Synthesis of Nanosilica Fillers for Experimental Dental Nanocomposites and Their Characterisations

Tuan Noraihan Azila Tuan Rahim[1], Dasmawati Mohamad[1]*, Abdul Rashid Ismail[1] and Hazizan Md Akil[2]

[1]School of Dental Sciences, Universiti Sains Malaysia,
16150 Kubang Kerian, Kelantan, Malaysia
[2]School of Material and Mineral Resources Engineering, Universiti Sains Malaysia,
14300 Nibong Tebal, Pulau Pinang, Malaysia

*Corresponding author: dasmawati@kck.usm.my

Abstract: *The aim of this study was to synthesise nanosilica fillers for use in the fabrication of experimental dental nanocomposites and to evaluate their properties, including surface and mechanical properties. Monodispersed, spherical silica nanoparticles were synthesised via a sol-gel process, and a size range of 10–20 nm was obtained. Surface treatment of the nanosilica was carried out with the silane coupling agent γ-methacryloxypropyltrimethoxysilane (MPS) to reduce agglomeration of nanosilica. Experimental dental nanocomposites with two different filler contents, 30 and 35 wt%, were fabricated and polymerised with a light curing unit for 40 s. The surface morphology, surface roughness, flexural strength and elastic modulus were evaluated and compared. A nanocomposite with 35% filler content showed higher filler compaction, lower surface roughness and higher elastic modulus than a nanocomposite filled with 30% filler. However, the nanocomposite filled with 30% filler content showed higher flexural strength. Based on the results obtained, the synthesised nanosilica is a promising material for the fabrication of dental nanocomposites for tooth-filling applications.*

Keywords: nanosilica, dental nanocomposite, mechanical properties, surface roughness

Abstrak: *Tujuan kajian ini dijalankan adalah untuk mensintesis pengisi nanosilika untuk kegunaan dalam fabrikasi nanokomposit ujikaji pergigian dan penilaian terhadap sifat-sifat komposit termasuk sifat permukaan dan mekanikal. Partikel nanosilika yang monosebaran dan berbentuk sfera disintesis melalui proses sol-gel dan saiz sekitar 10–20 nm diperolehi. Pengolahan permukaan bagi pengisi nanosilika dijalankan menggunakan agen penkupel silana, γ-metakrlosipropiltrimetoksisilana (MPS) untuk mengurangkan aglomerasi nanosilika. Nanokomposit ujikaji dengan kandungan pengisi yang berbeza, 30 dan 35 brt% difabrikasi dan dipempolimerkan menggunakan unit pematangan cahaya selama 40 s. Morfologi permukaan, kekasaran permukaan, kekuatan fleksural dan modulus elastic dinilai dan dibandingkan. Nanokomposit diisi 35% kandungan pengisi menunjukkan kepadatan pengisi yang lebih tinggi, kekasaran permukaan yang lebih rendah dan modulus elastik yang lebih tinggi berbanding komposit berpengisi 30%. Walaubagaimanapun, nanokomposit diisi 30 brt% kandungan pengisi menunjukkan kekuatan fleksural yang lebih tinggi. Berdasarkan keputusan yang didapati, nanosilika*

yang disintesis merupakan bahan yang berpotensi dalam fabrikasi nanokomposit pergigian untuk aplikasi tampalan gigi.

Kata kunci: nanosilika, nanokomposit pergigian, sifat mekanikal, kekasaran permukaan

1.   INTRODUCTION

Since 1970, visible-light-cured dental composites have been used extensively in dentistry due to their aesthetic characteristics and their particular properties. Before their introduction, dental amalgams were the materials of choice for stress bearing dental fillings for more than 150 years.[1] The presently available dental composites consist of a polymer matrix (organic phase), inorganic filler particles (dispersed phase), a filler-matrix coupling agent (interface), and minor additives including polymerisation initiators, stabilisers and colouring pigments.[2] Recent improvements have been achieved mainly through the discovery of organic monomers, modifications in formulation and filler technology, advances in light curing equipment and the introduction of efficient photoinitiators. Despite these achievements, there are ongoing efforts to improve the performance of current composites regarding their aesthetic properties, polymerisation shrinkage and mechanical properties.

Dental composites have traditionally been classified according to their filler particle sizes, including macrofilled composites, microfilled composites, hybrid composites and recently, nanocomposites with filler sizes below 100 nm. The development of nanotechnology has led to a significant improvement in the evolution of dental composites. This technology produces a smoother surface with higher translucency and polishability, comparable to those of microfilled composites, while their physical properties and wear resistance remain equivalent to those of several hybrid composites.[3]

Nanosilica filler is a typical filler used in dental composites, which has gained popularity in spite of criticism and predicted failures. One of the most important techniques used to prepare nanosilica fillers is the sol-gel process. Nanofillers synthesised using this method are reported to have a distinct spherical shape with a narrow size distribution that is useful for dental applications.[4,5] The extremely small nanoparticle size provides low visual opacity in unpigmented dental composites, which allows researchers to prepare a wide variety of shades and opacities of dental composites and thus provide highly aesthetic restorations. Furthermore, spherically shaped nanosilica particles provide superior polishability[6] and tend to distribute mechanical stress more uniformly than irregularly shaped particles, which leads to improved mechanical properties.[7]

This article describes a study on the development of a dental nanocomposite that has the aesthetic properties required for cosmetic restorations with improved surface roughness and acceptable mechanical properties. The nanosilica fillers with size range 10–20 nm were synthesised according to the methods of Jafarzadeh et al.[5] However, in this study, a silane coupling agent was introduced to the nanosilica gel prior to the drying process. Subsequently, experimental nanocomposites were prepared with selected monomers ratios and filler contents, and the surface morphology, surface roughness and mechanical properties were evaluated in order to prove their applicability and reliability. It was hypothesised that the experimental nanocomposites incorporated with monodispersed silica nanoparticles would improve the surface and mechanical properties of the composites.

2.   EXPERIMENTAL

2.1   Reagents and Materials

Tetraethyorthosilicate (TEOS, 99%, Fluka), absolute ethanol (C_2H_5OH, 99.8%, Systerm), ammonia (NH_3, 25% Merck), γ-methacryloxypropyl-trimethoxysilane (γ-MPS, Sigma Aldrich), acetic acid (CH_3COOH, 25%, Merck), bisphenol A glycidyl methacrylate (BisGMA, Esstech), diurethane dimethacrylate (UDMA, Aldrich), triethylene glycol dimethacrylate (TEGDMA, Fluka), camphorquinone (CQ, Aldrich), (2-dimethylaminoethyl) methacrylate (DMAEMA, Merck) and distilled water were used in this work. The chemicals were employed without any further purification.

2.2   Synthesis of Nanosilica Fillers

Nanosilica was synthesised by adding a 5 ml of TEOS in 30 ml of absolute ethanol under a low frequency ultrasound bath (Model 5510, Branson) for 15 min at room temperature. Then, 1 mL of distilled water was dropped into the reaction media with a feed rate of 0.2 mL min^{-1}. The sonication was continued for 1.5 h at room temperature to complete the hydrolysis process. Next, 2 ml of ammonia (catalyst) was dropped into the mixture at a feed rate of 0.03 mL min^{-1}. The gel was centrifuged (Biofuge primo, Heraeus) for 7 min at 4000 rpm to separate the silanised nanosilica from the solution. The mixture was washed with ethanol and distilled water prior to and after centrifugation. For silanisation, 1 g of nanosilica gel was added into 50 ml 1% γ-MPS, and then acetic acid was added to the mixture until a pH of 3.5 was reached. The mixture was stirred for 1 h, followed by centrifugation and washing, through the same protocol as described above. The mixture was then frozen at –70°C. The samples were dried under vacuum in a freeze dryer (Modulyo D, Thermo) for 48 h and

then in an oven at 80ºC overnight. The silanised nanosilica powder was ball-milled overnight. These steps were repeated to prepare nanosilica fillers without silanisation.[5]

2.3   Fabrication of Experimental Dental Nanocomposites

Two series of experimental dental nanocomposites, namely ENC1 and ENC2, were fabricated by mixing the monomer matrix and fillers in a mass ratio of 30/70 and 35/65, respectively. The monomer matrix (BisGMA, UDMA and TEGDMA) was mixed in a mass ratio of 30/20/50 for 5 min. This mass ratio was selected by Asmussen *et al*.[8] because it gives the most appropriate mechanical properties for the composites. Then, 0.5 wt% camphorquinone as an initiator and 0.5 wt% DMAEMA as an accelerator were added.[9] The mixture was hand-mixed with silanised nanosilica fillers at 29 wt% and 34 wt% filler loading. Then, 0.5 wt% zinc oxide was added as an anti-microbial agent,[10–11] and 0.5 wt% zirconia was added as a colorant and also to improve the mechanical properties. Therefore, the total filler loading for each experimental dental composite was 30 wt% (ENC1) and 35 wt% (ENC2).

The paste was then inserted into test moulds and light cured with a light curing unit (Elipar Freelight 2 LED, 3 M ESPE) at an intensity of 1500 mW/cm². The light was illuminated on both surfaces, top and bottom, through clear matrix strips for 40 s. The 40-s curing time was used to cure the experimental nanocomposites because it is commonly used by clinicians. The tip distance of the light curing unit was maintained at 1–2 mm from the composite surface.

2.4   Characterisation

2.4.1   Transmission electron microscopy (TEM) observation

Transmission electron microscopy (TEM, Philips CM12) was used to observe the morphology of the samples (unsilanised and silanised nanosilica) and determine their particle size. The suspension of nanosilica was prepared by diluting the nanosilica powder with ethanol and ultrasonicating it for 10 min. A drop of suspension was placed on a carbon-coated copper grid. The ethanol was subsequently evaporated at room temperature, leaving the nanosilica on the grid. The particle size was determined using Docu Version 3.2 image analysis software.

2.4.2   Field emission scanning electron microscopy (FESEM) observation

Additional field emission scanning electron microscopy (FESEM, Zeiss Supra 35VP) investigation was carried out to characterise the filler morphology

and distribution as well as the failure pattern of the composites. The bar-shaped specimen (25 × 2 × 2 mm) was prepared and broken after 1 min of immersion in liquid nitrogen. Prior to FESEM observation, the specimens were mounted on SEM stubs and gold sputtered for better electrical conduction.

2.4.3   Surface roughness

The specimens of 5 sample sizes, n = 5, were prepared in acrylic moulds (5 × 2 mm). The means of the surface roughness of the dental composites were assessed with contact mode AFM (Model Q250, Ambios Technology). Three areas were randomly selected with a scan area of 40 μm × 40 μm and a resolution of 512 pixels to obtain the surface roughness value, R_a. The R_a values were analysed with ScanAtomic SPM control software. Three-dimensional images with sizes of 10 μm × 10 μm were acquired for each specimen.

2.4.4   Flexural strength and elastic modulus

The test was carried out according to ISO specification 4049.[12] Bar-shaped specimens (25 × 2 × 2 mm) with 10 sample sizes, n = 10, were made in a split steel mould. The specimens were stored in distilled water at 37ºC for 24 h before the test. The flexural testing was measured by a three-point bending test with a span length of 20 mm using a Universal Test Machine (Model 3366, Instron) at a crosshead speed of 1 mm min^{-1} with a 10-kN load cell. The flexural strength and flexural modulus were calculated based on the following equations:

$$\text{Flexural strength} = 3PL/2bd^2$$
$$\text{Elastic modulus} = L^3 m/4bd^3$$

where P is the maximum force applied, L is the span length, b is the width, d is the thickness and m is the slope of initial straight line deflection curve.

3.   RESULTS AND DISCUSSION

3.1   TEM Observation

Monodispersed and spherical silica nanoparticles were synthesised via the sol-gel process according to Jafarzadeh et al.[5] Figure 1 shows that nanosilica spheres with a size range of 10–20 nm were obtained. Figure 2 and 3 show TEM images of the nanosilica without and with silanisation, respectively. Less agglomeration of nanosilica was observed after silanisation. The surface treatment was one of the crucial criteria for developing a successful dental composite. When the sizes of the fillers are below 25 nm, aggregation and

agglomeration of silica nanoparticles occur. Therefore, the synthesised nanosilica were treated with a silane coupling agent, γ-MPS, to reduce agglomeration, enhance filler dispersion and improve the interfacial adhesion between the polymer matrix and fillers.[13] These improvements may also result in the enhancement of surface and mechanical properties.
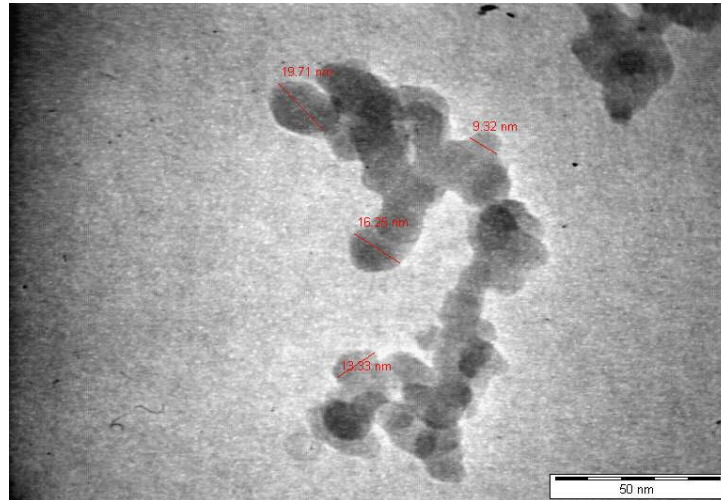

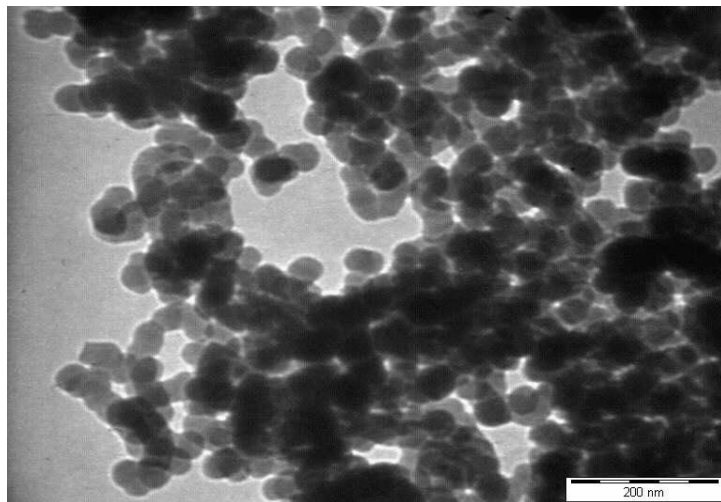Figure 1: Silica nanoparticles measurements.

Figure 2: TEM image of silica nanoparticles without surface treatment. High agglomeration of silica can be seen.
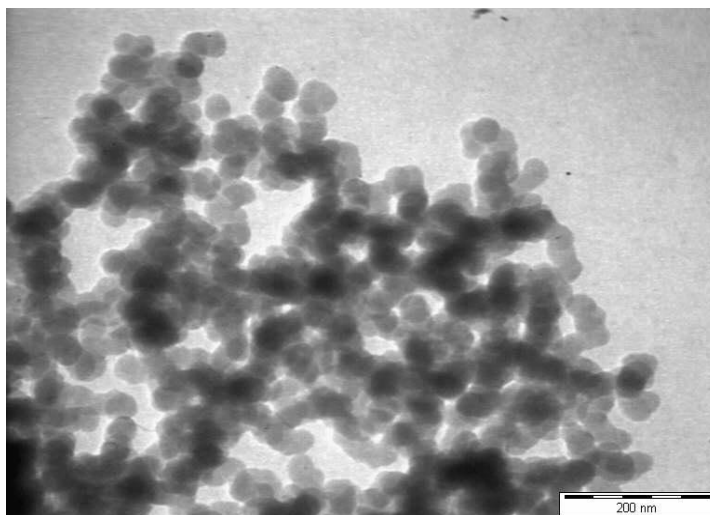
Figure 3:   TEM image of silica nanoparticles with surface treatment. Markedly reduced agglomeration can be seen. The nanosilica particles are relatively monodispersed.

In this study, nanosilica was used as a filler, which was mixed with selected monomer resins and additives for dental restorative application. The use of nanosilica fillers was expected to have some advantages and improve the properties of the composite fabricated. Klapdohr and Moszner[14] claimed that monodispersed nanofillers in a polymer matrix lead to nanocomposite materials with excellent mechanical properties, good processability and high transparency.

3.2   FESEM Observation

A FESEM micrograph of each material is shown in Figure 4 and 5 at two different magnifications. FESEM observation was carried out to investigate the filler distribution in the polymer matrix and the failure pattern of the composites. Differences in surface features can easily be seen by comparing Figure 4(b) and Figure 5(b), although the difference in the filler concentration between the composites was quite small. ENC2 shows a more homogenous filler distribution and higher compaction of filler particles compared to ENC1. The fracture surface for ENC1 shows many voids, indicating that less filler occupied the polymer matrix (Figure 4(b)). However, both nanocomposites exhibited cohesive failure. Matrix filler debonding could not be observed by FESEM because the filler size was in the nano range.
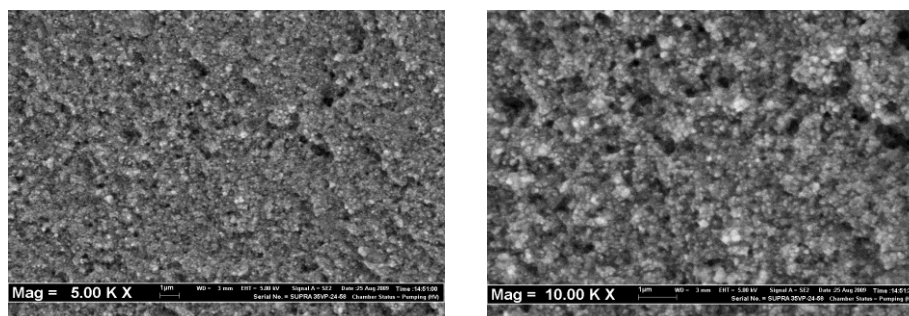
Figure 4: FESEM micrograph of fractured surface of ENC1 at different magnification (a) 5000 X, (b) 10000 X. Flat surface texture can be seen indicating cohesive failure has occurred.

3.3   Surface Roughness

In the characterisation of dental composites, the surface roughness is also important. Roughness has a major impact on the aesthetic appearance and discoloration of restorations.[15–17] High surface roughness of composites also contribute to bacterial plaque, debris and stain accumulation, which lead to secondary caries, gingival inflammation, superficial staining and reduction of the restoration gloss.[18] Nano size fillers have been shown to improve the surface roughness because they can be dispersed more homogeneously in a polymer matrix compared to micron size fillers.[15]

In this study, significant differences were observed in the surface roughness values, R_a, for both experimental nanocomposites (Table 1). ENC2 showed lower R_a than ENC1, which can be explained by the amount of filler and the filler distribution in the composite. As shown by 3D image of ENC2 (Figure 7), the fillers were uniformly distributed and highly compacted, and they therefore enhanced the surface smoothness. Conversely, the AFM image of ENC1 (Figure 6) shows the inconsistency of the filler packing, which led to a high surface roughness. These assumptions were also in agreement with Botta *et al*.[18] and Marghalani.[19] Although the R_a values differed, the values were still below 200 nm, which was reported as an initial point for bacterial plaque accumulation and risk for caries and periodontal inflammation.[20] Hence, the composite surfaces evaluated in this study can be assumed to have a smooth surface, which presents no risk of plaque accumulation.

Table 1: Properties of the experimental nanocomposites (S.D.).

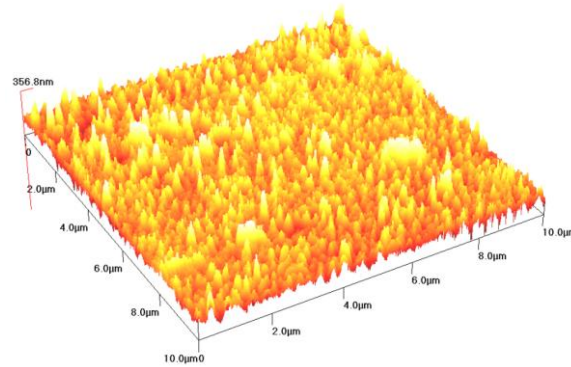| Materials	Flexural strength (MPa)	Modulus (MPa)	R_a (nm)
ENC1	85.97 (9.02)	3626.00 (274.92)	38.56 (5.03)
ENC2	73.55 (8.35)	4143.11 (347.14)	29.95 (3.37)

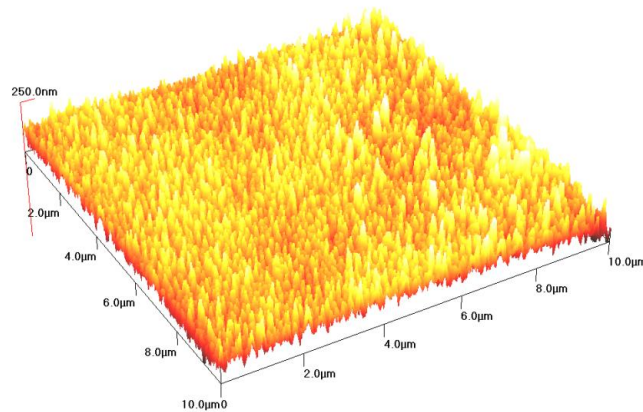Figure 6: AFM image acquired in the contact mode of ENC1 with matrix strip.

Figure 7: AFM image acquired in the contact mode of ENC2 with matrix strip.

3.4   Flexural Strength and Elastic Modulus

The flexural test is widely employed in dental research to examine the mechanical behaviour of dental composites because it combines the effects of compressive deformation (adjacent to the point at which the load is applied) and tensile deformation (on the opposite side of the specimen).[21] According to Table 1, both experimental nanocomposites showed acceptable flexural strength

values, which complied with the ISO standards (above 50 MPa).[12] This result is also in agreement with previously published studies,[6,21-22] which evaluated experimental nanocomposites filled with nanosilica.

In general, the physical and mechanical properties of composites improved with the amount of filler added. Many recent studies[23-25] have found increases in properties such as flexural strength, compressive strength, hardness and elastic modulus with the amount of filler added. Most dental composites on the market, even though claiming to be nanocomposite, contain higher loadings of micron size fillers compared to nanofillers. Thus, they are able to be filled with around 70–80 wt% of filler. However, in this study, the fillers used were all nanosilica fillers, and they exhibited a very high surface area for filler loadings up to 35 wt%.

ENC1 presented a slightly higher mean flexural strength than ENC2. Both composites contained the same type of monomer resin and fillers, and the only difference was the filler content. The incorporation of an overload filler content probably reduced the flexural strength, which is in agreement with the results of other studies.[7,26] Adabo *et al*.[26] reported that a more highly filled material, which presents a higher elastic modulus, suffers fragile fracture more easily. The FESEM micrograph of ENC2 (Figure 5 (b)) very clearly shows compaction of the filler packing in the polymer matrix compared with ENC1 (Figure 4 (b)) with the appearance of many voids.

Another important mechanical parameter provided by the flexural test is the elastic modulus, which measures the ability of the composite to flex under stress. If a composite is too stiff, it may chip easily. However, if it is too flexible, it may not withstand the forces of the mouth. In general, the modulus of the composite improves in direct relation to the amount of filler added. Based on the results obtained (Table 1), the modulus of ENC2 was significantly higher than that of ENC1, which is consistent with the theory. Both results were also above the minimum requirement, which is 3.5 GPa, provided by a manufacturer of anterior dental composites.[27]

4.   CONCLUSION

The synthesis of silica nanofillers was carried out prior to fabrication of experimental dental nanocomposites. Subsequently, the properties were evaluated, and the samples were compared to each other and also to ISO requirements and other published studies. All composites tested complied with the minimum requirements given by ISO standards. The filler size, content and distribution had significant effects on the composite properties.

5. ACKNOWLEDGEMENTS

6. REFERENCES

1. Soh, M. S., Sellinger, A. & Yap, A. U. J. (2006). Dental nanocomposites. *Curr. Nanosci.*, 2(4), 373–381.
2. Chung, S. M., Yap, A. U. J., Chandra, S. P. & Lim, C. T. (2004). Flexural strength of dental composite restoratives: Comparison of biaxial and three-point bending test. *J. Biomed. Mater. Res.*, 71B(2), 278–283.
3. Mitra, S. B., Wu, D. & Holmes, B. N. (2003). An application of nanotechnology in advanced dental materials. *J. Am. Dent. Assoc.*, 134(10), 1382–1390.
4. Nirschl, H. (2003). Nanoscale particles in medical products. *Adv. Eng. Mater.*, 5(8), 556–559.
5. Jafarzadeh, M., Rahman, I. A. & Sipaut, C. S. (2009). Synthesis of silica nanoparticles by modified sol-gel process: The effect of mixing modes of the reactants and drying techniques. *J. Sol-Gel Sci. Technol.*, 50(3), 328–336.
6. Rüttermann, S., Wandrey, C., Raab, W. H. M. & Janda, R. (2008). Novel nano-particles as fillers for an experimental resin-based restorative material. *Acta Biomater.*, 4(6), 1846–1853.
7. Tian, M., Gao, Y., Liu, Y., Liao, Y., Hedin, N. E. & Fong, H. (2008). Fabrication and evaluation of Bis-GMA/TEGDMA dental resins/composites containing nano fibrillar silicate. *Dent. Mater.*, 24(2), 235–243.
8. Asmussen, E. & Peutzfeldt, A. (1998). Influence of UEDMA, BisGMA & TEGDMA on selected mechanical properties of experimental resin composites. *Dent. Mater.*, 14(1), 51–56.
9. Atai, M., Nekoomanesh, M., Hashemi, S. A. & Amani, S. (2004). Physical and mechanical properties of an experimental dental composite based on a new monomer. *Dent. Mater.*, 20(7), 663–668.
10. Fang, M., Chen, J. -H., Xu, X. -L., Yang, P. -H. & Hildebrand, H. F. (2006). Antibacterial activities of inorganic agents on six bacteria associated with oral infections by two susceptibility tests. *Int. J. Antimicrob. Agents*, 27(6), 513–517.

11. Liu, Y., He, L., Mustapha, A., Li, H., Hu, Z. Q. & Lin, M. (2009). Antibacterial activities of zinc oxide nanoparticles against *Escherichia coli* O157:H7. *J. Appl. Microbiol.*, 107(4), 1193–1201.

12. International Organization for Standardization. (2000). ISO 4049, Section 7.11: Dentistry—Polymer-based filling, restorative and luting materials. Geneva: International Organization for Standardization.

13. Kim, J. W., Kim, L. U. & Kim, C. K. (2006). Size control of silica nanoparticles and their surface treatment for fabrication of dental nanocomposites. *Biomacromolecules,* 8(1), 215–222.

14. Klapdohr, S. & Moszner, N. (2005). New inorganic components for dental filling composites. *Chemistry and Materials Science,* 136(1), 1434–4475.

15. Janus, J., Fauxpoint, G., Arntz, Y., Pelletier, H. & Etienne, O. (2010). Surface roughness and morphology of three nanocomposites after two different polishing treatments by a multitechnique approach. *Dent. Mater.*, 26(5), 416–425.

16. Lu, H., Roeder L. B., Lei, L. & Powers, J. M. (2005). Effect of surface roughness on stain resistance of dental resin composites. *J. Esthet Restor. Dent.*, 17(2), 102–108.

17. Sarac, D., Sarac, Y. S., Kulunk, S., Ural, C. & Kulunk, T. (2006). The effect of polishing techniques on the surface roughness and color change of composite resins. *J. Prosthe. Dent.*, 96(1), 33–40.

18. Botta, A. C., Duarte S., Jr., Paulin Filho, P. I. & Gheno, S. M. (2008). Effect of dental finishing instruments on the surface roughness of composite resins as elucidated by atomic force microscopy. *Microsc. Microanal.,* 14(5), 380–386.

19. Marghalani, H. Y. (2001). Effect of filler particles on surface roughness of experimental composite series. *J. Appl. Oral Science*, 18(1), 59–67.

20. Bollenl, C. M. L., Lambrechts, P. & Quirynen, M. (1997). Comparison of surface roughness of oral hard materials to the threshold surface roughness for bacterial plaque retention: A review of the literature. *Dent. Mater.*, 13(4), 258–269.

21. Chen, C. -Y., Huang, C. -K., Lin, S. -P., Han, J. -L., Hsieh, K. -H. & Lin, C. -P. (2008). Low-shrinkage visible-light-curable urethane-modified epoxy acrylate/SiO$_2$ composites as dental restorative materials. *Compos. Sci. and Technol.*, 68(13), 2811–2817.

22. Du, M. & Zheng, Y. (2008). Degree of conversion and mechanical properties studies of UDMA based materials for producing dental posts. *Polym. Compos.,* 29(6), 623–630.

23. Ikejima, I., Nomoto, R. & McCabe, J. F. (2003). Shear punch strength and flexural strength of model composites with varying filler volume fraction, particle size and silanation. *Dent. Mater.*, 19(3), 206–211.

24.   Beun, S., Glorieux, T., Devaux, J., Vreven, J. & Leloup, G. (2007). Characterization of nanofilled compared to universal and microfilled composites. *Dent. Mater.*, 23(1), 51–59.

25.   Masouras, K., Silikas, N. & Watts, D. C. (2008). Correlation of filler content and elastic properties of resin-composites. *Dent. Mater.*, 24(7), 932–939.

26.   Adabo, G. L., Cruz, C. A. D. S., Fonseca, R. G. & Vaz, L. G. (2003). The volumetric fraction of inorganic particles and the flexural strength. *J. Dent.*, 31(5), 353–359.

27.   Cavex Holland. (2009). Quadrant Anterior Shine Composite product information. Retrieved 2 January 2010, from http://www.cavex. nl/3/3_qua_ans_pi.html