



THE EFFECT OF HEAT TREATMENT OF AN IONOMER GLASS ON ITS SURFACE CHARACTERISTICS AND CEMENT-FORMING PROPERTIES

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The surface properties of G338 ionomer glass powder, both in as-received and heat-treated, have been studied in order to identify the reason that heat-treatment gives a cement that sets quicker but is weaker. Samples of G338 glass were analysed by X-ray fluorescence spectroscopy and the density determined by gas pycnometry. As-received and heat-treated (at 240 °C) glass powders were examined by Scanning Electron Microscopy. Specific surface area (BET) and pore volume were determined with low temperature nitrogen sorption, using eight individual powder samples. Thermo-gravimetric analysis was carried out on as-received G338 in the range 30 - 900 °C ramped at 10 °C min⁻¹ in an inert atmosphere. Results showed the appearance of the as-received and heat-treated G338 powders to be the same, as were the specific surface areas and pore volumes. The density was found to be 2.6438 (\pm 0.0093) g·cm⁻³ and the XRF results were consistent with the known composition of the glass. Thermo-gravimetric analysis showed that the glass powder lost mass four steps, which were attributed to variations in states of water-binding on the surface of the glass. These findings lead to the conclusion that the observed differences in the setting properties of the glass G338 with poly(acrylic acid) and the strength of the resulting cements are not due to physical differences between the powders but to variations in the amount and state of surface water. Specifically, these variations are between differences in water binding to silanol groups that occur on glass surfaces.

INTRODUCTION

Glass-ionomer cements are widely used in dentistry for the repair of teeth. Their uses include full restorations, liners and bases, repair of Class V cavities, orthodontic bracket adhesives and fissure sealants [1, 2]. These materials are tooth-coloured and possess a degree of translucency that means that they are considered to be aesthetic repair materials [1].

Glass-ionomer cements are prepared by mixing an ion-leachable glass powder with a solution of polymeric water-soluble acid [1-3]. The most common acid used in polyacrylic, but some commercial brands use acrylic/ maleic copolymer instead [3]. Commercial brands are also typically formulated with some of the polymeric acid mixed dry into the glass powder. This allows the amount of the acidic polymer in the final mixed cement to be high without making the acid solution unworkably viscous. The use of large amounts of polymeric acid in the cement causes the resulting cement strong [4], a feature necessary to ensure good durability in clinical use. Glasses used in glass-ionomer cements are complex materials, generally based on calcium aluminasilicate mixtures with added phosphate and fluoride [2, 3, 5]. Certain brands employ strontium compounds in place of calcium, and these compounds are capable of undergoing similar setting reactions and producing strontium carboxylate salts as a major product of setting [6].

Practical ionomer glasses are not only complex in terms of their chemical composition, they are also typically at least partly phase-separated [5]. Once glass of this type that has been widely studied is known as G338, and its pre-firing composition is shown in Table 1. Glasses of this type are known to be used in commercial brands of glass-ionomer cement, even if the details of their composition differ slightly from those of G338.

The glass G338 has a structure that is partly phaseseprated, undergoing a process known as spinodal decomposition during cooling from the melt [7]. The resulting solid glass consists of two interlocking phases, one of which is richer in calcium than the overall glass and reacts preferentially with acid during the setting reaction.

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Table 1.	Pre-firing	composition	of glass	G338.
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Component	%
SiO ₂	24.9
Al ₂ O ₃	14.2
Na ₃ AlF ₆	19.2
CaF ₂	12.8
AlF ₃	4.6
AlPO ₄	24.2
Other oxides	0.1

Since the early work on phase relationships in G338, much interest has been focused on details of the chemistry of glasses, such as the role of fluoride as a structure-breaker within the glass [8] and the changes in coordination number of aluminium as it moves from the glass to the cement matrix [9]. Other studies have been aimed at developing workable glasses that do not contain aluminium, for example by including zinc [10, 11] or germanium [12]. These studies have been successful in producing glasses capable of undergoing acid-base reactions with aqueous polyacrylic acid, and in some cases the biological properties have been found to be superior to those of cements made with conventional aluminium-containing glasses [13, 14]. However, such glasses have not yet found application in practical biomedical cements, and glass-ionomer cements for use in dentistry remain based on calcium or strontium alumino-silicate glasses [1-3].

Recent studies have considered the state of water on the surface of these practical ionomer glasses. One proposal is that siloxane groups in the surface of the glass powder undergo hydrolysis as part of the setting reaction, thereby generating silanol groups [15]:

 $-Si-O-Si- + H_2O \rightarrow -Si-OH + HO-Si-$

The exact opposite has been suggested in another publication, based on observed reductions in peak intensities in the FTIR spectra of setting cements [16]. However, the peaks concerned are broad, and part of the change appears to be peak broadening. Nonetheless, further work is necessary to distinguish between these two competing suggestions.

We have previously shown that the glass G338 loses mass on heating, some 1.19 % of the initial mass of the powder, but can only regain 0.43 % by mass even under conditions of high humidity [17]. In the same study, it was shown that the setting time of G338 with a specific commercial polyacrylic acid solution was 16.0 minutes for the as-received glass powder, but 12.5 minutes for the heat-treated one. Despite the faster setting, the latter powder gave a significantly weaker cement as measured in compression at 24 h, i.e. 93.5 MPa compared with 125.9 MPa [17]. These findings are consistent with heat-treatment leading to loss of surface silanol groups and formation of siloxane groups, i.e. the reverse of the hydration reaction shown above. We have now carried out further studies on the effect heat treatment on G338 glass powder. These have included determination of the surface characteristics of as-received and heat-treated glass powders, their appearance using scanning electron microscopy and the detailed kinetics of mass loss using thermo-gravimetric analysis.

EXPERIMENTAL

Materials and Methods

All of the work in this study employed a sample of glass G338 obtained from First Scientific Dental (Elmshorn, Germany), which had the pre-firing composition given in Table 1, and had been ground to a fine powder, mean size approximately 4 μ m (87.7 % at 10 μ m or less). The composition of this material was confirmed by X-ray fluorescence spectroscopy using a MiniPal spectrometer (Malvern Panalytical BV, The Netherlands). Determinations were carried out in an atmosphere of helium gas and the radiation source was an X-ray tube with a rhodium cathode. Two energies, 13 kV and 25 kV, were used in the determinations.

The density of as-received G338 was measured by gas pycnometry using an Ultrapyc 1200e pycnometer (Quatachrome Instruments, Florida, USA) and helium gas. Thermogravimetric analysis was carried out in the temperature range 30 - 900 °C using a Clarus TGA1 machine (Perkin Elmer, Massachusetts, USA). The temperature was ramped between 30 °C and 900 °C at 10 °C·min⁻¹ and the sample was kept under an atmosphere of helium gas flowing at 40 ml·min⁻¹.

Scanning electron micrographs were recorded for both sets of powders using a JEOL JM-6380LA instrument.

Finally, low temperature nitrogen sorption was used to determine the specific surface area (BET) and pore volume on G338 powders degassed respectively at 2 °C and 240 °C. Eight individual powder samples were used and means and standard deviations determined. Differences were tested for significance using the Student *t*-test.

RESULTS

The density of the G338 powder was found to be 2.6438 (\pm 0.0093) g·cm⁻³. Thermogravimetric results are shown in the trace in Figure 1, from which it can be seen that mass was lost on heating and that such loss involved two clear major steps, at 642 °C and 834 °C respectively. These were shown by distinct peaks in the differential plot. There were also two minor steps, at around 730 °C and around 780 °C, as shown by changes in slot of the differential plot.

Figure 1 shows the X-ray fluorescence spectra of G338. The elemental analysis assigned from the peaks are consistent with the known composition of this glass, which has a calcium-based formulation.

Figure 2 shows SEM images of the powders of G338, both in the as-received and heat-treated states. There are no obvious differences between the images for the two glass powders, which suggests that the heat

treatment did not cause any major changes in the state of particle agglomeration or morphology.

Results for low temperature nitrogen sorption are shown in Table 2. These showed that there was no significant difference between the specific surface areas of the two glass powders (p < 0.01). Similarly there was no significant difference (p < 0.01) between the pore volumes of the two powders. Overall, this suggests



50 µm

Figure 1. X-ray fluorescence spectra of G338 powder.



a) G338 Glass (as received)

b) G338 Glass (240 °C)



d) G338 Glass (240 °C)



c) G338 Glass (as received) Figure 2. Scanning electron micrographs of G338 powder.

that heat treatment does not alter the morphology of the particle surfaces, at least not in a way detectable by nitrogen adsorption.

Table 2. Properties of cements made from different samples of glass G338 (17).

	Standard deviation		
Sample	Setting time (min)	Compressive strength (MPa)	
As-received G338	16.0 (1.75)	125.9 (11.4)	
Heat-treated G338	12.5 (0.25)	93.5 (8.6)	

DISCUSSION

For G338, there are no observable differences between the as-received and the heat-treated powder and this suggests that the variations in setting speed and cement strength are related to chemical composition at the surface of the glass particles. Certainly there do not seem to be any physical consequences of heat treatment that would account for these observations.

The thermo-gravimetric results suggest that there is a considerable mass loss on heating the G338 powder, and that this mass loss occurs in four steps. There is an initial distinct mass loss at 642 °C followed by two minor losses, at around 730 °C and around 780°C respectively, and then a second major loss at 834 °C respectively. The most likely cause of this mass loss is removal of water. It has previously been shown that heating G338 at 240 °C for 24 h leads to a 1.19 % reduction in mass, and this has previously been attributed to loss of water [17]. Heating up to 900 °C causes a much greater mass loss, and we attribute this to loss of water in much stronger states of binding than that lost at 240 °C.

If this mass loss is due to water, thermo-gravimetric analysis suggests that there are four distinct steps involved. This is consistent with known states



Figure 3. TGA results for G338 glass (including differential plot).

of water binding on the surface silica-based powders [18]. The most easily removed would be a loosely bound film, some of which begins to be lost at much lower temperatures, but most of which is lost at 642 °C. Following this, we need to consider the probable effect of two possible types of surface silanol group. These silanols, which have been identified on the surface of silica powders [18], are, respectively, out-of-plane and in-plane and they have different properties. The out-of-plane are strong and highly acidic, whereas the in-plane are weak and of low acidity. Water molecules forming hydrogen bonds with these groups would be bound with different strengths, water molecules associated with the out-of-plane silanols being more strongly bound than those associated with the in-plane silanols.

Lastly, there is the possibility of loss of water by dehydration of pairs of silanol groups, as previously proposed [17]. This would be expected to be the most difficult of all the water-loss processes and to require the most energy. Thus we propose that this is the process that is responsible for the relatively large mass loss occurring at 834 °C.

The major finding from the detailed study of the as-received and heat-treated powders is that there is no difference in morphology between them. In other words, heating G338 at 240 °C does not lead to changes in particle morphology or agglomeration, and it does not alter the porosity or specific area of the particle surfaces. Despite this, there is a distinct difference between the setting reactions of the two powders, both in terms of the speed and the eventual strength of the set cement [17].

There have been few previous studies of the specific surface area of ionomer glass powders. Instead powders are typically characterised in terms of their particle size and possibly particle size distribution. The limited number of results from previous studies indicates that there is a broad range of specific surface areas observed in ionomer glasses. In a patent for a new type of such glass for dental applications, Todo et al reported that glass powders had BET specific surfaces areas in the range 2.5 - 4.0 $\text{m}^2 \cdot \text{g}^{-1}$ [19]. In a detailed study of experimental ionomer glasses, Crowley et al reported a slightly wider range, i.e. 1.76 - 4.36, with the majority being close to 2 $m^2 \cdot g^{-1}$ [20], which is lower than that reported by Todo et al [19]. Lastly, a more recent study of an experimental strontium-based glass reported a value of $0.73 \text{ m}^2 \cdot \text{g}^{-1}$ [21]. Taken together, these results are consistent with our findings for G338 but not identical. The values for this particular glass are slightly on the low side compared with those quoted for both commercial glass powders [19] and conventional experimental glass powders [20]. However, they are higher than the value reported for the experimental strontium glass powder [21].

Two of these studies also report values for the density of the glass powders studied. The patented glass

powders had densities in the range $2.4 - 4.0 \text{ g}\cdot\text{cm}^{-3}$ [19], whereas the experimental strontium-based glass powder had a density of 2.2 g $\cdot\text{cm}^{-3}$. Our results show that G338 glass is within the range of the commercial material, but is higher than that of the experimental glass powder.

Heat treatment of G338 has previously been reported to give changes to the cement-forming properties of the glass [17]. Specifically, the setting time of as-received G338 with a commercial polyacrylic acid solution was 16.0 minutes, compared with 12.5 minutes for the heat-treated one. Compressive strengths at 24 hours were 125.0 and 93.5 MPa respectively [17]. Previous studies of the effect of acid washing on glass powders showed that acid-washing slowed down the setting reaction and led to weaker cements [20]. Indeed, this pattern of slower setting speeds leading to weaker cements is well established, using various techniques such as application of heat [22], ultra-sonication [23] or controlled changes in composition [24] to control the setting speed. This previous finding of increased setting speed leading to weaker cements is thus unusual with this class of material.

The differences in reported properties have not been found to correlate with any observable changes in the glass powder arising from the heat treatment. The powders appeared the same under SEM, and had comparable measured surface properties. Again, this contrasts with studies in which acid-washing was used to control setting speed. These studies showed that there was an effect on BET specific surface area when glasses were washed in acetic acid and that working and setting times went down as specific surface area went up [20]. However, the effect of acid-washing on specific surface area varied with the glass, generally increasing it, but in one case decreasing it. Since acid washing is known to selectively attack more basic regions of glasses with partial phase-separation, any effect on specific surface area seems bound to depend on precise details of the glass composition.

CONCLUSIONS

The effect of heat treatment on the surface properties of G338 ionomer glass has been investigated. No differences were observed between as-received and heat treated specimens using SEM, and no significant differences between the measured values of specific surface area or pore volume. Thermo-gravimetric analysis up to 900 °C showed mass loss that occurred in four steps, two major and two minor. These are consistent with a four-step loss of water from the glass powder surfaces. The proposed steps are (i) loss of loosely bound surface water, (ii) step-wise loss of water hydrogen bonded to two distinct types of surface silanol groups, and (iii) dehydration of silanol groups to form -Si-O-Si- linkages in the surface.

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