

Diffusivities of Dialkyl Phthalates in Plasticized Poly(vinyl butyral): Impact on Binder Thermolysis

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Hot-stage/Fourier transform infrared microspectroscopy (FTIR-M) was used to determine the diffusivities of a series of dialkyl phthalates in poly(vinyl butyral) (PVB) spin-coated films. The diffusivities ranged from 10^{-12} to 10^{-10} cm²/s for the isotherms investigated (60° to 150°C). In their respective temperature regimes, dimethyl phthalate and diethyl phthalate exhibited nonlinear diffusion behavior, while dibutyl phthalate (DBP) and dioctyl phthalate (DOP) exhibited Fickian behavior in PVB. The activation energies for DBP and DOP diffusion in the PVB-based films were calculated to be 76.3 and 114.7 kJ/mol, respectively. The diffusivity of DBP was used to compare the relative importance of diffusion and capillary migration in the thermolysis of PVB-DBP binders from ceramic greenware. Comparison of the calculated DBP loss due to diffusion alone could not account for the observed removal rates. A characteristic diffusion length is calculated from the experimental observations. [Key words: diffusivity, binders, plasticizers, polymers, Fourier transformation infrared spectroscopy (FTIR).]

I. Introduction

MULTICOMPONENT binder systems are often employed as ceramics processing aids. The primary components of these systems, polymers and organic plasticizers, have a two-fold function: the polymeric components provide strength to the formed ceramic piece, while the plasticizing components provide the flexibility¹ necessary to avoid damage to the green piece during handling and mechanical forming operations, such as via punching.

The binder system can comprise 20 to 45 vol% of the ceramic green body formed by tape casting or injection molding processes. These organic additives, however, are transient and must be removed during firing before sintering begins. The selection of optimal removal conditions requires an understanding of physical and chemical issues such as binder distribution processes, mass and heat transport, chemical degradation mechanisms, and associated ceramic surface interactions. Much of this work is ongoing, and until recently, little had been published on these processes.²⁻⁵

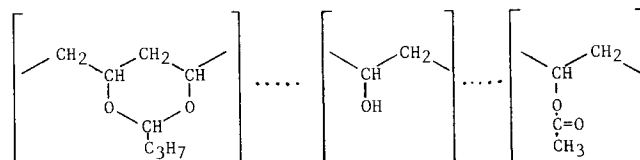
Two types of processes that occur during thermolysis must be distinguished: the removal of volatile constituents and the removal of volatile degradation products. The first process refers to the removal of solvents, plasticizers, and other low molecular weight components in the binder system. These materials are distributed within the green body at some initial concentration and have an appreciable vapor pressure relative to the polymeric components. As these species diffuse to the surface of the green body and evaporate, their concentration

decreases. In contrast, volatile products have an initial concentration equal to zero, but their concentration grows during thermolysis and then diminishes as they diffuse to the surface of the green body. Generally, both degradation reactions and volatile transport occur simultaneously during thermolysis, although there are cases where selective removal of binding constituents is preferred, such as injection molding.

The distribution of binder in the green body determines the path length over which volatile species must diffuse, while the pore structure of the ceramic affects the mass transfer resistance. Volatiles present within the polymer above their boiling points can form bubbles during thermolysis.⁶ To avoid bubble formation, it is necessary to remove volatile materials slowly so they can diffuse out of the green body.

Binder formulations based on phthalate-plasticized poly(vinyl butyral) (PVB) are frequently used for tape casting ceramics.⁷ In previous work,⁸ the distribution of binder in alumina-poly(vinyl butyral)-dibutyl phthalate (Al₂O₃-PVB-DBP) tape-cast sheets as a function of extent of thermolysis was determined. A significant result from this work was that capillary forces influenced the distribution of PVB-DBP in these green tapes during thermolysis. Direct observations of DBP removal from binder-filled two-dimensional model microstructures were made by hot-stage/optical microscopy.⁹ These observations confirmed that PVB-DBP is redistributed by capillary forces during the thermolysis process. The removal rate of DBP or other volatile species depends upon their diffusivity in PVB and the path length over which diffusion occurs. Migration of PVB-DBP due to capillary forces affects this path length. Diffusivities of phthalic esters (e.g., DBP) in PVB are needed to determine both the characteristic path length and the relative contribution of capillarity to PVB-DBP removal from these green tapes.

PVB is commercially prepared by an acid-catalyzed butyraldehyde condensation reaction with poly(vinyl alcohol) (PVA). Because of incomplete conversion, the resulting polymer is actually a copolymer of PVB and PVA. The chemical structure of PVB is as follows:



A small number of residual acetate groups may be present from poly(vinyl acetate), which is a precursor for PVA. The relative amounts of the different substituents depend on the synthesis conditions. The PVB* used in this study is nominally 9.0% to 13% by weight PVA and 0% to 2.5% by weight poly(vinyl acetate), and has a molecular weight range of 90 000 to 120 000 g/mol.

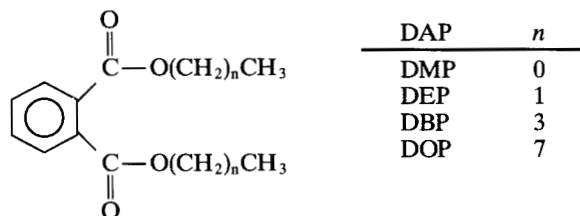
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In this study, the diffusivities of a series of dialkyl phthalates in PVB are measured. Dialkyl phthalates of varying molecular weight (specifically dimethyl (DMP), diethyl (DEP), dibutyl (DBP), and dioctyl (DOP) phthalate) were chosen to reveal fundamental diffusion parameters. The molecular weights of these DAPs are representative of other organic species which typically must be removed during thermolysis, such as plasticizers, waxes, or polymer degradation products. The chemical structure of these DAP species is shown below:



The diffusion studies were performed at isothermal temperatures below the decomposition temperature of PVB ($T < 170^\circ\text{C}$) to avoid complications arising from structural changes in the polymer and the presence of other volatile species which result from degradation.

Thin films of phthalate-plasticized PVB were examined using hot-stage/Fourier transform infrared microspectroscopy (FTIR-M). IR spectra of these films were collected with time at isothermal conditions. The intensity of the C=O ester functional group (1720 cm^{-1}) present in the dialkyl phthalates was measured by FTIR-M. The average concentration of DAP in the PVB film is related to the intensity at 1720 cm^{-1} . The diffusivity of DMP, DEP, DBP, and DOP in PVB can be determined by monitoring the change in intensity of this peak versus time for a given temperature.

II. Experimental Procedure

Stock solutions of PVB-DAP and PVB were made which contained by weight 90% solvent, 6.67% PVB, and 3.33% DAP (for DMP, DEP, DBP, and DOP), and 93.3% solvent and 6.7% PVB, respectively. The solvent used was a 1:1 mixture of methyl ethyl ketone (MEK) and toluene. Appropriate amounts of these stock solutions were weighed out to form solutions for spin coating and bulk polymer film casting.

PVB-DAP films with varying amounts of DAP (0 to 14 mol%) were formed by spin coating. The casting solutions were pipetted onto gold-coated glass cover slides (diameter = 22.0 mm) so that the solution completely covered the surface of the slide. Each sample was spun[†] at 3000 rpm for 30 s. The cover slides were weighed before and after spin coating to determine the thickness of the polymer films. The approximate thickness for all films was $2.5\ \mu\text{m}$.

These PVB-DAP (0 to 14 mol%) films were examined at room temperature by FTIR-M, and a calibration curve relating the intensity at 1720 cm^{-1} to the concentration of DAP was plotted. A separate group of PVB-DAP films (nominally 12.5 mol% DAP) was examined by hot-stage/FTIR-M. The hot-stage attachment[‡] was placed onto the FTIR microspectrometer[§] stage. Each sample was placed onto a glass microscope slide ($25\text{ mm} \times 75\text{ mm}$) for support and loaded into the heating cartridge of the hot stage. The samples were heated at a rate of $30^\circ\text{C}/\text{min}$ to a specific hold temperature. The Linkam controller maintained the T_{hold} to $\pm 0.2^\circ\text{C}$. The IR spectra of the binder films were collected in reflectance mode. The application of the gold coating to the cover slide enhanced the signal-to-noise ratio of the reflected IR beam. Nitrogen gas was passed over the samples during thermolysis. The IR

spectra were collected for 30 scans at a resolution of 16 cm^{-1} . These parameters were selected to minimize the collection time, which was about 4 s for each spectrum. The aperture was set so the IR beam sampled the film in a circular area $50\ \mu\text{m}$ in diameter. These conditions remained the same throughout the experiments.

PVB-DAP films with varying amounts of DAP (0 to 14 mol%) were also formed by bulk casting. The casting solutions were pipetted onto watch glasses (50 mm in diameter) and allowed to dry partially covered for 48 h. Films were produced with an approximate thickness of $50\ \mu\text{m}$. Square pieces ($5\text{ mm} \times 5\text{ mm}$) were cut from each film, placed into aluminum pans, and covered. Differential scanning calorimetry[¶] was performed over the temperature range -45° to 140°C at a heating rate of $30^\circ\text{C}/\text{min}$. Each sample was cycled through the temperature range twice and the T_g was determined from the midpoint of the second transition. Table I lists the T_g 's of pure PVB and PVB-DAP bulk films; the width of the transition region was 10° to 40°C and was proportional to the plasticizer content in the films.

III. Results and Discussion

(1) Diffusivity Measurements

IR spectra representative of the spin-coated PVB film and PVB-DAP films are shown in Figs. 1 and 2, respectively. The pertinent IR frequency range for these films is between 3000 and 1700 cm^{-1} . The following absorbance peaks are observed in this range: CH_3 at 2960 cm^{-1} , CH_2 at 2870 cm^{-1} , and C=O at 1720 cm^{-1} . Comparison of these IR spectra (see Figs. 1 and 2) indicates the peak at 1720 cm^{-1} is present only in the DAP-containing films; this is expected, based on their chemical structures. The intensity of the 1720 cm^{-1} peak is measured in absorbance units (measurement error ± 0.01 units) and is linear with respect to the concentration of DAP, [DAP], in the films as shown in Fig. 3. This behavior is predicted by the Beer-Lambert law. The intensity of this peak (1720 cm^{-1}) was used to determine the [DAP] in these films.

PVB-DAP (12.5 mol%) films were investigated by hot-stage/FTIR-M over the following temperature ranges: 60° to 80°C (DMP), 70° to 90°C (DEP), 70° to 110°C (DBP), and 110° to 150°C (DOP). These temperatures were selected based on the film thickness, the IR spectra collection time, the PVB decomposition temperature, and the diffusivity of the respective DAP. The maximum measurable DAP diffusivity was approximately $10^{-9}\text{ cm}^2/\text{s}$. Larger diffusivities caused the plasticizer to be removed too quickly from the film for these experimental conditions.

[†]DSC-7 with TAC 7/7 controller, Perkin-Elmer, Norwalk, CT.

Table I. DSC Data for PVB Powder and PVB-DAP (0 to 14 mol%) Films

Sample description	DAP (mol%)	T_g ($^\circ\text{C}$)
PVB (powder)	0	74.9
PVB + DMP	3.4	46.0
	10.7	31.0
	11.7	29.9
PVB + DEP	3.0	43.5
	9.4	23.6
	12.0	22.3
PVB + DBP	4.9	40.3
	10.5	22.3
	12.6	12.7
PVB + DOP	5.6	34.3
	10.1	21.6
	14.2	2.0

[†]Model 1-EC101D-R485 photo-resist spinner, Headway Research, Garland, TX.

[‡]THM-600 with TMS controller, Linkam, Surrey, U.K.

[§]Bruker Instruments, Billerica, MA.

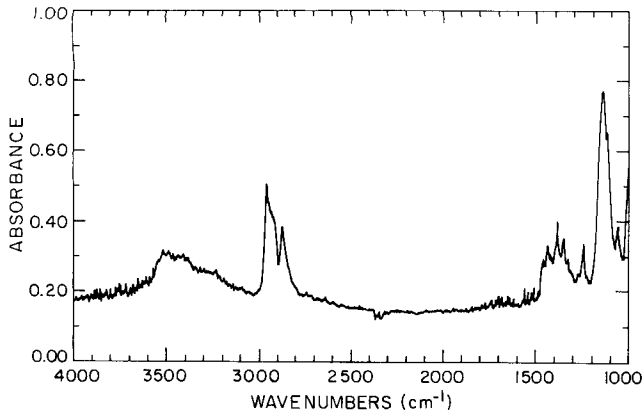


Fig. 1. IR spectrum of PVB film (spin-coated) in absorbance units.

IR spectra of the PVB-DAP (12.5 mol%) films were collected as a function of time at the isotherms stated above. During these isothermal holds, the plasticizer (DAP) diffuses to the surface of the film, where it is removed by evaporation. Plasticizer transport by diffusion in the film is the rate-limiting step. An example of IR spectra collected from a PVB-DBP (12.5 mol%) film held at $T_{\text{hold}} = 100^\circ\text{C}$ is shown in Fig. 4. The intensity of the peaks at 2960, 2870, and 1720 cm^{-1} decreases with time due to the loss of DBP from the film (see Fig. 4). The ratio of the absolute intensity, $I(t)$, of the 1720 cm^{-1} peak to the initial intensity, I_0 , in absorbance units can be determined from the series of collected IR spectra; this intensity ratio is equivalent to the ratio of the instantaneous concentration, $[C](t)$, to the initial concentration, $[C]_0$, of the plasticizer in the film. Thus, the profile of $I_0/I(t)$ (1720 cm^{-1}) measured over time by hot-stage/FTIR-M is comparable to an isothermogravimetric analysis (I-TGA) of each film.

Equation (1) is applicable to the diffusion process occurring in these films based on their geometry. This relationship was derived by performing a separation of variables (position and time) analysis:^{10,11}

$$[c](t) = \frac{8[c]_0}{\pi^2} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} \exp\left(\frac{-(2j+1)^2\pi^2Dt}{4l^2}\right) \quad (1)$$

where D is the diffusivity (cm^2/s), l is the film thickness (cm), and t is the time (s). The power series solution is valid over all times, but it is particularly useful when the first-term approximation holds. Comparing the relative magnitudes of the first and second terms indicates this approximation applies for these PVB-DAP (12.5 mol%) films. Equation (2) represents

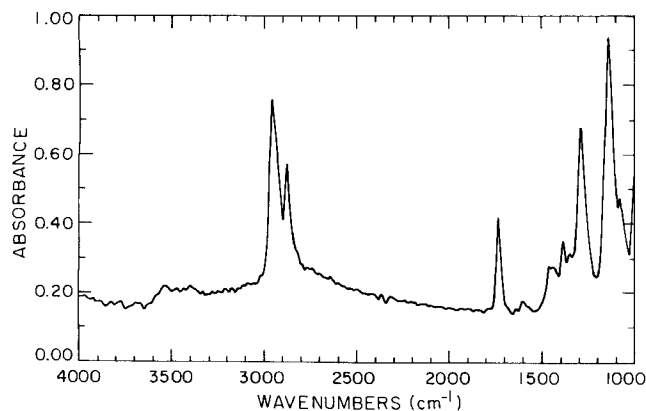


Fig. 2. IR spectrum of PVB-DBP film (spin-coated) in absorbance units.

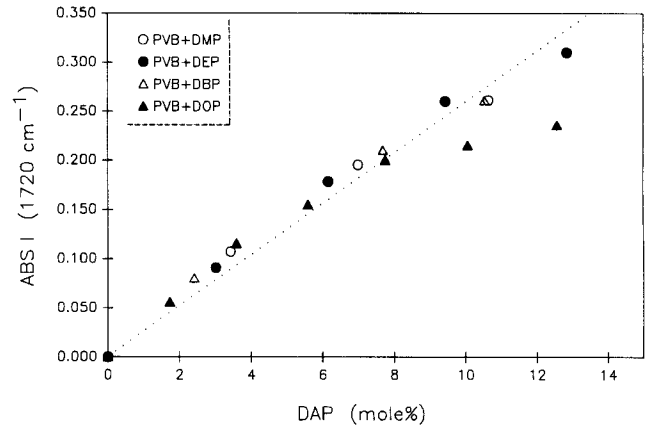


Fig. 3. Calibration curve of the absolute intensity of the C=O peak (1720 cm^{-1}) in absorbance units as a function of DAP concentration in the PVB-DAP films.

this simplified form:

$$\frac{[c](t)}{[c]_0} = \frac{8}{\pi^2} \exp\left(\frac{-\pi^2Dt}{4l^2}\right) = \frac{I(t)}{I_0} \quad (2)$$

Further modification of Eq. (2) yields Eq. (3), which is valid from $0 < I(t)/I_0 < 0.8$:

$$\ln\left(\frac{I(t)}{I_0}\right) = \frac{-\pi^2Dt}{4l^2} + \ln\left(\frac{8}{\pi^2}\right) \quad (3)$$

Figures 5 to 8 show $\ln(I(t)/I_0)$ as a function of time for each set of PVB-DAP films. The slope of each curve is directly proportional to the diffusion coefficient of DAP (DMP, DEP, DBP, and DOP) in PVB at T_{hold} (refer to Eq. (3)). Least-squares analysis was used to fit the data shown in Figs. 5 to 8. Only the data shown in Figs. 7 and 8 exhibit a linear correlation with time. The correlation coefficient (r) was calculated to be $r > 0.993$ for the PVB-DBP curves and $r > 0.965$ for the PVB-DOP curves. The degree of linearity is related to the diffusion behavior of the plasticizer in the PVB-based films. The PVB-DBP and PVB-DOP exhibit Fickian behavior, while the PVB-DMP and PVB-DEP films exhibit non-Fickian behavior over the temperatures investigated.

Cooperative movement of several monomer units (polymer segments) is required for diffusants whose size is comparable to or larger than the monomer unit of the polymer.¹²⁻¹⁴ The

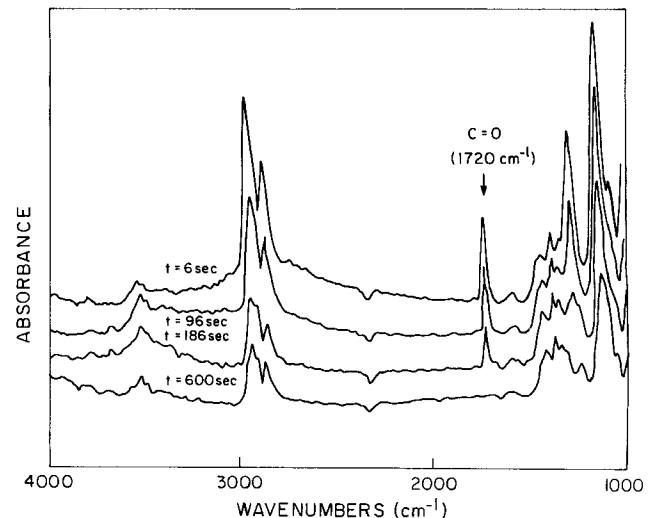


Fig. 4. IR spectra of PVB + 12.5 mol% DBP film as function of time at $T_{\text{hold}} = 100^\circ\text{C}$.

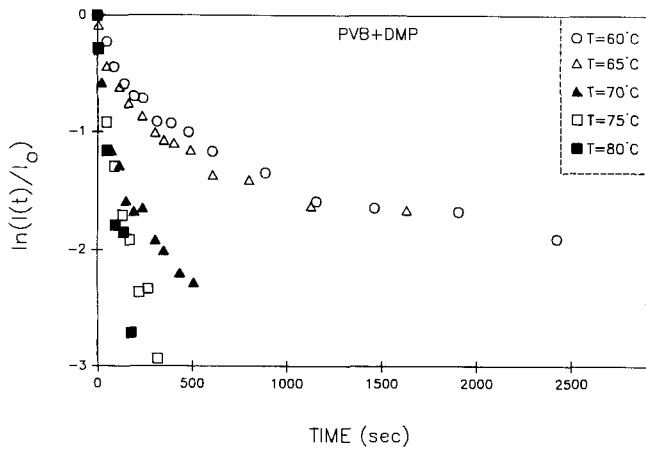


Fig. 5. $\ln [I(t)/I_0]$ as a function of time for PVB + 12.5 mol% DMP films at $T_{\text{hold}} = 60^\circ, 65^\circ, 70^\circ, 75^\circ,$ and 80°C .

DAPs studied are larger than the PVB monomer unit based on their respective molecular weights. Deviations in Fickian behavior can be expected in polymer-diffusant systems at temperatures near ($\pm 15^\circ\text{C}$) the T_g of the pure polymer.¹⁴⁻¹⁶ Non-Fickian anomalies result from the finite rates at which the polymer structure may change in response to the sorption or desorption of diffusant molecules.¹⁷ At temperatures above T_g ($\approx T_g + 15^\circ\text{C}$), polymers can respond rapidly to changes in their condition, and thus Fickian behavior is observed. Based on this, we expect Fickian behavior only for PVB-DBP and PVB-DOP films.

The slope of each curve shown in Figs. 7 and 8 was determined to within 95% confidence limits from the least-squares analysis. From this, an average diffusivity (and range) of DBP and of DOP in the PVB-based films is calculated (refer to Eq. (3)) and is reported in Table II. The slope of each curve shown in Figs. 5 and 6 is dependent on time (i.e., non-Fickian), and therefore an average diffusivity of DMP or of DEP in the PVB-based films cannot be calculated using Eq. (3).

Diffusion is an activated process based on an Arrhenius function of temperature. The activation energy (E_a) associated with a given polymer-diffusant system represents the energy necessary to form a hole large enough to accommodate diffusant movement. Therefore, E_a would be expected to increase as the diffusant size (or molecular weight) increased. A plot of $\log(D_{\text{ave}})$ versus reciprocal temperature for DBP and DOP diffusion in the PVB-based films is shown in Fig. 9. The slope of each curve is proportional to E_a for the diffusion process. E_a was calculated to be 76.3 kJ/mol for DBP diffusion and 114.7 kJ/mol for DOP diffusion in the PVB-based films. The activation energies for diffusion of DMP and of

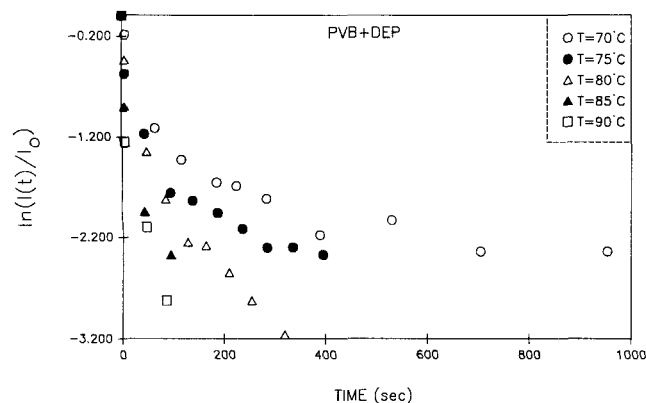


Fig. 6. $\ln [I(t)/I_0]$ as a function of time for PVB + 12.5 mol% DEP films at $T_{\text{hold}} = 70^\circ, 75^\circ, 80^\circ, 85^\circ,$ and 90°C .

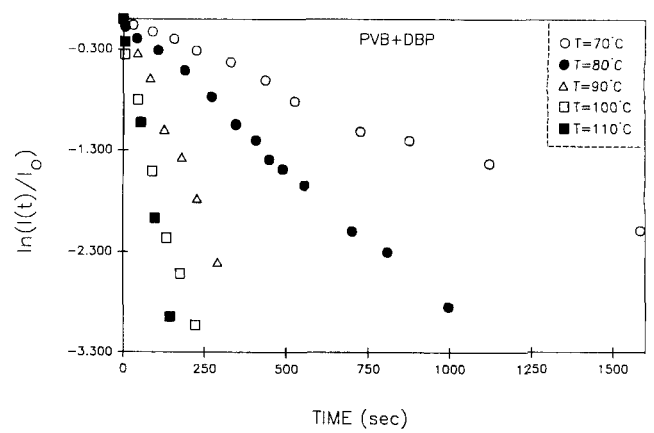


Fig. 7. $\ln [I(t)/I_0]$ as a function of time for PVB + 12.5 mol% DBP films at $T_{\text{hold}} = 70^\circ, 80^\circ, 90^\circ, 100^\circ,$ and 110°C .

DEP in these films are not reported because of their anomalous diffusion behavior in the temperature ranges investigated.

(2) Applications to Binder Thermolysis

The diffusivities of organic molecules in polymers are useful kinetic parameters for characterizing the thermolysis of binders within ceramic green bodies. The diffusivity of DBP in PVB can be used to estimate the characteristic diffusion length of DBP in tape-cast alumina-PVB-DBP sheets during removal and to determine the relative contribution of capillary migration to the removal process.

Capillary forces do not affect all binder systems during thermolysis, because the viscosity of the binder may remain too high even at elevated temperature. This is true when: (1) the time scale for removal of volatile constituents is much faster than the capillary-induced migration of the binder, (2) the length scale over which capillary forces act is much smaller than the dimensions of the green body, or (3) the binder system is highly cross-linked.⁹

Recent studies have shown that PVB-DBP is redistributed within the particulate network of the tape during thermolysis because of capillary forces.^{8,9,18} These tapes contained 40 vol% binder, with a PVB-to-DBP ratio of 2:1 by weight. A schematic model of the distribution of PVB-DBP during DBP removal from the tape is shown in Fig. 10, which depicts a region around developing pores. In order to remove DBP, it must diffuse through regions of plasticized PVB to reach the penetrating vapor-binder interface. Thus, the characteristic diffusion length should correspond to the distance between the developing pores.

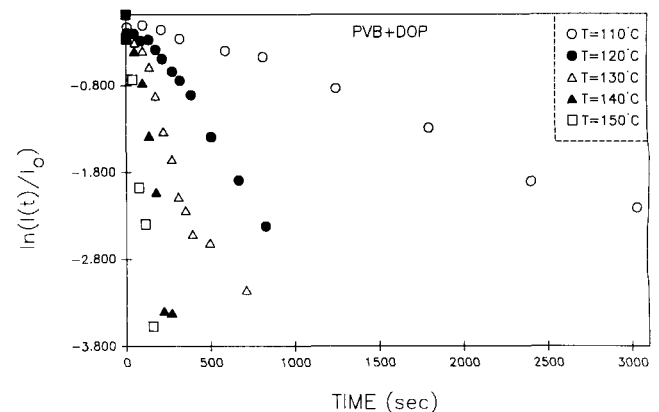


Fig. 8. $\ln [I(t)/I_0]$ as a function of time for PVB + 12.5 mol% DOP films at $T_{\text{hold}} = 110^\circ, 120^\circ, 130^\circ, 140^\circ,$ and 150°C .

Table II. Diffusivities of DAP Diffusants in PVB–DAP (12.5 mol%) Films

T_{hold} (°C)	Diffusivity ($\times 10^{10}$ cm ² /s)		
	D_{min}	D_{ave}	D_{max}
	DBP		
70	0.31	0.34	0.36
80	0.70	0.72	0.75
90	1.91	2.06	2.21
100	2.92	3.37	3.82
110	4.57	5.06	5.55
	DOP		
110	0.14	0.17	0.20
120	0.63	0.71	0.78
130	1.03	1.26	1.48
140	2.53	3.37	4.20
150	4.49	5.50	6.51

Estimates of the diffusion length (l) can be derived from the experimental rate at which DBP is removed from alumina–PVB–DBP tapes as determined by I-TGA. The mass flux (J) of DBP from these tapes was reported to be 5×10^{-8} g/(cm²·s) at 143°C and 3.2×10^{-7} g/(cm²·s) at 164°C.⁸ The rate of mass loss is nearly constant throughout DBP removal (based on I-TGA data), and therefore the controlling distance over which DBP must diffuse is also constant and can be estimated from

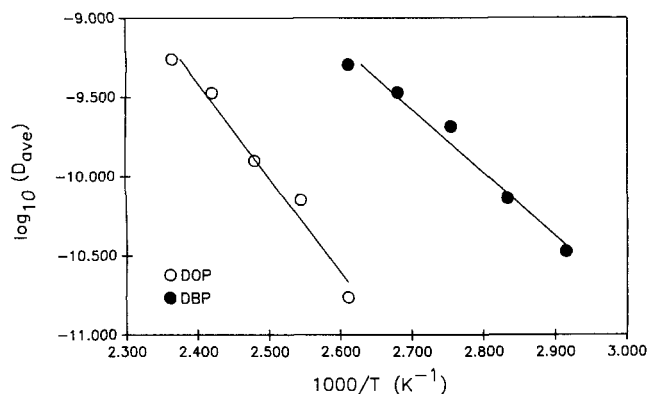
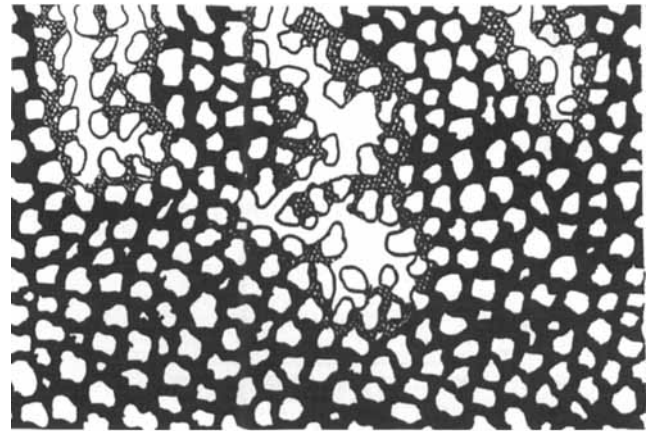
$$J = -D_{\text{eff}} \frac{\Delta c}{l} \quad (4)$$

where D_{eff} is the effective diffusivity (cm²/s), and Δc is concentration gradient (g/cm³). Δc equals 0.154 g/cm³, which is the initial concentration of DBP per unit volume of the green tape.

The effective diffusivity (D_{eff}) of the plasticizer within the alumina–PVB–DBP tape accounts for the presence of the ceramic particles and for the tortuous nature of the pores. D_{eff} can be evaluated from¹⁹

$$D_{\text{eff}} = \frac{D_{\text{DBP}}\epsilon}{\tau} \quad (5)$$

where D_{DBP} is the diffusivity of DBP in PVB, ϵ is the void fraction of the particulate bed, and τ is the tortuosity factor. D_{DBP} was calculated to be 5.16×10^{-9} cm²/s at 143°C and 1.49×10^{-8} cm²/s at 164°C using the Arrhenius relationship ($E_a = 76.3$ kJ/mol). The void fraction (ϵ) is approximately 0.4 for these green tapes, and this region is initially filled with binder. The tortuosity (τ) typically ranges from 3 to 7 for packed powder beds; a value of 5 was chosen to represent these tapes. Based on these values, D_{eff} was calculated to be 4.12×10^{-10} cm²/s at 143°C and 1.20×10^{-9} cm²/s at 164°C using Eq. (5). Thus, the presence of packed ceramic particles in the tape reduces the diffusivity of DBP (D_{eff}) by an order of magnitude relative to its diffusivity (D_{DBP}) in a PVB-based film.

**Fig. 9.** $\log D_{\text{DAP}}$ versus reciprocal temperature for PVB–DBP and PVB–DOP films.

■ Binder region with nominal DBP concentration
 ▨ Binder region containing DBP concentration gradient
 □ Alumina

Fig. 10. Schematic model of the distribution and removal processes which occur during thermolysis of alumina–PVB–DBP green tapes.

A characteristic length (l) for DBP diffusion in the green tape at various temperatures was calculated using Eq. (4) and was found to be 12 μm at 143°C and 4 μm at 164°C. These distances are on the order of several particle diameters in length. It is unclear whether tortuosity is relevant for these distances. Neglecting tortuosity results in lengths of 64 μm ($T = 143^\circ\text{C}$) and 28 μm ($T = 164^\circ\text{C}$). Therefore, the error in l is assigned to be 12 to 64 μm at 143°C and 4 to 28 μm at 164°C. These values of l are clearly representative of the distance between developing pores and not of the thickness of the green tape (300 μm). Interestingly, l decreases as the temperature increases, which indicates the mass flux of DBP increases faster with temperature than is accounted for by increased D_{DBP} alone. This phenomenon could occur because of an increase in the rate at which pores develop in the tape as temperature increases. The porosity development in the green tape is dependent upon the viscous nature of the PVB–DBP system, since capillary forces influence the removal process.⁸ The viscosity of PVB–DBP decreases with increasing temperature, and thus the viscous resistance to flow decreases. A decreasing characteristic diffusional length can be explained by the increasing importance of capillary forces at higher temperature.

The length scale over which capillary forces act on the PVB–DBP system in these alumina–PVB–DBP composites was determined to be on the order of the dimensions of the tape.⁸ The importance of capillary migration of PVB–DBP can be shown by comparing the DBP removal behavior that was observed (I-TGA) with the expected DBP removal if capillary forces did not act. Expected DBP removal rates can be calculated by adjusting Eq. (2) to the form below:

$$\frac{[\text{DBP}](t)}{[\text{DBP}]_0} = \frac{8}{\pi^2} \exp\left(\frac{-\pi^2 D_{\text{eff}} t}{4l^2}\right) \quad (6)$$

where $[\text{DBP}](t)/[\text{DBP}]_0$ represents the fractional loss of DBP from the tape, D_{eff} is the effective diffusivity, t is the time, and l is the length. The length (l) was chosen to be the half-thickness of the green tape ($l = 150 \mu\text{m}$); this value is the expected path length for DBP diffusion if capillary forces did not influence the distribution of PVB–DBP during thermolysis.

Figures 11(A) and (B) compare the observed DBP loss (I-TGA) and the calculated DBP loss (Eq. (6)) from the com-

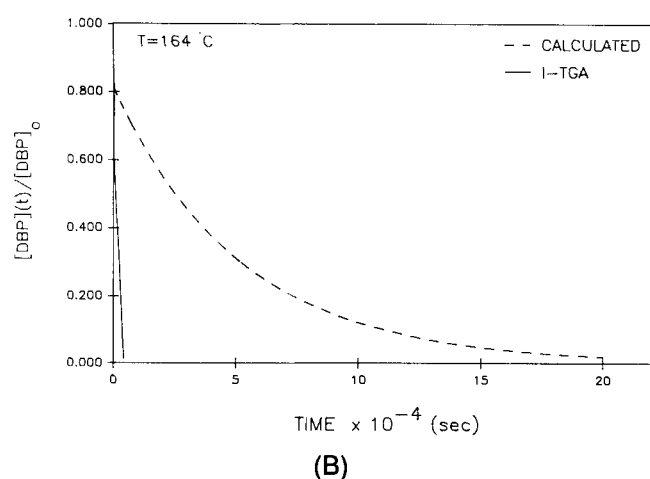
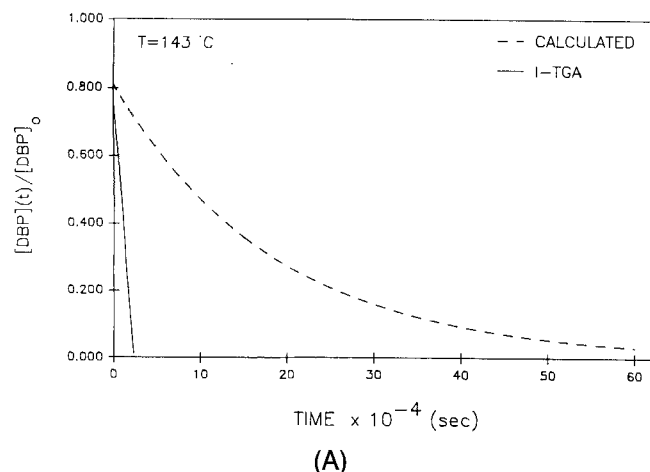


Fig. 11. Comparison of the calculated loss of DBP ($[DBP](t)/[DBP]_0$) versus time using corrected diffusivities (for the particulate bed) to the experimental loss observed by I-TGA: (A) $T = 143^\circ\text{C}$ and (B) $T = 164^\circ\text{C}$.

posite at 143° and 164°C , respectively. The rate of DBP removal is proportional to the slope of each curve. The effects of capillary migration are apparent. First, the time required for removal of 98% of the DBP is decreased by two orders of magnitude when capillary migration of PVB-DBP occurs. Secondly, the rate of DBP loss remains constant over the entire removal period because of capillary migration of the PVB-DBP. The diffusion model predicts a continuously falling rate of DBP removal from the composite during thermolysis. This comparison suggests that capillary forces can significantly enhance the removal of volatile constituents from ceramic green bodies.

IV. Conclusions

The removal of a plasticizing constituent from polymer-based films and ceramic green tapes was studied to afford an understanding of the fundamental issues involved in removing organic molecules during thermolysis. The investigation of plasticizer removal at temperatures below the polymer decomposition temperature allowed the thermolysis process to be simplified by eliminating complexities which result from polymer degradation (e.g., structural changes of the polymer and diffusion of other volatile species).

Two important points were illustrated by this investigation: first, the diffusivities of DAP plasticizers in PVB were quite low (10^{-12} to 10^{-10} cm^2/s) over the temperatures investigated, and secondly, capillary redistribution of PVB-DBP during thermolysis leads to a significant enhancement in the rate at which DBP can be removed from alumina-PVB-DBP green tapes relative to the expected removal rates due to diffusion alone.

Evidence presented in this paper demonstrates that the distribution of binder and the kinetics of the removal process are intimately coupled. The development of a penetrating porosity during the initial stages of binder removal as a result of capillary redistribution can reduce the path length over which species must diffuse to a length scale on the order of the particle size, as shown for the alumina-PVB-DBP tapes. This reduction in diffusion length relative to the dimensions of the green body expedites the removal process.

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