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Brief Introduction to Rheology

Rheology is defined as the study of flow and deformation of matter. This definition was introduced by Prof. Bingham (along with his colleague Markus Reiner), of the Lafayette College (USA) [1]. This definition was accepted by the Rheology Society by the time of its foundation in 1929. The term was inspired in the greek term *panta rhei* meaning "everything flows".

The practical importance of rheology embraces many processes from the daily life, like preparing a mayonnaise or baking a cake, or spreading an ointment or shampooing, to industrial processes like polymer processing, oil extraction, paints, etc. (figure 1). Rheology is also very important in biomedical applications like hematology (figure 1). The scientific basis of rheology is classical mechanics, Hooke's law for (classic) solids and Newton's law for (classic) liquids, however the classical definition of solid and liquid is inadequate not only for everyday purposes but for engineering ones as well. Considering the classic definition, a fluid is any substance that deforms continuously when subjected to small shearing stresses, and so mayonnaise is a solid and a glass is a liquid because it creeps very slowly (the windows in old churches, for instance, present smaller thickness on the top than on the bottom, due to creep).

Classic solids and liquids are not so common; actually, almost all materials are combinations of these two states of matter and they are called viscoelastic materials and are characterized by their viscoelasticy, which depends on not only the actual values of stresses applied to them but also on time. Depending on the ratio of a characteristic time of the material and a characteristic time of the process – called Deborah Number, named by Prof. Reiner – the material may behave essentially like a "solid" or a "liquid" [2]; for instance a ball of Silly Putty will bounce like an elastic solid if it is dropped suddenly, however it will flow if left to rest on a container. Some examples of viscoelastic materials are: foods, biofluids, cosmetics and pharmaceutical products, polymers, freshly mixed cement, hydraulic grouts and asphalts.

The main objective of rheology is the establishment of relationships between stresses, strains and time and, in a gross sense, a rheological measurement tells us how "hard" or "soft" a material is or, in other words, if it behaves more like a "solid" or a "liquid".

As the term viscoelasticity indicates, the deformation or flow of the material is characterized by its viscosity and elasticity. To measure them, different type of measurements may take place. In the case of "liquid-like" materials (fluids) – the only ones that will be considered here – different types of deformations may be applied: steady-state shear flow, oscillatory-shear flow, transient shear flow and extensional flow, briefly described by the equations in table 1. Mixed flows may also be found but will not be considered here.

Type of measurement	Governing equation	Comments
Steady state shear flow	$\eta(\dot{\gamma}) = \sigma(\dot{\gamma})/\dot{\gamma}$	η – steady state shear viscosity σ – steady state shear stress $\dot{\gamma}$ – shear rate
Dynamic shear flow	$\sigma(t) = \gamma_0[G'sin(\omega t) + G''cos(\omega t)]$	γ_0 – strain amplitude G' – storage modulus – real part of the complex modulus G* = G'+iG"; part of σ in phase with the strain G" – loss modulus – complex part of G*; part of σ lagged with the strain by δ, the phase angle
Transient shear flow	$\eta(\dot{\gamma},t) = \sigma(\dot{\gamma},t)/\dot{\gamma}$	t - time
Extensional flow	$\bar{\eta}(\dot{\varepsilon}) = \bar{\sigma}(\dot{\varepsilon})/\dot{\varepsilon}$	$\bar{\eta}$ – extensional viscosity $\dot{\varepsilon}$ – extensional strain rate $\bar{\sigma}$ – extensional stress The extensional viscosity may be time-dependent or not; in this last case, it is called steady state extensional viscosity

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Fig. 1. Examples of processes governed by rheology.

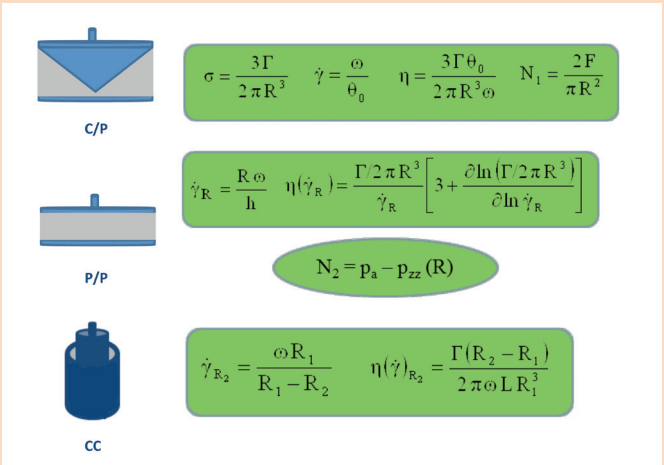

Fig. 2. Different geometries used in rotational rheometers and their governing equations.

To measure the rheological functions, different apparatus may be used, from the most simple ones, like viscosity cups and falling-ball viscosimeters, which allow for the determination of the viscosity, to the most sophisticated rheometers – of rotational, extensional and capillary types, allowing – depending on the rheometer – the determination of shear viscosities, complex viscosities, complex modulus and their components, normal stress differences (that will be talked about later on), extensional viscosities etc., as a function of rate or frequency deformations [3]. For shear flow, rotational rheometers may work with different geometries, cone/plate, plate/plate and concentric cylinders, as presented in figure 2 and measure the resulting shear stresses (and normal stress differences) when a shear deformation is imposed, or alternatively, the resulting shear deformation when shear stresses are imposed [3].

Viscoelastic fluids can be classified accordingly to the way the fluid responds to an applied stress or strain in, for time independent and non-linear behaviour, shear thinning and shear thickening, if the viscosity decreases or increases with the increase of the shear rate, respectively, or plastic, if there is a minimum shear stress needed to start the flow, called yield stress [4,5] (fresh mix cements and hydraulic grouts, for instance, are materials that present yield stress). In the linear viscoelastic regime the frequency dependent storage and loss modulus (G' and G'') are measured, revealing the mechanical behaviour of the material at rest, while the flow curve, $\eta(\gamma)$, shows how the material behaves under a continuous deformation [6]. In case of time dependent behaviour, the viscosity, at a constant shear stress, may decrease or increase with the increase of the shear rate, in which case the fluid is named thixotropic (a characteristic behaviour very important in paint applications or toothpaste, for instance) or rheopectic, respectively [7,8] – see figure 3. In extensional flow, the same kind of behaviour may be found with the fluid presenting an increase or decrease of the extensional viscosity, with the increase of the extensional stresses applied. Important to point out that a fluid may have, for instance, a shear-thinning behaviour in shear flow but present thickening behaviour in extensional flow [3].

Besides the shear rate, rheological functions – like viscosity or complex modulus – also depend on other parameters like temperature, pressure, molecular structure, etc. Temperature is a key factor in rheology; an increase in temperature leads to a decrease in viscosity that, in many situations, may follow an Arrhenius law (WLF equation may be necessary to represent the dependence of polymer viscosity) [9]. When dealing with macromolecules, which is the case with polymers and polymer based products, the molecular weight and molecular weight distribution, may also be determinant for their rheology, an increase in molecular weight leading to an increase in viscosity with an exponent that may vary with the degree of polymerization and shear rate [9].

The flow curve, $\eta(\gamma)$, shows how easily the material can be processed or shaped into a useful product. Actually the way the materials behave under flow is of major importance when

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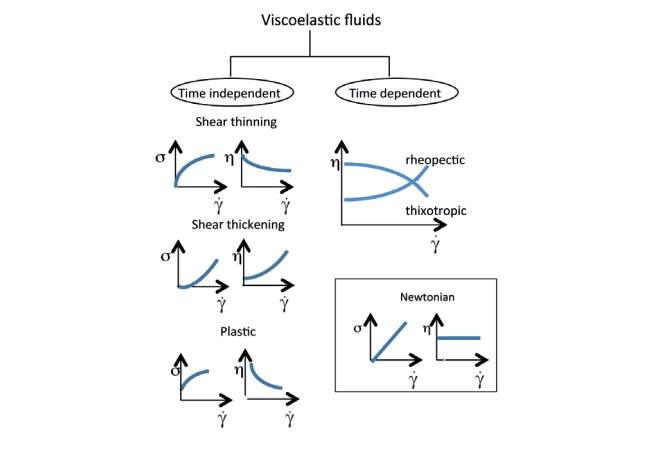

Fig 3. Classification of viscoelastic fluids according to their response under applied shear stresses. In the insert, the Newtonian behaviour (for pure viscous fluids) is presented for comparison.

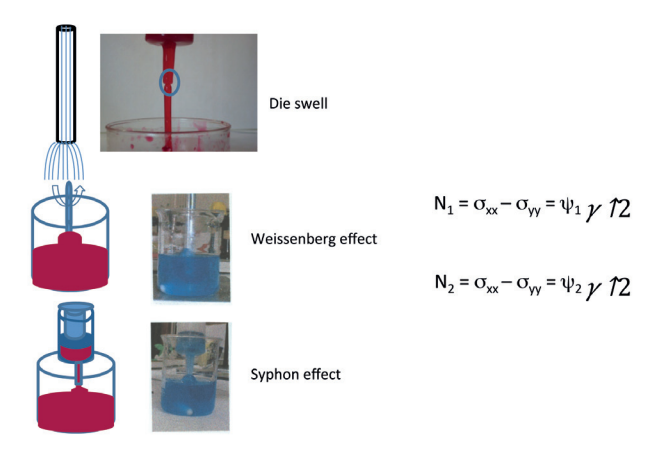

Fig. 4. Definition of first and second normal stress differences and effects observed due to the fact that these differences are not zero, as in the case of Newtonian fluids.

considering its processing; for instance, it is much easier and less expensive, to mould a material with shear thinning than shear-thickening behaviour, since an increase in viscosity will demand an increase in processing temperature.

Another rheological parameter, of major importance in some materials, namely in polymers, is the first normal stress difference, N_1, which is a consequence of the elasticity of the material and is responsible for some striking phenomena observed with polymers, the die swell (observed when a molten polymer or a polymeric solution exit a die or a capillary), the Weissenberg effect (the polymer climbs the spinning rod) and the syphon effect, just to name three (see figure 4), and have to be taken into account when processing those materials [3,9]. There is also the second normal stress difference, N_2, however, this parameter presents a significantly lower value than N_1, and is frequently neglected. The definition of the normal stress differences may be also seen in figure 4. Note that Newtonian fluids have zero normal stress differences.

Rheology is not only the measurement of rheological functions, it also deals with the establishment of constitutive equations, modeling of experimental data and numerical simulation, but these subjects are out of the scope of this brief introduction. Many references may be found for those more interested in these important aspects of rheology [10–12].

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[1] E.C. Bingham (1922) *Fluidity and Plasticity*, McGraw-Hill, New York.
[2] M. Reiner (1964) *Physics Today,* volume **17(1)**, 62.
[3] H.A. Barnes, J.F. Hutton and K. Walters (1989) *An Introduction to Rheology*, Elsevier Publishers.
[4] R.B. Bird, D. Glance, B.J. Yarusso (1982) *Rev. Chem. Eng.*, **1**, 1–70.
[5] P. Coussot (2005) *Rheometry of Pastes, Suspensions and Granular Materials*, Wiley, New York.
[6] R.G. Larson (1999) *The Structure and Rheology of Complex Fluids*, Oxford University Press.
[7] H. Barnes (1997) *J. Non-Newtonian Fluid Mech.*, **70**, 1–33.
[8] J. Mewis, N. Wagner (2009) *Advances in Colloid and Interface Science*, **147-148**, 214–227.
[9] L.E. Nielsen (1977) *Polymer Rheology*, Marcel Dekker, Inc.
[10] R. G. Owens, T.N. Phillips (2002) *Computational Rheology*, World Scientific Publishing Co.
[11] M.P. Allen, D.J. Tildesley (1988) *Computer Simulation of Liquids*, Oxford University Press.
[12] D.C. Rapaport (2004) *The Art of Molecular Dynamics Simulation*, Cambridge University Press.