Rheological studies of the setting of water-based cements

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Abstract—The time dependent viscosity of five types of water-based luting and filling materials was measured and compared with an idealized model. Differences between the materials were explained in terms of their structure formation. The shear rates involved in manipulating the material and the forces involved in seating a crown were calculated from model systems.

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Introduction

The flow and deformation behaviour (or rheology) of cements and filling materials has a profound influence on their manipulation and use. The flow behaviour of an ideal material may involve a stage of near constant viscosity so that the material can be thoroughly mixed and easily manipulated, followed by a region of rapid increase in viscosity so that the filling material (for a restoration) is retained in the preparation or so that the crown is retained in position (for a luting material). The shear rate dependency of the viscosity, or the manner in which the consistency is affected by the rate of shearing motion in the material, is also important because this can have bearing on the optimum rate of seating a crown.

Combe, Watts, and Greener have studied the time-dependent change in viscosity of zinc polycarboxylate cements and glass ionomers using an extrusion-style capillary rheometer. A disadvantage with this technique is that the material is subjected to a range of shear rates in the instrument so that detailed experiments are required before fundamental information can be obtained. These workers found that the viscosity rose steadily after mixing and that the material was Newtonian (viscosity independent of shear rate) initially but became progressively dilatant (viscosity increasing with shear rate) within the shear rate range 0.05-65 s⁻¹ as the reaction proceeded. This differed from the results obtained by the present authors using a cone and plate rheometer in which the material experienced a constant shear rate. This work indicated that the materials were near-Newtonian (between shear rates of 0.3 and 60 s⁻¹), and that while the zinc polycarboxylate cements showed a steady rise in viscosity with time, the glass ionomer cements exhibited a region of less rapid rise followed by a region of accelerated increase in viscosity. The study by Vermilyea, Powers, and Craig also indicated that zinc phosphate and zinc polycarboxylate cements were Newtonian. However, their

<table>
<thead>
<tr>
<th>Code</th>
<th>Brand</th>
<th>Manufacturer</th>
<th>Batch code</th>
<th>Recommended mixing ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSP</td>
<td>Lumicon silico-phosphate</td>
<td>Bayer, Leverkusen, West Germany</td>
<td>0009Z/0010Z</td>
<td>(P/L = 2.0)</td>
</tr>
<tr>
<td>KSP</td>
<td>New Kryptex</td>
<td>S. S. White Dental Manufacturing Co. Ltd. London, U.K.</td>
<td>577909/1146716</td>
<td>3.25-3.75 g/ml (P/L=2.06-2.37)</td>
</tr>
<tr>
<td>WS</td>
<td>S. S. White Filling Porcelain (improved)</td>
<td>S. S. White Dental Manufacturing Co. London, U.K.</td>
<td>61246179/1146716</td>
<td>3.3 g/ml (P/L=2.33)</td>
</tr>
<tr>
<td>AS</td>
<td>Achall biolochromic Silcap</td>
<td>Vivadent, Schaan, Liechtenstein</td>
<td>014Z10-1768</td>
<td>2.25 g/ml (Capsulated)</td>
</tr>
</tbody>
</table>

Table 1 lists the code numbers, brand names and powder-liquid (P/L) mass ratios used in the study of three zinc phosphate cements, one zinc polycarboxylate cement (for comparative purposes), three silicophosphates, three silicates and two glass ionomers (for comparative purposes). The materials were mixed on a glass slab according to their manufacturers' instructions at 21 ± 1°C and 50 ± 10% relative humidity, transferred to a cone and plate rheometer, and their viscosity monitored as a function of their setting time (θ) measured from the commencement of mixing. To minimize dehydration effects, the material between the cone and plate of the rheometer was maintained at 100 per cent RH by use of an environmental chamber accessory to the rheometer. Depending on the fluidity of the mix, shear rates between 0.17 s⁻¹ and 2.66 s⁻¹ were used. During each viscometry run, however, the shear rate was kept constant.

**Materials and methods**

The first purpose of the present study was to investigate the time dependent viscosity at low shear rates of the five common types of water based cement and filling material and rationalize this in terms of their setting mechanism. The second aim was to calculate theoretically the shear rates experienced by the material in its clinical usage.  

Model systems of the zinc phosphate and silicate cements were prepared from HZP cement liquid by addition of freshly prepared aluminium hydroxide (from aqueous solutions of NaOH and Al(NO₃)₃) or zinc hydroxide (from aqueous solutions of NaOH and ZnCl₂). Similar model systems were also prepared by the addition of either 5 mmol/g CaCl₂, 3 mmol/g ZnCl₂, or 1.5 mmol/g Al(NO₃)₃, to HZP liquid which had been partly neutralized with an aqueous solution containing 5 mmol/g NaOH and 5 mmol/g KOH. Contrary to that previously found with the polyelectrolyte cement liquids, no increase in viscosity was visually apparent until precipitation of salts occurred.

Results and discussion

Viscosity and structure

Figure 1 shows the change in viscosity (η) with time (θ) for the zinc phosphate cements and compares this with that of the zinc polycarboxylate cement DL. It has been previously shown⁴ that the latter behaviour is typical of zinc polycarboxylate cements so that it can be concluded that a strong analogy exists between the zinc phosphate and polycarboxylate cements. As shown by the data for the zinc phosphate cement DZP, alteration of the P/L ratio did not affect the basic shape of the curve but merely changed the initial viscosity and the rate of setting as was found previously⁴ for the zinc polycarboxylate and glass ionomer materials.

The viscosity behaviour for the silicate and glass ionomer/materials is shown in Fig. 2. In contrast to the zinc oxide based materials, the viscosity increased only slowly in the initial stages and then rose at an increasing rate which may be considered to be close to the behaviour of an ideal material. As might be expected from the formulation of silicophosphates (the powder contains fluorooxaluminio-silicate and zinc oxide), the behaviour of these materials (Fig. 3) appeared to be intermediate between the zinc phosphate and silicate cements.

The analogous behaviour of zinc phosphate cement with zinc polycarboxylates and of the silicates with glass ionomers suggests that their setting mechanisms may be similar. Based on chemical⁵ and rheological studies⁶ it has been suggested that the setting of glass ionomers is due to the branching of the polymeric acid chains by the calcium and aluminium ions extracted from the calcium fluoro-alumino-silicate glass and that this polymerization and eventual gelation process occurs homogeneously throughout the aqueous phase. In contrast, for the polycarboxylate cements, it has been suggested⁴ that the

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zinc ions released from the zinc oxide particle cause chain branching and then gelation of the neighbouring polymeric acid producing a reaction zone surrounding the particles which grow as the reaction proceeded. It is known\textsuperscript{11,12} that the setting of zinc phosphate cements results in the formation of an amorphous zinc phosphate matrix, while for the silicate cements,\textsuperscript{13,14} the matrix is composed of small amounts of crystalline CaF\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}(OH)\textsubscript{2}, and amorphous calcium and zinc aluminophosphates and larger amounts of aluminium phosphates. The potential for the formation of polymeric aluminium phosphate species has been recognized by Wilson and Kent,\textsuperscript{15} and the formation of linear and cross-linked polymeric metal phosphates\textsuperscript{16} is well known. In contrast to the polynuclear based materials,\textsuperscript{7} it appears unlikely that the rise in viscosity with reaction time for the zinc phosphate and silicate cements is caused by an increase in the viscosity of the liquid phase by soluble polymeric species, because the calcium, zinc and aluminium phosphates have limited solubility. Also, the addition of aluminium or zinc hydroxide to a zinc phosphate liquid or of concentrated solutions of Ca\textsuperscript{2+}, Zn\textsuperscript{2+} and Al\textsuperscript{3+} to partly neutralized zinc phosphate liquid did not produce any substantial rise in the viscosity of the solution before precipitation occurred. Therefore, it would appear that if polymeric species are formed, they are precipitated and that the rise in viscosity of the cement is caused by the increasing fracture of particles in mixed cement.

The influence of the volume fraction of particles (\(\phi\)) on the viscosity of a suspension (\(\eta_s\)), is given\textsuperscript{17,18} by:

\[
\eta_s = \eta_0 \left(1 + k_1 \phi + k_2 \phi^2\right)
\]

where \(\eta_0\) is the viscosity of the liquid, \(k_1\) is ideally 2.5 and \(k_2\) represents a crowding factor. For the polyelectrolyte cements\textsuperscript{12}, \(k_1\) was of the order of 11, possibly due to the irregular particle shape and \(k_2\) was negligible. This implies that \(\eta_s\) may be approximately linearly related to the mass fraction of the metal phosphate precipitated and thus the extent of reaction. If this is so, then the contrasting behaviour between zinc phosphates and silicates must lie in their phosphate precipitation behaviour. Possibly the calcium and aluminium ions are liberated from the silicate glass as soluble fluoride complexes\textsuperscript{19} which diffuse from the particles and do not immediately react with the phosphate ions whereas the zinc ions released from the zinc oxide powder may immediately react with the phosphate ions and precipitate.

### Viscosity and shear rate

Because the viscosity of the cements may show shear rate dependence, it is instructive to estimate the shear rate involved in their use. For spatteration of the material, a suitable model is that in which the material is subjected to simple shear\textsuperscript{(Fig. 4)}. The shear rate (\(D\)) in this case is given\textsuperscript{20} by:

\[
D = \frac{V}{h}
\]

where \(V\) is the transverse velocity and \(h\) is the thickness of material. Thus for the mixing procedure, shear rates of 10 to 50 s\textsuperscript{-1} would be expected. For calculations involving the setting of a crown, an idealized cross-sectional geometry is given in Fig. 5. If parallel plate...
geometry' is used to represent the flow of the material in the occlusal area of the crown and Pochettino geometry is (Fig. 5) represents the sliding motion between the crown and the tooth; then the average shear rates (derived from those given by Okai) are:

Parallel plate: $D = V \frac{a}{h^2}$

Pochettino: $D = 2V[f(b + a)ln b/a]$  

where $V$ is the velocity in the direction of the force (F).

Assuming that the rate of seating is 2 mm/min, the shear rates in the occlusal area and at the sides of the crown can be calculated to be 0.08 s⁻¹ and 0.38 s⁻¹ respectively when the gap (h) in the occlusal area is 1.0 mm or 2.0 mm and 12.6 s⁻¹ when h is 0.03 mm. These values are considerably smaller than the shear rate value of 2000 s⁻¹ estimated by Lortong and colleagues for the shear rates involved in seating. The reason for this is that the major resistance to seating (as discussed below) is not caused by the flow of the material in the occlusal area or the sliding action at the wall but arises from the volumetric flow of material from the occlusal area into the decreasing cavity between the walls. This flow behaviour is modelled by the penetrometer geometry in Fig. 5. From

the analyses of Smith, Perry and Schremp it can be shown that the averaged shear rate of the material between the walls of the cylinders is given by:

$$D = 2V \left[ \frac{a^2 + b^2}{(b-a)^2} \right] \ln(b/a) \quad (b^2-a^2)$$

where $r = [(a^2 + b^2)/2]^{1/2}$

For the occlusal gaps (h) of 2.0, 0.1 and 0.03 mm, equation (5) gives shear rates of 16, 1633 and 18200 s⁻¹, respectively, for a seating rate (V) of 2 mm/min.

The forces ($F_1$, $F_2$, $F_3$) due to fluid flow in the three model geometries of Fig. 5 can be calculated from the equations of Okai and are:

Pochettino geometry: $F_1 = 4\pi \rho V (b + a) ln b/a$  
Parallel plate geometry: $F_2 = 3\pi \rho \frac{h}{2} \frac{V^2}{a}$  
Penetrometer geometry: $F_3 = 2\pi \rho \frac{V^2}{b}(b^2-a^2)/(b^2-a^2)$  

Substitution of the dimensions for the idealized geometry of Fig. 5 into these equations reveals that the ratio $F_1/F_2/F_3$ is $5 \times 10^{-5}/9 \times 10^{-1}$ when the occlusal gap (h) is 1 mm, decreasing to $4 \times 10^{-8}/8 \times 10^{-1}$ when h is 0.01 mm. Thus the major force in seating is due to the pumping of the fluid from the occlusal area and through the gap between the walls. This force may be reduced by venting the crown or by ensuring that there is adequate spacing at the walls (for example by die spacing). Because the present calculations have neglected the particulate nature of the cement, the force due to the pumping action is underestimated. This occurs because when the gap (h) at the occlusal surface is 0.1 mm, the gap between the walls is 0.008 mm which is of the order of the particle diameter. Thus an additional friction mechanism occurs. This frictional force is best minimized by ensuring that there is a sufficient wall spacing.

Conclusions

Measurements of the rheology of five types of luting and filling materials reveal that the silicates (and to a lesser extent the glass ionomers) exhibit a relatively constant viscosity region prior to a rapid rise, whereas the viscosity of the phosphate and polyacrylate cements rises steadily. For the non-polymeric materials this appears to be related to the rate of growth of the reaction phase.

Model calculations of shear rates show that those used in the present study are of the same magnitude as those involved in mixing. Because much higher shear rates are generated in seating a crown, the present data may have less relevance. The major resistance to the seating crown has been shown to be due to a pumping action. This may be best minimized by die spacing.

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