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

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

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 (Harirahrainthiran 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 carboxomer resins) are high-molecular-weight homo- and copolymers of acrylic acid heavily cross-linked (intra-molecularly) with a polyalkenyl polymer; 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 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 Ettler 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).

![Fig. 1 A greatly simplified schematic representation of a Carbopol dispersion](image-url)