NON-NEWTONIAN FLUIDS

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Summary

This chapter reviews non-Newtonian fluids. A first classification establishes fluids as compressible and incompressible, according to their response to an externally applied pressure. Then, a general classification of incompressible materials is carried out attending their behavior under a force or a deformation. As result, in terms of ideal material response, a solid material with viscoelasticity is known as a "viscoelastic solid". In the case of liquids, there is more ambiguity so far as terminology is concerned. The terms "viscoelastic liquid", "elastic-viscous liquid", "elastic liquid" "memory fluid" are all used to describe a liquid showing viscoelastic properties. This chapter is focused on the viscous behavior of incompressible fluids under shear stress and shear rate leading to Newtonians and non-Newtonian fluids. Liquids whose behavior cannot be described on the basis of the Navier-Stokes equations are called "non-Newtonian liquids". In other words, a non-Newtonian fluid is one whose flow curve shows an apparent viscosity that depends on flow conditions such as flow geometry, shear rate, etc. and sometimes even on the kinematic history of the fluid element under consideration. Accordingly, firstly an overview of the non-Newtonian time independent behavior (i.e. corresponding to a steady state flow) has been carried out. Then, the time-dependent effects will be addressed. Non-Newtonian fluids can be phenomenologically modeled. In this sense, several mathematical expressions will be described to model non-Newtonian steady-state and time-dependent viscous flows. Finally, we have paid attention to a controversial, but with apparent engineering applications, rheological parameter: the "yield stress".

Non-Newtonian Fluids

Fluids can be firstly classified as “compressible” and “incompressible” according to their response to the externally applied pressure, i.e. whether or not the volume of an element of fluid is dependent on its pressure. A second classification of fluids may be according to their response to an applied shear stress or shear rate, leading to the so call “Newtonian” and “non-Newtonian” fluids (Chhabra and Richardson, 1999). While compressibility influences the flow characteristics of gases, liquids can normally be regarded as incompressible and their response to shear forces is the main goal of this chapter.

1. General Classification of Solids and Fluids

Regarding incompressible materials (not only fluids), they are considered in a more general classification attending their behavior under a force or a deformation. Thus, the simplest and probably the first relation between force and deformation is Hooke’ law, the force is proportional to the deformation (Barnes et al, 1993):

$$\sigma = G\gamma \qquad (1)$$

where σ is the force per unit area or stress, γ is the relative change of strain, and G is the constant of proportionality or elastic modulus, which is an intrinsic property of a solid. According to this, Hookean materials do not flow and are linearly elastic. Therefore, stress remains constant until the strain is removed and the material returns to its original shape. Hooke's law can be used to describe the behavior of many solids (steel, egg shell, dry pasta, etc.) when subjected to small strains, typically less than 0.01. However, the strain range over which the relationship is linear varies greatly, e.g., ≈2-3 for rubbers, ≈0.2-1 for most polymer gels, ≈1 for gelatin gels, ≈0.003-0.03 for many particle gels (yoghurt), and ≈0.0002 for bread dough, margarine, and cast iron. Only brittle materials such as cast iron, ceramic products, potato crisps, and several hard biscuits, are linearly elastic up to the point where they fracture (Van Vliet and Lyklema, 2005). Robert Hooke developed his "True Theory of Elasticity" in 1678 and proposed that "the power of any spring is in the same proportion with the tension thereof", i.e. a double tension leads to a double extension. This forms the basic premise behind the theory of classical (infinitesimal-strain) elasticity (Barnes et al., 1993).

At the other end of the spectrum, Isaac Newton, in the "Principia" published in 1687, proposed the following hypothesis for liquids: "The resistance which arises from the lack of slipperiness of the parts of the liquid, other things being equal, is proportional to the velocity with which the parts of the liquid are separated from one another" (Barnes et al., 1993). Thus, for a Newtonian fluid in laminar flow, Newton’s law has the following form:

$$\sigma = \mu\dot{\gamma} \qquad (2)$$

where, the shear rate, $\dot{\gamma}$, may be expressed as the velocity gradient in the direction perpendicular to that of the shear force. The force per unit area required to produce the

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motion is F/A and is denoted by σ and is proportional to the "velocity gradient" (or shear rate). The constant of proportionality, μ, is known as the coefficient of viscosity and results from the lack of slipperiness. Gases, simple organic liquids, solutions of low molecular weight inorganic salts, molten metals and salts are all Newtonian fluids.

Although Newton introduced these ideas, it was not until the nineteenth century that Navier and Stokes independently developed a consistent three-dimensional theory for what is now called a Newtonian viscous liquid (Barnes et al., 1993). The governing equations for such a fluid are called the Navier-Stokes equations. Moreover, a Newtonian fluid possesses a constant viscosity and it also satisfies the complete Navier-Stokes equations. Thus, for instance, the well-known Boger fluids display constant shear viscosity but, also, normal stress during flow (Boger, 1977; Prilutski et al., 1983). For that reason, they are considered as non-Newtonian fluids.

As a result, two limiting elastic and viscous behaviors can be considered in terms of the laws of Hooke and Newton. Both of them are linear laws, which assume direct proportionality between stress and strain, or strain rate, whatever the stress. However, phenomenologically, it is possible to provide a wider classification of materials according their rheological behavior. As a starting point, we will first consider ideally viscous and ideally elastic behavior (Figure 1). However, the range of stress over which materials behave linearly is invariably limited. In other words, material properties such as rigidity modulus and viscosity can change with the applied stress. The change can occur either instantaneously or over a long period of time, and it can appear as either an increase or a decrease of the material parameter.

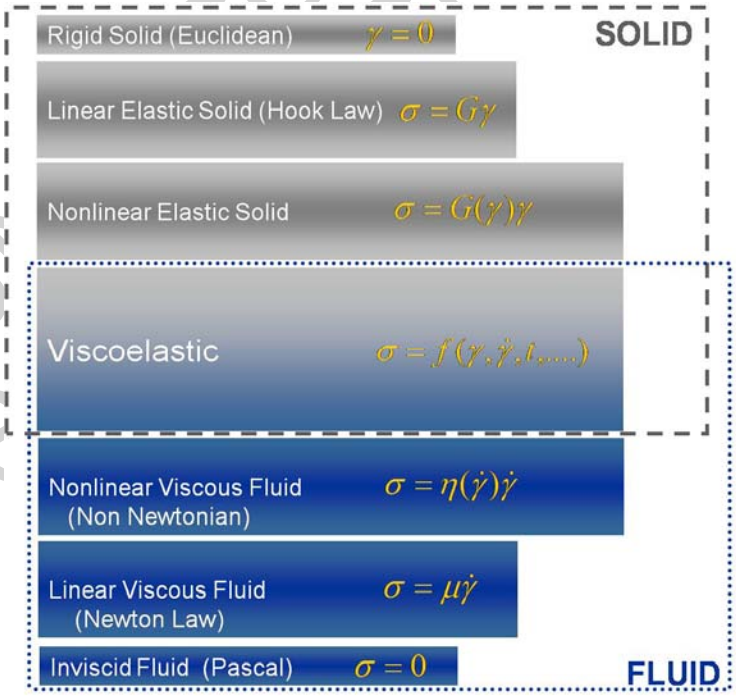

Figure 1. Material classification in simple shear (adapted from Darby, 1976)

In that sense, material properties often depend on strain or strain rate (non-linear

behavior). Moreover, the properties of a material may depend on the deformation time, resulting in non-equilibrium behavior. As result, for many materials the effect of a stress or strain generally consists of a partly viscous contribution and a partly elastic one; they are viscoelastic. The ratio between these two contributions mostly depends on the speed of deformation. A portion of the total classification spectrum is shown in Figure 1.
Moreover, a given material can behave like a solid or a liquid depending on the time scale of the deformation process. Then, it will be possible to include a given material in more than one of these classifications depending on the experimental conditions. The scaling of time in rheology is achieved by means of the "Deborah number", which was defined by Professor Marcus Reiner as follows (Barnes et al., 1993):

$$De = \frac{\tau_{\text{rel}}}{t_{\text{obs}}} \qquad (3)$$

where t_{obs} is a characteristic time of the deformation process being observed and τ_{rel} is a characteristic time of the material. The rheological behavior of materials with one single relaxation time can be classified according to their Deborah numbers: purely elastic or solid behavior when De is very high, purely viscous or liquid behavior when De is very low, and viscoelastic behavior for intermediate values of De. The important conclusion is that the distinction between solid and fluid behavior not only depends on an intrinsic property of the material but also on the duration of observation (Van Vliet and Lyklema, 2005).

Accordingly, a solid may be defined as a material that will not continuously change its shape when subjected to a given stress, i.e. for a given stress there will be a fixed final deformation, which may or may not be reached instantaneously on application of the stress. On the other hand, a liquid as a material that will continuously change its shape, that is, it will flow when subjected to a given stress, irrespective of the magnitude that stress.

In the same way, the term "viscoelasticity" may be used to describe behavior which falls between the classical extremes of Hookean elastic response and Newtonian viscous behavior (Figure 1). In terms of ideal material response, a solid material with viscoelasticity is invariably called a "viscoelastic solid" in the literature. In the case of liquids, there is more ambiguity so far as terminology is concerned. The terms "viscoelastic liquid", "elastic-viscous liquid", "elastic liquid" are all used to describe a liquid showing viscoelastic properties. In recent years, the term "memory fluid" has also been used in this connection. Moreover, liquids whose behavior cannot be described on the basis of the Navier-Stokes equations are called "non-Newtonian liquids". Such liquids may or may not possess viscoelastic properties. This means that all viscoelastic liquids are non-Newtonian, but not all non-Newtonian liquids are viscoelastic (Barnes et al, 1993).

Regarding its flow behavior, a non-Newtonian fluid is one whose flow curve shows an apparent viscosity, shear stress divided by shear rate, which is shear rate and, sometimes, shear time dependent. Accordingly, such materials may be conveniently grouped as follows (Chhabra and Richardson, 1999):

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- Fluids for which the rate of shear at any point is determined only by the value of the shear stress at that point at any instant; these fluids are known as "time independent", "equilibrium behavior", "purely viscous" or "inelastic" fluids.
- More complex fluids for which the relation between shear stress and shear rate depends, in addition, upon the duration of shearing and their kinematic history; they are called "time-dependent fluids" or "non-equilibrium behavior".

This chapter deals with the non-Newtonian fluid behavior, and the discussion will be limited to shear deformations. According to the previous general classification, a first study of the non-Newtonian time independent behavior (i.e. corresponding to a steady state flow) will be carried out. Then, the non-equilibrium or transient flow behavior, due to combined time and shear rate effects, will be addressed. Finally, we will pay attention to a controversial, but with engineering applications, rheological parameter, the "yield stress".

2. Steady-state Viscous Behavior

2.1. Shear Thinning/Thickening and Structured Fluids

Figure 2 shows a graphical overview of basic relationships between stress and shear rate for fluids and fluid-like materials subjected to shear deformation. In practice, a combination of these simple relationships can often be observed, particularly when the mechanical behavior is studied over a large range of shear rates or stresses.

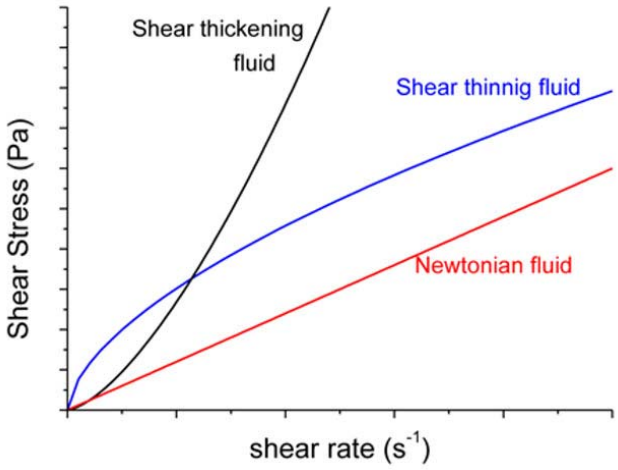

Figure 2. Steady-state flow behavior of Newtonian and non-Newtonian fluids.

The simplest relationship between shear stress and shear rate is linear (Figure 2). Fluids obeying such behavior are called Newtonian fluids. Only one material parameter, the Newtonian viscosity, μ, suffices to define fully their rheological behavior under shear. The viscosity is given by the slope of the line, and is independent of shear rate and shear time.

Regarding non-Newtonian fluids, the relationship between shear rate and stress is not

linear (Figure 2). Then, a shear rate-dependent viscosity is obtained, called apparent viscosity, $/\eta = \sigma / \dot{\gamma}$. If the fluid viscosity decreases with increasing shear rate, the observed behavior is known as shear-thinning; on the contrary, when viscosity increases a shear-thickening behavior develops (Figure 3) (Van Vliet and Lyklema, 2005; Barnes et al., 1993).

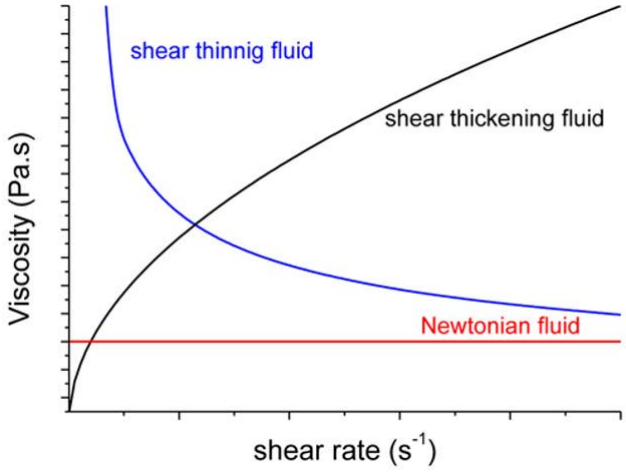

Figure 3. Plot, on linear-scale, of the steady-state viscous behavior of Newtonian and non-Newtonian fluids.

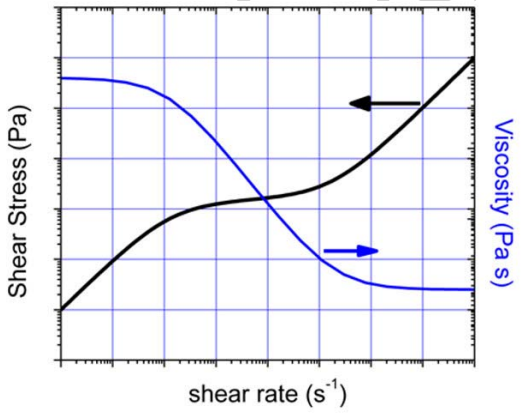

Figure 4. Log-log scale plot of the flow behavior of structured fluids.

Probably, the most common type of time-independent non-Newtonian fluid behavior observed is shear-thinning. However, most shear-thinning fluids with a complex microstructure also exhibit Newtonian behaviors at low and high shear rates. The resulting values of the apparent viscosity at very low and high shear rates are known as the zero-shear-rate-limiting viscosity, η_0, and the high-shear-rate-limiting viscosity, η_∞. Thus, the apparent viscosity of a shear-thinning fluid decreases from η_0 to η_∞, with increasing shear rate. Theses fluids are known as “structured fluids” because shear rate affects material microstructure and their viscous behavior changes according to such a microstructure. Data in a sufficiently wide range of shear rates may illustrate this complete viscous behavior (Figure 4).

Examples of structured fluids are, for instance, concentrated food emulsions, which show a marked non-Newtonian behavior. This behavior has been related to droplet deformation, flocculation or the non-Newtonian behavior of the dispersed phase (Pal, 1998). The general evolution of viscosity with shear rate (or shear stress) shows three different regions, a constant viscosity, η_0 , at low shear rates (or shear stress), a power-law decrease in viscosity, and finally a constant viscosity, η_∞ , at high shear rates, characteristic of an unflocculated system.

However, the complete structured fluid behavior, showing those three regions, is difficult to obtain, and, often, different rheometers are required to achieve this objective. An alternative procedure is the use of a master curve. For instance, the combined influence of both shear rate and disperse phase fraction (also emulsifier concentration) on viscosity was modeled by applying a superposition method, which yielded a master flow curve in which the shift factor affecting shear rate was a function of the oil weight fraction (Partal et al., 1994). This master flow curve may be fitted to any of the well-known models used in structured fluid, by including the influence of the dispersed phase volume fraction, ϕ, in the different parameters.

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Biographical Sketches

Pedro Partal is Professor of Chemical Engineering at the Chemical Engineering Department, University of Huelva. He was born in Sevilla in 1968 and received his bachelor's degree in Industrial Chemistry from University of Sevilla, Spain, in 1991. He completed his Ph.D. in 1995 with Dr. Antonio Guerrero at University of Sevilla. He was assistant professor at University of Huelva from 1994 to 2000 and Secretary of the Chemical Engineering Department of the University of Huelva (1997-2000). He became Director for Research Affairs at University of Huelva from 2000 to 2003 and Director of the R&D Centre on Food Technology of the University of Huelva, CIDERTA, in 2004. He is involved in PhD studies on "Complex Fluid Engineering" at the University of Huelva. He is external examiner of the National Evaluation and Foresight Agency (Ministry of Science and Innovation, Spain) in Food Technology (2000-2009).

His research activity is related to the Product Design and Development, with specific interest in the microstructure, rheology and processing of complex materials (food emulsions and gels, biopolymers, bioplastics, bitumen, lubricants, surfactants, etc.). In general, he is involved in topics related to fluid flow and heat transfer of non-Newtonian fluids. Researcher in at least 39 research projects sponsored by the public funds or by the industry, he is coauthor of more than 60 papers in peer reviewed journals, coauthor of a review on Food and Emulsion Rheology, coauthor of several chapters in specialized books, coeditor of a book on rheology entitled "Progress in Rheology: Theory and Applications", and author of more than 40 communications in International Conferences.

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