

Study of the Composition Effect of Glass Ceramic and Silver on Poly(vinyl butyral) Thermal Degradation with Thermogravimetric Analysis

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ABSTRACT: The thermal degradation of poly(vinyl butyral) (PVB)/glass ceramic, PVB/Ag, and PVB/glass ceramic/Ag composites was investigated with thermogravimetric analysis in nitrogen and air. Thermogravimetric data revealed that the compositions of both inorganic materials in air could greatly influence the thermal degradation of PVB. The degradation reactions of PVB/ceramic and PVB/Ag composites began earlier and accelerated rapidly at lower temperatures. The overall degradation period was obviously shortened for the thermal degradation of PVB/Ag in air,

whereas a longer time was required for the PVB/ceramic composite than for PVB. Moreover, dual effects of ceramic and Ag on the thermal degradation of PVB were observed for PVB/ceramic/Ag composites. In addition, the catalytic effects of ceramic and Ag on the degradation reaction of PVB in air were verified with a kinetic analysis. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2142–2149, 2004

Key words: composites; kinetics (polym.); thermogravimetric analysis (TGA)

INTRODUCTION

Low-temperature cofired ceramic (LTCC) technology has been focused on electronic device processing in recent years. The essential issues of LTCC processing are the product quality and yield for manufacturing; the product quality of ceramic devices is much influenced by the thermal processing or so-called firing cycle. The firing cycle usually includes polymer-binder burnout, metal/ceramic cofiring, ceramic sintering, and cooling stages.

Electronic ceramic devices can be poor in quality because of the defects in the ceramic body, such as delamination or cracks, generated during the firing cycle.¹ The operation of polymer-binder burnout is one of the critical steps influencing LTCC product quality. Recent studies examined controlling the rate of the polymer burnout to avoid the formation of defects of the ceramic body and the small amount of carbon residue left.^{2,3} Therefore, the phenomenon of polymer burnout needs to be understood to operate and control the process properly. However, interpreting polymer burnout conditions depends on a knowledge of the polymer degradation kinetics from a

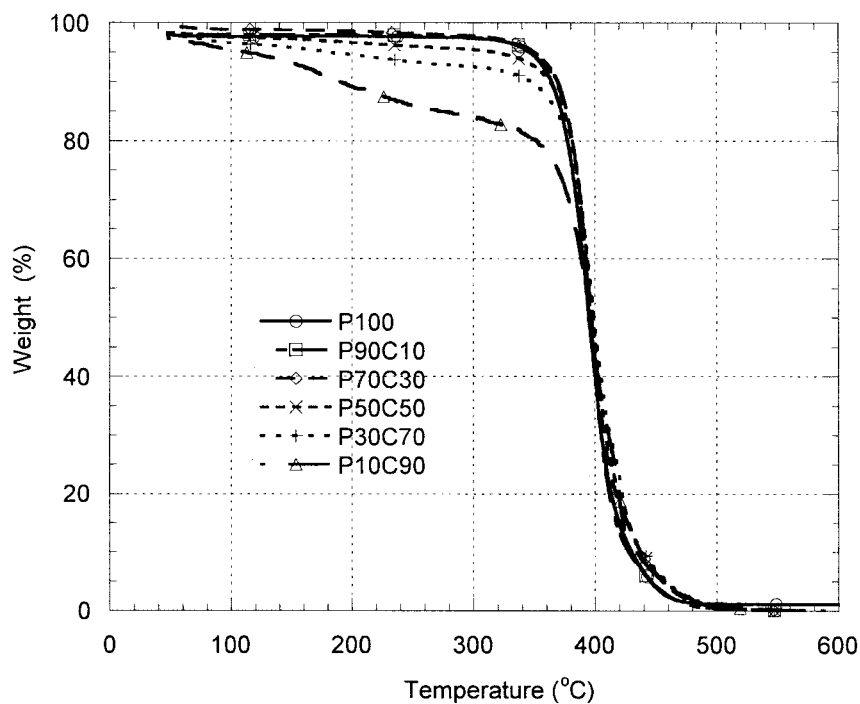
chemical-reaction point of view. Therefore, understanding the kinetics of polymer thermal degradation is important for operating the binder burnout process in LTCC technology.

Poly(vinyl butyral) (PVB) is a highly adhesive agent commonly used as a polymer binder to form flexible and high-impact-strength composites at low temperatures in electronic material processing.^{3–6} PVB thermal degradation has been kinetically investigated with different analytical tools and methods. One way of studying polymer degradation is to measure the weight loss of the PVB binder with thermogravimetry (TG)⁷ or the decomposition gas that evolves from PVB with TG/Fourier transform infrared^{8,9} or gas chromatography/mass spectrometry.⁹ These analytical data can be applied to the interpretation and demonstration of the kinetics of polymer thermal degradation.

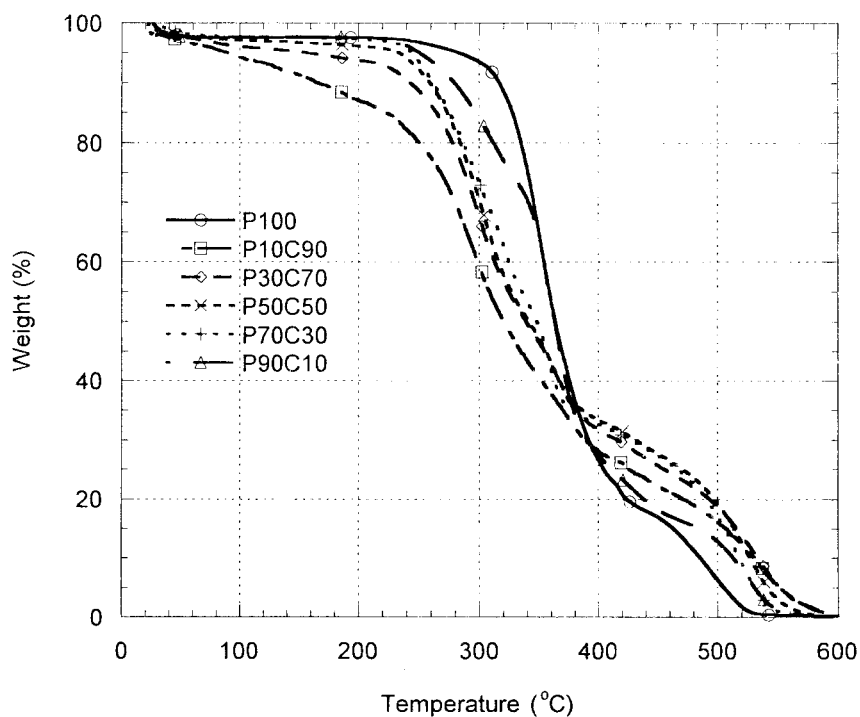
The raw materials of electronic ceramic devices are usually composed of a PVB binder, ceramic, and a metal, such as Ag. Previous studies have confirmed that the kinetics of PVB thermal degradation are strongly affected by the presence of ceramic. The compositions of these raw materials are sometimes different, depending on the recipes of the devices in practical industrial cases. The interaction of the thermal degradation of PVB with ceramic and Ag is not clearly known for these cases. The study of the composition effects of ceramic and metal on the thermal degradation of PVB is useful for practical applications. However, not much research has been discussed on the

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(a)



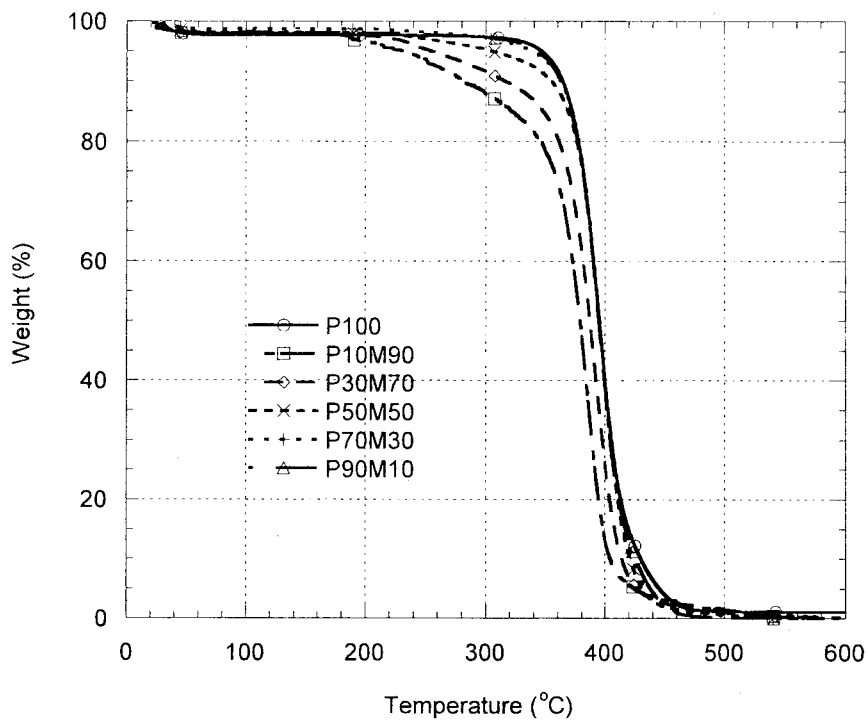
(b)

Figure 1 TG curves of PVB/ceramic samples (e.g., P30C70, which was 30 wt % PVB and 70 wt % ceramic) at 10°C/min (a) in nitrogen and (b) in air.

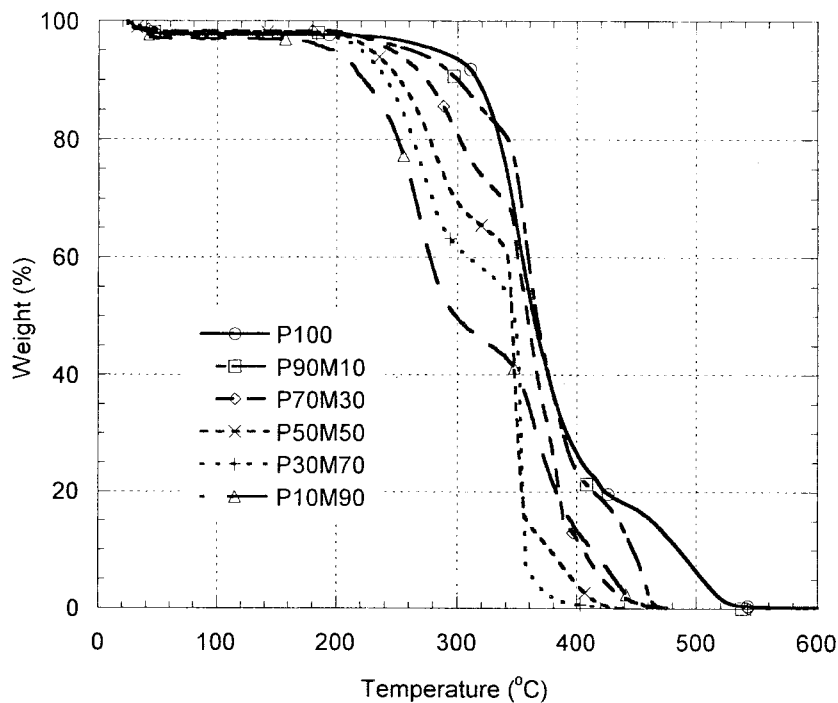
composition effects of ceramic and metal on the kinetics of the thermal degradation of PVB.

In this work, the effects of glass ceramic and Ag on the thermal degradation of PVB were studied with TG anal-

ysis in different atmospheres. Different compositions of PVB/ceramic, PVB/Ag, and PVB/ceramic/Ag samples were used to perform a kinetic analysis of the thermal degradation of PVB. The influence of ceramic and silver



(a)



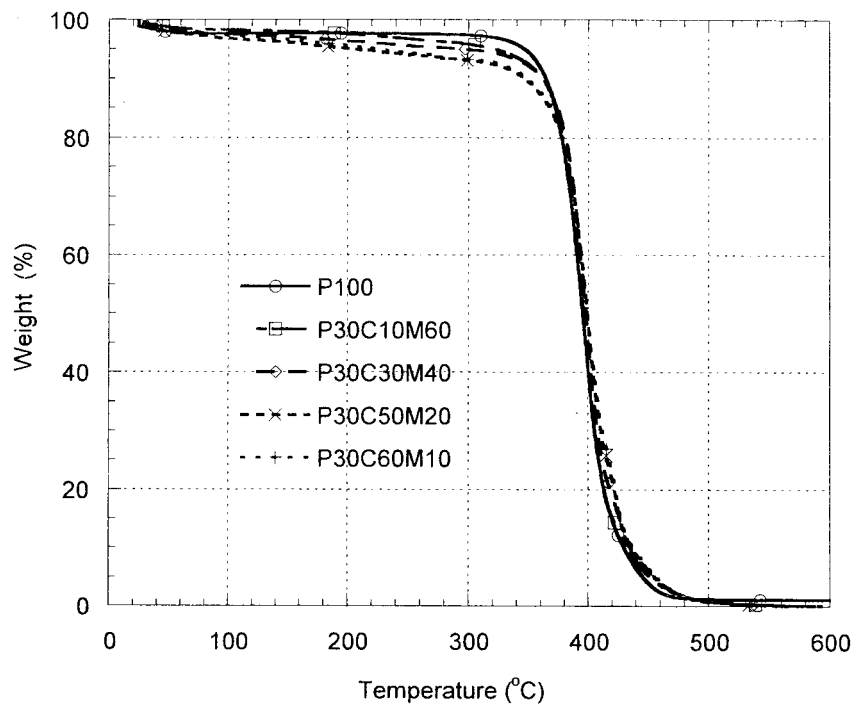
(b)

Figure 2 TG curves of PVB/Ag samples (e.g., P70M30, which was 70 wt % PVB and 30 wt % Ag) at 10°C/min (a) in nitrogen and (b) in air.

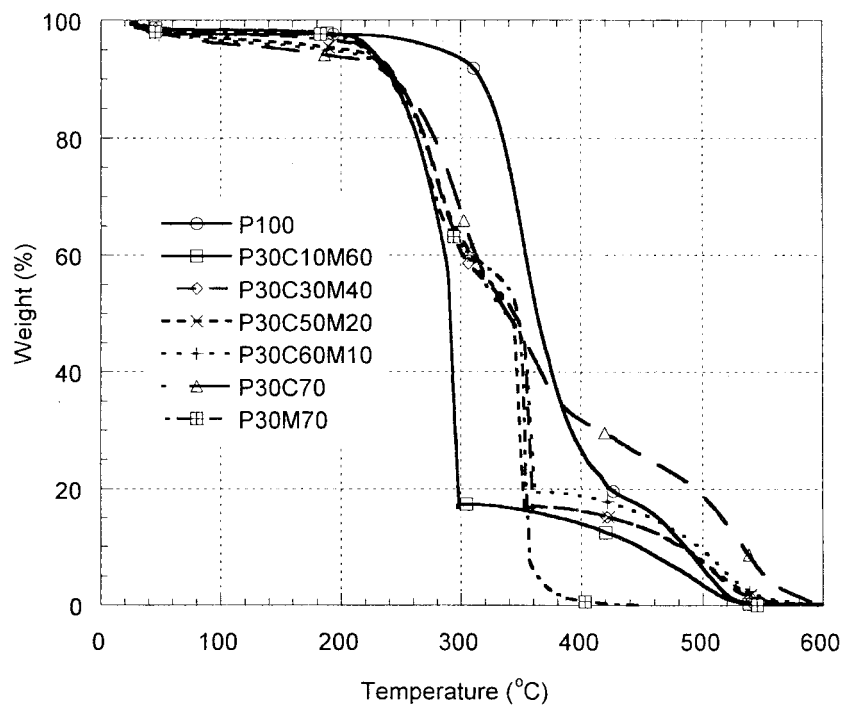
on the thermal degradation of PVB was elucidated from the analytical results. In addition, the kinetic analysis was examined for all these cases to evaluate the PVB degradation rate with respect to the operating temperature and the composition of the inorganic materials.

EXPERIMENTAL

A commercial PVB sample (type B-90) was used in this work. The weight-average molecular weight was approximately 85,000, and its glass-transition tempera-



(a)



(b)

Figure 3 TG curves of PVB/ceramic/Ag samples (e.g., P30C50M20, which was 30 wt % PVB, 50 wt % ceramic, and 20 wt % Ag) at 10°C/min (a) in nitrogen and (b) in air.

ture was 74°C. A commercial glass ceramic of the LTCC industry was used that consisted of Al_2O_3 , B_2O_3 , and SiO_2 . The average particle size was 3.1 μm the density was 2.52 g/cm^3 , and the transformation temperature was 500°C. An electronic-grade silver

powder was used with a density of 3.5 g/cm^3 and a particle size of 0.9 μm . The samples were prepared and mixed fully with a mixer. The sample preparation was based on mixed composites of two or three components, the components being PVB, ceramic, and Ag,

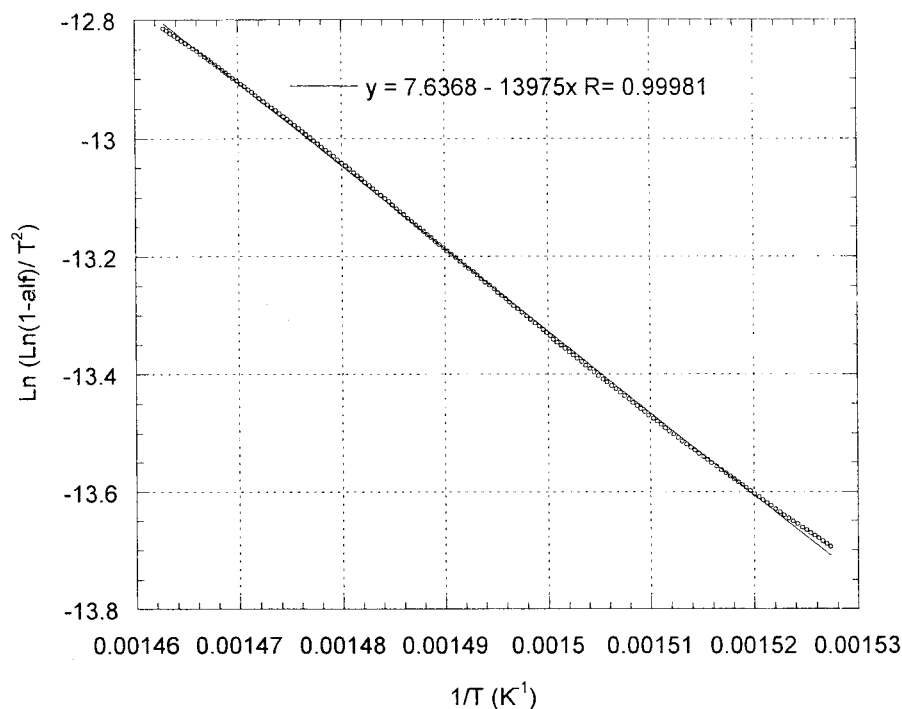


Figure 4 Curve fitting of transformed TG data for P70C30 used to determine the kinetic parameters.

the concentrations of which ranged from 10 to 100%. The prepared samples were denoted $P_iC_jM_k$ (where i is the weight percentage of PVB, j is the weight percentage of ceramic, and k is the weight percentage of Ag).

A Pyris 1 thermogravimetric analyzer provided by PerkinElmer (Shelton, CT) was used for the TG data collection and measurements. Before the experiments, the weight measurement of the TG instrument was calibrated with a 100-mg platinum standard supplied by PerkinElmer. In addition, the temperature was calibrated by the Curie points of nickel and alloy materials provided by PerkinElmer. The sample weight and temperature were well controlled, and the furnace temperature of the TG instrument could go up to 1300°C. The sample weight and sample temperature were recorded on a continuous basis. About 10 mg was used in each experiment, and the TG instrument

was programmed for a heating rate of 10°C/min. The flow rate of the carrier gas was kept at 90 cm³/min.

RESULTS AND DISCUSSION

PVB/Ceramic thermal degradation

The thermal degradation of PVB revealed different degradation paths in different environments, as demonstrated by TG curves. In nitrogen, the weight change of the PVB (P100) degradation was around 400°C, as shown in Figure 1(a), whereas the thermal degradation of the P100 sample in air was mainly distributed on two apparent weight change regions shown in Figure 1(b). The first region was located around 300 and 350°C, and the other was between 400 and 600°C. In addition, the thermal degradation period of P100 was longer in air than in nitrogen because

TABLE I
Kinetic Parameters of PVB with Different Ceramic Compositions for the First Degradation Step

Sample	In nitrogen				In air			
	E_a (kJ/mol)	σ	$\ln A$ (L/min)	σ	E_a (kJ/mol)	σ	$\ln A$ (L/min)	σ
P100	167	10	29	1.9	145	12.7	26	2.6
P90C10	260	11	46	2.0	55	7	8	1.4
P70C30	226	27.2	39	4.8	51	3.2	8	0.9
P50C50	224	24.3	39	4.4	59	5.6	10	1.2
P30C70	178	12.8	31	2.3	56	0.6	9	0.1
P10C90	119	18	20	3.3	40	1.5	6	0.4

σ = standard deviation.

TABLE II
Kinetic Parameters of PVB with Different Ag Compositions for the First Degradation Step

Sample	In nitrogen				In air			
	E_a (kJ/mol)	σ	$\ln A$ (L/min)	σ	E_a (kJ/mol)	σ	$\ln A$ (L/min)	σ
P100	167	10	29	1.9	145	12.7	26	2.6
P90M10	227	35	40	6.4	158	1.2	28	0.3
P70M30	236	25	41	4.6	72	8.2	12	2.1
P50M50	208	17	36	3.1	73	12.3	13	3.1
P30M70	221	3.6	39	0.6	80	13.6	15	3.3
P10M90	197	21	32	8.2	62	8.4	11	2

σ = standard deviation.

the carbon residue generated from the earlier degraded PVB in air needed a higher temperature for oxidation in the last degradation period.

Samples of PVB with different percentages of the ceramic, denoted $PiCj$, were studied to demonstrate the effects of different ceramic compositions on the thermal degradation of PVB. Figure 1(a) shows the TG curves of the thermal degradation of PVB/ceramic samples in nitrogen. The main weight change was around 400°C. The curves for the weight change indicate that the main thermal degradation of PVB was little affected by the presence of the ceramic.

TG curves of PVB/ceramic thermal oxidative degradation are presented in Figure 1(b). In air, the weight-change curves were in two regions [Fig. 1(b)]. The first degradation region was between 200 and 350°C; the other region ranged from 350 to 600°C. Under the initial degradation conditions, the addition of the ceramic could ignite the reaction earlier at a lower temperature than for P100. However, the degradation of the PVB/ceramic composites was slower and took longer to complete than that of P100 in the last degradation region. Moreover, the PVB/ceramic degradation period was longer in air than in nitrogen for all these cases.

PVB/Ag thermal degradation

The thermal degradation of PVB with different percentages of Ag in nitrogen and air is shown in Figure

2(a,b), respectively. In nitrogen, the TG curves of PVB decomposition significantly changed around 400°C for all the samples. This implies that the thermal degradation of PVB was not much affected by the presence of Ag. However, the TG curves were much different for the thermal oxidative degradation of PVB with different amounts of Ag in comparison with P100 [Fig. 2(b)]. Moreover, the initial degradation conditions began earlier, and the degradation rate was accelerated at a lower temperature as the Ag concentration increased. The weight of PVB/Ag samples rapidly changed from 60 to 20% around 350°C and was completely lost at a lower temperature than that of P100. This suggests that the mechanism of the thermal degradation of PVB could be altered by the presence of Ag in air. In addition, the degradation period for all the PVB/Ag composites was shorter in air than that of P100 [Fig. 2(b)].

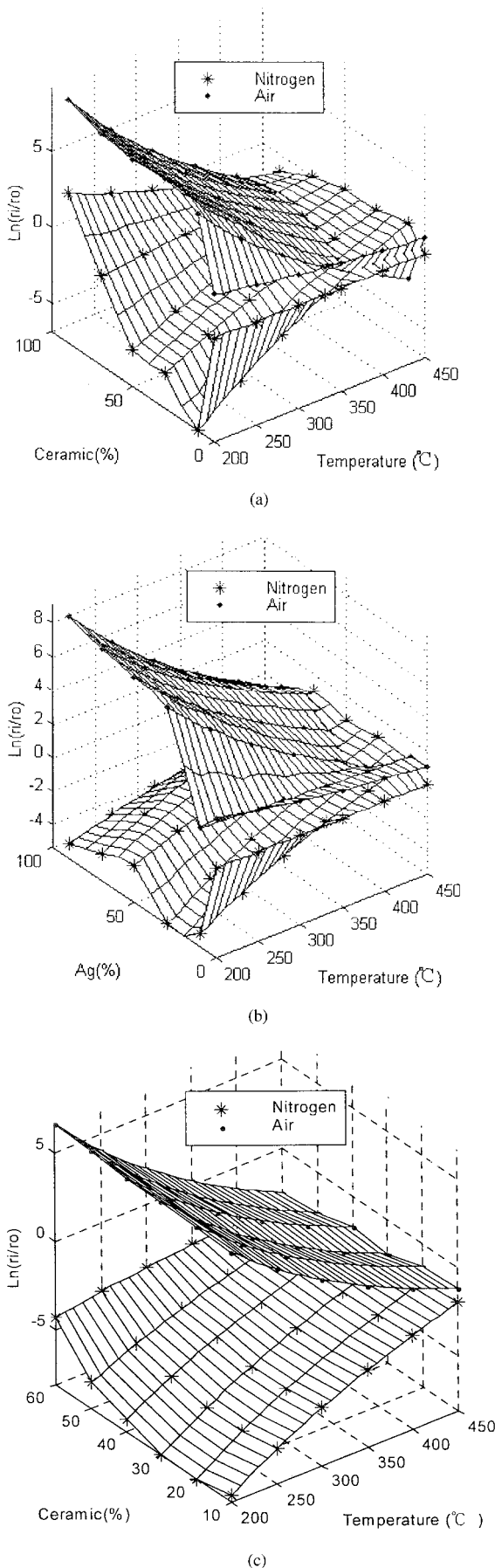
PVB/Ceramic/Ag thermal degradation

According to TG data analysis, both ceramic and Ag could interact with PVB in air to promote the degradation reaction earlier at a lower temperature. In addition, the mechanisms of the thermal oxidative degradation for PVB, PVB/ceramic, and PVB/Ag seemed different according to the TG curves in air. It was interesting to determine if there were dual effects of ceramic and Ag on the thermal oxidative degradation of PVB with both inorganic materials.

TABLE III
Kinetic Parameters of PVB with Different Ceramic and Ag Compositions for the First Degradation Step

Sample	In nitrogen				In air			
	E_a (kJ/mol)	σ	$\ln A$ (L/min)	σ	E_a (kJ/mol)	σ	$\ln A$ (L/min)	σ
P30C10M60	232	8.4	38.0	1.6	84.2	5.9	14.2	1.4
P30C20M50	236	7.1	38.4	1.4	81.6	17.6	13.7	4.0
P30C30M40	235	5.4	38.2	0.96	73.8	8.6	11.7	2.0
P30C40M30	225	5.9	36.5	1.1	76.0	5.2	12.3	1.2
P30C50M20	214	7.8	34.5	1.4	68.2	2.7	10.4	0.6
P30C60M10	183	34.1	29.0	6.1	64.1	3.5	9.6	0.8

σ = standard deviation.



TG measurements were taken of PVB/ceramic/Ag composites subjected to thermal degradation. The TG curves of these samples in nitrogen and air are given in Figure 3(a,b), respectively. In nitrogen, the weight changes of these PVB/ceramic/Ag samples significantly varied around 400 $^{\circ}\text{C}$, similarly to those of PVB/ceramic and PVB/Ag samples. This further confirmed that these inorganic materials little influenced the thermal degradation of PVB in nitrogen.

In air, the TG curves of the PVB/ceramic/Ag samples changed with respect to the ceramic and Ag compositions. The TG curves changed abruptly between 60 and 20% weight changes for these composites. This phenomenon was attributed to the presence of Ag, which affected the thermal degradation of PVB between 300 and 350 $^{\circ}\text{C}$ in comparison with the P30M70 case in Figure 3(b). Moreover, the degradation process took longer to be completed in the last degradation period for the PVB/ceramic/Ag samples than for the P30M70 case. This could be explained by the effect of ceramic on the thermal degradation PVB, as shown by the TG curves of P30C70 and P30M70 in Figure 3(b). Therefore, dual effects of ceramic and Ag composite materials on the thermal oxidative degradation of PVB existed in these cases.

Kinetic analysis of the thermal degradation of PVB

A kinetic analysis of the thermal degradation of PVB was carried out with the TG data with an analytical method. The kinetic equation can be written as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp(-E_a/RT) \times f(\alpha) \quad (1)$$

where α is the conversion, T is the temperature, β is the heating rate, A is the Arrhenius frequency (pre-exponential) factor, R is the universal constant and E_a is the activation energy. The integration form of eq. (1) for this nonhomogeneous chemical reaction can be approximately expressed as follows:

$$\ln \left[\frac{F(\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta(E_a + 2RT)} \right] - \frac{E_a}{RT} \quad (2)$$

where $F(\alpha)$ is the integral form of function $f(\alpha)$. A linear relation was expected from a plot of $\ln[F(\alpha)/T^2]$ versus $1/T$. E_a and A were determined on the basis of the algorithm. The slope of this line provided a value of $-E_a/R$. A detailed description of this method was

Figure 5 Degradation rate ratio of (a) PVB/ceramic, (b) PVB/Ag, and (c) PVB/ceramic/Ag thermal degradation in different environments.

reported by Yang et al.⁷ In this work, $f(\alpha)$ was assumed for a simple first-order form to be $f(\alpha) = (1 - \alpha)$. Figure 4 presents the transformed TG data fit to eq. (2) in a quite linear form for P70C30. Thus, we could reasonably assume that the first-order form of the reaction could be used in this work. The slope represented the term $-E_a/R$, and the intersection included A . The values of E_a and A were obtained with this procedure for all these cases.

Tables I–III list the data for the computed kinetic parameters for the PVB/ceramic, PVB/Ag, and PVB/ceramic/Ag samples in nitrogen and air. The E_a values for P100 were 261 kJ/mol in nitrogen and 147 kJ/mol in air. Moreover, the E_a values for thermal degradation of PVB in all cases were much lower in air than in nitrogen. These data indicate the significant kinetic effect of the operating environment on the thermal degradation of PVB.

In general, the PVB degradation rate can be defined as $r = d\alpha/dt$, where t is time, or

$$r = A \exp(-E_a/RT) \times f(\alpha) \quad (3)$$

The relative ratio of the degradation rate combined with eqs. (1) and (3) can be expressed as follows:

$$\ln\left[\frac{r_i}{r_0}\right] = \ln\left[\frac{A_i}{A_0}\right] - \frac{E_{ai} - E_{a0}}{RT} \quad (4)$$

where r_i and r_0 are the rates of the thermal degradation of PVB with inorganic materials and pure PVB under nitrogen conditions, respectively, and A_i and A_0 and E_{ai} and E_{a0} are the corresponding pre-exponential factors and activation energies, respectively.

Figure 5(a–c) illustrates the rate ratio $[\ln(r_i/r_0)]$ associated with the composite compositions and temperatures in nitrogen and air. The degradation rate ratios of r_i for PVB/ceramic, PVB/Ag, and PVB/ceramic samples to r_0 for P100 in nitrogen are compared. The r_i value of PVB with inorganic materials in air was about 3000 times greater than that of P100 in nitrogen at a lower temperature. This implies that the ceramic and Ag interacted strongly with PVB during the thermal

degradation in air. The reaction pathways of PVB/ceramic and PVB/Ag thermal degradation were different according to the TG curves. Therefore, the apparent catalytic effect of the ceramic and Ag on the thermal oxidative degradation of PVB could be verified with the kinetic analysis. The mechanisms of the thermal degradation of PVB with inorganic materials should be further identified in detail for the reaction pathways with other analytical instruments.

CONCLUSIONS

The effects of the ceramic and Ag concentrations on the thermal degradation of PVB were studied in nitrogen and air with TG analysis. In nitrogen, these inorganic materials little affected the thermal degradation of PVB. In air, the catalytic effects of the materials on the thermal degradation of PVB were evaluated with a kinetic analysis using the TG data. The thermal degradation of PVB began earlier, and the degradation rates accelerated more quickly, in the presence of these inorganic materials at lower temperatures. The overall degradation period of the thermal degradation of PVB was shortened by the presence of Ag, whereas the degradation of PVB with ceramic took longer to complete. Dual effects of the presence of ceramic and Ag on the thermal oxidative degradation of PVB were observed for PVB/ceramic/Ag composites. The results of the kinetic analysis could provide knowledge of polymer-binder burnout to LTCC engineers for process design and operation.

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