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Characterisation and properties of Nanohybrid Dental Composite (NhDC) reinforced with zirconia and alumina

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A trial nanohybrid dental composite (NHDC) was developed using silica extracted from biowaste rice. **Aim:** This study aims to test the effect of mixture of the silica and other filler which is zirconia and alumina, focusing on the characterization and their properties. Nano-silica obtained from rice husk was used as NHDC filler. **Methods:** Nanosilica white powder, derived from rice husk, was used. There were three groups: Group I, Zr (2%) and Al (3%); group II, Zr (3%) and Al (2%); and group III, Zr (3%). The distribution of filler particles and the chemical structure of filler particles were determined by FESEM images and FTIR test. Then, testing on Vickers hardness (VHN) and fracture strength (FS) of the samples was performed. **Results:** The distribution of filler particles showed a uniform distribution, and each peak element of the fillers was shown in the FTIR spectrum images. There was significantly increased on VHN and FS after addition of zirconia and alumina. **Conclusion:** This study concluded that zirconia and alumina strengthen the NHDC properties with addition of zirconia and alumina filler.

Keywords: Composite resins. Aluminum oxide. Zirconium. Spectroscopy, fourier transform infrared. Flexual strength.

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Introduction

Prior research improved dental composites in filler development till the 1990s. Filler sizes[1] and composition of dental fillers have changed dramatically over the years. Along with filler size and composition, the amount of filler[2] has been varied throughout a wide range[3]. Nowadays, resin composite consists of organic resins, inorganic fillers and initiator systems[4]. As coupling agents, silane derivatives are covalently linked to inorganic fillers to increase filler particle bonding[5,6].

The material of dental composite advancement can be classified into three categories: development of the filler phase, modification of resin monomers or introduction of new monomer systems[7], development of the initiator system[8] and introduction of new monomer systems[9,10]. The majority of dental composites used in dental restorations are made up of a resin matrix and silane-treated nonporous inorganic fillers in a variety of sizes and shapes[11]. In 1985, the average size of the inorganic filler was used to classify composite filling materials, and it remained the standard in subsequent studies[12]. In this study, we are employing zirconia and alumina as fillers in the reinforcement of dental composite, which is a limited study found. The characteristics of fillers were established using FTIR and FESEM equipment, and the properties will be evaluated using Vickers hardness and fracture strength.

Materials and Methods

i-Materials and Reagents

The experimental nanohybrid composite was prepared using resin matrix and filler at a 52/48 ratio. For the resin matrix, 50% urethane dimethacrylate (UDMA) (Merck KGaA, Germany) was used as a base-monomer and 50% TEDGMA (Sigma Aldrich, Germany) as a diluent. Three types of fillers were used in the study which were silica (SiO_2), zirconium oxide (ZrO_2) and aluminium oxide (Al_2O_3). This study used a sol-gel technique as in past study[13], nano-sized zirconia was purchased from US Research Nanomaterials (USA) and macro-sized alumina was purchased from Merck KgaA (Germany). Camphorquinone (CQ) (Merck Schuchardt OHG, Germany) and DMAEMA (Merck, Germany) also were added as visible light photo-initiator and co-initiator, respectively.

ii-Extraction of silica powder and silanisation

Rice husks were gently washed with water and dried in a 110°C hot air oven overnight[14]. The dried rice husks were treated to 1M HCl solution in a hot water bath for 90 minutes and dried again in a hot air oven. Then, 10% NaOH solution was added in the dried husk at 90°C to extract silica as described from a previous study[15]. All fillers were dried at 80°C in oven after silanisation using 6 wt.% γ-MPS. FTIR analysis was used for characterization.

iii-Fabrication of NHDC

Camphorquinone (0.01 wt.%) and DMAEMA (0.01 wt.%) was mixed in a matrix resin (UDMA/TEGDMA, 50/50 wt.%). The silanated fillers were added to the mixture and blended homogeneously.

The trial nanohybrid dental composite (NHDC) was grouped into three groups depending on the percentage of zirconia and alumina component: Group I, Zr (2%) Al (3%); Group II, Zr (3%) Al (2%); and Group III, Zr (3%) Al (0%). A negative control group was no addition of filler other than silica whereby commercial Z250XT (3M ESPE, St. Paul, MN, USA) was a positive control group.

iv- Characterisation and mechanical tests

The NHDCs were characterised using Fourier Transform Infrared Spectroscopy (FTIR), IRTracer 100 (Shimadzu, Japan) and FESEM (FEI Nova NanoSEM 450, US), followed by their mechanical tests.

Fracture Strength (FS) Test

To test FS, a split stainless steel mould (25 × 2 × 2 mm)[16-18] was used to prepare *n*=6 samples per group. All samples were cured using the light-emitting diode curing unit (Elipar™ Freelight 2 LED, 3 M ESPE). The samples were tested at a crosshead speed of 0.75 mm/min[14] using a universal testing machine (Model AG-X Plus Series Shimadzu, Japan) for FS test.

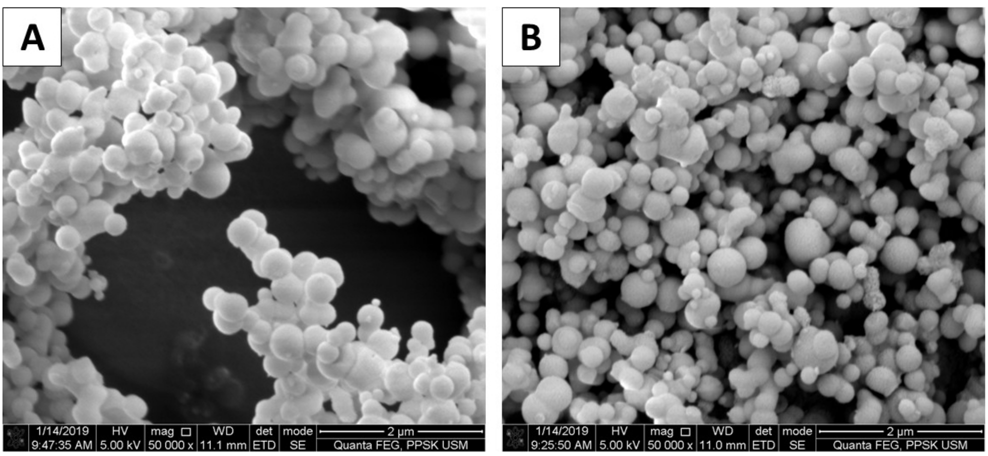
Vickers Hardness (VHN) Test

To test VHN, an acrylic mould (5 mm diameter and 2 mm thick) was used to prepare *n*=6 samples per group. All samples were tested for VHN using a Vickers' hardness tester (Model VM 50, FIE) with 1 kg load 15 seconds dwelling time[19].

Results

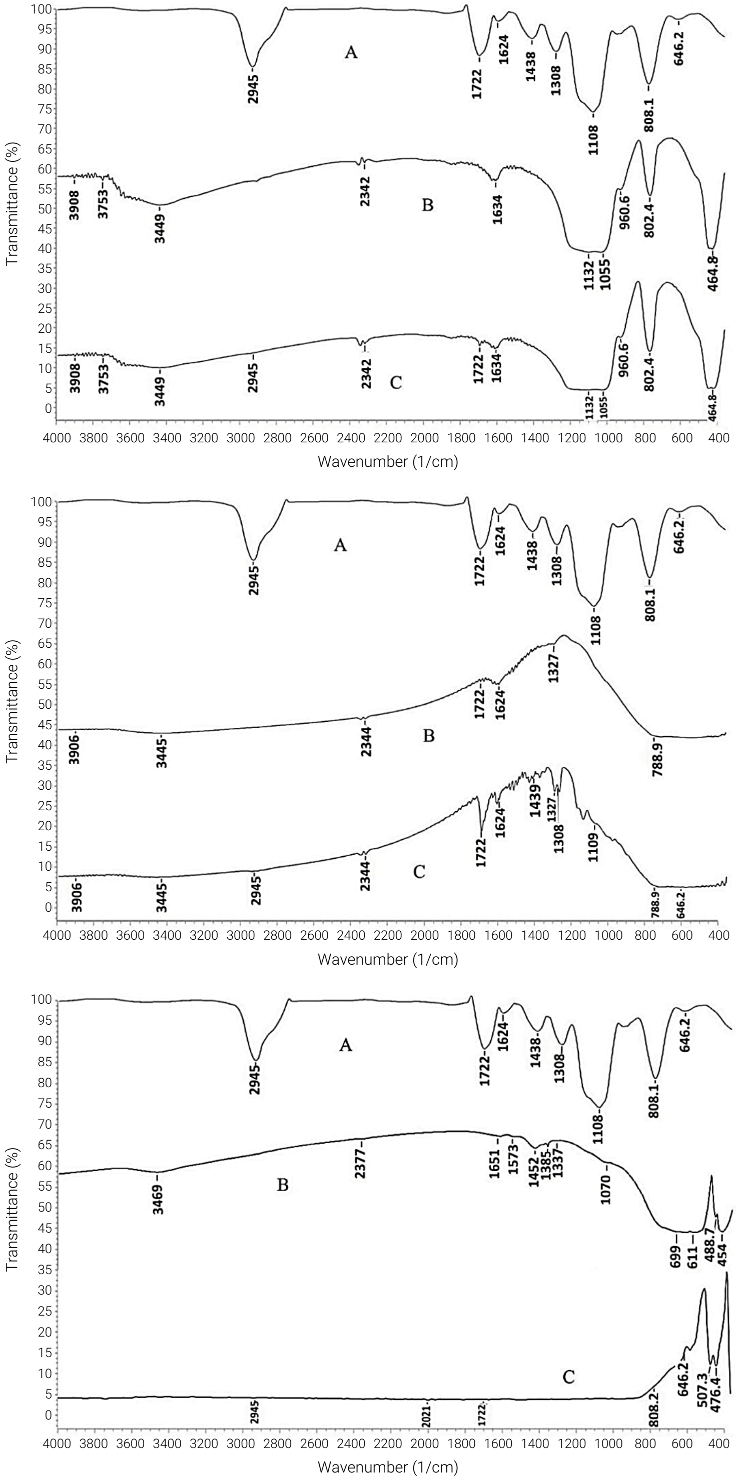
Characterisation of Silica Powder from Rice Husk

i-FESEM



(a) unsilaned silica powder (left) (b) silaned silica powder (right)
Figure 1. FESEM images of silica powder

ii-FTIR



(b) Zirconium oxide (ZrO_2) nanoparticles (c) Alumina (Al_2O_3) microparticles
Figure 2. FTIR spectra of fillers (a) Silica (SiO_2) nanoparticles

Fracture Strength

Table 1.Fracture strength evaluation of experimental NHDC

NHDC	Mean, MPa (SD)	F statistic (df)	p-value
No reinforced filler	73.387 (23.401)$^{\pi}$		
Reinforced Zr (3%) & Al (2%)	70.003 (3.453)$^{\pi}$		
Reinforced Zr (2%) & Al (3%)	80.943 (12.317)$^{\pi}$	9.560 (4,25)	p = 0.0001*
Reinforced Zr (3%) only	81.512 (16.253)$^{\pi}$		
Commercial Filtek™ Z250XT	127.325 (26.911)*		

Statistical significance of differences among groups was determined using One-way ANOVA, followed by post-hoc Tukey Test. *Significance level set at p = 0.05. The asterisk symbol (*) represents a statistically significant difference when compared to no reinforced filler NHDC (negative control). The pi constant symbol (π) represents a statistically significant difference when compared to Commercial Filtek™ Z250XT (positive control). SD = standard deviation; Zr = zirconia; Al = alumina

Vickers Hardness

Table 2. Vickers hardness evaluation of experimental NHDC

NHDC	Mean, HV (SD)	F statistic (df)	p-value
No reinforced filler	24.310 (4.040)$^{\pi}$		
Reinforced Zr (3%) & Al (2%)	29.250 (7.910)$^{\pi}$		
Reinforced Zr (2%) & Al (3%)	34.400 (11.080)$^{\pi}$	22.77 (4,25)	p = 0. 0001*
Reinforced Zr (3%) only	34.560 (2.730)$^{\pi,*}$		
Commercial Filtek™ Z250XT	61.760 (8.360)*		

Statistical significance of differences among groups was determined using One-way ANOVA, followed by post-hoc Tukey Test. *Significance level set at p = 0.05. The asterisk symbol (*) represents a statistically significant difference when compared to no reinforced filler NHDC (negative control). The pi constant symbol (π) represents a statistically significant difference when compared to Commercial Filtek™ Z250XT (positive control). SD = standard deviation; Zr = zirconia; Al = alumina

Discussion

Characterisation of Silica Powder from Rice Husk

i-FESEM

Figure 1 shows SEM images of the synthesized nanosilica before and after silanization at 50,000x magnification. Figure 1a (unsilane silica powder) shows that the surface silica is agglomerated and heterogeneous before silanization, while Figure 1b (silanized silica powder) shows that the treated silica surface is uniform and widely distributed.

ii-FTIR

Figure 2 depicts the FTIR spectra of the coupling silane agent γ-methacryloyltrimethoxypropylsilane (γ-MPS) (A), the filler untreated γ-MPS (B), and the filler treated with γ-MPS (C). Figure 2a depicts the silica's FT-IR spectrum. The intense peak at 1722 cm^{-1} in the γ-MPS spectrum reflects hydrogen bonding between silanol groups, and the band at 2945cm^{-1} represents the stretching vibrations of the CH_3 and CH_2 groups (Figure 2a A). The spectra of SiO_2 nanoparticles (Figure 2a B) showed the symmetrical stretching vibration of the siloxane bond, Si-O-Si, at 1055 cm^{-1}. The silanol Si-OH symmetry stretching and bending vibration bands, which are found at 802.4 cm^{-1} and 464.8 cm^{-1}, respectively. The findings of Halvorson et al.[20](2003) are compatible with the SiO_2 spectrum[20]. The presence of the stretching vibrations of C-H at 2945 cm^{-1} and C=O at 1722 cm^{-1}, in the spectra of the treated silica nanoparticles served as evidence that silica silanisation with γ-MPS was effective (Figure 2a C).

The strong peak at 1722 cm^{-1} points to hydrogen bonds between γ-MPS silanol groups (Fig. 2b A) in particles of zirconia. The symmetric and asymmetric stretching vibrations of γ-MPS's alkyl groups, CH_3 and CH_2, can be linked to the band at 2945 cm^{-1}. As mentioned by Zidan et al.[21](2021) the peak between 3650 to 3200 cm^{-1} were attributed to O–H (hydroxy group) bending vibration on the nanozirconia particles[21]. According to Patel et al.[22](2017), the absorption at the lower peaks are due to Zr–O and Zr–O_2–Zr vibrational stretch, respectively[22]. The stretching vibration C=O (carbonyl group) at 1722 cm^{-1} corresponds to Zr-O bending vibration, which confirms the successful of treated ZrO_2 nanoparticles with γ-MPS (figure 2b C). Meanwhile, the silanisation for alumina was shown in figure 2 C. The formation of the Al_2O_3 structure is confirmed by the peak at 1722 cm^{-1} corresponding to the Al-O bending mode. A strong peak at 1722 cm^{-1} indicates hydrogen bonding between γ-MPS silanol groups. Symmetric and asymmetric stretches (alkyl groups) of γ-MPS can be determined at the band of 2945 cm^{-1}.

Fracture strength

Fracture strength (FS) testing provides a reliable predictor of clinical durability[23]. Experimental NHDCs with a reinforced Zr and Al fillers significantly rise the fracture strength values ($p<0.05$) compared to the control group (control group). However, it is still inferior to the Z250XT on the market. No reinforcing filler, reinforcing Zr (3%) and Al (2%) were less than 80 MPa. A lower fracture strength may be due to poor interfacial interaction preventing an efficient stress transfer between the components. In such cases, adding filler particles is expected to increase the number of weak links[6,24]. The incorporation of alumina[25-26] and zirconia as a filler in the composite could help in increase fracture strength[27-29]. The contents of nanoparticles and microparticle fillers can have a significant effect in increasing the fracture strength of dental composites[26].

Vickers hardness

Hardness was used to determine how easy it was to complete the restoration and how long it lasted[30]. The hardness values of the experimental NHDC reinforced Zr (3%) & Al (2) were significantly higher than the no reinforced filler (control group) (Table 3) ($p < 0.05$). Addition of Al_2O_3 filler[31-32] into composites increases the hardness of the composites, as suggested by Kiran et al.[32] (2018). Furthermore, the zirconia filler reinforcement significantly improved the Vickers hardness[33-34]. This advantage is likely due to the properties of the ZrO_2 particles and the interfacial shear strength between the nanofiller and the resin matrix[35].

It can be concluded that an ideal dental composite resin should have low Vickers hardness and high fracture strength to be clinically suggestive of long-term success in dental restorations. Adding zirconia and alumina fillers to nanohybrid dental composites was shown to increase the Vickers hardness and fracture strength of the composites.

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Conflicts of Interest

None.

Data Availability

Datasets related to this article will be article upon request to the corresponding author.

Author Contribution

Nurul Najwa Mohd Nordin: Conceptualization, Methodology, Investigation, Formal analysis, Writing- Original draft. **Noor Huda Ismail:** Validation, Visualization. **Dasmawati Mohamad:** Validation, Visualization. **Mohd Firdaus Yhaya:** Supervision, Validation. **Raja Azman Raja Awang:** Supervision, Writing- Reviewing and Editing. All authors actively participated in discussing the manuscript's findings and have revised and approved the final version of the manuscript.

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