

# A REVIEW OF THE RHEOLOGY OF FILLED VISCOELASTIC SYSTEMS

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## **ABSTRACT**

We are concerned here with the effect of added filler particles on the linear and non-linear rheological properties of viscoelastic systems. Whilst the addition of spherical or near-spherical filler particles will almost always *increase* the level of both the linear and the non-linear viscometric properties (so leading to increases in pressure drops, etc.), we usually find a *decrease* in the level of the elasticity (in its various measures combining the first normal stress difference and the shear stress), as manifested in such important practical features such as extrudate swell, melt fracture, size of entry vortices, stress relaxation, Weissenberg effect, etc. However, the addition of high-aspect-ratio, fibre-like fillers can *increase* the elasticity as well as the viscosity. Occasionally, the absorption of chemical species from the continuous phase onto the surface of the disperse phase particles can complicate matters due to depletion of the continuous phase.

**KEYWORDS:** Viscoelastic; Polymer; Worm-like micelles; Particles; Filler.

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## **1. INTRODUCTION**

Suspended particles of various morphologies dispersed in viscoelastic liquids form the basis of many products and product precursors of industrial and commercial interest, ranging from polymer melts with fillers of disparate shapes, through ceramic pastes with polymeric binders, to consumer products such as toothpastes and medicines which have, for instance, crystalline, precipitated or ground-up solids as functional components suspended in a polymeric liquid phase. Viscoelastic detergent systems also come into this category, especially those formed from worm-like micelles.

Fillers are added to polymer melts in order to—among many other things—reduce the cost of, or increase the stiffness of the resultant solid polymer articles. On the other hand, polymer binders and thickeners are often added to aqueous dispersions of functional dispersed particulate material to improve the physical stability and aesthetic appearance ('thick and creamy'). For every-day consumer products, solid particles are frequently added to polymer and/or detergent thickened liquid bases to

produce an abrasive effect, as for instance in toothpastes, facial scrubs and hard-surface cleaners.

All these products are dispersions of solid particles in viscoelastic, shear-thinning liquids. We are concerned here with investigating the consequences of the presence of particles on the rheological properties of such liquids; in particular the viscosity and the non-linear, steady-state viscoelastic properties such as first (primary) and second (secondary) normal-stress differences as well as the extensional viscosity, which, depending on the particular molecular microstructure involved, can be quite different in its form from the shear viscosity. We will also mention linear viscoelasticity to complete the picture, although this is rarely of any real practical consequence. Arising from a combination of the non-linear viscoelastic and the shear stress components are the overt “elasticity” properties such as extrudate swell, melt fracture, size of entry vortices, stress relaxation, etc. In this context Cogswell [1] notes that ‘the elastic response of filled melts is usually reduced relative to that of the resin’, but many will wonder if he and the many who makes such statements are referring to the storage modulus, the first normal stress difference or to the observable elasticity manifestations such as extrudate swell.

While this study is important in its own right, it is also instructive as a simple exemplar for the study of the rheology of heterogeneous assemblages, and goes some way to showing how we can investigate these more complex systems that are often found in real products with their many “rheologically” active components.

The filler particles that we are interested in here can often be considered to be large enough—super-micron—to neglect Brownian motion, so that generally the effective phase volume relative to the maximum phase volume, is the primary controlling factor. Under these circumstances this parameter is a function of shape, morphology and the particle size distribution, but not necessarily of size itself. However, for some systems colloidal effects can be important, and for instance particle-particle attraction can lead to the formation of flocs that can have a profound effect on the linear and non-linear rheology.

## 2. PREVIOUS WORK

In his review of the situation current in 1985 with regard to suspensions in polymeric liquids, Metzner [2] noted that as far as any increase in viscosity was concerned “remarkably ... the best empirical expression for the effect of fillers on viscosity] available is probably the very simple form originated by Maron and Pierce”. He then uses this simple expression—see below for details—throughout his review to capture the form of data for various situations, saying ‘its use is recommended generally, albeit with caution’. He went on to discuss the elastic case, and concluded that at that time ‘there are only limited data with which to assess these effects, and no evident theoretical calculations’. He then noted results that showed that in capillary experiments the Bagley end correction for the pressure drop into the pipe was appreciably smaller for filled systems than for a polymer melt alone. He then recorded the observations of a number of workers that extrudate swell decreased, and more so as the concentration of particles was increased. With regard to linear viscoelastic measurements, he registered findings that suggested that  $G'$  rose slower than  $G''$  when

particles were added to a melt, so “In other words, the comparative importance of the elastic forces decreases as the solids concentration levels increase’. He then noted that at that time the only normal stress data he knew of was for suspensions of fibres which ‘the normal stresses rise slightly more rapidly than does viscosity’.

With respect to practical polymer processing and the addition of fillers, many areas have been reviewed, by Shenoy, in his book entitled “Rheology of Filled Polymer Systems” [3].

### 3. GENERAL OBSERVATIONS ON THE ADDITION OF PARTICLES

The addition of particles to a flowing liquid—with the inevitable accompanying local disturbance of the flow-lines—will obviously result in even the simplest situation (such as that found in simple Couette flow) becoming quite complicated. So, what might have started out as a steady-state, simple-shear flow—say in a cone-and-plate geometry with its constant shear rate—changes into a situation where locally in the liquid phase in the vicinity of the particles there is

- an increase in, and spatial variation of, the shear rate in the continuous phase;
- transient behaviour of local liquid elements as particles come towards and move past each other; (i.e., Eulerian vs. Lagrangian steadiness); and
- the introduction of extensional components into the local liquid flow as particles move past, over, towards or away from each other.

Because of the introduction of these complications, rheological properties other than viscosity can *potentially* become important even in the change in overall viscous dissipation. So that, just as the viscosity could be complicated by the presence of normal-stress differences, so too could the modified normal-stress differences be affected by unusual changes brought about in the viscosity! Indeed, See et al [4] recently concluded that ‘the Newtonian case itself contains many unresolved issues, and the viscoelastic case is even further complicated by the dependence of the carrier fluid’s response to deformation history’.

The end result of all these considerations could be a situation where, even when thinking about the increase in viscosity due to the addition of particles, no simple universal statements can be made based *only* on the original shear-viscosity behaviour of the continuous phase, and the altered viscosity curve would be a function of the *complete* polymeric continuous phase rheological behaviour, and not just the steady-state shear viscosity behaviour. So, if we find any simple useful expressions, we will be very thankful!

Theory and experiment show that the presence of particles in simple Newtonian liquids can lead to a *negative* first normal stress difference and a *positive* second normal stress difference. On the other hand, polymers systems always have a positive first normal stress difference and a (smaller), but negative, second normal stress difference. It is perhaps hardly surprising therefore that the combination of polymers

and particles, although giving an increase in viscosity, can, overall, give a much smaller increase in the first normal stress difference.

#### 4. FILLER PARTICLES

Obviously the particular effects found by adding particles as fillers will depend strongly on the nature of the individual filler particle and the way in which these particles interact with one another. These factors will now be considered. Last in this section, we will discuss the fact that added particles will not only change the rheological properties of a non-Newtonian liquid, but they can interfere with the measurement of these properties.

The simplest situation we can imagine is that the filler particles are present as geometric entities that only alter the flow lines of the continuous-phase liquid. For a given shear rate, the resulting distortion of the flow-lines leads to increased dissipation, hence an increase in viscosity. The minimum disturbance to flow is caused by spherical particles, while any other shape will usually give a greater distortion to the flow lines. (The exception to this is for aligned fibres.) Any tendency of particles to clump together – as for instance in flocculation - will also increase the distortion of flow lines.

##### Kinds of fillers

Typical inorganic and *organic* fillers used in polymers (i.e., plastics), etc., are:

alumina	asbestos	barium sulphate
calcium carbonate	calcium fluoride	<i>carbon black</i>
clays	diatomaceous earth	feldspar
ferromagnetics	fly ash	glass fibres
gypsum	<i>jute fibre</i>	kaolin
<i>lignocellulosics</i>	magnesium hydroxide	nylon fibres
mica flakes	<i>microcrystalline-cellulose</i>	powdered metals
quartz	silicas	<i>starch / ground rice</i>
talc	titanium dioxide	<i>wood flour/fibres</i>

with shapes ranging from spheres (solid, porous or hollow), through relatively short flakes, to long fibres, as well as other irregular shapes with differing degrees of porosity, see Falcone [5] and Wypych [6].

The properties of these filler systems that determine their particular contribution to the viscous and non-linear viscoelastic properties of the polymeric systems that they are added to, include their:

- concentration (as *effective* phase volume including porosity);
- shape (shape distribution, aspect ratio of fibres);
- particle-size distribution (possibly bi- or multimodal);
- surface properties (e.g., surface charge density via solution pH);
- adsorbed species (polymers or surfactants), and the
- hydrophobic/hydrophilic nature of the particles *vis-à-vis* the continuous phase.

These considerations are important in a number of respects including the *effective* phase volume of the particles, via the “openness” and strength of any flocs present resulting from particle-particle attraction. The particle interactions, which determine the degree of flocculation, are often decided by solution properties such as pH, electrolyte level, as well as dissolved polymers acting as straightforward thickeners or causing depletion flocculation. The degree of adsorption of polymers onto particle surfaces can often be controlled by competition with surface-active species such as surfactants present in solution. All these factors should be taken into account in any consideration of the overall rheology of filled systems.

Once the particle-surface take-up of polymer is complete, the viscoelastic properties begin to rise as usual as more polymer is added to the solution. This will be strongly particle-size dependent via the surface area, and if more particulate material is added, an increase in the level of viscoelastic properties would eventually ensue when the surface absorption is saturated. Other chemical moieties can transfer from the continuous phase onto the particle surfaces, and this could also cause some decrease in the viscosity of the continuous phase. In liquid-like systems, the particles can be centrifuged out and the effect on the liquid viscosity can then be measured directly. Another source of chemical interaction is the opposite – the dissolving or desorption of chemical moieties from the particles into solution. This can change the solution pH, or the general chemical composition, which in turn can lead to changes in the rheology.

In polymer melts certain dispersants are often added to affect the later solid properties. These can often act as dispersal aids to overcome the natural tendency of added particles to be attracted together by van-der-Waal’s forces to form flocs. These can have a profound affect on the flow properties since they affect the effective phase volume enormously. These alter particle/particle interactions, and also the way the particles key into the *solid* polymer, which affects the ultimate solid polymer strength, but there is only little evidence that they affect the particle/melt interaction, which is simply “non-slip”.

The level of linear properties such as the storage and loss moduli,  $G'$  and  $G''$ , are always raised with filler addition. This usually takes the form of a progressive increase in the level of the properties as more filler is added. However, sometimes a secondary mechanism can be seen such as the development of a plateau usually from a pseudo-network set up between flocs or chains of particles.

### Particle interactions

Particle-particle interactions (other than hydrodynamic) have been summarised by Barnes [7] and Quemada and Berli [8] and they include:

- Hydrophobic/hydrophilic interactions which usually exist where the dispersed phase is hydrophilic and the continuous phase is hydrophobic, and this leads to the particles treating the continuous phase as a hostile environment and being attracted to one another. This will mean that even traces of moisture on the particles can lead to flocculation, as happens when water is added to molten chocolate and the sugar particles—dispersed in cocoa butter oil—become moist;
- The particles can occasionally be charged, leading to repulsion;
- For very small particles, van der Waals attraction can lead to flocculation.

Similarly non-hydrodynamic continuous phase / particle interactions include:

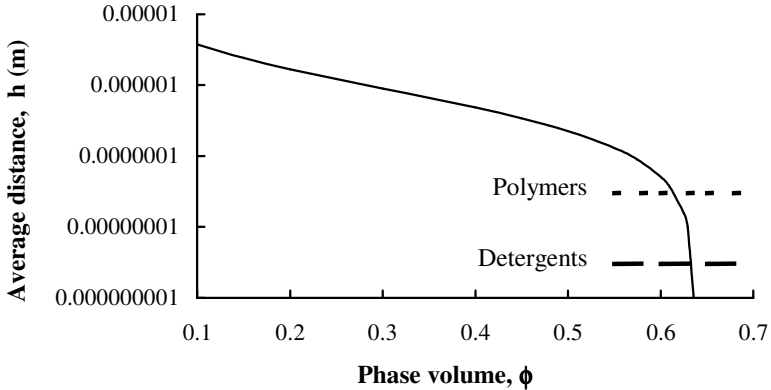
- absorption of polymers from the continuous phase can increase the effective particle size,
- species depletion from the continuous phase, especially of the thickening is due to surfactant species,
- depletion flocculation of particles; see Kiratzis and Luckham [9] and Robins [10],
- de-flocculation of particles by addition of additives.

At very high phase volumes, the average distance between particles of diameter,  $d$ , that we are considering, say  $10\ \mu\text{m}$ , becomes very small, and any surface effects between particles becomes very important. An average value of  $h$  in terms of  $d$  in terms of phase volume  $\phi$  is given by

$$\frac{h}{d} = \left[ \left( \frac{1}{3\pi\phi} + \frac{5}{6} \right) - 1 \right]. \quad \dots\dots\dots(1)$$

Figure 1 shows the average distance,  $h$ , between such  $10\ \mu\text{m}$  particles calculated according to the equation, see Barnes et al [11]. In this situation, the maximum phase volume of the randomly close-packed suspension of “bare” particles is  $\phi_m = 2/\pi$ , i.e., 0.6366.

As we see, the interparticle distance decreases steadily until the phase volume is around 0.55, thereafter the interparticle distance begins to decrease rapidly, and any colloidal decoration on the particle surface becomes very important to the rheology, and simple formulae for the effect of filler phase volume on viscosity fail. Typical effective layer thicknesses of polymers, and electrical double layers on charged particles are of the order of 10 – 20 nm, while detergents molecules absorb to a



**Figure 1:** Average interparticle distance as a function of phase volume for a suspension of 10  $\mu\text{m}$  diameter spheres: broken horizontal lines show when two 15 nm absorbed polymer layers or two 1.5 nm detergent layers on adjacent particles just touch.

thickness of around thickness of around a tenth of that value. This shows that at high concentrations, interparticle interactions will become quite significant, even though they are not apparent at lower concentrations. They become particularly important even for the definition of the phase volume, since small increases in effective phase volume calculated on the basis of the “core” radius plus a layer thickness have very large effects on viscosity at these phase volumes.

**Problems with particles in rheometers**

Barnes [12] has shown that the presence of particles that are large, compared with the dimensions of the enclosing measuring geometry, can lead to problems. He concluded that wall effects could only be ignored if the particle size is smaller than 1/10<sup>th</sup> of the gap size in the rheometer for concentrations around 25%, but above that value of phase volume, the allowable particle size would be even smaller. Indeed, above 50%, the size ratio would have to be smaller than 1/100<sup>th</sup>! As this has rarely been the case for filled polymer systems with very high phase volumes, it is questionable that the data is invariant to gap size. Of course, if enough data was collected over a range of gap sizes, a simple correction could be made, but this has not often been the case.

If a cone-and-plate geometry is used to measure a concentrated suspension, even with a large truncation of 100  $\mu\text{m}$ , then to ensure that no problem arises, particles

smaller than a micron would be necessary. However particles of this size could well interact colloiddally, and we are no longer looking at the effect of phase volume alone.

This cautionary note should be sounded because not all studies of the viscosity of filled systems comply with the requirements demanded, and the results quoted have caused confusion.

## 5. GENERAL COMMENTS ON VISCOELASTIC SYSTEMS

Viscoelasticity usually arises from the presence of polymers in the continuous phase, or otherwise as melts. The flow properties of such systems arise – for a given molecular weight and concentration – from the particular polymer architecture, ranging from linear coils (e.g., polyacrylamide), through lightly branched coils to highly cross-linked “microgels” such as xanthan gum or the various kinds of Carbopol, as well as melts with similar linear and branched polymers, although polymer melts are never as cross-linked as Carbopol, see Roberts and Barnes [13]. By and large, the level of viscoelasticity often arises from the extent to which the polymer coils can be unwound into high-aspect-ratio entities. So we can have polymer systems that vary considerably in the viscoelastic levels even though they have the same viscosity curve. Some non-polymeric systems such as dispersions of worm-like surfactant micelles can also show viscoelastic properties, since they too have the basic elements of polymer-like entanglements of extended structures. In fact these are often called “living” polymers, see Barnes [7].

## 6. VISCOSITY OF FILLED SYSTEMS

### Newtonian continuous phase

We will assume first that the viscosity of a filled polymeric system is simply a function of the viscosity of the continuous phase – or that the liquid is a generalised Newtonian liquid. We will see how far workers have got using this assumption.

Although the measurement of the viscosity of spherical particles suspended in a Newtonian liquid must be one of the most common rheological parameters to be measured, this seemingly simple determination is fraught with difficulties. Among them are the effects of:

- particle size,
- particle-size distribution,
- shear rate,
- smooth walls,
- particle migration,
- particle interactions – colloidal and hydrophilic/hydrophobic, and
- form of the flow, i.e., shear vs. extensional.

These effects are hardly important until the phase volume is around 30% and/or approaches 60% for monodisperse spheres or the equivalent values vis-à-vis the maximum phase volume for other fillers. The result is that there is considerable variation in results, with up to an order of magnitude difference possible as one approaches 60% phase volume.

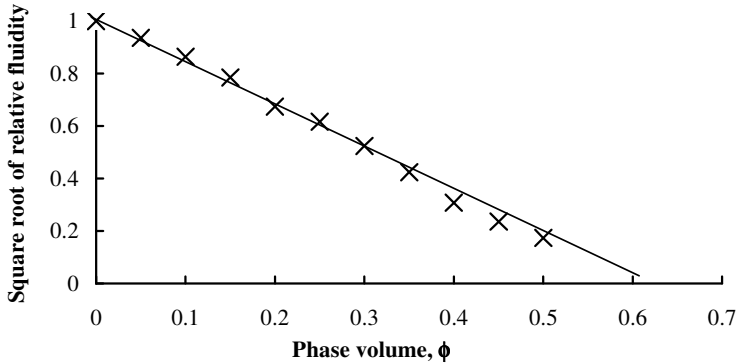
The viscosity,  $\eta$ , of a suspension of particles in a Newtonian liquid of viscosity,  $\eta_0$ , has often been well accounted for by the simple equation:

$$\frac{\eta}{\eta_0} = \left[ 1 - \frac{\phi}{\phi_m} \right]^{-2}, \quad \dots\dots\dots(2)$$

where  $\phi$  is the phase volume of the added filler particle and  $\phi_m$  is the maximum phase volume, where the latter parameter relates to the phase volume at which the suspension viscosity,  $\eta$ , is infinite, or put another way, the suspension fluidity  $1/\eta$  is zero. At least four names of workers have been connected with this remarkably simple, but very useful equation. Maron and Pierce seem to have priority in time from the mid-1950s [14], although anyone reading their paper would not find it easy to extract their formula. In the mid-1970s Quemada independently re-derived the equation [15], as did Kitano in the early 1980s [16]. However, the equation is actually a generalisation of Baker’s venerable formula dating from as far back as 1913, viz.  $\eta/\eta_0 = (1 - k\phi)^x$  [17]. The equation was particularised in the Krieger-Dogherty equation [18], with  $k$  as  $1/\phi_m$  and the exponent  $x$  written as  $-[\eta]\phi_m$ , where  $[\eta]$  is the intrinsic viscosity appropriate to the particular filler particles and describes their thickening power. This exponent was shown by Barnes et al [11] to centre around 2 for many diverse situations, see table 1. This arises in part because any increase in  $[\eta]$  is compensated for by a corresponding decrease in  $\phi_m$ , so that the product is often still around -2. If we force  $[\eta]$  to be the Einstein value of 2.5, then  $\phi_m$  would be 0.8, which would certainly be the case for a wide particle size distribution of spherical particles.

System	$[\eta]$	$\phi_m$	$[\eta]\phi_m$
Spheres (submicron)	2.7	0.71	1.92
Spheres (40 $\mu\text{m}$ )	3.28	0.61	2.00
Ground gypsum	3.25	0.69	2.24
Titanium dioxide	5	0.55	2.77
Glass rods, 30x700 $\mu\text{m}$	9.25	0.268	2.48
Quartz grains 53-76 $\mu\text{m}$	5.8	0.371	2.15

**Table 1:** The parameters of the Kreiger-Dougherty equation for a number of different systems, taken from [11], where details of the original sources of data used to produce the numbers can be found. The values of  $[\eta]\phi_m$  centre around 2.



**Figure 2:** The Maron-Pierce equation tested using Vladimir Vand’s 1948 suspension data [31], yielding the expected straight-line relationship and predicting a value of  $\phi_m$  of 0.606 from the intercept on the phase volume axis.

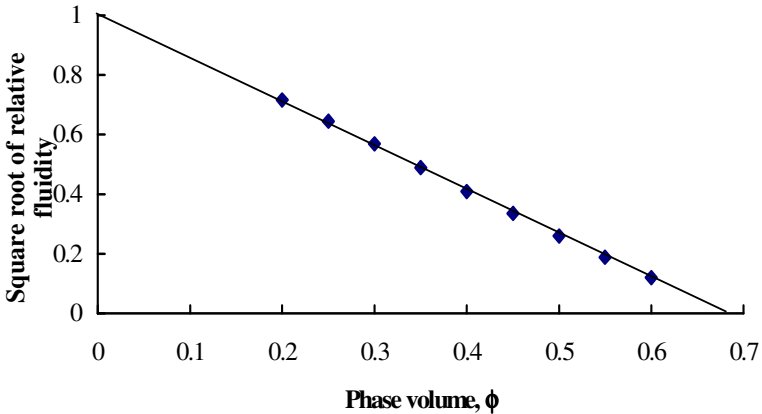
To ascertain if this equation fits a particular set of experimental data, it can be rearranged simply to give

$$\sqrt{\frac{\eta_0}{\eta}} = 1 - \frac{\phi}{\phi_m}, \quad \dots\dots\dots(3)$$

so that, if the square root of the relative fluidity,  $\eta_0/\eta$ , of the suspension is plotted against the phase volume of filler particles,  $\phi$ , a straight line should result for data that can be described by the equation. The value of  $\phi_m$  is then the intercept on the  $\phi$  axis. Figures 2 and 3 show interesting “historical examples” of viscosity data that can be used to test the equation.

A number of workers have remarked on the usefulness of this equation, and they have called it by various combinations of the names of its originators, for instance Gallegos and Franko [19], followed Tsai et al [20] in calling it the Maron-Pierce-Kitano (M-P-K) model. A number of some very different systems that can—according to the authors—be described reasonably well by the equation are shown in table 2, showing yet again the versatility of this simple model for quite wide-ranging systems.

The effect of particle size distribution, particle shape and even porosity can all be taken account of by the appropriate choice of the maximum phase volume,  $\phi_m$ .



**Figure 3:** The Maron-Pierce equation tested using data read off Thomas’s 1965 compilation of corrected suspension viscosity, see [32], yielding the expected straight-line relationship and predicting a value of  $\phi_m$  of 0.681 from the intercept on the phase-volume axis.

### Non-Newtonian continuous phases

If the continuous phase is non-Newtonian, then as we have already said, the local shear rate in the continuous phase of a suspension is higher than the overall shear rate in the kind of simple shear flow found in a cone-and-plate or concentric-cylinder viscometer. One consequence of this is that the viscosity of the continuous phase is lower than that which would pertain relative to the overall shear rate. This to some extent offsets the increase in viscosity due to the presence of the particles. A simple proof of the fact that local shear rates are higher is seen when we look at the shape of the viscosity/shear-rate curves of suspensions.

Figure 4 shows a hypothetical case of an inelastic non-Newtonian liquid with increasing levels of added (non-interacting) filler particles. The first important thing to observe is the shear-rate for the onset of shear thinning. This moves to lower and lower values of the overall shear rate as more particles are added. Then we note that the effect of the addition of particles on the viscosity is greater in the low-shear-rate Newtonian part of the curve, and eventually at high enough shear rate, the curves become parallel, each showing power-law behaviour, and the effect of added particles is smaller than in the Newtonian part of the curve. So we see the offsetting effect of the increased local shear rate. In effect we are starting from a lower base in terms of viscosity when particles are added. This also means that a simple vertical shift in the viscosity will not account for effect of added particles at all shear rates.

Reference	System(s)	Filler(s)
Liu and Tseng [21]	Wax	Zirconia (50-60%) $\phi_{max} \sim 70\%$
Bomal and Godard [22]	Polyethylene melt	Calcium carbonate with various surface treatments
Sato [23]	Water or methanol	Titanium dioxide, with/without PVP. $\phi_{max}$ values agree with sedimentation. Aqueous flocculated, methanol dispersed.
Wierenga and Philipse [24]	Water	Rods & rod-like fibres
Wierenga and Philipse [25]	Water	Boehmite rods, FD virus rods (charge effects seen)
Ayora et al [26]	Polyvinyl chloride (PVC) melt	Natural fibres - henequen leaves, coconut husk, bovine leather
Friedrich et al [27]	Polystyrene (PS) melt	Glass beads with and without PS grafting (extra $G'$ plateau)
Joshi et al [28]	Polybutylene terephthalate (PBT)/high density polyethylene (HDPE) / ionomer blends (melts)	Short glass fibres (10 – 30%) various aspect ratios and length distributions
Dames and Morrison [29]	Bimodal dispersions with colloidal interactions'	Particles above 0.25 microns
Lepez et al [30]	HDPE, polystyrene	Polydisperse glass beads (10 – 53 $\mu\text{m}$ )

**Table 2:** Systems whose viscosity/phase-volume relationship have been described by the MPKQ equation.

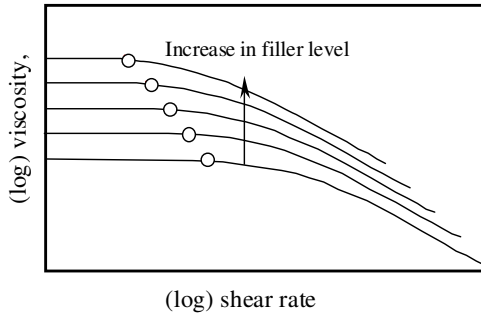
On the other hand, if we now look at the situation not in terms of the same overall shear rate, but, following Highgate and Whorlow's idea from 1970 [33], we look at the viscosity in terms of the overall *shear stress*, a much simpler picture emerges, see figure 5. Because of the continuous nature of shear stress, it is the same everywhere in simple flow situations such as small-angle cone-and-plate and small-gap concentric cylinder geometries. Thus, unlike the shear rate, it is uniform in the continuous phase, the particles, and even the enclosing walls of the viscometer. This means that we can now attempt to use the MPKQ equation at any given shear stress, and produce a vertical shift only to predict the viscosity. This is shown successfully for a number of systems in figures 6 - 9.

This will lead to the simple conclusion that if we translate this back to a controlled shear-rate situation, then for a power-law liquid, the effect of added

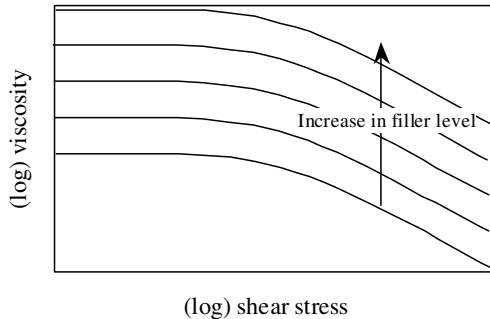
particles could be accounted for by a KD or Quemada-type equation, simply raised to the power  $n$ , the power-law index, hence the  $-2$  exponent becomes  $-2n$ , Barnes [7].

### Interacting particles in non-Newtonian liquids

If the continuous phase is shear thinning, *and* there is a strong interaction between the particles, which usually gives rise to flocculation, then it is possible to get the kind of behaviour shown in figure 10, where there is a double shear-thinning behaviour but usually only the part shown has been seen in practice, and this is typical of carbon black in rubber and certain fillers in polymer melts. If the particles are hydrophilic, then in hydrophobic polymer melts, they would flocculate, albeit lightly. This flocculation would easily be broken down over a narrow range of shear stress, as

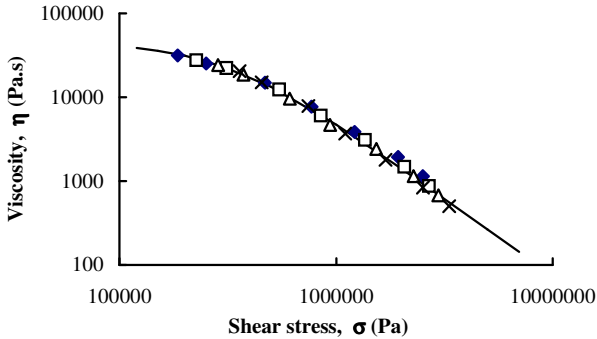


**Figure 4:** A schematic diagram of the viscosity/shear-rate curves found on adding filler particles to a shear-thinning liquid. Both vertical and horizontal shifts would be needed to bring the curves into coincidence.

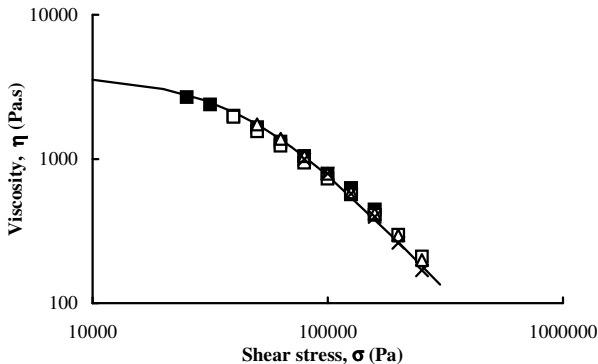


**Figure 5:** A schematic diagram of the viscosity/shear-stress curves found on adding filler particles to a shear-thinning liquid. The curves could be superimposed using a single vertical shift.

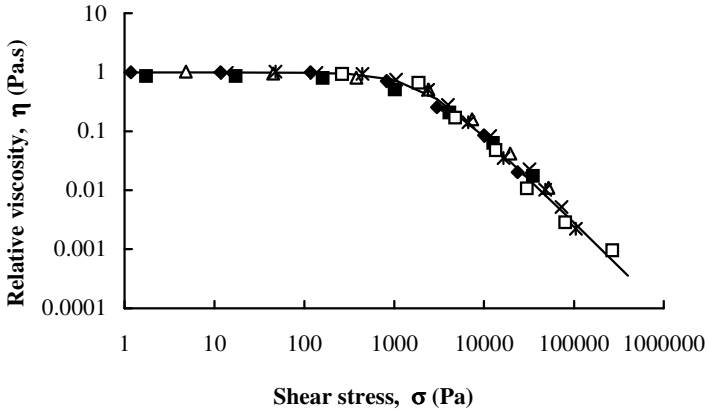
illustrated in figure 10. The typical shear-thinning behaviour of the continuous phase melt is then seen at even higher shear stresses. Similar effects can be found with either filler separately. Great care should be taken in interpreting this kind of curve as a double shear-thinning mechanism, because wall-slip effects can give the same shaped curve, but as an artefact, see Barnes [37].



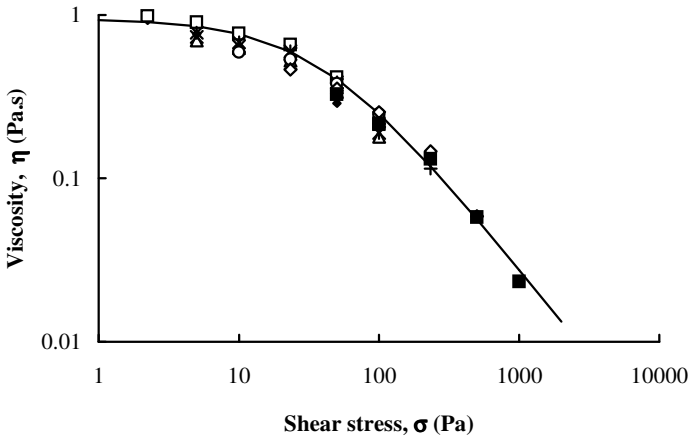
**Figure 6:** Yilmazer's [34] data for glass beads (10-40  $\mu\text{m}$ ) in ABS polymer at 220  $^{\circ}\text{C}$ , with phase volumes of 0, 0.093, 0.195 and 0.302 respectively. Data shifted vertically down to the unfilled situation using the MPKQ equation with  $\phi_m = 0.692$ . The solid line is given by  $\eta = 45000 / (1 + (0.0000032 \cdot \sigma)^{1.85})$  Pa.s.



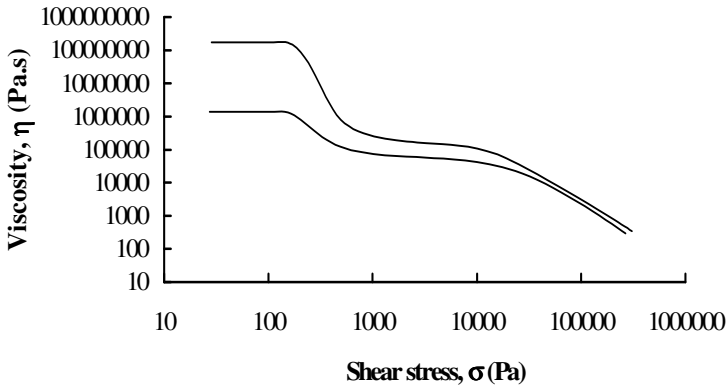
**Figure 7:** Sousa's [35] data for an HDPE melt filled with diatomite (diatomaceous earth, a silica-based amorphous, complex, 80% porous mineral) at phase volumes of 0, 0.09, 0.113, 0.174 and 0.235 respectively. Data shifted vertically down to the unfilled situation using the MPKQ equation with  $\phi_m = 0.305$ . The solid line is given by the empirical equation  $\eta = 3800 / (1 + (0.000022 \cdot \sigma)^{1.75})$  Pa.s.



**Figure 8:** Data of Poslinski et al [36] for 15 micron glass spheres in commercial grade thermoplastic, phase volumes of 0, 0.13, 0.26, 0.35, and 0.46 respectively, plotted as the relative viscosity with respect to  $\eta_0 = 117$  Pa.s. Data shifted vertically down to the unfilled situation using the MPKQ equation with  $\phi_m = 0.526$ . The solid line given by the empirical equation  $\eta_r = 1/(1+(0.0005.\sigma)^{1.5})$ .



**Figure 9:** Viscosity versus shear stress data for glass ballotini in 1.5% by weight aqueous CMC at 21.5 °C. Phase volumes 0, 0.02, 0.26, 0.3, 0.35, 0.4, 0.45, 0.5 and 0.55 respectively. Data shifted vertically down to the unfilled situation using the MPKQ equation with  $\phi_m = 0.582$ . The solid line is given by  $\eta = 0.95/(1+(0.177.\sigma)^{1.075})$  Pa.s.



**Figure 10:** A sketch of the viscosity/shear-stress results of Kim and White [38] for two mixtures of talc and calcite in polystyrene (10:12:78 and 05:05:90 v/v ratios) at 200°C, using sandwich (30–300 Pa), cone & plate (500–10,000 Pa) and capillary (20,000–300,000 Pa) rheometers to cover the whole stress range.

## VISCOELASTICITY OF FILLED SYSTEMS

### Linear viscoelasticity

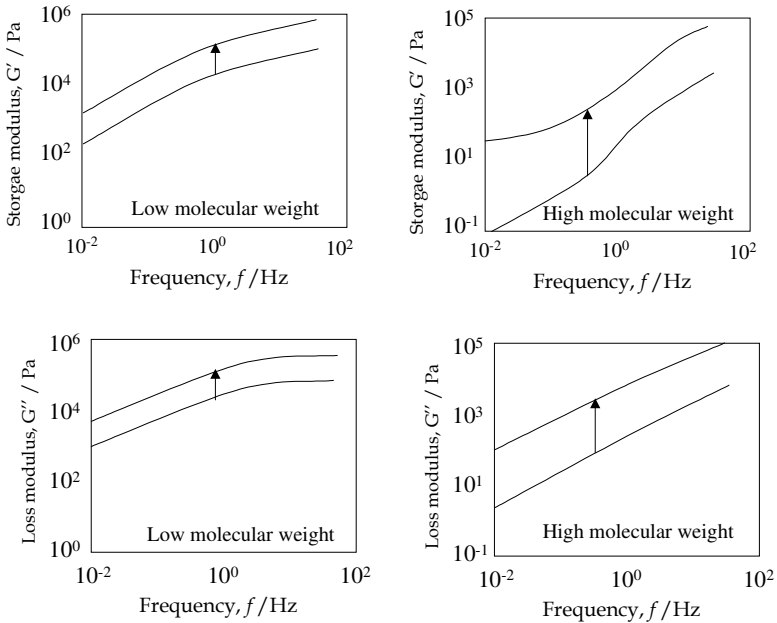
The linear region in which we measure the oscillatory properties decreases as the amount of filler is increased. At least this is so with respect to strain, but as with the case of large amplitude data, if stress is the variable, then the region of linearity is similar. With stress-controlled rheometers this becomes a particular advantage. The linear viscoelasticity parameters such as the storage and loss moduli  $G'$  and  $G''$  are - in the absence of complications due to depletion - always increased by the addition of fillers, and in the simplest case the factor we used above, i.e.,  $1/(1 - \phi/\phi_m)^2$  was sufficient in many cases to describe this increase quite well. In these cases the Cox-Merz relationship works well. If the particles interact, then we have a more complicated situation akin to flocculation. Then we have the appearance of extra longer relaxation mechanisms, and often the appearance of a plateau-like network effect, see figure 11.

There have been quite a number of publications on this area, but the results have been contradictory, with some workers claiming that the effect of filler is the same for  $G'$  and  $G''$ , while some suggest a greater effect on  $G'$ . Walberger and McHugh [39] recently reviewed the position, and added their own results to the debate. They concluded that there is always a considerable increase in both moduli,  $G'$  and  $G''$ , but that where the increase in both functions with addition of filler is not the same, the effect on  $G'$  seems to be greater. For the highest molecular weight polymer continuous phase used, the effects of filler on  $G'$  and  $G''$  were the same and this was

independent of frequency, see figure 11, and this coincides with the findings of See et al [4] for their tests at high frequencies. However for higher molecular weight, there was a greater increase in  $G'$  is particularly true at lower frequencies, see figure 11. Although this finding is contradictory to the earlier, but it seems to be supported the others, at least to the point that the effect of fillers on both moduli are the same.

Walberger and McHugh [39] should be read carefully to assess their arguments, but for our purpose, we need to take out the point that there is *always* a considerable increase in each modulus. As we shall see, this is certainly *not* the case for *non-linear* viscoelasticity. A number of workers have suggested that the effect on the moduli can be described by the Kitano equation, used elsewhere.

What is clear is that the  $G'$ ,  $G''$  curves can be used diagnostically to assess the state of dispersion, since a flocculated system will show up as an extra low-frequency  $G'$  plateau. In the simplest case we have a simple vertical shift, but often these interactions show a greater effect of filler at lower frequencies, suggesting an extra effect due to network-type interactions.



**Figure 11:** Sketches of the results of Walberger and McHugh [39], showing the relative effect of the addition of 60% filler on the linear viscoelastic moduli for low and high molecular weight PDMS respectively.

While linear data is not particularly relevant for real applications in processing, an investigation of the curves of filled versus unfilled systems can be useful in looking for particle-particle interactions. In this context Hornsby [40] cites interesting examples of fillers which interact—presumably via flocculation—to give more than a simple vertical shift, among these are titanium dioxide in LDPE, carbon black in polystyrene, talc in polystyrene and even glass beads ( $\sim 44 \mu\text{m}$ ) in polypropylene. At very high phase volume, shear thickening can set in, and he cites a zirconia/wax binder injection moulding formulation in the range of ceramic filler phase volume 55 to 70%. The appearance of a new rubber-like plateau in  $G'$  is seen for a number of systems, such as very small ( $0.15 \mu\text{m}$ ) calcium carbonate in polypropylenes, and  $0.53 \mu\text{m}$  magnesium hydroxide in polypropylene. This goes along with a high viscosity plateau at low shear stress and extreme shear thinning to just above the melt viscosity.

As to the actual amount by which the moduli increase, a number of workers have found that a MPKQ-type equation is obeyed. Lepez et al [30] measured the complex viscosity of two thermoplastic polymer melts (high density polyethylene and polystyrene) filled with polydisperse glass beads ( $10\text{-}53\mu\text{m}$ ) has been studied in the domain of linear viscoelasticity as a function of frequency, temperature, and filler concentration. In the experimental windows examined, the complex viscosity can be well described by a new empirical model, which contains a Cross type viscosity model for the frequency dependence, a MPKQ-type model for the filler concentration dependence.

See et al [4] showed that the oscillatory properties of a suspension of increase with the addition of  $60$  and  $80 \mu\text{m}$  particles in either  $1 \text{ Pa}\cdot\text{s}$  silicone oil or  $3\%$  Separan aqueous polymer solution such that  $G'$  and  $G''$  increase *pro rata* by the same amount, and approximately fit the MPKQ theory, with values of  $\phi_m$  of  $0.6$  and  $0.72$  respectively. (However, the gap is  $1000 \mu\text{m}$ , so the highest values at  $0.4$  phase volume might be a little suspect, see Barnes [12].)

### **Normal stress differences**

Highgate and Whorlow [33] claimed that their 1970 study of  $100 \mu\text{m}$  micron methacrylate spheres in various polymer systems was ‘the first systematic study of the influence of dispersed particles on the normal stress developed in viscoelastic fluids’. They showed that if the shear stress was taken as the basis of comparison, then there was a simple vertical shift in viscosity which was virtually independent of shear stress. They also showed that this was true for the first normal stress difference, but the increase was smaller. On average, the viscosity increase – based on the same shear stress values - found by adding  $7\%$  phase volume of spherical particles was about  $25\%$ , (including that for a Newtonian liquid), while the increase in first normal stress difference was only about half that value.

However, to gain an overall understanding of the effect of fillers, we need to consider first the general area of ‘elasticity’. A number of ways of combining shear stress  $\sigma$  and normal force  $N_1$  data have been suggested in order to produce a measure of “elasticity” at any given shear rate  $\dot{\gamma}$  or shear stress  $\sigma$ , among them are:

**Elasticity**,  $S$  or  $s = N_1/\sigma$ ,

**Recoverable shear stress ratio**,  $S_R = N_1/2\sigma$

**Maxwell relaxation time**,  $\lambda = N_1/2\sigma \dot{\gamma} = S_R / \dot{\gamma}$

**Shear modulus**,  $G = \eta / \lambda = 2\eta\sigma\dot{\gamma} / N_1 = 2\sigma^2 / N_1 = 1 / S_R$ , since  $\eta\dot{\gamma} = \sigma$ ,

**Weissenberg Number**,  $N_{We} = \lambda V / D = VN_1/2\sigma \dot{\gamma} D = N_1/2\sigma = S_R$ ,  
if we make the simple assumption that  $\dot{\gamma} = V/D$ .

$S_R$  has also been called the ultimate recovered strain  $s_\infty$ . The Weissenberg number is of course the ratio of elastic to viscous force, which is essentially the same as  $S_R$ , see Han [41] who says that  $\lambda$  is also ‘used to determine the elasticity of one fluid relative to another’, and gives examples of  $S_R$  for various polymer melts and concludes that ‘nylon 6 and PET are much less elastic than HDPE, PP, and PS’.

**Note that properly speaking, “elasticity” (however defined) is always associated with the ratio of normal stress difference to viscous stress and not just the level of normal stress difference or any other such parameter. This must be emphasised, since in many peoples’ minds “elasticity” means nothing more than the level of the normal stress difference or perhaps the storage modulus.**

For a given shear rate and geometry, when fillers are added they usually have a greater effect on shear stress than normal stress, then, all else being equal,  $S$ ,  $S_R$ ,  $\lambda$ ,  $N_{ew}$ , all *decrease*, while on the other hand  $G$  alone *increases*.

In the case of flow from a large tube into a smaller tube and subsequent flow out of the smaller tube into a larger one, the so-called entry and reattachment lengths are functions of the Weissenberg number, so they will usually decrease with increase in filler content. In this context, as early as 1958 Philippoff and Gaskins [42] had suggested that  $e$ , the entrance correction for pipe flow would be given by the normal viscous correction plus  $S_R/2$ .

The situation with respect to the non-linear viscoelastic parameters, such as normal force differences, is more complicated. Fillers increase viscosity, but increase normal stresses much less, and sometimes there have even been suggestions that they *decrease*  $N_1$ , however great care should be taken in examining these situations. Since normal stresses in suspensions of particles in Newtonian liquids can apparently lead to negative normal forces, then it is not surprising that strange things happen! Whatever else, we can say that beyond any argument, particles increase the viscosity more with increase in added filler than they do the normal stress differences. This means that the “elasticity” parameters and manifestations, which are some functions of the normal stress difference divided by the shear stress, will always *decrease*, while both the normal stress difference and the shear stress individually increase.

When viewed as a function of shear stress, the normal stress of filled systems would always lie on the same line as unfilled if both increased equally with the addition of filler (as often happens with increase in temperature). However, in almost all cases, when viewed as a function of *shear stress* rather than shear rate, the effect of filler is to *reduce* the level of the normal stress. (The opposite is true for long fibres, since the normal stress rises faster than the shear stress when they are added, especially at high shear rate).

It is obvious that all the complications of particle rearrangement and flocculation also have a complicated bearing on normal stresses. When the Cox-Merz and the analogous Al-Hadithi-Barnes-Walters (see Barnes et al [11]) empirical relationships are tested for particle-in-polymer systems, the former sometimes works, but the latter always fails because the first normal stress difference is too low.

Whereas the presence of particles in a viscoelastic liquid will always lead to an increase in viscosity, the effect on the normal forces is not of the same order. The difficulty probably arises from the inherent complex effect of particles in producing normal forces in Newtonian liquids. This can lead to either positive or negative normal stresses for either first or second normal stress differences, with either the first or second being greater.

Using a suspension balance formulation, in addition to conventional rheometry, Zarraga et al [43] found that for large particles (~ 43 and 74 microns) suspended in a Newtonian liquid,  $N_1$  and  $N_2$  were both negative, with the magnitude of  $N_2$  greater than  $N_1$ . Zarraga and Leighton [44] then calculated the normal stresses in a dilute suspension of hard spheres undergoing simple shear at low Reynolds number. The normal stress differences  $N_1$  and  $N_2$  were negative. However under other specific particle conditions, either  $N_1$  or  $N_2$  can become the prevailing normal stress difference. They also found that although the magnitude of  $N_1$  and  $N_2$  increased with the solids volume fraction  $\phi$ , in general the ratio  $|N_1/N_2|$  decreased as loading increased, Zarraga et al [45]. Indeed they suggested that, in large part, the normal forces were independent of that of the dissolved polymers at high solids loading ( $\phi \geq 0.3$ ). The magnitude of  $N_2$  at high concentrations approached that measured for similar suspensions in Newtonian fluids. Measurements of the surface deformation of the suspension near a rotating rod at different concentrations and shear rates confirmed the complex nature of the overall normal stresses.

Foss and Brady [46] reported that a Stokesian Dynamics, a molecular-dynamics-like simulation technique predicted that a monodisperse suspension of Brownian hard spheres in simple shear flow for  $P_e < 10$ , i.e., Brownian motion dominates the behaviour, the first normal stress difference is positive and the second negative. However, the first normal stress difference changes sign when hydrodynamics dominate. They claimed that the simulation results are shown to agree well with both theory and experiment.

White et al [47] found that for a glass-fibre-filled polypropylene melt, the presence of glass fibres increases the shear and normal stresses, with the latter showing a pro-rata greater increase. The effect of fibres seems to depend strongly on their length, so that a large increase results from long fibres, while short fibres behave like normal fillers and result in a decrease in elasticity.

Reference	Polymer system(s)	Filler(s)	Effect(s)
Chand [48]	LDPE/PP blends	Red mud particles	Recoverable shear strain decreased when mud added
Varghese et al [49]	Natural rubber	Acetylated sisal fibre	Decrease in elasticity
Joseph et al [50]	LDPE	Short sisal fibre	Decrease in elasticity
Takahashi et al [51]	Acrylonitrile-butadiene-styrene (ABS)	Soft and hard butadiene particles	Hard particles decreased strain-hardening of extensional viscosity, soft particles not so large decrease.
Choi et al [52]	Polyisobutylene/polybut-ene Boger fluid	Kaolinite (platey)	Elasticity increases
Ramkumar et al [53]	Ethylene vinyl acetate copolymers with maleic anhydride functional groups	Wheat starch	Shorter relaxation times
Kobayashi et al [54]	Polystyrene	Potassium titanate whiskers	Strain-hardening eliminated
Dreval [55]	Linear polyethylene 1,4-polybutadiene	Carbon black, silica, calcium carbonate, glass fibres	Shorter relaxation times, so elasticity decreased
Takahashi and Takimoto [56]	LPDE	Glass beads, glass flakes, talc, glass fibres	Extensional strain-hardening weaker as glass beads > glass flakes > talc.
Choi et al [57]	PIB solutions	Kaolinite	Weissenberg effect decreased
Aral and Kalyon [58]	Polydimethyl siloxane	Hollow glass spheres	Range of linearity decreased, for high loadings $N_1$ becomes negative. Extrudate swell and Weissenberg effect suppressed
Bayram et al [59]	Hydroxy-terminated polybutadiene	Glass beads	Cox-Merz valid for filled polymer.
Ohl and Gleissle [60]	Polyisobutylene	34.5 % filled	$N_2/N_1$ negative, but much larger for filled polymer.
Choi et al. [61]	Polyisobutylene/polybut-ene (Boger-type liquid)	Kaolin particles	Rod-climbing increased.

**Table 3:** Viscoelastic effects found on the addition of particles to polymeric systems.

Table 3 shows various other effects found on the addition of fillers to viscoelastic polymeric melts and liquids, note the fibre examples.

**A quantitative description**

If we now attempt a quantitative description of the effect of filler particles on the normal stress differences, we can attempt a MPKQ-type formulation by analogy to the viscosity description, as either

$$\frac{N_1}{N_{10}} = \left( 1 - \frac{\phi}{\phi_m} \right)^{-2} \dots\dots\dots(4)$$

to account for the decrease in  $N_1$ , or

$$\frac{N_2}{N_{20}} = \left( 1 - \frac{\phi}{\phi_m} \right)^2 \dots\dots\dots(5)$$

to account for the increase in  $N_2$ , all compared at a particular shear stress.

This is tested using the recent data of Mall-Gleissle et al [62] in figures 12 and 13, where we see that the description is very good.

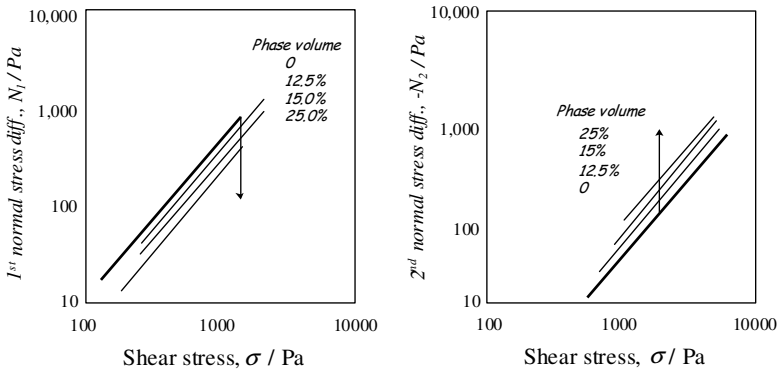
**Extensional viscosity**

The extensional viscosity of relatively inelastic shear-thinning systems always follows the shear viscosity once the relevant factors for scaling the two viscosities and deformation rates have been taken into account, e.g., Barnes and Roberts [63]. In this case the effect of fillers is the same for both kinds of viscosity. This is illustrated by the work of Evans and Greener [64] illustrated in figure 14.

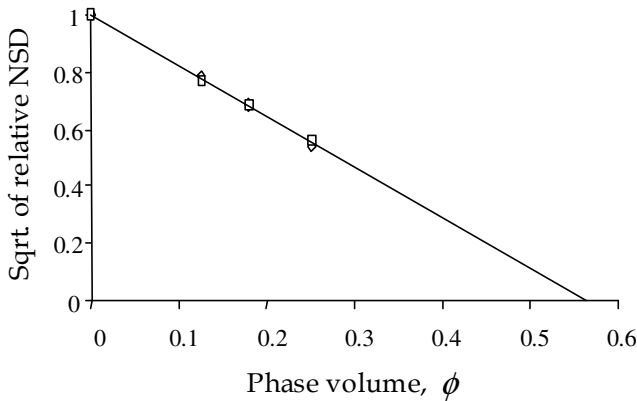
If the filler that is added can align in some way, then the increase in extensional viscosity will be greater than that observed for shear viscosity, although the general shape of the curve remains the same. This is shown in figure 15 where we see the effect of the addition of thin mica sheets to a polymer melt. For more elastic systems, the extensional viscosity can increase with increasing extension rate. The addition of filler particles usually suppresses this effect, see figure 16.

This suppression of “strain hardening” by the addition of fillers has been observed by a number of workers, among them Kobayashi et al [65] with a polystyrene-potassium titanate whisker melt and HDPE/glass beads, see Kobayashi et al [66]. The same group also showed [67] that adding different kinds of filler can change the shape of the evolving elongational viscosity very profoundly from strain-rate thickening to strain-rate thinning, see sketches - shows virgin, 20% talc (1.7 micron aspect ratio 1.6), glass fibre 13 microns thick aspect ratio 23, see figure 17.

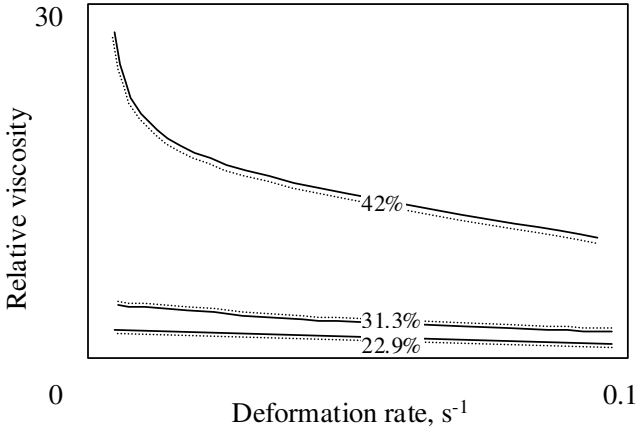
The elimination of the increase in extensional viscosity with extension rate “elastic” effects is in line with the decrease of elasticity by the addition of fillers described above.



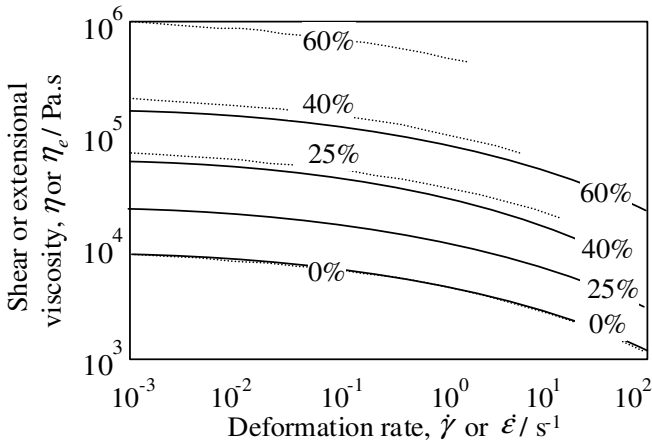
**Figure 12:** A schematic representation of the results of Mall-Gleissle, et al, [62] showing the first and second normal stress differences for dispersions of 0.5  $\mu\text{m}$  glass spheres in silicone oil. Note that the decrease in  $N_1$  almost exactly matched by the increase in  $N_2$  and at  $\phi \cup 0.3$ ,  $|N_2| \sim |N_1|$ .



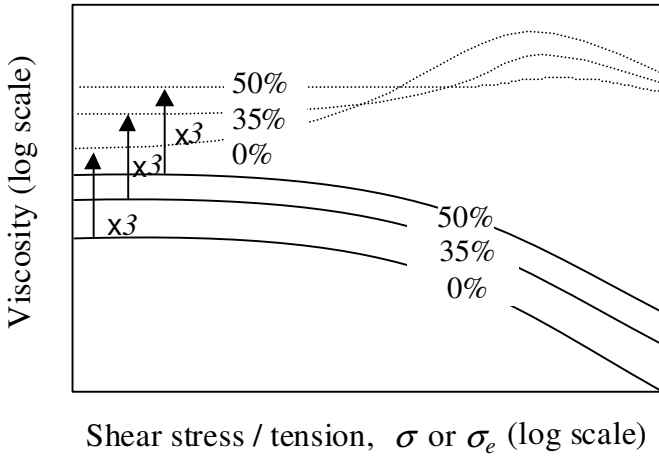
**Figure 13:** Maron-Pierce/Quemada/Kitano (M-P/Q/K) type model applied to data of Mall-Gleissle et al [62], on 0.5  $\mu\text{m}$  glass beads in 400 Pa.s Dow Corning silicone oil. The square root of the relative normal stress difference as either the normal form for the first normal stress difference (seen as diamonds) which decreases, or the inverse for the second normal stress difference (seen as squares) which increases. The intercept gives the maximum phase volume  $\phi_m$ , as 0.564.



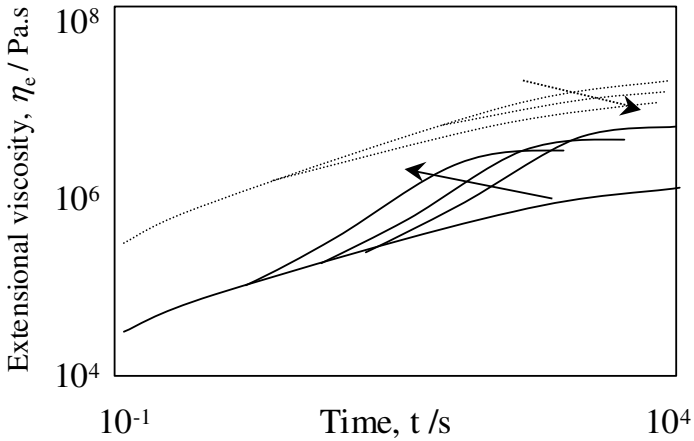
**Figure 14:** Data of Greener & Evans [64], for various phase volumes of alumina in polyisobutylene, plotted as the relative viscosity versus the relative deformation rate. Trouton ratio is 3 in all cases, the shear viscosity being the solid line and extensional viscosity being the dashed. Note that these are linear plots.



**Figure 15:** The effect of mica filler level on the shear (dotted lines) and one- third of the extensional (solid lines) viscosity of a polymer melt whose viscosity only decreases with increasing deformation rate, see Barnes [63].



**Figure 16:** The shear and extensional viscosities of an LDPE melt with various phase volumes of glass beads, see Barnes [63].



**Figure 17:** A sketch of the evolution of extensional viscosity of an LDPE melt filled with talc, as shown by Takahashi et al [67]. The arrow shows the effect of increase in the extension rate, showing the movement from extension thickening to extension thinning.

White et al [49] found that for a glass-fibre-filled polypropylene melt, the presence of glass fibres substantially increased the elongational viscosity at low extension rates, but this decreased rapidly at high deformation rates.

**PRACTICAL IMPLICATIONS**

**First normal stress difference – effect on processing**

Having seen how fillers can affect the shear stress and first and second normal stress differences, and hence the elasticity, we need to now consider how these factors themselves affect typical processing situations.

The origin of tube-flow measured parameters, such as entry and exit pressures, extrudate swell, vortex and reattachment lengths, etc., has been a matter of debate. Mitsoulis et al [68] found that normal stresses are responsible for most of the phenomena, while ‘the elongational viscosity tends to increase the end (Bagley) correction and decrease the (extrudate) swelling’. On the other hand Luo and Mitsoulis [69] used a numerical method to predict the flow of a K-BKZ integral model (simulating LDPE and HDPE) and found that strain-thickening elongational viscosity is responsible for the rapid entry vortex growth shown in LDPE.

The importance of the particular nature of the extensional viscosity – with respect to time and extension rate – has been shown to strongly influence contraction-type flows, so that for instance the strain thickening elongational viscosity is shown to be primarily responsible for the rapid entry vortex growth exhibited by LDPE melts, see Luo and Mitsoulis [69]. This kind of behaviour, together with inertial effects, has been shown to control vortex intensity and pressure drop across contractions under the kinds of high flow rates experienced in the industrial processing of polymer melts Tanoue et al [70] and Boger [71].

Tanoue et al [70] used a simplified Criminale-Ericksen-Filbey model to show numerically that as the primary normal stress difference increases, the corner vortex grows but the entrance pressure drops slightly, while inertia has the opposite effects and dominates at high flow rate. Both the vortex intensity and the entrance pressure drop for a fluid with strain-thickening elongational viscosity are larger than those for the fluid with strain-thinning elongational viscosity.

The extent of extrudate swell of a viscoelastic liquid emerging from a long tube, is given by the empirical Tanner equation [72]:

$$\frac{D_e}{D} = \left[ 1 + \frac{I}{2} \left( \frac{N_I}{2\sigma_w} \right)^2 \right]^{1/6} \dots\dots\dots(6)$$

where *D* is the diameter of the tube, and *D<sub>e</sub>* is the eventual diameter of the extrudate. The shear stress and the normal-stress difference values are evaluated at the wall of the tube.

This shows us that the ratio is directly controlled by the value of *S*, the elasticity, but that it only changes slowly with that value. For small values of extrudate

swell, say to nearly twice the exit diameter, a very simple linear approximation to the  $D_e/D$  versus  $S$  relationship is  $S = 20(D_e/D - 1)$ , see figure 18.

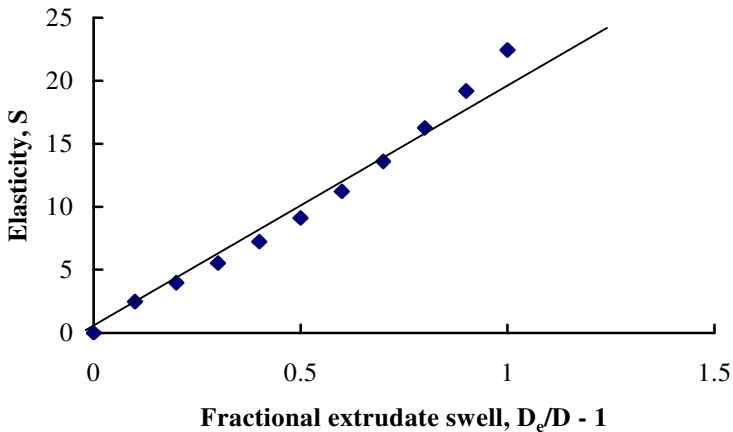
For ‘engineering calculations’, the simple inverse expression  $D_e/D = 1 + S/20$  is very useful. The value  $N_1/2\sigma$  is of course the ‘recoverable shear stress ratio’,  $S_R$ , mentioned above, so we can write this in the even simpler and more memorable form  $D_e/D = 1 + S_R/10!$  As mentioned above, the addition of fillers (apart from long, thin fibres) decreases the value of  $N_1/2\sigma$ , and thus decreases the extrudate swell. At levels of filler of about 40%, a typical polymer melt, which would swell by up to 40% when unfilled (i.e.,  $S_R \sim 4$ ), will show no visible increase at all, i.e.  $S_R < 0.01$ , see examples in Shenoy [3].

Tables 4 and 5 show the practical effects of fillers of different kinds in a wide range of systems. Table 4 shows only the expected decrease in extrudate swell, but table 5 shows more complex results.

**Particle deformability**

The effect of the deformability of the dispersed particles is important in many practical applications. As we have seen, the addition of hard particles decreases the elasticity of a viscoelastic liquid (and with it the extrudate swell), however if the added particles are made to become more and more deformable, the effect changes and eventually, the addition of *very* deformable particles leads to the *increase* the extrudate swell found with no added particles.

A particularly interesting example of this is the work of Fujiyama and



**Figure 18:** Predicted value of extrudate swell from Tanner’s expression compared with the linear approximation  $S = 20(D_e/D - 1)$

Kawasaki [82] on isotactic polypropylene blended with high-density polyethylene, where they found *increased* extrudate swell for dispersed domains of lower viscosity. Conversely, but proving the same point, George, et al [90] found that for a polypropylene melt filled with butadiene rubber domains, hardening the rubber domains by vulcanisation *decreased* extrudate swell.

Reference	Polymer system(s)	Filler(s)	Effect(s)
Roy et al [73]	Natural rubber, HDPE	Short carbon fibres	Extrudate swell decreased.
Haworth and Jumba [74]	HDPE	Calcium carbonate	Extrudate swell decreased.
Joshi et al [75]	PBT/HDPE/IONO blends	Short glass fibres	Extrudate swell decreased.
Kumar et al [76]	Neoprene and acrylic rubbers	Carbon black	Extrudate swell decreased.
Leblanc and Benoit-Cervantes [77]	Polybutylene terephthalate	Short glass fibres	Extrudate swell inhibited.
Kim et al [78]	Various polymers	Carbon black	Extrudate swell decreased.
Roy and Gupta [79]	Styrene- <i>isoprene</i> -styrene block copolymer	Short carbon fibres Coir fibre	Extrudate swell decreases with increase in fibre content, especially at high loadings
Nah and Kim [80]	Natural rubber	Reclaimed rubber powder 70-2000 $\mu$ m	Decrease in extrudate swell.
Nah and Kaang [81]	Styrene-butadiene rubber	Rubber powder	Increase in viscosity, especially at low stress and decrease in extrudate swell.

**Table 4:** Published systems where there is a decrease in extrudate swell on the addition of particles.

Reference	Polymer system(s)	Filler(s)	Effect(s)
Liang et al [83]	Low-density polyethylene	Glass beads	Extrudate swell decreases with increasing bead diameter.
Freakley and Sirisinha [84]	Styrene-butadiene rubber	Carbon black	Extrudate swell governed by recoverable strain and relaxation time.
Basu et al [85]	Isotactic polypropylene	Chopped jute fibres glass fibres	$N_1$ and extrudate swell for glass beads lower than jute fibres
Suh and White [86]	Polyethylene polypropylene	Talc	Annular swell decreased.
Mijangossantiago and Dealy [87]	Medium density polyethylene	Calcium carbonate	Extrudate swell decreased. With coupling agent, swell increased.
Khanna and Slusarz [88]	Polypropylene	Talc	Extrudate swell, entry pressure drop and elastic compliance all decreased.
Fajdiga and Susteric [89]	Various rubbers	Carbon black	Extrudate swell decreased with amount and surface activity

**Table 5:** Published systems where there are mostly extrudate swell effects, but other effects are also seen.

### **Fibres**

Yilmazer [34] measured the shear viscosity and extrudate swell ratio of acrylonitrile-butadiene-styrene filled with glass beads and glass fibres. The relative viscosity of the composites increased with filler content, but decreased with shear rate. At low shear rates, the fibre-filled systems had higher relative viscosities than bead filled systems. At high shear rates, the opposite was observed. The extrudate swell ratio of the unfilled material increased linearly with the logarithm of the shear rate. Systems highly filled with glass beads or fibres showed a maximum in the extrudate swell ratio at medium shear rates. The magnitude of the maximum in the extrudate swell ratio increased with filler content and the die length, up to a certain length, in a series of dies that had the same radius.

White et al [49] also found that for a glass-fibre-filled polypropylene melt, the presence of glass fibres increases the shear and normal stresses, with the latter showing a pro-rata greater increase. The glass fibres also substantially increased the elongational viscosity at low extension rates, but this decreased rapidly at high deformation rates. The ratio of die-ends pressure losses to shear stress was significantly increased with increasing glass fibre content, but the extrudate swell was substantially reduced.

### **Second normal stress difference**

There are two important practical situations where the second normal-stress difference is a key controlling factor, namely cases where layers of different viscoelastic liquids are flowing over each other, as in co-extrusion, and also flow of viscoelastic liquids in curved or non-circular straight pipes. The latter is very important in heat transfer situations where heat exchangers are often in the form of coiled pipes and the secondary flows present give enhanced heat transfer, see Barnes and Edwards [91]. Secondary flow in non-circular ducts is also controlled by the second normal-stress difference, and this too has important implications in heat transfer situations, etc.

In the layered-flow situation, the second normal-stress difference is a key controlling parameter in the general stability of the interface, and this will dictate the maximum speed at which layered or co-extrusion flows can take place, and this has economic implications in terms of maximum equipment utilisation. Brady and Carpen [92] showed that any multi-layer flow situation will show this type of behaviour if there is a discontinuity in normal-stresses between the two adjacent flowing fluids with different rheologies. Specifically they showed that fluids with a negative second normal-stress difference can be unstable with respect to “transverse or spanwise” perturbations. They illustrated the instability mechanism for two-layer Couette and falling-film flows of viscous suspensions, but they state that any similar situation will be similarly affected. Then it has been shown that in such situations, not only can the interface become unstable, but in plain co-extrusion situations, the interface can evolve from planar to where one liquid can engulf the other, and this has been called ‘encapsulation’. This is a known phenomenon, and Sunwoo and co-workers [93, 94] carried out a theoretical study that described the situation well. They showed that by varying the magnitude of the second normal-stress difference and its ratio in the adjacent fluids, they were able to control the interface profile and the degree of encapsulation along the downstream direction. Although the parameters that they used for the viscoelastic models were fitted by using the shear viscosity data only, quantitative agreements between the numerical results and the experimental co-extrusion data were quite satisfactory.

Flow in curved pipes is equally controlled by the second normal-stress difference. Although theoretical studies have their mathematical difficulties, see Robertson and co-workers [95, 96] it has been shown that the characteristic secondary flows are also drastically attenuated and in some cases completely inhibited by the second normal-stress difference, see Fan et al [97]. This would greatly reduce the good heat transfer and enhanced mixing that exist in such situations.

	<b>Simple shear viscosity</b> $\eta$	<b>Linear visco-elasticity</b> $G', G''$	<b>Non-linear viscoelasticity</b> $\gamma N_1, N_2$	<b>Extensional viscosity</b> $\eta_e$
<b>No filler</b>	Cross-type behaviour	Cox-Merz relates linear VE to shear viscosity	$N_1$ positive, $N_2 \sim -N_1/10$ . ABW relates non-linear to linear VE	Varies from 3 times $\eta$ to overshoot, depending on elasticity
<b>(Near) spherical non-interacting</b>	Increase viscosity and local shear rate	Similar increase in both $G'$ and $G''$ , or $G'$ smaller increase	$N_1$ increases slowly, so that elasticity decreases. But $ N_2 $ increases more than $N_1$	Depends on 'elasticity', $\eta_e$ and simply mirror $\eta$ , or overshoot can be decreased.
<b>(Near) spherical interacting, depletion or flocculation</b>	Depletion can cause decrease. Flocculation can give second shear-thinning mechanism. Apparent yield stress possible	Depletion can cause decrease. Flocculation can give second, low-frequency plateau in $G'$	Not enough data to generalise	Not enough data to generalise
<b>Long fibres</b>	More shear thinning	Large increase	Large increase	Large increase

**Table 6:** Summary of the effects of fillers on the rheology of polymeric systems.

Lastly, Brady and Carpen [94] showed that the second normal stress difference as controlling different kinds of interface instabilities.

## SUMMARY

When solid particles are added to viscoelastic solutions, liquids or polymer melts, then, providing no absorption of the thickening species from the solvent takes place, all the viscoelastic parameters increase, according to the summarised version given in table 6. However, the normal stresses do not increase as much as the shear stress, with the result that there is a decrease in certain “elasticity” phenomena which depend on the ratio of the two stresses. The paradox is then that although the level of the normal stress increases markedly, the visible effects of “elasticity” decrease to give what looks like a less “elastic” liquid. These effects include post-extrusion swelling and pre-extrusion vortex formation, as well as other visible effects.

## REFERENCES

1. Cogswell F N, "Polymer Melt Rheology, a Guide for Industrial Practice", George Godwin, London, (1981), p. 87.
2. Metzner A B, *J. Rheol.*, 29 (1985) 739-775.
3. Shenoy A V, "Rheology of Filled Polymer Systems", Kluwer Academic Publishers, Dordrecht, (1999).
4. See H, Ping J and Nhan P-H, *Rheol. Acta*, 39 (2000) 131–137.
5. Falcone S, Chapter on "Fillers" in Vol. 10, pp. 745–761, *Kirk-Othmer Encyclopaedia of Chemical Technology*, 4<sup>th</sup> Edition, Ed. M. Howe-Grant, John Wiley and Sons, New York, (1993), ISBN 0-471-52678-9.
6. Wypych G, "Handbook of Fillers", William Andrew Publishing, Norwich, NY USA, (1999).
7. Barnes H A, "A Handbook of Elementary Rheology", The University of Wales Institute of Non-Newtonian Fluid Mechanics, Aberystwyth, (2000), ISBN 0-9538032-0-1.
8. Quemada D and Berli C, *Advances in Colloid and Interface Science*, 98 (2002) 251-285.
9. Kiratzis N E and Luckham P F, *J. Euro. Ceramic Soc.*, 19 (1999) 2605–2612.
10. Robins M M, *Current Opinion in Colloid & Interface Science*, 5 (2000) 265–272.
11. Barnes H A, Hutton J F, Walters K, "An Introduction to Rheology", Elsevier, Amsterdam (1989).
12. Barnes H A, *J. Non-Newtonian Fluid Mech.*, 94 (2000) 213-217.
13. Roberts G P and Barnes H A, *Rheol. Acta*, 40 (2001) 499-503.
14. Maron S H and Pierce P E, *J. Coll. Sci.*, 11(1956) 80–95.
15. Quemada D, *Cr. Acad. Sci. B. Phys.*, 281 (1975), 173-176 and *Rheol. Acta*, 16 (1977) 82-94.
16. Kitano T, Kataoka T and Shirota T, *Rheol. Acta*, 20 (1981) 207–209.
17. Baker F, *Chem. Soc.*, 103 (1913) 1655.
18. Krieger I M and Dougherty T J, *Trans. Soc. Rheol.*, 3 (1959) 137-152.
19. Gallegos C and Franco J M, in "Rheology of Food Emulsions", in "Advances in the Flow and Rheology of Non-Newtonian Fluids", Part A, Ed. D.A. Siginer et al, Elsevier, Amsterdam, 1999.
20. Tsai S C, Botts D and Plouff J, *J. Rheol.*, 36 (1992)1291-1305.
21. Liu D M and Tseng W J, *J. Mat. Sci.*, 35 (2000) 1009-1016.
22. Bomal Y and Godard P, *Polym. Eng. & Sci.*, 36 (1996) 237-243.

23. Sato T J, Dispersion Sci. & Tech., 17 (1996) 83-96.
24. Wierenga A M and Philipse A P, Colloid & Surf. A – Physicochemical and Eng. Aspects, 137(1-3) (1998) 355-372.
25. Wierenga A M and Philipse A P, Langmuir 13 (1997) 4574-4582.
26. Ayora M, Rios R, Quijano J and Marquez A, Polym. Composites, 18 (1997) 549-560.
27. Friedrich C, Scheuchpflug W, Neuhausler S and Rosch J, J. Appl. Polym. Sci., 57(4) (1995) 499-508.
28. Joshi M, Maiti S N and Misra A, Polymer, 35 (1994) 3679-3685.
29. Dames B, Morrison B R and Willenbacher N, Rheol. Acta, 40 (2001) 434-440.
30. Lepez O, Choplin L and Tanguy P A, Polymer Engineering and Science, 30 (1990) 821-828.
31. Barnes H A, Applied Rheology, 10 (2000) 248-253.
32. Thomas D, Journal of Colloid Science, 20 (1965) 267-277.
33. Highgate D J and Whorlow R W, Rheol. Acta, 9 (1970) 569-576.
34. Yilmazer U, Polymer Composites, 10 (1989) 1–7.
35. Sousa J A, Proc. IX Intern. Congr. Rheol., ed. B. Mena et al, (1984), pp. 439–446.
36. [36] Poslinski A J, Polinski M E, Ryan R K and Gupta J, J. Rheol, 32 (1988) 703-735.
37. Barnes H A, J. Non-Newtonian Fluid Mech., 56 (1995) 221 – 251.
38. Kim K J and White J L, Polym. Eng & Sci., 39 (1999) 2189–2198.
39. Walberer, J A and McHugh, A J, J. Rheol., 45 (2001) 187–201.
40. Hornsby P R, Advances in Polymer Science, 139 (1999) 155-217.
41. Han C D, “Multiphase Flow in Polymer Processing”, Academic Press, New York, (1981).
42. Philippoff W and Gaskins F H, Trans. Soc. Rheol., 2 (1958) 263.
43. Zarraga I E, Hill D A and Leighton D T, J. Rheol., 44 (2000) 185-220.
44. Zarraga I E and Leighton D T, Physics of Fluids, 13 (2001) 565-577.
45. Zarraga I E, Hill D A and Leighton D T, J. Rheol., 45 (2001) 1065-1084.
46. Foss D R and Brady J F, J. Fluid Mech., 407 (2000) 167-200.
47. White J L, Chan Y and Oyanagi Y, J. Soc. Rheol. Japan, 6 (1978) 1-7.
48. Chand H, Research and Industry, 40 (1995) 193-202.
49. Varghese S, Kuriakose B, Thomas S, Premalatha C K and Koshy A T, Plastics Rubber and Composites Processing and Applications, 20 (1993) 93-99.

50. Joseph K, Kuriakose B, Premalatha C K, Thomas S and Pavithran C, *Plastics Rubber and Composites Processing and Applications*, 21 (1994) 237-245.
51. Takahashi T, Wu W G, Toda H, Takimoto J, Akatsuka T and Koyama K, *J. Non-Newtonian Fluid Mech.*, 68 (1997) 259-269.
52. Choi H J, Vinay S J and Jhon M S, *Polymer*, 40 (1999) 2869-2872.
53. Ramkumar D H S, Bhattacharya M and Zhang D, *Polymer Networks and Blends*, 7 (1997) 51-59.
54. Kobayashi M, Takahashi T, Takimoto J and Koyama K, *Polymer*, 36 (1995) 3927-3933.
55. Dreval V E and Borisenkova E K, *Rheol. Acta*, 32 (1993) 337-351.
56. Takahashi T, Takimoto J I and Koyama K, *Polymer Composites*, 20 (1999) 357-366.
57. Choi H J, Lee H J, Lim S T and Jhon M S, *Polymer Eng. and Sci.*, 39 (1999) 469-473.
58. Aral B K and Kalyon D M, *J. Rheol.*, 41 (1997) 599-620.
59. Bayram G, Yilmazer U and Orbey N, *J. Applied Polymer Sci.*, 70 (1998) 507-514.
60. Ohl N and Gleissle W, *Rheol. Acta*, 31 (1992) 294-305.
61. Choi H J, Sim I S, Lim S T and Jhon M S, *J. Applied Polymer Sci.*, 75 (2000) 572-575.
62. Mall-Gleissle S E, Gleissle W, McKinley G H and Buggisch H, *Rheol. Acta*, 41 (2002) 61-76.
63. Barnes H A and Roberts G P, *J. Non-Newtonian Fluid Mech.*, 44 (1992) 113-126.
64. Greener J and Evans J R G, *Journal of Rheology*, 42 (1998) 697-709.
65. Kobayashi M, Takahashi T, Takimoto J and Koyama K, *Polymer*, 36 (1995) 927-3933.
66. Kobayashi M, Takahashi T, Takimoto J and Koyama K, *Polymer*, 37 (1996) 3745-3747
67. Takahashi T, Takimoto J-I and Koyama K, *Polymer Composites*, 20 (1999) 357- 366.
68. Mitsoulis E, Vlachopoulos J and Mirzsa F A, *Polym. Eng. Sci.*, 25 (1985) 677-689.
69. Luo X L, Mitsoulis E, *Journal of Rheology*, 34 (1990) 309-342.
70. Tanoue S, Kajiwara T, Funatsu K, *J. Society of Rheology Japan*, 21 (1993) 123-129.
71. Boger DV, *Experimental Thermal and Fluid Science*, 12 (1996) 234-243.

72. Tanner R I, "Engineering Rheology", Clarendon Press, Oxford, (1985).
73. Roy D, Bhattacharya A K and Gupta B R, J. Elastomers and Plastics, 25 (1993) 46-58.
74. Haworth B and Jumpa S, Plastics Rubber and Composites, 28 (1999) 363-378.
75. Joshi M, Maiti S N and Misra A, Polymer 35 (1994) 3679-3685.
76. Kumar N R Gupta B R and Bhowmick A K, Polymer Engineering and Science, 33 (1993) 1002-1008.
77. Leblanc J L and Benoit-Cervantes G, Kautschuk Gummi Kunststoffe, 51 (1998) 840-846
78. Kim J K, Han M H, Go J H and Oh S C, J. Applied Polymer Sci., 49 (1993) 1777-1789.
79. Roy D and Gupta B R, J. Applied Polym. Sci., 49 (1993) 1475-1482.
80. Nah C and Kim H, Polymer-Korea, 21 (1997) 648-656.
81. Nah C and Kaang S, J. Polym. Eng., 17 (1997) 323-338.
82. Fujiyama M and Kawasaki Y, J. Applied Polymer Sci., 42 (1991) 481-488.
83. Liang J Z, Li R K Y, Tang C Y and Cheung S W J, Applied Polym. Sci., 76 (2000) 419-424.
84. Freakley P K and Sirisinha C J, Applied Polymer Sci., 65 (1997) 305-315.
85. Basu D, Banaerjee A N and Misra A J, Applied Polymer Sci., 46 (1992) 1999-2009.
86. Suh C H and White J L, Polymer Engineering and Science, 36 (1996) 1521-1530.
87. Mijangossantiago F and Dealy J M, Polymer Engineering and Science, 31 (1991) 1176-1181.
88. Khanna Y P and Slusarz K R, Polymer Engineering and Science, 33 (1993) 122-124.
89. Fajdiga B and Susteric Z, Kautschuk Gummi Kunststoffe, 46 (1993) 225-229.
90. George S, Ramamurthy K, Anand J S, Groeninckx G, Varughese K T and Thomas S, Polymer, 40 (1999) 4325-4344.
91. Barnes, H A and Edwards M F, "Mathematics of Heat Transfer", pp. 1-12, eds. Topholme G E and Wood AS, Clarendon Press, Oxford, (1998), ISBN 0 19 850358 X.
92. Brady J F and Carpen I C, J. Non-Newtonian Fluid Mech., 102 (2002) 219-232.
93. Sunwoo K B, Park S J, Lee S J, Ahn K H and Lee S J, J. Non-Newtonian Fluid Mech., 99 (2001) 125-144.
94. Sunwoo K B, Park S J, Lee S J, Ahn K H and Lee S J, Rheol. Acta, 41 (2002) 144-153.

95. Jitchote W and Robertson A M, *J. Non-Newtonian Fluid Mech.*, 90 (2000) 91-116.
96. Coscia V and Robertson A M, *Math. Models & Methods in App. Sci.*, 11 (2001) 1055-1071.
97. Fan Y R, Tanner R I and Phan-Thien N, *J. Fluid Mech.*, 440 (2001) 327-357.