# Binder removal studies in ceramic thick shapes made by laminated object manufacturing

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## Abstract

Binder removal was studied in a body of alumina made by Laminated Object Manufacturing (LOM) with polymethyl methacrylate as binder, benzyl butyl pthalate and polyethelene glycol as plasticisers and glyceryl trioleate as dispersant with an optimized solids loading of 58% by volume. The burnout of the organics from laminated cuboids of different thickness was carried out in nitrogen atmosphere at different temperatures between 200 and 300 °C. The variation of the organic content from the core to the surface was also determined by thermogravimetric analysis (TGA) and FTIR studies. The organic content of the body at a particular temperature exposed for a particular time was modeled based on the parameter, $S$ ($\propto D_{eff}/l^2$) where $D_{eff}$ is the effective diffusivity and $l$ is the diffusion path length. The variation of $S$ as a function of exposed surface area per unit volume of the cuboids is linear. Since the dependence of $S$ on temperature follows an Arrhenius behaviour, the value of S can be predicted at any temperature and for any exposed surface area per volume of the cuboids. Thus the model can be used to estimate the organic content of the body exposed for a certain duration at a particular temperature.
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## 1. Introduction

Solid Freeform Fabrication (SFF), is an effective approach to directly build 3D components without molding, hard tooling and much human intervention.[1] This approach has several advantages over the traditional processing routes in terms of design flexibility and direct fabrication of complex geometries to net shape.[1] Laminated Object Manufacturing (LOM) is a technique used to make functional components directly by cutting 2D sheets of materials using laser in CAD defined contours and by laminating the layers to obtain the 3D shape.[2] LOM using ceramic/metal tapes as feed materials is currently employed to make complex 3D ceramic functional components. Tape casting is a binder assisted forming technique that requires the addition of high volume percentage of organics prior to shape forming.[3]

Different kinds of organics are present as binders, plasticisers, and dispersants in the dried ceramic tapes. These organic content ranges from 35 to 60% by volume and needs to be removed prior to densification. For the defect free manufacturing of complicated shapes, the removal of such a substantial volume of organic processing aids from the body is a very critical step.[4–9] Some studies on the theoretical modeling of binder removal from single tape cast layers and injection molded bodies have been reported.[10,11] While there are several studies on debinding, very few studies have been done on the experiments and theoretical modeling of binder removal from thick ceramic shapes made by techniques like SFF.

Polymethyl methacrylate (PMMA) based ceramic tapes have not been reported as being used as feed materials for LOM. However, polyvinyl butyral based ceramic tapes have been used for making feed materials for LOM using a non-aqueous based solvent system. A variety of ceramic bodies of PZT, alumina, silicon nitride, silicon carbide have been made using this system.[13]

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The objective of this study is to investigate the removal of organics as a function of atmosphere, time, temperature and shape of the object. Thermogravimetry was used to obtain the experimental data and a model based on diffusion was proposed to satisfactorily explain the experimental data.

## 2. Experimental

Tapes of alumina made by the doctor blade technique were used as feed material for LOM. The system consists of alumina powder (ACC A16 grade, particle size: 0.6 μ, surface area: 8–10 m$^2$/g), polymethyl methacrylate (PMMA) as binder, benzyl butyl pthalate (BBP) and polyethelene glycol (PEG) as plasticisers and glyceryl trioleate (GTO) as dispersant, of composition reported in Table 1. A nonaqueous solvent system of an azeotropic mix of toluene and butanol (22:8 by volume) was used for casting. The solids loading was optimised to 58% by volume.[12] Flexible tapes of alumina with a thickness of 0.5–0.55 mm were obtained after drying.

Tape cast single layers and the pure organic constituents were subjected to thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in nitrogen and air with a simultaneous TGA/DTA analyser (PL-STA, Polymer Laboratories Inc.). Cuboids of dif-

ferent thicknesses of 24, 15 and 6 mm with the same cross sections of 8×8 mm$^2$ were made using previously optimised lamination conditions at a pressure of 3.0 kg/cm$^2$ and temperature of 90 °C with solvent spray in between laminates.[12]

Samples were heated to 200, 250 and 300 °C with a heating rate of 10 °C per minute and soaked for different durations of 0.5, 1, 1.5 and 2 h in flowing nitrogen in a tubular furnace. The weight loss was determined gravimetrically. Gravimetric weights were taken instantaneously at the set temperature and corresponding weights were taken at different soaking times.

Fig. 1a depicts the cuboids used in our experiments. The length (*l*) and width (*w*) of the cuboid was chosen as 8 mm for all the samples and the thickness (*d*) was varied from 6 to 24 mm. Sections from the centre of the laminated cuboid were cut as shown in Fig. 1b and strips were then cut from the core to the surface. FTIR studies were conducted on a pellet containing powder of green ceramic tape with organic mixed with KBr.

## 3. Results and discussion

### 3.1. Degradation of pure organics and single tapes

The degradation behaviour of the pure organics in air and nitrogen atmosphere showed an exothermic behaviour in air and an endothermic behaviour in inert atmosphere. This is in agreement with the reported degradation behaviour of PMMA in both atmospheres.[14] The degradation temperature range of the pure organics was obtained in nitrogen atmosphere and is shown in Table 2.

The DTA data (Fig. 2) of single tapes in both nitrogen and air atmosphere showed oxidative and exothermic removal in ambient atmosphere. This can lead to localized heating in a thick body and defects like hot spots,

Table 1
The proportions of different constituents

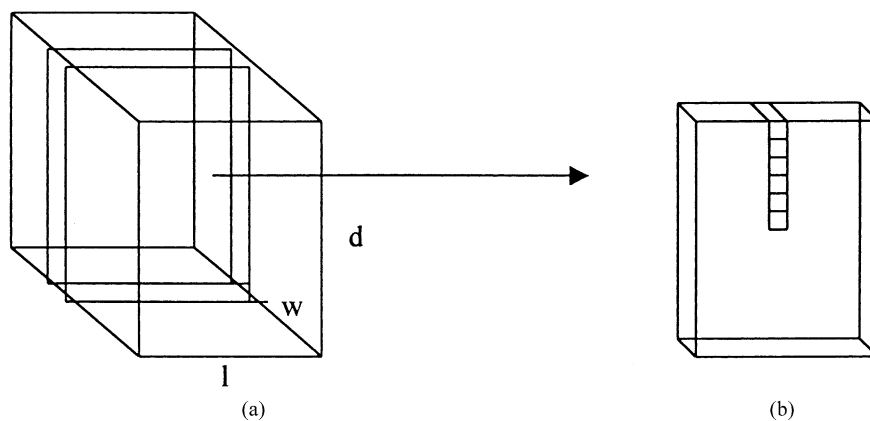| Constituents | Materials | Volume% |
|---|---|---|
| Ceramic Powder | Alumina | 29.52 |
| Solvent | Butanol–toluene mix | 49.14 |
| Binder | Polymethyl methacrylate | 9.08 |
| Plasticiser I | Polyethylene glycol | 3.50 |
| Plasticiser II | Benzyl butyl pthalate | 5.26 |
| Dispersant | Glycerol trioleate | 3.50 |



Fig. 1. Schematic of the laminated body from which samples for TGA and FTIR study were obtained: (a) The first section perpendicular to lamination direction; (b) the second section from which the samples in the form of strips were obtained.

Table 2
Degradation temperature range for the organics in nitrogen

| Organics | Degradation Temp Range, °C |
|----------|----------------------------|
| PMMA | 250–405 |
| BBP | 208–340 |
| PEG | 165–270 |
| GTO | 170–420 |
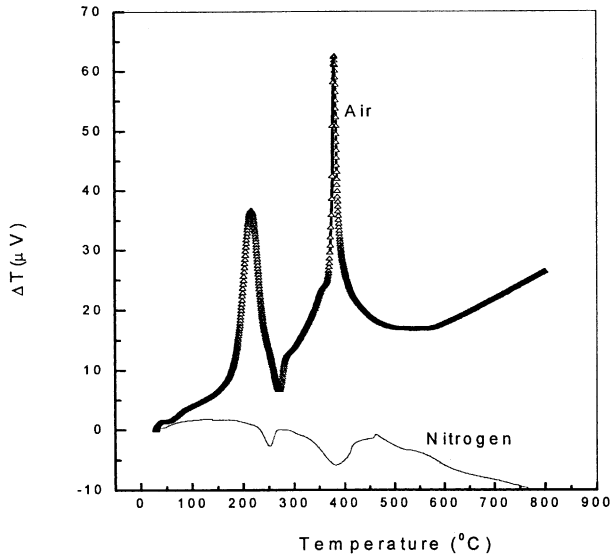


Fig. 2. DTA plot of single tapes in air and nitrogen atmosphere.



Fig. 3. TGA plot of single tape in nitrogen atmosphere (a) and the corresponding derivative plot (b).

delamination or anisotropic shrinkage. Nitrogen was therefore chosen as the removal atmosphere.

### 3.2. Multistage binder removal

The TGA plot and the derivative plot of single tapes and the derivative plot (Fig. 3) in nitrogen atmosphere showed a two step removal. The initial removal of lower molecular weight components was by diffusion through the liquid non-volatile polymer matrix and the higher temperature removal corresponds to that of the higher non-volatile component. Based on the degradation temperature range of the individual organics, it can be inferred that the initial removal corresponds to PEG, BBP, GTO while the later removal is due to PMMA.

### 3.3. Depth profile of organics during removal

The TGA data of strips cut from one central section of the laminated body as shown in Fig. 1 from the core to the surface showed differential content of organics. Fig. 4 indicates organic removal for samples of thickness (*d*) 15 and 24 mm heated to 250 °C. The data shows higher organic content near the core than near the surface. The rate of organic decrease is much higher near the core than near the surface. This behaviour is different
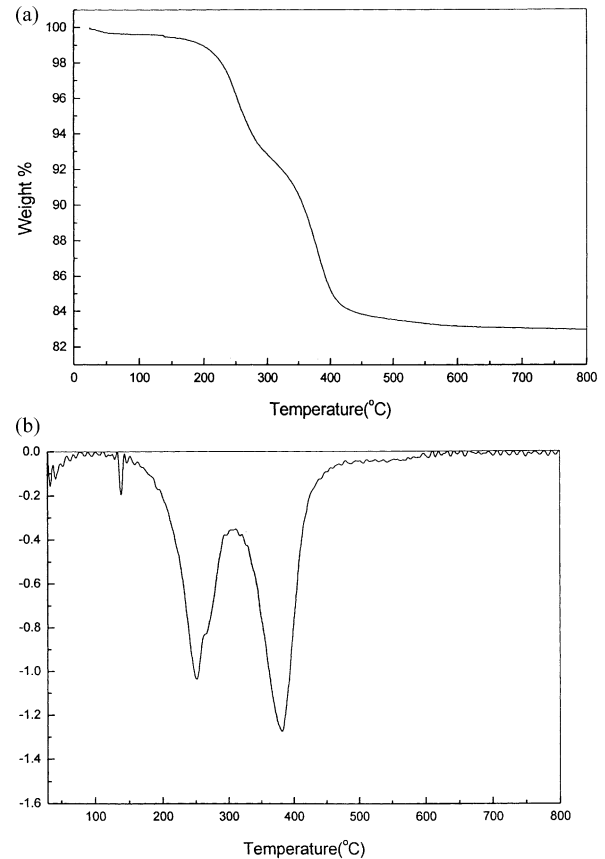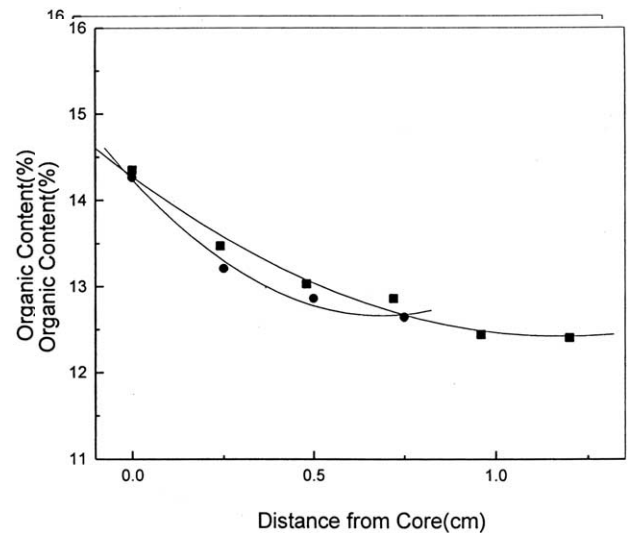


Fig. 4. Variation of the organic content (%) from core to surface for samples with $d = 24$ mm (■) and 15 mm (●) at 250 °C.

from that predicted by a theoretical model of removal of monocomponent binder system from a single tape cast sheet.[10] This might be because of the multi-component binder system or due to other parameters influencing the volatilization.

The FTIR data (Fig. 5) shows at 250 °C for a 15 mm length sample shows the relative peak intensities at 1730 cm$^{-1}$ (corresponding to C=O stretching) decreasing from the core to the surface. However, no quantitative conclusions can be made from the FTIR data but this data verifies the observations in Fig. 4.

### 3.4. Modeling of binder removal

The removal kinetics of the organics in the body was measured by the gravimetric weights taken at initial and at different soaking durations for different isothermals. The ratio of the instantaneous and initial weights as a function of time at 250 °C is shown in Fig. 6a. The debinding kinetics is assumed to be diffusion controlled for this system and the weight loss plot (Fig. 6a) at a fixed temperature obeys the equation[11]

$$\frac{M_t}{M_0} = \frac{8}{\pi^2} \sum_0^\infty \frac{1}{(2n+1)^2} \exp\left[-(2n+1)^2 \frac{\pi^2}{4} \frac{D_{eff}}{l^2} t\right] \quad (1)$$

where $M_0$, $M_t$ refer to the initial weight and at time $t$, respectively. In Eq. (1) $l$ is the diffusion length through a slab and $t$ is the debinding time. This equation is the solution for the one dimensional diffusion through a slab of a finite thickness. Only the first term ($n=0$) of Eq. (1) is used for data evaluation, as the succeeding terms in the series expansion become very small.[11] Thus Eq. (1) can be written as

$$\frac{M_t}{M_0} = \frac{8}{\pi^2} \exp\left(-\frac{\pi^2}{4} \frac{D_{eff}}{l^2} t\right) \quad (2)$$

Eq. (2) was used by Angermann and Vander Biest[11] to determine the degradation behaviour of a binder system using low density polyethylene (LDPE) from cylindrical injection molded bodies.

$D_{eff}$ is the effective diffusivity of the organics in the system and is given by

$$D_{eff} = D\frac{\varepsilon}{\tau} \quad (3)$$

$D$ denotes the diffusivity of the organics in the system, $\varepsilon$ is the porosity of the laminated body (i.e. volume content of the organics in the body) and $\tau$ is the tortuosity of the diffusion path (ratio of the length of the diffusion path with and without powder particles).[4,11] Fig. 6b shows the logarithmic plot of $M_t/M_0$ as a function of time for different thickness ($d$) samples. The slopes of the respective plots correspond to $S$ ($=\pi^2 D_{eff}/4l^2$).

The removal of the organic is assumed to be from all the surfaces of the cuboid excepting the surface resting on the floor of the furnace. As the binder removal depends mainly on the exposed surface of the sample, the variation of $S$ with the exposed surface per unit volume (A/V) was plotted at different temperatures and is shown in Fig. 7. The surface of the cuboid resting on the floor of the furnace (corresponding to 8×8 mm$^2$) was assumed not to contribute to any binder loss and was not used to evaluate the exposed area of the sample As it can be reasonably assumed that $D_{eff}$ is independent of thickness at a given temperature,[10] the increase of $S$ at a particular temperature with A/V can be attributed to the decrease of the diffusion
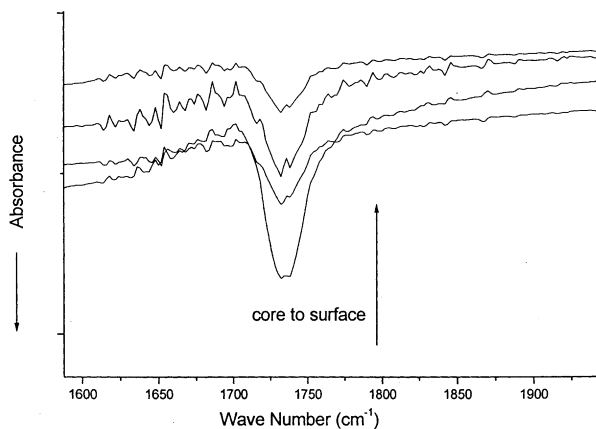


Fig. 5. FTIR data showing relative changes in peak intensity at 1730 cm$^{-1}$ corresponding to C=O stretching from core (bottom curve) to surface (uppermost curve) for a sample heated to 250 °C with $d=15$ mm.
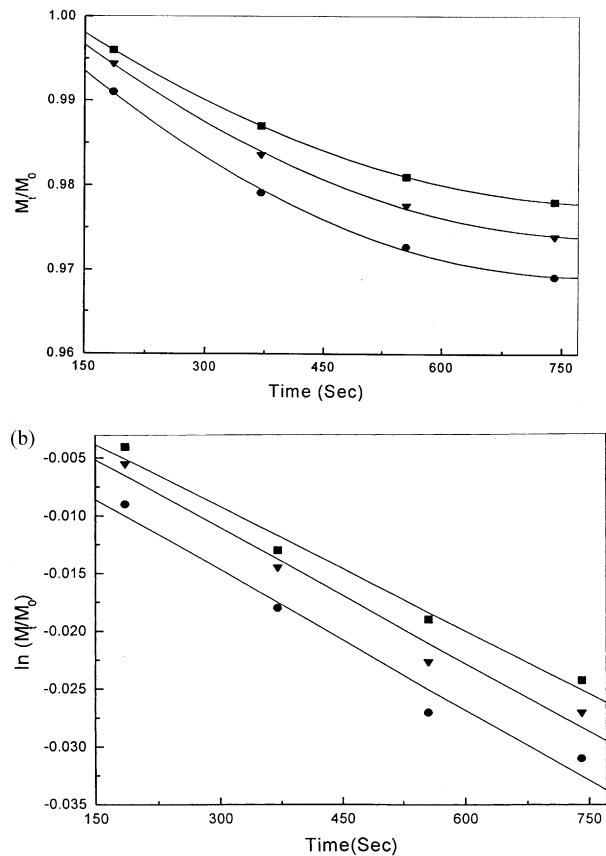


Fig. 6. (a) Variation of $M_t/M_0$ with time for samples with $d=6$(●), 15 (▼), 24 (■) mm heated to 250 °C (b) corresponding logarithmic plot.
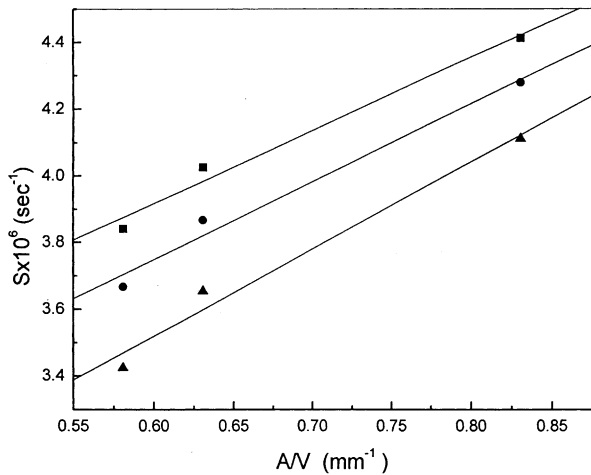
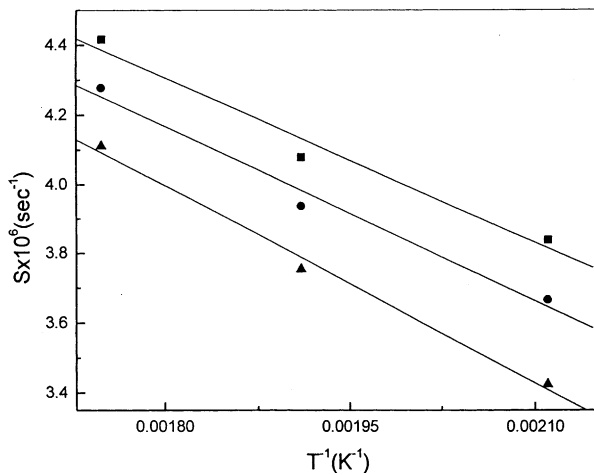Fig. 7. Variation of S with the exposed surface area per unit volume (A/V) at T = 200 (▲), 250 (●), 300 (■)°C.



Fig. 8. Arrhenius plot of S with temperature for samples with d = 6 (□), 15 (●), 24 (▲) mm.

path length *l*. The increase of S with increasing A/V may be due to the decrease in average distance between two pores as postulated by Angermann and Van Der Biest.[11]

The Arrhenius plot of S with temperature for samples with different d is linear and is shown in Fig. 8. Thus S can be predicted for any temperature for a particular A/V of the cuboids. For example, if one is interested in determining the value of $M_t$ at any given temperature and time for a fixed A/V, then one can determine S from Fig. 8 and using this value of S, the ratio of $M_t/M_0$ can be determined using Eq. (2). Thus this model can be used to predict the organic content of a cuboidal body exposed for a certain time at a particular temperature.

## 4. Summary and conclusion

The binder removal studies were carried out in a LOM made body of alumina ceramics. TGA and

FTIR were used to study the binder removal from laminated cuboids. The degradation behaviour of the pure organics was studied. The binder removal atmosphere was selected based on the endothermic behaviour of the degradation behaviour of single tapes in nitrogen atmosphere. The depth profile of the organics in the laminated sample was determined and the gravimetric weight change of the cuboidal samples was fitted to a model based on diffusion.

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