Optimisation of Flexural strength in Zirconia nanoclusters of the Bis-GMA & TEGDMA based dental composites

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Abstract. Chewing food is a dynamic and continuous process. tooth is an important component which can not be neglected. Accordingly to WHO(world health organization) report nearly 100% people have decay once in life. Decay can be filled with gold, silver amalgam. Composites have advantages by providing natural colour of tooth, less tooth removal required to fill cavity and natural tooth structure can be maintained. The aim of this work is to present an analysis of the composites and furnish dentists with a basis that can provide criteria for choosing one or another to suit their treatment. The mechanical properties of composite resins are importantly depends upon filler content. Dental composites are using silica, quartz and alumina glass as filler for long time. Zirconia is the latest addition as filler. Chewing of food is a dynamic situation in which many forces are acting in all possible direction, the most important being the flexural force. Our aim is to optimise the flexural strength in Zirconia nanoclusters of the Bis-GMA & TEGDMA based dental composites. The aim of work is to find out best combination of composite material.

1. Introduction
The purpose of this paper to obtain higher flexural strength of dental composite by using zirconia and hydroxyapatite as a filler. Proper composition of Zirconia, hydroxyapatite and silica is used to have favourable outcome by gaining optimum flexural strength now a days people have many problems such as dental decay, cavities, and root canal infections mainly cause due to bacterial infections. These problem hampers the tooth structure [1]. For treatment of the affected tooth, dentists recommend the removal of the dental caries and filling of the cavities with appropriate materials. Human health get affected during filling of cavities with dental amalgam. So, now in recent times, polymer composites have showed remarkable advantages over those traditional ones. Excellent properties such as biocompatibility, antibacterial and nontoxic ness makes them use highly as a dental restorative material. More than that its advantages over aesthetic makes it more popular. Also, Physical, mechanical, thermal and tribological properties of polymer composites is good [2]. Bisphenol A-glycidyl methacrylate (Bis-GMA) polymer composites are the favourable and most commonly practice in dentistry for anterior and posterior tooth filling. It has low polymerization shrinkage, low volatility, and high viscosity. Urethane dimethacrylate has lower viscosity but higher toughness than Bis-GMA [15].Recently, reinforcements based on Nano fillers with saline treatment are being widely used in dental polymer composites [3].
Dental adhesives are applied to restorative materials to tooth structure [1]. Adhesion to the enamel is much durable than the dentin due to the dynamic properties of the wet dentin [2,3].Dentin is a hydrated biological dynamic compositwhich consists of30% water and organic materials and 7...
0% minerals [11;12]. A weak bonding between the restorative materials and dentin results in problems such as secondary caries, sensitivity after restoration, colour change and micro leakage. Several mechanisms are involved in the adhesion between dental adhesives and tooth structure including physical adsorption, micro mechanical interlocking, chemical and ionic bonding and acid base interactions[7;8]. In the developments of dental adhesives attempts have been made to improve the mechanisms or to impart more mechanisms in the adhesion providing a stronger and more reliable bond for adhesive dentistry.

2. Materials and Methods

The monomer system can be viewed as the pillar of the composite resin system. Bis-GMA (bisphenol glycidyl methacrylate) and TEGDMA (triethylene glycol dimethacrylate) continue to be the most used monomers for manufacturing present-day composites [7]. Recent studies reveal introduction of zirconia as filler for improvement in mechanical properties. The resin matrix was a visible light cured system composed of Bis-GMA (Bisphenol A Glycidyl Methacrylate) and TEGDMA (Triethylene glycol dimethacrylate) as matrix and Nano filler amounts of percentage volume shown in table 1 the resin specimens were polymerized by means of the ICI light. The light output was monitored before and after use by means of a light meter designed to measure the output in the critical wave length range. Minimal acceptable output was established at 1200 W/m². The nano hybrid fillers were: silica, hydroxyapatite and Zirconia with varying volume percentage as mentioned in table 1.

| Process parameters | Level 1 | Level 2 | Level 3 |
|--------------------|---------|---------|---------|
| Hydroxyapatite%    | 5.8     | 11      | 15.4    |
| Zirconia%          | 4.7     | 9.6     | 14.3    |
| Silica%            | 4.1     | 7.8     | 12.7    |

Table 1 Percentage of filler volume at each level.

| Experiment number | Filler volume levels | Flexural strength | Signal to noise Ratio |
|-------------------|----------------------|-------------------|----------------------|
|                   | Hydroxyapatite | Zirconia | Silica | 75.91 | 37.606 |
| 1.                 | 1               | 1        | 1      | 41.92 | 32.448 |
| 2.                 | 1               | 2        | 2      | 30.55 | 29.700 |
| 3.                 | 2               | 3        | 3      | 44.83 | 33.031 |
| 4.                 | 2               | 1        | 2      | 54.98 | 34.804 |
| 5.                 | 2               | 2        | 3      | 32.05 | 30.116 |
| 6.                 | 3               | 1        | 3      | 34.26 | 30.695 |
| 7.                 | 3               | 2        | 1      | 19.28 | 25.702 |
| 8.                 | 3               | 3        | 2      | 75.91 | 37.606 |
| 9.                 | 3               | 3        | 2      | 41.92 | 32.448 |

Table 2 Taguchi L9 orthogonal array for flexural strength.

One more filler which was responsible for improvement in mechanical properties was Zirconia. Presently few commercially available dental composite is using Zirconia Nano clusters. So in addition to silica and hydroxyapatite we have added Zirconia nanoparticles as filler. Matrix used his combination of the following components: 1) bisphenol A glycidyl methacrylate (Bis-GMA)
2) triethylene glycol dimethacrylate (TEGDMA)
We have varied the volume fraction of the three fillers namely. 1) Hydroxyapatite. 2) Silica. 3) Zirconia

2.1 Preparation of test specimen for flexural strength:
The test specimens for flexural strength experimental composites were made by the following procedure. A hydroxyapatite rectangle of 25x3x3mm used as a mold for the preparation of a rectangular test specimen for flexural strength. Each mold was positioned upon polyester film of 0.1 mm thick. The mold was slightly overfilled with the test composite and all air bubbles were excluded. A second piece of polyester film was placed ont the material in the mold and covered with a hydroxyapatite plate, then pressure was applied gently, thus exuding excess material from the mold. Each of the 3 molds filled with the composite were prepared for flexural strength and placed in a visible light irradiation apparatus & irradiated for 15 min, then turned upside down and irradiated for another 15 min. The light-cured specimen was removed from its mold and stored in distilled water at 37°C for 24 hr prior to testing. The rectangular specimen was tested in a universal testing machine (Make-Autograph) & utilizing a crosshead speed of 1 mm/min. Three specimens of each experimental group were tested. The mean value of the three was accepted as an observed strength of the tested composite resin. The purpose of the study was to study the contribution of different filler particles of Dental composites in the market to investigate their mechanical properties and their filler contents.

2.2 Procedure adopted for testing Flexural strength:
The ASTM Standard adopted was ASTM D7264 [5]. We measured the width and thickness of the specimen on the performance of dental composite in general and flexural strength in particular. Experimentation was done and testing of all the leading commercially available brands to the nearest 0.01 mm (0.001 in.) at several points along its length. Calculate and record the minimum value of the cross-sectional area was calculated. We measured the length of the specimen and recorded the value. Test specimen was placed flexural testing machine. We move the crosshead of the testing machine until it just contacts the top of the tool plunger was adjusted. The test machine is equipped with an automatic recording device, record the complete load-deformation curve. After the yield point has been reached it may be desirable to increase the speed from 5 to 6 mm/min (0.20 to 0.25 in./min) and allow the machine to run at this speed until the specimen breaks.

2.3 Preparation of test specimen for flexural strength
We have taken three levels of filler volume percentages, Low, medium and high. These three levels are shown in table 1. We have varied the three levels of the volume percentage of silica, hydroxyapatite and Zirconia. By L9 (Taguchi’s orthogonal array) we have nine experimental composites. For each trial three readings are taken and the average flexural strength is calculated. The graphs for each filler and flexural strength is plotted keeping the other volume percentage constant, to study the contribution of each filler in the flexural strength. Then we have calculated Regression equation for each mechanical property and Analysis of variance (Table No 2) and Sensitivity analysis (Table No 3) for each mechanical property.

![Figure 1 experimental setup for flexural strength](image-url)
2.4 Taguchi experiment: Design and analysis
Traditional experimental design procedures are too complicated and not easy to use. When the number of process parameters are increases, at large number of experimental works have to be carried out. Dr Genichi Taguchi has designed a method which reduces the number of experiments by the use of an orthogonal array. The information the behaviour of the process is obtained from a plan of experiments with the objective of acquiring data in a controlled way. This design of high-quality system called Taguchi’s design method which reduces efforts of conducting a number of experiments, thus saving time and cost and enabling discovery significant factors quickly. But the main advantage of Taguchi’s method is by conducting less experiments, we get a reliable result and also the higher the value of sum of square of an independent variable, the more it has influence on the performance parameter. One can also calculate the ratio of individual of square of a particular

Independent variable to the total sum of squares of all the variables. This ratio gives the percent contribution of the independent variable on the performance parameter. In addition to above, one could also find the optimal solution to the problem. A statistical analysis of variance (ANOVA) and signal to noise ratio (S/N ratio) can be employed to study the influence of different filler volume percentages on flexural strength values. Following are the steps followed in Taguchi’s optimization study (Taguchi 1990; Ross 1996). (1) Select noise and control factors. (2) Select Taguchi orthogonal array. (3) Conduct experiments and measure the flexural strength for each of the experimental composites. (4) Analyse results (signal-to-noise ratio). (5) Predict optimum .(6) Confirmation experiment.

2.5 Planning of experiments:
Here Taguchi method is used, which includes the experiment design theory and the quality loss function concept. The degrees of freedom for three parameters in each of three levels were calculated as follows: degree of freedom (DOF) = number of levels – 1. For each factor, DOF is as follows: for hydroxyapatite DOF= 3 – 1 = 2; for zirconia, DOF = 3 – 1 = 2; for silica, DOF = 3 – 1 = 2. Taguchi L9 orthogonal array was used, which has three columns at three levels and nine rows corresponding to the number of tests [11]. Nine experiments were conducted at different parameters in this study. L9 orthogonal array has eight DOFs, in which six were assigned to three factors (each one 2 DOFs) and two DOF were assigned to the error. Table 4 shows the degree of influence of the process parameters, i.e. the filler content (volumetric percentage), three factors each at three levels, are taken into account [11]. The flexural strength was tested for each experimental composite with filler volume percentage corresponding to each level. The flexural strength values corresponding to each experimental composite are shown in table 2.

3. Results and discussion
3.1 Regression analysis:
A mathematical model was developed with the volumetric percentages of three fillers in the composite, namely, hydroxyapatite, zirconia and silica and its effect on the flexural strength. The correlation between factors (hydroxyapatite, zirconia, silica and flexural strength) was obtained by multiple linear regressions. To derive the models, the standard commercial statistical software package ‘MINITAB’ is used

\[
CS = 31.733 + 1.518 A_1 + 0.917 A_2 - 2.435 A_3 + 2.044 B_1 + 1.183 B_2 - 3.227 B_3 + 1.340 C_1 - 1.340 C_2 - 0.000 C_3
\]

3.1a Analysis of the signal to noise ratio: For the minimization of quality characteristic variation due to uncontrollable parameters the response variation is studied using signal-to-noise ratio (S/N ratio) as enumerated in Taguchi method. In the dental composites, larger flexural strength will be better, so the flexural strength was considered as the quality characteristic and the concept of ‘the larger-the-better’ [11] was used. The S/N ratio used for this type response is taken as ‘larger-the-better’ and given by the relation

\[
S/N = - 10 \log_{10} \left( \frac{1}{n} \sum \frac{1}{y^2} \right) \quad (1)
\]

Where y is the measured value in a run/row and n the number of measurements in a trial/row (n = 1 in this case). Equation (1) was used to calculate the S/N ratio. The S/N ratios and the corresponding values of flexural strength are shown in table 2. For the volumetric percentages of hydroxyapatite zirconia and silica concentrations, the flexural strength response table and the rank are shown in table 3. A greater S/N ratio value will give better performance, irrespective of the performance characteristic. The greater S/N ratio value will give the optimum level filler volume percentage. The optimal flexural strength was obtained at hydroxyapatite= 5.8 (level 1), zirconia= 4.7 (level 1), silica= 4.1 (level 1), based on the analysis of the S/N ratio.

Larger is better
The effect of the process parameters on the flexural strength is shown in figure 1, which is evaluated using statistical software package MINITAB.

### 3.2 Analysis of variance (ANOVA)

For finding out the differences in the average performance of the groups of items tested, a statistical tool named ANOVA, which is an objective decision-making tool is used. At a specific confidence level, the mean square is compared with an estimate of experimental error in ANOVA. The interaction and significance of all the main factors are tested. The following equation is used to find out the total sum of squared deviations $SST$ from the total mean S/N ratio, $n_m$

$$SS_T = \sum_{i=1}^{n} (n_i - n_m)^2 \quad (2)$$

where $n_i$ is the mean S/N ratio for the $i$th experiment and $n$ the number of experiments in the orthogonal array.

For calculation of $P$, i.e. percentage contribution

$$P = \frac{SS_d}{SS_T} \quad (3)$$

where $SS_d$ the sum of the squared deviations. Table 4 shows the results of ANOVA. To find out the significance of a factor, a ratio of the mean square error to the residual error is taken and called as $F$-ratio, named after Fisher. Fisher test is used to study the significant effect on quality characteristic by the design parameters. To study the effect of the filler volume percentage on the flexural strength we use the percentage (%) shown in table 4. From table 4, it can be seen that nano filler hydroxyapatite has 26.97%, zirconia has 44.15% and silica has 12.48%, which influences on the flexural strength, respectively.
Table 4. Analysis of variance (ANOVA) results for FLEXURAL strength of dental composite.

| Source | DF | Adj SS | Adj MS | F-Value | P-Value | Total % |
|--------|----|--------|--------|---------|---------|---------|
| A      | 2  | 579.3  | 289.6  | 1.65    | 0.3     | 26.97   |
| B      | 2  | 948.2  | 474.1  | 2.69    | 0.2     | 44.15   |
| C      | 2  | 268.0  | 134.0  | 0.76    | 0.5     | 12.48   |
| Residual | 2 | 351.8  |        |         |         | 16.38   |
| Total  | 8  | 214.7  |        |         |         | 100     |

Table 5. Fillers used in the experimental dental composite.

| Experimental dental composite no. | Filler volume percentages |
|----------------------------------|---------------------------|
|                                  | Hydroxyapatite | Zirconia | Silica |
| 1                                | 5.8            | 4.7      | 4.1    |
| 2                                | 5.8            | 9.6      | 7.8    |
| 3                                | 5.8            | 14.3     | 12.7   |
| 4                                | 11             | 4.7      | 7.8    |
| 5                                | 11             | 9.6      | 12.7   |
| 6                                | 11             | 14.3     | 4.1    |
| 7                                | 15.4           | 4.7      | 12.7   |
| 8                                | 15.4           | 9.6      | 4.1    |
| 9                                | 15.4           | 14.3     | 7.8    |

3.3 Confirmation test:
Taguchi strongly recommended a confirmation test for verifying the results [11;14]. The experiments are conducted with the optimum conditions and the strength is found. This flexural strength is compared with that calculated value using the relation enumerated above. We had obtained optimum filler volume as A1B1C1 and the flexural strength found experimentally was 71 MPa.

4. Conclusions
(1) In our study, we have prepared a experimental dental composite. Contemporary dental composite use hydroxyapatite and silica individually or in combination as fillers. Zirconia was introduced as nano filler. We have used three nanofillers, namely, hydroxyapatite, zirconia and silica in combination (conglomerate).
(2) It is observed that the influence of zirconia as a filler material on experimental dental composite is very significant and highest in our study, effect of zirconia on flexural strength being 44.15%. Statistical results (at a 95% confidence level) show that the zirconia, hydroxyapatite, silica affect the flexural strength by 44.15%, 26.97% and 12.48% of the experimental dental composites.
(3) Statistically designed experiments based on Taguchi methods were performed using L9 orthogonal arrays to analyse the flexural strength as a response variable. Conceptual S/N ratio and ANOVA approaches for data analysis drew similar conclusions.
(4) In this study, the analysis of the confirmation experiment for flexural strength has shown that Taguchi parameter design can successfully verify the optimum filler volume percentages (A1B1C1), which are hydroxyapatite = 5.8% (A1), zirconia = 11% (B1) and silica = 15.4% (C1).
(5) The confirmatory experimental tests results are matching with the optima value of flexural strength calculated.

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