Predicting Refractive Index of Fluoride Containing Glasses For Aesthetic Dental Restorations

Abstract

Objective Dental restoration aesthetics, particularly the translucency of modern dental restorative filling materials depends on the Refractive Index (RI) match between the different components in the material. In the case of dental composites (DC), the RI of the polymer must match the RI of the filler otherwise the material is optically opaque and has limited depth of cure. In the case of glass ionomer cements (GICs), the RI of the ion-leachable glass must match the RI of the polysalts to engineer a smart material with a tooth-like appearance. The RI of oxide glasses can be calculated by means of Appen factors. However, no Appen factors are available for the fluoride components in dental glasses. Therefore, the objective of this study is to empirically derive composition-specific Appen factors for the metal fluorides in complex multicomponent glasses for use in dentistry. **Methods** Two series of bioactive glasses and two series of ionomer-type glasses were produced for this study. Refractive indices of all glasses were then measured by the Becke Line technique. Thereafter, composition-specific factors for the metal fluorides were derived. **Results** It was found that increasing metal fluoride content reduces the RI of multicomponent dental glasses linearly. A series-specific Appen factors for the metal fluorides were successfully derived and allow RI calculation to within 0.005. **Significance** This paper proposes a modified Appen Model with composition-specific Appen factors for the metal fluorides for the development of dental restoratives with enhanced aesthetics and improved depth of cure of dental composites.

Key Words: aesthetics; glass ionomer cement; dental composite; fluoride; refractive index; translucency

1.0 Introduction

The aesthetics, particularly the translucency is an important feature of dental restorations. In order to obtain a translucent glass ionomer cement (GIC) or a dental composite (DC) it is essential to match the refractive index of the glass to the polymer or the polysalt cement matrix to avoid light scattering at the interfaces. Light scattering at the interfaces results in an opaque material. In DCs, light scattering because of a RI mismatch between the resin and the glass filler causes light attenuation and strongly influences the depth of cure of the composite material [1]. Furthermore, in photoactive resin based composites RI mismatch between the resin and the filler increases light scattering, however the RI of the resin changes dynamically during the curing process [2]. This can either increase or decrease light scattering depending on the refractive index match, i.e. if the RI of the filler matches the RI of the uncured resin, then light scattering will increase as the material polymerizes and if the RI of the resin is lower, then as the material polymerizes, light scattering will decrease and so will the opacity and light transmission through the material. Optimum RI matching and careful design of the DCs may produce DC materials with considerably improved optical properties. The only alternative way to obtain a highly translucent cement is to have well dispersed nano-sized particles where the dimensions of the particles are smaller than the wavelength of the visible light. Such fine scale powder particles are particularly difficult to manufacture as they have a high tendency to aggregate once mixed essentially forming larger clusters to reduce their high surface energy. Furthermore, it is difficult and costly to produce such nano particles particularly from melt-derived glasses. It is notable that translucent glass-ceramics are also produced by matching the RI between the different components in these multiphasic materials i.e. crystal phase/s and the residual “glassy” phase.

In the case of fluoride free glasses the RI of the glass can be calculated within about 0.01 by the means of Appen factors [3], which are empirically derived factors calculated on the basis of previous measurements of RIs of oxide glasses. Appen factors have been successfully used to calculate not only RI but also thermal expansion coefficients [4]. The RI of an oxide glass can be calculated using the following equation:

$$n_d = \frac{\Sigma^{n}{}_{i=1} n_{d,i} c_i}{100} \quad (1)$$

Where $n_{d,i}$ is the Appen factor (Table 1) for the respective oxide component and C_i is the mol % of the oxide component.

However, Appen factors for the metal fluorides are not available. Consequently, the refractive index of fluoride-containing glasses cannot be readily predicted. Fluoride components are known to reduce the RI of various glasses [5] and fluoride-containing glasses are attractive components for dental composites and particularly for GICs. The anticariogenic effects of fluoride have been long known [6]. Based on Scanning Electron Microradiography (SMR) *in vitro* studies, optimum fluoride concentrations under acidic conditions have also been proposed by Mohammed et al. [7].

However, despite the importance of RI it has rarely been measured for fluoride containing dental glasses there is only one peer reviewed article published in the literature. This article demonstrates how increasing CaF_2 content in bioactive glasses allows design of dental composite materials with improved optical properties, such as improved depth of cure and reduced light transmission [8]. Improved depth of cure of the DC will also result in increased longevity of the tooth restoration due to minimized shrinkage and increased polymerization.

The ability to model the role of metal fluorides on the RI of multicomponent glasses also allows the prediction of RI of fluorine-containing glass-ceramics (GCs) used in restorative dentistry, particularly GCs based on fluorapatite and fluormica phases. Since translucency is required for aesthetics, it is important to match the RI of the crystal phase to the residual glass phase. In these glass-ceramics, relatively large interlocking crystals are required to provide optimum strength and fracture toughness, as well as machinability in the case of mica glass-ceramics [9]. GCs containing nano-sized crystal phases would provide the desired aesthetics, however at the expense of mechanical properties and machinability. Therefore in summary it is necessary to develop a model by which RIs of fluoride-containing glasses can be predicted.

The objectives of this paper are to:

i) Measure the RI of two types of the fluoride-containing glasses used in glass (ionomer) cement formulations and as potential remineralising additives in various dental restorative materials.

ii) To develop Appen Factors for fluoride-containing glasses so that RIs of these glasses may be calculated which will allow the design of restoratives with improved translucency.

2.0 Materials and Methods

2.1 Glass Synthesis

Two series of bioactive glasses containing fluoride components were produced. These are given in Tables 2 to 3. The bioactivity of these two series of bioactive glasses was previously studied by Mneimne et al. [10] and Lynch et al. [11] respectively. In these glasses the metal fluorides were added to the composition rather than substituted for the metal oxide. All glasses were melted in platinum/rhodium 80/20 crucibles. Details of the synthesis conditions are given in the respective papers [10] and [11]. The first series of ionomer-type glasses (Table 4) are based on the series $4.5SiO_2 3Al_2O_3 1.5P_2O_5 (5-X)CaOXCaF_2$. In this series of ion-leachable glasses CaO is substituted for CaF_2 on a molar basis. These glasses were synthesized using a method described earlier by Stanton and Hill [12]. A second series of high fluorine ionomer-type glasses (Table 5) were provided by Cera Dynamics Limited (Stoke-on-Trent, UK). These high fluorine glass samples were produced in a custom-built cold-top furnace to prevent fluorine volatilization. Full chemical analyses of the industrially manufactured glasses was carried out by X-ray fluorescence. These glasses have much higher fluorine contents than the laboratory synthesized ionomer glasses whose compositions were designed to prevent fluorine loss as volatile silicon tetrafluoride [13].

2.2 Measurement of RI

Fluoride-containing glasses are prone to rapid crystallization [12] and fluoride loss on casting therefore as opposed to using Abbé refractometer refractive indices of the samples were measured by the Becke line test [14]. The refractive indices all fluoride-containing amorphous powdered glass samples were measured using polarized light microscopy by mounting the amorphous glass samples in suitable immersion liquids (Cargille, USA) and making observations of the Becke line. The immersion liquids have known refractive index values ranging from 1.45 to 1.70 with 0.01 intervals. Refractive Index measurements were performed at room temperature (~20 °C) using the sodium D line. The microscope was calibrated prior to each measurement using a known RI glass sample. Digital images of the glass samples were captured using a digital camera (Q Imaging, Canada) affixed to the microscope and digitised by manufacturer's software.

2.3 Appen factors

First, eq. (1) was used to calculate RIs of all glass samples. Since no Appen factors are available for the metal fluorides, the metal fluoride component contribution to the RI was underestimated. To compensate for this, multiple factors were tried for the respective metal fluoride (CaF_2/SrF_2) component until the calculated RI value matched to within 0.005 to experimentally derived RI value.

3.0 Results

All glasses used in the study were found to be amorphous by X-ray powder diffraction analyses. Figure 1(a-c) shows the RI as a function of CaF_2 , SrF_2 and F content for phospho-silicate bioactive glasses and alumino-silicate ionomer-type glasses. There is a linear decrease in RI with metal fluoride/elemental fluorine content. A comparison of the experimental and calculated RI values for Mneimne et al. [10] series of bioactive glasses shows a good correlation between the two (Figure 1(a)). However, for more complex F series of bioactive glasses containing additional oxide components it can be observed that there is a slight deviation between the experimental and calculated values with Ca/SrF_2 contents (Figure 1(b)). Figure 1(c) shows the RI for a series of ionomer glasses based on $4.5SiO_2 3Al_2O_3 1.5P_2O_5 (5\text{-}X)CaOXCaF_2$. The RIs calculated using Appen factors agrees well with the experimentally determined RIs. Figure 1(d) shows the RI as a function of F content for the industrially manufactured high fluorine (PF) series (Table 4) of glasses. In summary, there is a clear linear relationship between fluoride content (either as elemental F or as a metal fluoride) and refractive index of the glasses studied. Table 6 shows series-specific Appen factors derived from this study.

4.0 **Discussion**

Based on the experimentally derived RIs of the fluorine-containing glass samples, a linear (R^2=0.98) correlation between elemental fluorine/metal fluoride content and the refractive index of glasses is clearly observed. Generally, fluorine containing glasses have larger atomic spacings and therefore more disrupted structure. Larger spacing in the glass network results in the reduction in glass density and thus is attributed to lower refractive index. It has been long known that there is a linear correlation between density and refractive index in glasses [15]. However, many materials other than glasses do not exhibit this phenomenon. It may not be surprising that incorporation of fluoride lowers the dielectric constant of the glasses which is observed in other dielectric materials [16] and results in reduced polarizability and henceforth a reduction in refractive index.

For the first series of bioactive glasses developed by Mneimne et al. [10] calculated and measured RI values are matching within 0.005. In this series, it was found that CaF_2 contributes to the RI by a factor of 1.42, which is quite close to the RI of crystalline CaF_2, which at room temperature is 1.4338 [17]. It is notable that solid-state ^{19}F MAS-NMR studies of related glasses by Brauer et al. [18] have shown fluorine to be present as F-M(n) species where M is largely Ca with a small fraction of Na and n is close to four molecular dynamics simulations by Christie et al. [19] predict the formation of F-Ca(n) species. Thus in these glasses the fluorine exists in a fluorite like F-Ca(4) environment and it is therefore not surprising that the RI can be predicted based on a model assuming the presence of a fluorite-like environment. Furthermore, Brauer et al. [20] measured the density of CaF_2 containing bioactive glasses and showed the density could be predicted based on the assumption of fluorine existing in a CaF_2 like environment and using a density factor for crystalline CaF_2. It is worth noting that in the present glasses, as well as the ones studied by Brauer et al. [20] the CaF_2 was added to the glass rather than being substituted for CaO and in these glasses there is no change in the non-bridging oxygen content and the Q speciation of the silicon remains constant. In the original studies of Hench et al. [21] and more recently by Lusvardi et al. [22] CaF_2 was substituted for CaO which results in changes in the non-bridging oxygen content of the glass and the silicon speciation as well as potential loss of fluorine as silicon tetrafluoride during melting.

The calculations for the second series of bioactive glasses (Table 3) [11] with strontium and potassium components have also been performed by assuming the nominal proportions of CaF_2 and SrF_2 incorporated in the original glass composition. It was found that metal fluorides contribute to the RI by a factor of 1.45 (CaF_2) and 1.47 (SrF_2), which is higher than the factor for the first series. In the final melted glass composition the fluorine might be expected to form more F-Ca(n) species than F-Sr(n) species since Ca^{2+} has a slightly smaller ionic size than Sr^{2+} and this might be expected to favour F-Ca(n) speciation. In addition there is likely to be mixed F-Ca/Sr(n) and F-Na(n) sites where Na and Ca is more prevalent than Sr and this may an effect on the RI and hence may explain why the Appen factor for the metal fluoride component in this series is higher.

Appen factor for CaF_2 for the first series of aluminosilicate glasses (Table 4) was found to be 1.59, which is much higher when compared to the RI of crystalline CaF_2. In addition, it was also found that Appen factor for P_2O_5 is different from that published by Appen [3] and is around 1.48 for this series of glasses. This may be due to different phosphorus speciation in glass compositions containing aluminium and can be linked to several structural aspects [23].

Characterization by ^{19}F, ^{31}P, ^{29}Si and ^{27}Al MAS-NMR [24] indicate that the structure of ionomer type glasses is much more complex than the fluoride containing bioactive glasses. The fluorine can exist as Al-F-Ca(n), as well as F-Ca(n) and the proportion of these two species changes with the glass composition [24]. The assumption of the glass consisting of a CaF_2 free glass plus CaF_2 like species in the calculation of the RI is only partially valid and neglects the presence of Al-F-Ca(n) species. In addition substituting CaF_2 for CaO may also reduce the non-bridging oxygen content of the glass, which will also influence the RI. In addition increasing fluorine content can cause the Al to move from Al(IV) to higher coordination states of V and VI.

Due to the complexity of the second series of high-fluorine ionomer-type glasses (Table 5) the data is expressed as measured RI as a function of elemental fluorine content. These compositions contain excessive amounts of fluorine and further structural characterization is ongoing. However, RIs that all within the compositional domain of this series of glasses can also be predicted based on the amount of elemental fluorine in mol% using equation for straight line expressed in Figure 1(d).

Most commercial ionomer glasses also contain small amounts of sodium whereby it forms Al-F-Na(n) species in the glass in addition to Al-F-Ca(n) and F-Ca(n) species. Furthermore, many commercial glasses also contain strontium [23], which will result in Al-F-Sr(n) and F-Sr(n) speciation in addition to mixed species if calcium is included in the composition. In general the amount of sodium in ionomer glass compositions is typically less than 1% so the formation of Al-F-Na(n) species is not likely to have a large influence on the RI of ionomer-type glasses.

In regard to glass ionomer cements it is necessary that the RI of glass matches the RI of the polysalt matrix. This can be quite well facilitated in cement compositions where the initial difference between refractive index of the glass and the refractive index of the polyacid solution is lower.

5.0 Conclusions

The RI of fluoride containing bioactive glasses correlates linearly with metal fluoride content and the RI can also be predicted readily using Appen factors close to that of fluoride containing crystalline phases, such as CaF_2 as proposed in the study. The RIs of the more complex ionomer glasses also demonstrate a linear relationship with fluoride content. Nonetheless, the paper proposes a modified Appen Model with new composition-specific Appen factors for the metal fluorides for the development of highly translucent dental materials and improved depth of cure of dental composites. The present study also provides a very useful tool for the design of highly advanced restorative materials which can exhibit bioactivity alongside improved aesthetics and increased restoration longevity.

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Tables

Table 1: Appen factors for various oxides [3]

Oxide	Appen Factor
SiO_2	1.4585
Al_2O_3	1.52
P_2O_5	1.31
Na_2O	1.575
ZnO	1.71
K_2O	1.575
CaO	1.73
SrO	1.775

Table 2: Compositions of laboratory bioactive alkali phospho-silicate glasses (mol %) [10]

	SiO_2	P_2O_5	CaO	CaF_2	Na_2O
B2	36.41	6.04	24.74	4.53	28.28
C2	34.60	5.74	23.51	9.28	26.87
D2	32.95	5.47	22.38	13.62	25.59
E2	31.37	5.21	21.31	17.76	24.36
F2	28.40	4.71	19.29	25.54	22.06

Table 3: Compositions of multicomponent bioactive glasses in mol% [11]

	SiO_2	P_2O_5	CaO	CaF_2	SrO	SrF_2	Na_2O	K_2O	ZnO	CaF_2 + SrF_2
F0	44	5	15	0	15	0	10	10	1	0
F4	41.91	4.76	14.29	2.38	14.29	2.38	9.53	9.53	0.95	4.76
F13	38.01	4.32	12.96	6.81	12.96	6.81	8.64	8.64	0.86	13.62
F17	36.19	4.11	12.34	8.88	12.34	8.88	8.22	8.22	0.82	17.76
F25	32.76	3.72	11.17	12.77	11.17	12.77	7.45	7.45	0.74	25.54
F32	29.61	3.36	10.09	16.36	10.09	16.36	6.73	6.73	0.67	32.72

Table 4: Compositions of model laboratory ionomer-type glasses in mol %

	SiO_2	Al_2O_3	P_2O_5	CaO	CaF_2
LG99	32.14	21.43	10.71	14.29	21.43
LG95	32.14	21.43	10.71	20.00	15.71
LG134	32.14	21.43	10.71	25.00	10.71
LG115	32.14	21.43	10.71	28.57	7.14
LG116	32.14	21.43	10.71	35.71	0.00

Table 5: Compositions of high fluorine ionomer-type glasses produced by Cera Dynamics Limited (mol %)

	SiO_2	Al_2O_3	P_2O_5	Na_2O	CaO	SrO	Fluorine
PF124	20.00	14.47	1.87	5.15	0.13	8.47	49.90
PF125	28.71	17.48	2.12	1.67	0.09	15.63	34.30
PF126	23.35	13.30	2.05	5.32	0.12	8.86	47.00
PF127	29.16	15.88	2.56	1.66	0.08	15.51	35.15
PF128	25.03	15.90	7.44	1.67	23.61	0.46	25.89
PF129	25.73	17.34	8.37	1.32	26.98	0.08	20.18
PF130	27.85	18.14	4.34	1.55	27.80	0.02	20.30
PF131	26.17	17.73	4.21	1.48	12.59	16.01	21.81

Table 6: Empirically derived Appen factors

	CaF_2	SrF_2	P_2O_5
[8]	1.42	-	-
[9]	1.45	1.47	-
LG	1.59	-	1.48