Journal of Non-Newtonian Fluid Mechanics 192 (2013) 48–65

Contents lists available at SciVerse ScienceDirect

Journal of Non-Newtonian Fluid Mechanics

journal homepage: http://www.elsevier.com/locate/jnnfm

Review

Non-Newtonian viscosity in steady-state shear flows

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ARTICLE INFO

Article history:
Received 22 May 2012
Received in revised form 25 September 2012
Accepted 26 September 2012
Available online 16 November 2012

Keywords:
Non-Newtonian viscosity
Relaxation spectra
Yielding
Thixotropy
Inhomogenious flow
Shear banding

ABSTRACT

Different possible mechanisms of non-Newtonian behavior of polymeric and multi-component materials in shearing are discussed. There are two main types of the non-Newtonian media: fluids with the maximal (zero-shear-rate) Newtonian viscosity and yielding visco-plastic materials. Numerous intermediate and superimposing situations can also exist. The main concept of the non-Newtonian viscosity of such elastic fluids as polymer melts is based on definition of their "structure" as the set of relaxation modes modified by deformation. Shear-induced relaxation spectrum transformations lead to non-linearity, formation of anisotropic structures, and changes in the macromolecule entanglement topology. A general approach to quantitative description of non-Newtonian flow of polymer melts is achieved if to assume that the dominant reason of non-linear flow properties is molecular-weight distribution of polydisperse polymers with continuous flow-to rubbery transition from the side of slow relaxation modes with increasing shear rate.

The non-Newtonian viscosity of such multi-component systems as numerous suspensions, emulsions, and mixtures is characterized by transition from the flow curves with the zero-shear-rate viscosity to the yield-type behavior. The latter is the direct evidence of a spatial structure which changes in shearing. The yield stress value can be rigorously determined only for rigid structures. For soft matters, the structural breakdown/buildup processes are a time dependent (thixotropic/rheopectic) phenomenon, and the concept of yielding becomes uncertain. Nature of structures in various multi-component materials can be very different but just their existence determines a possibility of non-linear effects in shearing. A special type of the non-Newtonian flow is instability and inhomogeneity of a stream. Different forms of these phenomena (shear banding, layered flow, surface distortions, periodic oscillations, concentration separation, and movement of large structural aggregates) are known. In such situations, the "measured" non-Newtonian viscosity can appear an artifact depending on the size factor.

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http://dx.doi.org/10.1016/j.jnnfm.2012.09.015

1. Introduction

The concept of non-Newtonian flow of polymer melts and multi-component fluids (polymeric and colloid solutions as well as other dispersions) is a cornerstone of rheology to the same extent as the linear Newton law and the Navier–Stokes equations as its consequence are the base of the dynamics of viscous fluids. Meanwhile, the overwhelming majority of publications devoted to the problem of non-Newtonian flow consider a concept of some "structure" of a fluid as a key to various approximations of the non-Newtonian phenomena. However the very mechanism (or mechanisms) of the non-Newtonian shear viscosity remains disputable and requires more definite answers than intuitive references to the "structure" of polymeric or colloid multi-component fluids.

The first rheological papers were devoted to visco-plastic media which definitely have inherent structure formed by a disperse phase [1–3]. The same "structure" concept was presumed in discussing viscous properties of colloid systems and their non-Newtonian viscosity was initially called "*Structurviskosität*" [4,5]. Then polymer solutions treated like "colloid systems" were considered as structured fluids as well [6]. However majority of flexible-chain polymer melts and polymer solutions are definitely amorphous structureless fluids [7]. It was experimentally proven that "*in amorphous state the conformation of the polymer molecule is undistinguishable from that in* θ *solvent and that the Debye scattering function is valid ... for unperturbed chains ... as low as 10 A*" [8]. Surely, numerous types of specific structure formations are possible. The most evident cases are LC polymer solutions, clustering in dilute polyethylene oxide solutions [9,10], and polyelectrolyte gel formation, e.g. in poly(acrylic acid) solutions [11]. These systems demonstrate various non-Newtonian effects and the mechanisms of these effects can be different depending on a fluid microstructure. However below (in Section 2), we will discuss more simple model case of structureless polymeric fluids. For such fluids, it is necessary to search for the understanding of non-Newtonian behavior not directly related to their physical microstructure.

These preliminary arguments allows us to distinguish two principle schemes of the non-Newtonian behavior shown in Fig. 1.1: visco-plastic behavior with the yield stress, τ_Y, and a full flow curve with maximal or upper (zero-shear-rate) Newtonian viscosity, η_0. Formally, these schemes cover various main possible cases of steady state shear flow.

This paper is devoted to reviewing different possible basic situations in manifestation of the non-Newtonian steady state shear viscosity and discussion of possible mechanisms standing behind this phenomenon.

2. Flow curves of visco-elastic fluids

2.1. Viscosity and viscoelasticity

It is reasonable to suppose that flow curves observed for polymeric fluids are inherently related to their elasticity and reflect peculiarity of their relaxation properties. This might be also true for elastic colloidal systems, such as micellar colloids and emulsions.

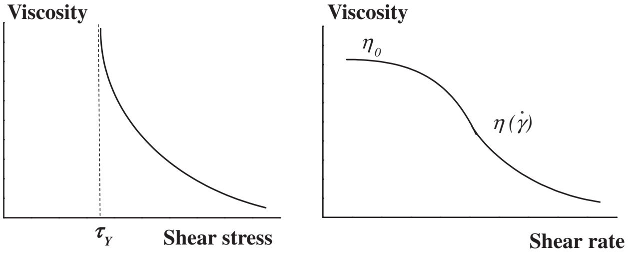

Fig. 1.1. Flow curves of viso-plastic (*left*) and non-Newtonian (*right*) fluids.

The first analysis of the correlation between viscosity and visco-elasticity was carried out by Oldroyd [12] who showed that the flow induced deformation of liquid droplets dispersed in another fluid leads to visco-elastic effects due to the action of surface forces. Much later, Kroy et al. came to the so-called "similarity rule" [13]. According to their rigorous fluid dynamic argumentation, the shear rate (non-linear) dependence of apparent viscosity, $\eta(\dot{\gamma})$, is similar to an expression for the real part of a frequency dependent of the complex viscosity, $\eta'(\omega)$:

$$\eta'(\omega) \cong \eta(\dot{\gamma}) \tag{1}$$

Besides, the following relationship was also obtained

$$\eta'(\omega) \cong \frac{\sigma_{11} - \sigma_{22}}{2\omega}, \tag{2}$$

where $(\sigma_{11} - \sigma_{22})$ is the first normal stress difference.

The last one was also obtained earlier in [14] from the different argumentation.

Similar relationships also appeared in various phenomenological theories of visco-elastic media (see, e.g. [15,16]).

The most frequently cited correlation between the apparent viscosity and the complex dynamic viscosity was formulated in [17] as the well known empirical Cox–Merz rule:

$$\eta(\dot{\gamma}) = |\eta^*|(\dot{\gamma}) \tag{3}$$

which is close to Eq. (1).

There is a lot of experimental data obtained for polymer solutions and melts which confirm the above written relationships (see for example [18–20,59–67,101–109,139–147,10,11,21,22] among many others). An attempt to give the molecular model explanation of this empirical rule is also known [23]. The latest molecular approach to the understanding of the Cox–Merz rule for polydisperse polymers was proposed in [24].

So, deformation of dispersed particles (including macromolecules) in shear flows simultaneously results in both, non-Newtonian behavior and visco-elasticity regardless the physical mechanism of elasticity, either it is surface properties or segmental movement of chain macromolecules.

These similarities can be accepted as the starting point for understanding the visco-elastic mechanism of the non-Newtonian shear flow. The decrease in the apparent viscosity should be considered as a consequence of the changes in relaxation properties of a fluid being a function of deformation rate. The decrease in the non-Newtonian viscosity with increasing deformation rate reflects the degeneration of slow relaxation processes. As a result, their input to viscous dissipation becomes lower along with the increase in the deformation rate. It corresponds to the continuous modification of a relaxation spectrum from the slow relaxation modes side.

Then this mechanism of non-Newtonian behavior can be discussed in terms of a relaxation spectrum. In the frames of the general viscoelasticity theory, the zero-shear-rate (linear) Newtonian viscosity, η_0, is expressed as the sum of dissipative losses in all relaxation processes [25]:

$$\eta_0 = \int_0^\infty \theta F_0(\theta) d\theta \tag{4}$$

where $F_0(\theta)$ is a (linear) relaxation function directly related to a relaxation spectrum.

In the transition to a non-linear region, $F_0(\theta)$ is modified by suppression of slow relaxation modes. This conception was advanced in [26,27] and is developed in the modern form in many publications by M. Wagner with coauthors (see the review [28]). The final