

The rheology of aqueous emulsions prepared by direct emulsification and phase inversion from a high viscosity alkyd resin

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Abstract

A comparison of the rheological properties of dispersions of an alkyd resin in water prepared by direct emulsification and phase inversion has been conducted. These dispersions have application as the base dispersion in the manufacture of the new generation of water based gloss paints. An experimental investigation of the effect of dispersed phase fraction, droplet size and dispersion age on the rheological properties of dispersions produced by each emulsification route has been carried out. The droplet size distributions of the dispersions are also characterised. It was found that phase inversion always gave a smaller droplet size distribution than direct emulsification. Surprisingly it was found that for a given dispersed phase fraction, the dispersions with a smaller droplet size, produced by the phase inversion route, have a lower zero shear rate viscosity than those produced by the direct emulsification route. The rheology of the direct emulsification samples was also observed to change with age, whilst with phase inversion samples the rheology was stable. It is proposed that this and other differences observed between the two methods of manufacture can be associated to the presence, or otherwise, of excess surfactant in the aqueous phase. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Emulsions; Phase inversion; Droplet size; High viscosity; High dispersed phase

1. Introduction

Alkyd resin dispersions are used in the paint industry as the basis for the new generation of environmentally friendly water based gloss paints (see, for example, [1,2]). These dispersions, of a highly viscous resin (above 200 Pa s at 20 °C) dispersed in water, can be manufactured by direct emulsification or via phase inversion to produce a

final product dispersion generally containing 50–60% dispersed phase volume. When manufacturing dispersion by direct emulsification the alkyd resin, oil, phase is simply added to the aqueous phase. Energy then imparted to the system by mixing is used to create the new surfaces of the droplets and thus form an oil-in-water dispersion. During manufacture by phase inversion, however, water is initially added to the agitated alkyd phase until a critical dispersed phase fraction is reached and the dispersion inverts to produce the required oil-in-water dispersion.

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Commercial dispersions are further processed following initial manufacture to add the remaining constituents of the finished paint, including, for example, pigments. During both the formation process and subsequent processing of the dispersions, knowledge of the rheological properties is important for effective processing to be achieved. The high viscosity of the alkyd resin presents difficulties during dispersion manufacture. Therefore, the choice of manufacturing route can be crucial to controlling the resulting droplet size distribution and thus rheological properties of the dispersion, and in the case of a finished paint, the wetting and film forming characteristics.

The rheological properties of emulsions are in general complex and are governed by droplet interactions (see, for example, [3,4]) and these are in turn affected by numerous factors including dispersed phase fraction, continuous phase viscosity, droplet size distribution, droplet deformability, surfactant concentration, temperature and dispersion age. The viscosity enhancement caused by the suspension and interaction of droplets within an immiscible liquid has been the subject of numerous studies and [5–7] for example, give good reviews on this subject.

As the dispersed phase fraction of a dispersion is increased, the dispersion rheology changes significantly as the frequency of droplet interaction increases. [8] developed an expression to describe this viscosity enhancement at low concentrations for hard spheres, which was subsequently modified by [9] to account for droplet deformability. Further studies have led to expressions for viscosity enhancement at higher dispersed phase fractions, for example, the semi-empirical equation of [10]. Over the wide range of dispersed phase fraction that can be achieved, the frequency of droplet interactions changes greatly [11]. Below a volume fraction of order 0.3, droplets can essentially move freely past each other, however, as the dispersed phase fraction is increased droplet interactions increase, until above fractions of 0.74, when the droplets become tightly packed and movement of droplets past one another becomes severely impaired. As the dispersed phase fraction changes through this range, the rheological characteristics of the dispersion also consequently

change from Newtonian, to shear thinning, to a viscoelastic type of behaviour [7].

The interfacial rheology of the droplets can significantly influence droplet interactions, which are enhanced by the presence of a surfactant (see, for example, [3,12]). At high surfactant concentrations, excess surfactant micelles, which can form in the continuous phase also influence the rheological characteristics of dispersions by inducing depletion flocculation [13,14], Pal and Rhodes, 1989). For a given dispersed phase fraction smaller droplets undergo a greater number of droplet interactions and therefore decreasing the droplet size of a monodispersed dispersion increases the viscosity, an effect which decreases as the dispersion droplet size distribution broadens (see, for example, [15,12]).

It is well known that the manufacturing route can affect the droplet size distribution of dispersions (see, for example, [16,17]). Direct emulsification will occur provided sufficient energy can be imparted to the system to break-up the dispersed phase and suspend it as droplets in the continuous phase. Phase inversion, however, can be achieved through two routes. One route involves changes to the relative phase concentrations and is termed catastrophic phase inversion. Alternatively changes to the hydrophilic/lipophilic balance (HLB) value of the surfactant [18], which is a measure of the surfactant's affinity for the aqueous or oil phase, can also cause phase inversion and is known as transitional phase inversion. The former route has been found to generate a similar droplet size distribution to formation by direct emulsification [29] whereas in the latter case a much smaller droplet size distribution can be achieved. This difference has been attributed to the formation of a co-continuous phase during the moment of phase inversion that has a very low interfacial tension [19].

In this paper, investigation of how manufacturing route affects the rheological properties of dispersions has been conducted for a single alkyd resin system. The rheology, as a function of deformation, age history and dispersed phase fraction has all been explored.

2. Experiments and modelling

Rheological tests were carried out using a Rheometrics dynamic spectrometer (RDSII), which is a controlled strain rheometer. Experiments were conducted using either a 50 or 25 mm (for viscoelastic samples) parallel plate geometry. Mackley et al. [20] have earlier demonstrated the applicability of a KBKZ type constitutive equation with a Wagner damping function, k , to describe the rheological characteristics of a range of complex fluids and this method has been used here to model the rheological response of the dispersions under test.

The so-called KBKZ model is a strain dependant integral constitutive equation that uses a discrete set of Maxwell elements to give a spectrum of relaxation times that describe the fluids linear viscoelastic behaviour. Non-linearity is then introduced via a strain dependent damping function, k , the Wagner damping function. This class of constitutive equations is described well by Larson [21].

The procedure used to obtain the rheological characteristics of a material consists of several sequential tests. Initially, a strain sweep is carried out to investigate the extent of any viscoelastic behaviour. This test is then repeated to ensure that a consistent test response is achieved. From the strain sweep data a strain is chosen at which to conduct a frequency sweep. A strain is selected at which the material response is independent of strain and the torque reading is well within the range of the force transducer. A discrete relaxation spectrum is then calculated from a best fit to the frequency sweep data using a rheometrics software package, and its accuracy checked by using the result to re-calculate the variation of the dynamic moduli with frequency. For viscoelastic

dispersions, step strain experiments are then performed. Where these tests were possible, a Wagner type damping coefficient could be obtained and used to predict the steady shear response, which is compared with the experimental steady shear curve. For full details of the experimental protocol used see [20].

The constituent components of the dispersions to be used are given in Table 1 and their respective Newtonian viscosities specified.

3. Material samples

Samples of dispersions with a range of dispersed phase fraction were manufactured by direct emulsification and via phase inversion (by the catastrophic route [29]). The mixing techniques of oscillatory flow mixing (OFM) (see for example, [22]) and a conventional stirred tank were utilised for this, as described by Watson [23]. The dispersions contain a surfactant system (consisting of a non-ionic surfactant and a co-solvent) at concentrations (10% by mass of surfactant and 5% co-solvent) that result in a significant excess of surfactant. In general this leads to the formation of dispersions with a stable droplet size distribution in unsheared material where droplet coalescence is considered to be negligible. Representative samples of these dispersions were readily obtained by simply using a spatula to place a sample of the dispersion into the test area of the rheometer. A new sample was used for each test, before which thorough cleaning of the sample plates with white spirit (in which the alkyd resin is soluble) and then distilled water was carried out. By varying the mixing intensity at which dispersions were manufactured, dispersions with a range of droplet size distributions were manufactured.

Table 1
Physical properties of the materials used for the production of alkyd resin dispersions

Material	Viscosity at 20 °C (Pa s)	Density at 20 °C (kg m ⁻³)	Melting point (°C)
Alkyd resin	200	1050	–
Surfactant	–	1100	40
Co-solvent	Approx. 10 ⁻³	950	–

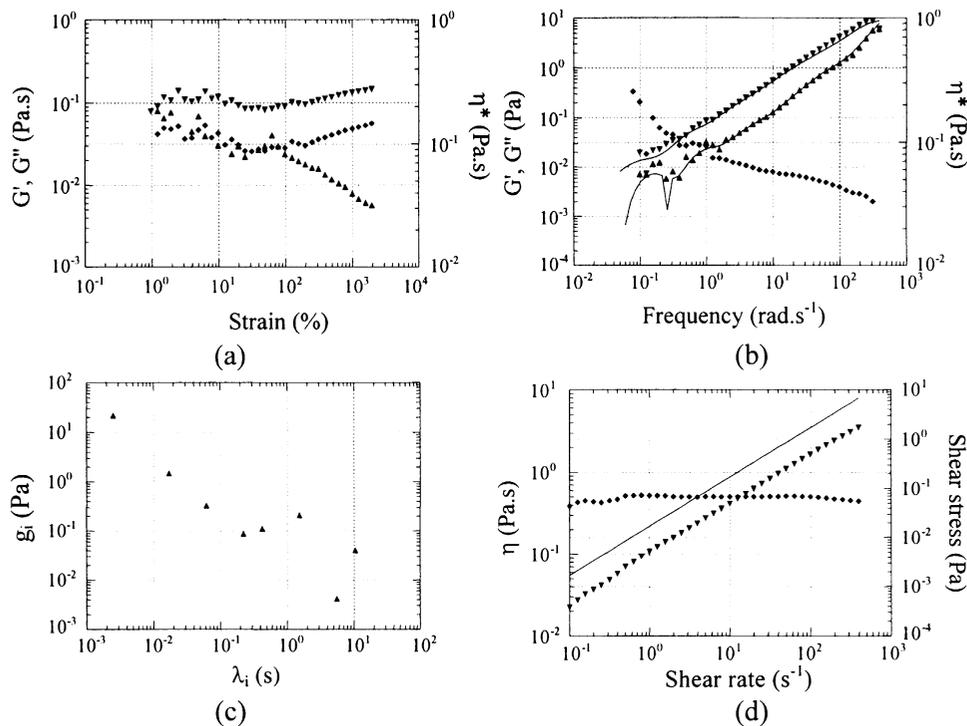


Fig. 1. Rheological characterisation of an alkyd resin dispersion containing 50% dispersed phase, manufactured by direct emulsification with 10% surfactant and $x_{50} = 7.3 \mu\text{m}$. Tests conducted at 20 °C. (a) Strain sweep $\omega = 1 \text{ rad s}^{-1}$, (▲) G' , (▼) G'' (◆) η^* . (b) Frequency sweep $\gamma = 30\%$, (▲) G' , (▼) G'' , (—) fit, η^* (◆). (c) Spectrum of relaxation times. (d) Steady shear measurements (◆) η , (▼) shear stress, Wagner prediction (—) calculated using $k = 0$.

When manufacturing dispersions by direct emulsification, samples with 10, 20, 30, 40 and 50% dispersed phase were prepared for testing. With the mixing apparatus available dispersed phase volumes greater than 50% could not be achieved. However, for the alkyd resin system used, phase inversion from a water-in-oil to oil-in-water dispersion occurs at an alkyd resin concentration of around 92% [23] and hence, when utilising the phase inversion route samples with higher dispersed phase volumes could also be produced. Thus samples with 20, 30, 40, 50, 60, 70, 80 and 90% dispersed phase were prepared for analysis via phase inversion. A dispersion of 5% water in alkyd was also tested. All these dispersions were stable over the duration of the testing procedure.

For the alkyd resin in water dispersions, droplet size distributions were obtained using a Sympatec

laser light scattering particle size analyser (for details of the operation of this type of particle size analyser see, for example, [24]).

4. Results

4.1. Manufacture by direct emulsification

4.1.1. Effect of dispersed phase fraction

Fig. 1 shows an example of the rheological characteristics of a fresh dispersion manufactured by direct emulsification and containing 50% dispersed phase, in this case with a median droplet size (x_{50}) of approximately $7 \mu\text{m}$. Tests were carried out at 20 °C using a 100 g cm force re-balance transducer and a 50 mm diameter parallel plate at a gap of 0.5 mm. Fig. 1(a) shows the dynamic strain sweep, conducted at a frequency

of 1 rad s^{-1} , and shows that the alkyd resin dispersion is a dominantly viscous material. A linear region is observed at the lower strains investigated, with a slight thickening of the dispersion occurring at strains above 100%. A possible explanation for this behaviour may be provided by the mechanism of depletion flocculation caused by the presence of excess surfactant micelles in the continuous phase [25,13]. This effect is caused by a decrease in osmotic pressure between approaching droplets as the excess surfactant micelles are excluded from the gap between the droplets, thus forcing the droplets together. The strain sweep data suggests this may happen as the strain is increased during the test and the droplets are forced past each other with increasing frequency and intensity.

The dynamic frequency sweep, shown in Fig. 1(b), was conducted at 30% strain and shows that the complex viscosity decreases with increasing frequency of deformation. Prediction of the dynamic moduli, using the relaxation spectrum shown in Fig. 1(c), is good, however, the structure of the discrete spectrum shows little physical significance. The dispersion is able to relax significantly in a very short time and hence step strain experiments could not be performed.

The relatively high volume fraction of dispersed phase tested in the example of Fig. 1 suggests that the material will exhibit shear thinning properties, however, as shown in Fig. 1(d) the experimentally measured apparent viscosity is essentially constant over the wide range of shear rates tested. Consequently, the non-linear damping parameter in the Wagner KBKZ type equation is put to zero [20]. The model prediction of the steady shear behaviour is also shown in Fig. 1(d). The consistent over prediction of the experimental data by the model suggests that wall slip between the rheometer plate and sample of dispersion is occurring during the experimental simple shear data acquisition. This observation is also consistent with recent work carried out in this laboratory [26].

Reducing the dispersed phase fraction decreases the number of droplet interactions and therefore the dispersion viscosity. The essentially Newtonian behaviour observed for a dispersion with 50% dispersed phase, as shown in Fig. 1, is re-

tained over the range of dispersed phase fractions investigated and below 30% dispersed phase the viscosity is independent of deformation rate throughout the range tested. Fig. 2 shows the variation of apparent and complex viscosity with dispersed phase fraction for dispersions with a median droplet size, $x_{50} = 7.3 \text{ }\mu\text{m}$. In this example, the value of the complex viscosity is arbitrarily taken at a strain of 1000%, however, only in the case of the highest phase volume of 50% does the choice of strain affect the result. The steady shear data shows near Newtonian behaviour for all shear rates tested, as shown in Fig. 1(d) for example. In Fig. 2 an increase in dispersed phase fraction causes an increase in the dispersion viscosity as expected, however, the apparent experimental steady shear viscosity is consistently greater than the experimental measured complex viscosity over the range of dispersed phase fractions investigated. This difference showed a reproducible trend and at present we have no clear interpretation to explain this effect.

The Krieger–Dougherty equation [10],

$$\eta_r = \left[1 - \left(\frac{\Phi}{\Phi_p} \right) \right]^{-[\eta]\Phi_p} \quad (1)$$

where: η_r , relative viscosity; Φ , dispersed phase fraction; Φ_p , maximum packing fraction; and $[\eta]$, intrinsic viscosity = 2.5 for hard sphere dispersion; has been fitted to the data. A maximum packing

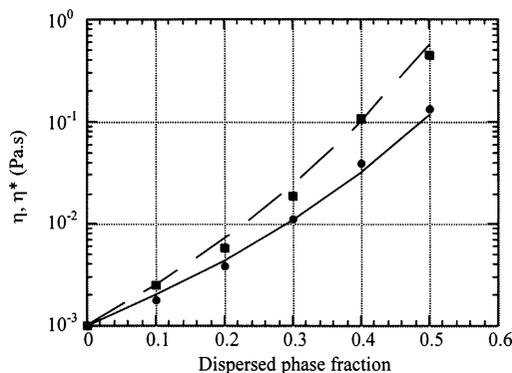


Fig. 2. Variation of apparent (■) and complex viscosity (●) measurement with dispersed phase fraction, (—) Krieger–Dougherty fit $\eta = 6.5$ for complex viscosity and $\eta = 8.75$ for apparent viscosity.

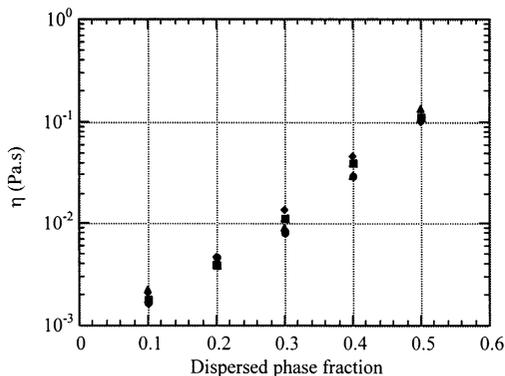


Fig. 3. The variation of apparent viscosity at a strain of 1000% with dispersed phase fraction for a range of droplet size distributions for dispersions manufactured by direct emulsification, (●) $x_{50} = 12.8 \mu\text{m}$, (◆) $x_{50} = 9.1 \mu\text{m}$, (▲) $x_{50} = 7.7 \mu\text{m}$, (■) $x_{50} = 7.3 \mu\text{m}$.

fraction of 0.92, based on the average dispersed phase fraction required to achieve phase inversion for this system, has been used [23]. The alkyd resin droplets behave as soft polyhedra and are therefore able to pack together to a high dispersed phase fraction. This is greater than that possible by dispersions of hard spheres, as assumed by the Krieger–Dougherty equation. The hard spheres assumption also results in an intrinsic viscosity of 2.5 generally being used with the equation. However, to fit the viscosity data of these alkyd resin dispersions, values for the intrinsic viscosity of 6.5 and 8.75 have been required for the complex and apparent viscosities respectively.

4.1.2. Effect of droplet size

In dispersions containing 50% dispersed phase there will be significant droplet interactions and therefore dispersions with different droplet size distributions will be expected to exhibit different rheological properties, the effect diminishing as the dispersed phase fraction decreases (see, for example, [7,27]). Fig. 3 shows the effect of droplet size distribution on the variation of the apparent and complex viscosity of these alkyd resin dispersions over a range of dispersed phase fractions. The corresponding droplet size distributions, on a volume basis, of the dispersions are shown in Fig. 4. Fig. 3 shows that there is generally little consis-

tent variation between samples with varying droplet size distribution. The polydispersity shown in the droplet size distribution data of Fig. 4 will, however, make it difficult for any significant variation in rheological characteristics with droplet size distribution to be observed. Polydispersity is known to influence the observed rheology with smaller droplets able to fit in the voids between larger droplets and thus reduce the effective viscosity enhancement of the droplets [14], an effect that becomes more significant as the polydispersity increases. The high degree of polydispersity shown in Fig. 4, which is essentially consistent in each dispersion tested, will therefore be expected to have a large influence over the dispersion rheology. This result also suggests that the possible influence of excess surfactant on the dispersion rheology, as seen in Fig. 1, is greater than any effect resulting from variation in dispersion droplet size.

4.1.3. Effect of dispersion age

Dispersions were left to age at room temperature for up to a week and the rheological properties tested at various intervals during this time. Of the dispersions manufactured by direct emulsification only those containing 50% dispersed phase were tested because sedimentation became a problem in dispersions with lower dispersed phase concentrations over this time scale.

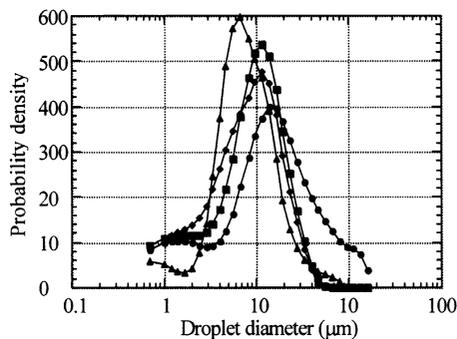


Fig. 4. Comparison of the droplet size distributions of the dispersions used for the rheological characterisations shown in Fig. 3, (●) $x_{50} = 12.8 \mu\text{m}$, (■) $x_{50} = 9.1 \mu\text{m}$, (◆) $x_{50} = 7.7 \mu\text{m}$, (▲) $x_{50} = 7.3 \mu\text{m}$.

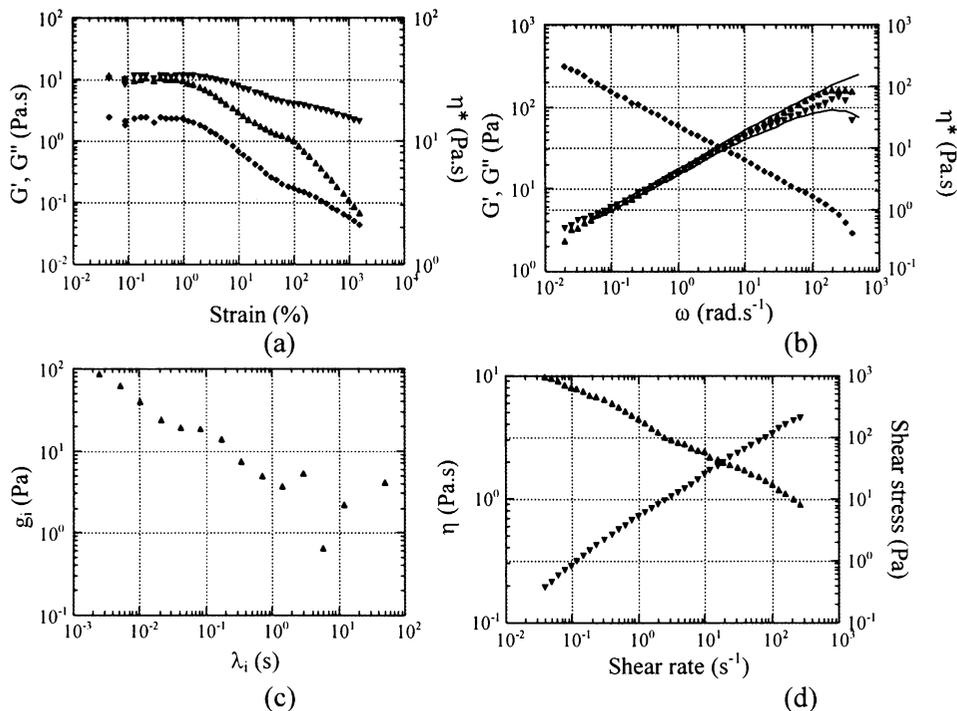


Fig. 5. Rheological characterisation of an alkyd resin dispersion manufactured by direct emulsification containing 50% dispersed phase, conducted after 3 days at 20 °C. (a) Strain sweep $\omega = 1 \text{ rad s}^{-1}$, (▲) G' , (▼) G'' , (◆) η^* . (b) Frequency sweep $\gamma = 1\%$, (▲) G' , (▼) G'' , (—) fit, (◆) η^* (c) Spectrum of relaxation times. (d) Steady shear measurements (▲) η , (▼) shear stress.

Fig. 5(a) shows a dynamic strain sweep of a 50% dispersed phase dispersion aged for 3 days carried out at a frequency of 1 rad s^{-1} . The response is more characteristic of a 'typical' liquid–liquid dispersion with higher dispersed phase fraction than that of the fresh dispersion shown in Fig. 1, with a linear region present at low strains before internal structures are broken and the material viscosity begins to decrease. The elastic and viscous moduli are of comparable magnitude initially and the viscous modulus dominates at higher strains. This response suggests that when the dispersions are left to age, the droplets are able to interact to form an internal network of flocs, resulting in a significant increase in the low strain rate viscosity of the dispersion. This structure is subsequently destroyed under higher deformation rates.

A frequency sweep was conducted within the linear region at a strain of 1%, and is shown in Fig. 5(b). Prediction from the relaxation spectrum

of Fig. 5(c) is generally good although a slight under prediction of the viscous modulus is seen at higher frequencies. In the relaxation spectrum an initial decrease of relaxation strength with an increase in relaxation time is seen, but at higher relaxation times the relaxation strength increases, indicating the influence of the elastic modulus at lower strains.

Under steady shear, the dispersion shows the classic shear thinning type of behaviour of a liquid–liquid dispersion, as shown in Fig. 5(d). Meaningful data from step strain experiments could not be obtained as the dispersion relaxes before the deformation has been fully applied. Therefore fitting of the Wagner model is not possible.

Fig. 6 shows how the variation of complex viscosity with strain changes with dispersion age. A large increase in viscosity is seen over the first 3 days as internal structures develop within the dispersion, however, only a refinement of this

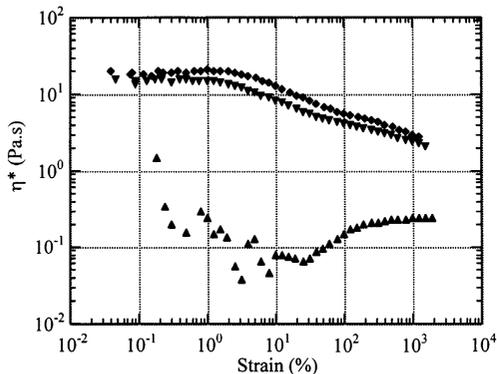


Fig. 6. Change in the variation of complex viscosity with strain at 20 °C for a dispersion manufactured by direct emulsification containing 50% dispersed phase aged over 7 days, $\omega = 1 \text{ rad s}^{-1}$, (▲) 0 days, (▼) 3 days, (◆) 7 days.

structuring occurs subsequently, as further viscosity increases are slight and the shape of the response remains the same. The presence of the surfactant prevents coalescence from occurring and over this period of ageing the droplet size distribution remains constant, as shown in Fig. 7. Therefore, the evolving rheological characteristic is a result of the formation of an inter-droplet network. Weak inter-droplet interactions are seen in the non-linear region at low strains in tests on the fresh dispersion, Fig. 1(a), indicating the potential for the formation of flocs seen in the aged dispersions.

Fig. 8 shows how the complex viscosity of

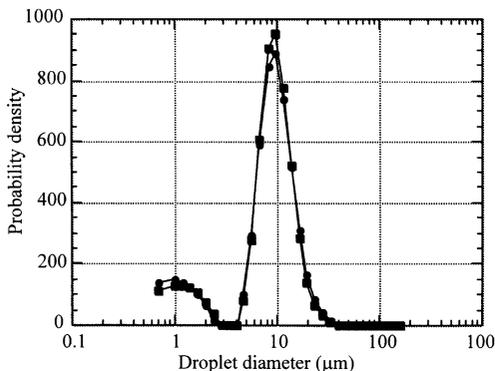


Fig. 7. Variation of droplet size distribution with dispersion age of 50% dispersed phase dispersions used for Fig. 6, (●) 0 days, (■) 7 days.

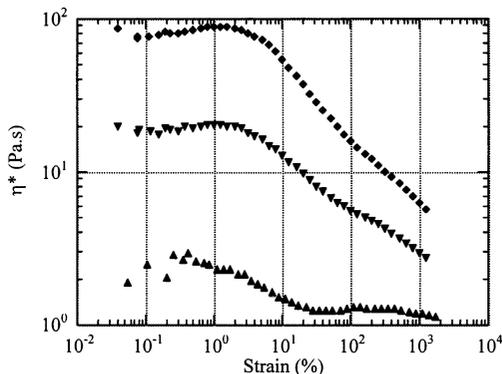


Fig. 8. Variation of complex viscosity with strain for 7-day-old 50% dispersed phase dispersions with a range of median droplet sizes manufactured by direct emulsification, (▲) $x_{50} = 14 \mu\text{m}$, (▼) $x_{50} = 8 \mu\text{m}$, (◆) $x_{50} = 5 \mu\text{m}$.

dispersions, with the range of droplet size distributions shown in Fig. 9, change with strain. This shows that the droplet size distribution of the dispersion has a large effect on the viscosity for aged dispersions compared with the freshly manufactured dispersions. This is despite the significant polydispersity of the dispersion shown in Fig. 9. A linear region is present for dispersions with smaller droplets, whereas the dispersion with a median droplet size of 14 μm thins to a constant viscosity after small increases in strain. All the dispersions have the same dispersed phase fraction of 50%, but in the sample with the smallest median droplet size there will be a greater number

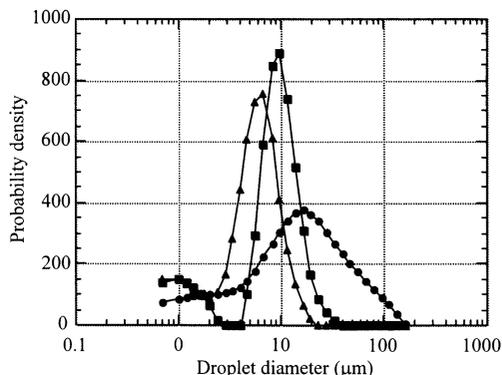


Fig. 9. Droplet size distribution of dispersions used to obtain data for Fig. 8, (●) $x_{50} = 14 \mu\text{m}$, (■) $x_{50} = 8 \mu\text{m}$, (▲) $x_{50} = 5 \mu\text{m}$.

of inter-droplet interactions, thus enabling more complex internal structures to develop within the dispersion and a greater increase in viscosity generated. The increase in droplet packing of a more polydispersed sample decreases the effective viscosity enhancement of the droplets in comparison with dispersion with a more monodisperse size distribution [14]. Thus, the difference between samples shown in Fig. 9 is enhanced by the large variation in polydispersity. This result shows that the droplet size has an influence when flocs have had time to form, probably by depletion flocculation, but, as shown in Fig. 3, does not when these flocs are not present.

4.2. Manufacture by phase inversion

Fig. 10 shows the rheological characteristics of 90% dispersed phase dispersion manufactured via phase inversion. These tests were conducted at 20 °C using a 25 mm parallel plate at a gap of 0.8 mm and a 100 g cm torque transducer. A dynamic strain sweep conducted at a frequency of 1 rad s⁻¹ is shown in Fig. 10(a). The dispersion is dominantly elastic at lower strains with a significant linear region. Once a sufficiently large strain, of around 10% is reached, the dispersion viscosity begins to decrease and the viscous modulus becomes gradually more influential, becoming dominant above strains of 100%. This type of response is typical of a liquid–liquid dispersion with a high dispersed phase fraction (for example, [7,28]).

A frequency sweep, carried out at 0.1% strain, is shown in Fig. 10(b). The complex viscosity decreases considerably with frequency of deformation and the elastic modulus is dominant for the majority of the frequency range investigated. Prediction of the viscous modulus is good when using the relaxation spectrum shown in Fig. 10(c) but the elastic modulus is under predicted. From the step strain data of Fig. 10(d) damping coefficients of 1.3 at 100% strain and 0.84 at 300% strain were found. The step strain tests do not produce parallel responses and consequently estimation of the damping factor is unreliable. This dependency of the damping factor on strain makes prediction of the steady shear data of Fig. 10(e), which shows that the dispersion has charac-

teristic shear thinning properties, difficult. The large discrepancy in the prediction of experimental steady shear data is believed to be a result of slip between the dispersion and rheometer plates during measurement, as reported by [26] for certain emulsion systems.

The rheological response of 50% dispersed phase dispersion manufactured by phase inversion is shown in Fig. 11. Fig. 11(a) shows a strain sweep carried out at a frequency of 1 rad s⁻¹ indicating the general Newtonian type behaviour of dispersions manufactured by phase inversion at this dispersed phase fraction. A frequency sweep at 30% strain is shown in Fig. 11(b) and shows a slight decrease in complex viscosity with increasing frequency of deformation, with the viscous modulus again dominant. Increasing relaxation strength increases the relaxation time linearly throughout the range, as shown in Fig. 11(c), which predicts the frequency sweep data well. A slight shear thinning is observed under steady shear with a constant viscosity approached above a shear rate of 100 s⁻¹. It was not possible to obtain meaningful step strain data due to the fast relaxation of the sample before deformation had been fully applied. Therefore, fitting of the Wagner model for this sample has not been possible.

The rheological response described in Fig. 11 is significantly different to that for a dispersion produced by direct emulsification and is more typical of that expected of dispersion behaviour. The linear strain sweep and shear thinning behaviour was not seen in dispersions produced by direct emulsification at the same dispersed phase fraction. The smaller droplets generated by phase inversion reduce the level of excess surfactant present, thus decreasing the possibility of the formation of flocs by depletion flocculation. This allows the droplets to move past each other more freely as the shear rate increased during a steady shear test.

As with direct emulsification, below 50% dispersed phase, dispersions retain a Newtonian characteristic. However, as the dispersed phase increases above 50% the viscoelastic properties gradually increase until those of 90% dispersed phase, as shown in Fig. 10, are observed.

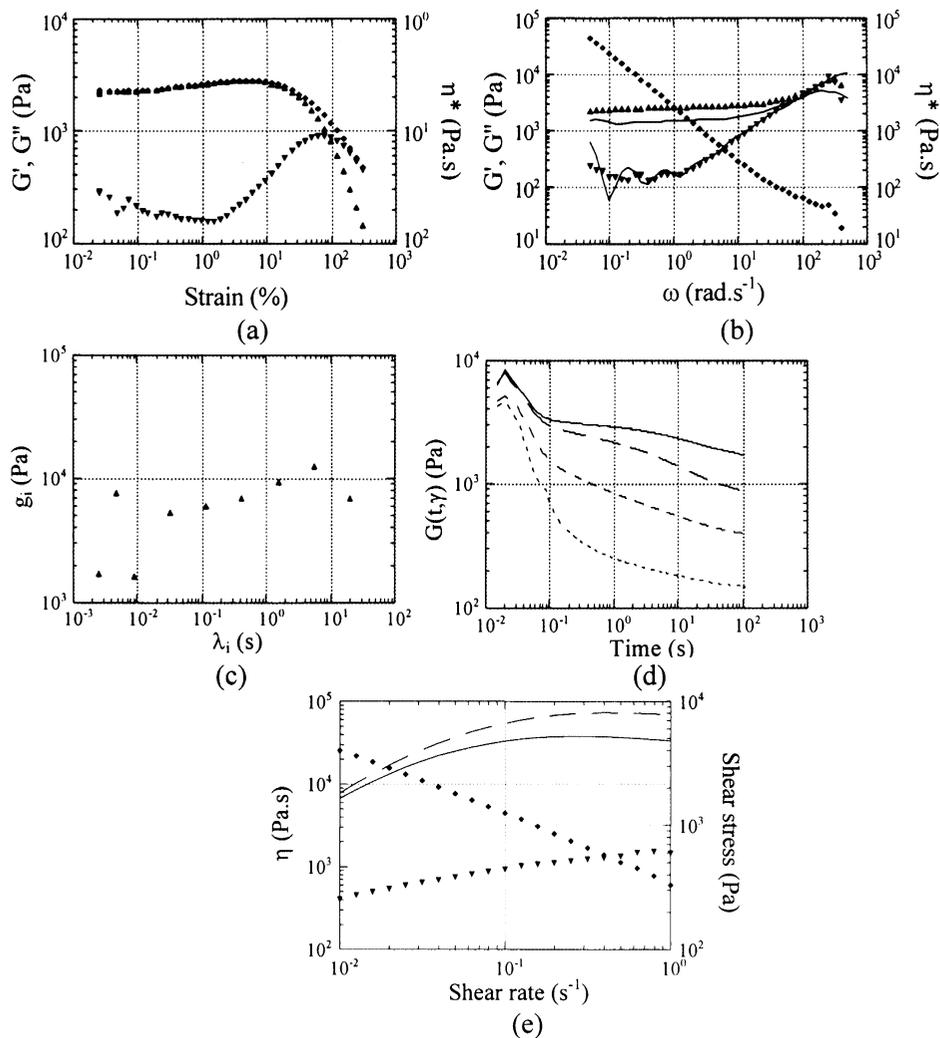


Fig. 10. Rheological characterisation, at 20 °C, of a dispersion manufactured via phase inversion containing 90% dispersed phase and with $x_{50} = 1.2 \mu\text{m}$. (a) Strain sweep, $\omega = 1 \text{ rad s}^{-1}$ (▲) G' , (▼) G'' , (◆) η^* . (b) Frequency sweep, $\gamma = 0.1\%$, (▲) G' , (▼) G'' , (◆) η^* . (c) Spectrum of relaxation times. (d) Step strain data for strains of 10, 30, 100 and 300 from top to bottom, respectively, from which values of $k = 1.3$ for 100% strain and $k = 0.8$ for 300% strain were calculated. (e) Steady shear measurements (◆) η , (▼) shear stress and predicted response for each value of k ($k = 1.3$ top line).

4.2.1. Effect of droplet size

Dispersions with a narrow range of droplet size distributions are produced by the phase inversion route. Over this range, from about 0.8 to 1.5 μm , no influence of droplet size on the rheological characteristics of the dispersions was observed. This result is similar to that seen for dispersions manufactured by direct emulsification.

4.2.2. Effect of dispersion age

In contrast to direct emulsification the rheology of dispersions manufactured by phase inversion does not change with age. This is illustrated in Fig. 12 which shows the change of strain sweep for a dispersion with 80% dispersed phase aged over 2 days. There is little difference in response over this time and if anything the moduli show a

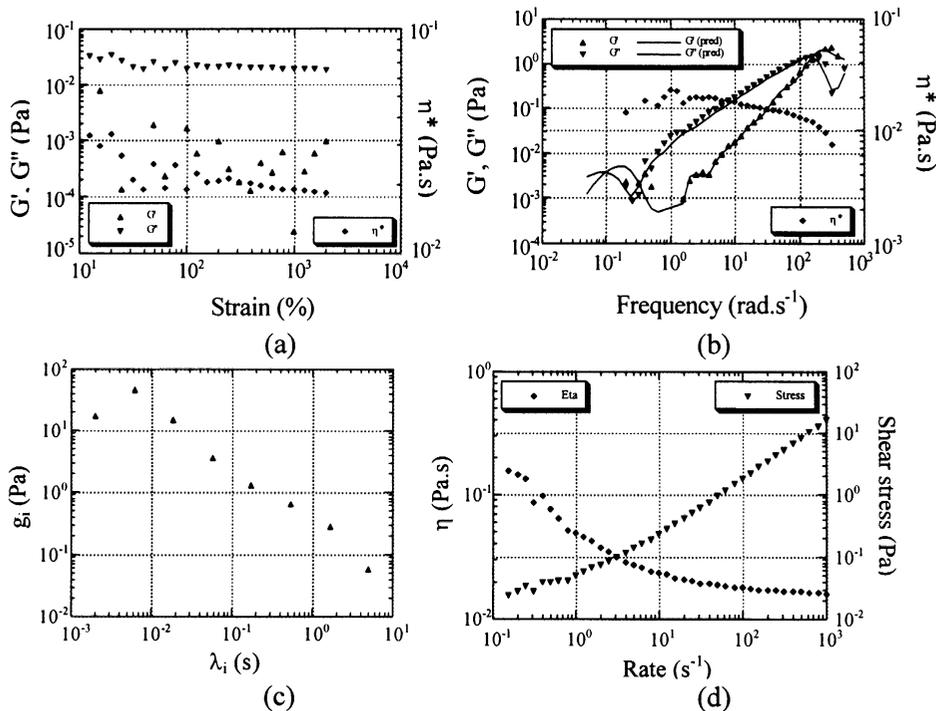


Fig. 11. Rheological response, at 20 °C, of a dispersion with 50% dispersed phase manufactured by phase inversion. (a) Strain sweep, $\omega = 1 \text{ rad s}^{-1}$, (\blacktriangle) G' , (\blacktriangledown) G'' , (\blacklozenge) η^* . (b) Frequency sweep, $\gamma = 30\%$, (\blacktriangle) G' , (\blacktriangledown) G'' , (\blacklozenge) η^* . (c) Spectrum of relaxation times. (d) Steady shear measurements (\blacklozenge) η , (\blacktriangledown) shear stress.

slight decrease in magnitude, suggesting a reduction in internal structure rather than the formation of flocs seen in dispersions produced by the direct emulsification route. Further ageing of the dispersions did not have any further effect on the response.

At lower dispersed phase fractions the situation is the same. This is illustrated in Fig. 13, which shows the change of strain sweep for a 50% dispersed phase dispersion, which has been aged for 12 days.

This age stability is a significantly different trend to that seen in dispersions manufactured by direct emulsification. As indicated above, the droplet sizes produced by phase inversion are significantly smaller than those generated by direct emulsification, with median sizes around 1 μm compared with 7–14 μm , respectively, for the dispersions used in this investigation. The same

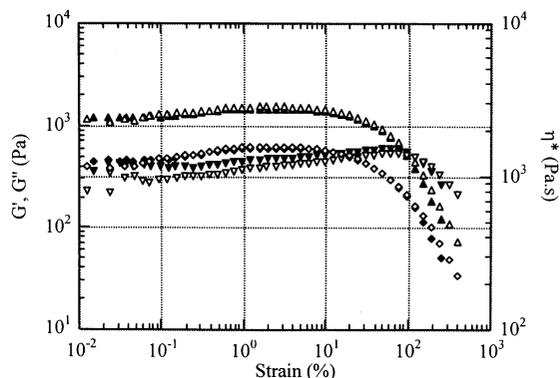


Fig. 12. Change in strain sweep response, at 20 °C, with dispersion age for an 80% dispersed phase dispersion manufactured by phase inversion, (\blacktriangle) G' , (\blacktriangledown) G'' , (\blacklozenge) η^* , (\triangle) G' after 2 days, (\triangledown) G'' after 2 days, (\lozenge) η^* after 2 days.

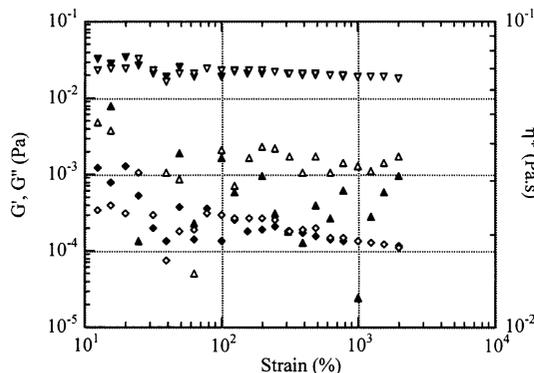


Fig. 13. Change in strain sweep response, at 20 °C, with dispersion age for a 50% dispersed phase dispersion manufactured by phase inversion, (▲) G' , (▼) G'' , (◆) η^* , (△) G' after 2 days, (▽) G'' after 2 days, (◇) η^* after 2 days.

concentration of surfactant was used during manufacture by both routes and therefore there is considerable less excess surfactant present in dispersion produced by phase inversion than those manufactured by direct emulsification. This decrease in excess surfactant can be expected to reduce the occurrence of depletion flocculation. Figs. 12 and 13 suggest that there is not sufficient excess surfactant to cause any flocculation to occur and the droplets are able to move past each other in both the fresh and aged dispersions.

4.3. Comparison between manufacturing methods

There are several differences in the rheological response of dispersions manufactured by each emulsification route. For a given dispersed phase fraction (Figs. 1 and 11) the viscosity of the dispersion produced by phase inversion is significantly lower, by almost an order of magnitude. Shear thinning behaviour in the steady shear test is seen with phase inverted dispersions, but not by fresh dispersions manufactured by direct emulsification.

Fig. 14 shows the change in complex viscosity and apparent viscosity at 20 °C with dispersed phase fraction for dispersions manufactured by both direct emulsification and phase inversion. The Newtonian viscosity of the dispersion was found where possible. This only affects the results

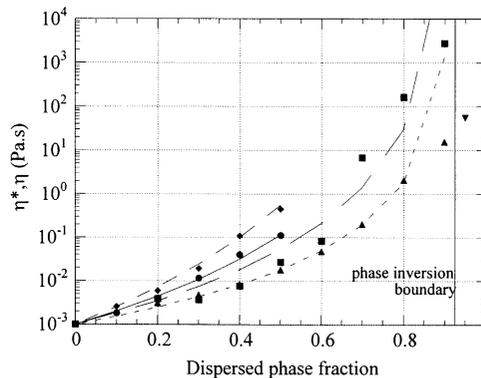


Fig. 14. Variation of complex and apparent viscosities, at 20 °C, with dispersed phase fraction of dispersions manufactured by direct emulsification (DE) and phase inversion (PI). The Krieger–Dougherty (K–D) equation has been fitted to each set of data. The viscosity of the base alkyd resin mix and a 5% water-in-alkyd dispersion are also shown. (●) η^* (at $\gamma = 1000\%$) DE, (—) fit for $\eta = 6.5$; (■) η^* PI, (—) fit for $\eta = 5.5$; (◆) η (at 100s⁻¹) DE, (—) fit for $\eta = 8.75$; (▲) η (at 100s⁻¹) PI, (—) fit for $\eta = 4$; (▼) 5% water in alkyd.

for dispersions with high dispersed phase fractions manufactured by phase inversion. The droplet size distributions of these dispersions are shown in Fig. 15 and show that dispersions manufactured via phase inversion contain significantly smaller droplets with a much narrower distribution. The production of smaller droplets by the phase inversion route is unexpected as catastrophic inversion occurs when the dispersed phase fraction is changed and this has been shown to generate droplets of a similar size to those obtained from

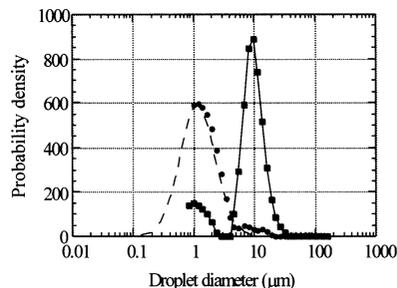


Fig. 15. Comparison between the droplet size distribution of a dispersion manufactured by direct emulsification (DE) and via phase inversion (PI). A log-normal distribution has been fitted to the distribution obtained from the phase inversion route. (●) PI, (—) log-normal distribution fit, (■) DE.

direct emulsification [29]. This indicates that the influence of the surfactant on the emulsification process, as well as the rheology, is significant.

The Newtonian viscosity of a 5% water in alkyd dispersion was found and is also shown in Fig. 14. All the curves show the same expected trend of increasing viscosity with increasing dispersed phase and as the alkyd fraction is increased the dispersion viscosity increases up to the phase inversion boundary after which a decrease in viscosity is observed towards that of the neat alkyd resin [5]. This figure shows clearly that for an equivalent dispersed phase fraction dispersions produced by phase inversion have a significantly lower viscosity than those produced by direct emulsification. This is an unexpected result as the smaller droplet size distribution produced by phase inversion would be expected to increase the dispersion viscosity for a given dispersed phase fraction [7]. Therefore, this suggests that the presence of excess surfactant micelles has a greater effect on the dispersion viscosity than the decrease in droplet size achieved through utilisation of phase inversion. Also, whereas dispersions manufactured by direct emulsification have a greater apparent viscosity than complex viscosity at a given dispersed phase fraction, the reverse is seen for dispersions manufactured by phase inversion. This difference is significant at higher dispersed phase fractions. The difference between the two mixing methods will be enhanced after a period of ageing as flocs form in the dispersions manufactured by direct emulsification.

5. Conclusions

Experimental rheological data of alkyd resin dispersions manufactured by direct emulsification and phase inversion together with the associated droplet size distributions have been presented.

Dispersions manufactured by direct emulsification for the range studied are weakly viscoelastic with the Newtonian viscosity following a Krieger–Dougherty relation. Surprisingly, the apparent viscosity is consistently greater than the complex viscosity over a range of dispersed phase fractions. This is an effect that at present we

cannot explain. Dispersions manufactured by phase inversion show viscoelasticity at higher dispersed phase fractions (above 80%), but near Newtonian behaviour at lower dispersed phase fractions (below 50%). A KBKZ type model has been fitted to the data and within the linear viscoelastic region we obtain a good fit, however, the steady shear prediction is poor, especially for dispersions manufactured by phase inversion which we believe is a result of wall slip.

For a given dispersed phase fraction and surfactant concentration, the viscosity of dispersion manufactured by phase inversion is significantly less than that produced by direct emulsification. This is surprising, as Pal and Otsubo and Prud'homme [27,30] for example, have shown smaller droplets produce dispersions with a higher viscosity for a given dispersed phase fraction. The effect of ageing on the rheology of the dispersions is significant for the direct emulsification route with viscoelasticity increasing with time. Utilisation of the phase inversion route yields dispersions with significantly smaller droplet size distributions and with greater ageing stability. A possible explanation of this result is that the excess surfactant in the direct emulsification sample is causing viscoelastic structuring in the aqueous phase by depletion flocculation.

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