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The influence of Al/Si ratio and post melting thermal treatment on the reactivity of aluminate –silicate glasses used for dental cements preparation

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The influence of both glass powders composition (Al/Si ratio) and post-melting treatment temperature on some of the properties (setting time, compressive strength and solubility) of the silicate dental cements was investigated. Two silicate cements were used in this study. The properties of the studied cements comply with the required for dental cements regarding the setting time, mechanical strength and solubility. In order to study the interaction processes X-ray diffraction analyze (XRD), scanning-electron microscopy (SEM) and electron-dispersion spectroscopy (EDS) analyses were used. The reactivity of the tested aluminate-silicate glasses towards the partial neutralized ortho-phosphoric acid solution increases with the increase of the Al/Si ratio. The glass powder reactivity can be reduced by supplementary thermal treatments at low temperatures (600^{o}C). The silicate cements could be used for anterior restoration due to their high aesthetic properties.

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Keywords: Silicate dental cement, Silicate-aluminate glass, Al/Si ratio, Post melting thermal treatment

1. Introduction

The silicate cement represents a dental binding material, prepared by the mixing of a solid compound (powder) with a aqueous solution of partially neutralized orto-phosphoric acid. This type of cement can be used for the restoration of the front teeth and for dental crowns fixing [1, 2]. Silicate dental cement exhibits better mechanical properties and hydrolytic stability as compared to ZnO – phosphate cement [1-3]. It has, also, a cariostatic action due to its fluoride content [1-3].

The solid compound is a finely grounded aluminate-silicate glass. The glass was prepared by melting and quenching in water of a mixture containing SiO_2, Al_2O_3, CaO and F^- as principal components [1-5]. The properties of the silicate cement are influenced by the oxide and phase composition of the glass powder, the melting temperature and the post-melting thermal treatment, the neutralization degree of the phosphoric acid solution and the solid-liquid ratio in the mixture of the two compounds [1-5].

This paper brings information concerning the influence of the chemical composition and the post melting thermal treatment on the reactivity of the glass powders and on the properties of the resulted silicate dental cement.

2. Materials and methods

Two SiO_2-Al_2O_3-CaF_2 glasses with 0.95 and 1.07 Al/Si ratio and with the same amount of fluorite were prepared (table 1).

Table 1. The chemical composition of the glasses.

Glass symbol	The composition of the glass (%)				Al/Si
	Si^{4+}	Al^{3+}	Ca^{2+}	F^-	
M1	27.41	26.17	23.81	22.60	0.95
M2	25.88	27.71	23.81	22.60	1.07

The glass was prepared by the melting and subsequent quenching of a mixture of aluminate-silicate gel (prepared by the sol-gel method using as precursors TEOS and $Al(NO_3)_3$) and fluorite.

The thermal treatment was performed at 1300°C for 30 minutes and the shock quenching was carried out by pouring the melt directly into ice cold distilled water. After drying, the glasses were ground up to total passing through the 45 μm sieve. In order to modify the glasses reactivity, the powders were thermally treated at 600°C for 1 hour.

The liquid compound was an aqueous phosphoric acid solution, partially neutralized at 23°C with Al_2O_3 and ZnO, corresponding to a molar ratio Al_2O_3/ZnO = 1.39.

The standard consistency, setting time and solubility of the resulting dental cements were assessed according to the BS 3365: Part 2: 1987 and BS EN 29917:1994 standards.

The compressive strength was tested on paste specimens (cylinders with ϕ = h = 10 mm), kept at 37°C, one hour in the mold and after in distilled water up to 7days.

Room temperature XRD measurements used for the study of the interaction processes during the hardening of

the dental cements were performed with a SHIMADZU XRD 6000 diffractometer, using Ni-filtered CuKα radiation (λ=1.5418 Å) with scan step of 0.02° and counting time of 0.6 s/step, for diffraction angles 2 theta ranged between 5 and 60°.

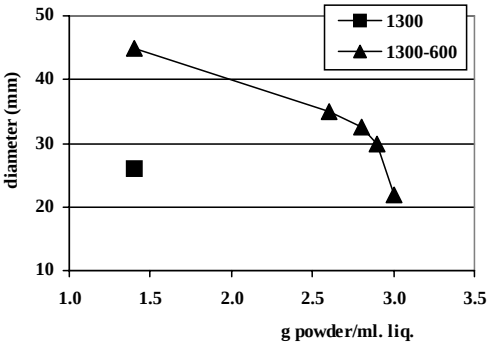
The hardening structure and morphology of the resulted dental cement was investigated by SEM & EDS analysis using a HITACHI S2600N equipment.

3. Results

3.1 The properties of silicate cements

3.1.1 The consistency of the cement pastes

The values for standard consistency –figure 1, show that the increase of the Al/Si ratio determines an increase of the powders reactivity and therefore the amount of powder necessary for the standard consistency diminishes.



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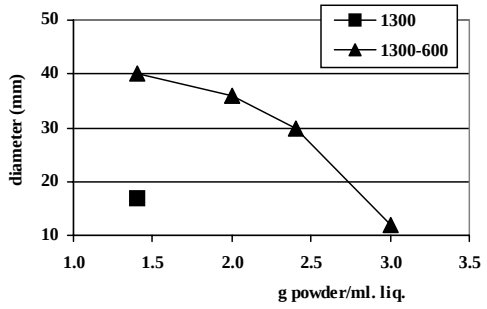

b

Fig. 1. The flow slump diameter obtained from 0.5 ml cement paste prepared with glass M1 (a) and M2 (b) versus the powder/liquid ratio; 1300 – glass prepared by melting at 1300°C/30 min.; 1300-600 – glass prepared by melting at 1300 °C and subjected to a post melting treatment at 600°C/1 hour.

3.1.2 The setting time

The setting time and consistency values for the cements prepared by using M1 and M2 glasses are presented in figure 2.

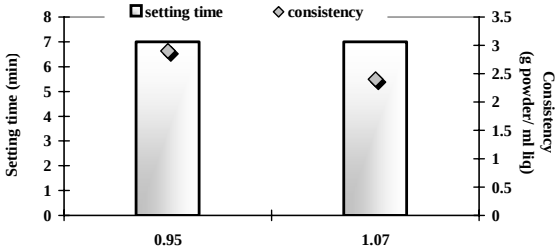

Fig. 2. The influence of the Al/Si ratio (of the solid compound - glass) on the silicate dental cement setting time and standard consistency.

3.1.3 Compressive strength

The mechanical strength values assessed on the compositions with setting times values between four and ten minutes are presented in Fig. 3.

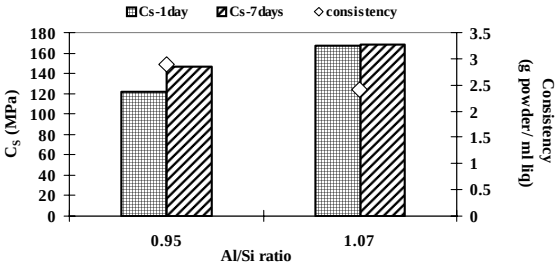

Fig. 3. The influence of the solid compound (glass) Al/Si ratio on the silicate dental cements compressive strength (C_s).

3.1.4 The solubility in neutral and acid solutions

The solubility values presented in table 2 brings information regarding the hydrolytic stability of the studied aluminate-silicate-phosphate cements.

Table 2. The solubility values of aluminate-silicate-phosphate cements prepared by using M1 and M2 glasses subjected to the post-melting treatment (at 600°C for 1 h).

Powder (Al/Si)	Solid/liquid ratio (g powder/ ml liq.)	C_S (MPa) after:		$S_{24\,h}$ (%)	
		1 day	7 days	Distilled water (pH=6.6)	Lactic acid (pH=5)
M1 (0.95)	2.9	122.3	146.75	0.46	0.58
M2 (1.07)	2.4	167.52	168.15	0.22	0.5

3.2 Interaction processes at the hardening of silicate cements

The XRD patterns of the M1 and M2 glasses and of the corresponding silicate dental cements pastes hardened for 1 day and 7 days are presented in Figs .4 and 5.

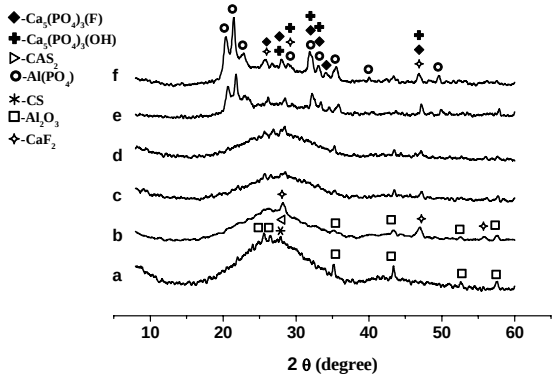

Fig. 4. XRD patterns of: a – M1 glass prepared by thermal treatment at 1300°C/ 30 minutes; b – M1 glass prepared by thermal treatment at 1300°C/30 minutes and subjected to a post-melting treatment at 600°C/1 hour (M1-1300-600); c, d – hardened silicate cements based on M1-1300-600 glass after 1 day and 7 days of hardening; e, f – M1-1300-600 binding masses hardened 1 day and 7 days respectively, subjected to an additional thermal treatment at 650°C/1 hour.

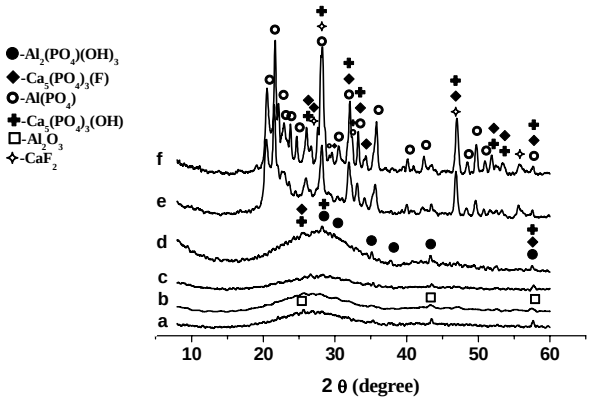

Fig. 5. XRD patterns of: a – M2 glass prepared by thermal treatment at 1300°C/ 30 minutes; b – M2 glass prepared by thermal treatment at 1300°C/30 minutes and subjected to a post-melting treatment at 600°C/1 hour (M2-1300-600); c, d – hardened silicate cements based on M2-1300-600 glass after 1 day and 7 days of hardening; e, f – M2-1300-600 binding masses hardened 1 day and 7 days respectively, subjected to an additional thermal treatment at 650°C/1 hour.

The SEM images and EDS spectra performed on 1 day hardened cements are presented in Figs. 6 and 7.

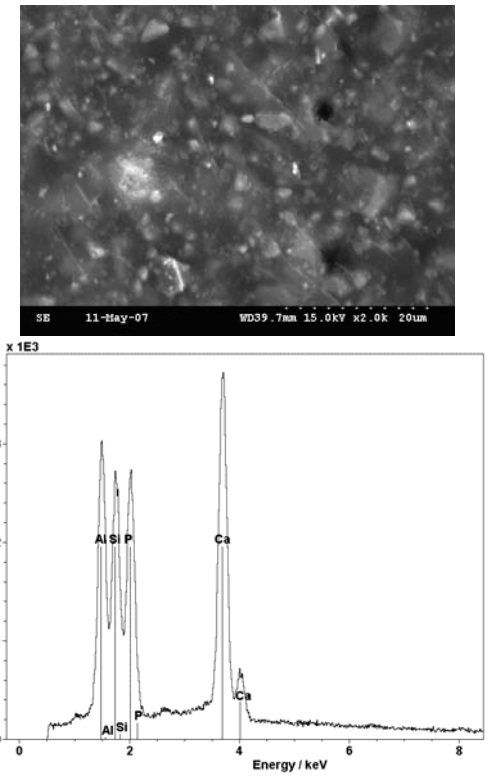

Fig. 6. SEM image (a) and EDS spectrum (b) analysis of 1 day hardened silicate dental cement based on M1 glass (prepared at 1300°C/30 minutes and subjected to a post melting treatment 600°C/1h).

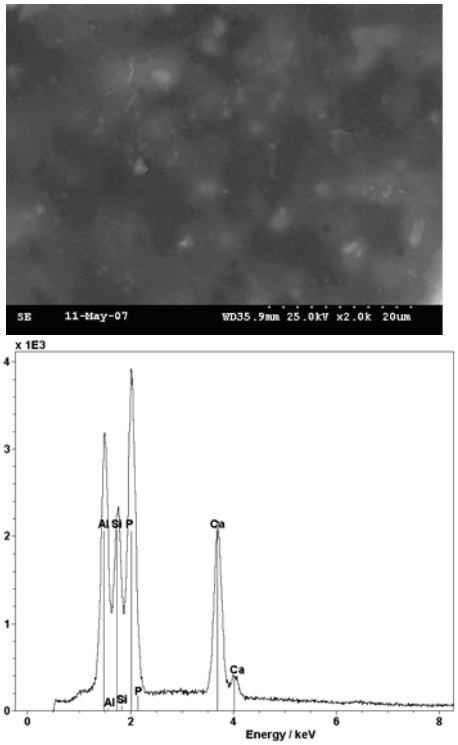

Fig. 7. SEM image (a) and EDS spectrum (b) analysis of 1 day hardened silicate dental cement based on M2 glass (prepared at 1300°C/30 minutes and subjected to a post melting treatment 600°C/1h).

4. Discussion

4.1 The properties of silicate cements

4.1.1 The consistency of the cement pastes

According to Wilson et al. [6] the most important factor in determining the cement properties is Al/Si ratio. The glass network consists mainly of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra in an alternating sequence [7, 8]. The oxygen linkage between adjacent aluminum and silicon tetrahedral is vulnerable to theacid attack. The Al^{3+} ion has a weaker field than that of Si^{4+} ion and as a result it interacts less strongly with the electron clouds of the oxygen anions leaving them with sufficient residual polarisability to be susceptible to acid attack [7]. Consequently, the increase of the Al^{3+}content will lead to the increase of the glass reactivity versus the phosphate solution.

The reactivity of the M1 and M2 glasses was very high, therefore the standard consistency was obtained only for very small solid/liquid ratios, inadequate for dental cements.

The post-melting thermal treatment of the glass powders at 600°C for 30 minutes deactivate the glass as a result of crystallization processes. From this point of view Hill and co-workers noticed the fluorite crystallization at the glass surface [7]. Therefore, the reactivity of the powders towards the phosphoric acid solution diminishes and it is possible to include a bigger amount of powder in one ml of liquid (increase of the standard consistency).

4.1.2 The setting time

A high value of Al/Si ratio determines an increase of the glass reactivity and consequently a decrease of the powder/liquid ratio.

Due to the different powder/liquid ratio used for cements preparation the two complementary effects (of the Al/Si ratio and powder/liquid ratio) lead to the same setting time value for both studied masses.

4.1.3 Compressive strength

As it was already mentioned the studied aluminate-silicate-phosphate cements develop good mechanical strengths, between 122-167 MPa after 24 hours and 146-168 MPa after 7 days. For composition M1 (with a lower value of the Al/Si ratio i.e. a lower reactivity) the hardening processes carry on at later ages (after 24 hours), so the mechanical strength increases with almost 42 % in the next 7 days.

4.1.4 The solubility in neutral and acid solutions

The increase of the Al/Si ratio determines the decrease of the dental cement solubility in water and lactic acid. The lower solubility values corresponding to the dental cements prepared with M2 glass are very likely due to the high compressive strength values of this masses (see also figure 3).

So, the solubility of the cement is given by the solubility of the binding matrix, but depends by the thickness and the uniformity the binding layers witch surrounds the unreacted glass grains.

4.2 Interaction processes at the hardening of silicate cements

The reaction products formed during the dental cement hardening are mainly amorphous phases – see the hallo present at 2θ=20-30° on XRD patterns.

The following crystalline compounds were identified on the XRD patterns of the 7 day hardened cement based on M2 glass (figure 5 – d): augelite - $Al_2(PO_4)(OH)_3$ (1.58 Å; 1.60 Å; 1.69 Å; 1.74 Å; 1.83 Å; 1.85 Å; 1.89 Å; 1.94 Å; 1.97 Å; 2.06 Å; 2.08 Å; 2.48 Å; 3.04 Å; 3.15 Å; 3.31 Å; 3.48 Å; 4.04 Å; 4.69 Å), fluorohydroxyapatite - $Ca_5(PO_4)_3(F)$ (1.76 Å; 1.93 Å; 2.66 Å; 2.71 Å; 2.76 Å; 2.83 Å; 3.15 Å; 3.48 Å) and hydroxyapatite - $Ca_5(PO_4)_3(OH)$ (1.71 Å; 1.74 Å; 1.77 Å; 1.79 Å; 1.83 Å; 1.89 Å; 1.94 Å; 2.14 Å; 2.27 Å; 2.59 Å; 2.66 Å; 2.71 Å; 2.76 Å; 2.83 Å; 3.09 Å; 3.48 Å; 3.84 Å; 4.04 Å).

In order to obtain additional information regarding the nature of the products formed, the hardened cements were subjected to an additional thermal treatment at 650°C for one hour; this treatment favors the crystallization of the amorphous phases, therefore facilitate their identification by X-ray diffraction.

On the XRD patterns of these specimens the following phases were identified: $AlPO_4$ (2.51 Å; 3.87 Å; 3.91 Å; 4.01 Å; 4.09 Å; 4.31 Å), $Ca_5(PO_4)_3(F)$ (1.76 Å; 1.93 Å; 2.69 Å; 2.75 Å; 2.81 Å; 3.22 Å; 3.41 Å), $Ca_5(PO_4)_3(OH)$ (1.76 Å; 1.93 Å; 2.69 Å; 2.78 Å; 2.81 Å; 3.41 Å), and CaF_2 (1.64 Å; 1.93 Å; 3.17 Å; 3.22 Å).

Besides the correlation between the intensity of the $AlPO_4$ XRD peaks and the Al/Si ratio in the solid compound (glass) has to be also pointed out. According to the XRD data, a higher amount of crystalline $AlPO_4$ is formed in the cement based on M2 glass - with a higher Al/Si ratio and consequently, with a higher reactivity.

The SEM micrographs show, for both specimens, the presence of irregular grains included into an amorphous binding matrix. For the cement prepared using the glass M2, the grain size is smaller as compared with the cement prepared with glass M1 (with smaller Al/Si ratio and consequently a smaller reactivity). This data are in good agreement with the phosphor content in the binding matrix assessed by EDS- figures 6b and 7b. This element is present in a higher quantity in M2 specimen as compared with M1, mainly due to the substantial increase of the binding matrix content.

One can assume that the better compressive strength and the smaller solubility of dental cements prepared with M2 glass (with a higher value of Al/Si ratio) are mainly due to the presence of this aluminate-phosphate matrix.

5. Conclusions

The hardening properties of the studied silicate cements are influenced by the chemical and phase composition of the glasses, i.e. their Al/Si ratio.

The reactivity of the M1 and M2 glasses was very high therefore, the standard consistency was obtained only for very small solid/liquid ratios, inadequate for dental cements.

The post-melting thermal treatment of the glass powders deactivates the glass as a result of the crystallization processes. Therefore, the reactivity of the powders towards the phosphoric acid solution diminishes and it is possible to include a bigger amount of powder in one ml of liquid (the standard consistency increase).

Good properties were obtained for the dental cements prepared with M2 glass (1.07 Al/Si ratio) – the compressive strengths after 24 hours of hardening was 150 MPa and the solubility in different mediums (distilled water and lactic acid aqueous solution) was smaller than 0.5%. The compressive strengths of the cements prepared with the M1 glass (0.95 Al/Si ratio) are smaller but increases up to 7 days (tested in this work).

There is a good correlation between the reactivity of the solid compound towards the phosphoric acid solution and the properties of the prepared cements. A higher value of the Al/Si ratio determines an increase of the glasses reactivity and, consequently, a decrease of the powder/liquid ratio, but no major modification of the setting time of the paste was noticed.

A lower reactivity of the glass powder is beneficial because it allows the increase of the powder/liquid ratio. This has a positive effect on both the interaction process and the amount of the formed products (aluminum-phosphate hydrates) in the binding matrix.

Acknowledgements

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