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Porosity in water-based dental luting cements

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The porosity in glass ionomer, zinc polycarboxylate and zinc phosphate dental cements has been studied using an optical microscopic technique. Pores of approximately 20 μm diameter were observed in all three materials. In addition, finer pores were seen in zinc oxide-containing cements. It has been postulated that the larger pores are due to entrapment of air during mixing and the finer porosity results from loss of excess water. The deleterious effects of such porosity are discussed.

1. Introduction

The inclusion of voids in water-based dental cements is a likely consequence of the manufacturing methods and clinical procedures employed with these materials. Diverse origins of porosity in the final set structure may be envisaged. For example, air, present in the individual components (dissolved in the liquid part or held in the powder) may be retained in the set material. Air may also become entrapped during mixing because of the highly viscous nature of the cement mix and further porosity may develop after completion of the setting reaction when excess liquid diffuses out from the hardened mass.

The presence of voids in luting cements may affect the cements in a number of adverse ways, particularly where the lute is exposed to the oral cavity at the margins of cemented restorations. With the possible exception of resin-based composite cements, dental cements must be viewed as brittle materials with low fracture toughness. In such brittle materials, the presence of pores will increase the likelihood of mechanical failure [1]. Cracking of the cement will exacerbate erosion, and increase the surface area where pores are exposed to oral fluid increasing dissolution rates. Pores with dimensions greater than the wavelength of light will also be responsible for reduced translucency and exposed pores may further impair aesthetics by becoming stained. In the case of adhesive cements, porosity occurring at the interfaces between tooth and cement or cement and restoration will reduce the contact area, lowering the overall bond strength.

If porosity in dental cements is to be minimized, a better understanding of the nature and origin of such voids is necessary. In particular, information is required about the number, size and morphology of such pores, which will determine the extent of their likely adverse effects. Furthermore, a knowledge of the origins of such porosity might be facilitated by characterizing the pattern of voids.

To date little quantitative information has been reported in the literature concerning characterization of pores in aqueous dental cements. A scanning electron microscopic examination of a silver-reinforced glass ionomer restorative cement indicated the presence of pores in this material, together with extensive cracking between the pores, although the latter may have been due to dehydration during sample observation in the SEM [2]. Pore-size distribution in a zinc carboxylate cement has also been investigated by mercury porosimetry [3], which indicated the presence of submicrometre voids (< 200 nm) only.

The aim of the present investigation was to develop a simple method of visualizing and quantifying porosity in water-based luting cements prepared under clinically relevant conditions, with minimal introduction of microstructural artefacts.

2. Methods and materials

Samples of three water-based luting cements listed in Table I, were prepared for microscopic examination as follows: approximately 0.4 g cement was mixed to luting consistency following the manufacturer's recommended procedures. Mixing was carried out on a cold glass slab to prevent premature setting. Sufficient of each mix to give a total area of approximately 200 mm was transferred to a glass slide measuring 14 mm × 14 mm and a second glass slide was positioned to cover the cement. The sandwich was then compressed in between the platens of a micrometer screw gauge, which was tightened to produce film thicknesses of 50 and 100 μm. The samples were allowed to set for the time recommended by the manufacturer then removed from the micrometer and placed in an 37 °C oven for a further period of approximately 30 min.

Each cement film, still sandwiched between the glass slides, was viewed by transmitted light with a Zeiss Axioskop optical microscope (Carl Zeiss, Oberkochen, Germany) at × 100 magnification. Photomicrographs were produced for each material and these were examined using a Kompira image analyser (Kompira, Salsburgh, Scotland) to obtain the area fraction of pores in each microstructure. For every material, three areas, each 0.16 mm, were randomly selected for analysis.

TABLE I List of materials studied

Material	Type	Manufacturer
AquaCem, batch no. 910115	Glass ionomer	De Trey Dentsply, Weybridge, UK
Poly-F Plus, batch no. 910226	Polycarboxylate	De Trey Dentsply, Weybridge, UK
De Trey Zinc, batch no. 880606	Zinc phosphate	De Trey Dentsply, Weybridge, UK

TABLE II Area fraction porosity measurements

Material	Porosity (%)		Mean pore size ± S.D. (μm)		Pore size range (μm)	
	50 μm film	100 μm film	50 μm film	100 μm film	50 μm film	100 μm film
AquaCem	6.4	5.5	15 ± 6	21 ± 7	6–63	9–46
Poly-F Plus	1.4[a]	1.0[a]	21 ± 5[a]	16 ± 4[a]	8–31[a]	9–26[a]
De Trey Zinc	3.1[a]	1.5[a]	14 ± 7[a]	12 ± 4[a]	5–46[a]	7–28[a]

[a] Figures do not include microporosity below 5 μm.

Figure 1 Unreacted glass ionomer powder.

A sample of as-received glass ionomer powder was examined microscopically in transmission. The powder was suspended in microscope lens immersion oil under a glass cover slip to improve image quality.

3. Results

Fig. 1 illustrates the unreacted powder used to form the polyalkenoate cement. Surface dimpling of the polymeric component is apparent. All particles are less than 25 μm across. Fig 2–4 show cement films of glass ionomer, zinc polycarboxylate and zinc phosphate viewed through the glass cover slip. The thickness of these films was 100, 50 and 100 μm, respectively. The results of area fraction porosity determinations and mean pore sizes are given in Table II.

4. Discussion

The aim of the present study was to develop a technique for the imaging of porosity in luting cement films, produced under conditions similar to those experienced clinically. It was considered important to minimize introduction of artefacts during sample preparation, e.g. pull-out of particles by polishing techniques. Compressing the cement film between two glass slides eliminates the need for such procedures, but may affect the flow behaviour of the cement due to the unrealistically smooth adherend surfaces and different surface chemistry compared with prepared teeth. It was considered that elongation of pores during compression could occur in both test samples and in the clinical situation.

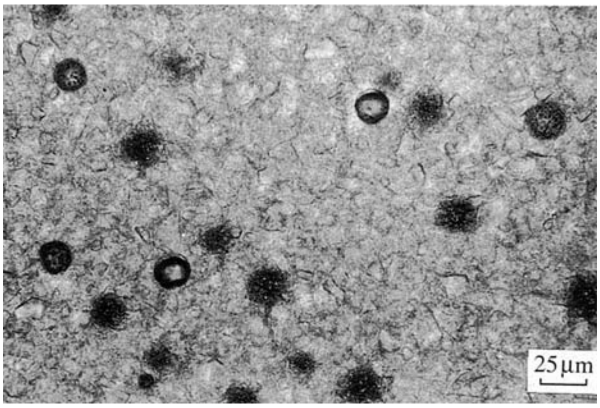

Figure 2 100 μm thick film of glass ionomer cement.

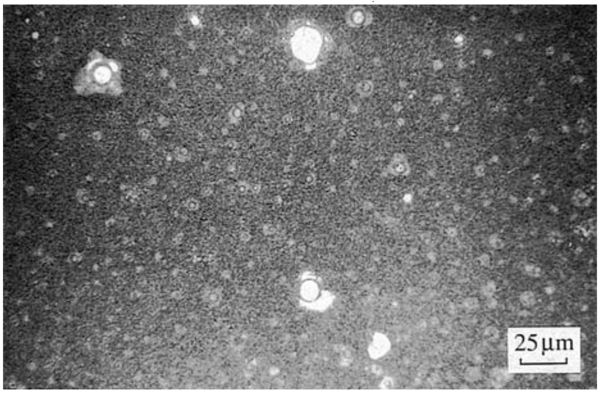

Figure 3 50 μm thick film of polycarboxylate cement.

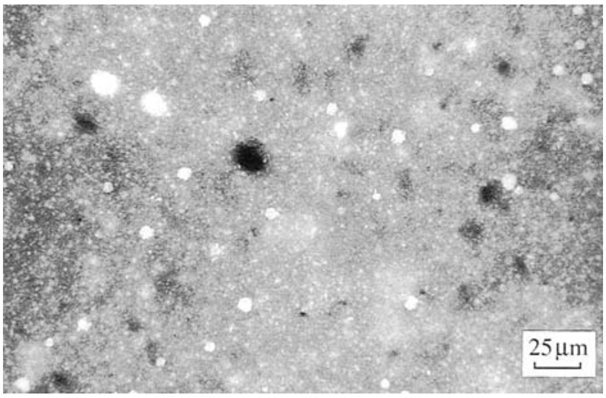

Figure 4 100 μm thick film of zinc phosphate cement.

Inspection of the unreacted glass ionomer powder revealed polymer particles with a heavily dimpled appearance (Fig. 1). It is possible that this porosity extends below the surface and is part of a sponge-like structure in the poly (acrylic acid) particles. Such porosity would introduce air into the cement mix.

Examination of Figs 2–4 reveals porosity in all samples of set cement. In addition to roughly spherical porosity in the glass ionomer film (Fig. 2), unreacted cores of glass are resolved. Some pores are hemispherical due to contact with the glass plate. Others are present within the body of the cement film and both types of pore were included in the area fraction determination. These pores ranged from 9–46 μm in the 100 μm film, with a mean size of 21 μm. A similar distribution was also observed in the 50 μm film. Applying the criterion of Birchall [4] for hydraulic cements, such pores must be considered as micro- rather than macropores (> 200 μm) and as such will have limited impact on compressive strength. Submicrometre porosity was not detected in glass ionomer cement by this technique. The area fraction of pores in the 100 μm glass ionomer film was slightly less than in the thinner film, possibly due to greater compression in the latter, where pores were of a size similar to the thickness of the film. There was no evidence of cracking in the cement film.

Within the polycarboxylate cement films, a bimodal distribution of pores was observed as shown in Fig. 3. A large number of very fine pores, approximately 1 μm diameter, are visible in addition to larger pores. The technique used in this study did not permit quantification of pores of this size. Porosity measurements include only the larger pores (> 5 μm), which must therefore be an underestimate of total porosity. Exclusion of the finely dispersed porosity might explain the relatively low measured value compared with the glass ionomer cement film. The question of why such fine porosity was observed in the polycarboxylate cement but not in the glass ionomer is difficult to explain, although the existence of fine porosity had been reported previously [3]. The amount of water added to the mix is similar in each case as are the mixing procedures. However, the nature of the acid–base setting reactions may account for the different pore structures observed. The added water which is principally present as a solvent, together with the water generated by the reaction, may be free to collect into ultrafine globules during and after setting and ultimately diffuse through the set cement leaving behind pores. However, in the glass ionomer cement, most water is bound into the gel matrix and is not free to form pools. Alternatively, ultrafine porosity may exist undetected in the latter although a scanning electron microscopy examination of a similar material did not resolve such pores [2]. Determination of ultrafine pores may require a vapour intrusion porosimetry technique. Whilst such fine porosity is unlikely to affect the mechanical properties of the cement, solubility may be affected adversely.

In the case of the zinc phosphate cement, a similar situation to that observed in the zinc polycarboxylate cement existed. A bimodal distribution of pore sizes was observed, and again only larger pores > 5 μm were included in the image analysis. The origin of the fine pores is likely to differ from the larger pores and may be related to the ability of excess water molecules to collect into microglobules. The mean size of the larger pores was similar to the other cements examined, the lower value of porosity measured being due to omission of the fine micropores.

In conclusion, all examples of water-based dental luting cements examined contained residual porosity. Pores of approximately 20 μm were observed in all materials and may have a similar origin, the most likely being incorporation of air during mixing. Additional fine porosity was observed in both polycarboxylate and zinc phosphate films. In this case, the pores probably originated from excess solvent water. Such excess was probably bound in the hydrogel matrix of the glass ionomer. Because the pore size did not exceed 100 μm in any area of film selected for analysis, the likely effect on mechanical strength is limited. However, the fine porosity observed in the polycarboxylate and zinc phosphate cements may have a deleterious effect on the resistance to erosion and staining potential. Opacity will also be increased.

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