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The role of particle size and polymer molecular weight in the formation and properties of an organo-ceramic composite

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The role of particle size and polymer molecular weight in the formation and properties of a calcium aluminate cement–poly(vinyl alcohol) composite was investigated. Banbury mixing studies, in combination with poly(vinyl alcohol) solution rheology, showed paste formation to be dependent on the polymer degree of polymerization and concentration. Both polymer molecular weight and cement particle size have an effect on the mechano-chemistry, the "window of processibility", and mechanical properties of the hardened matrix. Increasing the polymer chain length appears to accelerate the mechanically induced crosslinking reactions between the polymer and cement hydration phases, thereby diminishing the processing window. Decreasing the cement mean particle size has a similar effect. Polymer degree of polymerization and cement particle size distribution are shown to be important factors in the mechanical properties of the hardened composite. Scanning electron microscopy (SEM) micrographs show that wide polydispersity in the grain phase is important in attaining a macro-defect-free microstructure.

1. Introduction

Calcium aluminate cement–poly(vinyl alcohol) composites (CAC–PVA) are high strength organo-ceramics whose microstructure consists of well dispersed cement grains imbedded in a continuous polymer matrix. The superior mechanical properties of this composite are due in part to a mechanically induced crosslinking reaction which takes place between the particulate and polymer phases during the mixing process [1]. Mixing transforms the initially damp powder to a dough-like, viscoelastic paste. The latter step enhances the processibility, resulting in the need for much less water in the mix (w/c = 0.1 versus 0.5 for normal cement paste), thereby reducing the major source of large pores or defects in the hardened state. The resulting, macro defect-free microstructure contributes to the exceptional properties of the composite.

Previous studies on CAC–PVA organo-ceramics [1–4] have shown that quantitative information on the mixing mechano-chemistry and resultant properties of the polymer–particle network can be generated using Banbury mixing. For a given set of mixing conditions, the resultant mixing torque curves exhibit a characteristic shape which can be classified into four distinct regions associated with

1. the transformation of the organo-ceramic formulation from a damp powder to flowable paste;
2. mechano-chemical degradation of the PVA molecules, and paste flow;
3. mechanically induced crosslinking reactions which produce the polymer–particle network (whose concentration is highest at the point of maximum crosslink density); and
4. degeneration of the paste, which ultimately reverts to a friable mass.

Hence, there exists a "window of processibility" within which paste properties and the resulting hardened composites are optimum.

This type of processing protocol, in conjunction with microscopy studies of the hardened composite, has been used as part of a comprehensive study in the authors' laboratories of the processing–structure–property dynamics of the reactive CAC–PVA organo-ceramic system. Previous reports have focused on the role of processing variables, such as mixing times and rates, in the evolution of the paste mechano-chemistry and morphology [1, 4]. The present paper focuses on the influence of the material variables. Of primary interest are the role of CAC particle size, PVA molecular weight, and the amount of water in the formulation. In this paper the authors wish to show how these material variables affect paste formation during mixing as well as the morphology and mechanical properties of the hardened composites.

2. Experimental procedure

2.1. Materials

CAC–PVA pastes were prepared using the material proportions reported in the patent literature [5]. The formulation (reduced proportionally to accommodate the capacity of the internal mixer) was composed of

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40 g calcium aluminate cement (Lafarge Secar 71, whose primary constituents are calcium aluminate and calcium dialuminate), 2.8 g of an 80% hydrolysed poly(vinyl alcohol–acetate) copolymer of various molecular weights [Nippon Gohsei: Gohsenol KH-17 s (degree of polymerization, DP = 2225); Kuraray: PVA 403S (DP = 330), 405S (DP = 580), 410S (DP = 945), 415S (DP = 1410), 420S (DP = 2050), 424HS (DP = 2600), and 435S (DP = 3350)], 4.6 ml deionized water and 0.3 g glycerine.

The effects of CAC particle size and water content were studied using mixes formulated with the Gohsenol KH-17 s PVA. Bulk CAC was air classified into three different particle size ranges: 0–6, 5–22 and 19–100 μm, and having mean particle sizes of 2.8, 9.2 and 36 μm, respectively. Elemental analysis of the three powders by X-ray florescence showed insignificant differences in composition.

2.2. Procedure

A Haake–Buchler Rheocord System 90 with a water cooled Banbury-type internal mixer attachment (Rheomix 600) is used to monitor paste development during shear mixing. The mixing head is coupled to a drive unit via a transducer which measures the torque needed to rotate a pair of Delta conical rotors in opposite directions at a given speed during mixing. The left blade rotates clockwise at a rate 1.5 times faster than the right. *In situ* sample temperature is also measured through a thermocouple imbedded in the midsection of the mixing bowl. A plexiglass window mounted in the face plate allows visualization of the mixing dynamics. All the mixing studies are conducted at an initial temperature of 27 °C.

Starting formulations were blended in a planetary mixer at low speeds for 90 s to produce a damp, homogeneous powder which was then fed to the Banbury mixer at a uniform rate using a 5 kg stationary weight. Paste samples were extracted from the mixer at various times and hardened for mechanical and morphological analysis following earlier procedures [1, 3]. Flexural strengths of the hardened composites were determined using the biaxial test method. Discs of 29 mm in diameter were cored from hardened composite sheets, and tested on a universal testing machine at a crosshead speed of 5 mm min^{-1}.

Linear viscoelastic characteristics of the PVA solutions were measured on a constant stress Bohlin CS rheometer. Cone-and-plate and couette geometries were used, the former for the more concentrated PVA solutions. The Cox–Merz [6] rule was used to determine the zero shear viscosity of concentrated solutions from dynamic measurements. Semi dilute solutions were measured with the couette geometry, while a double gap couette device was employed for dilute solutions (less than 10 centipoise pure, c.p.). Zero shear viscosities of the semi dilute and dilute solutions were measured from stress sweep experiments.

An Hitachi S-530 scanning electron microscope (SEM) was used for microstructural examination of the hardened composites. Approximately 0.5 mm was removed from the composite surface to eliminate surface effects in the SEM specimens. These samples were further polished to a 0.3 μm surface finish, using alumina polishing powder and isopropyl alcohol as lubricant, then sputter coated with gold.

3. Results and discussion

Fig. 1 shows mixing torque curves generated at 100 r.p.m. and 27 °C with composites formulated using three different PVA molecular weights. In all cases, the characteristic four region behaviour results [1–4]. As shown, the "window of processibility" diminishes with increasing molecular weight. Moreover, the mixing torque in the processing window increases with PVA molecular weight. Since the polymer viscosity increases with increasing molecular weight, the corresponding pastes are more viscous, resulting in elevated torque levels during processing. On the other hand, the torque at the point of maximum crosslink density is seen to remain constant, regardless of PVA molecular weight. Since the viscosity and stiffness of the composite paste are due to a mechanically induced crosslinking reaction, the constant torque value at the maximum suggests that the overall extent of the polymer–particle reaction remains unchanged.

Previous reports [1, 3, 4, 7] have shown that a quantitative measure of the overall reaction rate can be obtained from the length of the processing window. Since the latter is inversely proportional to the reaction rate constant associated with the mixing mechano-chemistry [3, 7], the temperature dependence is expected to follow an Arrhenius-type behaviour. Fig. 2 shows data taken at two different mixer r.p.m. for the various polymer molecular weights studied. In each case, the average temperature within the "window of processibility" was used. Each data set can be fitted with least squares lines, which (within the error of the experiment) have the same slope. This suggests that the activation energy, and hence the CAC–PVA reaction type, is independent of polymer molecular weight. In lieu of showing the entire set of parallel linear fits, a single representative line is shown. The slopes from the straight line fits yield an overall

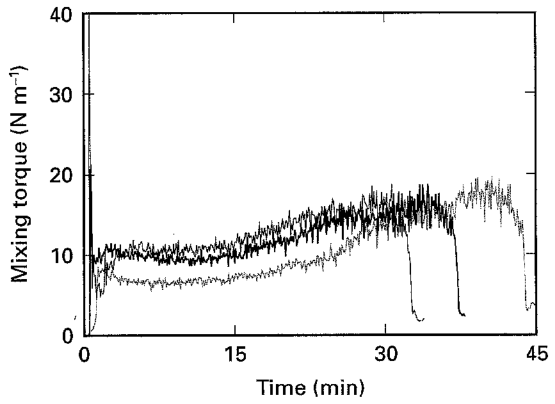

Figure 1 Mixing torque curves generated at 100 r.p.m. and 27 °C with composites formulated using three different PVA molecular weights. "Window of processibility" decreases with increasing PVA degree of polymerization. (···) DP = 1000, (—) DP = 2050, (—) DP = 3600.

activation energy of 54 kJ mol^{-1} for the CAC–PVA reactions. Consistent with previous studies [3, 7], the magnitude of this activation energy suggests that the mechano-chemistry involves a free radical crosslinking reaction.

Fig. 3 shows the length of the "window of processibility" as a function of PVA molecular weight for pastes mixed at 100 r.p.m. and an initial temperature of 27 °C. The monotonic decrease in the length of the processing window suggests that the overall reaction rate increases with PVA molecular weight. This is consistent with a previously proposed reaction mechanism [1], which postulates that mechanical work is needed to rupture the PVA chains, thereby yielding free radicals which initiate reactions with the hydrating CAC phase. Since higher molecular weight polymers are more susceptible to mechano-chemical degradation at a given mixing rate and temperature [8], increased chain scission and, therefore, PVA free radical concentration in the paste is expected. Consequently, the CAC–PVA reaction rate increases and the "window of processibility" is diminished. The increased rate of reaction with PVA molecular weight is also consistent with theory [9], and experimental results from shear induced reactions of polyethylene films [10].

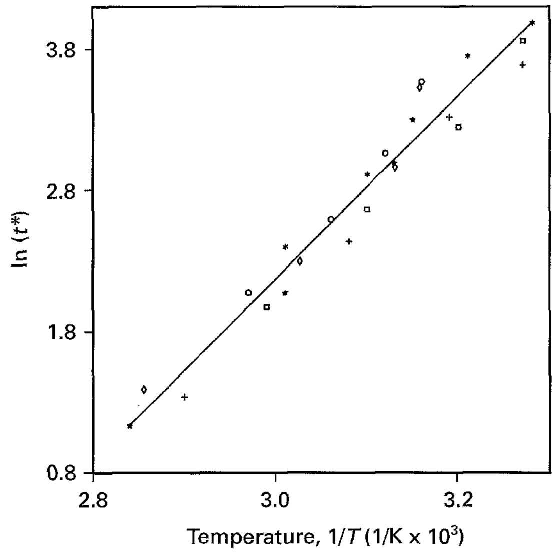

Figure 2 Logarithm of the length of the "window of processibility", t^*, versus the inverse of average temperature of composites formulated with three different DP and mixed at two rotor speeds. K410S: (*) 100 r.p.m., (○) 200 r.p.m. KH17s: (□) 100 r.p.m., (◇) 200 r.p.m. K435S: (+) 100 r.p.m., (★) 200 r.p.m. Solid line represents the collective least squares fit of the six data sets.

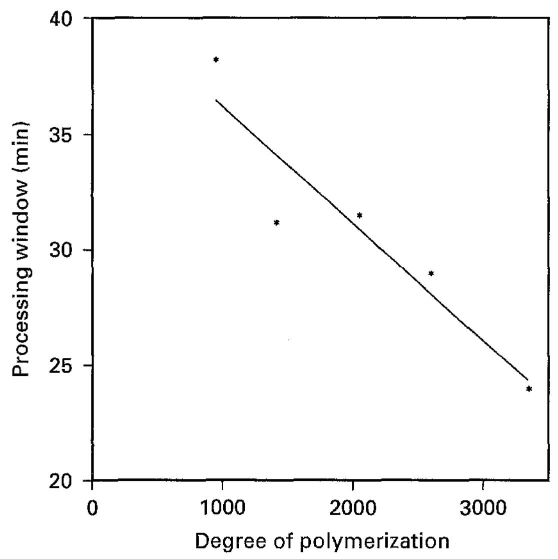

Figure 3 Length of the processing window as a function of PVA degree of polymerization. Solid line is least squares fit of data.

3.1. PVA solution rheology

For processing purposes, formulations with lower molecular weight polymer PVA would be more desirable due to the lower paste viscosity. However, reducing the degree of polymerization of the PVA from 945 to 580 failed to produce a paste when mixed with the standard batch size. When the size of the mix was increased from 40 to 55 g cement (other components of the formulation scaled proportionally), even the lowest molecular weight PVA (DP = 330) yielded a paste upon mixing. These observations suggest that more intimate mixing is required for short chain polymers to form a cohesive mass. Apparently, higher molecular weight PVA chains favour the formation of entanglements which are necessary for creating a cohesive matrix for the ceramic grains. However, for a given concentration, one would expect there to be a critical polymer molecular weight below which an entanglement network, and hence the organo-ceramic paste, cannot be formed. Similar behaviour would be expected with changes in the polymer solution concentration, where the conditions become less favourable for entanglements below a critical polymer concentration. In order to test this hypothesis Fig. 4 shows the concentration dependence of the measured

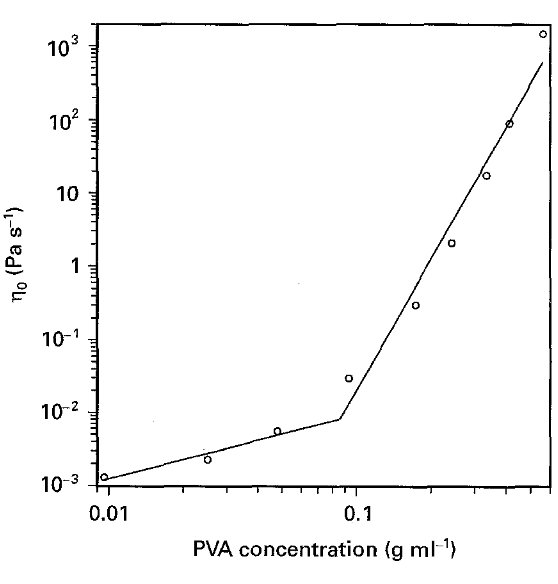

Figure 4 Zero shear viscosity of the K405S PVA (DP = 580) solution as a function of concentration. Solid lines represent linear fit of the data, and intersect at the critical concentration. Above the critical point, formation of a physically entangled polymer network is favoured.

zero shear viscosity for the 405S PVA (DP = 580) solution. The data clearly show the transition occurs at a critical concentration of about 0.08 g ml^{-1}, a characteristic of entanglement formation [11, 12]. Below this transition the viscosity is proportional to concentration; while, above the critical point, it varies with concentration to the third power.

Mixing with varying concentrations of the Kuraray 405S PVA showed that paste formation is dependent on the amount of polymer in the composite formulation. Formulations with PVA concentrations (in the organo-ceramic material) exceeding the critical point formed a cohesive, dough-like paste. Below the critical concentration, however, the damp powder remained crumbly when mixed. These results clearly demonstrate that paste formation is directly related to the formation of molecular entanglements during mixing. Although decreasing the water content in a "PVA poor" system can produce polymer concentrations above the critical conditions, there is a physical limitation below which surface wetting of most or all the cement grains becomes impossible. According to Tokita and Pliskin [13], wetting is essential for the formation of a single mass. Thus, the water content in the formulation also plays a critical role in paste formation. Once paste is formed, the amount of water in the initial formulation can greatly affect the mixing dynamics and chemistry, as shown in Fig. 5. The "window of processibility" is longer and the mixing torque is generally lower for pastes containing more water. However, mixing torque at the point of maximum crosslink density increases with water content in the composite formulation.

Since the viscosity of the composite paste decreases with increased water content, it is to be expected that lower stress levels are needed to cause the material to deform, i.e. flow, under an applied stress. In consequence, at a given mixing r.p.m., lower stresses exist in the system, hence fewer PVA free radicals are expected to form [8]. As a result, mixing torque levels are depressed and the "window of processibility" is lengthened. Water is also a reactant in this system. As such, its increase may lead to further development of the reactions between the polymer and the cement hydration products [1], thereby resulting in elevated torque levels at the point of maximum crosslink density, while simultaneously widening the processing window.

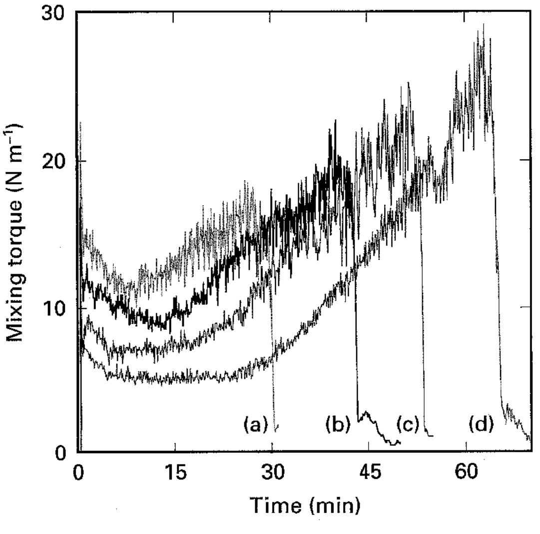

Figure 5 Mixing torque plot showing the effects of the amount of water in the composite formulation. Mixing conditions are the same as those shown in Fig. 1. Wt % modes to water: (a) 8.5, (b) 9.6, (c) 10.6, (d) 12.6.

3.2. Particle size effects

Fig. 6 illustrates the effect of CAC particle size on the mixing torque. Although the general shape of the torque curve remains unchanged, the "window of processibility" clearly decreases and the mixing torque increases with decreasing mean particle size. The elevated torque levels are believed to be due to increased paste viscosity [14], consistent with the behaviour seen in highly filled polymer systems at constant fill fraction [15]. Moreover, increased surface area associated with the smaller CAC particles results in higher reaction rates, and thus, a smaller processing window. Torque values at the point of maximum crosslink density increase with decreasing mean particle size. Changes in the number of particle contacts (per unit volume) and interstitial pore sizes, both of which are associated with grain dimensions [16], are possible explanations for the difference in the mixing torque levels. Composites mixed with the bulk CAC required the highest torque to mix at the point of maximum crosslink density. Apparently, since bulk CAC powder has the widest particle size distribution, packing is more efficient (no interstitial voids) [16], and a stiffer paste therefore results.

3.3. Morphology

The effects of particle size on packing in the hardened composite are evident in the SEM micrographs of Fig. 7. In this case, the hardened composites were processed at 100 r.p.m. for 10 min using CAC powders of different mean particle sizes. These micrographs reveal defects whose magnitude corresponds to the different grain dimensions, and are consistent with the

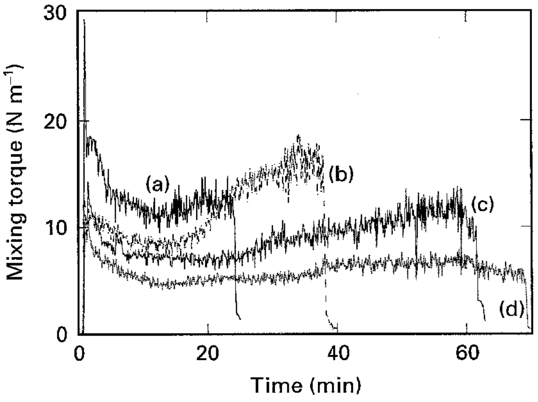

Figure 6 Mixing torque plot showing the effects of CAC particle size: (a) 2.8 μm, (b) bulk, (c) 9.2 μm, (d) 36 μm. Mixing conditions are the same as those shown in Fig. 1.

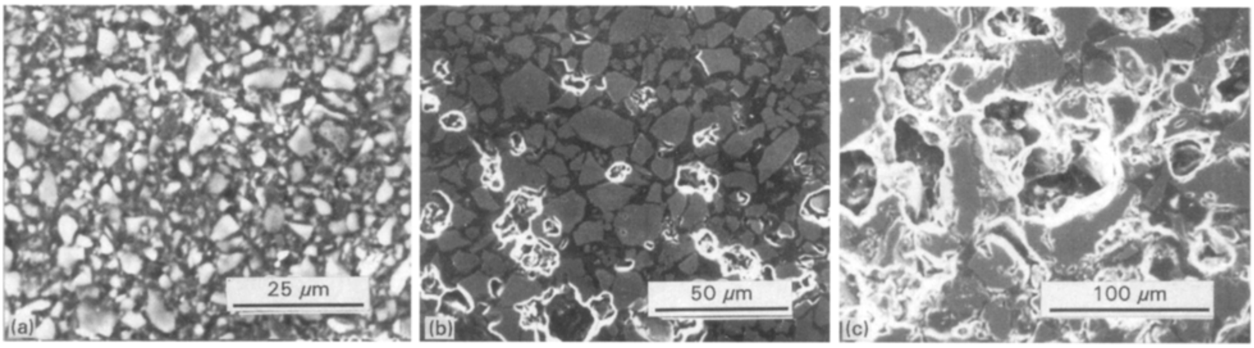

Figure 7 SEM micrographs showing the effect of mean CAC particle size (a) 2.8 μm, (b) 9.2 μm, and (c) 36 μm. Defect dimensions are on the order of the grains that make up the composite. Composites were formed from pastes mixed for 10 min at 100 r.p.m. and an initial temperature of 27 °C.

packing behaviour of monodispersed, spherical particulate systems where the interstitial pore size increases with the dimensions of the particles [16]. The large interstitial pores apparently lead to sizable imperfections in the microstructure. Fig. 8 shows an SEM micrograph of a composite formulated with bulk CAC powders and mixed at identical conditions to those shown in Fig. 7. The composite exhibits the "classic" macro defect-free microstructure, where the CAC grains are well dispersed in a continuous matrix devoid of large pores [3, 4]. These micrographs indicate that a broad particle size distribution may be important for the development of a macro defect-free composite. By contrast, PVA molecular weight shows little effect on the SEM-level microstructure of the hardened composites. Specimens processed with PVA of DP from 945 to 3350 were found to exhibit near identical, macro defect-free microstructures (much like Fig. 8).

3.4. Mechanical properties

Table I shows flexural strengths of hardened composites formed from pastes which were processed for 15 min at 100 r.p.m. and an initial temperature of 27 °C. The flexural strength shows a monotonic increase with PVA molecular weight. Although the (SEM-level) macro morphology of the hardened composites did not change with PVA molecular weight, the sub micrometre microstructure and associated microchemistry is expected to be different for composites formulated with the different PVA molecular weights. Previous studies [1, 4] showed that polymer–particle reactions lead to the formation of an interphase zone between the CAC and bulk PVA in the composite microstructure. The development of the interphase, which is seen to correspond with an increase in porosity and thickness of that layer, improves the mechanical properties of the hardened composites [1, 4]. Appropriately, composites formed with higher molecular weight PVAs, which are expected to show increased development of the interphase region (since higher reaction rates result as PVA molecular weight increases), show an increase in flexural strength.

Mechanical properties of hardened composites formulated with CAC powders of different mean particle sizes, and processed for 10 min at 100 r.p.m. and an initial temperature of 27 °C are shown in Table II. Flexural strengths of composites made up of the two smaller mean particle sizes (2.8 and 9.2 μm) are

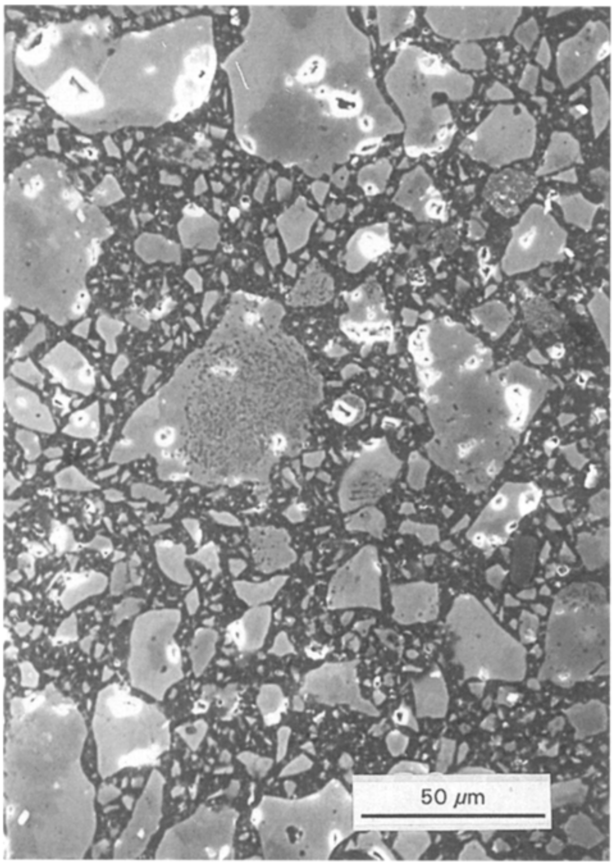

Figure 8 SEM micrograph of hardenend composite formulated with bulk CAC powders. The composite is macro defect-free. Processing conditions were identical to those in Fig. 7.

TABLE I Flexural strengths of hardened composites formulated with PVA of varying degree of polymerization. Composites were mixed for 15 min under conditions mentioned in Fig. 1

Mixing speed (r.p.m.)	Degree of polymerization	Flexural strength (MPa)
100	945	154
100	1410	177
100	2050	173
100	2600	181
100	3350	223

TABLE II Flexural strengths of hardened composites formulated with mean particle sizes of 2.8, 9.2 and 36 μm. Composites were mixed for 10 min under conditions mentioned in Fig. 1

Mixing speed (r.p.m.)	Mean particle size (μm)	Flexural strength (MPa)
100	2.8	137
100	9.2	150
100	36.0	51
100	Bulk: 7.7	224

similar, and about three times larger than that of the composite formulated with 36 μm mean particle size CAC powders. However, all three composites are inferior compared to the standard/normal organo-ceramic material which was processed with bulk CAC powders. Particle packing, as is evident from Figs 7 and 8, plays a critical role in the final mechanical properties of the PVA–CAC composites.

4. Conclusions

Results from mixing studies in combination with PVA solution rheology suggest that paste formation in CAC–PVA composites is only possible when the polymer binder phase is composed of a critical concentration and/or molecular weight PVA, beyond which a network of entangled polymer chains forms. Pastes formed from the different PVAs show a constant activation energy during the reaction phase of mixing which indicates that the polymer–particle reaction type is independent of polymer chain length. However, the reaction rate apparently increases with the polymer DP as evidenced by the reduced "window of processibility". The increased PVA DP in the composite also increases the flexural strengths of the hardened material. Particle size and polydispersity of CAC showed similar effects as those exhibited when varying PVA molecular weight. However, these studies suggest that composites formulated with bulk CAC are favoured for their processing and mechanical properties.

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