MIXER-TYPE RHEOMETRY

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Summary

Mixer-type rheometers belong to the category of process rheometers, and allow the possibility to extract rheological information directly from a batch or semi-batch process during and at the end of the preparation of a complex liquid-like product. Using a Couette analogy, it is shown that the torque-rotor speed data can be transformed into shear stress-shear rate curves, which are in fairly good agreement with off-line measurements obtained in conventional rheometers.

Several applications in different industrial sectors are presented in order to illustrate the interest of the mixer-type rheometry in the manufacturing of complex liquid-like products.

1. Introduction

The demand from the market place for very sophisticated products combining several functions and properties is still significantly growing. In order to properly satisfy these needs, appropriate formulations are required. Until now, formulation recipes are based on in-house know-how and experienced individuals. Efforts to integrate most of the aspects of such formulation recipes have recently been made in particular concerning process follow-up and monitoring during the preparation of formulated products using rheological measurements obtained with mixer-type viscometers or rheometers [1,2]. The approach makes direct use of the reactor in which the formulated product is elaborated. The reactor is equipped with an appropriate mixing device, whose characteristics may vary depending on the mixing requirements during the process

manufacturing, on the preparation protocols, on the nature of the phases under consideration, on the process operation mode (batch or semi-batch), and on the industrial application sector : food, cosmetic, toiletries, pharmaceutical, paint, polymer, coatings, adhesives, specialty chemicals, etc... In these industrial sectors, the formulated products are generally viscous and rheologically complex substances. Moreover, during practically the whole elaboration process, the substance into the reactor may have a complex and evolving rheological behavior. As a consequence, the possibility for *in situ* characterizing the formulated product during and at the end of its elaboration process using mixer-type rheometry constitutes a significant and interesting improvement for engineers.

Mixer-type rheometry belongs to process rheometry. The advantages for batch and semi-batch process operations of being able to determine at least the viscosity or better the viscous behavior of liquid (precursors, intermediate and final) products on-line (or in-line) during their manufacture (in other words *in situ*) are obvious :

- Time as well as effort is saved as compared to the conventional procedure, in which a representative sample has to be taken and analyzed in an off-line viscometer. This viscometer has to be carefully loaded and subsequently cleaned

- Continuous follow-up (monitor) of viscosity evolution becomes available

- In certain conditions, a control function may be introduced for eventual alteration of the viscosity (or viscosity evolution) by processing or chemical variables.

Generally a mixer-type rheometer is in fact an in-line rheometer, even if in reality and for convenience the on-line terminology is used. "In-line" means that all the fluid in the reactor is analyzed, for example with the use of a bypass loop. The desirable features of good in-line rheometer are: the representativity of the samples, the relatability (with off-line determination), the reliability and the robustness. Details concerning these features are presented in a review [3] as well as a quite complete discussion on process viscometry. However, this review doesn't discuss on the mixer-type category of process viscometers. The purpose of this chapter is to fulfill this drawback. In the first part, a theoretical development based on a Couette analogy will be presented, that allows to quantitatively analyzing the torque-rotational speed data in order to extract viscous rheograms. In the second part, several case studies will illustrate how mixer-type rheometry can be used as an interesting tool for better understanding specific product manufacturing processes.

2. Couette Analogy

The Couette analogy consists in replacing the mixing chamber of any reactor and its mixing device by a coaxial cylindrical bob rotating in a cylinder (Couette geometry). This analogy has been widely used, mostly in situations allowing to predict the power consumption in agitated vessels containing non-Newtonian viscous fluids, and in particular those obeying to the Power-law model :

$$\eta = m\dot{\gamma}^{n-1} \tag{1}$$

In which η is the viscosity, m the consistency index, n the flow index (in most cases: $n < 1$, the fluid exhibits a shear-thinning behavior), and $\dot{\gamma}$ is the rate of deformation tensor amplitude.
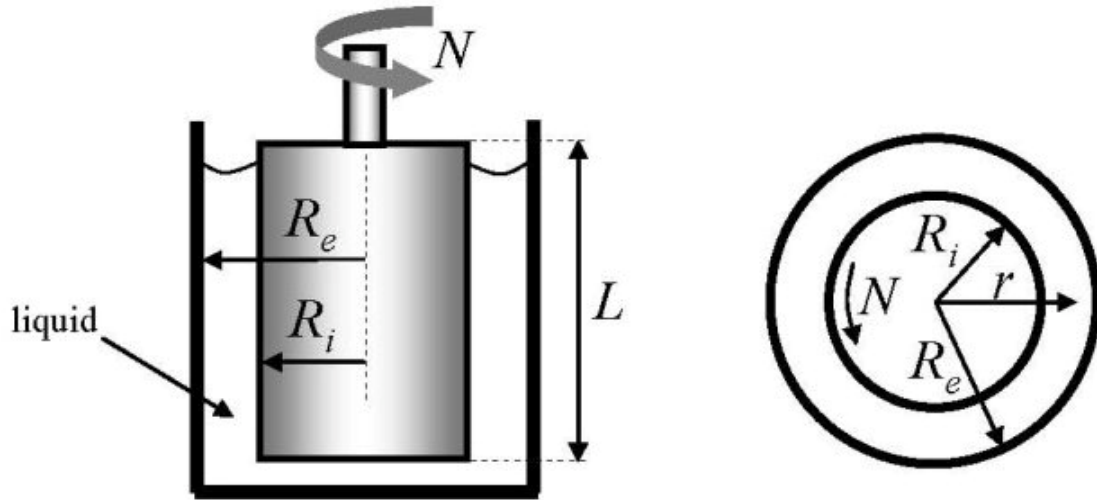

Figure 1. Couette geometry: the internal cylinder is rotating with a velocity :

$$V_{\theta}\big|_{r=R_{\mathrm{i}}} = 2\pi NR_{\mathrm{i}}$$

In Couette geometry (Figure 1), in laminar regime and neglecting the end effects, it is easy to salve the equations of change and to obtain all needed information, for instance:

- the rate of deformation (shear rate) profile :

$$\dot{\gamma}_{r\theta}(r) = -\frac{4\pi N}{n}\left(\frac{R_{\mathrm{i}}}{r}\right)^{2/n} \bigg/ \left(1-\left(\frac{R_{\mathrm{i}}}{R_{\mathrm{e}}}\right)^{2/n}\right) \qquad (2)$$

Where R_{i} and R_{e} are the radius of the internal cylinder and the one of the external one respectively, and N the angular rotational speed of the inner cylinder. $\dot{\gamma}_{r\theta}$ is the component of the rate of deformation tensor, here a negative quantity ($= -\dot{\gamma}$).

- the shear stress profile

$$\tau_{r\theta}(r) = \frac{C}{2\pi Lr^{2}} \qquad (3)$$

In which C is the transmitted torque and L the height of the inner cylinder.

The Couette analogy (see Figure 2) is based on the fact that the Couette analogue of the agitated vessel gives the same torque measurement for the same imposed rotational speed of the impeller (mixing device).
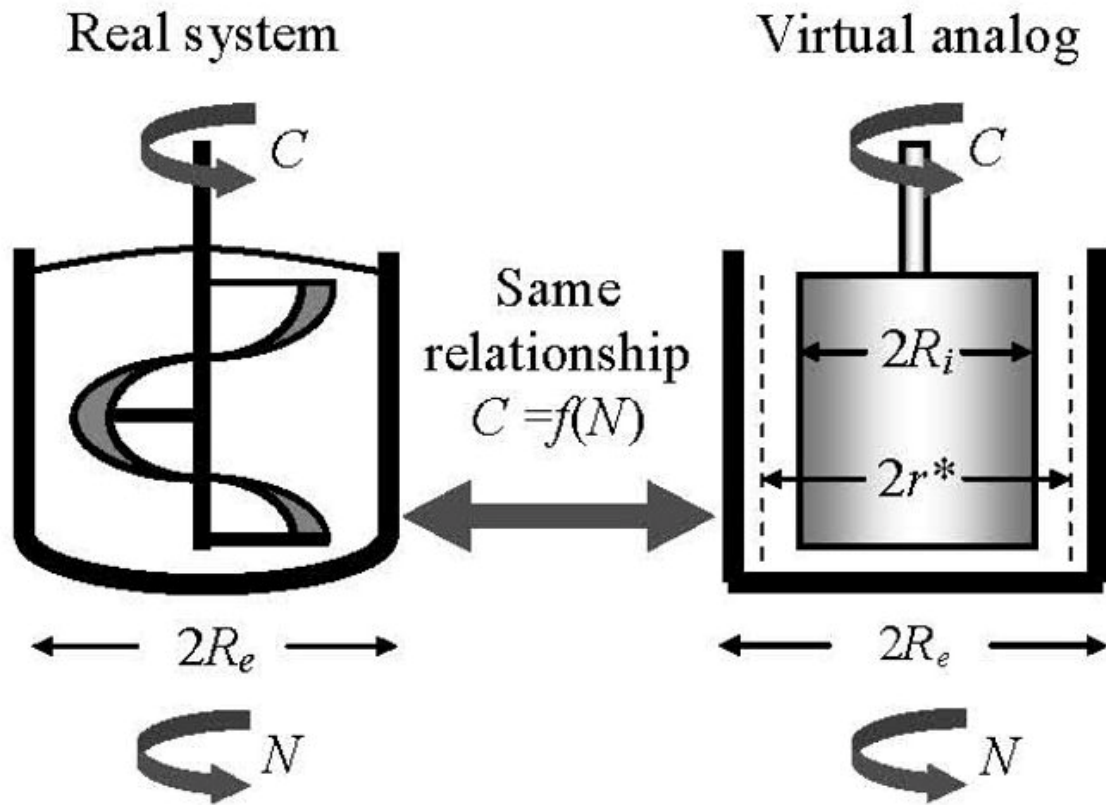
Figure 2. Principle of the Couette analogy

From Eqs. (2) and (3) and the definition of the transmitted torque:

$$C = 2\pi R_e^2 L \tau_{r\theta}\big|_{r=R_e} = 2\pi R_i^2 L \tau_{r\theta}\big|_{r=R_i} \tag{4}$$

It is easy to deduce the value of the radius of the inner cylinder for the Couette analogue of the agitated vessel (whose external radius remains R_e):

$$R_i = R_e \left/ \left(1 + \frac{4\pi N}{n} \left(\frac{2\pi m L R_e^2}{C} \right)^{1/n} \right)^{n/2} \right. \tag{5}$$

As in the case of the work by Bousmina et al. [4], who analyze batch mixer devices (internal mixers) used in the plastic industry, it has been demonstrated [5] that equation (5) is a very weak function of the power-law index n, specially for those values ranging from 1 to 0.15, which are typical values encountered in many cases of non-Newtonian shear-thinning complex fluids. As a consequence, R_i can be determined through a calibration procedure that makes use of a Newtonian fluid ($n = 1$) of known viscosity.

Furthermore, once R_i has been determined, it has been shown [5], that a position r^* in the gap exists where the shear rate $\dot{\gamma}_{r\theta}$ depends only slightly on the power-law index, in

other words on the rheology of the fluid even in the case of large gaps. This optimal position r^* in the gap can be determined either analytically or graphically (see [5] for details).

Equation (2) can then be used in the specific case of a Newtonian fluid ($n = 1$), for calculating the shear rate at the optimal position r^*, together with Eq. (3) at the same position, in order to calculate the viscosity:

$$\eta = -\frac{\tau_{r\theta}|_{r*}}{\dot{\gamma}_{r\theta}|_{r*}}$$

(6)

At the optimal position r^*, for any given fluid, equation (2) reduces to a linear relationship between the shear rate and the rotational speed of the inner cylinder N of the Couette analogue of the agitated vessel.

$$\left|\dot{\gamma}_{r\theta}(r^*)\right| = K_{\dot{\gamma}}N$$

(7)

Because N is also the rotational speed of the impeller in the real agitated vessel, $K_{\dot{\gamma}}$ is nothing but the well-known Metzner-Otto constant, K_s [6].

This is a very important result provided that, using this analysis, the Metzner-Otto constant can be *calculated* for a given impeller-vessel configuration without knowing a priori the rheology of the fluid, and without any time-consuming experimental procedure. At the same time, this analysis validates the empirical Metzner-Otto approach, which has been extensively used to determine an effective shear rate in an agitated vessel (in laminar regime and even slightly beyond) containing non-Newtonian fluids, and which is routinely recommended as a standard procedure in the mixing community.
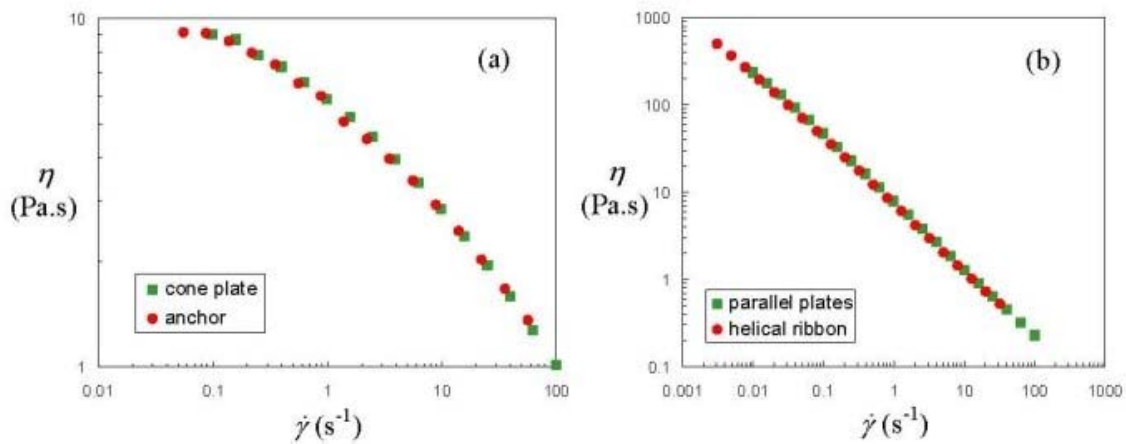

Figure 3. Viscous rheograms in conventional and "rheo-reactor" geometries at 25°C (a) aqueous solution (2% by weight) of carboxymethyl cellulose (b) salad dressing (Maille)

In the particular situation, where the conventional geometries used in rheometry

(classical Couette, double Couette, cone and plate, parallel plates) are replaced by a small size impeller-vessel configuration (the size depends on the rheometers but it can be up to 250 ml), we call it a "rheo-reactor" configuration, complete viscous rheograms can be obtained. Some examples are given in Figure 3.

For complex non-Newtonian fluids in two rheo-reactor configurations: an anchor-vessel and a helical ribbon-vessel. The viscous rheograms are compared with those obtained for the same fluids with conventional configurations and the agreement is excellent: no more than 5% error has been obtained.

If the rheometer can perform mechanical spectroscopy, it has been shown, that the Couette analogy can be transposed and conservation (G') and loss (G'') moduli can be calculated knowing the stress and the deformation γ_o in the virtual Couette geometry, at the r^* position, given by :

$$\gamma_o = 2\theta\left(\frac{R_i}{r^*}\right)^2 \bigg/ \left(1-\left(\frac{R_i}{R_e}\right)^2\right) \qquad (8)$$

Where θ is the deformation angle.

In Figure 4, the mechanical spectra for the same fluids as in Figure 3 are presented and compared with those obtained with conventional geometric, showing again very good agreement.
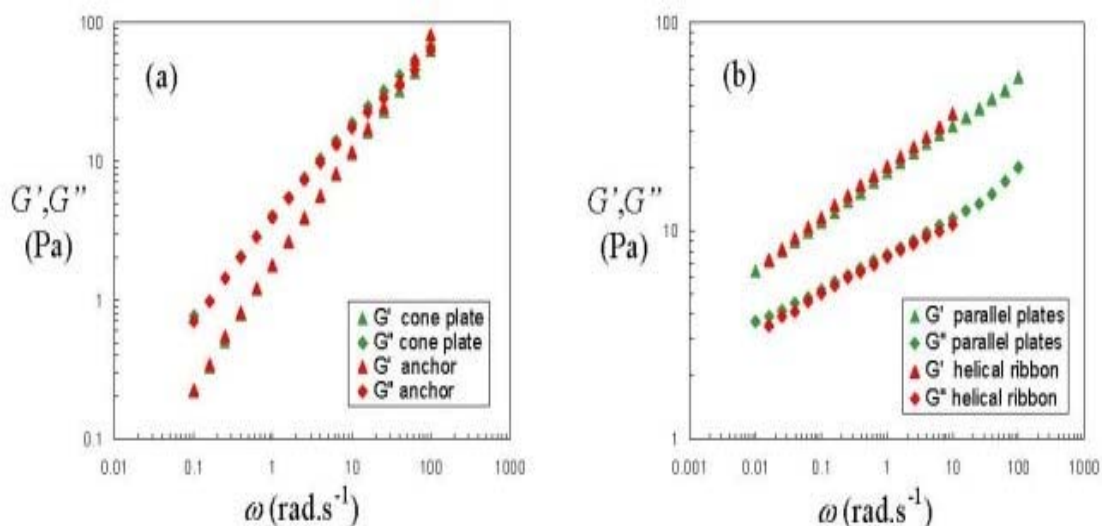

Figure 4. Mechanical spectra in conventional and "rheo-reactor" configuration at 25°C (a) aqueous solution (2% by weight) of carboxymethyl cellulose (b) salad dressing (Maille)

In fact, these rheo-reactors are much more than simple mixer-type rheometers, provided they can be used to simulate or mimic to some extent "real life" process conditions in batch or semi-batch modes under well-controlled temperature conditions.

Mixing is a very common unit operation. It can be used for mixing miscible liquids, for dispersing immiscible liquids or solids in liquids, for re-suspending solid particles that have sedimented out ... Torque measurements, in specific mixing conditions, allow to determine fundamental macroscopic quantities such as power consumption, macromixing time (t_m) and circulation time (t_c) in a stirred vessel as illustrated in Figure 5.
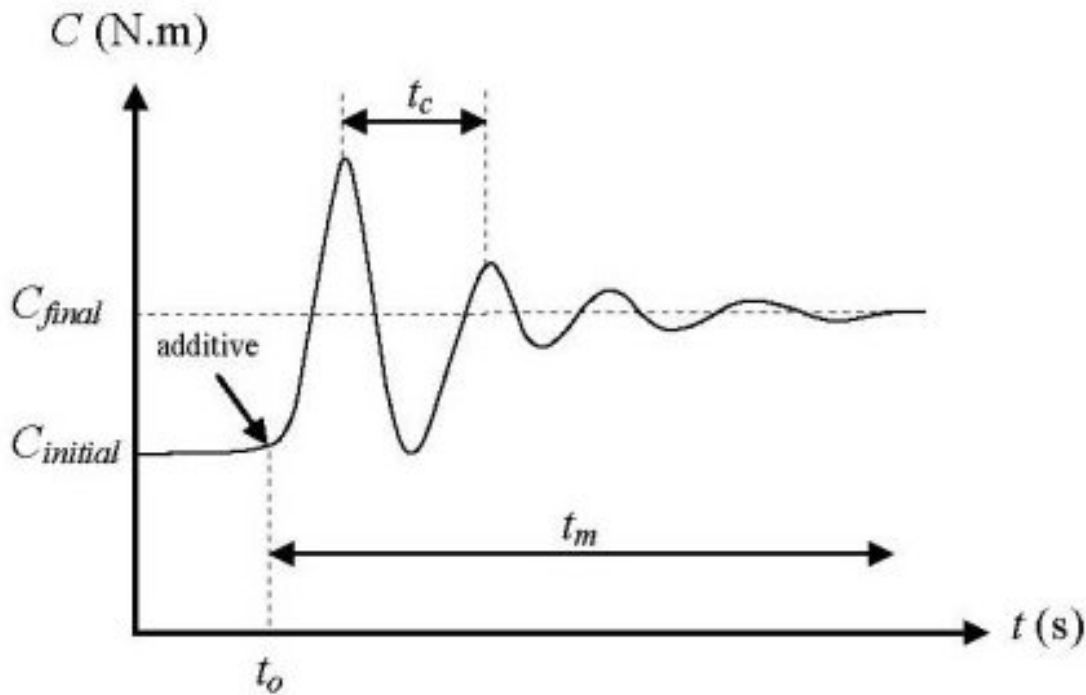

Figure 5. Macromixing and circulation times' determination: at time t_o, a viscous-modifier additive has been incorporated (the illustrated torque response may depend on the way the additive is incorporated).

Torque measurements also allow possible overloading and damage prevention to the impeller, particularly in start-up or re-homogenization conditions when the fluids are very viscous and/or elastic. In addition, torque measurements will be of paramount importance for the determination of the best conditions for the sequential incorporation of rheology-modifier additives. All these torque information are very useful for formulators as far as the definition of the preparation protocols are concerned. Furthermore, between the formulation steps, it is possible to perform in situ rheological analysis without any sampling procedure, i.e. directly into the rheo-reactor. This analysis will provide with information concerning the rheological (and/or structural) evolutions and the influence of additive incorporation conditions as well.

When the rheology-modifier additives interact with the medium, through chemical reactions, physical or physical-chemical modifications, the rheo-reactor allows performing in situ rheological monitoring. The kinetic study of the involved mechanisms requires that the kinetics of the rheological evolution is slow with respect to the experimental time (t_{exp}) needed for a rheological characterization. If F is an

appropriate rheological function to be monitored, the mutation number N_{mu} [7] defined by:

$$N_{\mathrm{mu}} = \frac{t_{\mathrm{exp}}}{F} \frac{\partial F}{\partial t} \qquad (9)$$

has to be not more than a few percent. This can however actually be checked only a posteriori.

Now, with the help of Fourier Transform Mechanical Spectroscopy (FTMS), it is possible to study relatively fast rheological kinetics over a certain frequency window and t_{exp} is determined by the fundamental frequency ω_0 through:

$$t_{\mathrm{exp}} = \frac{2k\pi}{\omega_0} \qquad (10)$$

Where k is the number of cycles per measurement. This technique allows a more precise gel point determination in gelation processes [8]. In addition, it is possible to study the influence of the additives incorporation conditions on the rheological evolution kinetics. This is particularly useful in the cases where interactions are flow- or strain- induced.

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Biographical Sketch

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