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# The physical chemistry of light-curable glass-ionomers

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This paper reviews aspects of the physical chemistry of light-curable glass-ionomer cements. These materials have a tendency to undergo phase separation in solution and, when set, to take up water and swell. Other likely features of their behaviour include: (i) retardation of the ionic curing reaction by the presence of organic components; (ii) modification of the photochemical cure process by the presence of ionic species; and (iii) gradual phase separation on setting, leading to a domain structure in the solid state. The paper concludes that longer-term clinical studies are needed to demonstrate whether these features lead to durable materials or to materials containing inherent physico-chemical weaknesses that will limit their overall usefulness.

## 1. Introduction

Light-curable glass-ionomer cements for use as lining materials in dentistry became commercially available in the late 1980s [1]. They are hybrid materials prepared by the incorporation of photopolymerizable components into a conventional acid–base mixture [2,3]. They consist of a complex mixture of components, and may include:

(a) poly(acrylic acid) or a modified poly(acrylic acid);
(b) a photocurable monomer such as hydroxyethyl methacrylate, HEMA, or a photocurable side chain grafted onto the poly(acrylic acid);
(c) a further photopolymerizable molecule conventionally used in dental composite resin filling materials, such as bisGMA or similar substance;
(d) an ion-leachable glass; and
(e) water.

These cements set by a number of competing reactions and they have complex structures. They were launched initially as liners/bases, and as such have been shown to have good adhesion to bovine dentine [4] and to release clinically useful amounts of fluoride [5]. They have been shown, too, to behave as mild hydrogels [6,7], taking up water on exposure to moisture, and generally becoming weaker and more plastic. The clinical consequences of this have been discussed [6]. More recently, restorative grades of light-curable glass-ionomers have become available, and longer-term exposure studies have shown that one of these materials, Fuji II LC (ex. GC Corporation, Japan), swelled in water, though it did not become weaker and remained brittle in failure [8].

In a hitherto unpublished study, we examined a further commercial liner/base material, and found that the liquid component had undergone phase separation on storage. This was not immediately apparent, and led to cements being prepared from what proved to be a resin-rich liquid containing little or no polymeric acid. Resulting cements, which could not undergo an acid–base setting reaction, were found to exhibit very large swelling on soaking in water. This highlighted an important aspect of these materials, namely their inherent thermodynamic tendency to undergo phase separation and the importance of overcoming such a tendency by careful attention to obtaining long-term compatibility between the components. However, it also raised in our minds the question of the overall effect of probable thermodynamic instability on the formulation, setting and durability of these cements. This in turn has led us to consider likely further effects on each other of the notionally separate setting mechanisms.

All of these topics are covered in the current paper. The paper is broken down into three areas, namely solution chemistry and the problems of phase separation; setting chemistry and the ways in which photopolymerization may interfere with the acid–base processes; and solid-state chemistry, especially the longer-term development of strength and the problems of swelling in water. In all three cases, much of the argument is based on inferences from the wider physico-chemical literature. This is necessary because of the very unusual nature of the materials under

consideration, which appear to be a unique blend of hydrophilic and hydrophobic components, setting by competing mechanisms, and for which there do not seem to be any obvious parallels in other areas of technology.

## 2. Solution chemistry

Before considering the particular case of the components of light-curable glass-ionomers, we need to consider the general case of the interaction of two polymers in solution. It is well established that the general result of mixing two polymers, whether in solution or in the melt, is a two-phase system [9]. This is explained in terms of thermodynamics:

The free energy of mixing can be calculated from the Gibbs equation:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

For mixing to occur spontaneously a necessary (but not sufficient) condition is that $\Delta G_{mix}$ be negative. Because the number of specific polymer–polymer interactions is small, because of steric effects, enthalpy changes for mixing of solutions of polymers tend to be small [10]. At the very least, this makes the $\Delta H_{mix}$ term small, so that it makes only a minor contribution to $\Delta G_{mix}$. For chemically dissimilar polymers, favourable interactions between similar segments of the same kind of molecule may be disrupted, thus making $\Delta H_{mix}$ positive, i.e. opposed to the mixing process.

Entropy of mixing, too, is small, for reasons that become clear from the application of the Flory–Huggins lattice theory. This states that

$$\Delta S_{mix} = -R(N_1 \ln \phi_1 + N_2 \ln \phi_2)$$

where $R$ is the gas constant, $N_i$ is the number of moles of component $i$ and $\phi_i$ is the volume fraction of component $i$. Since polymers have high molar mass, the number of moles per unit part of the solution is small. Due to the small size of the $N_i$ terms, the $\Delta S_{mix}$ term is very small; in the limit of infinite molar mass, it is zero.

The overall effect of these two thermodynamic terms being small is that $\Delta G_{mix}$ for polymers is itself small. Thus there is little thermodynamic driving force for spontaneous mixing, with the net result that blends of polymer melts or of polymer solutions are generally not miscible.

These broad generalizations do not apply in all circumstances, for instance:

(a) for oligomers, the entropy of mixing term is not negligible;
(b) with chemically similar polymers, where the enthalpy of mixing is likely to be small, and very low $\Delta S_{mix}$ may be sufficient to drive the process; and
(c) where polymers can develop large and specific interactions, such as hydrogen bonding, between the different types of molecule. In such cases, $\Delta H_{mix}$ is large and negative, and hence swamps the low $\Delta S_{mix}$ term.

The argument so far has been expressed in terms of thermodynamic miscibility. For real polymers, however, it may not be necessary to achieve true miscibility. A stable, intimate dispersion of one polymer solution phase in the other may be sufficient. Provided the dispersion remains intact over reasonable time periods, a condition known as "compatibility", the mixture may be satisfactory. For the polymeric components of light-curable glass-ionomers, while true miscibility probably cannot be achieved, with care, the more limited goal of compatibility can be.

None of the commercial materials has been available for very long, hence any problems of slow phase separation may not have had the chance to occur. The one exception to this, which was described earlier, has since been reformulated. Thus, in the main, compatibility does seem to have been achieved. This may be helped by the fact that, in a number of cases, the components of these cements are copolymers. Copolymers are generally more miscible with other polymers than homopolymers [9], a fact which arises because interactions with the second polymer reduce any unfavourable interactions between the different segments of the same molecule [11].

The presence of organic molecules in an aqueous solution has the effect of altering the conformation of dissolved polyelectrolytes. This has been shown experimentally for poly(acrylic acid) in the presence of methanol [12]. Methanol was found to reduce "goodness" of water as a solvent for the polymer, thus moving the system closer to the Flory theta-temperature,i.e. closer to phase separation. Although the actual experiments were carried out under what are formally described as "semi-dilute" conditions, hence far removed in terms of concentration from the polymer solution used in glass-ionomer cements, there are parallels between this study of poly(acrylic acid) solutions and an early study of glass-ionomer cements. Some years ago, in an attempt to overcome gelation in concentrated aqueous solutions of poly(acrylic acid), Crisp *et al.* [13,14] added methanol to the mixture. They found that the setting reaction of such mixtures with a calcium fluoro–alumino–silicate glass was slower than for poly(acrylic acid) in water alone, a fact they attributed to esterification of the carboxylic acid groups on the polymer [14]. It seems more likely, particularly in view of the findings of Klooster *et al.* [11], that the methanol had reduced the solvating power of the water, and led to the polymer adopting a more tightly coiled (hence less reactive) conformation. Similar effects seem likely to occur with HEMA in light-curable glass-ionomer cements.

## 3. Setting chemistry

Setting chemistry is complicated for light-curable glass-ionomers. In principle, on irradiation the setting occurs rapidly by the photochemical cross-linking reaction, and more slowly by the acid–base reaction. In practice, these two reactions cannot take place without reference to each other: the photochemical reaction will be affected by the polar nature of the acid–base medium, and the acid– base process will be

affected by the presence of relatively hydrophobic entities, and also by the reduced diffusion coefficients of the reactive species through the cross-linked network.

No data are available for the effect of either reaction on the other, but much is known generally about what influences the rate and mechanism of reactions, so that certain effects can be predicted with some confidence. For example, many years ago Hughes and Ingold formulated their rules on solvent effects [15], as follows:

(a) Where the activation step involves an increase in electronic charge, polar solvents will increase the rate of reaction.
(b) By contrast, where the activation step involves a decrease in electronic charge, polar solvents will decrease the rate of reaction.

Thus the presence of the polar poly(acrylic acid) molecule in water is likely to alter the rate of the photopolymerization reaction, though it is not possible to state firmly whether or not this is disadvantageous. Conversely, the presence of the non-polar photopolymerizable molecules (and, in certain light-curable cements, segments) will alter the rate of the acid–base reaction, and this will be disadvantageous. This effect would compound the already reduced rate of acid–base reaction experienced with the reduction in diffusion coefficients for the bulky reacting species as the photopolymerized network undergoes development.

The usual mechanism of the acid–base setting reaction in conventional, "self-curing" glass-ionomers must involve proton transfer from the acid to the base. Such reactions have been analysed as having three component steps [16]:

1. Diffusion of acid and base to the point where a hydrogen-bond forms between them.
2. Proton transfer via the hydrogen-bond, possibly mediated via water molecules.
3. Diffusion apart of the products [16].

All three of these steps will be affected by the presence of the hydrophobic, crosslinked structure. For steps (1) and (3), as we have seen, diffusion coefficients decrease, thereby adversely affecting the rate of reaction. For step (2), the relative reduction in concentration of water will also have the effect of reducing reaction rate. This may indeed be part of the explanation for the slightly reduced rate of reaction found by Crisp *et al.* [12] for conventional, self-curing glass-ionomer cements containing methanol.

A further feature of the setting reaction is a natural tendency for the reacting mixture to phase separate as the reaction proceeds. Recent experimental work has shown that phase separation occurs when HEMA is copolymerized with ethylene glycol dimethacrylate in aqueous solution in the presence of an ionic salt [17]. This system is clearly a relevant model for what happens in a light-curable glass-ionomer cement.

There are two driving forces for phase separation. First, as HEMA undergoes polymerization, it ceases to be water-soluble [18]. This will compound the general tendency of mixtures of polymer solution to phase separate. Second, as the acid–base reaction proceeds, and the poly(acrylic acid) becomes progressively more neutralized, so more hydrophobic organic species become less soluble in the aqueous phase. This is the well-known phenomenon of "salting out", which is responsible for such effects of the development of cloudiness when salts are added to surfactant–water systems [19].

## 4. Solid-state chemistry

The phase-separating tendency as light-curable glass-ionomers undergo setting means that the product itself is likely to contain domains of different phases. There are parallels in the microstructure of materials such as carboxylated rubbers [20] and lightly sulfonated fluoropolymers [21]. These latter materials have been particularly widely studied and shown to have a clustered morphology in which the ions, with some co-ordinated water molecules, are associated in domains in an otherwise hydrophobic fluoropolymer matrix. These domains are formed due to the highly unfavourable thermodynamic state of neutralized functional groups plus ions in a non-polar medium. Small-angle X-ray scattering has been used to determine the size of these domains in certain of these materials [22] and there is no question that they occur in a variety of related materials. Similarly, they have been assumed to occur in ethylene–acrylic acid copolymers containing only low levels of neutralizable functional groups [23]. It thus seems to be a general structural feature of polymeric materials based on mixed hydrophobic/ionic components that the ions form discrete assemblies within the organic matrix. We can therefore expect this kind of microstructure in fully set light-curable glass-ionomers. These are almost certainly the sites to which the water migrates as it is taken up. There is no evidence, yet, about what effect such hydrophobic domains have on the longer-term durability of these cements, though clearly this is an important point for experimental consideration.

## Conclusions

This paper has discussed a number of aspects of the probable physical chemistry of light-curable glass-ionomers. The tendency to undergo phase separation in the solution state and to take up water and swell when set have been demonstrated experimentally. Other features expected from a general consideration of physical chemistry, such as inhibition of the respective curing reactions, and a domain structure in the solid state, have not yet been observed experimentally. However, these are new materials, and data on them is far from complete. We hope that this paper has called attention to some of the structural and chemical features of these materials worthy of attention in the immediate future. In addition, a vital piece of work to be done is to determine just how these materials behave clinically. They represent an important and potentially versatile addition to the clinician's armoury. But, conceived as hybrids of composite resins

and glass-ionomers, we still need to ask "Do they combine the best features of their parents? Or the worst?"

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