

“Research Note”

**THE EFFECT OF THE ADDITION OF ZrO₂, TiO₂ NUCLEATING AGENTS ON
SETTING, WORKING TIMES AND COMPRESSIVE STRENGTH
OF A GLASS IONOMER DENTAL CEMENT***

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Abstract – The effect of the addition of nucleating agents such as ZrO₂ and TiO₂ on setting, working times and the compressive strength of a SiO₂-Al₂O₃-MgO-CaF₂ restorative glass ionomer cement has been investigated using differential thermal analysis and X-ray diffraction. The addition of 2.5% ZrO₂ resulted in the formation of anortite, MgF₂ and CaF₂ crystalline phases more than the addition of the same amount of TiO₂, and hence the setting, working times and compressive strength of the glass ionomer cement were notably increased. An increase in the heat treatment time caused an increase in the formation of the named crystalline phases.

Keywords– Glass ionomer dental cement, nucleation, crystalline phase, compressive strength

1. INTRODUCTION

Glass ionomer dental cements are formed by the setting reaction of an aqueous solution of a polyalkenoic acid such as acrylic or itaconic acid and an ion-leachable glass powder frequently containing SiO₂, Al₂O₃, CaF₂ and sometimes PO₄³⁻ and oxides such as Na₂O, CaO and BaO [1-4]. The hard cement is usually formed within a 2-10 minute setting time, having a compression strength around 200 N/mm². This value is compared with reported values of 96-386 N/mm² for human enamel [1].

The effects of crystalline phase formation on physical and mechanical properties, as well as working and setting times of a specific glass ionomer cement, have been studied by Wilson [5]. It was found that anortite phase formation in the glass causes a reduction of Ca, Al cations, and therefore working and setting times, as well as mechanical properties of the resulting cement have notably been increased. The incorporation of nucleating agents in the powder enhances the formation of such crystalline phases, which are increased via the proper heat treatment [5,6].

Thermal analysis of a glass containing the principal components, CaO using the pyrohydrolysis method and nucleating agents such as TiO₂, ZrO₂ and silver was studied by Hill [6]. It was reported that these nucleating agents were ineffective in the named glass at temperatures above the glass transition. That is, they can not induce liquid-phase separation upon heating for the crystallization of anortite to occur at high temperatures.

The purpose of this study was to evaluate the effects of nucleating agents such as TiO₂ and ZrO₂, and the heat treatment time on the crystalline phase formation in a SiO₂-Al₂O₃-MgO-CaF₂ glass, and thereby to compare the working, setting times and the compressive strength of glass ionomer cement with those of the conventional restorative cement.

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2. MATERIALS AND METHOD

a) Materials

Alumina (Al_2O_3) was obtained from the Martinswerk Company of Germany. Silica (SiO_2), magnesium oxide (MgO), kryolite (NaAlF_6), aluminum phosphate (AlPO_4), zirconia (ZrO_2) and titanium oxide (TiO_2) were all obtained from the Merck Chemical Company. The purity of all the above materials was greater than 99%.

The liquid part of the glass ionomer cement was chosen to be the commercial Fuji ionomer II restorative material. A four component glass, namely SiO_2 - Al_2O_3 - MgO - CaF_2 (mole ratios, 5:2:2:1.5) was prepared as the basic glass (MZTO). The formulation of this glass was chosen somehow to form the anortite and cordierite phases after the heat treatment. Along with the above components, AlPO_4 and Na_3AlF_6 were added to the formulation of the glass (see Table 1).

Table 1. Glass components

Component	Weight%
SiO_2	34.22
Al_2O_3	23.27
CaF_2	19.17
MgCO_3	13.34
AlPO_4	7
Na_3AlF_6	3

b) Glass preparation without the presence of the nucleating agents

The components listed in Table 1 were mixed together and ball milled for 2 hours. The mixture was transferred to zircon crucible and vacuum dried. Zircon decomposes at $1650\text{ }^\circ\text{C}$, therefore it was safe to use the crucible at $1300\text{ }^\circ\text{C}$ [10]. It was then heated at $1300\text{ }^\circ\text{C}$ with a heating rate of approximately $10\text{ }^\circ\text{C}/\text{min}$ in the air for 1 hour. The glass melt was then chock quenched by pouring it into demineralized water. The frit was then ground in a planetary mill to produce a fine powder, with the average particle size of approximately $100\text{ }\mu\text{m}$.

c) Glass preparation with the presence of the nucleating agents

Glasses listed in Table 2 were prepared containing different amounts of nucleating agents, TiO_2 and ZrO_2 , and classified as MZ and MT glasses.

Table 2. Glasses with different amounts of nucleating agents

Nucleating agents	MZT0	MZ1	MZ2	MZ3	MZ4	MT1	MT2	MT3	MT4
ZrO_2 (Wt%)	0	2.5	5	7.5	10	0	0	0	0
TiO_2 (Wt%)	0	0	0	0	0	2.5	5	7.5	10

d) Differential thermal analysis (DTA)

Differential thermal analysis (DTA) experiments for determining the crystallization temperatures of the samples were performed on Model 404 S, Netzsch instrument of Germany. The crucibles used were made of platinum, and Al_2O_3 powder was used as the reference material. The DTA experiments were conducted at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$, and a maximum temperature of $1100\text{ }^\circ\text{C}$. After reaching the crystallization temperature, each sample was heat treated at this temperature for 1hr. The samples were then poured into demineralized water and the resulted frits were ground in a planetary mill to obtain fine powders.

e) Heat treatment of the samples

In order to increase and study the amount of phase formation and also the development pattern of the crystalline phases, MT1 and MZ1 samples were heat treated longer at a rate of $20\text{ }^\circ\text{C min}^{-1}$ up to the crystallization temperature. The heat treatment times of these samples are listed in Table 3.

f) Powder X-ray diffraction (XRD)

Powder XRD was conducted on a Siemens D500 from Germany. In these experiments, $K_{\alpha} = 0.54 \text{ \AA}$, and the samples analyzed from $\theta = 0-60^{\circ}$.

Table 3. Holding time of MZ1 and MT1 samples in the treatment furnace

Sample	heat treatment time(hr)
MZ1, MT1	0
MZ1(t ₁), MT1(t ₁)	1
MZ1(t ₂), MT1(t ₂)-	2
MZ1(t ₃), MT1(t ₃)	3

t₁₋₃ are the heat treatment times

g) Physical and mechanical tests

In order to study the effects of heat treatment on working, setting times and the compressive strength of the ionomer cements, Fuji II liquid was used as the liquid part of the cement. The working, setting times and compressive strengths were then measured in accordance with ISO 9917 and BS 29917 standards [7, 8].

3. RESULTS AND DISCUSSION

Figures 1 and 2 show the DTA curves for MZ and MT samples, respectively. In each figure, the curve for the MZT0 sample is drawn for the comparison. Exotherms, endotherms and glass transition temperatures (T_g) listed in Table, were obtained from the DTA curves. As can be seen from Table 3, the MZT0 sample has the lowest exotherm among MZ and MT samples. Also, it was noticed that the MT4 sample has two exotherms, a broad peak at 820 °C and a small sharper one at 850 °C.

The approximate glass transition temperatures of the samples, except for MZ3 and MZ4, are more or less the same as for the MZT0 sample.

Table 4. Exotherm, endotherm and glass temperatures of the samples

Sample	MZT0	MZ1	MZ2	MZ3	MZ4	MT1	MT2	MT3	MT4
Exotherm(°C)	758	840	856	834	834	810	810	834	840 850
Endotherm(°C)	1010 1100	1018 1100	1018 1100	1024 1100	1100	1130	1100	1000	1000
T _g (°C)	630	635	640	700	750	620	620	650	670

As seen in Table 4, the glass transitions (T_g) of the samples were noticeably changed by the addition of larger amounts of TiO₂ and ZrO₂ (MZ₃, MZ₄ and MT₃, MT₄). This is because with low amounts of TiO₂ and ZrO₂, that is 2.5 and 5 percents, the viscosity of the glass phases, which is an important and effective factor on the glass transition, does not change. But for the higher amounts of nucleating agents (7.5 and 10 percents) these phases act as the original phases, and therefore the glass transition temperatures are increased. That is, the increase in the viscosity changes the glassy temperatures to higher degrees. These changes are even more pronounced for higher amounts of ZrO₂, because this nucleating agent increases the viscosity more than TiO₂, and hence results in a higher T_g of the related samples.

According to Table 4, with the addition of, for example 2.5% of TiO₂ to the samples, the crystallization temperature of the powder increases from 758°C to 810°C. This increase is due to refractoriness of the glass. It is also noticed from the XRD patterns that this results in a higher anortite phase in the MT1 sample than in the MZT0. This is due to the easier atomic transitions at the higher temperature, however the changes in the crystallization temperature are not so much for those samples with higher amounts of TiO₂, that is 5, 7.5 and 10 percents.

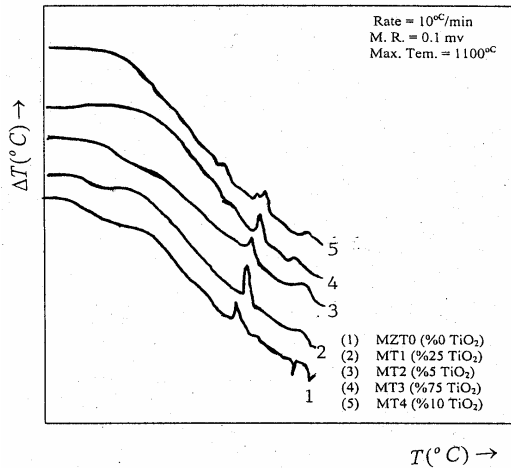


Fig. 1. DTA thermograms for MT samples

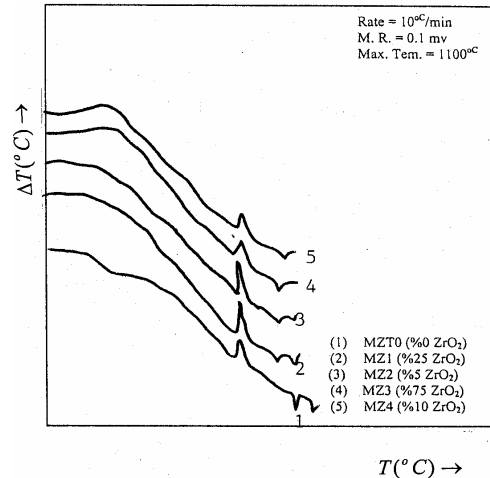


Fig. 2. DTA thermograms for MZ samples

The XRD patterns of the samples, each one heat treated at the crystallization temperature, are shown in Figs. 3 and 4. It is noticed from Fig. 3 that among MT samples, the MT1 has more crystalline phases such as anortite, MgF_2 and CaF_2 . This sample contains 2.5wt% TiO_2 as the nucleating agent. At the same time, Fig. 4 indicates that MZ1 has the highest crystalline phases among the MZ samples. An XRD comparison of the MZ1 samples revealed that the crystalline phases in the former are more pronounced. This means that ZrO_2 is a more efficient nucleating agent in these experiments.

The effect of the heat treatment time on the formation of the crystalline phases of the sample contains ZrO_2 (MZ1), indicating that the elapse of time enhances the crystalline phase formation (Fig. 5). Although there is little difference in the anortite peak of 100 in the 2 and 3 hr heat treated samples, new phases are formed during the 3 hr heat treatment, and also the rest of the peaks are sharper and more pronounced. In these figures, a= anortite, m= MgF_2 , s= Mg_2SiO_4 and c= CaF_2 phases.

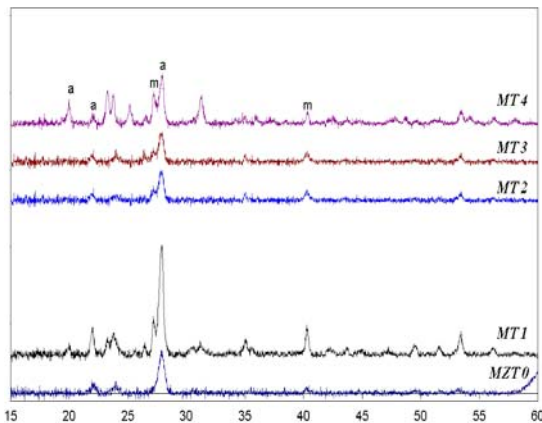


Fig. 3. Powder XRD pattern of MT samples

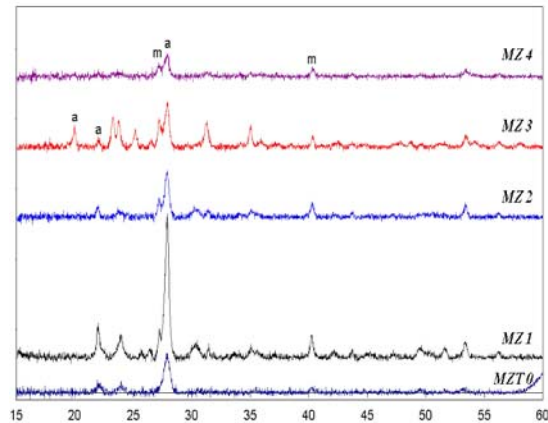


Fig. 4. Powder XRD pattern of MZ samples

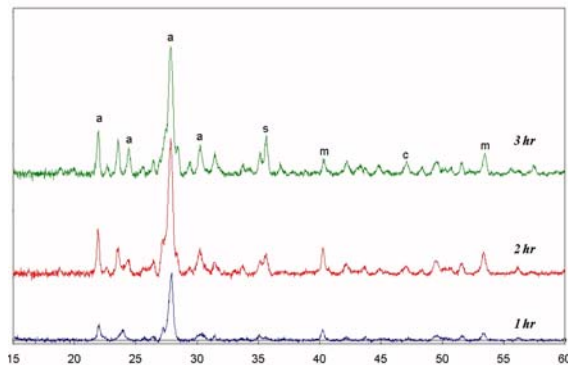


Fig. 5. The effect of heat treatment time on the crystalline phase formation of the MZ1 powder

Heat treatment of the samples increases the working and setting times. This is due to the formation of the anortite phase ($CaO \cdot Al_2O_3 \cdot 2 SiO_2$) and so a decrease of Al, Ca cations from the glass has occurred [9]. The heat treatment time also has an effect on the working and setting times of the MZ1 sample. The results of the related experiments are listed in Table 5. The working and setting times of MZ1 powder, when mixed with the Fuji II liquid, is more than twice as much as for the sample MZ1, which is not heat treated. This was also true with the compressive strength of the MZ1 sample that underwent heat treatment.

For a comparison of the results with those of the conventional cement, it is noticed from Tables 5 and 6 that the setting and working times, as well as the compressive strength, are all higher than the conventional restorative cement. The effect of nucleation can even be seen in MZ1 which has not undergone heat treatment. The working, setting times and compressive strength of this sample (with 2.5% ZrO_2) are respectively 1.7, 1.27 and 1.06, times the conventional restorative cement, while for sample MZ1(t_3) these ratios are 3.91, 3.1 and 1.18 times, respectively. This means that although the compressive strength and working times of the sample are increased as a result of the formation of the crystalline phases, the setting times are also increased. In order to lower the setting times, an appropriate accelerator such as tartaric acid could be added to the liquid part of the ionomer cement, which will be considered for further studies.

Table 5. Effect of heat treatment time on working setting times of the ionomer cement

sample	Setting time (min-sec)	Working time (min-sec)	Time of the heat treatment (hr)
MZ1	6.70	2.55	0
MZ1(t_1)	12.75	4.36	1
MZ1(t_2)	13.36	4.75	2
MZ1(t_3)	15.26	6.12	3
Conventional Restorative cement	4.00	2.00	-

Table 6. Effect of the heat treatment time on compressive strength

	Conventional restorative cement	MZ1	MZ1(t_1)	MZ1(t_2)	MZ1(t_3)
Compressive strength(MPa)	174	181	185	194	205

4. CONCLUSIONS

Heat treatment of samples increases the working and setting times of the cements (Table 4). The results of the compressive strengths, as listed in Table 5, indicate that restorative cement samples all have a higher strength compared to that of the conventional restorative cements obtained by mixing the Fuji II restorative liquid with the powder. As listed in Table 6, the heat treatment time of 3 hrs, has a profound effect on the compressive strength of the resulting cement MZ1 (t_3) and increased the strength of the conventional restorative cement by approximately 16 percent.

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REFERENCES

1. Bowen, R. L. (1963). Glass ionomer cements, *J. Am. Dent. Ass.*, 66, 307.
2. Wilson, A. D., Crisp, S., Prosser, H. J., Lewis, B. G. & Merson, S. A. (1980). Aluminosilicate glasses for polyelectrolyte cements. *Ind. Eng. Chem. Prod. Res. Dev.*, 19, 263-70.
3. Ducheyne, P. (1985). Bioglass coatings and bioglass composites as implant materials. *J. Biomed. Mater. Res.* 19, 273-9.

4. Ogino, M., Hench, L. L. (1980). Formation of calcium phosphate films on bioactive glasses. *J. Non-Cryst. Solids*, 38, 673-38.
5. Wilson, A. D. & Mclean, J. W. (1988). *Glass ionomer cements*. Chicago, IL: Quintessence Books, 16-24, 125-163.
6. Hill, R. G., Goat, C. & Wood, D. (1992). Thermal analysis of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-CaF}_2$ glass. *J. Am. Ceram. Soc.*, 7(4), 777-85.
7. British Standard Institution (1994). *Specification for dental water-based cements*. BS EN.
8. International Standards Organization (1991). *International standards for dental water-based cements*. ISO 9917.
9. Prosser, H. J., Powis, D. R. & Wilson, A. D. (1984). Characterization of glass ionomer cements. The physical properties of current restorative materials. *J. of Dentistry*, 12(3) 231-240.
10. Grayson, M. (1984). *Encyclopedia of glass, ceramics, and cement*. John Wiley and Sons, New York, 748.

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