



## Dissolution kinetics of water-soluble polymers: The guar gum paradigm

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### ABSTRACT

The ability of many water/electrolyte soluble polymers (WSPs), such as guar galactomannan, to form molecular solutions when dispersed in water is important industrially, for example in food applications, and in controlling the release of drugs in the gastrointestinal tract. Certain WSPs, including guar, are also referred to generically as 'soluble fibre' and some of these fibre preparations are currently available on prescription in the UK and elsewhere. The functional and exploitational properties of such polymers are reliant on the solution viscosity, which is, in turn, dependent on the rate and extent of dissolution in the aqueous solvent. This work extends previous experimental work on the effect of particle size on the dissolution (hydration) rate of guar gum powders over a wide range of particle sizes. In this earlier work, the main experimental variable was the solution viscosity, but we extend this by calculating a new effective concentration from the viscosity and exploring the dissolution rates in terms of this variable. The advantages and limitations of this approach are discussed, and a number of dissolution models, some well known and others novel, are explored. These include  $t_{50}$ , diffusion limited and chemical kinetics models. In view of the results, we suggest because of the particulate size, the model based on chemical kinetics appears the most successful. Aqueous guar gum is a model "entanglement solution" system, so the work should have applicability to many other WSP systems.

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### 1. Introduction

The ability of many water-soluble polymers (WSPs) such as guar galactomannan, to form molecular solutions when dispersed in water is of importance in a number of technological processes. In the pharmaceutical sector, for example, the functional properties of these polysaccharides are of importance for controlling the release of drugs in the gastrointestinal tract. (Chourasia & Jain, 2004; Friend, 2005; Montejo, Barcia, Fernandez-Carballido, & Molina-Martinez, 2004) Moreover, nutraceutical preparations that contain one or more water-soluble non-starch polysaccharides (NSPs) as the bioactive ingredient, are promoted commercially for their potential health benefits e.g. bulk-forming laxative and blood glucose-lowering effects in the treatment of diabetes. (Ellis & Morris, 1991; Guo, Skinner, Harcum, & Barnum, 1998; Judd & Ellis, 2006; Patrick, Gohman, Marx, DeLegge, & Greenberg, 1998; Slavin & Greenberg, 2003) Such water-soluble NSPs are often referred to generically as 'soluble fibre' in the medical and nutritional literature, and some fibre preparations are currently available on prescription in the UK. (Joint Formulary Committee, 2006) Water-soluble polymers are also used as excipients and bulking agents in a large number of formulations. "Viscosifying" guar gum solutions also occur in other

applications. For example in the oil industry, guar gum and its derivatives are major ingredients in drilling muds and fingering fluids, (Goel, Shah, & Asadi, 2000; Kesavan & Prudhomme, 1992; Perez, Siquier, Ramirez, Muller, & Saez, 2004; Zhou & Shah, 2004) and in the textile industry they are employed as "sizes" to help to improve printing quality. (Kesavan & Prudhomme, 1992; Schneider & Sostar-Turk, 2003; Turk & Schneider, 2000).

A number of factors are known to influence the hydration or dissolution process of WSPs, including their molecular weight and final solution concentration. In our recent series of papers on the dissolution (hydration) of guar powders, (Wang, Ellis, & Ross-Murphy, 2002, 2003, 2006) we have confirmed that another major determinant of hydration kinetics is particle size, which reflects the changes in surface area exposed to water. Commercial samples tend to have a particle size typically in the range 40–80  $\mu\text{m}$ , but in the last of these three publications (Wang et al., 2006) we used a range extended up to  $\sim 0.5$  mm. Here, the (weight average)  $M_w$  was maintained (effectively) constant, as was the initial nominal, concentration of polymer in the particulate material,  $C_0$ . This is an important step, because it appears that many literature studies, including those involving tableting (see below), have not been able to de-convolute the effects of particle size from those of molecular weight.

Although the present paper concentrates entirely on guar, this system is now accepted as a model water-soluble "viscosifying"

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or “thickening” polymer and the approach should serve as a standard for other WSPs, such as the cellulose ethers. Indeed the guar gum system is, to use an expression sadly somewhat over-employed – but here, we would argue, entirely appropriate – a paradigm. The literature evidence for this is extensive, but essentially goes back to work published by one of the current authors in the 1980s, where guar was demonstrated to be a model “entanglement solution” system. (Richardson & Ross-Murphy, 1987; Robinson, Ross-Murphy, & Morris, 1982) This work now seems to be part of the accepted canon.

Previously our studies have shown that development of (zero shear) viscosity on hydration of guar samples could be generalised on a single master curve by shifting the data appropriately along the time axis, as shown in Fig. 1. Central to the arguments developed in this paper is the consideration of this data in terms of the concentration of polysaccharide. Consequently, we re-examine the experimental data from our last paper, (Wang et al., 2006) but with a quite different emphasis.

In our earlier papers (Wang et al., 2002, 2003, 2006) we monitored the dissolution process purely in terms of the development of viscosity, and since this is published we give only essential details. To pre-empt the obvious question, why did we not simply follow the concentration with time, as is the convention standard for low molecular weight species particularly in the pharmaceutical area? Here we argued that, for these high molecular weight materials, the concentration, calculated by direct chemical analysis will not relate to fully hydrated material, so the value obtained will differ from that calculated from viscosity measurements, except for the “ultimate viscosity”. This is the value defined here as the viscosity measured for fully hydrated material, after long times.

Indeed in an earlier paper (Wang et al., 2002) we explained why we adopted the procedure of fitting the viscosity directly, rather than the concentration of dissolved material. To quote directly: “this (monitoring the concentration) would be more appropriate from the viewpoint of conventional chemical kinetics, but even though we centrifuged the extracted samples to remove totally undissolved (“filler” phase) material, we still do not have an equilibrium system. In other words, the viscosity even after filtration has a complex contribution from molecularly dissolved polymer, supramolecular but essentially hydrated material and solvent, so

the relationship between the measured viscosity at any time ( $<\infty$ ) is not necessarily a direct one. Consequently the idea that we use the ultimate viscosity versus concentration plots to back calculate the concentration of molecularly dispersed material is one we dismissed fairly early on”. To quote “we were not convinced there was, at any particular shear rate, a one-to-one mapping between concentration and the measured viscosity of the still hydrating system”. (Wang et al., 2002) the evidence for much of the above comment, including the evidence for supramolecular structure and the nature of undissolved material, follows from our work using the so-called pressure cell method to generate molecular solutions. (Patel, Picout, Ross-Murphy, & Harding, 2006; Picout, Ross-Murphy, Errington, & Harding, 2001, 2003; Picout, Ross-Murphy, Jumel, & Harding, 2002).

However, what this does allow us to do now is to calculate values of what we define as  $C_{\text{eff}}$ , the effective concentration of the system contributing to this viscosity. This is evaluated from the (zero shear rate) solution viscosity and, in the present text, we explore its dependence on time,  $t$ . Accepting the hypothesis above, the relationship between  $C_{\text{eff}}$  and the nominal initial concentration  $C_0$  is that generally  $C_{\text{eff}} < C_0$ , but that  $C_{\text{eff}} \rightarrow C_0$  as the hydration time,  $t \rightarrow \infty$ .

Since this is not an experimental paper *per se* we have not given any more than nominal particulars; full details are given in the earlier publications. (Wang et al., 2002, 2003, 2006) We note that other workers have also used the time development of viscosity to follow dissolution (most references in the papers above). For example, a recent publication by Larsen and co-workers (Larsen, Gaserod, & Smidsrod, 2003) applies a similar technique to alginate polymers, but the sample  $M_w$ 's are appreciably lower than those here (typically by  $>10\times$ ) so the viscosities are also markedly lower. One of the figures (their Fig. 2) also shows that log shear stress is proportional to polymer concentration – which suggests that their data are in the un-entangled, or dilute, regime. Under these circumstances it is likely that the above problems do not occur, and

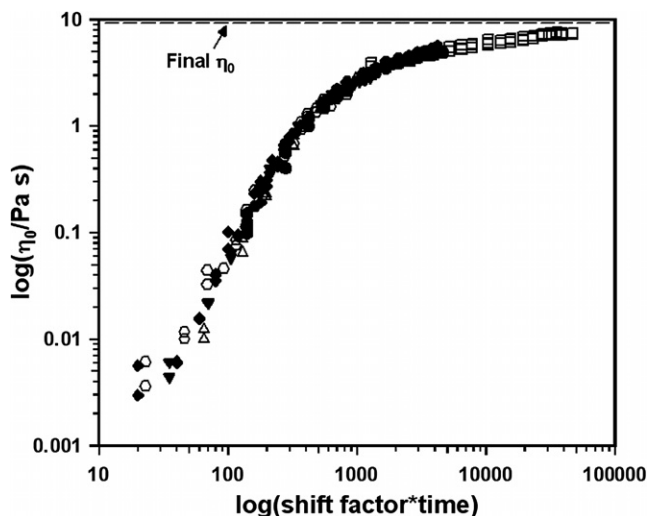


Fig. 1. Master curve of log viscosity versus scaled time, produced from viscosity versus time hydration data by applying shift-factor symbols: sample 1: filled diamond; sample 2: open hexagon; sample 3: filled triangle down; sample 4: open triangle up; sample 5: filled circle; sample 6: open square. Curves are cubic polynomial regressions to the means of the replicate measurements. Reproduced from Carbohydrate Polymers 64, 239–246 (2006) with permission from Elsevier Science.

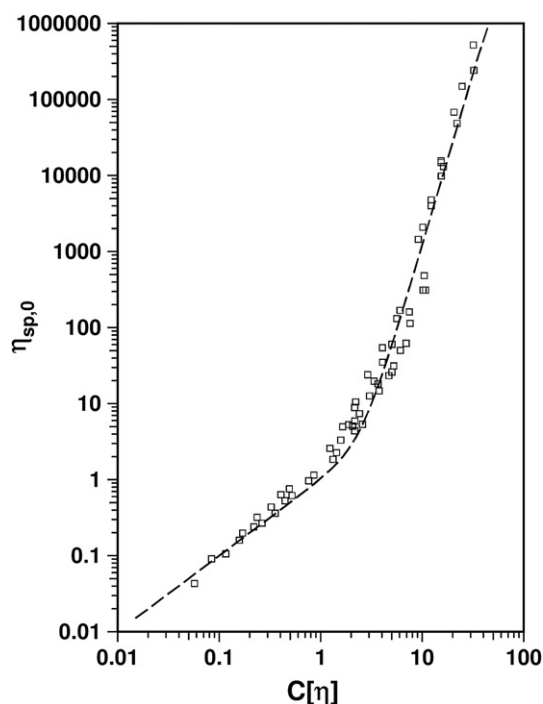


Fig. 2. Guar data from Robinson et al. (1982) plotted in the master plot form, and fitted to a modified Kulicke expression. The best fit, as is usual in this presentation, which spans 8 decades, corresponds to minimising the sum of squared of  $\log(\eta_{\text{sp},0})$  differences.

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