Physical and mechanical properties analyses of zirconia reinforced experimental nanohybrid dental composite (NHDC) from rice husk

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Abstract

Reinforcement of zirconia into dental composite is developed to improve strength. This study aimed to analyze the effects of zirconia on Vickers hardness (VHN), microstructure, compressive strength (CS), and degree of conversion (DC) of experimental nanohybrid dental composite (NHDC). Specimens were prepared according to zirconia reinforcement and mixing methods: Negative control (without zirconia), Mixing method I (3 wt % zirconia), Mixing method I (5 wt % zirconia), Mixing method II (3 wt % zirconia), Mixing method II (5 wt % zirconia), and Positive control (Filtek Z250; 3M ESPE). VHN, CS and DC were analyzed using hardness tester, universal testing machine, and Fourier transform infrared (FTIR) spectroscopy, respectively. VHN were significantly increased (3 wt % and 5 wt %) ($p < 0.001$). DC was reduced; however, DC values were all above the acceptable 60 %. An increased compressive strength with the zirconia (3 wt % and 5 wt %) compared to negative control, however the differences were not statistically significant ($p > 0.05$). Representative scanning electron microscopy micrographs revealed a pattern of homogenous distribution of the filler in all samples. There was no significant difference in physical and mechanical properties between NHDCs fabricated using different mixing methods. Zirconia reinforcements may increase the CS and VHN of NHDC, without compromising the DC.

Keywords: Nanohybrid composite, zirconia, physical and mechanical properties

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Introduction

Composite resin is a synthetic resin usually acrylic based, to which a glass or natural silica filler has been added. It is used mainly in dental restorative procedures. Composite resin possesses the aesthetics of a real tooth and is physically stable. Fillers directly affect physical properties. Therefore, resin composites are classified according to filler features. The introduction of well-dispersed inorganic particles into a resin matrix has proven to be extremely effective in improving the performance of polymer composites [1, 2]. Fillers used in dental resins can directly affect the property of a composite resin. Some of these properties are radiopacity, wear resistance and elastic modulus [3]. Hence it is known that, the nature and characteristic of a filler particle in composites can determine its mechanical strength and the wear resistance [4].

Due to the significant differences a filler can make, resin composites have been classified according to filler features, such as type, distribution or average particle size [5]. There has been an introduction to nanohybrid and nanofilled composites in addition to the traditional composite materials which are microhybrid and macrofilled. These two new types of composite provide a superior polish and gloss retention [6]. In this study, a nanohybrid composites has been produced for the testing of its mechanical property upon the introduction of additional filler in terms of types and percentage. Nanohybrids take the approach of combining nanomeric and conventional fillers [7]. Nanohybrids have the strength and the durability of hybrid composites while attaining the superior aesthetics of nanofilled composite. For this particular study, an experimental nanohybrid composite that utilizes silica from biomass waste as a filler. The silica was extracted from rice husk through precipitation using acids. A silica filler with a small surface area is produced for the best mechanical property in a composite. From this study, a nanohybrid composite can be produced, however, it remains inferior to that of a commercialized composite resin [8]. This experimental NHDC requires further work to improve its mechanical and physical properties. Since the modification and reinforcement of fillers has been shown to improve the dental composite properties [9, 10], this study focused on the role of zirconia as a reinforcement filler in modifying the experimental NHDC properties.

To determine whether the effect of additional zirconia fillers in the composite can improve the experimental nanohybrid dental composite mechanical property, zirconia is added at different percentages and at different sequences to produce a new type of composite for further testing. This is because it is known that the shape, amount and size of particles reinforcing the composite can clearly affect the property [11]. As there are lesser interparticle spacing when finer particles are used, the softer resin matrix will be protected and prevented from filler plucking. [12]. As an example, a positive effect of the presence of nanofiller particles was observed by an improvement in flexural strength, surface hardness and fracture toughness [13, 14, 15]. Zirconia became the choice of filler used for the improvement of the experimental composite as it is a super hard material and translucency. This is credited by its peculiar atomic arrangement which gives it such a mechanical property [16].

An optimal degree of dispersive and distributive mixing is vital for polymer processing and the main problem is to disperse fillers uniformly into the polymer matrix [17, 18]. This study was aimed to evaluate the property of zirconia on an experimental silica reinforced nanohybrid composite at different percentages and with different mixing methods on Vickers hardness, surface microstructure using scanning electron microscopy (SEM) coupled to energy dispersive X-ray spectrometry (EDS) and compressive strength, as well as degree of conversion.

Materials and Methods

Materials

Silanated nanosilica was produced after purification from rice husk. Bisphenol A glycidyl methacrylate (BisGMA) (Esstech, Inc., Essington, PA, USA) and triethylene glycol dimethacrylate (TEGDMA) (Sigma-Aldrich, USA) dental resins, zirconium oxide nanopowder (ZrO_2, 99+%, 40 nm) (US Research Nanomaterials, Inc., USA), DL-champhor-quinone (CQ) (Merck, Schuchardt OHG, Germany) and (2-dimethylaminoethyl)-methacrylate (DMAEM) (Merck, Schuchardt OHG, Germany) were mixed with silanated nanosilica.

Fabrication of experimental NHDC

Nanohybrid dental composites were prepared using silanated nanosilica filler particles derived from rice husk as shown in Figure 1. Characterization of the silaned nanosilica was done with scanning electron microscopy (SEM). Zirconia was incorporated into the nanohybrid dental composite for improvement of physical and mechanical properties.

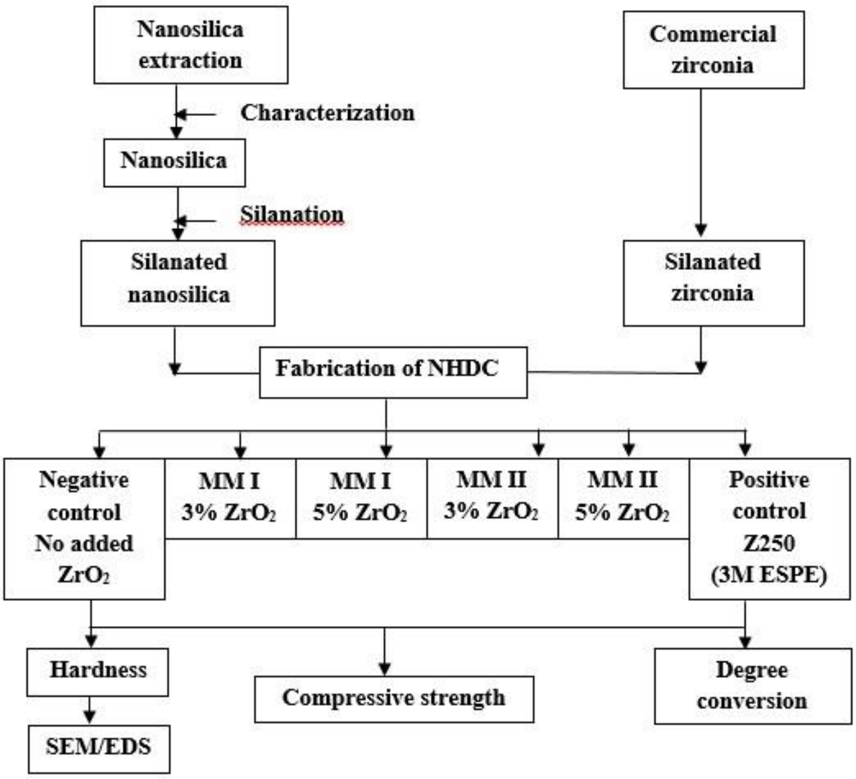

Figure 1 Flow chart of study design

The experimental NHDC was fabricated with a filler/matrix ratio of 50/50. The resin matrix of BisGMA and TEGDMA (60/40), 0.5 wt% CQ, and 0.5 wt% DMAEM were added and mixed into a porcelain dish. The silanated nanosilica and ZrO_2 nanopowder were added into the mixture by hand spatulation according to the formulation described in Table 1. This new NHDC paste was vortexed for 2 minutes and then, placed in porcelain dishes and covered with aluminium foil.

Table 1 Formulation of experimental NHDC

Groups	Filer/Resin (50/50)		
	Filler loading (%)		Resin
	Silica	Zirconia	
CTR	50	-	BisGMA/TEGDMA (60/40)
MM I 3%	47	3	
MM I 5%	45	5	
MM II 3%	47	3	
MM II 5%	45	5	
Z250	N/A	N/A	

The experimental NHDC were divided into 4 groups based on the percentage of zirconia filler reinforcements and mixing method used: Mixing method I, (MMI 3 wt % zirconia), Mixing method I (MMI 5 wt % zirconia), Mixing method II (MMII 3 wt % zirconia), Mixing method II (MMI 5 wt % zirconia). Experimental NHDC without zirconia reinforcement (CTR) was use as negative control, and commercial dental composite resin, Filtek Z250 (3M ESPE, USA) was used as positive control. These experimental NHDCs were then subjected to the test for the evaluation of their physical and mechanical properties: Microhardness test, SEM/EDS analyses, compressive strength, and degree of conversion.

Microhardness Test

A total of 60 disks were prepared by placing the composite resin into a plastic mold of 5 mm diameter × 2 mm height. Both surfaces were covered with slide glasses and LED-based dental light curing unit (Celalux II; Voco, Germany) for 60 seconds, using a light beam directed at the top and bottom surfaces for 30 seconds each. Then, each specimen was polished using silicon carbide abrasive papers (Sof-Lex discs; 3M ESPE, St Paul, MN) with increasing grit sequence from course, fine and extra-fine. The set specimens were then stored in distilled water for 24 hours at 37 °C to mimic the natural intraoral environment. After which, Vickers hardness was evaluated with a microhardness tester (VM-50, Fuel Instruments & Engineering PVT. LTD., India). A load of 9.81 N was applied to the resin disks for a dwell time of 15 seconds, and the scores were recorded in hardness Vickers (HV). The test was performed 30 times for every restorative composite resin, and the procedure was divided into 10 indentations for each resin disk. Descriptive statistics, including the mean and standard deviation, were calculated, and Tukey's post hoc multiple comparison test (one-way analysis of variance) with significance predetermined at $P<0.05$ was carried out.

SEM/EDS Analysis

Based on the results of the microhardness test, the specimen with the value that was closest to the mean value was selected and sent for scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) testing.

Before viewing the specimen under the SEM (Quanta 650 SEM, FEI, Germany) and xT microscope control SEM software, a sputter coating was needed to improve contrast and make it electrically conductive for SEM analysis. The SEM images of a specimen for each study group were recorded at magnification of 20,000x.

Compressive Strength Test

For compressive strength test, the samples consist of 10 cylindrical specimens from each study group with measurement of 4mm in diameter x 6mm of height. All 60 samples were tested using Instron Universal Testing Machine (Shimadzu, AGX-2 plus) at a crosshead speed of 1mm/min.

Degree of Conversion Test

For degree of conversion test, the samples consist of five specimens from each study group with measurement of 8-10mm in diameter x 0.10-0.15 mm of height or thickness. All 30 samples were tested using Fourier transform infrared (FTIR) spectroscopy.

Results and discussion

Spherical shaped filler particles and the variation of the particle size are factors that could influence the properties of the dental composite. The silica particles obtained for the experimental nanohybrid dental composite based on previous studies are dense and spherical in shape. At a feed rate of 1 ml/min, the silica particles are perfectly spherical in shape with a size range of 54–414 nm [19]. In comparison to several commercial dental composites. The hybrid or nanohybrid spherical shape of the filler allows an increased filler load to improve the mechanical properties [20]. Figure 2 shows SEM micrographs of nano-porous silica particle at magnification of 20,000x and 100,000x.

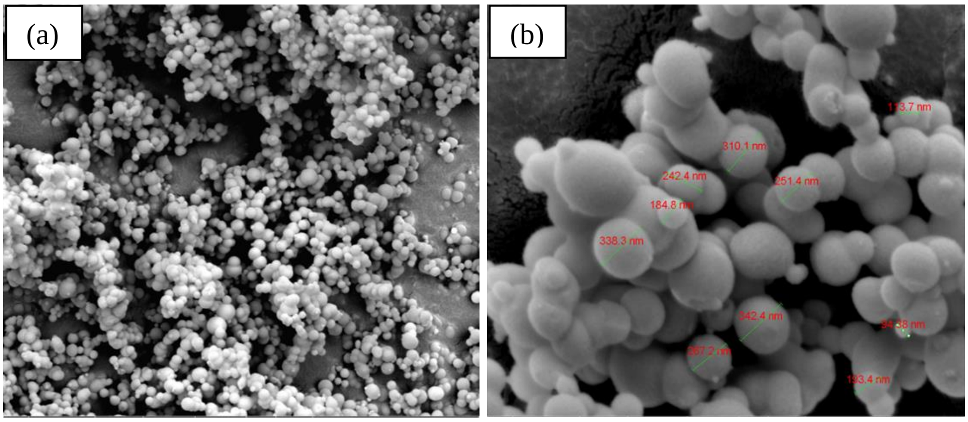

Figure 2 SEM micrographs of nanosilica particle on magnification (a) 20, 000x and (b) 100, 000x

This study was carried out to determine if zirconia fillers were able to help increase the mechanical property, Vickers hardness of experimental nanohybrid composite dental composite from rice husk. Silica was extracted from rice husk to be used as a filler to produce an experimental nanohybrid composite. However, the inferior mechanical property provides room for modification and improvement to produce a commercially acceptable composite. Table 2 shows the mean (SD) values of Vickers hardness for each group of specimens. There is a linear increase of the Vickers hardness upon the addition of filler percentages from 3% to 5%. It is also important to note that the increase of Vicker's hardness as compared to that of the control group shows a significant increase. However, the Vicker's hardness remains inferior to that of a commercially available composite (Filtek Z250, 3M ESPE).

Table 2 Vickers hardness (VHN) of the experimental NHDC

Composite	Mean VHN (SD)	F statistic[a] (df)	*p* value[a]
CTR	16.290 (2.152)		
MM I (3%)	28.520 (2.486)[b]		
MM II (3%)	30.950 (2.051)[b]	1747.629 (5, 54)	< 0.001
MM I (5%)	39.420 (1.834)[c]		
MM II (5%)	42.100 (2.508)[c]		
Z250	95.090 (1.164)		

Statistical significance of differences among groups was determined using One-way ANOVA[a], followed by post-hoc Tukey's test. Significance level set at $p = 0.05$. The same letter indicates a statistically significant difference ($p < 0.05$).

In terms of the different mixing method, it is noted that there is a slight but insignificant increase in the Vicker's hardness. Mixing method II which incorporates the zirconia into the experimental nanohybrid dental composite at the end of the mixing shows a more superior mechanical property. However, based on a different study, zirconia is a major contributing factor in the improvement of mechanical property of dental composite. It is undoubted that an increase of filler increases the overall mechanical property. However, Further, we can find out the exact volume percentage of zirconia, silica and glass which will give maximum effect in the improvement of mechanical properties [16]. This can be done by using optimization procedures to distinguish which filler can play a larger role in determining the overall Vickers hardness.

Based on the results produced, it is proven that there is an increase in hardness of nanohybrid dental composite upon zirconia reinforcement. This increase applies to both 3% and 5%. This result shows an alignment with previous study that hardness increases as filler content increases [21]. Although zirconia has been proven to increase the physical properties of dental composite [22], this study does not prove whether it is zirconia itself that increased the hardness, or it is due to the overall increase in filler volume that lead to the increase in hardness of the nanohybrid dental composite. When comparing the zirconia reinforced experimental nanohybrid dental composite to the commercially available dental composite (Z250, 3M ESPE), it is proven from the results that the hardness is significantly inferior. However, the loading method may need to be improved, besides the need to increase filler volume up to 60% which is the highest volume allowed for a round filler particle such as zirconia [23].

To ensure that zirconia fillers can provide its maximum positive effect on the properties of the experimental nanohybrid dental composite, it is ensured that the zirconia are spherical in shape as well. This is because spherical equiaxial fillers are free from tangling from other fillers or each other. This allows a more homogenous dispersion of filler within a composite matrix [24]. When compared with irregular filler particles, composite with spherical fillers show lower shrinkage stress values. This is due to the increase in the dispersion of fillers within the matric where stress can be evenly distributed [25].

The preparation of the zirconia reinforced experimental nanohybrid composite was done by a single operator. This allows the mixing and preparation of the composite to be standardized where the force and mixing is similar. The force and direction of mixing can alter the distribution of the filler content in the composite if the operators are changed for each composite. This is because the processing method, morphology and filler dimensions, microstructure of the matrix, and matrix/filler interaction can affect the mechanical properties of composite materials [26]. A good degree of dispersive and distributive mixing is very important for polymer processing and the main problem is to disperse fillers uniformly into the polymer matrix [17, 18]. Hence, this study justifies the use of only a single operator throughout the study. Other than that, the operations of the Vickers hardness tester should also be carried out by the same operator as it requires a similar set up of the pyramid indentor in terms of distance for each specimen. Hence, this precaution ensured that mixing does not cause any significant differences in increase of hardness.

Figure 3 (a) and (b) shows that the fillers of the control group and MM I 3% zirconia are spherical in shape. The energy dispersive X-ray spectrometry (EDS) of the control group shows that there is a high concentration of silica filler. The silica filler is noted to be homogenously distributed in the composite. Figure 3 (c) shows spherical fillers between irregularly shaped fillers at 20,000X magnification. It is noted that silica fillers are more homogenously distributed as compared to that of zirconia fillers. The zirconia fillers show tendency to agglomerate in certain regions which cause for a less homogenously distributed pattern.

A combination of relatively small and varied size fillers allows a denser packing which in turn increases the possible filler volume-fraction of the resin-composites [27, 28]. Hence, an idea is to produce differently sized silica fillers through different feed rate and mixing speeds. From this mixture of different sizes, it is possible that there can be an increase in mechanical property when zirconia fillers of the similar percentages are added. Spherical fillers are less noticed in the MM II 3% zirconia group and MM II 5% zirconia as shown in Figure 5 (d) and (e). It is also shown in Figure 5 (f) that fillers are homogenously distributed with high concentration of zirconia filler.

Table 3 shows the compressive strength (MPa) of the study groups. Zirconia reinforcement in this study shows an increase pattern of compressive strength of nanohybrid dental composite. However, the increase of compressive strength of nanohybrid dental composite is not significant and unfortunately the compressive strength values are still much more inferior compared to the commercially available dental composite resin.

From this study, we found out that there was a pattern of increased compressive strength of nanohybrid dental composite upon 3% of zirconia reinforcement. However, upon adding another 2% of zirconia, which makes it to 5% of zirconia reinforcement, there was no changes found in the compressive strength of nanohybrid dental composite. Although zirconia has been proven to increase the compressive strength [22] but we are not sure whether zirconia itself or the increased total filler volume that actually leads to the increased of compressive strength.

When comparing the compressive strength of zirconia reinforced experimental nanohybrid dental composite to the commercially available dental composite (Z250, 3M ESPE), it has been proven that the result is significantly inferior. This is expected due to the overall higher filler content as compared to the nanohybrid dental composite. Based on the data, it shows that zirconia reinforcement has potential in improving the physical and mechanical properties of the nanohybrid dental composite. However, there may be a need of modification in the filler loading method [29].

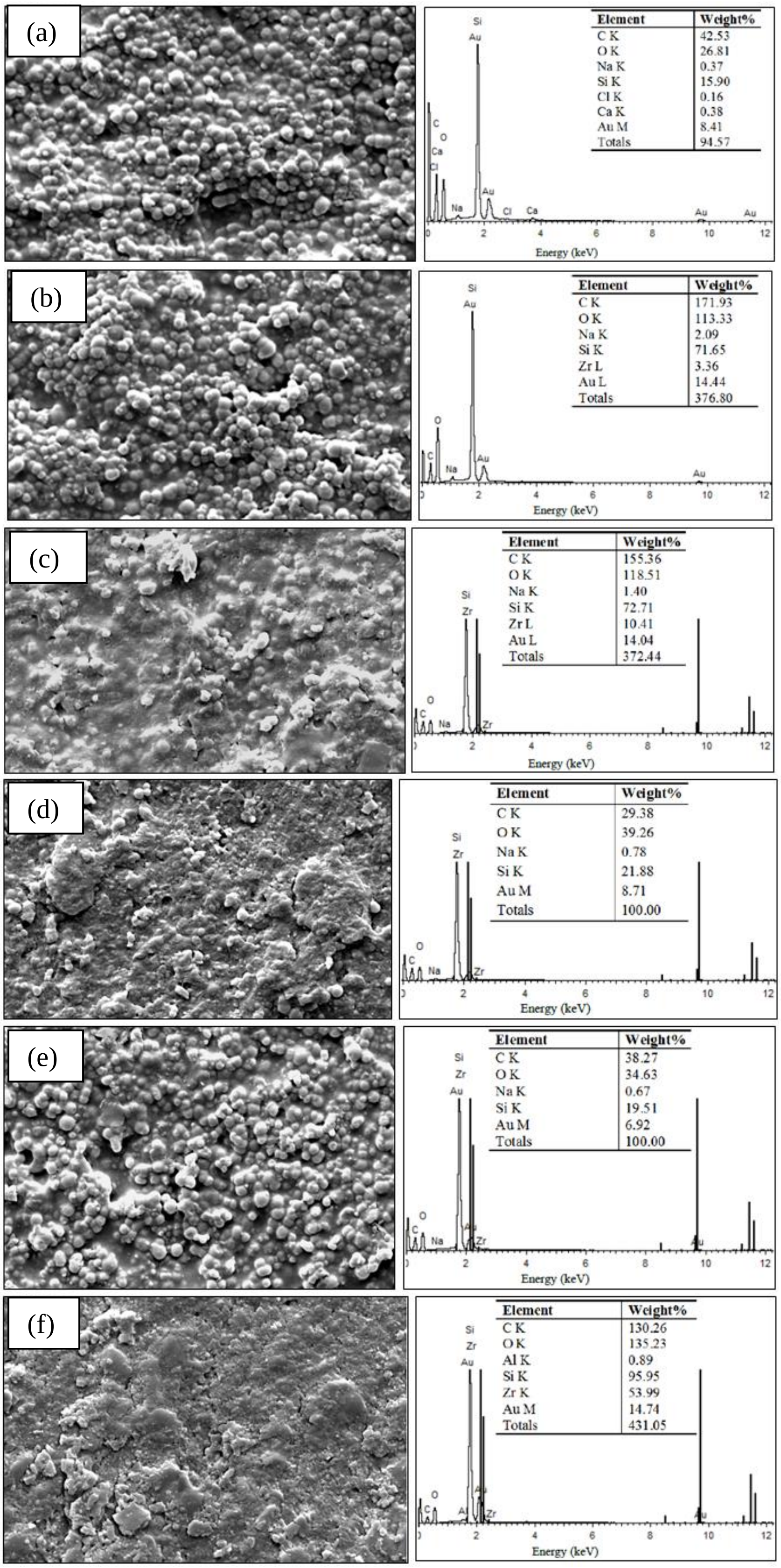

Figure 3 Representative of SEM micrographs on magnification of 20, 000x and EDS results: (a) CTX, (b) MM I 3% ZrO_2, (c) MM I 5% ZrO_2, (d) MM II 3% ZrO_2, (e) MM II 5% ZrO_2, (f) Z250 (3M, ESPE)

Table 3 Compressive strength of composite materials

Composite	Compressive strength (MPa) Mean (SD)	F statistic[a] (df)	*p* value[a]
CTR	132.838 (16.133)[bc]		
MM I (3 %)	188.326 (29.117)[bc]		
MM I (5 %)	176.768 (17.401)[c]	23.889	< 0.001
MM II (3 %)	167.027 (41.205)[c]	(5, 54)	
MM II (5 %)	161.951 (32.645)[c]		
Z250	316.303 (78.923)[c]		

Statistical significance of differences among groups was determined using One-way ANOVA[a], followed by post-hoc Tukey's test. Significance level set at *p* = 0.05. The same letter indicates a statistically significant difference (*p* < 0.05).

Zirconia reinforcement in this study shows decrease in degree of conversion of nanoybrid dental composite as shown in Table 4. This is expected as based on the previous study, filler was shown to reduce the degree of conversion of composite resins [30].

Table 4 Degree of conversion of composite materials

Composite	Degree of conversion (%) Mean (SD)	F statistic[a] (df)	*p* value[a]
CTR	71.778 (3.887)[bcde]		
MM I 3 %	61.840 (3.700)[b]		
MM I 5 %	64.998 (3.791)[c]	7.254	< 0.001
MM II 3 %	63.454 (2.321)[d]	(5, 24)	
MM II 5 %	60.952 (2.895)[e]		
Z250	66.191 (2.437)		

Statistical significance of differences among groups was determined using One-way ANOVA[a], followed by post-hoc Tukey's test. Significance level set at *p* = 0.05. The same letter indicates a statistically significant difference (*p* < 0.05).

Although the degree of conversion decreases with zirconia reinforcement, the values of degree of conversion of the experimental groups in this study are still above 60% which is the acceptable value (60 to 80%) for dental composite resin [31]. Even with the overall increase in the mechanical property of the experimental nanohybrid dental composite, it is still inferior to that of a commercially available dental composite. Besides, the experimental nanohybrid dental composite is considerably less aesthetic due to its opaque appearance. Further studies and modifications can be done in order to improve the aesthetic of the composite so that is can be readily accepted by patients. In addition to only have zirconia as a reinforcement for the experimental nanohybrid dental composite, it is wise to consider a different filler in addition to the nanosilica that is extracted from rice husk.

Conclusions

Zirconia fillers are able to increase the Vicker's hardness of the experimental nanohybrid dental composite (NHDC). However, we may need to improve on the filler loading method and probably increase the total filler volume up to 60%, which is the highest volume allowed for round filler particles of zirconia. Zirconia reinforcement has potential in improving the mechanical and physical properties of NHDC.

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Author Contributions

All authors contributed to research design and execution, outcomes interpretation, and manuscript writing.

Disclosure of Conflict of Interest

The authors declare no conflicts of interest in this work.

Compliance with Ethical Standards

The ethical approval has been obtained from the Human Research Ethics Committee, Universiti Sains Malaysia (USM/JEPeM/17020137).

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