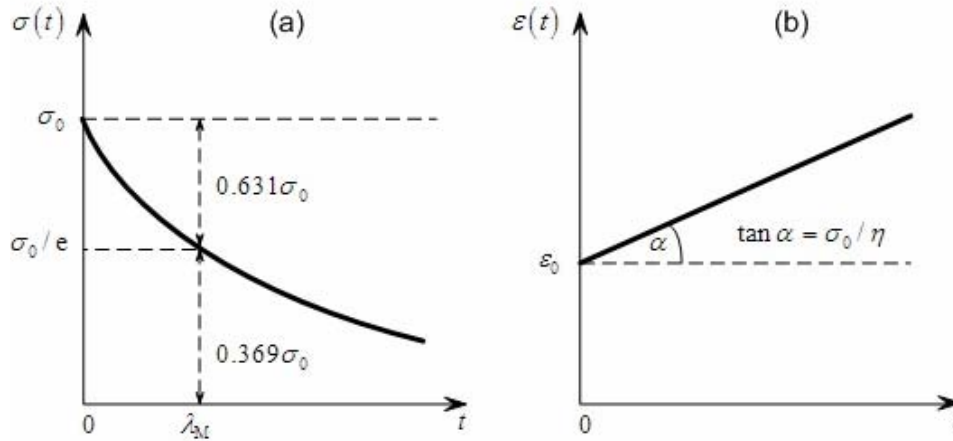$$E(t) = \frac{\sigma(t)}{\varepsilon_0} = E \exp(-t/\lambda). \tag{8}$$

Figure 3. Response of a Maxwell model to a) a step strain, and b) a step stress

By letting $\sigma(t) = \sigma_0 h(t)$, we obtain the response of the Maxwell model to a step stress, shown in Figure 3b. In this case Eq. (4) reduces to,

$d\varepsilon = \dfrac{\sigma_0}{\eta} dt$, and after integration

$$\varepsilon(t) = \varepsilon_0 + \frac{\sigma_0}{\eta} t. \tag{9}$$

We find the creep compliance, $D(t)$, by dividing strain by the applied stress σ_0,

$$D(t) = \frac{\varepsilon(t)}{\sigma_0} = \frac{\varepsilon_0}{\sigma_0} + \frac{t}{\eta} = \frac{1}{E} + \frac{t}{\eta} = D + \phi \cdot t, \tag{10}$$

where the reciprocal of the viscosity, $\phi = 1/\eta$, denotes the so called *fluidity* (readiness to flow). The first term, $D = 1/E$, represents the compliance of the spring, whereas the second term, $\phi \cdot t = t/\eta$, the compliance of the dashpot. From this observation we may postulate the following very important rule: When elements are added in series their compliances may be added! Later we will use this rule to intuitively derive the creep compliances of more complex models.

The Voigt Model

In the case of the Voigt model a spring and a dashpot are connected in parallel, as shown in Figure 2b. Now the strains in both elements are the same, and the stresses are additive,

$$\sigma(t) = \eta \dot{\varepsilon}(t) + E\varepsilon(t).$$ (11)

Following the analogous procedure as previously, we may find the responses to a step strain,

$$\sigma(t) = E \cdot \varepsilon_0,$$ (12)

and a step stress with magnitude σ_0,

$$\varepsilon(t) = \frac{\sigma_0}{E}\left[1 - \exp(-t/\lambda_V)\right] = \sigma_0 D\left[1 - \exp(-t/\lambda_V)\right] = \varepsilon_\infty\left[1 - \exp(-t/\lambda_V)\right],$$

which are shown in Figure 4, where in Fugure 4a $\sigma_0 = \varepsilon_0 E$. Here $\lambda_V = \eta/E$ is again characteristic parameter with units of time, which we will call now the *retardation time*. The relaxation and retardation times are commonly called the *response times*. With ε_∞ we denote the final value of the strain at $t = \infty$. By letting $t = \lambda_V$ we find

$$\varepsilon(t = \lambda_V) = \varepsilon_\infty(1 - 1/e) = 0.631\varepsilon_\infty.$$ (13)

The corresponding relaxation modulus and creep compliance are,

$$E(t) = \frac{\sigma_0}{\varepsilon_0} = E_0 = E,$$ (14)

and

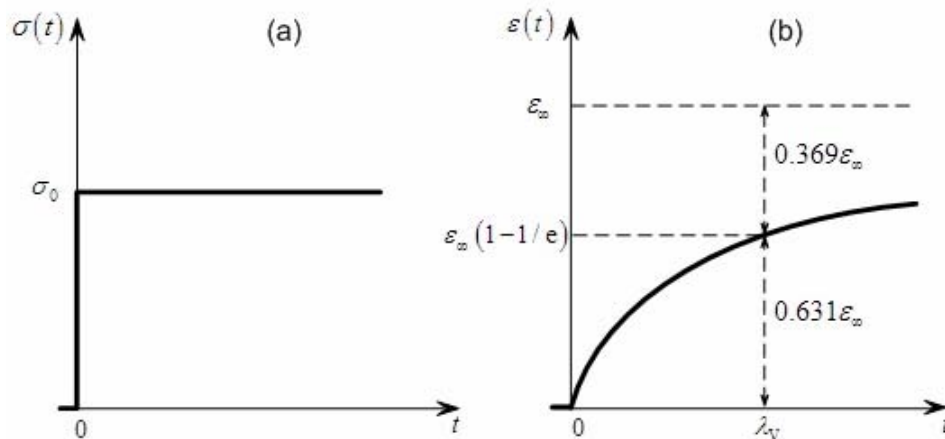$$D(t) = D\left[1 - \exp(-t/\lambda_V)\right].$$ (15)

Figure 4. Response of a Voigt model to a) a step strain, and b) a step stress

From Figure 3 and Figure 4 we may observe that Maxwell model is capable to represent a relaxation behavior, and fails in modeling the creep behavior, whereas the Voigt model does well in describing a creep behavior, and fails in modeling the relaxation process. Strictly speaking, the two rheological models are not able to model responses of real engineering materials. Placing a spring in parallel with the Maxwell unit or in series with the Voigt unit remedies this deficiency to some extend, and furnishes what is known as models of the standard linear solid (SLS).

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Bibliography

Christensen R.M. (2010). *Theory of Viscoelasticity: Second edition*, 378 pp. USA: Dover Publications, Inc. [Complete and consistent description of the linear theory of the viscoelastic behavior of materials. Relevant theoretical formulations are derived from a continuum mechanics viewpoint, followed by discussions of problem-solving techniques.]

Ferry J.D. (1980). *Viscoelastic Properties of Polymers*, 641 pp. USA: John Wiley & Sons, Inc. [Assemblage of information in the field of viscoelasticity of amorphous polymers needed for performing measurements and interpreting the results.]

Knauss W.G., Emri I., Lu H. (2008). Mechanics of Polymers: Viscoelasticity. *Springer Handbook of Experimental Solid Mechanics* (ed. W.N. Sharpe, Jr.), pp. 49–95. New York, USA: Springer Science+Business Media. [The guidance to the experimentally inclined researcher in characterization of time-dependent behavior of materials to be used in engineering design applications.]

Tschoegl N.W. (1989). *The Phenomenological Theory of Linear Viscoelastic Behavior / An Introduction*, 769 pp. Germany: Springer-Verlag. [This book provides a full exposition of the phenomenological theory of linear viscoelastic behavior described through the use of the Laplace transformation.]

Tschoegl N.W., Knauss W.G., Emri I. (2002). Poisson's Ration in Linear Viscoelasticity – A Critical Review. *Mechanics of Time-Dependent Materials* **6**, 3–51. [This paper develops the linear theory of the time- or frequency-dependent Poisson's ratio, and reviews work on its experimental determination.]

Tschoegl N.W., Knauss W.G., Emri I. (2002). The Effect of Temperature and Pressure on the Mechanical Properties of Thermo- and/or Piezorheologically Simple Polymeric Materials in Thermodynamic Equilibrium – A Critical Review. *Mechanics of Time-Dependent Materials* **6**, 53–99. [This paper presents a critical review of models proposed to describe the effect of temperature and/or pressure on time-dependent thermorheologically and/or piezorheologically simple polymeric materials.]

Wineman A.S., Rajagopal K.R. (2000). *Mechanical Response of Polymers – An Introduction*, 328 pp. Cambridge, UK: Cambridge University Press. [This book provides a thorough introduction to polymers from a mechanical engineering perspective, treating stresses and deformations in structural components made of polymers.]

Biographical Sketches

Igor Emri has made major experimental and theoretical contributions to the understanding of the effect of thermo-mechanical loading on the time-dependent behavior of polymers in the non-equilibrium solid state, and in the process of their solidification.

He is a Full Member of the Russian Academy of Engineering (1996), the Russian Academy of Natural Sciences (1997), the Slovenian Academy of Engineering (1998), the European Academy of Sciences and Arts (2006), an Associate Member of the Slovenian Academy of Sciences and Arts (2005), and Fellow of the European Academy of Sciences (2010).

Marina Gergesova is a postgraduate student at the Faculty of Mechanical Engineering, University of Ljubljana. The main subject of her research work is numerical methods of solving inverse problems in linear theory of viscoelasticity.