Characterisation of time-independent and time-dependent rheological behaviour simultaneously by multiple loop experimentation

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Revised: 2 October 2016 / Accepted: 6 October 2016 / Published online: 7 November 2016
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Abstract Flowable food materials express complex flow behaviour and are conventionally subjected to individual time-independent and time-dependent experiments. The present study proposes a single experiment to determine both these characteristics simultaneously in addition to determining the ‘isoviscosity’ to quantify and compare these properties by using a model food system like chickpea flour dispersion. The method employed here consists of the generation of five loops having increasing and decreasing shear-rates along with yield stress measurement in between them. The conventional rheological model like Herschel–Bulkley equation has been employed to determine the rheological properties that are affected as the number of loop increases. Though used in a model food system, the method is also expected to find applications in non-food non-Newtonian liquid systems for convenience.

Keywords Rheology · Liquid food · Method for characterisation · Chickpea batter

Introduction

Several liquid samples, including raw materials and processed foods, exhibit time-independent properties as well as time-dependent behaviour. The conventional practice is to determine these two characteristics separately from a different set of experiments. These knowledge are useful in understanding the behaviour of the material under stress

and/or deformation/flow, and over time. The applications of these properties lie in the design of processing systems and product development particularly for deciding the mode and method of transfer, selection of raw materials and appropriate processing equipment (Ravi and Bhattacharya 2004; Dattatreya et al. 2011).

The rheological properties of liquids are popularly depicted as flow behaviour, which are determined through two separate experiments, namely the time-independent and time-dependent characteristics. In the time-independent study, the characteristics of the material are determined on the assumption that they are independent of time; these properties are conventionally characterised over a range of shear-rate or shear-stress to understand how the rheological indices are affected by shear-rate/stress. The resultant data are usually subjected to fitting to empirical models like power law, Herschel–Bulkley (HB), Cross equations, etc. to obtain various rheological indices like flow behaviour index, consistency index, etc. (Barnes et al. 1989). The time-independent characterisation of the material is thus made based on these calculated values. On the other hand, the time-dependent characteristics are determined as a function of the time of shearing. The most common test include shearing at a particular shear-rate for a short time or the generation of a loop formed by the values obtained during the increasing shear-rate experiment followed by the decreasing shear-rate studies (Bhattacharya 1999). The perception of sensory texture in the mouth is also affected by the fundamental mechanical parameters of liquids and solids. The thixotropic behaviour also indicates that any disturbance of a product before and during the loading in the mouth or an instrument affect the viscosity or the perceived thickness. Hence, the question remains about the possibility of combining both the time-independent and time-dependent tests into a single unique

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test which can provide the required scientific understanding and convenience to researchers for research investigation as well as routine testing. In the loop testing, a hysteresis occurs due to the development of two non-coinciding curves in the case of a non-Newtonian fluid and the enclosed area depicts the work or energy for structural changes occurring during the short span of experimentation. The modelling of the forward and backward curves employing conventional rheological models is a possible approach that can characterise fluids in terms of measurable objective indices.

The objective of the present work is to employ a single unique experiment to determine both the time-independent and time-dependent behaviour of a model liquid sample comprising multiple loops (in addition to determining the yield stress) followed by modelling the forward and backward curves to characterise the status of the fluid undergoing shear damage and recovery.

Materials and methods

Split pulses (*dhals*) of chickpea (*Cicer arietinum*) or Bengalgram were procured from the local market followed by grinding to obtain fine particles (average particle size 25.7 μm) using a pilot plant model pulveriser (Pilots India, Thrissur, Kerala, India) which was operated below 45 $^{\circ}\text{C}$ to avoid starch gelatinisation. A 40% (w/w) dispersion containing chickpea flour solids (dry solid basis) was prepared in duplicates by thorough mixing with distilled water. The dispersion was examined for the presence of yield stress by shearing the samples at the shear-rate of 10 s^{-1} for 30 s followed by relaxation for 60 s; yield stress was taken as the value of stress at the end of relaxation period (Dhanalakshmi et al. 2011). The dispersion was also subjected to time-dependent flow characterisation by generating five loops (cycles) wherein the shear-rate was progressively increased up to a shear-rate of 500 s^{-1} in 60 s to generate 50 data sets comprising shear-rate, shear-stress and apparent viscosity. The sample was immediately subjected to decreasing shear-rates up to 0 s^{-1} in 60 s to generate one loop. At the end of completing one loop, the yield stress was again determined as mentioned earlier. The method was repeated to generate a total of 5 loops and associated yield stress measurements. All measurements were performed at 25 ± 0.1 $^{\circ}\text{C}$ using a stress-controlled rheometer (Model # RS 6000, Thermo Scientific, Karlsruhe, Germany) with a temperature-controlled water bath, and fitted with a coaxial cylinder geometry (# Z20) whose stationary cup had an internal diameter of 20 mm. All experiments were repeated thrice.

The shear-stress versus shear-rate data were subjected to a common rheological model like Herschel–Bulkley

equation (Eq. 1) wherein the experimental yield stresses (σ_0) were used, and the non-linear analysis software supplied by the equipment manufacturer was employed to calculate the rheological parameters such as consistency index (k) and flow behaviour index (n). The apparent viscosity was reported as the ratio of shear-stress (σ) and shear-rate ($\dot{\gamma}$) where the latter was taken as 100 s^{-1} for comparison of results.

$$\sigma = \sigma_0 + k (\dot{\gamma})^n \quad (1)$$

If the shear-stress is plotted against shear-rate, the hysteresis loop developed has an area of shear-rate multiplied by shear-stress meaning an unit of Pa/s. This unit is equivalent to $(\text{N/m}^2)(1/\text{s})$ or $(\text{Nm/s})(1/\text{m}^3)$ or $(\text{energy/shear-time})(1/\text{volume})$. Hence, the area of the hysteresis loop has the dimension of energy required to breakdown the thixotropic structure per unit volume of sample (Roopa and Bhattacharya 2009). The area enclosed by the individual loops were noted by using the software provided by the equipment manufacturer.

The term ‘isoviscosity’ shows the attainment of the same apparent viscosity. As the rheological status changes with the number of loops and during increasing or decreasing shear-rates, the apparent viscosity is expected to change. Hence, a same viscosity value or isoviscosity is expected to occur at different shear-rates as the sample is non-Newtonian in nature. In such a situation, for comparison of results, isoviscosity values such as 400, 500 and 700 mPas were selected in the present investigation. Thus, this index indicates the rheological status of samples during the increasing followed by decreasing shear-rates and during different loops. The isoviscosity values were determined from Eq. (1) by assigning the values of experimental yield stress (σ_0); the values of k and n , computed earlier from Eq. (1) for the increasing and decreasing curves of different loops, were also substituted to find the shear-stress (σ). Finally, the σ values were divided by the experimental shear-rates to obtain the apparent viscosity of the system. Latter, the isoviscosity values such as 400, 500 and 700 mPas were selected as examples to construct the sample curves of apparent viscosity against shear-rate and shear-stress (Fig. 1).

Results and discussion

The sample five loop (cycle) graphs showing shear-rate, shear-stress and apparent viscosity against the time of shearing are shown in Fig. 1. The maximum shear-stress and apparent viscosity decreases with the time and number of loops. It means that the structural degradation occurs continuously with an increase in the number of loops. Structural degradation is associated with the microstructural changes and affects the flow properties;

Fig. 1 A sample plot of **a** shear-rate and shear-stress against time, showing isoviscosity lines, and **b** shear-rate and apparent viscosity against shearing time of chickpea flour dispersion comprising five loops of increasing and decreasing shear-rates

it is the result of the competition between breakdown due to flow stresses, build-up due to in-flow collisions and Brownian motion (Barnes 1997). The lines of isoviscosity, defined as the same viscosity during different loops, are also shown in Fig. 1a. The magnitudes of isoviscosity increase in between the loops meaning the phenomenon of reassociation of the structural elements which finally increases the shear-stress and subsequently the resistance to flow.

The term ‘isoviscosity’ gives an experimental idea about the rheological stability of a non-Newtonian sample especially when subjected to increasing and decreasing rates of shear. A sample is expected to be stable under applied varying shear if the ‘isoviscosity’ line is nearly parallel to the axis of the independent variable (time). This is expected for a Newtonian sample. If the line is irregular with decreasing trend, it is a situation with thixotropic sample which happens for samples that are viable for structural changes like most of the food dispersions.

The rheological parameters for the model system of 40% chickpea flour dispersion, obtained from the loop experiments, are shown in Table 1. The popular rheological model of Herschel–Bulkley (HB) is suitable to fit the shear-rate/shear-stress data as the correlation coefficient (r) is higher than 0.998 (significant at $p \leq 0.01$). The flow behaviour index (n) of HB model increases due to shearing indicating a shift towards Newtonian characteristics. However, in the first increasing shear-rate step, the n values are below 0.5 and thus the samples exhibit pronounced shear-thinning characteristics. The existence of yield stress in chickpea flour samples has been reported (Kampf and Peleg 2002). The experimental yield stress decreases as the number of loop increases. The initial yield stress of the undisturbed system is higher than that of the remaining loops meaning a marked change in the structure even in the first loop. The apparent viscosity (η), consistency index (k) and the area of the loop also decrease with the number of loops exhibiting the phenomenon of thinning.

The time-dependency characteristics including the phenomenon of thixotropy has been detailed by Weltmann (1943), and Green and Weltmann (1943, 1946); the basic principles of the hysteresis loop, equations of thixotropic breakdown and the interpretation of a single loop to characterise thixotropy have been reported. Four different tests have been indicated of which the double consistency curve method deals with the generation of up and down curves (by increasing shear-rate followed by decreasing the same after attaining its highest level) to obtain an enclosed loop called hysteresis loop. However, the use of the generation of multiple loops has not been reported earlier. Further, the simultaneous measurement of time-independency and time-dependency from the proposed single measurement is possible. The quantification of these characteristics is the progressiveness over the existing systems.

A liquid material may show the phenomenon of thixotropy when it is sheared at a constant shear-rate (Chhabra and Richardson 2008). Its apparent viscosity or the corresponding shear-stress decreases with the time of shearing. If the flow curve is measured in a single experiment in which the shear-rate is continuously increased at a constant shear-rate from zero to a higher value and then decreased at the same rate to zero again, a hysteresis loop is formed. The height, shape and enclosed area of the hysteresis loop depend on the duration of shearing, the rate of increase/decrease of shear-rate, and the past kinematic history of the sample. In general, the larger the enclosed area, the stronger is the time-dependent behaviour of the materials. Hence, hysteresis loop is not observed for time-independent fluids meaning that the enclosed area of the loop is zero. In addition, the breakdown of structure by shearing is reversible in some cases. Upon removal of shearing action

Table 1 Rheological characteristics of a model system during multiple loop or cycle testing

Parameter	Cycle 1		Cycle 2		Cycle 3		Cycle 4		Cycle 5	
	Increasing	Decreasing	Increasing	Decreasing	Increasing	Decreasing	Increasing	Decreasing	Increasing	Decreasing
Yield stress (mPa)	49.7 ± 8.3		40.3 ± 6.2		31.9 ± 4.7		26.0 ± 3.2		22.1 ± 4.1	
Apparent viscosity, η (mPas) ^a	868.1 ± 24.5	458.1 ± 5.5	485.9 ± 9.7	392.9 ± 6.1	420.4 ± 22.5	354.0 ± 7.6	371.6 ± 10.5	325.4 ± 8.1	340.7 ± 11.2	304.1 ± 9.4
Consistency index, k (Pas ⁿ)	9.24 ± 0.96	0.79 ± 0.04	1.79 ± 0.08	0.74 ± 0.05	1.29 ± 0.06	0.67 ± 0.03	1.05 ± 0.06	0.6 ± 0.02	0.88 ± 0.05	0.55 ± 0.02
Flow behaviour index, n (–)	0.486 ± 0.018	0.874 ± 0.010	0.721 ± 0.005	0.859 ± 0.011	0.757 ± 0.007	0.860 ± 0.008	0.777 ± 0.008	0.865 ± 0.005	0.795 ± 0.007	0.870 ± 0.003
Area of the loop (Pas ^{–1})	15,860 ± 511		5025 ± 424		3260 ± 235		2523 ± 166		1988 ± 154	

Initial yield stress of model system (before loop experiment): 250.5 ± 43.5 mPa

^a Apparent viscosity values are reported at a shear-rate of 100 s^{–1}

or allowing for some time to rest, the sample regains a part of the initial value of apparent viscosity which may be called as the build-up of structure.

Conclusion

A multi-loop or multi-cycle method for characterisation of flowable materials like food dispersions can be used for simultaneous characterisation of time-independent and time-dependent behaviour from a single experiment instead of the conventional method wherein they are individually examined from two separate tests. The method thus provides convenience to researchers and routine analysts for characterisation of non-Newtonian liquids. A further advantage of this method is that it offers a detailed picture about the extent of shear-induced breakdown and regaining of rheological status.

Acknowledgements The authors thank the Council of Scientific and Industrial Research (CSIR), New Delhi for the Grant of Junior Research Fellowship (JRF) to Mr. Shanthilal J. to conduct the Ph.D. programme.

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