# Rheological phenomena occurring during the shearing flow of mayonnaise

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## Synopsis

A rheometrical study reveals that mayonnaise exhibits apparent wall slip in both small amplitude oscillatory shear flow and torsional flow. Whereas in the case of small amplitude oscillatory shear classical techniques are applicable for extracting bulk material properties, this is not the case for torsional flow. Progressively increasing the shear stress in torsional flow manifests another flow phenomenon that dominates the slip process. It is argued that ‘‘particles’’ within the mayonnaise migrate radially towards the center of the geometry. Spectroscopic techniques are employed to confirm that, following an experiment, material at the rim of the geometry differs from that towards the center. Experiments performed in a cone-and-plate geometry yield results that are qualitatively similar to those obtained in torsional flow tests thus indicating that the migration is not due solely to the radial shear-rate gradient that is present in torsional flow. © *1998 The Society of Rheology.* [S0148-6055(98)00206-5]

## I. INTRODUCTION

Mayonnaise is an oil-in-water emulsion containing salt, vinegar, emulsifiers, and flavoring materials. Many rheometrical studies of mayonnaise have been performed and have highlighted complex flow phenomena exhibited by the material. Indeed, mayonnaise has been shown to be shear thinning, viscoelastic, and thixotropic, it has a yield stress, and in some studies apparent wall slip has been observed. (It is well known, of course, that the term ‘‘yield stress’’ must be used with care and is, at best, a good engineering concept. The authors do not attempt to quantify such a measure.) In addition the effects of temperature and storage time on the product have been examined. One of the many difficulties encountered during the characterization of such a complex material is isolating and quantifying individual effects. There is a reasonable amount of literature on the rheological behavior of mayonnaise and related products and those publications most pertinent to this study are now reviewed.

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In 1974 Tiu and Boger (1974) published a paper with the optimistic title ''Complete rheological characterization of time-dependent food products.'' In the paper rheological data are obtained from mayonnaise samples. The mayonnaise is shown to exhibit shear-thinning and time-dependent behavior, and possess a yield stress. Consequently, the authors fitted the data to a modified Herschel–Bulkley model containing a structural parameter to account for the time-dependent effects.

A study on a range of fluid food materials, which included mayonnaise, was performed by Kokini and Dickie (1981). Stress overshoots during the development of the shear stress were observed, for most of the foods studied, during constant shear-rate experiments performed with a cone-and-plate geometry. After this initial transient behavior the foods showed power-law behavior both in viscosity and first normal-stress coefficient. An attempt was made to model the shear-stress response using the Bird–Leider [Leider and Bird (1974)] equation, though only crude agreement was obtained.

An investigation similar to that performed by Kokini and Dickie (1981) was carried out by Bistany and Kokini (1983). Their study revealed that relationships between viscometric functions and linear viscoelastic functions, such as the Cox–Merz rule, that hold for polymeric materials, did not hold for the food materials considered. The authors suggest that the failure of the food material to follow such relationships is due to a significant structure breakdown that occurs during flow.

The time-dependent flow properties of a commercial mayonnaise were investigated by Figoni and Shoemaker (1983). Constant shear-rate experiments were conducted for four shear rates using a cone-and-plate geometry. As the experiments proceeded, the stress applied to the samples decayed due to the structural breakdown of the mayonnaise under steady shear. The experimental data were modeled by fitting them to a series of first order functions.

The transient flow of mayonnaise in a Couette geometry has been investigated by Campanella and Peleg (1987). Shear rates were limited to 15 $s^{-1}$ since at higher rates the mayonnaise had a tendency to break up and cause a severe slip problem. It was found that mayonnaise can exhibit stress overshoots of the order of 70% above the steady-state value. The authors were able to model their experimental results using a modified version of a constitutive relation proposed by Larson (1985) for polymer melts.

Paredes *et al.* (1988) examined the effect of temperature on five commercial salad dressings. The dressings were characterized using a Couette geometry over a range of temperatures. The measurements showed that an increase in temperature led to a decrease in the viscosity of all the dressings and a decrease in the yield stress of four of the five dressings. The time-dependent nature of the dressings was also investigated at two temperatures and thixotropic breakdown was found to be faster at the lower temperature.

The viscoelastic properties of some commercial salad dressings were studied by Muñoz and Sherman (1990). They performed oscillatory-shear tests on mayonnaise, reduced calorie mayonnaise, and salad cream. On comparing the magnitude of the complex viscosity of the samples with the shear viscosity it was found that the magnitude of the complex viscosity was significantly higher than the shear viscosity. Muñoz and Sherman claim that this is due to the destruction, during the measurement of the shear viscosity, of the network structure formed between the lipoproteins.

Gallegos *et al.* (1992) found that a higher oil content produces a significant increase in the elastic characteristics of mayonnaise. Increasing temperature though, led to a decrease in both the storage modulus, $G'$, and the loss modulus, $G''$. On increasing the strain from 5% (in the linear viscoelastic region) to 80% (in the nonlinear viscoelastic region) an instantaneous decay in the complex viscosity was observed. (It is, of course, nonsensical to speak of complex viscosity when the strain is in the nonlinear region.) When a strain of 5% was reimposed there was an instantaneous recovery of the viscosity to an intermediate value (due to the elastic recovery of deformed flocs) followed by a time-dependent recovery (due to refloculation of oil droplets). The viscosity did not reach the level it had prior to the 80% strain though, due to an irreversible breakdown that was attributed to the coalescence of oil droplets.

Pons *et al.* (1994) studied the effect of temperature on the rheology of a range of normal and light mayonnaises. Data obtained from shear-rate sweeps were fitted to the power-law model and a large range of values was obtained for the consistency coefficient. Extreme values in the range belonged to light mayonnaises and statistical analyses of the results did not reveal definitive differences between normal and light mayonnaises. In addition, all of the samples tested were found to be shear thinning. Yield stresses, determined from the Casson model, were found to decrease with increasing temperature. All the samples were thixotropic and the light mayonnaises with a higher consistency showed a higher rate of structural breakdown.

Ma and Barbosa-Cánovas (1995a), (1995b) characterized two batches of mayonnaise in a parallel-plate geometry. In one batch the oil concentration of the mayonnaise was varied while in the other the Xanthan gum concentration was varied. Apparent wall slip was observed for all samples in torsional flow and was attributed to formation of a boundary layer a few tens of nanometers thick. In oscillatory shear, however, there was no evidence of apparent wall slip. As the concentration of either the oil or the Xanthan gum was increased the yield stress, elastic modulus, and complex viscosity were all found to increase due to the development of structure within the mayonnaise.

Franco *et al.* (1995) examined the effect of processing variables on the rheology of oil-in-water salad dressing emulsions. They looked for and found no evidence of apparent wall slip occurring during steady-state-shear flows on their emulsions [contrary to Ma and Barbosa-Cánovas (1995a)]. In oscillatory-shear experiments, the storage modulus of the emulsions was always higher than the loss modulus over the frequency range studied indicating a tendency towards elastic behavior. In addition, a plateau region was observed on plotting the loss modulus against the frequency and it was conjectured that this may be related to the formation of entanglements among proteins and sucrose stearate molecules, which increase the stability of the emulsion. In steady-state flow, a dramatic structural breakdown occurred which led to a significant difference between the shear viscosity and the complex viscosity. An increase in energy input and temperature during processing led to higher viscosity values and improved stability of the emulsion.

In their study on the stability of salad dressings Turgeon *et al.* (1996) performed oscillatory-shear tests on various oil-in-water emulsions. The dynamic tests were performed in a parallel-plate geometry to measure the emulsions in their rest state. Only one gap (1 mm) was used and the authors show that the loss tangent, $\tan d = G''/G'$, decreases with increasing protein content and a more stable emulsion is obtained.

Mayonnaises and salad creams have widely varying compositions and it is therefore not surprising that they exhibit different behavior. As a consequence, it is not reasonable to compare different samples without detailed knowledge of the microstructure. In the work that follows a single, highly flocculated commercial mayonnaise is used and there is no attempt to make comparisons between samples. Rather, the aim is to highlight generic flow processes and the effects that they have on rheometric data acquisition and interpretation.

## II. EXPERIMENTAL APPROACH

### A. Rheometry

The literature review on mayonnaise and related materials, presented in Sec. I, has shown that such materials exhibit complex and varied rheological behavior. Many of the studies summarized compare a given rheological characteristic for different varieties of the product. In addition, there are discrepancies between some of the results. Therefore in this study attention is restricted to a single mayonnaise in an attempt to isolate different rheological phenomena exhibited, determine the origin of the behavior, and deduce how different phenomena may suppress or exacerbate each other. Initial experiments were performed to investigate whether mayonnaise exhibits apparent wall slip. [Several techniques, including the use of roughened plates, are useful for eliminating slip effects in some (but not all) materials. The intention here though, is to highlight, not eliminate, the slip phenomenon and to try to shed some light on the processes involved.]

An in depth review of apparent wall slip was given recently by Barnes (1995). Apparent slip occurs in multi-phase systems when the dispersed phases migrate away from solid boundaries leaving a thin layer of lower-viscosity liquid. This depleted layer acts as a lubricant between the solid boundaries and the bulk material so that most, or all, of the deformation occurs within the depleted layer. In a parallel plate rheometer apparent slip is signified by a decrease in the apparent viscosity of the material following a decrease in the gap between the two plates, for a given stress level. This is because in larger gaps, more of the bulk material is deformed, and thus has a greater contribution to the measurement of the apparent viscosity.

To determine whether mayonnaise exhibits apparent wall slip, a TA Instruments (Leatherhead, UK) controlled stress rheometer (CSR) fitted with a parallel-plate geometry (diameter 50 mm) was used to perform oscillatory-shear and constant-stress torsional-flow experiments. The upper plate was transparent so that the sample could be observed during the experiments which were carried out at plate separations ranging from 0.25 to 3 mm and at a temperature of $20 \pm 0.1\,^{\circ}\mathrm{C}$. A single commercial mayonnaise (Hellman's ''Real'' Mayonnaise, CPC (UK) Ltd.) was used for all of the experiments to restrict the variation of the results. The exact recipe of the mayonnaise is therefore not known.

Preliminary small-amplitude oscillatory-shear experiments were performed to determine the strain range over which a linear response was obtained. At angular frequencies of 6.29 and 251.3 rad/s the response was found to be linear up to strains of at least 0.142 and 0.059, respectively. Consequently, oscillatory-shear experiments were carried out at a fixed strain of 0.05 over an angular-frequency range of 0.025–250 rad/s. A fresh sample of mayonnaise was loaded between the plates at the widest gap (3 mm) and excess mayonnaise was removed with a spatula. The free surface of the sample was covered with silicone oil since it had been observed in the preliminary experiments that evaporation at the edge of the sample can have a significant effect on the measurements. After performing the experiment the plate separation was reduced with the sample *in situ*, excess mayonnaise was removed once more, and the free surface re-covered with silicone oil. This process was repeated until the range of gaps had been covered. The resulting dynamic rigidity, $G'$, and dynamic viscosity, $\eta'$, data obtained from the series of experiments are shown in Fig. 1. Data for $\eta'$ corresponding to angular frequencies below 10 rad/s were suspect since the associated stress levels were too small to be determined reliably. The figure shows that both $G'$ and $\eta'$ decrease as the plate separation decreases which is indicative of apparent wall slip. The occurrence of apparent slip in the oscillatory tests is somewhat surprising. However, all precautions were taken to ensure the

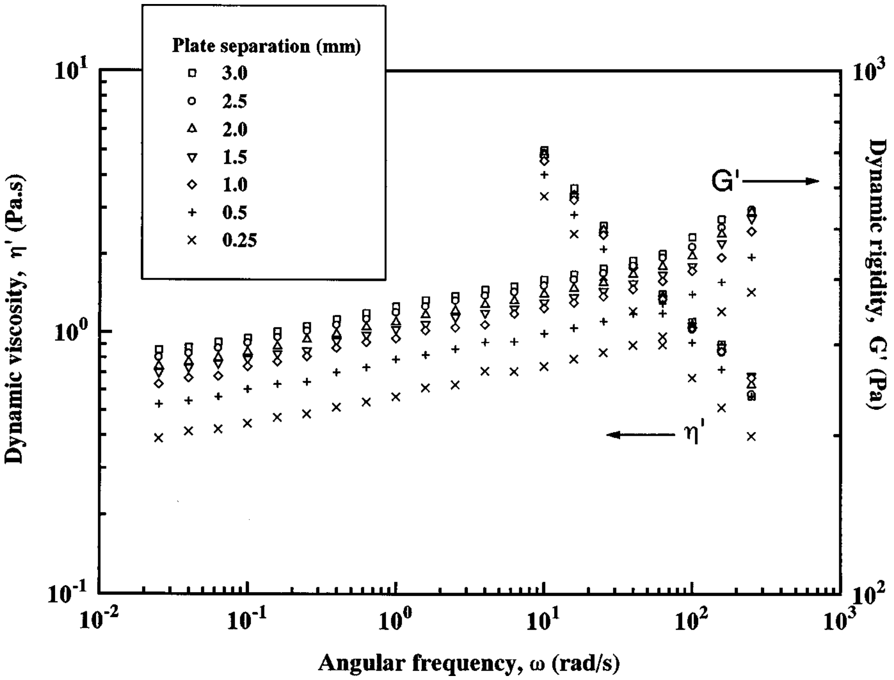

**FIG. 1.** The dynamic rigidity and dynamic viscosity of mayonnaise obtained over a series of small amplitude oscillatory shear tests with different gaps.

accuracy of the data, including comparisons with results for silicone oils of comparible viscosity which showed no slip effects under the same experimental conditions.

Ma and Barbosa-Cánovas (1995a) looked for but did not find evidence of apparent wall slip for mayonnaise in small-amplitude oscillatory shear. However, they only conducted experiments with plate separations of 1 and 1.5 mm. Examination of Fig. 1 shows that there is very little difference in the values obtained for the dynamic quantities at gaps of 1 mm and above and therefore the smaller plate separations used here need to be considered to reveal existence of slip. In addition, it is reasonable to assume that the curves obtained for the larger gaps are representative of the behavior of the bulk material. Examining the data for $\eta'$ once more it can be concluded that mayonnaise exhibits thinning characteristics.

Similar series of experiments were performed applying a constant stress to the sample to determine whether apparent wall slip could also be detected in torsional flow. Figure 2(a) shows the results obtained from a series of torsional flow experiments in which a stress of 30 Pa was applied for 20 mins. An immediate observation is that the apparent viscosity decreases by almost 2 decades as the plate separation is decreased. Even though the gap is reduced, the samples are subjected to the same nominal kinematics and the decrease in apparent viscosity with plate separation indicates the presence of a significant slip region.

It is also noteworthy that all the curves have a similar shape. During the first minute of the flow there is a substantial decrease in the apparent viscosity which is probably due to the destruction of the network formed between lipoproteins that coat the oil droplets in the mayonnaise. As time proceeds the apparent viscosity continues to decrease, albeit at a slower rate, and appears to tend towards a steady-state value.

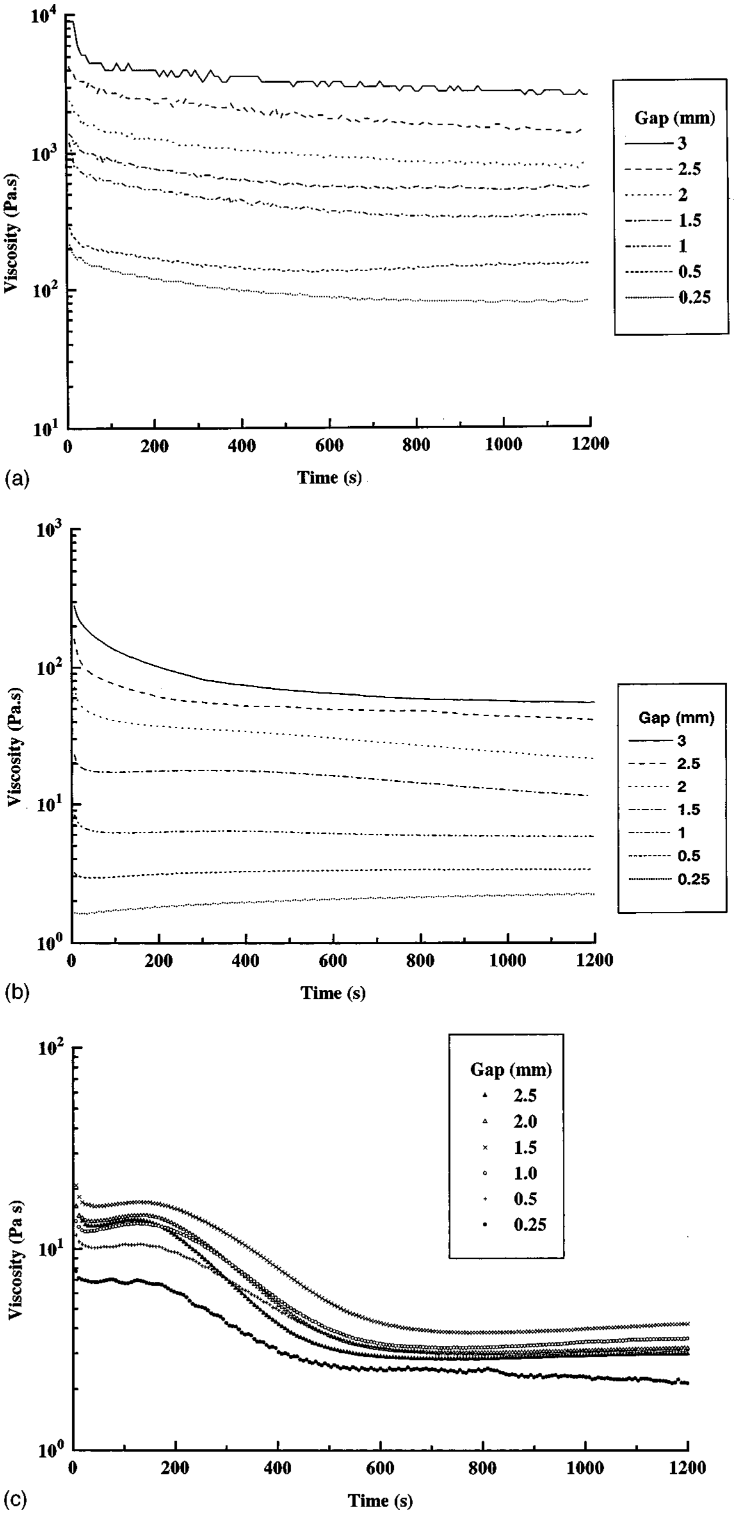

**FIG. 2.** The apparent viscosity of mayonnaise obtained over a series of torsional flow tests with different gaps. The shear stress applied was (a) 30 Pa, (b) 60 Pa, (c) 90 Pa.

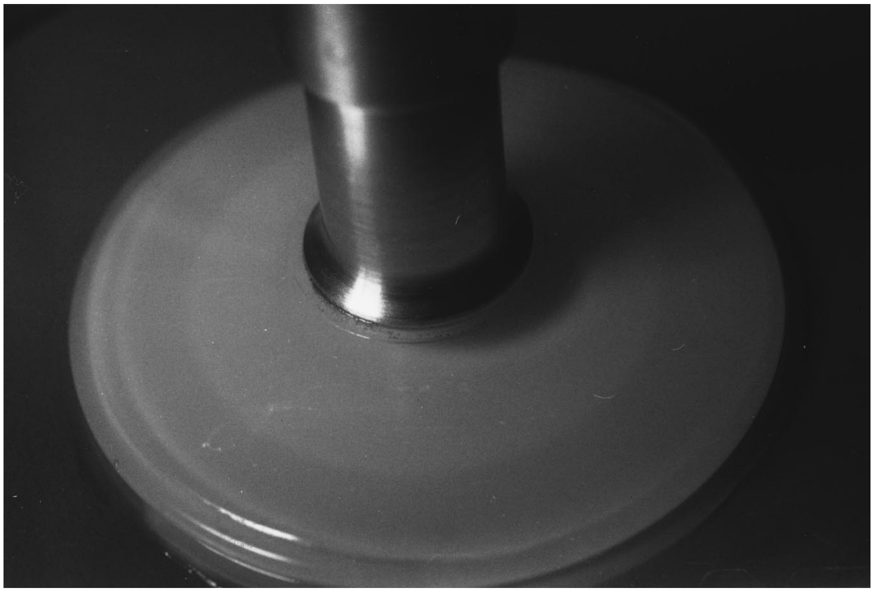

**FIG. 3.** Photograph of the torsional flow geometry showing the sample has divided into two distinct regions beneath the transparent upper plate. Note that the optical effects at the very edge of the plate are due to a bevel on the plate.

Similar results were obtained on applying a constant stress of 60 Pa and a plot of viscosity versus time is given in Fig. 2(b). Once again as the plate separation is decreased the apparent viscosity decreases and, for the range of separations considered, the decrease is on the order of 2 decades. The shape of the curves are similar to those in Fig. 2(a), however all but one of them possess another feature. The curves for plate separations of 2.5 mm and below all contain an inflexion which indicates that the rate at which the viscosity decreases is not monotonic. Indeed, the viscosity actually *increased* for periods in some of the experiments.

*Contrary to the behavior shown in Fig. 1 the curves in Figs. 2(a) and 2(b) do not converge as the plate separation is increased. Consequently the shear viscosity of the bulk material cannot be inferred without a detailed model of the slip process.*

On performing a similar series of torsional flow experiments at a stress of 90 Pa the results were markedly different from those presented in Figs. 2(a) and 2(b), as shown in Fig. 2(c). It can be seen in Fig. 2(c) that there is no distinct ordering of the curves and the variation of the apparent viscosity between the different curves is far less than that shown in Figs. 2(a) and 2(b). In addition, the form of the curves differs from that presented previously with the inflexion being far more prominent. It appears that the slip behavior, which was very distinguishable in the experiments performed at 30 and 60 Pa, is being dominated by another flow phenomenon.

It was observed that, following an experiment in which the sample had been subjected to a stress of 90 Pa, distinct regions, one at the rim and the other at the center of the geometry, had formed as shown in Fig. 3. A distinct variation of color tone across the radius of the acrylic plate develops during the time the shearing is applied. It appears that a phase separation occurs which may be attributable to a radial ‘‘particle’’ migration within the bulk material.

To highlight the flow behavior observed in the constant-stress experiments a series of constant-shear-rate experiments was performed on samples that had been stirred prior to

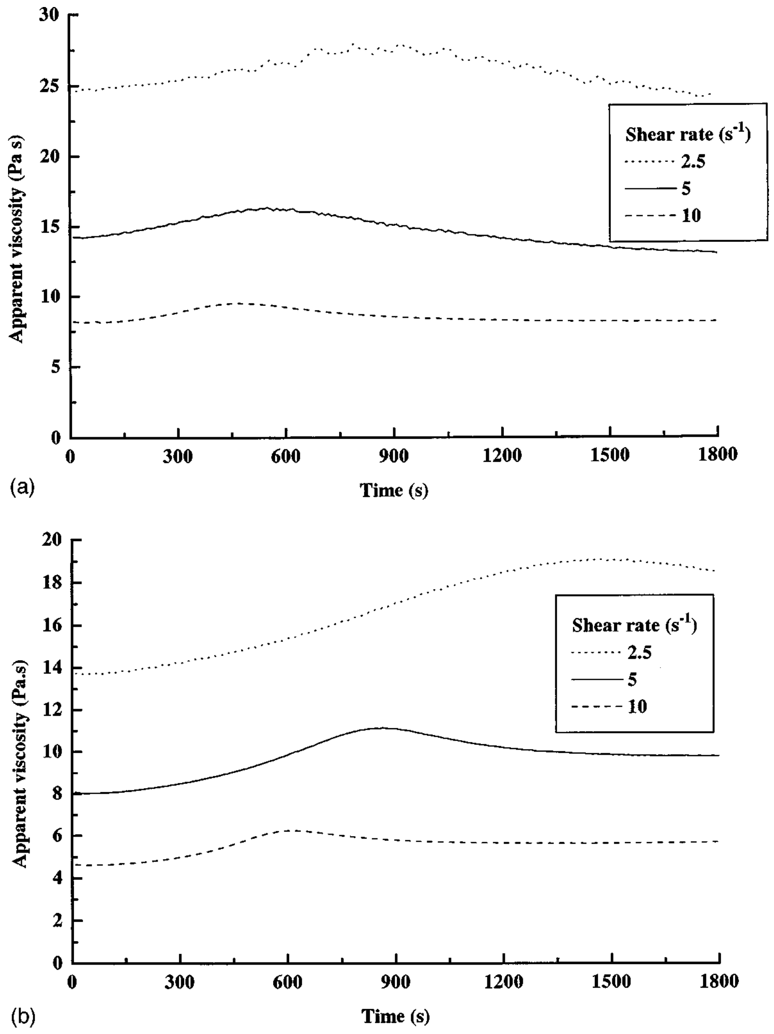

**FIG. 4.** The apparent viscosity of stirred mayonnaise obtained at different shear rates using (a) torsional flow, gap 1 mm, (b) cone-and-plate flow.

the experiment in order to destroy the structure formed by the lipoprotein network. Note that the samples were stirred and not presheared since preshearing may have induced particle migration. The results of three torsional flow experiments, in which the gap between the plates was 1 mm, are presented in Fig. 4(a). Since the structure had been destroyed upon stirring the samples there is no longer an initial decrease in apparent viscosity and it is clear that all three curves rise, peak, and then fall towards a steady-state measure of the apparent viscosity. It is difficult to put forward structural recovery after stirring as an explanation for the initial stress rise given the observed subsequent fall in the stress level and the fact that the stress peaks earlier in time for higher shear rates.

The evidence thus far suggested that particle migration is responsible for this transient behavior. To determine whether the particle migration is due to the radial shear-rate gradient that is present in torsional flow similar experiments were performed using a cone (4°, diameter 50 mm) and plate geometry on the CSR. Results from three experiments are presented in Fig. 4(b) and it is clear that the curves have the same qualitative characteristics as those presented in Fig. 4(a). (A quantitative comparison between the results obtained in torsional flow and cone-and-plate flow cannot be made due to the fact that the material also exhibits extraordinary apparent wall slip, as shown earlier.) Hence the particle migration/phase separation does not result solely from the radial shear-rate gradient that exists in torsional flow.

In order to confirm that some form of ''phase separation'' is the fundamental cause of the observed behavior it was decided to apply spectroscopic fingerprinting techniques to samples taken from the rim and the centre of given experiments.

## B. Spectroscopic analyses

To determine whether material at the rim of the geometry differs from that towards the center, samples were taken from both regions and analyzed using pyrolysis mass spectrometry and Fourier transform infrared spectroscopy.

### *1. Introduction*

Pyrolysis mass spectrometry (PyMS) and Fourier transform infrared spectroscopy (FT-IR) are physico-chemical methods which measure predominantly the bond strengths of molecules and the vibrations of bonds within functional groups, respectively [Griffiths and de Haseth (1986); Meuzelaar *et al.* (1982)]. Therefore, they give quantitative information about the total biochemical composition of a sample. Within the food industry PyMS has been used to authenticate orange juice [Aries *et al.* (1986); Goodacre *et al.* (1997)] and scotch whisky [Aylott *et al.* (1994)], and to detect the adulteration of milk and extra virgin olive oil [Goodacre *et al.* (1992), (1993)], while other olive oil studies have concentrated on regional classification [Salter *et al.* (1997)]. FT-IR has also been exploited within the food area for the authentication of vegetable oils [Lai *et al.* (1994)], fruit purees [Defernez *et al.* (1995); Kemsley *et al.* (1996)], and green coffees [Dupuy *et al.* (1995)]. Another vibrational spectroscopy technique which measures Raman scattering has also been applied to the analysis of foods [Baeten *et al.* (1996); Ozaki *et al.* (1992); Sadeghi Jorabchi *et al.* (1991)].

### *2. Materials and methods*

*Pyrolysis mass spectroscopy (PyMS):* 1 $\mu$l of the mayonnaise sample from each of four independent constant-shear-rate experiments was evenly applied to clean iron–nickel foils which had been partially inserted into clean pyrolysis tubes. Samples were run in triplicate. Prior to pyrolysis the samples were oven dried at 50 °C for 30 min and the foils were then pushed into the tubes using a stainless steel depth gauge so as to lie 10 mm from the mouth of the tube. Viton O-rings were next placed approximately 1 mm from the mouth of each tube to form a vacuum seal between the tube and the mass spectrometer.

Pyrolysis mass spectrometry was then performed on a Horizon Instrument PyMS-200X (Horizon Instruments Ltd., Heathfield, U.K.). For full operational procedures see Goodacre and Kell (1996) and Goodacre *et al.* (1993), (1994). Conditions used for each experiment involved heating the sample to 100 °C for 5 s followed by Curie-point pyrolysis at 530 °C for 3 s with a temperature rise time of 0.5 s.

PyMS data may be displayed as quantitative pyrolysis mass spectra [e.g., as in Fig. 5(a)]. The abscissa represents the 150 $m/z$ (mass/charge) ratios, while the ordinate contains information on ion count for any particular $m/z$ value ranging from 51 to 200. Data were normalized as a percentage of the total ion count to remove the influence of sample size *per se*.

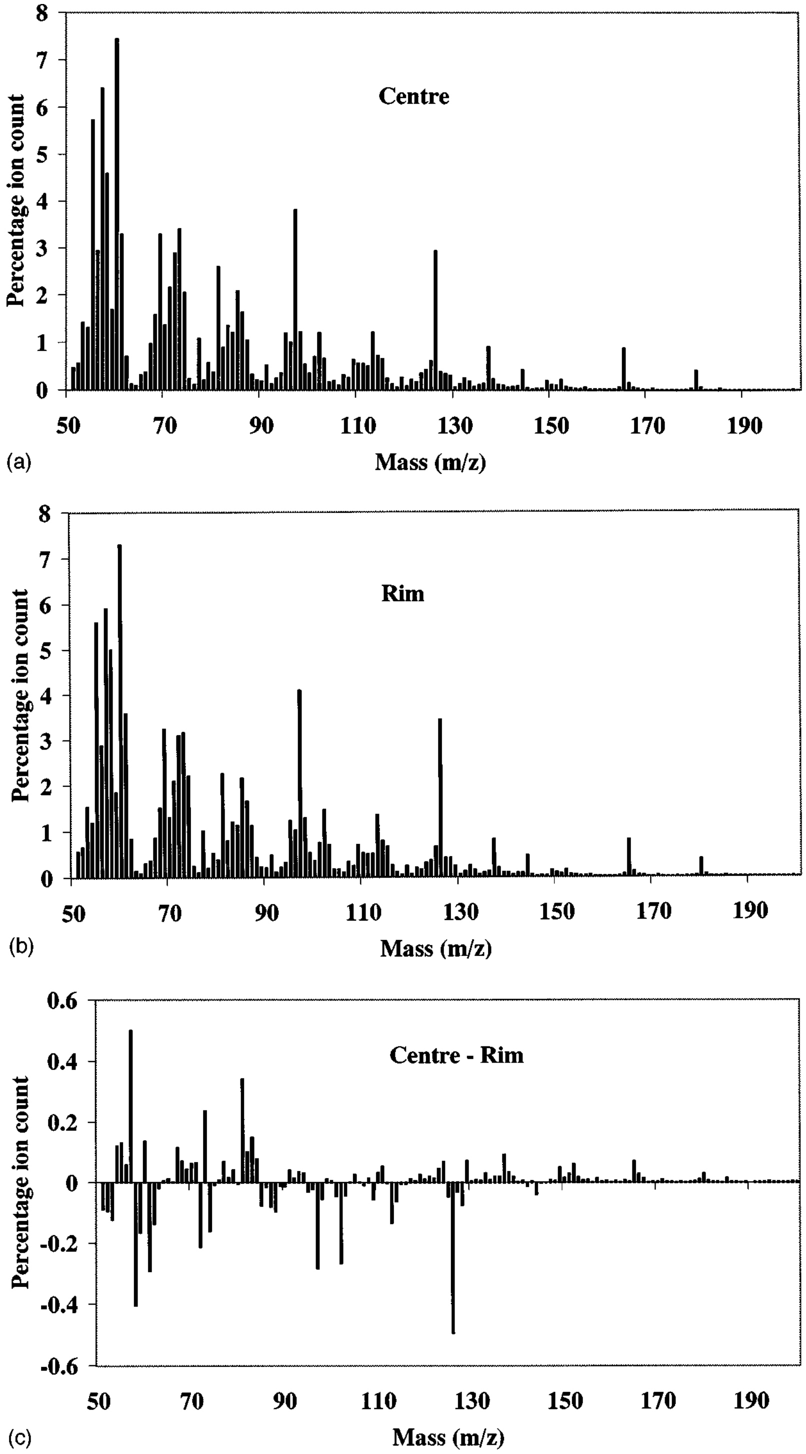

**FIG. 5.** Pyrolysis mass spectra of mayonnaise samples taken from the center (a) and the rim (b) of the torsional flow geometry following an experiment. (c) The difference between the two spectra shown in (a) and (b).

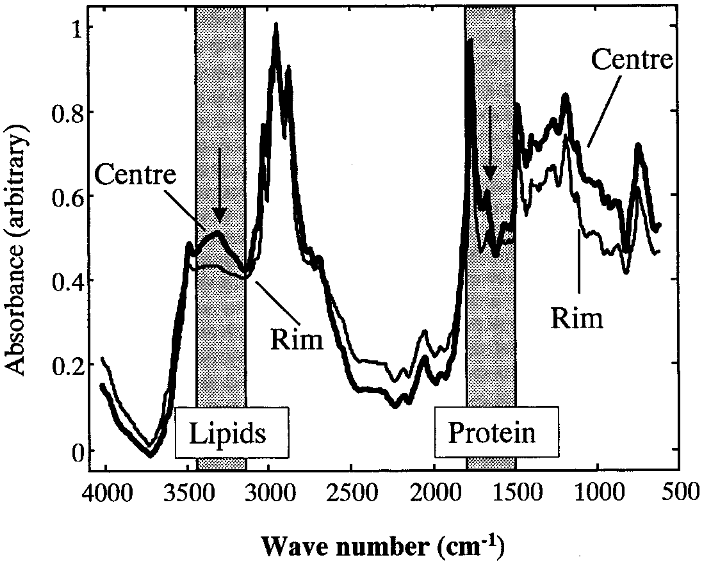

**FIG. 6.** Fourier transform infrared spectra of mayonnaise samples taken from the center and the rim of the torsional flow geometry following an experiment.

The normalised PyMS data were processed with the GENSTAT package [Nelder (1979)] which runs under Microsoft DOS 6.2 on an IBM compatible PC. This method has been previously described by Gutteridge *et al.* (1985). The initial stage involved the reduction of the data by principal component analysis (PCA) [Causton (1987); Jolliffe (1986)]; this is a well known technique for reducing the dimensionality of multivariate data while preserving most of the variance. Data were preserved by keeping only those principal components (PCs) whose eigenvalues accounted for more than 0.1% of the total variance. Discriminant function analysis (DFA) was then used to discriminate between groups on the basis of the ten retained PCs (which accounted for 99.57% of the total variance) and the *a priori* knowledge of which spectra were replicates [MacFie *et al.* (1978); Manly (1994); Windig *et al.* (1983)].

*Diffuse reflectance-absorbance Fourier transform infrared (FT-IR) spectroscopy:* 10 $\mu$l of the mayonnaise samples were applied evenly onto a sand-blasted aluminum plate. Prior to analysis the samples were oven dried at 50 °C for 30 min. Samples were run in triplicate. The FT-IR instrument used was the Bruker IFS28 FT-IR spectrometer (Bruker Spectrospin Ltd., Banner Lane, Coventry, UK) equipped with a mercury–cadmium–telluride (MCT) detector cooled with liquid nitrogen. The aluminium plate was then loaded onto the motorized stage of a reflectance thin layer chromatography (TLC) accessory [Bouffard *et al.* (1994); Goodacre *et al.* (1996); Winson *et al.* (1997)].

The IBM-compatible PC used to control the IFS28, was programmed (using OPUS version 2.1 software running under IBM O/S2 Warp provided by the manufacturers) to collect spectra over the wave number range 4000–600 $\text{cm}^{-1}$. Spectra were acquired at a rate of 20 $\text{s}^{-1}$ and the spectral resolution used was 4 $\text{cm}^{-1}$. To improve the signal-to-noise ratio, 256 spectra were coadded and averaged. Each sample was thus represented by a spectrum containing 882 points and spectra were displayed in terms of absorbance as calculated from the reflectance–absorbance spectra using the OPUS software. Typical FT-IR spectra are shown in Fig. 6.

ASCII data were exported from the OPUS software used to control the FT-IR instrument and imported into MATLAB version 4.2c.l (The MathWorks, Inc., 24 Prime Par Way, Natick, MA, USA), which runs under MICROSOFT WINDOWS NT on an IBM-compatible PC. To minimize problems arising from baseline shifts the following procedures were implemented:

(1) the spectra were first normalized so that the smallest absorbance was set to 0 and the highest to +1 for each spectrum;
(2) the normalized spectra were detrended by subtracting a linearly increasing baseline from 4000 to 600 $\mathrm{cm}^{-1}$;
(3) finally the smoothed first derivative of these normalized and detrended spectra was calculated using the Savitzky–Golay algorithm [Savitzky and Golay (1964)] with five-point smoothing.

To reduce the dimensionality of the FT-IR data MATLAB was also employed to perform PCA (according to the NIPALS algorithm [Wold (1966)]); of the original 882 spectral points 98.55% of the total variance was retained in the first 10 PCs which illustrates the power of this technique. Next these 10 PCs were used as inputs to the DFA algorithm with the *a priori* knowledge of which spectra were replicates. DFA was programmed according to Manly's principles [Manly (1994)].

## 3. Results and discussion

Typical PyMS and FT-IR spectra obtained from samples taken from the rim and center of the parallel-plate geometry following a constant-stress experiment, are shown in Figs. 5(a), 5(b), and 6, respectively. For PyMS there was very little qualitative difference between these spectra, although on closer inspection quantitative differences may be observed. These differences are highlighted in Fig. 5(c) in which the normalized spectrum obtained for the rim sample is subtracted from that obtained from the sample taken from the center. The FT-IR spectra all show broad and complex contours and again there was relatively little qualitative difference between the spectra. Such spectra readily illustrate the need to employ multivariate statistical techniques in the analysis of both PyMS and FT-IR data.

DFAs were used to observe relationships between the mayonnaise samples taken from the four independent experiments from their PyMS and FT-IR spectra. The 24 spectra were coded so as to give eight groups, one for each sample (i.e. the replicate pyrolysis mass spectra were the *a priori* groups and so do not bias the analysis in any way) and the PyMS and FT-IR data were analyzed by DFA as detailed earlier. The resulting ordination plots are shown in Figs. 7 and 8, respectively.

It can be seen that in the DFA plot from the PyMS analysis of the mayonnaise samples (Fig. 7) that, with the exception of the sample taken from the rim of experiment 3 ($R3$), the rim and center samples can be discriminated by the first discriminant function (DF1). DF1 by definition accounts for the most variance between the data [Manly (1994)], therefore this result shows that the center and rim samples are, in general, biochemically distinct as judged by PyMS. Likewise in the DFA analyses of the FT-IR data from the mayonnaise samples (Fig. 8) a combination of the first and second DF can be used to separate the samples into two classes: one for samples taken from the rim and the other for samples taken from the center of the parallel-plate geometry. It is noteworthy that the way in which DFA was performed was on replicates only so the fact that two classes can be seen is a natural phenomenon and not introduced due to the multivariate analysis.

It is worthwhile making some observations in order to clarify certain aspects of the FT-IR data in Fig. 6. The normalization procedure described earlier ensures that the minimum absorbance at $\approx 3700\ \mathrm{cm}^{-1}$ and maximum absorbance at $\approx 2900\ \mathrm{cm}^{-1}$ are

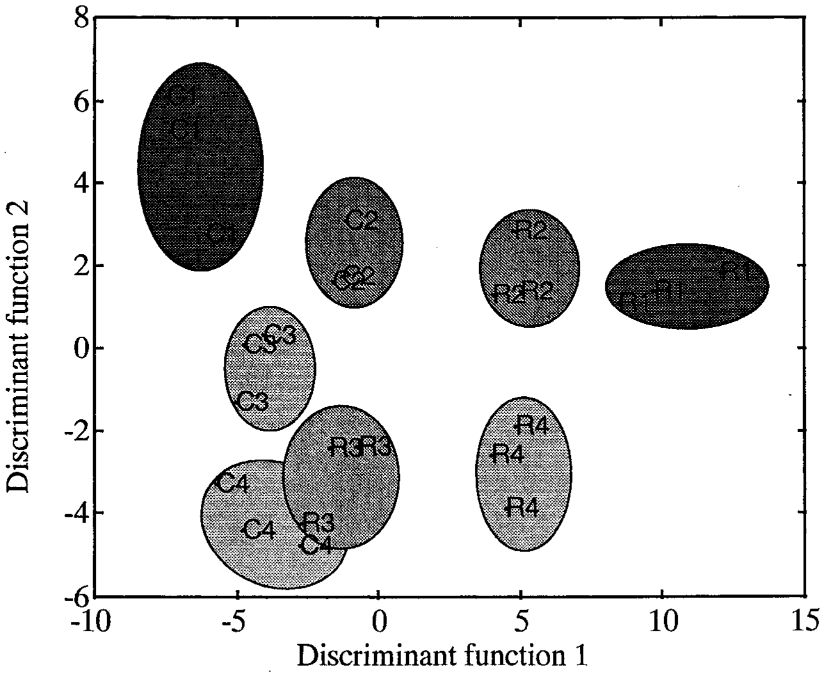

**FIG. 7.** Discriminant function analysis plot obtained from the PyMS analysis of mayonnaise samples from four independent experiments.

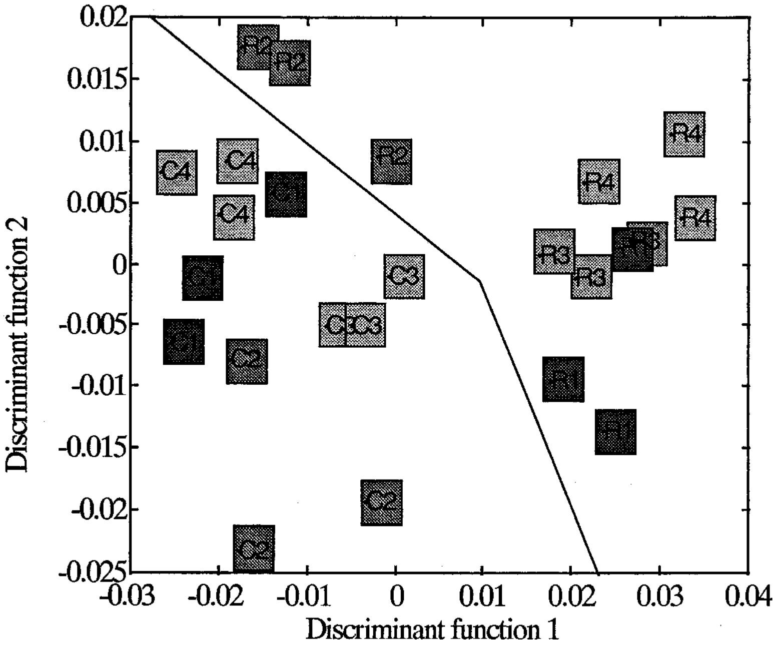

**FIG. 8.** Discriminant function analysis plot obtained from the FT-IR analysis of mayonnaise samples from four independent experiments.

scaled to lie at 0 and 1, respectively. The region between 2500 and 2000 $\mathrm{cm}^{-1}$ contains very little information (other than any residual absorbance from carbon dioxide) and the baseline shift in this region is due to reflectivities in the sample holder. Also, the region 1500–600 $\mathrm{cm}^{-1}$ is the ''fingerprint region'' which contains a wealth of information which is difficult to assign to any particular chemical species due to the common absorbance that occurs in this region [see, for example, Naumaun *et al.* (1991)]

Hence, that the ''fingerprints'' of samples taken from the rim and center of the torsional flow experiments as measured by PyMS and FT-IR are distinct, means that the material taken from the rim differs chemically from that taken from the center. More specifically the center samples were enhanced in protein (amide region at 1690–1620 $\mathrm{cm}^{-1}$) and lipids (alkyl groups absorbing at $\approx 3300\ \mathrm{cm}^{-1}$), see Fig. 6.

## III. DISCUSSION

It is generally accepted that upon shearing a concentrated suspension in a Couette geometry, particles within the suspension will migrate to regions of low shear stress [see Leighton and Acrivos (1987), Abbott *et al.* (1991), Phillips *et al.* (1992), Mondy *et al.* (1994), Chow *et al.* (1994), and Phan-Thien *et al.* (1995) for example]. Whether or not particle migration occurs in torsional flow however remains open to debate. Neither Chapman (1990) nor Chow *et al.* (1994) observed particle migration on subjecting monodisperse suspensions of poly(methyl methacrylate) (PMMA) spheres to torsional flow. More recently though, Krishnan *et al.* (1996) did witness migration of particles in bidisperse suspensions consisting of monosdispere PMMA spheres and different sized acrylic spheres, used as tracer particles, suspended in a mixture of Triton X-100, water, and anhydrous zinc chloride. In suspensions in which the tracer particles were larger than the PMMA spheres the tracer particles were observed to migrate towards the rim of the torsional flow geometry. Conversely, in suspensions in which the tracer particles were smaller than the PMMA spheres the tracer particles were observed to migrate towards the center of the geometry.

Several constitutive equations have been proposed for concentrated suspensions based on diffusive flux arguments [Leighton and Acrivos (1987), Phillips *et al.* (1992), Krishnan *et al.* (1996)] and kinetic theory [Nott and Brady (1994)]. Of these only the model proposed by Krishnan *et al.* (1996) has been shown to predict particle migration in torsional flow although it is clear that the work of Nott and Brady (1994) contains mechanisms that can predict the phenomenon.

The results here not only provide further experimental evidence of particle migration in torsional flow, but also concur with the theoretical diffusive flux arguments. Indeed, if the experimental conditions used here are related to the analysis of Phillips *et al.* (1992) then a significant migratory effect would be obtained within the relevant time scales for particles of 10–20 $\mu$m in size. This is within the range of species size associated with mayonnaise and oil-in-water suspensions [Muñoz and Sherman (1990); Yilmazer *et al.* (1991)]

## IV. CONCLUSIONS

The results from a rheometrical study of mayonnaise have been presented. It has been shown that this soft–solid material exhibits apparent wall slip in *both* small-amplitude oscillatory-shear flow between parallel disks and torsional flow. In the case of small-amplitude oscillatory-shear flow, as the gap between the disks is increased the dynamic measurements converge and it is reasonable to assume that the limiting values are consistent with the behavior of the bulk material. As such it was possible to conclude that mayonnaise also exhibits thinning behavior. In torsional flow though, the measurements did not converge and the shear viscosity of mayonnaise *cannot* be determined from simple rheometrical flow experiments without a detailed model of the slip process occurring at and in the vicinity of the solid boundaries.

As the stress applied to the samples in torsional flow experiments was increased another flow phenomenon evolved that masked the slip process. The behavior became apparent from inflexions in plots of the apparent viscosity against time. Examination of samples following an experiment revealed that two distinct regions had formed within the geometry; one at the rim, the other at the center. It has been conjectured that the behavior results from radial ''particle'' migration which leads to a phase separation. To confirm the material at the rim of the geometry differed from that at the center, subsamples taken from both regions were analyzed using pyrolysis mass spectrometry and Fourier transform infrared spectroscopy.

It has also been shown that the flow phenomenon occurs in a cone-and-plate geometry and therefore does not result solely from the radial shear-rate gradient present in torsional flow.

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