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Thermal Decomposition Behaviour of Poly(propylene carbonate)

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Abstract: Thermal analysis techniques including thermal gravimetric analysis (TGA), differential thermal analysis (DTA), and TG–FTIR were employed to investigate the thermal decomposition behaviours of poly(propylene carbonate) as a neat polymer and in the presence of AlN powder. It was found that the decomposition of poly(propylene carbonate) followed a depolymerisation mechanism and left no detectable residues. The combustion reaction in air enhanced the decomposition of the PPC binder in air only slightly compared to acrylic and PVB binders. In the presence of AlN powder, the PPC binder left primarily "gas phase mediated char" on the powder surface. © 1998 Elsevier Science Limited and Techna S.r.l. All rights reserved

1 INTRODUCTION

Organic polymer binder is used extensively in ceramic manufacturing processes such as tape casting or injection moulding. The importance of the binder is to impart workability and green strength to a ceramic green body during processing prior to sintering. It is important to control the burnout of the organic binders in order to prevent the development of flaws and to minimise carbon residues that may inhibit sintering.

Poly(propylene carbonate) (PPC) is formed by catalytically reacting carbon dioxide with propylene oxide.[1] The PPC binder decomposed cleanly via an unzipping mechanism even in an inert atmosphere,[2] which makes it suitable for ceramic powders that should not be exposed to an oxidising environment. Although the PPC binder is not widely used in ceramics, its clean burnout property should find more applications in the future.

Aluminum nitride (AlN) is a promising ceramic material for electronic packaging substrates because of its high thermal conductivity. Thermal conductivity, however is strongly dependent on the oxygen content. Since PPC is known to burn out cleanly in a nitrogen atmosphere, PPC was considered as a binder for tape casting of substrates.[3] As the work progressed, however, it was shown that PPC left less residual char than was desirable for a low thermal conductivity AlN (with 3 wt% Y_2O_3).[3]

There is not much published information regarding the thermal decomposition behaviour of polymer binder in the presence of ceramic powder. Sun *et al.*[4] studied the thermal decomposition behaviour of acrylic binder in the presence of Al_2O_3 powder. They found that the decomposition mechanism was dominated by depolymerisation, both as the neat binder and as a binder/ceramic mixture, but a higher temperature was required to burn out binder completely from the binder/ceramic mixture. They attributed this requirement to a surface reaction between acrylic binder and alumina powder at elevated temperatures, which was confirmed by an FTIR absorption peak for the carboxylate ion such that the surface reaction was no longer exclusively depolymerisation.

Shih *et al.*[5] and Scheiffele and Sacks[6] investigated poly(vinyl butyral) (PVB) binder burnout behaviour both as a neat binder and in the presence of Al_2O_3 powder. They found that PVB decomposes first by side group elimination and then by scission. In air the oxidative effect lowered the initial pyrolysis temperature but also caused

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both crosslinking and cyclisation which delayed the latter stage of pyrolysis to a higher temperature. The PVB decomposition mechanism in Al_2O_3/PVB mixtures was very similar to that of the neat polymer. Their experimental results (Fig. 3 in Ref. 5 and Fig. 1 in Ref. 6) show, however, that the binder's initial decomposition temperatures were reduced for Al_2O_3/PVB mixtures in both N_2 and air atmospheres. Masia *et al.*[7] also found that the oxides powder decreased the initial decomposition temperature of PVB binder. They concluded that oxides have a catalytic effect on thermal decomposition of the polymer.

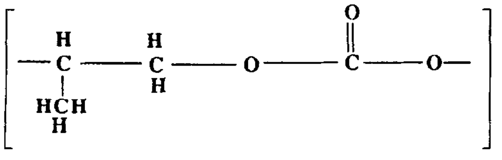
In both the study of Sacks and colleagues[5,6] and that of Masia *et al.*[7] PVB left a larger amount of residual char than acrylic binders. Whitman[8] studied the mechanisms of residual carbon formation of acrylic and PVB binders in the presence of alumina powder, and divided char formation into two mechanisms. The residual carbon resulting from pyrolysis of organic samples in isolation (from the neat polymer) was referred to as "intrinsic char", and char on powder surfaces from condensation of the volatile pyrolysis products was referred to as "gas phase mediated char". He did not consider the possibility of adsorbed binder reacting directly to form char, as described above. Whitman found that the amount of "gas phase mediated char" depended on the nature of the volatile species. Some volatile species are more reactive. For instance, one of the five acrylic binders he tested yielded almost 100% gas phase mediated char, whereas others were mostly intrinsic char.

In this work, the thermal decomposition mechanism of poly(propylene carbonate) polymer was investigated in air and nitrogen atmospheres using thermal gravimetric analysis (TGA) and FTIR, and the amount of intrinsic and "gas phase mediated char" was determined using AlN as the ceramic powder.

2 EXPERIMENTAL

2.1 Materials

Polymer binder used in this study was a poly(propylene carbonate) polymer with trade name QPAC-40M (PAC Polymers Inc. Greenville, DE). The PPC binder was a thermoplastic copolymer with the following structure:



$$\left[-\mathrm{CH(CH_3)}-\mathrm{CH_2}-\mathrm{O}-\mathrm{C(=O)}-\mathrm{O}-\right]$$

The aluminum nitride powder used was manufactured by Dow Chemical Co. and has a 3.1 m^2 gm^{-1} surface area. The supplier's chemical analysis indicates that it contains 1.07% of oxygen, 0.16% of carbon and less than 300 ppm of metal impurities.

2.2 Thermal gravimetric analysis (TGA)

Perkin-Elmer low temperature TGA (TAC 7, Perkin Elmer) was used to monitor the weight change during binder pyrolysis. The neat PPC binder and an AlN tape with 10 wt% of PPC binder were examined with TGA in air and nitrogen atmospheres at temperatures up to 600°C at a heating rate of 5°C min^{-1}.

2.3 FTIR

A sample of 5 wt% PPC in KBr powder for FTIR (1700 × FTIR, Perkin Elmer) analysis was prepared by mixing KBr powder (analysis grade, Fisher Scientific Co., NJ, USA) with the PPC melt uniformly.

2.4 TG–FTIR

For TG–IR analysis, a 45-mg PPC sample was heated from room temperature to 600°C at a rate of 30°C min^{-1}. Volatile products of the polymer binder from the TGA were flushed through a PTFE transfer line to a heated gas cell that is located inside the TG–IR interface. Infrared spectra of volatile products from the TGA instrument were recorded once every 20 s by Fourier Transform Infrared Spectroscopy.[9]

2.5 Carbon content analysis

Carbon content in the AlN samples was analysed with a LECO EC12 carbon detecting instrument, via a combustion infrared detection method by Luvak Inc., MA. A sample with 0.167% of carbon was used as a standard.

3 RESULTS AND DISCUSSION

3.1 Thermal decomposition behaviour of poly(propylene carbonate)

By direct observation of the poly(propylene carbonate) binder thermal decomposition on the top of a hot plate, it was found that the neat PPC polymer decomposed to a liquid intermediate and then vapourised away without leaving any detectible residual carbon. Figure 1 shows the weight loss of

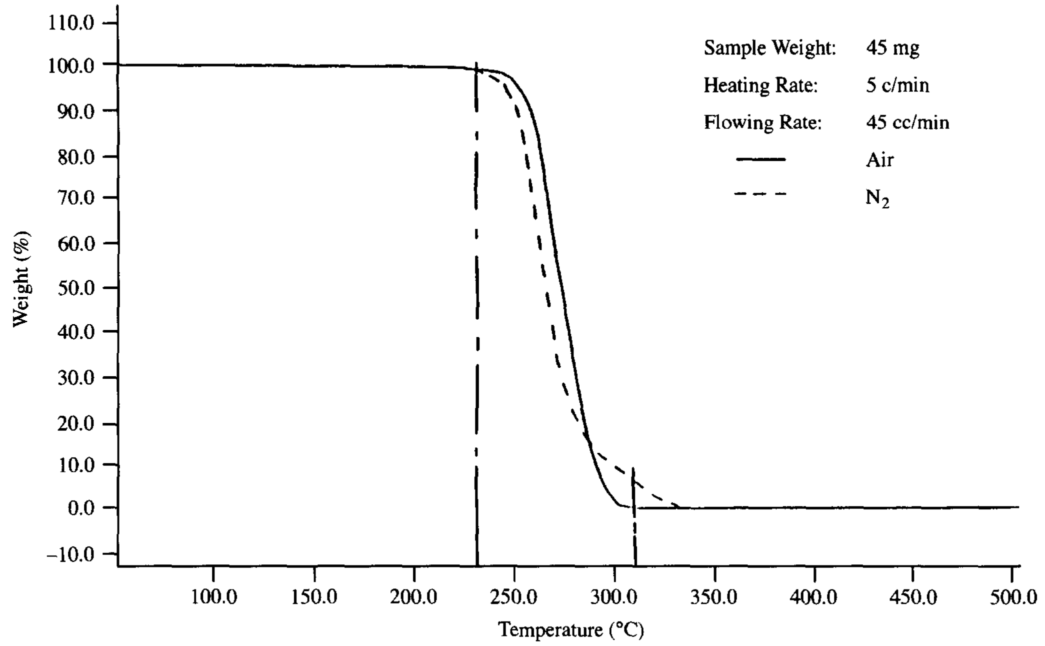


Fig. 1. TGA measurement of the pyrolysis of poly(propylene carbonate) in both air and flowing nitrogen.

PPC binder during its burnout in flowing air and nitrogen. These TGA curves indicate that poly (propylene carbonate) can be pyrolysed completely both in air and in nitrogen and that weight loss of the PPC binder occurs in a narrow temperature range which can be described as a single step weight loss. These characteristics are typical of depolymerisation reactions. The initial thermal decomposition took place at about 10°C lower in N_2 than in air but slowed down after 85% of the binder burning out in the N_2 atmosphere and its final decomposition temperature was delayed to 340°C.

Figure 2 shows a DTA plot of poly(propylene carbonate) polymer in both air and nitrogen atmospheres. In both cases a single peak is observed and the maximum decomposition rate was at about 260°C. The endothermal peak in the nitrogen atmosphere was broader than that in air. The final decomposition temperature in nitrogen was also higher than that in air.

TG–FTIR was used to further study the poly (propylene carbonate) polymer thermal decomposition mechanism. Figure 3 gives the FTIR spectrum of poly(propylene carbonate). The C–H stretching peak is at 2985 cm^{-1}, C = O peak at 1860 cm^{-1}, the C–H bending peak at 1460 cm^{-1}, and C–C stretching vibration at 1261 cm^{-1}, respectively. Figure 4 shows a multiple FTIR spectrum stack plot of the PPC polymer volatiles which were collected during the pyrolysis of the binder in air and nitrogen. This figure is a three-dimensional representation to allow an overview of the spectra. The y-axis (positive to the right) represents wavenumber, the z-axis is absorbance, and the x-axis from front to back represents the spectra number, which is proportional to time or temperature. Figure 4(b) indicates that the FTIR spectra from the volatile products of PPC binder burnout in nitrogen had the same feature as that of propylene carbonate,[10] the same peak positions, and the same peak intensity ratio indicating that the volatile species are the monomers or segments of the polymer. The result offers further evidence that the PPC binder decomposes by a depolymerisation mechanism. It is proposed that poly(propylene carbonate) decomposed by a depolymerisation mechanism into a propylene carbonate liquid. Monomer propylene carbonate vapourised away without leaving a residue.

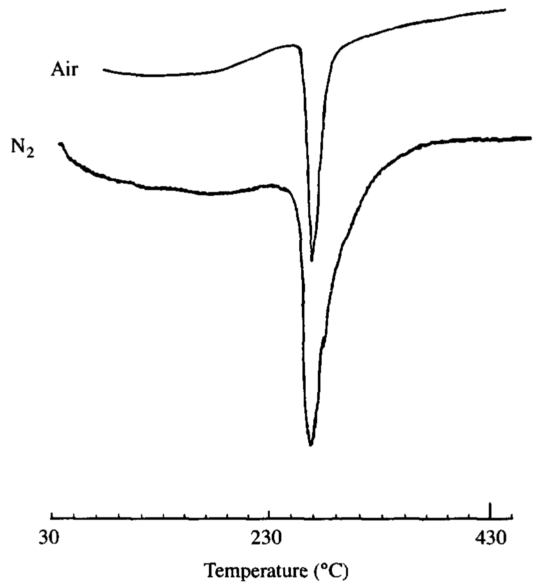


Fig. 2. DTA results from pyrolysis of poly(propylene carbonate). Sample weight was 60 mg, heating rate was 5°C min^{-1}, and flow rate was 40 cc min^{-1}.

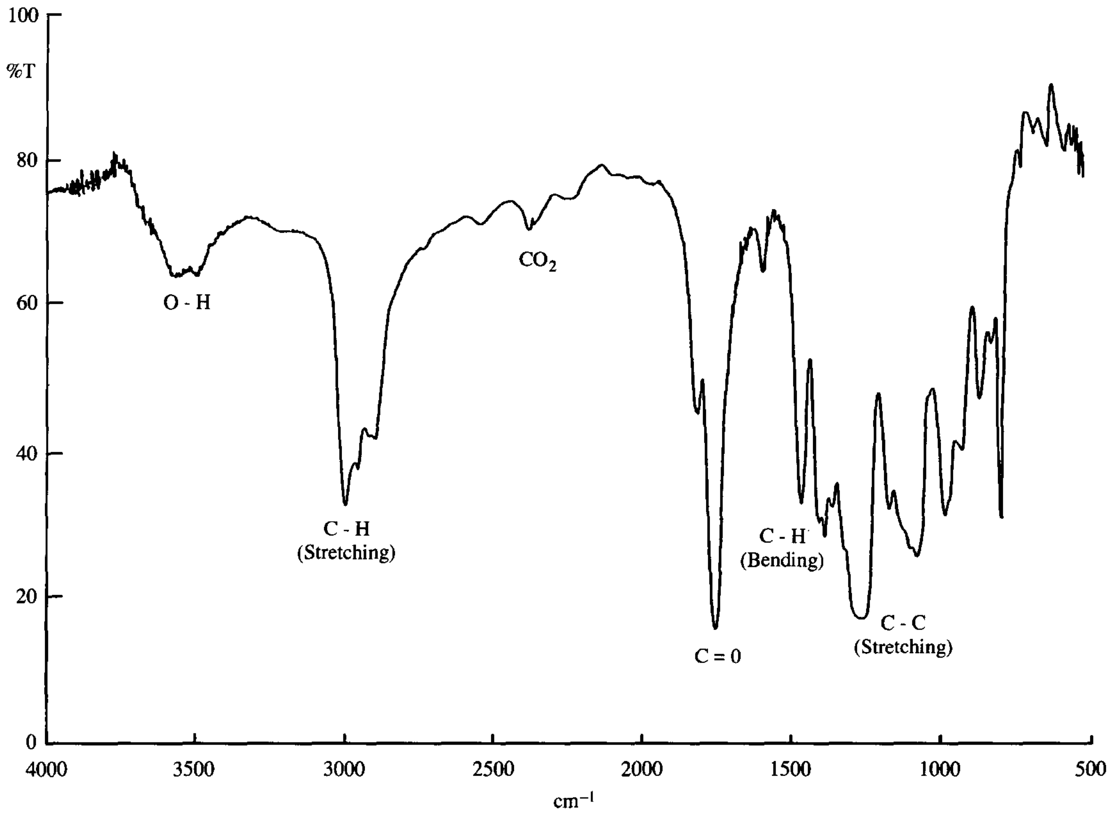


Fig. 3. FTIR spectrum of poly(propylene carbonate).

Figure 4(a) shows the IR spectra from PPC binder burnout in air. There were strong CO_2 peaks in addition to the peaks from propylene carbonate. Thermal decomposition of the PPC binder in air is enhanced by combustion to produce carbon dioxide and water. Figure 4 indicates also that with temperature increase, all of the absorption peaks reach a maximum intensity at the same temperature. Figure 5 gives the IR thermograms of the PPC binder which indicates the amount of volatile products produced upon thermal decomposition, and the temperature or time when the volatile products were generated. By comparing the thermograms for O_2 and for N_2 it can be concluded that the depolymerisation and combustion together in air generated more volatile products than the depolymerisation in N_2 alone.

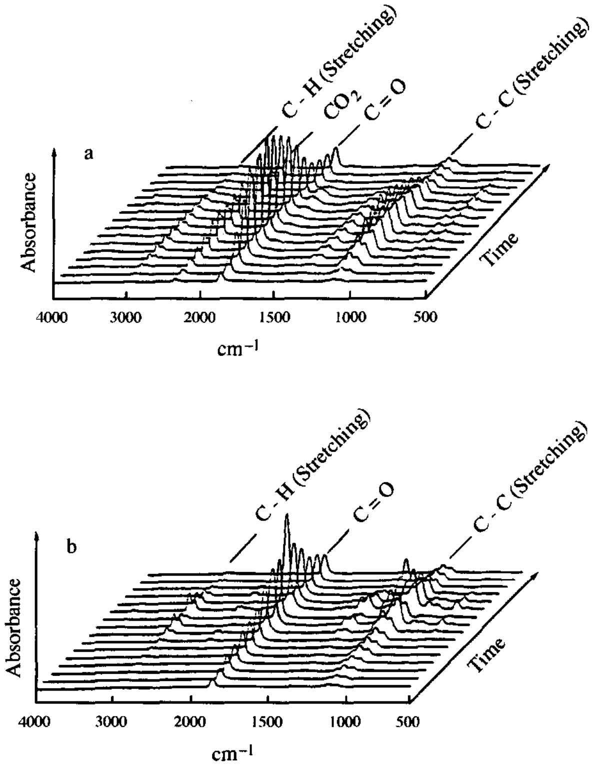


Fig. 4. Multiple FTIR spectra of the volatiles during pyrolysis: (a) in air, (b) in nitrogen.

4 PPC BINDER BURNOUT BEHAVIOUR IN THE PRESENCE OF AlN POWDER

The TGA curve of the neat PPC binder and PPC/AlN powder mixture cast into a tape is shown in Fig. 6(a) and (b) for air and nitrogen. Table 1 lists the initial (T_i) and final (T_f) thermal decomposition temperatures for the PPC binder and compares it with results for neat PVB and a PVB/AlN mixture cast into a tape. Both the initial and final decomposition temperatures decreased when the PPC binder was burned out in the presence of AlN. Furthermore, the initial decomposition temperatures of the PPC binder decreased more significantly in air than in the nitrogen atmosphere.

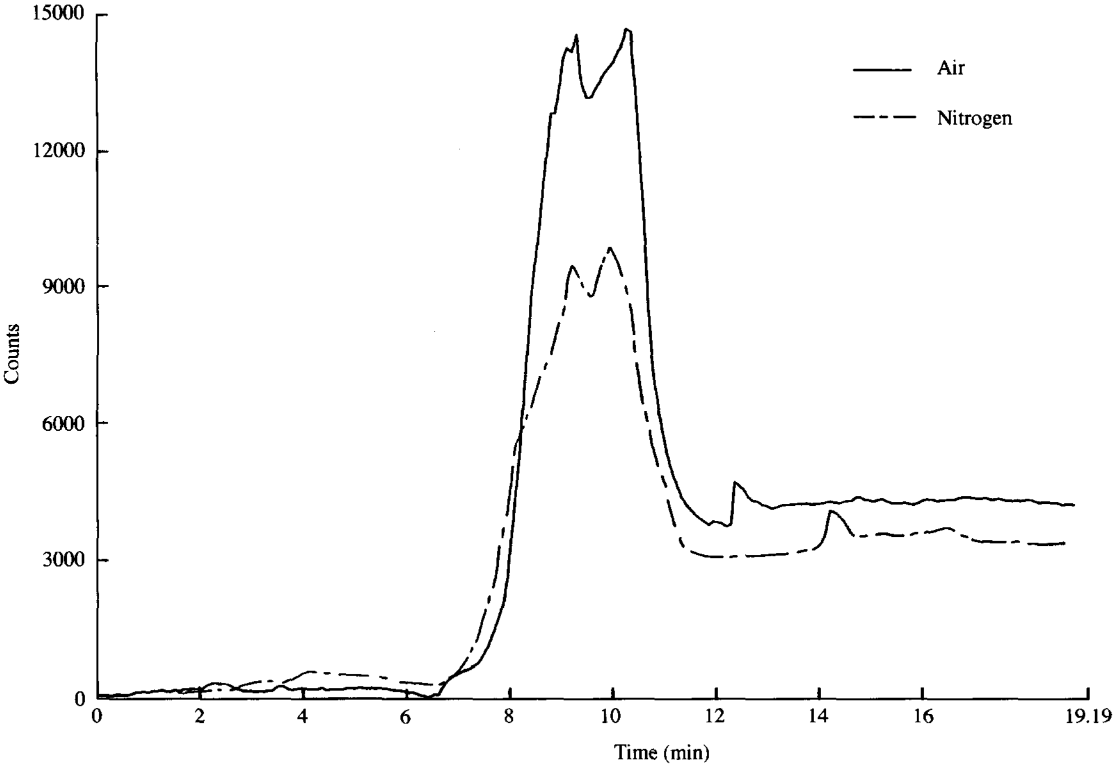


Fig. 5. IR thermogram of poly(propylene carbonate) from TGA–IR.

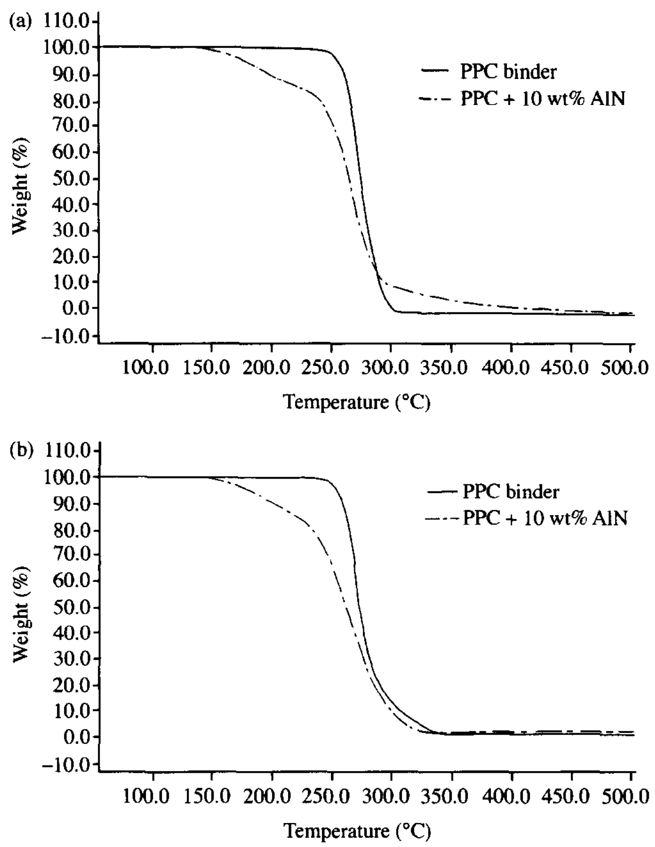


Fig. 6. (a) TGA plots of PPC binder and PPC/AlN mixture in air; (b) TGA plots of PPC binder and PPC/AlN mixture in nitrogen.

At the same time, (T_f–T_i) increased which meant that the thermal decomposition rate was slowed down. Masia *et al.*[7] showed evidence that for the PVB/alumina system the decrease in T_i in the presence of alumina powders was due to a catalytic effect of the oxide surface. They also found that the effect of alumina on the initial decomposition temperature was much greater in air than in argon

Table 1. Initial and final thermal decomposition temperatures from TGA

Sample	T_i(°C)	T_f(°C)	ΔT
PPC in air	255	300	45
PPC in N_2	250	340	90
PPC/AlN in air	200	275	75
PPC/AlN in N_2	220	320	100
PVB in air	340	500	160
PVB in N_2	360	425	65
PVB/AlN in air	250	475	225
PVB/AlN in N_2	320	400	80

atmosphere, the same trend as observed here. Presumably the oxide layer on the AlN powder surface had the same catalytic effect on the thermal decomposition of the binders in this study. From XPS it was found that the surface of AlN powder was covered with a layer of aluminum oxide and oxynitride mixture.

Table 2 lists the weight per cent of residual carbon after pyrolysis of PPC and PVB, both as a neat polymer and in the presence of AlN powder. Although the PPC binder alone left no char to within the limits of detection even after the binder pyrolysis in a nitrogen atmosphere, a significant amount of residual carbon was detected in the AlN/binder mixture after pyrolysis. Figure 7 compares the residual carbon from binder/powder mixtures of PVB, acrylate and PPC measured by combustion analysis. The residual carbon content does not vary greatly with the type of binder when pyrolysed in air pyrolysis but the variation is large for pyrolysis in nitrogen.

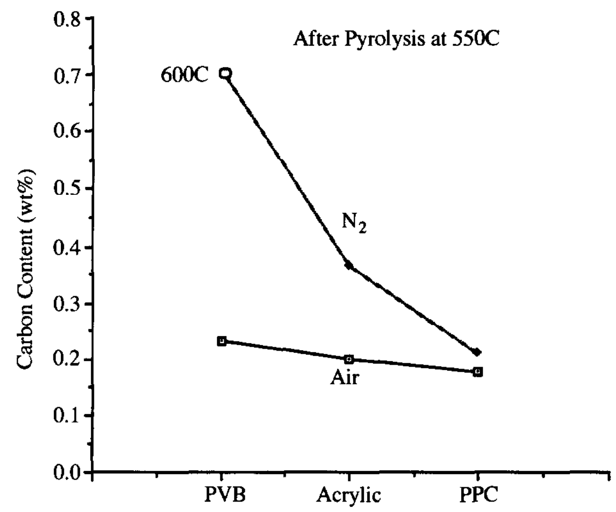


Fig. 7. A comparison of residual carbon from 10%binder/powder mixtures. Note: percentages are based on weight of binder + powder.

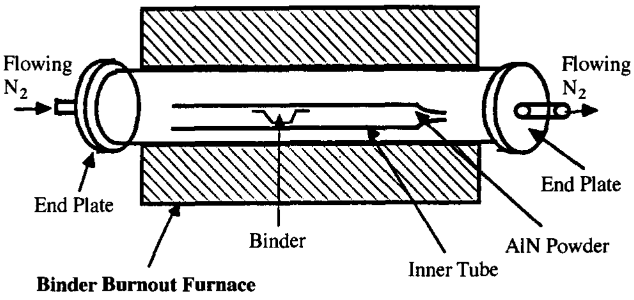


Fig. 8. Furnace used to collect "gas phase mediated char" and "intrinsic char."

To better understand the mechanism of formation of residual carbon on the powder surface, the portion of the total residual carbon which was "gas phase mediated char" was determined. Figure 8 shows the experimental set-up. Five grams of AlN powder and 0.5 gram binder were placed in the inner tube depicted in the figure and heated to 600°C at a heating rate of 5°C min^{-1}. The furnace was kept at 600°C for 30 min and then was cooled down at 10°C min^{-1}. Flowing dry air or nitrogen gas forced the volatiles through the AlN powder bed. In comparison, in a separate experiment, 5 g of AlN powder was mixed with PPC and pyrolysed directly for 30 min at 600°C. Table 3 shows that the amount of residual carbon for the two experiments was approximately equal. This indicates that the residual carbon originated almost entirely from adsorbed volatile species on the

Table 2. Weight per cent of residual carbon after binder pyrolysis at 600°C taken from TGA measurements. The weight per cent of residual carbon from AlN tape was based on the amount of polymer binder in the tape

	PVB	PVB/AlN	PPC	PPC/AlN
Air (TGA)	0.0	0.3–0.5	0.0	0.1–0.3
N_2 (TGA)	1.4–1.6	3.0–3.5	0.0	0.8–1.5
Air(combustion)*		1.2		0.6
N_2 (combustion)*		4.9		1.8

* LECO instrument, Luvak Inc., Boylston, MA.

Table 3. Oxygen and carbon analysis for the AlN powders by combustion analysis and XPS

Sample	Combustion			XPS C/O
	O%	C%	C/O	
AlN/GPMC in air*	1.32	0.167	0.13	0.21
AlN/GPMC in N_2*	1.30	0.275	0.21	0.52
AlN tape/BBO in air	1.28	0.175	0.14	0.20
AlN tape/BBO in N_2	1.27	0.290	0.23	0.50

* AlN powder with "gas phase mediated char" after PPC burned out in air and N_2, respectively.

** AlN tape with 10% of PPC binder. Binder burned out in air and N_2, respectively.

powder which subsequently charred. XPS surface analysis of the powder coated with char, shown in Table 3, revealed that the C/O ratios were very close to that of combustion analysis for AlN powder.

5 CONCLUSION

Thermal decomposition behaviour of poly (propylene carbonate) depended on the pyrolysis atmosphere. The final decomposition temperature in nitrogen was higher than that in air. The neat PPC binder could be burned out completely in both air and nitrogen atmospheres. The PPC binder decomposes via a depolymerisation mechanism into a propylene carbonate liquid. Propylene carbonate vapourised away without leaving residual carbon. Combustion reaction enhanced the PPC binder decomposition in air atmosphere.

In the presence of AlN powder some residual carbon was generated on the AlN powder surface due to the interaction between the AlN powder surface and the volatile pyrolysis products.

ACKNOWLEDGEMENTS

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