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Thermoanalytical characterisation of new dental ionomer biocomposites

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Thermoanalytic properties of four new glass ionomer cements were investigated using thermal techniques such as thermogravimetry (TG) and differential thermal analysis (DTA). The materials contain in the same ratio different copolymers and a mixture of two glass powders with preponderance of a fluoroaluminosilicate type glass. The X-ray diffraction analysis shows that these materials are all in the vitreous state. The thermal analysis traces have similar characteristics and indicate water removal, decomposition of hydroxyl groups, thermal decomposition process of the polymeric network and a dissociation process without mass loss. The last process is more likely to point out the glass transition taking place in the inorganic glass phase.

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1. Introduction

Glass ionomer cements have a great demand in dentistry due to several clinical advantages compared with other restorative materials [1]. One of the assumed advantages of GICs is that their coefficient of thermal expansion is thought to be similar to that of tooth [2]. Glass ionomer cements (GICs) are glass and polymer composite materials in which the glass phase acts both as a filler and as a source of cations to cross-link the polymer chains. They are prepared by combining a basic fluoroaluminosilicate glass powders and copolymer, water and a dilute solution of tartaric acid [3–8].

GICs are widely applied in dentistry for cementing metal prostheses or for filling cavities in carious teeth. It has been reported that these cements have great potential also for use in the field of orthopedic surgery instead of the conventional acrylic bone cement [9]. The hardening reaction of the cement is based on gelation of the polymeric acid by cross-linking of the carboxyl groups in the acid with $A1^{3+}$ and Ca^{2+} ions released from the cement powder [10, 11].

GICs are widely used for various dental applications as luting cements, bases, anterior filling materials and bone cements [7, 8]. The properties associated with this class of cements include good biocompatibility, good ability to bond chemically with tooth and fluoride release in the dental surface adjacent. These properties are major advantages over the composite resin and amalgams. The slow rate of the setting reaction of glass ionomer cements is one of the problems associated with their clinical use [1, 12]. The glasses used in commercial GICs are all of the aluminosilicate type, containing additionally calcium and fluoride ions in the composition.

The purpose of the present study was to investigate the thermoanalytical properties of four new ionomer biocomposites syntesised with identical inorganic phase and different copolymers.

2. Materials and methods

The inorganic/organic charge ratio in the investigated GISs is 2/1. They contain identical inorganic phase and only differ through the copolymer component. The organic phase consists of 50% water and 50% copolymer. 3% tartaric acid solution was also added. Tartaric acid acts as an accelerator that aids in the extraction of ions from the aluminosilicate glass, facilitates their binding to the polymer chains and also strengthens and hardens the cement [13].

The major constituent of many composite dental materials are the reinforcing filler particles [14]. The inorganic phase which acts both as filler and as a source of cations to cross-link the copolymer chains was prepared by combining powder of a basic fluoroaluminosilicate glass S1 (SiO_2 49%, Al_2O_3 22%, CaF_2 29%) in a ratio of 7/8 with powder of glass M1 (ZnO 16,72%, CaO 23,8%, Na_2O 9,33%, SiO_2 50,14%) in a ratio of 1/8.

The samples codes are C-B1, C-B2, C-T1 and C-T4 and derive from the type of the different copolymers that were used.

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The prepared composite systems were analyzed by X-ray diffraction (XRD) using CuK$_\alpha$ radiation (λ = 1.5418 Å). Thermal analysis was carried out in air on a Shimadzu TGA-50 thermobalance.

3. Results and discussion

The X-ray diffractograms for the investigated systems are illustrateds in Fig. 1. As can be seen all the samples are in the vitreous state, as expected for glasses.

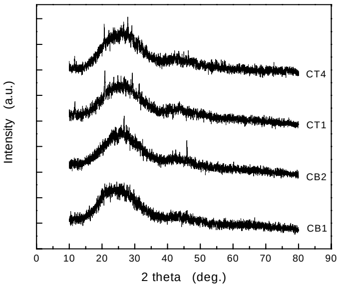

Fig. 1. XRD patterns of the studied glass ionomer cements.

This behavior indicates that the addition of different copolymers has no strong influence on the vitreous characteristic of C-B1, C-B2, C-T1 and C-T4 systems. Thus, regardless of the type of the copolymer present in our systems no crystalline phase was observed after the preparation process of the composite samples.

The thermal change traces for the investigated samples have also similar characteristics, as can be observed in Fig. 2, where, up to 1200 °C, all non isothermal DTA/TG curves exhibit four thermal ranges. The DTA curves show endothermic and exothermic heat effects which go along with the various chemical and physical processes, while the TG curves show the weight changes of the samples against steadily increasing temperature.

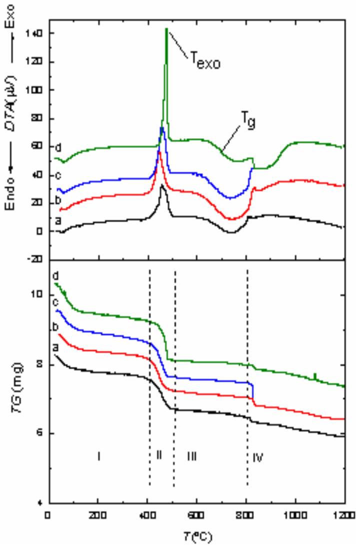

Fig. 2. DTA/TG curves of the studied glass ionomer cements (a – CT4, b – CB2, c – CB1 and d – CT1).

The four thermal change stages are related to water release, the decomposition of hydroxyl groups, thermal decomposition process of the polymeric network and a dissociation process without mass loss.

The first decomposition step (I) indicated by the first weight loss observed on the TG curves is assignable to removal of adsorbed and chemisorbed water and up to 400°C the thermal decomposition corresponds to the decomposition of the hydroxyls present in the samples [15]. The endothermic processes observed in this temperature range proves the occurrence of gel-like hydration products [16].

With further heating the sample, in the temperature range 400-500 °C (II) the bonds between the polymer chains of the cements are released, as revealed by the exothermic peak observed around T = 450 °C. Moreover, this thermal phenomena may also represent a dehydroxylation reaction [17, 18]. On the other hand, the high intensity of this peak could be connected with the effect of mutual interaction of the hydration products with the polymer used in the synthesis [16]. At the same time one remarks a dependence of the exothermic peak temperature on the polymer added to ionomer glass cement (Table 1).

At even higer temperatures, for $T > 500$°C, begins the third stage (III); the DTA plots exhibit at $T \sim 740$ °C a pronounced endothermic peak that may be attributed to a dissociation process without mass loss. In the last stage (IV) at approximately 810-830 °C a small exothermic peak is observed, accompanied by mass loss. The small exothermic peak is most probably due to the formation of a crystalline phase in these samples [5].

Tacking into account that in these compounds the major phase is the inorganic glass powder mixture of S1 and M1 silicate glasses, we assume that in the temperature region proceeding the apparent endothermic peak occurring around 740 ^{o}C has to be looked for the glass transition process in S1 and M1 glasses. In this case, the glass transition temperature seems to be slightly influenced by the copolymer used in the initial synthesis of the ionomer composites. It is obviously that the thermal analysis curves are envelopes of events arising both from organic and inorganic phases linked in composite samples. Assuming that region III in DTA profiles (Fig. 2) is related to glass transition of S1 and M1 glasses introduced in identical amounts in the investigated GICs, one remarkes the effect of the used copolymer on the apparent glass transition temperature, T_g, of these composites (Table 1). The T_g values for the composites syntetised with B1 and B2 copolymers are lower than for that of the composites syntetised with T1 and T4 copolymers.

The estimated total mass loss (Table 1) are very close for the composites CT1, CT4 and CB2, while a lower mass loss was evaluated for the composite CB1.

Table 1. Temperature of the first exothermic peak occurring in DTA curves, apparent glass transition temperature and mass loss estimated from TG curves.

Sample	CB1	CB2	CT1	CT4
T_{exo} (^oC)	459	447	455	475
T_g (^oC)	665	670	693	685
mass loss (%)	22.20	27.81	28.38	28.66

The glass phase seems to have a high thermal stability as compared with other ionomer glass systems. Hill et al. reported for a SiO_2-Al_2O_3-CaO-CaF_2 ionomer glass [19] a sharp glass transition at about 645 ^oC and two exotherms corresponding to liquid-liquid phase separation and to crystallisation of the remaining glass phase.

4. Conclusions

Thermal analysis and XRD results on four new GICs were comparatively discussed. The vitreous state is confirmed in all cases, regardless of the type of the copolymer entering the investigated GICs. The DTA/TG analysis evidence in the range from room temperature to 1200°C similar events, but they are slightly affected by the added copolymer. The thermoanalytical behaviour differs first of all through the polymer chain scission in these cements. The glass transition temperature is also influenced by the used copolymers.

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