Bio compatible glass for ionomeric cements

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Ionomeric cements are usually made from vitreous powders of $CaO-CaF_2-Al_2O_3-SiO_2$ composition and aqueous solutions of polyacrylic acids (PAA). Their main advantage consist in the quick working, without cracking or major thermal increases, as well as their high mechanical strength. The chosen vitreous materials are fluoro-alumino-silicatic, from quaternary system $CaO-Al_2O_3-SiO_2-F$, with some amounts of soda oxides. For the projection of annealing programs are plotted the thermal expansion curves, with the Linseis, L 75 type, dilatometer and are calculated the characteristic temperatures. The thermal expansion coefficients, on 20-320 ^oC temperature domain, are determined, and measured the density of the samples, by hydrostatic method. The bio-compatibility of the samples is evaluated with the aid of micrographic analyze, made in phase contrast, of the culture osteoblastes in the presence of samples. It is calculated the viability of the human embrionary osteoblastes in the presence of powdered samples.

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1. Introduction

In the last 20 years appeared new preoccupations, concerning the study and practical realisation of a new type of materials, the so-called glass-ionomer cements. A short definition of such materials say that the glass-ionomer cements are polymers obtained from the reaction of polyacrylic acid with some special alumino-silicate glass, who is able to change ions. Those systems are, in principle, ionic polymers made from polymer matrix that bend together the glass particles surrounded by a silica gel.

The ionomer cements of glass are usually vitreous powders from composition $Ca0-CaF_2-Al_2O_3-SiO_2$ in aqueous solution of polyacrylic acid (PAA). Their major advantage consist in the quick put in work, without cracks or major raises of the temperature, together with the high mechanical strength.

The major disadvantage of actual classes of ionomer cements of glass is the weak, almost inexistent, ability to create bonds with the bone, the so-called weak bioactivity.

A recent classification refers at four main types: type I – adhesives binders; type II – restoring cements; type III – cements for basic obturation; type IV – cements for bonts restoring.

The vitreous powder materials must be carefully selected for the compatibility with the utilization demands and also for the technical solution chosen for their fabrication and application. The most important characteristics of the glasses for those demands are the type of glass, the oxide system, the temperature T_g, the thermal linear expansion coefficient in the field of interest, the granular distribution, the properties of flow and wetting at the working temperature, the compatibility of the glass composition with the proposed medical application.

2. Experimental

The chosen oxide compositions are presented in Table 1.

Table 1. The chosen oxide compositions, in the quaternary fluoro-calco-alumino-silicate system.

No.	Oxide or element	Proportion [grav. %]				
		SCI 1	SCI 2	SCI 3	SCI 4	SCI 5
1	SiO_2	37,5	37,2	47,5	47,6	47,6
2	Al_2O_3	21,8	23,2	21,1	23,8	21
3	CaO	13,8	13,6	10,3	10,3	6,9
4	Na_2O	8,1	10,3	7	7	10,5
5	P_2O_5	4,4	0	2,8	0	2,8
6	F	14,4	15,7	11,3	11,3	11,2

For the silica introduction it was used the quartz of Uricani, U1, containing 40-60 ppm Fe_2O_3, copper oxides 1.6 ppm and titanium oxide 3.4 ppm. The humid quartz was dried at 120^{o}C, in stove with ventilation and then sieved to the sieve of 0.02 mm. As raw material for the phosphorus oxide it was utilized the aluminium phosphate, which contains over 96% useful compound. For the aluminium oxide introduction it was used the industrially made alumina, with more than 98% Al_2O_3, purified in the National Institute for Glass to 99.9% purity.

The natrium oxide was introduced as natrium fluoride - NaF, prepared in the National Institute for Glass, from fluorhydric acid and natrium carbonate containing over 98% Na_2CO_3, EXTRA quality, with maximum 30 ppm Fe_2O_3, according to the standard 99/78. For the calcium

oxide it was used the calcium fluoride – CaF_2, also prepared in NIG, from HF and CaO, having purity over 98%. The fluorine was introduced as calcium and natrium fluorides, prepared as indicated.

The raw materials, dried in electrical stove, were triturated in a mechanical agate triturator and then sieved on metallic sieves of 0.01-0.02 mm, on a vibrating installation. The dosage was realized with an analytical balance, of 100 g. The homogenization was realized on the homogenization installation, in porcelain vessels, for 4 hours.

The melting took place in superkanthal furnace, in crucibles made from aluminous fire clay. The stirring of the melts was done with cordhardt made stirrers. The glass was casted in metallic moulds, at temperatures between 1000 and 950°C. The samples were cooled and then introduced in the annealing furnace, equipped with kanthal resistances. The melting program is presented in Table 2.

After annealing, the obtained glasses were broken in jaw breaker ant milled in planetary mill, provided with balls and vessels made of porcelain. The final granulation was between 10 and 50 μm.

The annealing programs were established using the thermal expansion curves, plotted with a Linseis type dilatometer, model L75. The density of the glasses was determined by the hydrostatic method.

Table 2. The melting-homogenizing-refining program for the glasses SCI3 and SCI4.

Hour [h]	Temperature [°C]	Atmosphere	Observations
0	1325	Neutral-slow oxidant	Alimentation
0h30min	1325	Neutral-slow oxidant	Alimentation
1	1325	Neutral-slow oxidant	Alimentation
1h30min	1325	Neutral-slow oxidant	Alimentation
1h45min	1325	Neutral-slow oxidant	Alimentation
2	1325	Neutral-slow oxidant	Alimentation
3	1350	Neutral-slow oxidant	Plate; Sample
4	1350	Neutral-slow oxidant	Decreasing
4h 30 min	1325	Neutral-slow oxidant	Stirring
5	1300	Neutral-slow oxidant	Stirring
5h30min	1275	Neutral-slow oxidant	Stirring
6	1250	Neutral-slow oxidant	Sample
6h30min	1225	Neutral-slow oxidant	Sample
7	1200	Neutral-slow oxidant	Sample
7h30min	1175	Neutral-slow oxidant	Sample
8	1150	Neutral-slow oxidant	Stirring
8h30min	1125	Neutral-slow oxidant	Stirring
9	1100	Neutral-slow oxidant	Stirring
9h30min	1075	Neutral-slow oxidant	Sample
10h	1050	Neutral-slow oxidant	Sample
10h30min	1025	Neutral-slow oxidant	Sample
11h	1000	Neutral-slow oxidant	Moulding

For the test of biocompatibility of synthesised vitreous materials they were introduced sterile fragments of those materials in osteoblasts cultures. The osteoblasts were maintained in culture for 72 hours, with pieces of vitreous materials introduced in there from the first moment. The proliferation of the osteoblasts in the presence of vitreous materials pieces was put in evidence with the aid of phase contrast optical microscopy.

For the testing of the physiologic state of the osteoblasts adherent on the bio glass support there were made cytotoxicity and cell proliferation determinations. The cells in the exponential growing phase were exposed to the action of the vitreous materials. The number of survivor cells was indirectly determined, through the reduction of the MTT colorant (the [3-(4, 5 /dimethyltyayol-2-yl)-2, 5-difenyltetrazoly bromide] 5 mg/ml in salt phosphate tampon). The quantity of the MTT-formazan produced was spectrophotometrically determined after the dissolution in isopropyl alcohol, by reading the optical density of the sample at the wavelength of 570 nm, comparatively to that of the isopropyl alcohol.

3. Results and discussions

The characteristic temperatures for two compositions are presented in table 3.

Table 3. The characteristic temperatures for the glasses SCI 4 and SCI 5, determinated from the thermal expansion curves, plotted with the LINSEIS dilatometer.

No.	Propriety	Sample SCI 4	Sample SCI 5
1	The dilatometric temperature TD [°C]	589,7	551,2
2	The upper annealing point Tsr [°C]	519,7	484,2
3	Temperature of vitreous transition TG [°C]	499,3	468,8
4	The lower annealing point Tir [°C]	471,4	449,5

The thermal expansion curves are presented in Figs. 1 and 2. The coefficient of thermal expansion, on the 20-300°C domain, are shown in Table 4.

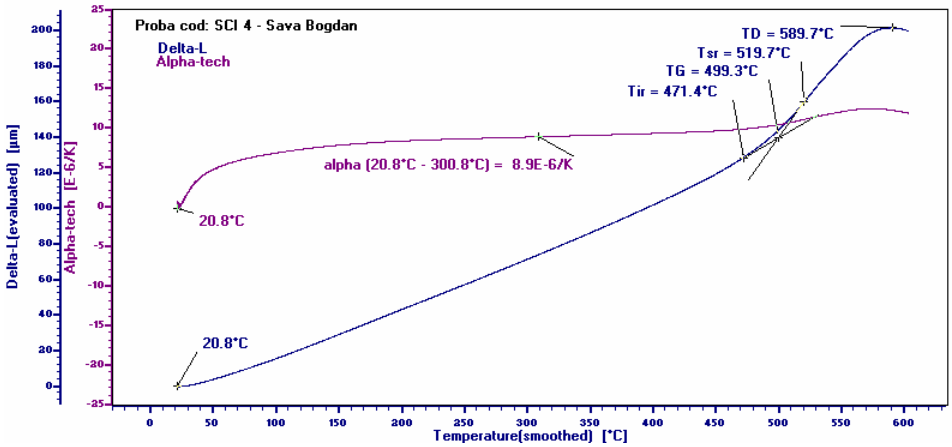

Fig. 1. The thermal expansion curve for the sample SCI4.

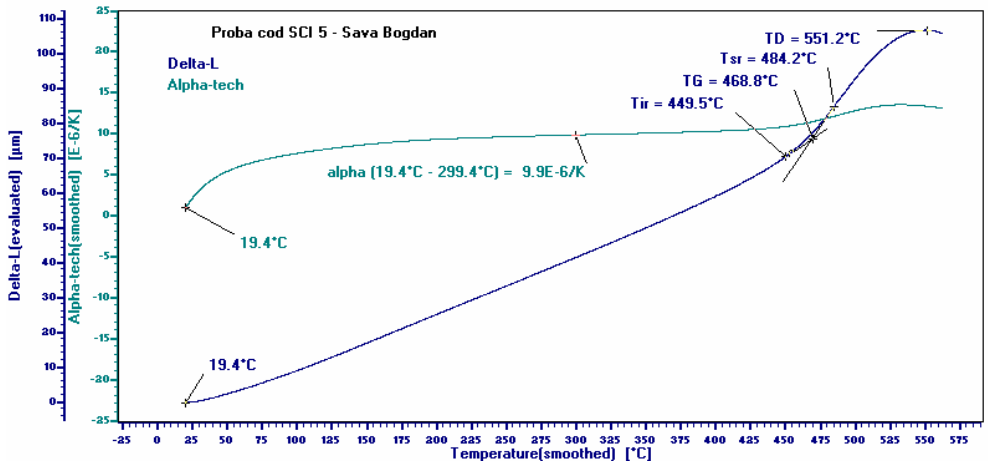

Fig. 2. The thermal expansion curve for the sample SCI5.

Table 4. The coefficient of thermal expansion, for glasses SCI 4 and SCI 5.

No.	Sample	Coefficient of linear thermal expansion $\times 10^{-6}$ [1/K]
1	SCI 4	8.9
2	SCI 5	9.9

The density of the samples is presented in Table 5.

Table 5. The density of the samples SCI 1, 2, 4 and 5, hydrostatic measured.

No.	Sample	Density [g/cm^3]
1	SCI 1	2.5876
2	SCI 2	2.8669
3	SCI 4	2.4734
4	SCI 5	2.4672

The proliferation of the osteoblasts in the presence of vitreous materials pieces is presented in figures 3-6.

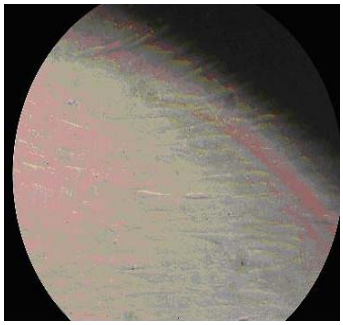

Fig. 3. Micrograph in phase SCI1 (x100). It can be seen the cells with cytomorphologic aspect normal in the vicinity of the piece.

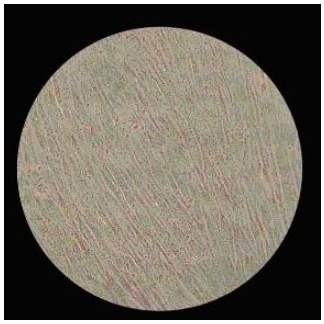

Fig. 4. Micrography in phase contrast of the osteoblasts in contrast of the osteoblasts in culture, in the presence of sample culture, in the presence of sample SCI1 (100). There are observed cells with cytomorphologic aspect normal, confluent to some distance to the piece.

Fig. 5. Micrography in phase contrast, in the presence of sample SCI4 (100). One observes cells with cytomorphologic aspect normal.

Fig. 6. Micrography in phase contrast in culture, in the presence of sample SCI4 (100). It can be seen cells with cytomorphologic aspect normal, confluent at distance to the piece.

Table 6 presents the results of the tests of cytotoxicity and cell proliferation, for the samples code SCI1, and SCI4.

Table 6. The percent viability of the human embryonal osteoblasts in the presence of the vitreous samples.

Sample	$DO_{570\ nm}$	% viability in rapport to the witness
Witness	0.856	100
SCI1	0.909	106
SCI4	0.817	95

4. Conclusions

Due to the quality of raw materials, and also to the judicious established thermal treatment programs there were obtained vitreous materials in the quaternary fluoro-calco-alumino-silicate system, with amounts of soda oxides, materials which represent the vitreous part of the glass-ionomer cements.

The osteoblasts proliferation tests show that the tested samples, namely samples SCI1 and SCI4 present a very good biocompatibility. The osteoblasts have proliferated till the surface of the vitreous material pieces.

The microscopic data for these samples were in perfect correlation with those of cytotoxicity. In comparison with the witness sample the percents of viability were of 106 and 95, respectively, which show the absence of the cytotoxicity and, more over, in the case of the sample SCI1, with percentage over 100%, the cell proliferation. That proves the importance of the presence of phosphorus oxide in glass for ionomer cements, which determines the increasing of the viability percent over 100%.

The pH determination for the culture media in the presence of the vitreous samples didn't show any difference to the value of the witness sample, respectively pH=7.4.

References

[1] R. G. Craig, Restorative dental materials, 10th ed. St Louis (1997).
[2] C. J. Wang, P. L. Millstein, D.Nathanson, J. Prosthet. Dent. **67**, 786 (1992).
[3] G. J. Mount, An atlas of glass-ionomer cements: a clinician's guide, Martin Dunitz Ltd., London, (1990).
[4] S. K. Sidhu, M. Sheriff, T. F. Watson, J. Dent. Res. **76**, 1495 (1997).
[5] I. K. Mausner, G.R.Goldstein, M. Georgescu, J. Prosthet. Dent **75**, 129, (1996).
[6] E. J. Jr. Swift, A. H. Lloyd, D. A. Felton, J. Am. Dent. Assoc. **128**, 195 (1997).
[7] S. Fujisawa, Y. Kadoma, Biomaterials **18**, 701 (1997).

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