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# Effects of a combined supercritical extraction/thermal cycle on binder removal cycle time, yield, and residual carbon of multilayer ceramic capacitors

Brandon Abeln<sup>a</sup> and Stephen J. Lombardo<sup>a,b,\*</sup>

<sup>a</sup>Department of Chemical Engineering, University of Missouri, Columbia MO 65211, USA <sup>b</sup>Department of Mechanical & Aerospace Engineering, University of Missouri, Columbia MO 65211, USA

A combined cycle, consisting of a supercritical extraction cycle (SCE) followed by a thermal cycle (TC), was used to remove binder from green multilayer ceramic capacitors. The dielectric was barium titanate and the binder consisted of poly(vinyl butyral) plasticized with phthalates. Supercritical extraction of approximately one-third of the binder leads to an increase in the porosity and gas permeability of samples and to a decrease in the adhesion strength between layers. The partial removal of the binder also resulted in a decrease in cycle time and defects following the combined SCE/TC. Samples subjected to the combined SCE/TC also had 25-30% less residual carbon as compared to samples subjected to a thermal cycle alone.

Key words: Supercritical extraction, Binder, Residual carbon, Barium titanate, Multilayer ceramic capacitor.

#### Introduction

In the manufacture of noble-metal and base-metal multilayer ceramic capacitors (MLCs), mixtures of organic additives are used to aid in the fabrication, handling, and lamination of green tapes. In addition to these general benefits, the binder influences specific properties of the MLC such as the green strength, the adhesion strength between layers, and the permeability to gas flow. These properties depend not only on the amount and type of binder, but also on the conditions of the lamination process via the lamination time, temperature, and pressure [1-3].

Although the binder plays a number of important roles during processing, it ultimately must be removed [4, 5] and this is traditionally accomplished in furnacing operations in which the organic constituents of the binder are either vaporized, oxidized, or pyrolyzed into gas phase species. The evolution of these species into the pore space of the green body thus leads to an increase in pressure, which in turn causes stress [6-8] within the component that ultimately may lead to defects such as fracture or delamination [9-14]. To avoid failure of green components during binder removal- and thus increase yield-several strategies are available. Most often, once a binder system has been developed, heating schedules are specified in which multiple ramp rates, hold temperatures, and hold times are selected so that the rate of binder decomposition is sufficiently retarded in order to minimize the pressure and hence stress within the green body. Thus, in practice, specification of an ideal heating schedule becomes a compromise between

extraction of plasticizers may lead to 40-60% removal of the organic fraction [19, 20], depending on the components in the binder blend, and substantial partial extraction of binder can lead to increases in both the porosity and gas permeability of the green body. Even though SCE may not be capable of fully removing all of the organic constituents, a subsequent thermal cycle (TC) may be used to remove any remaining organic species. This thermal cycle may be realized as a separate furnace operation or as part of the sintering cycle, and may be conducted under

oxidizing, reducing, or inert conditions.

achieving a short cycle time and a high product yield. To avoid the aforementioned drawbacks associated

with the thermal removal of binder, supercritical extraction

(SCE) has been proposed and demonstrated as an

alternative processing route [15-25]. Under supercritical

conditions, organic species dissolve into the supercritical

fluid and then diffuse out of the green body, thus effecting

binder removal without additionally increasing the pressure

in the pore space. It is well known that SCE is most

effective in removing organic species of lower molecular

weight such as short chain waxes [16-18] or plasticizers

[19-21, 24, 25]. For the case of MLCs, this preferential

In summary, although supercritical extraction can remove binder, either partially or nearly completely from green bodies, its efficacy as an alternative processing strategy in terms of benefits to cycle time and yield– the same issues which pertain to thermal debinding– have not been specifically addressed in the literature. It is thus one aim of this study to demonstrate that a combined supercritical extraction/thermal cycle (SCE/TC) can be used to decrease the overall processing time while avoiding defects and thus maintaining a high yield. This combined cycle may be rapid because supercritical extractions times can be short, often on the order of hours, and the aforementioned

<sup>\*</sup>Corresponding author:

Tel : +573-884-1644 Fax: +573-884-4940

Fax: +5/3-884-4940

E-mail: LombardoS@missouri.edu

increases in porosity and gas permeability of the green body may consequently facilitate a subsequent rapid thermal cycle. In addition to this objective, we have also observed in earlier work that changing the conditions of an upstream process step in the manufacture of MLCs, namely in the lamination conditions, can also influence the yield during binder removal [3], and thus we report and discuss on this aspect of processing for the combined SCE/TC as well.

Finally, we note that another shortcoming of thermal debinding is that carbonaceous residues may remain in the green body and these may either inhibit sintering or degrade the electrical properties of the final components. The role of carbon contamination on device performance is especially important in the processing of MLCs with base metal electrodes in which non-oxidative conditions during binder removal are typically used at temperatures above 270 °C in order to avoid oxidation of the base-metal electrode material [26-30]. We therefore additionally demonstrate that a combined SCE/TC can also impact the residual carbon present in base-metal MLCs, which is a current processing trend for MLCs.

## **Experimental**

For determining the effect of SCE/TC on the yield and cycle time for binder removal from multilayer bodies, green tapes were prepared which consisted of 86.6 wt% barium titanate powder (Ferro X7R422H, Ferro, Niagara Falls, NY), 6.7 wt% poly(vinyl butyral) (PVB) resin (Butvar B98, Richard E. Mistler, Inc., Yardley, PA), 5.1 wt% butyl benzyl phthalate (Santicizer 160, Richard E. Mistler, Inc.), and 1.7 wt% Menhaden fish oil (Richard E. Mistler, Inc.). A uniaxial press (Model 2518, Carver Inc., Wabash, IN) was used to laminate 17 individual green tapes, each approximately 150  $\mu$ m thick, at 5 MPa for 10 minutes at either 85 °C or 95 °C into MLCs; the dimensions after lamination were 2.0 × 1.5 × 0.25 cm and 2.0 × 1.5 × 0.23 cm, respectively.

The porosity and permeability of four laminated tapes were measured after lamination, after SCE, and after the combined SCE/TC. The porosity,  $\varepsilon$ , was determined using Archimedes' method. The permeability measurements, which have been described in more detail elsewhere [31, 32], were performed by measuring the molar flux,  $N_m$ , of N<sub>2</sub> gas through tapes of disc shape. For a pressure drop from  $P_1$  to  $P_2$  across a sample of thickness, L, the permeability,  $\kappa$ , can be determined from the flux data with:

$$\kappa = -2RTN_m \mu \frac{L}{P_2^2 - P_1^2} \tag{1}$$

where *R* is the gas constant, *T* is the temperature, and  $\mu$  is the viscosity of the gas.

The adhesion strength between layers was determined by performing peel tests, which have been described in more detail elsewhere [2, 3, 33, 34]. First, two substrates were fabricated, each containing two laminated green tapes of 4.0 cm length by 1.0 cm width. These two substrates were layered, partially separated by mylar, and then laminated to form a T-shaped peel sample. For the peel test, the two unlaminated parts of the T shape were placed in the grips of a tensile tester (TA TX Plus Texture Analyzer, Stable Micro Systems Ltd, Surrey, UK). During testing, the load was measured as a function of displacement as the top crosshead moved at a speed of 0.4 cm s<sup>-1</sup>. When the extension due to strain is negligible, the adhesion strength,  $\sigma$ , is given by:

$$\sigma = \frac{F_1}{b} \tag{2}$$

where  $F_1$  is the applied force and b is the sample width. The adhesion strength is reported as the average of three samples.

The supercritical extraction experiments were conducted in a SS 316 (6.25 cm diameter, 500 ml) Parr high pressure non-stirred vessel equipped with a thermocouple well located in the vessel cover. The vessel was placed in a controlled-temperature furnace which maintained the temperature within ±2 °C. Extraction experiments were conducted in a semi-continuous mode of operation using  $CO_2$  as the supercritical fluid. The SCE cycle was comprised of a purge step, a pressurization step, a dwelling step, and a depressurization step. The purge consisted of a three minute exposure to flowing CO2 at room temperature and pressure to remove air from the extraction vessel. The vessel was next pressurized with carbon dioxide from 0.1 MPa to 10 MPa with a compressor over 3-4 minutes at room temperature. The vessel was then thermally pressurized to  $30 \pm 1$  MPa as the temperature was increased to 90 °C. The dwell lasted for 1 h as pressure and temperature were held constant. The vessel was then depressurized isothermally over a 6 h period to atmospheric conditions. After depressurization, the extraction efficiency was determined from the weight loss of the MLCs, normalized by the total amount of organic phase initially present.

Thermal oxidation of the binder in the MLCs was conducted in air in a box furnace. The TC consisted of a ramp at either 7.5 or 10 K·minute<sup>-1</sup> to 600 °C, a 1 h soak at 600 °C, followed by cooling to 40 °C. Fig. 1 shows the segments of the SCE cycle (~8 h total duration), the TC (~6 h total duration), and also the combined SCE/TC (~14 h total duration).

For determining the effect of the combined SCE/TC on the residual carbon content, the green tapes consisted of 87.7 wt% barium titanate powder (AD 342N, Ferro, Niagara Falls, NY), 8.8 wt% poly(vinyl butyral) (PVB) resin (BMS, Sekisui, Troy, MI), and 3.5 wt% dioctyl phthalate (Sigma-Aldrich, St. Louis, MO). The dried tapes were  $\sim$ 22 µm thick. To prepare the nickel metal electrode pastes, nickel powder at 75.8 wt% (JFE Ni Powder, JFE Mineral Co., Japan), 15.1 wt% barium titanate (BT 01, Sakai Chemical Industry Co., Japan), 4.6 wt% Witco Emphos (Witco Corp., Greenwich, CT), and 4.6 wt% ethyl cellulose



**Fig. 1.** The supercritical extraction cycle and the thermal cycle used in this study for determining yield and cycle time of MLCs. For comparison, part of a typical cycle from industry is also shown.

(N-4, Ashland Aqualon, Wilmington, DE) were combined in a solvent and then screen printed onto the tapes. Next, 30 tapes were laminated in a hydrostatic press at ~21 MPa at 65 °C for 20 minutes, and the resulting dimensions of the MLCs were  $2.54 \times 2.54 \times 0.067$  cm. Samples were also prepared without the Ni electrode material.

For these samples, SCE was performed with carbon dioxide at 90 °C and 30 MPa for three 1-h exposures. Following SCE, the TC was conducted in the box furnace in air with a ramp of 1 K·minute<sup>-1</sup> to 270 °C followed by a 12 h dwell period and then cooling to 40 °C. Fig. 2 shows the segments of the SCE cycle (~6 h total duration), the TC (~19 h total duration), and also the combined SCE/TC (~25 h total duration).

The carbon content was measured with a residual carbon analyzer (Model C-144, LECO, St. Joseph, MI) by pulverizing the MLCs into a powder yielding an average particle diameter of approximately 1 mm. For each type of sample, the average percent residual carbon (%RC) and 90% confidence intervals were calculated from 5 samples at each condition. To determine the precision and accuracy of the RC measurements, a 1% carbon standard was evaluated prior to analyzing the samples.

# **Results and Discussion**

#### Effect of SCE/TC versus TC on cycle time and yield

For the first experiment, an MLC, laminated at 85 °C and 5 MPa for 10 minutes, was subjected to a TC alone with a heating rate of 7.5 K·minute<sup>-1</sup>. As seen in the images in Fig. 3(a), the top surface in the central portion of the substrate experienced a large defect during the TC; no damage was evident on the sides of the sample. Another MLC, laminated at the same conditions, was then subjected first to supercritical extraction; the sample lost 36 weight% during this step and displayed no defects afterwards. This



Fig. 2. The supercritical extraction cycle and the thermal cycle used in this study for determining residual carbon content of MLCs.



**Fig. 3.** Side and top images of MLCs laminated at 85 °C, 5 MPa for 10 minutes. a) Sample after a TC conducted with a 7.5 K minute<sup>-1</sup> ramp to 600 °C with a 1 h hold. b) Sample after a combined SCE/TC after exposure first to supercritical CO<sub>2</sub> at 90 °C, 29 MPa for 1 h followed by a 6 h depressurization. The MLC was then exposed to a thermal cycle identical to (a).

sample was then subjected to the TC portion of the cycle, where the binder was completely removed, *e.g.*, the total weight loss was 100%. Fig. 3(b) shows that after the combined SCE/TC, no defects were evident in the sample.

In the second experiment, the above procedure, for the same lamination conditions, was repeated, but this time during the TC the samples were heated at a higher rate of 10 K·minute<sup>-1</sup>. Fig. 4 shows that for the TC, the MLC once again experienced defects in the top surface and also large delaminations on the edge of the sample. For the MLC subjected to the combined SCE/TC, the top surface exhibited no defects but the edge now showed two small regions of delamination. Thus, an increase in the heating rate during the TC has lead to defects in samples subjected to both processes, although the severity is much worse for the TC alone. This suggests that the evolution of pressure, and hence stress, during the TC exceeded the strength of the green body in both cases.

Additional experiments were conducted, but now the lamination temperature was increased from 85 °C to 95 °C.



**Fig. 4.** Side and top images of MLCs laminated at 85 °C, 5 MPa for 10 minutes. a) Sample after a TC conducted with a 10 K minute<sup>-1</sup> ramp to 600 °C with a 1 h hold. b) Sample after a combined SCE/TC after exposure first to supercritical  $CO_2$  at 90 °C, 29 MPa for 1 h followed by a 6 h depressurization. The MLC was then exposed to a thermal cycle identical to (a). The arrows indicate delaminations.



**Fig. 5.** Side and top mages of MLCs laminated at 95 °C, 5 MPa for 10 minutes. a) Sample after a TC with a 7.5 K·minute<sup>-1</sup> ramp to 600 °C with a 1 h hold. b) Sample after a combined SCE/TC after exposure first to supercritical CO<sub>2</sub> at 90 °C, 29 MPa for 1 h followed by a 6 h depressurization. The MLC was then exposed to a thermal cycle identical to (a).



**Fig. 6.** Side and top images of MLCs laminated at 95 °C, 5 MPa for 10 minutes. a) Sample after a TC with a 10 K·minute<sup>-1</sup> ramp to 600 °C with a 1 h hold. b) Sample after a combined SCE/TC after exposure first to supercritical CO<sub>2</sub> at 90 °C, 29 MPa for 1 h followed by a 6 h depressurization. The MLC was then exposed to a thermal cycle identical to (a).

**Table 1.** Summary of defect formation in MLCs after exposure to a thermal cycle (TC) alone or a combined supercritical extraction cycle/thermal cycle (SCE/TC) versus lamination temperature and heating rate of the TC

Lamination Temperature (°C)	Heating Rate (K minute <sup>-1</sup> )	TC Failure (Yes/No)	SCE/TC Failure (Yes/No)
85	7.5	Yes*	No
85	10	Yes	Yes*
95	7.5	Yes*	No
95	10	Yes	No

\*Sample experienced only slight damage

Fig. 5(a) shows that for the TC alone, in which the heating rate was 7.5 K·minute<sup>-1</sup>, defects occur in the green body; these defects, however, are not located on the surface but instead are restricted to the edges of the sample in the form of large regions of delamination. Fig. 5(b) shows that after the combined SCE/TC, no defects were evident in the sample.

In the final set of experiments, MLCs laminated at 95 °C were subjected to a TC alone, but now at the higher heating rate of 10 K·minute<sup>-1</sup>. For this heating rate, Fig. 6(a) shows that the sample subjected to the TC alone exhibited defects on both the top and edges. The MLC subjected to the SCE/TC, however, exhibited no defects after the combined cycle, although defects were observed at this heating rate for a sample laminated at 85 °C.

The MLC yield relationships presented above between a TC alone versus a combined SCE/TC as a function of TC heating rate and lamination temperature are summarized in Table 1. All samples subjected to the TC alone, regardless of the lamination temperature and heating rate in the TC, experienced defects, although the severity was worse for the higher heating rate. For samples subjected to the combined SCE/TC, the yield of defect-free parts was higher in three of the four sets of conditions as compared to the TC alone. An alternative way to view the yield results is that for a given type of heating cycle (TC versus SCE/TC) the propensity or severity of defect formation increased in three of the four cases as the heating rate was increased.

To clarify the trends in Table 1, the sample porosity, gas permeability, and adhesion strength were measured at different points in the process, and these data, along with sample weight loss, are summarized in Table 2. For lamination at 5 MPa for 10 minutes at 85 or 95 °C, each substrate

**Table 2.** Porosity, permeability, adhesion strength, and weight loss for ceramic tapes as 4-layer substrates after lamination, after SCE, and after a combined SCE/TC

		Aft	er Lamin	ation		А	fter SCE			А	fter SCE/	TC
Lam. Temp. (°C)	ε(-)	$\kappa$ (m <sup>2</sup> )	σ (N/m)	Wt. Loss (%)	ε(-)	$\kappa$ (m <sup>2</sup> )	$\sigma  (N\!/\!m)$	Wt. Loss (%)	ε(-)	$\kappa$ (m <sup>2</sup> )	σ (N/m)	Wt. Loss (%)
85	0.19	~ 0	48.4	< 0.5	0.32	$3.4\times10^{-16}$	33.3	36.5	0.49	*	*	~100
95	0.18	$\sim 0$	59.5	< 0.5	0.34	$4.0\times10^{-16}$	45.5	38.5	0.48	*	*	~100

\*indicates samples were too fragile to measure

experienced less than 0.5% weight loss, and the permeability of the laminated green tapes was too low to be measured. The fractional porosity decreased slightly from 0.19 to 0.18 as the lamination temperature was increased from 85 °C to 95 °C whereas the adhesion strength between layers increased from 48.5 to 59.5 N m<sup>-1</sup>. This latter type of behavior for the effect of lamination on the adhesion strength is consistent with previous work [2, 3] whereby at higher lamination temperature, the viscosity of the sample, via the binder, decreases, and thus the interpenetration or flow of the tapes during lamination is enhanced, thereby increasing the adhesion strength.

Following lamination, samples were subjected to SCE in carbon dioxide at conditions of 90 °C at 29 MPa for 1 h. For the substrate laminated at 85 °C, SCE resulted in a 36.5% weight loss of the organic content and an increase in the fractional porosity from 0.19 to 0.32. Supercritical extraction, likely via the weight loss and concomitant change in porosity, lead to an increase in the permeability, which was now measurable, and a decrease in the adhesion strength from 48.5 to 33.3 N m<sup>-1</sup>. Similar trends in the porosity, permeability, and adhesion strength following SCE were observed for the samples laminated at 95 °C.

After the TC in air, the substrates experienced  $\sim 100\%$  weight loss of the organic fraction, which corresponds to a porosity value of 0.48 for substrates laminated at 85 °C and 0.49 for substrates laminated at 95 °C. The complete loss of binder during the TC rendered the samples too fragile for handling and testing; this behavior likely reflects a further decrease in the adhesion strength and masks an increase in the gas permeability.

To summarize this section, the combined SCE/TC leads to rapid binder removal cycles with high yield as compared to cycles practiced in industry for samples of similar dimensions, compositions, and physical properties (See Fig. 1). This likely arises because of the partial removal of binder during SCE, which increases the porosity and permeability of the samples, which in turn facilities gas flow and thus mitigates the buildup of pressure and hence stress within the green body.

# Effect of SCE/TC versus TC on residual carbon

Table 3 summarizes the average percent weight loss for MLCs subjected to an SCE cycle alone, a combined SCE/TC cycle, or a TC alone. For MLCs with and without Ni, both types of samples experienced 29-30% weight loss during SCE at 90 °C, 30 MPa, for three 1 h cycles. After SCE/TC and TC alone, the samples lost up to 97-100% of the organic fraction, irrespective of sample type or prior processing conditions. The results above suggest that weight loss alone determined gravimetrically is insufficient to conclude which process is superior for binder removal.

To differentiate between the different processing routes, residual carbon analysis was conducted. Fig. 7 shows the %RC for the MLC samples with and without nickel electrodes. For both types of samples, the combined SCE/TC leads to 25-30% less carbon as compared to the TC alone.

**Table 3.** Average percent weight loss after SCE, after SCE/TC or after TC at the indicated maximum temperatures

Cycle Type (Maximum Temperature)	MLC With Ni Weight Loss (%)	MLC Without Ni Weight Loss (%)
SCE (90 °C)	29	30
SCE (90 °C)/TC (270 °C)	97	~100
TC (270 °C)	97	99



**Fig. 7.** Percent residual carbon with 90% confidence intervals for MLC samples with and without nickel electrodes subjected to SCE/TC and TC alone.

In addition, the use of SCE/TC leads to substantially less variability in the residual carbon content, as indicated by the 90% confidence intervals. Because of the overlap of confidence intervals in Fig. 7, the sample means were compared for equality using a 90% confidence interval, one-sided test. This test indicates that for the MLCs with and without nickel, the differences in the means are statistically significant, which indicates the SCE/TC process is effective in lowering the %RC as compared to the TC alone.

The origin of the lower %RC for SCE/TC as compared to the TC alone may be attributed to the fact that during the SCE step, the binder, namely the low molecular weight plasticizer component, is removed by dissolution into the supercritical fluid and then diffusion out of the body and not by thermal degradation. Thus, removing one-fourth to one-third of the binder by this process leads to less organic being present which can subsequently crack to carbonaceous residue during the TC. Alternatively, the removal of the plasticizer, with the resultant creation of porosity, may allow for more facile oxidation of the remaining organic fraction during the TC without concomitant carbon deposition.

# Conclusions

In this study, we have demonstrated that a combined supercritical extraction and thermal cycle can be used to remove binder from green MLCs, and this binder removal effects both cycle time and yield. Supercritical extraction of a fraction of the binder results in an increase in the gas permeability and a decrease in the adhesion strength of the MLCs. Following the SCE segment, the MLCs then survive a rapid TC that they did not survive without prior SCE, which indicates that the trade-off in the increase in gas permeability following SCE has a more pronounced effect than the reduction in adhesion strength. This rapid cycle is much shorter than typical cycles of 50-150 h used in industry for samples of similar size and physical properties. The yield of the MLCs was also seen to depend on other upstream processing variables such as the conditions of lamination, whereby increasing the lamination temperature leads to a large increase in the adhesion strength, which persists even following partial binder removal via SCE.

Finally, the combined SCE/TC also has an effect on the residual carbon content of MLCs. Utilization of the SCE/TC leads to 25-30% less carbon as compared to a TC alone and to much less sample-to-sample variation. This reduction in carbon content and variation was observed in MLCs prepared both with and without nickel electrodes.

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