3 Continuum Theories for the Viscoelasticity of Flexible Homogeneous Polymeric Liquids

3.1 Introduction

There are two primary reasons for seeking a precise mathematical description of the constitutive equations for viscoelastic fluids, which relate the state of stress to the state of deformation or deformation history. The first reason is that the constitutive equations are needed to predict the rheological behavior of viscoelastic fluids for a given flow field. The second reason is that constitutive equations are needed to solve the equations of motion (momentum balance equations), energy balance equations, and/or mass balance equations in order to describe the velocity, stress, temperature, and/or concentration profiles in a given flow field that is often encountered in polymer processing operations. There are two approaches to developing constitutive equations for viscoelastic fluids: one is a continuum (phenomenological) approach and the other is a molecular approach. Depending upon the chemical structure of a polymer (e.g., flexible homopolymer, rigid rodlike polymer, microphase-separated block copolymer, segmented multicomponent polymers, highly filled polymer, miscible polymer blend, immiscible polymer blend), one may take a different approach to the formulation of the constitutive equation. In this chapter we present some representative constitutive equations for flexible, homogeneous viscoelastic liquids that have been formulated on the basis of the phenomenological approach. In the next chapter we present the molecular approach to the formulation of constitutive equations for flexible, homogeneous viscoelastic fluids.

In the formulation of the constitutive equations using a phenomenological approach, emphasis is placed on the relationship between the components of stress and the components of the rate of deformation (or strain) or deformation (or strain) history, such that the responses of a fluid to a specified flow field or stress can adequately be described. The parameters appearing in a constitutive equation are supposed to represent the characteristics of the fluid under consideration. More often than not, the parameters appearing in a phenomenological constitutive equation are determined by curve fitting to experimental results. Thus phenomenological constitutive equations shed little light on the effect of the molecular parameters of the fluid under investigation to the rheological responses of the fluid.

Basically, there are three types of continuum-based constitutive equations: differential-, integral-, and rate-type. Differential-type constitutive equations are of the form that contains a time derivative (or derivatives) of either the stress tensor, the rate-of-strain tensor, or both. Integral-type constitutive equations are of the form in which the stress tensor is represented by an integral over the strain history or rate-of-strain tensor. Rate-type constitutive equations are of the form that contains neither a time derivative nor an integral, and thus the stress tensor is expressed explicitly as a function of the rate-of-strain tensor. In this chapter we present examples of all three types of phenomenological constitutive equations for viscoelastic fluids, including the material functions from each. There are monographs (Bird et al. 1987; Larson 1988; Truesdell and Noll 1965) that are devoted entirely to the formulation of various phenomenological constitutive equations for viscoelastic fluids.

3.2 Differential-Type Constitutive Equations for Viscoelastic Fluids

3.2.1 Single-Mode Differential-Type Constitutive Equations

Let us consider the simplest mechanical model, in which one spring is attached to one dashpot, as schematically shown in Figure 3.1. When a force F is acting on the spring downward at $t = 0$ (i.e., in one-dimensional flow), the stress–strain relationship for the spring (i.e., Hookean material) may be described by

$$\sigma = G\gamma \tag{3.1}$$

where σ is the stress (the force divided by the cross-sectional area), γ is the strain defined by $(L_0 - L)/L_0$, in which L_0 is the initial length of the spring (i.e., at $t = 0$) and L is its length at time t, and G is the proportionality constant, called the "elastic modulus." Conversely, the stress response of the dashpot (i.e., purely viscous

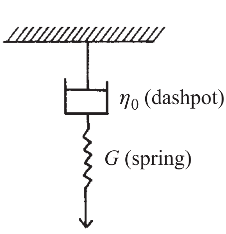

Figure 3.1 A "spring and dashpot" mechanical model for a viscoelastic fluid.

Newtonian fluid) to an applied deformation rate may be described as

$$\sigma = \eta_0 \dot{\gamma} \tag{3.2}$$

where $\dot{\gamma} = \mathrm{d}\gamma/\mathrm{d}t$ is the strain rate (or rate of strain) and η_0 is the proportional constant,[1] often referred to as "viscosity." In other words, the spring exhibits purely an elastic effect (i.e., as a Hookean solid) and the dashpot exhibits purely a viscous effect (i.e., as a viscous fluid).

Therefore, the total strain of the spring and dashpot at any time t is the sum of that due to the spring (reversible) and that due to the dashpot (irreversible). Combining Eqs. (3.1) and (3.2) and generalizing the resulting expression to a three-dimensional form (i.e., in tensor form), we obtain

$$\boldsymbol{\sigma} + \lambda_1 \frac{\partial \boldsymbol{\sigma}}{\partial t} = 2\eta_0 \mathbf{d} \tag{3.3}$$

where $\boldsymbol{\sigma}$ is the extra stress tensor and $\mathbf{d}$ is the rate-of-strain (or the rate-of-deformation) tensor (see Chapter 2). Equation (3.3) is referred to as the classical Maxwell mechanical model. Note that $\lambda_1 = \eta_0/G$ in Eq. (3.3) is a time constant, often referred to as the relaxation time. Equation (3.3) is capable of qualitatively explaining many well-known viscoelastic phenomena, such as stress relaxation following a sudden change in strain and elastic recovery following a sudden release of imposed stress.

However, Eq. (3.3) is valid only for extremely small strain rates because the spring and dashpot mechanical model is based on the premise that the Hookean material is subjected to an infinitesimally small displacement gradient. In order to overcome this limitation, Oldroyd (1950) proposed a generalization of Eq. (3.3) by replacing the partial derivative $\partial/\partial t$ with the convected derivative $\mathfrak{d}/\mathfrak{d}t$ (see Chapter 2), yielding

$$\boldsymbol{\sigma} + \lambda_1 \frac{\mathfrak{d}\boldsymbol{\sigma}}{\mathfrak{d}t} = 2\eta_0 \mathbf{d} \tag{3.4}$$

which is referred to as the convected Maxwell model. In Chapter 2 we discussed the physical interpretation of the convected derivative. In steady-state simple shear flow, whose velocity field is given by Eq. (2.11), Eq. (3.4) with the contravariant components of the convected derivative of $\boldsymbol{\sigma}$ (see Eq. (2.107)) yields (see Appendix 3A)

$$\begin{Vmatrix} \sigma^{11} & \sigma^{12} & \sigma^{13} \\ \sigma^{21} & \sigma^{22} & \sigma^{23} \\ \sigma^{31} & \sigma^{32} & \sigma^{33} \end{Vmatrix} + (-\lambda_1 \dot{\gamma}) \begin{Vmatrix} 2\sigma^{12} & \sigma^{22} & \sigma^{23} \\ \sigma^{22} & 0 & 0 \\ \sigma^{32} & 0 & 0 \end{Vmatrix} = 2\eta_0 \begin{Vmatrix} 0 & \dot{\gamma}/2 & 0 \\ \dot{\gamma}/2 & 0 & 0 \\ 0 & 0 & 0 \end{Vmatrix} \tag{3.5}$$

from which it follows

$$\eta(\dot{\gamma}) = \eta_0; \quad N_1 = 2\eta_0 \lambda_1 \dot{\gamma}^2; \quad N_2 = 0 \tag{3.6}$$

It can easily be shown that Eq. (3.4) with the covariant components of $\boldsymbol{\sigma}$ (see Eq. (2.104) for the definition of the covariant convected derivative) yields the following material