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Studies on the structure of light-cured Glass-ionomer cements

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The behaviour of two commercial light-cured glass-polyalkenoate ("Glass-ionomer") cements has been studied in terms of changes in strength following storage under various conditions. Unlike conventional glass-polyalkenoates, these materials cure partly by a photochemical polymerization process, in addition to the normal acid-base setting reaction. Results presented in the current paper show that these hybrid materials are able to take up a considerable amount of water when stored in either water or physiological saline solution. This leads to an observed change of failure mode in compression from purely brittle to partly plastic. These changes are accompanied by a reduction in compressive strength. Overall, the behaviour of the light-cured Glass-ionomers was found to be similar to that of hydrogels. This finding is discussed in light of the information it gives about the underlying microstructure of these materials.

1. Introduction

The term "Glass-ionomer" (or more correctly "glass-polyalkenoate") is applied to a class of materials of a similar basic type used in restorative dentistry [1]. They are acid-base cements derived from aqueous polymeric acids, such as poly(acrylic acid) homopolymer or acrylic/itaconic copolymers. The glass component is usually a fluoroalumino-silicate [1], though other non-fluoride glasses have been used, either straightforward aluminosilicates [2] or aluminoborates [3]. They may also be reinforced by incorporating finely divided metal, such as silver–tin alloy, into the cement [4].

A further development of this class of material has been the incorporation of photopolymerizable components to form hybrid cements known as light-cured Glass-ionomers [5, 6]. These became commercially available in the late 1980s [7]. The advantage of these materials is that the initial set of the cement, the photochemical polymerization, gives the cement good early protection against attack by moisture [7]. The early susceptibility of the simple acid-base Glass-ionomers has long been recognized as a weakness [1] and is overcome in clinical use by coating the cement with a varnish or petroleum jelly [8].

As stated earlier, these cements are cured initially by photochemical means and, because light can penetrate to only a limited depth, they must be used in thin layers (2 mm maximum). As a result, these light-cured cements have been recommended for clinical use as lining materials. Special materials are used for lining cavities to minimize the pulpal irritation caused by certain restorative materials [9].

Light-cured Glass-ionomers consist of a complex mixture of components. These are (i) poly(acrylic acid) or a modified poly(acrylic acid), (ii) a photocurable monomer such as hydroxyethyl methacrylate (HEMA), or a photocurable side chain grafted on to the poly(acrylic acid), (iii) an ion-leachable glass, and (iv) water. Consequently, they set by a number of competing reactions to give complex structures.

The initial setting reaction is the photochemical polymerization. Depending on the precise details of the formulation, this process is either a copolymerization of the HEMA with the polymer side chains or homopolymerization of the functional groups in the side chains.

Subsequently, the acid-base reactions typical of Glass-ionomers takes place. This process is designed to be slower than in conventional Glass-ionomers [5, 6]; it is also probably impeded by the development of photopolymerized network. By analogy with previous studies [1], these reactions may be assumed to be as follows.

1. Decomposition of the glass under the influence of the polyacid, leading to release of Ca^{2+} ions and Al^{3+} species, these latter probably being in the form of complex oxyanions containing several aluminium atoms [2].
2. Rapid reaction of the Ca^{2+} ions with the polyacid chains, followed by slower reaction of Al^{3+} species gradually released from the anionic complex [10].
3. Gradual hydration of the silicate fragments released in step 1 to yield a matrix of increased strength and greater resistance to desiccation [2].

Although the broad outline of the setting reactions in these hybrid materials is clear, several points of detail remain to be elucidated. For example, the precise nature of the matrix formed as these cements set is uncertain, since the relative importance of the photo-

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polymerization and the acid-base reactions has not yet been determined. It is also not clear how the properties of these cements change with time. For conventional Glass-ionomers, by contrast, it is known that compressive strength generally increases as the cements age [1]. However, recent results have shown that this is not always true and that Glass-ionomers derived from copolymers tend to become weaker on ageing in water, apparently due to slight hydrolysis of the matrix [11].

A final feature of these hybrid cements that has not previously been discussed in the literature is the role of water within them. In conventional Glass-ionomers water is known to occur in at least two different states, classified as evaporable and non-evaporable [12]. The basis for this classification is whether the water can be removed by vacuum desiccation over silica gel [13]. The alternative terms "bound" and "unbound" have also been applied to these different states of water combination.

In Glass-ionomers formed from the homopolymer of acrylic acid the unbound water represents up to 5% by mass of the total cement, while the bound water is 18–28% [12]. This amount of bound water is equivalent to five or six water molecules to each acid group and to each associated metal cation. Hence at least 10 water molecules are involved in the hydration of a single coordinated metal ion at a carboxylate site.

The ratio of bound to unbound water in conventional Glass-ionomer cements has been found to increase with time [1]. This causes the cements to become less susceptible to the effects of desiccation as they age. It also correlates with the increase in compressive strength.

In the present study, attention has been paid to understanding the role of water in hybrid cements. Cements have been aged in a variety of environments, ranging from highly desiccating air (i.e. stored over concentrated sulphuric acid) to immersion in pure water. Specimens have been stored for varying lengths of time and the effects of the different ageing periods and conditions on the mass, volume, dimensions and compressive strength have been determined. From the results obtained, it has been possible to gain a better understanding of the relative importance of the two setting processes and of the role of water within these materials.

2. Materials and methods

The commercial light-cured Glass-ionomer cements under investigation were Vitrebond (3M, Dental Products Division, Minnesota, USA) and *XR*-Ionomer (Kerr, Michigan, USA). Vitrebond consists of poly (acrylic acid) with grafted side chains of allyl isocyanate, together with 25% hydroxyethyl methacrylate (HEMA), glass powder and water. *XR*-Ionomer consists of a similar poly(acrylic acid) graft copolymer, though with fewer side chains, together with glass powder and water; it does not, however, contain HEMA.

Compressive strength specimens were prepared by using a modified standard split mould. In this apparatus, a stainless steel cylinder of height 10 mm, diameter 6 mm, is placed inside the mould leaving a depression (2 mm × 6 mm) into which the cement may be packed. After irradiation of this 2 mm depth of cement, a washer of height 2 mm is placed under the specimen, so that the hole in the washer coincides with the position of the specimen in the mould. The specimen is then pushed down into the 2 mm gap provided by the washer and a further depression (2 mm × 6 mm) is available for packing. In the current work, this process was repeated until a cylindrical specimen of standard size had been made from six layers (2 mm × 6 mm) of cement. Irradiation was brought about by using a blue light source designed for curing dental cements (Heliolux II, ex. Vivadent, Leicester). The Vitrebond samples were cured for 30 s per layer, the *XR*-Ionomer for 40 s. These times are in line with those in the directions for clinical use supplied by the manufacturers. It was the minimum cure time, causing sufficient through polymerization, to enable the layer to be pressed down into the mould.

The cements were stored in the mould for 1 h at 37 °C, then weighed and measured. They were then stored in either (i) air at ambient humidity, (ii) rigorously dried air (i.e. over conc. H_2SO_4), (iii) pure water, or (iv) physiological saline. Storage was at 37 °C in all cases. After 1 day, 7 days or 90 days, specimens were weighed, measured and their compressive strength tested. Six specimens were made for storage under each set of conditions.

The load at failure in compression, used to calculate the compressive strength of a material, was measured by using an Instron 1185 Universal Testing Machine, at a crosshead speed of 1 mm min^{-1}.

The initial water content of each liquid component was determined by placing a weighed amount of each sample in specimen bottles that had previously been stored over concentrated sulphuric acid at 37 °C until their mass was constant. The samples were themselves stored under these conditions until they attained constant mass, from which the amount of water lost was calculated.

3. Results

The results for compressive strength of specimens of the two different light-cured Glass-ionomer cements are shown in Table I.

These results show interesting differences between the specimens. In air at ambient humidity, a progressive increase in mean strength was found for both *XR*-Ionomer and Vitrebond. Application of Student's *t*-test to these data showed the increase to be significant for *XR*-Ionomer at the 99% confidence level, whereas for Vitrebond the increase was significant at the 95% level but not at the 99% level.

In dry air, the specimens lost integrity during storage, presumably due to loss of water to the surroundings. Specimens stored in wet conditions, either in pure water or in saline, were weaker by comparison with those stored in air at ambient humidity. In all cases this was significant at the 99% confidence level.

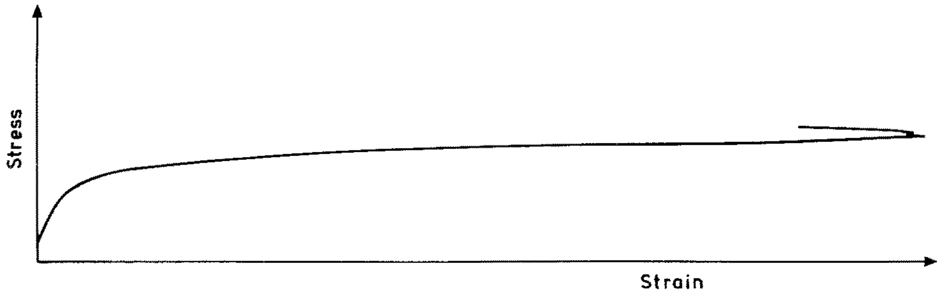

Figure 1 Instron trace for XR-Ionomer stored in dry air for one day showing brittle fracture.

Storage in water led to an increase in the compressive strength of Vitrebond with time that was significant at the 99% confidence level; by contrast the change for XR-Ionomer was not statistically significant. Both materials behaved differently in saline. XR-Ionomer gave specimens that were significantly stronger after 90 days in saline than after 90 days in pure water (99% confidence level); Vitrebond gave specimens that were marginally stronger after storage in saline than in water, a result that was significant at the 95% confidence level, but not at the 99% level.

In addition to these changes in compressive strength, there were changes in the mode of failure of specimens stored in aqueous environments compared with those stored in air. The former underwent failure that showed significant plastic character, the specimens becoming barrel-shaped before fracture. The stress–strain curve changed shape, as illustrated. Fig. 1 shows the trace obtained from a specimen stored in dry air for one day, which exhibited almost pure brittle fracture, while Fig. 2 shows the trace obtained for the same cement stored in saline for an identical length of time. This latter specimen exhibited significant plastic deformation before fracturing, as well as failing at a lower stress.

The results for differences in compressive strength can be compared with results for changes in mass and in volume, as shown in Tables II and III respectively.

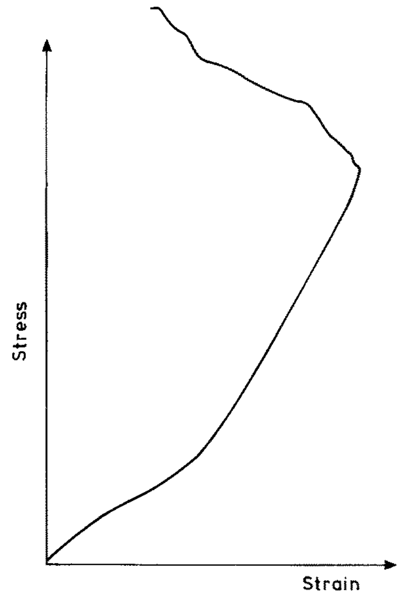

Figure 2 Instron trace for XR-Ionomer stored in physiological saline for one day showing some plastic deformation.

These results show the following two important features: (i) in the desiccating atmosphere specimens underwent considerable reduction in both mass and volume, and (ii) in wet conditions, i.e. in either pure water or physiological saline, samples increased in mass and in volume.

TABLE I Results for the determination of compressive strength. There is no result to quote for the samples stored over concentrated sulphuric acid for 7 and 90 days. This is because the specimens either disintegrated during storage or broke while they were being measured with the micrometer screw gauge. The column s gives the standard deviations in the results

Storage		Compressive strength (MPa)			
Medium	Duration (days)	XR-Ionomer (%)	s	Vitrebond (%)	s
Air	1	73	5	80	10
	7	83	8	73	5
	90	126	30	100	14
Dry air	1	73	34	110	9
	7	–		–	
	90	–		–	
Water	1	52	3	64	7
	7	64	9	47	7
	90	41	12	41	5
Saline	1	49	3	72	6
	7	58	11	56	8
	90	65	8	45	3

TABLE II Reduction in mass as a percentage of initial value. In each case the value quoted is the mean of the six values obtained for that set of conditions. A negative value indicates an increase in mass and a positive value indicates a mass loss. The column s gives the standard deviations in the results

Storage		Percentage mass loss			
Medium	Duration (days)	XR-Ionomer (%)	s	Vitrebond (%)	s
Air	1	0.6	0.1	0.5	0.1
	7	1.0	0.3	1.0	0.2
	90	2.8	0.4	4.4	0.4
Dry air	1	10.7	0.6	7.6	0.2
	7	14.0	0.5	11.0	0.4
	90	17.0	0.6	13.8	1.1
Water	1	– 1.5	0.6	– 3.6	0.2
	7	– 2.2	0.4	– 3.4	0.4
	90	– 2.9	0.3	– 2.3	0.4
Saline	1	– 1.5	0.2	– 2.8	0.2
	7	– 2.0	0.6	– 3.2	0.5
	90	– 1.6	0.3	– 2.0	0.2

TABLE III Decrease in volume as a percentage of initial value. In each case the value quoted is the mean of the six values obtained for that set of conditions. A negative value indicates an increase in volume and a positive value indicates a decrease in volume. The column *s* gives the standard deviations in the results. There is no result to quote for the samples stored over concentrated sulphuric acid for 7 and 90 days. This is because the specimens either disintegrated during storage or broke while they were being measured with the micrometer screw gauge

Storage		Percentage volume decrease			
Medium	Duration (days)	*XR*-Ionomer (%)	*s*	Vitrebond (%)	*s*
Air	1	1.2	0.5	0.5	0.4
	7	1.8	0.4	0.6	0.5
	90	5.9	0.9	7.6	0.9
Dry air	1	16.6	1.1	10.6	0.4
	7	–		–	
	90	–		–	
Water	1	– 2.7	0.9	– 4.7	0.4
	7	– 3.9	0.9	– 4.8	1.0
	90	– 3.8	1.0	– 2.3	0.8
Saline	1	– 3.1	0.7	– 3.5	1.0
	7	– 3.0	0.7	– 3.9	1.0
	90	– 2.7	0.8	– 2.3	1.4

TABLE IV Calculation of bound and unbound water in light-cured glass-ionomer cements

	XR-Ionomer	Vitrebond
Powder/liquid ratio (wt/wt)	1.4:1	1.4:1
% of cement mass due to liquid component	42	42
% of water in liquid component	61.5	51.3
% of cement mass due to water	25.8	21.5
% of cement mass lost due to desiccation	17.0	13.8
% of water lost on desiccation	66	64
% of water bound[a]	34	36
% of water unbound	66	64

[a] As evaluated from the results for storing over concentrated sulphuric acid for 90 days.

Results for the determination of water content of the aqueous components of the two cements are shown in Table IV. From these values, the amount of water present initially in the cements and the amount lost after storage of the cement specimens for 90 days over concentrated sulphuric acid were calculated. These values are also shown in Table IV.

4. Discussion

The results reported in this paper give considerable information on the correlation between structure and physical properties for these light-cured Glass-ionomer cements. They show firstly that for both of the commercial light-cured Glass-ionomer cements studied there is an increase in strength on storage in air at ambient humidity. This is similar to the behaviour of acid-base Glass-ionomer cements [1], and the fact that the light-cured cements behave in the same way implies that similar maturation processes take place in these latter cements. Such processes continue for some time after the initial hardening reaction is complete [1], and their occurrence in the light-cured cements demonstrates that the various acid-base reactions are able to continue despite the formation of the photopolymerized network.

The results in the current paper also show that the light-cured cements undergo profound changes on storage in water or saline. Compressive strength has been found to decrease with increasing storage time and specimens stored in water were found to be consistently weaker than cements of similar age stored in air. The mode of failure in compression was also found to be different for water-stored as opposed to air-stored samples, being more plastic rather than almost purely brittle. Failure of cements stored in aqueous environments came after considerable distortion of the test specimens, which became barrel-shaped. By contrast, specimens stored in air at ambient humidity underwent sudden catastrophic failure with little observable deformation.

The change in failure mode has been shown to relate to the fact that water is taken up by the specimens. In aqueous environments, the specimens undergo considerable swelling, taking up water which acts as a plasticizer once inside the cements.

Results for specimens stored in physiological saline showed that there was less reduction in compressive strength than for specimens stored in pure water. However, for each type of cement, there was a considerable weakening effect compared with storing in air at ambient humidity. Uptake of water as assessed by determination of changes in mass showed that less water was taken up on storage in saline than on storage in water.

These findings can be accounted for readily in terms of the underlying chemistry of the materials. In both cases, the photochemical polymerization leaves a structure that contains a high proportion of hydrophilic functional groups. This is the classic structure of a synthetic hydrogel.

Hydrogels, which are often prepared from copolymers of HEMA, are materials designed to take up large amounts of water, possibly up to 80% by mass [14]. Hydrogels have a variety of uses in medicine, including as devices for controlled drug delivery and as soft contact lenses [15]. Owing to their high degree of hydration, hydrogels generally have low mechanical strengths. Moreover, strength is related to the amount of water taken up, the greater the uptake the weaker the resulting swollen hydrogel [16].

Swelling of hydrogels arises as a consequence of the affinity of the network structure for water [12]. Due to the light crosslinking, the hydrogel is unable to dissolve, hence its affinity for water has to manifest itself as water uptake. The hydrogel continues to take up water until the chemical potentials of water in the gel and of water surrounding the gel are balanced. As water enters the hydrogel, it solvates the hydrophilic segments of the network, causing elongation of the polymer molecules. Since there are limits to the extensibility of the polymer molecules, it follows that there are limits to the extent to which the network can swell. Hence there are also limits to the amount of water that hydrogels can take up.

The differences between the behaviour of the light-cured Glass-ionomers on storage in pure water and in physiological saline are also characteristic of hydrogels. Swelling depends on the osmotic pressure surrounding the gel, which in turn depends on the chemical potential of the water outside the gel. The chemical potential of water is affected by the presence of dissolved solutes, which means that dissolved compounds in the aqueous phase surrounding a hydrogel always alter the degree of swelling of the hydrogel. This is significant in the current work, since it means that large swelling in pure water does not imply there will necessarily be comparable swelling in saliva.

Since conventional acid-base Glass-ionomers do not swell to any appreciable extent in aqueous environments, the swelling behaviour of these light-cured cements must be assumed to be caused by strongly hydrophilic functional groups in the photopolymerized part of the matrix. In Vitrebond, this polymeric structure may include both poly(HEMA) and graft copolymers of HEMA as well as the carboxylic acid and carboxylates arising from the modified poly(acrylic acid) component. In *XR*-Ionomer, only these latter groups are present, but in greater proportion than in Vitrebond. Hence both cements have some capacity for acting as hydrogels and taking up water. When they do so, like typical hydrogels, their dimensions increase (i.e. they swell) and their strength decreases.

5. Conclusions

From the results reported in this paper, we conclude that the two light-cured Glass-ionomers set to form materials that show some of the characteristics of hydrogels. As such they swell in aqueous environments to give materials that are of lower compressive strength than equivalent materials stored in air at ambient humidity. Swelling occurs to a lesser extent in physiological saline, due to the fact that water has a lower chemical potential in saline solution than in the pure state. Consequently in saline solution, the driving force for swelling is less than in pure water. This indicates that *in vivo*, when exposed to saliva in the mouth, the swelling of these hybrid cements may not be as severe as we have shown it to be in pure water.

Desiccation of these materials causes severe loss of water, up to 66% of the total water originally present in the system. Such desiccation causes complete loss of integrity of the specimens, showing that the presence of water is necessary to build up the structure of these cements.

Specimens stored in pure water or in saline failed in compression by a different mode from specimens stored in air at ambient humidity. On loading they became progressively more barrel-shaped before failure, indicating that they had a significantly plastic character. By contrast the specimens stored in air at ambient humidity failed catastrophically with minimal deformation, indicating that they were essentially brittle materials. This change from brittle to plastic behaviour following immersion in water is also a characteristic of hydrogels.

The increase in strength with time that was found for the specimens stored in air at ambient humidity indicates that there are secondary reactions taking place within the cement. These are typical of the maturation processes of acid-base Glass-ionomers, and have recently been attributed to hydration of a silicate network that develops gradually after the formation of the polysalt matrix [2]. We conclude that the changes in compressive strength with time indicate that these maturation processes also occur in the hybrid cements. They thus become less like hydrogels and more like conventional Glass-ionomers as they age.

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References

1. A. D. WILSON and J. W. McLEAN, "Glass ionomer cement" (Quintessence Publishers, Chicago, USA, 1988).
2. E. A. WASSON and J. W. NICHOLSON, *Brit. Polym. J.* **23** (1990) 179.
3. M. A. WILSON and E. C. COMBE, *Clin. Mater.* **7** (1991) 15.
4. A. G. W. WALLS, J. ADAMSON, J. F. McCABE and J. J. MURRAY, *Dent. Mater.* **3** (1987) 113.
5. J. M. ANTONUCCI, J. E. McKINNEY and J. W. STANSBURY, "Resin modified Glass-ionomer dental cement", US Patent 7 160 856 (1988).
6. S. B. MITRA, "Photocurable ionomer cement systems", European Patent Application 88 312 127.9 (1988).
7. A. D. WILSON, *Int. J. Prosthodontics* **3** (1990) 425.
8. M. S. A. EARL, W. R. HUME and G. J. MOUNT, *Aust. Dent. J.* **30** (1985) 298.
9. D. F. WILLIAMS and J. CUNNINGHAM, "Materials in clinical dentistry" (Oxford University Press, 1979).
10. J. W. NICHOLSON, P. J. BROOKMAN, O. M. LACY and A. D. WILSON, *J. Dent. Res.* **67** (1988) 1451.
11. J. A. WILLIAMS and R. W. BILLINGTON, *J. Oral. Rehab.* **18** (1991) 163.
12. H. J. PROSSER and A. D. WILSON, *J. Chem. Tech. Biotech.* **29** (1979) 69.
13. A. D. WILSON and S. CRISP, *Brit. Polym. J.* **7** (1975) 279.
14. D. G. PEDLEY, P. J. SKELLY and B. TIGHE, *ibid.* **12** (1980) 99.
15. F. G. HUTCHINSON, "Medical and pharmaceutical applications of water soluble polymers", in "The chemistry and technology of water-soluble polymers", edited by C. A. Finch (Plenum Press, New York and London, 1983).
16. J. KALAL, "Water sensitive chemically cross-linked gels", in "The chemistry and technology of water-soluble polymers", edited by C. A. Finch (Plenum Press, New York and London, 1983).

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