Optimization of Curing Behavior of Si$_3$N$_4$ UV Resin for Photopolymerization 3D Printing

Chuanru Cao$^1$, Cao Wang*$^1$, Zhe Zhao$^{1,2}$

$^1$ School of Materials Science and Engineering, Shanghai Institute of Technology, Shanghai, 201418, China

$^2$ Department of Materials Science and Engineering, KTH Royal Institute of Technology, Stockholm SE-100 44, Sweden

* wangcaoc@gmail.com (W.Cao); $^2$ zhezhao@kth.se (Z. Zhao)

Abstract: Silicon nitride (Si$_3$N$_4$) ceramics are widely used in mechanical and thermal management applications due to their excellent properties. To overcome the difficulties in traditional Si$_3$N$_4$ ceramic forming techniques, it is interesting to see the possibility of making complex-shaped silicon nitride ceramic component with novel 3D printing methods. In this study, we aim to study the effect of photo-initiators on the curing behavior of pre-formulated Si$_3$N$_4$ ceramic UV resin suspension. To elucidate the potential multi-factor interactions, a statistic experiment design was implemented in a sequence of screening and optimization by using Modde software. It was found that the kinds of photo-initiators, total amount of initiators and the mixture ratio between initiators have a great influence on the curing properties of silicon nitride UV ceramic resin. Based on these results, a formula was selected based on the criterion of using least amount photo-initiator while reaching the highest curing thickness.

1. Introduction

Silicon nitride is one of the most promising functional ceramics with excellent high temperature resistance, thermal stability and thermal shock resistance[1-2]. Recently, the development of material adding manufacturing technology provides a fast and convenient technical method for manufacturing complex shapes and high precision ceramics[3-5]. In the fabrication of ceramic complex devices, DLP is a promising material addition manufacturing technology[6-7]. Through the projection of ultraviolet light onto the ceramic suspension, the ceramic suspension can be quickly polymerized and solidified, and then a layer of green body can be made. Up to now, most of the works have been focused on oxide ceramics, but very few works have been reported on no-oxide ceramics by DLP method, such as Si$_3$N$_4$[8-13]. The main problem is that silicon nitride powder has large absorbance and refractive index, and the refractive index of silicon nitride powder is also very different from that of resin. Therefore, when silicon nitride ceramics are fabricated via DLP method, its curing depth is low[14]. So the molding of silicon nitride ceramics is difficult. The curing effect of ceramic suspension is the key factor to affect the manufacturing technology. Photopolymerizable suspensions have been used in dental resins[15], patterned substrates[16] and ceramic additive manufacturing[17].

The suspension of photopolymerization is composed of ceramic particles dispersed in liquid monomer. Photoinitiator (PIs), as a photoactive substance, initiated polymerization under light. The polymerization behavior is influenced by the kinds of photoinitiators, the concentration of
photoinitiator. This behavior can be modified by an inert dye that absorbs photons without producing free radicals and does not produce inhibitors that destroy free radicals. UV scattering also affects photopolymerization due to the refractive index comparison between ceramic particles and monomers. Once the photopolymer is polymerized, a through-pore matrix is formed around the ceramic particles and condensed onto the green flake material[18]. UV curing process has great advantages, can eliminate evaporation, avoid high shrinkage and cracking risk. Selecting the appropriate photoinitiator to induce monomer to produce better polymerization, so as to increase the curing depth of silicon nitride, this is an urgent problem for us to solve.

In this work, the purpose of this study is to investigate the effect of initiators on the curing effect of silicon nitride ceramics on the basis of UV curing. In this respect, to elucidate the potential multi-factor interactions, a statistic experiment design was implemented in a sequence of screening and optimization by using Modde software, the effects of photoinitiators, total amount and ratio on curing depth will be studied.

2. Experimental procedure

2.1. Materials
The Si₃N₄ powder used in this study is silicon nitride(purity > 99.9%, Zhejiang Province jiaxing Ceram Plus Tech. Ltd., China). The resin used contains one functional group, two functional groups and three functional groups(Zhejiang Province jiaxing Ceram Plus Tech. Ltd., China), respectively, as the major UV curable monomer system. CPM-D-13 (Zhejiang Province jiaxing Ceram Plus Tech. Ltd., China) was selected as dispersant to modify silicon nitride. 2-isopropylthioxanthone (ITX, Chengdu sicheng guandian materials. Ltd., China), 1-hydroxycyclohexyl phenyl ketone (184, Chengdu sicheng guandian materials. Ltd., China), 2-methyl-1-(4-methyl-Phenyl)-2-morpholin-1-propanone (907, Chengdu sicheng guandian materials. Ltd., China), 2,4,6-trimethyl-1-benzoyldiphenylphosphineoxide (TPO, Sinopharm Chemical Reagent Co., Ltd., China); (2-Benzyl-2-dimethylamino-1)-4-morpholinphenyl butanone (369, Chengdu sicheng guandian materials. Ltd., China) was used in this study as photo-initiator. The ceramic suspension with the same composition was prepared and solidified under the UV light of 405nm.

2.2. Method
Before the preparation of the silicon nitride ceramic suspension, the silicon nitride powder was firstly modified by added dispersant, and the content is 3wt% of silicon nitride powder. UV curable ceramic suspensions were prepared by adding modified powder into mixed resin monomer. After ball milling for 2h with a speed of 200 rpm. The addition of ceramic particles in a photocurable system greatly influences the polymerization of the resin which is then limited by two physical phenomena, namely the absorption and the scattering due to ceramic particles [19]. The absorbance of silicon nitride ceramic suspension was measured by UV spectrophotometer. Figure 1 shows the absorption spectra of the prepared silicon nitride in the range 200–800nm. It can be seen that silicon nitride has almost all absorption in the whole wavelength range. Among them, the absorbance of silicon nitride is the largest at 200nm, and it decreases rapidly in the wavelength range of 200-300nm. The absorbance of silicon nitride decreases slowly in the wavelength from 300 to 800nm, while at the wavelength of 800nm, the absorbance of silicon nitride is still about 0.75.

According to the different reaction mechanism of each photoinitiator, based on UV curing system, five kinds of ITX, 184, 907, TPO, 369 initiators were selected, and the content is 3wt% of silicon nitride powder, the Modde software was used to screen and optimize the system. By entering the range of initiator content that it need to add, setting the relevant factors, then the software automatically filters and optimizes, and the statistical experiment design was carried out. Eighteen groups of photoinitiators with different proportions were obtained, the Si₃N₄ slurry was prepared according to the results of the software. Photopolymerization experiments were carried out on the prepared silicon nitride ceramic suspension, the slurry was put into the UV curing box at 405nm for 30s. To access the curing ability of
different ceramics under the UV light, the curing thickness was measured by using a Absolute origin
electronic digital display caliper (Guiling guanglu digital measurement and control Co., Ltd., China)
after erasing the uncured slurry carefully. The measured curing results were input into Modde software.
The relationship between the five initiators and the curing behavior of silicon nitride slurry was
obtained by internal analysis of the software, and the most effective combination of photoinitiators
was selected.

![Figure 1. Light absorption spectra of the Si$_3$N$_4$ sample prepared.](image)

3. Results and discussion
Based on a mixture design model provided with Modde software, the ratio between five different
photoinitiators, namely TPO,369,184,907 and ITX, was adjusted in order to screening the most
effective photoinitiators for silicon nitride UV resins to be cured efficiently. Different combinations of
five photoinitiators were obtained by Modde software. To find the optimal ratio of the five
photoinitiators, different curing thicknesses were obtained by testing. The Si$_3$N$_4$ slurry was exposed
for 30 seconds under UV light with wavelength of 405nm, the curing thicknesses results are shown in
Table 1. When the composition of TPO,369,184,907,ITX is 0.1, 0.1, 0.1, 0.6, 0.1 and 0.225, 0.225,
0.225,0.225, 0.1, respectively, the curing thickness is the largest and the curing thickness is 70μm.
When the composition of the five initiators is 0.1, 0.1, 0.1, 0.1, 0.6, the curing thickness is the smallest
and the curing thickness is 40μm. The results were inputted into Modde software. After optimization
and screening, statistical experiments showed that photoinitiators 184,369 and TPO had little effect on
the curing effect of silicon nitride slurry, while initiators 907 and ITX had great influence on the
curing effect of silicon nitride slurry. The analysis of Modde software shows that the effect of initiator
907 on the curing of silicon nitride slurry is positive correlation, and the effect of initiator ITX on the
curing of silicon nitride slurry is negatively correlated, as shown in Figure 2. To be noticed, the positive
correlation for 907 indicate that increased concentration can increase the curing depth while the
negative correlation for ITX means that the concentration of ITX should be reduced.

In order to select the optimal amount of photoinitiator, only photoinitiator 907 and ITX were
selected based on the criterion of using least amount photo-initiator while reaching the highest curing
thickness. According to Table 1, when the ratio of initiator 907 to ITX is 6: 1, the curing effect is
optimal, and the curing thickness is 70μm. In order to study the best amount of photoinitiator curing in
silicon nitride suspension, the total amount of photoinitiator was tested, as shown by Table 2. The total amount of initiator is increased from 3 wt% to 6 wt%, the curing thickness is 60 μm, 70 μm, 60 μm, respectively. When the total amount of 907 and ITX is 4 wt%, the curing effect is optimal.

Table 1. Optimization of five photoinitiators to obtain the curing depth of Silicon Nitride suspension tested in different proportions by using Modde software.

| TPO  | 369 | 184 | 907 | ITX | Thickness(μm) |
|------|-----|-----|-----|-----|---------------|
| 0.6  | 0.1 | 0.1 | 0.1 | 0.1 | 50            |
| 0.1  | 0.6 | 0.1 | 0.1 | 0.1 | 50            |
| 0.1  | 0.1 | 0.6 | 0.1 | 0.1 | 60            |
| 0.1  | 0.1 | 0.1 | 0.6 | 0.1 | 70            |
| 0.1  | 0.1 | 0.1 | 0.1 | 0.6 | 40            |
| 0.4  | 0.15| 0.15| 0.15| 0.15| 60            |
| 0.15 | 0.4 | 0.15| 0.15| 0.15| 60            |
| 0.15 | 0.15| 0.4 | 0.15| 0.15| 50            |
| 0.15 | 0.15| 0.15| 0.4 | 0.15| 50            |
| 0.15 | 0.15| 0.15| 0.15| 0.4 | 50            |
| 0.1 | 0.225| 0.225| 0.225| 0.225| 60           |
| 0.225| 0.1  | 0.225| 0.225| 0.225| 60           |
| 0.225| 0.225| 0.1  | 0.225| 0.225| 60           |
| 0.225| 0.225| 0.225| 0.1  | 0.225| 50           |
| 0.225| 0.225| 0.225| 0.225| 0.1  | 50           |
| 0.2  | 0.2  | 0.2  | 0.2  | 0.2  | 50           |
| 0.2  | 0.2  | 0.2  | 0.2  | 0.2  | 50           |
| 0.2  | 0.2  | 0.2  | 0.2  | 0.2  | 50           |

According to figure2, we can see that the 907 is positively correlated with the curing depth while ITX is negatively correlated with the curing depth of the silicon nitride UV resin. Therefore, under the premise of selecting the best total amount of initiator 4wt%, In order to choose the optimal proportion...
of photoinitiator, the ratio of 907 to ITX is gradually increased from 6:1 to 10:1. The curing thickness of silicon nitride suspension is 70μm, 70μm, 60μm, 50μm, respectively. As shown in figure3, curing depth varies with the ratio of 907 to ITX. When the ratio of initiator to initiator is 6:1 and 7:1, the curing thickness of silicon nitride suspension is the optimization.

| Weight dose | Photoinitiator ratio | Thickness(μm) |
|-------------|----------------------|---------------|
| 3wt%        | 6:1                  | 60            |
| 4wt%        | 6:1                  | 70            |
| 5wt%        | 6:1                  | 60            |
| 6wt%        | 6:1                  | 60            |

**Figure 3.** Control the ratio of 907 to ITX to 6:1, change the total amount of photoinitiator from 3wt% to 6wt%, test the curing thickness.

**4. Conclusions**

Initiators (907, ITX, 369, 184, TPO) play an important role in silicon nitride suspensions. The curing thickness of silicon nitride suspension was increased by irradiating resin monomer with ultraviolet light of 405 nm. Modde software showed that initiator 907 and ITX had an obvious effect on the curing effect of silicon nitride suspension, while 369, 184 and TPO made little difference on that. According to the principle of using least amount photo-initiator to reach the highest curing thickness, 907 and ITX were selected. The total amount and proportion of the initiators were studied respectively. The results showed that when the ratio of 907 to ITX ranged from 6 to 7, and the total amount of 907 and ITX was 4 wt%, the curing effect of silicon nitride suspension is optimal.

**Acknowledgment**

This work was supported by the National Key R&D Program of China (No.2017YFB1103500 & No.2017YFB1103502). The results of the study expressed in this paper are that the author's views do not necessarily reflect the views of the NKPC.
References

[1] Krstic Z and Krstic V D 2012 Silicon nitride: The engineering material of the future J. Mater. Sci. 47 535–52

[2] Kim J , Schubert H and Petzow G 1989 Sintering of Si₃N₄ with Y₂O₃ and Al₂O₃ added by coprecipitation J. Eur. Ceram. Soc. 5 311–9

[3] Yang Y, Song X, Li X, Chen Z, Zhou C, Zhou Q and Chen Y 2018 Recent Progress in Biomimetic Additive Manufacturing Technology: From Materials to Functional Structures Adv. Mater. 30 1–34

[4] Zocca A, Colombo P, Gomes C M and Günster J 2015 Additive Manufacturing of Ceramics: Issues, Potentialities, and Opportunities J. Am. Ceram. Soc. 98 1983–2001

[5] Abouliatim Y, Chartier T, Abelard P, Chaput C and Delage C 2009 Optical characterization of stereolithography alumina suspensions using the Kubelka-Munk model J. Eur. Ceram. Soc. 29 919–24

[6] Chartier T, Badev A, Abouliatim Y, Lebaudy P and Lecamp L 2012 Stereolithography process: Influence of the rheology of silica suspensions and of the medium on polymerization kinetics - Cured depth and width J. Eur. Ceram. Soc. 32 1625–34

[7] Hu K, Wei Y, Lu Z, Wan L and Li P 2018 Design of a Shaping System for Stereolithography with High Solid Loading Ceramic Suspensions 3D Print. Addit. Manuf. 5 311–8

[8] Yang Y, Chen Z, Song X, Zhu B, Hsiao T, Wu P I, Xiong R, Shi J, Chen Y, Zhou Q and Shung K K 2016 Three dimensional printing of high dielectric capacitor using projection based stereolithography method Nano Energy 22 414–21

[9] Chen Z, Song X, Lei L, Chen X, Fei C, Chiu C T, Qian X, Ma T, Yang Y, Shung K, Chen Y and Zhou Q 2016 3D printing of piezoelectric element for energy focusing and ultrasonic sensing Nano Energy 27 78–86

[10] Schwentenwein M, Schneider P and Homa J 2014 Lithography-Based Ceramic Manufacturing: A Novel Technique for Additive Manufacturing of High-Performance Ceramics Adv. Sci. Technol. 88 60–4

[11] He R, Liu W, Wu Z, An D, Huang M, Wu H, Jiang Q, Ji X, Wu S and Xie Z 2018 Fabrication of complex-shaped zirconia ceramic parts via a DLP- stereolithography-based 3D printing method Ceram. Int. 44 3412–6

[12] Schwentenwein M and Homa J 2015 Additive manufacturing of dense alumina ceramics Int. J. Appl. Ceram. Technol. 12 1–7

[13] Song X, Chen Z, Lei L, Shung K, Zhou Q and Chen Y 2017 Piezoelectric component fabrication using projection-based stereolithography of barium titanate ceramic suspensions Rapid Prototyp. J. 23 44–53

[14] Griffith M L and Halloran J W 2005 Freeform Fabrication of Ceramics via Stereolithography J. Am. Ceram. Soc. 79 2601–8

[15] STANSBURY J W 2000 Curing Dental Resins and Composites by Photopolymerization J. Esthet. Restor. Dent. 12 300–8

[16] Lee H D, Pober R L, Calvert P D and Bowen H K 1986 Photopolymerizable binders for ceramics J. Mater. Sci. Lett. 5 81–3

[17] De Hazan Y, Heinecke J, Weber A and Graule T 2009 High solids loading ceramic colloidal dispersions in UV curable media via comb-polyelectrolyte surfactants J. Colloid Interface Sci. 337 66–74

[18] Tomeckova V and Halloran J W 2010 Cure depth for photopolymerization of ceramic suspensions J. Eur. Ceram. Soc. 30 3023–33

[19] Hird M J 1976 Transmission of ultraviolet light by films containing titanium pigments—applications in u.v. curing Pigment Resin Technol. 5 5–14