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Yield stress measurements in suspensions: an inter-laboratory study

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Abstract

The first international inter-laboratory study, involving six laboratories, has been conducted to examine issues associated with yield stress measurements in suspensions. The initial focus of the project was to evaluate the reliability and reproducibility of several common yield stress measuring techniques employed in different laboratories and with different instruments. Aqueous suspensions of colloidal TiO_2 at concentrations of 40-70 wt% solids were used as the test fluids. A wide range of instruments and techniques employing both direct and indirect methods were used to determine the yield stress of the samples prepared according to a prescribed procedure. The results obtained indicated that although variations of results existed among different techniques, direct yield stress measurements using static methods produced more reliable and repeatable results than other methods. Variability of the yield stress measured using different techniques within any laboratory however was less significant than variability of the results among different laboratories. The nature and condition of the test suspensions was identified as the most likely factor responsible for the poor reproducibility of yield stress measurements from different laboratories.

Keywords : yield stress, suspensions, inter-laboratory study, yield stress measurement

1. Introduction

A strong interest in yield stress fluids in the last two decades has led to developments of a variety of experimental methods and techniques for measuring the yield stress property (Nguyen and Boger, 1992). While each method has its own merits and limitations, and although some techniques may be more popular than the others, no single method has been universally accepted as the standard for measuring the yield stress. Since yield stress measurements are notoriously difficult to interpret, it is not unusual to find variations in the results obtained from different methods with the same material, prepared and tested in the same laboratory (e.g., James *et al.*, 1987; Steffe, 1996; Zhu *et al.*, 2001; Uhlherr *et al.*, 2005). Such variability is often attributed to the differences in the principles employed by different techniques, the definition of the yield stress adopted and the time scale of the measurements involved (Cheng, 1986; Nguyen and Boger, 1992; Barnes, 1999). The variable nature of yield stress measurements has led to a suggestion that an absolute yield stress is an elusive property and any agreement of results from different techniques is accidental (Steffe, 1996; Barnes, 1999). As the first collaborative attempt to examine the issues concerning yield stress measurements, an international round robin exercise involving six laboratories has recently been conducted to evaluate the reliability and reproducibility of several common techniques used for yield stress measurements on identical samples tested in different laboratories and with a variety of instruments. The ultimate aims of this inter-laboratory program are to define the most suitable methods for measuring the yield stress of suspensions; and to produce a reference yield stress fluid that researchers can use to calibrate their instruments or validate their methodology for yield stress determination.

The laboratories participating in the first phase of this round robin program were those of D.V. Boger (University of Melbourne, Australia), P.J. Carreau (Ecole Polytechnique, Montreal, Canada), P. Coussot (Laboratoire des Matériaux et des Structures du Génie Civil, France), D. De Kee (Tulane University, USA), Q.D. Nguyen (University of Adelaide, Australia), C. Tiu (Monash University, Australia), and H. Usui (Kobe University, Japan). A wide range of instruments and techniques employing both direct and indirect methods were used to determine the yield stress of colloidal TiO_2 suspensions, prepared according to a recommended procedure. In this paper, the results collected to date in the first phase of the inter-laboratory study

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are presented, compared and analyzed and the trends emerging from the findings are identified and discussed.

2. Experimental materials and techniques

2.1. Overview

Aqueous suspensions of colloidal TiO_2 particles were selected as test samples for yield stress measurements in the round robin program. Each participating laboratory was provided with the same material in powder form which was acquired commercially by one laboratory and mailed in sealed containers. The participants were requested to prepare their own suspension samples for testing following the recommended protocol described below. The participants had the freedom of using any type of instruments and techniques available in their laboratories to carry out the necessary measurements to determine the yield stress. Details of the experimental conditions and techniques employed by all the round robin participants are summarized in Table 1.

2.2. Test material and preparation

The test suspension samples were prepared from a commercial TiO_2 pigment, Tronox CR-826, purchased from Kerr-McGee Chemical LLC. The solid particles contained 93 wt% TiO_2 with an average particle diameter of 0.2 μm. Aqueous 0.01 M KCl solution was used as the dispersing medium to make up suspensions at two recommended test concentrations of 50 and 60 wt% solids. Mechanical agitation for at least 1 hour was used to disperse the powder in the suspending liquid. The suspension pH was adjusted to 7.0 ± 0.1 by adding HCl or KOH. All measurements were conducted at a constant temperature of 25°C.

2.3. Techniques for yield stress measurements

A total of nine different techniques consisting of both

Table 1. Details on experimental materials and techniques used in the round robin program

Laboratory	Samples tested	Sample preparation	Technique	Instrumentation	Sample conditioning before measurement
Adelaide	TiO_2 suspension 40-60 wt% solids	Mechanical agitation 2 hrs @300 rpm, rested 24 hrs, pH 6.9	Steady-shear measurement Extrapolation	Stress controlled rheometer Bohlin CVO50, vane-cup geometry	Thoroughly mixed for 10 min
			Stress ramp Creep test	Stress controlled rheometer Bohlin CVO50, vane-cup	Presheared at 100 s^{-1} for 5 min
			Vane technique	Rate controlled rheometer Haake RT55, vane device	Thoroughly mixed for 10 min
Kobe	TiO_2 suspension 50-60 wt% solids	Mechanical stirring 1 hr @100 rpm, pH 7.0	Steady-shear measurement Extrapolation	Rate controlled rheometer Iwamoto Seisakusho IR200, cone-plate	Restirred 1 min
			Shear stress ramp	Stress controlled rheometer Rheometric SR-5, cone-plate	Presheared 10 min at 31 s^{-1}, rested 30 s
Monash	TiO_2 suspension 50-60 wt% solids	Mechanical agitation 24 hrs, pH 7.0	Steady-shear measurement Extrapolation	Rate controlled rheometer Haake RV20, grooved bob-cup	Presheared 10 min at 10 s^{-1}, rested 10 min
			Stress ramp Creep test	Stress controlled rheometer Rheometric DSR, vane-cup	Presheared 10 min at 10 s^{-1}, rested 10 min
			Vane technique	Rate controlled rheometer Haake RV20, vane device	Presheared 10 min at 10 s^{-1}, rested 10 min
			Static equilibrium	Cylindrical Penetrometer	Presheared 10 min at 10 s^{-1}, rested 10 min
Tulane	TiO_2 suspension 40-70 wt% solids	Stirring with spatula 1 hr, pH 7.0	Steady-shear measurement Extrapolation	Stress controlled rheometer SR5000, plate-plate	Restirred 1 min
LMSGC	TiO_2 suspension 50-60 wt% solids	Mechanical stirring at least 1 hr, pH 7	Static equilibrium	Inclined plane device	Thoroughly mixed
Melbourne	TiO_2 suspension 60 wt% solids	Sonication 2 min, pH 7.7	Vane technique	Rate controlled rheometer Haake RE50, vane device	Hand stirred 1 min

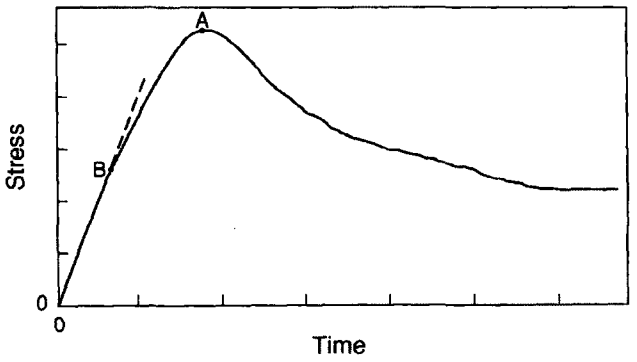

Fig. 1. A typical force (or torque)-time response curve for the vane or slotted plate technique.

direct and indirect measurements of the yield stress were employed in the round robin program. Table 1 lists the methods used and the experimental conditions employed by the participating laboratories. Only a brief description of the methods used is given here. More detailed information about the specific techniques and procedures employed can be found in the literature cited.

2.3.1. Vane technique

Since its first development by Nguyen and Boger (1983; 1985), the vane has grown in popularity as a simple and effective technique for direct measurement of the yield stress property. In the rate-controlled mode of operation, a four-bladed vane fully immersed in the fluid is rotated at a constant and sufficiently slow rate and the torque exerted is recorded as a function of time. For yield stress fluids, the torque-time curve obtained, as shown in Fig. 1, would show a maximum (point A), at which the fluid is considered to yield along a cylindrical surface circumscribed by the vane blades. The yield stress (σ_y) can thus be calculated from the peak torque (M_{max}) and the vane dimensions, diameter (D) and length (L):

$$M_{max} = \frac{\pi D^3}{2}\left(\frac{L}{D}+\frac{1}{3}\right)\sigma_y \tag{1}$$

Due to its special geometry, the vane tool offers several advantages which include eliminating of wall slip, allowing the fluid to yield within itself, and minimizing the disturbance caused to the sample by the insert of the testing element.

In this study, the vane technique was employed in three laboratories (Adelaide, Melbourne and Monash) for measuring the yield stress (Table 1).

2.3.2. Slotted plate technique

The plate technique was developed and used at Tulane University for determining the static yield stress of suspensions (Zhu *et al.*, 2001). The experimental procedure involves measuring the force acting on a vertical plate, constructed with rectangular slots to prevent slip at the surface, being lifted through the suspension. Fig. 1 shows a typical force-time response for a constant speed of the moving plate. This technique assumes that the fluid starts to yield at point B, corresponding to the end of the linear elastic deformation, from which the static yield stress can be computed as follows:

$$\sigma_y = \frac{F_r}{A} = \frac{F-F_i}{A}, \tag{2}$$

where A is the surface area of the plate, F_r is the net force acting on the plate after the initial force, F_i , due to the combined weight of the plate and attaching wire less the buoyant force, is subtracted from the measured force, F.

2.3.3. Cylindrical penetrometer technique

In this technique, pioneered by Uhlherr *et al.* (2002) at Monash University, the yield stress was determined based on the static equilibrium of a cylinder falling under gravity in a yield stress fluid. The penetrometer consisted of a hollow cylinder with a hemispherical bottom end. When the penetrometer is gently released in a fluid with yield stress, it will fall toward the equilibrium position when the force due to gravity is balanced by the resistance forces due to shear yield stress and buoyancy. Assuming that the shear stress is uniform over the immersed surface, the yield stress of the fluid can be determined as follows:

$$\sigma_y = \frac{g\left[m-\rho\pi d^2\left(\frac{l}{4}+\frac{d}{12}\right)\right]}{\pi d\left(l+\frac{\pi d}{8}\right)} \tag{3}$$

where m is the mass of the penetrometer, d is the cylinder diameter, l is the immersed length, ρ is the suspension density, and g is gravity.

2.3.4. Inclined plane technique

At the Laboratoire des Matériaux et des Structures du Génie Civil (LMSGC), the yield stress of TiO_2 suspensions was determined using the inclined plane method developed by Coussot *et al.* (1996). An amount of the well mixed suspension was gently poured over a large plane made of plywood and allowed to spread. At static equilibrium, when the spreading stops, the final thickness of the fluid layer (h) may be related to the fluid yield stress by a force balance. If slip or other perturbing effects (sedimentation, surface tension, and evaporation) can be neglected and if the thickness of the layer is much smaller than its longitudinal and lateral dimensions, the yield stress can be calculated from:

$$\sigma_y = \rho g h \sin\alpha, \tag{4}$$

where ρ is the fluid density, g is gravity, and α is the angle of inclination of the plane.

Alternatively, the yield stress can be determined by measuring the critical angle of the plane inclination at which an initially static fluid layer with a finite thickness starts to

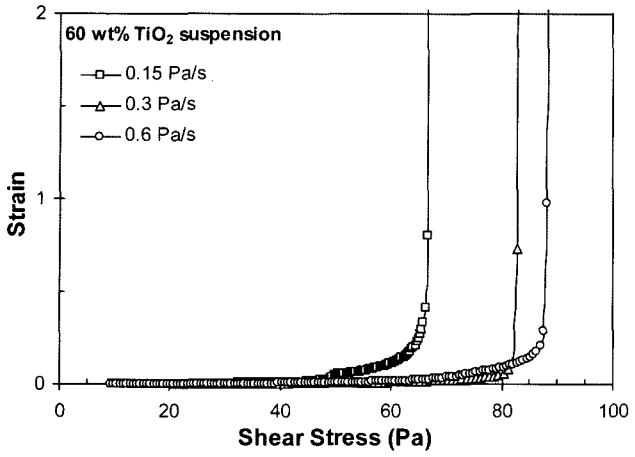

Fig. 2. Typical stress ramp test profiles.

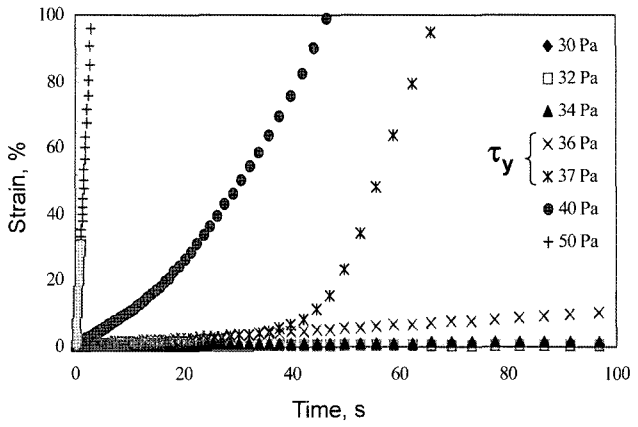

Fig. 3. Typical creep test profiles.

flow. The latter procedure also provides a convenient way to study the evolution of the yield stress in thixotropic fluids due to structure reformation at rest.

2.3.5. Stress ramp technique

Stress ramp tests were carried out in four participating laboratories using stress-controlled rheometers, equipped with either the vane or cone-plate geometry. Details of the systems used are summarized in Table 1. In a ramp test, the shear stress is increased linearly at a constant rate from zero to a level well above the yield stress and the resulting deformation is recorded. Fig. 2 shows typical stress-strain profiles obtained for a TiO_2 suspension. Initially, the strain increases linearly with increasing stress, indicating the solid-like behaviour. When the stress reaches a certain critical value, continuous flow can be observed and the slope of the strain-stress curve rapidly increases. The yield stress of a material can be determined by extending the two straight lines corresponding to solid-like and liquid-like behaviour to a point of intersection (Zhu *et al.*, 2001). It is evident from Fig. 2 that the stress ramp rate has a definite effect on the yielding process of the suspension: the lower the applied ramp rate, the smaller the critical stress observed. Therefore, only the results obtained at the lowest rates of stress sweep reported by the participants were used for comparison.

2.3.6. Creep technique

Stress-controlled rheometers were also employed to determine the yield stress by creep measurements in four different laboratories using the vane geometry. The experimental set up and conditions employed were similar to those used for the stress ramp method (see Table 1). In a creep test, constant stresses in a range covering the yield stress are applied in successive steps to the sample and variations of the strain with time are measured. If the applied stress is less than the yield stress, the sample behaves as a solid and the measured strain is small. When the applied stress is larger than the yield stress, the strain tends to infinity and a constant strain rate is achieved. Fig. 3 illustrates a typical creep strain versus time profile for a 60 wt% TiO_2 suspension. The critical shear stress which causes a significant increase in the creep rate over a short period can be taken as the suspension yield stress. It is obvious that the measurement time frame plays an important role in the determination of the critical shear stress. A prolonged creep time can cause the failure of the material structure at lower stresses (Uhlherr *et al.*, 2005). For the data in Fig. 3, stress levels were changed at 100 s intervals, since it was found that the sample would start flowing within such a time frame.

2.3.7. Indirect methods

Indirect methods involve extrapolation of the steady shear rheological data to determine the yield stress (Nguyen and Boger, 1992). Both stress-controlled and shear rate-controlled rheometers, employing different measuring geometries were employed in five participating laboratories to obtain steady shear data for TiO_2 suspensions (Table 1). Care was taken by the participants to ensure that wall slip and other effects that could affect the measurements at low shear rates were minimized or avoided. The yield stress was obtained by (i) graphically or numerically extrapolating the shear stress-shear rate flow curve at low shear rates to zero shear rate, and (ii) fitting the shear stress-shear rate data using two non-linear models for yield stress fluids, such as the Casson and Herschel-Bulkley models.

3. Results and discussion

3.1. Steady shear flow behaviour

Fig. 4 shows the steady shear flow property data for the TiO_2 suspensions tested at various solids concentrations. The data are presented both as shear stress versus shear rate flow curves (Fig. 4a) and apparent viscosity versus shear stress plots (Fig. 4b) to demonstrate that the TiO_2 suspensions tested have a yield stress, which strongly

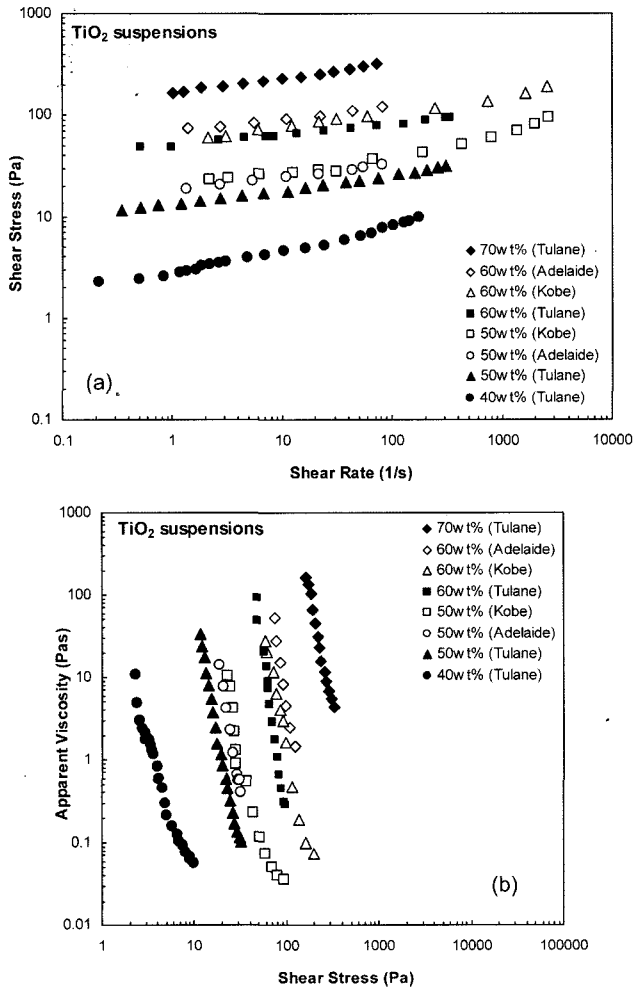

Fig. 4. Steady-shear flow data for the TiO_2 suspensions. (a) Shear stress-shear rate flow curves; (b) Apparent viscosity versus shear stress plots.

depends on the solids concentration. For the two recommended test concentrations of 50 and 60 wt% solids, the results provided by three different laboratories show fair agreements, considering the differences in the rheological instruments and flow geometries employed (see Table 1). It should be noted that although the TiO_2 suspensions were found to be thixotropic, the results reported in Fig. 4 and used for yield stress determination by indirect methods were obtained under the equilibrium shear flow condition.

3.2. Comparison of yield stress results from different techniques

All yield stress results obtained using different methods for the suspensions tested at two solids concentrations of 50 wt% and 60 wt% are collected in Table 2. Values obtained from techniques employed by more than one laboratory are presented as arithmetic averages and relative standard deviations based on the data provided by different laboratories. For those techniques involving single laboratories, the mean values and relative standard deviations, if available, are shown as received from the participants. Generally, a cursory inspection of the results reveals that the mean yield stress values determined from different methods are fairly consistent and comparable in magnitude. Some variations of the results from different methods do exist, as would be expected, due to the different principles inherent in the techniques used for measuring the yield stress property. Such differences among the different techniques, however, are less significant than the variability of the results within some individual techniques, as employed by different laboratories.

For a more meaningful and direct comparison of the results, the different methods used have been divided into

Table 2. Comparison of yield stress results from different methods for the TiO_2 suspensions

Method	No. of Labs	50 wt% TiO_2		60 wt% TiO_2	
		Mean σ_y (Pa)	STD (Pa)	Mean σ_y (Pa)	STD (Pa)
Direct Methods - Static					
- Vane	3	19.2	2.0	56.8	4.9
- Slotted plate	1	10.5	-	32.0	-
- Penetrometer	1	10.7	1.0	60.9	-
- Inclined plane	1	14.8	-	40.3	-
Direct Methods - Rheometric					
- Stress ramp	4	14.5	8.9	46.5	23.7
- Creep	3	8.3	2.4	39.3	19.6
Indirect Methods - Extrapolation					
- Flow curve extrapolation	4	15.0	6.8	48.0	20.0
- Casson model	4	14.5	9.0	43.7	26.3
- Herschel-Bulkley model	2	7.6	3.5	39.0	18.5
All Methods	6	13.5	6.6	45.8	18.1

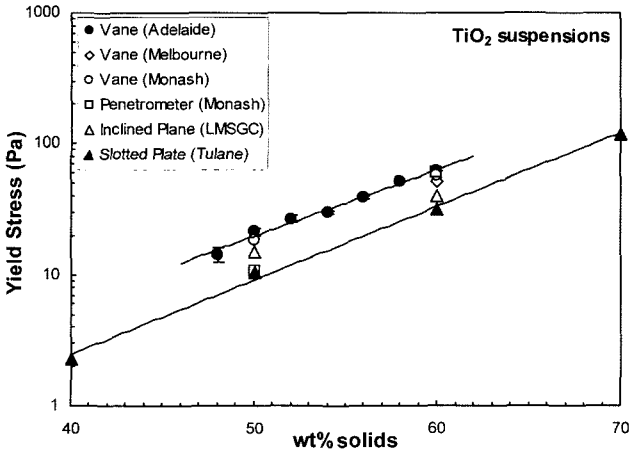

Fig. 5. Comparison of yield stress measured by the static direct techniques for the TiO_2 suspensions. The lines shown are trend lines based on vane (upper) and slotted plate (lower) results.

three groups, based on the similarity of their measuring techniques. As stipulated in Table 2, the first group consists of four direct methods, including the vane, slotted plate, penetrometer and inclined plane techniques, which were designed specifically for measuring the yield stress under static conditions and independent of conventional rheological measurements. The second group consists the shear stress ramp and creep techniques, which are also considered as direct methods but involve measurements using controlled-stress rheometers. The third group includes all indirect methods, in which the yield stress is determined by extrapolation of the conventional rheological data.

The results produced by the first group of techniques are presented in Fig. 5 as yield stress versus solids concentration for the TiO_2 suspension. Additional data from the vane and slotted plate techniques at several different concentrations are also included for comparison and trend indication. The results indicate that the measured yield stress varies among the four different static methods. At a fixed solids concentration, the yield stress is highest as measured with the vane technique and lowest with the slotted plate technique. The ratio of the two yield stress values is about 2 and independent of solids concentration of the suspension. The difference in the yield property measured by these two direct techniques, which are essentially similar in operation as stress growth experiments at a constant strain rate, arises from different interpretations of the yield stress. The plate method considers the yield stress as the critical shear stress corresponding to the end of the elastic deformation region (point B on the force-time response in Fig. 1), when viscoelastic flow commences. In the vane technique, the yield stress is defined at the maximum of the shear stress versus time (or strain) response (point A, Fig. 1), denoting the start of fully viscous flow. Consequently, the yield value determined by the plate technique is consistently smaller than that obtained by the vane method. Together, these techniques provide critical shear stress values that define the lower and upper bounds of the yield stress of the suspension. These limits of the yield stress have sometimes been referred to as the "static" and "dynamic" yield stresses, respectively (e.g., Liddell and Boger, 1996; Uhlherr *et al.*, 2005).

Values of the yield stress measured using the cylindrical penetrometer and inclined plane techniques are comparable and fall within the limits set by the vane and plate data (see Fig. 5 and Table 2). These two direct methods basically employ the same principle of static equilibrium to determine the yield stress as the limiting shear stress remaining in the suspension when flow stops. The yield stress measured using the penetrometer technique agrees with the slotted plate result for the 50 wt% suspension and with the vane result for the 60 wt% sample. The inclined plane method produced yield stress values which are approximately average of the vane and slotted plate results. Furthermore, while the critical (yield) stress could be defined unambiguously from certain characteristics of the stress-deformation response (Fig. 1) with the vane and plate techniques, it was somewhat more difficult to decide objectively when flow actually stopped and a state of static equilibrium was achieved in the penetration and inclined plane techniques.

Of the four direct static methods compared, only the vane technique was employed in more than one laboratory. The results obtained in three different laboratories indicate good consistency of the yield stress determined using the vane, with a maximum standard deviation of ±10% for both TiO_2 samples (see Table 2).

Overall, the relative standard deviations about the mean yield stress measured using the four direct static methods

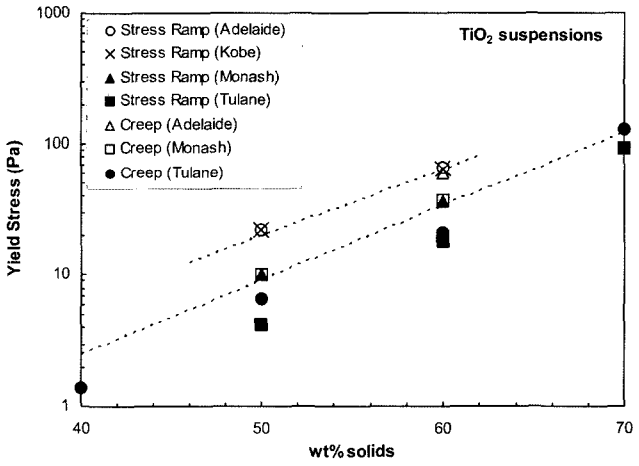

Fig. 6. Yield stress measured by direct (dynamic) methods. The dotted lines are trend lines from the vane (upper) and slotted plate (lower) results.

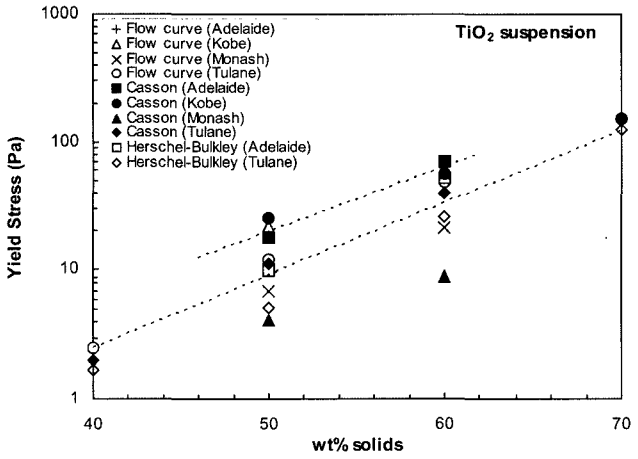

Fig. 7. A comparison of yield stress results determined by extrapolation of steady-shear data. The dotted lines are trend lines from the vane (upper) and slotted plate (lower) results.

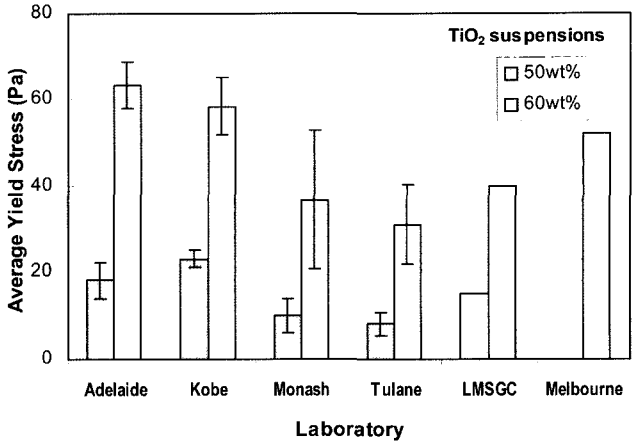

Fig. 8. Comparison of mean yield stress results from different laboratories for the TiO_2 suspensions. The bar height represents average yield stress values obtained from all different techniques used in a given laboratory. The error bars represent standard deviations within individual laboratories.

are ±31% and ±24% for the 50% and 60% TiO_2 suspension, respectively.

Fig. 6 compares the yield stress results produced by the stress ramp and creep techniques. These direct methods are similar in principle and operation, both using stress-controlled rheometers to determine the yield stress as the critical shear stress required to initiate flow. The stress ramp technique, employed in four laboratories, produced considerably diverse results, with standard deviations greater than ±50%. Yield stress results from creep measurements conducted in three laboratories also show large scatterings, with deviations ranging from ±30% to ±50%. Overall, the measured yield stress values exhibit a greater degree of variation and inconsistency compared to the data obtained using the static direct methods presented earlier. Furthermore, the average yield stress obtained from stress ramp is comparable to the upper yield stress limit defined by the vane technique, while the mean yield stress produced by the creep tests is closer to the lower limit indicated by the slotted plate results. Both controlled stress techniques were strongly influenced by the measurement time scale, the effects of which appeared as the dependence of the measured yield stress on the rate of shear stress application in stress ramp experiments and on the observation time frame used in creep tests (Uhlherr, 2005).

Yield stress results obtained by indirect measurements (extrapolation from flow curves and yield stress model fits) are presented in Fig. 7. Compared to the direct methods, extrapolation of steady-shear data generally produces larger variability in yield stress values. Direct extrapolation from the flow curves and extrapolation by data fitting using the Casson model produced comparable yield stress results. Application of the Herschel-Bulkley model resulted in lower yield stress values. Two laboratories reported difficulty in extracting meaningful yield stress by means of the Herschel-Bulkey model, and did not provide any data. Of all the indirect techniques used, extrapolation by means of the Casson model resulted in the largest variation of the yield value with standard deviations ranging from ±60% to ±63%. The combined errors from yield stress determination by all indirect methods used are ±55% and ±46% for the 50% and 60% TiO_2 suspensions, respectively.

3.3. Comparison of yield stress results from different laboratories

Fig. 8 depicts yield stress results reported by all participating laboratories for the TiO_2 suspensions at the two test concentrations. Each bar in the figure is a measure of the average yield stress value determined by all different techniques employed by a given laboratory, and the error bars represent the within-laboratory standard deviations. It may be seen that the results vary widely among different laboratories and the distributions are similar for both concentrations. Some laboratories, e.g. Adelaide and Kobe, reported consistently high yield stress values, whereas Tulane tended to produce the lowest yield stress values. Although the choice of techniques employed in different laboratories may be important in affecting the overall within-laboratory results, it may not be the main reason for such significant inter-laboratory differences. As also shown in Fig. 8, variations in measured yield stress exist in all laboratories where more than one technique was used to determine the yield stress. The standard deviations about the mean yield stress from individual laboratories are similar for both concentrations and range from ±10% to ±40%, depending on the choice and combination of the methods

employed. However, the comparison in Fig. 8 also reveals that dispersions of results obtained from different techniques employed within individual laboratories are relatively smaller than the variations of results among the different laboratories. This suggests that variability of the yield stress determined is not only due to random variations from the techniques and instruments used but also to systematic differences between laboratories. Consequently, we may say that the reproducibility of yield stress measurements among the participant laboratories was poor compared to the repeatability of the measurements with different techniques employed within individual laboratories.

3.4. Statistical data analysis

A detailed analysis of the precision of all different techniques used and the reproducibility of the measurements among all participating laboratories was not possible because not all different techniques were employed by all participants. For some methods, e.g. slotted plate, penetration and inclined plane techniques, only single sets of results were reported by the laboratories which developed and used them. Also two participating laboratories provided results obtained from only one technique which were insufficient to estimate the repeatability of the measurements in those particular laboratories. Nevertheless, an approximate statistical analysis of the results has been attempted using the data reported by four laboratories (Adelaide, Kobe, Monash and Tulane), in which multiple techniques were employed for yield stress determination. Using data pooled from different techniques and grouped in the same way as described earlier, the precision values of the measurements were estimated following the procedure recommended in the ASTM standard E691-99. The results are summarized in Table 3 in terms of the repeatability standard deviation (s_r), which is a measure of the average within-laboratory variation, and the reproducibility standard deviation (s_R), which takes into account both between-laboratory variability and within-laboratory variability that affect inter-laboratory differences. The results show that within any laboratory, direct measurements employing static techniques yield the most repeatable results (with lowest s_r), whereas indirect determination of the yield stress based on extrapolation of rheological data are the least repeatable (with highest s_r). For any group of techniques, s_R is several times larger than s_r, indicating a poor reproducibility of the measurements among the different laboratories as compared to the repeatability of the measurements within a given laboratory. We also note that direct yield stress measurements using the static techniques produce the most reproducible results while those based on controlled-stress rheometry give the least reproducible results among the different laboratories.

3.5. Effects of sample preparation and conditioning

The statistical analysis of the results has clearly demonstrated that the repeatability of yield stress measurements using different methods within a given laboratory was better than the reproducibility of the measurements among different laboratories. Since within-laboratory variability already includes experimental and systematic errors associated with the techniques and instruments employed, other additional effects may be responsible for the large between-laboratory variations in the measured yield stress. The most likely contributing factors may come from the characteristics and condition of the suspension samples used in the round robin. Firstly, the samples as tested in the participating laboratories were probably not identical due to variability in the methods employed for sample preparation (see Table 1). Although all participants used the same raw materials and ingredients, the various techniques (hand stirring, mechanical agitation, sonication...) employed to disperse solid particles in liquid could affect the final state of the colloidal suspension samples. Secondly, the samples were not conditioned in the same way prior to yield stress measurement: in some laboratories the suspensions were tested in a well mixed state, and in others the samples were presheared and allowed to rest for a period of time, ranging from 1 to 10 minutes, before each test (see Table 1). Since the suspensions tested showed time-dependent flow behaviour, shear history would have an effect on the yield stress measured in different laboratories. As illustrated in Fig. 9 using the data for the TiO_2 suspensions, the yield stress measured in a previously sheared sample increases steadily with time of rest due to

Table 3. Variability analysis of yield stress measurement based on results from four different laboratories (Adelaide, Kobe, Monash and Tulane) for the TiO_2 suspensions

Method	50 wt% TiO_2			60 wt% TiO_2		
	Mean σ_y (Pa)	s_r (Pa)	s_R (Pa)	Mean σ_y (Pa)	s_r (Pa)	s_R (Pa)
Direct Methods - Static	15.5	0.8	5.6	50.2	2.2	15.9
Direct Methods - Rheometric	12.4	1.6	8.6	39.8	3.2	22.3
Indirect Methods - Extrapolation	13.3	3.7	7.9	44.5	9.4	22.0
All Methods	14.9	3.7	8.2	49.3	9.0	20.6

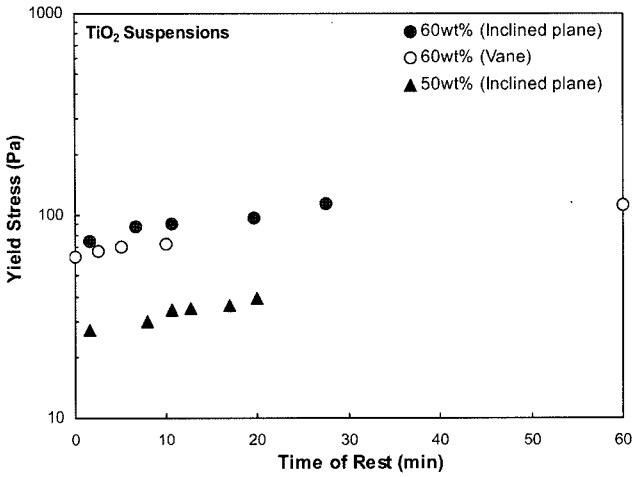

Fig. 9. Yield stress of TiO_2 suspensions measured using the vane and inclined plane techniques as a function of time of rest after previously sheared to equilibrium.

a recovery of the broken down structure in the static state. Thus a sample left undisturbed for 10 minutes after being completely mixed would possess a yield stress that is some 25% higher than that tested immediately after mixing without rest. Furthermore, yield stress measurements on samples with a partially recovered (thixotropic) structure are more likely to be affected by experimental time scale and techniques employed than measurements with the materials at the equilibrium structural state (Cheng, 1986). A recent study by Coussot *et al.* (2002) has demonstrated a complex interplay between yielding and thixotropic behaviour of suspensions that makes yield stress measurements, without a carefully controlled shear history, very difficult to interpret.

4. Conclusions

The initial focus of this inter-laboratory study was to evaluate the reliability and reproducibility of yield stress measurements using different methods and in different laboratories. Overall, the data obtained in six laboratories using a variety of techniques suggested that the measured yield stress varies with both methods and participants. However, when the results were properly analyzed certain consistent trends emerged and helped to identify the factors that affect practical yield stress measurements. Among the different techniques employed, direct methods were found to produce more reliable and repeatable results than indirect methods, which rely on extrapolation from shear viscosity data. Of the direct methods, the techniques specially designed to determine the yield stress under static condition and independent of conventional rheological measurements gave the most consistent yield stress results with lowest deviations among different laboratories. A statistical analysis of the data from four different laboratories clearly indicated that the repeatability of yield stress measurements using different methods within any given laboratory was much better than the reproducibility among different laboratories. The nature and condition of the suspension samples tested were identified as a likely factor responsible for the large between-laboratory deviations. A lack of proper control of the shear history and time-dependent effects in thixotropic suspensions may also contribute to the poor reproducibility of yield stress measurements using any techniques.

This inter-laboratory study clearly highlighted the need for a uniform sample preparation and conditioning procedure and a well controlled shear history if accurate and reproducible results are to be obtained from yield stress measurements with suspensions. It also identified the importance for a follow up study, which will concentrate on direct measurement techniques and sample preparation. We also plan to include other yield stress materials, e.g. electro-rheological fluids, as part of the future round robin exercise.

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