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New measurements of the flow-curves for Carbopol dispersions without slip artefacts

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Abstract The thickening properties of many commercial thickeners are difficult to measure because of wall slip artefacts. Here we report a series of experiments on a typical thickener where these artefacts have been successfully eliminated. As a result, complete, steady-state flow-curves of aqueous Carbopol 980 (the toxicologically preferred version of the older and more well-known Carbopol 940) dispersions are reported for a range of concentrations of 0.045–1.0 wt%. The vane-and-basket flow geometry was used to avoid slip problems at low shear stress, with the geometry housed in a TA AR1000-N controlled-stress rheometer, whilst a Haake RV2

viscometer with an SV2P and MV2P concentric-cylinder geometries were used at higher shear rates. The flow-curves obtained show a smooth but steep transition from a very high Newtonian viscosity at low shear stress to a much lower viscosity at high shear stress. No real yield stresses were detected, but the higher shear rate results can be fitted to the Herschel-Bulkley model, which assumes an *apparent* yield stress. The various model parameters are displayed as a function of Carbopol concentration.

Key words Wall slip · Carbopol · Dispersion · Herschel-Bulkley · Vane · Controlled-stress rheometer

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Introduction

Thickeners added to the aqueous phase of liquid products confer many important advantages in terms of consumer acceptability and long-term physical stability, etc. However, the measurement of the complete flow curves for some of these materials has not been easy because of wall-slip artefacts. Here our aim is to produce such flow curves for one important commercial thickener without the inevitable artefacts found in naïve measurements using unmodified, smooth geometries. These measurements are obtained for a wide range of concentrations.

For the last 50 years or so, Carbopol – the well-known B.F. Goodrich commercial polymeric thickener – has, in its many variant forms, been one of the most widely used thickening and gelling agents for commercial aqueous

products in the personal, home care and pharmaceutical areas. Carbopol dispersions and gels are useful vehicles for many functional ingredients, and are found in dozens of everyday products, ranging from toothpastes, through tile cleaners, to (artificial) tears (Unlü et al. 1991).

A typical Carbopol's exceptionally good optical clarity and thickening power – even less than 0.1% can give excellent thickening – make it very effective and economical, whilst used at slightly higher concentrations (typically above 0.5%) it produces an easily rubbed-on, transparent, '*smooth, luxurious gel*'. It is not only beloved of the product developer, but is also much-used by the rheologist and chemical engineer because of its versatility in imparting extreme non-Newtonian properties without excessive elasticity or stringiness (i.e. abnormally high extensional viscosity), and being *so* shear thinning that it appears to have a yield stress. For

this reason it has been used for model systems in mixing (Galindo and Nienow 1992; Amanullah and Nienow 1998; Amanullah et al. 1997; Galindo et al. 1996; Moore et al. 1995), pumping and heat transfer investigations (Lin et al. 1996; Lin and Ko 1995; Oliver and Shoji 1992; Loulou et al. 1992) and general flow experiments over and around objects (Hariharaputhiran et al. 1998; Wu and Thompson 1996; Cho et al. 1992).

Carbopol microstructure

Carbopol has been described as a microgel, that is to say a collection of highly cross-linked polymer particles, which individually are gelled but together act effectively as a concentrated dispersion even though the actual concentration is low. The exterior of the particles is decorated with dangling free ends of gel strands, and these interact strongly with their corresponding members on adjacent microgel particles (Carnali and Naser 1992) (see Fig. 1) to give a very high viscosity at low shear stress.

Most Carbopol-type polymers (also called carbomer resins) are high-molecular-weight homo- and copolymers of acrylic acid heavily cross-linked (intra-molecularly) with a polyalkenyl polyether; see the manufacturer's various websites, e.g. <http://www.homecare.bfgoodrich.com/products/carbopol.html>. The viscosity of any Carbopol dispersion is sensitive to pH, with a broad maximum in viscosity from around pH 5–10, with a considerable decrease in viscosity above and below this general range. Electrolyte addition also decreases the viscosity, since Carbopol is a polyelectrolyte. Once properly prepared, the shear-thinning properties of the high-clarity gels result in easy pumping and

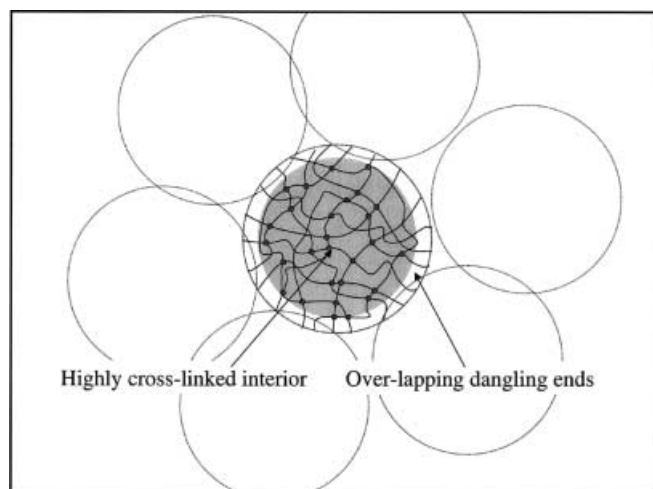


Fig. 1 A greatly simplified schematic representation of a Carbopol dispersion

dispensing via such means as trigger pumps and sprays. Normally, increasing the temperature decreases the viscosity, but some anomalous viscosity-temperature behaviour has been reported (Park and Irvine 1997).

Although its complete flow behaviour from low to high shear stress is important for suspending and thickening, few reports of the complete characterisation of the steady-state flow-curves over a range of concentrations have been published, while some, which have been published, are marred by slip artefacts (see below). This has caused a lot of confusion, and needed to be rectified, hence the reason for this work.

We report here on a comprehensive set of experiments using Carbopol 980, which is the toxicologically preferred version of the older and more well-known Carbopol 940, being polymerised in a co-solvent system. The manufacturer's promotional literature for Carbopol 980 claims that '*it is an efficient thickener at high viscosity and forms sparkling, clear, water or hydro-alcoholic gels*', and suggested applications include '*clear gels, hydro-alcoholic gels, and creams*', see www.personalcare.bfgoodrich.com/products/carbopol/980.html.

Our samples were made up from 0.045–1.0% (expressed in grams of dry Carbopol powder dispersed in 100 ml of de-mineralised water) according to the manufacturer's recommendations (see www.homecare.bfgoodrich.com/products/carbopol.html), and neutralised to pH 7. The dispersions produced, although very viscous, were quite 'short', i.e. non-stringy.

Rheological characterisation

Early attempts at characterisation of aqueous Carbopol dispersions using simple Brookfield-type 'dip-in' viscometers (with rotating bobs and discs immersed in large containers of liquid) resulted in their description as Bingham or power-law fluids (Meyer and Cohen 1959; Bauer et al. 1961; Testa and Etter 1973; Barry and Meyer 1979), while later, using data from typical laboratory viscometers with defined shear fields, the Herschel-Bulkley model was suggested (Atapattu et al. 1995). However, any serious attempt at characterising these dispersions over a wide range of shear stress must anticipate and correct for the kind of slip problems that we soon encountered in our experiments. This problem is most severe at low shear stresses, and occurs when unmodified, smooth-walled flow geometries are used. Figure 2 shows a typical example of such a flow-curve, where a 0.075% dispersion of Carbopol 940 was measured in a controlled-stress rheometer with a typical cone-and-plate smooth, polished geometry. The form of the curve is quite typical of the large collection of 'slip' results shown by Barnes (Barnes 1995).

In order to overcome these slip problems, we have used the vane geometry popularised primarily by Nguyen (Nguyen and Boger 1981) in the early 1980s for the measurement of the yield stress of concentrated suspensions, but augmented by us with the addition of a slender gauze basket inserted inside an outer cylinder (Barnes 1995), which eliminates slip there also, while, at the same time, giving a better-defined shear field. The particular rheometer used to house this flow geometry was a TA AR1000-N (TA Instruments, Leatherhead, England, KT22 7UQ). All the measurements were made at 25 °C. Great care was taken to eliminate any electronic or mechanical zero errors in the rheometer to give reliable viscosity data at low shear stresses.

Measurements of the viscosity at higher shear rates were made using the Haake RV2 viscometer, using the unmodified SV2P and MV2P concentric-cylinder geometries. At these higher shear rates slip is not a major problem, since the flow-curve rejoins the no-slip curve (as in Fig. 1 above 10 Pa), and any minor slip effects are insignificant.

The end product of both ranges of measurements is a set of smooth flow-curves decreasing monotonically but quickly from a very high viscosity at low shear stress to a much lower viscosity at high shear stress; see Fig. 3.

Parameters as a function of concentration

Figure 4 shows the various measured parameters as a function of Carbopol concentration. What is immediately noticeable is that the rate of increase from the lowest used concentration to around 0.1% is phenomenal, with a log slope of around 16, while above this

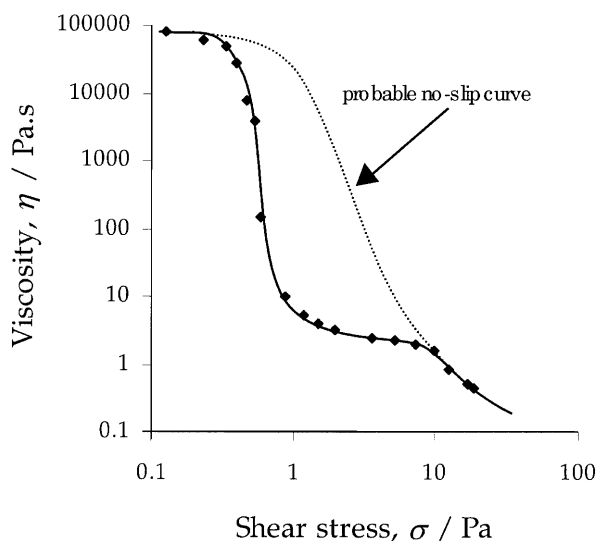


Fig. 2 A typical example of a Carbopol 940 flow-curve with slip at the smooth boundaries of the rheometer

value the slope drops dramatically to around unity. The critical stress shown is the value of the shear stress where the viscosity/shear-stress slope is a maximum or, put another way, what appears to be the yield stress (if it had one!), which for all practical purposes is the stress at a shear rate of around 0.01 s^{-1} . The behaviour of the critical stress follows that of the zero-shear-rate viscosity in terms of concentration.

High shear-rate behaviour

As indicated above, workers had previously (Atapattu et al. 1995) described the high shear rate behaviour using a Herschel-Bulkley model for the shear stress, i.e. an apparent yield stress plus a power-law viscous component, i.e. $\sigma = \sigma_o + k\dot{\gamma}^n$. Although this does not have the correct limit of a Newtonian asymptote at the highest shear rates, it does nevertheless give quite a good fit to the data in the range in which it has been collected (see Fig. 5) where seven of the most appropriate data sets are plotted.

Discussion

If care is taken to eliminate slip artefacts, then Carbopol dispersions show the typical properties of concentrated systems. The results so obtained show that the very high Newtonian-plateau viscosity seen at very low shear stresses is left quickly as the shear stress increases past a critical range. This could be because the entanglements between the surface polymer strands of adjacent micro-gel particles disappear as the flow 'combs' them out. On

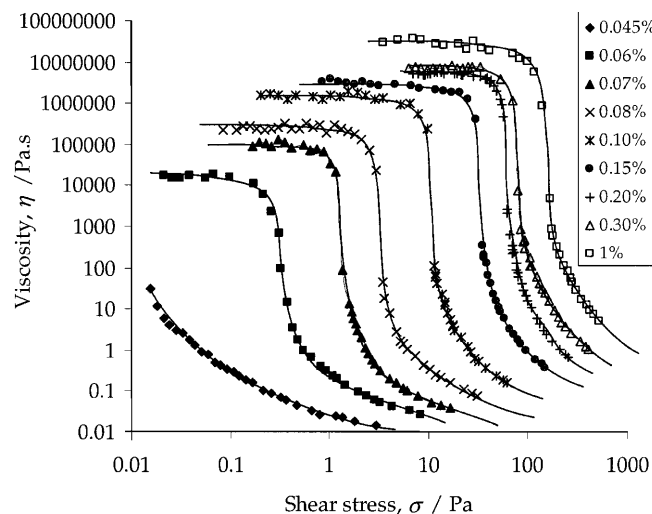


Fig. 3 Viscosity vs shear stress for a range of Carbopol 980 aqueous dispersions: *solid lines* are to guide the eye

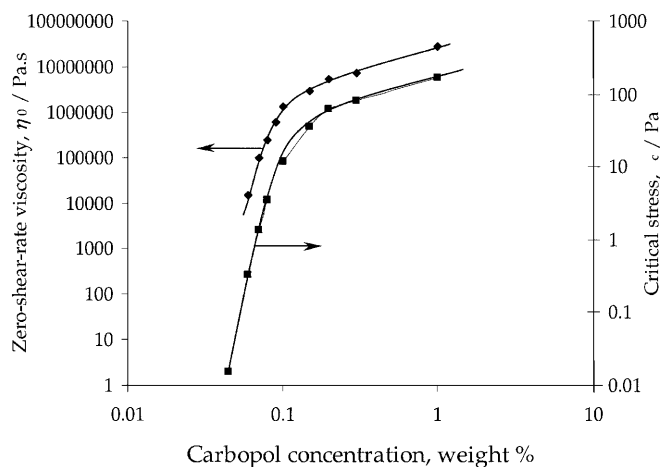


Fig. 4 Some rheological parameters as a function of Carbopol concentration

the other hand, it could be that the breakdown of structure is via clumps of microgel being broken down progressively as the shear stress is increased. This latter explanation would certainly account for the observed slip effects, where these clumps act effectively as large particles, which are the usual cause of problems at smooth walls (Barnes 1995). However, the viscosity levels off at a higher shear stress, and the microgel particles behave in the same way as a suspension, albeit with a high effective phase volume.

Although we have successfully eliminated artefacts due to slip effects, it might well be that in any real application, slip does indeed take place, so great care has to be used in utilising these results. Even sedimentation – appropriate to the shear stress range where slip is encountered – cannot be studied without due consideration, particularly if the shear stress applied by the particles on the surrounding liquid is high enough to be in the ‘slip’ region.

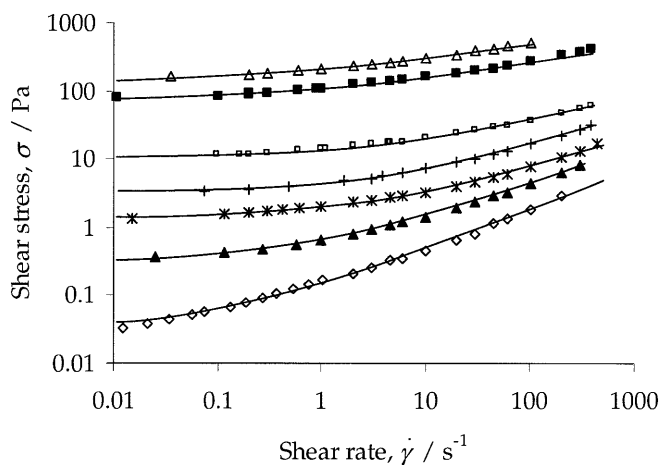


Fig. 5 A plot of the shear stress vs shear rate for a range of Carbopol concentrations (lowest concentration, lowest curve, etc.), fitted to the Herschel-Bulkley model using appropriate fitting parameters, as follows:

	0.045%	0.06%	0.07%	0.08%	0.10%	0.30%	1.00%
σ_0	0.03	0.300	1.25	3.0	10.00	70	115
k	0.12	0.345	0.67	1.4	3.75	40	100
n	0.60	0.550	0.50	0.5	0.45	0.35	0.3

Although Carbopol dispersions have no real yield stress, the abrupt transition from very high to low viscosity over a relatively narrow range of shear stress means that, on the one hand, small particles will appear to be stationary in suspension – although in reality they are moving very slowly – while the suspension as a whole can be poured out or expressed through a nozzle quite easily under the conditions of high shear stress and low viscosity. The same behaviour accounts for many other phenomena such as ‘cavern formation’ in mixing, and ‘dead spots’ in flow through complex geometries.

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