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A Water-Based System for Ceramic Injection Moulding

R. J. Huzzard[a] & S. Blackburn[a,b]

[a]Interdisciplinary Research Centre in Materials for High Performance Applications, [b]School of Chemical Engineering, The University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK

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Abstract

Water-based binders for injection moulding of ceramics use low moulding temperatures allowing moulding and die temperatures to be similar. Most of the binder system can be driven off as water vapour, cutting process time, reducing burn-out problems and causing less environmental pollution. The difficulties with removing moulded articles from the die must be overcome. To address this problem, gel strength was measured on solutions up to 8 wt% of ten commercially available cellulose derivatives at four temperatures between the gel temperature and the boiling point of water. A paste with rheology that permits mould filling was made from the binder that showed highest gel strength. This was used in moulding trials. A similar formulation based on a low-strength binder was also studied for comparison. The paste based on the highest gel strength binder showed significantly less deformation on release from the die, allowing the processing advantages of the system to be realised. © 1996 Elsevier Science Limited.

1 Introduction

Injection moulding is an established route for mass production of ceramics of complex shapes.[1,2] The continuing commercialisation of this technique will require shorter process times, better shape retention and the control of defects in the compact.

Aqueous binder systems have been introduced which use low moulding temperatures.[2,3] Moulding and die temperatures can be similar, reducing shrinkage and consequent moulding defects. Most of the binder system can be driven off as water vapour, cutting process time, reducing burn-out problems and leaving a rigid structure with better shape retention. The ability of the moulded material to withstand ejection from the die presents a serious limitation to the use of water-soluble binders in injection moulding. Successful systems exhibiting thermal gelation to solidify the component have been reported.[2–5]

The systems investigated here are based on cellulose, a linear polymer of anhydro-glucose and b-*O*-glucopyranosyl. Where injection moulding of ceramics is concerned, work on cellulose derivatives has focused on the preparation and properties of the binder systems. Mutsuddy[2] recently reviewed the literature. Cellulose ethers are generally soluble in cold water but insoluble in hot water. Properties of the gels were considered in detail by Sarkar.[6] Gelation of aqueous solutions of cellulose derivatives is caused by hydrophobic interaction. At temperatures below the gel point, the molecules are hydrated. As temperature increases the water of hydration is gradually lost, allowing cross-linking to occur and eventually resulting in a rigid gel. Gel formation is reversible and time-dependent. The degree of substitution is categorised by the number of available hydroxyl units, three per unit, which are substituted. This number need not be an integer, since substitution may vary from unit to unit. The temperature at which gelation occurs (the gel point) and the strength of the resultant gel are affected by molecular weight, concentration, the presence of additives and the degree and the nature of substitution. Substituent groups include hydroxypropyl- or methyl-. The main source of information is from manufacturer's literature where test methods may vary and few standards currently exist (Table 1).

Thermal gelation temperatures from 50 to 90°C are possible by varying the methyl and hydroxypropyl substitution. Cellulose derivatives have been classified for gel strength using the cone penetration test.[6] The dependence of gel strength on degree of substitution and molecular weight was established. As temperature increases above the gel point, cross-linking continues and the gel

Table 1. Properties of cellulose derivatives used in solution as binders

Chemical name	*%Methyl deg of sub 3 = 100%*	*%Hydroxypropyl*	*Viscosity 2% solution at 20°C (mPa s)*	*Trade name*
HPMC[a]	1·6	0·2	4000–6000	HPM 5000DS[h]
HPMC	—	—	—	20/2311[i]
HPMC	1·6	0·2	80–120	HPM100DS[i]
HPMC	1·6	0·2	12000–17000	B2/15[h]
HPMC	1·6	0·2	350–550	HPM450P[h]
MC[b]	1·9	—	17–23	MM20P[h]
MC	60	—	12–18[e]	Methocel A15LV[i]
HPMC	60	—	3500–5600[f]	Methocel F4M[i]
HPMC	46	—	3500–5600[f]	Methocel K4M[i]
MEC[c]	3·5–6·5	14·5–6·5[d]	10–60[g]	MEC[h]
HPMC	—	—	—	DP588[h]

[a] HPMC Hydroxypropylmethylcellulose.
[b] MC Methylcellulose.
[c] MEC Methylethylcellulose.
[d] Ethyl substitution.
[e] USA Standard (D1347).
[f] USA Standard (D2363).
[g] 2·5% solution.
[h] Courtaulds Chemicals, PO Box 5, Spondon, Derby DE21 7BP.
[i] Croxton and Garry Ltd, Curtis Road, Dorking, Surrey RH4 1XA, UK on behalf of the Dow Chemical Company, USA.

strength gradually rises to a maximum and then falls as the cellulose molecules precipitate out.[2] Small changes in degree of substitution can have a large effect on gel strength, e.g. a small quantity of hydroxypropyl substitution increases gel strength. The interaction of substituent groups is complex: methyl substitution in hydroxypropylmethylcellulose is responsible for gelation, but hydroxypropyl substitution increases gel strength significantly. Measured at 65°C, gel strength increases with the log of molecular weight up to a gel strength of about 150,000 Pa but becomes independent of molecular weight at higher strengths.[6] Substances with a high affinity for water, such as glycerol, remove water from the solution and increase the cellulose concentration, thereby increasing gel strength. It follows that gel strength will be affected in highly concentrated suspensions where the surface of the dispersed phase has a different affinity for water than for the cellulose molecule. The scarcity of commercially available derivatives limits the usefulness of these observations. Gelation temperature varies with concentration of cellulose and degree of hydroxypropyl substitution.[2]

Several attempts have been made to improve the rigidity of the gel. Zhang[7] adapted Meer's method[8] to provide gel strength data on agar systems which reflected ejection of a component from an injection moulding die. Hot solutions of agar derivatives have low viscosities, and the gels form on cooling. Gel strength has been measured at a temperature around 20°C.[7] Injection moulding mixes based on agar therefore require a barrel temperature between the gel point of the agar and the point at which evaporation of water is unacceptably high. The die temperature must be lower than the gel point of the agar so that the moulded component solidifies. The reverse applies for gels that are formed on heating such as those found in cellulose systems. It is therefore essential to measure gel strength over a range of temperatures from the gel point up to nearly 100°C. The resultant moisture loss from the die rather than the barrel may prove advantageous in the case of injection moulding of pastes based on cellulose gels. A range of cellulose and agar derivatives have been studied here to assess their suitability for use in ceramic injection moulding.

2 Experimental Procedure

2.1 Gel preparation

Various commercially available cellulose derivatives (Table 1) were assessed. These grades are generally classified by the manufacturers using viscosity at low shear rate. Table 1 shows the manufacturers' figures, although the tests are not directly comparable. Other systems, typically agar, have been successfully used as water-soluble binders for injection moulding. For this reason, an agar solution (Steetley Chemicals, grade 940 Gel) was included in the study at 4, 6, and 8 wt% for comparison. A reactive, calcined alumina (RA107LS) from BA Chemicals Ltd, with mean particle size 0·5 μm, was used in the moulding formulations.

Solutions of the cellulose derivatives were prepared in covered 100-ml beakers using deionised water at 90°C such that 200 g of an 8 wt% (+/–0·2%) binder solution resulted. The powdered binder was slowly shaken into the hot water in small portions with continuous gentle agitation. The stirring continued whilst the mixture was allowed to cool. The mixture thickened as the cellulose dissolved and the solution was allowed to continue cooling without further agitation. Care was taken with the preparation since air entrapment could lead to a lower strength gel. In practice a slight excess of water was used to allow for losses due to evaporation. The agar solutions were made in much the same way as described above, but a gel formed on cooling. Any disruption of the gel led to low gel strength results. Less excess water was needed in the case of agar, mainly because the test temperature was lower (24°C), confining evaporation losses to the preparation stage. All of the gels were aged for approximately 18 h prior to testing.

Problems preparing 8 wt% agar solutions have been reported previously[6] and this gel proved difficult to measure here due to the surface roughness. In view of this, the agar was repeated at lower concentrations. Gel strength was measured by Meer's method.[7] Several modifications were necessary (Fig. 1). The apparatus incorporated a hot plate and water bath to facilitate heating. An Instron load frame (TT BM) fitted with a load cell (A30–40, 1–50 kg range) was used to plot load displacement curves for the penetration of the 6 mm diameter probe. The probe had a 0·1 mm radius to reduce surface stress concentration.

The covered, as prepared, cellulose solutions were reheated to the required test temperature in a water bath with pumped circulation. The test was carried out as the temperature at the centre of the gel reached the selected temperature of the water bath. Care was taken to ensure minimal disruption of the gel. In addition, a small glass water bath was heated with the gel to reduce heat loss during the test. The beaker was placed in the glass water bath and the assembly transferred to the hot plate. Gel temperature was measured with a thermocouple during the test. The probe was lowered nearly to the gel surface and then pushed into the gel at 5 mm min^{-1}. The gel surface deformed and then broke, with further penetration continuing to a depth of 10 mm. The load versus displacement curve was plotted (Fig. 2). The measurement was repeated at four points, each 8 mm from the side of the beaker. All of the tests on agar solutions were carried out in a controlled environment (24°C and 50% relative humidity). Gel strength, G (MPa) was calculated from the load, L (MN) and the cross-sectional area under load, A (m^2) using the equation

$$G = L/A.$$

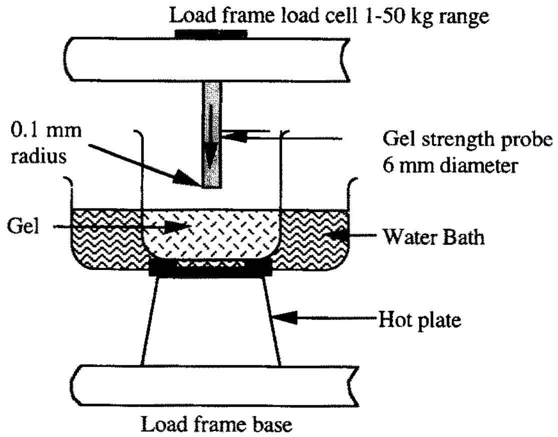

Fig. 1. Modified gel strength measurement equipment.

2.2 Gel point measurement

Gel point is usually determined on cooling from the temperature at which a gel has sufficiently low viscosity to run down an inverted tube.[7] Cellulose gels, however, exhibit considerable hysteresis, and the resultant gel point measurement is much lower than the value obtained on heating. The latter transition is of greater interest for injection moulding purposes. In view of this, the gel point of a given solution was obtained by recording the temperature at which viscosity rises rapidly on heating.[6] Viscosity measurements were carried out on 8 wt% solutions of HPM5000DS and HPM450P on the Carrimed 150 cone and plate measurement system using a 20 mm cone diameter and 2° cone angle.

2.3 Paste preparation

Premixing of the pastes was carried out in a Kenwood planetary mixer prior to 30 min cooled mixing in a Werner and Pfleiderer double-lobe mixer. As a final mixing stage, the paste was extruded through a 6 mm die prior to evaluation.[9] The compositions are given in Table 2. The system was investigated by capillary rheometry using the load frame and barrel depicted in Fig. 3. A series of dies with lengths of 12·5, 25 and 37·5 mm

Table 2. Paste compositions

	Paste 1		*Paste 2*	
	Weight %	*Volume %*	*Weight %*	*Volume %*
RA107LS	79·4	49·80	79·4	49·80
Deionised water	19	47·45	19	47·45
HPM5000DS	1·6	2·75	—	—
MPM450P	—	—	1·6	2·75

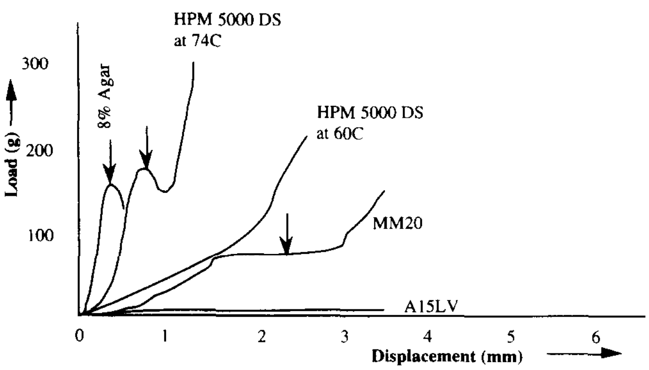

Fig. 2. Load versus displacement plots for various binder solutions.

and a diameter of 2 mm were fitted in place of the mould and gate system. Each paste was extruded at ram speeds of 1, 2, 5, 10, 20, 50 and 100 mm min^{-1}. Stress and shear rate at the wall were calculated in each case.[10] Injection moulding was carried out using the arrangement shown in Fig. 3 with an injection speed of 150 mm min^{-1}. This gave a volumetric flow rate of 1250 mm^3 s^{-1} into a cylindrical mould of 27·5 mm diameter by 18 mm length. The barrel and die temperatures were 50°C and 80°C respectively. Residence times in the mould of 2, 5 and 10 min were used for each paste.

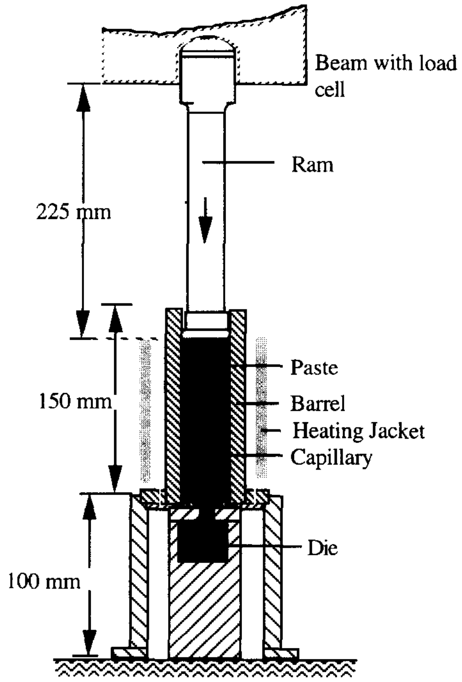

Fig. 3. Injection moulding equipment.

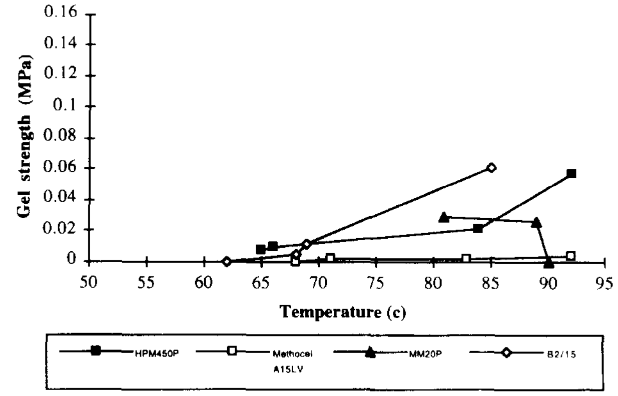

Fig. 4. Gel strength versus temperature curves for low-strength binders.

3 Results and Discussion

3.1 Gel strength

The various cellulose derivatives showed differences in appearance. HPM5000DS formed a rigid, colourless gel at 24°C. MEC solutions always separated into a clear, colourless liquid and a white, opaque liquid that were easy to remix on gentle agitation. Separation was observed to a lesser extent with MM20P, 20/231 and Methocel A15LV. The other cellulose derivatives gave colourless solutions.

The point of rupture was obtained from the load versus displacement plots for agar gels (Fig. 2). Most of the curves for cellulose derivatives gave a zero gradient at a point that coincided with the observed rupture of the gel. In this case the solutions exhibited residual strength not found in the agar gels. This gave rise to three types of rupture curve illustrated in Fig. 2. In gels such as HPM5000DS, rupture was followed by a load relaxation. On further penetration of the probe, the load increased above that of the initial fracture. It is not possible to comment on the implications of this increased load after failure for the injection moulding process. In MM20P at 80°C to 90°C, there was little relaxation after fracture. No relaxation after fracture was detected in HPM5000DS solution at 60°C. The weakest gels, for example Methocel A15LV, showed little resistance to penetration. The behaviour of Methocel F4M and K4M was similar to Methocel A15LV.

The methyl cellulose gels, A15LV and MM20P and methylethylcellulose (MEC) did not have sufficient strength to be considered for injection moulding (Fig. 4). The high-viscosity HPMC grades were expected to give the highest gel strengths. The trials give the expected results, except that the B2/15 showed lower gel strength than HPM5000DS and HPM100DS gave a higher strength than the HPM450P. Methocel K4M and F4M gave surprisingly low-strength materials. These two grades have methyl substituents to initiate the gel, but the high level of substitution may have had a deleterious effect on the gel strength. DP588 was an experimental grade that gave low strengths. Gels from grades HPM5000DS, HPM100DS and 20/231 gave more

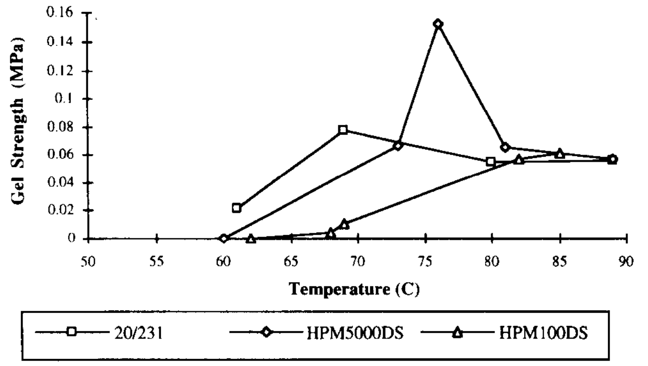

Fig. 5. Gel strength versus temperature curves for high-strength binders.

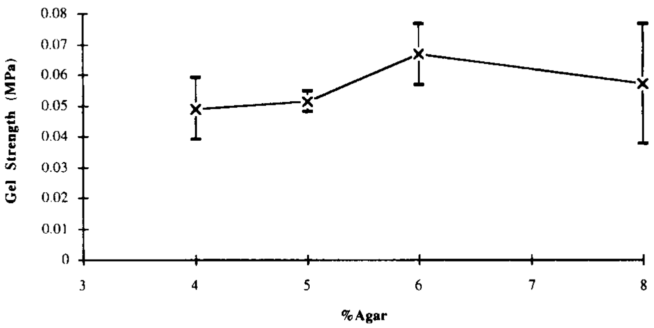

Fig. 6. Gel strength versus percentage weight of agar.

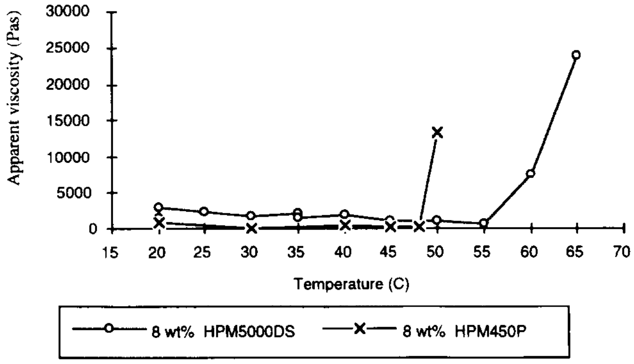

Fig. 7. Gel point determination from viscosity versus temperature at a shear rate of 0·03 s^{-1}.

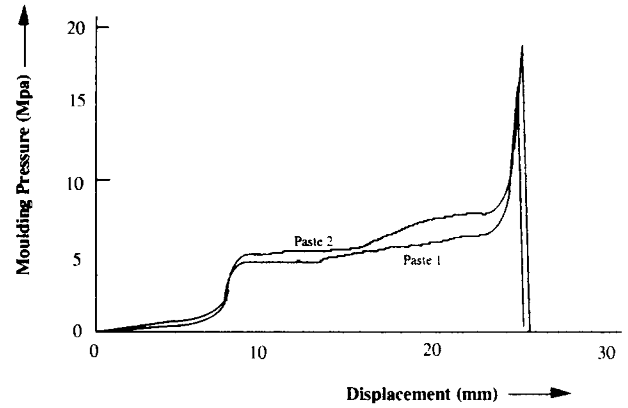

Fig. 8. Injection pressure versus displacement curves for pastes 1 and 2.

promising results as shown in Fig. 5. The low-strength gels obtained from B2/15 confirmed that molecular weight was not the only important factor in determining gel strength.

The trends for gel strength against temperature were similar for all of the cellulose solutions. For example, above the gel point, the gel strength of HPM5000DS rose to a maximum of 0·14 MPa, (+/– 0·04) before falling to 0·08 MPa(+/– 0·02) as the temperature rose to 90°C. The high molecular weight HPM5000DS gels consistently showed the highest strength across a range of temperatures. The 8 wt% agar gel gave an uneven surface. The error bars in Fig. 6 show the resulting wide variation of results which improved at lower concentrations due to the smoother surface.

3.2 Gel point

The viscosity–temperature relationship at a shear rate of 0·03 s^{-1} is shown in Fig. 7. Close to the gel point the material slips against the measuring surface giving unreliable results at high shear rates. The point at which the viscosity rises rapidly was taken as the gel point. The gel points for 8 wt% HPM5000DS and 8 wt% HPM 450P were 50 and 60°C, respectively.

3.3 Pastes

In view of the high gel strength over a range of temperatures, HPM5000DS was selected for paste formulation 1 (Table 2). HPM450P is used in extrusion of ceramics and was also selected for paste formulation to provide a comparison. The solids of both pastes were chosen such that they were suitable for injection moulding. A power law model was used to describe the rheology of each paste.[10] In each case the apparent viscosity was less than 1000 Pa s over the shear rate range of 100–1000 s^{-1}.

The moulding pressure versus piston displacement curves are plotted in Fig. 8. There was an initial pressure rise to overcome the yield value of the paste in the barrel and force the paste through the gate into the empty die. The pressure then rose gradually as the mould filled. The rapid increase in pressure occurred as the air was forced out of the mould.

Both pastes showed unacceptable levels of distortion after 2 min in the die (0·4 and 0·6 mm) and severe cracking resulted. Using paste 1, a rigid cylinder was formed by increasing the residence time in the mould to 5 min. The cylinder was removed without significant distortion (0·1 mm) or cracking. Under the same conditions, paste 2 showed considerable distortion (0·4 mm). After 10 min residence time, both compacts retained their shape. The improvement in mould removal of the compact from paste 1 is due to the higher strength conferred by the HPM5000DS.

4 Conclusions

Cylinders of 27·5 mm diameter and 18 mm in height were considered beyond the scope of ceramics injection moulding before the advent of water-based systems. The use of higher gel strength binders now gives the opportunity to reduce residence time in the mould and improve the feasibility of these systems.

Solutions of commercially available cellulose derivatives have been investigated. High gel strength was achieved by using HPM5000DS in solution without compromising the rheological requirements for injection moulding.[10] The work also confirms that hydroxypropyl substitution and molecular weight are important factors in increasing gel strength.

Acknowledgements

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