



**Flow Dynamics of Time-dependent and Viscoplastic Fluids
in Couette Geometry**

by

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Abstract

This work studies the flow behaviour of fluids exhibiting time-dependent and yield stress characteristics in a Couette flow geometry. Methods for characterizing this type of fluids using a concentric cylinder viscometer have been developed and demonstrated for a number of materials.

The flow behaviour at steady state conditions has been theoretically analyzed. The existence of yield boundary has been quantified and discussed. A simple approach called the " r_c method" has been proposed to obtain shear stress-shear rate pairs of data for the time-dependent yield stress fluids in a concentric cylinder viscometer. This method uses a reference radius r_c instead of bob surface to evaluate the fluid properties, which gives more accurate results than existing methods. The location of r_c , for ideal Bingham fluid at fully sheared condition, depends only on the geometry factor. However, the r_c method can be used for other flow conditions within acceptable errors under certain circumstance which has been validated by experimental work.

The unsteady state flow behaviour using modified flow model approach has been successfully simulated for both time-independent and time-dependent yield stress fluids. The simulation results suggest that, under the current experimental conditions, the unsteady flow occurs in a much shorter time than that due to the change of the thixotropic fluid structure. Therefore, the flow of a thixotropic fluid can be adequately simulated with steady state assumption.

The accurate description of the rheological properties of the time-dependent yield stress fluid, which is necessary for the simulation of the flow pattern, can not be obtained by the existing modelling methods. Therefore, a new modelling approach, overcoming such

limitations, has been proposed to quantify the change of the flow model parameters with time and shear.

The yield boundary measured using visualization technique compares well with the theoretical prediction when the yield stress measured by the vane method is used as yield criterion. The dynamic behaviour of yield boundary is shown to be predictable if the knowledge of basic rheological flow properties is known. However, the phenomenon of moving yield boundary is more complex than the ideal concept because of the intricate nature of the microstructure.

Declaration

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference had been made in the text.

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Chapter 1

Introduction

It is well known that many suspensions, like slurries, pastes, food products etc. exhibit yield stress, a critical shear stress below which the fluid behaves like a solid and does not flow. The yield stress behaviour is caused by the complex formation of the fluid internal structure. The internal structure is derived from the interparticle links due to flocculation and aggregation. This structure may be broken down during shearing effect and recover at rest. Such behaviour leads to the time-dependent characteristic (thixotropy) of the structure, as well as the change of the rheological property of the fluid. The presence of the yield boundary which separates the yielded flow and unyielded flow has always been an important topic both in theoretical study and industrial practices. Good knowledge of the rheology property of the fluid is required in industrial process design and control, especially in the handling of such type of fluid.

Viscometers have been widely used to measure the rheological property of fluids. It is usually employed to obtain viscosity or the shear stress-shear rate relationship which enable evaluation of the fluid property. Since the introduction of the first concentric cylinder viscometer by Couette in 1890, the original design has gone through many improvements. Due to a number of advantages such as ease of operation and lower cost as compared to other types of viscometers, the concentric cylinder viscometer has become one of the most widely used equipment to evaluate fluid properties. When using the concentric cylinder viscometer, the shear rate value can not be directly obtained from the measurement, however. In the past, various methods have been successfully developed to evaluate the fluid property specially for time-independent fluids. However, for fluids with yield stress and time-dependent

characteristics, there is no plausible way to evaluate their fluid properties primarily due to the lack of the knowledge of flow behaviour in such geometry.

The scope of the current work includes a study of flow behaviour of fluid with yield stress and time-dependent characteristics in the Couette geometry. The main purpose is to gain a better understanding of the flow behaviour of such fluids as well as finding the appropriate way of evaluating the fluid property. Ideal conditions are assumed in the theoretical study for the flow system, i.e. incompressible and homogenous fluid, tangential laminar flow; no slip at bob or cup surface; negligible end effects at the top and bottom of the rotating bob; and isothermal system. Three commonly used ideal viscoplastic flow models (Bird et al 1983) have been employed here; they are Bingham, Casson and Herschel-Bulkley models. The tangential flow of fluid in the annulus resulting from the rotating bob at a given speed, while the cup is maintained stationary. The flow geometry is analyzed in a cylindrical co-ordinates (r , θ , z). If the fluid is assumed to flow tangentially with the velocity components v_r and v_z equal to zero, the flow can be reduced to a simple one dimensional model. In addition, the yield stress and shear rate share the same sign as the shear stress which is positive. The respective flow models are shown as follows:

$$\text{Bingham model} \quad \tau = \tau_y + \mu \cdot \dot{\gamma} \quad (1.1)$$

$$\text{Casson model} \quad \tau^{1/2} = \tau_y^{1/2} + \mu^{1/2} \cdot \dot{\gamma}^{1/2} \quad (1.2)$$

$$\text{Herschel-Bulkley model} \quad \tau = \tau_y + \mu \cdot \dot{\gamma}^n \quad (1.3)$$

In the above equations, τ_y denotes the yield stress of the flow model, while μ is the model parameter which has different meaning and unit depending on the type of model used. The flow model parameters τ_y and μ may change with time of shear for the time-dependent fluid. In addition to the yield stress from flow model, the yield stress obtained by other approach (such as by vane method) is also used as the yield criterion in this study.

The present thesis is divided into the following sections. A review of the previous work related to the present study is given in **Chapter 2**. **Chapter 3** investigates theoretically

the general flow behaviour at steady state condition. The analytical expressions for flow parameters such as shear stress and shear rate distributions, location of yield boundary are presented. A critical value which distinguishes whether the flow is in fully or partially condition has been determined. A novel method (r_c method) for evaluating flow properties of the time-dependent and yield stress fluids based on the above analysis has been developed and discussed. The accuracy of the r_c method for different type of flow models and shearing conditions are analyzed in details. **Chapter 4** investigates the unsteady state shear flow behaviour for both time-independent and time-dependent yield stress fluids. Modified flow models are used to overcome the difficulty of determining the yield boundary by solving the equations of motions. The change of the yield boundary of the unsteady flow is studied under the partially sheared condition. **Chapter 5** describes the details of the experimental work which encompasses material selection, measurement apparatus and techniques used in the current study. Fluids with yield stress and time-dependent characteristic such as waxy maize starch, mayonnaise, kaolin and bentonite suspensions were used in the experimental study. The main experimental work included (1) measurement of shear stress-shear rate-time relationship using a concentric viscometer; (2) measurement of yield stress by the vane method; and (3) measurement of yield boundary using video imaging system. In **Chapter 6**, experiments were carried out on various time-dependent suspensions to verify the r_c method for evaluating fluid property. The accuracy of the r_c method on experimental results is analyzed and discussed. The rheological models of the tested suspensions are described by Bingham, Casson and Hershel-Bulkley flow models respectively. A new modelling approach has been adopted to characterize the time-dependent behaviour of the suspensions. The modelling results for the above suspensions are used in the following chapter to predict the transient behaviour of the yield boundary. In **Chapter 7**, the yield stress measured by the vane method was characterized under varying fluid structure due to shear. Numerical simulations were performed to predict the transient flow pattern, such as the shear stress and shear rate distributions as a result of thixotropic fluid structure. The dynamic behaviour of the

yield boundary is predicted by two different yield criteria, i.e. from the yield stress of flow model or the yield stress measured by the vane method. The simulation results of the location of the yield boundary are compared with the experimental measurements. The visualization on the appearance of yield boundary is also discussed. **Chapter 8** concludes the key findings of this work and provides further recommendations for the future work.

Chapter 2

Flow of Time-dependent Yield Stress Fluids - A Review

2.1 Thixotropic Yield Stress Fluids

Yield stress

Many fluids commonly encountered in industries and daily life such as concentrated suspension, pastes, foodstuffs, blood, solid rocket propellants, emulsions, foams have been shown to exhibit flow properties intermediate between solid and liquid (Bird et al 1983). For such fluid, when the applied stress is less than a critical value, they do not flow but deform plastically like a solid with definite strain recovery on the removal of stress. When the applied stress is larger than the critical value, the fluid flows like a truly viscous material. Bingham and Green (Bingham & Green 1920, Bingham 1922) firstly conducted measurements on viscoplastic flow and investigated its applications in industrial process. They defined the yield value as the force required to start the flow. Billington (1960) suggested that the yield value is the maximum force per unit area that the deformable particles (or aggregates) in a suspension can sustain without flow occurring. Many researchers have found that the yield stress behavior is common in structured suspensions. The particles in the suspension can interact among each other and aggregate to form chains, or flocs, and create three-dimensional network structure which gives rise to the solid-like spatial structure (Gillespie 1960, Fischer et al 1961, Davenport & Somper 1971, Nguyen & Boger 1983, Missaire et al 1990). The magnitude of the yield stress would be affected by the strength of the inter-linking chains and the number of links per unit volume of the suspension (Goodeve 1939). Studies on various type of materials having such fluid behaviour have been reviewed by Bird et al (1983), Nguyen & Boger (1983), Metzner (1985), and Kamal & Mutel (1985).

Thixotropy

The term "thixotropy" was first introduced by Peterfi in 1927 (Cheng 1987) in the study of the isothermal sol-gel transformation, and used by Freundlich (1935) to describe the isothermal, reversible gel-sol transformation in colloidal suspension. This term has later been extended in many ways such as: "isothermal reversible decrease of viscosity with increase of rate of shear" (Goodeve & Whitfield 1938); and "process of softening caused by remolding, followed by a time-dependent return to the original harder state" (Burgers & Scott Blair 1948). In 1975, the British Standards Institution revised the definition to the "decrease in viscosity under stress, followed by gradual recovery when the stress is removed". Cheng (1987) referred the variation of structure with time to the time-dependent nature of thixotropy, and he also gave a review on its various aspects.

The microstructures of colloidal suspensions have been widely studied (Olphen 1963, Reh binder 1965, Cheng 1987). Both the behaviour of yield stress and thixotropy arise from its internal structure formation, which are due to the interparticle forces acting between the dispersed species. The Van der Waals forces provide interparticle attraction. The repulsive forces can be resulted from electrical interaction of ionic double layer, steric interaction of adsorbed macromolecules or combined electrical and steric effects of polyelectrolytes. The dispersed species in stable colloid suspensions stay at the equilibrium state of Brownian motion and equilibrium force against sedimentation. The cohesion of the particles creates coagulations and forms chains. The particles along the chains contact its neighbours, so a random network of such chains is formed. The links between chains in the network can be broken down under shear and rebuilt at rest. The breakdown or recovery process of the network will lead to the change of fluid structure and properties, such as the yield stress and viscosity etc. The breakdown (or recovery) of yield stress with time of shear for various kind of fluids has been reported by many researchers (Moore 1959, Davenport & Somper 1971, Nguyen & Boger 1985, Cheng 1987, Garrido et al 1990). Moore (1959) used a "Plasticity

Model" to describe the internal structure change of the thixotropic yield stress material during the process of the shear stress, based on energy barriers theory. Hahn et al (1957) used the "flow unit" theory to described the shear stress-shear rate relationship for non-Newtonian flow, as it is believed that in the thixotropic fluid system, there exist entangled and disentangled molecules and the rheological transformation of the fluid from Non-Newtonian behaviour (entangled unit) to Newtonian behaviour (disentangled unit) as a result of shear.

2.2 Modelling of Time-Dependent Fluids

As time-dependent flow behaviour is important in industrial process, such as in fluid transportation, storage, mixing and etc., researchers have tried to formulate quantitative relationships between shear stress, shear rate and time. Slibar & Paslay (1964) suggested a set of constitutive equations to describe the deformation process of such thixotropic yield stress fluid, and time-dependent memory functions were assumed in those equations. Szilas (1984) used the "Grid-shell" theory to explain and simulate the thixotropic fluid phenomena, especially the hysteresis loop. Empirical equations based on the area of hysteresis loop were also used in the literature (Green & Weltmann 1943, Djakovic et al 1990). Huang (1972) used a thermodynamic approach to study the thixotropic fluid phenomena. His theory was based on entropy variation with respect to the change of molecular arrangement as a result of shear. Structure change with time under shear is usually analogous to chemical reaction process (Goodeve & Whitfield 1938), which is the most common approach to characterize the time-dependent fluid behaviour. Some physical values have been used to represent the quantity of the structure: number of links per unit volume (Hiemenz & Vold 1965, Ruckenstein & Mewis 1973); stress under a certain shear rate (Schnaare et al 1976); viscosity (Brown & Pinder 1971); yield stress (Billington 1960) etc. Moore (1959) introduced a general parameter λ to represent the structure quantity: $\tau = (\eta_e + c \cdot \lambda) \cdot \dot{\gamma}$. When $\lambda = 1$ indicates a complete structure build-up; and $\lambda = 0$ indicates the complete structure breakdown. In addition to the apparent viscosity, this concept of λ has been widely used and developed to represent the change of

other structure quantities. As λ is treated as the fraction of the structure, its physical values are usually believed to vary in proportion to the remaining structure. Hence, the fraction of the physical value is usually used to represent λ in the rate equation. A general formula of rate equation is written as (Nguyen 1983):

$$-\frac{d\lambda}{dt} = k \cdot \lambda^p - k_r \cdot (1-\lambda)^q \quad (2.1)$$

where λ is the fraction of structure remaining at time t , and clearly $(1-\lambda)$ is the fraction of the structure which has been broken at that time. The first term on the right side of Eq. (2.1) describes the structure break-down; and the second is the structure build-up process. Both the break-down and build-up rate constants k and k_r are usually functions of shear rate or shear stress, and p and q are orders of the structural break-down and recovery kinetics, respectively.

In addition, a rate equation based on an analogy with the irreversible chemical reaction has the following form:

$$-\frac{d\lambda}{dt} = k \cdot (\lambda - \lambda_e)^p \quad (2.2)$$

Here, the structure is assumed to break down without rebuilding until the structure reaches λ_e at equilibrium. So, $(\lambda - \lambda_e)$ is the remaining fraction of structure that can possibly be broken down.

Different reaction orders of p and q have been used in previous work, e.g. $p=1, q=1$ (Moore 1959); $p=2, q=1$ (Lapasin et al 1980); $p=2$, irreversible (Petrellis & Flumerfelt 1973). Other forms used have also been summarized by Nguyen (1983).

Various experiments have been devised to systematically investigate the time-dependent fluid behaviour and they can be classified as follows:

- (1) Measurement of the decay of suspension structure during the agitation process or its structure recovery when the suspension is allowed to rest after vigorous agitation (Nguyen 1983, Nguyen & Boger 1985b). See Figs. 2.1 and 2.2.

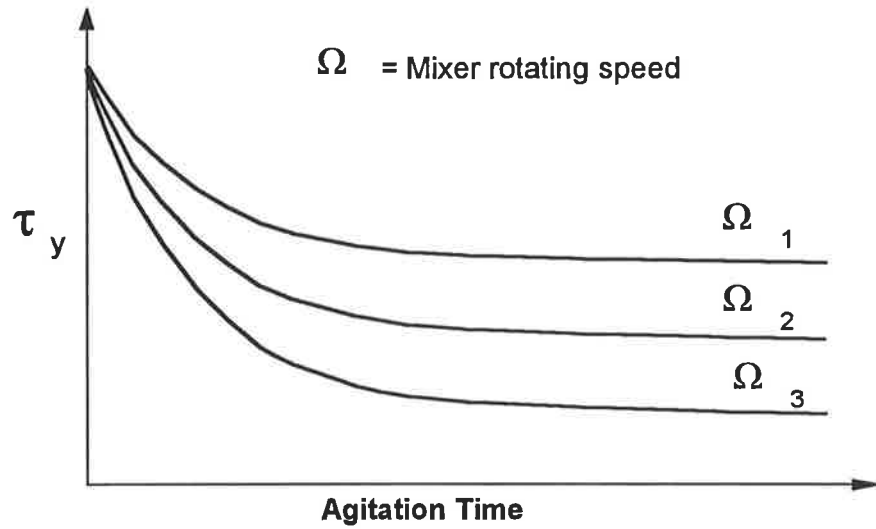


Fig. 2.1 The decay of the yield stress with time during agitation under different rotational speeds of mixer.



Fig. 2.2 The recovery of the yield stress with rest time.

- (2) Measurement of the shear stress $\tau(t)$ at the condition of varying shear rate $\dot{\gamma}$ (Fig. 2.3). The shear rate is usually increased linearly with time up to a maximum value and then decreased linearly to zero. The resulting relation of $\tau(t)$ versus $\dot{\gamma}$ for a given sweep time is called the "hysteresis loop" (Weltmann 1943). This is a very common method for practical applications, as it gives a rapid, though qualitative and limited indication of thixotropic properties of material (Mercer & Weymann 1974).

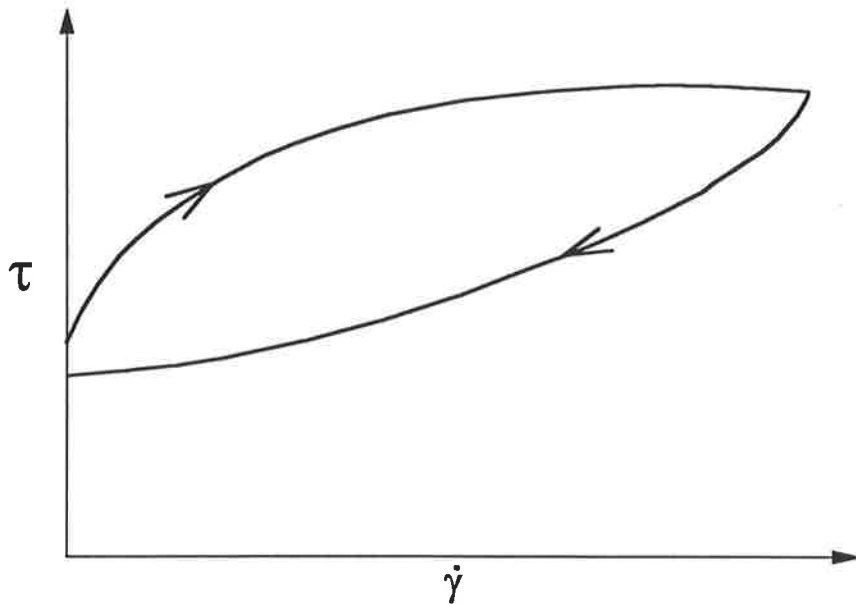


Fig. 2.3 The hysteresis loop of shear stress under cyclic shearing.

- (3) Measurement of shear stress $\tau(t)$ decaying with time t under a constant shear rate $\dot{\gamma}$. This is the most commonly used experimental procedure in literature (Fig. 2.4).

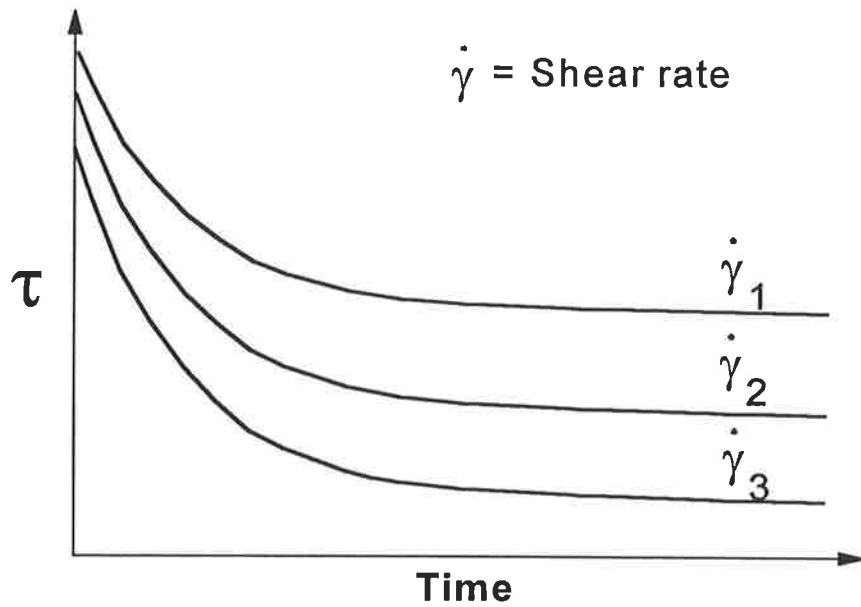


Fig. 2.4 Stress decay under different constant shear rates.

- (4) "Step-change-in-shear-rate" method (Cheng & Evans 1965) (Fig. 2.5). The shear rate is initially held constant at $\dot{\gamma}_r = E$, until shear stress reaches an equilibrium value. Then the shear rate is abruptly changed to a new value (say $\dot{\gamma} = a$) and the corresponding shear stress is recorded. After that, the shear rate is again changed back to $\dot{\gamma}_r = E$ until the stress reaches equilibrium state, which corresponding to the constant structure level of the reference shear rate $\dot{\gamma}_r = E$. By repeating the above shear rate change procedure (like $\dot{\gamma} = b, c \dots$) to obtain more pairs of shear stress-shear rate data, a flow curve is obtained at a constant structure level, which $\dot{\gamma}_r = E$ is its reference shear rate (Fig.2.6).

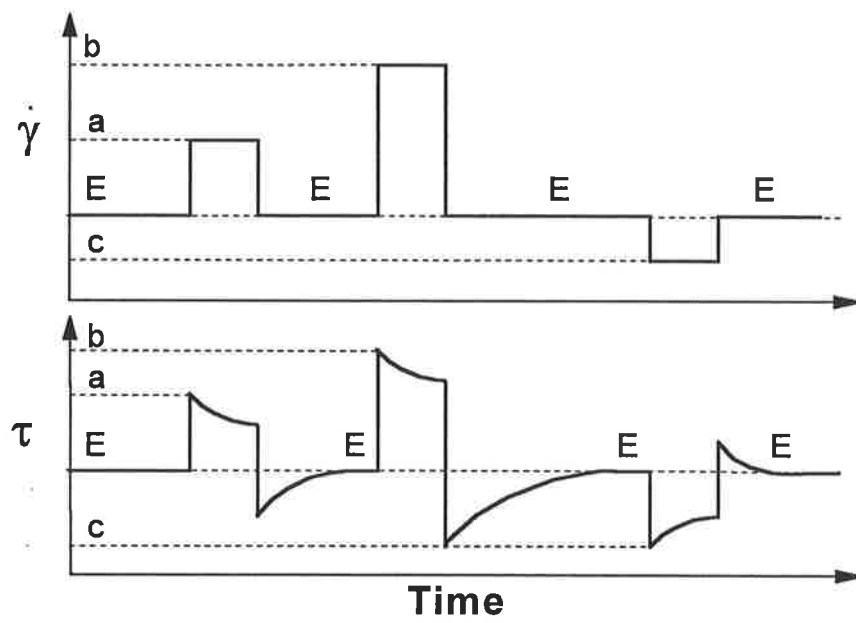


Fig. 2.5 Response of shear stress under step-change-in shear rate experiment to obtain a constant-structure flow curve.

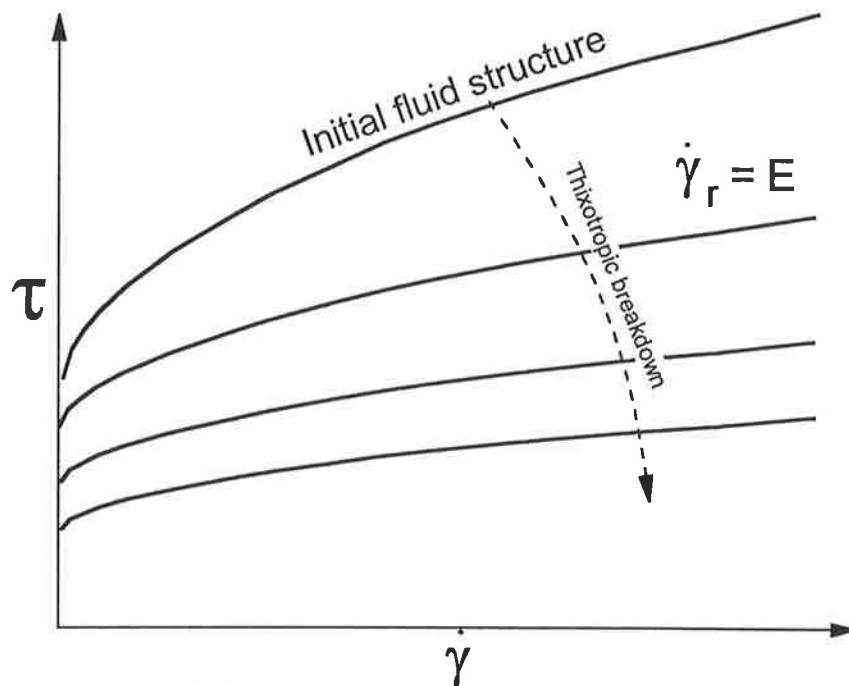


Fig. 2.6 A group of constant-structure flow curves.

Method (1) is usually used for some specific situations, and the results are straightforward for the practical application, such as fluid mixing, transportation, storage etc. Relation between agitation speed and average shear rate can be found in the literature (Metzner & Otto 1957, Nguyen & Boger 1985b). Coupling with some other measurements (viscometer, vane etc.), it is possible to determine (or formulate) the fluid property i.e. the flow curve or the change of yield stress with time, at rest or under a known average shear rate during the agitation. Method (2) has been used for qualitative comparison and enhancing the understanding the thixotropy of materials (Saunders 1967, Petrellis & Flumerfelt 1973, Liu & Soong 1983). Some studies were based on empirical equations, as mentioned earlier. Researchers are mostly concerned with the difference between the up and down curves of the hysteresis loop, as it represents the degree of thixotropy. Green & Weltmann (1943) suggested that the yield stress could be determined by the down curve, however they did not consider the structure change influencing the value of yield stress. Since the shear rate is changing linearly with time, it could be substituted into the rate Eq. (2.1) or Eq. (2.2), in which the rate constant is usually a function of shear rate. The change of structure parameter λ with time in Eq. (2.1) or Eq. (2.2) can be obtained for model prediction, and compared with experimental results (De Kee et al 1983, Garrido et al 1990). Theoretical simulations based on results of the shear rate changing linearly with time have been performed by Moore (1959).

Method (3) is a very basic experimental procedure commonly used for the modelling of thixotropic behavior, as it is directly related to the rate Eq. (2.1) or (2.2) where the rate constant will not change because the shear rate is a constant. It also offers a convenient way for model verification or justification. Methods (3) and (4) are also used together to characterize the thixotropic fluid based on constitutive equations which were initially introduced by Moore and developed later by other authors (Cheng & Evans 1965, Cheng 1987). The general form of constitutive equations suggested by Cheng & Evans (1965) consists of an equation of state and a rate equation:

$$\tau = \tau(\dot{\gamma}, \lambda) \quad (2.3)$$

$$\frac{d\lambda}{dt} = g(\dot{\gamma}, \lambda) \quad (2.4)$$

The experiments which usually performed to describe the thixotropic property or to determine the model parameters (Joye & Poehlein 1971, Petrellis & Flumerfelt 1973, Alessandrini et al 1982, Usui & Sano 1985) include: (i) conduct experiments using Method (3) to obtain shear stress decay curve under a constant shear rate; (ii) use Method (4) to obtain a group of constant structure λ curves (see Fig. 2.6) where each of the curves is related to a reference shear rate. An equilibrium flow curve can be determined from the group of constant structure curves. The details of the experimental and modeling procedures have been described by Cheng & Evans (1965).

2.3 The Determination of Yield Stress and Yield Boundary

The fact of the existence of the "true yield stress" has always been a matter of debate in the past (Evans 1992, Schurz 1992). The value of the yield stress measured has been found to be dependent on the instrument sensitivity, measurement limitation and the methods used (Keentok 1982, Barnes & Walters 1985, Avramidis et al 1991). However, the concept of the yield stress has been accepted and widely used both in theoretical studies and practical applications since Bingham and Green discovered that some materials were not truly viscous fluid. Nguyen and Boger (1992) gave a comprehensive review on various yield stress measurement methods, and the problems related to the yield stress determination. Some of the measurement methods which are more relevant to the current work are:

- Stress relaxation method. The yield stress is defined as the residual stress remaining in the fluid when the rotational speed of the viscometer is gradually or suddenly brought to rest. The measured yield stress is therefore influenced by the previous shear history for time-

dependent fluid. Other problems leading to the inaccuracy may also be due to wall slip, inertia, and damping characteristics of the rotating body.

- Vane method. The vane used in the vane method suggested by Nguyen and Boger (1983, 1985a), basically consists of four thin blades arranged at equal angles around a small cylindrical shaft. The measurement procedure involves slowly and constantly rotating the vane immersed in the fluid and recording the torque-time response. The yield stress value can be calculated from the maximum torque in the torque-time response curve. This approach assumes that after elastic deformation, the fluid yields along a localized cylindrical surface defined by the vane dimensions. This method overcomes the problem of wall slip which encountered in rotating cylinder. It is most suitable for fluids with high yield stress, and its accuracy has been confirmed by many workers. Since this method causes minimum disturbance to the test fluid, it is thus appropriate for measurement with time-dependent fluids.
- Indirect method. The yield stress can be obtained by extrapolating the shear stress-shear rate data (which may be fitted by a polynomial equation) to zero shear rate or inferred from a suitably fitted flow model. The yield stress value can not be regarded as the absolute material property, as it usually depends on the range of the data used and (or) the model assumed for the fluid.

The following are other measurement methods which are not considered in the current study:

- Creep/recovery experiment.
- Stress growth experiment.
- Cone penetration.
- Method based on static equilibrium of an immersed body.
- Static stability on an inclined plane.
- Exploitation of viscometer defects.

When testing a fluid with yield stress in the concentric cylinder viscometer, a yield boundary may exist to separate the fluid into a sheared flow and an unsheared plug flow region. This situation usually causes error in the measurement. The presence of the yield surface can be detected by drawing a "line" across the fluid surface with dyed particles, and then observe for the deformation of the line when the bob (or cup) is rotating (Schramm 1981). If only a part of the particles on the line move, then a plug flow zone exists in this measurement. However, it is usually not easy to visually observe the boundary using the above method due to very small gap size between the two cylinders or other obstructions such as water jacket. Horie and Pinder (1979) studied the thixotropic slurries with yield stress in a coaxial cylinder viscometer using a wide gap size. They found that only part of the fluid was sheared; and the higher the yield stress the thinner was the sheared layer. The yield boundary was measured with particle tracer (red nylon fibers about 1 mm long), and the yield boundary was found to increase with time until reaching an equilibrium value at a given rotating speed. When using particle tracer for flow visualization, the particle would follow the flow correctly if it is small and neutrally buoyant, as the inertial and gravitational forces decrease rapidly with the particle size (Gharib & Willert 1989).

2.4 Evaluation of Fluid Properties with Concentric Cylinder Viscometry

The original concentric cylinder viscometer, devised by Couette in 1890, consisted of a rotating cup and an inner bob which was supported by a torsion wire and rested in a point bearing in the bottom of the cup. The test fluid was placed in the annulus between the two concentric cylinders. In about a few decades, especially after 1940, improved versions of the cup and bob designs (either of the cylinders may be rotating) were developed and available commercially (Orosz et al 1972, Van Wazer et al 1963). Many commercial viscometers are equipped with a rotating inner cylinder with fixed and/or linearly varying rotating speed with time and a stationary cup. The torque is measured at the inner cylinder.

This instrument is very widely used because it usually costs less than cone and plate viscometer, requires smaller amount of sample, and is simpler to operate than capillary viscometer. It is commonly equipped with a water jacket to maintain constant and uniform temperature for the test sample. The range of measured shear rate can be varied by selecting the appropriate speed and gap clearance confined by the two cylinders. This instrument is generally limited to shear rate range of up to 1000 s^{-1} , and insensitive at shear rate below 1 s^{-1} (Nguyen & Boger 1992). One typical measurement error of this instrument is due to the additional shearing at the end(s) of the bob (i.e. end effect). Van Wazer et al (1963) derived mathematical expressions to account for the end effects and described ways to minimize it. Highgate & Whorlow (1969) showed that the error due to end effect could be severe when the non-Newtonian fluid behaviour is dominant. Usually, the bob is designed with a hollow base to trap air and hence reduce the end effect. Princen (1986) suggested that the hollow based bob may be more suitable for viscoplastic fluid where the air bubble can remain more stable at the base due to the yield stress. Another contributing factor for the measurement error is the slip effect. This phenomenon is generally complex, it may be due to the phase separation or concentration difference near the wall surface, especially when handling suspensions or two-phase fluids (Dobson & Tompsett 1973, Cheng & Richmond 1978). The usual method to minimize the slip effect is to use a bob with a grooved surface. Vein & Tovchigrechko (1992) described a method of correcting the primary data influenced by slip factor using the concentric cylinder viscometer. Turbulent flow can also be a source of error. It is more likely to happen in the experimental condition(s) with thin or low density fluid; high rotating speed; wide gap size (Tillmark & Alfredsson 1992). Finally, the effect due to the moment of inertia of the rotating bob has also been discussed by Van Wazer et al (1963).

In most theoretical studies, the fluid is usually assumed to behave ideally (Van Wazer, et al 1963) where it has the following conditions:

- incompressible fluid;
- steady state flow;
- laminar tangential flow;
- no end effect;
- no slip;
- isothermal system.

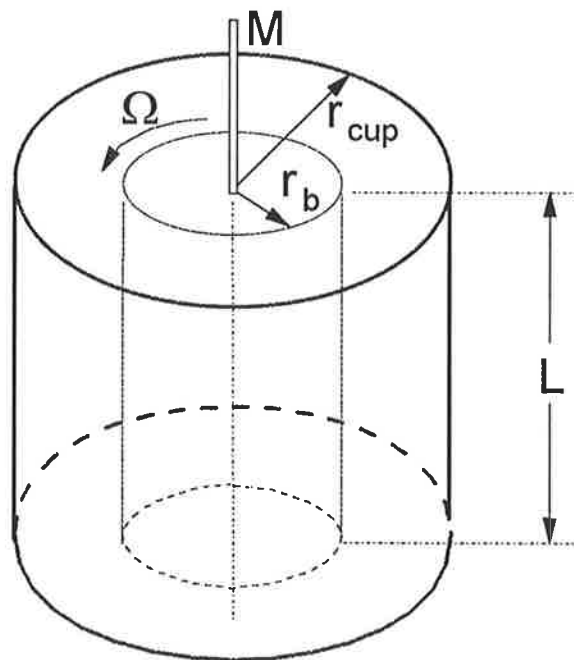


Fig. 2.7 Sensor system of a concentric cylinder viscometer.

In this type of viscometer, the shear stress (τ) and shear rate ($\dot{\gamma}$) data can be analyzed from the torque (M) and speed data (Ω). Knowing the geometry and torque of the bob (see Fig 2.7), the shear stress value at the surface of the bob can be derived from equation of motion (Bird et al 1960):

$$\tau_b = \frac{M}{2\pi \cdot r_b^2 \cdot L} \quad (2.5)$$

but the determination of shear rate at the bob surface is not that straight-forward if the flow model is not known. The shear rate at bob surface is determined by:

$$\dot{\gamma}_b = F(\tau_b) \quad (2.6)$$

$$\Omega = -1/2 \int_{\tau_b}^{\tau_o} \frac{F(\tau)}{\tau} d\tau \quad (2.7)$$

Various mathematical expressions for calculating the shear rate at bob surface can be obtained for different flow models as shown below (Van Wazer et al 1963):

Viscous fluid:

Newtonian fluid: $\tau = \mu \cdot \dot{\gamma}$

$$\dot{\gamma}_b = \frac{2\Omega}{(1 - \varepsilon^{-2})} \quad (2.8)$$

Simple power law fluid: $\tau = \mu \cdot \dot{\gamma}^n$

$$\dot{\gamma}_b = \frac{2\Omega}{n \cdot (1 - \varepsilon^{-2/n})} \quad (2.9)$$

Yield stress fluid:

Shear rate at bob surface can be obtained by substituting the shear stress at bob surface from flow model $\tau_b = f(\dot{\gamma}_b)$ into the equation of $\Omega = F(\tau_b)$ as listed below. It is for the condition where all the fluid in the annulus is sheared.

Bingham fluid: $\tau = \tau_y + \mu \cdot \dot{\gamma}$

$$\Omega = \frac{\tau_b}{2\mu} (1 - \varepsilon^{-2}) - \frac{\tau_y}{\mu} \ln \varepsilon \quad (2.10)$$

Power law fluid with a yield stress: $\tau = \tau_y + \mu \cdot \dot{\gamma}^n$

$$\Omega = \left(\frac{\tau_y}{\mu} \right)^{1/n} \int_1^\varepsilon \left(\tau_b / (\tau_y r^2) - 1 \right)^{1/n} dr / r \quad (2.11)$$

Ellis Model: $\dot{\gamma} = C_0(\tau - \tau_y) + C'_0(\tau - \tau_y)^{1/n}$

$$\Omega = C_0 \frac{\tau_b}{\varepsilon^2} [\varepsilon^2 - 1] + \tau_y \ln \varepsilon + C'_0 \int_1^\varepsilon (\tau_b / r^2 + \tau_y)^{1/n} dr / r \quad (2.12)$$

However, analytical expressions are complex for the last two flow models, and it is more convenient to obtain the shear rate at bob surface by numerical approach.

For viscoplastic fluids, a plug flow will exist (where $\dot{\gamma} = 0$) if the shear stress in this region (at some radius in the annulus) is less than yield stress. It is also referred to as partially sheared flow. Flow phenomena has been studied analytically by Reiner & Rivlin in 1927 (Bird et al 1960) and Paria (1959) for Bingham model; Batra & Das (1992) for Casson model. In their studies the cup was rotating while the bob remained stationary, and the conditions at which the fully and partially sheared may be distinguished have also been discussed. Schummer & Worthoff (1978) assessed the evaluation of the flow curves in Couette geometry for different type of fluids. They interpreted the shear rate data by assuming linear relation of $\dot{\gamma}$ with Ω (i.e. $\dot{\gamma} = C \cdot \Omega$) by using sum of least squares method. Optimum proportional constants, C , have been obtained for a few flow models, and they suggested that it is possible to use the constant from the Bingham model under fully sheared condition for other types of fluid with some error. Toorman (1994) studied flow behaviour of a yield stress fluid with Worrall-Tuliani rheological model in a Couette geometry. As the shear rate distribution could not be specified prior to the knowledge of the rheological model parameters, an iterative procedure was used to evaluate the pairs of experimental data (shear stress-rotating speed) to obtain the rheological model parameters and shear rate distributions as well as the yield radius.

Some numerical approaches have been developed to evaluate the shear stress shear rate data for time-independent fluids which does not require any specific flow model. Krieger et al (1952, 1953, 1954, 1968) described various mathematical expressions for evaluating the shear rate of non-Newtonian viscous fluid using different methods: (1) Multiple-bob method; (2) Two-bob method; (3) A single bob shearing in infinite cup radius; (4) Single-bob method and (5) A modified version of (4).

Methods (4) and (5) above are important in practice. Mathematical expressions for shear rate at bob surface are obtained by solving the shear rate Eq. (2.7).

For method (4):

$$\dot{\gamma}_b = (\Omega / \ln \varepsilon) \cdot [1 + \delta^{-1} \ln \varepsilon + \delta^{-2} (\ln \varepsilon)^2 / 3 - \delta' \cdot \delta^{-3} (\ln \varepsilon)^4 / 3 + \dots] \quad (2.13)$$

In which the shear rate equation is calculated by using Euler-Maclaurin series. Where the $\delta (= d \ln M / d \ln \Omega = d \ln \tau_b / d \ln \Omega)$ is the local gradient of the logarithmic plot of M or τ_b versus Ω , and ε is the radius ratio of the cup and bob, and $\delta' = d\delta / d \ln \Omega$. In practice the first two or three terms of the series should be sufficient to obtain reasonably accurate result for $\varepsilon \leq 1.2$.

For method (5):

$$\dot{\gamma}_b = \left\{ (2\Omega / \delta) / (1 - \varepsilon^{-2/\delta}) \right\} \cdot \left\{ 1 - C_1 \cdot \delta' \cdot \delta^{-1} + 3(C_2 + C_3) \cdot (\delta' \cdot \delta^{-1})^2 - C_2 \cdot \delta'' \cdot \delta^{-1} \dots \right\} \quad (2.14)$$

Where $\delta'' = d\delta' / d \ln \Omega$. Expressions for the coefficients C_i , are series functions of δ and Ω . Yang and Krieger (1978) demonstrated that this equation can yield accurate result with large gap systems up to $\varepsilon \leq 2.0$ for fully sheared fluid. The ideal data was generated from Williamson fluid and Bingham plastic models.

However, plug flow may exist in the annulus for yield stress fluid and unacceptable error will result if the above shear rate evaluation method is used (Yang & Krieger 1978). Therefore, it is necessary to know what is the effective gap width to use. For fully sheared condition, ε in the above equations is the radius ratio of the cup and bob. For partially sheared condition, the effective gap width should be the radius ratio of the yield surface and the bob, which is less than ε .

Darby (1985) examined the error for yield stress fluids following Bingham and Casson models using the Power-law approximation which is the leading term of the shear rate in Eq. (2.14) (i.e. $(2\Omega/\delta)/(1-\varepsilon^{-2/\delta})$). It was found that the obvious error may exist at condition when the stress at the cup surface approaches the yield stress. Nguyen & Boger (1987) suggested a two-step procedure to analyze the shear stress-speed data which included all flow situations. In their study, real experimental data and ideal data generated from Casson model were used. If the fluid is partially sheared, the shear rate Eq. (2.7) can be solved by substituting τ_y for τ_o , and differentiating both sides with respect to τ_b gives:

$$\dot{\gamma}_b = 2\Omega/\delta \quad (2.15)$$

Two different steps were considered, where the first step uses partially sheared condition of Eq. (2.15) to analyze the full range of stress-speed data, and the second step employs method (4) or (5) to analyze the full range of data. Two separate ranges of data under partially and fully sheared conditions could be distinguished graphically by comparing the results of the two steps.

In addition, MacSporran (1986, 1989) solved the shear rate Eq. (2.7) by using a piece wise cubic polynomial interpolation to approximate the shear rate, and a modified version with least-squares cubic spline method.

For time-dependent fluid with a yield stress, the shear rate at a given rotational speed not only varies with the radius position, but also with time. So the methods for time-independent fluid are not applicable in this case. When the concentric cylinder viscometer is used to characterize fluid behaviour of this type, an approximate value of shear rate has to be used. The most commonly used approximate value is the Newtonian shear rate at bob surface (i.e. Eq. (2.8)) (Weltmann 1943, Billington & Huxley 1966, Schramm 1981); or the average gradient of velocity across the gap (i.e. narrow-gap assumption: $\dot{\gamma}_b \approx \Omega / (1 - \varepsilon^{-1})$) (Van Wazer et al 1963, Stanislav 1982, Alessandrini et al 1982). The approximations above can yield reasonable result only when the gap is very narrow which may not be practical for suspension of coarse particles. So far there is no convincing theoretical approach available in literature on shear stress-shear rate evaluation using the concentric cylinder viscometer to characterize time-dependent and yield stress fluids.

In addition to the lack of theoretical basis on evaluation of shear rate for time-dependent and yield stress fluids of ideal isotropic structure, measurement using the coaxial cylinder viscometer for this type fluids has also been questioned. This problem is due to serious shear stress and shear rate variations in the annular space between the cylinders as well as with time, which in principle could cause a variety of different time-dependent structure responses in the fluid being tested (Cheng & Evans 1965, Oroscz et al 1973, Szilas 1984). It is not certain if the stress information obtained at the bob surface really represents the structure property in the entire annulus. This is especially the case for yield stress fluid under low rotating speeds (Cheng 1973); or when the gap between the two cylinders is not narrow enough (Charm 1962). It is suggested that the cone and plate viscometer might be more suitable for characterization of such time-dependent and yield stress fluids (Cheng 1973, 1987).

2.5 Unsteady State Shear Flow of Yield Stress Fluid in Couette Geometry

The unsteady state shear flow can be studied by solving the equation of motion and continuity (Bird et al 1960) which involve nonlinear differential equations. Bird & Curtiss (1959) obtained the analytical solution of unsteady velocity profile for Newtonian fluid in the Couette geometry. Analytical solution is obtained by solving the partial differential equation by methods of separation of variables and Laplace transform, with the boundary conditions set at the bob and cup surfaces. Paria (1959) studied the unsteady shear flow of Bingham fluids in Couette geometry (with the cup rotating) analytically using the method of Laplace transform. The flow is assumed to take place in the whole region of the annulus and the boundaries are set at the bob and cup surfaces. However, for the fluid with a yield stress, it is possible that a yield boundary may exist which separates the yielded and unyielded flow regions. When the equation of motion is used to solve the unsteady state shear problem, it has to be under the condition that the flow occurs everywhere within the boundary region (Oldroyd 1947b). So according to this criterion, there are two possibilities for the boundary condition, i.e. the boundary can be either at the rigid surface if the flow occurs fully within the geometry (gap), or at the yield surface if the flow occurs only for part of the fluid within the geometry. However, in many calculations with viscoplastic fluids, it is often difficult to determine the plug flow zone where no flow occurs. The solution of the yield boundary can not be determined explicitly from the equation of motion because it also forms the boundary condition. Oldroyd (1947a, b) suggested that unsteady rheology problem, i.e. the development of yield boundary could be analogous to heat conduction problem, and such analogy has been used and developed by many authors (Phan-Thien 1983, Sekimoto 1991).

Even at steady state condition, it has always been a difficulty problem to define the location of the yield boundary before solving the flow condition in a complex flow geometry. Modified viscoplastic model methods have been used so that the flow can be assumed to take place in the entire region of the fluid. In many cases, the flow model is assumed to contain

two regions separated by a small shear rate: above which, the fluid obeys the ideal viscoplastic model; and below which is a Newtonian fluid. The plug flow zone could be determined from the part where the stress is lower than the yield stress which is defined from the ideal viscoplastic model. With this concept, O'Donovan & Tanner (1984) for example, studied the Bingham flow in a parallel-plate plastometer with the small shear rate defined as $\tau_y / (999\mu)$ and Szabo & Hassager (1992) used eccentric annular geometries with the small shear rate defined as 10^{-4} 1/s, and more have also been summarized by Papanastasiou (1987). These approaches require the use of numerical methods which involve complex algorithms with numerous iterations to track the yield material and application of different constitutive equations of the flow models. Papanastasiou (1987) introduced a modified constitutive equation for Bingham plastic fluid which could be simply expressed by one equation to describe the flow curve for all shear rate. The one-dimensional expression is:

$$\tau = \left[\mu + \frac{\tau_y \cdot (1 - \exp(-n \cdot |\dot{\gamma}|))}{|\dot{\gamma}|} \right] \cdot \dot{\gamma} \quad (2.16)$$

The flow curve expressed by Eq. (2.16) is therefore continuous for the entire range of shear rate. This expression approaches the ideal Bingham flow model if a relatively large exponent n , is used to simulate a very quick stress growth at a relatively very low shear rate. Therefore, the main advantage for Eq. (2.16) is that there is no need to apply different constitutive equations when tracking the yield material.

Chapter 3

Steady Flow of Thixotropic Yield Stress Fluids

This chapter investigates the flow behaviour for three different model fluids at steady state condition based on ideal data simulation. The flow models include Bingham model, Casson model and Herschel-Bulkley model. Solutions for the general flow parameters such as shear stress distribution, velocity and shear rate profile, as well as the location of the yield boundary have been investigated. Critical parameters which distinguish between fully and partially sheared conditions have been derived for each of the three flow models. Most importantly, an approach called the " r_c method" has been proposed to evaluate thixotropic fluid property. This method has been analytically shown to provide a unequivocal way of characterizing thixotropic fluid property for Bingham model under fully sheared condition. This approach can also be applied to other flow conditions and models at some level of accuracy if certain conditions are applied. Errors derived as a result of such approximation have also been analytically evaluated.

3.1 Basic Equations

The geometry of the Couette flow is shown in Fig. 3.1. The fluid within the annular gap between two concentric cylinders is being sheared tangentially by the rotation of the inner cylinder (bob), while the outer cylindrical surface (cup) remains at stationary. The general form of the equation of motion in the θ -component of the cylindrical coordinates is shown as follows (Bird et al 1960):

$$\begin{aligned} & \rho \cdot \left(\frac{\partial v_\theta}{\partial t} + v_r \cdot \frac{\partial v_\theta}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{v_r v_\theta}{r} + v_z \cdot \frac{\partial v_\theta}{\partial z} \right) \\ &= -\frac{1}{r} \cdot \frac{\partial P_\theta}{\partial \theta} - \left(\frac{1}{r^2} \cdot \frac{\partial}{\partial r} (r^2 \tau_{r\theta}) + \frac{1}{r} \cdot \frac{\partial \tau_{\theta\theta}}{\partial \theta} + \frac{\partial \tau_{\theta z}}{\partial z} \right) + \rho \cdot \sigma_\theta \end{aligned} \quad (3.1)$$

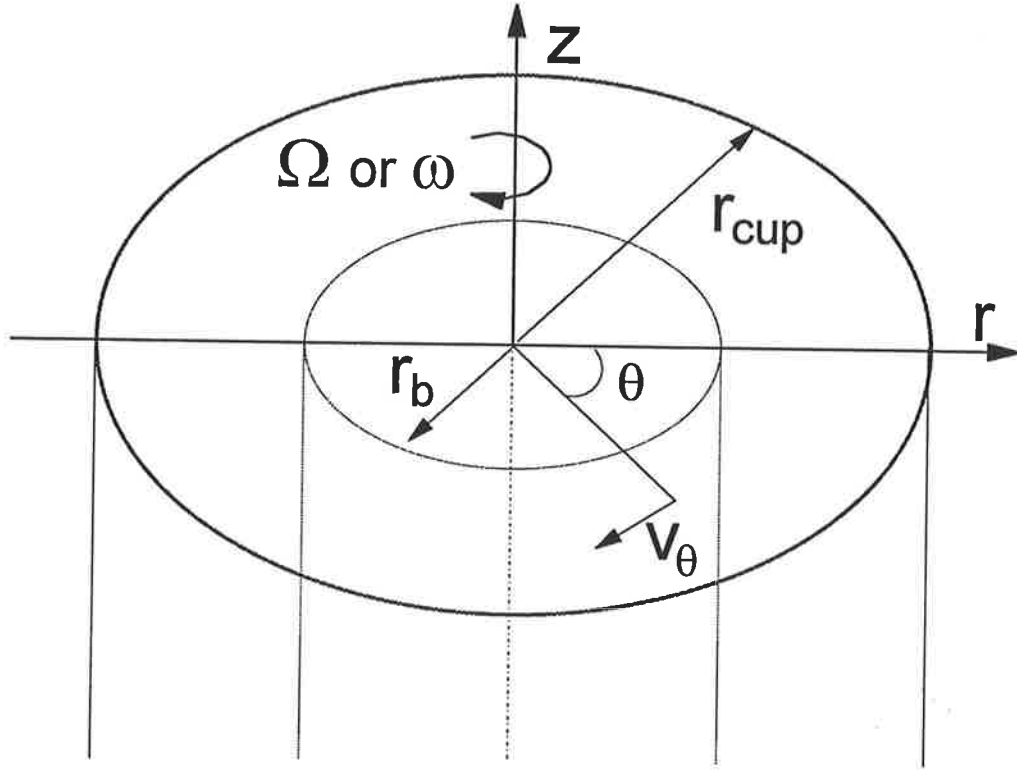


Fig. 3.1 The geometry of a Couette flow.

At steady state conditions with $v_r = v_z = 0$ and $v_\theta = r \cdot \omega$, the above equation is thus reduced to the following form, in which the pressure and body force are neglected:

$$\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \tau_{r\theta}) = 0 \quad (3.2)$$

Integrating equation (3.2) with a boundary condition at bob surface, an expression for the shear stress is obtained:

$$\tau_{r\theta} = \frac{M}{2\pi \cdot L} \cdot \frac{1}{r^2} \quad (3.3)$$

where M is the torque applied on the inner cylinder. As this is one dimensional flow, and the subscripts denoting the cylindrical co-ordinates will be omitted in the following sections and chapters for simplicity. The boundary conditions at the bob surface where $r = r_b$ are:

$$\left. \begin{aligned} \tau_b = \tau(r_b) &= \frac{M}{2\pi L} \cdot \frac{1}{r_b^2} = \tau(r) \cdot \frac{r^2}{r_b^2} \\ \omega &= \Omega \\ \dot{\gamma}(r_b) &= \dot{\gamma}_b \end{aligned} \right\} \quad (3.4)$$

while the boundary conditions at the cup, $r_{cup} = \varepsilon \cdot r_b$ are:

$$\left. \begin{aligned} \tau_{cup} = \tau(\varepsilon \cdot r_b) &= \frac{M}{2\pi \cdot L} \cdot \frac{1}{\varepsilon^2 \cdot r_b^2} = \tau_b \cdot \varepsilon^{-2} \\ \omega &= 0 \\ \dot{\gamma}(r_{cup}) &= \begin{cases} \dot{\gamma}_{cup}: & \text{fully sheared} \\ 0: & \text{partially sheared} \end{cases} \end{aligned} \right\} \quad (3.5)$$

Under partially sheared condition, the boundary condition is located at the yield boundary, $r = r_y$:

$$\left. \begin{aligned} \tau_y = \tau(r_y) &= \frac{M}{2\pi \cdot L} \cdot \frac{1}{r_y^2} = \tau_b \cdot \frac{r_b^2}{r_y^2} \\ \omega &= 0 \\ \dot{\gamma}(r_y) &= 0 \end{aligned} \right\} \quad (3.6)$$

The two flow conditions are defined as follows:

$$\text{Fully sheared:} \quad \tau_y \leq \tau_{cup} < \tau_b \quad (3.7)$$

$$\text{Partially sheared:} \quad \tau_{cup} < \tau_y < \tau_b \quad (3.8)$$

By definition, the shear rate is:

$$\dot{\gamma} = -r \cdot \frac{\partial \omega}{\partial r} \quad (3.9)$$

The angular velocity, ω , can be obtained by integrating Eq. (3.9):

$$\omega = \int_{r_o}^{r_o} \frac{\dot{\gamma}}{r} \cdot dr \quad \text{where} \quad \begin{array}{l} r_o = r_{cup} = \varepsilon \cdot r_b: \text{ fully sheared} \\ r_o = r_y: \text{ partially sheared} \end{array} \quad (3.10)$$

A similar expression for the angular velocity in term of shear stress can also be derived by using the relationship of Eq. (3.3) and substituting in Eq. (3.10):

$$\omega = -\frac{1}{2} \int_{\tau_o}^{\tau_o} \frac{\dot{\gamma}}{\tau} \cdot d\tau \quad \text{where} \quad \begin{array}{l} \tau_o = \tau_{cup} = \varepsilon^{-2} \cdot \tau_b: \text{ fully sheared} \\ \tau_o = \tau_y: \text{ partially sheared} \end{array} \quad (3.11)$$

In the past, flow behaviour has been seen analyzed in term of dimensionless parameters, especially for the fluid with a yield stress (Bird et al 1983, Darby 1985, Walton & Bittleston 1991, Briscoe et al 1992, Bittleston & Hassager 1992, Szabo & Hassager 1992). The dimensionless terms are usually defined by grouping a number of variables. Such grouping of variables into dimensionless terms reduces the number of variables and makes the analysis simple and general. In the study of flow in Couette geometry, Paria (1959) defined the "Bingham number" as $Bi = \tau_y \cdot r_b / (\mu \cdot V)$; and Batra & Das (1992) specified the "Casson number" as $Ca = \tau_y \cdot r_{cup} / (\mu \cdot V)$. τ_y and μ are the yield stress and viscosity and V is the rotational velocity of the cup.

In the current study, various dimensionless parameters are defined to characterize the flow model equations as summarized in Table 3.1.

Table 3.1 Dimensionless parameters

Variables	Dimensionless Parameters
Radius:	$r^* = r / r_b$
Shear stress:	$\tau^* = \tau / \tau_y$
Angular velocity:	$\omega^* = \omega / \Omega$
Shear rate:	$\dot{\gamma}^* = \dot{\gamma} / \Omega$
Yield numbers:	
Bingham model:	$Bi = \tau_y / (\mu \cdot \Omega)$
Casson model:	$Ca = \tau_y / (\mu \cdot \Omega)$
Herschel-Bulkley model:	$He = \left[\tau_y / (\mu \cdot \Omega^n) \right]^{1/n}$

In the following sections, the flow behaviour for the three different flow models under both fully and partially sheared conditions will be investigated. The shear stress at bob surface will be determined initially. Other flow parameters (such as the shear stress and shear rate distributions, velocity profile etc.) can also be determined with the knowledge of the shear stress at the bob surface.

Bingham model: $(\tau = \tau_y + \mu \cdot \dot{\gamma}, \quad \tau > \tau_y)$

The equation for Bingham model in dimensionless form is expressed as follows:

$$\tau^* = 1 + \frac{\dot{\gamma}^*}{Bi}, \quad \tau^* > 1 \quad (3.12)$$

using the relationship shown in Eq. (3.4), and Eq. (3.12) the dimensionless shear rate becomes:

$$\dot{\gamma}^* = Bi \cdot (r^{*-2} \tau_b^* - 1) \quad (3.13)$$

Fully sheared condition:

The dimensionless shear stress at bob surface under the fully sheared condition can be obtained by substituting Eq. (3.12) into Eq. (3.11) with boundary condition at bob surface:

$$\tau_b^* = \frac{2 \ln \varepsilon}{1 - \varepsilon^{-2}} + \frac{2}{1 - \varepsilon^{-2}} \cdot Bi^{-1} \quad (3.14)$$

Angular velocity in dimensionless form is obtained by substituting Eq. (3.13) into Eq.(3.10), with fully sheared condition:

$$\omega^* = \frac{Bi}{2} \left[(r^{*-2} - \varepsilon^{-2}) \tau_b^* - 2 \ln \left(\frac{\varepsilon}{r^*} \right) \right] \quad (3.15)$$

The distribution of shear rate under a given rotational speed can be obtained by substituting Eq. (3.14) into Eq. (3.13):

$$\dot{\gamma}^* = \frac{2r^{*-2}}{(1 - \varepsilon^{-2})} \cdot \left[1 + Bi \cdot \left(\ln \varepsilon - \frac{1 - \varepsilon^{-2}}{2} \cdot r^{*2} \right) \right] \quad (3.16)$$

Partially sheared condition:

By substituting Eq. (3.12) into Eq. (3.11) with boundary condition at bob surface, the shear stress at bob surface under the partially sheared condition is as follows:

$$\tau_b^* = \left[1 + \ln(\tau_b^*) \right] + \frac{2}{Bi} \quad (3.17)$$

The angular velocity is obtained by substituting Eq. (3.10) into Eq. (3.13), and with partially sheared condition and $r_y^* = \sqrt{\tau_b^*}$ (i.e. Eq. (3.6)):

$$\omega^* = \frac{\text{Bi}}{2} \left\{ \tau_b^* \cdot r^{*-2} - \ln(\tau_b^* \cdot r^{*-2}) - 1 \right\} \quad (3.18)$$

The corresponding shear rate distribution under a given rotating speed is obtained by substituting Eq. (3.13) into Eq. (3.17):

$$\dot{\gamma}^* = \text{Bi} \cdot \left\{ \left[1 + \ln \left[\left(1 + \frac{\dot{\gamma}^*}{\text{Bi}} \right) \cdot r^{*2} \right] + \frac{2}{\text{Bi}} \right] \cdot r^{*-2} - 1 \right\} \quad (3.19)$$

Using the similar approach, the dimensionless expressions for Casson and Herschel-Bulkley models are summarized as follows:

Casson model: $(\tau^{1/2} = \tau_y^{1/2} + \mu^{1/2} \cdot \dot{\gamma}^{1/2}, \quad \tau > \tau_y)$

$$\tau^{*1/2} = 1 + \left(\frac{\dot{\gamma}^*}{\text{Ca}} \right)^{1/2} \quad \tau^* > 1 \quad (3.20)$$

$$\dot{\gamma}^* = \text{Ca} \cdot \left(r^{*-1} \sqrt{\tau_b^*} - 1 \right)^2 \quad (3.21)$$

Fully sheared condition:

$$\tau_b^* (1 - \varepsilon^{-2}) - 4 \sqrt{\tau_b^*} (1 - \varepsilon^{-1}) + 2 \ln \varepsilon - \frac{2}{\text{Ca}} = 0 \quad (3.22)$$

$$\omega^* = \frac{\text{Ca}}{2} \left\{ \left[r^{*-2} - \varepsilon^{-2} \right] \cdot \tau_b^* + 2 \ln \left(\frac{\varepsilon}{r^*} \right) - 4 \sqrt{\tau_b^*} \cdot (r^{*-1} - \varepsilon^{-1}) \right\} \quad (3.23)$$

$$\left(\sqrt{\frac{\dot{\gamma}^*}{\text{Ca}}} + 1 \right)^2 \cdot (1 - \varepsilon^{-2}) \cdot r^{*2} - 4 \left(\sqrt{\frac{\dot{\gamma}^*}{\text{Ca}}} + 1 \right) \cdot (1 - \varepsilon^{-1}) \cdot r^* + 2 \ln \varepsilon - \frac{2}{\text{Ca}} = 0 \quad (3.24)$$

Partially sheared condition:

$$(\tau_b^* - 1) + \ln \tau_b^* - 4 (\sqrt{\tau_b^*} - 1) - \frac{2}{\text{Ca}} = 0 \quad (3.25)$$

$$\omega^* = \frac{\text{Ca}}{2} \left\{ \left[\tau_b^* \cdot r^{*-2} - 1 \right] + \ln(\tau_b^* \cdot r^{*-2}) - 4 (\sqrt{\tau_b^*} \cdot r^{*-1} - 1) \right\} \quad (3.26)$$

$$\left[\left(\sqrt{\frac{\dot{\gamma}^*}{Ca}} + 1 \right)^2 \cdot r^{*2} - 1 \right] + 2 \ln \left[\left(\sqrt{\frac{\dot{\gamma}^*}{Ca}} + 1 \right) \cdot r^* \right] - 4 \left[\left(\sqrt{\frac{\dot{\gamma}^*}{Ca}} + 1 \right) \cdot r^* - 1 \right] - \frac{2}{Ca} = 0 \quad (3.27)$$

Herschel-Bulkely model: $(\tau = \tau_y + \mu \cdot \dot{\gamma}^n, \quad \tau > \tau_y)$

$$\tau^* = 1 + \left(\frac{\dot{\gamma}^*}{He} \right)^n \quad \tau^* > 1 \quad (3.28)$$

$$\dot{\gamma}^* = He \cdot (r^{*-2} \tau_b^* - 1)^{1/n} \quad (3.29)$$

$$\frac{1}{He} = -\frac{1}{2} \int_{\tau_b^*}^{\tau_o^*} (\tau^* - 1)^{1/n} d\tau^* / \tau^* \quad (3.30)$$

where: $\tau_o^* = \tau_{cup}^* = \varepsilon^{-2} \cdot \tau_b^* \tau_b^*$ fully sheared condition

$\tau_o^* = 1$ partially sheared condition

Two numerical approaches have been adopted to solve the integral Eq. (3.30). The first method uses an integration technique while the second one uses a power series approach. Details of the approaches are described in Appendix 1. Although both methods give the same results, the second method is more convenient to use in solving the equation numerically. For the Power series approach, the solutions for fully and partially sheared conditions are as follows:

Fully sheared condition:

$$\frac{1}{He} = \sum_{p=0}^{\infty} \frac{\alpha_p(m)}{2(m-p)} \cdot (1 - \varepsilon^{-2(m-p)}) \cdot \tau_b^{*(m-p)} \quad (3.31)$$

$$\omega^* = He \cdot \sum_{p=0}^{\infty} \frac{\alpha_p(m)}{2(m-p)} \cdot (r^{*-2(m-p)} - \varepsilon^{-2(m-p)}) \cdot \tau_b^{*(m-p)} \quad (3.32)$$

$$\frac{1}{\text{He}} = \sum_{p=0}^{\infty} \frac{\alpha_p(m)}{2(m-p)} \cdot (1 - \varepsilon^{-2(m-p)}) \cdot \left[r^{*2} + \left(\frac{\dot{\gamma}^*}{\text{He}} \right)^{\frac{1}{m}} \cdot r^{*2} \right]^{(m-p)} \quad (3.33)$$

Partially sheared condition:

$$\frac{1}{\text{He}} = \sum_{p=0}^{\infty} \frac{\alpha_p(m)}{2(m-p)} \cdot (\tau_b^{*(m-p)} - 1) \quad (3.34)$$

$$\omega^* = \text{He} \cdot \sum_{p=0}^{\infty} \frac{\alpha_p(m)}{2(m-p)} \cdot (r^{*-2(m-p)} - 1) \cdot \tau_b^{*(m-p)} \quad (3.35)$$

$$\frac{1}{\text{He}} = \sum_{p=0}^{\infty} \frac{\alpha_p(m)}{2(m-p)} \cdot \left\{ \left[r^{*2} + \left(\frac{\dot{\gamma}^*}{\text{He}} \right)^{\frac{1}{m}} \cdot r^{*2} \right]^{(m-p)} - 1 \right\} \quad (3.36)$$

$$\text{where the } \alpha_p(m) = (-1)^{-p} \cdot \binom{m}{p}$$

However, if m ($m=1/n$) is an integer in the above series summations, then there exists a term that gives $(m-p) = 0$, which is undefinable. In this case, a theorem of limits is employed which defines that $m = m + \Delta x$ with Δx infinitively small i.e. $\Delta x \rightarrow 0$. Taking the term $(m-p)$ as Δx and, based on the theorem of limits (Ginzburg, 1963) the following relation holds:

$$\lim_{\Delta x \rightarrow 0} \frac{C^{\Delta x} - 1}{\Delta x} = \ln C \quad (3.37)$$

where C is any positive constant. This relationship is thus introduced into the series summations where applicable. Using this approach, the results for shear stress and shear rate at the bob can be obtained for any integer m . In addition, for integer value of m , only $p=m+1$ terms are required in the calculation while the rest of the terms (i.e. $p>m+1$) become zeros by definition. However, for non-integer m , an infinite number of terms is necessary in theory for the calculation. However, the value of the corresponding term also becomes smaller when p

is increased to a large value. Therefore, only a limited value of p is required to obtain a relatively accurate result. Appendix 1 showing that $p=10$ or greater is sufficient in the calculation. It is also interesting to note that when $m \rightarrow 1$, the analytical expressions for Herschel-Bulkley model as presented above can be reduced to those of Bingham model.

3.2 Critical Parameters for Fully and Partially Sheared Conditions

If shear stress at the cup surface is equal or greater than the yield stress, the fluid is considered to be under fully sheared condition. Otherwise, the fluid is under partially sheared condition. If the shear stress at the cup surface is equal to the yield stress, i.e. yield boundary is at cup surface, then the flow is said to be at the critical yield condition. Under fully sheared condition the following holds

$$\tau_b \cdot \varepsilon^{-2} \geq \tau_y \quad \text{or:} \quad \tau_b^* \cdot \varepsilon^{-2} \geq 1 \quad (3.38)$$

Using this relationship, the critical parameters (or critical yield number) which distinguish the fully and partially sheared conditions have been derived for these three flow models.

Bingham model:

For Bingham model, the fully sheared condition may be determined by applying the condition in Eq. (3.38) to Eq. (3.14):

$$Bi \leq \frac{2}{\varepsilon^2 - 1 - 2 \ln \varepsilon} \quad (3.39)$$

$$\text{Let } G_{Bi} = \frac{2}{\varepsilon^2 - 1 - 2 \ln \varepsilon} \quad (3.40)$$

as the critical parameter. When $Bi \leq G_{Bi}$, the fluid at fully sheared condition, otherwise it is partially sheared.

Similarly, by applying the condition in Eq. (3.38) to Eq. (3.22) and (3.31) gives:

Casson model:

$$G_{Ca} = \frac{2}{(\varepsilon - 1) \cdot (\varepsilon - 3) + 2 \ln \varepsilon} \quad (3.41)$$

Herschel-Bulkley model:

$$G_{He} = \frac{2}{\sum_{p=0}^{\infty} \frac{\alpha_p(m)}{(m-p)} \cdot (\varepsilon^{2(m-p)} - 1)} \quad (3.42)$$

Similar to the Bingham model, when $Ca \leq G_{Ca}$ or $He \leq G_{He}$, the fluid is fully sheared, otherwise is partially sheared. For Herschel-Bulkley model, when $m = 1$ (i.e. let $m = 1 + \Delta x$ with $\Delta x \rightarrow 0$) by substituting Eq. (3.37) into Eq. (3.42), it can be shown that the Herschel-Bulkley model is reduced to Bingham model Eq. (3.40).

It may be seen in Eqs. (3.40) and (3.41) that the critical parameters which specify the flow conditions (i.e. fully or partially sheared) for Bingham and Casson fluids depend only on the geometric factor, ε . Fig. 3.2 show the relationship of critical parameters G_{Bi} and G_{Ca} as functions of radius ratio for Bingham model and Casson models. At the same radius ratio condition, Bingham fluid requires lower critical parameter than Casson fluid to maintain a fully sheared condition. However, the critical parameter for Herschel-Bulkley model shown in Fig. 3.3 depends on the radius ratio as well as the power law index n ($1/m$). It is shown that the lower the power law index n , the more sensitive is the critical parameter to the change of the radius ratio. For all the three flow models, the larger the radius ratio the lower are the critical parameters. It means that larger radius ratios usually require lower yield numbers to maintain a fully sheared condition.

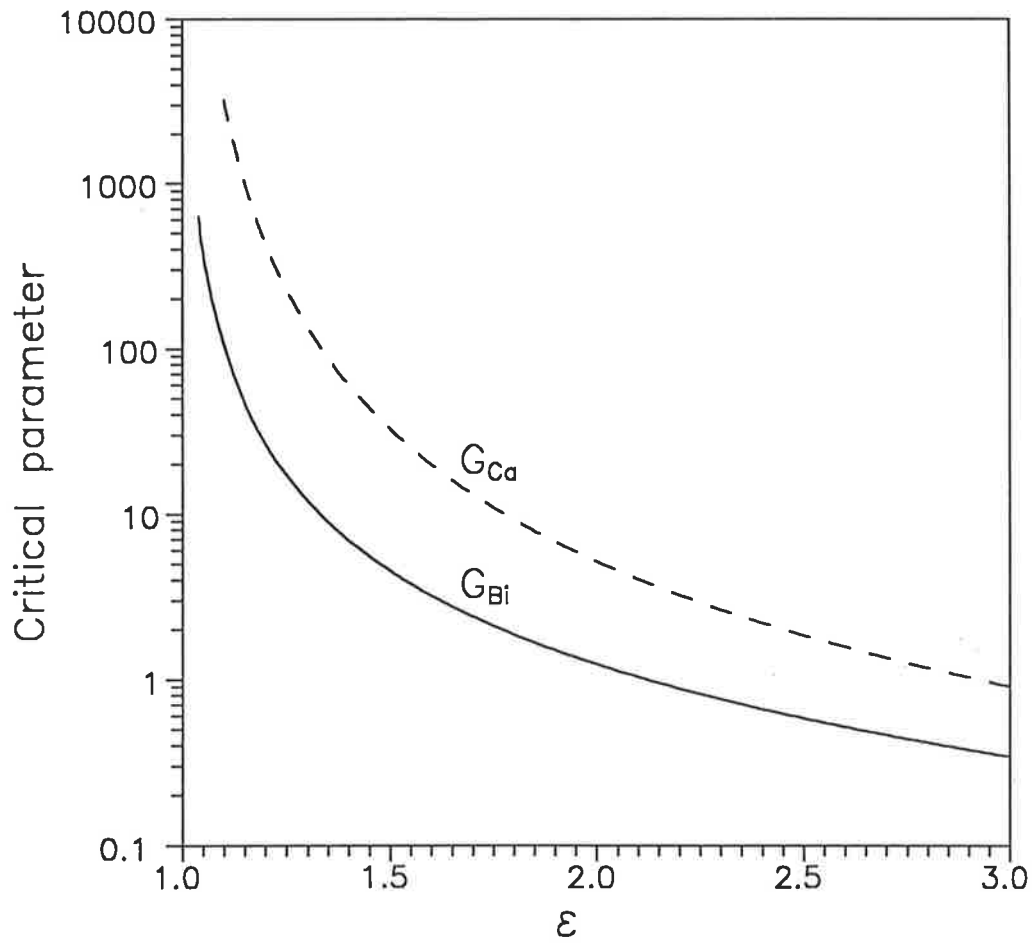


Fig. 3.2 The critical parameters G_{Bi} and G_{Ca} as a function of radius ratio for Bingham and Casson model respectively. The region below each curve is at fully sheared condition; and that above the curve is at partially sheared condition.

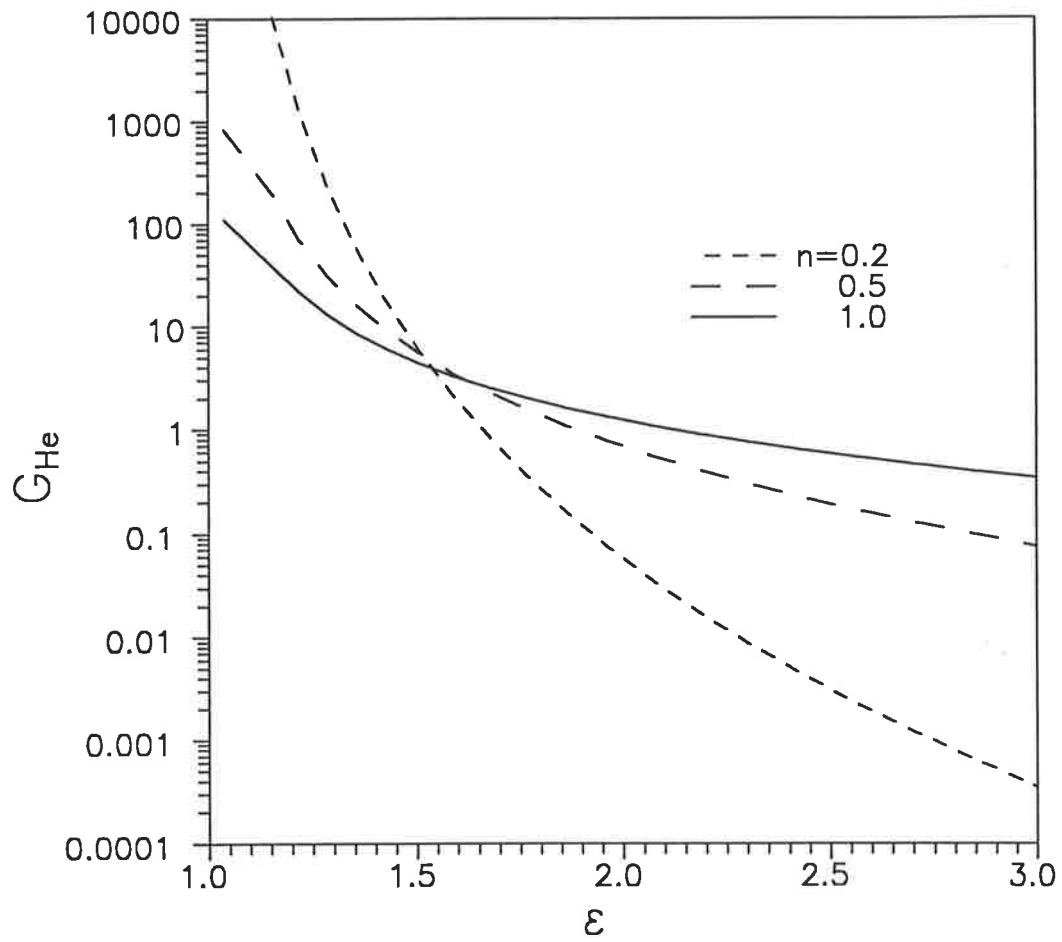


Fig. 3.3 The critical parameter G_{He} as a function of radius ratio and shear rate index for Herschel-Bulkley model. The region below each curve is at fully sheared condition; and that above the curve is at partially sheared condition.

Since the critical parameter for a given flow model corresponds to the condition where the yield boundary is at the cup surface, this gives a valuable expression relating the yield number and the yield boundary in an infinite cup medium (where the influence of the cup to the flow is irrelevant). This can be easily achieved by simply replacing the critical parameter (G_{Bi} , G_{Ca} or G_{He}) with a given yield number (Bi, Ca or He); and also the radius ratio ε with r_y^* in either Eq. (3.40), (3.41) or (3.42):

$$Bi = \frac{2}{r_y^{*2} - 1 - 2 \ln r_y^*} \quad (3.43)$$

$$Ca = \frac{2}{(r_y^* - 1) \cdot (r_y^* - 3) + 2 \ln r_y^*} \quad (3.44)$$

$$He = \frac{2}{\sum_{p=0}^{\infty} \frac{\alpha_p(m)}{(m-p)} \cdot (r_y^{*2(m-p)} - 1)} \quad (3.45)$$

3.3 Time-dependent Flow Phenomena

In this section, the change of the yield number and yield boundary with time is illustrated and discussed. From Eqs. (3.43), (3.44) and (3.45), the yield radius can be easily shown to increase monotonically with decreasing yield number or vice versa for all three flow models described earlier. For example, in the case of Bingham model, the derivative of Eq. (3.43) leads to:

$$\frac{d(\text{Bi}^{-1})}{dr_y^*} = r_y^* - r_y^{*-1} \quad (3.46)$$

The right hand side of Eq. (3.46) is always positive so that the Bi^{-1} has the same increasing or decreasing trend as r_y^* . Since the yield stress and viscosity change with time of shear, the yield number will also be a function of time, which can be determined according to Table 3.1. The yield radius is determined from Eqs. (3.43).

Fig. 3.4 show the change of yield number and yield boundary with time. In these result, the yield number is increasing with time while the flow may change from fully sheared to partially sheared conditions with the yield boundary reducing in size continuously. The fluid parameters used in the simulations can be found in Appendix 2. Similar results are also obtained for Casson and Herschel-Bulkley models which are presented in Appendix 2.

The transient behaviour of the yield number of thixotropic fluids depends on the way by which yield stress and viscosity vary in the process of structural breakdown. The yield number can either increase or decrease with time. As the bob rotating speed is constant, so either the yield number increasing or decreasing with time will depends on how the ratio of τ_y / μ is changing with time, i.e.

$$\frac{\tau_{y0}}{\mu_0} \rightarrow \frac{\tau_y(t)}{\mu(t)} \rightarrow \frac{\tau_{ye}}{\mu_e} \quad (3.47)$$

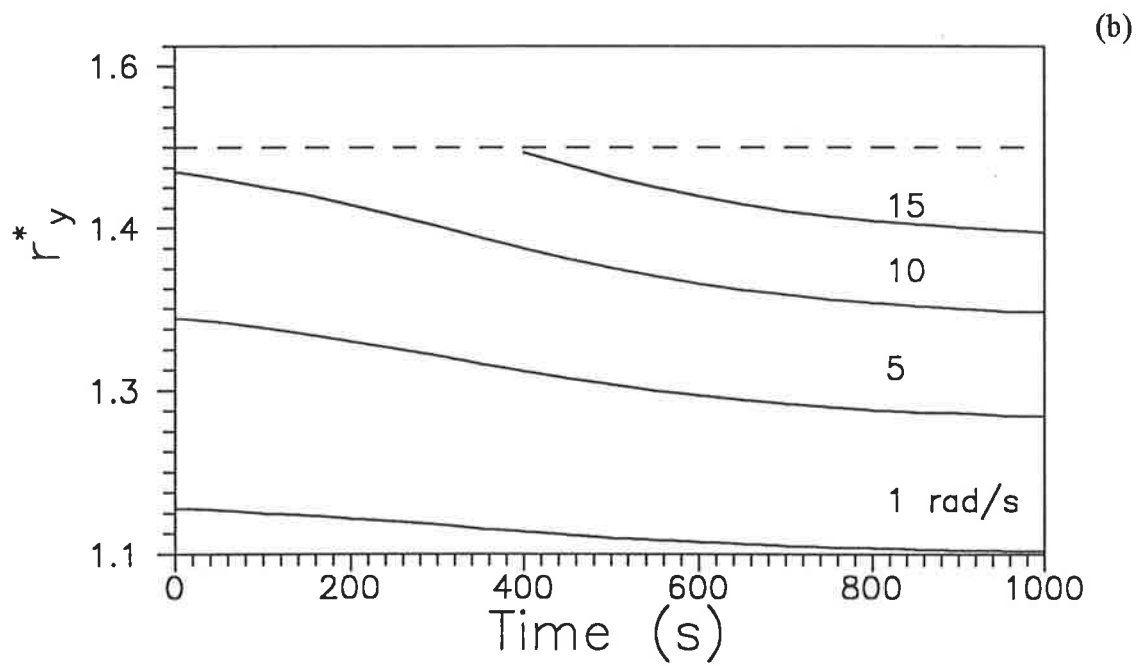
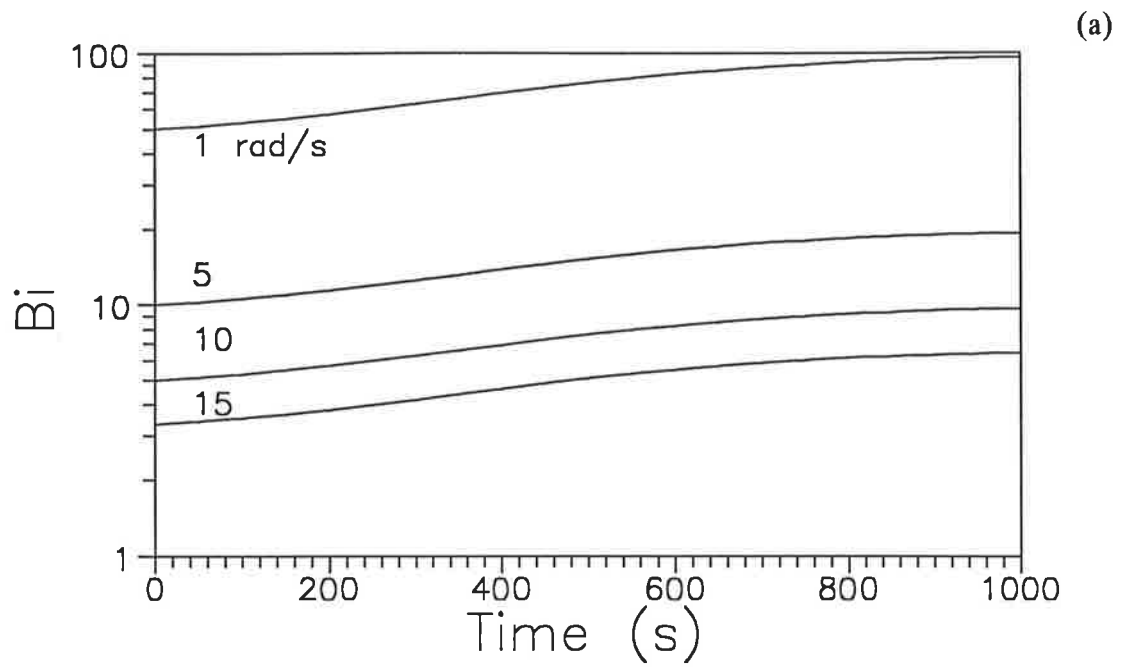


Fig. 3.4 The change of flow behaviour for thixotropic fluid based on Bingham model at $\epsilon=1.5$. (a) Yield number; (b) Yield boundary.

From the simulation results shown in Fig. 3.4, the ratio of τ_y / μ is changing from 5 (i.e. τ_{y0} / μ_0) to 10 (i.e. τ_{ye} / μ_e), so the yield number is increasing with time. However, if the fluid parameter is changed, then the yield number may show other trend instead of increasing with time. For example, let $\mu_e = 0.5$ instead of 0.1 (Pa.s), then the ratio of τ_y / μ can change from 5 (τ_{y0} / μ_0) to 2 (τ_{ye} / μ_e) which shows a decreasing trend with time. For real fluids the change of yield number with time may be more complex than the ideal data simulation. However, in the following, two simple cases will be discussed.

a) Monotonic increase of yield number with time:

If the flow is initially under partially sheared condition, then the yield radius will be decreasing with increasing time ($\Omega = 1, 5$ or 10 rad/s in Fig. 3.4 (b)). If the flow is at fully sheared condition, then there are two possibilities which will depend on the magnitude of the change of yield number. One possibility is that the flow may remain fully sheared at all time if the yield number could not increase sufficiently to reach critical yield number. While in the other case, there may exist a time t at which the yield number equals the critical yield number. When the shearing time is greater than t , the flow would change from fully sheared to partially sheared condition ($\Omega = 15$ rad/s in Fig. 3.4).

b) Monotonic decrease of yield number with time:

Under this condition, if a flow starts with fully sheared condition, it will remain under fully sheared condition at all time. If the flow starts with partially sheared condition, the yield radius under the ideal homogenous structure condition (Eqs. (3.43), (3.44) and (3.45)) would be expanding with increasing time. For thixotropic fluid, since only the fluid within the yield boundary is being sheared, the fluid parameters (such as yield stress and viscosity) outside the initial yield radius will be maintained at the initial unsheared conditions for all the time and is significantly different from that inside of the yield radius. This is because in any region beyond the initial yield radius, the continuously reduced shear stress in this region would never be enough to overcome the initial yield stress. Therefore, the yield radius should remain unchanged from its initial stage because the structure breakdown only occurs within the

sheared flow region. This initial yield boundary would behave like a cup surface for the fluid. Consequently, Eqs. (3.43), (3.44) and (3.45) can not be applied for the thixotropic fluid under partially sheared condition when the yield number is decreasing with time.

Generally, the yield radius ratio in an infinitive fluid medium condition can also be defined from Eq. (3.6) to give:

$$r_y^* = \sqrt{\tau_b / \tau_y} \quad (3.48)$$

While for a given radius ratio ε , the partially or fully sheared conditions can be determined by comparing ε and r_y^* . If r_y^* equal or greater than ε , then the flow is under fully sheared condition, otherwise partially sheared condition occurs.

When the yield stress value from the flow model is used as the yield criteria for τ_y in Eq. (3.48), then the change of yield radius ratio will be the same as for both cases (a) and (b). In case (a) where yield number is increasing (or decreasing $\sqrt{\tau_b / \tau_y}$) with time, then r_y^* will decrease with time, while in case (b) where the yield number is decreasing (or increasing $\sqrt{\tau_b / \tau_y}$) with time, then r_y^* will remain constant. However, as pointed out by Nguyen & Boger (1992), the yield stress determined from flow models might not be appropriately used as the true yield criterion, it is possible that the yield stress measured from direct method may be able to represent the true yield behaviour better in Eq. (3.48). This issue will be further discussed in Chapter 7. In such case, the change of yield boundary would not be influenced by the change of yield number, and it is only dependent on the condition in Eq. (3.48). However, under the condition when the calculated r_y^* increases with time, the expected yield radius ratio would remains constant because of the same reason discussed for case (b).

3.4 r_c Method for Bingham Model

Fig. 3.5 shows the calculated results of shear rate distribution for Bingham model at various shearing condition Bi. It is shown that the yield number is a function of shearing time i.e. Bi(t). During the shearing, if the yield number shows an increasing trend with time, then the shear rate value increases near the bob surface and decreases or even vanishes near the cup surface. Otherwise the shear rate value decreases near the bob surface and increases near the cup surface. This phenomenon leads to the fact that in the flow region near the bob and cup surface, the shear rate can change more significantly with time than the area between the surfaces of the bob and cup. In this plot there is a radius position where the shear rate value has a minimum change with Bi (or the change of fluid property with time) as compared to the shear rate at the bob surface which changes significantly with Bi.

Eq. (3.16) in section 3.1 describes the shear rate distribution for Bingham fluids under fully sheared condition. By rearranging Eq. (3.16), the following equation is obtained,

$$\frac{\dot{\gamma}}{\dot{\gamma}_N} = 1 + Bi \cdot \left(\ln \varepsilon - \frac{1 - \varepsilon^{-2}}{2} \cdot \left(\frac{r}{r_b} \right)^2 \right) \quad (3.49)$$

Where the $\dot{\gamma}_N$ is the Newtonian shear rate at radius r , i.e.:

$$\dot{\gamma}_N = \frac{2(r_b / r)^2 \cdot \Omega}{1 - \varepsilon^{-2}} \quad (3.50)$$

It is found from the Eq. (3.49) that there exists a radius position r_c which makes the coefficient of Bi equals to zero. The value r_c can be determined as follows:

$$r_c = r_b \cdot \sqrt{\frac{2 \ln \varepsilon}{1 - \varepsilon^{-2}}} \quad (3.51)$$

At this position, $\dot{\gamma}_c / \dot{\gamma}_N = 1$ and the shear rate $\dot{\gamma}_c$ is

$$\dot{\gamma}_c = \dot{\gamma}_N = \frac{2(r_b / r_c)^2 \cdot \Omega}{1 - \varepsilon^{-2}} \quad (3.52)$$

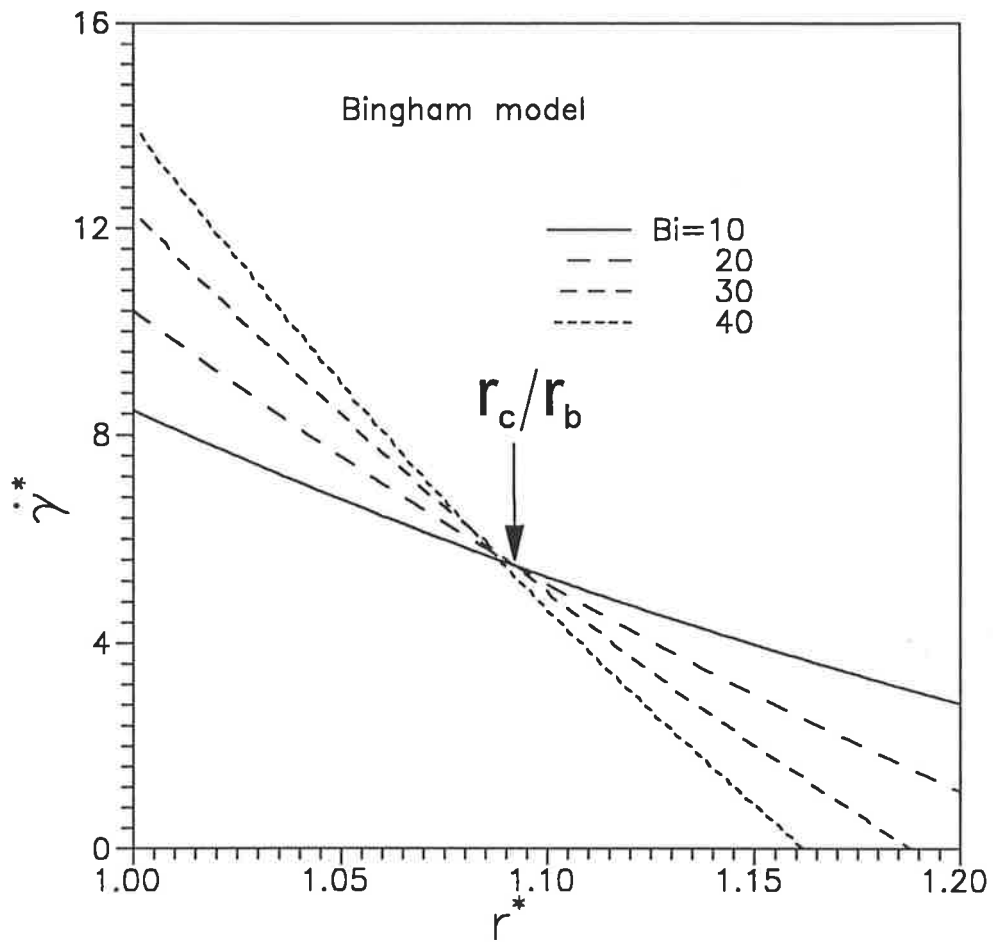


Fig. 3.5 Shear rate distribution of a Bingham flow for different values of yield number Bi , at $\varepsilon=1.2$. $Bi=10, 20$ are at fully sheared conditions; and $Bi=30, 40$ are at partially sheared conditions.

Substituting Eq. (3.51) into Eq. (3.52), gives:

$$\dot{\gamma}_c = \frac{\Omega}{\ln \varepsilon} \quad (3.53)$$

According to Eq. (3.51) the $r_c(\varepsilon)/r_b$ position is only a function of geometric factor ε and independent of the fluid parameters (such as yield stress and viscosity etc.). However, the shear rate $\dot{\gamma}_c(\varepsilon, \Omega)$ at position r_c depends on the ε and rotating speed Ω , viz. Eq. (3.52) or (3.53).

The shear stress τ_c at the critical position r_c can be determined from Eqs. (3.4) and (3.51):

$$\tau_c = \tau_b \cdot (r_b / r_c)^2 \quad (3.54)$$

For Bingham model at fully sheared condition, this $r_c(\varepsilon)$ position can be conveniently used as a reference location (instead of the bob surface) for evaluating fluid property. Each data pair (τ_b, Ω) can thus be conveniently converted to a pair of $(\tau_c, \dot{\gamma}_c)$ by means of the equations (3.53) and (3.54). The method for converting the shear stress-rotating speed pair of data into shear stress-shear rate pair of data using this approach, as in this work, is called the " r_c method". The value of shear rate at this reference point remains constant with time as long as the bob rotating speed is constant, no matter how much the shear rate will change at the bob surface (due to the change of the fluid property with time). The experimental transient data of shear stress versus time could be transformed in the following manner:

$$(\tau_b, t)_\Omega \rightarrow (\tau_c, t)_{\dot{\gamma}_c(r_c)} \rightarrow (\tau, t)_{\dot{\gamma}} \quad (3.55)$$

As reviewed in Chapter 2, the existing methods developed for evaluating the shear stress-shear rate relationship use the bob (or cup) surface as the reference position. The approximate methods which are either based on the Newtonian fluid approximation or average velocity gradient across the gap apply only under the condition of very small radius ratio. In addition, both these approximate methods assume that the shear rate is constant in the annulus. However, as illustrated in Fig. 3.5, the shear rate can vary significantly at the bob surface for different yield numbers under a given radius ratio. Obviously, the approximate

methods above will give inaccurate result when evaluating the time dependent and yield stress fluids. The more elaborate methods developed for time-independent fluids in evaluating shear stress-shear rate relation (section 2.4) also can not be applied to the time-dependent yield stress fluids due to the changing shear rate at the bob surface during shear. In view of such limitations discussed above, the r_c method as proposed here provides a more direct and accurate way to obtain shear stress-shear rate pairs of data for the time-dependent and yield stress fluid of Bingham model type.

The change of $r_c(\epsilon)/r_b$ position as a function of radius ratio for Bingham model at fully sheared condition is shown in Fig. 3.6. The calculation results show that the larger the radius ratio, the higher is the $r_c(\epsilon)/r_b$. From Eq. (3.54), the shear stress is smaller at larger $r_c(\epsilon)/r_b$ value. Consequently, the range of shear stress-shear rate data covered using this method to evaluate the fluid property is lower for a given rotating speed.

However, under the partially sheared condition, the critical position where the shear rate equals to $\Omega/\ln \epsilon$, will not be the same as the r_c position defined from the fully sheared condition. Instead, this location is shifted to a position which can be determined by substituting Eq. (3.52) into Eq. (3.19):

$$\frac{1}{Bi \cdot \ln \epsilon} = \left\{ 1 + \ln \left[\left(1 + \frac{1}{Bi \cdot \ln \epsilon} \right) \cdot \left(\frac{r_c}{r_b} \right)^2 \right] + \frac{2}{Bi} \right\} \cdot \left(\frac{r_c}{r_b} \right)^{-2} - 1 \quad (3.56)$$

It can be seen from the above equation that the $r_c(\epsilon, Bi)$ position under the partially sheared condition depends on both the radius ratio and the yield number.

Fig. 3.7 shows the change of $r_c(\epsilon, Bi)/r_b$ position with the yield number after the flow has changed from fully to partially sheared conditions for Bingham flow model. It is shown that under fully sheared condition, the critical radial position depends only on radius ratio like that in Fig. 3.6. However, as the yield number increases, the flow changes from fully to partially sheared condition, and the critical radial position moves closer to the bob surface.

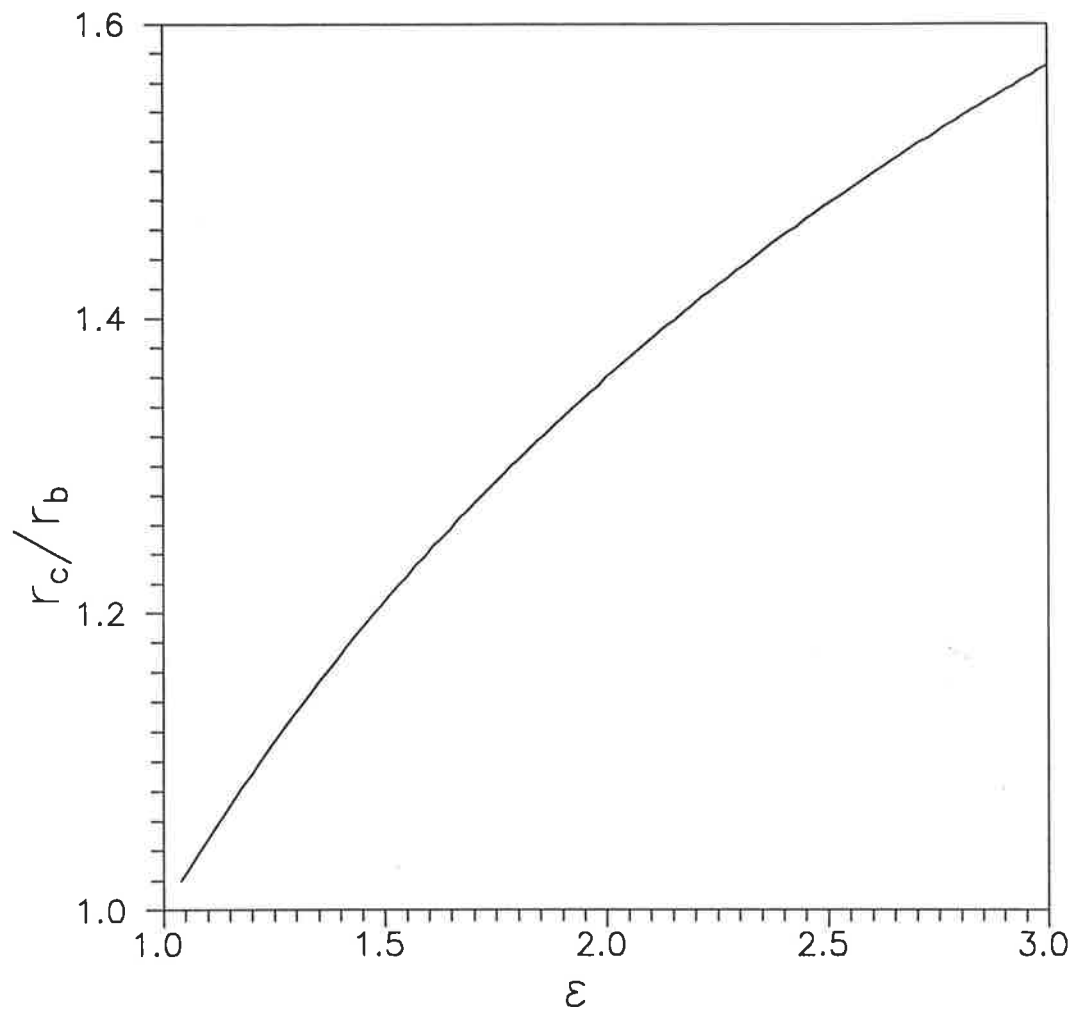


Fig. 3.6 The position of $r_c(\varepsilon)/r_b$ as a function of radius ratio for Bingham model at fully sheared condition.

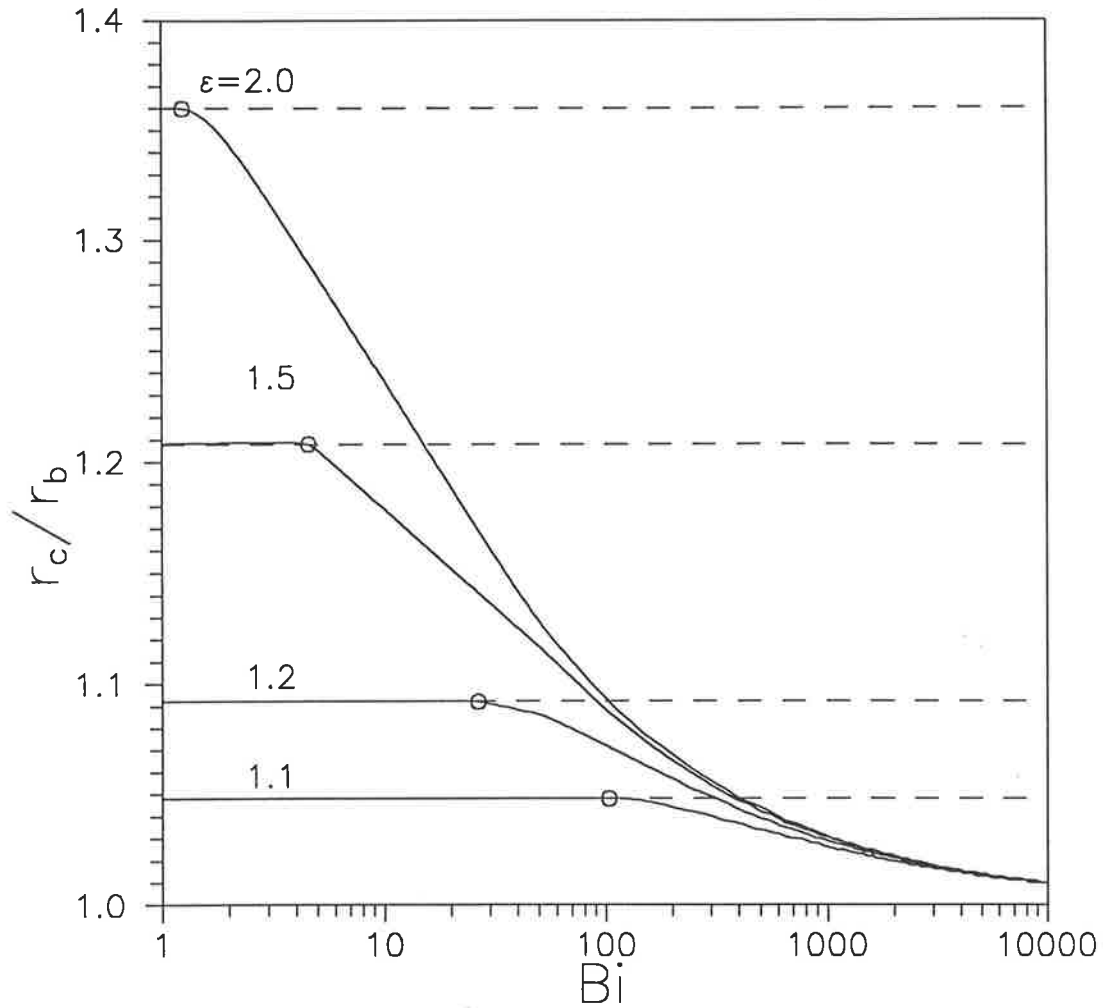


Fig. 3.7 The position of $r_c(\epsilon, Bi)/r_b$ as a function of yield number for Bingham model at fully and partially sheared conditions. The dashed lines indicate the $r_c(\epsilon)/r_b$ position for Bingham model at fully sheared condition. The circles represent the critical position at which the flow changes from fully to partially sheared condition as Bi is increased.

3.5 r_c Method for Other Types of Flow Models

In the previous section, the critical radius position $r_c(\epsilon, Bi)$ for Bingham model under partially sheared condition was shown to have a different expression than that under fully sheared condition. Fig. 3.8 and Fig. 3.9 show the shear rate distribution for different yield number for Casson and Herschel-Bulkley models respectively. It is found that, for both types of fluids the shear rate at some radial position varies with yield number at much lesser extent than that at the bob surface. This characteristic has led to the interest in further investigating the existence and location of such critical radius position for Casson and Herschel-Bulkley models in this section.

Casson model

Fully sheared condition

Substituting the Bingham shear rate at r_c position (Eq. (3.53)) into shear rate distribution (Eq. (3.24)) gives:

$$\left(\sqrt{\frac{1}{Ca \cdot \ln \epsilon}} + 1 \right)^2 \cdot (1 - \epsilon^{-2}) \cdot \left(\frac{r_c}{r_b} \right)^2 - 4 \left(\sqrt{\frac{1}{Ca \cdot \ln \epsilon}} + 1 \right) \cdot (1 - \epsilon^{-1}) \cdot \left(\frac{r_c}{r_b} \right) + 2 \ln \epsilon - \frac{2}{Ca} = 0 \quad (3.57)$$

Partially sheared condition

By substituting Eq. (3.53) into Eq.(3.27), the following expression is obtained:

$$\left[\left(\sqrt{\frac{1}{Ca \cdot \ln \epsilon}} + 1 \right)^2 \cdot \left(\frac{r_c}{r_b} \right)^2 - 1 \right] + 2 \ln \left[\left(\sqrt{\frac{1}{Ca \cdot \ln \epsilon}} + 1 \right) \cdot \left(\frac{r_c}{r_b} \right) \right] - 4 \left[\left(\sqrt{\frac{1}{Ca \cdot \ln \epsilon}} + 1 \right) \cdot \left(\frac{r_c}{r_b} \right) - 1 \right] - \frac{2}{Ca} = 0 \quad (3.58)$$

$r_c(\epsilon, Ca)/r_b$ for both fully and partially sheared conditions can be determined by solving the above equations numerically. The $r_c(\epsilon, Ca)/r_b$ position as a function of yield number and at different radius ratios are shown in Fig. 3.10. Both flow conditions i.e. fully and partially sheared, have been considered.

Herschel-Bulkley model

Fully sheared condition

Similarly, Eq. (3.53) is substituted into Eq. (3.33) and to obtain an expression

$$\frac{1}{He} = \sum_{p=0}^{\infty} \frac{\alpha_p(m)}{2(m-p)} \cdot (1 - \varepsilon^{-2(m-p)}) \cdot \left[\left(\frac{r_c}{r_b} \right)^2 + \left(\frac{1}{He \cdot \ln \varepsilon} \right)^{\frac{1}{m}} \cdot \left(\frac{r_c}{r_b} \right)^2 \right]^{(m-p)} \quad (3.59)$$

Partially sheared condition

For this condition, Eq. (3.53) is substituted into Eq. (3.36) to give

$$\frac{1}{He} = \sum_{p=0}^{\infty} \frac{\alpha_p(m)}{2(m-p)} \cdot \left\{ \left[\left(\frac{r_c}{r_b} \right)^2 + \left(\frac{1}{He \cdot \ln \varepsilon} \right)^{\frac{1}{m}} \cdot \left(\frac{r_c}{r_b} \right)^2 \right]^{(m-p)} - 1 \right\} \quad (3.60)$$

and $r_c(\varepsilon, He)/r_b$ for both fully and partially sheared conditions are then determined by solving the above equations numerically. Similar to section 3.1 the theorem of limits (i.e. Eq. (3.37)) is used to overcome the condition where $(m=p)$ for integer m . The results for $r_c(\varepsilon, He)/r_b$ as a function of yield number and different radius ratio for this flow model are shown in Fig. 3.11.

In Fig. 3.10 and Fig. 3.11, for a given radius ratio condition, when the yield number lower than the circle position, the fluid is at fully sheared condition, otherwise is at partially sheared condition. At fully sheared condition, the critical radius position has some limited deviations comparing to that of Bingham fluids. Such deviations become larger when yield number increasing to the partially sheared condition. Unlike the Fig.3.7 for Bingham model, the transitions between fully and partially sheared condition in Fig. 3.10 and Fig. 3.11 are smooth, and in the partially sheared region, the critical positions migrate towards near to the bob surface more slowly with increasing of the yield number. The critical radius positions $r_c(\varepsilon, Ca)/r_b$ and $r_c(\varepsilon, He)/r_b$ for Casson and Herschel-Bulkley models respectively are very close to the value of $r_c(\varepsilon)/r_b$ for Bingham fluids at relatively low yield number and radius

ratio less than 1.2. In general, as the radius ratio and yield number increase, larger deviations between the $r_c(\varepsilon, \text{Ca})/r_b$ and $r_c(\varepsilon)/r_b$, or $r_c(\varepsilon, \text{He})/r_b$ and $r_c(\varepsilon)/r_b$ are observed especially for partially sheared conditions.

In principle, if the critical position $r_c(\varepsilon, \text{Bi})/r_b$, $r_c(\varepsilon, \text{Ca})/r_b$ or $r_c(\varepsilon, \text{He})/r_b$ is known for a given test fluid and radius ratio condition, then it would be possible to obtain the relationship of shear stress-shear rate by using this position as the reference position. However, in practice, the value of this position is usually not known before the fluid property is characterized. It would be more convenient to use the $r_c(\varepsilon)$ based on Bingham model, for all fluids where it can be determined easily with only the knowledge of radius ratio. In next section, the errors as a result of this simplified approach in the evaluation of fluid property for conditions other than Bingham fluid under fully sheared condition are discussed.

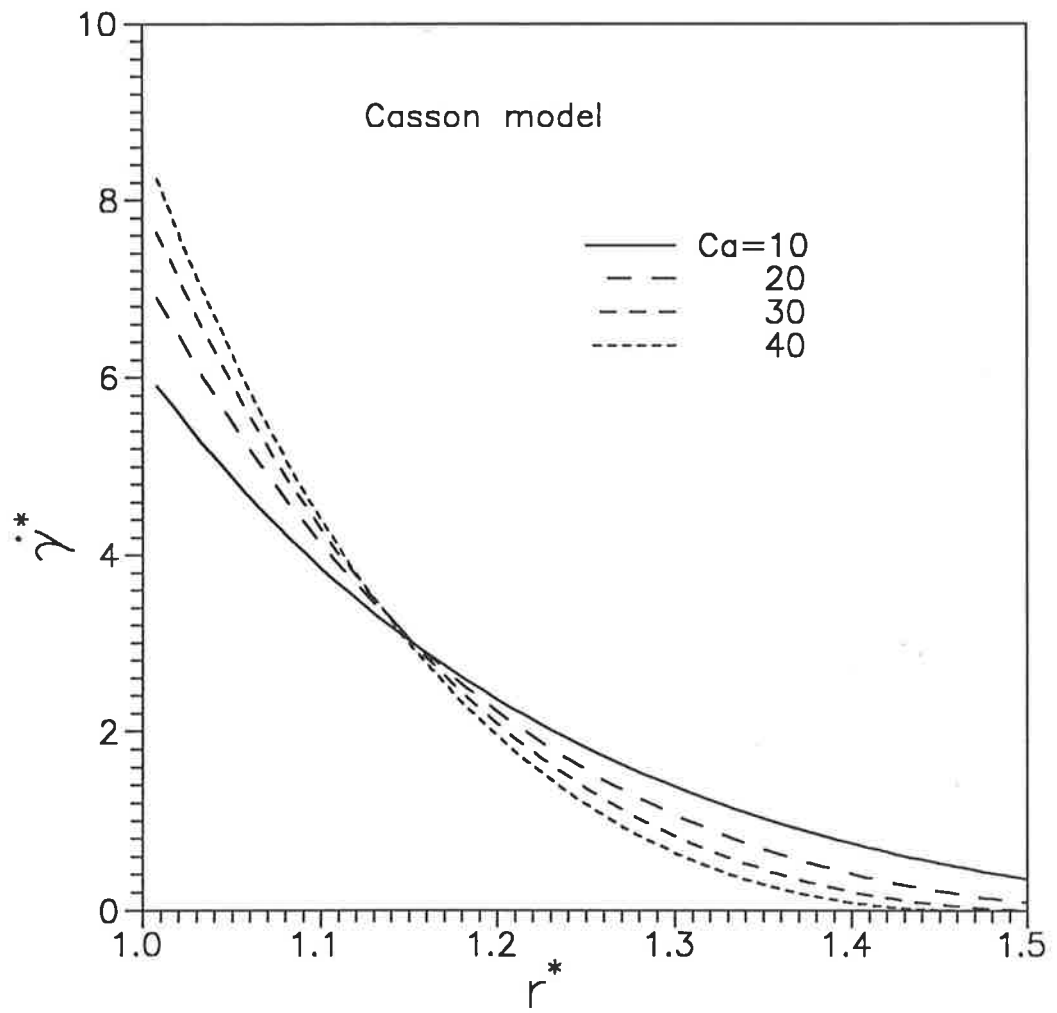


Fig. 3.8 Shear rate distribution of a Casson fluid for different values of yield number, Ca , at $\epsilon=1.5$. $\text{Ca}=10, 20$ are at fully sheared conditions; and $\text{Ca}=30, 40$ are at partially sheared conditions.

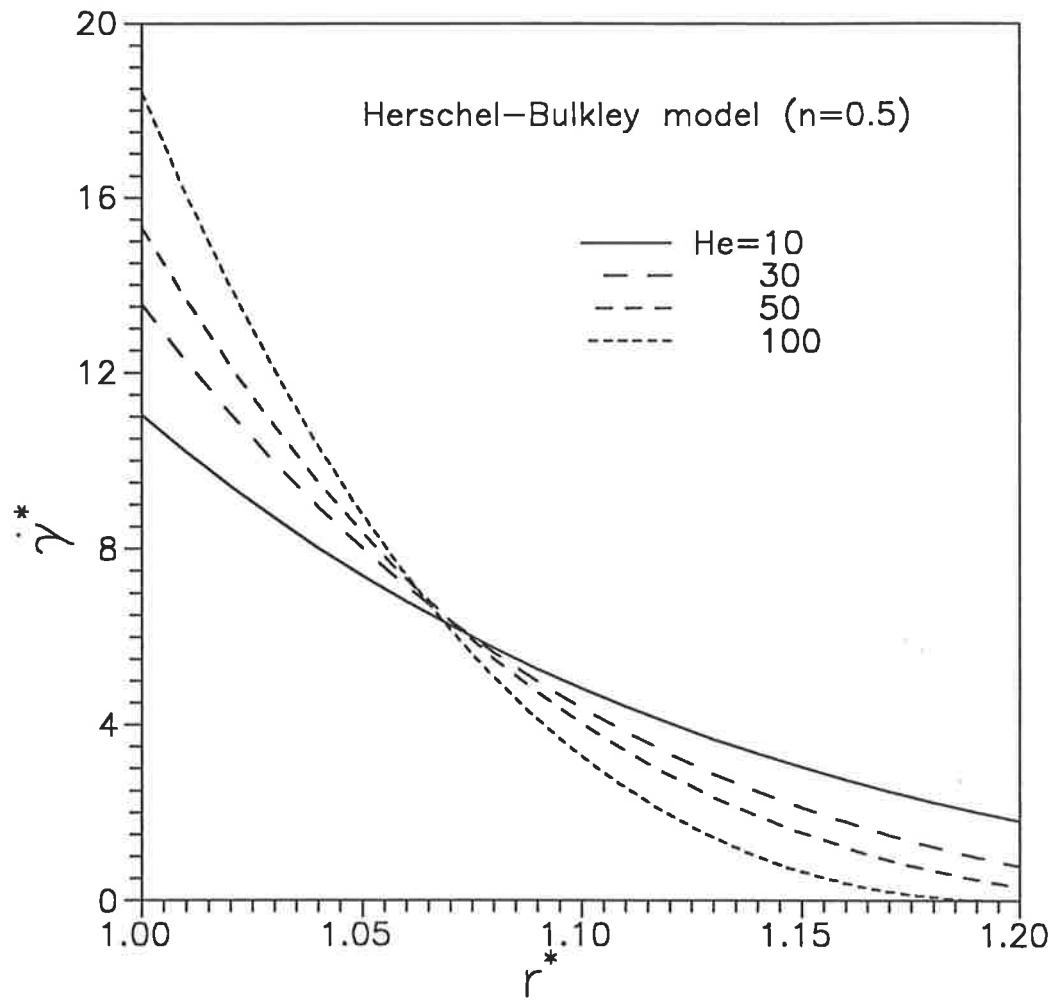


Fig. 3.9 Shear rate distribution of a Herschel-Bulkley fluid for different values of yield number, He , at $\varepsilon=1.2$. $He=10$, 30, and 50 are at fully sheared conditions; and $He=100$ is at partially sheared condition.

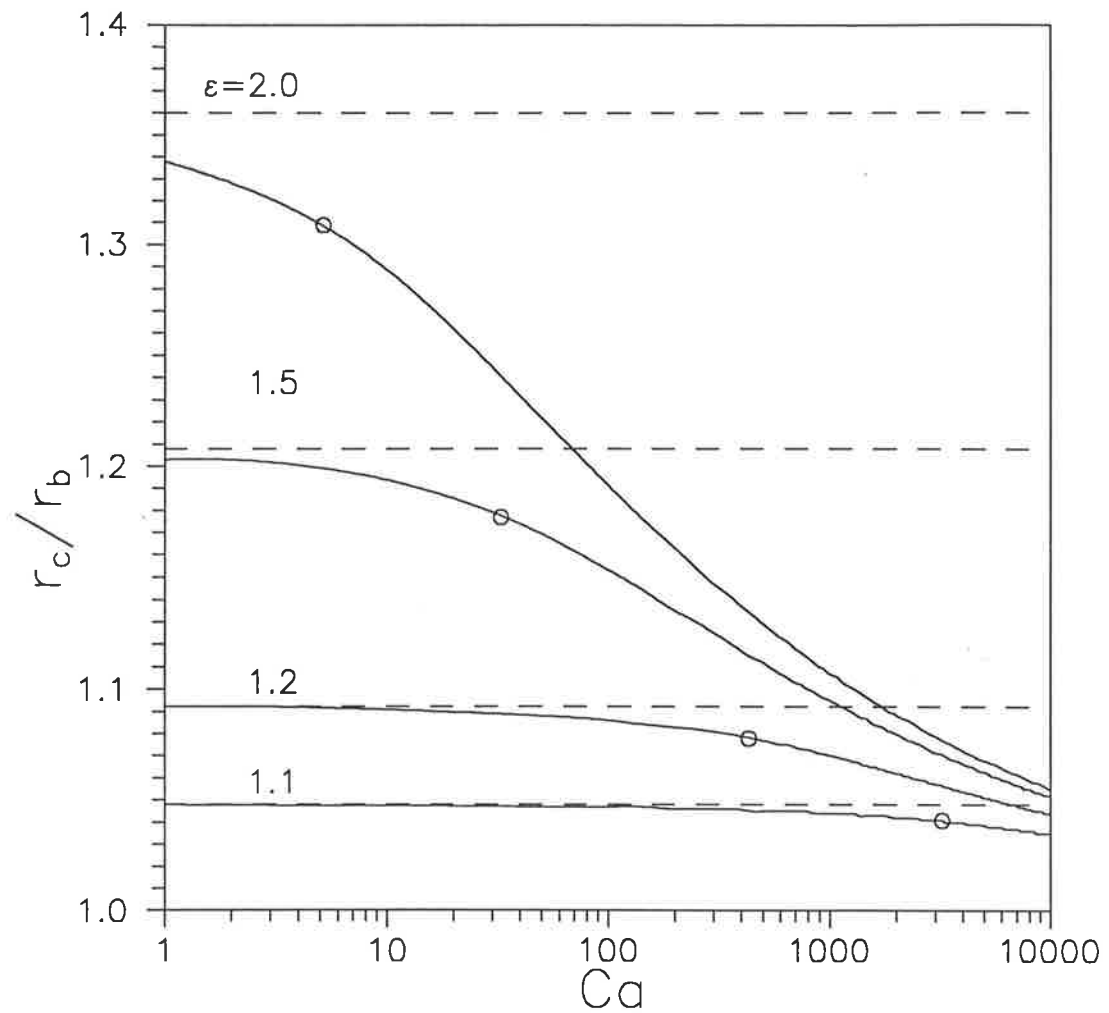


Fig. 3.10 The position of $r_c(\epsilon, Ca)/r_b$ as a function of yield number for Casson model at fully and partially sheared conditions. The dashed lines indicate the $r_c(\epsilon)/r_b$ position for Bingham model at fully sheared condition. The circles represent the critical position $r_c(\epsilon, Ca)/r_b$ at which the flow changes from fully to partially sheared condition.

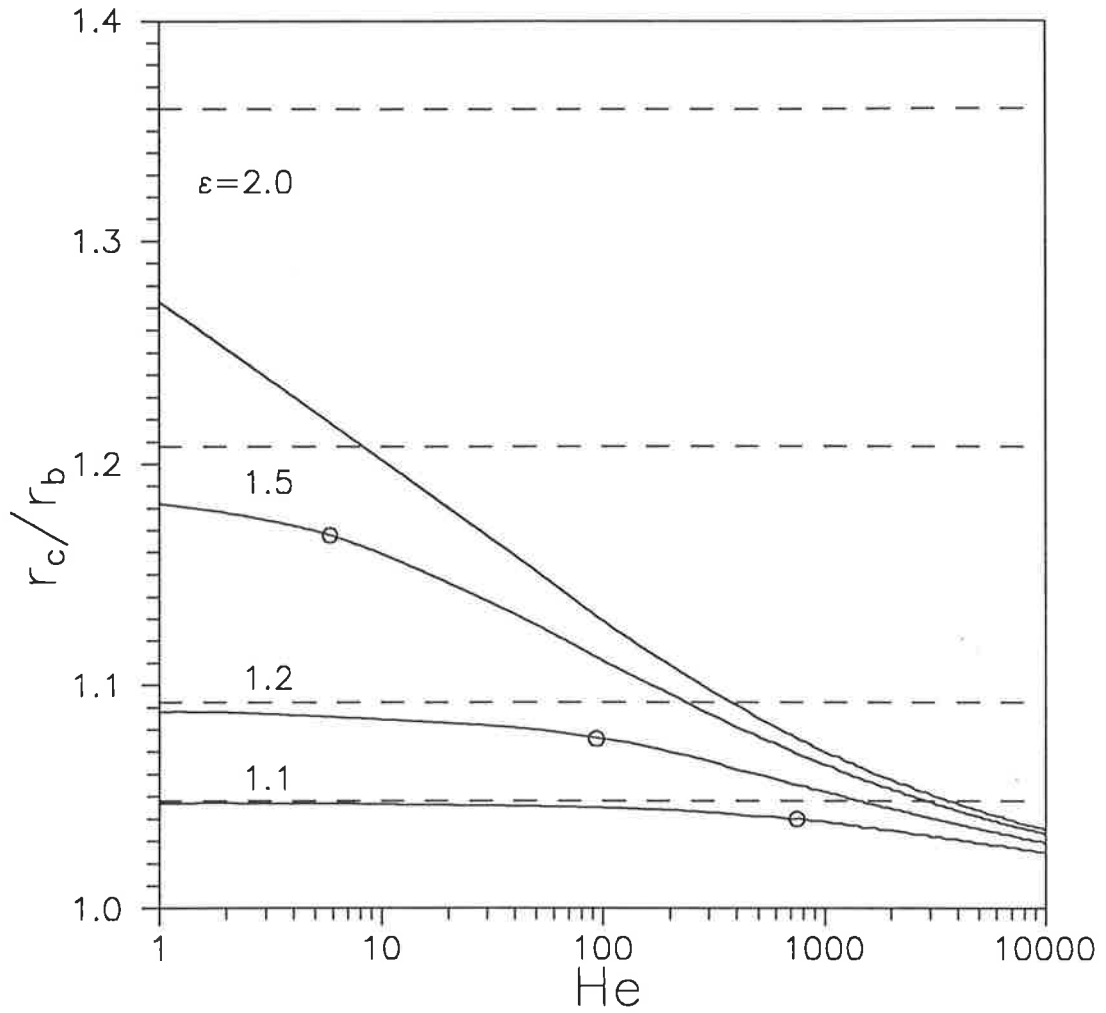


Fig. 3.11 The position of $r_c(\epsilon, He)/r_b$ as a function of yield number for Herschel-Bulkley ($n=0.5$) model at fully and partially sheared conditions. The dashed lines indicate the $r_c(\epsilon)/r_b$ position for Bingham model at fully sheared condition. The circles represent the critical position $r_c(\epsilon, He)/r_b$ at which the flow changes from fully to partially sheared condition.

3.6 Accuracy of the r_c Method in Determination of Rheological Properties

The r_c method is developed based on analysis of Bingham fluids at fully sheared condition. Thus if this method is used for other more general flow conditions, errors are expected. The errors derived for Casson and Herschel-Bulkley fluids at both fully and partially sheared conditions by using this r_c method are estimated in this section. The accuracy of using the r_c method for Casson and Herschel-Bulkley fluids varies depending on the situation. In some cases, this method can be used with relatively small errors.

Fig. 3.12 shows the schematic of a general flow curve and a Bingham flow curve. The r_c method uses the straight line o-c-b to approximate the real flow curve of o-c'-b, where the respective points are defined as follow:

- b: shear stress and shear rate at bob surface;
- o: shear stress and shear rate at cup surface;
- c: shear stress and shear rate at $r_c(\epsilon)$ position for Bingham fluid;
- c': shear stress at $\dot{\gamma}_c = \Omega / \ln \epsilon$ for actual fluid, $(\dot{\gamma}_c', \tau_c')$;
- c'': shear rate at τ_c determined by r_c for actual fluid, $(\dot{\gamma}_c'', \tau_c'')$;

The corresponding error for shear stress and shear rate is $(\tau_c - \tau_c')$ and $(\dot{\gamma}_c - \dot{\gamma}_c'')$ respectively. The accuracy of using the r_c method for a actual fluid, depends on both of the fluid and the operating conditions. For the fluid condition, it is better that the actual flow curve is relatively straight; and the actual fluid has a lower yield stress then the shear stress at the cup surface. For the operating condition, the larger the radius ratio, the longer is the line of o-c-b (due to more difference between τ_b and τ_o), which may result in the larger errors of $(\tau_c - \tau_c')$ and $(\dot{\gamma}_c - \dot{\gamma}_c'')$. Also the bob rotating speed should not be too low, that the shear stress at the cup surface is higher than the yield stress of the actual fluid to maintain a fully sheared condition.

The magnitude of these errors for shear stress are estimated in the following section. The error estimation for shear rate for different flow models is presented in Appendix 1. A

general symbol Yn is used to represent the yield number (Bi, Ca, or He) for the actual fluid for convenience.

a) Error estimation in shear stress for different flow models

The error of shear stress at the point of $\dot{\gamma} = \Omega / \ln \varepsilon$ is defined as:

$$\text{error}\% = \frac{\tau_c - \tau_c'}{\tau_c'} \times 100 = \frac{\tau_b^* \cdot \left(\frac{r_c(\varepsilon)}{r_b} \right)^{-2} - \tau_b^* \cdot \left(\frac{r_c(\varepsilon, Yn)}{r_b} \right)^{-2}}{\tau_b^* \cdot \left(\frac{r_c(\varepsilon, Yn)}{r_b} \right)^{-2}} \times 100 = \left[\left(\frac{r_c(\varepsilon, Yn)}{r_c(\varepsilon)} \right)^2 - 1 \right] \times 100 \quad (3.61)$$

The error for shear stress derived from using the r_c method depends on the given radius ratio and the yield number. The $r_c(\varepsilon)/r_b$ can be readily determined easily for a given radius ratio; and the $r_c(\varepsilon, Yn)$ can be derived for the different flow models in the sections 3.4 and 3.5.

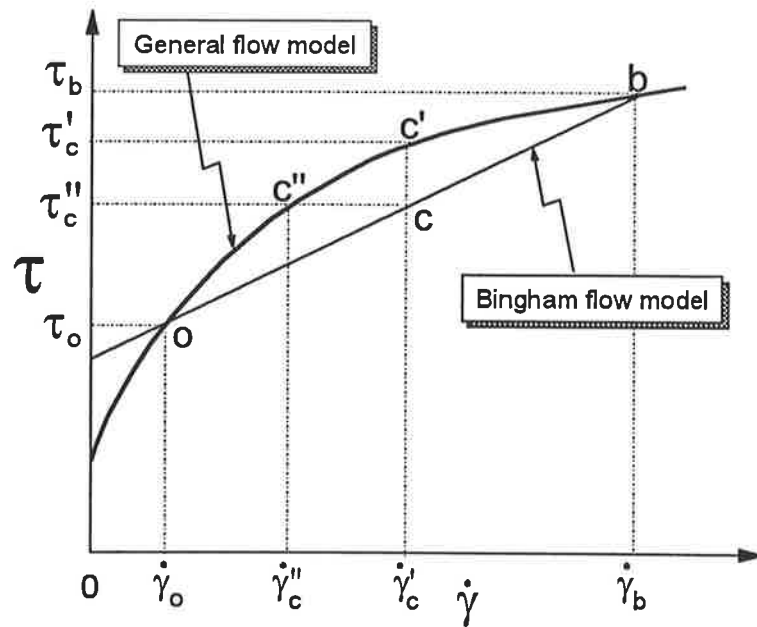


Fig. 3.12 A schematic showing the errors in determination of the shear stress-shear rate relationship for a typical fluid using the r_c method. Line o-c-b represents the flow curve for Bingham model and $\dot{\gamma}_c' = \dot{\gamma}_c$; $\tau_c'' = \tau_c$.

The shear stress is usually underestimated if the actual fluid is assumed as a Bingham type at a fully sheared flow condition, which is similar to that shown in Fig. 3.12. An example is shown here to calculate the error for Casson model. Using flow conditions of $\epsilon=1.2$ and $Ca=100$, flow is shown to be at fully sheared condition according to Eq. (3.41). From Eq. (3.51), $r_c(\epsilon)/r_b = 1.092$ and $r_c(\epsilon, Ca)/r_b = 1.086$ from Eq. (3.57). Therefore, the error for shear stress of -1.188% is determined by substituting the $r_c(\epsilon)/r_b = 1.092$ and $r_c(\epsilon, Ca)/r_b = 1.086$ in to Eq. (3.61).

b) Maximum possible error in shear stress in using the r_c method

Although the error from using the r_c method can be estimated as shown in the above section, the flow behaviour is usually not known in practice before the fluid property is being evaluated. Even if the flow behaviour is known, it is still tedious to fit the appropriate flow model, and go through the analytical procedure as described above. Consequently, a simple method for estimating the maximum possible error for shear stress, independent of the type of flow model, is proposed here.

As shown in earlier Figs. 3.7, 3.10, and 3.11 in section 3.4 and 3.5, the $r_c(\epsilon, Y_n)$ (where $Y_n = Bi, Ca$ or He) position always moves progressively towards the bob surface as the yield number is increased. Irrespective of the value of the yield number and radius ratio, the $r_c(\epsilon, Y_n)$ position always lies between $r_c(\epsilon)$ and r_b . The limiting case which represents the largest possible error is when $r_c(\epsilon, Y_n) = r_b$. Substituting this limiting condition where $r_c(\epsilon, Y_n) = r_b$ into Eq. (3.61), the maximum absolute error for the shear stress is:

$$\text{Error\%} \leq \left| \left(\frac{r_b}{r_c(\epsilon)} \right)^2 - 1 \right| \times 100 \quad (3.62)$$

From the above equation, the error is clearly larger for larger radius ratio. Fig. 3.13 shows a plot of this Error% against different values of radius ratio ϵ for all cases of flow models conditions. It can be shown that, the error for the radius $\epsilon = 1.048$ is less than 4.6%, while for $\epsilon = 1.141$, $\text{Error} \leq 12.1\%$. However, for the flow at a very high yield number (usually for high

yield stress, and at very low rotating speed), the actual error may approach the limit of the maximum error. In contrast, the maximum possible error on shear rate can be determined only when the flow model for the given fluid is known which will not be further discussed here.

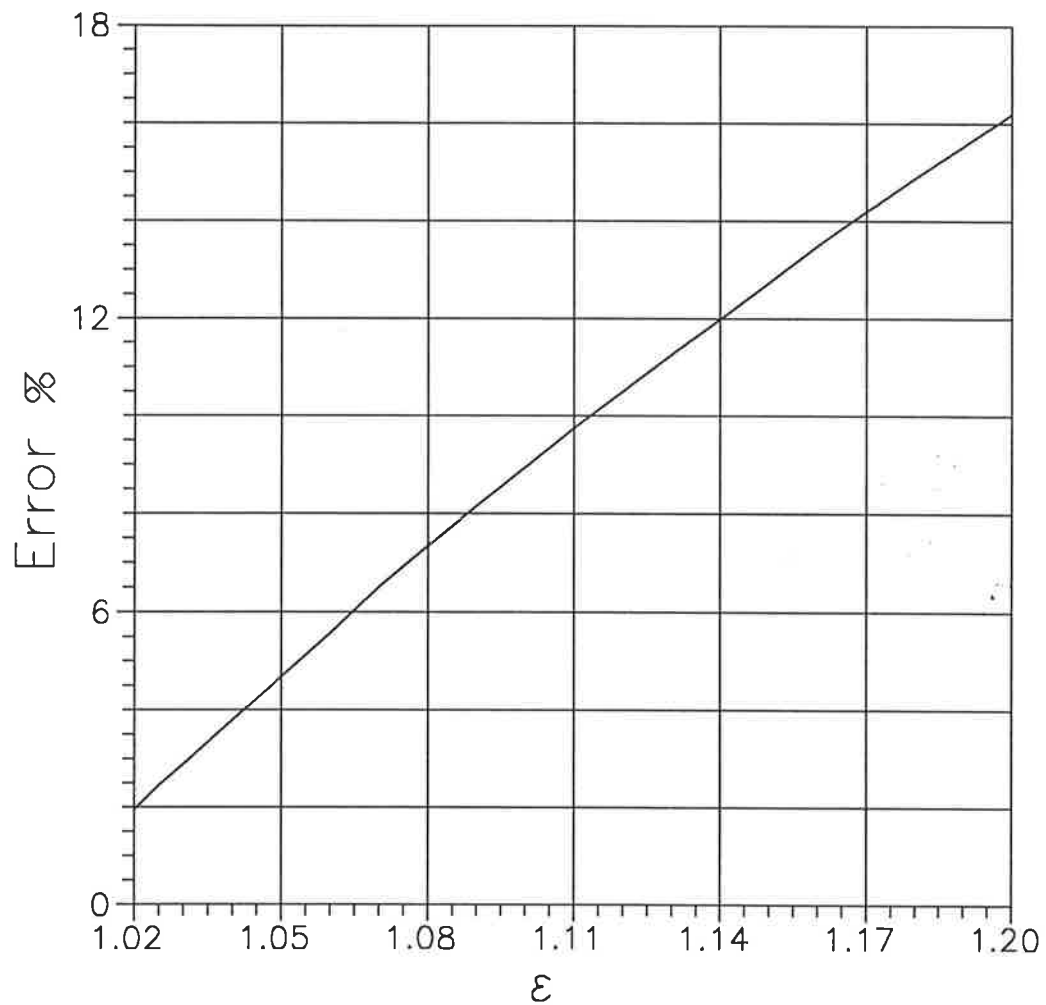


Fig. 3.13 Maximum possible error for shear stress estimated in using the r_c method for all flow conditions.

3.7 Further Discussion on the r_c Method

The analysis in section 3.4 to 3.6 concluded that the r_c method provides an improved approach to evaluate fluid property as compared to the usual approach by using the shearing surface. Good accuracy of using this method needs that the actual flow curve in Fig. 3.12 is reasonably straight in the range of o-c'-b and the shear stress at cup surface is greater than the yield stress. This method can be adopted with reasonable accuracy if the radius ratio used is not too large. Clearly, the use of narrow gap is limited to suspension consisting of very fine particles. Thus, it is required to know the range of gap size which is accurate enough for a given fluid and bob rotating speed when using the r_c method.

A practical method to check the accuracy of the r_c method is to use two sensor systems with ε_1 and ε_2 (say $\varepsilon_2 > \varepsilon_1$) to generate identical shear rate at their corresponding r_c positions. If both methods produce the same results of the flow property, then the r_c method can be used. If the results from both methods are not in good agreement then at least one of the radius ratio is too large. In addition to the limitation of the r_c method, it is possible that "other effects" such as slip factor, end effect, radial movement of particles by centrifugal force, and turbulence may also contribute to the disagreement between the two sensor systems. Such "other effects" will influence the experimental results at different extents for various sensor systems.

Fig. 3.14 shows a group of constant structure flow curves (i.e. $\lambda_1, \dots, \lambda_5$) for a yield stress time-dependent fluid. The decay of the shear stress under a constant rotating speed are represented by the intersecting lines τ_b and τ_{cup} which are the shear stress at the bob and cup respectively. If the constant structure flow curves within the region confined by the shear stress at bob and cup surfaces, highlighted in Fig. 3.12, can be well approximated by a straight line, then the error resulting from the r_c method would be relatively small.

The methods for the time-independent fluids (i.e. Krieger et al (1952, 1953, 1954, 1968), Yang & Krieger (1978)) have been developed to convert the experimental shear stress-speed data into shear stress-shear rate relationships for time-independent fluids. These

methods require the condition that all the shear stress-rotational speed pairs of data are obtained when there is no structure change on the given tested fluid. For time-dependent fluid, each individual curve in a group of constant structure flow curves, represents a constant fluid structure level. Therefore, under this special case, the methods developed for the time-independent fluid can be used to obtain the shear stress-shear rate pairs of data for a constant structure flow curve. The r_c method and the Krieger method for time-independent fluids (Yang & Krieger 1978) will be compared in obtaining the constant structure fluid curves using the experimental results in Chapter 6.

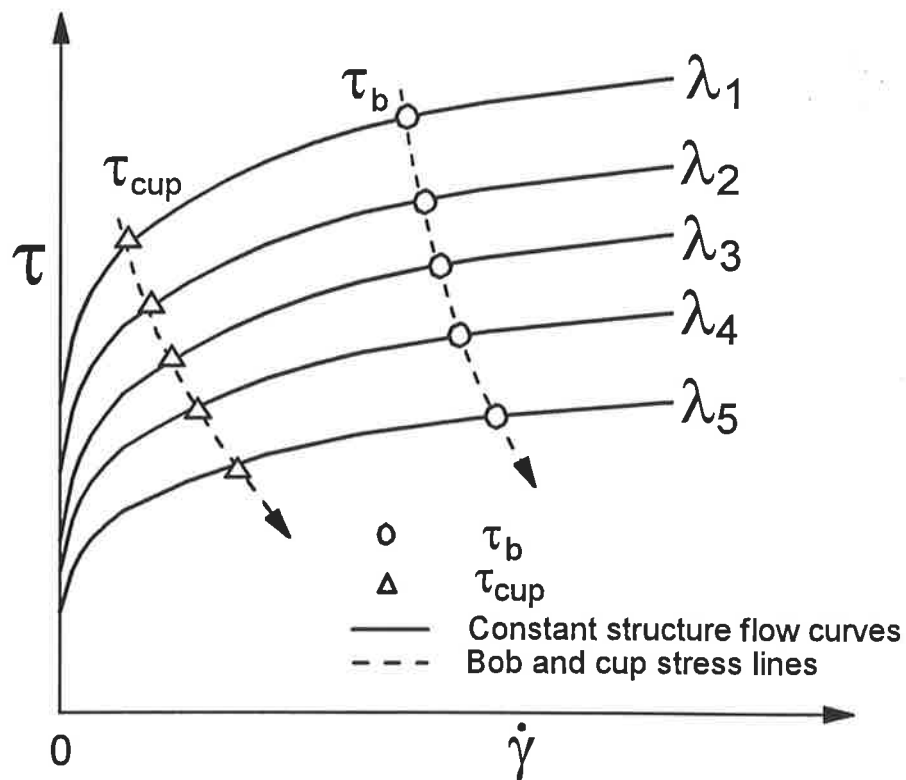


Fig. 3.14 A schematic showing the change of shear stress-shear rate values at bob and cup surfaces for a typical thixotropic fluid during shear.

Chapter 4

Unsteady Shear Flow

4.1 Introduction

In this chapter, the unsteady state shear flow is studied for three different flow models with yield stress. Transient phenomena of the flow such as velocity profile, shear rate distribution and yield boundary have been simulated. Both of the time-independent and time-dependent fluids have been considered.

The study of unsteady shear flow in various geometries involves solving of the equation of motion. The general form of the equation of motion has been described in section 3.1 (see Eq. (3.1)). The equation of motion for tangential Couette flow is expressed as follow:

$$\rho \frac{\partial v}{\partial t} = -\frac{1}{r^2} \cdot \frac{\partial}{\partial r} (r^2 \tau) \quad (4.1)$$

The respective variables are defined in Fig. 3.1. For the yield stress fluids, it is possible that only a part of the fluid region is yielded. However, Eq. (4.1) is only valid in the yielded flow region where the shear stress is greater than the yield stress. In the unyielded region, the shear rate in the fluid is zero and velocity remains constant. Therefore, the solution of the problem becomes more involved if the fluid has a yield stress because the yield boundary has to be determined before the differential equation can be solved. However, the boundary condition (i.e. yield boundary) is usually not known prior to the knowledge of the velocity profile which in fact forms the solution of the equation of motion.

Papanastasiou (1987) introduced a modified constitutive equation to approximate the ideal Bingham plastic fluid. Papanastasiou used this approach to analyze flow behaviour successfully in various complex geometries at steady state. This one dimensional flow of the modified constitutive equation, called Papanastasiou model in this study, is as follows:

$$\tau = \left[\mu + \frac{\tau_y (1 - \exp(-n|\dot{\gamma}|))}{|\dot{\gamma}|} \right] \cdot \dot{\gamma} \quad (4.2)$$

Papanastasiou model approaches the ideal Bingham model for large value of n (i.e. >50). One key feature of the Papanastasiou model which differs from the ideal Bingham fluid is that there is no critical shear stress value below which the shear rate is zero. So, the flow occurs throughout the fluid region. The main advantage of using this approach is there is no need to track the location of the yield boundary before the flow pattern can be solved. In this chapter, Papanastasiou model was adopted to approximate the ideal Bingham model and later extended to Casson and Herschel-Bulkley models. Such extension will be denoted as "modified" Bingham, Casson and Herschel-Bulkley models respectively. The modified flow models will be used in the equation of motion to solve the unsteady state flow problem. Since the flow as described by Eq. (4.2) is continuous throughout the whole region, the surfaces at the bob and cup are set as the boundary conditions. Again for generality, the variables are expressed in dimensionless forms as summarized in Table 4.1.

Table 4.1 Dimensionless variables

Variable	Dimensionless Term *
Velocity:	$\varphi = v / (r_b \cdot \Omega)$
Time:	$T = \mu \cdot t / (\rho \cdot r_b^2)$
Exponent	$N = n \cdot \Omega$
Eq. (4.2)	$\tau^* = \frac{\dot{\gamma}^*}{Bi} + \frac{\dot{\gamma}^*}{ \dot{\gamma}^* } (1 - \exp(-N \cdot \dot{\gamma}^*))$
<u>Boundary conditions:</u>	
At bob surface	$r^* = 1; \quad \varphi = 1$
At cup surface	$r^* = \varepsilon; \quad \varphi = 0$
<u>Initial conditions:</u>	$T = 0; \quad \varphi = 0$

* Other dimensionless shear stress, shear rate, radius and yield number have been defined in Table 3.1

The velocity profile can be solved from Eq. (4.1) by applying the appropriate flow model. The numerical subroutine DMOLCH, available in the IMSL (1987) was used to solve the partial differential equation (4.1). The subroutine uses the numerical method of Gear and method of lines with cubic Hermite polynomials (i.e. $H_3=x^3-3x$) in the spatial approximation (IMSL 1987). The error tolerance was set at 0.1%. Details of the numerical solver are described in the Volume II of the IMSL user's manual (IMSL 1987).

After solving for the velocity profile, the shear rate distribution is next determined by using a simple approximation method of finite difference. The radius r_i^* within the boundary is divided into I number of small intervals with i varies from 1 to I.

$$\bar{\dot{\gamma}}^*(\bar{r}_i^*) = -\bar{r}_i^* \frac{\partial(\varphi / r^*)}{\partial r^*} \bigg|_{\bar{r}_i^*} \approx -\bar{r}_i^* \frac{\Delta(\varphi / r^*)}{\Delta r^*} \quad (4.3)$$

where $\bar{r}_i^* = (r_i^* + r_{i+1}^*) / 2$, $\Delta r^* = r_{i+1}^* - r_i^*$, and $\Delta(\varphi / r^*) = (\varphi_{i+1} / r_{i+1}^*) - (\varphi_i / r_i^*)$.

A reasonable approximation can be obtained if the incremental radius Δr^* is small enough.

4.2 Unsteady Shear Flow for Time-Independent Fluids

4.2.1 Modified Bingham model

Papanastasiou model is used for the modified Bingham model. For $\dot{\gamma} > 0$, the dimensionless form of the modified Bingham model becomes:

$$\tau^* = \frac{\dot{\gamma}^*}{Bi} + (1 - \exp(-N \cdot \dot{\gamma}^*)) \quad (4.4)$$

A comparison of flow curves for ideal and modified Bingham model for different values of N in dimensionless form is shown in Fig. 4.1. It may be seen that when N is large, the modified Bingham model approaches the ideal Bingham model. A value of N equal to or greater than 100 was used in the modified Bingham model in this study.

Substituting the constitutive Eq. (4.4) into Eq. (4.1), the following equation is obtained:

$$\frac{\partial \phi}{\partial T} = -\frac{1}{r^{*2}} \frac{\partial}{\partial r^*} \left[r^{*2} \left(\text{Bi} \cdot \left(1 - \exp \left(-N \cdot \left(-r^* \frac{\partial(\phi / r^*)}{\partial r^*} \right) \right) \right) + \left(-r^* \frac{\partial(\phi / r^*)}{\partial r^*} \right) \right) \right] \quad (4.5)$$

Expanding Eq. (4.5), gives

$$\begin{aligned} \frac{\partial \phi}{\partial T} = & -\frac{2\text{Bi}}{r^*} \cdot \left[1 - \exp \left(-N \cdot \left(-r^* \frac{\partial(\phi / r^*)}{\partial r^*} \right) \right) \right] + 2 \cdot \frac{\partial(\phi / r^*)}{\partial r^*} \\ & + \left[\text{Bi} \cdot N \cdot \left(\exp \left(-N \cdot \left(-r^* \frac{\partial(\phi / r^*)}{\partial r^*} \right) \right) \right) + 1 \right] \cdot \left(\frac{\partial(\phi / r^*)}{\partial r} + r^* \cdot \frac{\partial^2(\phi / r^*)}{\partial r^{*2}} \right) \end{aligned} \quad (4.6)$$

When $\text{Bi}=0$, Eq. (4.6) reduces to the expression for Newtonian flow (Bird & Curtiss 1959). The calculated results using the current numerical method for $\text{Bi}=0$ (i.e. Newtonian fluid) are shown in Fig. 4.2 and compared with the analytical solution obtained by Bird and Curtiss (1959). The radius ratio used in the simulation is 5. This comparison was done to verify the accuracy of the numerical approach for solving the equation of motion. Further numerical simulations were then extended to other conditions which will be discussed in the following.

The transient velocity profile for $\text{Bi}=10$, is shown in Fig. 4.3. The radius ratio of this condition was selected as 1.6 which is larger than the yield boundary of an ideal Bingham model at steady state, i.e. 1.33 from Eq. (3.39). In this simulation, the radius ratio was divided into 160 intervals and T ranged from 0.001 to 10. The flow reaches equilibrium when $T>1$ and the numerical results at this time are also in good agreement with the analytical solutions for the ideal Bingham model at steady state as derived in section 3.1. The corresponding transient behaviour of shear rate distribution is also shown in Fig. 4.4. The shear rate distributions calculated numerically also agree well with the analytical solution for

ideal Bingham model at steady state, thus confirming the accuracy of the finite difference method used. In addition, the numerical shear rate profiles diminish in magnitude at the location of the yield boundary as calculated from ideal Bingham model at steady state, i.e. 1.33. In the following sections, the study of the transient flow behaviour is extended to modified Casson and Herschel-Bulkley models.

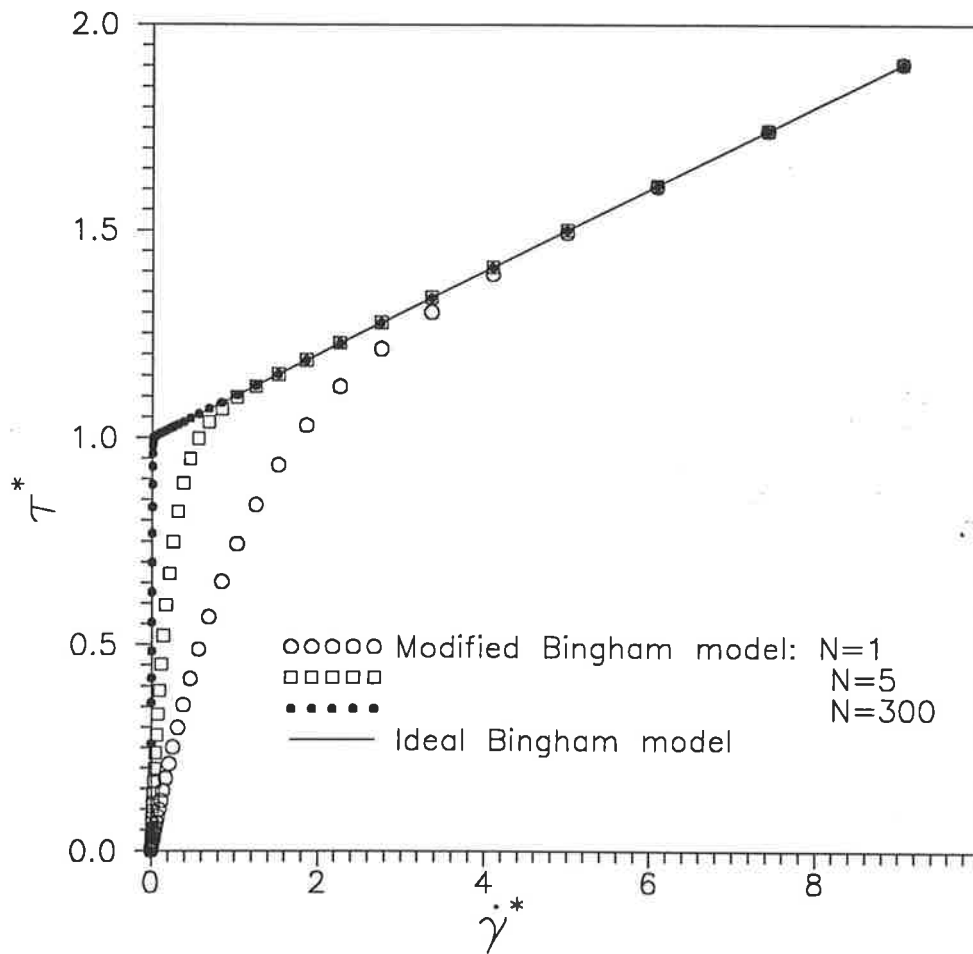


Fig. 4.1 Comparison of the ideal Bingham model and the modified Bingham model with different values of N .

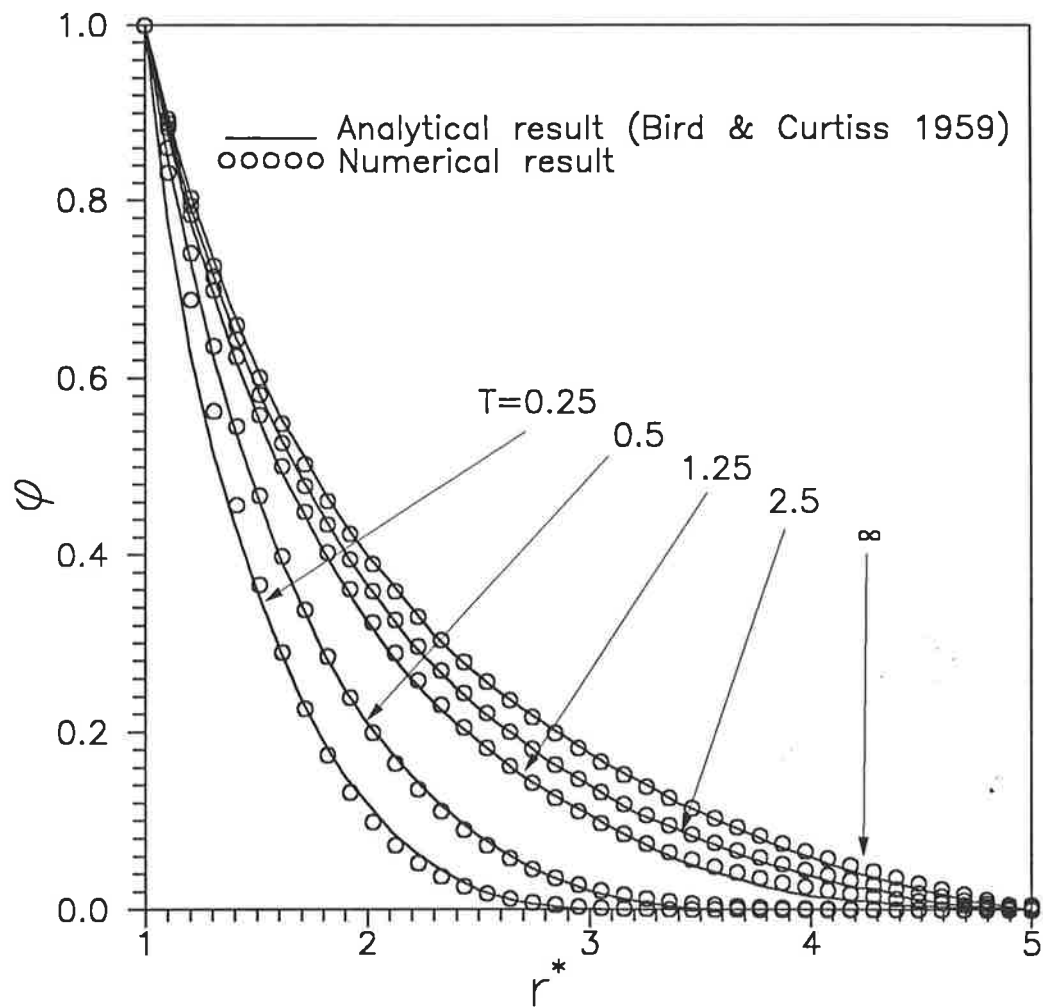


Fig. 4.2 Comparison of the velocity profile of the numerical result from modified Bingham model (when $Bi=0$); and the analytical result for Newtonian fluids (Bird and Curtiss 1959).

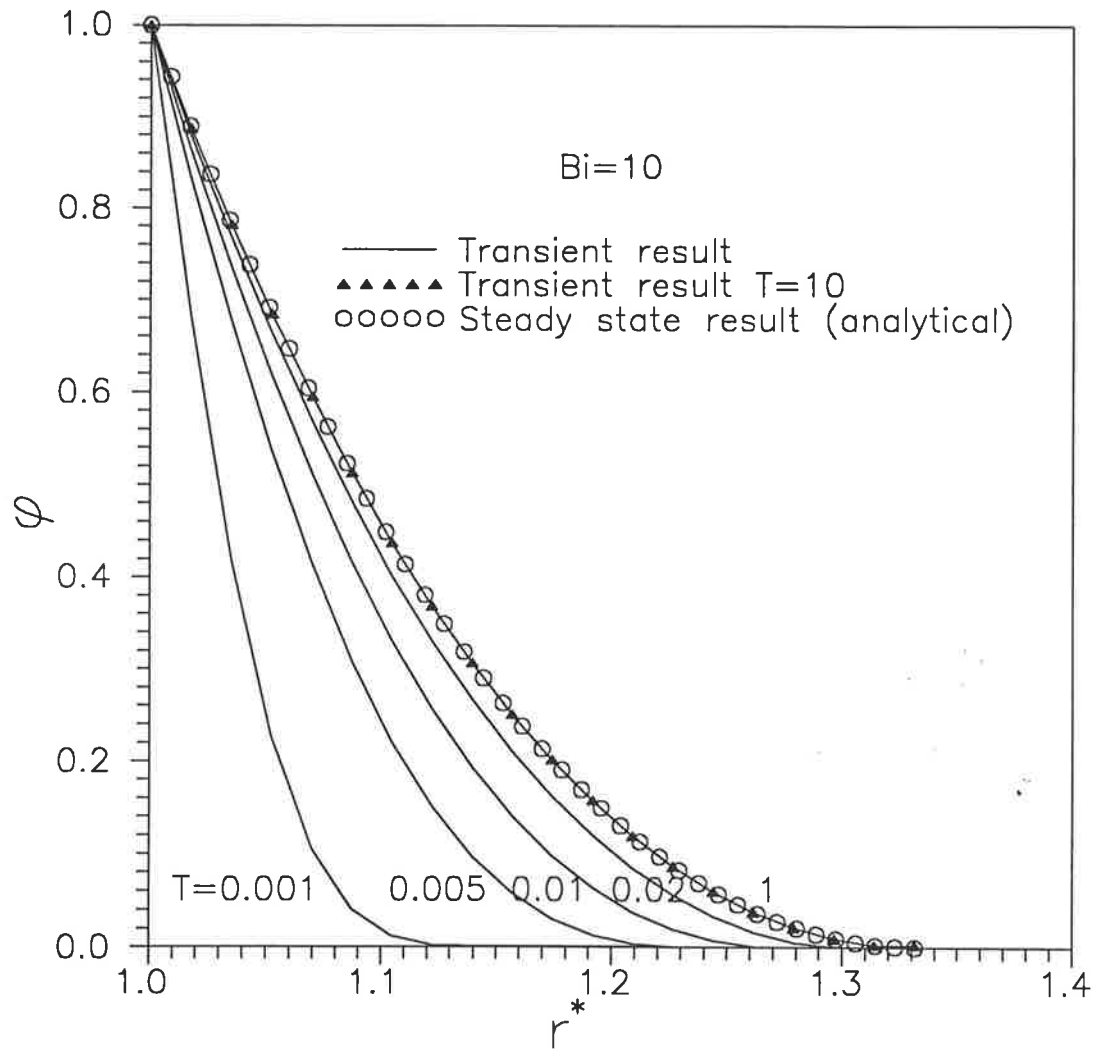


Fig. 4.3 Simulated transient velocity profile for a Bingham fluid with Bi=10.

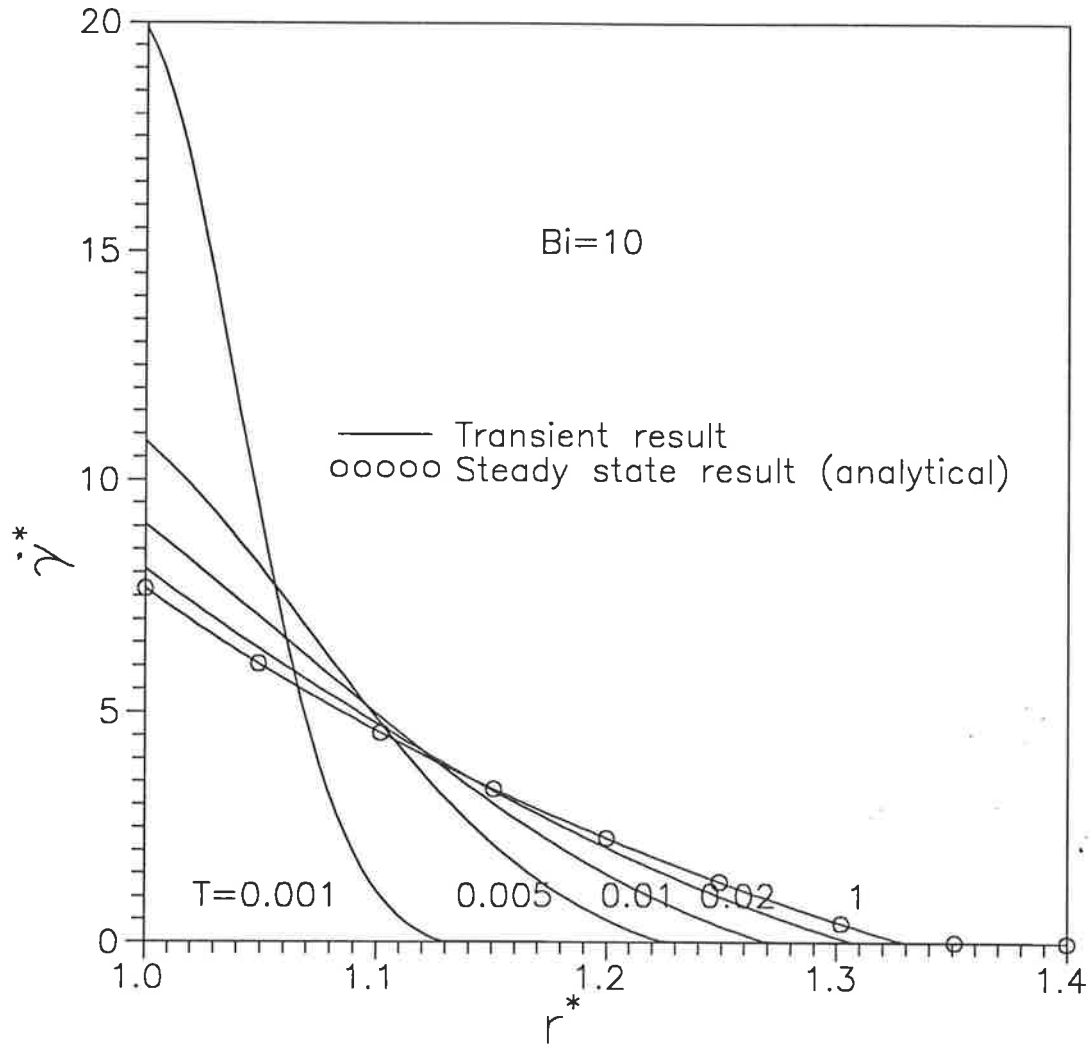


Fig. 4.4 Simulated transient shear rate distribution for a Bingham fluid with $Bi=10$.

4.2.2 Modified Casson model

Modified Casson model can be expressed as

$$\tau^{1/2} = \left[\mu^{1/2} + \frac{\tau_y^{1/2} \cdot (1 - \exp(-n \cdot |\dot{\gamma}|^{1/2}))}{|\dot{\gamma}|^{1/2}} \right] \cdot \dot{\gamma}^{1/2} \quad (4.7)$$

Similarly, for $\dot{\gamma} > 0$ the dimensionless form of Eq. (4.7) is

$$\tau^* = \frac{\dot{\gamma}^*}{Ca} + (1 - \exp(-N \cdot \dot{\gamma}^*)) + 2 \left[(1 - \exp(-N \cdot \dot{\gamma}^*)) \cdot \frac{\dot{\gamma}^*}{Ca} \right]^{1/2} \quad (4.8)$$

N equal to or greater than 100 is used in the following calculations for the modified Casson model. The corresponding equation of motion for the modified Casson flow is obtained by substituting Eq. (4.8) into Eq.(4.1):

$$\begin{aligned} \frac{\partial \phi}{\partial T} = & -\frac{1}{r^{*2}} \frac{\partial}{\partial r^*} \left[r^{*2} \left(Ca \cdot \left(1 - \exp \left(-N \cdot \left(-r^* \frac{\partial(\phi / r^*)}{\partial r^*} \right) \right) \right) \right) + \left(-r^* \frac{\partial(\phi / r^*)}{\partial r^*} \right) \right. \\ & \left. + 2Ca^{1/2} \left(1 - \exp \left(-N \cdot \left(-r^* \frac{\partial(\phi / r^*)}{\partial r^*} \right) \right) \right)^{1/2} \cdot \left(-r^* \frac{\partial(\phi / r^*)}{\partial r^*} \right)^{1/2} \right] \end{aligned} \quad (4.9)$$

and expanding Eq. (4.9) leads to

$$\begin{aligned} \frac{\partial \phi}{\partial T} = & -\frac{2Ca}{r^*} \cdot \left(1 - \exp \left(-N \cdot \left(-r^* \frac{\partial(\phi / r^*)}{\partial r^*} \right) \right) \right) + 2 \frac{\partial(\phi / r^*)}{\partial r^*} \\ & + \left(Ca \cdot N \cdot \exp \left(-N \cdot \left(-r^* \frac{\partial(\phi / r^*)}{\partial r^*} \right) \right) + 1 \right) \cdot \left(\frac{\partial(\phi / r^*)}{\partial r^*} + r^* \frac{\partial^2(\phi / r^*)}{\partial r^{*2}} \right) \\ & + Ca^{1/2} \left(1 - \exp \left(-N \cdot \left(-r^* \frac{\partial(\phi / r^*)}{\partial r^*} \right) \right) \right)^{1/2} \cdot \left(-r^* \frac{\partial(\phi / r^*)}{\partial r^*} \right)^{1/2} \\ & \cdot \left\{ -\frac{4}{r^*} + \left(\frac{\partial(\phi / r^*)}{\partial r^*} + r^* \frac{\partial^2(\phi / r^*)}{\partial r^{*2}} \right) \right. \\ & \left. \cdot \left[\left(1 - \exp \left(-N \cdot \left(-r^* \frac{\partial(\phi / r^*)}{\partial r^*} \right) \right) \right)^{-1} \cdot \exp \left(-N \cdot \left(-r^* \frac{\partial(\phi / r^*)}{\partial r^*} \right) \right) \cdot N + \left(-r^* \frac{\partial(\phi / r^*)}{\partial r^*} \right)^{-1} \right] \right\} \end{aligned} \quad (4.10)$$

When $Ca = 0$, Eq. (4.10) is reduced to the same expression for modified Bingham model (when $Bi=0$ in Eq. (4.6)), or the expression for Newtonian fluid by Bird and Curtiss (1959).

4.2.3 Modified Herschel-Bulkley model

Expression for the modified Herschel-Bulkley model is:

$$\tau = \left[\mu + \frac{\tau_y (1 - \exp(-n \cdot |\dot{\gamma}|))}{|\dot{\gamma}|^n} \right] \cdot \dot{\gamma}^n \quad (4.11)$$

For $\dot{\gamma} > 0$, the dimensionless form of Eq. (4.11) is

$$\tau^* = \left(\frac{\dot{\gamma}^*}{He} \right)^n + (1 - \exp(-N \cdot \dot{\gamma}^*)) \quad (4.12)$$

N equal to or greater than 100 is used in the following calculations for the modified Herschel-Bulkley model.

$$\frac{\partial \phi}{\partial T} = -\frac{1}{r^{*2}} \cdot \frac{\partial}{\partial r^*} \left[r^{*2} \left(He^n \left(1 - \exp \left(-N \cdot \left(-r^* \frac{\partial(\phi/r^*)}{\partial r^*} \right) \right) \right) + \left(-r^* \frac{\partial(\phi/r^*)}{\partial r^*} \right)^n \right) \right] \quad (4.13)$$

Expanding Eq. (4.13) leads to

$$\begin{aligned} \frac{\partial \phi}{\partial T} = & -\frac{2He^n}{r^*} \left(1 - \exp \left(-N \cdot \left(-r^* \frac{\partial(\phi/r^*)}{\partial r^*} \right) \right) \right) - \frac{2}{r^*} \left(-r^* \frac{\partial(\phi/r^*)}{\partial r^*} \right)^n \\ & + \left[He^n \cdot N \cdot \exp \left(-N \cdot \left(-r^* \frac{\partial(\phi/r^*)}{\partial r^*} \right) \right) + n \cdot \left(-\frac{\partial(\phi/r^*)}{\partial r^*} \right)^{n-1} \right] \\ & \cdot \left(\frac{\partial(\phi/r^*)}{\partial r^*} + r^* \frac{\partial^2(\phi/r^*)}{\partial r^{*2}} \right) \end{aligned} \quad (4.14)$$

When $n=1$, Eq. (4.14) is reduced to the same expression as that for modified Bingham model i.e. Eq. (4.6).

Simulation results for Casson and Herschel-Bulkley models as described in sections 4.2.2 and 4.2.3 are presented in Appendix 3, which includes the following figures.

The flow curves expressed in dimensionless forms for both modified Casson and Herschel-Bulkley models can approximate well the ideal flow models when N is large as shown in Fig. A3.1 and A3.4 respectively.

For modified Casson model, Fig. A3.2 shows the unsteady velocity profile for $Ca=10$, and the corresponding transient shear rate distribution is shown in Fig. A3.3. For modified Herschel-Bulkley model, the unsteady velocity profile ($He=10$, $n=0.5$) is shown in Fig. A3.5, and the corresponding shear rate distribution changing with time is shown in Fig. A3.6.

Similar to the earlier section 4.2.1 for the modified Bingham model, the numerical results of the velocity profiles obtained for modified Casson and Herschel-Bulkely models approach the analytical results for the both corresponding ideal flow models at steady state (see Figs. A3.2 and A3.5). Finally, the numerical shear rate profiles diminish in magnitude beyond the yield boundaries, i.e. $r_y = 1.78$ and 1.42 , obtained for the ideal Casson and Herschel-Bulkely models at steady state respectively (see Figs. A3.3 and A3.6).

This section has demonstrated that the transient flow behaviour can be satisfactorily simulated using the modified flow model approach. In the following section, the transient development of the yield boundary will be further explored.

4.3 Determination of Yield Boundary

It has been shown in section 4.2 that the modified flow models can approximate the behaviour of ideal flow models in predicting transient velocity and shear rate profiles. In this section the yield boundary will be determined by using these modified flow models. According to the modified flow models approach, there are no yield criteria imposed on the model description as those used for ideal flow models, i.e. section 3.1. However, in the following numerical simulation, a condition is imposed to define the yield boundary where the shear stress is equal to the yield stress specified in the modified flow model. Substituting

$\tau^* = 1$ into each of the modified flow models, the corresponding shear rates at the imposed yield boundary for the various flow models are as follows:

For modified Bingham model, i.e. Eq. (4.4):

$$1 = \frac{\dot{\gamma}_y^*}{\text{Bi}} + \left(1 - \exp(-N \cdot \dot{\gamma}_y^*)\right) \quad (4.15)$$

while for modified Casson model, Eq. (4.8):

$$1 = \frac{\dot{\gamma}_y^*}{\text{Ca}} + \left(1 - \exp(-N \cdot \dot{\gamma}_y^*)\right) + 2 \left[\left(1 - \exp(-N \cdot \dot{\gamma}_y^*)\right) \cdot \frac{\dot{\gamma}_y^*}{\text{Ca}} \right]^{1/2} \quad (4.16)$$

and for modified Herschel-Bulkley model, Eq. (4.12):

$$1 = \left(\frac{\dot{\gamma}_y^*}{\text{He}} \right)^n + \left(1 - \exp(-N \cdot \dot{\gamma}_y^*)\right) \quad (4.17)$$

In the above equations $\dot{\gamma}_y$ is the shear rate when the shear stress equal to yield stress of the fluid. Knowing the shear rate profile, it is possible to determine a yield boundary position bounded by radius $\bar{r}_i^*$ and $\bar{r}_{i+1}^*$ such that the condition $\bar{\gamma}_{i+1}^* \leq \dot{\gamma}_y^* < \bar{\gamma}_i^*$ applies. This position, defined as the yield radius r_y^* , can be determined by a simple linear interpolation method:

$$\left(\bar{r}_y^* - \bar{r}_{i+1}^* \right) / \left(\bar{r}_i^* - \bar{r}_{i+1}^* \right) = \left(\dot{\gamma}_y^* - \bar{\gamma}_{i+1}^* \right) / \left(\bar{\gamma}_i^* - \bar{\gamma}_{i+1}^* \right) \quad (4.18)$$

The flow develops from unsteady state into steady state conditions after the bob starts to rotate. For the time-independent fluid, the yield boundary at steady state (called $r_{y,\text{Max}}^*$) is of the largest boundary that can be developed from the unsteady motion. The radius ratio ε must be set large enough ($\varepsilon \geq r_{y,\text{Max}}^*$) so that the flow is always under partially sheared condition both at unsteady and steady states. The determination of such $r_{y,\text{Max}}^*$ has been discussed in section 3.2. In all the following simulations, the specified radius ratio was set in such a way that the gap size ranged from about 1 to 3 times the maximum thickness of the yield layer, i.e. $1 \leq (\varepsilon - 1) / (r_{y,\text{Max}}^* - 1) \leq 3$. In this study, accuracy of 3 decimal points was obtained when more than 25 intervals within the radius range $1 \sim r_{y,\text{Max}}^*$ were used. The boundary conditions of the non-linear partial differential equations for the time-independent

fluid are set at the bob and cup surfaces.

The dimensionless yield radii for the three ideal viscoplastic flow models (see section 3.2 in Chapter 3) at steady state with yield number $Bi=10$, $Ca=10$ and $He=10$ ($n=0.5$) are 1.33, 1.78 and 1.42 respectively. Fig. 4.5 show the velocity profiles at different times for several radius ratios for modified Bingham flow model. Similar results for the modified Casson and Herschel-Bulkley models are also presented in Figs. A3.7, and A3.8 in Appendix 3. From these plots, the flow phenomena under partially sheared flow conditions appear to be independent of the radius ratio (or boundary condition at the cup surface), which is also consistent with that predicted by using the ideal flow models.

The development of yield boundary from the unsteady state shear to steady state condition for modified Bingham model is shown in Fig. 4.6. Simulations were performed for $Bi=10$ and 100. The growth rate of yield boundary for $Bi=10$ is slower than that for $Bi=100$. The unsteady state yield boundary approaches that of the steady state value (from section 3.2) at approximately $T=0.1$ for $Bi=10$ and $T=0.006$ for $Bi=100$. Similar results for modified Casson and Herschel-Bulkey models are also presented Figs. A3.9 and A3.10 respectively in Appendix 3. In most cases, the unsteady flow reaches steady state at $T>1$.

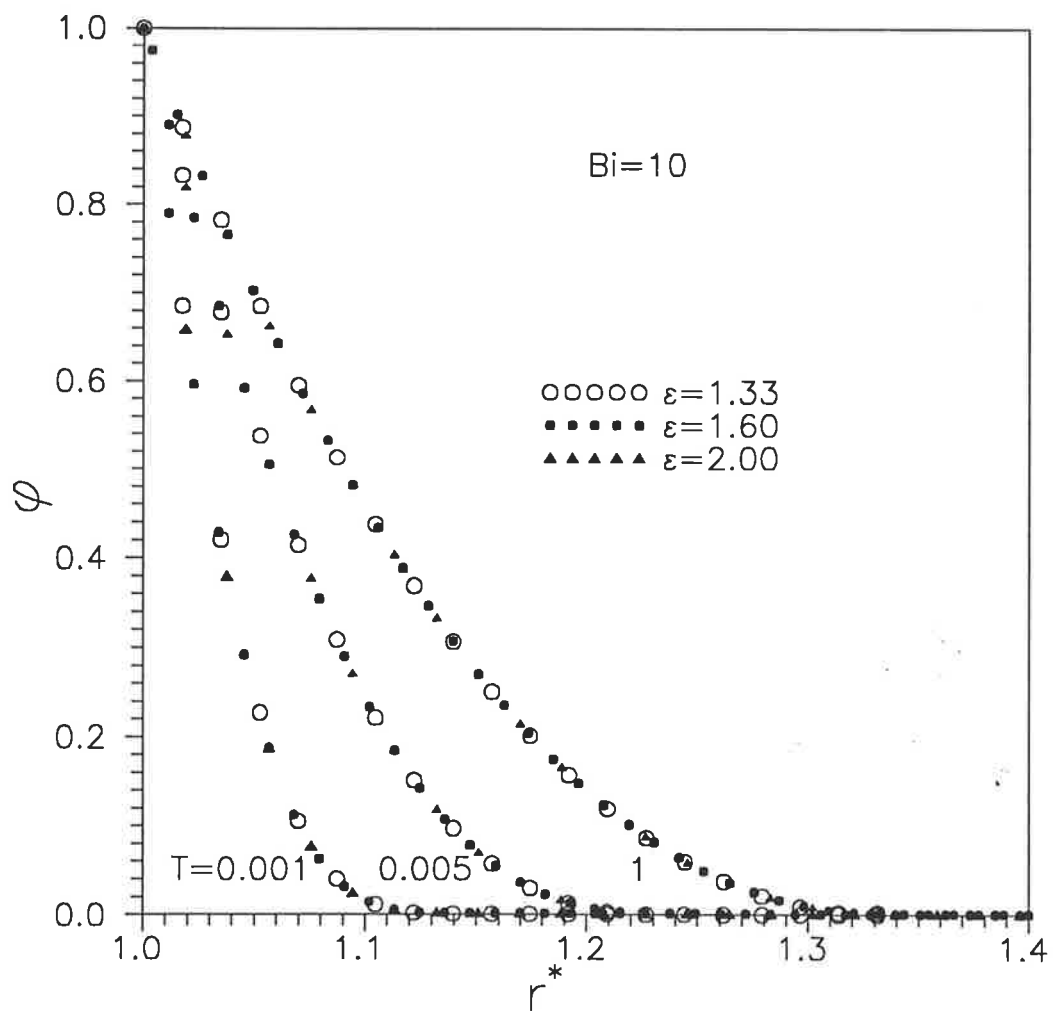


Fig. 4.5 Velocity profile at different times for the modified Bingham model with different radius ratios used for boundary conditions.

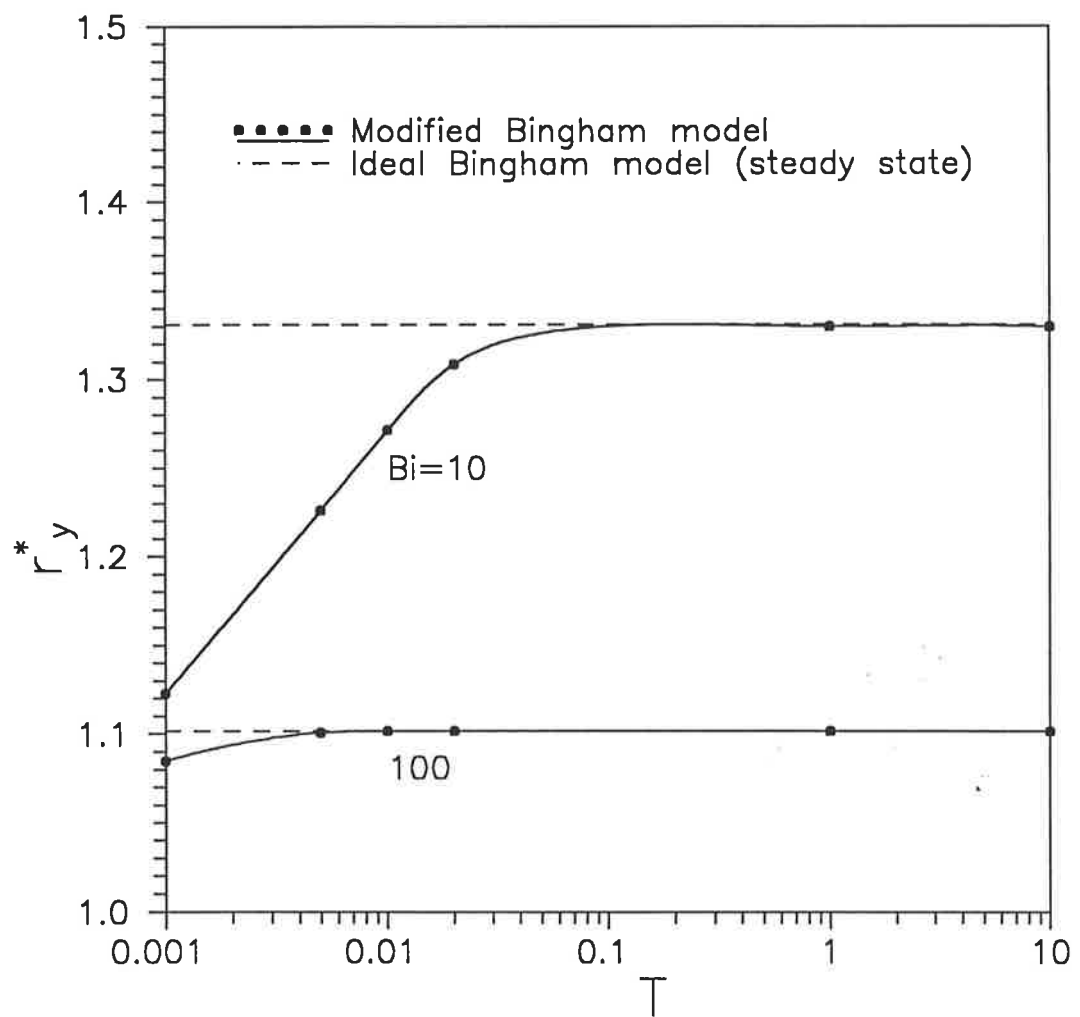


Fig. 4.6 The transient behaviour of yield boundary for the modified Bingham model.

4.4 Unsteady Shear Flow of Time-Dependent Fluids

4.4.1 Two time-influencing factors

The unsteady shear flow phenomena of a time-dependent (thixotropic) fluid depends on two time-influencing factors, i.e. the unsteady flow caused by the transient fluid motion, and the change of fluid properties by shear due to the thixotropic behaviour. Unlike the analysis for time-independent fluid discussed in earlier section, the yield number in this case will change with time, leading to an even more complex situation.

The time period of the unsteady state shear flow depends on various flow conditions which have been studied in the earlier sections. Such flow conditions include the time-independent flow model, yield number and dimensionless time $T = (\mu \cdot t) / (\rho \cdot r_b^2)$. For example, with a Bingham fluid having a yield number of 100, the flow reaches a steady state condition at $T=0.006$ (Fig. 4.6). For the fluid with a moderate viscosity and density say, $\mu = 1$ Pa.s and $\rho = 1000 \text{ kg/m}^3$ which is being sheared by a bob of radius 0.02 m, the flow will reach steady state in about 0.0024 second. However, if the bob radius is increased to 1 m, then the flow will reach steady state at about 6 seconds. Therefore, depending on the flow conditions, the unsteady state shear period may range from almost instantaneous to a few seconds.

However, the time required by structure change of thixotropic fluids would usually be longer, in the order of seconds, minutes, hours or even days, before reaching the equilibrium condition. Therefore, these two time-influencing factors could occur in a very different time scales in some cases. For example, the unsteady shear could require a very short time or almost instantly (say $t < 0.1$ second) to reach a steady state; while for thixotropic fluids it may take some time (say $t > 0.5$ second) before any noticeable structural change may take place. Hence, under this condition it is possible to study the effect of these two influencing factors on the flow behaviour quite independently. In such case, the initial structure of the fluid property is used to study the unsteady shear flow, and at steady state the flow behaviour is studied according to the thixotropic structure change from initial to equilibrium condition.

In general, without prior knowledge of the extent of the influencing factors, both factors need to be considered simultaneously. The following section discusses the behaviour of the yield boundary as a result of the combined effects of unsteady state shear and thixotropic structure variation.

Generally, the rate of change of structure may be characterized by a rate constant k which usually depends on the applied shear rate. However, there are some special cases where the rate constant k has found to be not sensitive to the applied shear rate (Billington 1960, Nguyen 1983). In the current study such two different cases (i.e. k is shear rate-independent and shear rate-dependent) are considered and solved by two separate methods, i.e. Methods I and II. In the first case, the rate constant is independent of shear rate, which the flow behaviour can be solved by Method I. While the second case considers the rate constant as a function of shear rate which the flow behaviour is solved by another Method II. While the flow behaviour under the first case can be solved numerically, the approach employed for Method II involves a complex numerical procedure.

The thixotropic structure change may be represented by an irreversible decay kinetics (Nguyen 1983):

$$\frac{d\lambda}{dt} = -k \cdot (\lambda - \lambda_e)^p \quad (4.19)$$

where the structure parameter λ is defined as:

$$\lambda = \frac{\mu(t) - \mu_e}{\mu_o - \mu_e} = \frac{\tau_y(t) - \tau_{ye}}{\tau_{yo} - \tau_{ye}} \quad (4.20)$$

where $\mu(\infty) = \mu_e$, $\tau_y(\infty) = \tau_{ye}$ and $\lambda(\infty) = \lambda_e$. Bingham model has been used to demonstrate the following simulation methods. The similar procedure can also be applied to other types of flow models.

4.4.2 Method I for shear rate-independent rate constant

Since k is a constant for any applied shear rate, the structure parameter depends only on shearing time. Integrating Eq. (4.19) with the condition of the first order break-down process ($p=1$); and combining with Eq. (4.20) gives

$$\mu(t) = \mu_e + (\mu_o - \mu_e) \cdot \exp(-k \cdot t) \quad (4.21)$$

$$\tau_y(t) = \tau_{ye} + (\tau_{yo} - \tau_{ye}) \cdot \exp(-k \cdot t) \quad (4.22)$$

The yield number Bi can be obtained from the following equation:

$$Bi(t) = \frac{\tau_y(t)}{\mu(t) \cdot \Omega} = \frac{1}{\Omega} \cdot \frac{\tau_{ye} + (\tau_{yo} - \tau_{ye}) \cdot \exp(-k \cdot t)}{\mu_e + (\mu_o - \mu_e) \cdot \exp(-k \cdot t)} \quad (4.23)$$

The equation of motion for time-dependent modified Bingham model is derived as follow:

$$\begin{aligned} \frac{\partial \phi}{\partial t} \cdot \frac{1}{(\mu(t) / \rho \cdot r_b^2)} = & -\frac{2Bi(t)}{r^*} \cdot \left[1 - \exp \left(-N \cdot \left(-r^* \frac{\partial(\phi / r^*)}{\partial r^*} \right) \right) \right] + 2 \cdot \frac{\partial(\phi / r^*)}{\partial r^*} \\ & + \left[Bi(t) \cdot N \cdot \left(\exp \left(-N \cdot \left(-r^* \frac{\partial(\phi / r^*)}{\partial r^*} \right) \right) + 1 \right) \right] \cdot \left(\frac{\partial(\phi / r^*)}{\partial r} + r^* \cdot \frac{\partial^2(\phi / r^*)}{\partial r^{*2}} \right) \end{aligned} \quad (4.24)$$

Unlike the case for time-independent Bingham fluids, viz. Eq. (4.6), it is not convenient to use dimensionless time in Eq. (4.24) since the viscosity term is also a function of time. Substituting Eqs. (4.21) and (4.23) into Eq. (4.24), the partial differential equation can be solved by a subroutine called DMOLCH from IMSL which is based on the "method of lines with cubic hermite polynomials" (also see section 4.2.). Fig. 4.7 shows the velocity profile solved by method I (i.e. Eq. (4.24)) at different times and rate constants for the modified Bingham model for time-dependent fluids. Fig. 4.7 (a) shows that there is a good agreement between the results from the method I (when $k=0$) and the time-dependent fluids which solved by Eq. (4.6) in section 4.2.1. Simulation results have been also obtained for other rate

constants i.e. $k=0.1$ and $k=1.0$ as shown in Fig. 4.7 (b) and (c). For a given rate constant k , the velocity develops gradually along the radius with increasing time. However, for a given time condition, the higher the k value, the shorter is radius range that the flow can develop. Fig. 4.8 shows that the simulated transient behaviour of the yield boundary using different rate constants. It also shows that the two different approaches ($k=0$ for Method I, and time-independent fluids) used give a similar result. In general, the yield boundary, initially at bob surface, increases with increasing time. As the time approaches infinity, the transient yield boundary approaches the equilibrium yield boundary calculated analytically from ideal Bingham model at steady state. Fig. 4.8 also shows two different yield boundary developments with different rate constants. At lower value of structural breakdown rate constant ($k=0.1$), the yield boundary advances at a faster rate reaching a peak value before it gradually decreases to an equilibrium value. For the much larger rate constant ($k=1.0$), the yield boundary develops at much slower rate before reaching the equilibrium state. It seems that at smaller structural breakdown rate constant, the initial flow behaviour is more dominated by the unsteady shear phenomenon as signified by the faster growth of yield boundary and the presence of a peak value. When the rate constant k is relatively high, the effective structural breakdown is more prominent and occurs at much earlier stage, and the peak value of yield boundary may not be present. Details of the simulation conditions are described in Appendix 4.

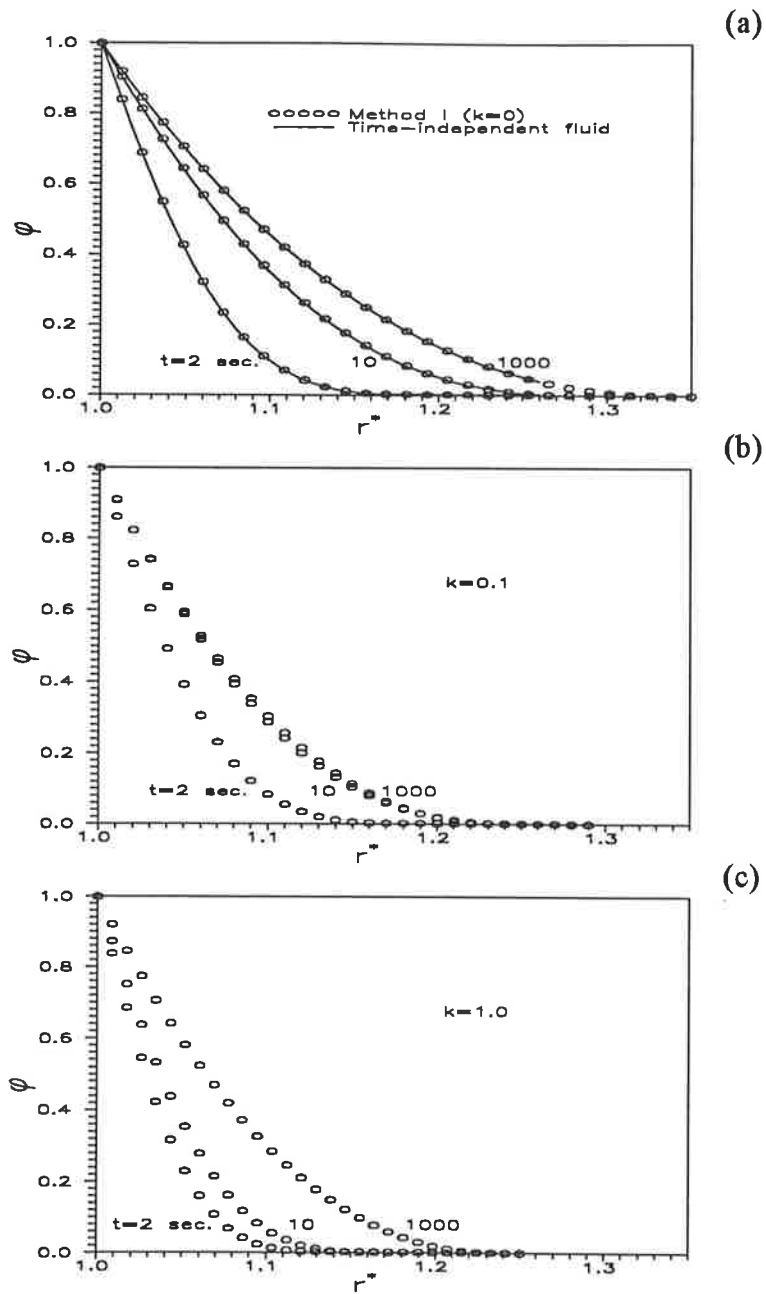


Fig. 4.7 Velocity profile solved by method I at different times and rate constants for the modified Bingham model for time-dependent fluids. (a) Comparison of the results from method I ($k=0$) and time-independent fluids; (b) $k=0.1$; (c) $k=1.0$.

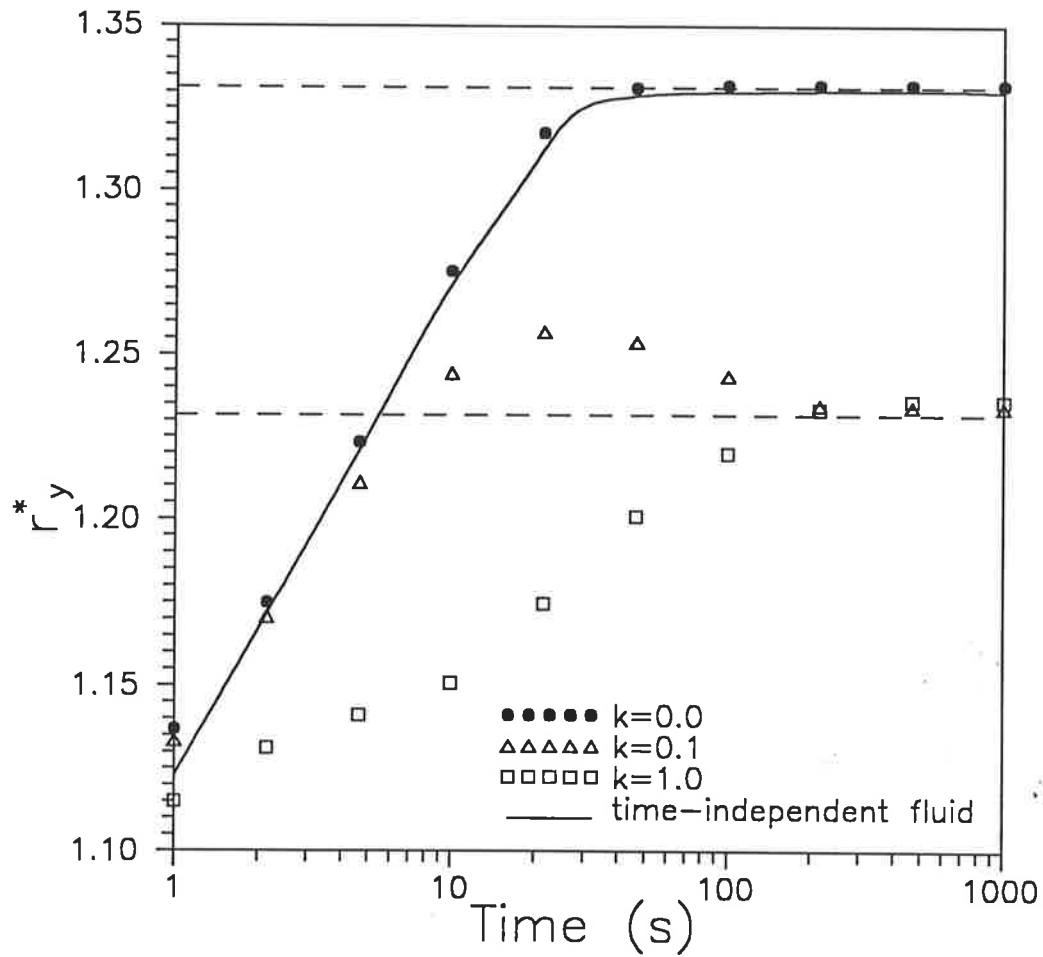


Fig. 4.8 The transient behaviour of yield boundary due to unsteady motion and structure breakdown using Methods I for the modified Bingham. The initial yield number Bi is 10 for fresh fluid and $Bi=20$ at equilibrium. The two dashed lines are the locations of yield boundary at steady state for ideal Bingham model with $Bi=10$ (upper) and $Bi=20$ (lower) respectively.

4.4.3 Method II for shear rate-dependent rate constant

To demonstrate the effect of rate constant which is dependent on the applied shear rate, a simple linear relationship for the rate constant k and shear rate is assumed:

$$k = a \cdot \dot{\gamma} + b \quad (4.25)$$

where a and b are constants. From this expression, the k value is different for different regions of the flow because the shear rate is different along the radius. The inclusion of shear rate dependency is therefore leading to a more complicated analysis than the former method. The determination of the corresponding rate constant k in the yielded region was determined using the method of finite difference in which the annulus was divided into small finite annular intervals (with $i=1$ to I) and the total time was divided into J time steps ($j=1$ to J). The first radial annular element (i.e. $i=1$) is the one nearest to the bob surface; while the first time element (i.e. $j=1$) is the initial time step. Flow parameters such as the velocity, shear stress and shear rate, were assumed to be constant within each annular element i and time step j .

The fluid velocity $v_{i,j}$ and shear rate $\dot{\gamma}_{i,j}$ distributions along the individual radial intervals were determined at different time steps. The corresponding value of k at each radial and time element was obtained from Eq. (4.25) using the result of the shear rate distribution. The flow behaviour as a result of structure change and unsteady motion can be simulated numerically at each incremental time step.

Mathematical descriptions of the numerical simulation

Since the shear rate value changes with time and radial position, the rate constant k (according to Eq. (4.25)) is also dependent on both time and radial position. If $k_{i,j}$ represents a rate constant value at a radial element i and time step j , then it can be defined according to Eq. (4.25) (i.e. $k_{i,j} = a \cdot \dot{\gamma}_{i,j} + b$) if the shear rate distribution is known. From $k_{i,j}$, the current overall rate constant for the yielded flow at time step j , may be defined as follows. The fluid structure in the yielded region is assumed to be uniform and the overall structure change is the cumulative result of the contributions from each radial element. Consider a radial element H from the bob surface, such that its radial position is just greater than r_y (i.e. $r_{H-1} < r_y < r_H$).

Each radial element from $i=1$ to $i=H$, is subject to structural breakdown at a rate $k_{i,j}$. Thus the overall rate constant at time j is obtained by:

$$k_j = \sum_{i=1}^H \frac{1}{H} k_{i,j} \quad (4.26)$$

The term $1/H$ is equivalent to the volumetric fraction of the fluid within one radial element in the total yielded fluid. For example, if there are 100 radial elements of fluid yielded, then the rate constant of each one of the 100 elements contributes 1% to the overall rate constant. According to Eq. (4.19) and Eq. (4.26) the overall structure change at a given time step j is defined as:

$$\frac{d\lambda_j}{dt} = - \sum_{i=1}^H \left(\frac{1}{H} \cdot k_{i,j} \right) \cdot (\lambda_j)^p \quad (4.27)$$

where λ_j is the structure parameter at the time step j . Using the first order kinetic process ($p=1$), the integral form of Eq. (4.27) is:

$$\ln \lambda_j = - \int_0^{t_j} \sum_{i=1}^H \left(\frac{1}{H} \cdot k_{i,j} \right) \cdot dt \quad (4.28)$$

The right hand side of Eq. (4.28) can be integrated numerically

$$\ln \lambda_j = - \sum_{j=1}^j \overline{\sum_{i=1}^H \frac{1}{H} \cdot k_{i,j} \cdot \Delta t_j} \quad (4.29)$$

where the time interval Δt_j is $t_j - t_{j-1}$. The average rate constant between time steps $(j-1)$ and j is:

$$\overline{\sum_{i=1}^H \frac{1}{H} \cdot k_{i,j}} = \sum_{i=1}^H \frac{1}{H} \cdot k(\dot{\gamma}_{i,j}) \quad (4.30)$$

in which: $\dot{\gamma}_{i,j} = \frac{\dot{\gamma}_{i,j-1} + \dot{\gamma}_{i,j}}{2}$ is the average shear rate at radial element i between these two time steps $j-1$ and j . At time step $j-1$, Eq. (4.29) can be written as:

$$-\ln \lambda_{j-1} = \sum_{j=1}^{j-1} \overline{\sum_{i=1}^H \frac{1}{H} k_{i,j-1} \cdot \Delta t_{j-1}} \quad (4.31)$$

From Eqs. (4.29) and (4.31) the following can then be conveniently represented as

$$-\ln \lambda_j = -\ln \lambda_{j-1} + \sum_{i=1}^H \frac{1}{H} k_{i,j} \cdot \Delta t_j \quad (4.32)$$

Eq. (4.32) shows the way in which the structure parameter λ_j at the current time step can be determined from the last time step. Knowing λ_j , the viscosity and yield stress at a given time step can also be determined from Eq. (4.20). Similarly, the yield number can be determined according to:

$$Bi_j = \frac{1}{\Omega} \cdot \frac{[\tau_{ye} + (\tau_{yo} - \tau_{ye}) \cdot \lambda_j]}{[\mu_e + (\mu_o - \mu_e) \cdot \lambda_j]} \quad (4.33)$$

Details of the simulation conditions and procedure used are described in Appendix 4. Fig. 4.9 shows the simulation results obtained from method II for different rate constants. In plot (a), (b), and (c), the parameter a is different and the parameter b is a constant. The larger the a , the larger is the k according to Eq. (4.25). For given parameters a and b , the velocity develops gradually along the radius with increasing time. However, for a given time condition, the higher the value a (hence the k), the shorter is the radius range that the flow can develop, which is similar to that shown in Fig. 4.7. Fig. 4.10 shows that the simulated transient behaviour of the yield boundary using different rate constants. It is worth noting that the two different methods ($k=0.1$ for Method I and, $a=0$, $b=0.1$ for Method II) used give a similar result. Similar to Fig. 4.8, the yield boundary, initially at bob surface, increases with increasing time. As the time approaches infinity, the transient yield boundary approaches the equilibrium yield boundary calculated analytically from ideal Bingham model at steady state. Fig. 4.10 also shows three different yield boundary developments with different rate constants. At lower value of structural breakdown rate constant ($a=0.0$; $b=0.1$), the yield boundary advances at a faster rate reaching a peak value before it gradually decreases to an equilibrium value. For slightly larger overall value of rate constant ($a=0.01$; $b=0.1$), the yield boundary

advances marginally slower and does not show any peak value. For the much larger overall rate constant ($a=0.1$; $b=0.1$), the yield boundary develops at much slower rate before reaching the equilibrium state. From the simulation result, it seems that if the rate constant is a function of shear rate (i.e. a is finite and relatively large) the effective structural breakdown is more prominent and occurs at much earlier stage, which is similar to the large k condition observed in Fig. 4.8.

4.5 Conclusions

Papanastasiou model is effective to approximate the ideal Bingham fluid in solving the unsteady state flow problem. The method using the modified flow model (from the Papanastasiou model) can also be successfully extended to other yield stress fluids such as Casson and Herschel-Bulkley models. The velocity and shear rate profile as well as the location of the yield boundary obtained for the unsteady state conditions have been verified to be accurate by comparing the result obtained from other analytical solutions (such as the result for Newtonian fluid or at steady state conditions).

Time-dependent flow phenomena as the effect of the unsteady shear and the time-dependent (thixotropic) structure change has also been discussed and studied. Numerical procedure has been developed to analyze the flow behaviour as the combined effect of these two time-influenced factors. The respective time scale for both time influencing factors, i.e. unsteady state shear and thixotropic fluid behaviour may or may not occur in the same time scale. It is dependent on flow conditions and the magnitude of the rate constant.

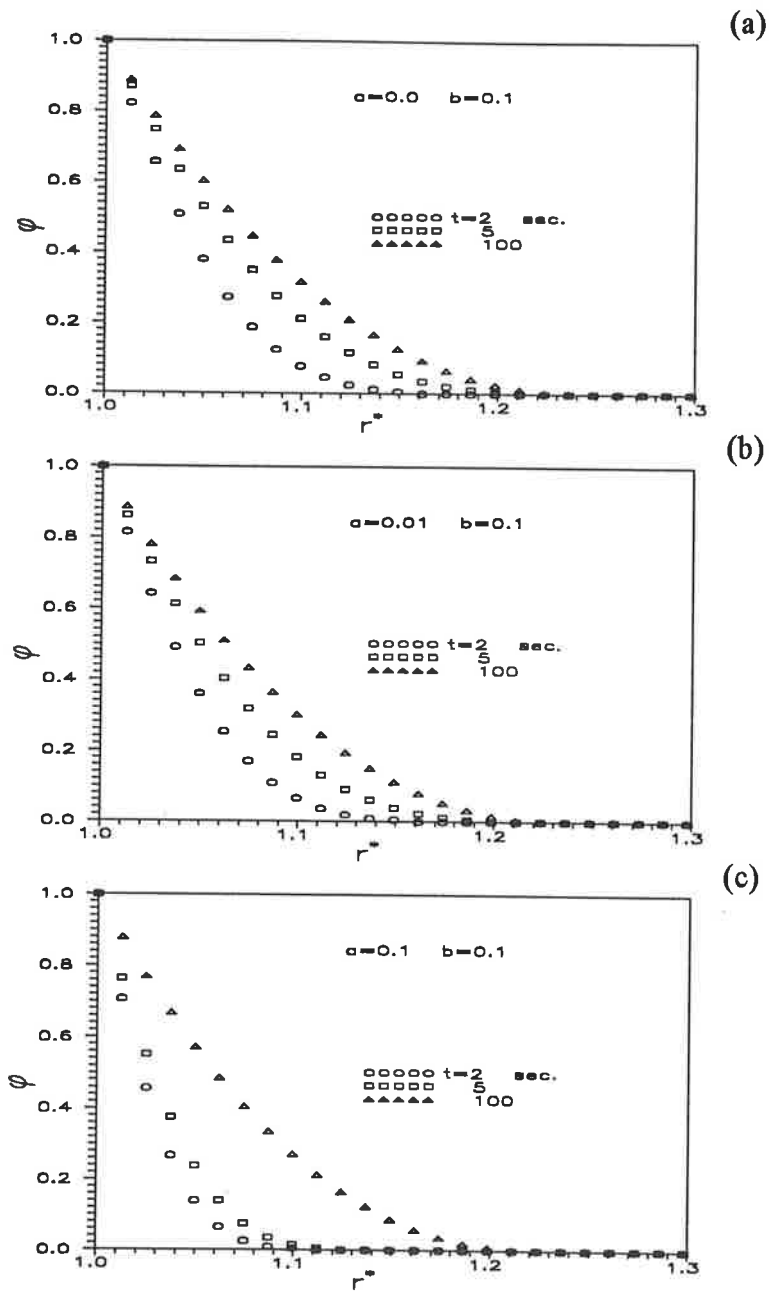


Fig. 4.9 Velocity profile solved by method II at different times and rate constants for the modified Bingham model for time-dependent fluids. (a) $a=0.0$, $b=0.1$; (b) $a=0.01$, $b=0.1$; (c) $a=0.1$, $b=0.1$.

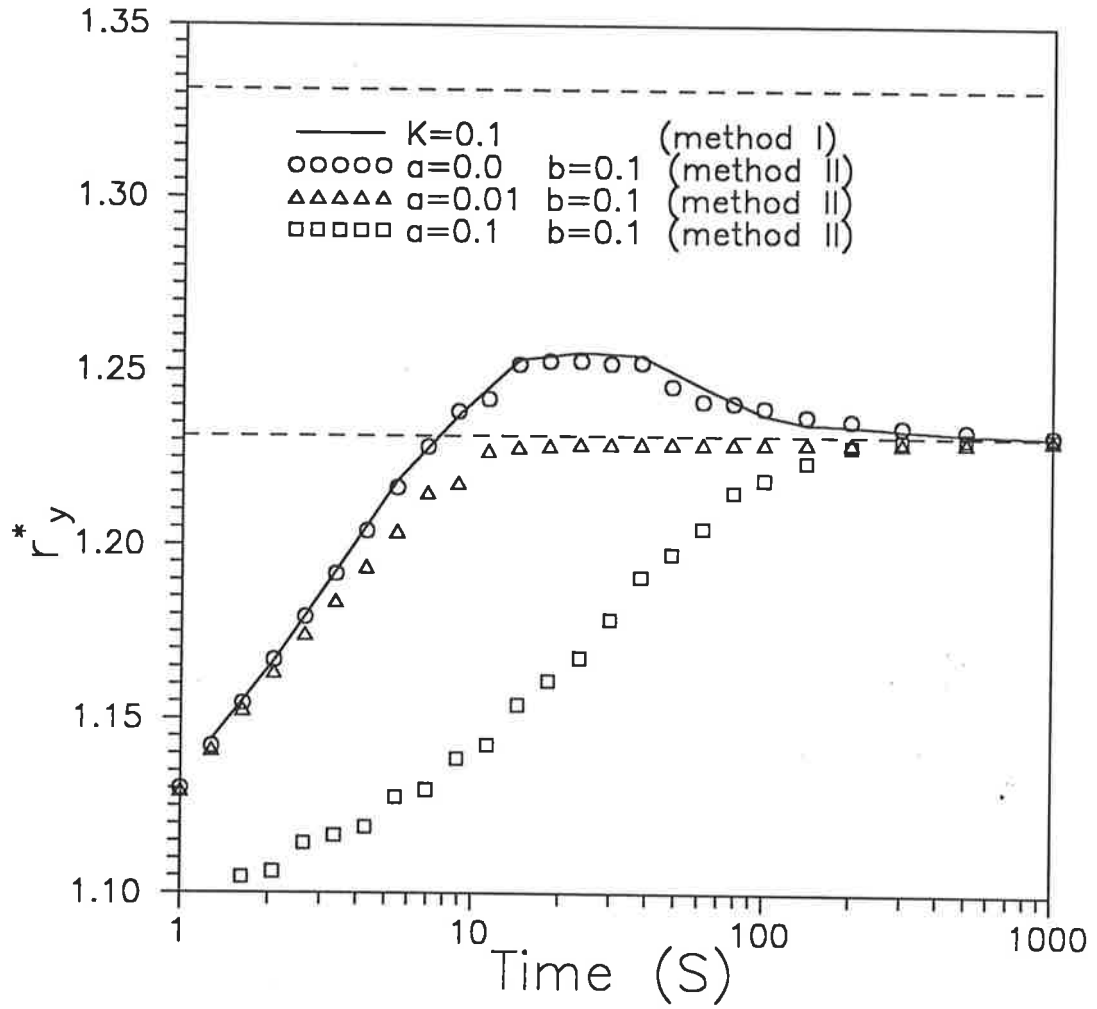


Fig. 4.10 The transient behaviour of yield boundary due to unsteady motion and structure breakdown using Methods I and II for the modified Bingham model. The initial yield number Bi is 10 for fresh fluid and $Bi=20$ at equilibrium. The two dashed lines are the locations of yield boundary at steady state for ideal Bingham model with $Bi=10$ (upper) and $Bi=20$ (lower) respectively.

Chapter 5

Experimental System

This chapter describes the details of the experimental work in this study which includes the selection and preparation of suspension materials, the measurement apparatus and the experimental procedures.

5.1 Material Selection and Characteristics

The first step of the experimental work requires a careful selection of the suspension materials. In this study, suspension materials were selected based upon the following considerations. The suspension should:

- exhibit thixotropic behaviour;
- be stable for a period of time;
- have measurable yield stress and flow property;
- be non-toxic for safe handling and disposal;
- be readily available at reasonable cost.

Based on the above considerations, the following materials were found to be the most suitable for the present experimental study, they are bentonite, kaolin, waxy maize starch and mayonnaise. Waxy maize starch, kaolin and bentonite were obtained in powder forms while the mayonnaise suspension was obtained in a pre-prepared bulk of 21 kg from a commercial source. The particle size distributions of these materials were measured by laser diffraction method using a particle sizer (Malvern Instrument, Series 2600). The physical properties of the solid powder materials are shown in Table 5.1 where the bulk particle densities were measured in a loosely packed condition, and the $d_{v,0.5}$ and $d_{2,3}$ are median diameter and Sauter mean particle size respectively. Fig. 5.1 shows the particle size distribution of the three

materials. The morphology of the materials were observed through a scanning electron microscope. Typical particle shapes as obtained from the scanning electron microscopy are shown in Fig. 5.2. The bentonite particles were found to be irregular while kaolin and starch particles were found to be flaky and round respectively.

Table 5.1 Physical properties of the selected materials in powder forms.

Material	Bulk density (loosely packed) (kg/ m ³)	d _{v,0.5} (μm)	d _{2,3} (μm)
Waxy maize starch	602	16	15
Kaolin	558	22	18
Bentonite	1006	7	5

5.2 Suspension Preparation

Batch Preparation

Although their particle size from the original stock were relatively fine, the kaolin and bentonite powders were further screened to eliminate all particles above 50 μm to ensure that the particles formed a stable suspension in water (i.e. without significant sedimentation). Since 97% of the starch powder was less than 50 μm (Fig. 5.1 (a)), it was used without further screening.

The suspension of kaolin or bentonite was prepared by mixing the powder with distilled water for about 2 hours at room temperature. Usually, about 1 to 3 liters of the suspension was prepared for any given batch.

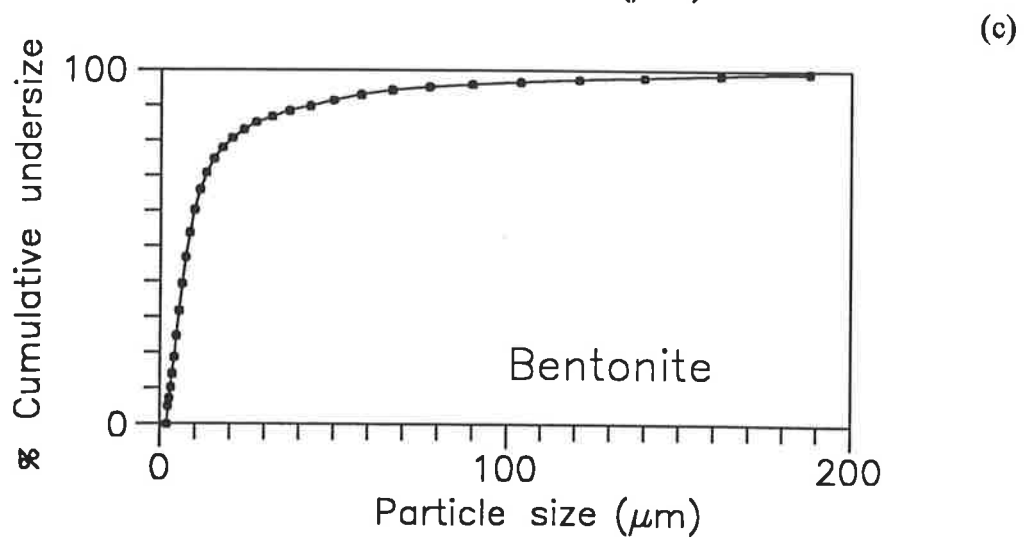
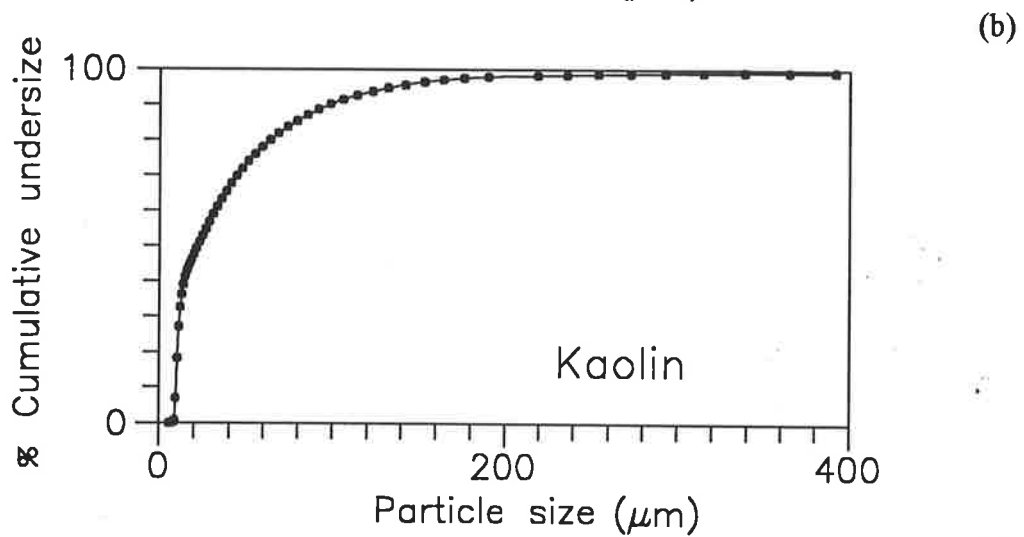
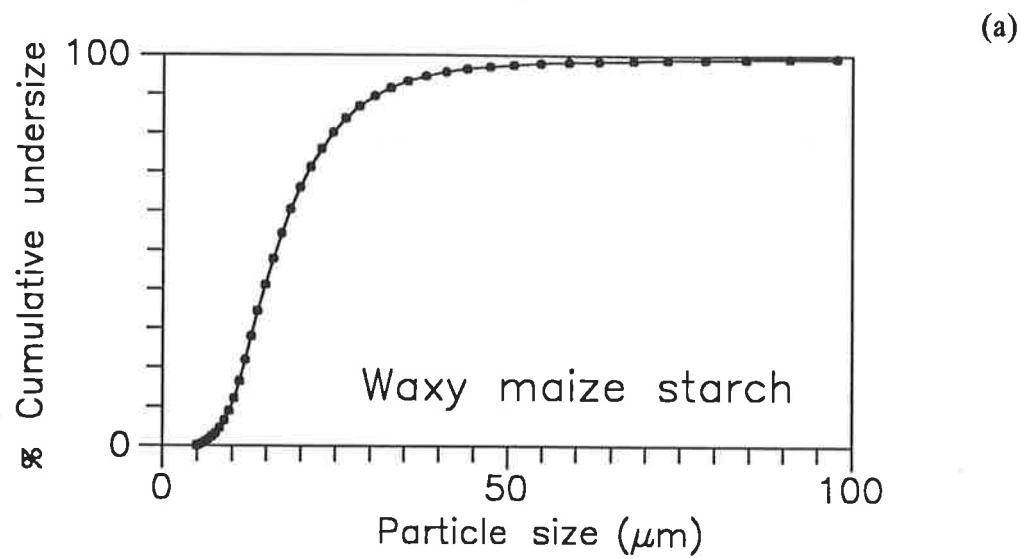
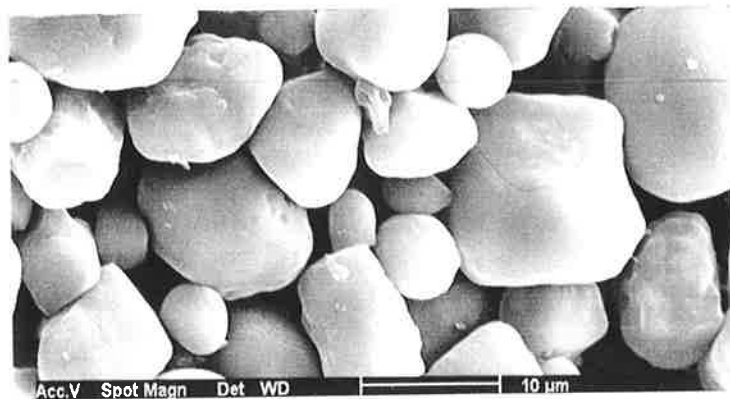
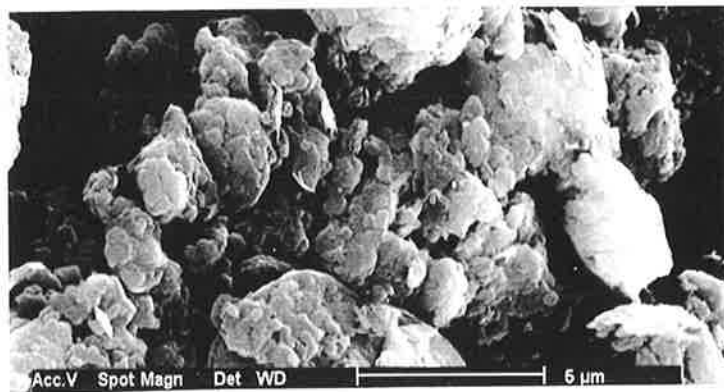


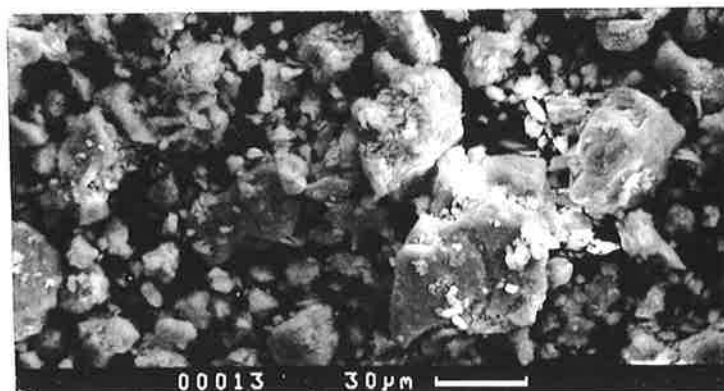
Fig. 5.1 Cumulative particle size distribution of the materials in powder form. (a) waxy maize starch; (b) kaolin; and (c) bentonite.



(a)



(b)



(c)

Fig. 5.2 Photo-micrograph of particles in powder form taken by a scanning electron microscope. (a) waxy maize starch; (b) kaolin; and (c) bentonite.

The preparation procedure for the starch suspension followed that by Kristensen et al (1995) and involved the following steps: (1) mixing the starch powder in a beaker of distilled water at 50 °C; (2) once a homogeneous slurry was obtained, the temperature was raised quickly to the gelatinisation point, i.e. 70 °C where the suspension became a transparent viscous liquid; (3) the suspension was then cooled down to room temperature before testing.

The mayonnaise suspension was stored in a refrigerator to ensure that it was maintained at constant quality. The test sample was taken out of the refrigerator a night before so that it reached a uniform room temperature for the test.

To further maintain the uniformity and consistency of the test samples, particularly for those materials to be prepared from powder form, every batch of suspension was prepared at the same mixing speed. In most cases, the solids concentration in the suspensions varied from 0 to 8 wt% for starch; 5 to 10 wt% for bentonite and 47 to 66 wt% for kaolin in the absence of other additives. The freshly prepared suspension was then allowed to rest for sometime in a sealed container before testing to prevent severe evaporation.

Optimum Rest Time for Suspension Before Testing

The optimum rest time required for the suspension material to reached a relatively stable structure before the samples could be tested was determined experimentally by measuring the change of the yield stress of the suspension with different rest time. The yield stress was measured by the vane method (Nguyen & Boger 1983, 1985a). From Figs. 5.3 and 5.4, the change of the yield stress with rest time for both kaolin and bentonite suspensions was found negligible after about a period of 48 hours. For consistency, the rest time was standardized to a 48-hour period for the kaolin and bentonite suspensions in the subsequent preparation stages.

However, the quality of the starch suspension was found to vary noticeably when it was left for 48 hours. This was probably due to either fermentation or bacteria growth.

Hence, the tests for waxy maize starch were conducted after the suspension was cooled down to room temperature, usually about 3 hours after gelatinisation.

The suspension of a given batch was required to be tested within one day to prevent any significant variation in fluid structure among the different test samples. The homogeneity of the prepared sample was also tested by measuring the torque (hence yield stress) at various locations in the stock suspension of a given batch by using the vane method. Torque measured at 21 different locations in a batch of 10% bentonite suspension gave a mean value of 2.045 Ncm with a standard deviation of 0.070 Ncm (see Appendix 5) which led to a percentage deviation of $\pm 3\%$. Therefore, it can be concluded that the suspension prepared through the procedures described above gives a reasonably homogeneous or uniform suspension structure.

Effect of pH and on Suspension Rheology

One other reason for imposing a time restriction for sample preparation and testing is that the pH of the suspension was also found to change slightly with time. The rheological property of colloidal suspension is usually very sensitive to the pH change. The cause of this change was originally attributed to the absorption of atmospheric CO₂ into the suspension. However, this change was not totally eliminated even with the container sealed at all time. Although the cause remains unclear, it was decided to use only the fresh material for all tests (i.e. no recycling of the material).

Fig. A6.1 in Appendix 6 shows the reduction of pH from 10.87 to 10.30 for the bentonite suspension (10%) after 7 days. In addition, the pH was also found to change with solids concentration for bentonite suspension where the pH was determined immediately after preparation (see Fig. A6.2 of Appendix 6).

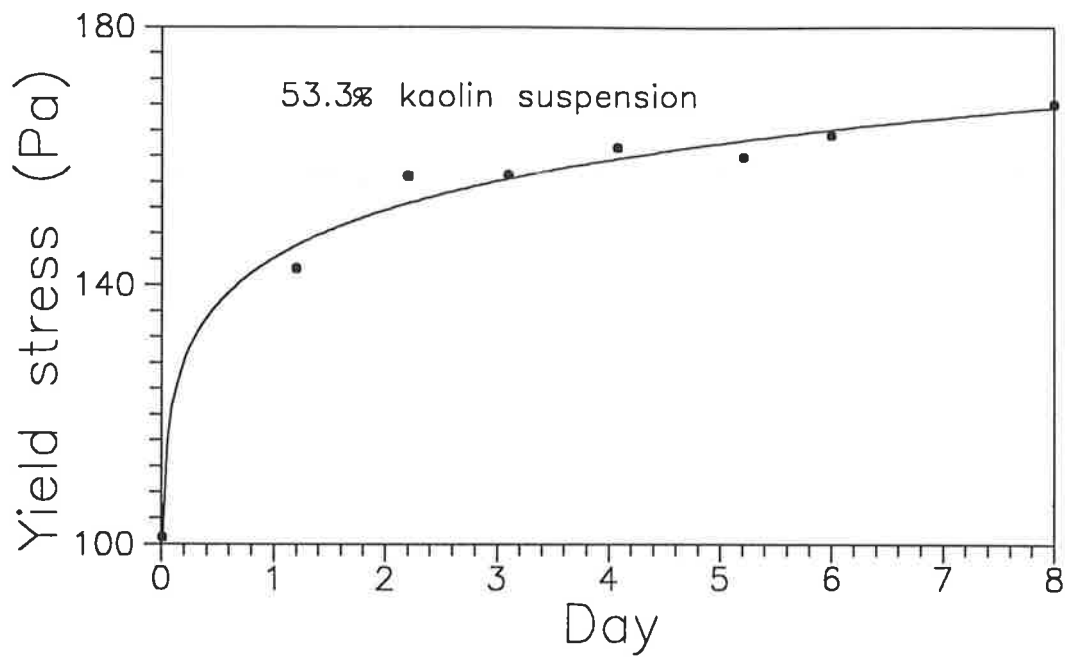


Fig. 5.3 The change of the yield stress value as measured by the vane method with different rest time for 53.3% kaolin suspension.

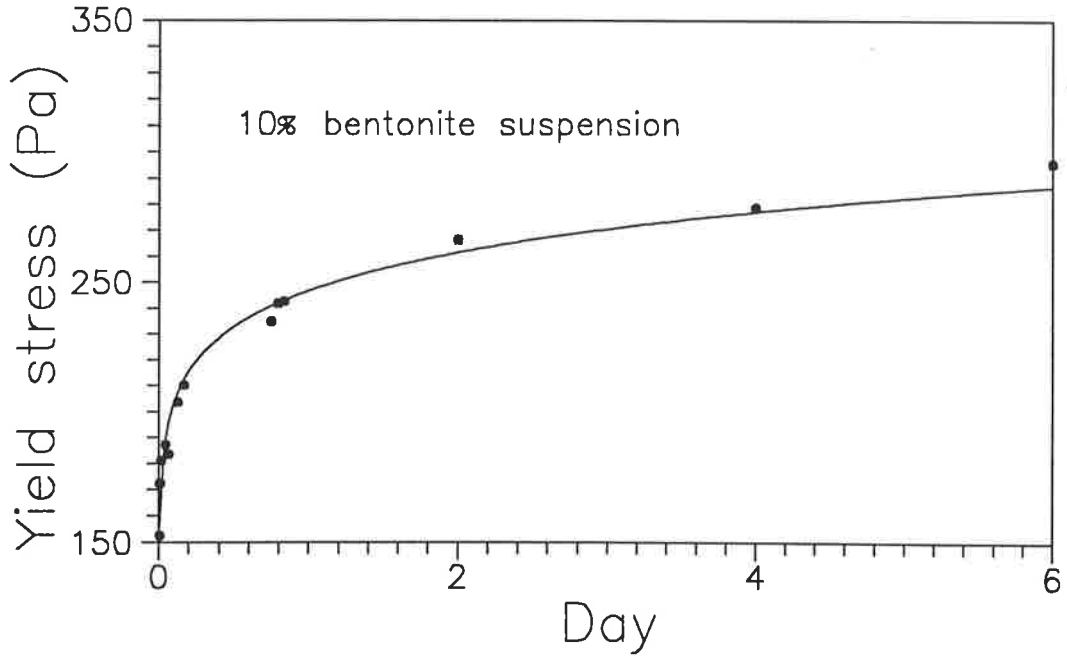


Fig. 5.4 The change of the yield stress value as measured by the vane method with different rest time for 10 wt% bentonite suspension in 0.625 g/L NaCl solution.

The experimental results in Tables A7.1 and A7.2 of Appendix 7 show that the pH values obtained directly from suspension were slightly higher than that measured from its filtrate (through filtration process) within a pH variation of about 0.3. In all the tests, the pH values of the filtrate were used to represent the suspension pH.

Selection of suitable Solids Concentration of Suspension

Finally, the suitable solids concentration of the suspensions to be used in this study was selected by considering the following factors:

- The suspension should be concentrated enough to exhibit stable and measurable yield stress;
- It should be viscous enough to show flow property within the measurable range of the available viscometer;
- The suspension should exhibit a measurable yield layer within the measurement capability.

With the above considerations, the suitable concentration of the suspension was determined by gradually adding and mixing the solid powder into a container of distilled water. The suitable concentration for kaolin suspension was found to be between 47 and 53.3 wt%. Similarly the suitable concentration for starch was found to be around 7 wt%.

However, the stable suspension of bentonite appeared to exist only in a very narrow range. Hence, the determination of the suitable concentration was slightly more difficult. For example, sedimentation was a problem if the solids concentration is below 5 to 6 wt%. Furthermore, at the low concentration, the overall texture of the unsheared edge of the suspension appeared to become less "coagulated". However, at concentration above 7 wt%, the bentonite suspension exhibits a relatively low viscosity compared to its yield stress, hence giving high value of τ_y / μ . The flow curve of such suspension gives a relatively high stress and also insensitive to the change of increasing shear rate. Consequently, the stress decay curves as a function of different rotating speeds would appear to be very close together, with

variation of the order of the experimental error. The sheared layer at concentration above 7 wt% was also found to be very small, e.g. for 8 wt% bentonite suspension, the sheared layer varied from 1 to 2 mm using a bob radius of 20.04 mm rotating at a speed of 50 rpm.

Numerous trials have been conducted to improve the rheological properties of the bentonite suspension with the aim of reducing the value of τ_y / μ , hence giving a better condition for the experimental demonstration in the later study. One of the approach is to change the ionic strength of the colloid suspension by addition of NaCl. The bentonite suspensions with different concentrations of NaCl were prepared. The results showing the influence of solids and NaCl concentrations on the suspension rheology are presented in Table A7.2 and Fig. A7.1 in Appendix 7. However, the problem of high τ_y / μ could not be totally overcome in this attempt. For the purpose of the present study, it appeared that the 8 wt% bentonite suspension with 0.006 Molar NaCl solution was the only satisfactory combination among the others. To improve the observation of the sheared layer, a larger bob with a radius of 54.8 mm was used.

Table 5.2 shows the physical properties of the selected suspensions used in the present study. The temperature of the experiments is at 18°C. Particle size in suspensions were measured with the particle size analyzer using a slurry feeder. The particle sizes for kaolin and bentonite suspension were smaller than those in their powder forms, because during the measurement in suspension, ultrasonic pulsation was used to break up the particle agglomerates. The waxy maize starch particle size in the suspension became larger than its powder form due to absorption of water by starch granules which led to swelling.

For the selected suspensions, bentonite was not used in the experimental verification of the r_c method because its shear stress value was insensitive to the applied shear rate as mentioned above. The suspension of mayonnaise, bentonite and kaolin (53.3 wt%) were used for the yield boundary measurement due to their reasonably well defined yield boundaries.

Table 5.2 Physical properties of the selected materials in suspension.

Material	Solid conc. wt%	Yield stress Pa (vane method)	Density Kg/m ³ (suspension)	d _{v,0.5} μm	d _{2,3} μm	pH
Mayonnaise	NA	31.5	1170	8	4	2.9
Waxy maize starch	7	7.0	1074	32	21	5.6
Bentonite	8	83.5	1075	5	4	10.3
Kaolin	53.3	145	1545	6	4	8.3
	47	33	1429	6	4	7.6

NA: not available.

5.3 Experimental Apparatus and Procedures

This section describes the experimental apparatus and procedures employed using a concentric cylinder viscometer. The yield stress was determined by the vane method while the yield boundary was measured by visual technique using an imaging system.

5.3.1 Concentric cylinder viscometer

Equipment

Fig. 5.5 shows the general setup of the concentric cylinder viscometer and computer system employed. The viscometer used was Haake RV100. The detailed descriptions of equipment and operating procedures are described in the user's manual provided by the manufacturer (Haake GmbH). Two types of measuring-drive-units, M5 and M10, were used. Their specifications are shown in Table 5.3.

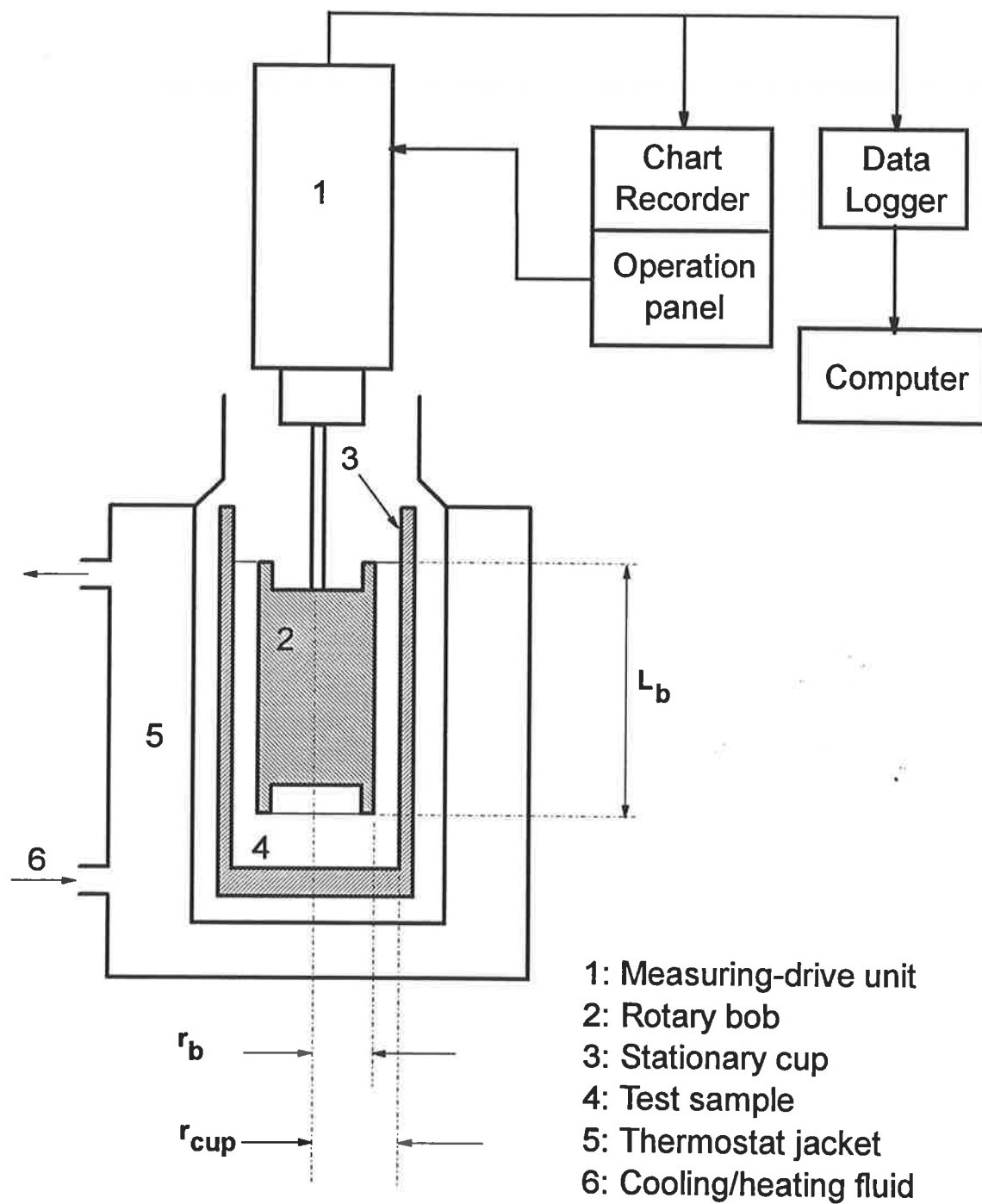


Fig. 5.5 A schematic of the concentric cylinder viscometer.

Table 5.3 Specifications of measuring-drive-units

measuring-drive-unit	maximum torque (Ncm)	maximum speed (rpm)	Error % in torque
M5	4.9	500	± 2
M10	9.8	1000	± 2

The full range of the rotational speed for both measuring-drive-units was tested by using an electronic counter with light sensor and, the error was found to be within $\pm 2\%$. The rotational speed used in the following study usually seldom exceeded 300 rpm.

The viscometer may be equipped with one of the three different sensor systems of measuring devices: MVI, MVII or MVIII. The dimensions of the bob and cup for different sensor systems are shown in Table 5.4.

Table 5.4 Specifications for different sensor systems.

Sensor system	MVI	MVII	MVIII
<u>Inner cylinder (bob)</u>			
radius, r_b (mm)	20.04	18.4	15.2
height, L (mm)	60	60	60
<u>Outer cylinder (cup)</u>			
radius, r_{cup} (mm)	21	21	21
Radius ratio, ϵ (r_{cup} / r_b)	1.048	1.141	1.382
Sample volume, (cm ³)	40	55	70
Temperature : max. (°C)	100	100	100
min. (°C)	-30	-30	-30

The MVI and MVII systems were used most often in this study. The viscometer was equipped with a water jacket so that the temperature of the test suspension could be maintained constant during the experiment. The measured stress value by the sensor was transmitted to and recorded by either a chart recorder or stored through a data logger (real-time interface module, RIM 1000) in a personal computer for later analysis.

Method

Before testing, the cup was carefully filled with the required volume of sample and it was slowly pushed upward with the bob inside until the bob was entirely submerged in the sample material. The position of the cup was then fixed with respect to the bob and the water jacket. The water circulating in the jacket was maintained at 18 °C with a variation of ± 0.5 °C in all experimental tests. Since the sample suspension had been affected by shear to a certain degree when the bob was slowly pushed into the cup, the sample in the cup was thus allowed to rest for 1 hour before the test commenced. This was done to ensure that all samples to be tested had almost the same initial state of structure. Additional precaution was also taken, if possible, to prevent the loss of sample moisture to the atmosphere by covering the exposed top surface of the suspension sample with a transparent plastic film and sealed with grease.

Measurements were performed either by using a cup and bob arrangement with a relatively narrow gap or, using a single bob rotating in an 'infinite' medium (i.e. a wide radius cup) to achieve a partially sheared condition, required for observation of yield boundary. The typical tests performed using the above configurations include:

- stress decay with time under a given rotational speed;
- step-change-in speed (hence shear rate) test at a constant structure level;
- hysteresis loop test by linearly increasing and decreasing the rotational speed;
- yield boundary measurement.

5.3.2 Vane method

In addition to using a sensor system described above, the measuring-drive-unit could be equipped with a vane to measure the yield stress. The yield stress can be determined from the maximum torque at very low rotating speed. The measuring criteria and procedures followed the methods developed by Nguyen & Boger (1983 and 1985a).

5.3.3 Visualization experiments

The location of the yield boundary has been studied theoretically in previous chapters. The purpose of the visualization experiment was to measure the yield boundary in suspension and to validate the theoretical prediction.

Selection of Tracer Particles

Tracer, either in the form of particles or solution, was used to assist in the detection of the yield boundary. Various types of tracers were tested to find the most suitable material. These include colored ink, wood dust, wax fragments, aluminum flakes, "lexan" plastic particles and carbon black particles. The colored ink was found unsuitable due to its tendency to disperse. The fibrous nature of the wood dust with its less distinctive color was found to be unsatisfactory as well. Although the wax fragments are relatively lighter than the aluminum flakes, their inclination to aggregate in room temperature also showed to be problematic. In this case, "lexan" plastic and the carbon black particles were found to be most suitable as tracer material due to its low density, non-aggregate tendency and distinctive colors i.e., white "lexan" particles for yellowish brown bentonite suspension background and, carbon black particles for milky white kaolin and light yellow mayonnaise suspensions. Both types of tracer particles were carefully screened to the size range from 44 to 100 μm .

Experimental Setup for the Visualization Technique

The experimental setup for the measurement of the yield boundary by visual technique using a video imaging system is shown in Fig. 5.6. The test sample was sheared using the viscometer configuration as discussed earlier. A front-silvered mirror which avoided the problem of double reflection was positioned, with the aid of a retort stand, at 45-degree angle just above the surface of the test suspension. The relative length scale of the image was calibrated prior to the experiment for quantitative measurement at the later stage. Sufficient lighting was also provided to ensure good image quality. Before commencing the test, a small

fraction of the tracer particles were sprayed across the surface of the suspension. Measurement of the yield boundary was performed by either still photography or video method. The video method provided a better way for detecting movement of the boundary and could be easily analyzed through the use of the appropriate image analysis software.

Photographic Method

The suspension was photographed by a still camera equipped with a macro lens at a fast shutter speed at different times during the shearing process. The yield boundary was delineated by differentiating between the moving and non-moving tracer particles, with the moving particles near the bob surface appearing to be blurred in the photograph. The yield boundary was measured by projecting the image on a large screen using a slide projector. Typical photographs showing the existence of the yield boundary for mayonnaise, kaolin and bentonite suspensions are shown in Fig. 5.7 (a), (b) and (c) respectively. For both mayonnaise and kaolin suspensions, carbon black was used as the tracer particles, while for bentonite suspensions "lexan" plastic particles were selected as tracer. The exposure time of the camera was set at 1 second which was found to be sufficiently long to distinguish the stationary and moving tracers. Bob rotational speeds used for mayonnaise, kaolin and bentonite suspensions were 5, 50 and 90 rpm respectively.

Video Imaging Method

The photographic technique had several disadvantages. The task of developing the film and analysis of the results proved to be extremely tedious, time consuming and costly. An alternative approach was adopted by using an integrated video and image analysis system which was being used and developed in-house by the Fluidization Research Group of this department. The video camera used was a CCD (charge-coupled device) with a macro lens of 25X magnification. Images showing the movement of the yield boundary were captured and recorded by a video cassette recorder (VCR). The recorded image sequences were then played back from the VCR and analyzed using the appropriate image analyzer hardware and

software. Briefly, the image analysis steps first involved digitization of the analog video signals from the VCR by a frame grabber into 512 by 512 picture elements (pixels). Then, through the use of a host personal computer and the appropriate computer software, the digitized image was analyzed following of the procedure as described in Appendix 8.

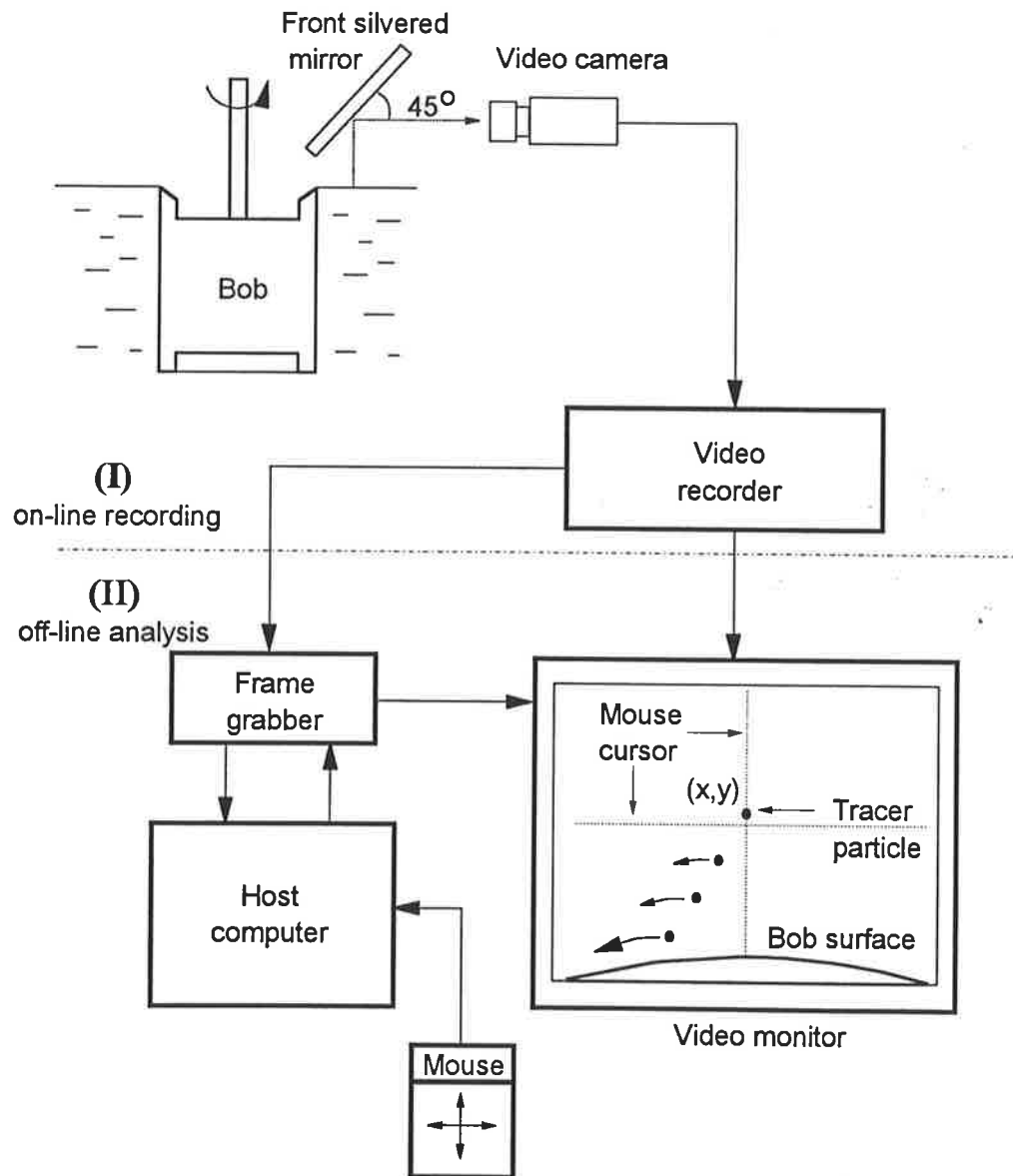


Fig. 5.6 A schematic of the experimental set up and data analysis for the yield boundary measurement using a video imaging system.

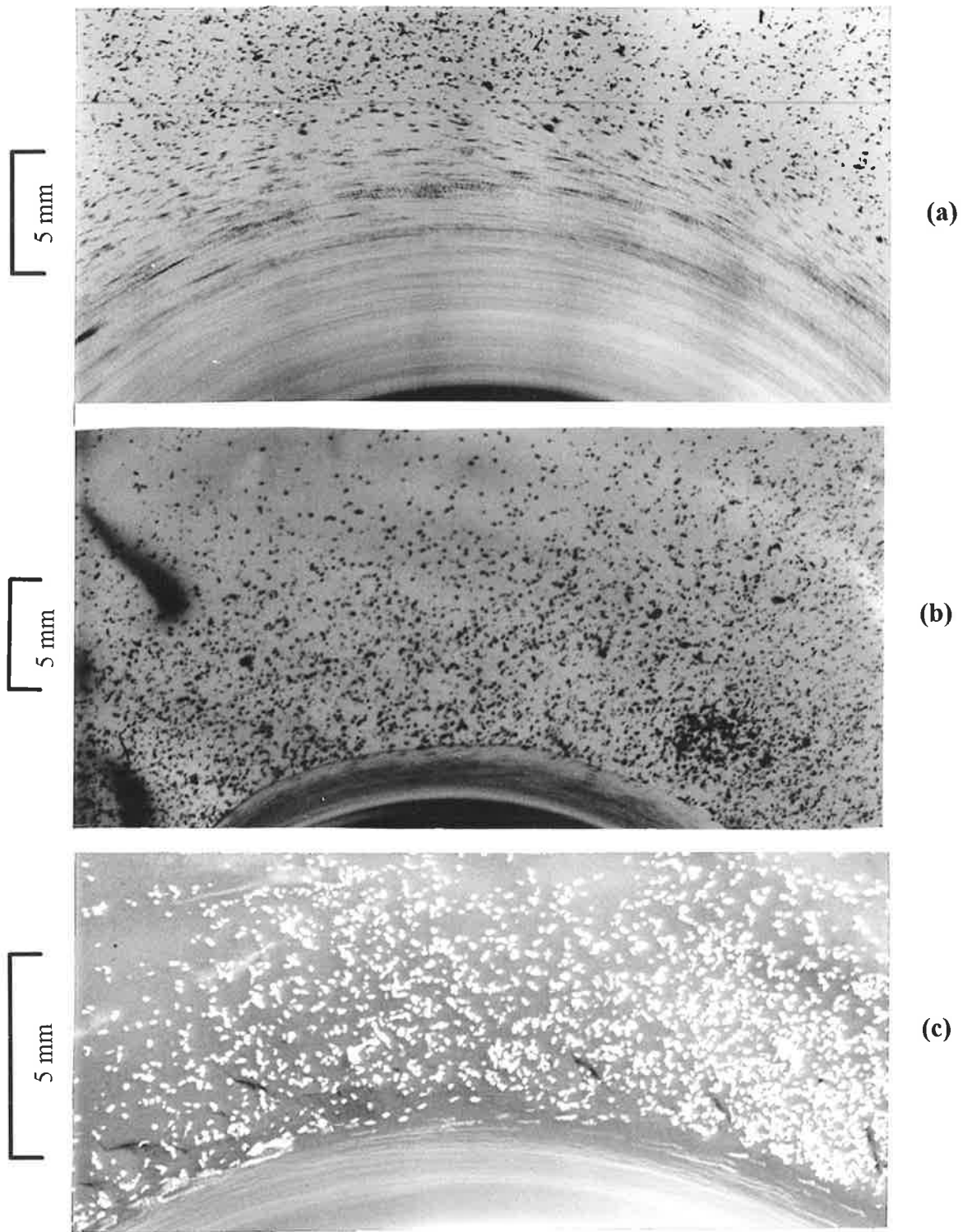


Fig. 5.7 Photograph showing the yield boundaries for different suspensions. (a) mayonnaise; at $\Omega = 5\text{rpm}$; (b) kaolin 53.3 wt%; at $\Omega = 50\text{rpm}$; and (c) 8 wt% bentonite suspension with 0.006 Molar NaCl; at $\Omega = 90\text{rpm}$. Camera exposure time was at 1 second

Chapter 6

Characterization of the Thixotropic Behaviour

To successfully characterize the thixotropic fluids, it is important that one can accurately obtain and interpret the experimental data and has the appropriate model to describe the time-dependent behaviour. In this chapter, the methods for interpreting and modelling such fluids is presented. Firstly, the r_c method is used to obtain more accurate shear stress-shear rate-time data from the experimental shear stress-speed data using a concentric cylinder viscometer. Secondly, a new and improved modelling approach is proposed to characterize the thixotropic fluids where the existing limitations from the previous methods will be overcome.

6.1 Experimental Work to Illustrate the r_c Method

The theoretical calculation procedures for shear stress and shear rate using the r_c method have been described in section 3.4. The shear stress and shear rate are related only to the geometric factor (i.e. ϵ) and rotation speed (Ω). In the following experimental study, the flow in the annular region of the concentric viscometer is maintained at fully sheared and laminar tangential flow condition. Such conditions could be achieved by a proper selection of the range of gap size and rotation speed depending on the nature of the fluids. Considering these factors, sensor systems MVI ($\epsilon=1.048$) and MVII ($\epsilon=1.141$) were found to be most suitable for the current experiments using the selected suspensions. While, sensor system MVIII ($\epsilon=1.382$) was occasionally used especially at lower shear rate conditions. Fig. 6.1 shows the calculated bob rotational speed as a function of shear rate at the corresponding r_c position for the three sensor systems employed.

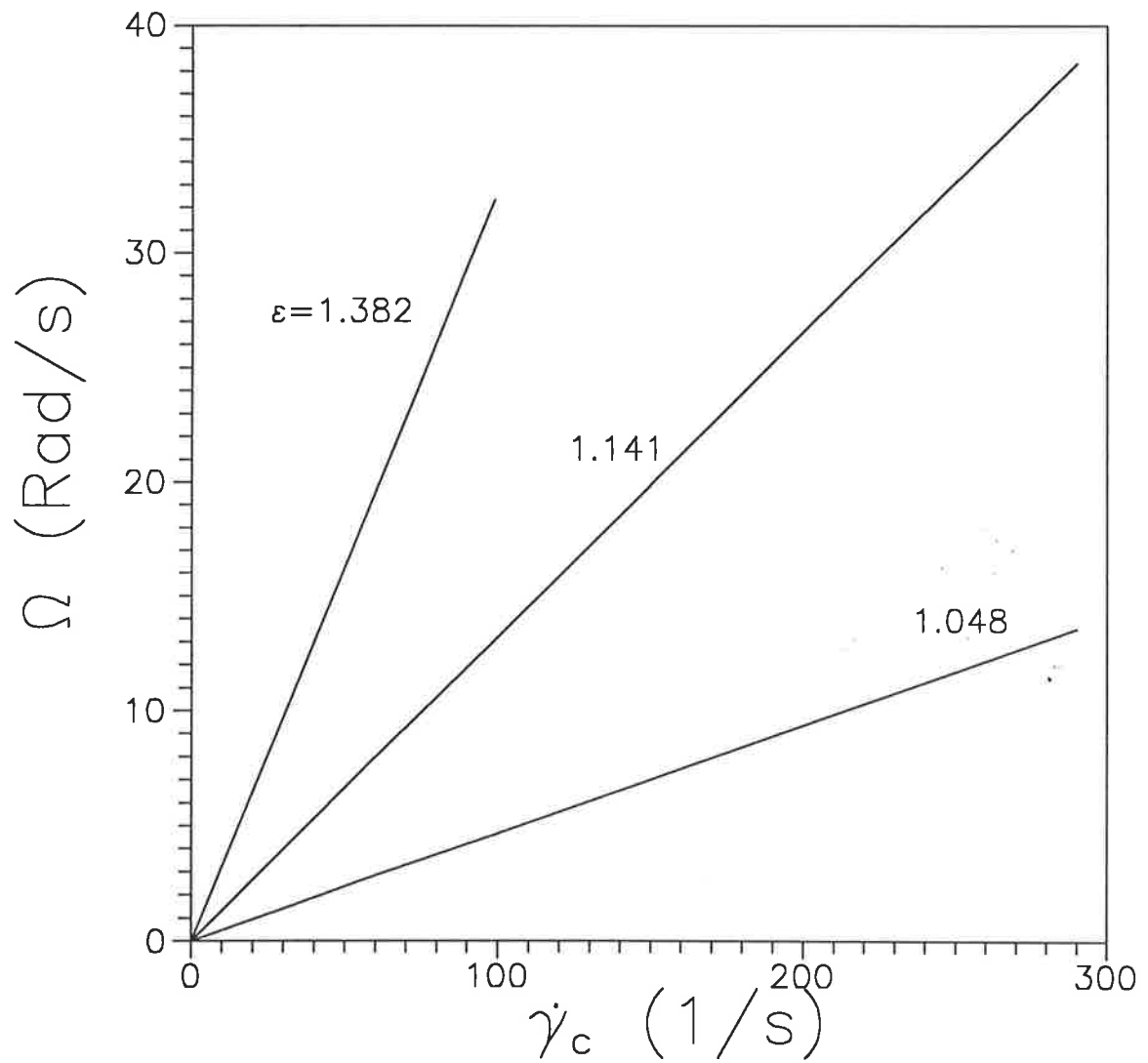


Fig. 6.1 Rotational speed of the bob as a function of shear rate at r_c position for three sensor systems. Speed is defined in Eq (3.52).

The experimental results have been analyzed following the r_c approach using three most commonly used experimental procedures for characterizing thixotropic fluids, namely (1) shear stress decay method (Goodeve & Whitfield 1938; Nguyen 1983; Cheng 1987); (2) constant structure flow curve method (Cheng & Evans 1965); and (3) hysteresis loop method (Moore 1959; Garrido et al. 1990). The following experiment results will demonstrate that the r_c method is a reliable method for interpreting the experimental data obtained for four different time-dependent yield stress suspensions.

For flow conditions other than the fully sheared Bingham flow, the error due to the r_c method increases with the yield number (in the case of any one of the three ideal flow models) and the radius ratio of the sensor system employed. According to the definition in Table 3.1, the value of yield number increases with the increasing value of (τ_y / μ) and inversely proportional to the rotational speed Ω . So the error in using r_c method depends on both the tested fluid structure condition (i.e. the value (τ_y / μ)) and the operating conditions (i.e. Ω and ϵ). The experimental results using three most commonly used experimental procedures are presented and discussed qualitatively in sections 6.1.1 to 6.1.3. More detailed quantitative analysis is presented in section 6.1.4.

6.1.1 Shear stress decay experiments under constant shear rate

In this method, the shear stress decay was measured under a constant rotational speed. The change of the shear stress with time under a given shear rate was calculated from experimental shear stress-time data at bob surface under a constant rotational speed (see section 3.4). The experiments were performed under different sensor systems and a series of constant shear rate conditions. Theoretically, the shear stress decay curve under a constant shear rate depicts the characteristic of the fluid structure and should be independent of the measuring approach. So, if the measurements from different sensor systems are accurate, they should produce identical results.

For each shear stress decay curve under a constant Ω , the value of (τ_y / μ) will vary with time of shear due to structure change. Similarly, the yield number will increase (or decrease) with increasing (or decreasing) value of (τ_y / μ) from the initial yield number. The trend of (τ_y / μ) changing with time is usually not known at this stage. However, the yield number is expected to be high if low rotational speed Ω is used.

The shear stress decay curves at r_c position for mayonnaise and waxy maize starch 7 wt% suspensions are shown in Figs. 6.2 and 6.3 respectively. The shear stress values obtained from three different sensor systems (i.e. $\varepsilon=1.048$, 1.141 and 1.382) under the same shear rate were found to be very close. Such good agreement for these two suspensions may because the experimental values of (τ_y / μ) are not excessively high and Ω s are also not too low to lead to noticeable errors in the r_c approach as discussed earlier. Figs. 6.4 and 6.5 present the shear stress decay results at r_c position for kaolin (53.3%) and kaolin (47%) suspensions respectively. A relatively good agreement was obtained for the shear stress values from two different sensor systems (i.e. $\varepsilon = 1.048$ and $\varepsilon = 1.141$) at a given shear rate except for those curves obtained at low shear rate conditions. This deviation is probably due to the high yield number (i.e. low Ω and high (τ_y / μ)) at the given sensor system conditions especially for the large gap sensor ($\varepsilon = 1.141$). This was also confirmed, although not presented, from the experimental tests using large gap sensor of $\varepsilon = 1.382$ sensor system. Clearly, the r_c method is not satisfactory for the sensor system of $\varepsilon = 1.382$ for the above kaolin suspensions as compared with the mayonnaise and waxy maize starch suspensions.

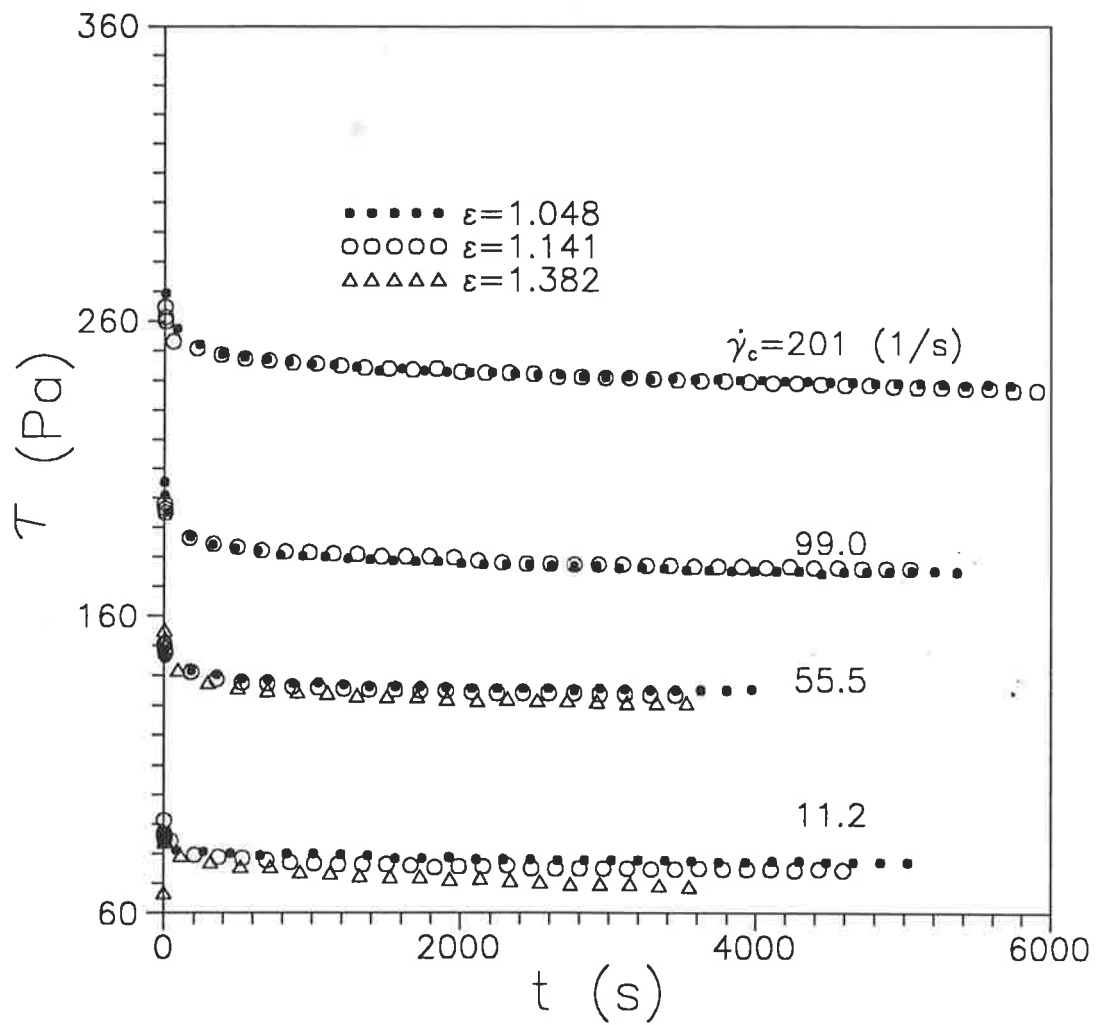


Fig. 6.2 Shear stress decay curves for mayonnaise suspension using the r_c method where the shear stress is specified at r_c location.

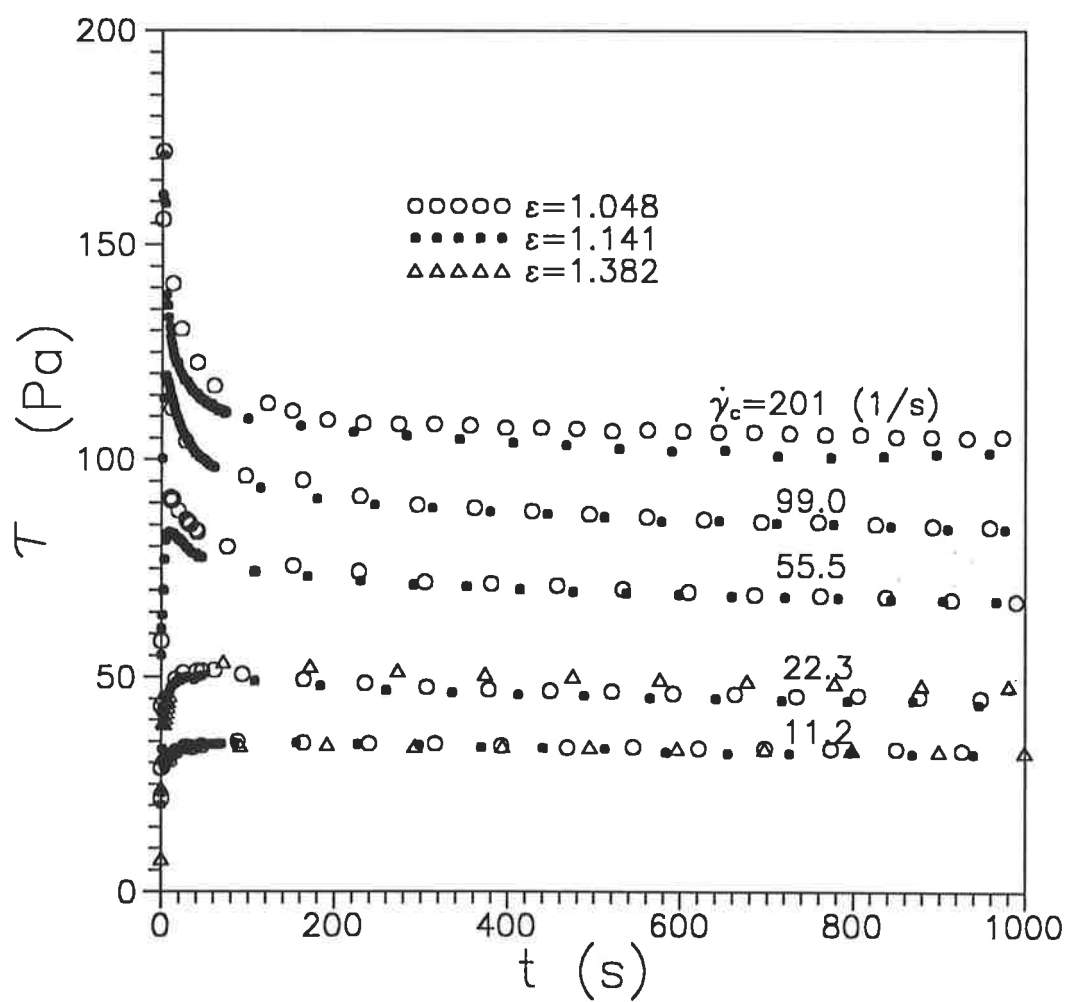


Fig. 6.3 Shear stress decay curves for waxy maize starch 7 wt% suspension using r_c method.

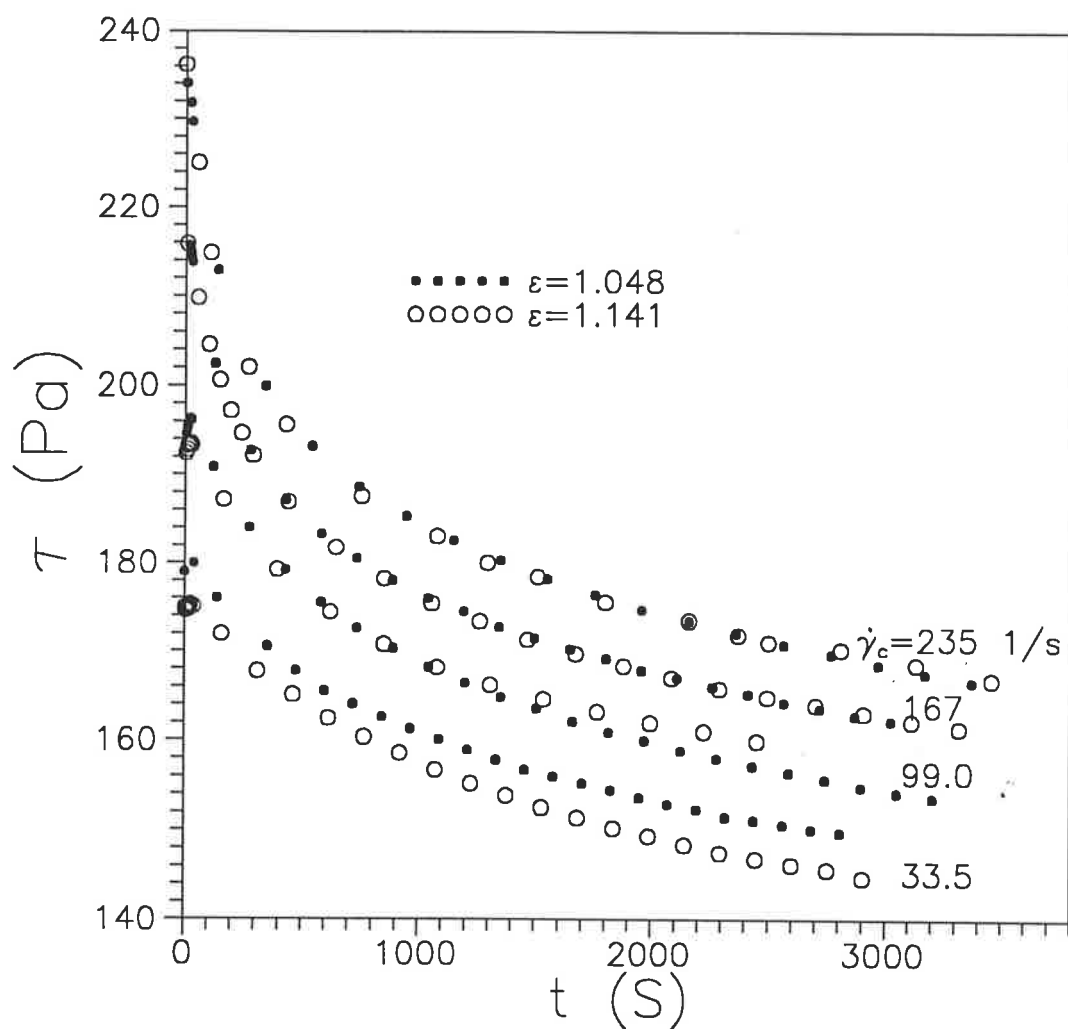


Fig. 6.4 Shear stress decay curves for kaolin 53.3 wt% suspension using the r_c method.

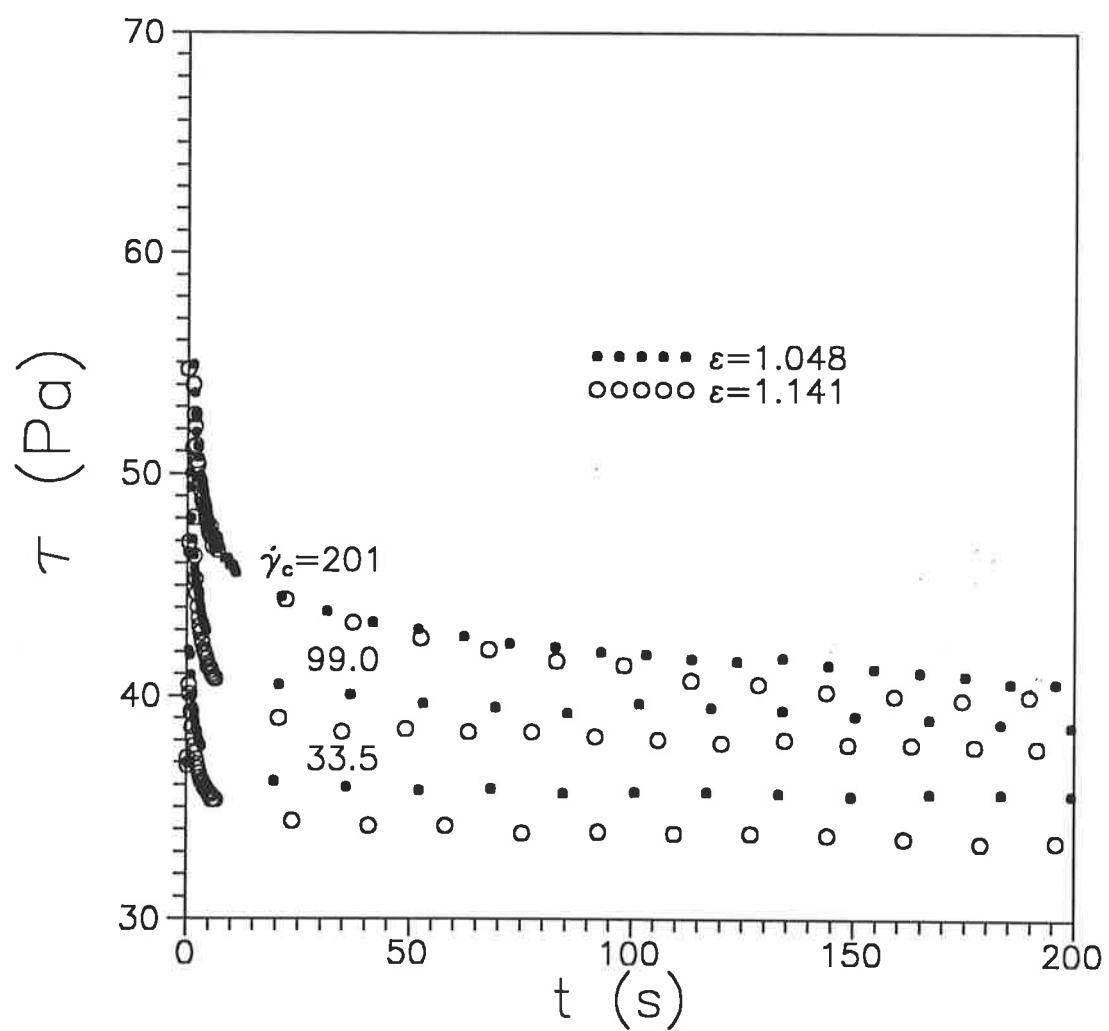


Fig. 6.5 Shear stress decay curves for kaolin 47 wt% suspension using the r_c method.

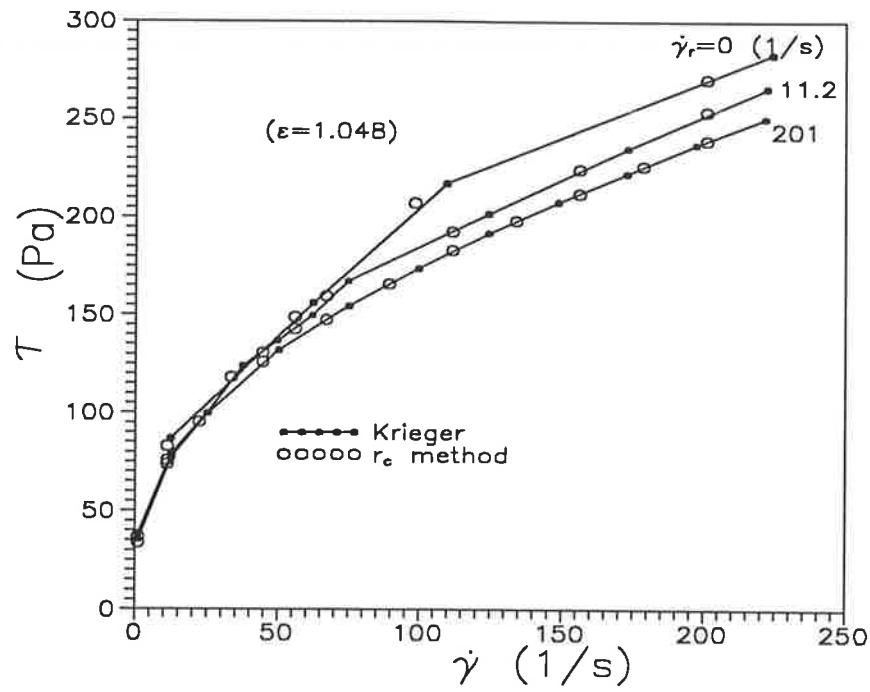
6.1.2 Constant structure flow curves at different reference shear rates

Constant structure flow curves were obtained by measuring the shear stress-change in speed data and converting into shear stress-change in shear rate relationship in this section. Constant structure flow curves are basic rheological properties for a given fluid and should be independent of the interpretation approach. So if the r_c method is accurate in this application, then it should produce identical results compared to other well developed method such as the Krieger method. As mentioned in section 3.7, the Krieger method which is used to convert the shear stress-speed data to shear stress-shear rate relationships for time-independent fluids can be used to obtain the constant structure flow curves from the experimental shear stress-speed data. In this section, the Krieger and the r_c methods are used and compared for the determination of constant structure flow curves from the step-change in speed (shear rate) experiments using two different sensor systems ($\epsilon = 1.048$ and 1.141).

Comparison of the constant structure flow curves obtained from the Krieger and the r_c methods for mayonnaise suspension is shown in Fig. 6.6. The constant structure flow curves for the reference shear rates above 55 1/s overlapped. This implies that only one structure level was reached beyond this reference shear rate. Unlike the mayonnaise suspension, this behaviour was not observed in the maize waxy starch suspension as shown in Fig. 6.7. Both mayonnaise and waxy maize starch suspensions exhibit a relatively low yield stress than that for kaolin 53.3 wt% and 47 wt% suspensions as shown in Figs. 6.8 and 6.9 respectively. The constant structure flow curves generated from the r_c methods in general have a slightly shorter shear rate range than that obtained by Krieger method because the shear stress and shear rate at r_c is smaller than that at the bob surface. It is interesting to note that good agreement between the two methods was observed even the fluids tested were not necessarily belonged to ideal Bingham fluid. This agreement has provided a stronger confidence in using the r_c method for other more general fluid types.

For each constant structure flow curve, the ratio (τ_y / μ) remains constant while Ω is varied. At low shear rate condition (i.e. low speed), the r_c method is more likely to give a large error under a given ε due to the possibility of a higher yield number. The another reason for the error is probably due to the poor measurement accuracy at the very low shear rate condition resulted from delayed shear stress response. For example, such delayed response can be seen in Fig. 6.3 at shear rate of 11.2 and 22.3 1/s where the initial shear stress responses were delayed about at least 40 seconds instead of reaching the peak shear stress value immediately. Due to such problem, the experimental data at shear rate below 30 (1/s) were assumed to be unreliable.

(a)



(b)

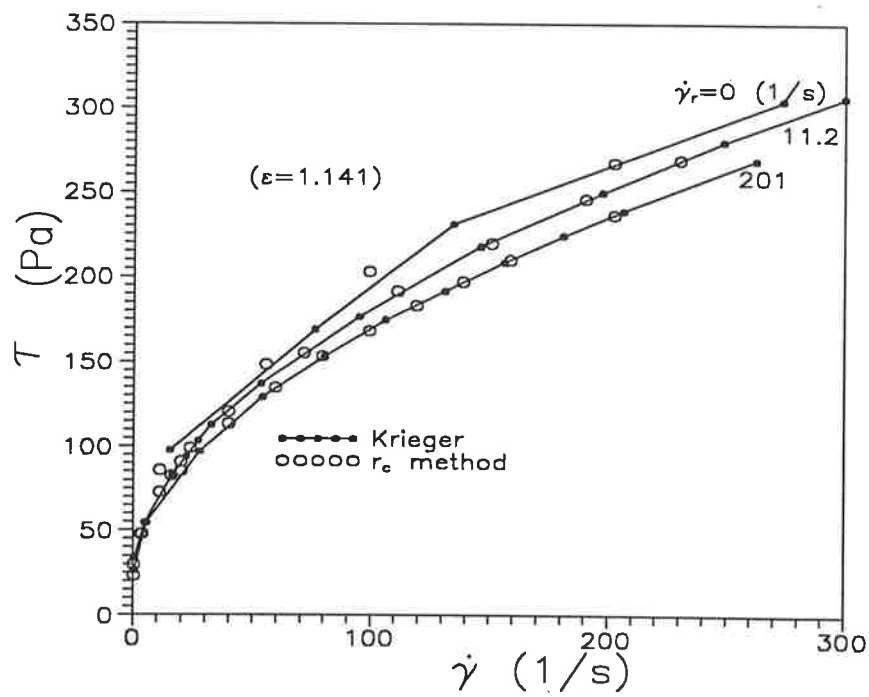


Fig. 6.6 Constant structure flow curves for mayonnaise suspension using the Krieger and the r_c methods. (a) $\epsilon = 1.048$; (b) $\epsilon = 1.141$.

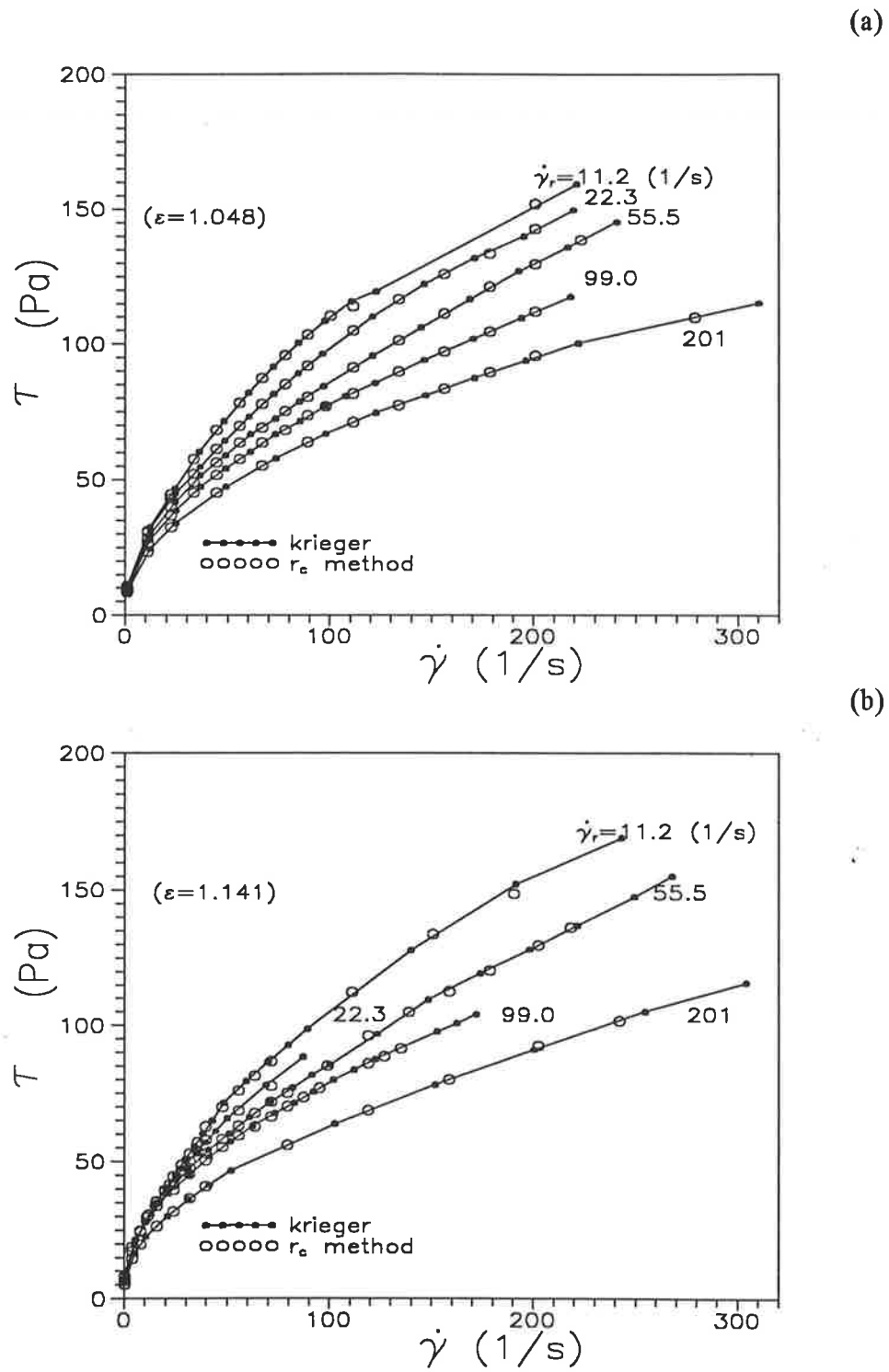


Fig. 6.7 Constant structure flow curves for waxy maize starch 7 wt% suspension using the Krieger and the r_c methods. (a) $\varepsilon = 1.048$; (b) $\varepsilon = 1.141$.

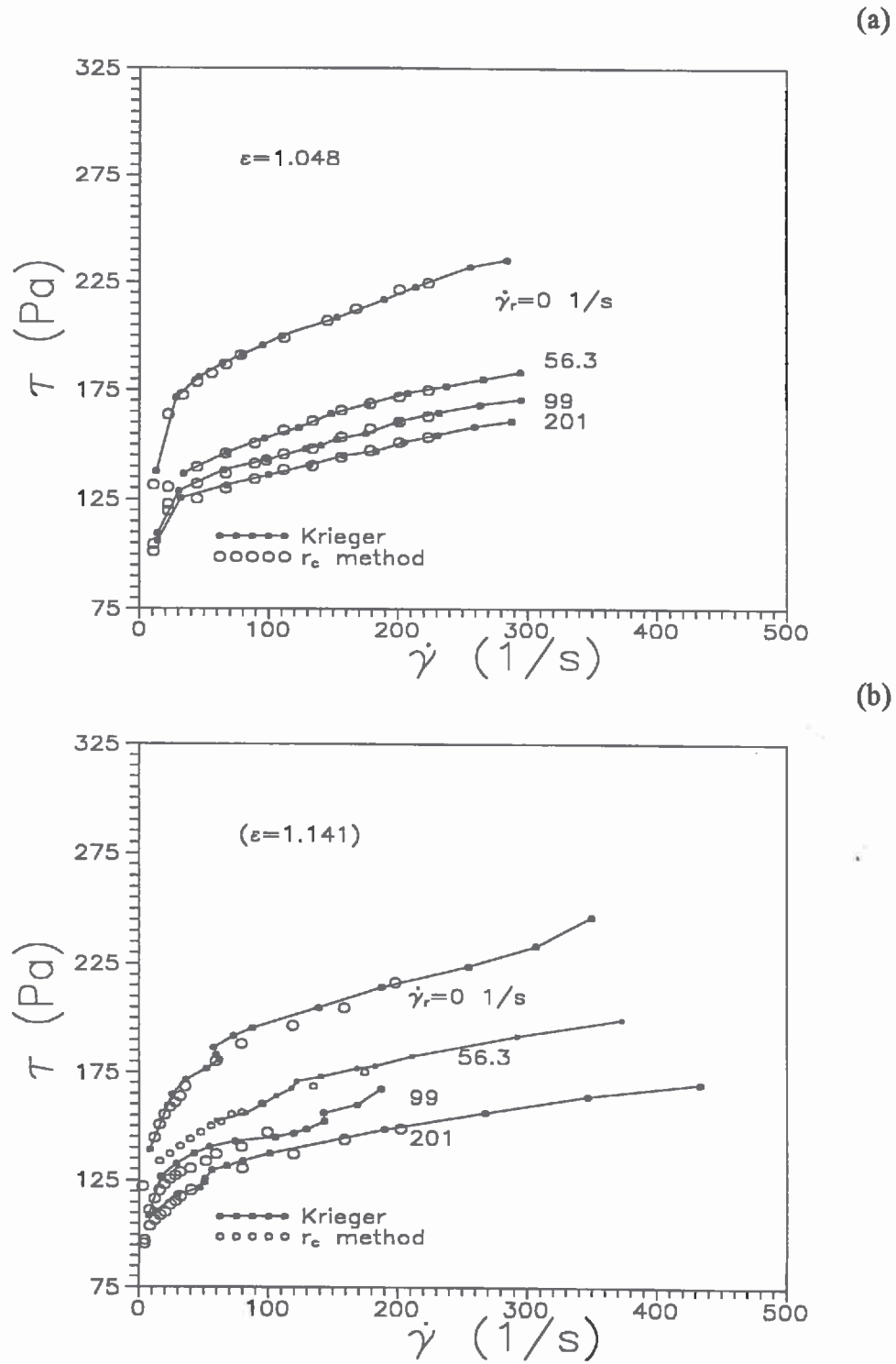
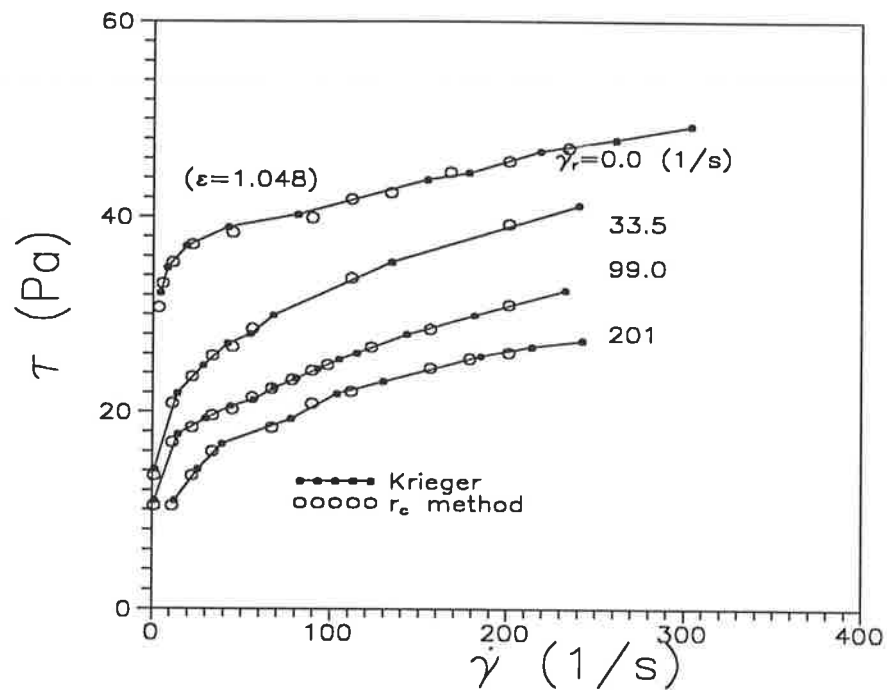


Fig. 6.8 Constant structure flow curves for kaolin 53.3 wt% suspension using the Krieger and the r_c methods. (a) $\varepsilon = 1.048$; (b) $\varepsilon = 1.141$.

(a)



(b)

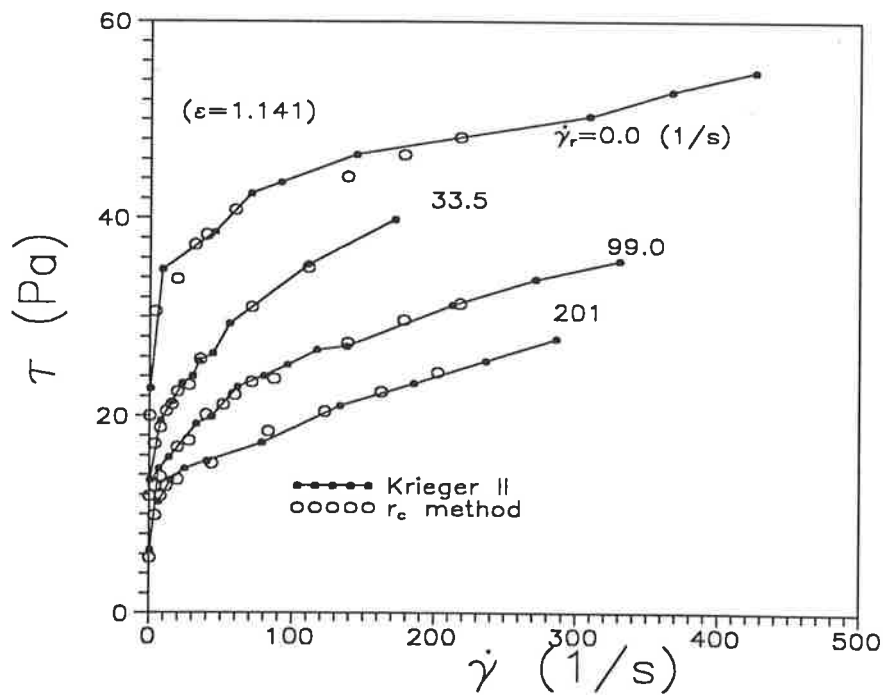


Fig. 6.9 Constant structure flow curves for kaolin 47 wt% suspension using the Krieger and the r_c methods. (a) $\varepsilon = 1.048$; (b) $\varepsilon = 1.141$.

6.1.3 Hysteresis loop

Hysteresis loop of the shear stress was obtained by linearly increasing and decreasing the rotational speed (shear rate). During the measurement, both Ω and the (τ_y / μ) were varied with time. Two different sensor systems ($\varepsilon = 1.048$ and $\varepsilon = 1.141$) were used and the results are compared in Figs. 6.10 to 6.13. The results for the mayonnaise suspension indicates a weaker thixotropic behaviour because the area enclosed by the hysteresis loop is relatively small. The results obtained from the two different sensor systems agree very well for the low yield stress fluids i.e. mayonnaise and waxy maize starch suspensions (Figs. 6.10 and 6.11). This is due to low values of (τ_y / μ) for mayonnaise and waxy maize starch suspensions. Consequently, relatively lower rotational speed could be used without resulting in large errors when using the r_C method. However, larger errors were observed for kaolin suspensions (Figs. 6.12 and Fig. 6.13) in the lower range of the shear rate (below 10 1/s), which may be due to the high value of (τ_y / μ) (i.e. high yield stresses) at low rotational speed. Good agreement between two sensor systems has been obtained for kaolin 53.3 wt% suspension at high shear rate range. In addition to the error at low shear rate range for kaolin 47 wt% suspension, it seems that there is some error also in the high shear rate range.

In the next section 6.1.4, more quantitative analysis of the experiment results in using the r_C method will be discussed.

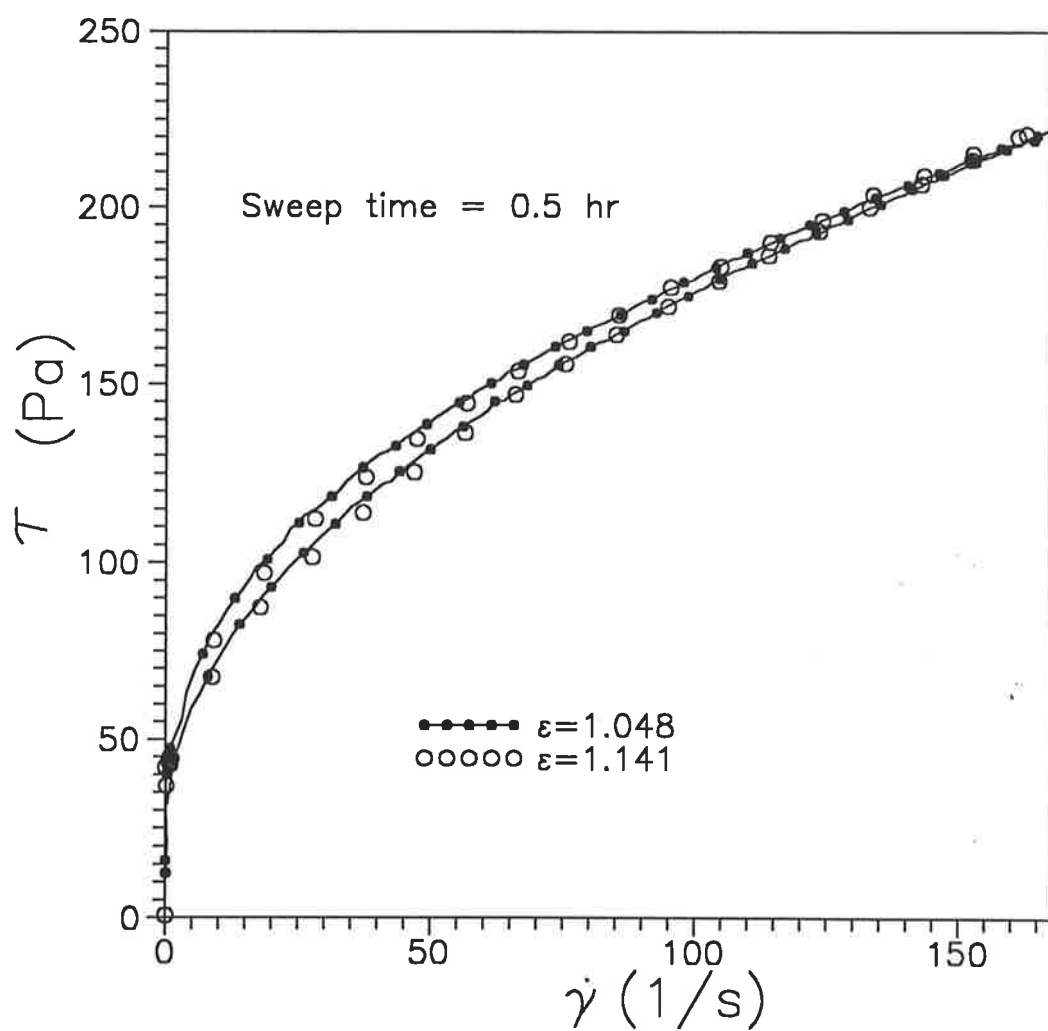
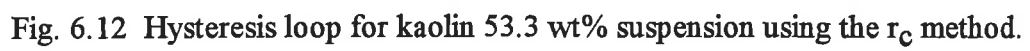


Fig. 6.10 Hysteresis loop for mayonnaise suspension using the r_c method.





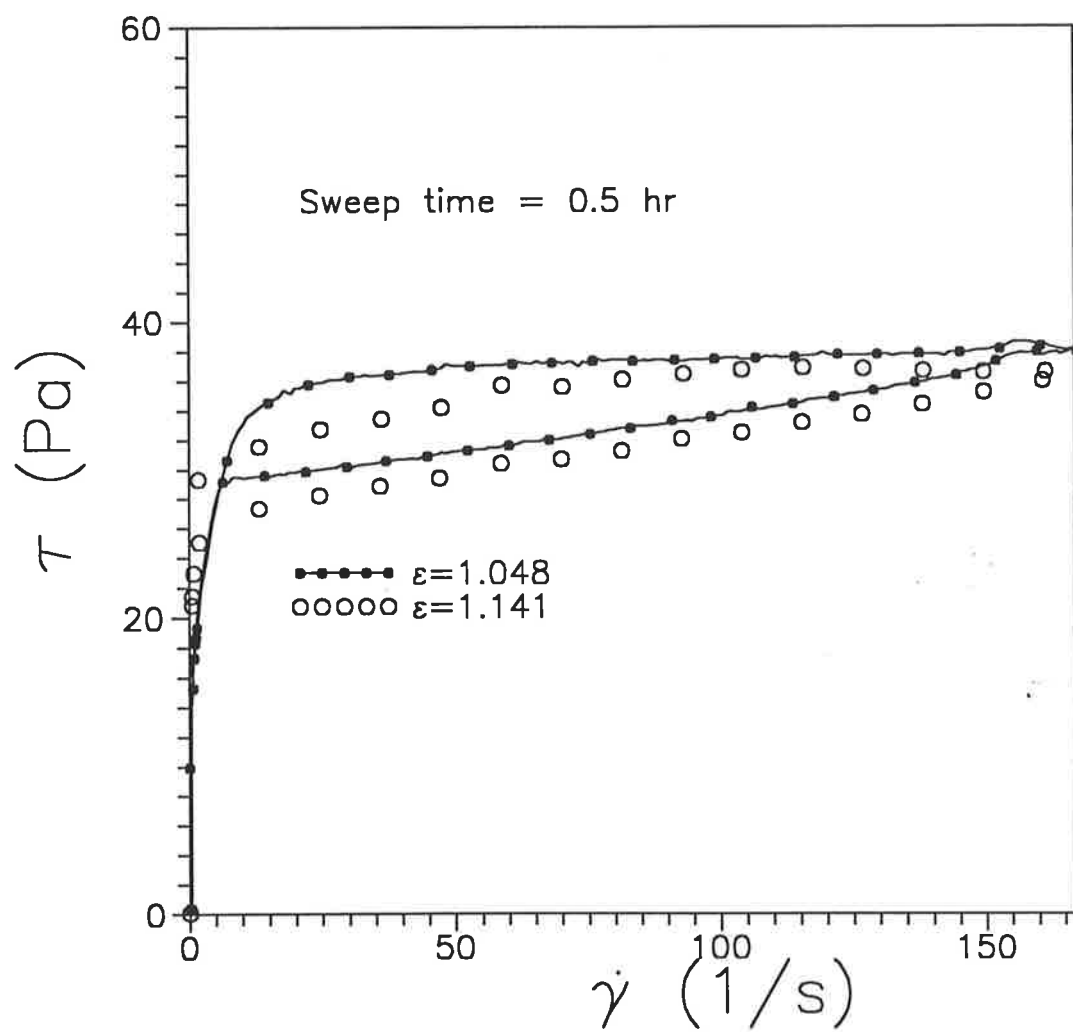


Fig. 6.13 Hysteresis loop for kaolin 47 wt% suspension using the r_c method.

6.1.4 Error estimation for the experimental results using the r_c method

The expected theoretical error when using the r_c method has been discussed earlier in Chapter 3. The radius position r_c / r_b can be determined from Eqs. (3.57) to (3.60) for Casson and Herschel-Bulkley models with $\dot{\gamma} = \Omega / \ln \varepsilon$. According to the Eq. (3.61), the error on shear stress can be determined with the knowledge of r_c / r_b . The following analysis considers three radius ratios used in the current experimental conditions, which are 1.048, 1.141 and 1.382. Figs. 6.14 (a) and (b) show the $r_c(\varepsilon, Ca) / r_b$ position and the corresponding error as a function of yield number with different radius ratios for Casson model. Similar plots for Herschel-Bulkley model are shown in Figs. 6.15 (a) and (b). From these plots, the error is found to be negative, implying that the shear stress is always underestimated because the r_c position moves closer to the bob surface than that for ideal Bingham fluid at fully sheared condition. The error increases with increasing value of yield number and it is also greater at larger radius ratio for a given yield number.

The yield number (for example, the $(\tau_y / \mu) / \Omega$ for the Casson fluid) depends on rotational speed of the bob as well as the value of (τ_y / μ) which is defined by the structure condition of a given fluid. For a given rotational speed, the higher the value of (τ_y / μ) the larger is the yield number. The maximum error for a given experimental condition can be estimated from the highest possible value of (τ_y / μ) that the fluid can exist. The values of (τ_y / μ) can be obtained by fitting the constant structure flow curves at different structure levels with appropriate flow model parameters. The experimental data for the constant structure flow curves for $\varepsilon=1.048$ are shown in Figs. 6.6 to 6.9. Among the four suspensions tested, mayonnaise and kaolin 47 wt% gave the highest possible values of (τ_y / μ) at the initial structure level. On the other hand, the waxy maize starch and kaolin 53.3 wt% gave the highest (τ_y / μ) at structure level when $\dot{\gamma}_r = 201(1/s)$.

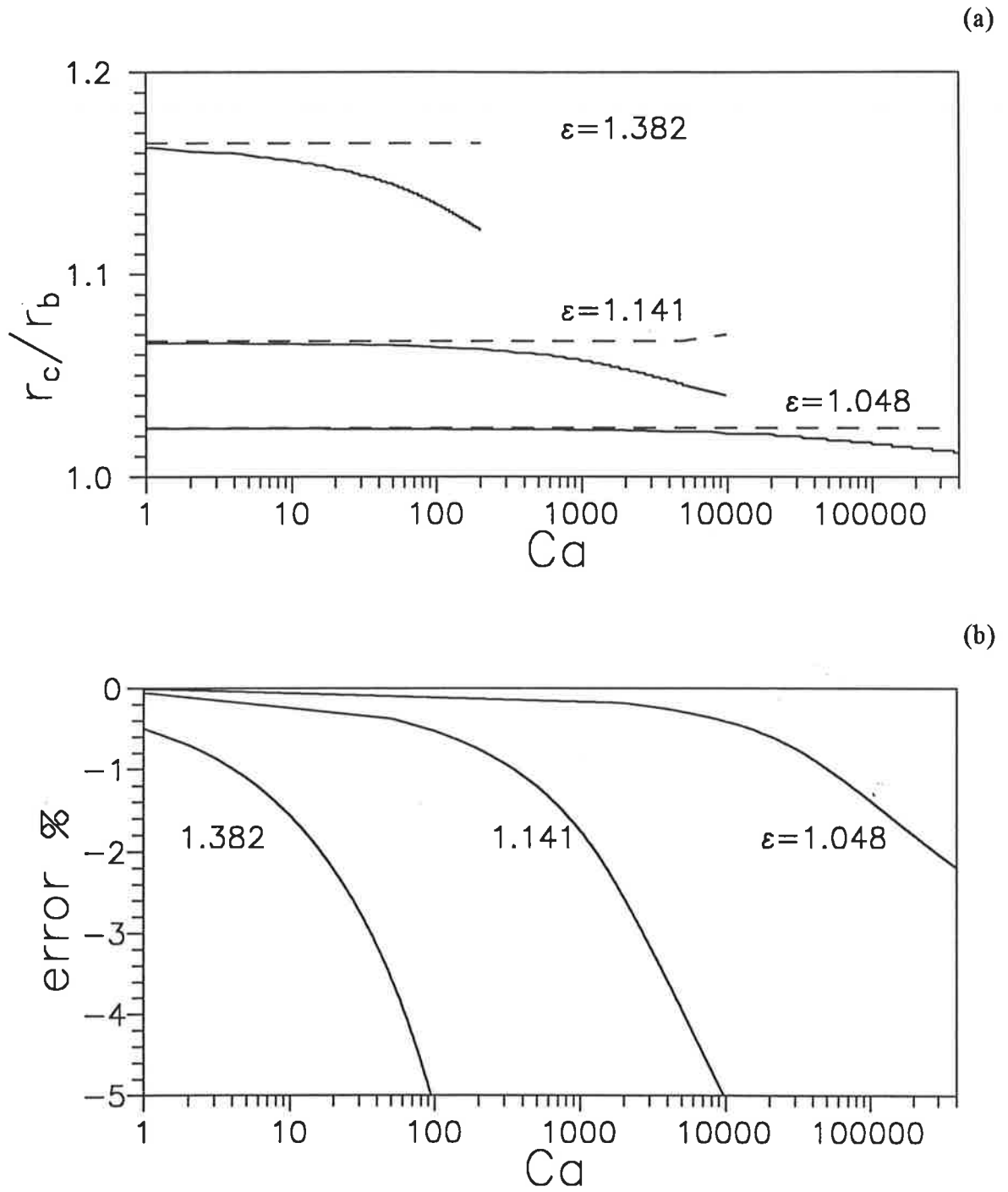


Fig. 6.14 (a) solid lines are the $r_c(\epsilon, Ca)/r_b$ and dashed lines represent the $r_c(\epsilon)/r_b$ of Bingham model at fully sheared conditions. (b) percentage error of shear stress as a function of yield number for Casson fluid.

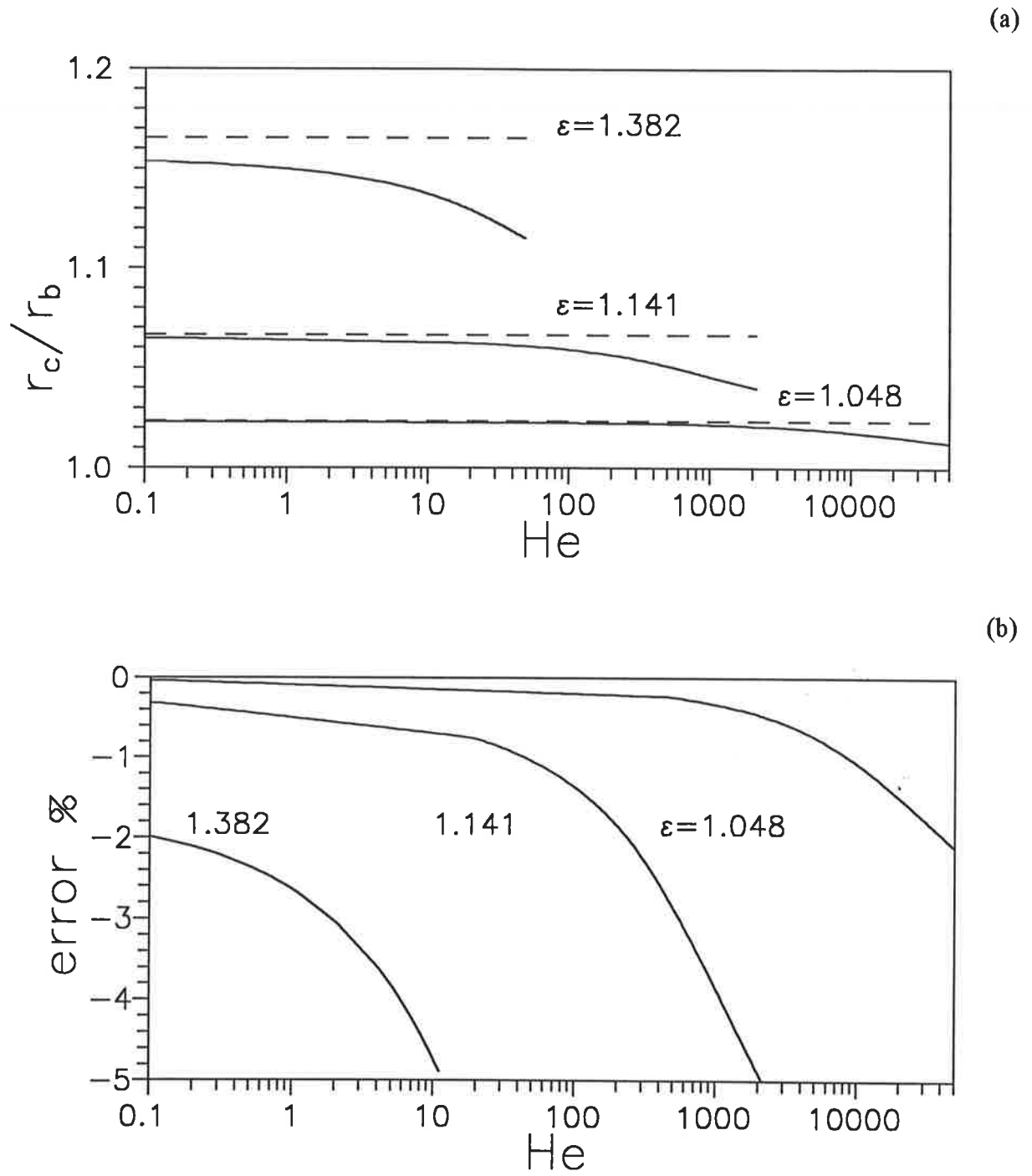


Fig. 6.15 (a) solid lines are the $r_c(\epsilon, He)/r_b$ and dashed lines represent the $r_c(\epsilon)/r_b$ of Bingham model at fully sheared conditions. (b) percentage error of shear stress as a function of yield number for Herschel-Bulkley fluid.

If an error margin of 5% is set for the shear stress, then from the relationship between error and yield number it is possible to determine the lower limit of the rotational speed for a given fluid. It has been shown in section 3.6 that the maximum error for $\epsilon=1.048$ is 4.6% in shear stress. Thus no matter how large the yield number (or how low the rotational speed) is, the error would not exceed 5% at this radius ratio condition. Table 6.1 tabulates the lower limits of the rotational speed for radius ratios 1.141 and 1.382 using four different test suspensions. The power law index of Herschel-Bulkley model (denoted as H-B) in Table 6.1 is 0.5. The values of τ_y and μ were obtained by linear fitting the constant structure flow curves (those obtained by the Krieger method) which had a correlation coefficients greater than 0.980. The highest value of (τ_y / μ) was calculated for a given fluid. The yield number, Yn (i.e. Ca or He) was determined from Fig. 6.14 (b) or 6.15 (b) at error equals to 5%. The lower limit of the rotational speed which gives an error of 5% is determined from $\Omega = (\tau_y / \mu)^2 / \text{He}$ for Herschel-Bulkley model, and $\Omega = (\tau_y / \mu) / \text{Ca}$ for Casson model.

Table 6.1. The lower limit of the rotating speed with error of less than 5%.

suspension	flow model	τ_y	μ	τ_y / μ	ϵ	Yn	Ω (rad/s)
mayonnaise	H-B	24.8 Pa	17.5	1.417	1.141	2130	9.43×10^{-4}
			Pa.s ^{0.5}	(1/s) ^{0.5}	1.382	10	2.01×10^{-1}
waxy maize starch	H-B	7.0 Pa	6.11	1.146	1.141	2130	6.16×10^{-4}
			Pa.s ^{0.5}	(1/s) ^{0.5}	1.382	10	1.31×10^{-1}
kaolin (53.3 wt%)	Casson	107 Pa	0.0181	5912	1.141	9750	6.06×10^{-1}
			Pa.s	1/s	1.382	90	65.69
kaolin (47 wt%)	Casson	33 Pa	0.00518	6370	1.141	9750	6.53×10^{-1}
			Pa.s	1/s	1.382	90	70.78

Knowing the lower limit of the rotational speed, it is possible to find the corresponding shear rate using the relationship shown in the Fig. 6.1. As summarized in Table 6.1, the lower limits of the bob speed for mayonnaise and waxy maize starch are relatively low for both radius ratios 1.141 and 1.382. The estimated limit also helps to explain why good agreement was obtained for the experimental conditions used for mayonnaise and waxy maize starch suspensions as discussed in the earlier section. The results of the error analysis suggest that the fluid property of mayonnaise and waxy maize starch suspensions can be accurately evaluated by the r_c method using all the above sensor systems. However, for both the kaolin suspensions, the r_c method at the sensor system $\epsilon=1.382$ is not accurate, because with this sensor system the lower limit of rotational speed is much higher than the normal experimental condition. A large deviation at the condition of $\epsilon=1.382$ for the kaolin suspensions has also been found experimentally. To ensure the error is less than 5%, the rotational speed used for the kaolin 47 wt% and 53.3 wt% suspensions at the condition of $\epsilon=1.141$ has to be larger than 6.06×10^{-1} and 6.53×10^{-1} (rad/s) respectively. In addition, the above analysis suggests that the error observed in stress decay and hysteresis loop experiments at large value of shear rate for kaolin 47 wt% suspension (Figs. 6.5 and 6.13) might be mainly resulted from "other effects" (like slip effect, or particle radial movement due to centrifugal effect, etc.) instead of only from using the r_c method.

In summary, the applicability of the r_c method has been confirmed by using different sensor systems for a majority of suspensions used in the experiments.

6.2 Modelling of Time-dependent Fluids

From the theoretical studies described in Chapter 3, we know that the flow pattern, such as velocity profile, shear rate, shear stress distributions etc., are dependent on the type of flow model and yield number (such as Bi, Ca and He) of the flow. During the shearing, the

structure of the fluid undergoes changes which in turn also affect the flow pattern. To simulate the change of these flow patterns, it is important to have the knowledge of the type of the flow model for the fluid, and of how the yield number changes with time and shear.

6.2.1 Previous modelling methods

The existing modelling methods for thixotropic fluid have focused on the prediction of shear stress-shear rate-time relationship. The transient shear stress measurements are usually performed at a given constant shear rate. Kinetic models are used to describe the change of structure parameter(s) with time. The structure parameter, λ , is usually defined from the apparent viscosity term (or shear stress) (Tiu & Boger 1974, Nguyen 1983, Cheng 1987, Kristensen et al 1995), for examples:

$$\tau(t) = \eta(t) \cdot \dot{\gamma} \quad (6.1)$$

$$\text{either } \lambda(t) = \eta(t) / \eta_0 \quad (\text{ or } \lambda(t) = \tau(t) / \tau(0) \text{ as } \dot{\gamma} = \text{const.}) \quad (6.2)$$

$$\text{or } \lambda(t) = \frac{\eta(t) - \eta_e}{\eta_0 - \eta_e} \quad (\text{ or } \lambda(t) = \frac{\tau(t) - \tau_e}{\tau(0) - \tau_e} \text{ as } \dot{\gamma} = \text{const.}) \quad (6.3)$$

In Eqs. (6.1), (6.2) and (6.3), only the dependency of time for the apparent viscosity or shear stress is considered and they contain no details about the type of flow model and its model parameters. Therefore, in such cases, it is not possible to determine the flow model and the yield number for yield stress fluids.

In addition, other methods have been proposed and used to describe the change of time-dependent fluid structure where the flow model parameters are assumed to decay in certain ways (Davenport & Somper 1971, Alessandrini et al 1982). For instance, in the method used by Alessandrini et al (1982), λ is defined as follows:

$$\lambda(t) = \frac{\tau_y(t) - \tau_{ye}}{\tau_{yo} - \tau_{ye}} = \frac{\mu(t) - \mu_e}{\mu_o - \mu_e} \quad (6.4)$$

Comparing with Eqs. (6.1), (6.2) and (6.3), one can see that only equation (6.4) can describe the change of the yield number with time. The transient yield number, Y_n , can be expressed as:

$$Y_n = \left(\frac{\tau_y(t)}{\mu(t)} \right)^{\frac{1}{n}} \cdot \frac{1}{\Omega} = \left(\frac{\tau_{ye} + (\tau_{yo} - \tau_{ye}) \cdot \lambda(t)}{\mu_e + (\mu_o - \mu_e) \cdot \lambda(t)} \right)^{\frac{1}{n}} \cdot \frac{1}{\Omega} \quad (6.5)$$

If $n=1$, the expression is then led to the yield number for Bingham and Casson fluids, i.e. Bi and Ca. The underlying assumption of Eq. (6.5) is that the transient change of the flow model parameters (τ_y and μ) follow the same kinetic process (i.e. Eq. (6.4)). It will be shown later that Eq. (6.4) does not provide the only choice for describing the structure change because the experimental results could also be successfully predicted using other combination of structure decay parameters. This feature will be illustrated in the following analysis. Taking the 53.3 wt% kaolin suspension for example, a second order kinetics (detailed derivation will be given in section 6.3) for the flow model parameters (τ_y and μ) with two individual structural breakdown rate constants (k_{τ_y} , k_{μ}) is assumed, i.e.

$$\tau_y(t) = \tau_{ye} + (\tau_{yo} - \tau_{ye}) \cdot (1 + k_{\tau_y} \cdot t)^{-1} \quad (6.6)$$

$$\mu(t) = \mu_e + (\mu_o - \mu_e) \cdot (1 + k_{\mu} \cdot t)^{-1} \quad (6.7)$$

Using the Casson model (also from section 6.3) to represent the flow model we then have:

$$\tau^{1/2}(t) = [\tau_{ye} + (\tau_{yo} - \tau_{ye}) \cdot (1 + k_{\tau_y} t)^{-1}]^{1/2} + [\mu_e + (\mu_o - \mu_e) \cdot (1 + k_{\mu} t)^{-1}]^{1/2} \cdot \dot{\gamma}^{1/2} \quad (6.8)$$

In addition to the condition of $k_{\tau_y} = k_{\mu}$, which is the original case of Eq. (6.4), other combinations for rate constant, i.e. $k_{\tau_y} = 0.5k_{\mu}$ and $k_{\tau_y} = 0.25k_{\mu}$, are studied and compared. Model parameters of the equilibrium value i.e. τ_{ye} and μ_e can be found in Appendix 11 (for kaolin (53.3 wt%) suspension). Fig. 6.16 shows that under the three different structure parameter assumptions, all the predictions give reasonably good fit with the experimental data (obtained from Fig. 6.4 when $\varepsilon = 1.048$). The statistical analysis of the fittings is shown in Appendix 9. The results indicate that with the same experimental stress decay curve, there are multiple combinations of structure parameters ($\tau_y(t)$ and $\mu(t)$) to describe the breakdown process. Although the transient behaviour of yield number is distinct for different combinations of breakdown process (see Eq. 6.5), the initial and equilibrium yield number will remain constant since they have been pre-specified.

A group of "constant-time flow curves" can be obtained by interpolating the shear stress decay curves at different constant shear rates for a constant time of shear (Ritter & Govier 1970, Tiu & Boger 1974). The "constant-time flow curves" have been used to determine the change or decay of the yield stress and viscosity at different time. However, this is only valid for two specific conditions, namely (a) the rate constant of structure breakdown is independent of the applied shear rate; (b) the equilibrium structure conditions such as τ_{ye} and μ_e are independent of the applied shear rate. These conditions are explained in details in Appendix 10. As indicated above, there is no reliable modelling method which can determine the actual transient changes of basic parameters of the flow model. In the following section, a novel modelling procedure will be proposed and used to circumvent existing problems and limitations.

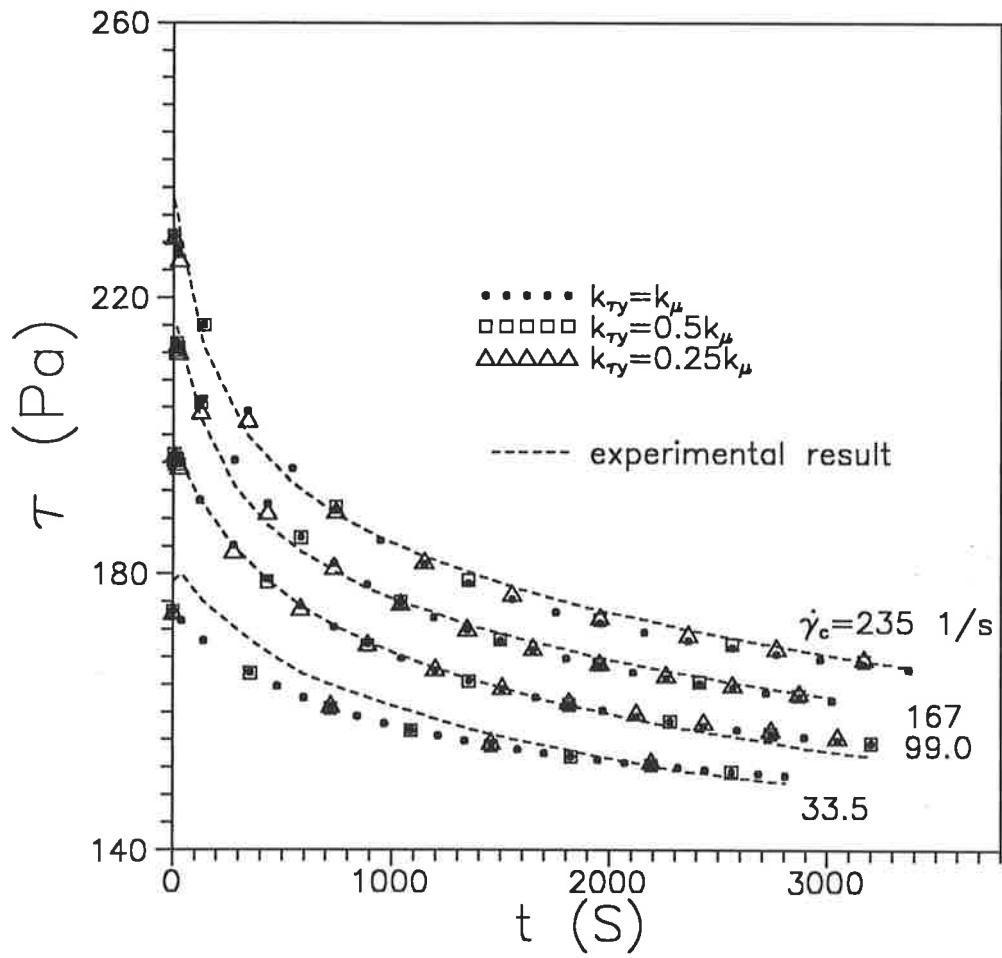


Fig. 6.16 Simulation for shear stress decay curves from thixotropic fluid model based on different rate constant assumptions. Eq. (6.8) was used as the time-dependent fluid model. The rate constant was determined by fitting with the experimental data.

6.2.2 New modelling method

In this section, a new modelling procedure for the characterization of the time-dependent flow model parameters will be described. Fig. 6.17 illustrates how to obtain the time-dependent flow model parameters when a fluid is being sheared at a constant shear rate. Two samples A and B are assumed to be taken out from the same fresh suspension. Shear rates $\dot{\gamma}_A$ and $\dot{\gamma}_B$ are applied to samples A and B respectively with $\dot{\gamma}_A < \dot{\gamma}_B$. Because sample A is experiencing lower rate of shearing than that of sample B, the structure of sample A will break down slower than that of sample B. When the structure of sample A approaches an equilibrium state (when $t \rightarrow \infty$), its structure corresponds to a certain structure level (i.e. a constant structure flow curve as shown in Fig. 6.17 which can be obtained by step-change-in shear rate experiment). Since the applied shear rate in sample B is higher (i.e. $\dot{\gamma}_B > \dot{\gamma}_A$) than sample A, then its structure breakdown process will also be faster. This also implies that sample B will reach the same structure level as that of sample A at equilibrium state in a shorter time period (say t_b). Therefore, the flow model parameters for sample B at time t_b could be obtained from the constant structure flow curve of sample A. The following section describes the method of determining the time t_b .

From the general form of the constitutive equations viz. Eqs. (2.3) and (2.4), the shear stress is a function of applied shear rate and structure level for a given fluid: $\tau = \tau(\dot{\gamma}, \lambda)$ (Cheng 1987). Any given pair of $(\tau, \dot{\gamma})$ data in a group of the constant structure flow curves is corresponding to a certain structure level (which is related to λ). If the shear rate in sample A at equilibrium state is changed from $\dot{\gamma}_A$ to $\dot{\gamma}_B$, a shear stress response of τ_B will be obtained and the pairs of $(\tau_B, \dot{\gamma}_B)$ data should be on the constant structure flow curve in Fig. 6.17. During the breakdown process of the sample B, the time t_b is determined when a shear stress τ_B is reached. The two samples A (at $t \rightarrow \infty$) and B (at t_b) would be at the same structure level condition because samples A and B have the same shear stress response at the shear rate $\dot{\gamma}_B$. Essentially, this implies that for any given shear stress-shear rate relation, there

exists a unique structure level as shown in the Fig. 6.18 (b) since there is no intersection between any two constant structure flow curves for the time-dependent yield stress fluid.

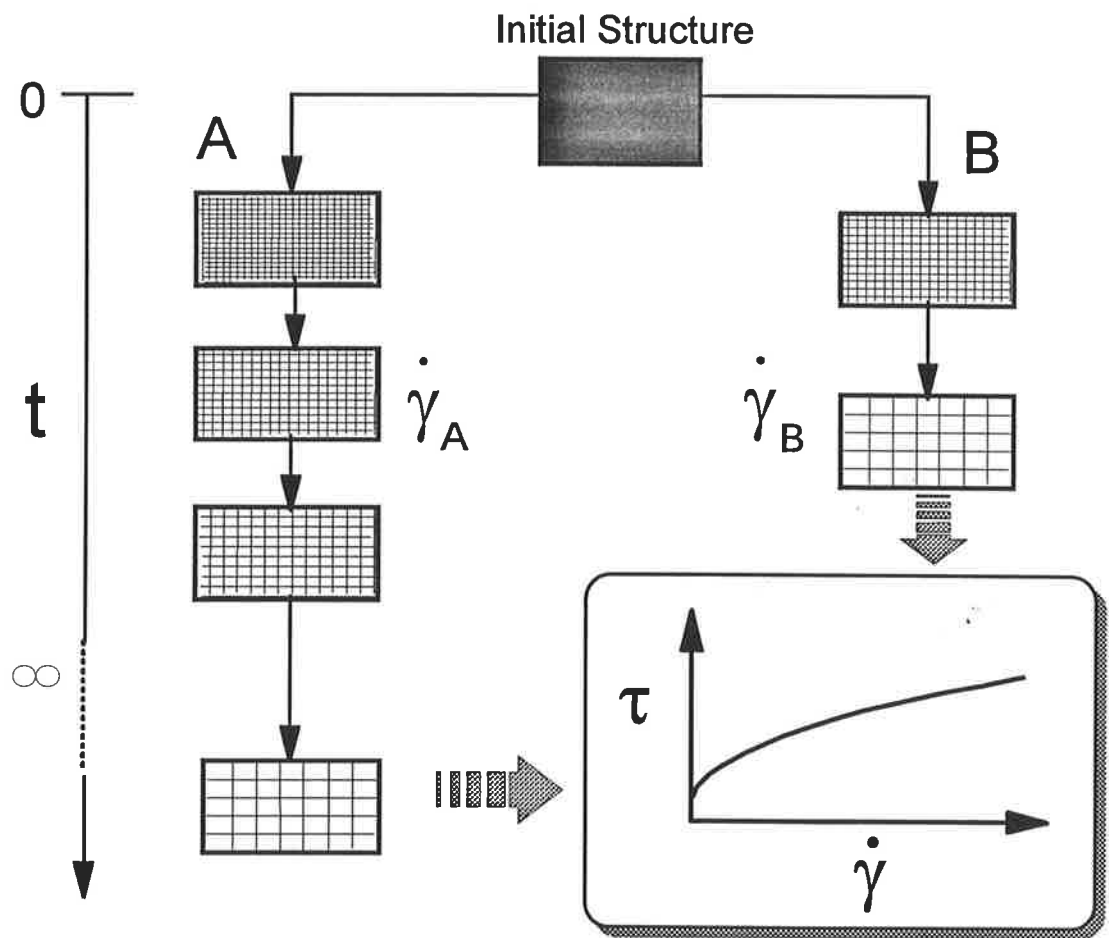


Fig. 6.17 Schematic showing the change of structure level under two different shear rates. The shading indicates different structure levels.

The experimental study for this work is similar to that described by Cheng & Evans (1965). The experimental steps include:

- obtaining the shear stress decay curves at different constant shear rates.
- shearing the suspension to the equilibrium stage at a given reference shear rate and then measure the shear stress and shear rate relationship by a step-change-in shear rate method.
- repeating the above procedure at different reference shear rates to determine a group of constant structure flow curves.

However, the way of interpreting the experimental data of the thixotropic fluids depends on the nature of the modelling method. Fig. 6.18 (a) shows a shear stress decay curve under a constant shear rate $\dot{\gamma}_s$. During the shear stress decay, the structure level of the suspension decreases continuously. Correspondingly, the flow curve tends to change gradually from its initial state to the equilibrium level. If knowledge of the time-dependent change of the flow curve during the constant rate of shear is known, then the time-dependent change of the basic flow model parameters can also be determined. Fig. 6.18 (b) shows a group of constant-structure flow curves. By intercepting the flow curves at line: $\dot{\gamma} = \dot{\gamma}_s$, then a set of stresses, $\tau_A, \tau_B, \tau_C, \tau_D, \dots$ at points A, B, C, D,... can be obtained. From these values of $\tau_A, \tau_B, \tau_C, \tau_D, \dots$ the corresponding time values at points A, B, C and D ... may be obtained for the decay curve shown in Fig. 6.18 (a). Consequently, the following pairs of data of shear stress and time can be obtained:

$$(\tau_A, t_A)_{\dot{\gamma}_s}, (\tau_B, t_B)_{\dot{\gamma}_s}, (\tau_C, t_C)_{\dot{\gamma}_s}, (\tau_D, t_D)_{\dot{\gamma}_s}, \dots \quad (6.9)$$

Furthermore, other pairs of data of the flow model parameters (τ_y and μ) may also be determined for the corresponding structure level, i.e.

$$(\tau_{yA}, t_A)_{\dot{\gamma}_s}, (\tau_{yB}, t_B)_{\dot{\gamma}_s}, (\tau_{yC}, t_C)_{\dot{\gamma}_s}, (\tau_{yD}, t_D)_{\dot{\gamma}_s}, \dots \text{ and} \quad (6.10)$$

$$(\mu_A, t_A)_{\dot{\gamma}_s}, (\mu_B, t_B)_{\dot{\gamma}_s}, (\mu_C, t_C)_{\dot{\gamma}_s}, (\mu_D, t_D)_{\dot{\gamma}_s}, \dots \quad (6.11)$$

So, the time-dependent change of flow model parameters under a constant shear rate can be specified. In the current study, since the constant shear rate is at r_c position, then the $\dot{\gamma}_c$ will be used to replace the value of $\dot{\gamma}_s$ specified above.

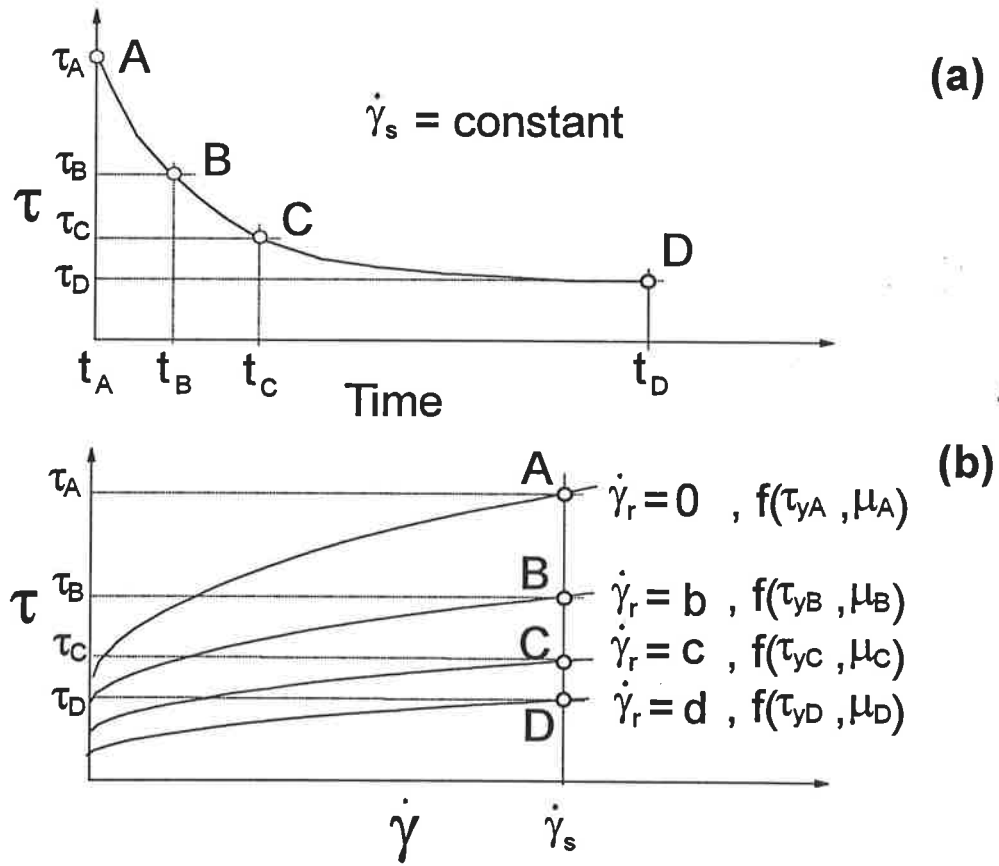


Fig. 6.18 Schematic diagram showing the new modelling method to obtain flow model parameters as a function of time under a constant shear rate.

6.3 Modelling Results for the Time-Dependent Suspensions

In this section, the use of the new modelling concept will be demonstrated on a number of suspensions that exhibit time-dependent characteristics. The results of this modelling will be subsequently used in Chapter 7 to simulate the flow pattern and transient behaviour of the yield layer.

6.3.1 Determination of transient parameters for the flow model

A procedure based on the principle discussed in section 6.2.2 is developed to analyze the experimental data (shear stress versus time data and constant-structure flow curves) in this section. The time-dependent flow model parameters (τ_y, μ) at a given constant shear rate $\dot{\gamma}_c$ can be determined from the plots similar to Figs. 6.18 (a) and (b). In principle, this task can be performed through graphical method but it is tedious and subjective. Hence, a numerical method is proposed as follows:

1 Fitting of the Experimental Data:

- Determine the type of flow model (i.e. Bingham or Casson or etc.) from a group of constant-structure flow curves (similar to Fig. 6.18 (b)) and its parameters $(\tau_{ye}, \mu_e)_r$ at each reference shear rates $\dot{\gamma}_r$. τ_{ye} and μ_e are the flow model parameters of a constant structure flow curve at equilibrium condition after being sheared by a reference shear rate $\dot{\gamma}_r$.
- Determine the functionality of the equilibrium parameters τ_{ye} and μ_e with reference shear rate $\dot{\gamma}_r$, at the constant structure conditions.
- Fit a function for the shear stress decay curve (shear stress versus time) under a constant shear rate $\dot{\gamma}_c$.

2 Data Generation:

After the above steps, the following steps enable the determination of the appropriate kinetic models for the time-dependent behaviour of the flow model parameters of the fluid (i.e. $\tau_y(t)$ and $\mu(t)$ as a function shearing time).

- Obtain a group of constant structure flow curves:

Use a series of reference shear rates to generate a series of constant structure flow curves, i.e. the flow model parameters $(\tau_{ye}, \mu_e)_r$

- Determine the shear stress value at $\dot{\gamma}_e$ on each constant structure flow curve:
Generate a series of shear stress $\tau_{e,r}$ by using the shear rate $\dot{\gamma}_e$ and $(\tau_{ye}, \mu_e)_r$ according to the corresponding flow model.
- Simulate the shear stress decay curve (shear stress versus time) using a constant shear rate $\dot{\gamma}_e$ and determine a series of time, t , when the shear stress equals to $\tau_{e,r}$:
From the shear stress versus time function under constant shear rate $\dot{\gamma}_e$, determine a series of solutions for time t from a series of shear stress values ($\tau = \tau_{e,r}$). Then the data of flow model parameters versus time under a given shear rate (like those in Eqs. (6.10) and (6.11)) can be obtained.

6.3.2 Kinetic models

In this modelling work, it is assumed that the structure of the thixotropic suspension breaks down irreversibly from the initial structure to equilibrium state under a constant shear rate without significant buildup. Let λ represents the dimensionless structure parameter of the fluid, the rate of structure breakdown could be expressed as (Kristensen et al 1995):

$$\frac{d\lambda}{dt} = -k(\lambda - \lambda_e)^p \quad (6.12)$$

Where $k = k(\dot{\gamma})$ is a shear rate dependent rate constant and p is the order of the breakdown process. Initially, at the fully structured state, $t = 0$: $\lambda = 1$; and at equilibrium state, $t = \infty$: $\lambda = \lambda_e$. At a constant applied shear rate, integration of (6.12) (when $p \neq 1$) from $t = 0$ to t gives:

$$(\lambda - \lambda_e)^{1-p} = (p-1) \cdot k \cdot t + (1 - \lambda_e)^{1-p} \quad (6.13)$$

The structure parameter λ can be taken as a general term to represent the dimensionless parameters τ_y and μ i.e. $\lambda(\lambda_{\tau_y}, \lambda_{\mu})$; similarly, for the rate constants, $k(k_{\tau_y}, k_{\mu})$. The structure parameters for τ_y and μ are defined as:

$$\lambda_{\tau_y} = \lambda_{\tau_y}(\dot{\gamma}_e, t) = (\tau_y(t) - \tau_{ye}) / (\tau_{y0} - \tau_{ye}) \quad (6.14)$$

$$\lambda_{\mu} = \lambda_{\mu}(\dot{\gamma}_e, t) = (\mu(t) - \mu_e) / (\mu_0 - \mu_e) \quad (6.15)$$

The initial flow model parameters at $\lambda(\lambda_{\tau_y} = 1, \lambda_{\mu} = 1)$ are: $\tau_y(0) = \tau_{y0}$, $\mu(0) = \mu_0$ while the flow parameters at equilibrium state $\lambda(\lambda_{\tau_y} = 0, \lambda_{\mu} = 0)$ are: $\tau_y(\infty) = \tau_{ye}$, $\mu(\infty) = \mu_e$.

Substituting Eqs. (6.14) and (6.15) into (6.13), we obtain:

$$(\tau_y(t) - \tau_{ye})^{1-p} = [(p-1) \cdot k_{\tau_y} \cdot t + 1] \cdot (\tau_{y0} - \tau_{ye})^{1-p} \quad (6.16)$$

$$(\mu(t) - \mu_e)^{1-p} = [(p-1) \cdot k_{\mu} \cdot t + 1] \cdot (\mu_0 - \mu_e)^{1-p} \quad (6.17)$$

where $\tau_y(t)$ and $\mu(t)$ are expressed as a function of time. Here, the same symbol of p is used in both Eqs. (6.16) and (6.17), however p may or may not be the same value for the $\tau_y(t)$ and $\mu(t)$ in the decay processes. The kinetic model parameters (such as the order of the reaction, rate constant, equilibrium values of the flow model parameters in Eqs. (6.16) and (6.17)) can be defined by fitting the time-dependent experimental data of the $\tau_y(t)$ and $\mu(t)$ when a constant shear rate is applied. If the time-dependent experimental data are obtained under a

number of constant shear rate conditions, the shear rate dependency of the above kinetic model parameters can be obtained (such as the rate constant, equilibrium values of the flow model parameters as a function of the applied shear rate).

6.3.3 Modelling results for time-dependent flow model parameters

The r_c method was used to convert the rotational speed to shear rate value for stress decay experiment. Although the r_c method and the Krieger method gave good agreement as shown in section 6.1.2, the Krieger method was used to determine the shear stress-shear rate pairs of data from shear stress-speed pairs of data in a constant structure flow curve because it can cover a wider range of shear rate. The radius ratio $\varepsilon=1.048$ is chosen because it is not large enough to cause any significant error, as discussed earlier. At relatively low rotational speeds, the initial experimental shear stress response was not very reliable (see section 6.1.2) which would not be considered in the model fittings.

In the preliminary tests, it was found that there were visible yield boundaries for the following suspensions: mayonnaise, bentonite and kaolin while no discernible boundary for waxy maize starch suspension was observed. So the modelling work was carried out for the first three suspensions.

6.3.3.1 Mayonnaise suspension

The constant structure flow curves for this suspension is fitted by the Herschel-Bulkley model as shown in Fig. 6.19. Figs. 6.20 and 21 show the change of equilibrium flow model parameters (τ_{ye}, μ_e) as a function of reference shear rate. The time-dependent data for the flow model parameters were obtained according to the steps suggested in section 6.3.1. Details of the function fitting for this suspension is described in Appendix 11. The change of flow model parameters with time are shown in Figs. 6.22, and 23. A second-order kinetic was

found to fit the decay data for the flow model parameters better than the other orders. When $p = 2$, from Eqs. (6.16) and (6.17), one obtains:

$$\tau_y(t) = \tau_{ye} + (\tau_{y0} - \tau_{ye}) \cdot (1 + k_{\tau y} \cdot t)^{-1} \quad (6.18)$$

$$\mu(t) = \mu_e + (\mu_o - \mu_e) \cdot (1 + k_{\mu} \cdot t)^{-1} \quad (6.19)$$

The decay rate constants of the above kinetics are tabulated in Table 6.2. The rate constants ($k_{\tau y}$ and k_{μ}) as function of applied shear rate are shown in Figs. 6.24 and 6.25 respectively.

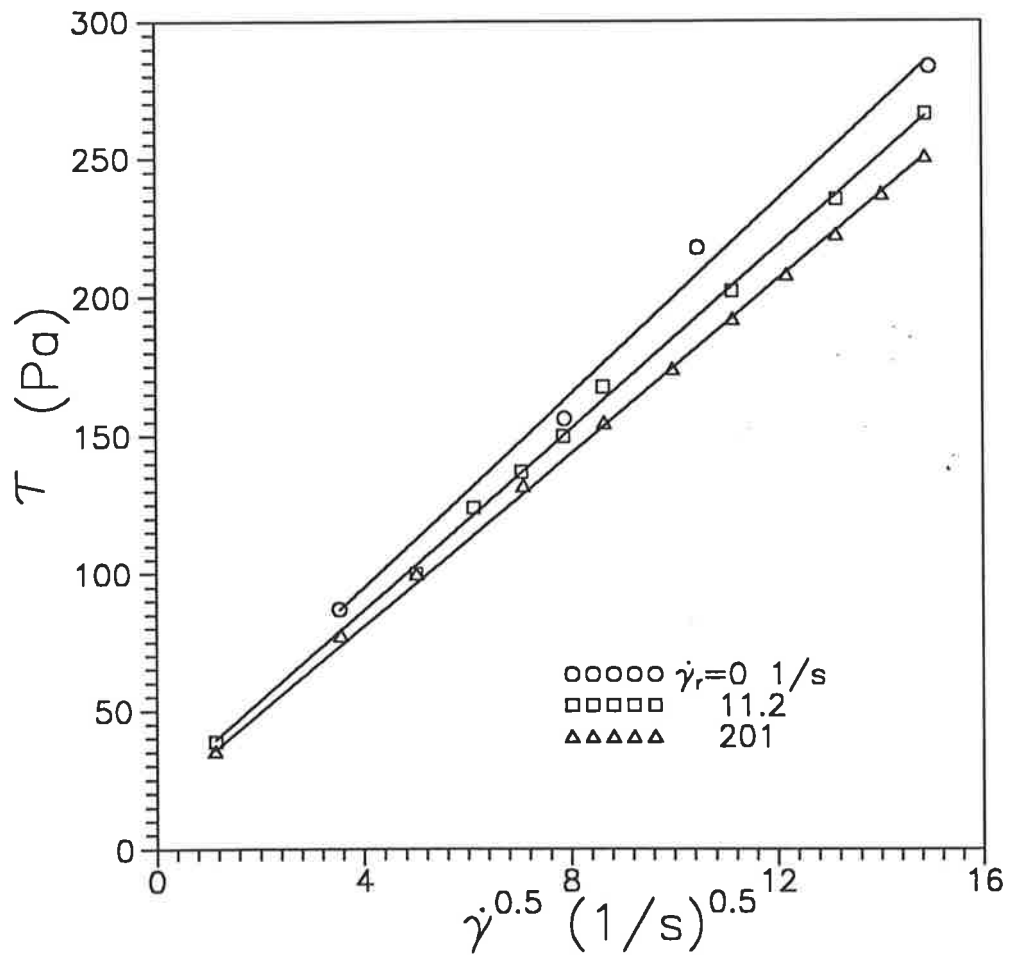


Fig. 6.19 Constant structure flow curves for mayonnaise suspension. Symbols are experimental data from Fig. 6.6 (a). Lines are model fittings.

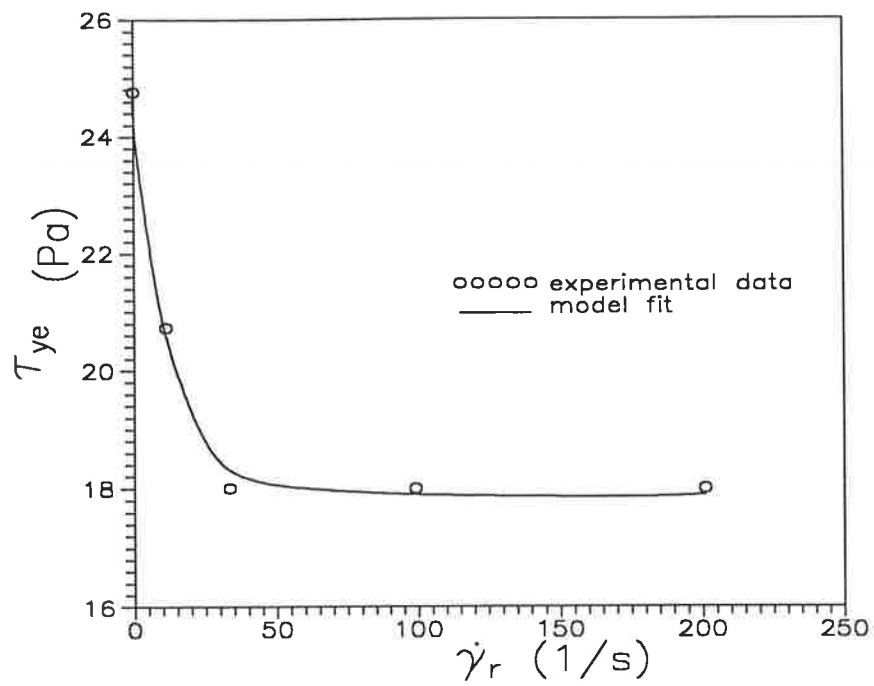


Fig. 6.20 Equilibrium flow model parameter τ_{ye} as a function of reference shear rate for mayonnaise suspension.

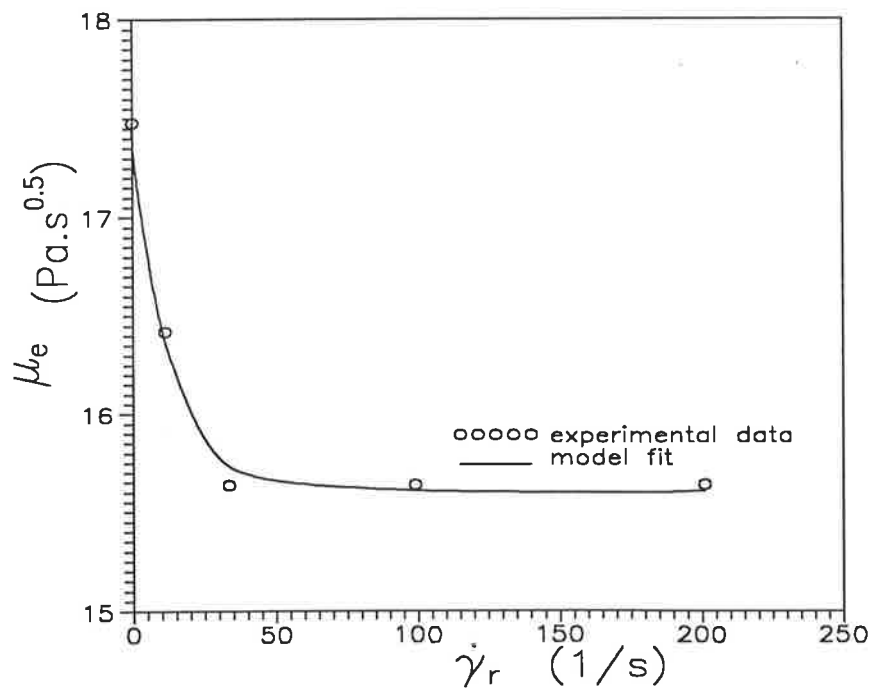


Fig. 6.21 Equilibrium flow model parameter μ_e as a function of reference shear rate for mayonnaise suspension.

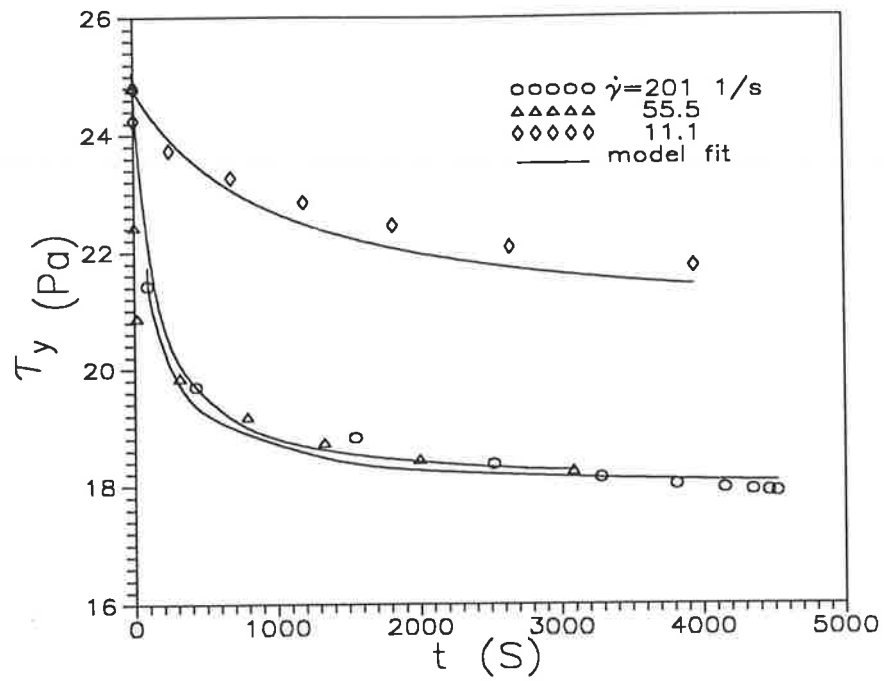


Fig. 6.22 Flow model parameter τ_y as a function of time at different applied constant shear rates for mayonnaise suspension.

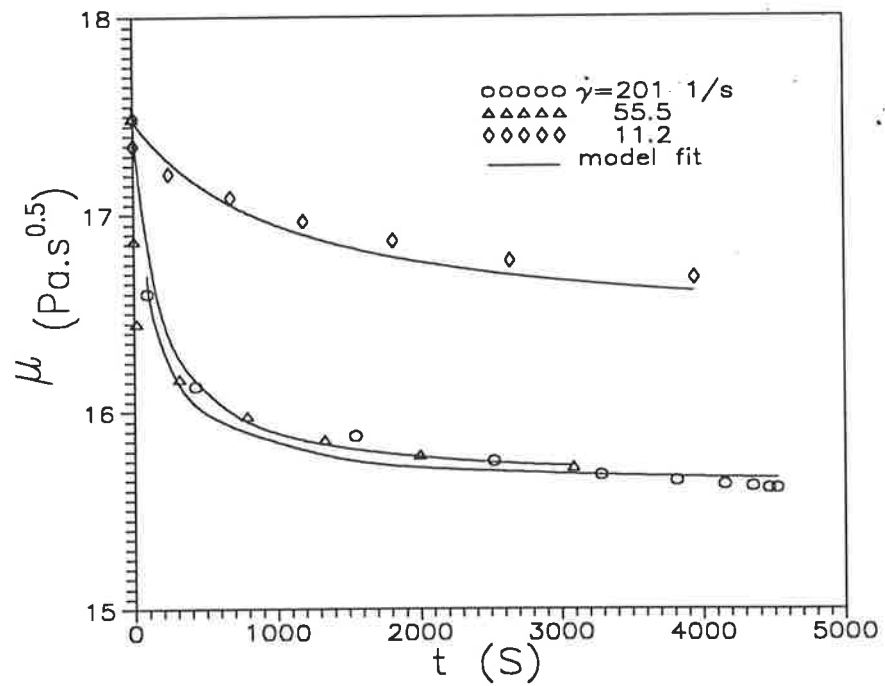


Fig. 6.23 Flow model parameter μ as a function of time at different applied constant shear rates for mayonnaise suspension

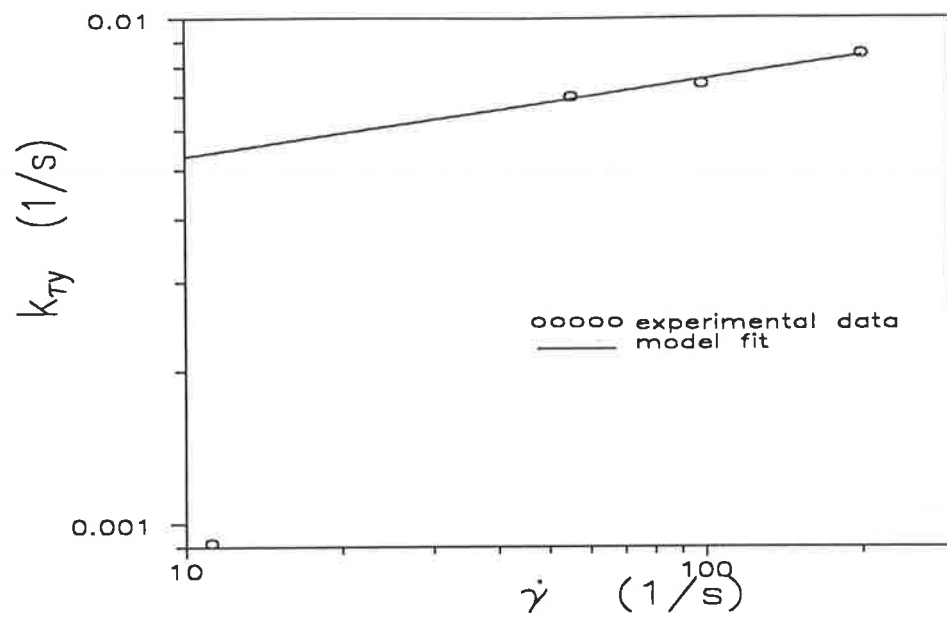


Fig. 6.24 Rate constant k_{Ty} as a function of applied shear rate for mayonnaise suspension.

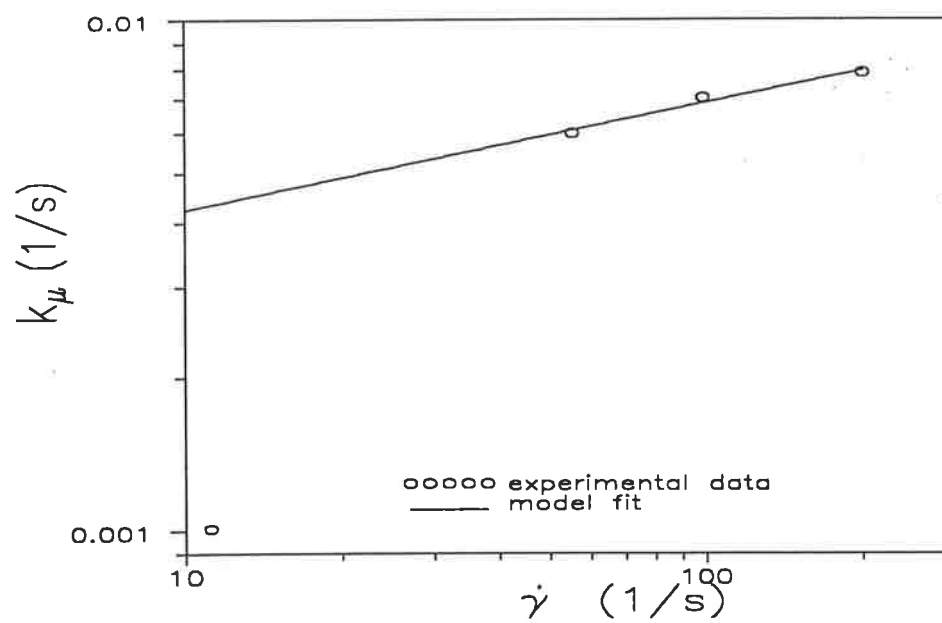


Fig. 6.25 Rate constant k_{μ} as a function of applied shear rate for mayonnaise suspension.

Table 6.2 Rate constant as a function of shear rate for mayonnaise suspension

shear rate (1/s)	k_{τ_y} (1/s)	correlation	k_{μ} (1/s)	correlation
11.2	0.00101	0.955	0.000917	0.965
55.5	0.00700	0.772	0.00600	0.774
99.0	0.00741	0.962	0.00704	0.958
201	0.00851	0.978	0.00788	0.976

The relationship between the rate constant and the applied shear rate is presented in Figs. 6.24 and 6.25 and can be conveniently correlated as:

$$k_{\tau_y} = 0.003738\dot{\gamma}^{0.1533} \quad (6.20)$$

$$k_{\mu} = 0.002615\dot{\gamma}^{0.2101} \quad (6.21)$$

It seems that the Eqs. (6.20) and (6.21) are more suitable for the shear rate higher than 55 1/s according to the Figs. 6.24 and 6.25. The corresponding parameters of the kinetic model for mayonnaise suspension described in Eqs. (6.16) and (6.17) have now been determined. So the time-dependent behaviour of the flow model parameters $\tau_y(t)$ and $\mu(t)$ can be simulated, which is necessary for the flow pattern simulation in later study. Similar procedures for the determination of the kinetic model parameters are performed for the remaining kaolin 53.3 wt% and bentonite 8 wt% suspensions.

6.3.3.2 Kaolin 53.3 wt% suspension

Casson model was used to fit the constant structure flow curves of this suspension as shown in Fig. 6.26. Figs. 6.27 and 6.28 show the change of equilibrium flow model parameters (τ_{ye}, μ_e) as a function of reference shear rate. The time-dependent data of the flow model parameters were obtained according to the steps suggested in section 6.3.1. Details of the function fitting for this suspension is described in Appendix 11. The flow model parameters ($\tau_y(t)$ and $\mu(t)$) versus time at different constant shear rates are shown in Figs.

6.29 and 6.30. Similarly, the data were best fitted by a second-order kinetic with rate equations for $\tau_y(t)$ and $\mu(t)$ similar to Eqs (6.18) and (6.19) respectively. The values of the rate constant are listed in Table 6.3. The rate constants (k_{τ_y} and k_{μ}) as function of applied shear rate are shown in Figs. 6.31 and 6.32.

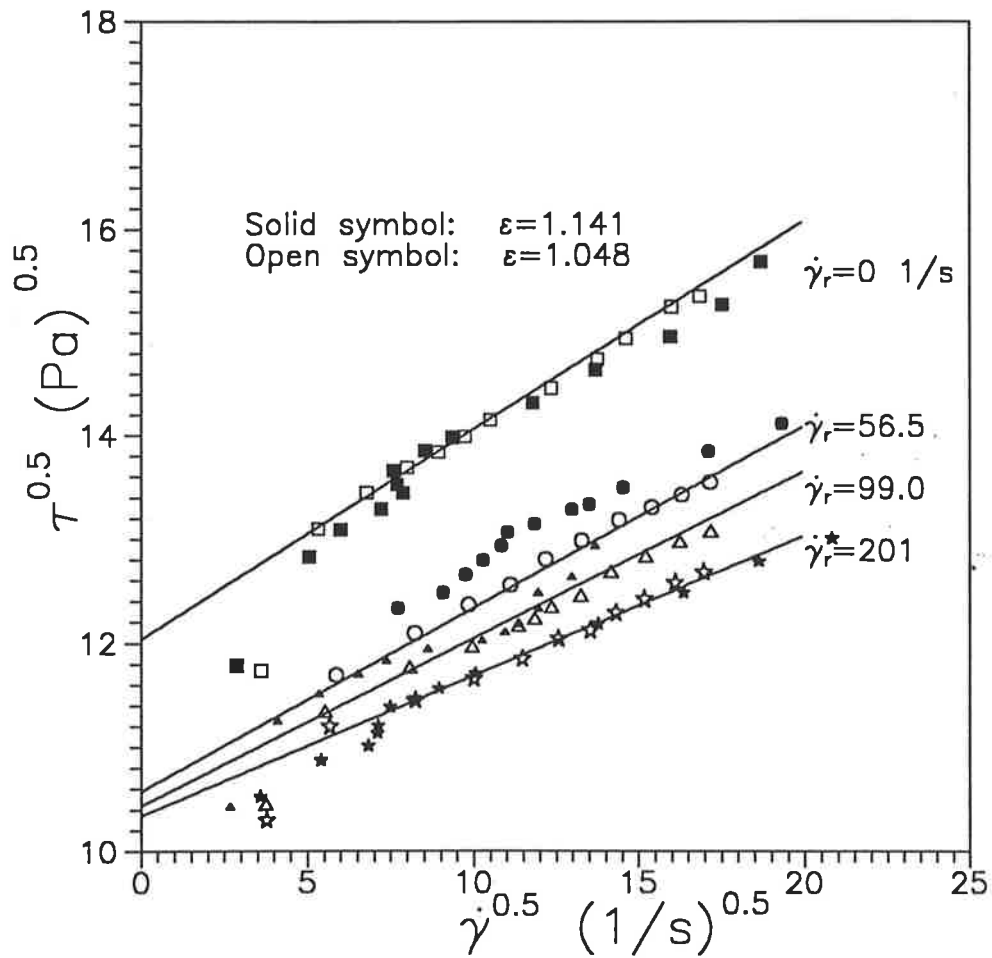


Fig. 6.26 Constant structure flow curves for kaolin 53.3 wt% suspension. Symbols are experimental data from Fig. 6.8 (a). Lines are model fittings.

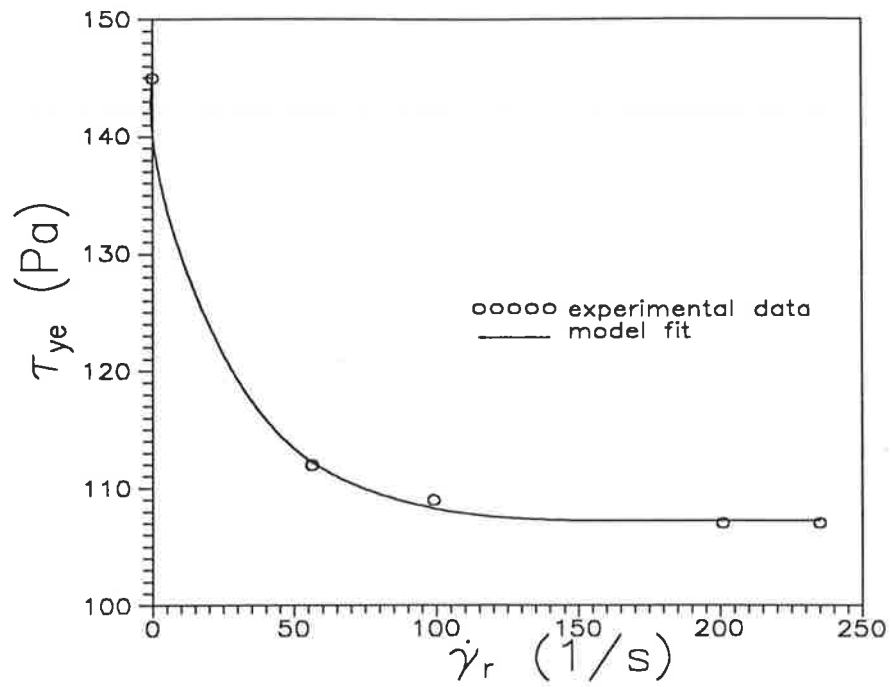


Fig. 6.27 Equilibrium flow model parameter τ_{ye} as a function of reference shear rate for kaolin 53.3 wt% suspension.

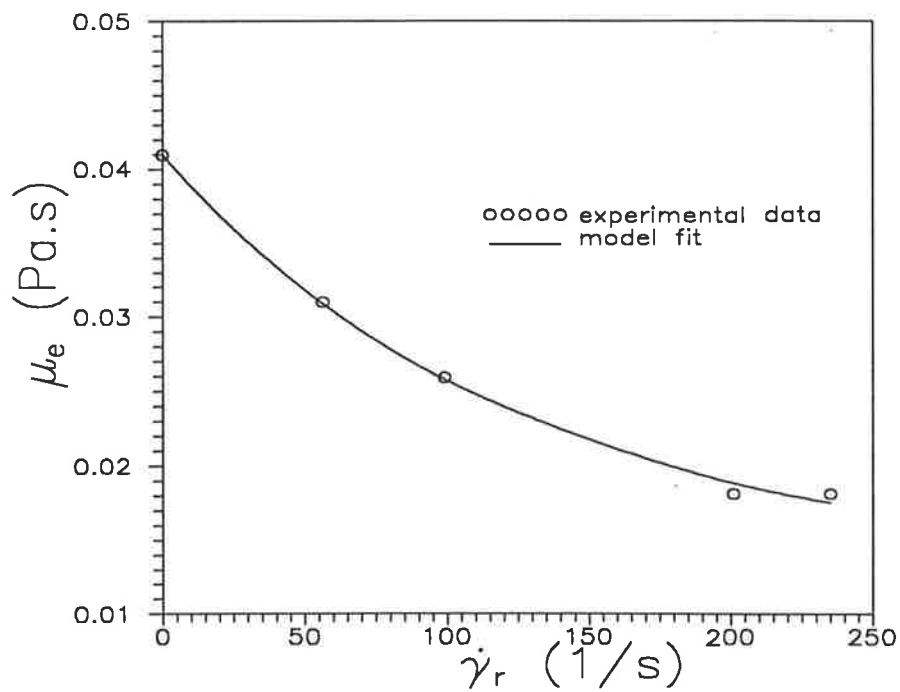


Fig. 6.28 Equilibrium flow model parameter μ_e as a function of reference shear rate for kaolin 53.3 wt% suspension.

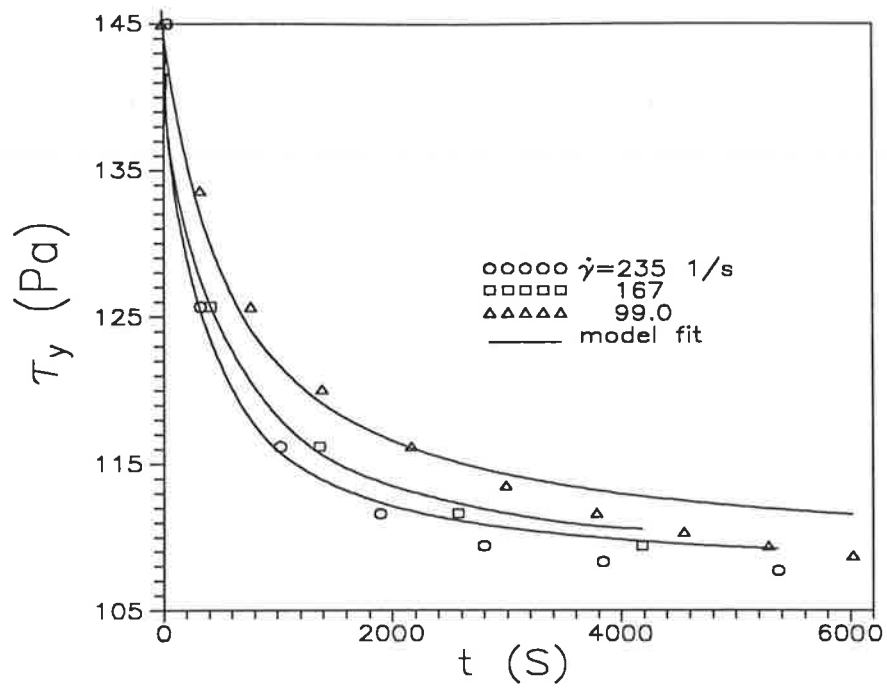


Fig. 6.29 Flow model parameter τ_y as a function of time at different applied constant shear rates for kaolin 53.5 wt% suspension.

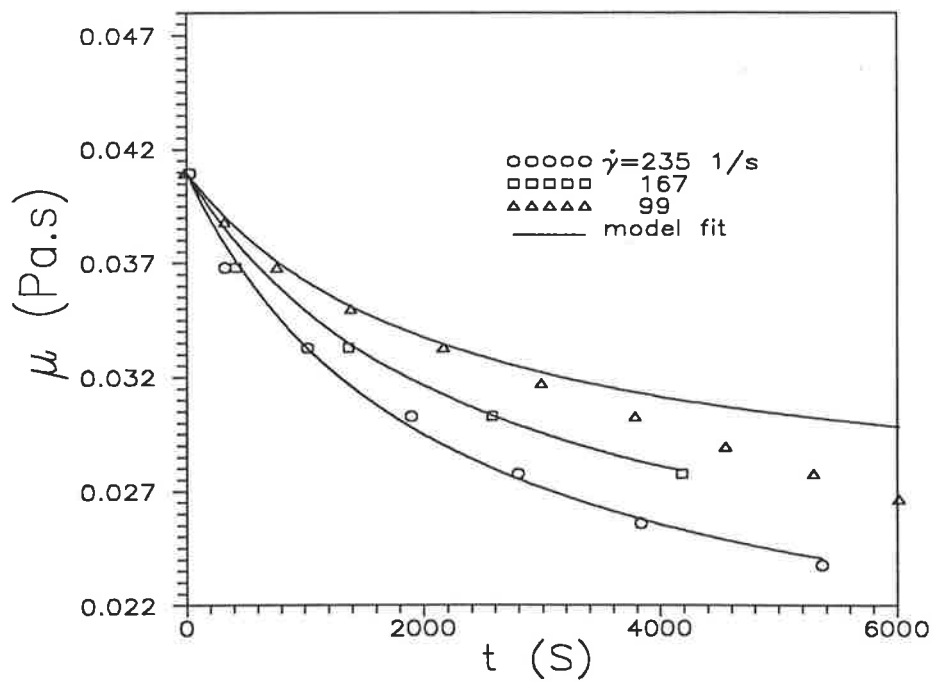


Fig. 6.30 Flow model parameter μ as a function of time at different applied constant shear rates for kaolin 53.5 wt% suspension.

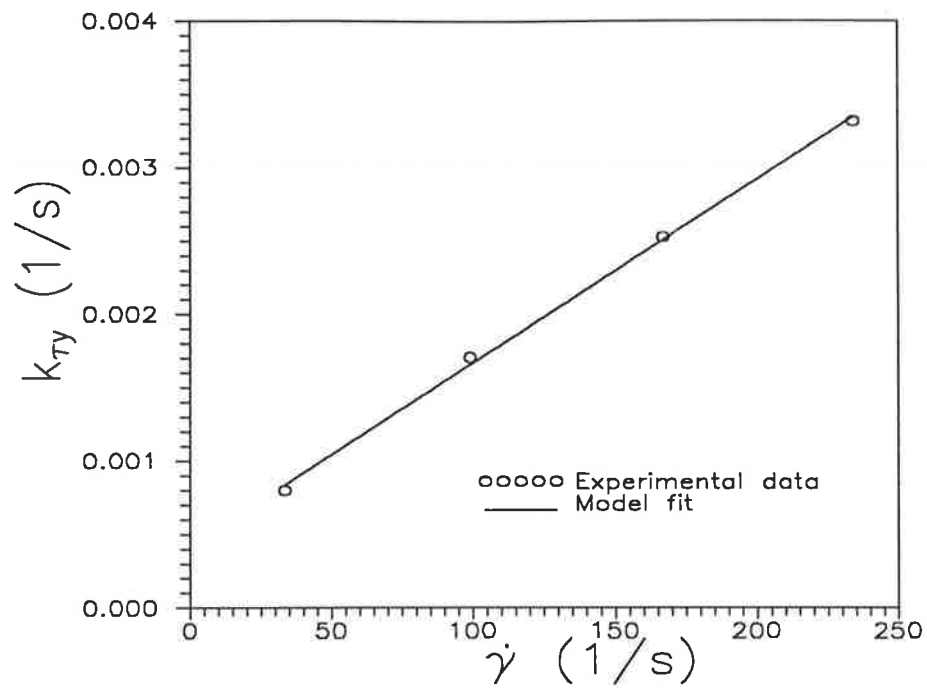


Fig. 6.31 Rate constant k_{γ} as a function of different applied shear rates for kaolin 53.3 wt% suspension.

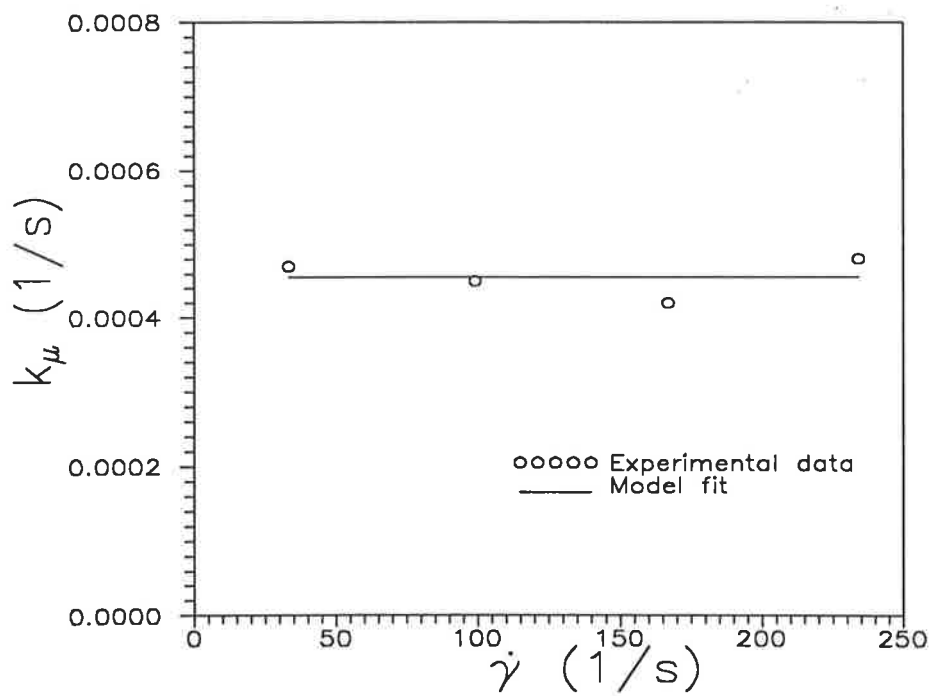


Fig. 6.32 Rate constant k_{μ} as a function of different applied shear rates for kaolin 53.3 wt% suspension.

Table 6.3 Rate constant as a function of shear rate for kaolin (53.3 wt%) suspension

shear rate (1/s)	k_{τ_y} (1/s)	correlation	k_{μ} (1/s)	correlation
33.5	0.00800	0.859	0.000470	0.890
99.0	0.00171	0.988	0.000450	0.949
167	0.00253	0.997	0.000420	0.988
234	0.00332	0.991	0.000480	0.997

The functional relationship of the respective rate constants with shear rate, as shown in Figs. 6.31 and 6.32 are defined as:

$$k_{\tau_y} = 1.251 \times 10^{-5} \dot{\gamma} + 4.210 \times 10^{-4} \quad (6.22)$$

$$k_{\mu} = 4.550 \times 10^{-4} \quad (6.23)$$

The parameters of the kinetic model for kaolin 53.3 wt% suspension described in Eqs. (6.16) and (6.17) with second-order kinetic, have now been determined. The Eqs. (6.22) and (6.23) show that the rate constant for the $\tau_y(t)$ is a function of shear rate, and the rate constant for $\mu(t)$ is a constant which is independent of shear rate. With the above modelling result for the $\tau_y(t)$ and $\mu(t)$, the time-dependent behaviour of the flow pattern can be simulated.

6.3.3.3 Bentonite (8 wt% with 0.006 Molar of NaCl) suspension

As shown in Fig. 6.33, Bingham model was found to fit the experimental data well. Fitting details are presented in Appendix 11. Interestingly, all the flow curves at equilibrium structure under different reference shear rates (10 to 201 1/s) lie on the same line. This means that for this type of suspension, the structure could only reach one equilibrium stage irrespective of the value of the shear rate. Clearly, for this unusual case, the current proposed modelling method can not be applied. Consequently, the analysis method suggested by

Alessandrini et al (1982) will be used (see section 6.2.1). The shear stress decay function for this type of fluid using Bingham model are expressed below:

$$\tau(t) = \tau_y(t) + \mu(t) \cdot \dot{\gamma} \quad (6.24)$$

Again, it was found that the second-order kinetic model fitted the experimental data better than other orders. By substituting Eqs. (6.16) and (6.17) into Eq. (6.24), the following expression is obtained:

$$\tau(t) = \tau_{ye} + (\tau_{yo} - \tau_{ye}) \cdot (1 + k_{ty}t)^{-1} + [\mu_e + (\mu_o - \mu_e) \cdot (1 + k_{\mu}t)^{-1}] \cdot \dot{\gamma} \quad (6.25)$$

where $k_{ty} = k_{\mu}$ and $p=2$. The experimental shear stress decay data was fitted with Eq. (6.25) by using different values of rate constant. The results of the fitted curves are shown in Fig. 6.34 and the values of the rate constants are tabulated in Table 6.4.

Table 6.4 The rate constant as a function of shear rate for 8 wt% bentonite suspension with 0.006 Molar of NaCl by assuming $k = k_{ty} = k_{\mu}$.

Shear rate (1/s)	k (1/s)	correlation
22.5	0.0155	0.9918
99.0	0.0172	0.9818
201	0.0182	0.9071

The linear relationship of the rate constant with the reference shear rate as shown in Fig. 6.35 is described as follows:

$$k = 1.102 \cdot 10^{-5} \dot{\gamma} + 1.588 \cdot 10^{-2} \quad (6.26)$$

The modelling method for bentonite suspension has its limitation because of the assumption that $k_{ty} = k_{\mu}$. However, the error would be limited as the breakdown process is bounded by the initial and equilibrium conditions which have been determined by experiments.

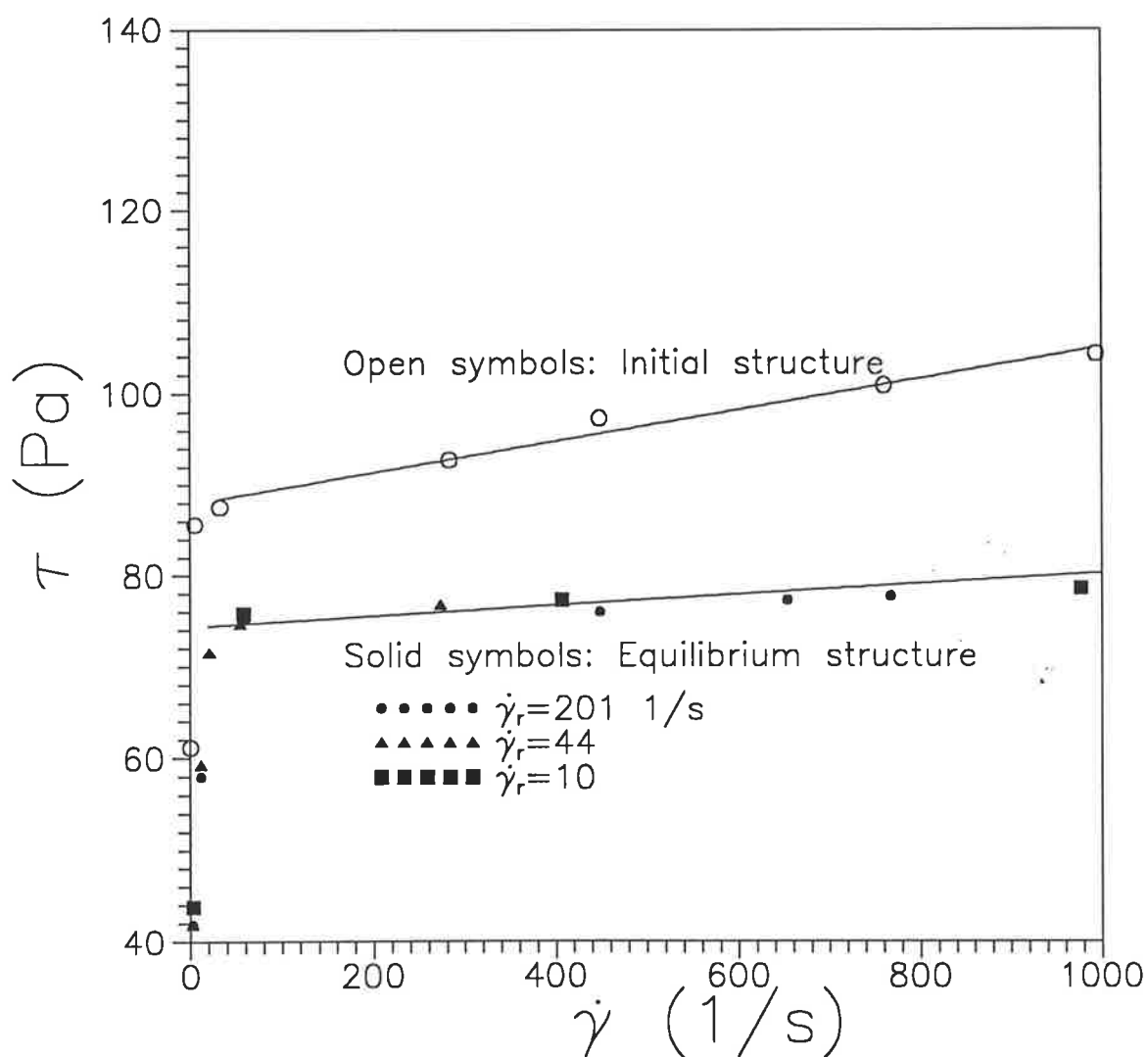


Fig. 6.33 Constant structure flow curves for bentonite (8 wt% with 0.006 Molar NaCl) suspension. $\varepsilon = 1.048$. Symbols are experimental data and lines are model fittings.

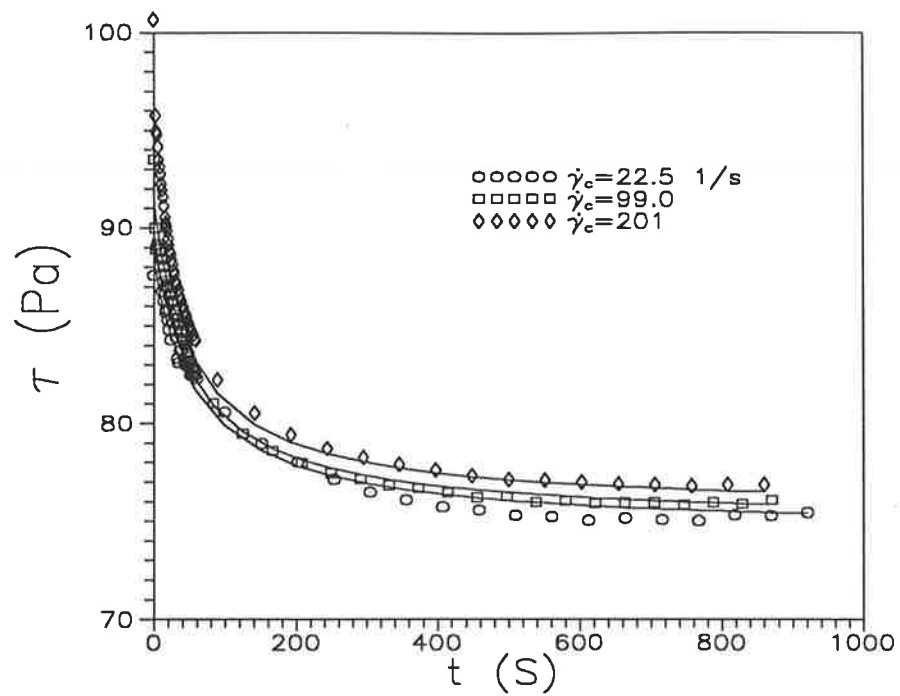


Fig. 6.34 Shear stress decay curves for bentonite (8 wt% with 0.006 Molar NaCl) suspension using the r_c method. $\varepsilon = 1.048$.

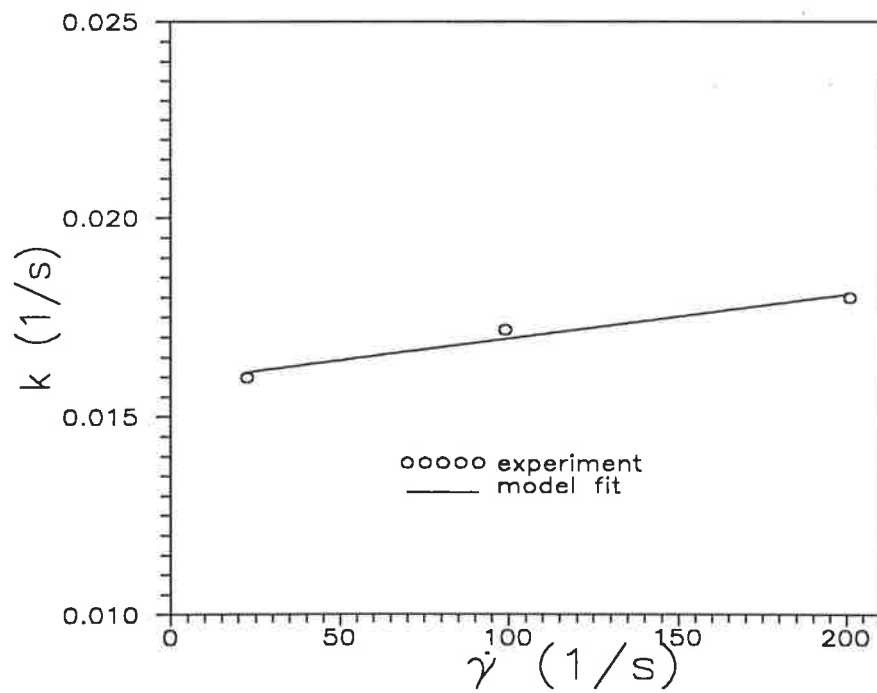


Fig. 6.35 Rate constant ($k = k_\gamma = k_\mu$) as a function of applied shear rate. Bentonite (8 wt% with 0.006 Molar NaCl) suspension.

6.4 Conclusions

The τ_c method has been proven experimentally to be a reasonable accurate approach to obtain shear stress-shear rate data for a number of suspensions at a wide range experimental condition. The accuracy of using the τ_c method for interpreting the experimental results has also been discussed analytically.

A new modelling method has been developed to quantify the change of the flow model parameters, which can not be obtained by existing modelling methods. With the new modelling method, the accurate description of the rheological properties of time-dependent yield stress fluids can be obtained, which is necessary for the simulation for the flow pattern.

Kinetic model parameters have been obtained for 3 different suspensions with the experimental data.

Chapter 7

Moving Yield Boundary

7.1 Introduction

A good understanding of yield behaviour of a fluid is important in industrial processes especially in fluid handling, mixing and transport. Although the location of yield boundary of the flow has been theoretically studied in the past for various flow geometries, the predictions of its location (for both time-dependent and time-independent fluids) from basic flow models have not been validated with the experimental results. The theoretical prediction of the yield boundary location based on ideal flow model would be clearly over-simplified as the yield stress of the real fluid is complex due to the nature of its internal micro-structure.

Horie & Pinder (1979) measured the location of the yield boundary (sheared radius) for a slurry with thixotropic and yield stress characteristics using a rotating cylinder. The radius of the cup was wide enough to maintain the flow in a partially sheared condition. The sheared radius was observed to increase with time until it reached an equilibrium value. The volume of the sheared fluid increased with time; and this phenomenon was postulated to be due to thixotropic Gel. $\leftrightarrow$ Sol. transformation. A rate equation based on chemical reaction was assumed for this process. However, since the reaction model parameters was based on the measurement of the sheared radius, the model was semi-empirical in nature.

For time-dependent fluids, the determination of the location of the yield boundary may be even more complex as the fluid structure changes simultaneously with shear. In this study, the change of the flow pattern and the yield boundary are simulated. The simulations utilize the modelling results of the real time-dependent fluids presented in Chapter 6.

The simulations were performed under the following considerations:

- As stated in the equation of motion, the flow will first experience unsteady motion then become fully developed after reaching steady state. The shear stress distribution as well as the movement of the yield boundary will take some time to develop before arriving at this steady state condition. Simulations for such phenomenon, based on the theory described in sections 4.2 and 4.3 with the flow model parameters at initial structure condition (Appendix 11), have been performed. The simulation results for the development of yield boundary during the unsteady state flow of the mayonnaise suspension is shown in Fig. 7.1. It was found out that at their initial structure conditions for the selected suspensions, the flow reached steady state within a time scale of the order of less than 0.1 second. In contrast, the extent of fluid structure change as a result of the thixotropic fluid behaviour for the same time scale of 0.1 second can be estimated according to the second order kinetic models. For example, by substituting the highest decay rate constant (Table 6.4, i.e. $k=0.0182$) into Eq. (6.18) or (6.19), the percentage of change (decay) during the time period of 0.1 second is only about 0.2% which is insignificant as compared to the overall structure change. This verifies that the unsteady state motion occurs within a time scale much shorter than the process for thixotropic time-dependent flow. Similarly, it is reasonable to assume that there is insufficient time for the thixotropic structural change to occur during the period of unsteady flow. Therefore, the simulation for flow influenced by thixotropic structural change can be adequately performed under steady state condition while ignoring the unsteady flow behaviour.
- When the flow starts to occur, the structure of the fluid within the flow region also begins to break down by the shearing effect. Consequently, the yield stress and viscosity start to decrease from their initial values. The flow pattern changes simultaneously with change in flow property. The sheared radius should also experience a change with increasing time. The numerical procedure used for the simulation is described in section 7.3.

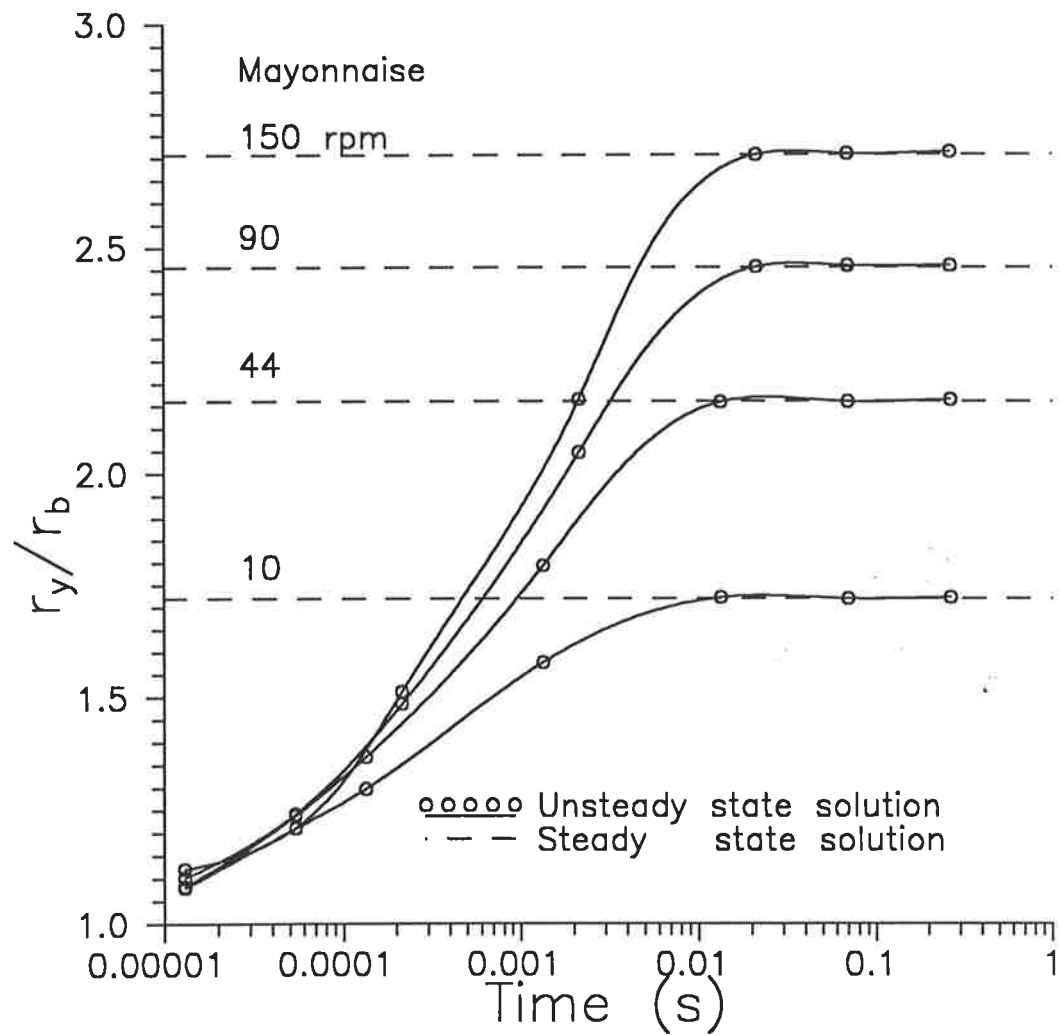


Fig. 7.1 Yield boundary development at unsteady state shear. Mayonnaise suspension. Bob radius $r_b=20.04$ mm. Flow model yield stress was used as the yield criteria.

- Accurate knowledge of the yield stress is very important as it is a critical parameter for determining the location of the yield boundary. A flow model is commonly used to fit the experimental flow curve data to obtain the flow model parameters such as yield stress and viscosity. Such fitting results are very subjective as it depends on the range and the number of the experimental data available, and the type of flow model used. The yield stress value obtained from the fitted flow model (denoted as "flow model yield stress") is not truly the absolute fluid property. In addition, there is no lowest limit of shear rate at which the data can be used to extrapolate the location of the true yield stress from the experimental shear stress-shear rate pairs of data. These limitations have been discussed by Nguyen & Boger (1992). Reliability of the experimental data at the lower range of shear rate of the flow curve is also questionable as discussed in section 6.1.2. To overcome these limitations, independent measurements for yield stress using the vane method (denoted as "vane yield stress") were performed following the procedure described by Nguyen & Boger (1983, 1985a). The time-dependent behaviour of the vane yield stress for the selected suspensions has been characterized and is shown in section 7.2. The determination of yield boundary using both the flow model yield stress and vane yield stress have been studied and compared with experimental results.

7.2 Vane Yield Stress as a Function of Time and Shear

The following describes measurement of the yield stress as a function of shearing time using the vane method which has been proposed by Nguyen & Boger (1983, 1985a). Since it was not possible to perform vane measurement on the sample which was sheared by a concentric cylinder viscometer, the following mixing method using a fan turbine impeller was employed to provide the shearing effect. The relationship between the average shear rate $\dot{\gamma}_m$ and the mixing speed Ω (rev / sec) can be simply expressed by:

$$\dot{\gamma}_m = 13 \cdot \Omega \quad (7.1)$$

for a wide range of fluids (Metzner & Otto 1957). The diameters of the mixer impeller and container were 108 mm and 145 mm respectively. Other experimental arrangements, such as the position of impeller and suspension height etc. followed that suggested by Metzner & Otto (1957). After a given time of mixing,, a small amount of the sample was taken out from the mixing container and the yield stress value of the sample was measured by using a single vane method. So at a given mixing speed of the impeller, the change of the yield stress of the suspension at different time was measured.

Fig. 7.2 shows the change of the vane yield stress with time for mayonnaise suspension under different mixing speeds. The decay characteristic of the vane yield stress was shown to be insensitive of the applied average shear rate. Therefore, it seems reasonable to assume the yield stress to be dependent only on the mixing time. The experimental data were fitted with a second order kinetic model (refer to Eq. (6.13), for $p = 2$) where the structure parameter is defined as:

$$\lambda = (\tau_{y,vane}(t) - \tau_{ye,vane}) / (\tau_{yo,vane} - \tau_{ye,vane}) \quad (7.2)$$

The expression of the yield stress measured by the vane method is

$$\tau_{y,vane}(t) = \tau_{ye,vane} + (\tau_{yo,vane} - \tau_{ye,vane}) \cdot (1 + k \cdot t)^{-1} \quad (7.3)$$

where the related parameters are:

$$\tau_{ye,vane} = 24.0 \text{ (Pa)} \quad \tau_{yo,vane} = 31.5 \text{ (Pa)} \quad k = 0.00131 \text{ (1/s)} \quad \text{correlation} = 0.96$$

Fig. 7.3 shows the vane yield stress as a function of mixing time under different rotation speeds of the mixer for kaolin 53.3 wt% suspension. It is clear from the plot that the vane yield stress for this suspension remains relatively constant at 145 Pa during the mixing.

The change of the vane yield stress with mixing time under different mixer speeds for bentonite (8 wt% bentonite with 0.006 M NaCl) suspension is shown in Fig. 7.4. Similar to the case for mayonnaise suspension, the experimental data was fitted with a second order kinetic model (see Eq (7.3)). Unlike the earlier case, the rate constant k was found to be a function of average shear rate which is tabulated in Table 7.1. The rate constant can be fitted by a linear function with the average shear rate as shown below, giving a correlation of 0.91.

$$k = 1.475 \times 10^{-4} \dot{\gamma}_{\text{m}} \quad (7.4)$$

Other corresponding values of the model parameters are:

$$\tau_{\text{ye,vane}} = 61.8 \text{ (Pa)}; \quad \tau_{\text{yo,vane}} = 83.5 \text{ (Pa)}$$

Table 7.1 The rate constant as a function of average shear rate for 8 wt% Bentonite suspension with 0.006 Molar of NaCl as obtained from vane yield stress measurement.

Average shear rate (1/s)	k (1/s)	correlation
21.7	0.00326	0.946
65.0	0.00771	0.973
86.7	0.01600	0.996

It should be noted that the mixing speeds used in the above studies were performed under 400 to 500 (rpm). This is because at higher mixing speed, the mixer motor would be overloaded. Incidentally, this limit is also close to the condition when the suspension exists in a very turbulent state (i.e. cavitation due to air bubbles in the suspension). Under this condition, the experimental readings fluctuated severely, leading to larger errors in the measurement. So, the maximum average shear rate used in the modelling of the transient vane yield stress behaviour is confined to 108 (1/s) corresponding to a mixing speed of 500 rpm.

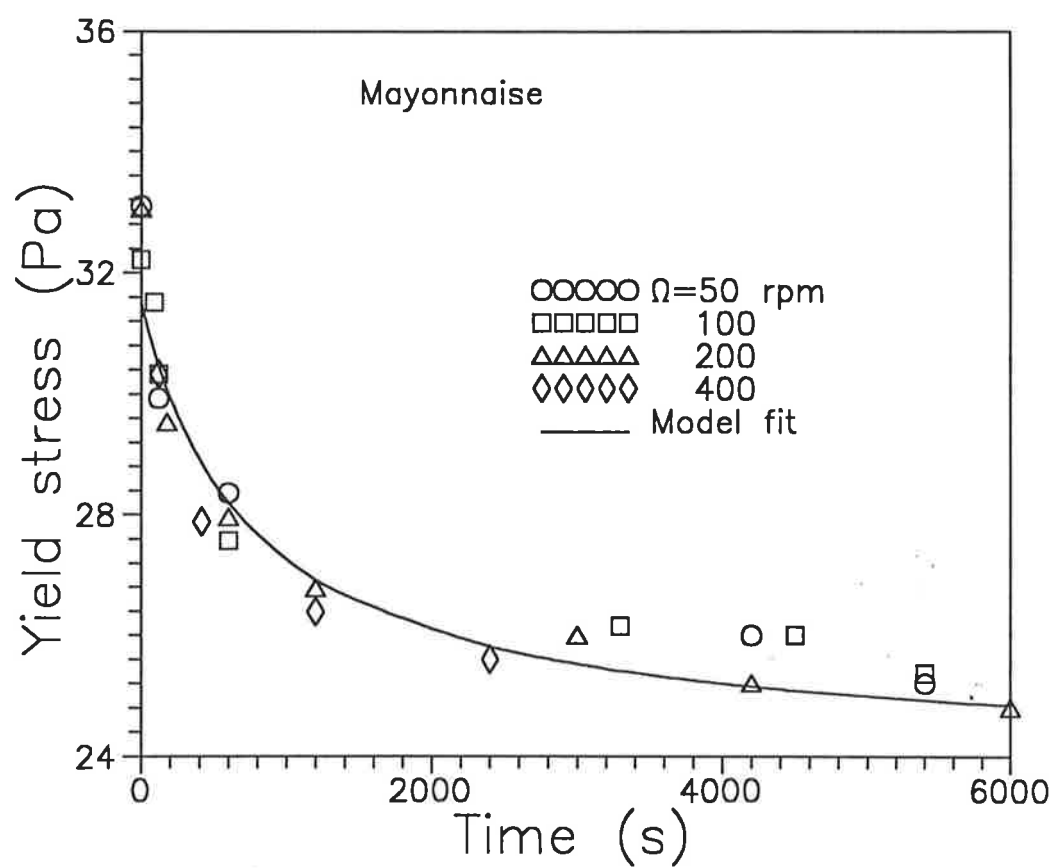


Fig. 7.2 Vane yield stress as a function of mixing time for mayonnaise suspension.

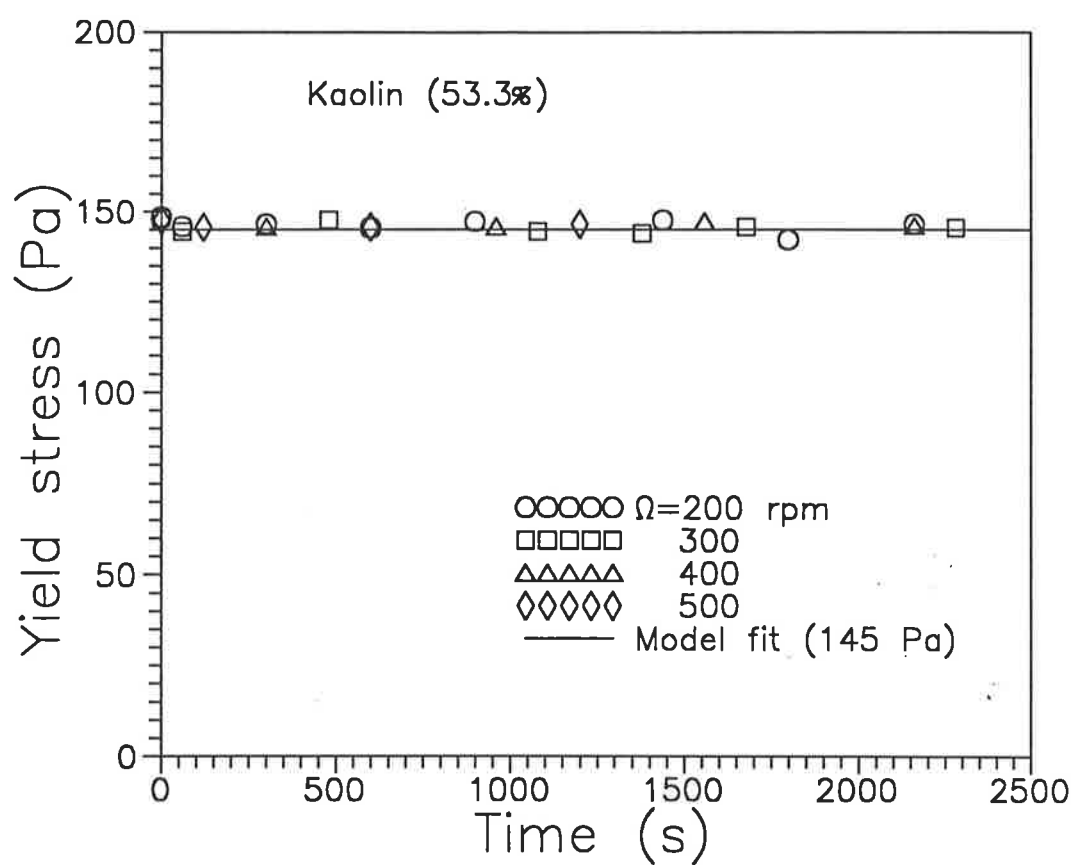


Fig. 7.3 Vane yield stress as a function of mixing time for kaolin 53.3 wt% suspension.

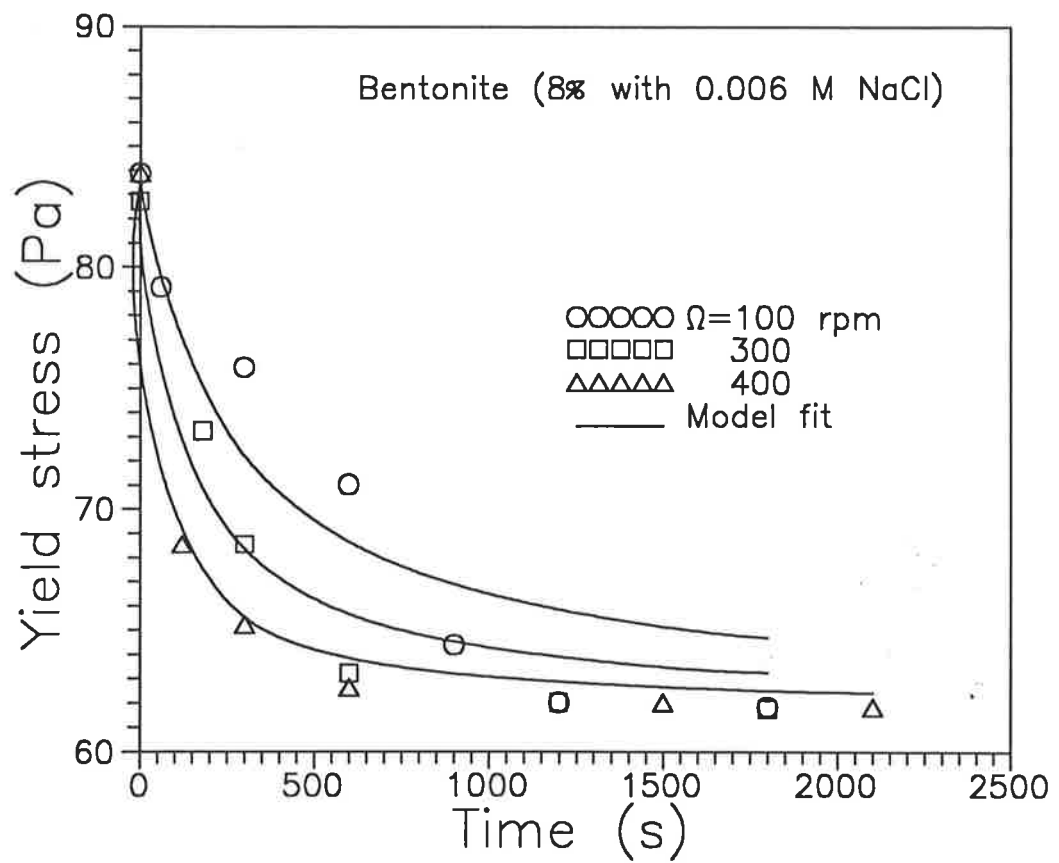


Fig. 7.4 Vane yield stress as a function of mixing time for bentonite 8 wt% with 0.006 Molar NaCl suspension.

7.3 Simulation Procedures

The present simulation is based on a single bob geometry shearing in an infinite fluid medium (i.e. very large cup) under a constant rotational speed to ensure partially sheared condition. Thixotropic flow models, defined in Chapter 6, are used for the selected suspensions. In the simulation, it was necessary to determine the shear stress distribution so that the yield boundary, representing cylindrical surface that separates the yielded and unyielded flow regions, could be determined basing on the yield criteria. In addition, it was important to know the shear rate distribution throughout the flow which was used to calculate the change of structure with time.

As the shear rate varies along the radius, there is no unique shear rate value which could be used to represent the shearing effect for the whole region of the flow. Finite difference method was used to treat this problem for every small intervals of radius and time as described in section 4.4.3. The shear stress and shear rate values within each radius and time intervals were then simulated at any radius and time steps.

$\lambda_{\tau_y, j}$, $\lambda_{\mu, j}$ and $\lambda_{\tau_{y,vane}, j}$ are the structure parameters for the flow model parameters (τ_y and μ) and vane yield stress at time t_j . The structure related quantities (τ_y , $\tau_{y,vane}$ and μ) at time t_j can be defined by:

$$\tau_y(t_j) = \tau_{ye} + (\tau_{yo} - \tau_{ye}) \cdot \lambda_{\tau_y, j} \quad (7.5)$$

$$\tau_{y,vane}(t_j) = \tau_{ye,vane} + (\tau_{yo,vane} - \tau_{ye,vane}) \cdot \lambda_{\tau_{y,vane}, j} \quad (7.6)$$

$$\mu(t_j) = \mu_e + (\mu_o - \mu_e) \cdot \lambda_{\mu, j} \quad (7.7)$$

If the flow model parameters could be defined, then according to the analysis in chapter 3 the flow parameters such as the shear stress, shear rate etc., can be simulated. The yield boundary

can be subsequently located with the yield criteria (either using flow model yield stress or vane yield stress). The following describes how to determine the structure parameters, and the equilibrium parameters (τ_{ye} , $\tau_{ye,vane}$ and μ_e) for the above Eqs. (7.5) to (7.7) from shear rate distribution.

The rate constant k , and the equilibrium parameters for the yield stress τ_{ye} and $\tau_{ye,vane}$, and viscosity μ_e , have been found to be functions of the applied shear rate according to previous modelling work in sections 6.3 and 7.2. At any given time, there exists a shear rate distribution and hence it is not possible to determine a unique quantity to represent the rate constant or equilibrium parameters for the overall flow.

It was assumed that the overall fluid structure within the yield boundary to be homogeneous. The overall change of the fluid structure in the sheared region is accumulated from the contributions of each radial element. Similar to the description in section 4.4.3, that the overall structure change at a given time step j is defined as:

$$\frac{d\lambda_j}{dt} = -\frac{1}{H} \sum_{i=1}^H (k_{ij}) \cdot (\lambda_j)^p \quad (7.8)$$

When $p=2$, the integral form of Eq. (7.8) is:

$$\frac{1}{\lambda_j} - 1 = \frac{1}{H} \int_0^{t_j} \sum_{i=1}^H (k_{ij}) dt \quad (7.9)$$

The right hand side of Eq. (7.9) can be integrated numerically i.e.:

$$\frac{1}{\lambda_j} = 1 + \frac{1}{H} \sum_{j=1}^j \overline{\sum_{i=1}^H k_{ij}} \cdot \Delta t_j \quad (7.10)$$

Eq. (7.10) can also be conveniently written as:

$$\frac{1}{\lambda_j} = \frac{1}{\lambda_{j-1}} + \frac{1}{H} \sum_{i=1}^H \overline{(k_{i,j})} \cdot \Delta t_j \quad (7.11)$$

In which the term $\frac{1}{H} \sum_{i=1}^H \overline{(k_{i,j})}$ has the same expression as Eq. (4.30) and $\Delta t_j = t_j - t_{j-1}$. Eq. (7.11) illustrates the way by which the current structure parameter λ_j (representing a general term for $\lambda_{\tau_y, j}$, $\lambda_{\tau_{y,vane}, j}$, $\lambda_{\mu, j}$) can be determined from the last time step (j-1) basing on the knowledge of the current time step values of the rate constant $k_{i,j}$ (representing a general rate constant term for τ_y , $\tau_{y,vane}$, and μ as function of time) in each of the radial element. $k_{i,j}$ can be defined from the shear rate distribution. The yield boundary is located between the r_{H-1}^* and r_H^* positions.

A general parameter ψ_e , which is a function of shear rate, is defined to represent the equilibrium parameters (τ_{ye} , $\tau_{ye,vane}$, and μ_e):

$$\psi_e = F(\dot{\gamma}) \quad (7.12)$$

An average quantity $\overline{\psi}_e$ is defined at a given time step j. $\overline{\psi}_e$ is calculated by summing up each small contribution from every radial element with the corresponding shear rate:

$$\overline{\psi}_e = \frac{1}{H} \sum_{i=1}^H F(\dot{\gamma}_{i,j}) \quad (7.13)$$

Naturally, this step will be simplified if the rate constant or equilibrium structure value is independent of the applied shear rate. Instead of accounting for the cumulative effects (i.e. Eq. (7.11) or (7.13)) for the rate constant and equilibrium structure quantities, only a single value for each quantity is required. Typical examples where those equilibrium quantities and rate constants are independent of shear rate have been illustrated in section 7.2.

Shear stress distributions were calculated according to the flow model and its time-dependent model parameters at any time of shear. As shown in Appendix 12, the shear stress distribution can be determined from the flow model which covers a wide range of shear rate data except for the narrow range of lower values. The yield boundary was then determined from this shear stress distribution where the shear stress is equal to the yield stress. Yield criteria either basing on the flow model yield stress or the vane yield stress have been considered.

Following the above calculation procedures, the shear rate distribution was determined from the shear stress distribution and flow model parameters at any given time of shear. The extent of structure change caused by shearing effect was then calculated according to the shear rate distribution. However, this structure change would also lead to the change of flow pattern such as the stress and shear rate distribution. Due to such interaction between the structure and flow pattern change, it is necessary to adopt a convergence method to solve for the effective change at any given time step. After obtaining the converged solution, the similar procedures were carried out for the next time step, until a required time length was reached for the simulation.

In the simulation, the methods used to calculate the shear stress and shear rate distribution and the yield boundary with a given flow model and the flow model parameters are referred to Chapter 3. The programming procedures are described as follows:

Radial boundaries were selected, and divided into a number of radial elements. These boundaries were selected in such a way that the simulation result of the yielded radius would not exceed it. The selected boundaries used in the simulation are shown below:

The selected boundary (r / r_b) for different simulation conditions.

	10 rpm	44 rpm	90 rpm	150 rpm
mayonnaise	2.00	2.40	2.70	3.00
kaolin	1.15	1.17	1.20	1.25
bentonite	1.12	1.12	1.15	-

The incremental radial element is increased according to an arithmetic series:

$$r_i / r_b = 1 + (\text{boundary} - 1) \cdot (i - 1) / (I - 1)$$

In which the i varies from 1 to I . A geometric series is chosen for the time step as the change of flow behaviour is much slower in the later time:

$$t_j = \Delta t \cdot (\text{base})^{j-1}$$

where the incremental base value is defined as: $\text{base} = (t_{\max} / \Delta t)^{1/(I-1)}$. j varies from 1 to J , with $t_0 = 0$ when $j=0$. $t_{\max}$ is the maximum value of time as specified by the user. For bentonite, mayonnaise and kaolin suspensions, $t_{\max}$ values were specified at 2000, 2800 and 4000 (sec) respectively. Δt denotes the first incremental time step. In the following, Y_n represents a general term for yield number (i.e. Bi, Ca, He) of different fluids and flow conditions.

Computational Program Structure:

At the initial time step $j = 0$; $t_j = 0$, the fluid parameters and flow conditions are:

$$\lambda_{\tau_y,0} = 1$$

$$\lambda_{\tau_{y,vane},0} = 1$$

$$\lambda_{\mu,0} = 1$$

$$\tau_y(0) = \tau_{y_0},$$

$$\tau_{y,vane}(0) = \tau_{y_0,vane}$$

$$\mu(0) = \mu_0$$

The shear stress, shear rate distribution and yield radius were calculated at $t=0$. Simulation continued from time $j=1$ as shown below.

The flow behaviour in the current time step is simulated based on the values of the parameters at the last time step. For example, to simulate the flow at time step j , the following computational steps were followed:

1. The flow conditions and fluid properties at time $j-1$ are known. The values of fluid parameters and flow condition for the time step j are guessed from those of previous time step ($j-1$), e.g.

$$\tau_y(t_j)(\text{guess}) = \tau_y(t_{j-1}); \quad Yn_j(\text{guess}) = Yn_{j-1}$$

$$\tau_{y,vane}(t_j)(\text{guess}) = \tau_{y,vane}(t_{j-1}); \quad H_j(\text{guess}) = H_{j-1}$$

$$\mu(t_j)(\text{guess}) = \mu(t_{j-1});$$

2. Shear stress and shear rate distributions, and yield radius at time step j were then calculated:

$$\tau_{i,j}, \quad \dot{\gamma}_{i,j}, \quad H_j$$

3. The change of the structure related values during the time step $j-1$ to j could be determined by using the calculated shear rate distributions. The structure related values at time step j were calculated from Eqs. (7.5~7), (7.11.), and (7.13).

$$\tau_y(t_j), \tau_{y,vane}(t_j), \quad \mu(t_j)$$

4. The flow condition at the time t_j step were calculated:

$$\tau_{i,j}, \quad \dot{\gamma}_{i,j}, \quad H_j, \quad Yn_j$$

5. Errors for the yield number was calculated as:

$$ERR = |Y_{n_j} - Y_{n_j}(\text{guess})| / Y_{n_j}$$

If ($ERR \leq \text{specified tolerance}$) then the computation proceeds to the next time step ($j+1$) following the similar procedures starting from step 1. If the error condition were not met, then new guessed values were updated with the current results:

$$\tau_y(t_j)(\text{guess}) = \tau_y(t_j) \quad Y_{n_j}(\text{guess}) = Y_{n_j};$$

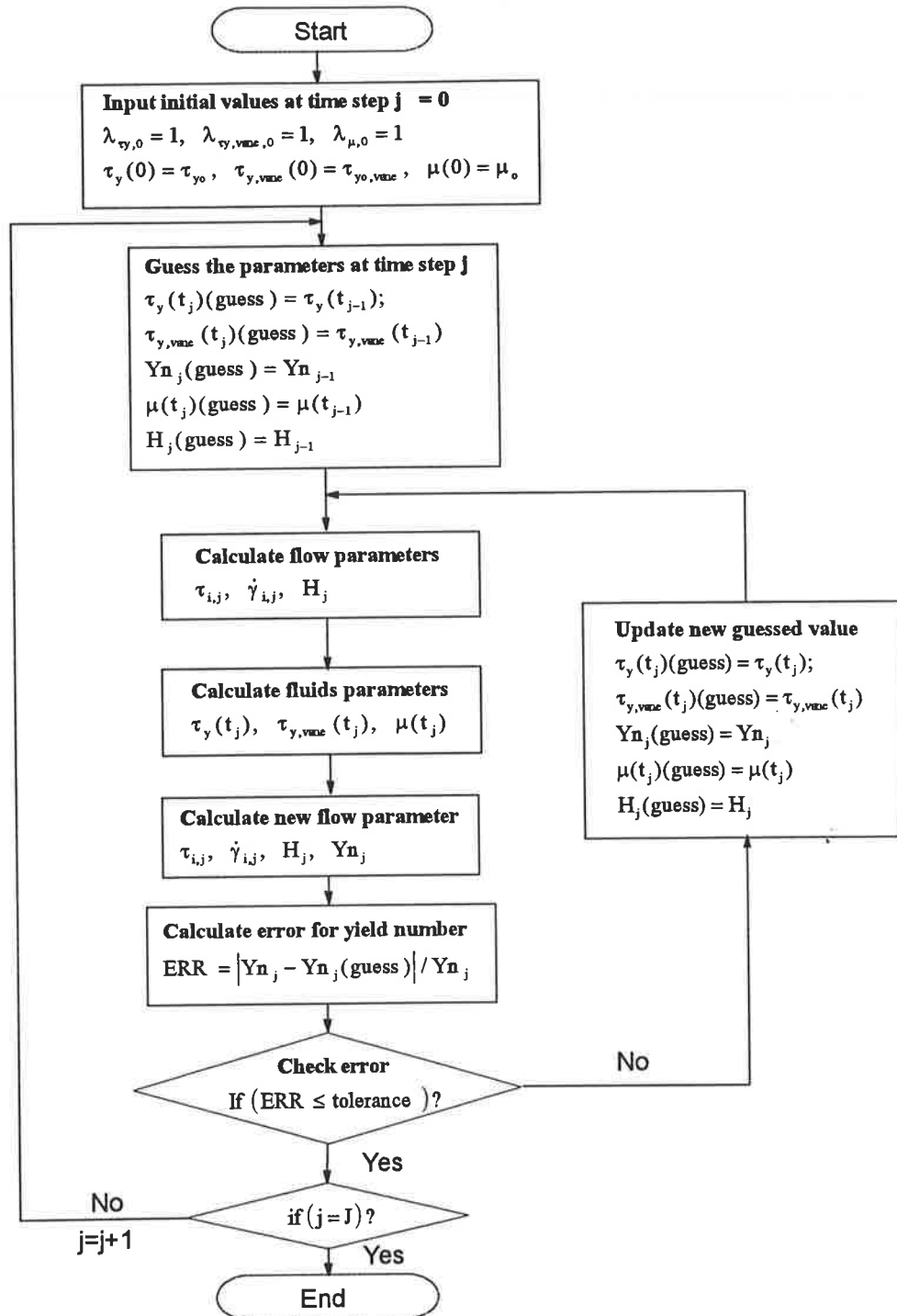
$$\tau_{y,vane}(t_j)(\text{guess}) = \tau_{y,vane}(t_j); \quad H_j(\text{guess}) = H_j.$$

$$\mu(t_j)(\text{guess}) = \mu(t_j);$$

and the calculations from step 2 were repeated for this time step until the error condition was satisfied.

6. The calculation was terminated when the time step j reached J as set by the user.

In all the simulations the specified tolerance was set at 1% for the yield number. It was found that when the I and J were greater than 20 in all the experimental conditions, the accuracy of the simulation results could not be improved further. However, in this study the number of radial and time steps were chosen as 30 and 90 respectively which were shown to be sufficient to obtain stable numerical solutions. The following shows the flowchart of the above program.



7.4 Results and Discussions

The radius of the yield boundary was measured for each of the three selected suspensions, i.e. mayonnaise, kaolin (53.3 wt%) and bentonite (8 wt% with 0.006 M NaCl) suspensions, in a cup with a large radius to ensure the partially sheared condition. The bob radius was 20.04 mm for mayonnaise and kaolin suspensions, and 54.8 mm for bentonite suspension. For the bentonite suspension, due to a high yield stress, the larger bob was used to attain larger sheared layer, providing better visual observation. The sheared radius was measured by using a video system as described in the experimental set up section (Chapter 5).

The parameters of the time-dependent flow models for different suspensions used in the simulation can be found in sections 6.3.3, 7.2 and in Appendix 11. The simulation results for mayonnaise suspension are compared with the experimental measurements as shown in Figs. 7.5 and 7.6. In both the experimental and simulation results, the change of the yield boundaries show a slight increasing trend with time. Comparison of the simulation results with the experimental data shows that the simulation result based on the vane yield stress as the yield criteria (in Fig. 7.5) can predict the experiment measurement (especially for the experimental condition $\Omega \geq 44$ rpm) better than that based on the flow model yield stress as the yield criteria (Fig. 7.6). Such finding suggests that the yield stress measured by the vane method offers a better yield criteria than the flow model yield stress. Fig. 7.7 compares the simulation results with the experimental data for kaolin suspension (53.3 wt%). In this case, the yield stress measured by the vane method is again the better yield criteria. The experimental yield boundaries for kaolin (53.3 wt%) suspension show an increasing trend initially then followed by a decreasing trend with time, while the simulation results based on vane yield stress as the yield criteria show only a decreasing trend with time. Comparison of the predicted yield boundary with experimental data for the bentonite suspension is shown in Fig. 7.8. Both the experimental and simulation (based on vane yield stress) results show a strong increasing trend with time. However, for the simulation based on the flow model yield

stress as the yield criteria, the results show a decreasing trend with time. This further confirms that vane yield stress is a better yield criteria to use for modelling these suspensions. Good agreements were obtained between the predicted yield boundary and the experimental data as shown in Figs. 7.5, 7.7 and 7.8. So this confirms that the modelling results for the time and shear dependent structural related parameters reasonably represent the characteristic of the tested fluids; and also with the current simulation procedures for the time-dependent yield boundaries of the flow can be reasonably described.

The following summarizes the key findings from the above experimental and theoretical studies on the transient movement of yield boundary in a Couette geometry:

1. In the current experiments, the yield boundary was observed to exist for three of the selected suspensions where the flow was separated into two regions, i.e. yielded and unyielded flow regions. This is confirmed from the tracer experiments on the surface of the yielded flow where they were observed to be in motion; while the other tracer on of unyielded flow region remained stationary. The dynamic behaviour of the location of the yield boundary has been simulated based on the fundamental rheological property (i.e. time-dependent behaviour of the flow model parameters and the yield stress measured by the vane method) of the fluids. In general, good agreements were obtained between the predicted yield boundary and the experimental data when the vane yield stress was used as the yield criteria (see Figs. 7.5, 7.7 and 7.8). For this reason, it is claimed that the modelling results for thixotropic fluids can reasonably describe the time dependent fluid behaviour, and the vane yield stress can better represent the actual yield stress of the fluids. It concludes that the yield behaviour of the time-dependent flow for a actual fluid can be predicted if the basic rheological property of this given fluid is known.

2. The appearance of the yield boundary varies with different types of suspensions depending on the nature of structure formation in these fluids. The actual yield boundary is in

fact more complex than the idealized yield boundary which is represented as a distinct and continuous circular ring. However, from the experimental observation for example in bentonite suspension, the yield boundary was not found to be smooth and continuous. The suspension material residing just outside the edge of the sheared radius was observed to have small cracked lines and slowly broken up into smaller clumps in the course of the experiment (see for example, the photograph for bentonite in Fig. 5.7 (c) in Chapter 5). This phenomenon may be considered to be comparable to the nature of breakage or crack found in most solid materials such as wood, plastic or brick. The material breaks first at the location where the bond between the internal structure is the weakest. The cracks propagate with the duration of shearing time. Clearly, this suggests that the formation of the internal structure is very complex. Consequently, apart from the experimental error, this phenomenon would also contribute to the scatter in the experimental data. Unlike the bentonite suspension, the yield boundaries for the mayonnaise and kaolin suspensions were seen to be smoother with no visible cracks present (see Fig. 5.7 (a) and (b)). The yield boundaries in the kaolin and bentonite suspensions appeared to be very distinct in comparison to that of mayonnaise suspension. The bentonite and kaolin suspensions had relatively narrow yield layer in contrast with the mayonnaise suspension under the same experimental condition. The existence of the distinct yield boundary and narrow yield layer for the bentonite and kaolin suspensions is due to the relatively high value of yield stress compared to the mayonnaise suspension.

3. According to the theoretical studies in chapter 3, if the calculated yield boundary indicates an increasing trend (i.e. $r_y^* = \sqrt{\tau_b / \tau_{y,vane}}$ increases with time.), then the idealized concept would suggest that the thickness of the sheared layer r_y^* remains constant for the actual time-dependent fluids. This is caused by the discontinuity of the fluid structure at the initial yield boundary (i.e. the structure of the fluid in the yielded region continues to break down, while that in the unyielded region remains at its initial fully structured state) for the idealized actual time-dependent yield stress fluids. However, from the experimental yield

boundary measurements, it was found that the yield boundary did increase with time for some suspensions (i.e. mayonnaise and bentonite suspensions as shown in Figs. 7.5 and 7.8 respectively) and they also agreed reasonably well with the simulation results when the vane yield stress was used as the yield criteria. The reason for the yield boundary to increase with time for the actual fluids is that the presence of the small shear stress in the unyielded region at the initial stage, though less than the yield stress, may slowly help to destroy some of the weakest bonds of the structure in that region. With this effect, the structure in the initially unyielded region would not stay at the fully structured state. Such slow progression would lead to the destruction of the structure near the yielded region. There was some evidence for such argument in the case for the bentonite suspension as discussed in previous point 2. So the idealistic concept in chapter 3, has been found experimentally to be unrealistic for some types of suspensions. Therefore, it is concluded that the yield boundary could increase in the same trend as the calculated yield boundary.

4. The deviation between the experimental observation and numerical simulation in the earlier time period for kaolin suspension might be explained by the elastic deformation and creep flow before the shear stress could totally overcome the initial yield stress to initiate flow. The related studies on creep behaviour at the shear stress close to the yield stress have been reviewed by Nguyen and Boger (1992). In the current visualization experiments for kaolin suspension, the undetectable creep deformation (by means of tracer motion) might take some finite time before the yielding occurring if the shear stress was slightly higher than the yield stress. When the cylinder initially started to rotate, there might exist a annular region where the shear stress was slightly higher than the yield stress. In this region, it is quite possible that some finite time is necessary before the strain can reach a measurable level to initiate the viscous flow. This behaviour might lead to a delayed detection in the visual measurements and might be the reason why the measured yield boundary in kaolin suspension took some time to reach the peak values. The creep behaviour was not considered in the

simulation work, which might lead to some deviation between the experimental observation and numerical simulation.

In conclusion, an improved understanding on the moving yield boundary of real fluids has been achieved, both qualitatively and quantitatively. The significance of this work is certainly beyond the Couette geometry. In general, the yield boundary for some fluids with yield stress is shown to be predictable if the knowledge of the basic rheological parameters of the fluid is known. However, the phenomenon of moving yield boundary is complex and influenced by a number of factors. The current simulation approach remains rather idealized in some ways and further sophistication on the modelling method is clearly required in the future. Nonetheless, this work presents, perhaps for the first time, an approach to predict the location of the yield boundary using the basic rheological and flow parameters of the real fluids. Current findings are relevant to industrial processes when handling such time-dependent yield stress fluids. It is recommended that more accurate and detailed studies are needed in the future on a variety of fluids.

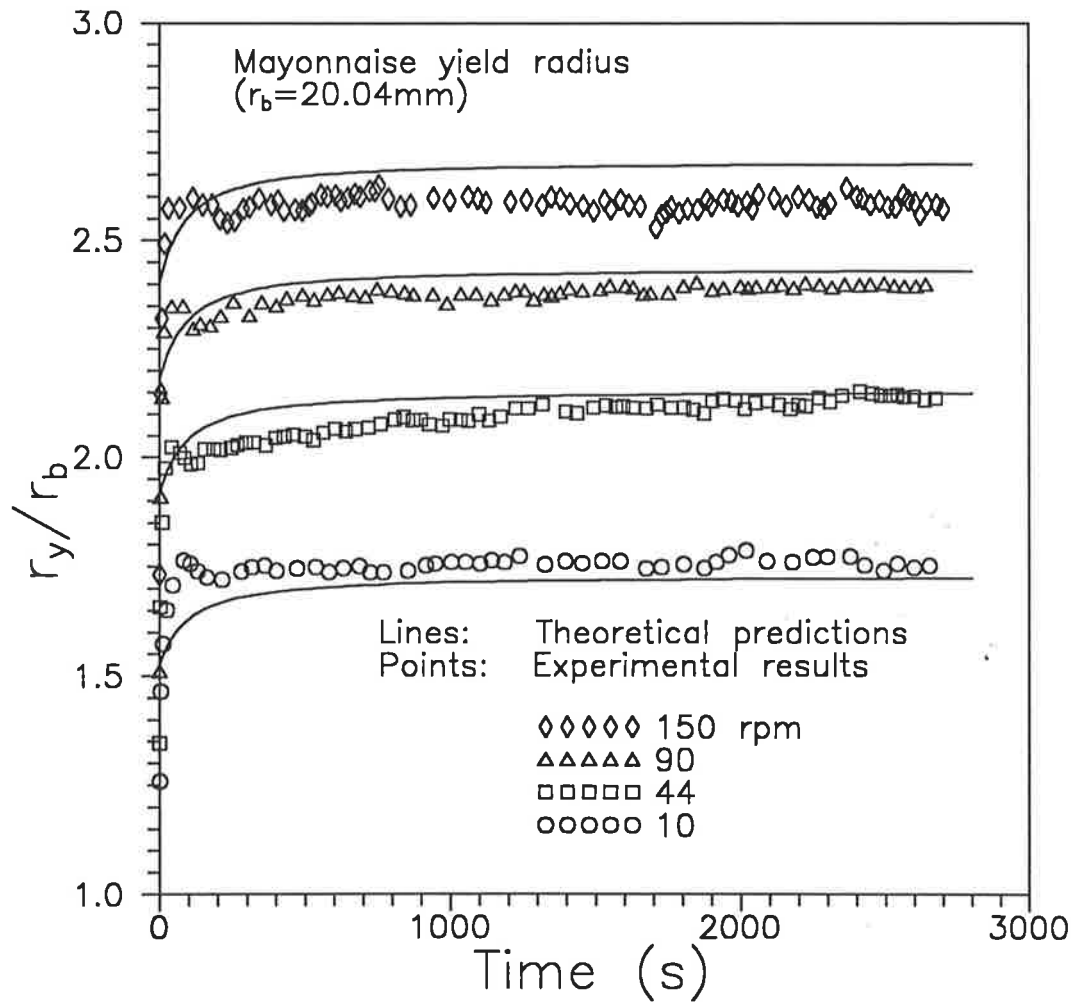


Fig. 7.5 Comparison of the theoretical transient behaviour of yield radius with experimental data for mayonnaise suspension at 10, 44, 90 and 150 rpm where the vane yield stress was used as the yield criteria. $r_b=20.04$ mm.

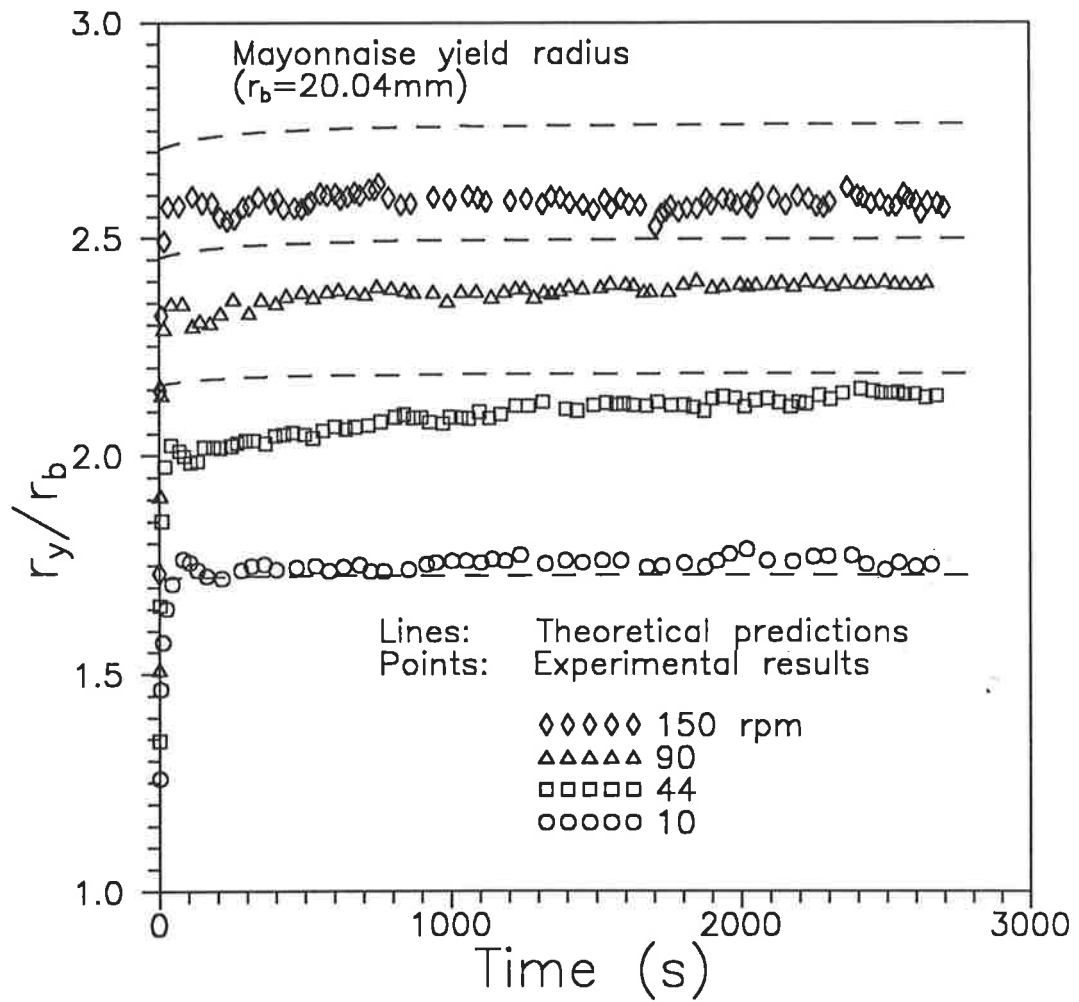


Fig. 7.6 Comparison of the theoretical transient behaviour of yield radius with experimental data for mayonnaise suspension at 10, 44, 90 and 150 rpm where the flow model yield stress was used as the yield criteria. $r_b=20.04\text{ mm}$.

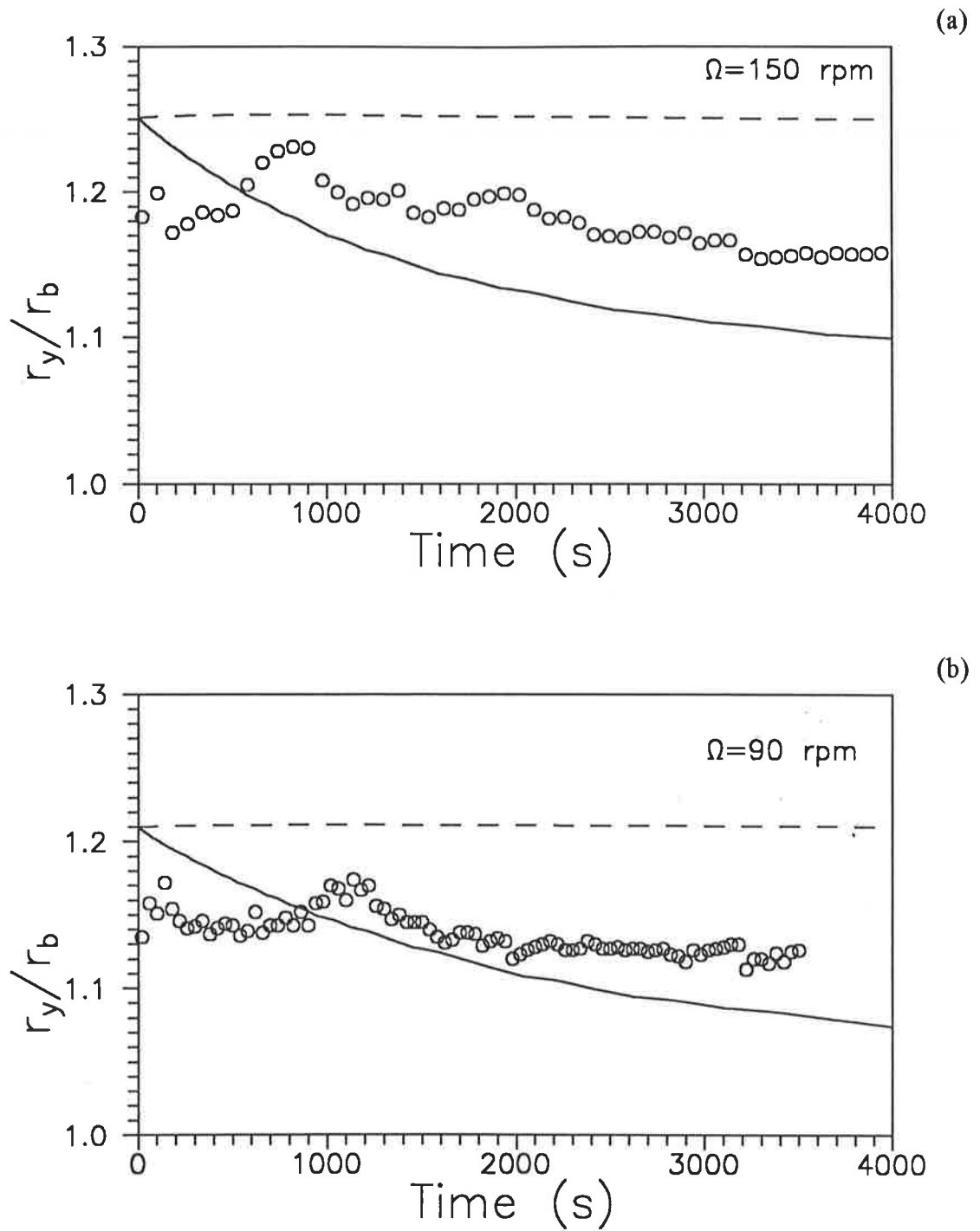


Fig. 7.7 Comparison of the theoretical transient behaviour of yield radius with experimental data for 53.3 wt% kaolin suspension. $r_b = 20.04 \text{ mm}$. Circles: experimental data. Solid line: prediction based on the vane yield stress as the yield criteria. Dashed lines: prediction based on flow model yield stress. (a) $\Omega = 150 \text{ rpm}$; (b) $\Omega = 90 \text{ rpm}$.

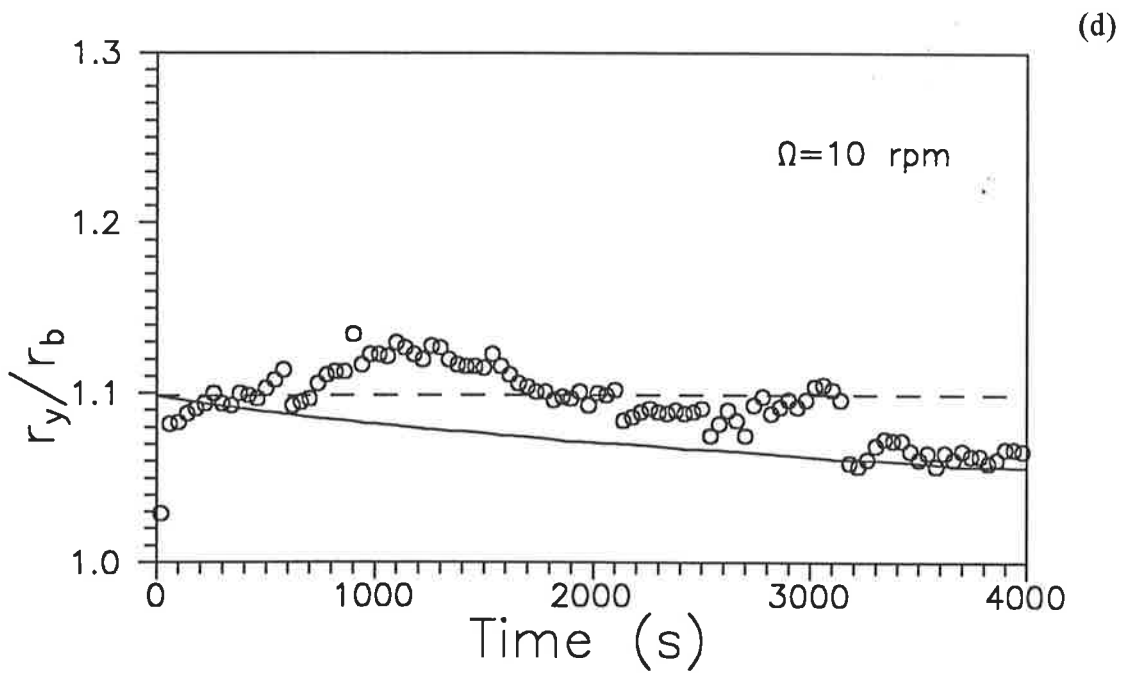
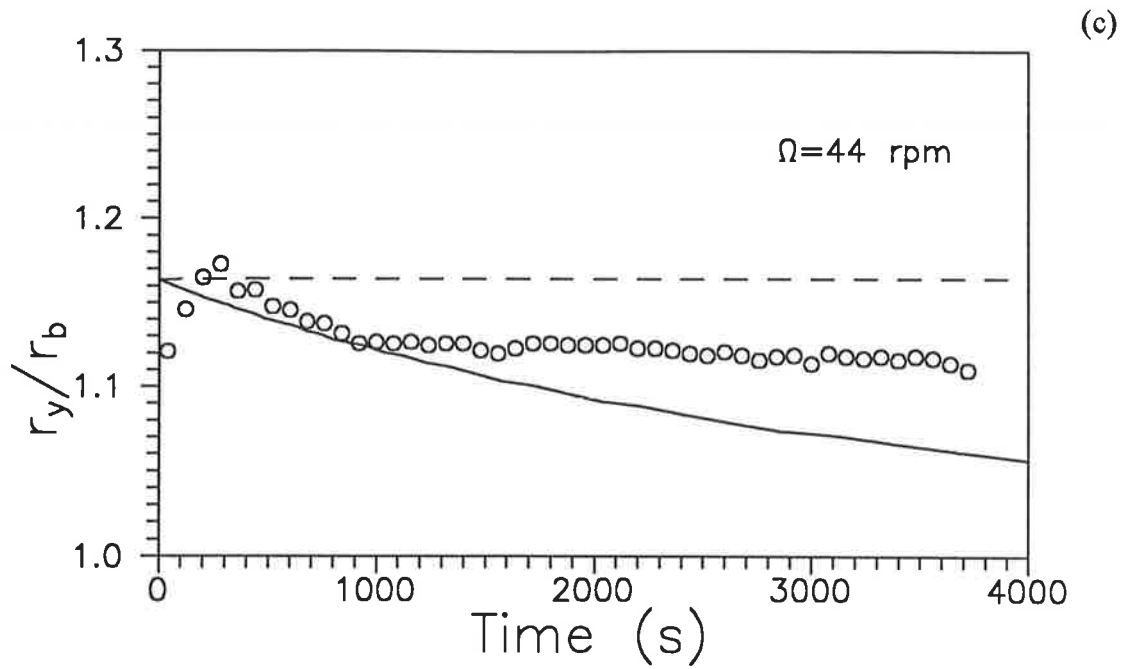


Fig. 7.7 Comparison of the theoretical transient behaviour of yield radius with experimental data for 53.3 wt% kaolin suspension. $r_b = 20.04 \text{ mm}$. Circles: experimental data. Solid line: prediction based on the vane yield stress as the yield criteria. Dashed lines: prediction based on flow model yield stress. (c) $\Omega = 44 \text{ rpm}$; (d) $\Omega = 10 \text{ rpm}$.

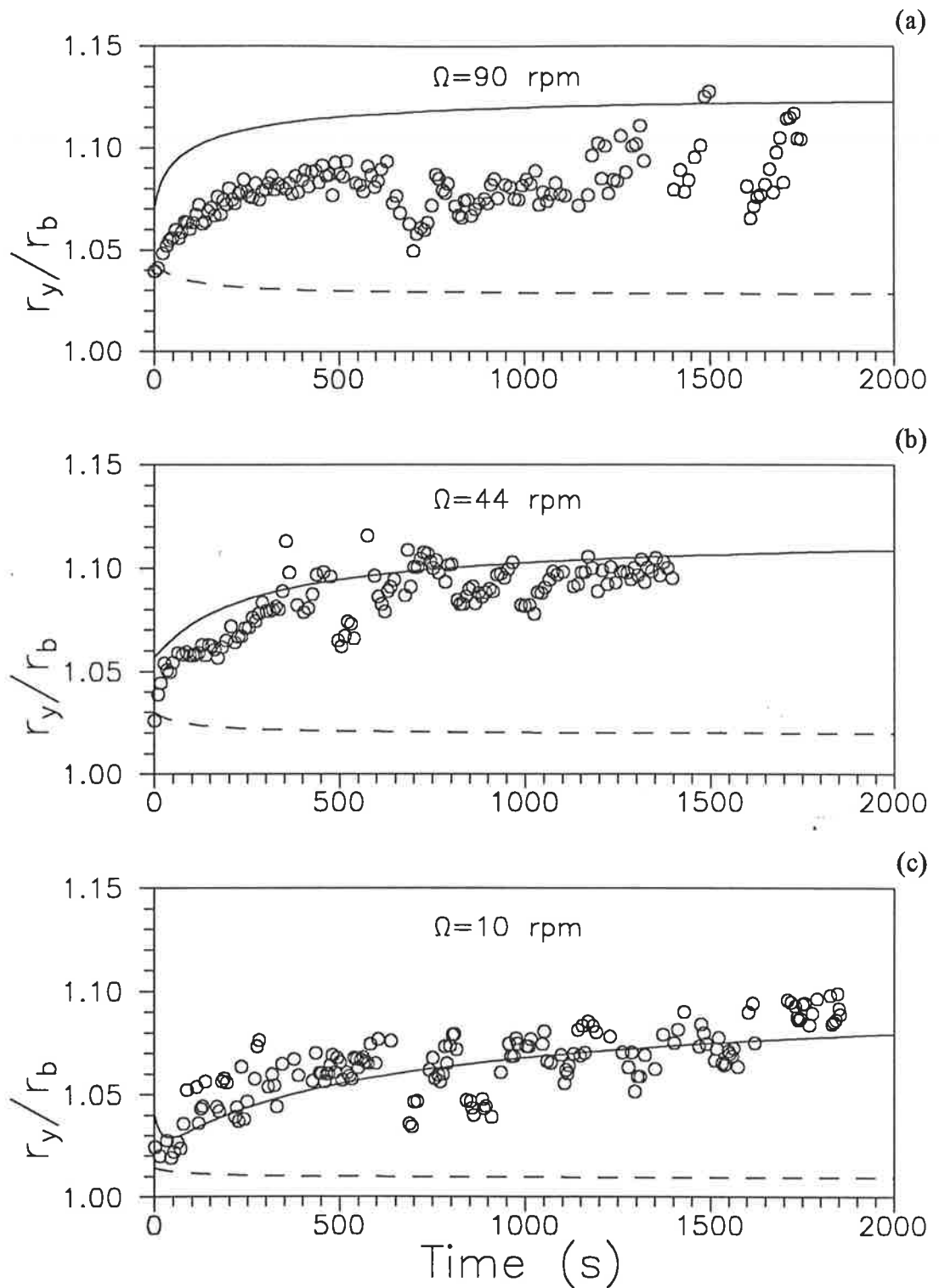


Fig. 7.8 Comparison of the theoretical transient behaviour of yield radius with experimental data for bentonite 8 wt% with 0.006 Molar NaCl suspension. $r_b = 54.80$ mm. Circles: experimental data. Solid line: prediction based on the vane yield stress as the yield criteria. Dashed lines: prediction based on flow model yield stress. (a) $\Omega = 90$ rpm; (b) $\Omega = 44$ rpm; (c) $\Omega = 10$ rpm.

Chapter 8

Conclusions and Recommendations

Conclusions

In this work, various aspects of flow behaviour of time-dependent yield stress fluids have been studied in a Couette geometry. It has examined some of the critical issues related to the characterization of time-dependent fluids. These topics have been methodically studied both theoretically and experimentally. Key results and findings from this work are summarized as follows:

- Analytical expressions for the distribution of flow parameters and location of yield boundary have been obtained to provide a better understanding of flow behaviour of fluids at both steady and unsteady state shear conditions.
- A method based on a critical radius (the r_c method) has been experimentally demonstrated as a reasonably accurate approach to determine the flow properties of time-dependent fluids with a yield stress using Couette rheometry. Its significance and potential applications have been discussed.
- A new modelling approach has been developed to characterize thixotropic yield stress fluids. This method offers a comprehensive way of quantifying the change of the rheological properties with time and shear which overcomes the limitations of the previous modelling approach.
- The experimental yield boundary, measured by visualization technique, has been successfully predicted from the theoretical model. This is the first time, to the knowledge of the author, that the yield boundary has been theoretically predicted from the basic rheological properties and compared with experimental results.

- The origin of the yield stress from the point view of microstructure formation is no doubt complex. In relation to the fundamental issues about the existence of the yield stress and the behaviour of the yield boundary, they vary from one type of fluid to the others. In conclusion, the overall implication of this work is significant and its application is clearly beyond that for Couette flow of yield stress fluids.

Recommendations

The following outlines recommendations for the future work based on this study:

- The application of the r_C method could also be extended to the "stress-controlled" concentric cylinder viscometer. In this case, the speed is the measured variable in the experimental result. Despite such variation, it is still convenient to convert the stress-speed data to stress-shear rate data by using the r_C position as a reference measurement point developed in this study.
- In practice, it is usually more convenient to assume a steady state condition in this Couette geometry. However, in some cases, it would be useful to know the time scale required for the flow to achieve fully developed condition. This information can be obtained by extending the simulation work described in Chapter 4. From the example shown in Fig. 4.6, the necessary times (in dimensionless form) required to achieve such fully developed state for $Bi=10$ and 100 are 0.1 and 0.006 respectively. Therefore, it is possible in principle to obtain a relationship of Bi and dimensionless time if additional calculations are performed for a wider range of Bi , say from 1 to 10000 . For any given flow condition for Bingham type fluids, one can estimate the necessary time scale for the flow to reach fully developed state from the above computed relation. The same approach can also be extended to Casson or Herschel-Bulkley type of fluids.

- The modelling method discussed in Chapter 6 has been used to obtain the transient behaviour of the flow model parameters. It should be noted that it is possible to obtain an identical result from an alternative approach. In Fig. 6.18 (a), the transient flow model parameters at states A, B, C and D could be obtained from a group of pairs of shear stress-shear rate data correspond to each of the A, B, C and D states. For example, at state B ($\tau_B, \dot{\gamma}_s$), one may change the $\dot{\gamma}_s$ to a new lower shear rate and get the corresponding shear stress response; and then go back to the original $\dot{\gamma}_s$ and wait until the shear stress returns to τ_B . The above procedure may be repeated to obtain a number of shear stress-shear rate responses. This experiment would be different from the conventional "step-change-in shear rate" experiment as the reference state ($\tau_B, \dot{\gamma}_s$) is not at the equilibrium shearing condition. No doubt further work is needed to substantiate this method experimentally.
- In the current study, the yielded region of the time-dependent yield stress fluid is assumed to exist in homogeneous structure condition. However, if the gap size is large, the flow region near the bob surface would suffer more shear force than the region far from bob surface, hence leading to a possible structure variation along the radius. The observed good agreement in the experimental work using the r_C method implies that the homogeneous assumption is at least valid for radius ratio up to 1.141 for the given kaolin suspensions and 1.382 for mayonnaise and starch suspensions. If the gap size is larger than the above limits, the homogeneous assumption may be under question. So far, there is no quantitative means for estimating this influence in the existing experimental work on yield boundary measurement for flow with a large yield layer. Such non-homogeneity factors could be affected by number of factors like nature of fluid, gap size, rotating speed, temperature. The simulation will become more complex if these factors are to be accounted for. Therefore, such inclusion is not warranted at present until further tests are performed in the future.

- It was found in Chapter 7 that the experimentally measured yield boundary could increase with time when the theoretical yield radius $r_y^* = \sqrt{\tau_b / \tau_{y,vane}}$ showed an increase with time. However, this behaviour is in contradiction to the theoretical indication discussed in Chapter 3. The explanation for this contradictory behaviour is mainly due to the fact that in the theoretical study the unyield region was considered as ideal solid and remained in the initial fresh structure at all time of shear. Such idealistic assumptions have been found experimentally to be unrealistic for some types of suspensions. However, it is again premature to conclude that the yield boundary always increase with time when the theoretical $r_y^* = \sqrt{\tau_b / \tau_{y,vane}}$ shows a increasing trend for all types of fluids and conditions. More experiments are clearly required for different types of fluids in the future.

Nomenclature

a	Model parameter for rate constant, [1/s]
A	Parameter in Eqn (A9-1), [Pa]
b	Model parameter for rate constant, [-]
B	Parameter in Eqn (A9-1), [Pa]
Bi	Yield number for Bingham model, [-]
c	A constant used in defining the apparent viscosity, [Pa s]
C	General constant specified according to text
C₀, C₁	Flow model parameter in Ellis model, [-]
Ca	Yield number for Casson model, [-]
e	The total number of pixels across the video screen, [pixel]
Δe	The uncertainty in boundary detection on the video screen, [pixel]
E	Calibration on the entire video screen, [mm]
ΔE	ΔE ₁ + ΔE ₂ , [mm]
ΔE₁	Error due to the instability of the rotating bob, [mm]
ΔE₂	Error due to subjective judgment on the video screen; [mm]
F	Any function
G_{Bi}	Critical yield number for Bingham model, [-]
G_{Ca}	Critical yield number for Casson model, [-]
G_{He}	Critical yield number for Herschel-Bulkley model, [-]
H	Location of the radial element where the yield boundary exists [-]
He	Yield number for Herschel-Bulkley model, [-]
I	Total number of intervals on radius, [-]
J	Total number of intervals on time, [-]
k	Rate constant for structure decay process, [1/s]
k_r	Rate constant for structure recover process, [1/s]

k_{τ_y}	Decay rate constant for flow model parameter τ_y , [1/s]
k_{μ}	Decay rate for flow model parameter μ , [1/s]
L	length of the bob, [m]
m	$1/n$, [-]
MVI	Sensor system $\varepsilon = 1.048$
MVII	Sensor system $\varepsilon = 1.141$
MVIII	Sensor system $\varepsilon = 1.382$
n	Shear rate index, [-]
n	Exponent value in modified flow model, [s]
N	$n \cdot \Omega$, [-]
P_o	Pressure, [Pa]
p	Number of terms in Maclaurin series, [-]
p	Kinetic order of the structure decay process, [-]
q	Kinetic order of the structure recover process, [-]
r	Radius, [m]
r_c	Critical radius position, [m]
r_{cup}	Radius of cup, [m]
r_o	Outer boundary condition, [m]
r_y	Radius of yield boundary, [m]
$r_{y,max}$	The maximum value of radius of yield boundary, [m]
Δr	Radius interval, [m]
t	Time, [s]
t_b	A time period for the fluid structure to reach certain structure level, [s]
T	Dimensionless time, [-]
M	Measured torque by the viscometer, [N m]
Δt	Time difference, [s]
V	Velocity, [m/s]

Δx	A positive value which approaches zero
Y_n	Yield number for Bingham, Casson and Herschel-Bulkley models, [-]

Greek Symbols

$\alpha_p(m)$	$(-1)^{-p} \cdot \binom{m}{p}$
δ	Local gradient of the logarithmic plot of τ_b versus Ω ($d(\ln \tau_b) / d(\ln \Omega)$)
σ	Acceleration, [m/s ²]
ε	Radius ratio of the bob and cup: r_{cup} / r_b , [-]
$\dot{\gamma}$	Shear rate, [1/s]
$\dot{\gamma}_c$	Shear rate at r_c position, [1/s]
$\dot{\gamma}_{\bar{m}}$	Average mixing shear rate, [1/s]
$\dot{\gamma}_N$	Newtonian shear rate, [1/s]
$\dot{\gamma}_r$	Reference shear rate, [1/s]
$\dot{\gamma}_s$	A constant shear rate, [1/s]
$\dot{\gamma}_y$	The shear rate at the location of yield boundary of modified flow model, [1/s]
φ	Dimensionless velocity, [-]
λ	Structure parameter, [-]
λ_e	Structure parameter at equilibrium state, [-]
λ_μ	Structure parameter for flow model parameter μ , [-]
λ_{τ_y}	Structure parameter for flow model parameter τ_y , [-]
μ	Flow model parameter for Bingham, and Casson: [Pa s]; Herschel-Bulkely: [Pa s ⁿ] fluids
μ_e	μ at equilibrium shearing condition, as in μ
μ_o	μ at initial (fresh sample) condition, as in μ
ψ_e	General term for equilibrium fluid property (i.e. τ_{ye} , μ_e , $\tau_{ye,vane}$)

η	Apparent viscosity, [Pa s]
η_o	Apparent viscosity η at initial (fresh sample) condition, [Pa s]
η_e	Apparent viscosity η at equilibrium shearing condition, [Pa s]
ρ	Density, [kg/m ³]
τ	Shear stress, [Pa]
$\tau(0)$	Shear stress at initial structure state, [Pa]
τ_e	Shear stress at r_e position, [Pa]
τ_o	Shear stress at equilibrium shearing condition, [Pa]
τ_o	Stress at outer boundary condition, [Pa]
τ_y	Yield stress, [Pa]
τ_{ye}	Yield stress at equilibrium shearing condition, [Pa]
τ_{yo}	Yield stress of fresh sample, [Pa]
$\tau_{y,vane}$	Yield stress as measured by vane method, [Pa]
$\tau_{ye,vane}$	Yield stress as measured by vane method at equilibrium mixing condition, [Pa]
$\tau_{yo,vane}$	Yield stress measured by vane method at fresh sample, [Pa]
Ω	Rotational speed, [rad/s] (or [rpm] if specified)
ω	Angular velocity, [rad/s]

Subscripts

b	Bob
cup	Cup
i	Radius interval index
j	Time step index
θ	Angular co-ordinate
r	Radial co-ordinate
z	Z co-ordinate

Superscripts

*	Dimensionless
—	Average
'	The position of pair of data on the flow curve in Fig. 3.12
"	The position of pair of data on the flow curve in Fig. 3.12



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Appendix 1

Calculations for flow at steady state

1. Determination of The Shear Stress at Bob Surface for Herschel-Bulkley Model

Method I - Integration approach

According to Eq. (3.30), let:

$$F(\tau^*) = \frac{1}{2} \int_{\tau_b^*}^{\tau^*} \frac{(\tau^* - 1)^{1/n}}{\tau^*} \cdot d\tau^* - \frac{1}{He}; \quad (A1.1)$$

When $\tau^* = \tau_b^*$ implies that $F(\tau_b^*) = 0$ as from Eq. (3.30). The value of $F(\tau^*)$ can be determined by a numerical integration routine available in IMSL solvers at any given value of τ^* . Newton method is used to determine the root τ_b^* of the equation $F(\tau_b^*) = 0$ in the following manner:

$$\tau_b^*(\text{new}) = \tau_b^*(\text{old}) - \frac{\left(\frac{dF(\tau^*)}{d\tau^*} \right) \Big|_{\tau_b^*(\text{old})}}{F(\tau_b^*(\text{old}))} \quad (A1.2)$$

where the $\tau_b^*(\text{new})$ is the current root, and $\tau_b^*(\text{old})$ is the last step root of equation $F(\tau_b^*) = 0$. When the $|\tau_b^*(\text{new}) - \tau_b^*(\text{old})|$ less than certain error tolerance, the $\tau_b^*(\text{new})$ is accepted as the root of the equation $F(\tau_b^*) = 0$, otherwise, the $\tau_b^*(\text{new})$ becomes $\tau_b^*(\text{old})$ and a new $\tau_b^*(\text{new})$ is further calculated. The error tolerance was set as $\tau_b^*(\text{new}) \times 10^{-4}$ in all

simulation. As required by this approach, the derivatives of $F(\tau)$ for two shear conditions are:

Fully sheared condition:

$$\frac{dF(\tau_b^*)}{d\tau_b^*} = \frac{1}{2} \frac{(\tau_b^* - 1)^{1/n}}{\tau_b^*} - \frac{1}{2} \frac{(\varepsilon^{-2}\tau_b^* - 1)^{1/n}}{\varepsilon^{-2}\tau_b^*} \quad (A1.3)$$

Partially sheared condition:

$$\frac{dF(\tau_b^*)}{d\tau_b^*} = \frac{1}{2} \frac{(\tau_b^* - 1)^{1/n}}{\tau_b^*} \quad (A1.4)$$

Method II - Power series approach

Rearranging Eq. (3.30) obtains:

$$\frac{1}{He} = -\frac{1}{2} \int_{\tau_o^*}^{\tau_b^*} (1 - \tau^{*-1})^{1/n} \cdot \tau^{*1/n-1} \cdot d\tau^* \quad (A1.5)$$

Let $1/n=m$ and using power series approximation (Maclaurin series) to expand the term in Eq. (A1.5):

$$\begin{aligned} (1 - \tau^{*-1})^m &\approx 1 - m \cdot (\tau^{*-1}) + \frac{m \cdot (m-1)}{2!} \cdot (\tau^{*-1})^2 - \frac{m \cdot (m-1)(m-2)}{3!} \cdot (\tau^{*-1})^3 \\ &\quad + \dots + (-1)^p \cdot \frac{m \cdot (m-1) \cdot (m-2) \cdot \dots \cdot (m-p+1)}{p!} \cdot (\tau^{*-1})^p \\ &= \sum_{p=0}^{\infty} \alpha_p(m) \cdot (\tau^{*-1})^p \end{aligned} \quad (A1.6)$$

where: $\alpha_p(m) = (-1)^{-p} \cdot \binom{m}{p}$.

Eq. (A1.5): can then be represented with the Maclaurin series:

$$\begin{aligned}\frac{1}{\text{He}} &= \frac{1}{2} \int_{\tau_o^*}^{\tau_b^*} \sum_{p=0}^{\infty} \alpha_p(m) \cdot (\tau^{*-1})^p \cdot \tau^{*(m-1)} \cdot d\tau \\ &= \frac{1}{2} \int_{\tau_o^*}^{\tau_b^*} \sum_{p=0}^{\infty} \alpha_p(m) \tau^{*(m-1-p)} \cdot d\tau^*\end{aligned}\quad (\text{A1.7})$$

Eq. (A1.7) can be integrated to give:

$$\frac{1}{\text{He}} = \frac{1}{2} \sum_{p=0}^{\infty} \frac{\alpha_p(m)}{(m-p)} \cdot \left[\tau_b^{*(m-p)} - \tau_o^{*(m-p)} \right] \quad (\text{A1.8})$$

Under fully sheared condition :

Substituting $\tau_o^* = \tau_b^* \cdot \varepsilon^{-2}$ into (A1.8) then the following is obtained:

$$\frac{1}{\text{He}} = \frac{1}{2} \sum_{p=0}^{\infty} \frac{\alpha_p(m)}{(m-p)} \cdot \left(1 - \varepsilon^{-2(m-p)} \right) \cdot \tau_b^{*(m-p)} \quad (\text{A1.9})$$

Under partially sheared condition :

Substituting $\tau_o^* = 1$ into (A1.8) then the following is obtained:

$$\frac{1}{\text{He}} = \frac{1}{2} \sum_{p=0}^{\infty} \frac{\alpha_p(m)}{(m-p)} \cdot \left[\tau_b^{*(m-p)} - 1 \right] \quad (\text{A1.10})$$

In the present analysis, both the results have been obtained by method I and method II. It is shown at the plot in Fig. A1.1 that the bob shear stress as calculated by both methods I and II gives good agreement when $p=10$ or greater.

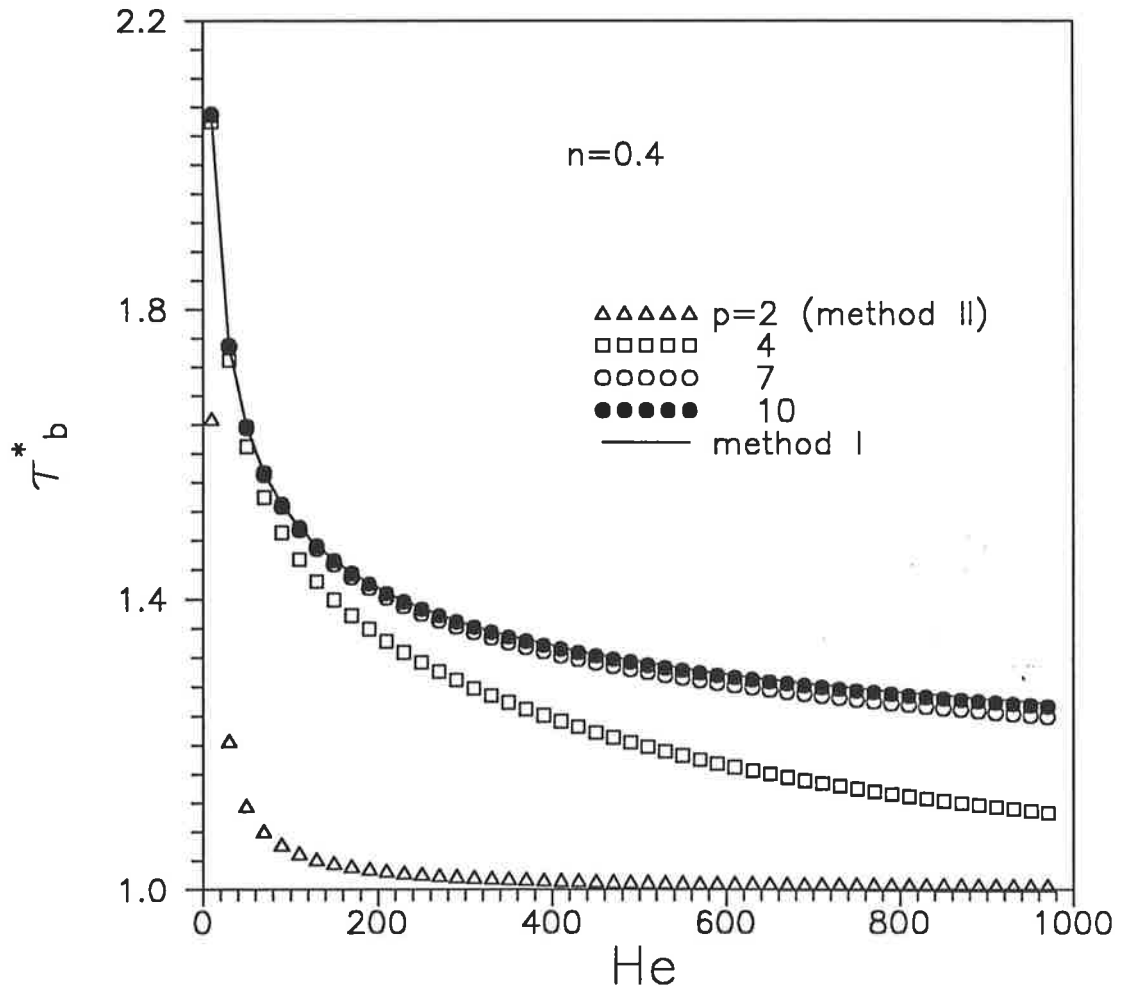


Fig. A1.1 Comparison of the shear stress calculation from method I and method II with different values p for Herschel-Bulkley model. The fluid is being sheared in an infinite medium.

2. Error Estimation for Shear Rate in Using r_c Method

From Fig. 3.12, the error for shear rate at τ_c can also be determined by:

$$\text{error}(\dot{\gamma})\% = \frac{\dot{\gamma}_c - \dot{\gamma}_c''}{\dot{\gamma}_c''} \times 100 = \left[\frac{\dot{\gamma}_c}{\dot{\gamma}_c''} - 1 \right] \times 100 \quad (\text{A1.11})$$

where $\dot{\gamma}_c''$ is the true shear rate at the $r_c(\epsilon)$ position for the actual flow curve because $\tau_c'' = \tau_c$ as shown in Fig. 3.12. The following will discuss the errors of shear rate (i.e. Eq. (A1.11)) for three different type of fluids. The $\dot{\gamma}_c$ can be determined by Eq. (3.52), while the $\dot{\gamma}_c''$ will be defined according to the given flow model as follow.

Bingham model: $\tau_c^* = \tau_b^* \cdot (r_c(\epsilon) / r_b)^{-2} = \tau_c'' = 1 + \dot{\gamma}_c'' / (\text{Bi} \cdot \Omega),$

Eq. (A1.11) becomes:

$$\text{error}(\dot{\gamma})\% = \left[\frac{1}{\text{Bi} \cdot \ln \epsilon \cdot (\tau_b^* \cdot (r_c(\epsilon) / r_b)^{-2} - 1)} - 1 \right] \times 100 \quad (\text{A1.12})$$

Under fully sheared condition, by substituting the Eq. (3.51) for $(r_c(\epsilon) / r_b)$ and Eq. (3.14) for τ_b^* into Eq. (A1.12), it can be proved that the error is equal to 0.

Casson model: $\tau_c^* = \tau_b^* \cdot (r_c(\epsilon) / r_b)^{-2} = \tau_c'' = \left\{ 1 + [\dot{\gamma}_c'' / (\text{Ca} \cdot \Omega)]^{1/2} \right\}^2$

Eq. (A1.11) becomes:

$$\text{error}(\dot{\gamma})\% = \left[\frac{1}{\text{Ca} \cdot \ln \epsilon \cdot (\tau_b^{*1/2} \cdot (r_c(\epsilon) / r_b)^{-1} - 1)^2} - 1 \right] \times 100 \quad (\text{A1.13})$$

Herschel-Bulkely model: $\tau_c^* = \tau_b^* \cdot (r_c(\varepsilon) / r_b)^{-2} = \tau_c^{*''} = 1 + [\dot{\gamma}_c'' / (\text{He} \cdot \Omega)]^n$

Eq. (A1.11) becomes:

$$\text{error}(\dot{\gamma})\% = \left[\frac{1}{\text{He} \cdot \ln \varepsilon \cdot (\tau_b^* \cdot (r_c(\varepsilon) / r_b)^{-2} - 1)^{1/n}} - 1 \right] \times 100 \quad (3.14)$$

In general, the error derived from using the r_c method depends on the given radius ratio and the yield number. For the error determination on shear rate (at a given shear stress $\tau_c = \tau_b \cdot (r_c(\varepsilon) / r_b)^{-2}$), the τ_b^* has to be determined. The shear rate is usually overestimated, which is similar to that shown in Fig. 3.12. An example is shown here to calculate the error for Casson model. Using flow conditions of $\varepsilon=1.2$ and $\text{Ca}=100$, flow is shown to be at fully sheared condition according to Eq. (3.41). From Eq. (3.51), $r_c(\varepsilon) / r_b = 1.092$. Therefore, the error for shear rate can thus be calculated by substituting $\tau_b^* = 1.796$ (from Eq. (3.22)) into Eq. (A1.13) which gives an error of 6.226%.

Appendix 2

Simulation result for flow at steady state

The parameters used in the simulation in Fig. 3.4, Fig. A2.1 and Fig. A2.2 are

$$\begin{array}{ll} \tau_{y_0} = 50 & \mu_o = 1.0 \\ \tau_{y_e} = 10 & \mu_e = 0.1 \end{array}$$

For Bingham, Casson and Herschel-Bulkley models, the dimension for τ_{y_0}, τ_{y_e} is Pa. The dimension for μ_o, μ_e is Pa.s for Bingham and Casson models. However for the Herschel-Bulkley model the power law index $n=0.5$ is used, so the dimension for the μ_o, μ_e is Pa.s^{0.5} in this case.

A simple structure parameter is assumed as follows:

$$\lambda = \frac{\tau_y(t) - \tau_{y_e}}{\tau_{y_0} - \tau_{y_e}} = \frac{\mu(t) - \mu_e}{\mu_o - \mu_e} \quad (\text{A2.1})$$

the decay of the structure is also assumed to follow a first order kinetic:

$$-\frac{d\lambda}{dt} = k \cdot (\lambda - \lambda_e) \quad \text{where: } k = 0.005(1/s) \quad (\text{A2.2})$$

At $\tau_y(\infty) = \tau_{y_e}$, $\mu(\infty) = \mu_e$ and $\lambda(\infty) = \lambda_e$ as $t \rightarrow \infty$.

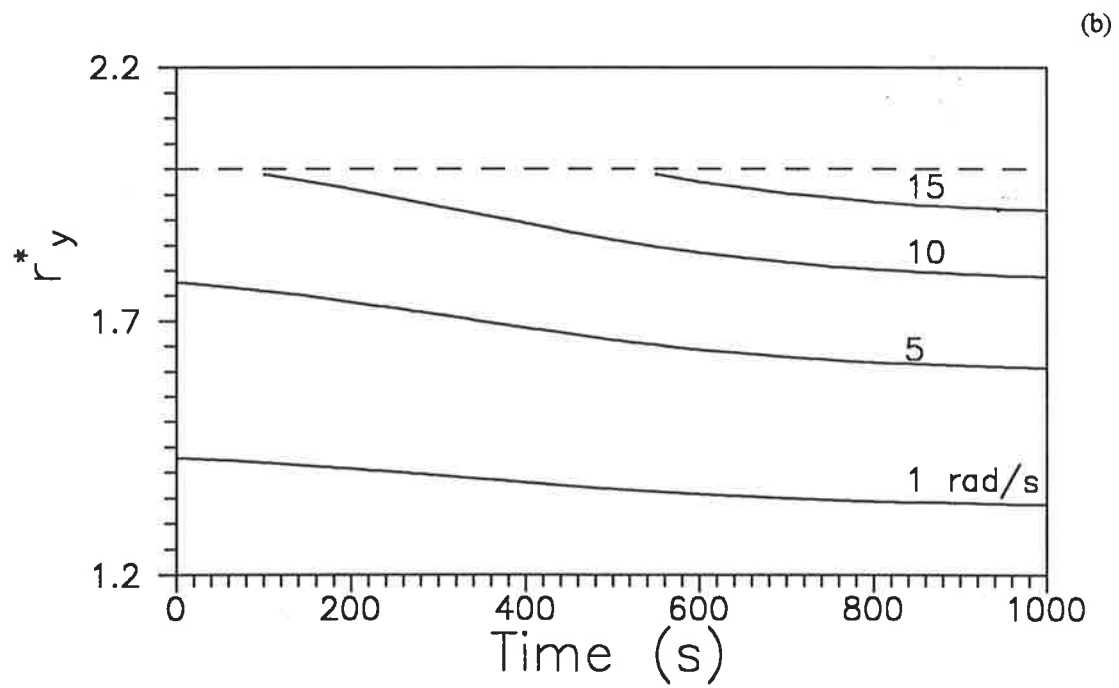
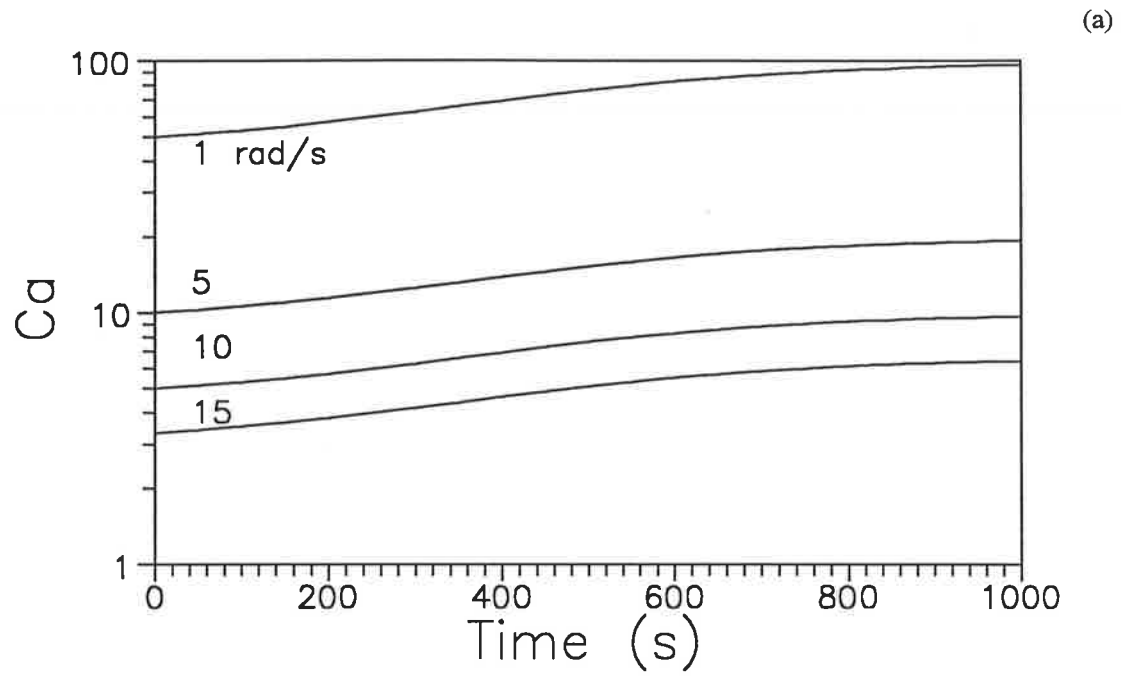


Fig. A2.1 The change of flow behaviour for thixotropic fluid of Casson model at $\epsilon=2.0$. (a) Yield number (b) Yield boundary.

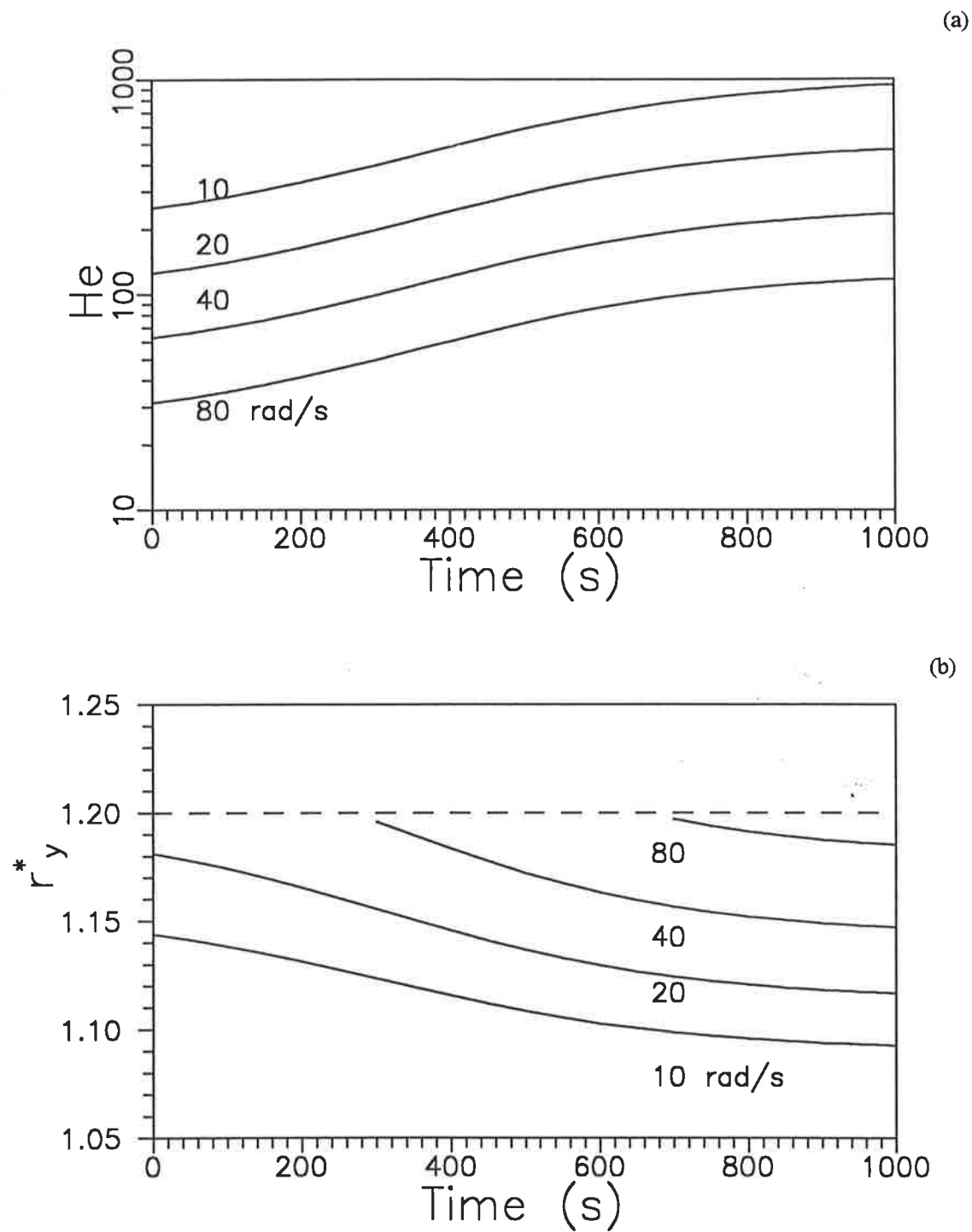


Fig. A2.2 The change of flow behaviour for thixotropic fluid based on Herschel-Bulkley model at $\epsilon=1.2$. (a) Yield number (b) Yield boundary.

Appendix 3

Simulation Result for Casson and Herschel-Bulkley Fluids at Unsteady State Conditions

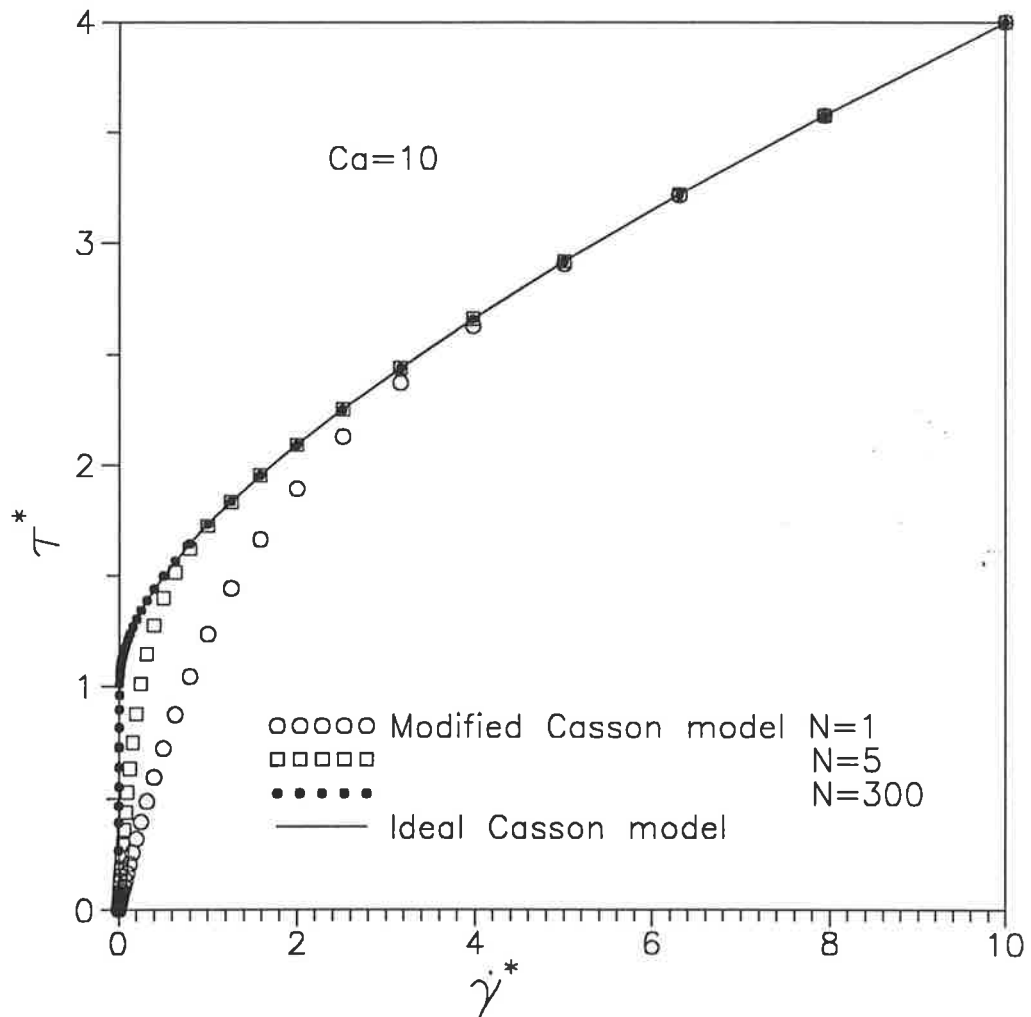


Fig. A3.1 Comparison of the ideal Casson model and the modified Casson model with different values of N .

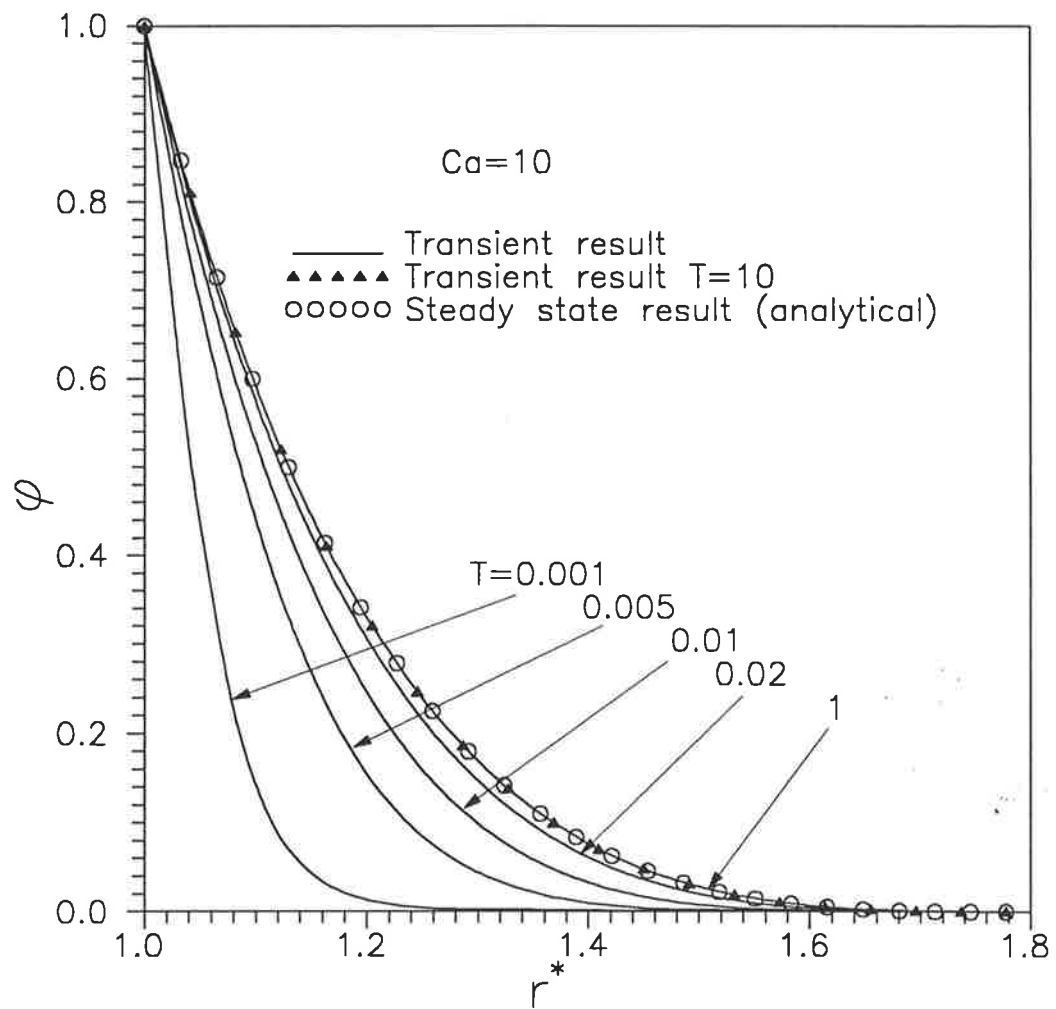


Fig. A3.2 Velocity profile at different time. The transient results were simulated from the modified Casson model; while the steady state results were obtained analytically from the ideal Casson model.

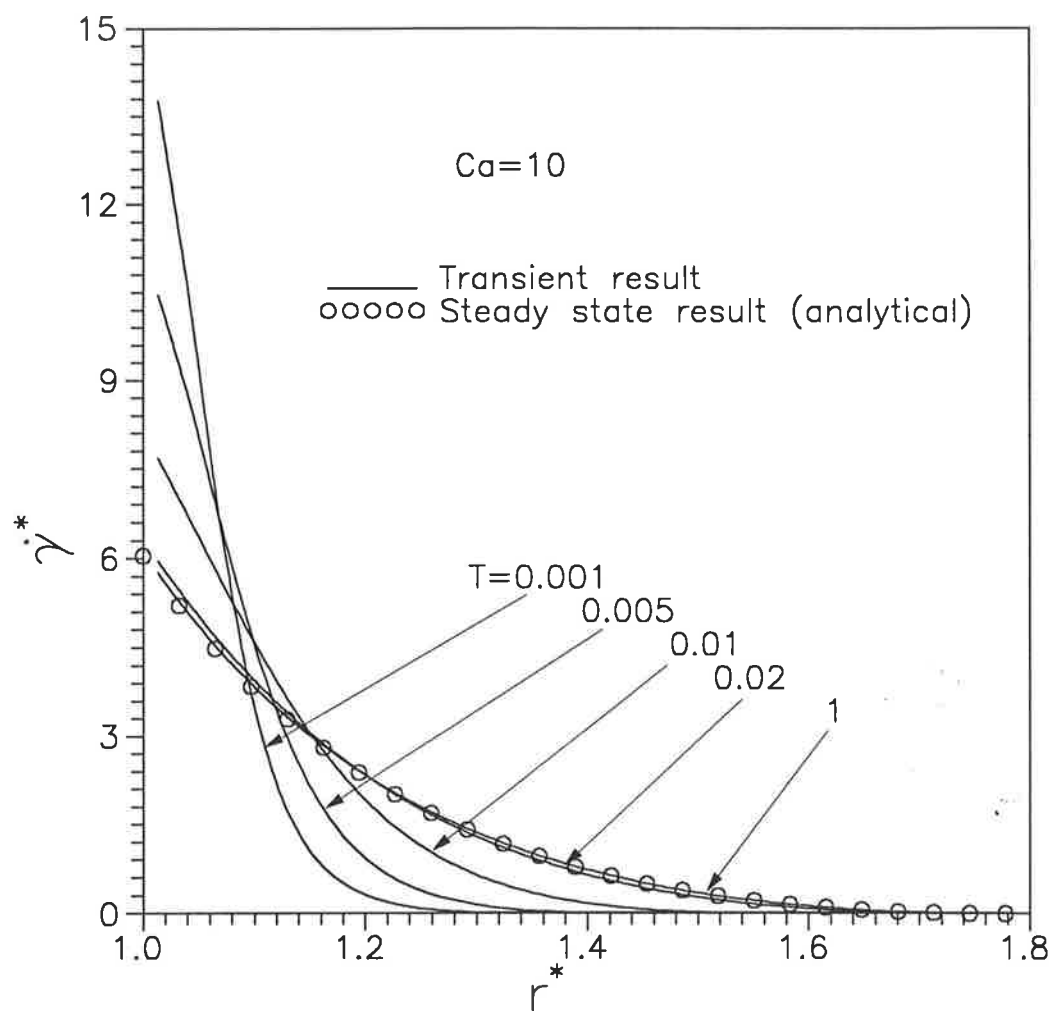


Fig. A3.3 Shear rate profile at different time. The transient results were simulated from the modified Casson model; while the steady state results were obtained analytically from the ideal Casson model.



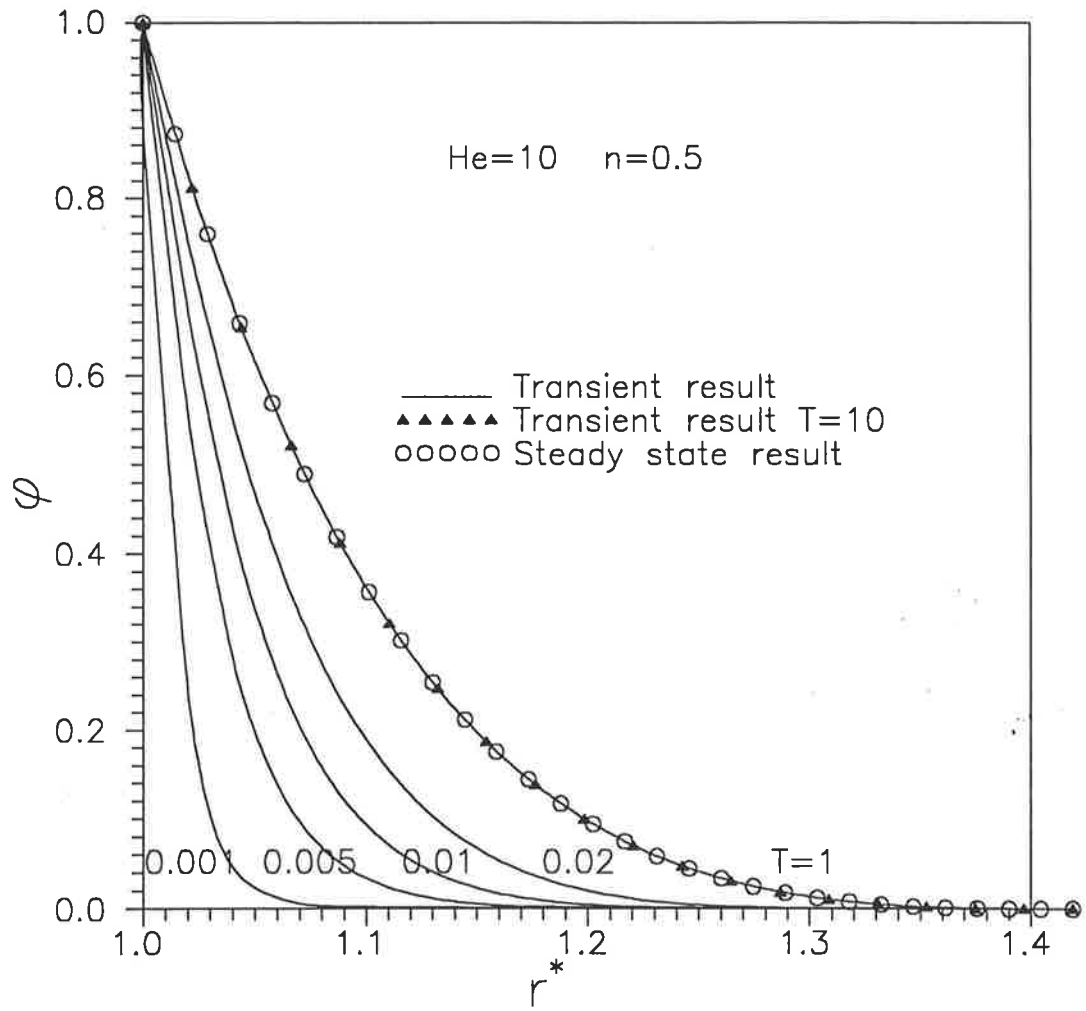


Fig. 3.5 Velocity profile at different time. The transient results were simulated from the modified Hershel-Bulkley model; while the steady state results were obtained from the ideal Hershel-Bulkley model.

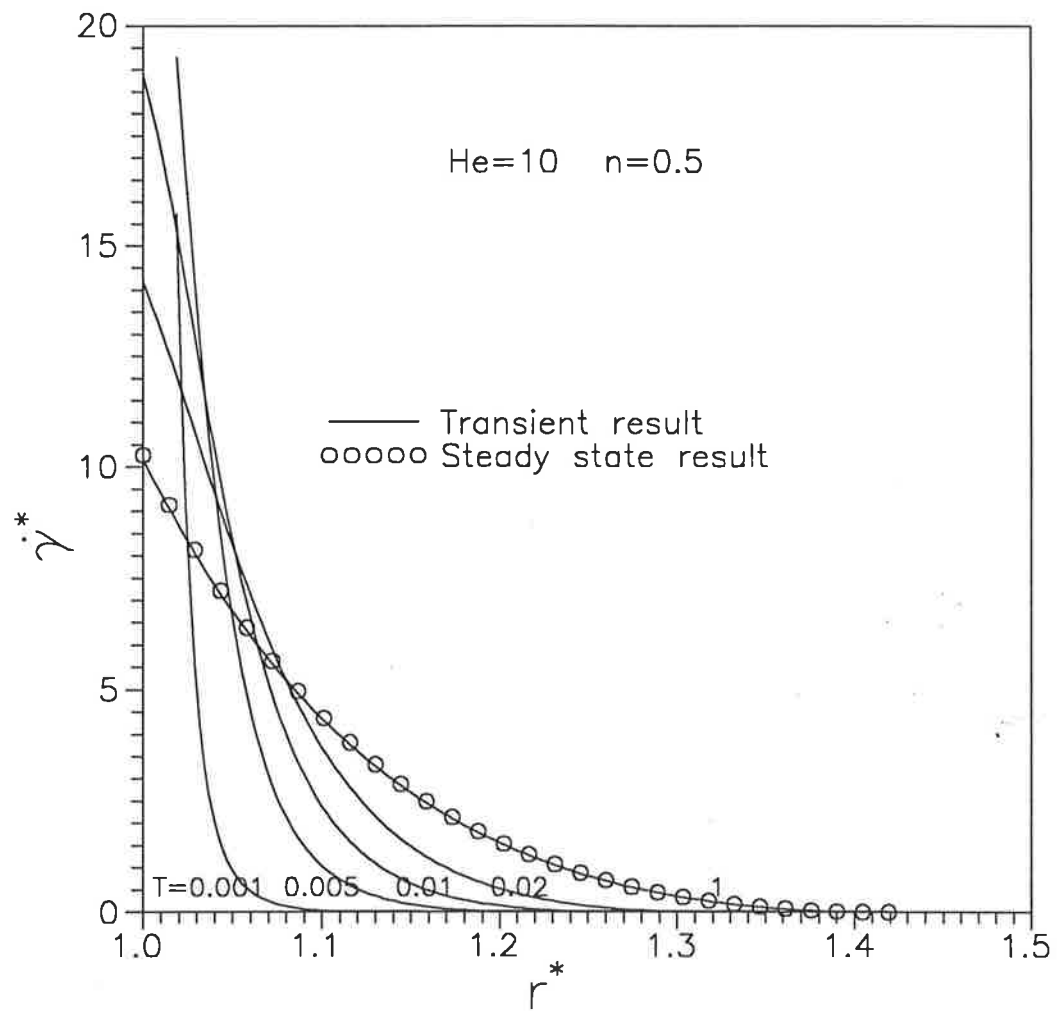


Fig. A3.6 Shear rate profile at different time. The transient results were simulated from the modified Herschel-Bulkley model; while the steady state results were obtained from the ideal Herschel-Bulkley model.

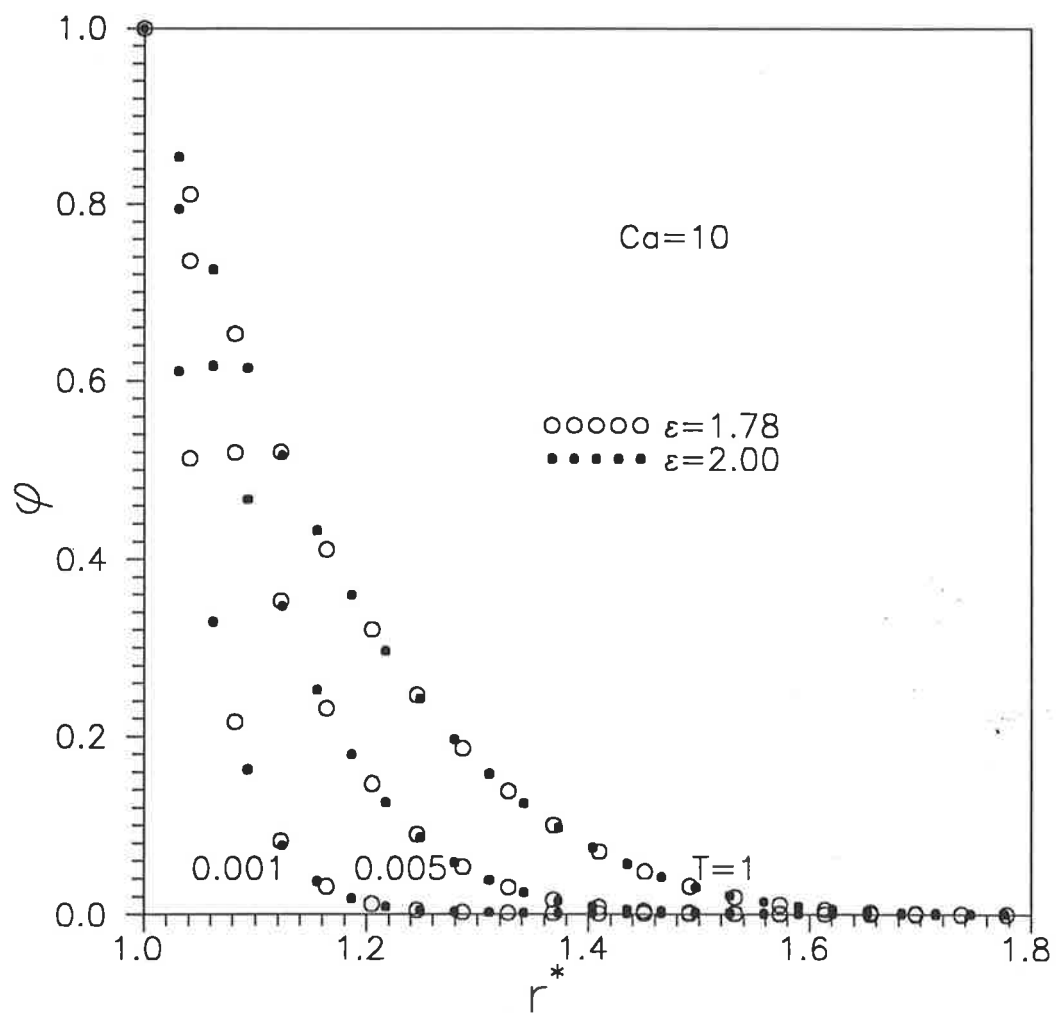


Fig. A3.7 Velocity profile at different time for the modified Casson model, in which different radius ratios were used for boundary condition.

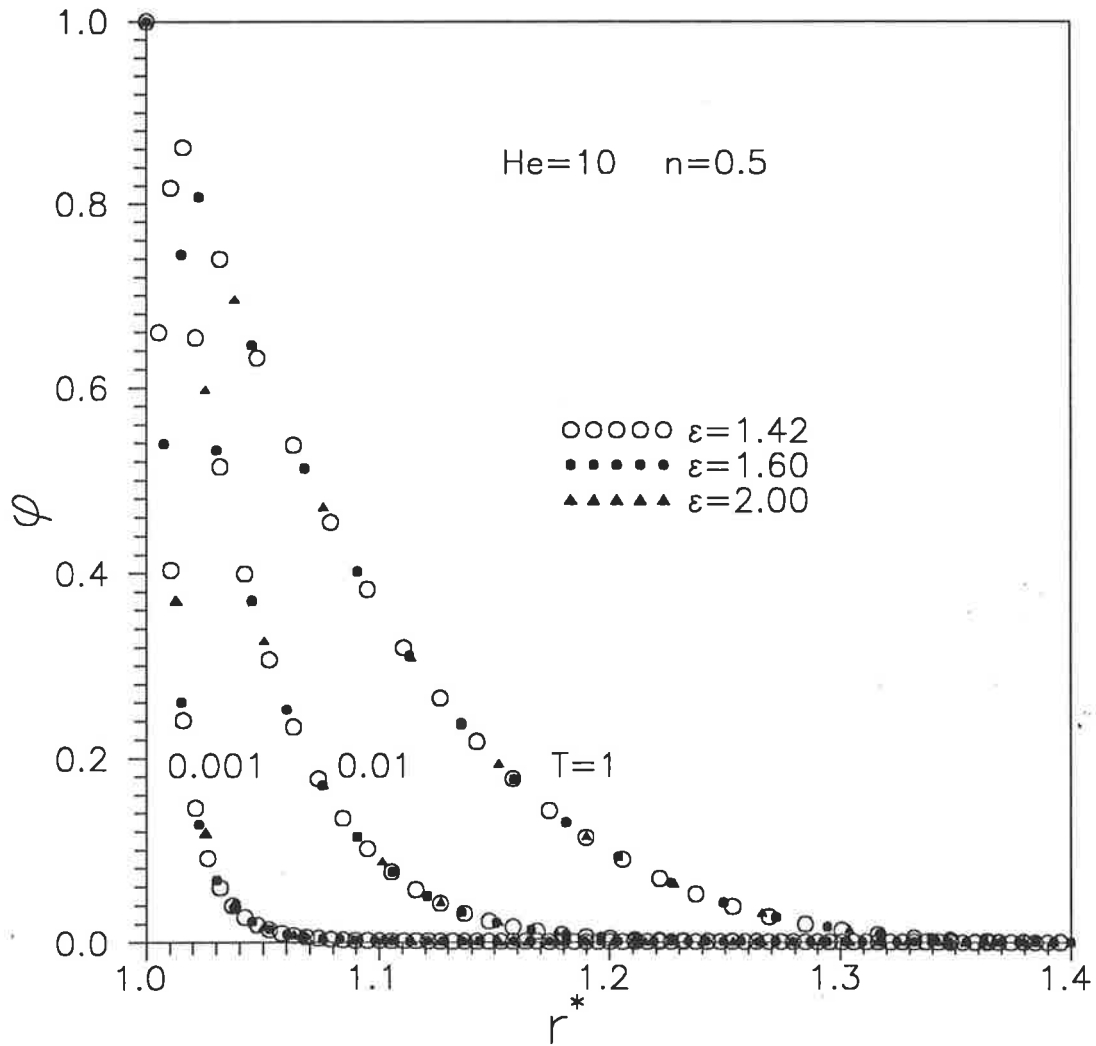


Fig. A3.8 Velocity profile at different time for the modified Herschel-Bulkley model, in which different radius ratios were used for boundary condition.

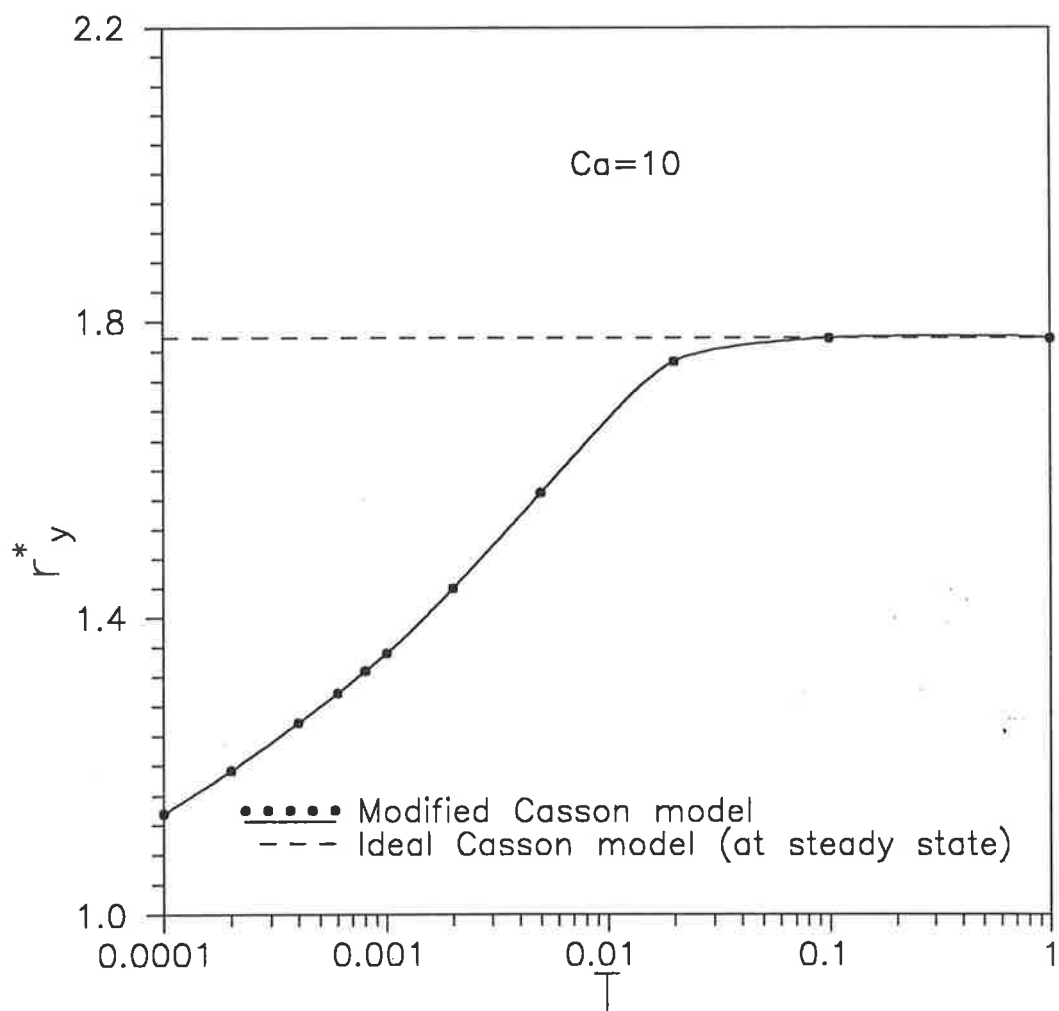


Fig. A3.9 The transient behaviour of yield boundary for the modified Casson model.

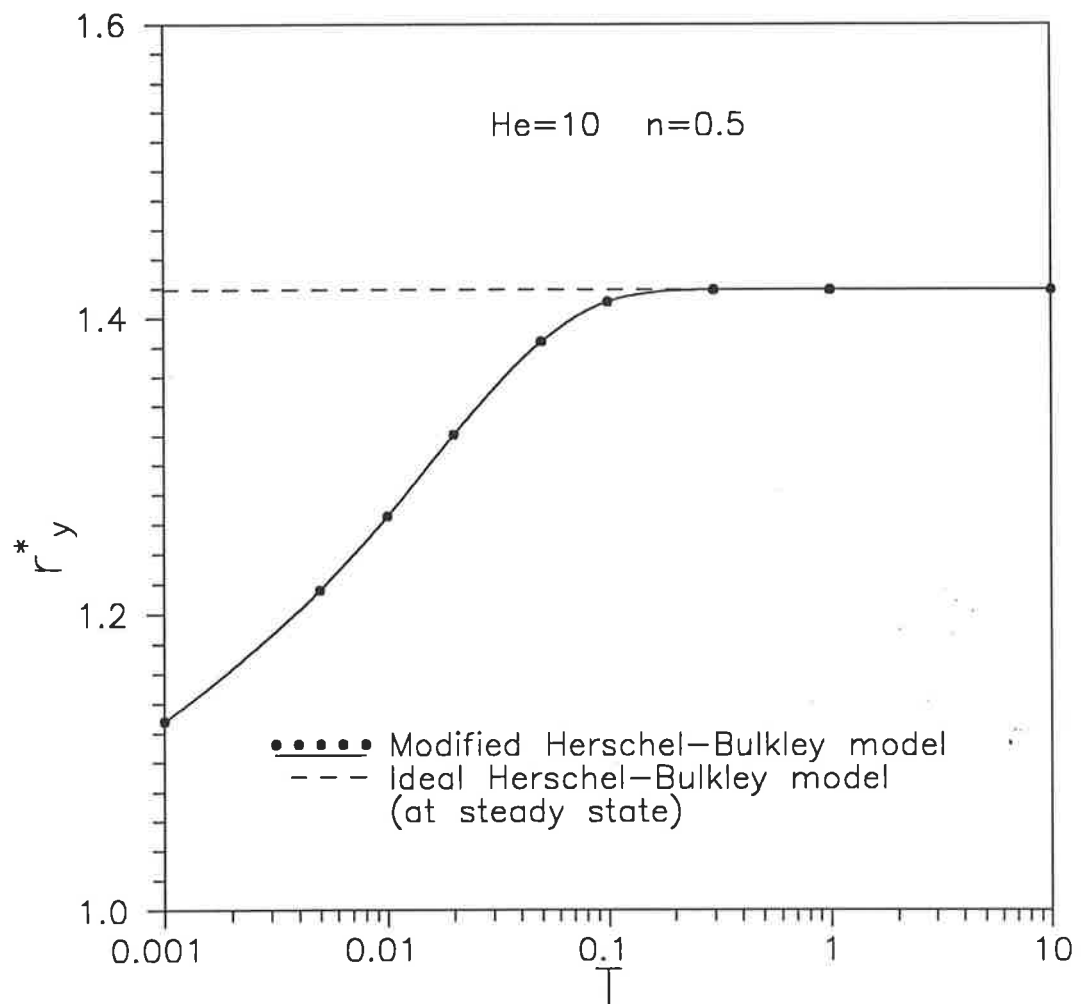


Fig. A3.10 The transient behaviour of yield boundary for the modified Herschel-Bulkley model.

Appendix 4

Brief Description of the Programming Procedures

The radius increment is taken as arithmetic series:

$$r_i / R = 1 + (\text{boundary} - 1) \cdot (i - 1) / (I - 1)$$

while geometric series for the time as the change of flow behavior is much slower in the later time:

$$t_j = \Delta t \cdot (\text{base})^{j-1}$$

the incremental base value is defined as: $\text{base} = (t_{\max} / \Delta t)^{1/(I-1)}$, where $t_{\max}$ is the maximum time value specified by the user; and Δt is the first incremental time step.

Computational Program Structure:

For the initial time step $j = 0$; $t_j = 0$; The initial fluid parameters and flow conditions are defined as:

$$\begin{array}{lll} v_{i,0} = 0; & \dot{\gamma}_{i,0} = 0; & H_0 = 1; \\ \mu_o; & \tau_{yo}; & Bi_0; & \lambda_0 = 1. \end{array}$$

and then the simulation is advanced to the time step $j = 1$. The simulation follows below description.

The flow behaviour in the current time step is simulated based on the values of the parameters at the last time. The following computational steps are followed:

1. Fluid parameters and flow conditions at time step $j-1$ is known, e.g.

$$\begin{array}{llll} v_{i,j-1}; & \dot{\gamma}_{i,j-1}; & H_{j-1}; & \\ \mu(t_{j-1}); & \tau_y(t_{j-1}); & Bi_j; & \lambda_{j-1}. \end{array}$$

2. The values of fluid parameters and flow condition for the time t_j step are guessed from that of last time step $j-1$, e.g.

$$\mu(t_j)(\text{guess}) = \mu(t_{j-1}); \quad \tau_y(t_j)(\text{guess}) = \tau_y(t_{j-1});$$

$$Bi_j(\text{guess}) = Bi_{j-1} \quad H_j(\text{guess}) = H_{j-1}$$

3. Velocity profile, $\phi_{i,j}$, for time step j is calculated from the above guessed values by Eq. (4.24) with the initial condition at time $= t_{j-1}$; $\phi_{i,j-1}$.
4. New shear rate, $\bar{\gamma}_{i,j}^*$, are calculated at time step j with $\phi_{i,j}$ and Eq. (4.3); and H_j can be determined by checking $\bar{\gamma}_{H-1,j}^* < \dot{\gamma}_y^* < \bar{\gamma}_{H,j}^*$; and r_y^* can be determined by interpolation method between r_{H-1} to r_H as shown in Eq. (4.18).
5. λ_j is determined from Eq. (4.32). Consequently $\tau_y(t_j)$, $\mu(t_j)$ and Bi_j can be determined by Eq. (4.20) and Eq. (4.33).
6. $ERR = |Bi_j - Bi_j(\text{guess})| / Bi_j$. If $(ERR \leq \text{Tolerance})$ (where Tolerance is specified by user), then the procedures are repeated starting from step (1) and the flow at the next time step $j=j+1$ is calculated.

If the above conditions are not satisfied then the updated values become the guessed values as shown below, and the calculations continue from step (3) again:

$$\mu(t_j)(\text{guess}) = \mu(t_j); \quad \tau_y(t_j)(\text{guess}) = \tau_y(t_j);$$

$$Bi_j(\text{guess}) = Bi_j; \quad H_j(\text{guess}) = H_j.$$

The calculation is terminated when the time step j reaches J , which is set by the user.

Parameters:

$$\tau_{yo} = 50 \text{ (pa)} \quad \rho = 1000 \text{ (kg / m}^3\text{)}$$

$$\tau_{ye} = 10 \text{ (pa)} \quad r_b = 1.0 \text{ (m)}$$

$$\mu_o = 1.0 \text{ (Pa.s)} \quad \Omega = 5 \text{ (rad/s)}$$

$$\mu_e = 0.1 \text{ (Pa.s)}$$

Values used in the numerical simulation:

$$I = 30; \quad J = 25;$$

$$t_{\max} = 1000 \text{ (Sec.)}; \quad \Delta t = 1 \text{ (sec)};$$

$$\text{Tolerance} = 1\% \quad \text{boundary} = 1.36$$

Appendix 5

Homogeneity of the prepared suspension

This experimental result illustrates the consistency and homogeneity of the freshly prepared suspension stock at a given batch. The following is the 10 wt% Bentonite suspension (After mixing and resting two days) in a diameter of 22.5 cm container. A scheme was proposed to designate different positions on the suspension surface which would be tested as shown in Fig. A5.1 A vane (high: 1.5cm, diameter: 1cm) was used to measure the torque at each specified location. The rigid boundaries of the container should not affect the measurement in the current experimental condition according to Nguyen and Boger (1983 and 1985)

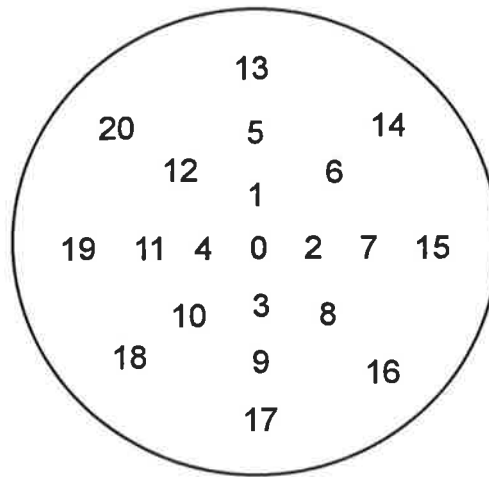


Fig. A5.1 Schematic picture showing the different location index s in a suspension surface to be tested using a vane.

According to the equation of yield stress determination (Nguyen & Boger 1985), the measured value of maximum torque is proportional to the value of the yield stress: $M_s \propto \tau_{y,s}$ for a given vane. So the expression for dimensionless yield stress can be determined by:

$$\frac{\tau_{y,s}}{\bar{\tau}_y} = \frac{M_s}{\bar{M}_s} \quad (A5.1)$$

In which the $\bar{M}_s$ and $\bar{\tau}_y$ are the average value of measured maximum torque and the average value of yield stress. And the $\bar{M}_s$ has been obtained by:

$$\bar{M}_s (\text{Ncm}) = \frac{\text{Summation of the torque in each locations } (\sum M_s)}{\text{The total number of the locations}} \quad (A5.2)$$

Table A5.1 The maximum torque and dimensionless yield stress values at different measured positions

s	$M_s (\text{Ncm})$	$\tau_{y,s} / \bar{\tau}_y$	s	$\bar{M}_s (\text{Ncm})$	$\tau_{y,s} / \bar{\tau}_y$
0	2.14	1.05	11	2.07	1.01
1	2.03	0.99	12	2.08	1.02
2	1.98	0.97	13	2.02	0.99
3	2.06	1.01	14	2.11	1.03
4	2.16	1.05	15	2.08	1.02
5	1.92	0.94	16	2.10	1.03
6	1.96	0.96	17	2.07	1.01
7	1.96	0.96	18	2.05	1.00
8	2.12	1.03	19	2.01	0.98
9	1.94	0.95	20	2.13	1.04
10	1.96	0.96			

$$\bar{M}_s = 2.045 (\text{Ncm}); \text{ with a standard deviation of } \pm 0.070 (\text{Ncm})$$

No clear trend for the yield stress variation with different positions of the suspension. The variation is small and appears to be random.

Appendix 6

The change of suspension pH with time and concentration.

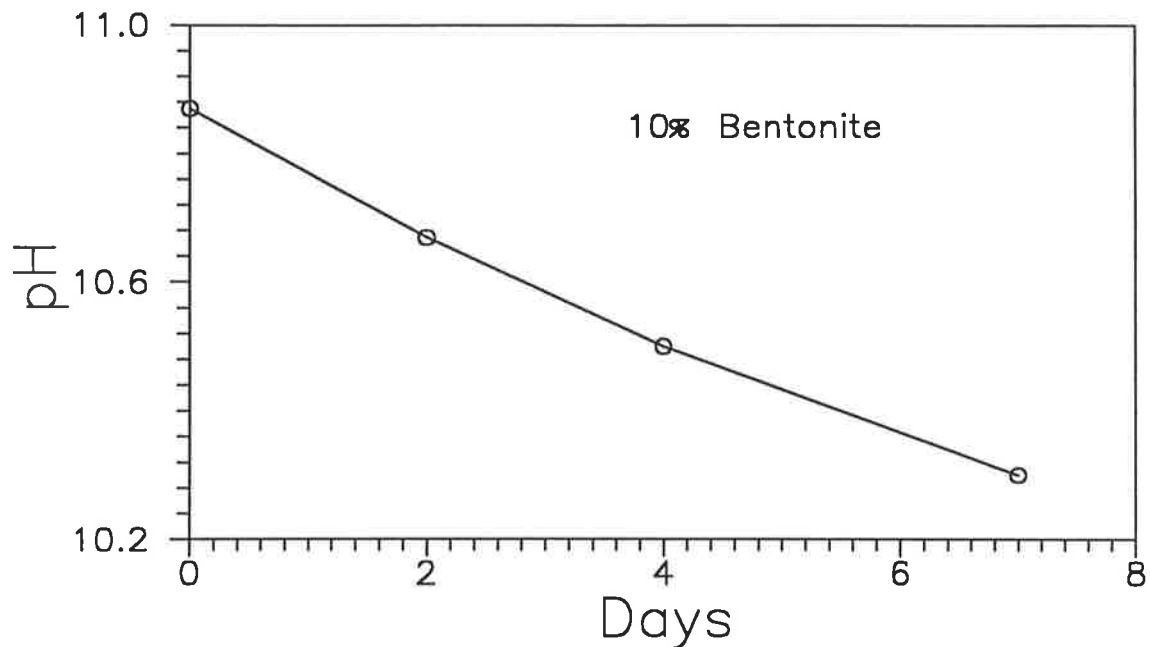


Fig. A6.1 The change of pH with resting time in days for 10% bentonite suspension.

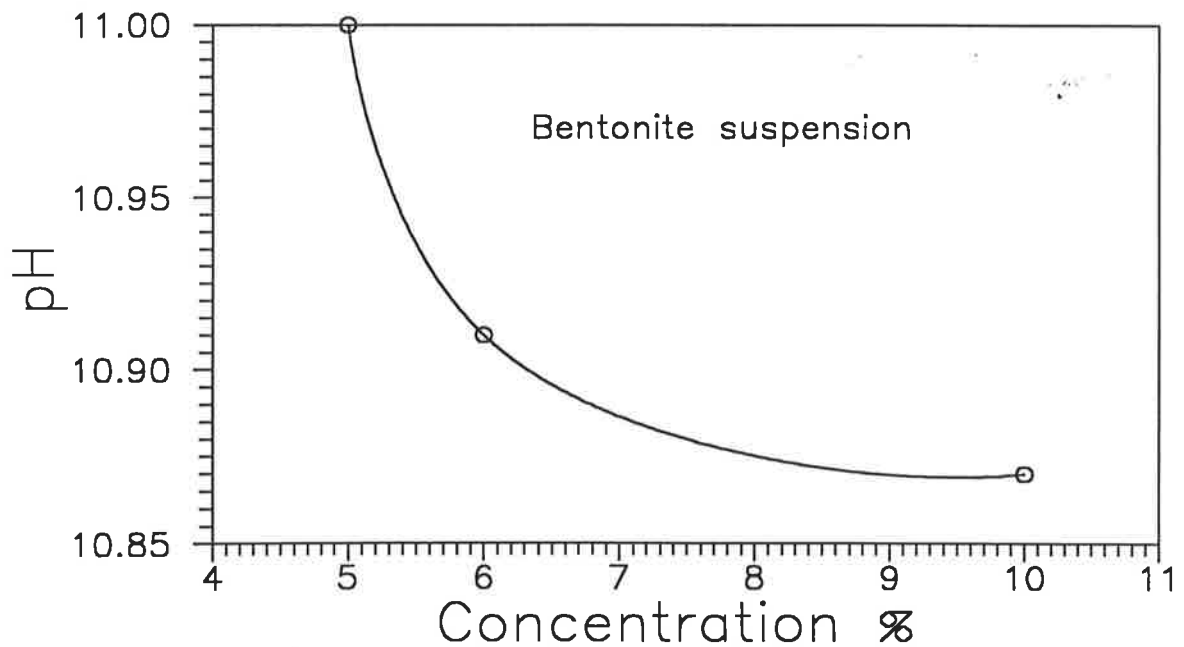


Fig. A6.2 The change of pH with suspension concentration for bentonite. pH was measured at the time just after the suspension had been prepared and it was determined in the suspension.

Appendix 7

Property of Bentonite suspension

Notations:

1. The measurement was carried out 2 days after the suspension had been made.
2. * indicates sedimentation appeared after 2 resting days.
3. The time-dependent behaviour of the suspensions was tested in a concentric cylinder viscometer by recording the shear stress decay with time under a constant shear rate. The "Rheopexy" indicates that the shear stress showed a increasing trend with time, while the "Thixotropy" means that the shear stress showed a decreasing trend with time (Olphen 1963) under a given condition in the following tables. However, the reason of why the suspension showed a behaviour of "Rheopexy" or "Thixotropy" under that given condition remains unclear in term of micro-structure theory, which is beyond the scope of this study.

Table A7.1 Bentonite in HCl water suspension

% Bentonite (w/w)	HCl (Molar)	pH (Suspension)	pH (Liquid)	Yield stress (Pa) (Vane method)	Yield stress (Pa) (Residual)	Yield stress (Pa) (Bingham model)	Time dependent
20	0.008	9.8	9.5	179.6	53.1	164.2	Rheopexy
20	0.010	9.7	9.6	62.0	9.02	61.1	Rheopexy
20	0.012	9.5	9.4	22.8	3.22	35.8	Rheopexy
20 *	0.016	8.8	8.8	/	/	/	Rheopexy
20 *	0.032	7.6	7.4	/	/	/	Rheopexy

Table A7.2 Bentonite in NaCl water suspension

% Bentonite (w/w)	NaCl (Molar)	pH (Suspension)	pH (Liquid)	Yield stress (Pa) (Vane method)	Yield stress (Pa) (Residual)	Yield stress (Pa) (Bingham model)	Time dependent
30	0.2	10.1	9.9	566.6	274.3	597.1	Rheopexy
30	0.3	10.1	9.9	120.2	41.5	131.5	Rheopexy
30 *	0.4	9.6	9.4	/	4.51	21.7	Rheopexy
20	0.2	10.3	10.1	110.8	40.0	110.4	Rheopexy
15.4	0.05	10.6	10.4	362.6	144.9	349.5	Rheopexy
7	0.006	10.8	10.6	57.2	28.6	58.1	Thixotropy
8	0.006	10.5	10.3	83.5	46.4	87.9	Thixotropy
8	0.01	10.5	10.3	69.0	32.5	73.1	Thixotropy (weak)
8	0.02	10.5	10.3	53.4	20.8	55.0	Neutral (approximate)
8	0.03	10.5	10.3	36.4	12.4	37.4	Rheopexy

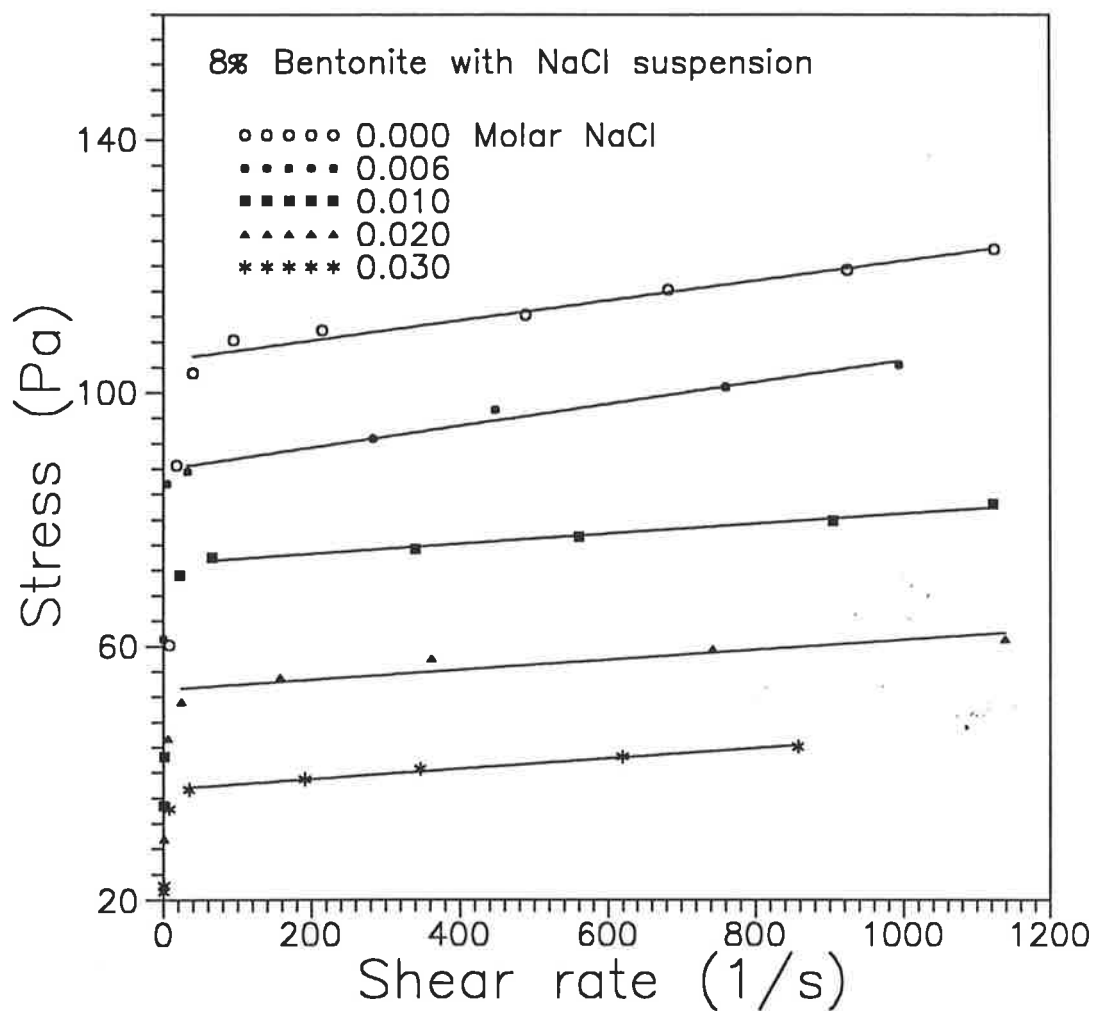


Fig. A7.1 Flow curves of 8 wt% bentonite suspension with NaCl. Experiments were carried out using single bob shearing in a wide radius container (partially sheared condition) after two days the suspension had been made. Step-change-in speed method was used. Shear rate was evaluated with the method suggested by Nguyen & Boger (1987).

Appendix 8

Image Analysis Procedure

The steps involving the measurement of the yield boundary progression using the image analyzer software "BOB.EXE" are described below:

- Setting up the video/computer system;
- Enter program parameters such as filename, bob radius etc.;
- Perform dimension calibration i.e. number of pixels per unit length in mm;
- Locate bob boundary and compute the relative bob center position;
- Start the measurement from tape;
- Continuously locate the boundary by using the mouse cursor (cross-hair). The time and the coordinates of the yield boundary were computed and recorded on computer.

Similar procedures were performed on the same experiment many times to obtain many data for better statistical results.

Error Estimation for Yield Boundary Measurement

The error in the determination of the yield boundary location can come from various sources, namely: (1) instability of the rotating bob; (2) human judgment on the video screen; (3) optical distortion; (4) accuracy of equipment placement such as horizontal and vertical alignment of the equipment; (5) vibration from surrounding and (6) other unknowns. At present, it is only possible to quantify the extent of error due to factors (1) and (2). Sources of error resulting from factors (3) to (6) were minimized if possible during all the experimental runs.

In the following, a combined error, ΔE , due to the factors (1) and (2) is estimated (i.e. $\Delta E = \Delta E_1 + \Delta E_2$) for the purpose of establishing the extent of accuracy using this method. Uncertainty due to bob rotation instability and vibration, ΔE_1 , has been tested and reported to

be about 0.040 mm. The error from human judgment on video screen can be estimated by $\Delta E_2 = (\Delta e / e) \cdot E$. Where Δe is the uncertainty in boundary detection using the mouse cursor on the video screen (in pixels) and e is the total number of pixels across the video screen (i.e. 512 pixels). E represents the true dimension of the image occupying the entire video screen. The uncertainty of Δe was 4 pixels which corresponded to about 3 mm on the video monitor screen. E depends on the magnification of the image. The following Table A8.1 tabulates the combined error ΔE for different suspensions. Also presented in the table are the ranges of the measured yield layer for different suspensions and the corresponding expected errors of the measurement (i.e. $\Delta E / \text{Measured yield layer}$) which range from 1.3 % to 18.3 %. The expected error is general larger for the smaller value of yield layer. It is shown that the Mayonnaise suspension has the smallest measurement error compared to the other suspensions.

Table A8.1 Estimation of error associated with yield boundary measurement.

Suspension	E (mm)	ΔE_1 (mm)	ΔE_2 (mm)	ΔE (mm)	Measured yield layer (mm)	Expected error (%)
Mayonnaise	50	0.04	0.39	0.43	12.02 ~ 32.06	3.6 ~ 1.3
Kaolin	23	0.04	0.18	0.22	1.20 ~ 5.01	18.3 ~ 4.4
Bentonite	12	0.04	0.09	0.13	1.10 ~ 7.67	11.9 ~ 1.7

Appendix 9

Fitting parameters for the Fig. 6.16

Table A9.1 Rate constant as a function of shear rate for 53.3% kaolin suspension by assuming $k = k_{ty} = k_{\mu}$.

shear rate (1/s)	k (1/s)	correlation
33.5	0.00110	0.9461
99.0	0.00125	0.9982
167	0.00141	0.9930
235	0.00156	0.9940

Linear fit of rate constant and shear rate in Table A9.1 is: $k = 2.290 \cdot 10^{-6} \dot{\gamma} + 1.024 \cdot 10^{-3}$

Table A9.2 Rate constant as a function of shear rate for 53.3% kaolin suspension by assuming $k = k_{ty} = 0.5k_{\mu}$.

shear rate (1/s)	k (1/s)	correlation
33.5	0.00106	0.9432
99.0	0.00111	0.9981
167	0.00114	0.9968
235	0.00118	0.9945

Linear fit of rate constant and shear rate in Table A9.2 is: $k = 5.821 \cdot 10^{-7} \dot{\gamma} + 1.001 \cdot 10^{-3}$

Table A9.3 Rate constant as a function of shear rate for 53.3% kaolin suspension by assuming $k = k_{ty} = 0.25k_{\mu}$.

shear rate (1/s)	k (1/s)	correlation
33.5	0.00093	0.9517
99.0	0.00095	0.9970
167	0.00095	0.9974
235	0.00094	0.9953

Linear fit of rate constant and shear rate in Table A9.3 is: $k = 9.40 \cdot 10^{-4} \dot{\gamma}$

Appendix 10

Constant time flow curves

In general, the values of yield stress and viscosity should not be obtained from the group of "constant time flow curves", as theoretically the shear stress-shear rate pairs of data on each individual "constant time flow curve" are not based on one constant structure. This could be done only when the group of "constant time flow curves" overlapping with the "constant structure flow curves", which are at the following two conditions: (a) the decay rate constants k for the yield stress and viscosity are not a function of shear rate; and (b) the equilibrium structure level is not dependent on the shear rate. In general case, the structure level depends not only on length of time the suspension being sheared but also on the magnitude of the shear rate which is applied to the fluid. In addition, it should be clear that, the stress values at a specified time, for different constant shear rate curves, are the consequence of different state of structure. Godfrey (1973) showed that the "constant time flow curve" (called "isochronous flow curves" in his paper) is different from the "constant structure flow curve".

For instance, if the rate constant k is expressed as a simple linear function of shear rate ($k = a \cdot \dot{\gamma} + b$), then the yield stress (Eq. (6.6)) of a suspension at a given time t after being sheared by two different shear rate conditions, say $\dot{\gamma}_1$ and $\dot{\gamma}_2$ can be expressed as follows:

$$\tau_y(t) = \tau_{ye} + (\tau_{yo} - \tau_{ye}) \cdot [1 + (a\dot{\gamma}_1 + b)t]^{-1} \quad \text{at } \dot{\gamma}_1 \quad (\text{A10.1})$$

$$\tau_y(t) = \tau_{ye} + (\tau_{yo} - \tau_{ye}) \cdot [1 + (a\dot{\gamma}_2 + b)t]^{-1} \quad \text{at } \dot{\gamma}_2 \quad (\text{A10.2})$$

Obviously, if the value of a is finite; or/and the equilibrium yield stress depends on the history shear rate, then mathematically the yield stress expressed in Eqs (A10.1) and (A10.2) will be different under different shear rate conditions. Similar argument is also applied to the viscosity term in Eq. (6.7).

Work has been conducted to extract the "constant time flow curve" data from the stress decay curve for Kaolin suspension (53.3 wt%) (Fig. 6.4) at some given time using the interpolation method described above. The result is shown in Fig. A10.1. The data fitted with a "constant time flow curve" with Casson model are:

$$t=0 \text{ (Sec)} \quad \tau^{1/2} = 147.7^{1/2} + 0.0401^{1/2} \dot{\gamma}^{1/2} \quad (\text{A10.3})$$

$$t=500 \quad \tau^{1/2} = 148.0^{1/2} + 0.0138^{1/2} \dot{\gamma}^{1/2} \quad (\text{A10.4})$$

$$t=1000 \quad \tau^{1/2} = 146.7^{1/2} + 0.00859^{1/2} \dot{\gamma}^{1/2} \quad (\text{A10.5})$$

$$t=1500 \quad \tau^{1/2} = 142.0^{1/2} + 0.00851^{1/2} \dot{\gamma}^{1/2} \quad (\text{A10.6})$$

$$t=2000 \quad \tau^{1/2} = 140.2^{1/2} + 0.00738^{1/2} \dot{\gamma}^{1/2} \quad (\text{A10.7})$$

$$t=2500 \quad \tau^{1/2} = 138.4^{1/2} + 0.00702^{1/2} \dot{\gamma}^{1/2} \quad (\text{A10.8})$$

In Eqs. (A.10.4)~(A10.8) the viscosity for the Casson model are much lower than the viscosity in the constant structure flow curves for kaolin suspension in Appendix 11, which was obtained with the step-change-in speed (shear rate) experiment. Only Eq. (A10.3) is similar to the initial structure flow curve (in Appendix 11, kaolin suspension, when $\dot{\gamma}_r = 0$). In the set of Eqs. (A10.3~8), only (A10.3) represents the constant initial structure condition.

One problem needs to mention here. When stress decay curve is measured with a concentric cylinder viscometer, a constant rotating speed is usually used for example, in Fig. 6.2~5. Shear stress-speed pairs of data could be obtained at a given time by interpolation method. However, the shear stress-shear rate pairs of data should not be evaluated from the shear stress-speed pairs of data (on the "constant time flow curve", apart at $t=0$) with the method for time-independent fluid, such as the methods developed by Krieger and his co-worker (1952, 1953, 1954, 1968). Because there is a structure variation among the shear stress-speed pairs of data in spite of the same shearing time. In this case, r_c method is most suitable to be used to convert the rotating speed value to the shear rate value.

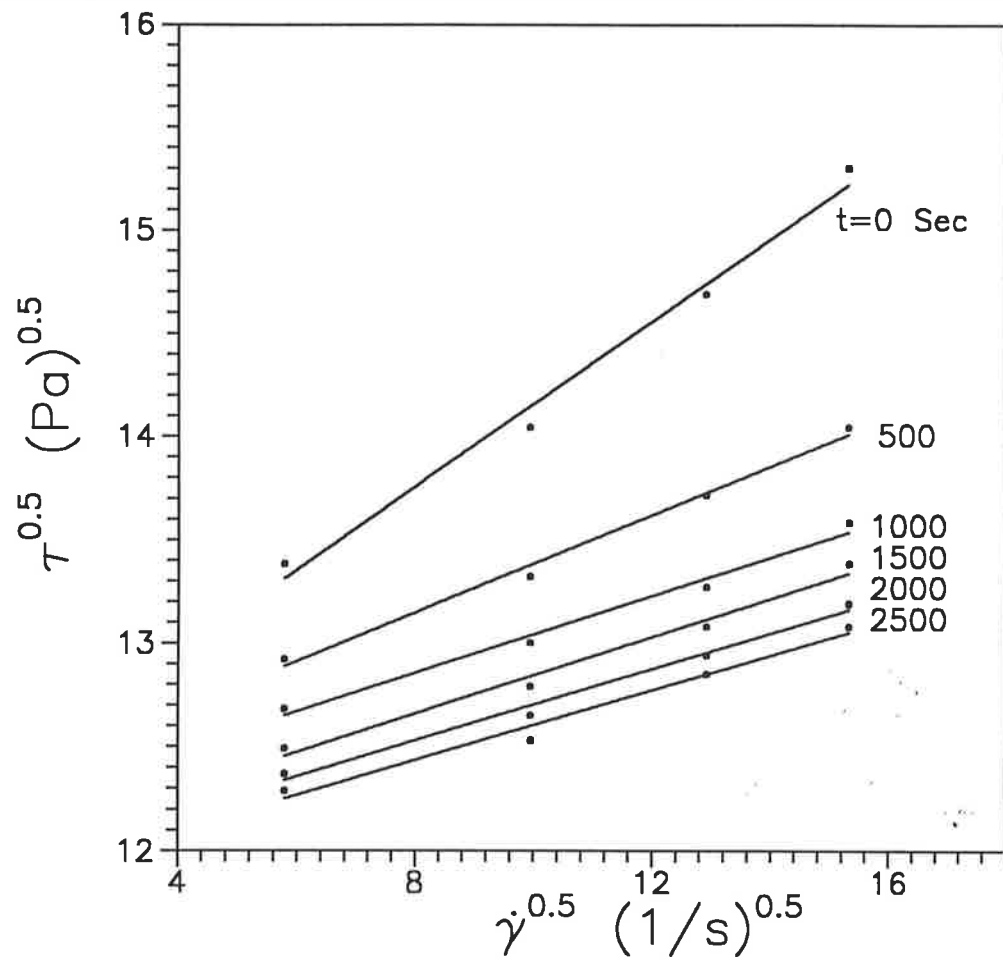


Fig. A10.1 Constant time flow curves for Kaolin (53.3%) suspension. The data was obtained by interpolation method in stress decay curves in Fig. 6.4 when $\varepsilon = 1.048$.

Appendix 11

Function fitting

1. Mayonnaise

In Fig. 6.19, it was found that the Herschel-Bulkey model could fit the constant flow curves well and the best fits are:

reference shear rate (1/s)	flow model	correlation
$\dot{\gamma}_r = 0$	$\tau(0) = 24.77 + 17.48\dot{\gamma}^{0.5}$	0.9966
$\dot{\gamma}_r = 11.2$	$\tau_e = 20.74 + 16.42\dot{\gamma}^{0.5}$	0.9995
$\dot{\gamma}_r = 55.5 \sim 201$	$\tau_e = 18.00 + 15.64\dot{\gamma}^{0.5}$	0.9996

When the reference shear rate range is $55.5 \leq \dot{\gamma}_r \leq 201$ (1/s), the constant structure flow curves are overlapped.

The equilibrium flow model parameters vary with reference shear rate can be obtained from above function, as shown in Figs. 6.20 and 6.21. Model fittings are:

$$\tau_{ye} = 17.9 + 6.91 \exp(-0.0839\dot{\gamma}_r)$$

$$\mu_e = 15.6 + 1.88 \exp(-0.0806\dot{\gamma}_r)$$

In Fig. 6.2 for the stress decay curves can be conveniently described by the following function:

$$\tau = \tau_e + A \cdot \exp(-k_1 \cdot t) + B \cdot \exp(-k_2 \cdot t) \quad (\text{A11.1})$$

The parameters for the above function (A11.1) at different constant shear rate applied are shown in the Table A11.1.

Table A11.1 Parameters of the fitting functions for stress decay curves

Shear rate (1/s)	τ_e (Pa)	A (Pa)	k_1 (1/s)	B (Pa)	k_2 (Pa)	Correlation
11.2	76.9	7.18	0.944	5.07	0.000509	0.9994
55.5	135	7.20	0.0996	7.29	0.00105	0.9995
99.0	175	16.0	0.0157	11.4	0.000638	0.99998
201	238	18.7	0.0108	12.9	0.000452	0.99989

2. Kaolin suspension

For the 53.3 wt% Kaolin suspension, it was found that the Casson model can fit the experimental data of the constant structure flow curve as illustrated in Fig. 6.26.

reference shear rate (1/s)	flow model	correlation
$\dot{\gamma}_r = 0$	$\tau(0)^{1/2} = 145.0^{1/2} + 0.04100^{1/2} \dot{\gamma}^{1/2}$	0.997
$\dot{\gamma}_r = 56.3$	$\tau_e^{1/2} = 112.0^{1/2} + 0.03100^{1/2} \dot{\gamma}^{1/2}$	0.995
$\dot{\gamma}_r = 99.0$	$\tau_e^{1/2} = 109.0^{1/2} + 0.02592^{1/2} \dot{\gamma}^{1/2}$	0.987
$\dot{\gamma}_r = 201$	$\tau_e^{1/2} = 107.0^{1/2} + 0.01814^{1/2} \dot{\gamma}^{1/2}$	0.994

When the reference shear rate $\dot{\gamma}_r$ (up to 400 1/s) is greater than 201 (1/s), the flow curve at equilibrium state did not change any further. So the flow curve at equilibrium state for $\dot{\gamma}_r = 201$ (1/s) might correspond to the lowest structure level which the fluid structure could possibly reach by shearing effect in the current experimental condition.

The equilibrium yield stress and viscosity varies with reference shear rate can be obtained from above data, as shown in Figs. 6.27 and 6.28. Model fittings for the equilibrium yield stress and viscosity are:

$$\tau_{ye} = 107.2 + 37.78 \exp(-0.03573 \dot{\gamma}_r)$$

$$\mu_e = 0.01345 + 0.02751 \exp(-0.008173 \dot{\gamma}_r)$$

In Fig. 6.4 for the stress decay curves, it was found that the same function, e.g. Eq. (A11.1) can fit the flow curves well. The parameters for the equation (A11.1) at different constant shear rate applied are shown in the table A11.2.

Table A11.2 parameters of the fitting functions for stress decay curves.

Shear rate (1/s)	τ_e (Pa)	A (Pa)	k_1 (1/s)	B (Pa)	k_2 (Pa)	Correlation
33.5	142.5	16.7	0.000882	11.1	0.000288	0.961
99.0	138.1	36.9	0.000274	21.7	0.00217	0.994
167	155.5	25.8	0.00552	37.0	0.000561	0.997
235	160.1	32.9	0.00610	42.4	0.000546	0.997

3. Bentonite 8 wt% suspension with 0.006 Molar of NaCl

Similar to the earlier approach used for the mayonnaise and kaolin suspensions, the constant structure flow curves for this suspension are as follows. (see Fig. 6.33):

reference shear rate (1/s)	flow model	correlation
$\dot{\gamma}_r = 0$	$\tau(0) = 87.91 + 0.01714\dot{\gamma}$	0.989
$\dot{\gamma}_r > 0$	$\tau_o = 74.35 + 0.005960\dot{\gamma}$	0.715

In the above, the reference shear rate $\dot{\gamma}_r = 0$ corresponds to the initial structure state.

Appendix 12

Determination of shear stress distribution

The following schematic picture shows the example of a flow curve, and the shear rate distribution. The fluid is being sheared by a rotating bob at a partially sheared condition.

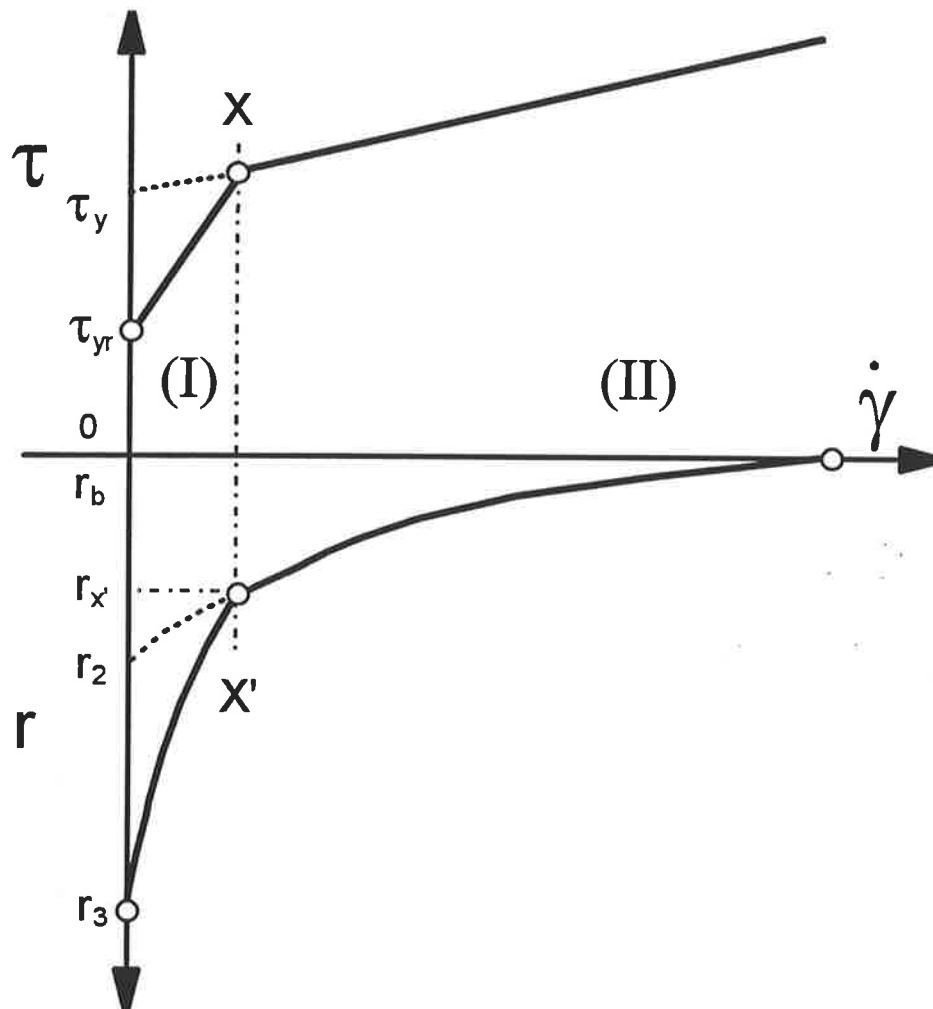


Fig. A12.1 Schematic shows a shear rate distribution at a for a given flow condition.

Assuming that in the low shear rate range (I), the fluid obeys a flow model:

$$(I) \quad \tau_{(I)} = F(\dot{\gamma}_{(I)}); \quad (A12.1)$$

and at the high shear rate range (II), the fluid follows a typical ideal flow model (for example Bingham flow model):

$$(II) \quad \tau_{(II)} = \tau_y + \mu \dot{\gamma}_{(II)} \quad (A12.2)$$

The extrapolated shear rate distribution from region (II) to (I) (i.e. dash line $x' \sim r_2$ in picture) is $\dot{\gamma}'_{(I)}$.

From the relationship of rotation speed (Ω) and shear rate, the following expression is obtained:

$$\Omega = \int_{r_b}^{r_3} \frac{\dot{\gamma}}{r} \cdot dr = \int_{r_b}^{r_x} \frac{\dot{\gamma}_{(II)}}{r} \cdot dr + \int_{r_x}^{r_3} \frac{\dot{\gamma}_{(I)}}{r} \cdot dr \quad (A12.3)$$

If the low shear rate range (I) is narrow (i.e. shear rate data in (I) approach zero) then the following relationship for the second term in Eq. (A12.3) holds:

$$\int_{r_x}^{r_3} \frac{\dot{\gamma}_{(I)}}{r} \cdot dr \xrightarrow{\dot{\gamma}_{(I)} \rightarrow 0} 0 \quad (A12.4)$$

If the following term replaced that in Eq. (A12.4):

$$\int_{r_x}^{r_2} \frac{\dot{\gamma}'_{(I)}}{r} \cdot dr \xrightarrow{\dot{\gamma}'_{(I)} \rightarrow 0} 0 \quad (A12.5)$$

then Eq. (A12.3) becomes:

$$\Omega = \int_{r_b}^{r_3} \frac{\dot{\gamma}}{r} \cdot dr \approx \int_{r_b}^{r_x} \frac{\dot{\gamma}_{(II)}}{r} \cdot dr + \int_{r_x}^{r_2} \frac{\dot{\gamma}'_{(I)}}{r} \cdot dr \quad (A12.6)$$

Substituting the relationship of shear rate with shear stress as well as radius with shear stress (see Chapter 3) for Bingham model (as an example), Eq. (A12.6) can be expressed as:

$$\Omega \approx -\frac{1}{2} \int_{\tau_b}^{\tau_y} \left(\frac{\tau - \tau_y}{\mu \tau} \right) \cdot d\tau \quad (A12.7)$$

So the shear stress τ_b can be solved from Eq. (A12.7) and the shear stress distribution can also be determined subsequently.