

GLASS FORMATION AND DISSOLUTION PROPERTIES OF Na₂O-CaO-P₂O₅ GLASSES IN SIMULATED BODY FLUIDS

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Abstract: Various compositions of $x\text{CaO} \cdot (70-x)\text{P}_2\text{O}_5 \cdot 30\text{Na}_2\text{O}$ glasses ($0 \leq x \leq 30\%$ mol %) are investigated in order to estimate glass formation, glass stability and activation energy of crystallization as well as dissolution properties of samples. Transparent vitreous samples were obtained in the entire composition range from 40 to 70 mol% P₂O₅. The glass transition temperatures and crystallization temperatures increased with CaO content. Dissolution properties in distilled water and simulated body fluids were measured. The dissolution behaviour depends on the CaO content introduced in glass sample. The dissolution rate increases with substitution degree of P₂O₅ by CaO in samples. In decaionised water and physiological serum one observes after 50 hours the occurrence of a shoulder in the release curve denoting that the glass dissolution is suppressed.

Key words: Phosphate glasses, dissolution properties.

1. INTRODUCTION

Glass systems allowing controlled release of components are intensely investigated [1-4] in the last decades. Phosphate glasses and glass-ceramics are well-known biocompatible materials. Simple phosphate glasses do not have enough chemical durability for usual glass applications. Therefore, studies on phosphate-based glasses have concentrated on insoluble compositions. However, new applications of soluble glasses were proposed [5-7]. Soluble phosphate glasses that slowly release active ingredients are used to cure trace element deficiencies in animals and as agricultural fertilizers. On the other hand, bioabsorbable materials, which degrade and are absorbed in the human body are useful as suture thread, in bone fracture fixation and as carriers in drug delivery. Phosphate based glasses are potential bioabsorbable materials because of their solubility. Furthermore, phosphate glasses can be melted at low temperature. This feature aids the incorporation of useful ingredients, which degrade at high temperature, such as therapeutic organic agents. In order to apply phosphate glasses for bioabsorbable materials, their dissolution behaviour and biocompatibility should be studied.

The aim of this paper is to investigate glass formation, glass stability and activation energy of crystallization as well as dissolution properties of various $x\text{CaO} \cdot (70-x)\text{P}_2\text{O}_5 \cdot 30\text{Na}_2\text{O}$ glasses.

2. EXPERIMENTAL

The investigated samples belong to xCaO(70-x)P₂O₅ 30Na₂O glass system (0 ≤ x ≤ 30 mol %). They were obtained from homogenized mixtures of CaCO₃, (NH₄)₂HPO₄ and Na₂CO₃ 10H₂O reagents of p.a. purity grade by melting at 1000°C for 15 minutes in sintered corundum crucibles in an electric furnace. The melts were quickly undercooled at room temperature by pouring onto stainless steel plates. Transparent vitreous samples were obtained in the entire composition range from 40 to 70 mol% P₂O₅.

The thermal analysis TG, DTG and DTA curves were recorded in the temperature range 20-1000°C by using a MOM equipment, at heating rates of 2.5, 5 10 and 20°C/min. The activation energy of the crystallisation (E_c) for different heating rates *a* = 5, 10 and 20°C/min was evaluated according to Kissinger's equation⁵ [8].

The corrosion behaviour was followed in static regime by samples immersion in desalinated water, physiological serum and chlorine acid solution with pH = 1.5. The mass of samples was measured after different immersion times, by using an analytic balance sensitive to 0.1mg. The glass surface area to solution volume ratio was around 15 m⁻¹ for all samples.

3. RESULTS AND DISCUSSION

Thermogravimetric and differential thermogravimetric curves show only a very small weight loss around 100°C denoting low water absorption of samples. The glass transition temperature corresponding to the quasi-endothermic peak as well as the crystallization temperature associated to the exothermic events from DTA curves are given in Table 1. The composition dependence of T_g is in agreement with the data reported for other alkali-lime-phosphate glasses [9].

Table 1.
Glass transition temperature (T_g), crystallisation temperature (T_{exo}) and glass stability for xCaO (70-x)P₂O₅ 30Na₂O samples.

x (mol %)	T _g (°C)	T _{exo} (°C)	S (°C)
0	515	637	122
10	563	702	139
20	575	705	130
30	582	703	123

The glass stability can be expressed^{7,8} by the difference of crystallisation and glass transition temperatures, $S = \Delta T = T_{cr} - T_g$. Larger values of ΔT lead to higher thermal stability of the glasses. One remarks an increase of glass stability by addition of CaO to 70P₂O₅ 30Na₂O glass matrix and an apparent maximum for the sample containing 10 % mol CaO.

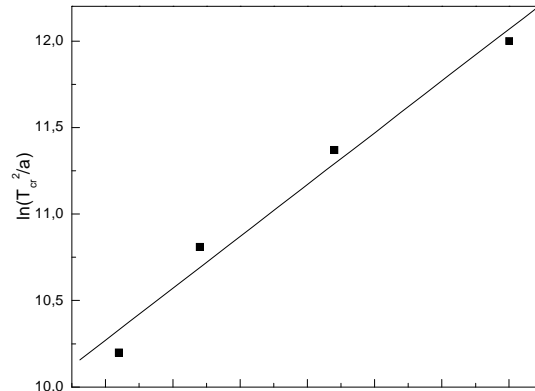


Fig. 1. - Plot of $\ln(T_{cr}^2/a)$ versus $10^3/T_{cr}$ of the samples with $x = 10$ mol %.

The activation energy of crystallisation was discussed according to Kissinger's formula, as given by equation:

$$\ln(T_{cr}^2/a) = E_t/RT_{cr} + \text{const.}$$

for different heating rate, a ($a = 2.2, 5, 10, 20$ degree/min), where T_{cr} is a temperature corresponding to the maximum of the DTA crystallisation peak, E_t is the effective activation energy of crystallisation and R is the gas constant.

Figure 1 shows the plot of $\ln(T_{cr}^2/a)$ versus the reciprocal crystallisation

temperature, T_{cr}^{-1} , for the different heating rates. A value of 51 kJ/mol was calculated for the activation energy of the sample with $x = 10$ % CaO using the slope from the linear fitting of Kissinger's equation.

The dissolution in simulated biological media are shown in Figures 2-4 which represent the time dependence of the relative mass loss expressed by the fraction f ($f = \Delta m/m$).

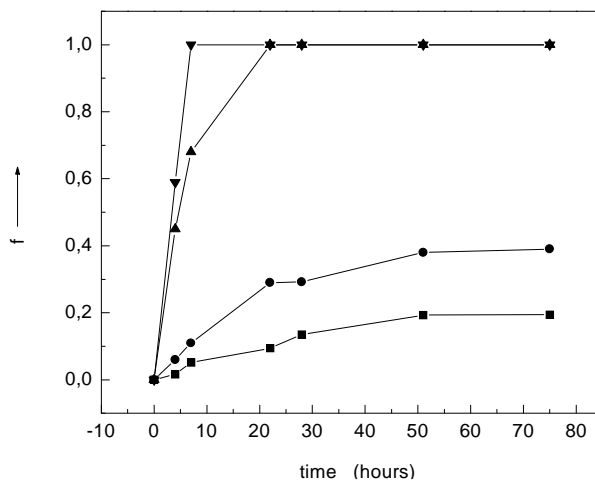


Fig. 2. - Dissolution rate of $x\text{CaO} \cdot (70-x)\text{P}_2\text{O}_5 \cdot 30\text{Na}_2\text{O}$ samples in chlorine acid solution; $x = 0$ (■), $x = 10$ (●), $x = 20$ (▲) and $x = 30$ (▼). The lines are only guide for eyes.

For all compositions the corrosion process is most pronounced in chlorine acid (pH = 1.5). In order to explain the different release of cations from the glass network in the investigated dissolution media beside the composition of glasses and solvents is necessary to take into account the short-range order characterizing the samples. The structural stability of cations in glass matrices is correlated with their local symmetry [10].

Pure vitreous P₂O₅ consists in a continuous random network (polymeric structure) of quasi-tetrahedral PO₄ units wherein phosphorous is four coordinated and only three of the oxygen atoms of each unit bridge to neighbouring units, while the forth is doubly bonded to the central phosphorous atom.

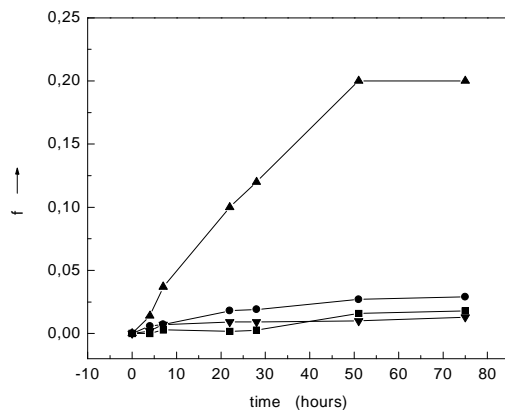


Fig. 3. - Dissolution rate of $x\text{CaO} \cdot (70-x)\text{P}_2\text{O}_5 \cdot 30\text{Na}_2\text{O}$ samples in physiological serum; $x = 0$ (■), $x = 10$ (●), $x = 20$ (▲) and $x = 30$ (▼). The lines are only guide for eyes.

The presence of the modifier like alkali and alkaline earth species decreases the number of bridging oxygens (P-O-P bridge) in PO_4 units, while its negative charge increases.

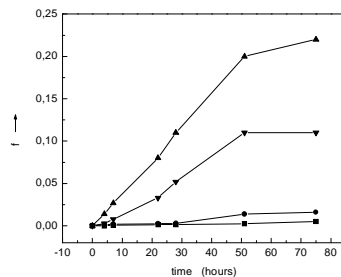


Fig. 4. - Dissolution rate of $x\text{CaO} \cdot (70-x)\text{P}_2\text{O}_5 \cdot 30\text{Na}_2\text{O}$ samples in decaionised water; $x = 0$ (■), $x = 10$ (●), $x = 20$ (▲) and $x = 30$ (▼). The lines are only guide for eyes.

Two PO_4 tetrahedra sharing an oxygen, that can be represented as $(\text{PO}_3)_2^{2-} - \text{O} - (\text{PO}_3)_2^{2-}$, form the $(\text{P}_2\text{O}_7)^{4-}$ pyrophosphate anions. Both in the melt and during the

quenching process will occur an equilibrium between the pyrophosphate anions and their products as follows [10] $(\text{PO}_3)^{2-} - \text{O} - (\text{PO}_3)^{2-} \leftrightarrow (\text{PO}_4)^{2-} + -\text{O} - (\text{PO}_2)$. The dissolution resistance has to be also related to the presence of Na₂O in the glass matrix, having in view that the alkali ions diminish the network consistency [11].

The initial stages of the aqueous reactions always results in the leeching of alkali and alkaline earth species from the surface of the glass to create a P₂O₅-rich surface layer. It is generally believed that in the initial stages of the leaching reaction, the contact of liquid water or vapour water with the glass surface leads to an exchange of alkali and alkaline earth ions in the glass with hydrogenated ions in the aqueous environment. (i.e., ion exchange or interdiffusion mechanism).

Another mechanism proposed is based on the diffusion of molecular water into the glass and its chemisorption at the non-bridging oxygen sites where alkali and alkaline earth species reside in the glass [12].

4. CONCLUSIONS

The addition of CaO to Na₂O-P₂O₅ glass matrix modifies the glass sample stability. The highest cations delivery was obtained for the samples containing 20 mol % CaO in all biological simulated media. The highest corrosion stability was observed in physiological serum. In decationised water and physiological serum one observes after 50 hours the occurrence of a shoulder in the release curve denoting that the glass dissolution is suppressed.

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