

Viscosity optimisation of photosensitive Al₂O₃ slurry for stereolithography based additive manufacturing

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Abstract

Viscosity of alumina slurry is a key factor affecting the quality of ceramics formed by stereo photolithography, but it is closely related to the resin distribution ratio, dispersant content, plasticizer content and solid content. Most researchers utilize the single factor method to study the composition and ratio of the slurry. In this study, orthogonal experimental design and back propagation artificial neural networks methods were combined to solve the optimisation problem of multi-objective and multi-factor influence on alumina slurry performances. The results of optimal composition and content allocation were achieved by back propagation artificial neural networks and experimental testing. It was shown that the optimal conditions are: resin composition HDDA : PPTTA = 4 : 1, DS-165A dispersant content of 3.86 wt.%, PEG plasticiser amount of 3.5 wt.% and the solid content of 75.74 wt.%. The predicted optimal viscosity value was 8787 mPa·s and the shrinkage rate could reach 14.57%. The optimal values of viscosity and shrinkage were consistent with the experimental results, the viscosity and shrinkage errors were only 4.06% and 3.856%, respectively. The average density and bending strength of the sintered samples were 3.979 ± 0.005 g/cm³ and 365 ± 61 MPa, respectively. According to the obtained data, stereolithography 3D printing alumina slurry with excellent flowability and low shrinkage was successfully prepared.

Keywords: stereolithography, Al₂O₃ slurry, orthogonal experiment design, artificial neural networks

I. Introduction

Stereolithography technology is a method to prepare basic photocuring units by curing the photosensitive resin monomer under the illumination of the ultraviolet (UV) laser [1,2]. This technology uses a point-bypoint scan to polymerise the photosensitive resin. UV laser scans a layer to obtain a layered 2D solid and then moves the platform to add a new layer of 2D solid on the solidified entity in the z-axis direction. This step is repeated until a 3D entity is aggregated [3–5]. This technology has high accuracy and good surface quality of the green body compared with other 3D printing technologies [6,7].

Ceramic slurry with high solid content and low vis-

cosity is the key to photocurable 3D printing [8]. Usually, the strength of a ceramic green body is improved and the shrinkage rate is decreased by increasing the solid content of the slurry. At the same time, the flowability of the slurry should be considered, which can be scraped without hindrance and can ensure that the parts can be printed smoothly [5]. Many factors affect the two behaviours, including acrylic monomer [9–11], dispersant [12,13], plasticiser [14–16] and solid content [17– 19].

Alumina is a widely used industrial material and researchers mostly utilize α -Al₂O₃ and γ -Al₂O₃ to prepare ceramic slurry. The ceramics prepared with γ -Al₂O₃ exhibit numerous pores in both intraparticle and intergranular regions while those obtained with α -Al₂O₃ show pores in only intergranular sections. Pore content in γ -Al₂O₃ is high, leading to low solid content [20]. Therefore, most researchers select α -Al₂O₃ to prepare

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the ceramic slurry. In the α -Al₂O₃ slurry, the increase in solid content can significantly improve the flexural strength, density and other properties of parts. However, it also brings problems such as particle agglomeration, increased slurry viscosity, increased mechanical resistance and part deformation. Thus, there is constant effort to optimise various α -Al₂O₃ ceramic slurry formulations and solve the above mentioned problems.

For UV-curable resin solutions, good rheology and high curing rate facilitate the formation of ceramic parts. Acrylate resins, cationic resins and acrylate oligomers are usually used as the main components. Acrylate resins are preferred over cationic resins in ceramic photocurable printing due to their higher curing rate. Furthermore, ceramic suspensions with low viscosity are typically achieved using acrylate monomers rather than acrylate oligomers [21]. In general, acrylate monomer is used as a component of UV-curable ceramic resin and involves the three following steps: i) generation and emission of free radicals by the photoinitiator under UV irradiation of the photoinitiator, ii) transformation of the acrylate monomers into the crosslinked polymer networks via photo-polymerisation and iii) immobilisation and trapping of the ceramic powder particles in these crosslinked polymer network structures [22].

Usually, two or more acrylate monomers [23] are mixed to obtain a UV-curable ceramic suspension with excellent curing properties and low viscosity [24]. However, different acrylic monomer mixtures have different viscosities and curing depths. Therefore, testing the rheological and curing properties of such suspension is necessary. Borlaf et al. [25] obtained a resin solution with HDDA, 17 wt.% of modified acrylic polyether polyol and 29 wt.% of benzyl alcohol. Then, they added 40 vol.% of alumina to obtain the optimal slurry ratio. The printed parts had a pore size of $400\,\mu\text{m}$ and a minimum clearance of 200 µm. Xu et al. [26] studied the adhesion properties of UV-cured alumina suspensions and the relationship between function and structure of UV-curable acrylate monomers. By combining several acrylic resins with different functional groups to study the curing depth, curing degree and a series of resin properties, the research showed that alumina suspensions formulated with 20 vol.% IBOA, 50 vol.% HDDA and 30 vol.% PPTTA exhibited excellent adhesion and suitable curing properties. The above mentioned studies all obtained lower viscosity and better flow properties. However, representative points are selected within the maximum range of experiments to arrange the experiment. Therefore, the optimal material ratio needs to be further studied.

In the alumina ceramic slurry system, α -Al₂O₃ powder has the polarity of the high-energy hydrophilic surface, whilst most of the photocurable polymers have the nonpolarity of the low-energy hydrophobic surface. The incompatibility leads to the poor dispersion of the α -Al₂O₃ ceramic suspension. Researchers explore different methods to improve the performance of the α -Al₂O₃ ceramic suspension, including direct surface modification of the α -Al₂O₃ powder or the addition of dispersant to the α -Al₂O₃ ceramic suspension. Most dispersants only act on the surface of the ceramic particles and do not participate in the polymerisation reaction of resin. Zhang et al. [27] studied two factors, dispersant type and solid content, as well as how they affected the property of the slurry. They showed that the viscosity reached 15.4 Pa·s at a shear rate of 200 1/s when the solid content was 60 vol.% and the concentration of KOS110 dispersant was 5 wt.%. Most researchers [8,28] consider the effect of layer recoating efficiency and believe that the slurry viscosity should be below 10 Pa·s at the shear rate of 30 1/s to ensure good green body printing. During the subsequent cleaning and drying process, the green body will also exhibit delamination, which is due to the rapid evaporation of the liquid on the printing surface and the formation of air bubbles [29]. The addition of plasticisers helps eliminate delamination of green bodies. Xing et al. [16] prepared a 48 vol.% alumina slurry by adding HDDA, PPTTA, alkylamine dispersant and plasticiser PEG and studied its mechanical properties. Higher plasticiser content was added to reduce the risk of deformation during shrinkage and decrease the material stress that may cause the stratification of the green body. PEG did not participate in the polymerisation process of the ceramic suspension. However, it acted as a connection between the cured monomer and the ceramic powder, which reduced the brittleness of the green body. The study also found that the density and flexural strength were independent of the plasticiser without delamination between adjacent layers [16]. However, considering the influence of wetting and recoating quality during photocuring, the optimal range of values for the content of PEG needs to be further determined.

A property of ceramic slurry is affected by many factors. Most researchers had a more detailed analysis of the composition selection of the slurry. However, most of them chose the representative point to study the influence of the component content of ceramic slurry on the properties of ceramic slurry, but neglected the influence of the small difference of the component content of ceramic slurry on the properties of ceramic slurry. Therefore, this study combines orthogonal experimental design with the predictive analysis of artificial neural networks, investigates the influence of resin distribution ratio, dispersant content, plasticizer content and solid content on the slurry properties, with the main goal to obtain the optimal values of all the results in the whole experiment. The influence rules of various factors on the viscosity and shrinkage were determined. The slurry proportions applicable for 3D printing were optimized. This method also has guiding significance for the formulation of other 3D printing slurries.

II. Experimental

2.1. Materials

In this experiment, spherical α -Al₂O₃ particles with the average size of 0.5 µm (Shanghai Xinchao New Materials Ltd.) were selected as precursor. Three kinds of photosensitive resins with different functionalities were utilized: isobornyl acrylate (IBOA), 1,6 hexanediol diacrylate (HDDA) and ethoxylated (5) pentaerythritol tetraacrylate (PPTTA, Shanghai Guangyi Chemical Ltd.). Photoinitiator 819 (Guangzhou Lihou Trading Ltd.) was utilized for the curing of alumina resin. Four kinds of reagents were employed as the dispersing agents: DS-165A (Tianjin Heppe-Philo New Materials Ltd.), sodium citrate (C₆H₅Na₃O₇), ammonium polyacrylate (C₃H₇NO₂) and polyvinylpyrrolidone (PVP, Beijing Wanjia Shouhua Biotechnology Ltd.). The plasticiser polyethylene glycol (PEG, Shanghai Maclean Biochemical Technology Ltd.) was used to improve the strength of the green body.

2.2. Slurry preparation

In this study, three steps are used to prepare the photocurable alumina slurry. Firstly, premixed UV-curable resin solutions were prepared by mixing the different UV-curable acrylate monomers, followed by the continuous stirring in the dark for 4 h. Secondly, the α -Al₂O₃ powder was dried in a drying oven at 180 °C for 24 h to remove the residual water, and the dried α -Al₂O₂ powder was deagglomerated by grinding and screening, by the use of a sieve with a mesh size of 149 µm. Ultimately, a certain content of α -Al₂O₂ powder was added into the prepared photocurable resin solution. A certain amount of free radical photoinitiator 819 was added to it and the selected dispersant was placed into the planetary ball mill. The slurry was placed in the environment of 45 °C, followed by milling at 400 rpm for 24 h to achieve uniform dispersion.

2.3. Printing process

The prepared ceramic slurry was placed in a photocurable ceramic 3D printer for single-layer testing. The 3D printing equipment and working principle are shown in Fig. 1. The supply cavity provided the slurry, which was then spread on the forming platform with the scraper. Ultraviolet laser scans a layer to obtain a layered 2D solid and then moves the platform to add a new layer of 2D solid on the solidified entity in the *z*axis direction. This step was repeated until a 3D entity was aggregated. The UV laser outputs a 5 W laser with a wavelength of 355 nm; the laser power was selected according to the quality of numerical forming and its range was controlled within 20% to 70%. The singlelayer laser printed thickness was determined based on the thickness of the model slice, which is four times the thickness of the model slice to ensure the connection to the previous layer without faults. The scraper speed was 50 mm/s, the platform speed is 3 mm/s and the laser scanning speed was 1800 mm/s.

2.4. Sintering process

The printed green body undergoes degreasing and sintering in the GF1750Q high-temperature sintering furnace. Based on previous experimental experience and references [30-32], the process is divided into three stages. From the room temperature to 200 °C is the first stage where the main change is the removal of physically adsorbed water from the ceramic green body. The second stage is between 200 and 300 °C while part of the resin began to decompose from ceramic green body. At the temperature between 300 and 700 °C, the resin is basically decomposed. At the temperature higher than 1150 °C, the organic polymer in the ceramic body is completely eliminated. Then it continued to heat up to 1700 °C to sinter the alumina. The whole process proceeded in the air atmosphere. The heating curve is shown in Fig. 2. C1 to C9 is the degreasing process with an average heating rate of 1 °C/min, C9 to C11 is the sintering process with an average temperature rate of 5 °C/min and C11 to C12 is the furnace cooling process.

2.5. Experimental methods

The orthogonal design method was utilized to optimise the combination of experiments. Amongst the various influencing factors of the alumina slurry, the



Figure 1. Experimental set-up for the 3D printing process with photocurable 3D printing equipment (a) and schematic of the photocurable 3D printing device (b)



Figure 2. Process curves for degreasing and sintering in which C1 to C9 is the degreasing process; C9 to C11 is the sintering process; C11 to C12 is the furnace cooling process

amount of dispersant (A, wt.%), the amount of plasticiser polyethylene glycol (B, wt.%) and solid content (C, wt.%) were selected as orthogonal design factors. Each factor is selected according to five levels. The level of influencing factors was set according to the relationship that the measured factors influence viscosity and shrinkage. Table 1 shows the horizontal range of each factor, which determines the degree of influence on the viscosity of the slurry.

Table 1. Factor levels

Level	Factor level				
Level	A [wt.%]	B [wt.%]	C [wt.%]		
1	3	2.5	70		
2	4	3	72		
3	5	3.5	74		
4	6	4	76		
5	7	4.5	78		

A three-layer back propagation (BP) neural network model was utilized to predict the influencing factors of photocurable ceramic slurry. This method does not presuppose the input and output relationship, but it utilizes existing data to learn the functional relationship between them. The network structure with 3 inputs, 2 outputs and 10 nodes hidden layers was used. The factors corresponding to the three experimental parameters were taken as the input of the network and the performance values were used as the output of the network under the corresponding conditions, as shown in Fig. 3.

All input and output values were normalised, *y*, and uniformly limited to the range from 0 to 1:

$$y = \frac{x - x_{min}}{x_{max} - x_{min}} \tag{1}$$

where *x* is the actual experimental values, and x_{max} and x_{min} are the maximal and minimal values all given in Table 2. The purpose of normalisation is to unify the



Figure 3. Three-layer artificial neural network model

different units of the factor and reduce the time to train the neural network. The experimental data shown in Table 2 are divided into two groups for training and testing the BP neural network. One group is the training set (20 datasets, samples 1–20 in Table 2), which is used for training until the network learns the relationship between input and output. The other group is the test set (5 datasets, samples 21–25 in Table 2), which verifies the generalisation ability of the neural network as an independent dataset. The trained and tested networks can complete the predictions for a new set of data.

III. Results and discussion

3.1. Resin distribution ratio and performance test

Many kinds and combinations of resin can be utilized for photocuring on the market. Thus, determining the composition and ratio of resin by single factor method is necessary and the amount of resin needs to be optimised. A premixed UV-cured resin solution was prepared using UV-cured acrylate monomers with different functionalities [33]. In the experiment, IBOA and HDDA were selected as low-functional group diluent monomers as the main components of the resin solution. Its proportion should be higher than 60% to ensure a lower viscosity for normal printing and the proportion of PPTTA should also be higher than 10%. In this way, a higher curing rate is needed to save time and a larger crosslinking density is required to ensure the performance requirements after degreasing and sintering. The resin composition is shown in Table 3. The prepared resins were tested for viscosity and depth of cure properties according to the data given in Table 3. The dripping time of each set of resins was measured by a dripping flow tester. Then, the viscosity of the resin was calculated according to Eq. 2:

$$V = \frac{T - 6}{0.223}$$
(2)

Laval		Factor level	Experimental results		
Level	A [wt.%]	B [wt.%]	C [wt.%]	D [mPa·s]	E [%]
1	1(3)	1(2.5)	1(70)	6180	18.05
2	1(3)	2(3)	2(72)	7560	17.21
3	1(3)	3(3.5)	3(74)	8340	15.24
4	1(3)	4(4)	4(76)	10860	14.19
5	1(3)	5(4.5)	5(78)	13620	12.79
6	2(4)	1(2.5)	2(72)	7080	17.28
7	2(4)	2(3)	3(74)	8160	15.17
8	2(4)	3(3.5)	4(76)	9780	13.51
9	2(4)	4(4)	5(78)	12120	12.47
10	2(4)	5(4.5)	1(70)	5420	18.01
11	3(5)	1(2.5)	3(74)	8220	15.36
12	3(5)	2(3)	4(76)	9920	14.05
13	3(5)	3(3.5)	5(78)	12640	12.88
14	3(5)	4(4)	1(70)	5940	18.44
15	3(5)	5(4.5)	2(72)	7240	17.73
16	4(6)	1(2.5)	4(76)	11100	14.39
17	4(6)	2(3)	5(78)	13200	12.91
18	4(6)	3(3.5)	1(70)	6380	18.36
19	4(6)	4(4)	2(72)	7420	17.75
20	4(6)	5(4.5)	3(74)	8260	15.36
21	5(7)	1(2.5)	5(78)	13980	12.96
22	5(7)	2(3)	1(70)	6200	18.56
23	5(7)	3(3.5)	2(72)	7680	17.98
24	5(7)	4(4)	3(74)	8360	15.89
25	5(7)	5(4.5)	4(76)	11340	14.86

Table 2. Design orthogonal table L25 (5³)

Table 3. Resin composition of photocuring alumina suspensions

	IDOA		DDTTA
Number	IBOA	HDDA	PPTIA
Number	[vol.%]	[vol.%]	[vol.%]
F1	80	0	20
F2	70	0	30
F3	60	0	40
G1	0	80	20
G2	0	70	30
G3	0	60	40
H1	20	50	30
H2	25	50	25
H3	30	50	20
H4	10	60	30
H5	20	60	20
H6	30	60	10

where V is the kinematic viscosity in mm^2/s and T is the outflow time sign. The photocuring ceramic 3D printer CeraBuilder 100Pro-D was utilized to conduct a single-layer test to obtain its curing depth and the optimal resin composition and ratio were selected.

Figure 4 shows results of viscosity test obtained by measuring the drop time of the resin solutions with compositions given in Table 3. The viscosity is lower when the drop time is shorter. In Fig. 4, it can be seen that H6 has the shortest drop time, which means that it has the lowest viscosity. Single layer printed blocks with different resin premix compositions are shown in Fig. 5 confirming that the printed block shape is complete. Figure 6 shows the relationship between the different laser powers and the cure thickness for the different components of resin premix. The curing rate is faster when the thickness is larger.

In the experiment, the F1, G1, H2, H3 and H6 groups had the drop time below 15 s. Amongst them, the group G1 has the largest curing thickness and the highest curing rate at the same laser power and scanning speed. The functional number of the reactive diluent greatly



Figure 4. Drop time data of resin solutions with different composition and ratios



Figure 5. Macroscopic morphology of different resin components obtained with the same laser power



Figure 6. Cure thickness of resins of different components at different laser power

influences the curing performance of the photocurable system and the physical and chemical properties of the cured film [34]. The active diluent monomer of the group G1 contains a large number of functional groups, large functionality, high activity of the photocuring reaction, fast photocuring reaction rate and large crosslinking density of the curing film. Thus, the group G1 is selected as the photocuring resin solution in all following experiments.

3.2. Selection and performance test of dispersant

The surface of alumina ceramic particles usually contains hydroxyl groups, which are hydrophilic. However, Fig. 7 shows that the selected photopolymer resins have chain ends of -CH₂, which have hydrophobic main chain structures and are all hydrophobic in nature [27]. Hydrophilic monomers can easily form hydrogen bonds with ceramic particles. Thus, the particles can be evenly dispersed in the suspension, whilst hydrophobic monomers cannot. Therefore, DS-165A, C₃H₇NO₂, PVP and $C_6H_5Na_3O_7$ were utilized in the experiment to ensure that the hydrophobic monomer forms a stable suspension. The species are determined by a univariate method. Choose four beakers and add 1 g of sieved alumina powder to 15 g of the optimal resin group premix. Then, add 5 wt.% of different types of dispersants into each beaker and stir them evenly with a planetary ball mill. Thereafter, place it into a graduated cylinder, seal it with plastic wrap and let it stand for 72 h in a dark environment at room temperature. The dispersion ability of the dispersant is ascertained by the static sedimentation stratification method [3]. Ultimately, the type of dispersant is determined.

Figure 8 shows the principle and physical diagram of the static sedimentation stratification method. A total of 1 ml of the measuring cylinder is equivalent to a height of 2 mm. Four different dispersants, namely, DS-165A,



Figure 7. Chemical structures of three different UV-curable acrylate monomers



Figure 8. Static settlement stratification of alumina suspension with different dispersants



Figure 9. The relationship between liquid solvent height and precipitation time with different dispersants

 $C_3H_7NO_2$, PVP and $C_6H_5Na_3O_7$ are utilised. The liquid solvent is changed over different times and the change pattern is shown in Fig. 9. As shown in Figs. 8 and 9, the dispersion stability of DS-165A is much better than those of the three other dispersants. The main component of DS-165A is a composition of a maleic acidstyrene-type modified copolymer with a surfactant and is positively charged on the surface. When the ceramic powder particles are added, the polymer molecules are quickly and tightly adsorbed to the particle surface and form a stable double electric layer. When the particles are close to each other, they will be affected by not only the electrostatic repulsion generated by the interaction between the electric double layers but also by the steric hindrance between the polymer molecules. Ultimately, the particles will be in a state of equilibrium, as shown in Fig. 10. This electrostatic steric hindrance stabilisation mechanism can prevent the dispersed particles from flocculating [35]. Compared with the two other mechanisms, it can maintain the stability of the slurry. Thus, in this work DS-165A dispersant was chosen as optimal.



Figure 10. Microscopic schematic diagram of the alumina surface in which the polymer molecules are adsorbed to the Al₂O₃ surface and form a stable double electric layer

3.3. Orthogonal experimental analysis

The orthogonal design table was designed according to the factors and levels in Table 1, as shown in Tables 2 and 4.

This study evaluates the influence of three factors on the slurry fluidity and line shrinkage rate by studying the influence of different levels of each factor on the slurry. The conditions and corresponding results for each trial are shown in Table 2. Table 4 contains 10 important parameters: K1, K2, K3, K4, K5, S1, S2, S3, S4 and S5. Ki (i = 1, 2, 3, 4, 5) is the sum of the viscosity corresponding to 'i' in Table 2, column 25. Si (i = 1, 2, 3, 4, 5) is the sum of the shrinkage rates corresponding to 'i' in Table 2, column 25.

The ranges R1 and R2 are the main indicators that can be intuitively analysed by orthogonal experiments. R1 is defined by Eq. 3 as the difference between the maximal K and the minimal K values in the corresponding coefficient column. R2 is defined by Eq. 4 as the difference between the maximal S and the minimal S values in the corresponding coefficient column.

$$R1 = \max(K1, K2, K3, K4, K5) - \min(K1, K2, K3, K4, K5)$$
(3)

$$R2 = \max(S1, S2, S3, S4, S5) - \min(S1, S2, S3, S4, S5)$$
(4)

Darameters	Data						
1 arameters	A [wt.%]	B [wt.%]	C [wt.%]				
K1	46560	46560	30120				
K2	42560	45040	36980				
K3	43960	44820	41340				
K4	46360	44700	53000				
K5	47560	45880	65560				
S 1	77.48	78.04	91.42				
S2	76.44	77.9	87.95				
S 3	78.46	77.97	77.02				
S 4	78.77	78.74	71				
S5	80.25	78.75	64.01				
R1	5000	1860	35440				
R2	3.81	0.85	27.41				

 Table 4. Orthogonal experimental parameters data

The ranges R1 and R2 reflect the influence degree of each factor on the viscosity and line shrinkage of the slurry. In general, the range values of each column are not equal, which indicates that the influence of each factor on the performance of the indexes is different. The effect of the indicator is greater when the value is larger. The factor with the largest numerical value is the factor with the highest influence. As shown in Table 4, the primary influencing factor on the slurry viscosity is the solid content, followed by the dispersant and polyethylene glycol contents, i.e. C > A > B. The solid content has the greatest influence on the linear shrinkage, followed by the dispersant and polyethylene glycol contents, i.e. C > A > B. In summary, the most important affecting factor of the viscosity and line shrinkage of the slurry is the solid content, followed by the content of the dispersant and the content of polyethylene glycol is the least important.

However, two objective functions are considered: meeting the minimum line shrinkage whilst the optimal value of the slurry viscosity is the best. Therefore, the orthogonal experiment only verifies the order of importance of each factor. It only considers the optimal value between these experimental points and not the optimal value for the entire experimental range. The BP neural network was applied below to evaluate the optimal value of the whole experimental range for solving the aforementioned problem.

3.4. Artificial neural network model analysis

A BP neural network is constructed using the orthogonal experimental results to further investigate the combined effects of the two objectives of slurry viscosity and line shrinkage. The data of the first 20 groups in Table 2 are normalised prior to training.

The BP neural network model consists of three neurons in the input layer and two neurons in the output layer. In the network design, the number of neurons in the hidden layer is set to 10. The training samples are trained according to the structure and algorithm of the model. Training stops when the mean squared error (*MSE*) level of performance is satisfactory. *MSE* that determines the performance of the network is calculated according to Eq. 5.

$$MSE = \frac{1}{N} \sum_{i=1}^{N} (y_i - y_k)^2$$
(5)

Figure 11 shows a training process diagram of the BP network. The network will stop when *MSE* is below 10^{-6} or reach 400 epochs. During the first 50 training cycles, *MSE* dropped rapidly and gradually approached the limit value, then fluctuated around the limit value. Within the entire 400 epochs, *MSE* did not reach 10^{-6} . The best training performance was $1.2065 \cdot 10^{-6}$ at epoch 194.



Figure 11. Termination condition plot of the BP network training process in which the network will stop when MSE is below 10^{-6} or reach 400 epochs

To confirm the accuracy of the BP neural network model, the remaining five sets of experiments (experiments 21–25 in Table 2) were used as test samples for the network. Table 5 shows the comparison between the experimental and predicted values tested by the BP neural network model. The error values are small, which means that the network prediction results are correct. Figure 12 shows the error between the predicted and actual values, which is small. Therefore, the BP neural network model is reliable.

3.5. Multi-objective optimisation

The 25 sets of orthogonal experimental data contain a certain gradient for each factor in the experiment, which makes the accuracy very poor and affects the experimental results. A refinement analysis is required in the multi-objective optimisation of BP neural networks to narrow the experimental data and obtain a result closer to the global optimal solution [36]. The method of refinement analysis is based on the degree of influence of various factors. The analysis is refined when more influencing factors are considered, whilst the best level is chosen when fewer influencing factors are regarded. In the above mentioned experiments, two main factors af-

	Slurr	Slurry viscosity [mPa·s] Shrinkage [%]				
No.	Experimental	Predicted	Difference [%]	Experimental	Predicted	Difference [%]
1	0.4658	0.4656	0.0429	0.1296	0.1302	0.4630
2	0.2064	0.2039	1.2112	0.1856	0.1838	0.9698
3	0.2558	0.2558	0	0.1798	0.1791	0.3893
4	0.2784	0.3049	9.5187	0.1589	0.1632	2.7061
5	0.3778	0.3779	0.0265	0.1486	0.1480	0.4038
(a) Training: R=0.99994 (b) Test: R=0.98935 (c) All: R=0.99764					All: R=0.99764	
0.45		. 🕺 .	0.45	20	0.45	

~= 1.1*Target + -0.01

Output 0.2

0.4

0.35

0.3

0.25

0.1

Table 5. Comparison of normalised experimental and predicted values in BP neural network model test

Target Target Target Figure 12. Error analysis diagram of the predicted and experimental values of: a) 20, b) 5 and c) 25 groups of tests

0.3

0.4

0.2

Output ~= 1*Target + -0.002

0.4 0.35

0.3 0.25

0.2

0.1

02

0.3

04



Figure 13. The influence of solid content and dispersant content on: a) viscosity and b) shrinkage

fecting the property of alumina slurry are the solid and dispersant contents. Therefore, the content of PEG was determined to be 3.5 wt.% and only two other important factors were considered. This work utilized the BP neural network to build a 3D model. In Fig. 13, two factors of solid content and dispersant were utilized as the independent variables and viscosity and shrinkage were utilised as the dependent variables. Two 3D surfaces were drawn based on the predicted values of the BP neural network. Figure 13a shows the change of viscosity where the viscosity gradually increases with the increment in solid content and dispersant content. The slurry viscosity should be below 10 Pa·s to ensure good green body printing, so it should be less than 0.5 (normalised data). Considering the lowest value of the actual slurry viscosity, it should be greater than 0.1 (normalised data). Figure 13b shows the change of shrinkage. The shrinkage gradually decreases with increasing the solid content and dispersant content. The range of the shrinkage is also between 0.1 and 0.5. Figures 14a and 14b show the projection of 3D-surfaces in this interval, which are

Output ~= 1*Target + 6.9e-0!

0.

0.35

0.3

0.25

0.2

0.1

0.2

0.3

0.4

the optimal viscosity and shrinkage ranges. In Fig. 14c two planes are placed in the same coordinate system; the intersection area was the range of values that meet both the best viscosity and shrinkage. Figure 14d presents an enlarged view of the intersection area. Under this condition, the ranges of the dispersant and solid contents were obtained. When the solid content is large, the mechanical properties of the parts will increase accordingly, therefore, the maximum solid content in the intersection area should be selected. When 3.86 wt.% of dispersant is added to the ceramic slurry with the solid content of 75.74 wt.%, the viscosity can reach 8787 mPa·s and the contraction rate is only 14.57%. These values should then meet the excellent liquidity energy and sintering performance.

IV. Experimental verification

The final experiments were conducted to verify the predicted optimal ceramic slurry formulation to confirm the rationality of the model trained by the artificial neu-



Figure 14. The range of solid and dispersant content when: a) viscosity range is between 0.1 and 0.5 and b) shrinkage range is between 0.1 and 0.5. Dependences shown in (a) and (b) presented in the same coordinate system are given in (c) with the enlarged view of the intersection area (d) - intersection area is the range of values that meet best viscosity and shrinkage



Figure 15. Changes after sintering and shrinkage ratio of alumina ceramic samples - (a, b, c) three solid and (d, e) porous samples

ral network. Three kinds of solid samples and two kinds of porous samples were prepared for measuring the viscosity of ceramic slurries and the linear shrinkage. The results are shown in Fig. 15. Viscosity of the slurry was 8430 mPa·s and the error from the predicted value was 4.06%. The average shrinkage error of three solid samples was 3.43%, and the maximum error was 5.7%; the average shrinkage error with the porous samples was 4.495%, and the maximum error was 7.14%. The type of sample has a certain influence on the shrinkage rate. No cracks and deformations are observed on the surface of the sintered parts. The results show that the slurry is suitable for 3D printing of complex structural parts. The formula obtained in this study was compared with the formulas of other researchers [16,20,37,38] to compare the viscosity of the slurry and the shrinkage after sintering under the similar solid content (75 wt.%/45 vol.%). The comparison (Table 6) shows that, under the same solid content, the ceramic slurry formula obtained by the combination of orthogonal experiment and artificial neural network has lower viscosity and similar shrinkage rate as other formulas. Therefore, the material formulation with 75 wt.% solid content has an advantage.

V. Properties and fractography after sintering

Test samples with the size of $100 \text{ mm} \times 5 \text{ mm} \times 5$ mm (marked as I, II and III) were prepared by using the optimized ceramic slurry and 3D printer. Figure 16a shows the density and bending strength of three samples after sintering. The maximal shrinkage rate as 14.85% and the maximal density was 3.983 g/cm³. Figure 16b shows the load-displacement curves obtained from three point bending test. The maximal and minimal bending strengths were 425 and 304 MPa, respectively.

Figure 17 shows the macroscopic and fracture morphologies of the sintered samples. It can be seen from the Fig. 17a that all 3D printed and subsequently sintered samples are complete. Figure 17b shows SEM photographs of fracture with the highest bending strength (II). It can also be seen that the alumina has a high degree of compactness and there are pores in the grain boundaries and inside the grains. Mainly intergranular fractures (such as in the red circle) and some transgranular fractures (such as in the blue circle) are obvious fracture steps. Figure 17c shows SEM

Table 6. Comparison of the solid content and shrinkage rate for similar samples

	-			8				
Al_2O_3 average	Acrylate	Photoinitiator	Dispersant	Additive	Solid	Viscosity	Shrinkage	Ref.
particle size [nm]	monomer		1		content	[Pa·s]	[%]	
152, 549, 1303	HDDA,	Irgacura 184	Irgacure 184 alkylamine	PEG-400	4 vol.%	30	22	[16]
	PPTTA	ligacule 104						
450	maleic		isobutylana		50 vol.%	30	14.51	[37]
	anhydride		isobutylelle					
10000	Clear Flepcl 04		$C_4H_6O_2$		75 wt.%	12.78	13.65	[20]
600	NPG2PODA	T 104			25	12.47	[20]	
	TMPTA	Irgacure 184	KH560		/5 wt.%	25	25 13.47	[38]
500	HDDA							this
	РРТТА	819	DS-165A PEG 75.74 wt.% 8.87 14.57	14.57	work			



Figure 16. Histogram of sample density and bending strength (a) and load-displacement curve obtained from the three point bending test (b)



Figure 17. Image of the sample bending fracture (a) and SEM micrographs of the fractured surface of sample II (b) and III (c)

photographs of the fractured sample with low bending strength (III). It can be seen from the figure that there are large pores in the sample. According to the principle of the minimum energy consumption of fracture, crack propagation path always goes along the surface with the weakest atomic bonding force, so the fracture mostly occurs in the voids and grain boundaries. These defects can be removed by subsequent optimization of the 3D printing process and debinding sintering process.

VI. Conclusions

This study combines the OED method with the artificial neural network method and determines the optimal solution of multi-objective and multi-factor influence on slurry performance and obtains α -Al₂O₃ ceramic slurry with good printing performance. As a result, method for the optimisation of photocuring 3D printing ceramic slurry formula was provided. Using the OED method, the solid content and the dispersant DS-165A content were determined to be the key affecting factors of the slurry rheology and shrinkage properties. The BP neural network is trained through the OED experimental data to obtain the predictive properties values, which show a good agreement with the experimental values. The optimal conditions obtained by this method are as follows: resin composition HDDA : PPTTA = 4 : 1, 3.86 wt.% of DS-165A as the dispersant, the amount of plasticiser PEG is 3.5 wt.%, and the solid content can reach 75.74 wt.%. The error between the obtained optimal viscosity and the actual value was 4.06%, the average shrinkage error of the three solid constructions was 3.43% and the maximum error was 5.7. The average shrinkage error of the porous construction was 4.495%, and the maximum error was 7.14%. The average density and bending strength of the sintered samples were $3.979\pm0.005 \text{ g/cm}^3$ and $365\pm61 \text{ MPa}$, respectively. The optimal alumina ceramic material formula obtained in this experiment is suitable for printing complex structural parts. This study also provides a reference for further research on multi-objective and multi-factor design of other ceramic slurries.

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