to become less oxygen-like, limiting the degree of excited-state mixing possible.[37]

These effects are manifested to a greater degree in the KTP-type structures reported in this work. Upon exchange for Na or Ag, the average cation–oxygen coordination distance drops from 2.9 to 2.6 Å, indicating a generally closer association of the cation with the framework. The differences lie in the relative preferences of the cations for the $(Ti–O)_n$ and the PO_4 (or AsO_4) oxygen atoms. In NaTP, as in KTP, the average bond valences for the Na–O(9,10) and the Na–O(1–8) interactions are essentially the same, so the optical nonlinearity of NaTP is impacted only by the overall closer sodium–oxygen contacts. In AgTP, silver plainly favors coordination with the titanyl oxygen atom O(9), disrupting conjugation in the $(Ti–O)_n$ chain. In NaTA, the closer coordination of sodium to the framework is counteracted by the increased basicity of the AsO_4 groups, which in effect draw these ions away from the titanyl chain. In this respect, NaTA behaves more like KTA than NaTP.

The low SHG intensity of AgTP is thus readily explained by both the high electronegativity of Ag (relative to K) and the strong coordination of Ag(1) and Ag(2) to the titanyl oxygen atoms. Similarly, the close association of Na with the Ti–O framework oxygen atoms reduces SHG intensity by an order of magnitude despite the similar electronegativities of Na and K. The looser Na coordination with the titanyl oxygen atoms in NaTA allows this material to have a strong nonlinear response. In addition, the effects of any increase in cation–framework covalency are likely to be mitigated by arsenate substitution, which should increase the basicity of the oxygen levels, facilitating their mixing with the metallic charge-transfer band orbitals.

6. Summary

For small cation isovalent analogues of KTP (e.g., α-$NaTiOPO_4$, α-$AgTiOPO_4$, and α-$NaTiOAsO_4$) the titanite ($CaTiOSiO_4$) structure is found to be thermodynamically favored at high temperature. Through ion exchange, however, we have synthesized β-$NaTiOPO_4$, β-$AgTiOPO_4$, and β-$NaTiOAsO_4$, three KTP isostructures which cannot be prepared directly from their constituent oxides. Though their Ti coordination environments are similar to those in KTP and KTA, their SHG intensities vary over 2 orders of magnitude. The Na and Ag atoms in these structures are lower coordinate than are the K atoms in KTP, probably due to their reduced size. Because NaTP and AgTP retain the long–short Ti–O bonding characteristic of KTP and other ferroelectric metal oxides with good NLO properties, localized bond-charge models do not adequately predict the low SHG intensities observed in these compounds. However, the correlation between SHG intensity and cation coordination and electronegativity agrees with the predictions of a more extended model in which cation–Ti–O(9,10) interactions alter excited-state mixing coefficients for a charge-transfer state and thereby influence nonlinear susceptibility. This is confirmed by single-crystal structural data and nonlinear optical results previously reported for KTP and KTA.

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Registry No. $Ag_{0.5}K_{0.5}TiOPO_4$, 138312-50-2; $Ag_{0.85}K_{0.15}TiOPO_4$, 124520-05-4; $Na_{0.2}K_{0.8}TiOPO_4$, 127005-70-3; $Na_{0.4}K_{0.6}TiOPO_4$, 127005-72-5; $Na_{0.55}K_{0.45}TiOPO_4$, 138312-51-3; $Na_{0.65}K_{0.35}TiOPO_4$, 138312-52-4; $Na_{0.95}K_{0.05}TiOPO_4$, 138312-53-5; $K_{0.13}Na_{0.87}TiOASO_4$, 138312-54-6; $NaTiOPO_4$, 110074-73-2.

Supplementary Material Available: Tables of anisotropic thermal parameters and all bond distances and angles within 3.2 Å (9 pages); tables of calculated and observed structure factors (24 pages). Ordering information is given on any current masthead page.

Effect of Silica on the Nonoxidative Thermal Degradation of Poly(vinyl butyral)

Robert L. White* and Jiu Ai

Department of Chemistry and Biochemistry, University of Oklahoma,
Norman, Oklahoma 73019

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Thermal degradation processes for poly(vinyl butyral) (PVB) are examined over the temperature range 50–1000 °C. The thermal degradation of neat PVB, PVB coated on silica, and PVB coated on silanized silica are compared. Thermal degradation of PVB in contact with silica proceeds through four stages. At low temperature, water is generated due to dehydroxylation. A second stage occurs between 350 and 450 °C, corresponds to the largest sample mass loss, and is characterized by evolution of oxygen-containing species. The third stage occurs between 400 and 600 °C and is characterized by evolution of unsaturated and aromatic species. The last degradation stage occurs between 600 and 800 °C and corresponds to removal of carbon-rich residue by the water–gas reaction. The water–gas reaction is inhibited by the presence of H_2.

Introduction

The increasing size and complexity of new integrated circuit (IC) designs has created a need for high-quality IC packaging technology. Substrate materials employed in IC packaging should be impermeable to moisture and have high resistance, high thermal conductivity, and a coefficient of thermal expansion that closely matches that for silicon. Ceramics possess these characteristics and are the materials of choice for constructing high-performance integrated circuit packages.[1]

Polymers are used in the ceramics industry as binders

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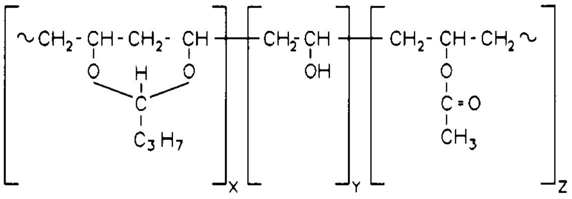
to hold ceramic precursors in place prior to sintering. Ideally, polymer binders decompose completely below temperatures required for ceramic sintering. Although complete decomposition can usually be achieved in oxidative sintering atmospheres, incomplete binder decomposition may be obtained in inert or reductive atmospheres. Nonoxidative sintering is often used in production of ceramic integrated circuit substrates to avoid oxidation of cofired metals.[2-7] During nonoxidative sintering, binder residue remaining at high temperature may interfere with sintering processes leading to flawed ceramics.

Poly(vinyl butyral) (PVB) is commonly employed as a ceramic binder in microelectronics applications.[8-11] This paper describes investigations of the effect of silica on the nonoxidative thermal degradation of commercial grade PVB. Thermal degradation of neat PVB, PVB coated on silica, and PVB coated on silica in which the majority of SiOH groups were removed by silanization are compared. PVB/silica mixtures were prepared in a manner that ceramic green bodies are typically formed. Thermal degradation processes were studied by correlating TGA, TGA-MS, and DRIFTS-MS[12] results for PVB samples heated by using temperature ramps similar to those employed in the early stages of ceramic sintering. Thermal degradation was carried out in inert atmospheres (e.g., He, Ar, N_2) and atmospheres containing H_2 and H_2O.

Experimental Section

Apparatus. Thermogravimetric analyses were performed with a Du Pont (Wilmington, DE) Model 951 TGA analyzer. TGA-MS measurements were made by connecting the gas outlet of the TGA analyzer to a Hewlett-Packard (Palo Alto, CA) 5985 quadrupole mass spectrometer by means of a Scientific Glass Engineering, Inc. (Austin, TX) MCVT-1-50 variable splitter valve. The TGA-MS interface was maintained at 200 °C by using heating tape. The DRIFTS-MS apparatus and procedures for acquiring variable temperature diffuse reflectance infrared and mass spectra have been described previously.[12] The DRIFTS-MS interface was modified to facilitate studies at atmospheric pressure by replacing the isolation valve with the variable splitter valve used for the TGA-MS interface. The DRIFTS sample holder accommodated sample masses of approximately 15 mg. The DRIFTS sample chamber purge gas flow rate was maintained at 10 mL/min during DRIFTS-MS measurements by using a Edwards High Vacuum, Inc. (Grand Island, NY) Model 825 mass flow controller. A heating rate of 8.15 °C/min from 50 to 550 °C was used for DRIFTS-MS measurements. DRIFTS measurements were made at a rate of 1 spectrum/min over the 4000–750 cm^{-1} range at 8-cm^{-1} resolution. TGA-MS mass spectra were acquired by using 70-eV electron bombardment ionization and scanning from m/z 10 to 200 at a rate of 3 spectra/min. DRIFTS-MS mass spectra were acquired by using 20-eV electron bombardment ionization and scanning from m/z 10 to 500 at a rate of 3 spectra/min. Ion source pressure was maintained at 2×10^{-5} Torr for TGA-MS measurements and 1×10^{-5} Torr for DRIFTS-MS measurements.

Reagents. Poly(vinyl butyral) (PVB) and silica were obtained from Hitachi, Ltd. (Hitachi-shi, Japan) and were used without purification. Commercial grade PVB is prepared by converting poly(vinyl acetate) to poly(vinyl alcohol) which is subsequently reacted with butanal. This process does not lead to complete conversion to poly(vinyl butyral) but instead results in a material containing residual acetate and hydroxyl groups:



The composition of the PVB used for experiments described here was $X > 75\%$, $Y = 18–22\%$, and $Z < 3\%$. Infrared spectra of this material contained a medium-intensity O–H stretching band at 3540 cm^{-1} and a small C═O stretching vibration band at 1736 cm^{-1}, which is consistent with this composition. 1-Butanol and ethanol (omnisolv grade) were purchased from EM Science (Gibbstown, NJ) and were not further purified prior to use. Chlorotrimethylsilane was obtained from Aldrich Chemical Co., Inc. (Milwaukee, WI) and was also used without further purification. Potassium bromide (KBr) powder employed for DRIFTS measurements was prepared by crushing scraps of high-purity KBr window material with a mortar and pestle. KBr powder was calcined by heating at 550 °C for 5 h in flowing air. Norit A decolorizing carbon was obtained from Pfanstiehl Laboratories, Inc. (Waukegan, IL). He (99.9995%), Ar (99.999%), N_2 (99.998%), and H_2 (99.9995%) gases were obtained from Union Carbide, Linde Division (Somerset, NJ). Water was sometimes added to the TGA gas stream by passing carrier gases over a heated tube containing water. The concentration of water in the carrier gas was varied by changing the temperature of the water in the tube. Water flow rates were calculated by measuring the weight loss of the tube containing water as a function of time.

Sample Preparation Procedures. Silanized silica was made from silica by reaction with chlorotrimethylsilane. Approximately 1 g of silica was heated in a quartz tube under vacuum at 1000 °C for 4 h. This promoted condensation of hydrogen-bonded SiOH groups and facilitated removal of organic impurities. The thermally treated silica was then placed into a round-bottom flask containing 15 mL of chlorotrimethylsilane, and the mixture was refluxed for 16 h. Exposed OH groups remaining after thermal treatment were removed by reaction with chlorotrimethylsilane:

$$(\text{-O-})_3\text{SiOH} + (\text{CH}_3)_3\text{SiCl} = (\text{-O-})_3\text{Si–O–Si(CH}_3)_3 + \text{HCl}$$

Removal of hydroxyl groups was verified by comparing a diffuse reflectance spectrum of silica with a spectrum obtained from the silanized silica. The DRIFTS spectrum of the silanized material exhibited significantly lower absorbance in the 3800–2500-cm^{-1} region compared to the DRIFTS spectrum of untreated silica. The measured surface areas of silica and silanized silica powders used for experiments described here were 16.7 and 10.6 m^2/g, respectively. Thermogravimetric analysis of silica and silanized silica samples in He revealed that the fraction of total sample mass lost after heating to 900 °C was 0.45% and 0.18%, respectively, for these two materials. The bulk of this mass loss was attributed to evolution of H_2O generated by silanol condensations. Nearly all of the observed mass loss occurred below 600 °C for both materials.

PVB coated on silica was prepared by dissolving 0.5 g of PVB in 50 mL of butanol, adding 4.4 g of silica, and rotoevaporating the mixture until the solvent was removed. PVB coated on silanized silica was prepared by dissolving 0.02 g of PVB in 20 mL of ethanol, adding 0.2 g of silanized silica, and rotoevaporating the mixture until the solvent was removed. PVB/KBr (10% w/w) was prepared by dissolving 0.03 g of PVB in 20 mL of butanol, adding 0.3 g of KBr, and rotoevaporating the mixture until the solvent was removed. PVB/KBr (1% w/w) was prepared by dissolving 0.019 g of PVB in 20 mL of butanol, adding 1.8 g of KBr, and rotoevaporating the mixture until the solvent was removed.

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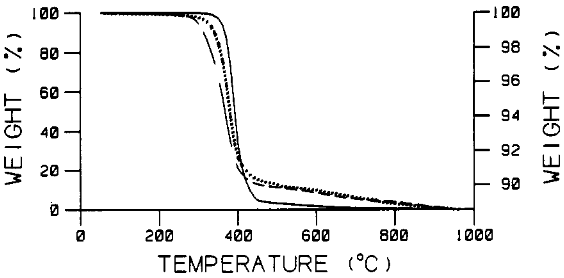

Figure 1. TGA weight loss curves for neat PVB (solid line), PVB coated on silica (dotted line), and PVB coated on silanized silica (dashed line). The left abscissa corresponds to the neat PVB curve, and the right abscissa corresponds to the PVB/silica and PVB/silanized silica curves.

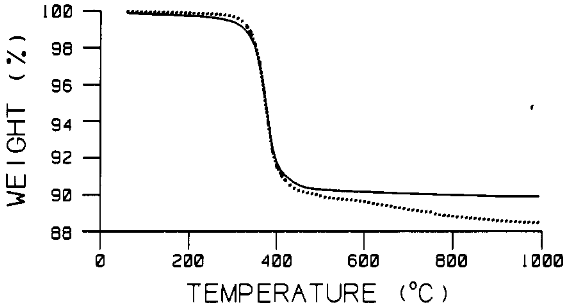

Figure 2. TGA weight loss curves for PVB coated on silica measured by using 50 mL/min of He (dotted line) and 50 mL/min of H_2 (solid line).

Results

The thermal degradation of poly(vinyl butyral) and the effect of silica on decomposition processes was studied by thermogravimetric analysis with He, Ar, N_2, and H_2 as carrier gases. Samples of neat PVB, PVB coated on silica, and PVB coated on silanized silica were analyzed. The effect of adding small amounts of H_2O (5–10 mg/L) to the carrier gas was also investigated. The purpose of adding H_2O was to investigate the effectiveness of the water–gas reaction which converts carbon-rich residues remaining after the initial stages of polymer degradation to CO and H_2. Because polymer sample masses employed for TGA analysis were typically less than 15 mg, the amount of polymer residue remaining for the water–gas reaction was small. To study this process more effectively, samples of approximately 5% carbon mixed with silica were prepared, and these samples were studied under the same conditions as polymer residues.

TGA weight loss curves for approximately 10 mg of neat PVB, 11% w/w PVB/SiO_2, and 11% w/w PVB/silanized SiO_2 are shown in Figure 1. Measurements were made in 50 mL/min of He by using a 8 °C/min heating rate. Similar results were obtained when Ar and N_2 were employed as the TGA carrier gas. First-derivative peak minima for the major weight loss steps in the curves shown in Figure 1 occurred at 390 °C for neat PVB, 376 °C for 11% PVB/SiO_2, and 370 °C for 11% PVB/silanized SiO_2. The fraction of polymer mass remaining above 400 °C was greatest for samples containing silica.

When the 11% PVB/SiO_2 mixture was thermally degraded in 50 mL/min of H_2, little mass loss was detected above 500 °C. Figure 2 shows that the major weight loss step for 11% PVB/SiO_2 was unaffected by changing the TGA gas from He to H_2. In fact, the first derivative of the TGA curve measured in H_2 had a minimum at 379 °C, which was close to the first-derivative minimum calculated for the curve measured when He was employed.

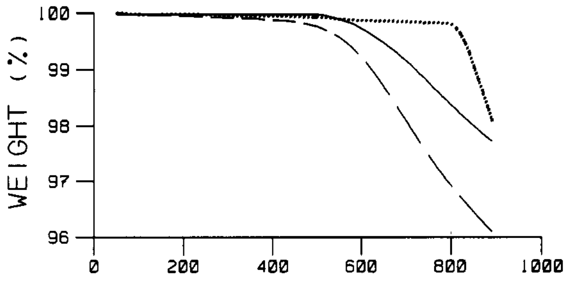

Figure 3. TGA weight loss curves for 5% carbon deposited on silica measured by using Ar (solid line), Ar/H_2 (dotted line), and Ar/H_2O (dashed line) for the carrier gas.

Table I. Maximum Ion Signal Temperatures

		T_M, °C		
m/z	probable origin(s)	PVB	PVB on silica	PVB on silanized silica
44	CO_2, acetaldehyde, butanal	386	379	369
58	acetone	386	376	362
60	acetic acid	389	379	376
70	2-butenal	379	376	362
72	butanal	386	379	369
78	benzene	393	386	379
84	3-penten-2-one	386	376	362
91	toluene, xylene	396	393	389
			434	427
96	2,4-hexadienal	393	383	379
106	benzaldehyde, xylene	389	383	376
			437	430

TGA experiments were performed to ascertain the effectiveness of the water–gas reaction and the effect of changing the atmospheric conditions on this reaction. Figure 3 contains thermograms illustrating the effect of H_2O and H_2 on the removal of carbon from samples containing silica. The solid line is a thermogram for a 5% mixture of carbon and SiO_2 obtained in 50 mL/min of Ar. The dashed line shows weight loss for the same mixture after 6 mg/L of H_2O was added to the Ar flow. The dotted line is a thermogram obtained by using 50 mL/min of a 9:1 Ar/H_2 mixture as the carrier gas. Figure 3 indicates that the water–gas reaction began to occur at about 600 °C and was accelerated when H_2O was added to the TGA carrier gas. Weight loss observed in the absence of added H_2O was probably caused by reaction of H_2O that desorbed from the walls of the TGA furnace tube and entered the gas stream. As shown in Figure 3, the addition of H_2 to the TGA carrier gas delayed carbon weight loss until the sample temperature exceeded 800 °C.

The TGA was coupled with a mass spectrometer in order to characterize species evolved during the thermal degradation of PVB. Samples of neat PVB, PVB coated on SiO_2, and PVB coated on silanized SiO_2 were studied by TGA-MS by using a 8 °C/min heating rate in 50 mL/min of He. TGA-MS results indicated that butanol (*m/z* 72) was the major degradation product for all samples. Ions representing other volatile species were also detected. Table I contains a list of temperatures corresponding to maximum ion signal (T_M) for ions previously detected by pyrolysis GC/MS, pyrolysis GC/FT-IR, and TGA-MS studies of PVB and found to represent specific volatile products.[13,14] Inspection of TGA-MS data revealed that the temperature profiles for ions derived from unsaturated and aromatic species were different from the *m/z* 72 bu-

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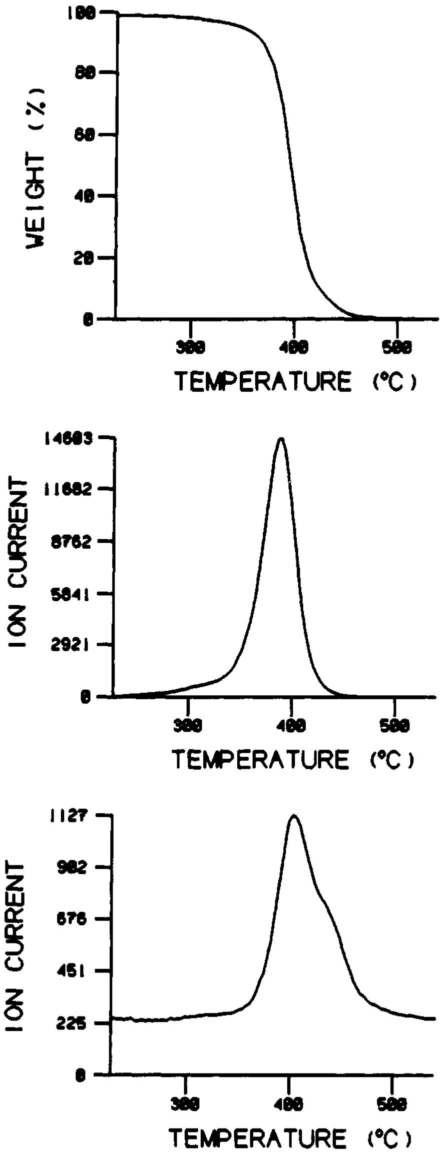

Figure 4. TGA weight loss curve (top) and ion signal temperature profiles for m/z 72 (middle) and 91 (bottom) measured by TGA-MS analysis of neat PVB.

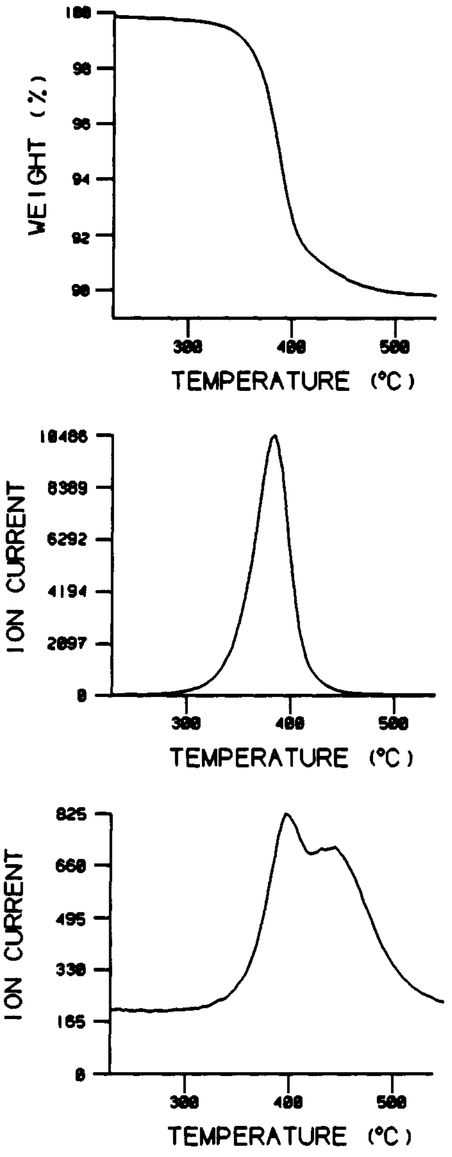

Figure 5. TGA weight loss curve (top) and ion signal temperature profiles for m/z 72 (middle) and 91 (bottom) measured by TGA-MS analysis of PVB coated on silica.

tanal temperature profile. For example, T_M values for m/z 78 (benzene), m/z 91 (toluene, xylene), m/z 96 (2,4-hexadienal), and m/z 106 (benzaldehyde, xylene) were significantly greater than m/z 72 T_M values for all samples analyzed. In addition, ion signal temperature profiles for m/z 91 and 106 appeared as two overlapping peaks (vide infra). T_M values for both components of these ion signal profiles are given in Table I.

Figure 4 shows the weight loss curve and ion signal temperature profiles for m/z 72 amd 91 obtained by TGA-MS analysis of neat PVB. m/z 72 and 91 ion signal maxima occurred at 386 and 396 °C, respectively. Whereas the m/z 72 ion signal temperature profile was symmetrical, the m/z 91 profile was asymmetric and returned to the baseline at a higher temperature than the m/z 72 profile. Figure 5 shows the weight loss curve and ion signal temperature profiles for m/z 72 and 91 obtained by TGA-MS analysis of 11% (w/w) PVB/SiO_2. The m/z 72 ion signal temperature profile had a maximum at 379 °C. The m/z 91 ion signal temperature profile comprised two overlapping peaks with maxima at 393 and 434 °C. Figure 6 shows the weight loss curve and ion signal temperature profiles for m/z 72 and 91 obtained by TGA-MS analysis of 11% (w/w) PVB/silanized SiO_2. T_M for the m/z 72 ion signal temperature profile (369 °C) was significantly lower than the m/z 72 T_M value measured for PVB/SiO_2. Unlike the m/z 72 ion signal temperature profile obtained for PVB/SiO_2, the m/z 72 temperature profile for PVB/silanized SiO_2 was asymmetric, exhibiting significant ion signal at temperatures below 300 °C. However, the m/z 91 temperature profile measured for the PVB/silanized SiO_2 sample was similar to that obtained for the PVB/SiO_2 sample. T_M values for the overlapping components of the m/z 91 ion signal temperature profile (389 and 427 °C) were close to those measured for the m/z 91 temperature profile obtained for PVB/SiO_2. After TGA-MS experiments, a brown residue was observed on the inside of the TGA furnace tube indicating that not all of the species evolved during thermal degradation was sampled by the mass spectrometer. Evidently, these species were not volatile enough to be transported through the 200 °C interface.

DRIFTS-MS was employed to examine functional group changes in the polymer residue that occurred during thermal degradation and to correlate these changes with volatile products. Linear relations between diffuse reflectance intensity (Kubelka–Munk units) and sample concentration cannot be obtained if samples are highly

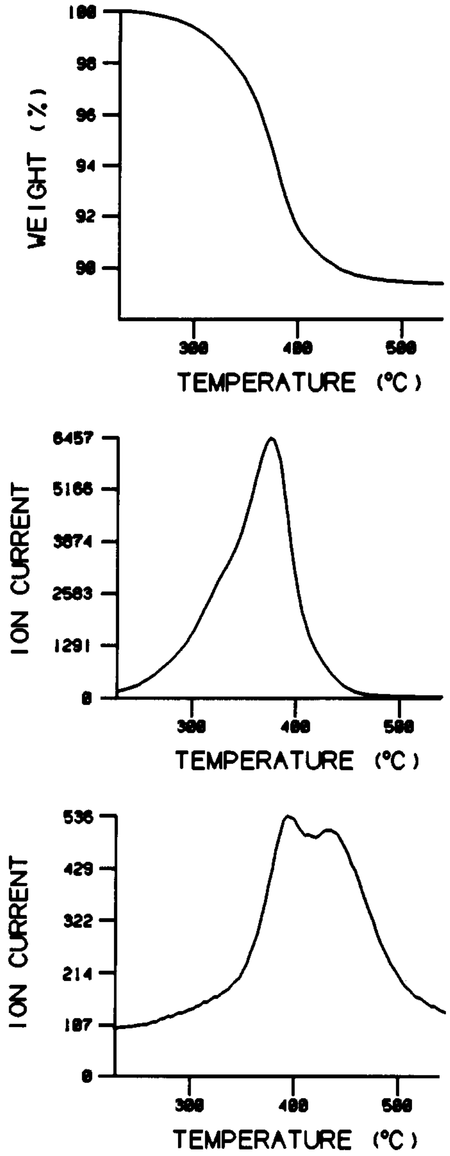

Figure 6. TGA weight loss curve (top) and ion signal temperature profiles for m/z 72 (middle) and 91 (bottom) measured by TGA-MS analysis of PVB coated on silanized silica.

absorbing.[15,16] Infrared absorbance bands for neat PVB were too strong in diffuse reflectance spectra to obtain linear relationships between band intensities and functional group concentrations. To obtain DRIFTS spectra that could be used for quantitative comparisons, it was necessary to mix samples with KBr so that the PVB component of analyzed samples was about 1% by weight. The effect of KBr on the thermal degradation of PVB was investigated by comparing thermograms for neat PVB and a 10% (w/w) PVB/KBr mixture. These thermograms were indistinguishable within experimental error, indicating that KBr had no effect on the thermal degradation of PVB. However, when 1% w/w PVB/KBr samples were prepared by coating PVB on KBr powder, changes in the TGA thermogram were noted. Compared to neat PVB thermograms, thermograms measured for 1% w/w PVB/KBr in which KBr particles were coated with PVB were characterized by a slightly lower temperature for the major weight loss step and a more distinct second weight loss step. Both of these effects may be attributed to an increase in surface area and decrease in polymer thickness for the 1% w/w PVB/KBr sample compared with neat PVB or mixed PVB/KBr. Additional evidence that KBr had no significant effect on PVB degradation below 550 °C was provided by the fact that no difference in volatile product identities or order of evolution was noted when mass spectral information acquired by TGA-MS analysis of neat PVB was compared with information obtained by DRIFTS-MS analysis of 1% w/w PVB/KBr.

The first stages of PVB thermal degradation involve evolution of water, acetic acid, and butanal. These processes leave the polymer residue with increased unsaturation and carbonyl content.[16-20] Figure 7 shows a portion of DRIFTS spectra measured at 50, 370, 386, and 411 °C during the thermal degradation of 1% w/w PVB/KBr. Initially (Figure 7a), PVB infrared spectra contained a carbonyl band representing acetate functionalities in the polymer. By 370 °C (Figure 7b), thermal degradation processes had led to the appearance of additional carbonyl absorbance bands near 1700 cm^{-1} and a broad C═C band spanning the 1620–1550-cm^{-1} range. Near T_M for m/z 72 (Figure 7c), carbonyl absorbance decreased and the C═C absorbance band reached maximum intensity. By 411 °C (Figure 7d), the carbonyl band had disappeared and the C═C band was greatly diminished.

Figures 8–10 show DRIFTS integrated band intensity (Kubelka–Munk function) temperature profiles for the 3000–2800-cm^{-1} C–H stretching vibration and the 3800–3100-cm^{-1} O–H stretching vibration wavenumber ranges and corresponding m/z 72 ion signal temperature profiles (dotted lines) measured for PVB, 11% w/w PVB/SiO_2, and 11% w/w PVB/silanized SiO_2 samples. All samples contained KBr and were prepared so that the PVB weight fraction was approximately 1%. Dehydroxylation was more easily characterized by observing changes in the O–H stretching vibration band in infrared spectra than by monitoring the m/z 18 ion signal because a large m/z 18 background was present during mass spectral measurements due to water desorbing from interface tubing and vacuum system walls. DRIFTS spectra indicated that hydroxyl loss began immediately after the start of the temperature ramp. The slope of the decrease in integrated band intensity for the O–H stretching vibration band was greatest for the sample containing silica (Figure 9). For this sample, the O–H stretching vibration band was comprised of contributions from PVB hydroxyls and silica silanols. The slope of the O–H stretching vibration integrated band intensity temperature profile for the sample containing silanized silica was greater than that for 1% (w/w) PVB/KBr. TGA analysis of silanized silica confirmed that the increased slope for the O–H integrated intensity temperature profile derived from PVB/silanized SiO_2 measurements was due to contributions from silanol dehydroxylation.

DRIFTS-MS measurements indicated that the presence of silica caused the C–H stretching vibration integrated band intensity and m/z 72 ion signal temperature profiles to be shifted to lower temperature. The C–H stretching vibration integrated band intensity exhibited the steepest decline for 1% (w/w) PVB/KBr (Figure 8). DRIFTS-MS temperature profiles for the sample containing silanized SiO_2 (Figure 10) indicated that significant thermal degradation occurred below 300 °C, which was consistent with

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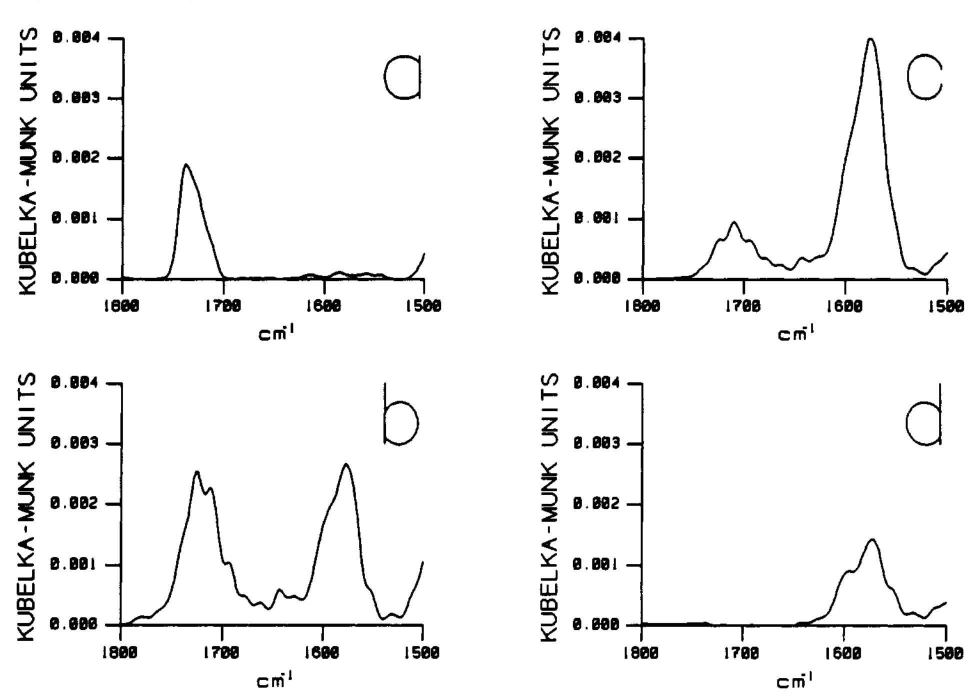

Figure 7. DRIFTS spectra obtained during thermal degradation of 1% w/w PVB/KBr at (a) 50, (b) 370, (c) 386, and (d) 411 °C.

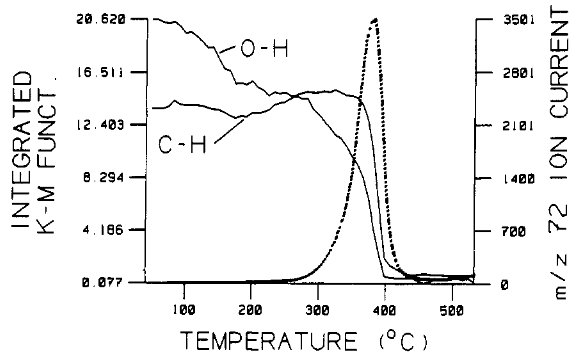

Figure 8. Integrated infrared intensity and m/z 72 ion current temperature profiles obtained by DRIFTS-MS analysis of 1% w/w PVB/KBr.

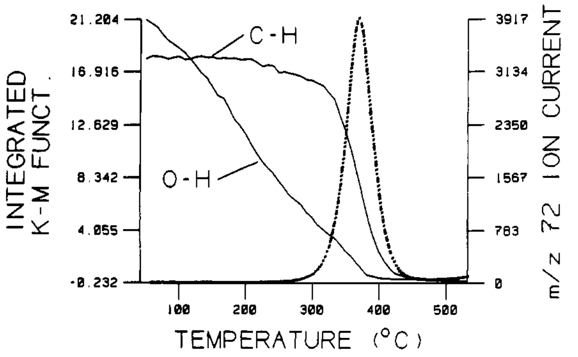

Figure 9. Integrated infrared intensity and m/z 72 ion current temperature profiles obtained by DRIFTS-MS analysis of PVB coated on silica and mixed with KBr such that the weight percentage of PVB was approximately 1%.

TGA-MS results (Figure 6).

Discussion

TGA-MS studies indicated that the thermal degradation products of neat PVB were the same and occurred at similar temperatures in He, Ar, and N_2. In the absence of oxygen, some carbon-rich residue was left above 1000 °C in all TGA analyses. For neat PVB this residue was small as evidenced by the fact that the sample weight approached zero. However, residue was visible as a dark film on the sample pan at the completion of TGA experiments. Carbon residues were also observed after TGA analyses of samples containing silica. In these instances, the normally white silica powder appeared gray.

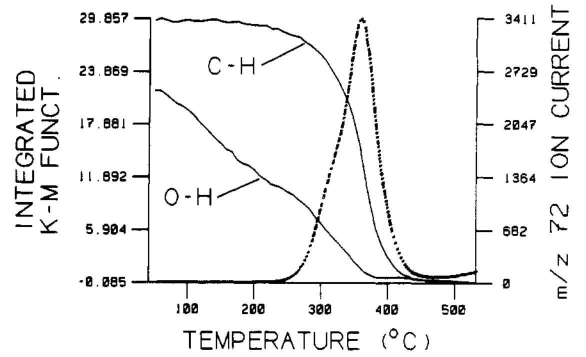

Figure 10. Integrated infrared intensity and m/z 72 ion current temperature profiles obtained by DRIFTS-MS analysis of PVB coated on silanized silica and mixed with KBr such that the weight percentage of PVB was approximately 1%.

DRIFTS-MS spectra measured in this study were consistent with those previously reported for the decomposition of PVB in vacuum[13] and indicated that butanal was the primary degradation product. PVB coated on SiO_2 decomposed in four steps. In the first step, which began immediately after the temperature ramp was started, PVB hydroxyl groups and silica silanols were lost in the form of water. The second step corresponded to the most weight loss and involved evolution of a variety of oxygen-containing species. Butanal was the major degradation product evolved during this step, which occurred between 350 and 450 °C. A third step between 400 and 600 °C was characterized by evolution of unsaturated and aromatic species. The final step in PVB decomposition occurred above 600 °C. This step consisted of the water–gas reaction in which carbon-rich residue remaining from the first three degradation steps was converted to CO and H_2. Mass spectra indicated that CO_2 was also generated during the water–gas reaction. Carbon dioxide can be formed from

CO at elevated temperatures by[21]

$$C(O) + CO = C + CO_2$$

In this reaction, C(O) represents a carbon–oxygen complex formed by reaction of H_2O with carbon. At temperatures between 700 and 1000 °C, the rate constant of the forward reaction exceeds the rate constant for the reverse reaction.[21,22]

TGA-MS results indicated that silica had a catalytic effect on the thermal degradation of PVB. Compared to neat PVB, the temperature corresponding to maximum rate of weight loss (T_M) was typically 10–15 °C lower for samples in which PVB was coated on silica. TGA-MS analyses showed that the major TGA weight loss for PVB consisted of two components. Butanal evolution predominated at the beginning of the sample mass decrease. The temperature at which butanal evolution occurred was lower when silica was present. The second component of the TGA weight loss for PVB occurred at higher temperature than butanal evolution and was characterized by evolution of unsaturated and aromatic species. TGA-MS profiles for m/z 91 (tropylium ion) indicate that this portion of the weight loss curve was shifted to higher temperature when samples contained silica or silanized silica.

Butanal evolution below 300 °C was enhanced when the number of SiOH groups was reduced by silanization. This inhibiting effect of SiOH groups was previously reported for PVB thermal degradation studies conducted in high vacuum.[13] SiOH groups may be responsible for restricting polymer chain movement during the early stages of decomposition. Removal of these groups may enable the polymer to more easily attain conformations that facilitate butanal elimination.

Nonoxidative ceramic sintering is often conducted in an atmosphere containing N_2, H_2, and H_2O. Nitrogen is used as an inert carrier to sweep sintering volatiles away from the ceramic product. Hydrogen is added to the nitrogen stream to maintain a reductive sintering atmosphere. Water is entrained in the gas stream to initiate the water–gas reaction to facilitate removal of polymer binder residue remaining after the primary degradation pathways are completed. Experiments conducted here indicate that the water–gas reaction is inhibited by the presence of H_2 in the carrier gas stream. This is to be expected because hydrogen is a product of the reaction of water with carbon. The presence of H_2 in the sintering atmosphere caused the water–gas equilibrium to shift in favor of carbon residue stability, raising the temperature at which carbon-rich residue was removed to above 800 °C (Figure 3).

Conclusions

This study supports findings by Masia et al.[9] that silica catalyzes the thermal decomposition of poly(vinyl butyral). The mechanism of silica catalysis of PVB thermal degradation is not yet known. However, TGA-MS results indicate that the presence of silica shifts the weight loss curve for PVB to lower temperature by lowering the activation energy for butanal evolution. In contrast, evolution of aromatic species was hindered by the presence of silica. Experiments described here indicate that the magnitude of the catalytic effect attributed to silica is dependent on the number of silanols in contact with the polymer. When exposed silanol functionalities were removed by silanization, the magnitude of the catalytic effect increased. This inhibiting effect of silanol groups on PVB thermal degradation was also observed for measurements made in high vacuum.[13] Removal of all silanol functionalities in an attempt to enhance the silica catalytic effect is not recommended because PVB adheres to oxide surfaces primarily through hydroxyl–hydroxyl interactions[23] and removal of silanol functionalities would deleteriously alter the properties of ceramic green bodies.

The temperatures at which the degradation processes occurred (T_M values) and the widths of the DRIFTS-MS ion signal temperature profiles reported here were different from those reported for PVB thermal degradation in high vacuum. Ion signal temperature profiles were broader for measurements made with PVB samples contained in high vacuum. This was due to the fact that mass transport of volatile species was diffusion limited in high vacuum and because temperature gradients throughout sample volumes were larger in vacuum than in the presence of carrier gas. In addition, it appears that activation energies for PVB thermal degradation processes differ when PVB thermolysis is carried out in high vacuum, resulting in discrepancies in T_M values for ion signal temperature profiles derived from measurements made in high vacuum compared to measurements made at near-ambient pressure.

Hydrogen is often added to sintering atmospheres to ensure that the sintering environment is reductive. Unfortunately, the effect of hydrogen on the water–gas reaction is undesirable. If the carbon-rich residue remaining after the early stages of PVB decomposition is responsible for flaws in ceramic products, the integrity of ceramic end products may be improved by sintering in inert instead of reductive atmospheres.

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Registry No. Silica, 7631-86-9.

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