

## Characterization techniques to predict mechanical behaviour of green ceramic bodies fabricated by ceramic microstereolithography

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**Abstract.** Ceramic microstereolithography (CMSL) has emerged as solid free form (SFF) fabrication technology in which complex ceramic parts are fabricated from ceramic suspensions which are formulated by dispersing ceramic particles in UV curable resins. Ceramic parts are fabricated by exposing ceramic suspension to computer controlled UV light which polymerizes resin to polymer and this polymer forms rigid network around ceramic particles. A 3-dimensional part is created by piling cured layers one over the other. These ceramic parts are used to build microelectromechanical (MEMS) devices after thermal treatment. In many cases green ceramic parts can be directly utilized to build MEMS devices. Hence characterization of these parts is essential in terms of their mechanical behaviour prior to their use in MEMS devices. Mechanical behaviour of these green ceramic parts depends on cross link density which in turn depends on chemical structure of monomer, concentrations of photoinitiator and UV energy dose. Mechanical behaviour can be determined with the aid of nanoindentation. And extent of crosslinking can be verified with the aid of DSC. FTIR characterization is used to analyse (-C=C-) double bond conversion. This paper explains characterization tools to predict the mechanical behaviour of green ceramic bodies fabricated in CMSL

### 1. Introduction

Ceramics known for their excellent thermal and mechanical properties which metals and polymers do not possess [1]. Many techniques have been developed for near net shaping of ceramics. Slip casting is one of the most attractive routes to fabricate ceramic parts by consolidating colloidal suspension in mould. Ceramic injection molding is another attractive technique to fabricate ceramic parts, however the cost moulds and operational cost is justified only when parts are produced in mass

Ceramic microstereolithography (CMSL) has recently emerged as solid free form fabrication of ceramics [2]. It has gained a lot of attention of science community across the world due to its capability to fabricate high aspect ratio ceramic structures with fine resolution. Ceramic parts are built in CMSL by curing UV curable ceramic suspensions and piling these cured layer one over the other. This technique can be used to fabricate millimetre and sub-millimetre ceramic parts for



microelectromechanical (MEMS) devices without using moulds [3]. This technique uses highly loaded ceramic suspension, obtained by dispersing ceramic particles in photo-curable resins. This technique can be considered as versatile as any ceramic parts can be fabricated as long as ceramic particles are dispersed with photo-curable resin.

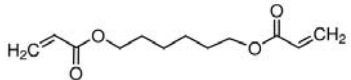
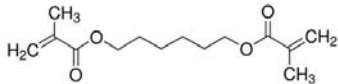
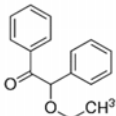
In order to formulate stable ceramic suspension for CMSL, study of colloidal chemistry is must as it influences curing behaviour under the exposure of UV light [4]. Various characterization techniques have been proposed for characterizing ceramic suspensions in terms of UV reactivity and flow behaviour. Flow behaviour is usually predicted by steady state rheology and that of suspension microstructure by dynamic rheology [5, 6]. In addition to this, UV reactivity of suspension is predicted either by photo DSC or real-time FTIR. However characterization techniques for as fabricated green ceramic parts is not yet extensively studied. This study is essential as sometimes as fabricated ceramic parts can be directly incorporated in MEMS [7, 8]. In such cases prediction of green ceramic strength is must. This paper describes characterization of green ceramic bodies in terms of their mechanical behaviour and cross link density. The ceramic parts were fabricated from ceramic suspension formulated in bifunctional acrylate and methacrylate resins.

## 2. Materials and methods

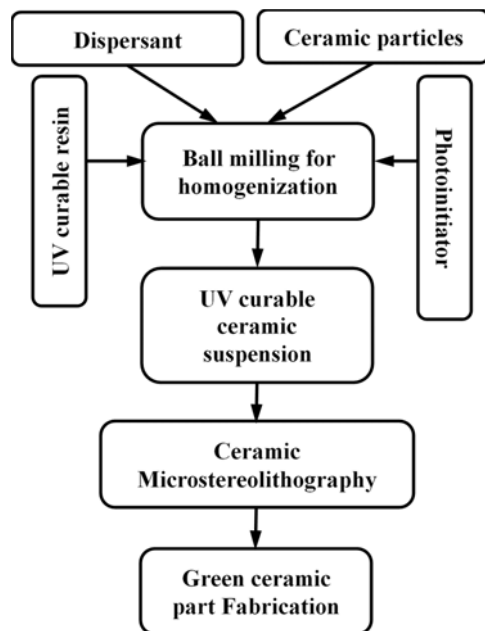
### 2.1 Materials

Table 1 shows molecular structure and physical properties bifunctional monomers and photoinitiator used in the present study. Both 1, 6 hexanediol diacrylate (HDDA) and 1, 6 hexanediol dimethacrylate (HDDMA) are bifunctional UV curable monomers with only difference is that  $-\text{CH}_3-$  group attached to both ends of HDDMA molecule. It is to be noted here that acrylate resins are more hazardous as compared to methacrylates. Benzoin ethyl ether was selected as photoinitiator. The selection of photoinitiator is based on its solubility in resins and its UV absorption characteristics. Refractive indices of both HDDA and HDDMA remains same as per manufacturer's specification and both of these absorb UV light in same range. Sub-micron alumina is chosen as ceramic material (Almatis CT3000, density-  $3.9\text{g/cm}^3$ ) whose average particle size ( $d_{50}$ ) is 0.5micron and surface area of  $6.2\text{m}^2/\text{g}$  as measured from BET.

**Table 1.** Properties and molecular structures of monomers and photoinitiators

Monomers	Monomer structure	Refractive index	Density (g/l)	Molecular weight (g/mol)
1, 6 Hexanediol diacrylate		1.45	1.01	226.27
1,6 Hexanediol dimethacrylate		1.45	0.982	254.0
Benzoin Ethyl ether (BEE)		1.57	1.101	240.30

## 2.2 Formulation of ceramic suspension



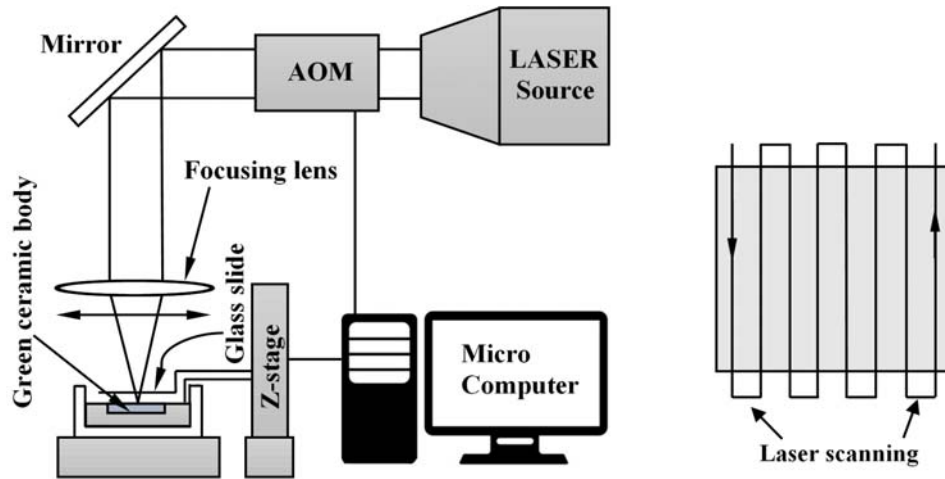
**Figure 1.** Flow chart showing ceramic suspension formulation and fabrication of green ceramic part

Ceramic suspensions is formulated as explained below. 10 ml of HDDA is taken in polypropylene bottle of 30ml capacity. 4 wt. % of BEE is added with respect to weight of powder and 2.5 wt. % of phosphate ester was added to improve solid loading. Now alumina powder was added incrementally till solid volume fraction reaches 0.40. The suspension is continuously pot milled using ceria stabilized zirconia balls (1:1 with respect weight of alumina powder) of mean diameter 2~3 mm for about 24 hours to get stable alumina suspension. The same procedure is repeated to formulate alumina suspension in HDDMA as well. The flowchart in figure 1 shows the general procedure followed to formulate ceramic suspensions in photocurable monomers for microstereolithography applications.

## 2.3 Experimental setup and fabrication of green ceramic part

Figure 2 (a) shows schematic of scanning based CMSL. A tightly focused Gaussian laser beam scans ceramic suspension with a speed of 1mm/sec. This CMSL is equipped with UV laser source (COBOLT Zouk) of maximum power of 20mW at 355nm. The exposure energy can be varied with the help of Accausto optical modulator (AOM) and neutral density filters. Power at resin surface was measured by power meter (OPHIR PD-300UV) equipped with silicon photodiode. Focal length of the Gaussian beam is adjusted such that it is focused at the interface of suspension and glass using Snell's law. Gaussian beam diameter was about 6 microns which is calculated based on wavelength of laser and size of lens. Mirrors are mounted on flexural mechanism driven by voice coils in order to achieve uniform spot characteristics over entire range of scanning [9]. The Z-stage carries a removable transparent glass slide which facilitate the focused laser beam to scan the ceramic suspension.

Stabilized ceramic suspension was placed in small glass tank. Many square shapes of size 2mmX2mm were fabricated for characterization at different energy doses. Figure 2 (b) shows Gaussian beam scanning pattern. The distance between successive scan lines was maintained at 6 microns. After fabrication ceramic part remained attached to the glass slide. The glass slide washed with acetone repeatedly so as to remove any uncured ceramic suspension from the cured part. The parts are dried at room temperature. As many as ten parts are fabricated at different energy doses for characterization.



**Figure 2. (a) Schematic of scanning based CMSL (b) Scanning pattern for fabrication**

### 3. Results and discussion

The parts fabricated from CMSL are essentially UV cured polymer-ceramic composites. Therefore characterization tools which are used for measuring mechanical properties of protective coatings are also applicable to parts fabricated in CMSL. Few known characterization techniques to measure mechanical properties are nano indentation, scratch test and dynamic mechanical thermal analysis etc.

#### 3.1 Mechanical behaviour with aid of nanoindentation

The mechanical properties of cured ceramic -UV curable resin composite are far better than that of cured neat resins possibly due to interfacial phenomena [10] UV curable resins generally imparts flexibility and ceramic particles provide greater hardness and impact strength [11] Another influencing parameter is compatibility of chemically modified particle surface with dispersion medium which not only helps to improve solid loading by reducing viscosity but also helps to improve mechanical properties of composites [12, 13]. Never the less size of particles, distribution of particles in reactive medium plays a major role in deciding mechanical properties of ceramic-resin composite.

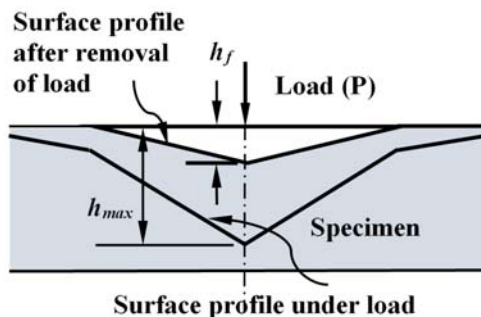
Green ceramic parts were fabricated at same power scales for both HDDA and HDDMA based suspension and at same scanning speed of laser beam. (1mm/s). Energy delivered ' $E$ ' at the resin surface is calculated using the formula.

$$E = \sqrt{\frac{2}{\pi}} \frac{P}{w_0 v_s} \dots\dots\dots (1)$$

Where ' $P$ ' is the UV power, ' $w_0$ ' is beam size ' $v_s$ ' is scanning speed. The following table shows power measured, exposure energy for HDDA and HDDMA based suspension. It is to be noted that exposure energy remains same for both HDDA and HDDMA based suspension as scanning speed and power scales have same values as per equation 1. The power levels and UV energy calculated at the resin surface are mentioned in table 2. HDDA\_ALU represents ceramic part fabricated from HDDA based suspension and HDDMA\_ALU represents ceramic part fabricated from HDDMA based suspension respectively.

**Table 2.** Exposure energy at suspension surface

Notation	Scanning speed (mm/sec)	Power (μW)	Energy on resin surface (mJ/cm <sup>2</sup> )
HDDA-ALU	1	64	851.1
HDDMA-ALU	1	64	851.1



**Figure 3.** Schematic of nanoindentation [14]

The mechanical behaviour of these green ceramic bodies can be characterized using nanoindentation. This characterization technique was proposed by W. C. Oliver et al to measure hardness, elastic modulus of material [14]. Figure 3 shows schematic of nanoindentation technique in which a maximum displacement ( $h_{max}$ ) that occurs when material is indented with a conical shaped indenter and permanent deformation ( $h_f$ ) that is left when the load ( $P$ ) is removed. There exist a non-linear behaviour between displacement and load [15, 16]. Based on this assumption the elastic modulus can be calculated using following complex modulus equation.

$$\frac{1}{E_r} = \frac{1-\nu_s^2}{E_s} + \frac{1-\nu_i^2}{E_i} \dots\dots\dots (2)$$

' $S$ ' is stiffness (slope of unloading curve) and determined experimentally as

$$S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A} \dots\dots\dots (3)$$

' $E_r$ ' is reduced elastic modulus ' $E_s$ ' and ' $E_i$ ' are elastic moduli of sample and indenter materials respectively. ' $A$ ' is the projected area of elastic contact. ' $\nu_s$ ' and ' $\nu_i$ ' are Poisson's ratio for sample and indenter materials respectively.

In the present experiment the maximum load ( $P$ ) was restricted to 300μN. As many as 10 indents were made on ceramic part at different locations to obtain consistent results. Following table shows reduced elastic modulus and stiffness values of parts. The values shown in the table 3 are average of 10 readings.

**Table 3.** Stiffness and reduced elastic modulus values of green ceramic parts

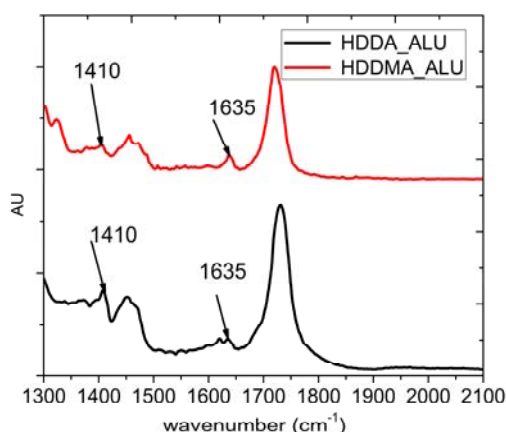
	S(μN/nm)	E <sub>r</sub> (GPa)
HDDA-ALU	10.67	4.20
HDDMA-ALU	12.74	4.73

As revealed from table 3 both stiffness and reduced elastic modulus for green ceramic parts fabricated from HDDMA suspension are greater than those fabricated from HDDA suspension under same exposure energy. Hence for the same energy dose mechanical behaviour of ceramic part fabricated from HDDMA based suspension is better over the ceramic part fabricated from HDDA based suspension. It appears that higher cross link density in HDDMA based ceramic part over that of HDDA based ceramic part contributing in improving mechanical behaviour for the same energy dose. However the extent of cross linking in HDDA and HDDMA based ceramic parts cannot be decided by this technique.

### 3.2 Glass transition temperature and double bond conversion

In order to ascertain the results obtained from nanoindentation green ceramic parts were analysed in DSC for their glass transition temperature. Glass transition temperature can be used as an indicative of extent of cross link density and at this temperature cross linked polymer (under UV exposure) transforms

from glassy material to rubber like [17, 18]. The green ceramic parts of both HDDA and HDDMA were heated at 10°C/min up to 500°C in air. It is obvious that the green ceramic part which has high cross-link density should give rise high glass transition temperature [19]. However as revealed from table 4 glass transition temperature of ceramic part fabricated from HDDMA suspension showed (277°C) as compared to glass transition temperature of ceramic parts fabricated from HDDA suspension (332°C).



**Figure 4.** FTIR spectra of green ceramic parts

These ceramic parts were further analysed in conventional FTIR using KBr as reference for their double bond conversion. Figure 4 shows FTIR spectra of green ceramic parts fabricated from HDDA and HDDMA suspensions. If the cross link density of HDDMA green ceramic parts is high then it should show higher double bond conversion. However at the energy dose used for curing the intensity of peaks at 1635 cm<sup>-1</sup> and 1410 cm<sup>-1</sup> for part fabricated from HDDMA based suspension is higher as compared to part fabricated from HDDA based suspension. This indicates lower double bond conversion for part fabricated from HDDMA suspension. Table 4 shows double bond conversion of cured part fabricated from HDDA and HDDMA formulations which are

calculated using equation 4. It is to be noted here that double conversion estimates the cross link density. Here intensity of peaks at 1635cm<sup>-1</sup> and 1410cm<sup>-1</sup> were recorded and intensity of peak at 1720cm<sup>-1</sup> was taken as reference. Subscript '0' stands for intensity of peak of uncured suspension and 't' indicates intensity of peaks of cured ceramic parts at specified energy doses [20]

$$\% \text{ Conversion} = \frac{\left( \frac{A_{1635} + A_{1410}}{A_{1720}} \right)_0 - \left( \frac{A_{1635} + A_{1410}}{A_{1720}} \right)_t}{\left( \frac{A_{1635} + A_{1410}}{A_{1720}} \right)_0} \dots\dots\dots (4)$$

**Table 4.** % double bond conversion and glass transition temperature of green ceramic parts

	% double bond conversion	Glass transition temperature (T <sub>g</sub> )
HDDA-ALU	67 %	332°C
HDDMA-ALU	58 %	277°C

Hence there is lower double bond conversion for ceramic parts fabricated from HDDMA suspension than that of HDDA suspension. Obviously curing behaviour of HDDA and HDDMA alumina suspension must be different at same energy dose. The curing mode or curing protocol has influenced on double bond conversion. It is known that methacrylates are less reactive than acrylates. Hence curing behaviour of both suspensions will be different though same energy dose is utilised to cure. And though double bond conversion is directly related to cross link density it alone does not give complete characterization of photocured cross linked polymer-composite as same double bond conversion may produce different extent of cross linking [21].

#### 4. Conclusion

Curing behaviour of HDDA and HDDMA based ceramic suspension found to be different as acrylates are more reactive than methacrylates at same energy dose. Nanoindentation results showed mechanical behaviour of green ceramic parts fabricated from methacrylate suspension better than those fabricated from acrylate suspensions. However further investigations by DSC and FTIR revealed that



nanoindentation alone cannot be used as characterization technique to predict mechanical behaviour of green ceramic parts. Also glass transition temperature as determined from DSC alone is not indicative of cross link density as same double bond conversion may produce different extent of cross linking.

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