Phase separation in an ionomer glass: Insight from calorimetry and phase transitions

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ABSTRACT

The G338 ionomer glass is a fluoro-alumino-silicate system, which is used as the powder component of glass ionomer cements (GICs) in dental applications. However, despite progress in understanding the nature of this glass, chemical identity of its separated amorphous phases has not yet been conclusively determined. In this work, we identify these phases by performing differential scanning calorimetry (DSC) and X-ray diffraction (XRD) analyses on both the as-received glass and heat-treated samples. We detected three glass transitions in the as-received G338 glass during DSC upscanning, implying the co-existence of three amorphous phases. Towards resolving the chemical identity of the three phases, we performed XRD analyses on samples subjected to dynamic heating, while further DSC and XRD analyses were performed on samples subjected to isothermal treatment. The results suggest that the three amorphous phases in G388 are Ca/Na–Al–Si–O, Ca–Al–F and Ca–P–O–F phases, respectively. However, the exact chemical compositions of the three phases still require further exploration. The results of this work are important for understanding the impact of phase separation within ionomer glasses on the setting behavior of GICs, and hence improving performances of GICs by optimizing the glass production conditions.

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1. Introduction

Many glass-forming melts exhibit liquid–liquid immiscibility, and when cooled the resulting glasses will be phase-separated [1]. Phase separation in these glass melts is a favorable thermodynamic process due to the decrease in the free energy. The ionomer glasses with composition ranges (wt.%) of ~20–36 SiO_2, ~15–40 Al_2O_3, ~0–35 CaO, ~0–10 $AlPO_4$, ~0–40 CaF_2, ~0–5 Na_3AlF_6, ~0–6 AlF_3 [2] are typical systems exhibiting metastable immiscibility [3]. They are used primarily to produce glass ionomer cements (GICs) and glass-ceramics. GICs, also called glass polyalkenoate cements, have been widely used in dentistry as luting cements and filling materials since their invention in the early

1970s. Their extraordinary properties, especially good biocompatibility and natural adhesion to the teeth and bone — amongst other advantages [4], have helped expand their applications to other fields of medicine, including otorhinolaryngological (ear–nose–throat) and maxillofacial augmentation and surgeries, use in orthopedic surgeries as bone cements and the potential use as bone graft substitutes [5–8].

Ionomer glasses appear opal, due to light scattering from the different phases, giving GICs a tooth-color like appearance; significant for dental use. According to an early study [9] on the glass microstructure, another version of ionomer glass, i.e., the G200 glass with a nominal composition (mol%) of 38.52 SiO_2, 12.97 Al_2O_3, 35.07 CaF_2, 1.89 Na_3AlF_6, 5.04 AlF_3, and 6.51 $AlPO_4$ has a tendency to be separated into two phases: a continuous calcium alumino-silicate matrix and partly crystalline calcium fluoride-rich droplets (sphere in matrix morphology). Controlled acid-etching experiments show the acids selectively attacking the amorphous phase of the droplets, the extent of which depends on the melting temperature [9]. It has been postulated that the setting reactions contain two overlapping stages: i) the rapid leaching of calcium cations from the droplets and ii) the subsequent slower

leaching of aluminium and calcium cations from the glassy matrix phase. Hence, the setting rate of GICs can be controlled by the separated phases in the ionomer glass, and the latter can be tailored by changing glass production conditions. Another study [10] has revealed that ionomer glasses readily crystallize in part to apatite, driven by the existing separated phases, imparting GICs with human biocompatibility. Studying the phase separation within the ionomer glass is crucial since it greatly helps advance our understanding of the glass structure–cement property relationship [11–15] for the GIC system. Having this knowledge in-hand will aid advancement of cement design for various applications through rational control of the glass production conditions and their contributions to the material properties of the cement.

One manner of demonstrating amorphous phase separation is by illustrating that the glass has more than one glass transition, indicative of several glassy phases, since each phase has a different glass transition temperature (T_g). Differential scanning calorimetry (DSC) provides a reliable and simple method for detecting existing T_gs in a glass. However, T_g is a dynamic characteristic temperature, which depends on the thermal history of the glass, the heating rate and the definition of T_g, owing to the fact that glass transition occurs over a range of temperatures rather than a single temperature [16]. As a result, there exists discrepancy in the literature T_g values even for the same system. To avoid this problem, a standardized method for determining T_g has been proposed in [16]. Therein, T_g is defined as the onset temperature of the glass transition peak on the second DSC upscan curve obtained at the heating rate of 10 K/min equivalent to that of the first downscan rate. The thus-derived T_g coincides with the temperature corresponding to the viscosity of 10^{12} Pa s for oxide glasses. Based on this standardized method, the T_g values in the current study are therefore determined from the second upscan curve obtained at a heating rate of 20 K/min following a cooling rate of 20 K/min. The faster rate used in the current study was chosen to ensure detection of glass transitions. DSC scans are furthermore used to detect the phase transitions (e.g., crystallization) in the glass during dynamic heating, while XRD is used to identify crystal types. Since crystal structures formed upon heating of a glass often resemble those of the corresponding amorphous phases present in the original glass, this allows for the indirect estimation of the chemical composition of different phases in the glass, hence assignment of the T_g values to their respective phases.

From our parallel study we have found that phase separation in the G338 glass plays an important role in strongly affecting chemical reactions at the interface between the glass and polyacrylic acid, and hence in influencing setting behavior and resultant mechanical properties of the GICs [17]. However, the following questions still remain regarding the G338 glass: 1) How many phases are present in the glass? 2) What is the chemical identity of the separated phases? 3) How do both dynamic and static heating protocols influence the phase separation within the glass?

In this work we answer these questions by performing systematic DSC and XRD measurements, heat-treatments, and through (cross-) referencing to the established literature. Resolving these questions can provide insight into phase separation in other fluoro-alumino-silicate glasses in addition to G338 glass.

2. Experimental

We chose commercial G338 glass, as an example of modern commercial ionomer glasses, for investigation. The nominal [18,19] and elemental compositions of the glass [20] are listed in Table 1. The glass was used as-received with a powder size of ≤40 μm.

The thermal response and the mass change of the glass powder sample during heating and cooling were measured using a simultaneous thermal analyzer (STA 449 C Jupiter, Netzsch, Selb, Germany) consisting of both differential scanning calorimetry (DSC) and thermogravimetry (TG) (Fig. 1). The measurements were conducted with a heating- and subsequent cooling rate of 20 K/min and using argon as both protective

Table 1
Nominal and elemental composition of the G338 glass.

Component	Mol%	Element	Atom%
SiO$_2$	39.05	Al	13.1
Al$_2$O$_3$	13.13	Si	9.8
CaF$_2$	15.45	P	3
Na$_3$AlF$_6$	8.61	Ca	4.1
AlF$_3$	5.10	O	53.6
AlPO$_4$	18.66	F	14.3
		Na	5.5

and purge gas with flow rates of 18 mL/min and 40 mL/min, respectively. The measurements of the baseline and a sapphire reference were conducted to determine the isobaric heat capacity (C_p). Approximately 20 mg glass powder was put into a platinum crucible and gently pressed to ensure good heat transfer. The powder was upscanned to 1088 K, then downscanned to room temperature. From the upscan curves we detect the glass transition and various phase transitions in the glass. From the characteristic temperatures of phase transitions, we designed the heat treatment protocols for the glass, and then conducted XRD analyses on the heat-treated samples.

In order to determine T_g, another 20 mg sample was loaded and subjected to two runs of up- and downscans. The first scan was carried out to ensure a controlled thermal history (i.e. the sample downscanned at 20 K/min prior to the second upscan), whereas the second scan was done at the same rate for the determination of T_g [16]. The isobaric heat capacity (C_p) curve for each measurement was calculated relative to that of the sapphire reference using the standard Netzsch analysis program. T_g was defined as the onset temperature of glass transition on the second upscan C_p curve, which is the cross point between the tangent line of the glass C_p and the melt C_p line (Fig. 2).

XRD analyses were conducted on the as-received glass as well as dynamically heated glass samples. According to the DSC upscanning protocol, the glass samples were dynamically heated in the DSC at 20 K/min in argon to each of the characteristic temperatures (e.g., onset or peak temperatures of the crystallization peaks of the DSC curves) and then cooled to room temperature (RT) at 20 K/min. Subsequently, they were reground to fine powder and measured with a PANalytical diffractometer (Empyrean, PANalytical, Almelo, the Netherlands) with Cu K(α) X-rays at 45 kV and 40 mA in the range of $2\theta = 5$–$70°$. Reflection spinner mode was used with an interval of 0.013°, enabling quantitative as well as qualitative XRD analyses. The Highscore program was used for assigning crystal peaks. The refraction peaks are assigned to
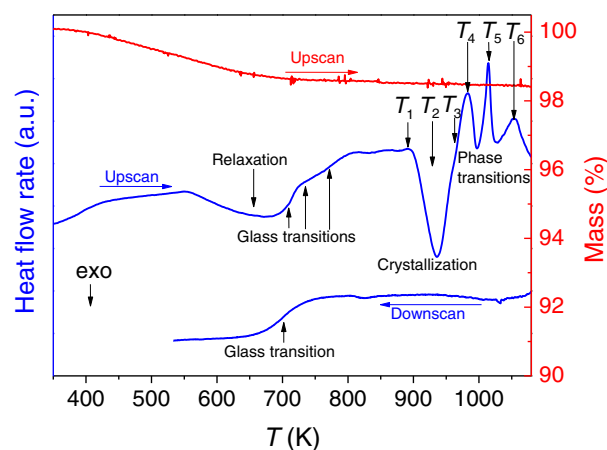
Fig. 1. Thermal responses of the as-received G338 sample during both the DSC upscan and downscan, respectively. Blue curves: Heat flow rate as a function of temperature (T). Red curve: Mass in percentage as a function of T. The relaxation, crystallization, phase transition peaks and the 6 characteristic temperatures (T_1 to T_6) are indicated with the vertical arrows.