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Rheological properties of the aqueous zirconia/colloidal zirconia binder sol system

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The slip behaviour of the zirconia/colloidal zirconia binder sol system has been characterized by rheological measurements. The effects of slip solid loading and methylcellulose polymer addition on rheology and on rheology as a function of ageing time have been examined. The optimum conditions for suitable slips used in the dip-coating process have been determined from the rheological properties of the slips.

1. Introduction

The basic requirements for suitable dip-coating slip, including a high solid content, high redispersed property of the slip sediment, and highly shear-thinning flow behaviour, have been reported in a previous work [1]. Obviously, to develop a suitable slip for the dip-coating process, it is necessary to understand the rheological behaviour of the slip. In spite of the potential application of a zirconia/binder sol system in the coating industry, systematic studies of the properties and behaviour of such a slip have not yet been carried out. The present study investigated the rheological behaviour of the aqueous zirconia/colloidal zirconia binder sol system. The primary objective was to determine the optimum conditions for stable and suitable slips for use in the dip-coating process.

2. Experimental procedure

Slips were prepared by mixing -325 mesh electrofused stabilized zirconia powders (chemical composition $ZrO_2 > 93.0\%$, $CaO < 4.5\%$, $SiO_2 < 0.5\%$, $Fe_2O_3 < 0.2\%$, $TiO_2 < 0.3\%$), colloidal zirconia sol (~ 20 wt % ZrO_2, nitrate stabilized). Different amounts (0 to 0.15 wt % based on dried batch) of methylcellulose polymer (viscosity of 2% aqueous solution at 25° C approximately 150 c.p.s. were added to the slips. The slips were ground by a centrifugal ball mill with rotation speed 320 r.p.m. for 20 min; the grinding media were spheres of dense zirconia oxide. The grinding chamber was spherical and made of zirconia oxide. The ratio of media to slips by weight was constant (1.5 : 1) for all experiments. Slip rheological flow characteristics were determined using a Brookfield Model LV Rheoset Viscometer (Brookfield Engineering Laboratories, Inc., Massachusetts, USA) shortly after milling. 8 cm^3 slip was used for each viscometry. The viscosity results were all reported at an LV4 spindle speed of 60 r.p.m. The slip properties were also measured by changing the shear rate (r.p.m.) from 0 to maximum (< 250 r.p.m.) with a computer program which controlled the rate of increase at 10 r.p.m. per 15 sec. After measurement, the slips were stored at room temperature in borosilicate glass containers which were covered with aluminium foil, and were kept in a $\sim 55\%$ r.h. atmosphere provided by the saturated magnesium nitrate solution. After every 24 h ageing, the slips were stirred at 60 r.p.m. for about 10 min, and the slip properties were measured again.

Sedimentation bulk density was determined by pouring the slip (of known weight) into a 25 ml graduated cylinder. The cylinder was covered with a flexible film to prevent water evaporation and the solids in the slip were allowed to settle by gravity until the sediment height no longer changed with time. The sedimentation bulk volume was determined directly from the sediment height in the graduated cylinder. The weight of ZrO_2 in the sediment was determined by multiplying the known weight of slip in the cylinder by the known weight percentage of ZrO_2 in the slip. Sedimentation bulk density was determined by dividing the weight of ZrO_2 by the bulk volume. Several slips were used for the dip-coating wax pattern process. The dip-coated surfaces were observed by scanning electron microscopy (SEM).

3. Results and discussion

From the results of viscosity–shear rate (r.p.m.) measurements for different solid content slips prepared at $pH \simeq 1.2$ (as the isoelectric point of ZrO_2 is $pH \simeq 6.5$ [2], it is expected to have a large electrostatic repulsive force at this pH value), as shown in Fig. 1, the 72 and 75 wt % slips exhibited a Newtonian flow behaviour, that is, the viscosity was independent of shear rate. This is characteristic of a well-dispersed suspension. The 78, 80 and 83 wt % solid content slips show non-Newtonian flow behaviour. In slips with high solid contents (83 wt %), the viscosity decreases significantly as the shear rate increases (i.e. a high shear thinning behaviour). Slips with intermediate solid contents (78 and 80 wt %) are relatively independent of shear rate. Despite the large electrostatic repulsive forces, flocculation occurs under conditions of high

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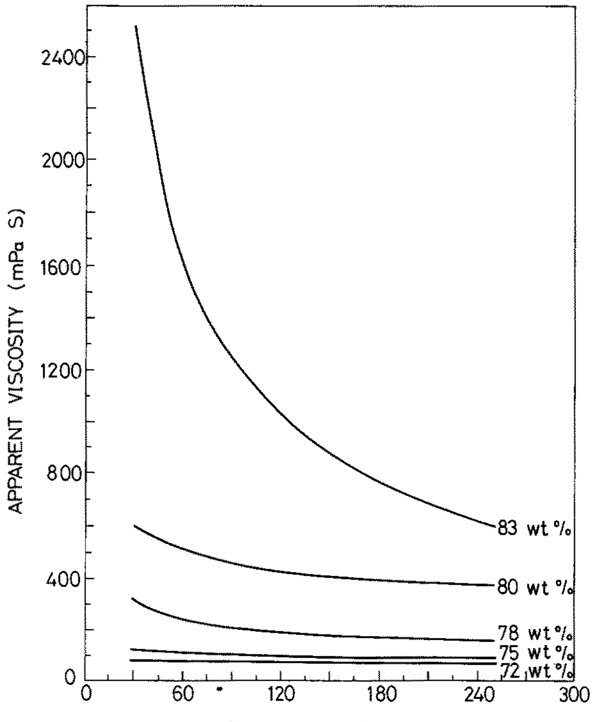

Figure 1 Plots of apparent viscosity against shear rate for different solid-content slips indicated.

solid loadings and low shear rates. Fig. 2 shows that the 72 to 80 wt % ZrO_2 slips were stable (kept near-constant viscosity) during a long period of ageing, whereas the 83 wt % slip was unstable, the viscosity changed widely from 1400 to 2000 mPa S at 60 r.p.m. These data correlate well with the rheological measurements (Fig. 1). For high solid loading and high shear thinning slip (83 wt %), it is relatively hard to redisperse the sediment by stirring at 60 r.p.m. This may be the reason why its viscosity changed with ageing time.

Because the 83 wt % slip has a high solid content and shear thinning behaviour, it seems to be an appropriate workable slip for the dip-coating process. To test this, a wax pattern was dipped into this slip. Examination of the coating layer indicated it produces a flabby and non-uniform surface. The irreversible phenomenon shown in Fig. 3 might explain why it does not produce a satisfactory coating. In flocculated slip, such as that with 83 wt % solid content, liquid is immobilized in the interparticulate void space of the flocs and floc networks. This increases the "effective" solid loading (relative to a well-dispersed slip), resulting in higher viscosity. If the flocs are broken down by shearing the slip, occluded liquid is released, the viscosity decreases and shear thinning flow behaviour is observed [3]. However, when the shearing force from a high r.p.m. is restored to a low r.p.m., the viscosity was lower than it was previously at the same shear rate, because having removed the shearing force, motion ceases and flocs begin to relink together. If the relinking rate is low, viscosity will be lower, as shown in Fig. 3. This results in the rheological behaviour called "thixotropy" [4]. The coating slip must flow evenly and must have constant properties to achieve a good-quality coated surface. Consequently, the unstable behaviour of 83 wt % slip due to its high degree of thixotropy is undesirable.

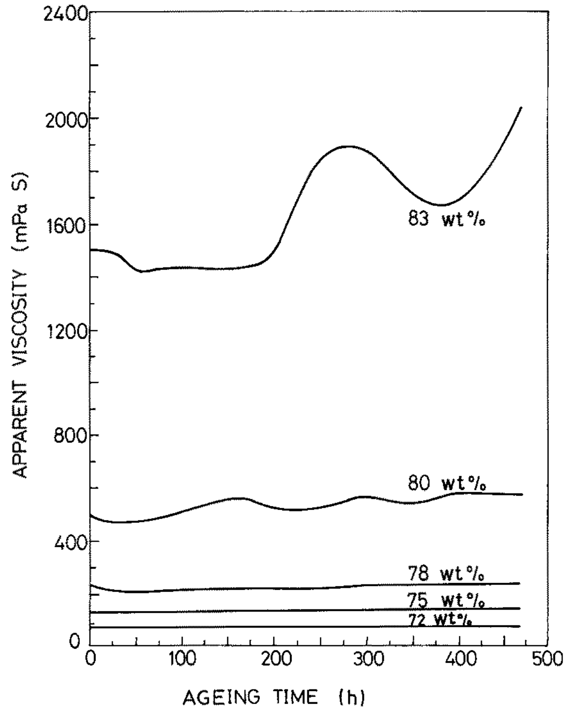

Figure 2 Plots of apparent viscosity against ageing time for different solid-content slips indicated.

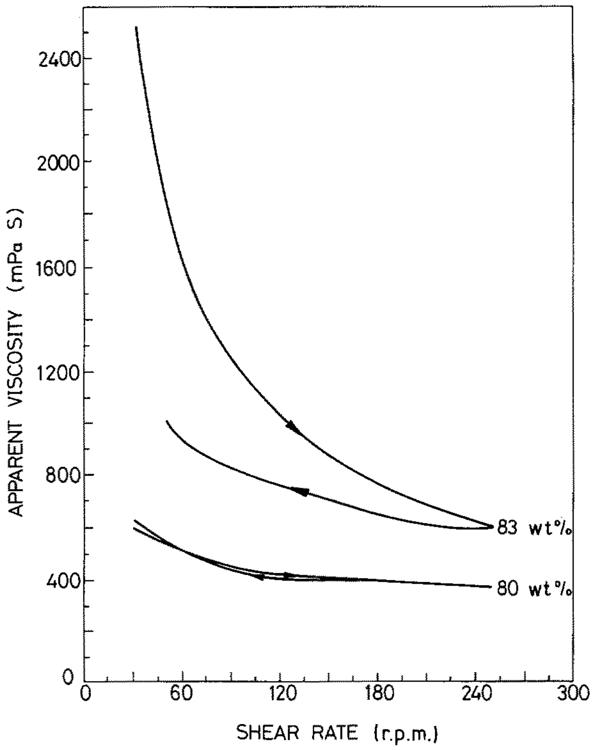

Figure 3 Hysteresis curves of apparent viscosity against shear rate for 80 and 83 wt % solid-content slips.

In contrast, the 80 wt % slip shows slightly thixotropic behaviour and is stable for long ageing times. However, the dip-coating test indicated that its viscosity is too low for it to remain on the pattern surface during the draining operation. Fig. 4 shows the flow behaviour of 80 wt % slip with different weight percentages of methylcellulose (MC) polymer additions. The rheology of the slip is strongly affected by the MC additions which increase the viscosity and change the flow characteristics from near-Newtonian

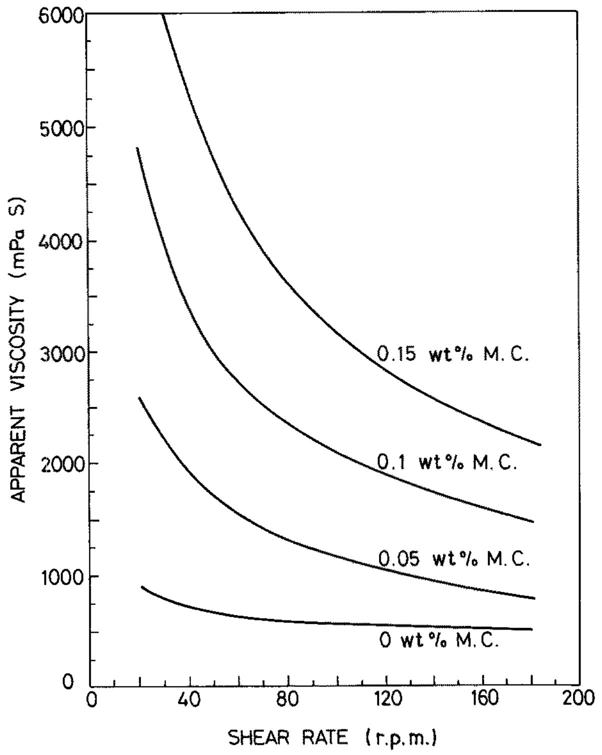

Figure 4 Plots of apparent viscosity against shear rate for 80 wt % slip with different amounts of methylcellulose additions.

to shear thinning behaviour. The addition of MC polymer to this slip probably results in the formation of soft flocs in which the particles are connected by polymer linkages. The soft floccules can form under low shear rate conditions, but tend to be broken up at high shear rates, occluded liquid being released and thus the viscosity decreases, so the shear thinning behaviour is observed. Fig. 5 shows viscosity–ageing time curves for 80 wt % slips with different amounts of MC additions. It indicates that increasing MC content of the slip is accompanied by increasing viscosity. In the early stage of ageing, the viscosity is unstable and becomes stable (relatively constant viscosity) after a longer ageing time. The MC polymer probably cannot initially produce a homogeneous coverage of all particles; however, the slip becomes more homogeneous and the viscosity reaches an equilibrium state and shows stable values after a longer stirring time. It was attempted to change the order of MC addition, and to add the MC to the slip before, instead of after, the milling process. The results indicate that a steady value of viscosity can be reached in the early stage of ageing. The sedimentation bulk density is plotted against weight per cent MC in Fig. 6. Sedimentation density decreases with increasing MC addition. This indicates that flocculation increases. The sediment of relatively well-dispersed slip without MC addition is very compact because particles can glide along one another until the packing is as dense as possible. Such a sediment makes redispersion difficult [5]. All slips with polymer additions are in a flocculated condition, the sediments show lower sedimentation densities, are rather loosely packed and will be easily re-incorporated into the dispersion by light stirring or shaking. On the other hand, MC additions are expected to increase the viscosity of the liquid medium and to slow down the settling. Therefore, slips with polymer additions would remain homogeneous for longer ageing times. In fact, controlling the sediment properties by controlling the degree of stability or of flocculation of the slip is very important in coating technology [1]. The use of the 80 wt %, 0.1 wt % MC slip for coating patterns has been successful. The relatively uniform coverage coating layer could adhere to the surface of the pattern

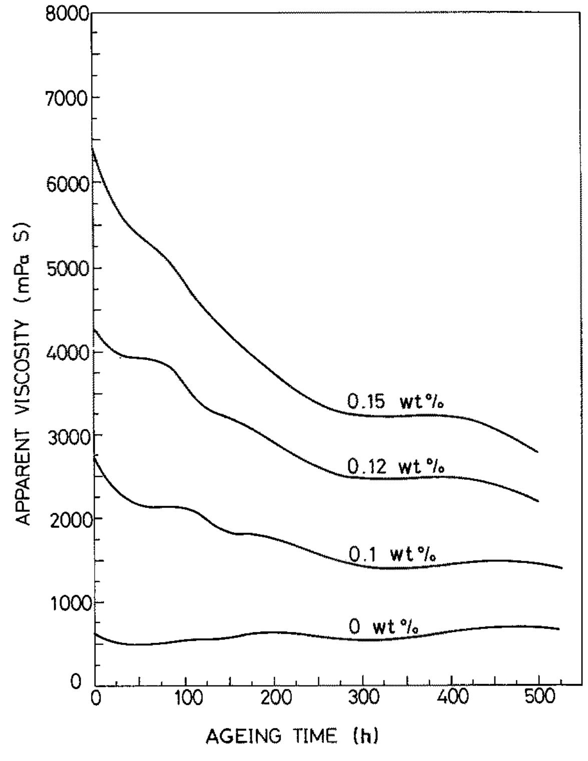

Figure 5 Plots of apparent viscosity against ageing time for 80 wt % slip with different amounts of methylcellulose additions.

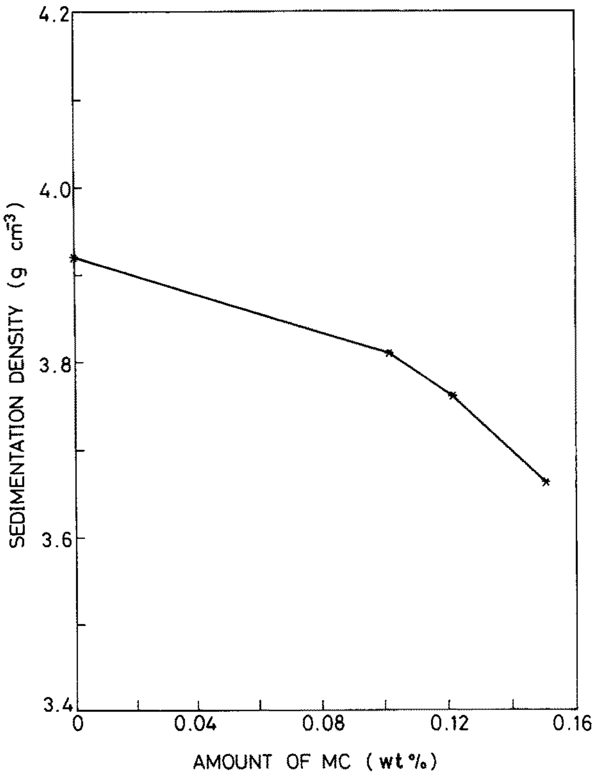

Figure 6 Plot of sedimentation bulk density against methylcellulose additions in the slips.

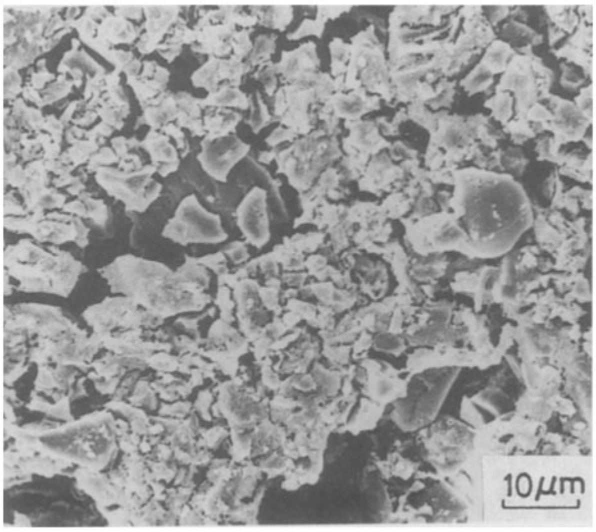

Figure 7 Scanning electron micrograph of a coated surface prepared from 80 wt %, 0.1 wt % MC slip.

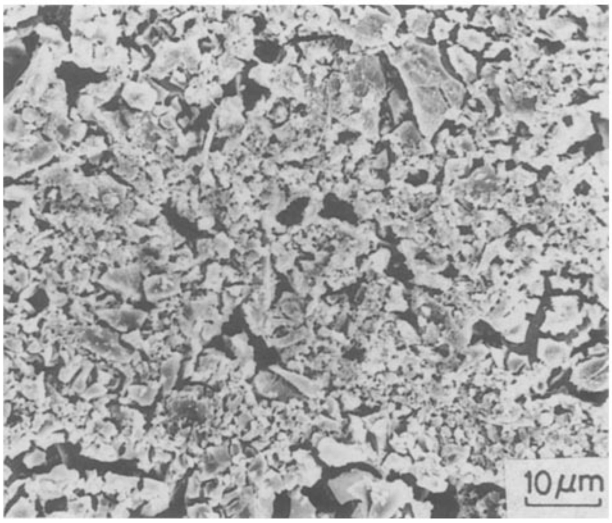

Figure 8 Scanning electron micrograph of a coated surface prepared from 80 wt % ZrO_2, 2.4 wt % Al_2O_3, 0.1 wt % MC slip.

(Fig. 7). In order to enhance sintering and to obtain a better mechanical strength of the coating layers, 2.4 wt %, 1 μm α-Al_2O_3 powder was added to 80 wt %, 0.1 wt % MC slip. The viscosity of this slip stayed in the stable range (about 1500 mPa S) for more than 25 d ageing. The microstructure of the coating surface prepared by dipping the wax pattern into this slip, as shown in Fig. 8, indicates a more uniform coating layer compared to that prepared by the slip containing no Al_2O_3.

4. Conclusions

Flocculation by a dissolved non-ionic, water-soluble MC polymer produces pseudoplasticity which is important in producing a low viscosity during dip coating, but a high viscosity is achieved once the coating has been deposited so that the slip can be "solidified" and allow uniform coverage of the surface to be coated. Such flocculated slips also produce easily redispersed loose sediment. In contrast, flocculation due to high solid loading in the slip (i.e. coagulated flocs) is an appropriate workable slip for the dip coating process.

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