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Dedicated to Prof. Antonius Kettrup on the occasion of his 60th birthday

BURNOUT OF ORGANIC COMPONENTS OF GLASS CERAMIC COMPOSITE TAPES

Thermoanalytical investigations

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Abstract

Glass ceramic composite tapes are composed of inorganic raw materials (borosilicate glasses and inert fillers) and organic additives (polymer binder, plasticizer, dispergent, residues of solvent from the tape casting process). Burnout of organics in air is a complex process of vaporization, depolymerization and oxidation. Conditions of this process can be simulated by thermal analysis of plasticizer, various binders and binder/plasticizer mixtures with alumina, prepared by impregnation of alumina powder with corresponding solutions and subsequent drying. This allows a quantitative interpretation of the results of burnout of tapes.

Keywords: burnout, ceramics, ceramic tapes, degradation, polymers, TG-DTA

Introduction

Glass ceramic composite tapes are intermediates for the production of LTCC multilayer substrates for hybride microelectronic circuits, multichip modules, and microwave packages [1–5]. These tapes contain an inorganic ceramic raw material dispersed in an organic matrix. In the ceramic firing process the matrix is burned out and the inorganic components form a dense body. Some aspects of the firing processes, mainly in and between the inorganic components, have been reported previously [6]. This paper deals with the burnout of the organic matrix.

Components of the organic matrix are

- polymeric binder – poly (vinyl butyral) or polyacrylate,
- plasticizer – dibutyl phthalate,
- dispergent – phosphoric acid ester,
- residues of organic solvents (alcohols, ketones) from the casting process.

Burning out these organics i.e. heating the tape in air one has to anticipate complex processes including their vaporization, decomposition and depolymerization, and oxidation. Thermal analysis in an air flow may be thought of as a model of the technical firing process.

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Experimental

Thermal analyses were performed in a symmetric SETARAM TAG 24 thermobalance equipped with simultaneous DTA measurement facilities. Samples were placed in open 100 μl platinum cups and heated in an air flow at 5 K min^{-1}, with a 1 h stop at 500°C.

Polymeric binder materials used to prepare the tapes and model samples were: PVB 1, poly(vinyl butyral) B 79; PVB 2, poly(vinyl butyral) B 98, white powders, both obtained from Monsanto; PAcr 1, polymethacrylate-acrylate B 72, colorless granulate; PAcr 2, polymethacrylate-acrylate A 21, colorless granulate; PAcr 3, polymethacrylate-acrylate A 11, white powder, all obtained from Rohm & Haas.

Results and discussion

Tapes

Figure 1 shows typical thermoanalytical curves of both a polyacrylate (PAcr) and poly(vinyl butyral) (PVB) based tape. Whereas TG and DTG curves exhibit reasonable reproducibility, the DTA curves of polyacrylates are dramatically affected by the heating rate, mass, geometry and packing density of the sample and the gas exchange. This influence has been discussed previously [6]. There occur simultaneously endothermal decomposition (depolymerization) and evaporation and exothermal oxidation of organic components. As long as sufficient oxygen has access to the sample, the exothermal process predominates in the DTA

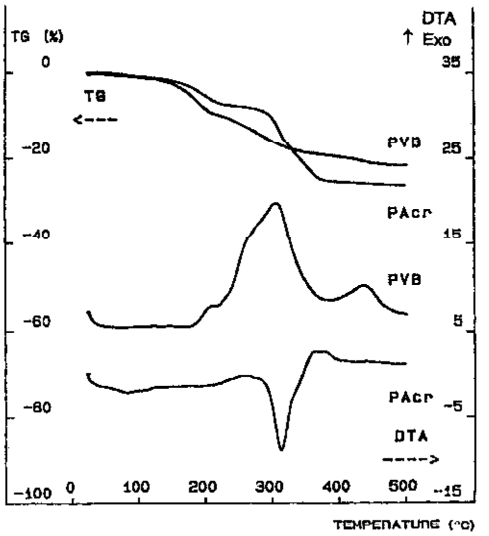

Fig. 1 TG and DTA curves of polyacrylate (PAcr) and poly(vinyl butyral) type (PVB) tapes, sample mass ≈20 mg

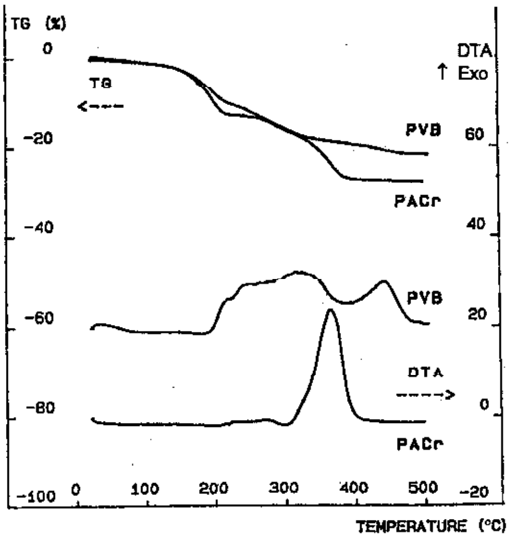

Fig. 2 TG and DTA curves of polyacrylate (PAcr) and poly(vinyl butyral) type (PVB) tapes, sample mass ≈10 mg, sample geometry optimized

signal. If however – as in the case of PAcr – there develops locally and temporarily shortage of oxygen by too rapid decomposition and poor exchange of gases, the endothermal effect of decomposition can predominate occasionally. To obtain reproducible DTA curves, this latter situation must be prevented. Therefore, with tape samples, measurements had to be performed using a small sample mass (<10 mg), an open crucible, and not too high heating rate (5 K $\min^{-1}$ or less). We have chosen 5 K $\min^{-1}$ to minimize experimental time. To achieve a reproducible geometry of sample that provides sufficient exchange of gases, a rectangular section of 4 by 12 mm was cut out, bent as a cylinder and placed vertically in the sample cup to touch its wall. With these conditions of measurement, we obtained reproducible thermoanalytical results for PVB and PAcr type tapes (Fig. 2).

Binders

We intended to compare the thermal behavior of tapes with that of their components. Thermoanalytical diagrams of binders in form of powders or granulates: 2 PVB binders (Fig. 3) and 3 PAcr binders (Fig. 4) exhibit irregular and – in case of PAcr – very different DTA curves, probably again affected by the various access of atmospheric oxygen for the oxidation of the decomposing polymers. As already known from corresponding tapes (Figs 1, 2), the decomposition of bulk binders of polyacrylate type started at lower temperature and ended at higher temperatures than that of poly(vinyl butyral) type. However, these results did not allow for any further conclusions concerning the decomposition of tapes.

Another procedure to prepare binder samples for TA proved more successful. A dilute solution of polymer (5 mass%) in a butanone-ethanol solvent was sucked in α-Al_2O_3 powder. TA measurements were performed after the majority of the solvent had evaporated from this impregnate. This procedure had the advantages that a very small mass of active sample (1... 2 mg on ≈25 mg alumina) came to the investigation, forming a large specific surface that was not drastically changed upon melting of the polymer, and easy exchange of gases was not restricted by melting. As a result, the decomposition/oxidation of polymers gave

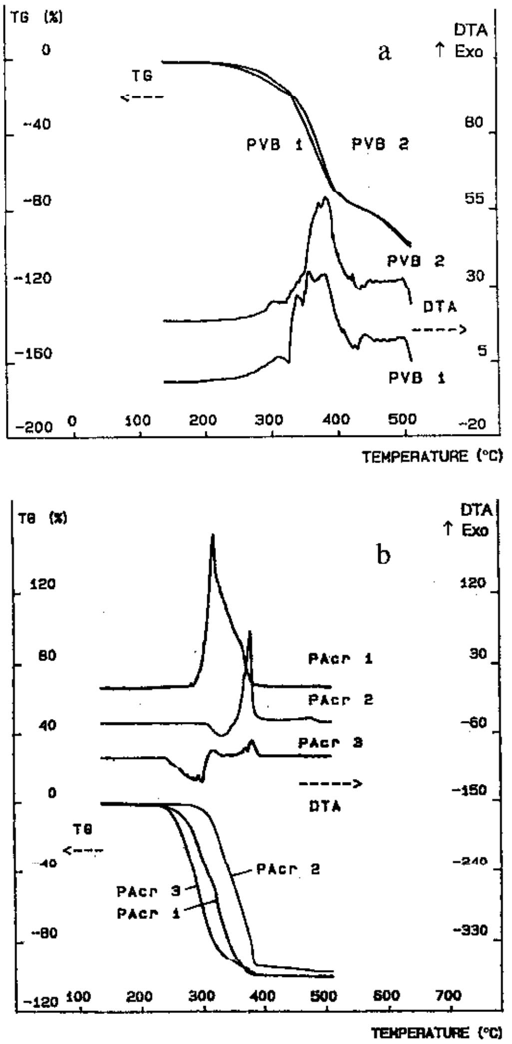

Fig. 3 TG and DTA curves of a) poly(vinyl butyral) binders (powders): PVB 1, B 79; PVB 2, B 98; b) polyacrylate binders: PAcr 1, B 72, granulate; PAcr 2, A 21, granulate; PAcr 3, A 11, powder

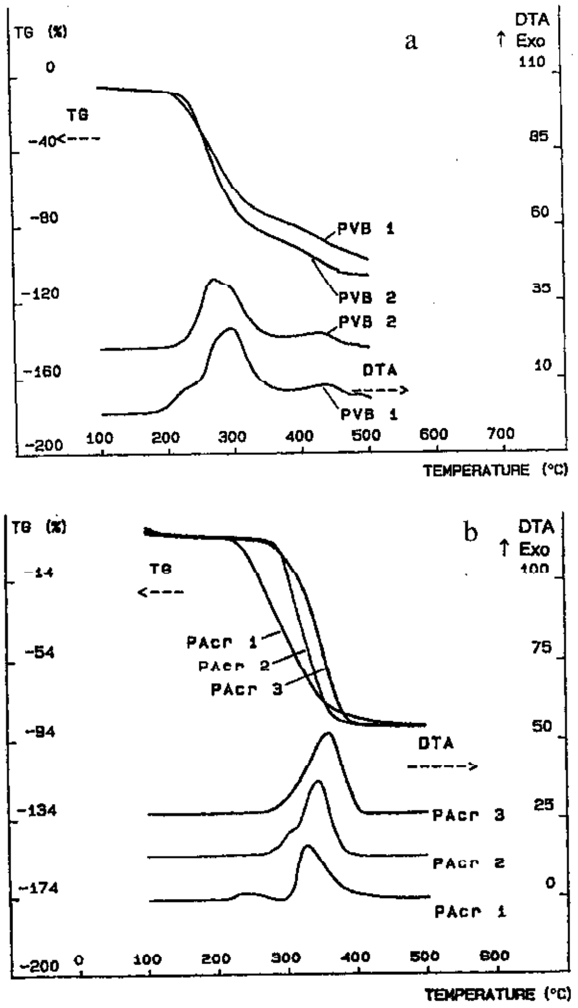

Fig. 4 TG and DTA curves of the polymer binders of Fig. 3 after solution impregnation in α-Al_2O_3 powder. (a) PVB binders, (b) PAcr binders

simple curves, only exothermic even in case of PAcr. The influence due to irreproducible sample geometry was cancelled. Any differences could be ascribed unambiguously to the different binders. Thus we have approximated the conditions of thermooxidative destruction of the polymer to those controlling the same processes when heating the tape.

Plasticizer

The other organic main component of the organic phase is the plasticizer dibutyl phthalate (DBP). In thermal analysis (Fig. 5) the bulk liquid exhibits TG

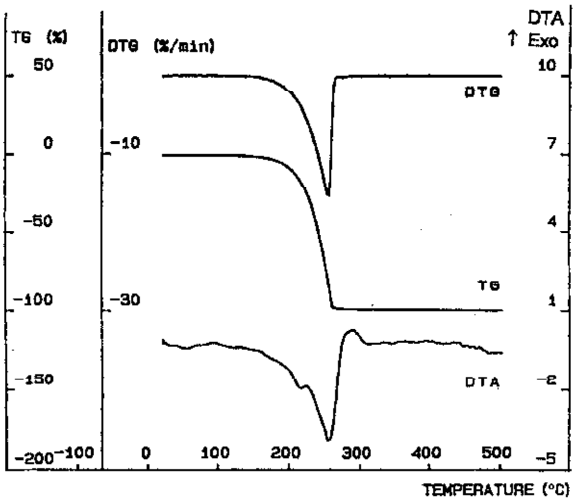

Fig. 5 TG, DTG and DTA curve of bulk plasticizer dibutyl phthalate

and DTG curves typical for the vaporization under non-equilibrium conditions below the boiling point. Vapour pressure and vaporization rate increase at rising temperature. At ≈260°C, much below the boiling point at atmospheric pressure (340°C [7]), the liquid is totally evaporated, vaporization ends abruptly. The evaporation gives rise to a relatively small endothermal DTA effect. It is followed by a smaller exotherm >260°C. The latter together with some irregularities in the endotherm above 200°C, and intermediate dark colouration of the

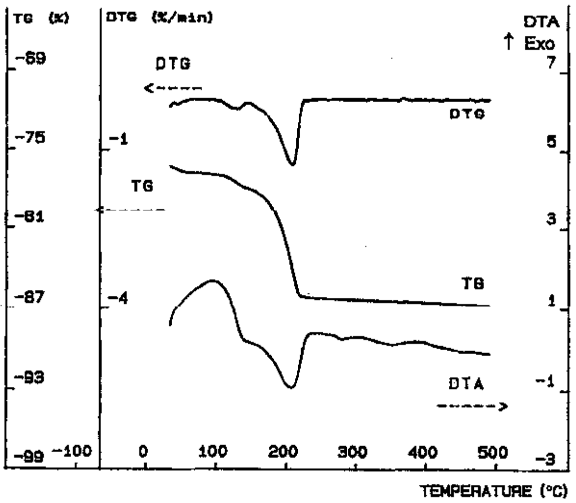

Fig. 6 TG, DTG and DTA curve of plasticizer dibutyl phthalate after solution impregnation in α-Al_2O_3 powder

heated sample suggest that some side reaction occurs parallel to the evaporation. Probably the plasticizer is partially decomposed into less volatile tar-like products and these residues were then oxidized at higher temperature after evaporation of the main amount of DBP.

Analogously to the binders (previous section), the plasticizer was applied as a dilute solution to impregnate an alumina powder, the majority of the solvent was evaporated by an air flow. Then, TA curves (Fig. 6) show endothermal mass loss in two partially overlapping steps below and above ≈150°C, presumably indicating the vaporization of residual solvent and plasticizer. Under these conditions with a sample mass of ≈2 mg, the vaporization is finished at 215°C and no hints were found to any decomposition. Therefore one may assume that the decomposition of the plasticizer occurs >215°C, if it is not vaporized at lower temperature.

Binder plus plasticizer

Next we studied the behavior of mixtures of (polymeric binders plus plasticizer) obtained by the technique of solution impregnation in alumina. As an example, Fig. 7 presents the thermoanalytical curves obtained with a mixture of the

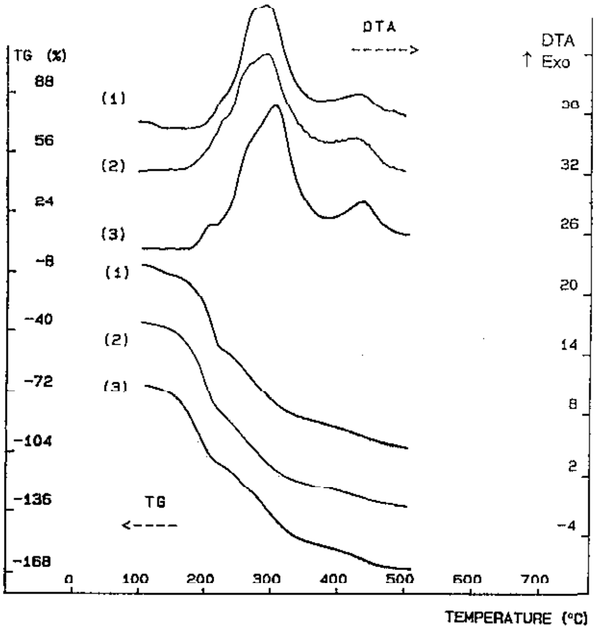

Fig. 7 TG and DTA curves 1) generated by weighted addition of curves of binders B 79 and B 98 and plasticizer (each measured separately after solution impregnation in α-Al_2O_3 powder); 2) of a binder/plasticizer mixture (after solution impregnation in α-Al_2O_3 powder); 3) of a tape prepared with the same binder/plasticizer system

two poly(vinyl butyral)s and dibutylphthalate. The results (curves 2) closely resembled those of real tapes (curves 3), prepared with the same system of two binders and plasticizer. Furthermore, it was possible to generate the same TA curves by the addition of TA signals obtained separately with pure binder and plasticizer, weighted according to their respective mass shares in the solution (curves 1). Thus the TA results obtained with the tapes can be interpreted as a summation of thermoanalytical curves of the main components binder and plasticizer.

Conclusions

The results allow to assign quantitatively the thermal effects of tapes (Fig. 2) to the processes as listed in Table 1.

Table 1 Thermal bevior of tapes and model systems

Temperatur interval	Mass change	DTA effect	Interpretation
120 ... 220°C	strong mass loss, increasing rate at increasing temperature	weak endotherm	evaporation of DBP
190 ... 490°C	mass loss in 2 overlapping steps: 1) strong mass loss, 2) weak mass loss	2 overlapping peaks 1) strong exotherm 2) weakly exotherm	decomposition and oxidation of PVB
or 270 ... 440°C	1 or 2 overlapping mass loss steps, (depending on polymer charge)	1 or 2 exothermal DTA peaks	decomposition and oxidation of PAcr

In case of PAcr type tapes the mass loss steps due to the evaporation of plasticizer and decomposition of polymer are sufficiently separated to allow for quantitative determination of the plasticizer content. In PVB type tapes the decomposition of polymer starts – as visualized by the exothermic effect – before the evaporation of PVB is concluded. This allows for a rough estimation of plasticizer content only.

Except polymer binder and plasticizer, the organic phase of tapes contains small amounts of residual solvents and dispergent. Solvents are evaporated below ≈130°C and do not affect the thermal analysis results of tapes above this temperature. The dispergent is decomposed very slowly and exothermically between

100 and 400°C. Due to its low content this process should hardly be visible on the TA diagrams if the 50-fold mass of polymer and plasticizer are burned simultaneously. Further studies have to deal with this subject.

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