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Porosimetry studies on polyacrylic acid–ZnO cements

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The porosity of ZnO–polyacrylic acid (PAA) composites was studied by mercury intrusion porosimetry and scanning electron microscope. There seems to be a dependence of the porosity on the ZnO/PAA ratio and a particular value for which the pore volume is a minimum. These results are analysed and explained in terms of the reaction kinetics.

1. Introduction

Research and development in materials for dentistry and some other similar applications represent a steadily growing field, not only because of their obvious practical importance, but also because there are still a number of scientific challenges related to this area that remain to be solved. Indeed, in order to become suitable for dental applications and the like, a specific material has to fulfil a number of requirements from both the materials science and the biocompatibility points of view. In this regard a number of publications, reporting mainly mechanical characterizations and *in situ* behaviour, can be found in the specialized literature [1–4]. In fact, these kinds of composite materials have a number of rather interesting properties such as their mechanical strength, their low-temperature processing requirements, etc., that represent an enormous source for many different practical applications.

Roughly speaking, these waterless cements are fabricated by the chemical mixing of a metal oxide and a polyelectrolite polymer. In particular, we have studied the system ZnO–polyacrylic acid (ZnO–PAA). A recent report by some of the present authors [5] has demonstrated that there are two key experimental parameters for controlling the final mechanical strength of such composites, namely the ZnO/PAA ratio and the curing or hardening time. Moreover, an empirical equation relating the above parameters has already been established.

Nevertheless, one very important variable that has not been studied sufficiently deeply in these cements is the porosity and its possible relationship to the final mechanical properties. In the present work porosimetry measurements of samples of dental-like cements with different ZnO/PAA ratios are reported and a discussion of this parameter to the chemistry of the materials is presented. The porosity measurements were basically performed by using mercury intrusion porosimetry (MIP) techniques and were supported by scanning electron microscopy (SEM) and optical microscopy (OM) observations.

2. Experimental procedure

Reagent-grade ZnO powder was used along with commercial PAA to prepare the cements. The PAA content of solids was determined to be approximately 30% and the corresponding average molecular weight was found to be approximately 121 000. As was explained in [6], the ZnO/PAA ratio that produces good samples (in terms of consistency and mechanical properties) is rather restricted. Moreover, a value of ZnO/PAA = 0.6 (expressed in g ZnO per ml PAA) was determined to be the best. Therefore, since we were interested mainly in samples that presented good mechanical behaviour, we analysed only samples with compositions ZnO/PAA = 0.5, 0.6 and 0.7.

The samples were prepared according to ASTM standard number D621-64 in order to check the mechanical properties of the specimens. The PIM measurements were performed in a Quantachrome Autoscan-60 machine, according to ASTM standard number D-4284. Samples were prepared for SEM observations by slicing the cylinders and coating the pieces with a thin aluminium layer. The SEM observations were carried out in a Jeol 35-CF microscope.

3. Results and discussion

Fig. 1 shows a typical plot of the MIP experiments performed in samples with ZnO/PAA ratios of 0.5, 0.6 and 0.7 (expressing, as before, the ZnO content by weight in g and the PAA content by volume in ml). The curve of Fig. 1 corresponds to ZnO/PAA = 0.6, which turns out to be the sample with the smallest pore volume, as can be observed from Table I, despite the fact that the overall shape of the porosimetry curves was very similar in all of the cases analysed.

According to the well-known Griffith criterion, the

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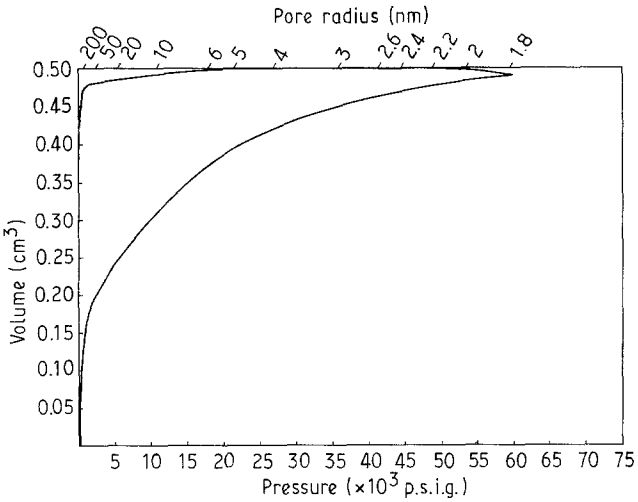

Figure 1 Typical mercury intrusion porosimetry curve of the cements studied. In this case ZnO/PAA = 0.6. (1 p.s.i. ≈ 6.9 kPa.)

fracture toughness σ_f is given by

$$\sigma_f = (E\gamma_f/4C)^{1/2}$$

where E is the elastic modulus of the material, γ_f is the surface free energy and C is the diameter of the largest pore present in the sample. In the case of the ZnO–PAA cements, the observed decrease in porosity as the ZnO/PAA ratio increases can be explained as follows: since the reaction between the ZnO and the PAA is schematically expressed as

$$ZnO + 2\{CH_2\text{–}CHCOOH\} \rightarrow \{CH_2{=}CHCOOH\}_2Zn\text{–} + H_2O$$

we can observe that crosslinking is taking place by the zinc being added to the polymeric chain as a sort of "bridge" because of its double valence. On the other hand, some of the ZnO particles that have not reacted for one reason or another would produce some porosity by simple geometrical packing actions. Therefore, the porosity must be related to the relative proportions of unreacted ZnO and PAA. Furthermore, according to the porosity measurements, a value of the ZnO/PAA ratio (ZnO/PAA = 0.6) seems to exist for which the porosity is a minimum compared with concentrations above and below that particular value. It is interesting to note that that value has also been found to correspond to the samples with the best mechanical properties [6]. In a first attempt to explain this behaviour, it could be thought that we are dealing simply with a supersaturation phenomenon. Some more careful analysis, currently under way, of the reaction that is taking place reveals, however, that under some specific physicochemical conditions (pH, concentration, temperature, etc.) the reaction can be reversible and some of the water would act as a solvent for both the reacted and the unreacted substances.

TABLE I Summary of porosimetry measurements

ZnO/PAA content ($g\,ml^{-1}$)	Pore volume ($cm^3\,g^{-1}$)
0.5	0.2264
0.6	0.1584
0.7	0.1828

On the other hand, microscopic observations have shown that near the centre of the samples unreacted polymer and oxide (see Fig. 2) are more likely to be found. This can be explained easily by the fact that, since the reaction is exothermic, the outer regions of the specimen would react more rapidly since they are allowed to have thermal exchange with the environment, whereas the inner regions, being thermally isolated, would have much slower reaction kinetics. This finding is important not only because it implies that geometry-dependent kinetics has to be taken into account for further studies, but also because it opens up the possibility of using some kinetics modifiers to control some of the hardening processes that take place in these materials.

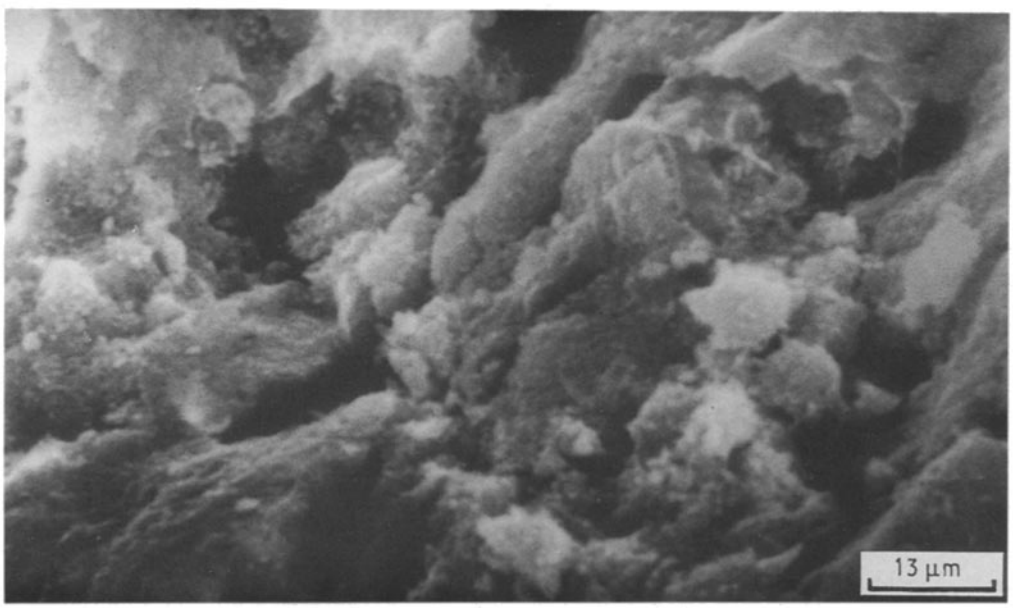

Figure 2 Scanning electron micrograph of a sample with ZnO/PAA ratio of 0.5. Notice the higher concentration of unreacted material near the centre of the sample.

4. Concluding remarks

From the results presented here it is possible to observe a clear dependence of the final porosity (as measured by MIP) on the chemical composition of the composite, observed after an almost complete curing, and the existence of a "best" ZnO/PAA value in terms of porosity that also coincides with the "best" value in terms of mechanical strength. Besides the obvious relevance of this for the mechanical behaviour of the composites, it also becomes important for many other properties such as humidity absorption and gas percolation through the sample. Also, since the hardening reaction in these cements basically consists of a crosslinking process of the polymer–metal composite, as we have explained, the formation of microstructure becomes a very important parameter to be taken into account if a better understanding of the kinetics of the phenomenon is to be achieved. In addition, the influence of some other physicochemical variables, such as the pH of the mixture, remains to be analysed. Some studies are currently under way and will be reported elsewhere.

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