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Pyrolysis of polyvinyl butyral (PVB) binder in thermoelectric green tapes

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Abstract

The pyrolysis of polyvinyl butyral (PVB) binder and other organic additives in thermoelectric green tapes, are analysed through differential thermal analysis (DTA), thermogravimetric analysis (TGA) and published results of fourier transformer infrared spectroscopy (FTIR). Based on these analyses the optimum balance of binder degradation mechanism, heating rate, burnout temperature and burnout atmosphere were determined. The maximum upper temperature at which pyrolysis can take place in an oxidising atmosphere, was imposed at 450°C, to avoid the risk of oxidising the thermoelectric material above this temperature, which could degrade its thermoelectric properties. Thermoelectric cast green tapes made with PVB formulation were found to leave char residue after pyrolysis at 450°C, estimated to be almost 20% of the total PVB content in the tape. Different pyrolysis atmospheres of air, argon, CO_2 and Ar/H_2O were used to minimise the char content. The best pyrolysis for the PVB was obtained with the use of CO_2 atmosphere at 450°C with a hold-out time of 5 h, which reduced the char residue to only 1%. Even with this small percentage, the char residue was in the form of a very fine black powder (soot) which covered the thermoelectric material powder in the tape, preventing its densification at the later stages of the sintering process. It was therefore concluded that the PVB system was not a suitable binder candidate to be used in the fabrication of thermoelectric generator by the tape casting method. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: PVB; Pyrolysis; Sintering; Tape casting; Thermoelectric materials

1. Introduction

The tape-casting method has been employed as a new fabrication method for the thermoelectric generators. The role of organic additives are essential in the processing of the thermoelectric green tape. They impart strength and flexibility in green tapes, to retain the desired shape before firing.

During firing, the organic additives must be completely removed from the tape before densification reaches an advanced stage, otherwise, residues may be retained within the tape 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.

Once the complete burnout of all organic additives was achieved without leaving any residues, the sintering process took place at a much higher temperature than the pyrolysis's temperature. The objective of the sintering process was to achieve densification of the material to its theoretical density.

2. Experimental procedure

Several cast thermoelectric green tapes with silicon germanium or iron disilicide powders were made with PVB formulation in order to optimise the green tape quality, the details of which are published in Ref. 1. Table 1 shows the general slurry composition with PVB binder

The PVB binders were obtained from Hoechst representative in the UK (Crestchem Ltd), under the commercial name of Mowtial Resins and were supplied as a

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Table 1
Types of organic additives used in the slurry composition for the thermoelectric green tapes

Function	Material
Thermoelectric powder	SiGe or $FeSi_2$
Dispersant	Glycerol trioleate
Solvent 1	Trichloroethylene
Solvent 2	Ethanol
Plasticizer	PEG600/PEG1000
Plasticizer	Diethyl phthalate
Plasticizer	Dibutyl phthalate
Binder	Mowtial B20H (PVB)
Binder	Mowtial B70H (PVB)

free-flowing fine-grained powder. The Mowtial has grades of 20, 30, 40, 60 and 70. The number refers to the increasing degree of polymerisation. A combination of two grades of Mowtial B20H and B70H were used according to the advice of the manufacturer. The plasticizer polyethylene glycol (PEG) was obtained again from Hoechst, in two different molecular weights grades, of 600 and 1000 and both are obtainable in a liquid/solid form. The rest of the plasticizers, diethyl phthalate and dibutyl phthalate, both in a liquid form, were obtained from BASF, UK, under the commercial name of "Palational A" and "Palational C", respectively. The solvents were both 99.9% pure and obtained from Fison, UK.

The differential thermal analysis (DTA) and thermogravmetric analysis (TGA) was carried out for the organic additives and the cast tapes using a Dupont differential scanning calorimetary 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

Figs. 1–5, show the DTA results carried out for each of the individual organic additives used in the PVB formulation. This analysis was carried out in air, at a heating rate of 10°C/min, until the reaction was complete.

These figures show clearly the temperatures at which the reactions start and end for each additive. No DTA analysis was carried out on the dispersant, glycerol trioleate, since it evaporated completely at 80°C. Fig. 6 shows the DTA comparison of all the organic additives used in the formulation.

The DTA analyses of these figures help in establishing two points:

1. The main reaction temperatures will decide the heating rate during the pyrolysis process. Hence, a different heating rate during the organic burn out of the tape could be imposed as the temperature approaches the beginning of each reaction.
2. The DTA analysis ensures the suitability of the organic additives selection for the burn out stage. It is important for the individual organic additives to burn out at different temperatures but within a narrow temperature range, in order to avoid disturbing the powder structure in the tape.

Once the DTA analysis was carried out for each individual organic additive, the pan that contained the samples in the DSC was checked for residues, by weighing using an accurate analytical balance. All the plasticizers used, PEG600, Palational A and Palational C, were burnt out completely without leaving any residues. While both PVB binders, left some residues that were visible in the pan.

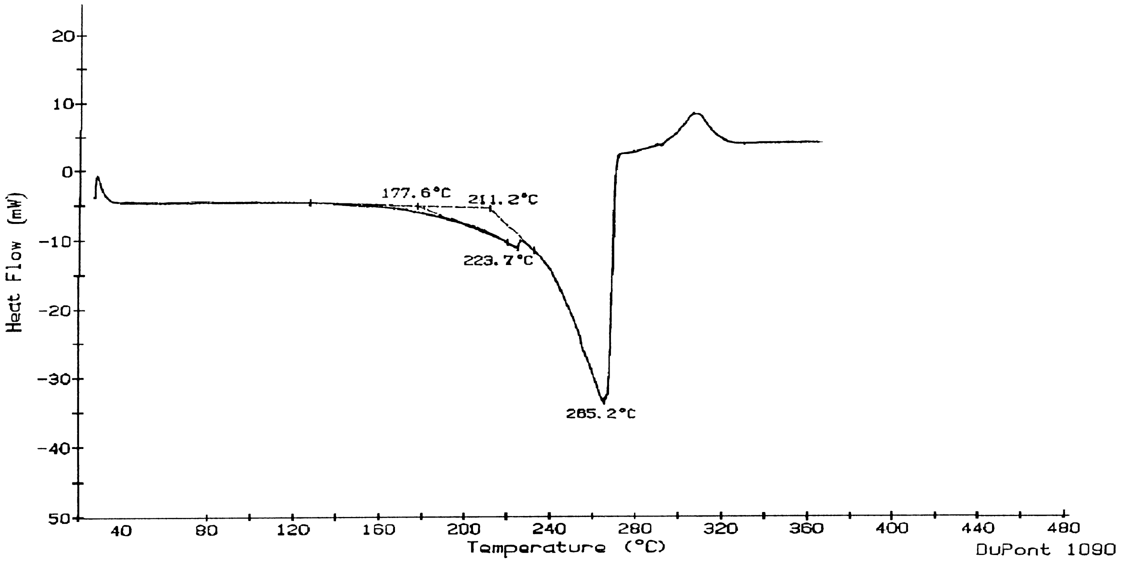


Fig. 1. DTA analysis of Palationol A (diethyl phthalate) plasticizer.

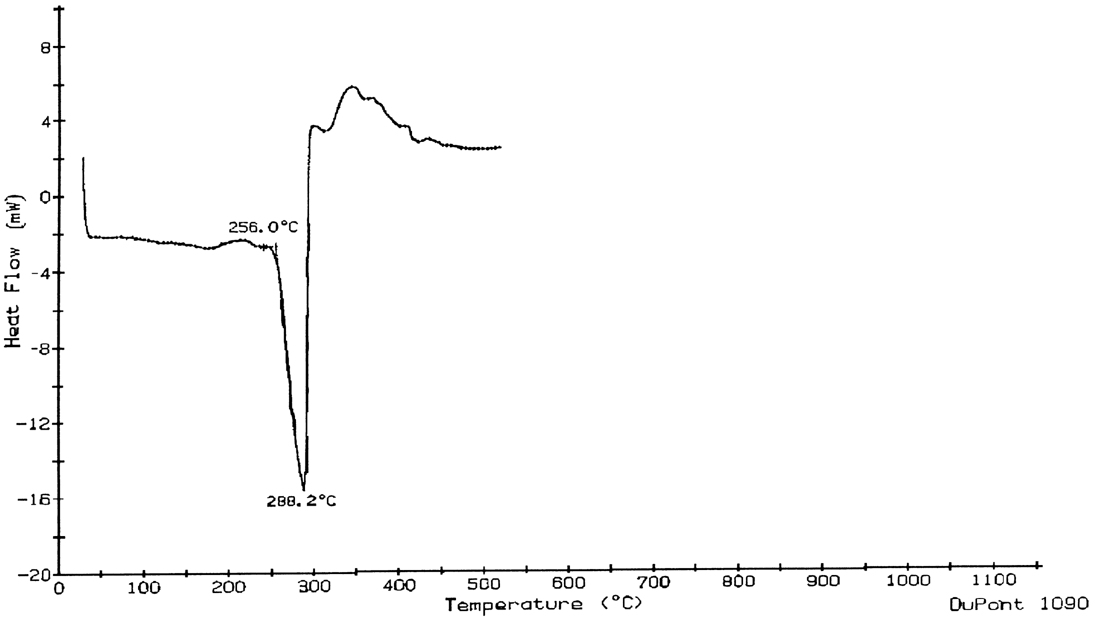


Fig. 2. DTA analysis of Palationol C (dibutyl phthalate) plasticizer.

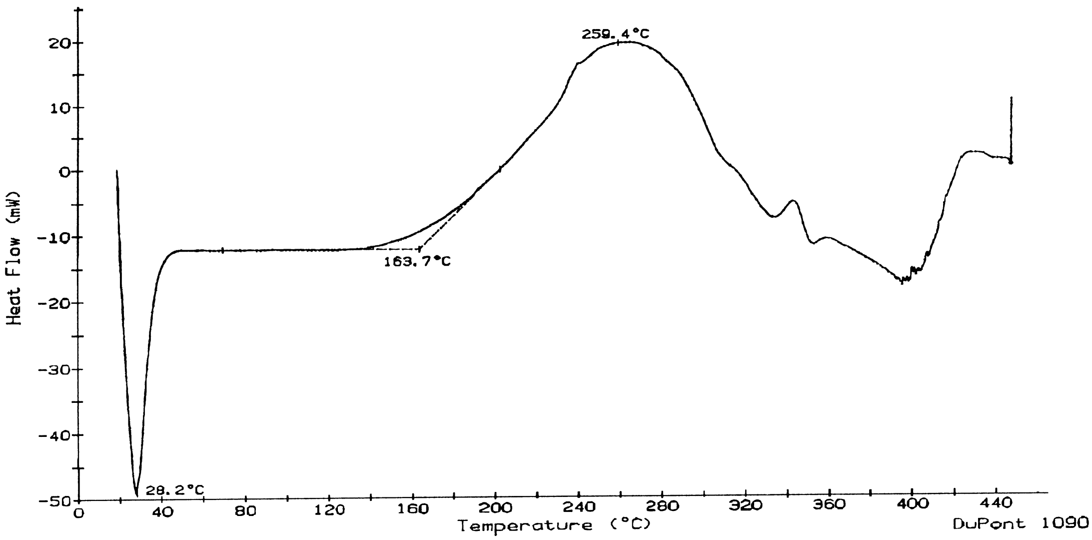


Fig. 3. DTA analysis of PEG 600 plasticizer.

TGA analysis was therefore performed on one of the PVB binders, in order to determine accurately the amount of residue by weight percentage. The TGA was only performed on the binder B70H, since both binders have the same chemical structure and they differ only in their relative molecular masses, of which B70H being the larger.

Fig. 7 shows the TGA analysis of the B70H binder, which shows the wt% loss of the binder, combined with the DTA data analysis, and the calculated rate of the wt% loss per min. The TGA analysis was carried out under airflow of 30 ml/min and heating rate of 20°C/min. The following observations about the PVB binder pyrolysis were made by examining Fig. 7:

1. The bulk of the weight loss, 'approximately 85%', for the PVB binder in air, occurred in the temperature range of 350–450°C, with the fastest rate of weight loss occurring in the temperature range of 397–447°C.
2. The PVB burnout was not completed by 600°C and the residue was estimated to be 2 wt%. This residue falls below 1 wt%, in the temperature range of 700–800°C, with almost no residue detected at 1000°C.
3. The large exothermic peaks were not associated with the primary first stage weight loss, but with the slower second stage weight loss, which occurred between the temperatures of 450–600°C. These

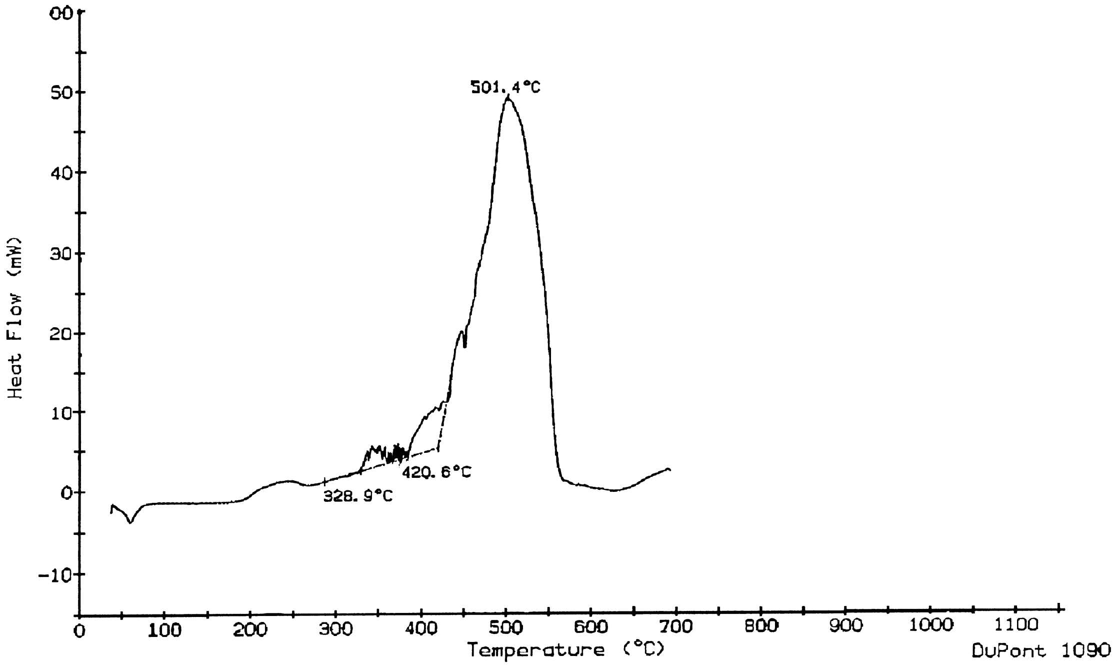


Fig. 4. DTA analysis of PVB binder (B20H).

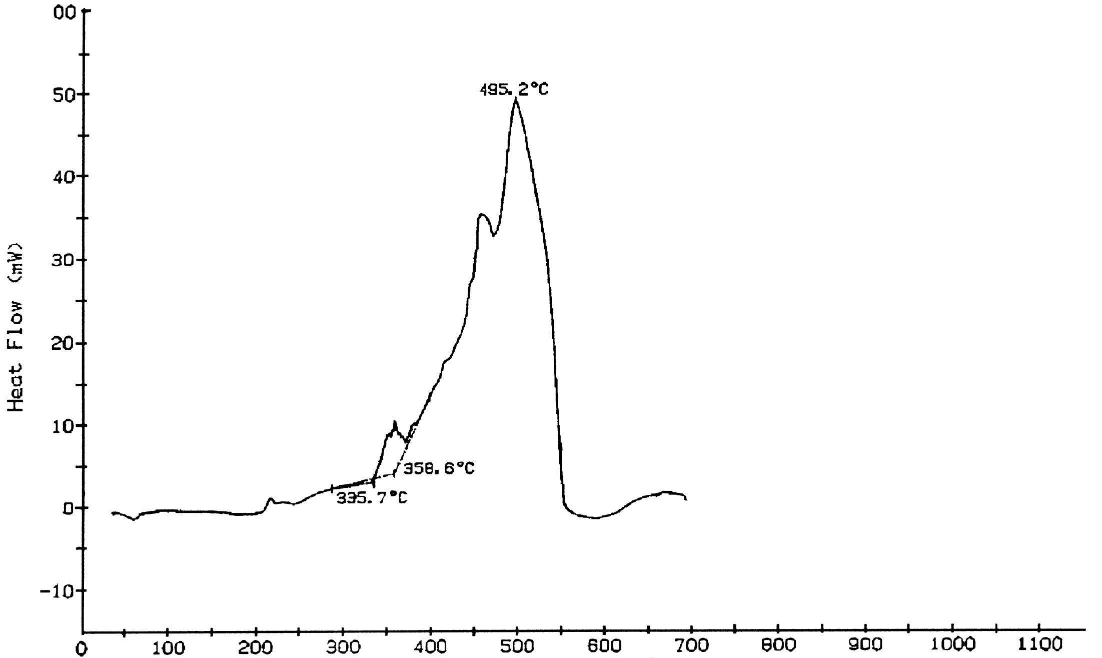


Fig. 5. DTA analysis of PVB binder (B70H).

exothermic peaks could be attributed to a large oxidisation reaction combined with a weight loss of volatile products.

Figs. 8 and 9 show the DTA, TGA and the rate of wt loss percentage analysis for two thermoelectric green tapes S4 and S2C, made by the tape-casting process out of SiGe powder, and containing 20.7 and 22.5% organic by weight. The relative powder packing of these tapes were 49.91 and 55.50%, respectively.

The two DTA curves show almost the same burn out characteristics and differ only in the magnitude of the reaction heat evolved, since two different sample sizes were used. It can also be noticed from Figs. 8 and 9,

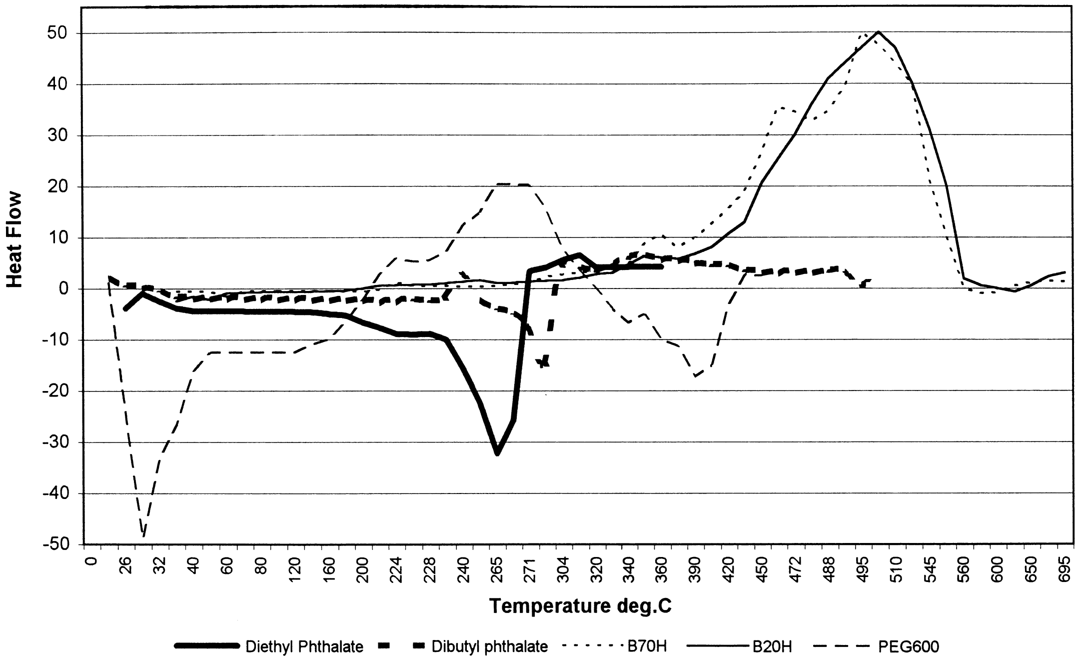


Fig. 6. Comparison of the DTA analysis for all the organic additives used in this project.

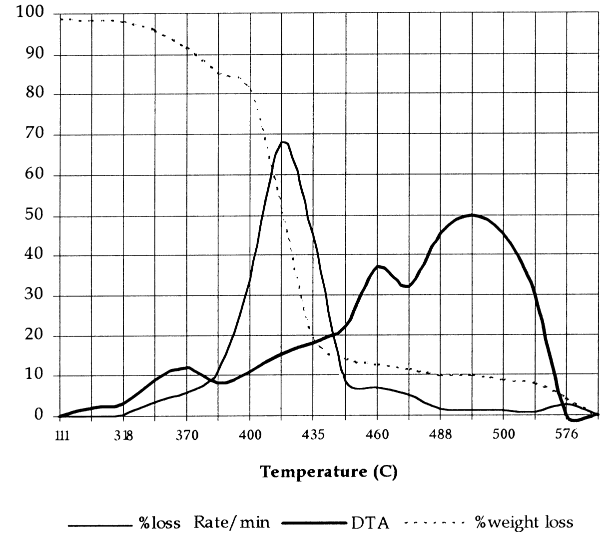


Fig. 7. Combined TG/DTA and wt% loss for the PVB (B70H) binder in air.

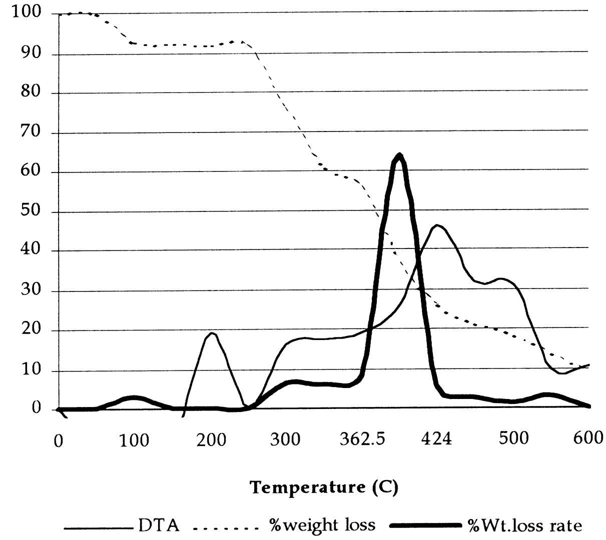


Fig. 8. TG/DTA and the rate of wt% loss for S4 tape.

that there was a baseline shift, represented by a higher flat line at temperature above 550°C, when compared to the flat line at the start of the pyrolysis at 50°C. This is usually due to increases in mass and specific heat of the tape, as a result of an oxidisation reaction.It can be seen that a large organic residue was left in both tapes after the pyrolysis process. Fig. 8 shows that 11.07% of the organic additives are left in the S2C tape at 592°C, comparing only to about 8.49% in the S4 tape in Fig. 9, at the same temperature. It was not possible to decide at which temperature, the complete burnout of the residual organic would occur, since the tapes started to increase in weight due to oxidisation above 592°C.

The difference in the organic residue in each tape, was due to different powder packing of 49.41 and 55.5% in the S4 and S2C tapes, respectively. The larger amount of residue left in S2C tape, was due to the larger interaction between the powder particles and the volatile organic additives, which sustained the residue as a char in the tape.

In order for a complete analysis of the results mentioned above to be carried out, published results[2] of

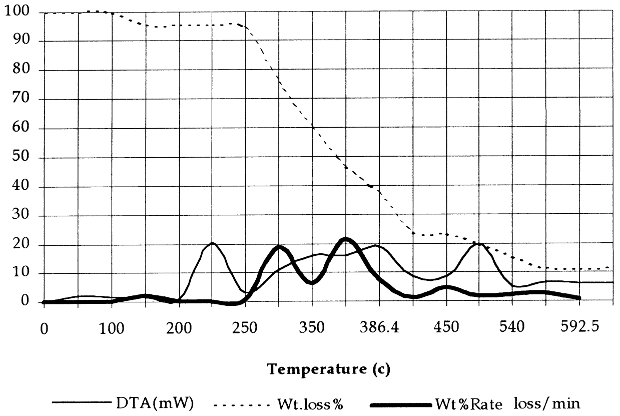


Fig. 9. TG/DTA and the rate of wt% loss for 2SC tape.

FTIR analysis spectra of the PVB binder residue at the indicated temperatures carried out in air and nitrogen, where studied in conjunction with results of the DTA and TGA, which is shown in Figs. 10 and 11. These figures have been magnified and the chemical structure that each peak represents was marked for clarity in Fig. 10.

In order to understand the FTIR analysis for the PVB binder pyrolysis process, the chemical structure of the PVB had to be identified clearly. The PVB is commercially prepared by an acid-catalysed butyraldehyde condensation reaction with polyvinyl alcohol (PVA). This reaction does not proceed to complete conversion to PVB and consequently the Mowtial binder always contains a certain proportion of polyvinyl acetate (PVAc) and polyvinyl alcohol (PVA). According to the manufacturer, the contents were 77.73% PVB, 2–3% PVA and 20–21% PVAc, as shown in Fig. 12.

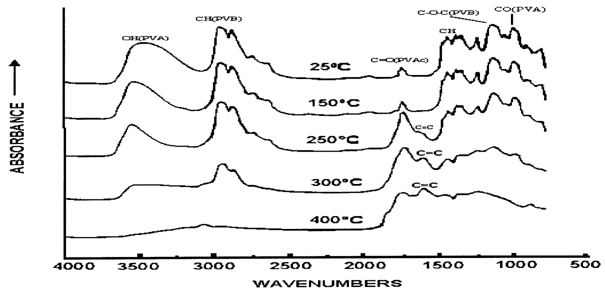


Fig. 10. FTIR analysis of PVB in air.[2]

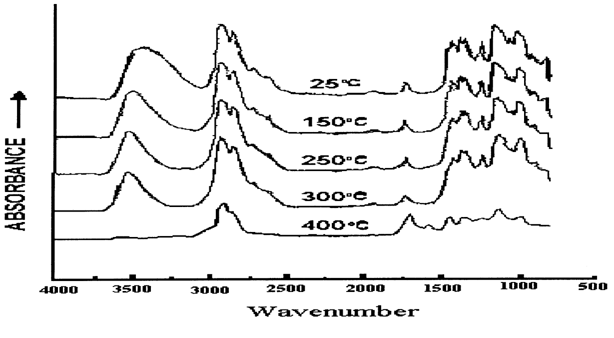


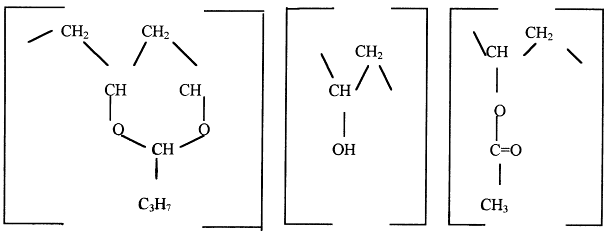
Fig. 11. FTIR analysis of PVB in nitrogen.[2]

A comparison of air and inert atmosphere pyrolysis of Figs. 10 and 11, could be made by comparing the two figures and it is shown in Table 2 below. The degradation mechanism of PVB and its removal from materials in an oxidising and other atmospheres were studied by many researchers.[3–10] Bakht[3] in his study of PVB up to 500°C in air, confirmed the development of an unsaturated hydrocarbons residue, which is very difficult to burn remains in the structure. Therefore, inevitable residues remain from the PVB structure, while the rest decompose and burn out as ethylene, propylene, carbon dioxide and volatiles.

The unsaturated nature of this hydrocarbon residues tends to form cyclic and cross-linking structures with double bonds leading to the formation of a carbonaceous char. Such structures need to breakdown at higher temperatures, than a linear chain polymer.

In the linear chain, breaking a chain bond at random, lowers the average molecular weight by a factor of 2, rapidly producing volatile products. However, when rings or cross-links are present in the chain, breaking a ring bond has no effect on the molecular weight, since the integrity is maintained by the other halves of the ring. The result is to delay the formation of volatile products to a higher temperature, where charring can occur. Hence the cyclic or the cross-link structure development leads to higher break-down temperatures with char formation, which needs even higher temperature to break it down. Table 3 shows the amount of energy needed to break down the different types of bonds.

The break down of the cyclic and cross-linked structure (i.e. high-energy bonds) was shown to occur between 400 and 500°C.[3] This was also confirmed by the DTA and TGA analysis of PVB in Fig. 7. The large exothermic peak observed at around 495°C, which occurred just after the primary weight loss stage had ended, was an indication of the oxidative break down of the cyclic and cross-linked structures that had developed at earlier stages of the pyrolysis.



PVB(77-78%) **PVA(2-3%)** **PVAc(20-21%)**

Fig. 12. The chemical structure of commercial PVB binder.

Table 2
Comparison of PVB pyrolysis in air and nitrogen

Air pyrolysis	Nitrogen pyrolysis
Side-group elimination begins at lower temperature of 250–300°C	Side-group elimination starts at 300–400°C
C–H peaks of PVB disappear at 400°C	Significant C–H peaks remain after 400°C
Development of unsaturated carbon peaks between 150 and 250°C	Development of smaller peaks of unsaturated carbon can be observed at 400°C

Table 3
Energy required to break the different kinds of chemical bonds[11]

Type of bond	Bonds strength (KJ/g mol)
C–C	368.36
C=C	720
C–H	435.3
C–O	360
C=O	531.6
O–H	498

Two conclusions were drawn from the examination of Figs. 10 and 11 for the FTIR of the PVB in air and nitrogen:

1. The oxidative degradation mechanism of the PVB was the only mechanism which achieved complete organic burnout. The development of cyclic and cross-link structures at lower temperatures tended to raise the temperature at which a complete burnout was achieved.
2. There was less development of cyclic and cross-linked structures at the lower temperature ranges in nitrogen, since oxidative degradation mechanisms were not possible in inert atmospheres. Therefore, one would expect a greater overall weight loss (i.e. less residues) at low temperature, using inert rather than oxidizing atmospheres.

The char formation was the product of dehydration of the polymer in an oxidising atmosphere which was "air". This char took the form of a very fine black powder, which covered the entire powder material, turning it black. Hence a visual examination of the sample colour was sufficient to determine whether the complete burn-out had been achieved. In order to demonstrate this effect, a white cast tape containing a ceramic compound of SiO_2–Al_2O_3–$H_3B_2O_3$ and PVB binder was made. As the tape was subjected to air pyrolysis, the tape colour was gradually changed from white to white–brown, in the temperature range of 150–200°C, and completely to black at 250°C and above. The heating continued at the rate of 2°C/min up to 800°C, with a return to the white colour of the ceramic in the temperature range of 750–800°C, indicating complete burn out of the char from the tape.

This high-temperature treatment in an oxidising atmosphere, unfortunately, cannot be applied to thermoelectric material, since there is a risk of oxidising the material above 450°C, as shown in Figs. 8 and 9, which tends to degrade its thermoelectric properties. Hence, the complete burn out of the organic binders had to be achieved at or below 450°C.

Two approaches were adopted to achieve the complete burn-out below 450°C. The first was to accelerate the char oxidation at low temperature and the second was to prevent char formation in the polymer structure during the early stages of the pyrolysis. Both these approaches required the use of reducing and/or inert atmospheres.

Three types of well known reactions normally used in decarburising steel were considered

$$C_s + 2_H(g) \leftrightarrow CH_4(g).......K = \frac{P_{CH_4}}{P^2_{H_2} \cdot a_C} \qquad (1)$$

$$C(s) + CO_2(g) \leftrightarrow 2CO_2(g).......K = \frac{P^2_{CO}}{P_{H_2O}.a_c} \qquad (2)$$

$$C(s) + H_2O(g) \leftrightarrow CO(g) + H_2(g).......\\ K = \frac{P_{CO}.P_{H_2}}{P_{H_2O}.a_C} \qquad (3)$$

The subscripts (s) and (g) refer to solid and gas, respectively, K is the equilibrium constant, which indicates the direction the reaction will proceed. While P describes the partial pressure of the gas involved in the reaction, and "*a*" denotes the activity of the solid, usually taken as 1.

Reactions (1) and (2) use the first approach for removing char, while the third reaction using H_2O prevents char formation in the early stages of pyrolysis.

During pyrolysis under different atmospheres, the hydrogen gas was introduced to the furnace as a mixture of argon and 5% hydrogen. The percentage of the hydrogen was chosen so as to be below the minimum flammable safety ratio of 7% H_2. Pure hydrogen atmosphere was not used due to the lack of suitable equipment. The H_2O was introduced by bubbling argon gas through a flask of water, prior to its introduction to the furnace, and the CO_2 was introduced directly to the furnace.

Calculation of the equilibrium constant K for each reaction shows that the use of hydrogen was useful only in removing some the char at 450°C ($K = 4.27$). Despite that hydrogen was found useful, since it prevents the formation of char as it reacts with unsaturated and cyclic hydrocarbon preventing cross-linking and thus char formation.[12] The CO_2 is a very effective atmosphere for removing char at 450°C, and the reaction would proceed very well to completion ($K = 1 \times 10^{24}$), turning all the char to $2CO_2$ volatile. The use of H_2O is only effective in removing the char above 650°C, but its use is to prevent the char formation at lower temperatures, rather than removing it after its formation.

Note that the samples are not at equilibrium in a static atmosphere since they are placed in a flow that removes any reactants and the results are influenced but not limited by the equilibrium.

In order to verify the pyrolysis analysis, and to use it to reduce the char content in tapes, over 50 samples have been treated under different atmospheric conditions and temperature hold-out times. Not all these results are reported as some of them were discarded and some of them were solely used to prove the repeatability of the results.

Fig. 13 shows the weight losses for two samples, treated under the same flow rate of air and argon. The figure confirms the PVB pyrolysis mechanism analysis of less char production under the inert atmosphere than under the air atmosphere; hence, more weight loss, since more organic additives were removed at lower temperatures in the case of the argon atmosphere. Above 450°C, only the oxidative mechanism is able to shift the char formed at lower temperatures.

Table 4 shows a comparison for the organic residues % fraction remaining in the tape up to 450°C, after pyrolysis treatments under different atmospheres of air, air/H_2O, Ar/H_2O, CO_2, or mixed atmospheres under different temperatures.

Table 4 confirms the proceeding analysis of the proylysis processes up to the temperature of 450°C. The following conclusions were drawn from the table about the use of various atmospheres:

1. The oxidizing atmosphere “air”, clearly led to the formation of char, which is only removed at the very high temperature of 750°C. The combination of air with water vapour, helps to reduce the char formation, if there was a short hold-out time at 450°C (see samples 1 and 3 in Table 4). Longer hold-out times under such atmospheres tended to oxidise the thermoelectric powder, effectively sealing the surface of the sample with a continuous oxide film with a “glassy layer”, thus preventing any additional burnout of the char or organics. Samples 4, 5 and 6 show increases in the sample weights due to oxidisation of the thermoelectric powder, when compared to sample 3.
2. The use of an inert atmosphere prevented the char formation due the oxidative mechanism (see comparison of samples 1 and 2). The introduction of an oxidising atmosphere of H_2O to argon above 150°C helped to shift larger amounts of organic additives as saturated carbon, which vaporised out of the tape at low temperatures. Comparison of samples 8, 9 and 10 showed the that the best temperature to introduce the H_2O, was above 350°C. This had a profound effect on reducing the residual organic to only 2.14% of the total present, nearly 17.2% less than the residual when air was used alone at 450°C.
3. The best atmosphere for the degradation of the PVB binder was found to be CO_2, which has reduced the residues to only 1% of the total. This might be due to the combined effect of CO_2, being an oxidative atmosphere, which can shift large amount of organic and a good oxdising medium for the char formed by the oxidative mechanisms. The introduction of the CO_2 at a very late stage of the 450°C, after a treatment under argon, was not so successful, as shown by comparing samples 11 and 12.

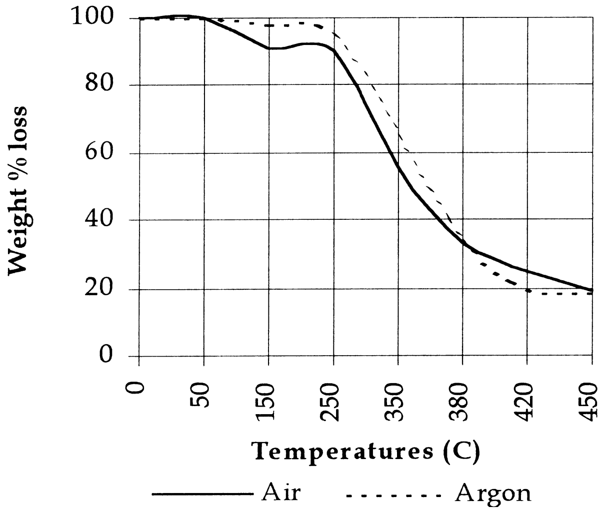


Fig. 13. Wt% loss of organic under air and argon atmospheres.

It should be noted, that for the inert atmospheres, argon was preferred to nitrogen, since the latter required preheating to prevent variation of temperature over the sample.

In conclusion, all atmospheres have failed to remove the PVB residues completely out of the tape. Even in the case of CO_2 atmosphere, which reduced the residues to only 1%, the char residue was in the form of a very fine black powder (soot) which covered the thermoelectric material powder in the tape, preventing its densification at the later stage of the sintering process. It was therefore concluded that the PVB system was not a suitable binder to be used in the fabrication of thermoelectric generator by the tape casting method.

Table 4
Organic residue fractions remaining in the tape after pyrolysis in different atmospheres

Sample no.	Atmospheres used at different temperatures						Hold out time at 450°C (H)	Residues %	Remarks[a]
	150°C	250°C	300°C	350°C	400°C	450°C			
1	Air	Air	Air	Air	Air	Air	1	19.3	1
2	Ar	Ar	Ar	Ar	Ar	Ar	1	18	1
3	Air/H_2O	Air/H_2O	Air/H_2O	Air/H_2O	Air/H_2O	Air/H_2O	0.6	14.17	1
4	Air/H_2O	Air/H_2O	Air/H_2O	Air/H_2O	Air/H_2O	Air/H_2O	2.3	19.13	1, 2
5	Air/H_2O	Air/H_2O	Air/H_2O	Air/H_2O	Air/H_2O	Air/H_2O	50	20.10	1, 2
6	Air/H_2O	Air/H_2O	Air/H_2O	Air/H_2O	Air/H_2O	Air/H_2O	100	31.4	1, 2
7	Ar	Ar/H_2O	Ar/H_2O	Ar/H_2O	Ar/H_2O	Ar/H_2O	4.1	4.9	1
8	Ar	Ar	Ar	Ar/H_2O	Ar/H_2O	Ar/H_2O	16.30	2.14	1, 3
9	Ar	Ar	Ar	Ar	Ar/H_2O	Ar/H_2O	6.16	92.40	1, 3
10	CO_2	CO_2	CO_2	CO_2	CO_2	CO_2	5	1	1
11	Ar	Ar	Ar	Ar	Ar	CO_2	3	13.66	1, 3
12	Ar	Ar	Ar	Ar	Ar	Ar/H_2O	2.5	11.6	1, 4

[a] Remarks: 1, All heating rates were 2 K/min up to 200°C, and 1 K/min up to 450°C. The flow rates of all gases were 1 l/min. 2, These percentages do not represent the fraction % of organic additives remaining in the tape, but rather an increase in weight of the sample due to oxidization. 3, The argon gas quality used in this experiment was of a normal grade (99% pure), containing in 1% of other gases such as Cl, N_2 but oxygen free. 4, Hold out times of 2.5 h at 400°C in air, and another 2.5 h at 450°C under Ar/H_2O.

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