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Poisson's ratio of glass-polyalkenoate ("glass-ionomer") cements determined by an ultrasonic pulse method

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Poisson's ratio has been determined for four glass-polyalkenoate cements; one experimental luting type, one experimental restorative type, one commercial restorative type (Chelon-Fil, ex. ESPE GmbH) and one cermet-reinforced cement [Chelon–Silver, also ex. ESPE]. An ultrasonic pulse method was employed for the Poisson's ratio determinations. For the restorative materials, including the cermet-reinforced cement, the values obtained were all in the region of 0.3. For the luting cement, on the other hand, the values found were in the range of 0.35. This difference was consistent with the relatively increased water content and reduced glass content of the luting cement. The cements based on poly(acrylic acid) showed slight, but statistically significant, increases in Poisson's ratio up to 80 days, whereas the cements based on poly(maleic acid) showed no significant changes in Poisson's ratio with time.

1. Introduction

Glass-polyalkenoate cements are widely used dental restorative materials [1]. In addition, they are increasingly finding use in other surgical applications, such as maxillofacial and ear, nose and throat surgery [2].

Glass-polyalkenoates are generally evaluated in terms of the compressive and/or flexural strength [3] or, more rarely, their fracture toughness [4]. To date, however, there has been no published experimental work on the determination of their Poisson's ratio, nor of the factors which affect this property.

Poisson's ratio (σ) of a material, a dimensionless term, is defined as the ratio of the lateral strain to the longitudinal extension measured in a uniaxial tensile test. [5]. For very small elongations it may alternatively be defined as the decrease in width of the specimen per unit width divided by the increase in length per unit length on the application of a tensile load [6]. Poisson's ratio for glass-ionomer cements has been shown in modelling studies to be a factor affecting the integrity of glass-ionomer cemented crowns [7] and orthodontic brackets [8]. This material property is also employed in calculating the *in vitro* biaxial flexural strength from the loads at failure for dental materials in the "shell test" [9]. Recent interest in evaluating glass-polyalkenoates by this test has made necessary the provision of data on Poisson's ratio for these materials. The current work has been undertaken both to do this, and to study the effect of factors such as age, composition and the presence of fillers on the values obtained.

Poisson's ratio for an experimental type I (luting) cement, an experimental and a commercial type II (restorative) cement and a silver-cermet-reinforced cement have been determined using an ultrasonic pulse method. In addition, Poisson's ratio for the glass component of such a cement has been evaluated. Although two of the materials were experimental, they were made from the glass G338 and 40% aqueous poly(acrylic acid). The glass G338 is widely used in commercial cements, although such cements use polyacids whose molar mass, polydispersity and concentration may differ from the particular polymer used in our experiments. Thus our experimental cements were representative of commercial glass-polyalkenoates.

The determination of Poisson's ratio using any experimental arrangement requires the measurement of displacement caused by the application of a stress. There are a number of static methods for determining this term. These include: first-principles calculations [10]; determination of the rigidity (K), shear (G) and Young's (E) moduli, using rectangular prisms [11], controlled stress rheometry [8] and three-point bend testing [9], respectively, from the expressions:

$$G = \frac{E}{2(1+\sigma)} \quad \text{or} \quad K = \frac{E}{3(1-2\sigma)}$$

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The ultrasonic pulse determination of Poisson's ratio is based on the fact that an ultrasonic pulse passed through a material in the longitudinal and transverse directions will undergo different propagation paths [14]. In practical terms, this will affect the time taken for the pulse to travel through the specimen in each mode. The method has been extended from its initial remit of metals and monocrystals to polycrystalline materials. The limiting factor in this latter case is that the size of the component crystalline materials must not be so large as to scatter the ultrasonic pulse, otherwise the successive echoes of the pulse would be impaired.

2. Materials and methods

In the apparatus used for the current experiments, the respective times taken by the pulses to travel through the test material in the two modes of vibration were measured. This was done by attaching two quartz crystals on opposite faces of the specimens. The quartz crystals used were either X-cut or AT-cut for longitudinal or transverse waves, respectively. Short pulses (0.75 μs) with a carrier frequency of 2–20 MHz were transmitted from one face of the specimen to the other at a frequency of 1000 Hz. The phase of the radio-frequency pulse was synchronous with the frequency in order that a steady pattern of the radio-frequency pulse could be seen on the oscilloscope tube. The received pulses were amplified by a wide-band amplifier having a bandwidth of 22 MHz and a gain of 80 dB, and displayed on a cathode-ray tube. The time base, which was synchronized with the transmitter frequency, was delayed by a crystal-controlled circuit. The arrival time of any pulse was measured by setting the delay circuits to bring the image of the pulse to coincide with the cross-wires of the microscope. The travel times of the pulses in the specimens were deduced from the relative arrival times of the first received pulse and the successive echoes which were received in multiples of twice the travel time. Under good conditions, i.e. when the specimens had flat and parallel sides, the travel time could be deduced with a standard deviation of about 1 part in 10000.

Poisson's ratio, σ, was determined by the expression:

$$\sigma = \frac{R^2 - 2}{2(R^2 - 1)}$$

where $R = V_L/V_t$, and V_L and V_t are the longitudinal and transverse velocities of the ultrasonic pulse, respectively. V_L and V_t are obtained by subtracting the delay time (T_0) built into the measurement, i.e. the reading with the probes touching each other, with no specimen present) from the time obtained with the specimens in place (T_x). T_x was then divided by the thickness of the specimen to obtain the relevant velocity terms.

The ultrasonic pulse employed in this study had a frequency of 2.5 MHz.

The glass-polyalkenoate cements studied were as follows: (i) an experimental type I (luting) cement; (ii) an experimental type II (filling) cement; (iii) a commercial filling cement [Chelon-Fil, ex. ESPE GmbH, Seefeld, Germany] and the equivalent silver-reinforced cement [Chelon-Silver]. The commercial products were mixed in accordance with the manufacturers' instructions. The experimental cements were prepared as follows: for the luting cement, 1.00 g of sub-45 μm glass G338 was mixed with 0.38 g of a 40% (by mass) aqueous solution of poly(acrylic acid) [Versicol E9, ex. Allied Colloids, Low Moor, Bradford, UK]. The restorative cement was prepared by mixing the same cement components, but at a powder:liquid ratio of 1.00:0.19. The glass G338 was prepared by us to a composition previously published [15] (see Table I). This glass is used in a number of commercial cements, as is poly(acrylic acid), though the concentration and molecular weight may differ slightly from the polymer used in these experiments.

TABLE I The composition of glass g338

Glass component	Composition by weight (%)
SiO_2	24.93
Al_2O_3	14.25
CaF_2	12.82
Na_3AlF_6	19.23
$AlPO_4$	24.22
AlF_3	4.56

Once mixed, cement pastes were packed into pre-waxed, open stainless steel cylindrical moulds of dimension 25 mm diameter by 3 mm height. The moulds were covered on both sides by circular, waxed stainless steel plates, clamped and placed in an oven pre-set at 37 ± 2 °C for 1 h to allow the cements to set. Set cements were removed from the moulds and placed in labelled containers of distilled water for storage at the same temperature prior to testing.

Poisson's ratio of the G338 glass was also determined. The details of its composition are presented in Table I.

Specimens for the determination of Poisson's ratio were made from these ingredients as follows: glass melts, fired at 1300 °C, were poured into pre-heated cylindrical graphite crucibles of dimensions 30 mm diameter × 70 mm height which were open at one end. The graphite crucibles containing the glass were immediately transferred back into a furnace which was already at the pre-set temperature of 800 °C. The furnace was turned off after 2 h of annealing the glass, and the crucible left to cool in the furnace. This was to ensure that the resulting glass cooled slowly enough not to crack. The cooled glasses were cut and machined to obtain cylindrical specimens with flat and parallel sides and of dimension 30 mm diameter × 3 mm height.

Poisson's ratio of the cements, determined in duplicate, were evaluated after 24 h, 80 days (3 months), and 253 days (9 months). For the glass, Poisson's ratio was determined on four specimens.

3. Results and discussion

Table II presents the results of Poisson's ratio for the cements evaluated as a function of time.

TABLE II Poisson's ratio of glass-polyalkenoate cements

Cement type	Poisson's Ratio (σ)		
	1 day	80 days	253 days
Luting cement	0.370 (0.001)	0.347 (0.006)	0.337 (0.011)
Filling cement	0.305 (0.003)	0.288 (0.006)	0.292 (0.002)
Chelon-Fil	0.297 (0.013)	0.305 (0.014)	0.328 (0.011)
Chelon Silver	0.332 (0.004)	0.310 (0.021)	0.311 (0.030)

The numbers in parentheses are the associated standard deviations

Statistical analysis of the results in Table II was performed using ANOVA. This showed that Poisson's ratio for the experimental luting cements was significantly greater (at the 95% confidence level) than that of the filling materials for all storage periods, and also greater than that of the commercial filling material, Chelon-Fil, after 24 h storage, also at the 95% level. Poisson's ratio for the glass G338 was also determined, and found to be 0.277 (standard deviation 0.003). Thus the finding that the luting cement, with relatively more water (Poisson's ratio 1.000) and relatively less glass, had a significantly higher Poisson's ratio was to be expected.

Table II shows that for both of the experimental cements, there is a statistically significant decrease in Poisson's ratio (at the 95% confidence level) between 1 and 80 days. The differences between 80 and 253 days were not statistically significant. These changes between 1 and 80 days correlate with other known changes in the properties of these cements, including compressive strength, translucency, and sensitivity to desiccation [1–3]. These slow maturation processes are known to continue long after the cement has set [1–3], and have now been shown to result in slight reductions in Poisson's ratio with time. The likely cause of this particular change is that of water becoming more tightly bound into the cement with time, probably forming a hydrated silicate structure [15]. This change in the mode of incorporation of water seems to cause it to exert relatively less influence on Poisson's ratio of the cement than it does in the "loosely bound" state. Although these changes were significant at the 95% level, they were only slight, and unlikely to be significant in the clinical use of these cements.

For the commercial cement studied, the values of Poisson's ratio were of the same order as those for the experimental restorative cement. However, unlike the experimental material, this cement apparently increased its Poisson's ratio with time, though these changes were not statistically significant. These findings are consistent with previous ones that have shown that the ageing characteristics of cements vary according to whether they are formulated from poly(acrylic) or poly(maleic acid) [16].

Finally, the silver-cermet reinforced cement was found to have a similar Poisson's ratio to other materials. Like the experimental poly(acrylic acid) cements, its Poisson's ratio went down very slightly with increasing age, but for this cement, the effect was not statistically significant.

4. Conclusions

Poisson's ratio of two experimental and two commercial glass-polyalkenoate cements have been accurately determined using an ultrasonic pulse method. The values obtained in this study for the three restorative cements were all in the region of 0.3, a value which has previously been assumed for these materials [8]. The luting cements were shown to have a greater Poisson's ratio than the restorative materials, i.e. approximately 0.35. The experimental cements, which were based on poly(acrylic acid), also showed slight but statistically significant increases in Poisson's ratio between 1 and 80 days, but not thereafter, which is consistent with known changes that occur in these cements with time. On the other hand, neither of the commercial cements, which were both formulated from poly(maleic acid), showed any significant changes in Poisson's ratio on ageing.

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