CHARACTERIZATION OF POLYPHOSPHATE GLASSES PREPARATION USING CRTA

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Abstract

We used CRTA for the study of both the elaboration and characterization of several polyphosphate glasses. We show that controlled transformation rate thermal analysis is able to remove a systematic error present in classical thermal analysis, in the study of the precursor of the phosphate glass. We show too that in CRTA, water release in the phosphate glasses can take place by diffusion phenomena at low temperature and that it is not due to the crystallization. These two examples illustrate some interests of this inverse method in the study of the decomposition of inorganic compounds with water release.

Keywords: controlled transformation rate thermal analysis, conventional thermal analysis, polyphosphate glasses

Introduction

The thermal preparation of polyphosphate glasses has been the subject of discussion for many years [1, 2]. Indeed several interpretations have been made for the thermoanalytical results obtained. Conventional thermal analysis has been able to quantity the different types of water in these systems. This is why we have turned to CRTA (an inverse sample determined thermal analysis method) for the study of both the preparation and characterization of several polyphosphate glasses.

In conventional thermal analysis, one measures a physical or chemical property X while a predetermined program of heating is applied to the sample. In Controlled transformation Rate Thermal Analysis, the roles of the "thermometer" and the "X-meter" are exchanged so that it is now the physical property X which is made to follow a predetermined program and which controls the heating of the sample (Fig. 1). The thermoanalytical information is obtained simply from recording of T vs. t, since the physical property X follows its predetermined program and does not necessarily need to be recorded.

The property X we consider, is the partial pressure of evolved gases above the sample which originate from the rate of reaction itself.

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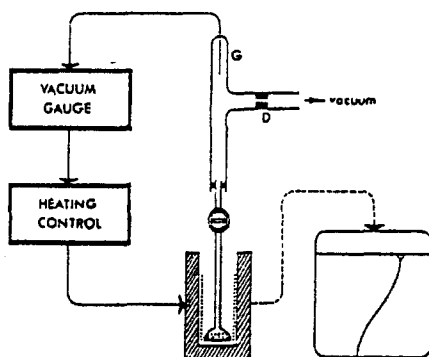
Fig. 1 Principle of the Controlled transformation Rate Thermal Analysis

The resolution power of CRTA results from the possibility of controlling the rate of transformation at such a low rate that the remaining temperature or pressure gradients through the sample are themselves low enough to avoid any overlapping of the successive steps. Under these conditions the reaction may take place simultaneously within the whole sample, the degree of synchronism then being limited only by the size of the grains or crystallites of the sample and not by the size of the sample or by the shape of the crucible. CRTA is also very interesting in the study of kinetics of thermodecompositions. A limitation appears for the use of such apparatus: the gas release must be compatible with the pressure sensor and the connection pieces.

CRTA has been used to characterize the decomposition of several inorganic compounds such as $Li_2SO_4 \cdot H_2O$ [3], $UO_2(NO_3)_2 \cdot 6H_2O$ [4], dolomite [5], industrial $Al(OH)_3$ gibbsite [6], etc. In the present study we have used this technique and compared it with classical thermal analysis (DTA, TG) in the study of polyphosphate glasses and one of their precursors.

To synthesize the phosphate glasses we have used a "soft chemistry" route: simple coacervation permits the synthesis of phosphates glasses at room temperature and in aqueous medium. After heating, these precursors give rise to glasses (Fig. 2).

Simple coacervation of polyphosphates [7] is a kind of flocculation which leads to a compound containing 50% of water and 50% of dry substances, in weight. It is obtained when sodium polyphosphate (Graham's salt) and cationic species are together in solution, for specific concentrations. We can adapt both the concentrations and the salts used to obtain a suitable formulation of the precursor and thus of the final product: the glass [8].
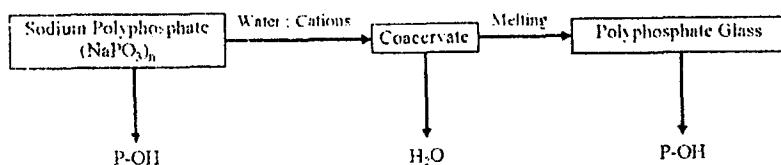

Fig. 2 Importance of water in the study of polyphosphates glasses obtained from coacervates

On heating the precursor transforms via several steps to a glass. One important step is the drying of the coacervate. After preparation, this system contains important amounts of water. So that, different kinds of water may be present into the structure, i.e. free water, phosphate hydrates, cation hydrates.

To control the drying of the precursor and the reactions which can take place with water, we have to know the structural state of water in our system.

When the coacervate has been heated up to ~900°C, it gives rise to a phosphate glass which still contains a small quantity of water. Contrary to silicate glasses, phosphate glasses are of a polymeric nature. They can be described by a sequence of $[PO_3^-]$ units in which P–OH groups can be present [1]. By condensation of polyphosphates, water can be released according to reaction 1:

$$P-OH + OH-P \rightarrow P-O-P + H_2O\uparrow \qquad (1)$$
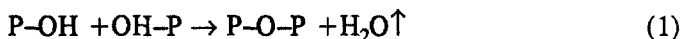
Ropp [2] indicates that this reaction takes place for temperatures higher than the crystallization temperature of the glass. It can be interesting to characterize the processes of P–OH decomposition and water release and also the relations which may exist between reaction 1 and the temperature (particularly the characteristic temperatures T_g, T_d and T_m).

Experimental

Sample preparation

The precursors of calcium-sodium polyphosphates glasses were formulated from coagulation between 3 mol kg^{-1} $(NaPO_3)_n$ and 2 mol kg^{-1} $CaCl_2$ or $MnCl_2$ solutions. Sodium polyphosphate, manganese chloride and calcium chloride were supplied by Merck. For classical method of glass achievement, the coacervate was heated at 1000°C for one hour in a platinum crucible.

Controlled transformation Rate Thermal Analysis

For all experiments, the residual pressure (or "vacuum") of the sample was kept constant at a value of $2 \cdot 10^{-3}$ mbar. The sample mass varied from 0.6 to 2.0 g.

DTA/TG

Differential Thermal Analysis and Thermogravimetric Analysis of glasses and coacervates were carried out using a TD/TG92 from Setaram, in carbon crucibles and in an argon atmosphere. Sample mass was about 50 mg.

Results and discussion

Coacervates

TG studies of polyphosphate coacervates (Fig. 3) show several mass losses. The DTA curves present an exothermic peak at ~90°C. Some authors [9, 10] interpreted
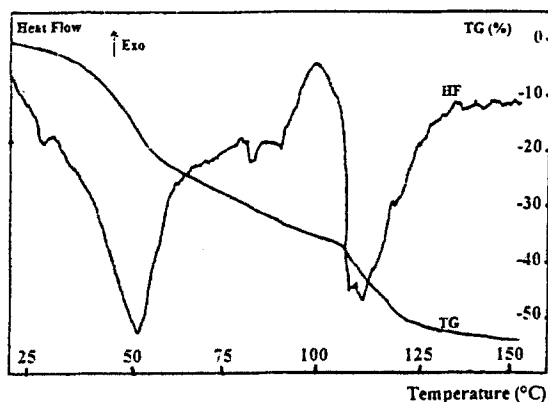
Fig. 3 DTA/TG curve obtained for a calcium-sodium coacervate, with a rate of heating of $0.5°C$ min^{-1}
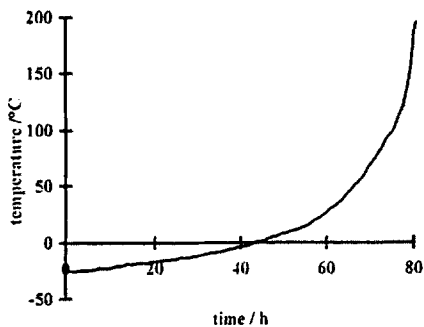

Fig. 4 CRTA curve obtained for a calcium-sodium coacervate, up to 200°C

these results, and concluded that different kinds of binding between water and the other particles exist in the coacervates. Some water molecules are then free in the bulk, some others make up of hydrates.

CRTA of calcium-sodium coacertate, Fig. 4, leads to a curve of temperature $vs.$ time. Dehydration of the glass precursors is continuous, with only one step. We conclude that no hydrate are present in the system. Water only gives rise to a continuous solvatation of the different species contained into the coacervate.

This conclusion utterly contradicts the direct interpretation of the results obtained by classical thermal analysis.

It is noteworthy that polyphosphates are easily hydrolyzed to give ortho and pyrophosphates. Accordingly, we induced this reaction, by heating a calcium-sodium coacervate at 80°C during 48 h. We have shown [11] that the CRTA of a such sample presents several steps. When the coacervate is heated, ortho and pyrophosphates appear in the system. These compounds possess some stable stoichiometric hydrates vhich decompose at temperatures up to 100°C. For example, monohydrated calcium orthophosphate, $Ca(H_2PO_4)_2 \cdot H_2O$, removes one H_2O molecule at 109°C.

These hydrates may be formed using the water present in the coacervate which are then observed by CRTA.

When the glass precursor is synthesised only one kind of water contributes to the structure of the system. In DTA/TG, the sample is heated with a constant programmed rate. So that, for temperatures lower than ~90°C, water released by evaporation gives rise to a weight loss. At ~90°C, another phenomenon appears because water is still present in the system, this is polyphosphate hydrolysis [1] (observed by an exothermic peak in DTA). This water should be released at lower temperature but the kinetics is too slow. The hydrolysis reaction then induces the formation of ortho and pyrophosphates which form stable hydrates as water is still present. These compounds release water at temperatures higher than 100°C, by decomposition and no longer via classical evaporation.

In CRTA, the temperature is maintained constant until all the water, which is able to be released at this given temperature, has disappeared. So that, when T ~90°C, the hydrolysis of the polyphosphate chains becomes impossible (this reaction requires the presence of H_2O) and the final product (a glass if the sample is heated up to ~900°C) preserves its polymeric nature. No ortho or pyrophosphates are formed.

If a coacervate is studied by classical thermal analysis, such as DTA and TG, a systematic error due to the analytical method appears. Controlled transformation rate thermal analysis is able to remove this error. This imparts an additional interest to CRTA.

Glasses

We studied water contained in several phosphate glasses. Glasses obtained by the heating of coacervates with several modifier cations in the vitreous network. We also studied the initial polyphosphate used in the elaboration of the coacervates, the sodium polyphosphate. This compound is in fact a glass but it contains only one modifier cation (Na^+).

TG study of polyphosphate glasses shows a small mass loss. It is verified for Graham's salt and glasses with several modifier cations (Fig. 5). We note that in these thermal curves, the loss of weight, due to water release, always occurs at the devitrification temperature (T_d), according to Ropp [2]. Classical thermal analysis shows that crystallization of the glass and water release occurs in the same temperature range. This indicates that the two reactions may be interdependent and if this is true, two possibilities exist:

– water release may induce the formation of nuclei at the time as molecular rearrangements,

– crystallization organizes the polyphosphates chains so that, it may make the condensation reaction, with water release, easier.

DTA/TG curves also show that the mass loss occurs roughly at the devitrification temperature and stops rapidly.

Ropp [2] indicates that a method which permits the dehydration of phosphate glasses consists of a series of melting and quenching of the glass.
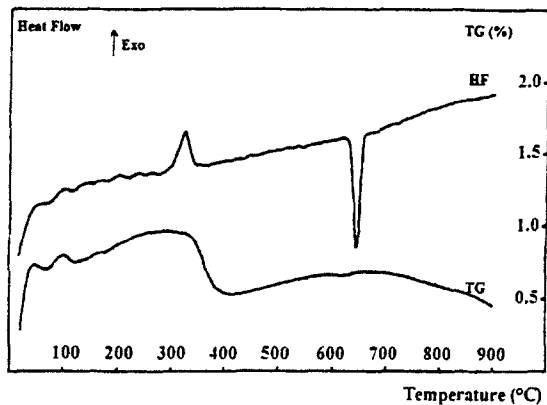
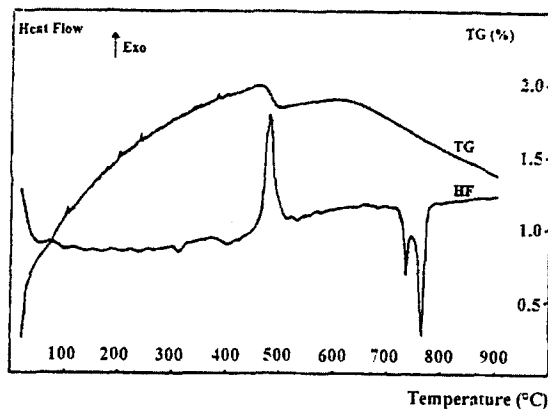**Fig. 5a** DTA/TG curves obtained for a sodium polyphosphate [Merck], with a rate of heating of $5°C$ min^{-1}

Fig. 5b DTA/TG curves obtained for a phosphate glass of formulation 52% P_2O_5–33% CaO– 15% Na_2O, with a rate of heating of $5°C$ min^{-1}

By CRTA, the regulation of temperature is a consequence of the gas flow, due to decomposition reactions. So that, if water release is directly induced by the devitrification, the CRTA curves must show a fast slope of temperature, up to T_d, before stabilization at this temperature. The experimental results obtained for sodium, sodium-calcium and sodium-manganese polyphosphate glasses are represented in Fig. 6. Water release begins at a temperature near 200°C, for all formulations. So, phosphate condensation which gives rise to water release is not at all dependent on the devitrification of the glass, at least under vacuum. We also note that this reaction occurs at $T < T_g$. At such temperatures, molecular rearrangements are totally impossible. This indicates that water formation in the glass occurs by a diffusional phenomena in the bulk.
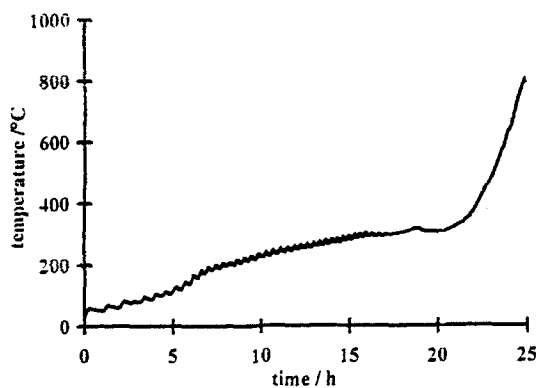
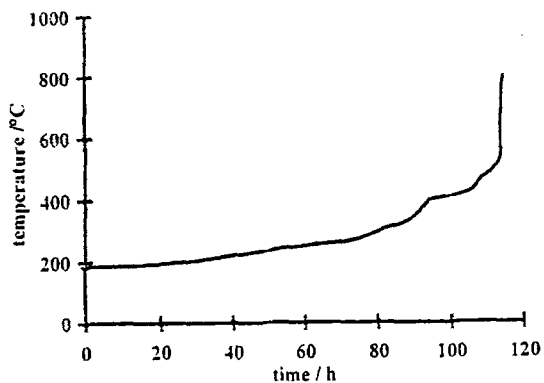Fig. 6a CRTA curve obtained for a sodium polyphosphate [Merck], up to 1000°C

Fig. 6b CRTA curve obtained for a phosphate glass of formulation 52%P_2O_5–35% MnO–13% Na_2O, up to 1000°C
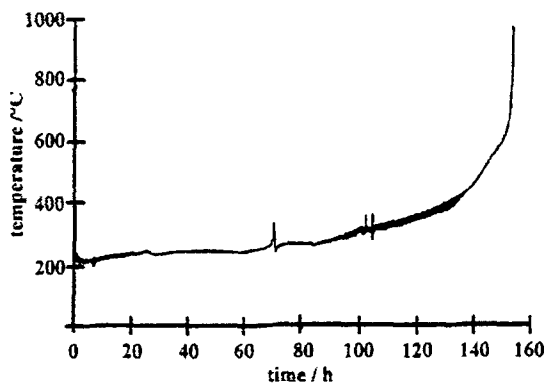

Fig. 6c CRTA curve obtained for a phosphate glass of formulation 52% P_2O_5–33% CaO–15% Na_2O, up to 1000°C

Conclusion

CRTA has been used to characterize the decomposition of several inorganic compounds. We used this inverse method and compared it with classical DTA and TG, in the study of polyphosphate glasses and one of their precursors (coacervates).

CRTA of coacervates utterly contradicts the direct interpretation of the results obtained by classical thermal analysis. We show that only one kind of water is present into the colloidal system. DTA/TG induce the hydrolysis of polyphosphates, which causes the formation of hydrated ortho and/or pyrophosphates. These compounds are then able to release water at higher temperatures. Controlled transformation Rate Thermal Analysis is able to remove this systematic error present in classical thermal analysis.

We also studied polyphosphates glasses by CRTA to characterize P–OH decompositions. Whereas a sudden loss of weight appears in TG at the crystallization temperature, CRTA curves show a continuous vapor release. P–OH decomposition then occurs from ~200°C up to the glass melting. The shape of the curve indicates that water release takes place by diffusion phenomena and that it is not due to the crystallization.

These two examples compare the results obtained by classical thermal analysis and by CRTA. They illustrate some interests of this inverse method in the study of the decomposition of inorganic compounds with water release.

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