

Pyrolysis of poly-methyl methacrylate (PMMA) binder in thermoelectric green tapes made by the tape casting method

Loey A. Salam*, Richard D. Matthews, Hugh Robertson

School of Engineering Systems and Design, South Bank University, 103 Borough Road, London SE1 0AA, UK

Received 15 February 1999; received in revised form 20 May 1999; accepted 27 May 1999

Abstract

The pyrolysis of poly-methyl methacrylate (PMMA) binder in thermoelectric green tapes, are analysed through differential thermal analysis (DTA), thermogravimetric analysis (TGA). These analyses confirmed that the main mechanism of the PMMA binder decomposition is the depolymerization or the unzipping mechanism. The best pyrolysis procedure was found to be in air to a maximum temperature of 410°C with 1.30–2 h hold out time. Some small amount of binder residue was found to remain in tapes after the pyrolysis procedure. This was suspected to be due to an interaction between the thermoelectric powder and the PMMA binder. Despite this small residue, the thermoelectric tape was sintered successfully to almost 95% of its theoretical density, in vacuum at 1200°C after 4 h. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: PMMA; Pyrolysis; Sintering; Tape casting; Thermoelectric materials; FeSi₂

1. Introduction

The tape casting process has been investigated as a new low cost fabrication process for thermoelectric generator. The process involve the production of flexible thermoelectric tapes by the addition of polymer binder, plasticizer and dispersant to the thermoelectric powder in a solvent mixture.

The role of these organic additives are temporary with a limited function of imparting strength and flexibility in green tapes during the process of cutting, shaping and lamination of these tapes. Once the tapes are laminated, the organic additives must be completely removed from the tapes before densification can reach an advanced stage, otherwise, residues may be retained within the tapes and alter the desired properties of the thermoelectric materials. The removal of the organic additives is generally called the pyrolysis process or organic burnout, and consists of thermal decomposition and evaporation of the organic additives and the subsequent removal of the volatile compounds from the thermoelectric tape.

In a previous paper,¹ the pyrolysis of the polyvinyl butyral (PVB) binder system formulation for the thermoelectric tapes was investigated. It was concluded that the PVB system was not a suitable binder candidate to be used in the fabrication process, due to the inability to remove all the its residues from the tape. These residues were identified as a unsaturated hydrocarbone, and was in the form of a very fine black powder (soot), which covered the entire thermoelectric material, preventing its densification during sintering. To tackle the problem, an alternative polymer binder system a poly-methyl methacrylate (PMMA) was used due to its low burnout temperature and its low char content.

2. Experimental procedure

Several cast thermoelectric green tapes with Iron Disilicide powders were made with PMMA formulation in order to optimise the green tape quality, the details of which are published in Ref. 2. The Iron disilicide powder samples were prepared by the mechanical alloying technique.³ The average particle size of the powder was 3.15 µm, the specific surface area was 1.5633 m²/cm³ and of irregular shape. Table 1 shows the general slurry composition with PMMA binder.

* Corresponding author. Tel.: +44-(0)171-815-7672; fax: +44-(0)171-815-7699.

E-mail address: salamla@vax.sbu.ac.uk (L.A. Salam).

The PMMA binders were of two types and obtained from Rohm and Hass (USA). The first under the commercial name of Acryloid B-67 was in the form of transparent white grains. While a second had the commercial name of Acryloid B-7 MEK, and was in the form of viscous liquid, with the binder already dissolved into a methyl-ethyl Keton solvent (MEK). The plasticizer dibutyl phthalate was in a liquid form, was obtained from BASF.UK, under the commercial name of "Palational C". The solvents were both 99.9% pure and obtained from Fison, UK.

The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) was carried out for the organic additives and the cast tapes using a Dupont differential scanning calorimetry cell (DSC). The pyrolysis procedure were carried out on the thermoelectric cast green tapes using a horizontal furnace under different atmospheres.

3. Results and discussion

While the PVB binder is commonly used in the tape casting process, because of its excellent green tape characteristic,^{1,2} the PMMA binder was used in this project for its low burnout temperature. The PMMA binders in general leave very small amounts of char after burnout.

The B-67 and the B-7MEK binders have been optimized for low char burnout by altering their chemical structures.⁴ These changes are a company proprietary, but it is thought that these changes involve the addition of oxidative additives, to oxidize the char to volatile CO or CO₂. Consequently, the amount of intrinsic char with these binders after pyrolysis, were quoted by the company to be <0.04% and <0.05% for the B-67 and the B-7MEK binders respectively, while the gas phase mediate char was estimated to be 0.0054% ± 0.0002 for both binders. These low residues compares favourably with the PVB binder char yield, estimated to be 0.34% and 0.00864% ± 0.0008 for the intrinsic and the gas phase mediate char, respectively.⁵

DTA and TGA analysis were conducted on the individual organic additives of the PMMA binder system shown in Table 1, with a DSC cell type Stanton Red-Croft STA-780 thermal analysis system. No analysis was connected on the dispersant glycerol trioleate, which was found to evaporate completely at 80°C.

Figs. 1–4, show the TG/DTA analysis for binder B-67 and B-7MEK in air and nitrogen atmospheres. These analysis were carried out under a heating rate of 5 K/min, to a maximum temperature of 1000°C, under a flow rate of 50 ml/min of air or nitrogen gas. The nitrogen which was a normal grade, was dried using a commercial gas drier (calcium chloride + molecular sieve). The B-67 was in the form of solid granules, which were hand-ground to a fine powder in a mortar and

Table 1

Types of organic additives used in the slurry composition for the thermoelectric green tapes

Function	Material
Thermoelectric powder	FeSi ₂
Dispersant	Glycerol trioleate
Solvent 1	Trichloroethylene
Solvent 2	Ethanol
Plasticizer	Dibutyl phthalate
Binder	Acryloid B-67 or B-7MEK

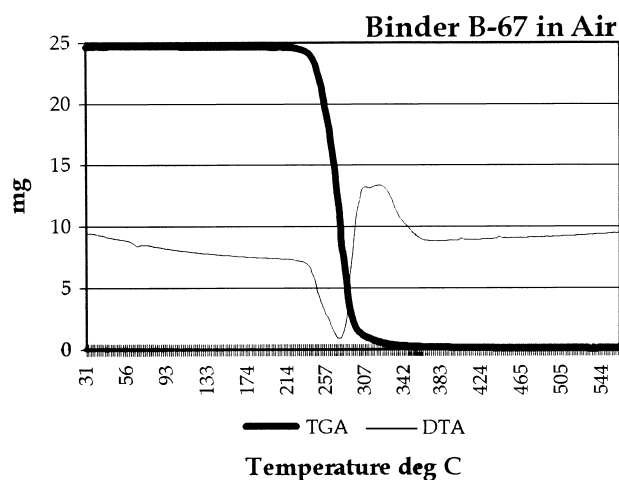


Fig. 1. TG/DTA analysis of B-67 (PMMA) binder in air.

pestle prior to testing. The B-7MEK, came as a dissolved solution containing 30% MEK solvent. The B-7MEK was left to dry in air, and then hand-ground to a fine powder under liquid nitrogen.

From Figs. 1 and 2 with air pyrolysis, it can be seen that the TG/DTA curves for B-67 and B-7MEK differ greatly. The bulk of the weight loss of B-67, almost 95%, occurs between temperatures of 230 and 375°C, with complete burnout just below 400°C. An endothermic peak starting at 230°C and ending at 310°C, is associated with the loss of almost 90% of the organic as volatile. This is followed up by an immediate exothermic peak, starting at 310°C and ending at 360°C. This exothermic peak is associated with the decomposition of less than 5% of the remaining binder, by an oxidative mechanism.

For the B-7MEK (Fig. 2), the bulk weight loss of around 80% of the binder, starts at a temperature of 260°C, which is higher than the B-67, and ending at a higher temperature of 390°C, with complete burn out of the B-7MEK at 447°C. A large and sharp exothermic peak associated with the second stage of the bulk weight loss was observed at around 350°C and ending at 390°C. This was followed by a much smaller exothermic peak starting at 400°C and ending at 420°C. Both these peaks are associated with the weight loss of the last 30% of the binder by an oxidative mechanism.

The effect of the nitrogen pyrolysis on B-67 decomposition is shown in Fig. 3, has delayed the complete burnout of the organic to a higher temperature of

420°C, compared to just below 400°C in the case of the air pyrolysis. The nitrogen pyrolysis had a similar effect on the B-7MEK binder as shown in Fig. 4. Figs. 5 and 6,

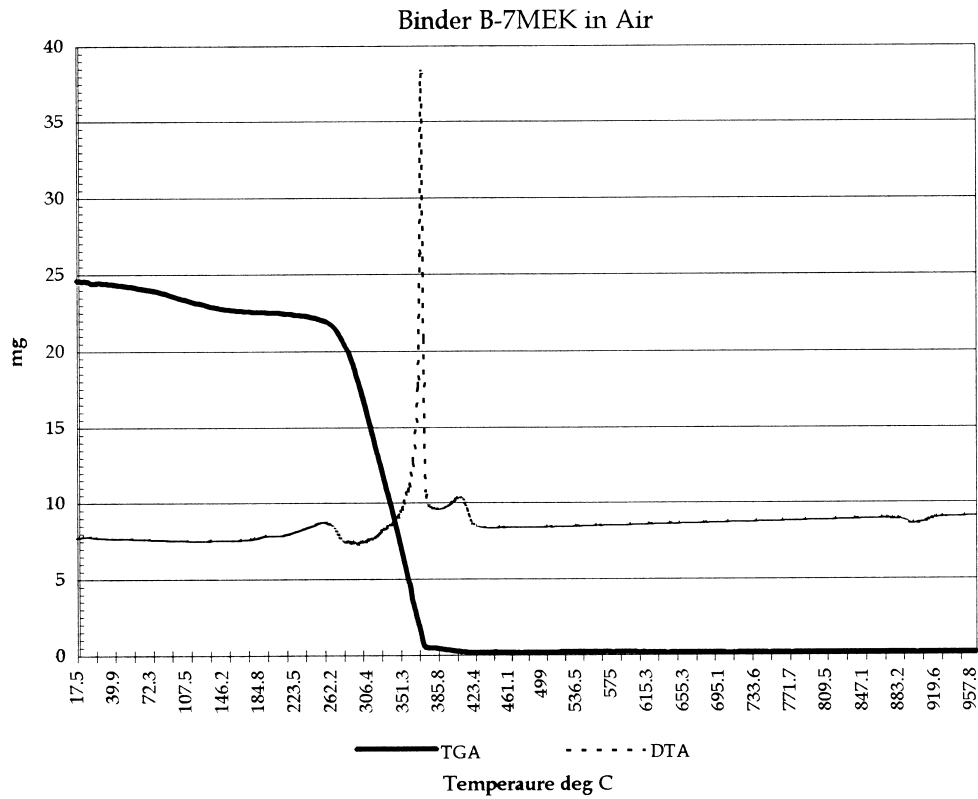


Fig. 2. TG/DTA analysis of B-7 MEK (PMMA) binder in air.

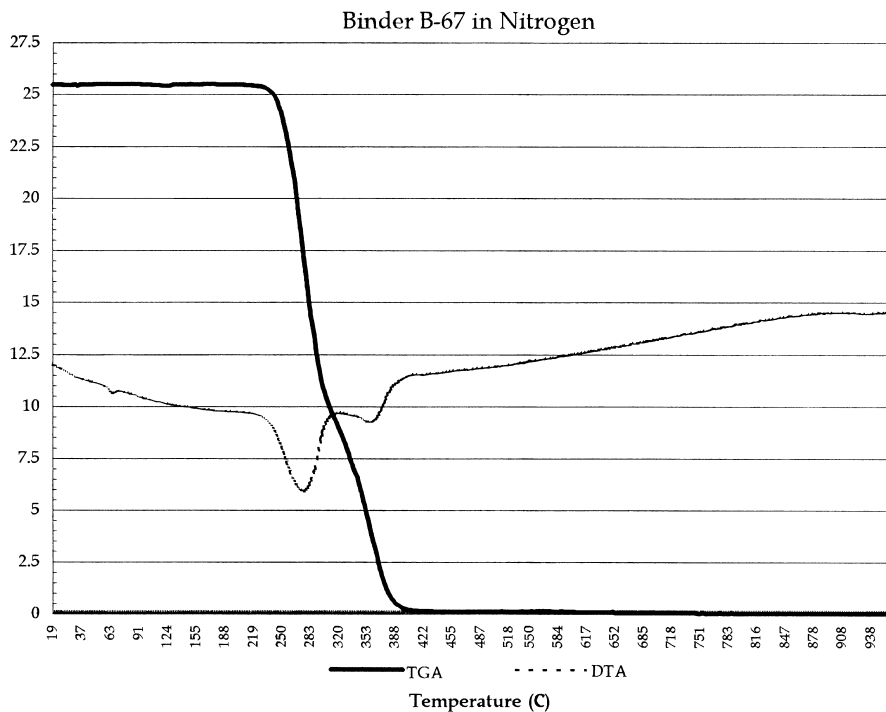


Fig. 3. TG/DTA analysis of B-67 (PMMA) binder in nitrogen.

show a comparison of the weight loss between B-67 and B-7MEK in air and nitrogen, respectively.

Figs. 7 and 8 show the TG/DTA analysis in air and nitrogen for the dibutyl phthalate plasticizer, used with the PMMA binder system. From the two figures, it can be seen that the plasticizer achieves complete burn out below 300°C, independent of the pyrolysis atmosphere.

TG/DTA analysis were also conducted for two green thermoelectric tapes S37 and S34 (0.3 mm thick) in air and nitrogen. The S37 tape, was made from the B-67 binder, and contained 10.17 wt% organic (7% of which binder), while tape S34 was made from the B-7MEK binder and contained 5.35 wt% (3.45% of which binder), see formulation in Table 1.

Figs. 9 and 10 show the TG/DTA analysis for tape S37 in air and nitrogen respectively. All the DTA reactions and weight losses were no different to those encountered for the TG/DTA analysis of the binder alone in air and nitrogen shown in Figs. 1 and 2.

Fig. 11 shows a comparison of the weight losses for tape S37 under air and nitrogen. The important difference between them is the increase in temperature under nitrogen by 50 K, to achieve the same weight losses when compared to that of air pyrolysis. More

importantly, there was no complete burn out for the organic under these atmospheres, but more organic residue was left in the tape under the nitrogen than under air. In the air pyrolysis more than 96% of the organic was burnt out at 395°C, in comparison to only 87% at 470°C, in the case of the nitrogen pyrolysis. Therefore the air pyrolysis had to be used rather than the nitrogen one, for cast tapes, to achieve a complete burnout at low temperatures.

In order to quantify the effect of the diffusion path length or the thickness of the tape on the binder burn out, a TGA analysis was carried for one layer and four laminated layers, of S37 tape, as shown in Fig. 12. From the figure it can be seen that the single layer tape started the weight loss at a lower temperature than the four layers, but the losses of the two tapes at 400°C, were different by less than 0.1 wt%.

Fig. 13 shows a comparison of the organic weight losses of tape S34 made with B-67 MEK binder in air and nitrogen. The S34 tape contained 5.35 wt% organic, 55.70% of which has been removed in the air pyrolysis below 400°C, compared to 62.61% of the total in nitrogen at temperature of 580°C. It is not clear, why the performance of B-7MEK was much worse than that

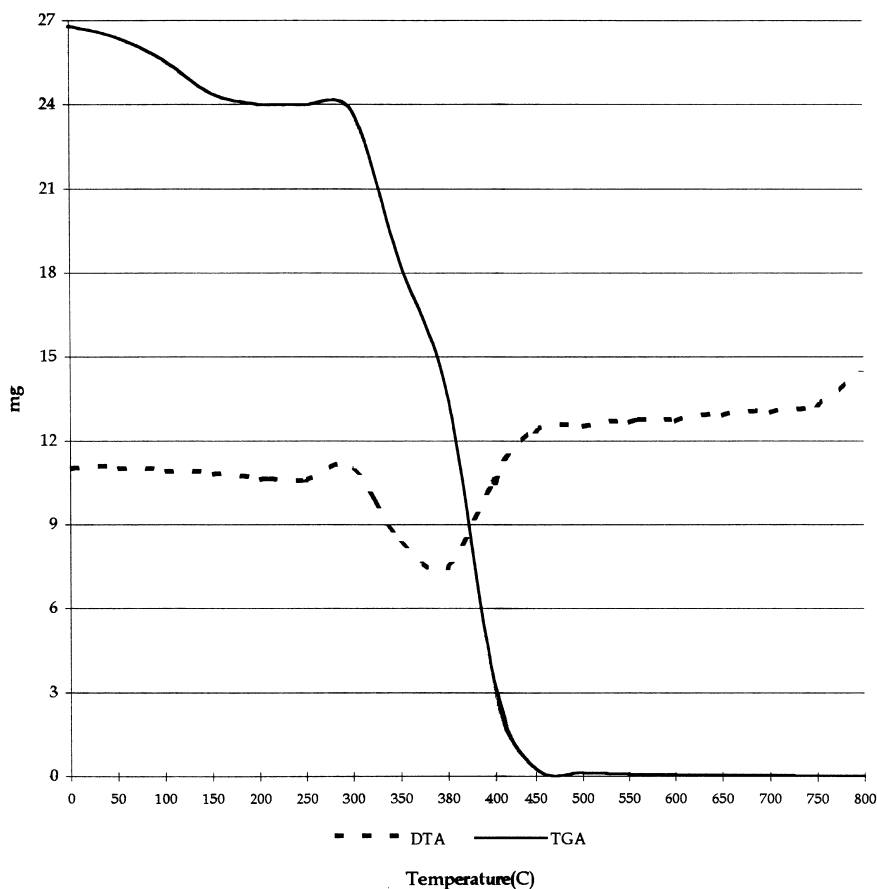


Fig. 4. TG/DTA analysis of B-7 MEK (PMMA) binder in nitrogen.

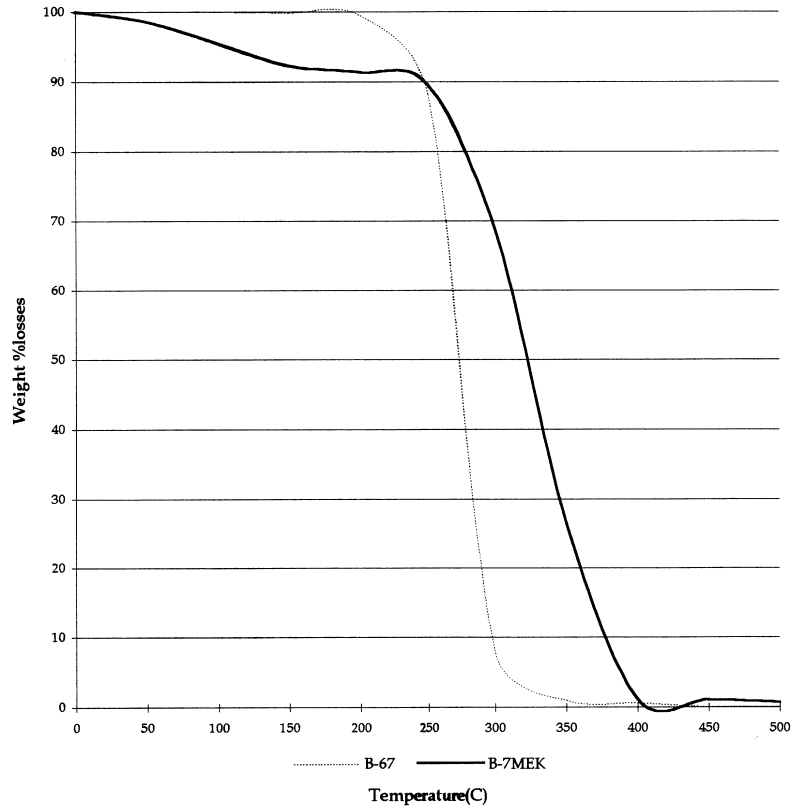


Fig. 5. Wt% loss comparison of B-67 and B-7 MEK binder in air.

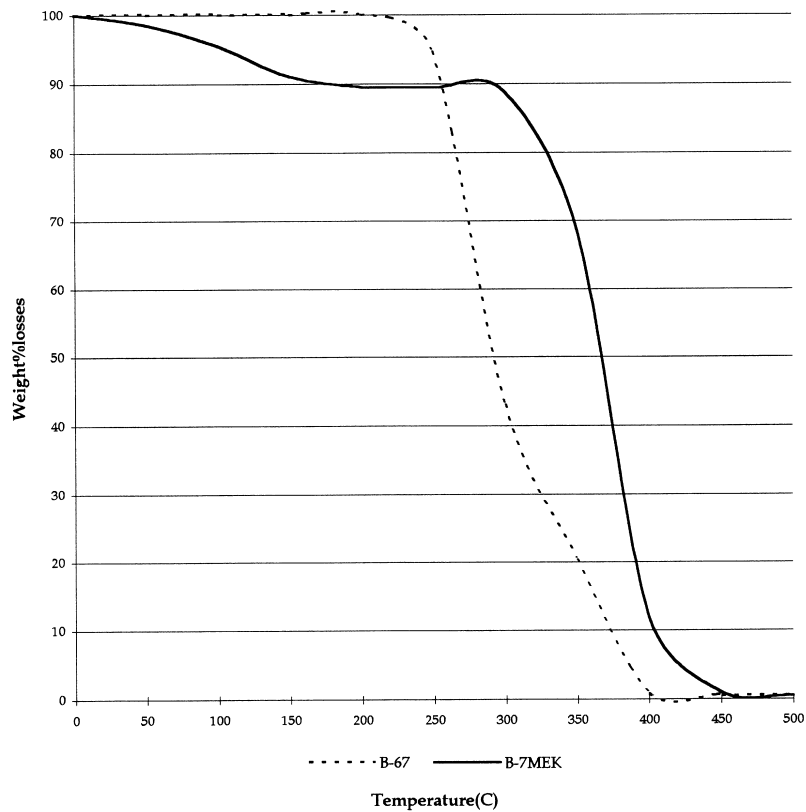


Fig. 6. Wt% loss comparison of B-67 and B-7 MEK binder in nitrogen.

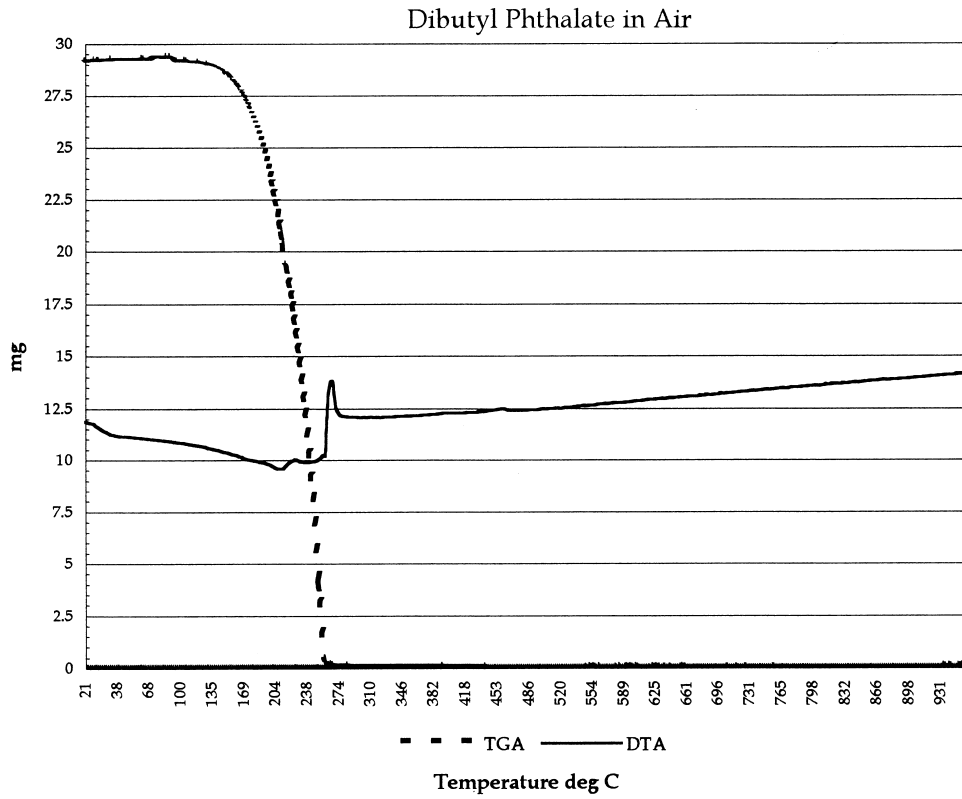


Fig. 7. TG/DTA analysis of dibutyl phthalate in air.

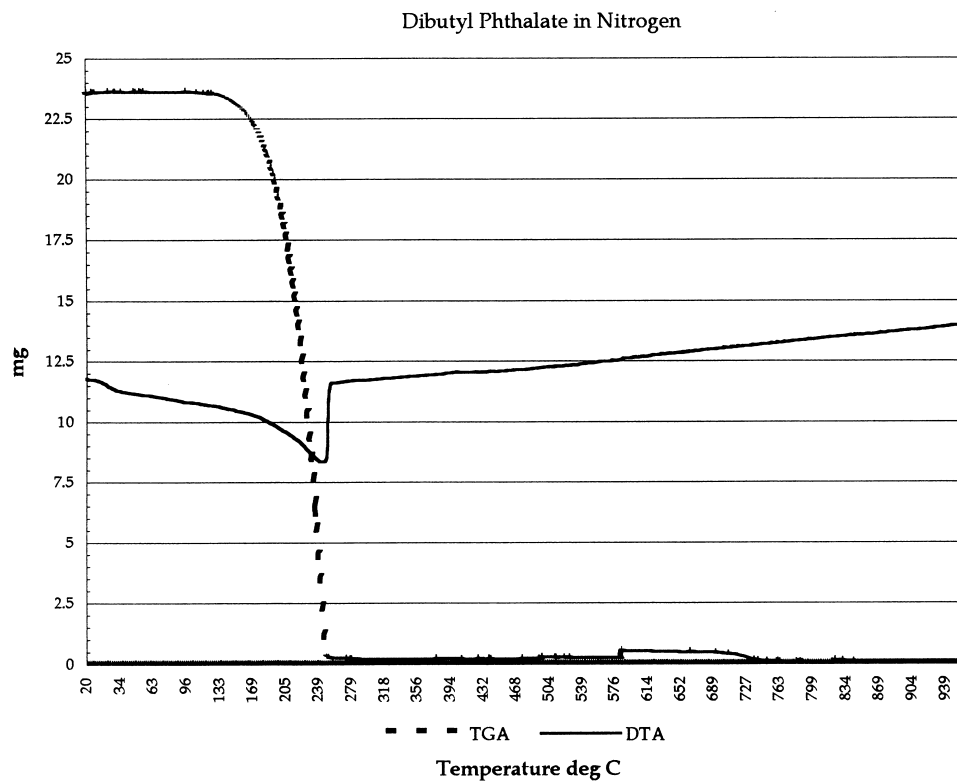


Fig. 8. TG/DTA analysis of dibutyl phthalate in nitrogen.

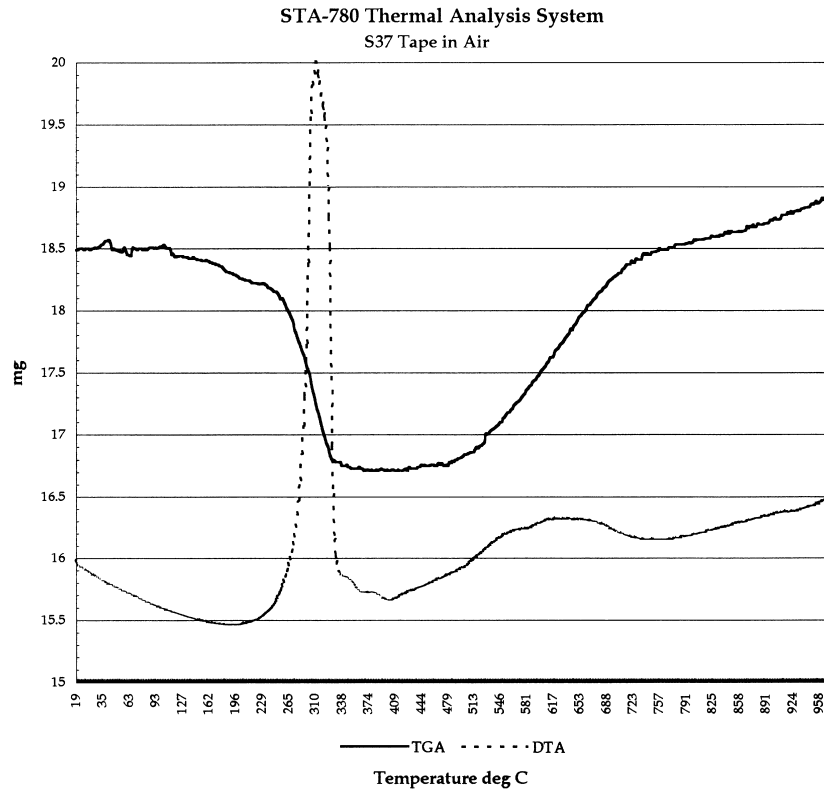


Fig. 9. TG/DTA analysis of tape S37 (B-67 binder) in air.

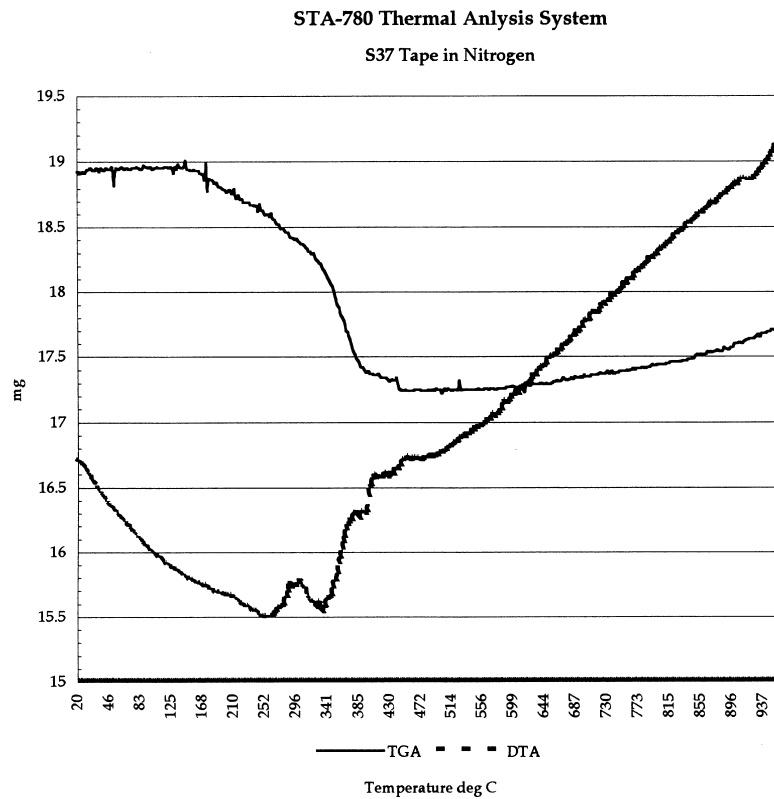


Fig. 10. TG/DTA analysis of tape S37 (B-67 binder) in nitrogen.

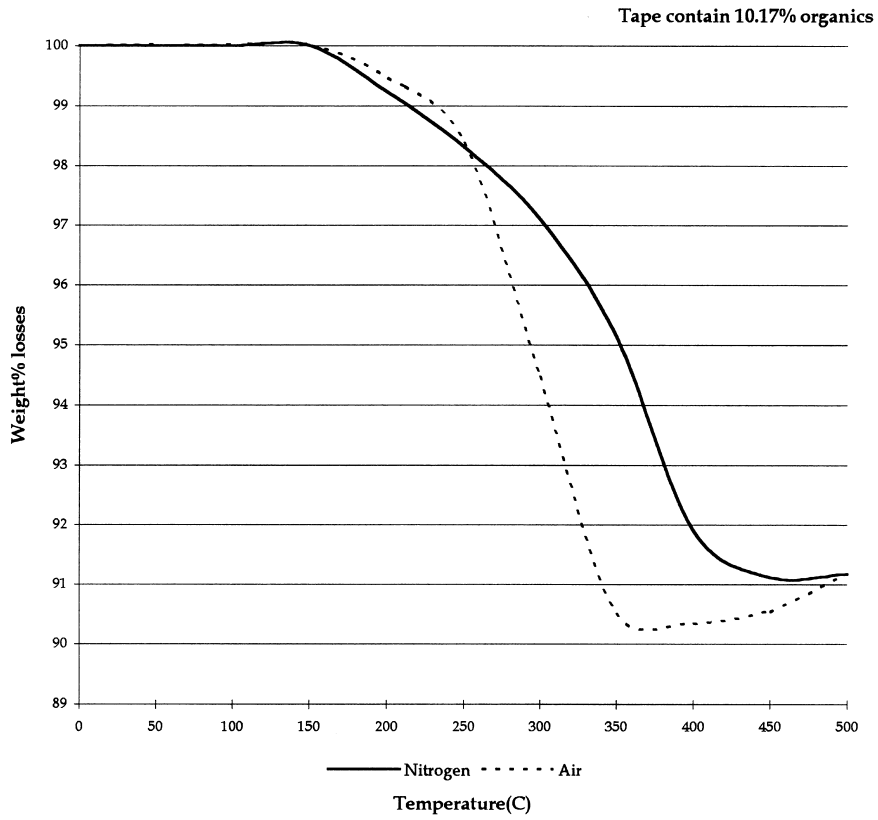


Fig. 11. Wt% loss comparison of tape S37 in air and nitrogen.

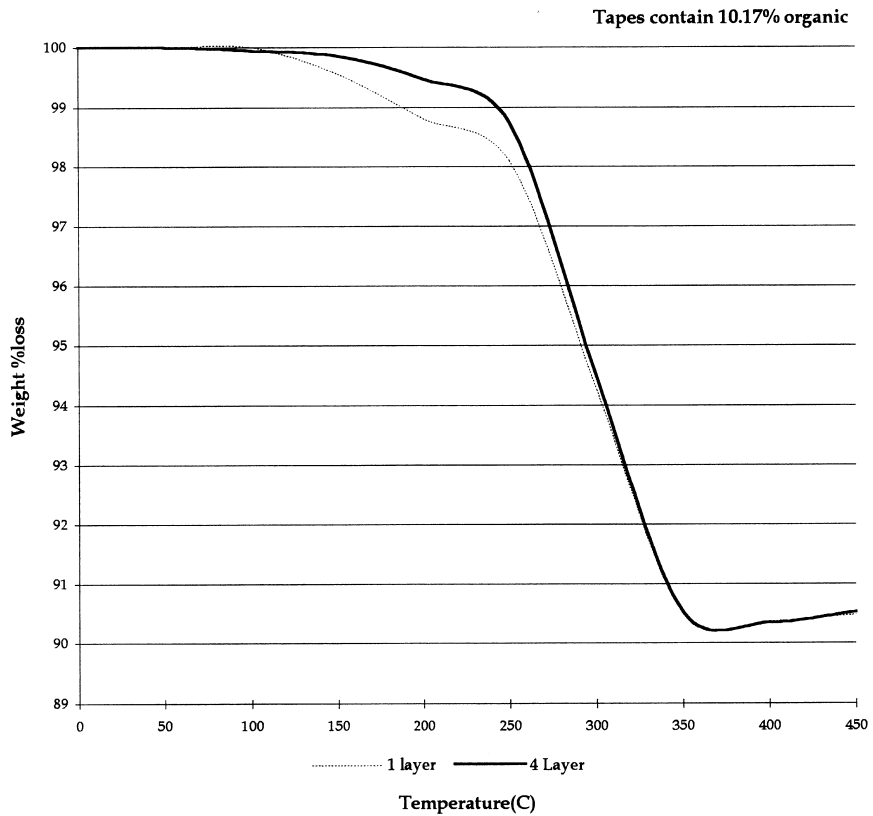


Fig. 12. Wt% loss comparison of 1 and 4 layers of S37 tape in air.

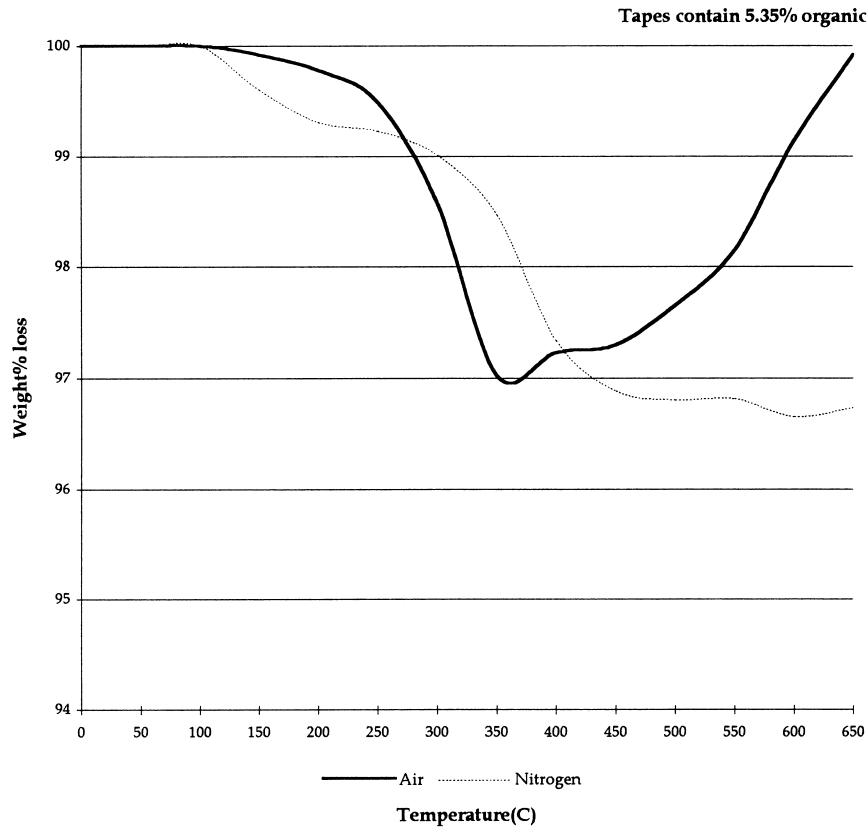


Fig. 13. Wt% loss comparison of tape S34 (B-7 MEK binder) in air and nitrogen.

of B-67 binder, since no information was given on what kind of structure manipulation was performed by the manufacturer on the two binders. Based on these results, it was decided to use the B-67 binder for the tape casting method, since it has an easier burn out characteristic than B-7MEK.

From the foregoing analysis, the pyrolysis mechanism for the PMMA binder appears to be extremely simple. It differs significantly from most other binders, which decompose thermally via complex mechanisms involving random bond scission, as described for PVB binder pyrolysis.¹

The main degradation mechanism occurs through the depolymerization of the binder, an exact reverse to the reaction used in the polymerization process of the binder. This mechanism is often referred to as an “Unzipping” reaction, which can be viewed as the reverse of the propagation step in addition polymerization shown in Fig. 14.⁴

The TG/DTA analysis of B-67 binder in air (Fig. 1) confirms that the degradation mechanism occurs through the depolymerization or unzipping mechanism, there are two indication of this behaviour.

1. The TGA curve shows that all the polymer weight losses occurs over a narrow temperature range 230–375°C, as expected for a polymer that

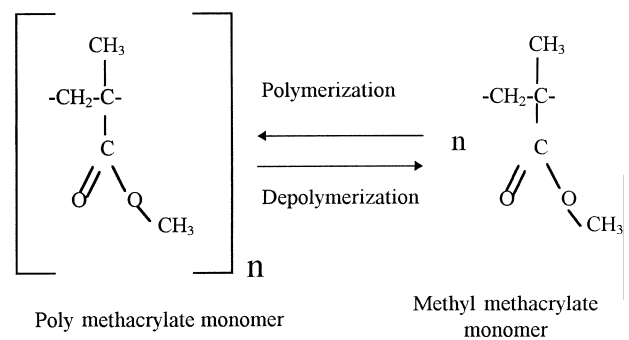


Fig. 14. Polymerization process of PMMA binder.

degrades by a single stage mechanism, such as depolymerization.

2. The DTA curve shows a single endothermic reaction which is consistent with the degradation mechanism of depolymerization.

The depolymerization mechanism usually does not differ in an oxidizing or inert atmosphere, but it could be retarded so that it occur at a higher temperature in an inert atmosphere. This was also confirmed by Fig. 2, for the B-67 binder pyrolysis in nitrogen, which shifted the complete burn out temperature upwards by 50 K.

The FTIR analysis for the PMMA binder pyrolysis in air carried out by Sun et al.⁶ showed that more than 95% of the degraded products were methyl methacrylate monomer, which confirm the unzipping reaction as the main pyrolysis mechanism.

The comparison between Figs. 1 and 9, for the B-67 binder and tape S37 pyrolysis in air, respectively, showed that a complete burnout of the binder was not achieved in the case of the tape. This indicates that there might be some further complications in the pyrolysis mechanism for B-67 binder in the presence of the thermoelectric powder.

Physical factors like the length of the diffusion path and the powder packing was discounted in this instance, since Fig. 12 showed that the weight losses was almost the same for 1 and 4 layer tapes. This was despite an increase in the length of the diffusion path and the powder packing density which usually occurs during tape lamination.

Therefore a binder–powder interaction was suspected to be the reason for the observed differences of the remaining small fraction of the binder in the tape pyrolysis. Two explanations were considered, which might effect the burnout of the last 4% of remaining binder in the tape, to undergo different degradation mechanism and which may form different degradation products than those of the unzipping mechanism for the bulk of the degraded binder.

Assuming that oxidisation occurs in some of the silicon powder within the matrix of the tape, a possible interaction could occur in two ways:

1. Depending on the powder metal–oxygen bonding, a surface reaction between the binder and the powder could increase. An increase in such reaction is observed, as the metal–oxygen bonding tends to be ionic and less if it is covalent.⁶
2. As the acidity of the powder was increased, an increase in the surface reaction was observed with the base character of the PMMA.⁷

The first observation was concluded by Sun and co-workers,⁶ as a result of a strong interaction between the PMMA binder and Al_2O_3 powder, which has an ionic bonding (less covalent), and even a greater degree of reaction was observed with the alkali halides. In contrast to the diamond powder with completely covalent bonding, which have no reaction with PMMA binder.

Applying this observation to the case of tape S37, if oxidization was assumed to take place, leading to the formation of SiO_2 , then the first observation is not applicable, since the Si–oxygen bonding is covalent. However some ionic bonding could take place between the corners of oxygen atoms and other ions like iron ions.⁸ Hence, an interaction between the PMMA and the thermoelectric powder could take place based on

such assumption, but this could be very weak and this explanation was discarded.

The second observation was based on an experiment carried out by Aruchany and co-workers,⁷ which showed, that an increase in the temperature of the PMMA decomposition was observed with decreasing PbO content (base character) in a glass mixture of $\text{PbO-SiO}_2\text{-B}_2\text{O}_3$. This indicated that the PMMA interacts strongly with more acidic surface, like those of SiO_2 . The interaction specifically occurs between the basic character of the ester group “ CH_3O ” of the PMMA and the acid-base SiO_2 . Despite this explanation much work is needed to verify the reasons for this specific behaviour of the PMMA with the thermoelectric powder.

Nevertheless, for thermoelectric tapes which were subjected to a maximum pyrolysis temperature in the range of 400–410°C, with a hold out time of 1.30–2 h, followed by sintering in vacuum at 1200°C for 4 h, have achieved a density of almost 95% of its theoretical density. This indicated that the small residue percentage remaining in tapes, had no detrimental effect on the sintering process or the thermoelectric properties of the material.

4. Conclusions

The pyrolysis of poly-methyl methacrylate (PMMA) binder in thermoelectric green tapes, are analysed through differential thermal analysis (DTA), thermogravimetric analysis (TGA). These analyses confirmed that the main mechanism of the PMMA binder is the depolymerization or the unzipping mechanism. The depolymerization mechanism usually does not differ in an oxidizing or inert atmosphere, but it could be retarded so that it occurs at a higher temperature in an inert atmosphere. However, the best pyrolysis procedure for PMMA was found to be in air to a maximum temperature of 410°C with 1.30–2 h hold out time. Some small amount of binder residue was found to remain in tapes after the pyrolysis procedure. This was suspected to be due to an interaction between the thermoelectric powder and the PMMA binder, which might be due to the interaction of the basic character of the ester group “ CH_3O ” of the PMMA with the acid-base SiO_2 . Despite this small residue, the thermoelectric tape was sintered successfully to almost 95% of its theoretical density, in vacuum at 1200°C after 4 h.

Acknowledgements

This work was performed as a part of a postdoctoral research contract with British Gas plc in 1994–1996. The authors acknowledge the help of Mr. David Lander from British Gas with the thermogravimetric analysis.

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