Original Article

Fabrication and its characterisation of zirconia and alumina reinforced experimental nanohybrid dental luting composite using silica from rice husk

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ABSTRACT

Objectives

Silanisation of dental filler strengthens the bonding within the resin matrix. This study aims to characterise silanated silica, zirconia, and alumina fillers, then nanohybrid dental luting composite cement (NHC) using the fillers.

Materials and Methods

Charaterisation of unsilanated and silanated silica, zirconia and alumina fillers was performed using FTIR and FESEM for microstructure analysis. Five NHC groups: silica only; 3 wt% zirconia; 3 wt% alumina; 3 wt% zirconia and 2 wt% alumina; and Rely-X^{TM} U200.

Results and Discussion

From the FESEM analysis, the silanated fillers were homogeneously dispersed in NHC.

Conclusion

NHC made of silica rice husk with reinforcement of zirconia and alumina has potential in the market.

Keywords

Alumina; Zirconia; Characterisation; Luting composite

INTRODUCTION

Tremendous development of dental cement has occurred for years to achieve excellent oral health [1]. Dental cement can be used in many dental applications, such as cementing dental veneers, crowns, and braces. The ever-expanding scope of nanotechnology offers scientists new opportunities to combat diseases in the future [2]. It has been recognized for handling diverse dental problems, its programs, teeth hypersensitive reactions, and root canal disinfection [3]. Nanotechnology is widely used to treat many dental issues, including dentistry and root canal therapy [4]. Because of its size, surface area, low density, and biocompatibility properties, nano-silica has been used as a nanofiller in dental

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composites on a large scale [5]. Different sizes of nano-silica have been extensively utilised to enhance dental cement's physical and mechanical properties [6]. It becomes a primary filler in dental resin-based cement [7].

In recent years, there has been a sharp rise in the use and demand for silica nanoparticles in various scientific and industrial applications, including catalysts, stabilizers, colouring, and synthetic mechanical polishing [8]. Quartz, tridymite, and cristobalite are the three most prevalent types of silica [9]. Another source of silica is produced from rice husk at a low cost [10]. Most Asian countries cultivate rice [11]. Cellulose, lignin, and ash are the three main components of rice seeds, which are covered by rice husks [12]. Silica (87-98%) makes up most of the rice husk ash, with traces of metallic metals [13]. Other fillers are zirconia and alumina, which are incorporated into luting cement. Zirconia is known to give superior translucency and strength to dental resin matrix. Besides, zirconia is used in medical bioengineering to support implant apart from titanium [14].

This study aims to characterise i) silica rice husk, zirconia, and alumina after silanisation and ii) experimental NHCs using silica from the rice husk reinforced with zirconia and alumina. The hypotheses of this study were that there was no effect on i) fillers after silanisation and ii) homogeneity of NHC after adding zirconia and alumina.

MATERIALS AND METHODS

Materials

The synthesis of silica from rice husk and its silanisation is followed by a previous study by Noushad et al. [15]. The silica and zirconia powder <50 nm (US Research Nanomaterials, Inc, USA) and alumina powder <50 nm (Sigma-Aldrich, USA) were silanated with 6 wt.% γ-methacryloxypropyltrimethoxysilane (γ-MPS) (Sigma-Aldrich, USA). The resins used were Bisphenol A-glycidyl methacrylate (Bis-GMA) (Esstech, Inc., Essington, PA, USA) and triethylene glycol dimethacrylate (TEGDMA) (Sigma-Aldrich, USA). Other materials used were DL-champhorquinone (CQ) (Merck, Schuchardt OHG, Germany), (2-dimethylaminoethyl) methacrylate (DMAEM) (Merck, Schuchardt OHG, Germany), and Rely-X™ U200 (3M ESPE, USA).

Filler characterisation

The three fillers were characterised for unsilanated and silanated stages for microstructure analysis using a field emission scanning electron microscope (FESEM) (FEI Quanta450, Germany) with energy dispersive X-ray (EDX) and Fourier transform infrared spectroscopy (FTIR) (Shimadzu IRTracer-100, Germany). The FTIR analysis was set up within 400 to 4000 cm^{-1}.

Preparation and characterisation of NHCs

Table 1 shows the composition of experimental NHCs using filler/resin (30/70). The silanated zirconia and alumina were added into the mixture of resins, 0.5 wt.% CQ, and 0.5 wt.% DMAEM. The disc-shaped samples (2mm x 2 mm) of NHC were then subjected to characterisation using FESEM with EDX.

Table 1 Composition of the experimental NHCs

Groups	Filler (30 wt.%)			Resin (70 wt.%)
	Si (wt.%)	ZrO_2 (wt.%)	Al_2O_3 (wt.%)	
0 wt.% ZrO_2/Al_2O_3	100	-	-	Bis-GMA/ TEGDMA (60/40)
3 wt.% ZrO_2	97	3	-	
3 wt.% Al_2O_3	97	-	3	
3 wt.% ZrO_2 and 2 wt.% Al_2O_3	95	3	2	
Rely-X™ U200	NA	NA	NA	NA

Si = Silica; ZrO_2 = Zirconia; Al_2O_3 = Alumina

RESULTS

FESEM analysis of filler characterisation

Figure 1 displays SEM images of silica at different magnifications. The size of the silica was between 74 and 430 nm, with a median of 145.72 nm and a mean (standard deviation) of 241.65 nm (133.15). Element distribution of silica particles includes silicon, oxygen, and carbon, as shown in Figure 2.

FTIR analysis of filler characterisation

The silanisation process of silica, zirconia, and alumina fillers with γ -MPS was successful, as shown by the

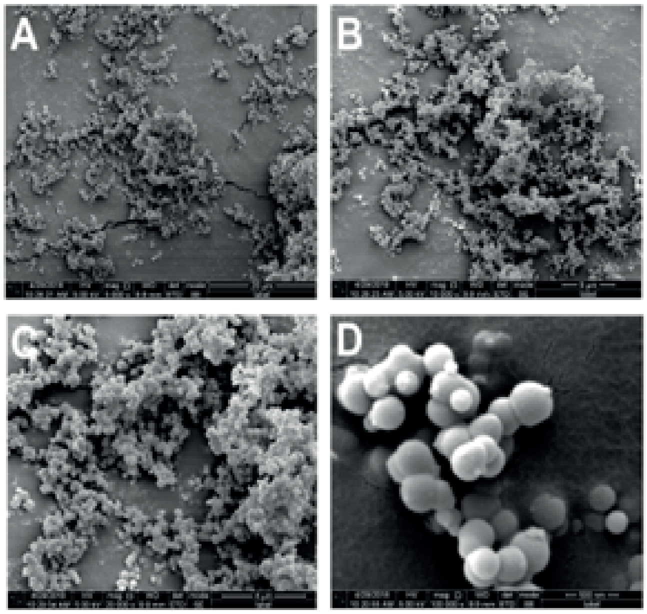

Figure 1. Scanning electron microscope analysis of silica. Magnification 5000x (A), 10000x (B), 20000x (C), and 100000x (D).

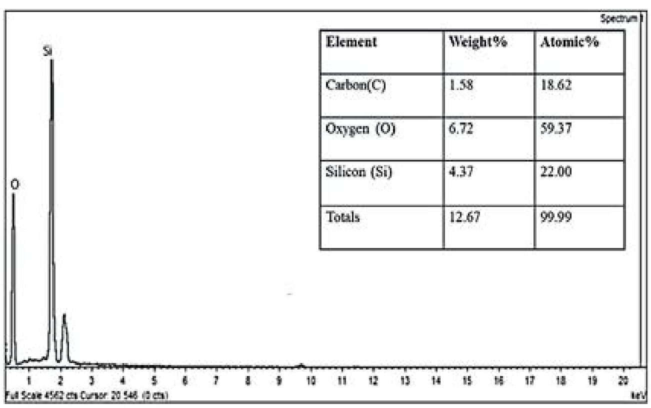

Figure 2. EDX spectrum showing the extracted silica's elemental composition in atomic and weight percentages.

FTIR spectra (Figure 3). The silanated silica filler spectra showed four more absorption peaks at 1458 cm^{-1}, 1634 cm^{-1}, 1722 cm^{-1}, and 2944 cm^{-1}, showing that γ -MPS and silica nanoparticles had chemically interacted (Figure 3-1C). The spectra of the silanated zirconia filler also show a few additional absorption peaks at 2944 cm^{-1}, 1634 cm^{-1}, 1380 cm^{-1}, and 599 cm^{-1}, showing that further chemical alteration has occurred (Figure 3-2C). Four additional absorption peaks at 2944 cm^{-1}, 1778 cm^{-1}, 1447 cm^{-1}, and 615 cm^{-1} were visible in the silanated alumina filler spectra, showing the successful treatment (Figure 3-3C).

FESEM analysis of NHC characterisation

SEM analysis of Figure 4 demonstrates agglomeration of NHC, which is a typical occurrence given that the filler particles are in the nano to macro size range [16]. Additionally, the EDX examination verified that the filler component was present for all experimental NHCs, which is comparable to the Rely-X™ U200 group.

DISCUSSION

Dental luting cement primarily aims to lute the indirect restoration to tooth substrate. Luting cement's superior physical and mechanical strength is essential for longevity. Therefore, studies continue to enhance these features of a luting agent [17]. Other reason, the ideal dental luting cement is to reduce the risk of microleakage that could compromise the longevity of tooth restoration[18].

Using the sol-gel technique for silica extraction, we can get a nanohybrid filler with a spherical form and a regulated particle size that meets our requirements for NHC fabrication. The spherical form and nanohybrid status of the rice husk silica, which has a size range of 74 to 430 nm, have been established. This result is congruent with the previous studies, which showed a diameter range of 48 to 534 nm [15, 19, 20]. The variety of nanoparticle size is essential to contribute good distribution, hence strengthening the bonding within the resin matrix [21]. Because of their small size, nanoparticles are known to clump together quickly. A surface treatment is needed to resolve this problem [22]. In this study, the surface of nanohybrid silica was successfully treated with γ-MPS to lessen agglomeration during the manufacturing of NHC.

Using sodium hydroxide solution, silica (SiO2) is removed from the rice husk and changed into sodium silicate, which is then treated with acid to generate gel (Na2SiO3 + H2O = SiO2 + 2NaOH). Siloxane bonds (Si-O-Si) and silanol groups (Si-OH) are produced by the combination of silicon and oxygen in silica powder [23]. Element carbon was also found, likely from the carbon tape used in the FESEM [24]. Following a prior investigation, FTIR analysis shows that absorption peaks confirm silica at 465 cm^{-1}, 802 cm^{-1}, 961 cm^{-1}, 1067 cm^{-1}, 1634 cm^{-1}, and 3448 cm^{-1} [25].

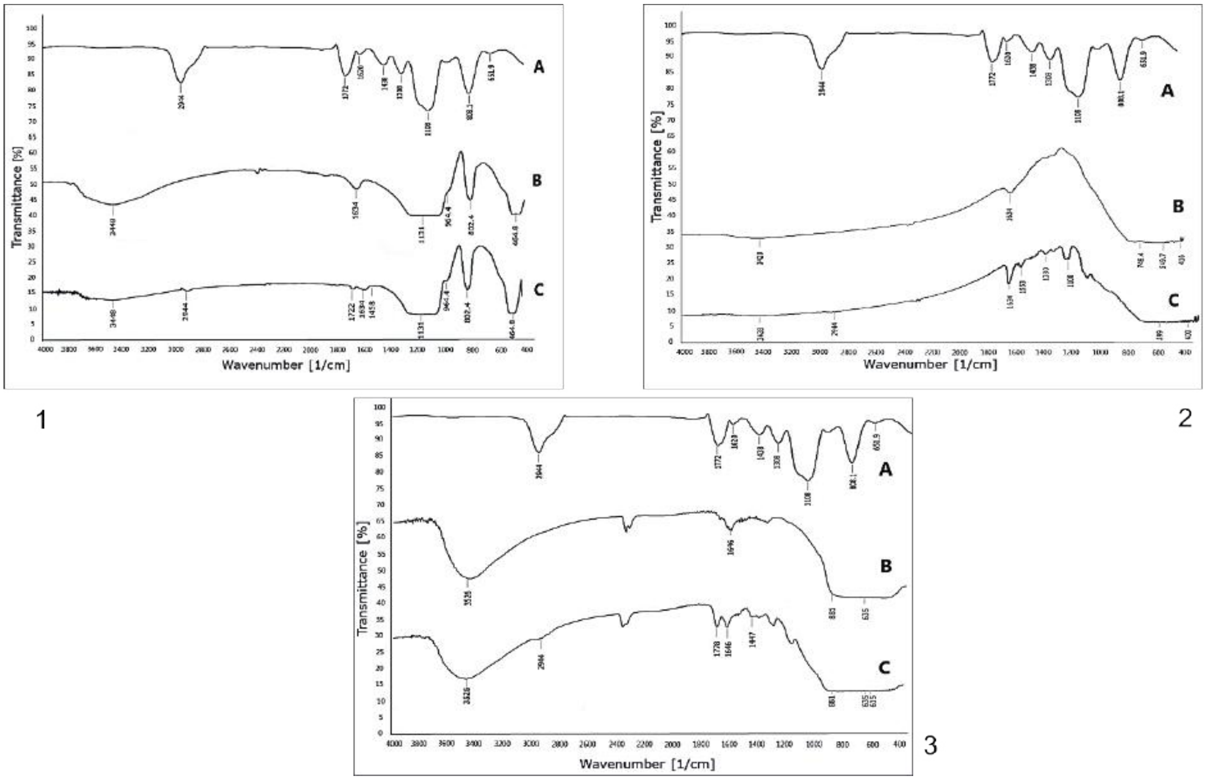

Figure 3. FTIR spectra of silica (1), zirconia (2), and alumina (3) before and after silanisation with γ-MPS. (A) Silane agent, γ-MPS, (B) Filler before silanisation with γ-MPS, (C) Filler after silanisation with γ-MPS.

Filler silanisation is crucial for the fabrication of composite resin. It has been discovered to enhance the composite resin's mechanical qualities, including reduced viscosity and reduced water sorption [26, 27]. The findings in this study demonstrated the silanisation of silica, alumina, and zirconia utilising γ-MPS to be successful (Figure 3). Therefore, the first hypothesis is rejected. This is consistent with the silica silanisation from a previous study [28]. Other previous studies also found that silanisation of zirconia and alumina filler are essential to support bonding within the resin matrix [29, 30]. Following a successful filler silanisation, the spherical shape fillers were equally disseminated in the resin matrix of the experimental NHCs.

The uniform dispersion of the fillers was unaffected by the addition of silanated alumina and zirconia to the resin composite. This emphasizes the requirement for efficient filler silanisation in the fabrication of composite resin [24, 31]. A well distribution of filler(s) in the resin matrix is important to reduce the risk of weak bonding. Apart silanisation, the homogenous mixture is another challenging. In this study, the mixture was performed using by hand spatula and same operator to avoid the discrepancies of steps and speed of mixing. The findings show the SEM images of zirconia and alumina reinforced NHCs represented similarity of the morphology the hybrid resin cement of the Rely-X^{TM} U200. Therefore, the second hypothesis is rejected. The physical and mechanical properties of the NHCs could be further investigated and improved as necessary. Moreover, the hybrid reinforcement of luting cement is used worldwide in many dental applications.

CONCLUSION

Within the study limitations, the conclusions include:

(1) Despite agglomeration, various particle filler sizes improve the homogeneity distribution considering the successful silanisation process with γ-MPS based on the outcome of FTIR and FESEM analyses.

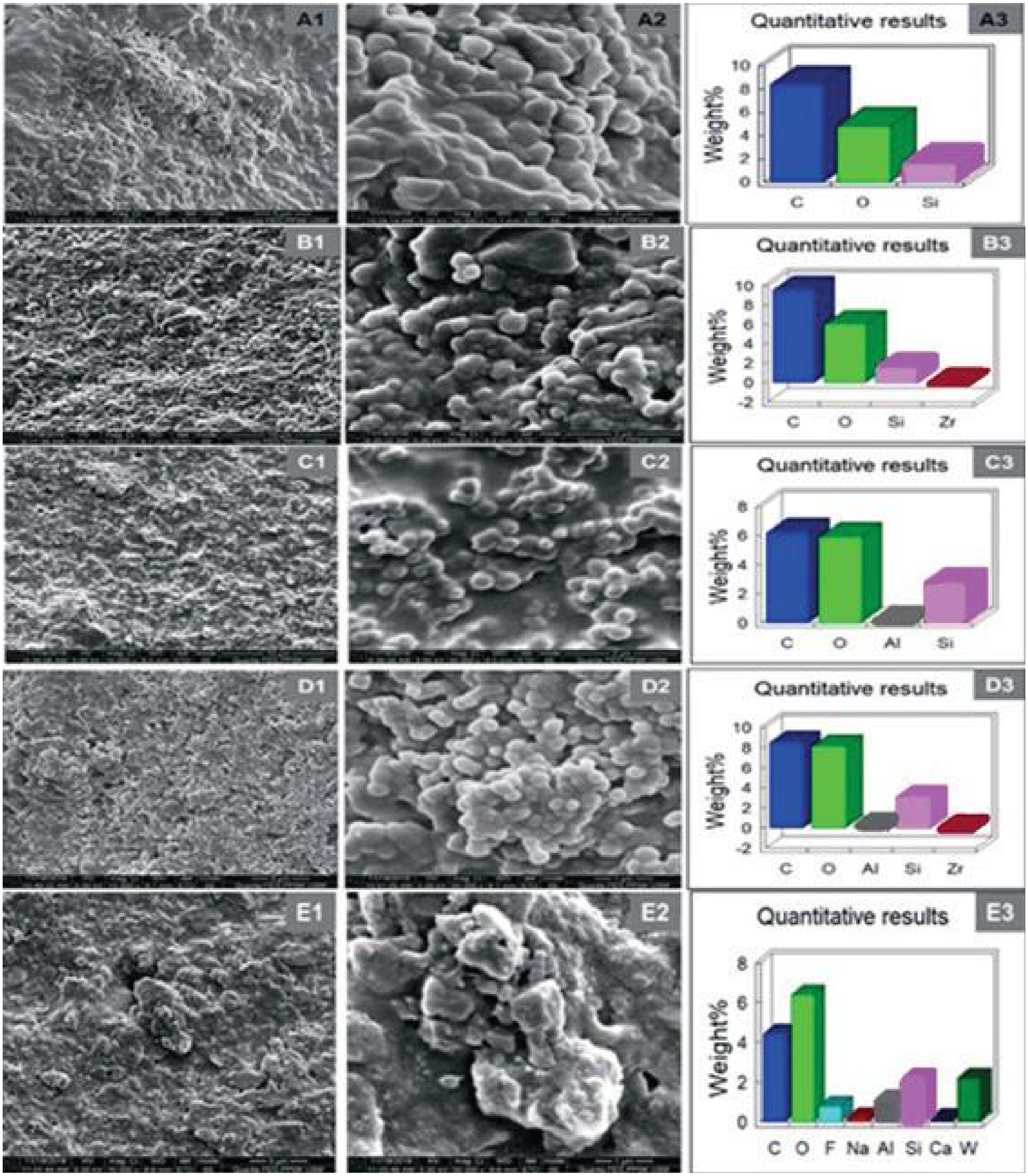

Figure 4. SEM/EDX analysis of experimental NHC. A = 0 wt.% ZrO_2/Al_2O_3; B = 3 wt.% ZrO_2; C = 3 wt.% Al_2O_3; D = 3 wt.% ZrO_2 and 2 wt.% Al_2O_3; E = Rely-X^{TM} U200; 1 = Magnification 10000X; 2 = Magnification 50000X; 3 = EDX's elemental distribution; C = Carbon; O = Oxygen; Si = Silicon; Zr = Zirconium; Al = Aluminium; F = Fluorine; Na = Sodium; Ca = Calcium; W = Tungsten; ZrO_2 = Zirconia; Al_2O_3 = Alumina.

(2) Hybrid reinforcement of zirconia and alumina added in the experimental NHC is comparable to the commercial Rely-X U200. Further exploration of the different reinforcement percentages could be beneficial as a potential luting cement in the market.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Declarations of Interest: none.

Compliance with Ethical Standards

The work is compliant with ethical standards.

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