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Thermal Analysis & Rheology

Parallel Superposition Rheology
of an Associatively Thickened Latex

by

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Introduction

Principles of parallel superposition

The rheological techniques of steady shear and oscillatory shear, and their use in investigating the properties of liquid and semi-solid materials, are well known. In superposition experiments the steady shear and oscillatory motions are applied to a sample simultaneously [1]. The direction vectors of the two motions may be either parallel (parallel superposition), or at right angles (transverse or orthogonal superposition). In both cases superposition moduli, analogous to those of simple oscillation, can be defined. For parallel superposition the shear stress at low amplitudes is given by [2]:

$$\sigma_{yx}(\gamma, \gamma_0, t) = \eta(\gamma) \bullet \dot{\gamma} + G_{\parallel}^*(\omega, \gamma, \gamma_0) \bullet \gamma_0 \sin \omega t \tag{1}$$

where $G_{\parallel}^*$ is the parallel complex modulus, γ is the steady shear rate, $\eta(\dot{\gamma})$ is the steady shear viscosity, and γ_0 and ω are the amplitude and frequency of the superimposed oscillation respectively. Then $G_{\parallel}' = \gamma_0 \cos \delta$, and $G_{\parallel}'' = \gamma_0 \sin \delta$, where δ is the phase angle between the oscillatory components of the shear stress and the shear strain.

The superposition can cause an interference from one motion on the response of the other, oddities such as negative values for the storage modulus may result, and interpretation of the results is difficult [3]. If the amplitude of oscillation is sufficiently low, however, a linear region is observed in which the parallel moduli are independent of amplitude, and the oscillation can be regarded as a linear perturbation of the steady shear. In this region the oscillation probes the shear induced steady state structure.

Parallel superposition rheology has previously been reported for polymer solutions [3, 4], and liquid crystals [2, 5], and more recently for polymer melts [6]. To the author's knowledge, however, particulate dispersions have not previously been investigated using this technique.

Principles of associative thickening

Surface coating and other formulations based on aqueous latices usually require the addition of rheology modifiers [7]. Since these modifiers have the effect of increasing the viscosity of the system, over at least part of the usual shear rate range, they are commonly referred to as thickeners. Conventional, non-associative, organic thickeners are aqueous soluble polymers such as cellulose ethers. Interactions between non-associative thickeners and the other principle components of the formulation, the latex binder and pigment particles, are in general weak or negligible. Formulating with such thickeners is therefore relatively straightforward, as the rheological performance of the complete system can simply be regarded as a combination of those of the thickener and the base formulation.

In contrast associative thickeners rely for their effect partly on strong interactions with other components of the formulation, in particular the latex binder [8]. They are aqueous soluble polymers, but unlike conventional thickeners, each molecule contains at least two hydrophobic groups. These groups accommodate themselves to the aqueous environment either by adsorbing on the surface of the latex particles, or by forming ensembles analogous to micelles. An extensive network is thereby built up throughout the system.

Associative thickeners confer many benefits on surface coatings, but the rheological performance of the complete system differs substantially from those of the thickener and base formulation combined [9], and the problem which this presents to a formulator will be recognized. Investigation of the rheological properties of associatively thickened systems and the mechanisms involved is therefore of considerable importance to the surface coatings industry. In this study the rheological technique of parallel superposition is used to investigate a commercial latex thickened with a commercial associative thickener.

Experimental

Materials

The latex used in this study was a 100% acrylic latex, supplied at 44.0% by volume in water, pH 9.0-9.5, specific gravity (dry powder) 1.13, (wet powder) 1.06. Particle diameter (light scattering) 452 ± 36 nm (95% confidence limits).

The thickener used was a commercial polyether urea polyurethane associative thickener, supplied at 25% solids in 80:20 water:diethylene glycol ether; specific gravity 1.03; Mw 30,865; Mn 16,770; polydispersity 1.8405.

Sample details

Three samples were prepared, containing 1.0, 2.0 and 5.0% thickener (total formulation) by weight (manufacturers recommendation 0.4 - 6.0%). Experiments were performed on each of these samples, along with the base (unthickened) latex.

Instrument

This work was carried out on a controlled strain Weissenberg Rheogoniometer manufactured by TA Instruments. A cone and plate geometry was used throughout. In this configuration the sample is placed between two circular plates, the lower of which is flat and horizontally mounted. The upper plate has the form of an inverted cone, truncated at the tip, with the virtual cone tip located in the plane of the surface of the lower plate. The lower plate is driven at a given rotational speed or angular frequency, and a simple numerical conversion provides the shear rate. Stress is transmitted by the sample to the upper plate, causing it to rotate against a precalibrated torsion bar on which the plate is suspended. This rotation is monitored by a linear displacement transducer, and the shear stress is simply calculated. Concentricity of the upper and lower plates is maintained by an annular air bearing of negligible friction.

The upper operating frequency of the instrument is governed by the natural frequency of the torsion bar, in the region of which the response becomes insensitive to to the material properties of the sample [10]. This effect becomes significant at about 70% of the natural frequency. The higher the compliance of the torsion bar the greater the sensitivity, but the lower the natural frequency. In this investigation two torsion bars were used.

Procedure

Experiments were conducted at 20°C throughout.

In all cases the sample was loaded onto the instrument by raising the upper plate, and placing an aliquot of sample on the lower plate. The upper plate was then lowered at an exponentially decreasing rate. The system was allowed to equilibrate for five minutes before shear was applied. Preliminary investigations had shown this time to be ample.

For the steady shear experiments shearing was then commenced, the shear rate being ramped up logarithmically over three minutes, over the range 10^{-3} to 10^3 s^{-1}. Thixotropic and transient effects were negligible over these timescales. Oscillatory and superposition measurements were performed at angular frequencies from 6.28 to 628 rad s^{-1} (0.1 to 100 Hz), superimposed on steady shears of zero, 1 and 10 s^{-1}. The sample loading and equilibration procedures were as for the steady shear experiments.

Linearity checks were conducted at all shear rates on selected samples by increasing the oscillation amplitude at an angular frequency of 6.28 rad s^{-1}. It was found that in all cases the moduli were independent of amplitude to at least 0.05 strain units. To ensure that this was universal all oscillatory and superposition experiments were conducted at oscillation amplitudes of both 0.02 and 0.05 strain units. Data taken at these amplitudes were in all cases superimposable within experimental error.

For the frequency ramp experiments steady shear was applied after equilibration, at the required rate, for one minute, before the superimposed oscillation was added. Oscillation was conducted for 10 seconds plus 10 cycles before the commencement of sampling, and a further 10 seconds plus 10 cycles while sampling. Preliminary investigations had also shown that under these conditions steady state was achieved before sampling commenced. It should be remarked in passing that any transient response could not be investigated in these circumstances, but that the preliminary investigations referred to showed that the instrument response was sufficiently rapid for these to be observable. It is intended that this should be the subject of a future investigation.

Results presented for the superpositon experiments are compilations of two data sets. Data in the range 0.63 to 62.8 rad s[-1] were obtained using the high compliance, low natural frequency torsion bar, and in the range 31.4 to 628 rad s[-1] using the low compliance, high natural frequency torsion bar. Excellent overlap was achieved between the data sets for each experiment.

Results and discussion

Steady shear viscosity results for the latex as supplied, and containing 1.0, 2.0 and 5.0% thickener, are presented in Fig. 1. In all cases the viscosity was seen to decrease with shear rate, approximately following a power law, but with asymptotic values for the viscosity at high and low shear rates. Similar results for both unthickened and thickened latices have been reported many times [11].

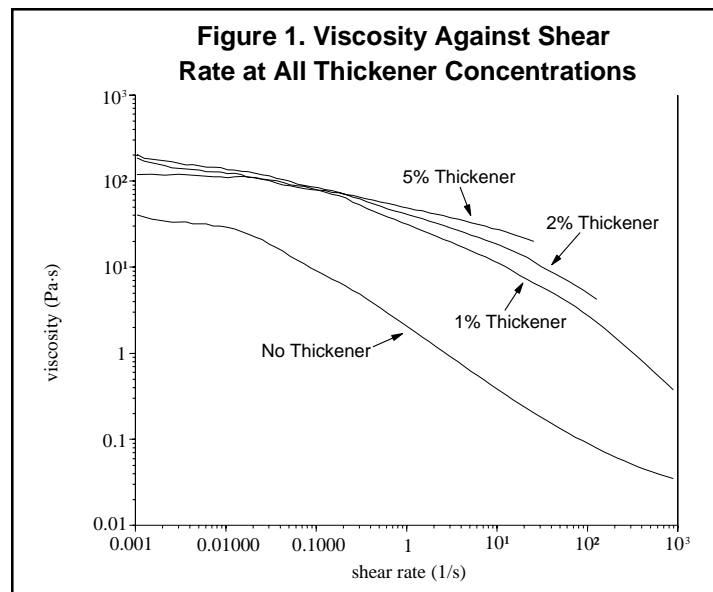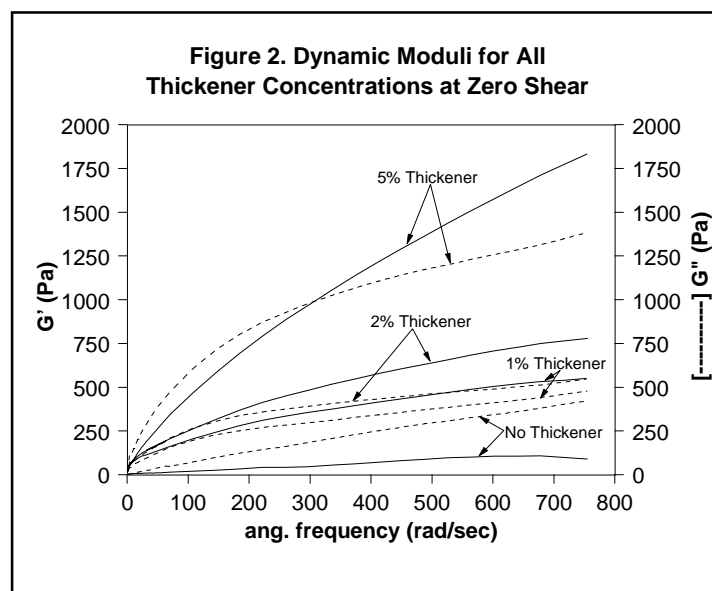Data presented are those obtained at an amplitude of 0.02 strain units.

Figure 1. Viscosity Against Shear Rate at All Thickener Concentrations

Fig. 2 shows $G_{\parallel}'$ and $G_{\parallel}''$ against frequency for all four samples at zero shear rate. As has been reported by previous workers for similar systems [12], both moduli are found to increase with frequency. It can be seen that besides increasing the viscosity, the thickener greatly increases the elasticity of the system. Figures 3 and 4 show $G_{\parallel}'$ and $G_{\parallel}''$ against frequency at added shear rates of 1 sec^{-1} and 10 sec^{-1} respectively. Again the trends in the moduli are as expected.
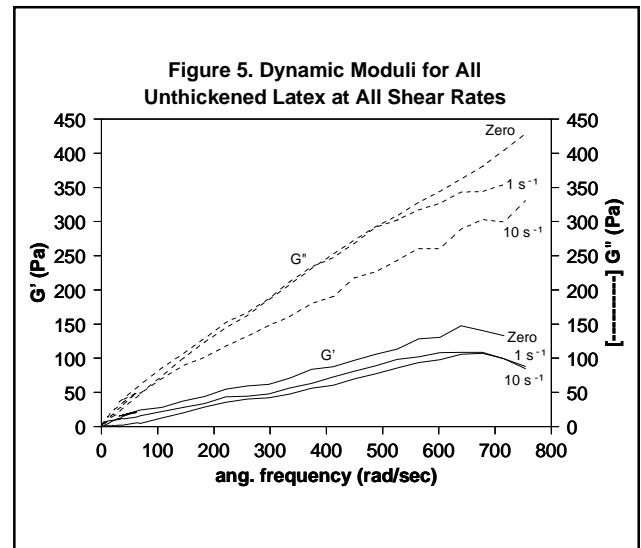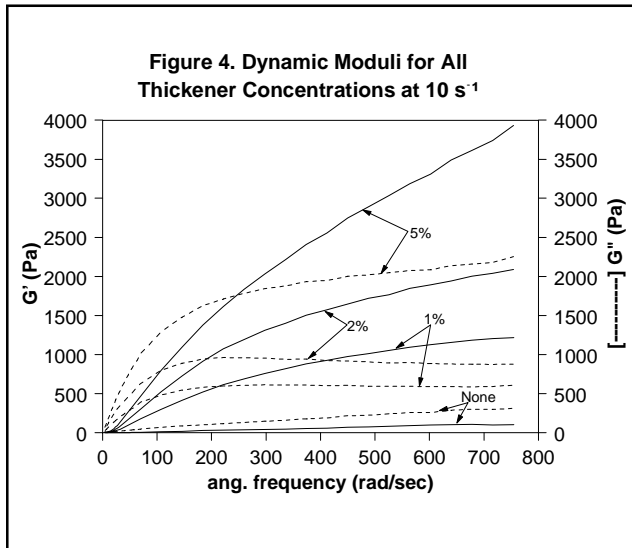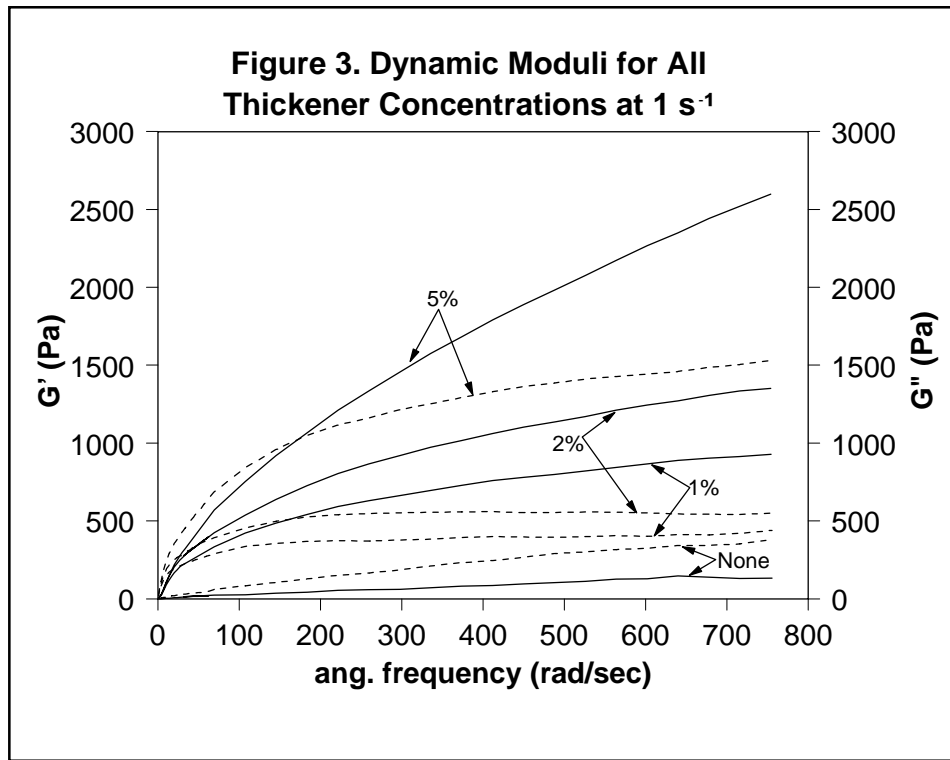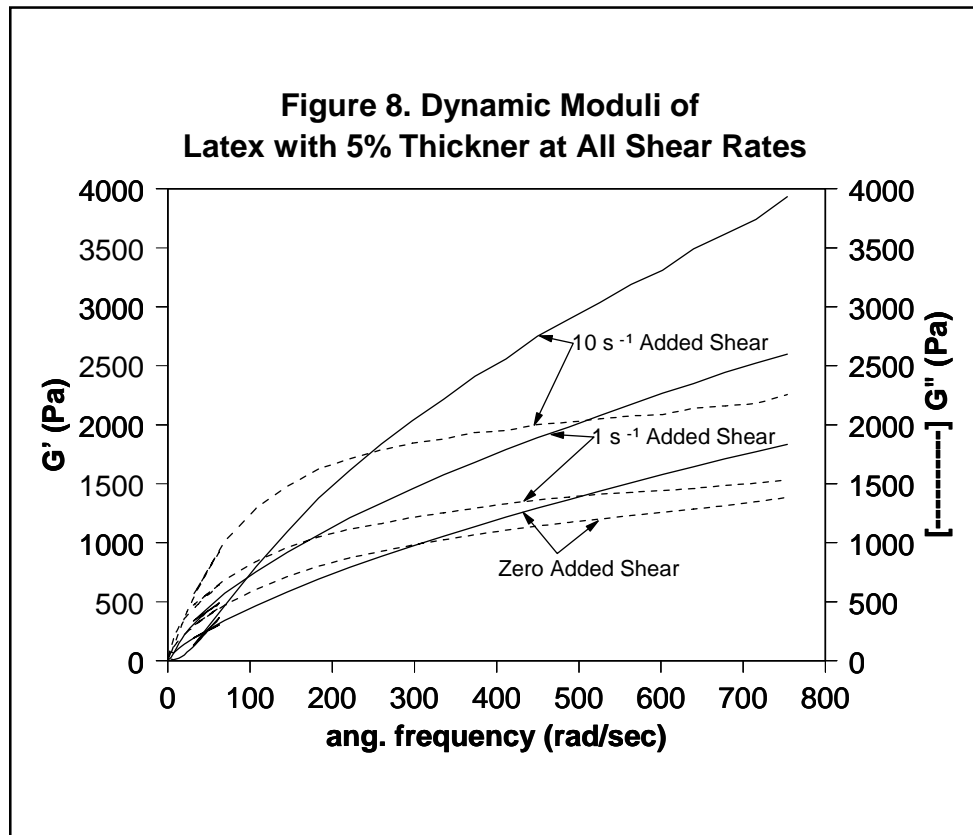

Figure 2. Dynamic Moduli for All Thickener Concentrations at Zero Shear

**Figure 3. Dynamic Moduli for All
Thickener Concentrations at 1 s^{-1}**

5%

2%

1%

None

G' (Pa)

G" (Pa)

ang. frequency (rad/sec)

**Figure 4. Dynamic Moduli for All
Thickener Concentrations at 10 s^{-1}**

5%

2%

1%

None

G' (Pa)

[--------] G" (Pa)

ang. frequency (rad/sec)

**Figure 5. Dynamic Moduli for All
Unthickened Latex at All Shear Rates**

Zero

1 s^{-1}

10 s^{-1}

G"

G'

Zero

1 s^{-1}

10 s^{-1}

G' (Pa)

[--------] G" (Pa)

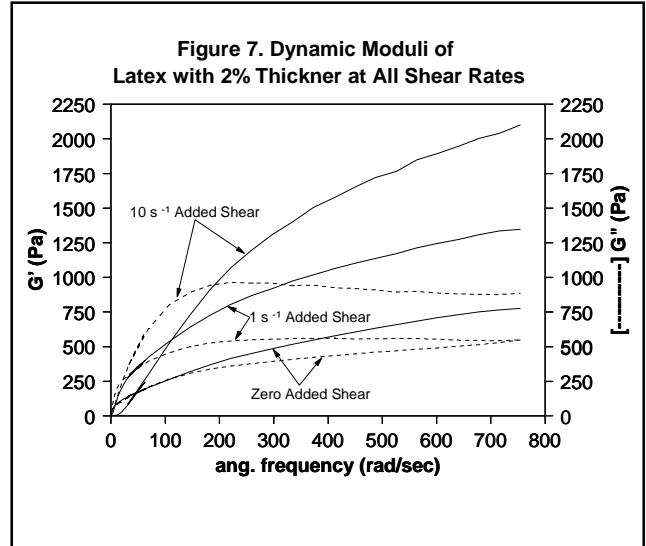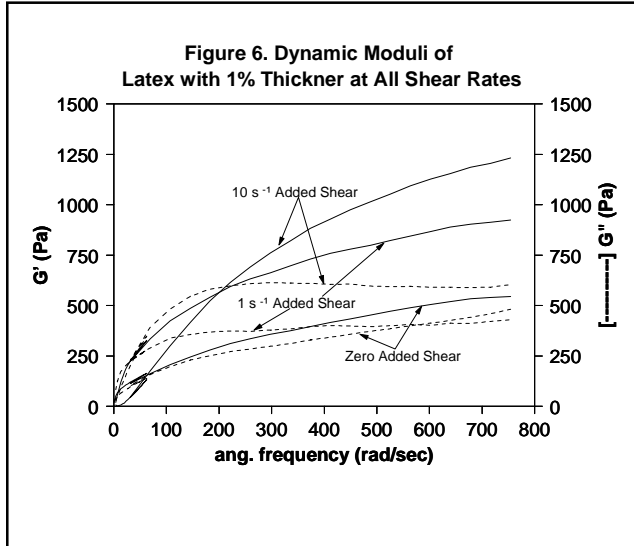ang. frequency (rad/sec)

Fig. 5 shows $G_{\parallel}'$ and $G_{\parallel}''$ against frequency at steady shear rates of zero, 1 sec^{-1} and 10 sec^{-1} for the unthickened latex. It can be seen that at all shear rates $G_{\parallel}'' > G_{\parallel}'$ over the entire frequency range. However an interesting feature of the data is that for $G_{\parallel}'$ the zero shear values lie between those of the 1 sec^{-1} and the 10 sec^{-1} added shear. This feature is discussed in detail below.

Figures 6 to 8 show $G_{\parallel}'$ and $G_{\parallel}''$ against frequency at added shear rates of zero, 1 sec^{-1} and 10 sec^{-1} for the samples containing 1.0%, 2.0% and 5.0% thickener respectively. It can be seen that in all cases the moduli increase with added shear rate. This trend is the reverse of that which has been reported by other workers for polymers and liquid crystals [2,3,4,5], and to the author's knowledge has not previously been reported for any system. Indeed it does seem remarkable that for shear thinning systems in which the steady state viscosity decreases with shear rate, the dynamic rheological functions increase with frequency.

Figure 6. Dynamic Moduli of Latex with 1% Thickner at All Shear Rates

Figure 7. Dynamic Moduli of Latex with 2% Thickner at All Shear Rates

Figure 8. Dynamic Moduli of Latex with 5% Thickner at All Shear Rates

Elasticity in dispersions is usually considered to be hydrodynamic or thermodynamic in origin; the former term referring to shear induced pressure gradients within the sample, the latter to Brownian and interparticle effects. Wagner and Russel have shown that the hydrodynamic and Brownian terms are likely to be orders of magnitude less than measured values [13], and it is therefore probable that the effects observed in the present case are substantially due to particle interactions

It has been suggested that the origin of shear thinning in latices is the displacement of the particles from random (Brownian) positions at zero shear, into two or one dimensional structures (rafts and strings) which align in the shear field. Structures of this type have been reported both for real systems and for computer simulations; the subject has recently been reviewed by Chen et.al. [14]. The experimental data presented here suggest that such structures are formed with or without the presence of thickener. However for dispersions in general, the high frequency limit of the storage modulus, $G_{\parallel}'(\infty)$, is proportional to the second derivative of the interparticle potential of mean force (the free energy of interaction between adjacent particles), $d^2E(R)/dR^2$, or, what is equivalent, the derivative of the interparticle force, $dF(R)/dR$, where R is the centre-centre distance between adjacent particles [15].

Characteristic times for structural changes are relatively long, and in the linear viscoelastic region we are therefore probing the form of the potential of mean force. There are a number of contributions to this potential for complex dispersions, in particular van der Waals attraction, and repulsion due either to electrostatic double layer interactions or steric overlap of adsorbed surfactant or polymer layers. The form of the potential is governed by the magnitude of each of these contributions. Although the potential of mean force is not directly available in the present case, it is reasonable to postulate that for the unthickened latex the form of its third derivative is not monotonic. In other words, the shear induced structures formed result in a reduction in the interparticle separation with increasing shear rates, but the derivative of the interparticle repulsive force is greater at longer and shorter separations than at intermediate separations. A sigmoidal repulsion of this form has been predicted by de Gennes for sterically stabilised dispersions [16]; rheological and other measurements confirm the prediction [17, 18].

For the thickened latices the presence of the associative thickener increases the repulsive force between the particles at low separations, where the thickener molecules are compressed away from entropically more favourable configurations. De Gennes' theory predicts an approximately exponential repulsion at separations of high compression of the adsorbed polymer, in which case, of course, d^nE/dR^n is monotonic for all values of n, and the observed trend in $G_{\parallel}'(\infty)$ is predicted.

It is worth remarking that these observations have further implications for the surface coatings technologist. For those processes in which the shear rate changes encountered are slow (brushing, pouring, pumping etc.) the steady state viscosities of the material are all that need be considered. However for those processes in which the shear rate changes more rapidly than can be accommodated by structural changes in the material (high speed printing, pulsatile pumping) difficulties may be encountered which the steady state viscosity will not reveal.

Conclusions

It has been shown that a latex thickened with an associative thickener is shear thinning, but that the parallel superposition moduli increase with applied shear rate. It is argued that this is due to the reduction in the interparticle separation at high shear rates, combined with a monotonic decrease in the third derivative of the interparticle potential of mean force. For surface coatings technologists the implication is that for most purposes the steady state viscosity is a reasonable guide to the performance of a material in application, but that under conditions in which the change in shear rate is rapid, for example pulsatile pumping and high speed printing, the use of conventional rheological techniques is insufficient. Superposition measurements are required in these circumstances.

Acknowledgements

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