

Comparison of the Effect of Metallic Nano-particles on the Water Contact Angle of Composite Resin

Shirinzad, M.* Kasraei, Sh.** Azarsina, M.***

* Assistant Professor, Department of Operative Dentistry, Dental Faculty, Hamadan University of Medical Sciences, Hamadan, Iran.

**Associate Professor, Dental Research Center, Department of Operative Dentistry, Dental Faculty, Hamadan University of Medical Sciences, Hamadan, Iran.

***Assistant Professor, Department of Operative Dentistry, Dental Faculty, International Branch of Shahid Beheshti University of Medical Sciences, Tehran, Iran.

ABSTRACT

Statement of the problem: Addition of metallic nano-particles to composite resins can change their water contact angle.

Purpose: The aim of this study was to evaluate the effect of addition of nano-particles of silver and zinc oxide to composite resins on their water contact angle.

Material and Methods: This in vitro study was performed on 60 composite resin samples. Nano-silver and nano-zinc oxide were added to composite resin at 0.5% and 1% by weight. SEM-EDX analysis was performed to confirm the homogeneity of the nano-particle distribution. Composite resin discs were made in molds measuring 10 mm in diameter and polished with silicon carbide papers. Water contact angle measurements were performed on 4 points on the surface of each sample, and the mean of the points was reported as the water contact angle of the sample. Two-way ANOVA, followed by the Tukey-HSD test and independent t-test with a significance level of 5%, were used for data analysis.

Results: The addition of nano-particles caused a reduction in the contact angle between water and composite resin ($P=0.000$). The interaction of the type of nano-particle and its concentration on the contact angle was significant ($P=0.000$). Water contact angle varied depending on the type of nano-particle ($P=0.000$) and its concentration ($P=0.028$).

Conclusion: Addition of silver and zinc-oxide nano-particles to composite resin reduced the water contact angle of composite resin.

Keywords: Nanotechnology, Silver, Composite Resins.

INTRODUCTION

Methacrylate-based composite resin restorations were introduced in the 1960s. These materials undergo free radical polymerization reaction, during which monomer molecules come closer to each

Corresponding Author: M. Azarsina Address: Assistant Professor, Dept. of Operative Dentistry, Dental Faculty, International Branch of Shahid Beheshti University of Medical Sciences, Jamalzade Street, Tehran, Iran. E.mail: azarsina2012@yahoo.com, Tel: 0098 21 88209020.

other resulting in 2–5% polymerization shrinkage.⁽¹⁾ In the recent decade, a new monomer system named “silorane” has been introduced, which is obtained from the reaction of oxirane and siloxane molecules.⁽²⁾ Silorane monomer exhibits a cationic ring opening polymerization mechanism, and in vitro studies have confirmed a reduced polymerization stress and shrinkage of <1% by volume.^(3–5)

Microorganisms accumulate more readily on composite resins compared to amalgam

and glass-ionomer restorations. Bacterial accumulation in dental biofilm is highly dependent on the characteristics of the material surface. The bacterial accumulation on the surfaces of these restorative materials can provide the bacterial source, leading to the development of secondary caries and periodontal diseases.^(6,7) Therefore, restorative materials with a low tendency for oral microorganisms are preferable.

Metals such as silver and zinc have been used as bactericidal and bacteriostatic agents. Silver, which has a significant antimicrobial activity, is also effective against *Streptococci* of the human oral cavity and periodontal pathogens; so, it might be useful as an antibacterial agent incorporated into dental restorations, especially when applied in nanometer sizes.^(1,8,9) Zinc oxide (ZnO) is an inorganic compound, which is in the form of a white powder and has the potential to inhibit dental plaque acid production by inhibiting *Streptococcus mutans* and *Lactobacillus*.⁽¹⁰⁾ Measuring water contact angle at the solid-air-liquid interface is a widely known technique used to investigate wettability of solid substrates. Contact angles change with surface topography, surface tension of the liquid surface energy of the substrate, and level of interaction between the liquid and solid.⁽¹¹⁾ Water contact angle is an effective factor on plaque accumulation on the surface of restorative materials.

Considering the fact that the incorporation of nano-particles to composite resins, for their antibacterial properties, can affect restoration contact angle measurements, the aim of the present study was to evaluate the effect of the addition of nano-silver and nano-zinc oxide particles to composite resins on the water contact angle of composite resin restorations.

Clinical Implications: Addition of nano-particles of silver and zinc-oxide to composite resins for their proved antibacterial properties can reduce contact angle of the composite resins, and as a result, increase their susceptibility to bacterial accumulation.

MATERIAL AND METHODS

This experimental study was performed on 60 composite resin discs. Nano-silver particles (TopNano Tech Co. Taipei, Taiwan) with an average size of 50 nm and nano-zinc oxide (Malekeashtar Faculty of Nano Tech. Isfahan, Iran) particles with 20 nm average size were added mechanically to composite resin as 0.5% and 1% by weight. The nano-particles were mixed with the composite resin by a plastic spatula continuously for 30 minutes in a dark room. SEM-EDX (Scanning electron microscopy with an energy dispersive x-ray analytical system) analysis was performed for one sample in each group to confirm the homogeneity of distribution of the nano-particles in composite resins. The samples were made in PVC molds measuring 10

mm in diameter and 1.5 mm in height. The composite resin was inserted into the mold and immediately covered with two glass slides from top and bottom. The specimen was light-polymerized using an LED (Demi LED Light Curing System, Kerr Corp, Orange, CA, USA) light-curing unit with a light intensity of 800 mW/cm^2 , measured with a radiometer, for 60 seconds from both sides. The samples were broken into two pieces with a chisel-like blade and the broken surfaces were gold sputter-coated (Sputter coater, EMITECH, K450X Ashford; Kent, England) in a thin 15-nm layer to prevent the sample surfaces from burning during SEM observation. Gold was finally removed from surface elements of the samples. The broken surfaces of each sample were observed under a scanning electron microscope (TESCAN, VEGAII, XMU, and Czech Republic) at $\times 350$. Following confirmation of the homogenous distribution of the nano-particles in composite resins, the samples of each study group were prepared by the same method as described above. Unloaded composite resin was used as the control group. All the samples were polished with 600-, 800- and 1200-grit SiC papers (991A Softflex, Germany) to obtain high-polished samples with identical surface roughness (R_a) values. Wettability of the samples was assessed by measuring distilled water contact angles on composite resins with a contact angle measuring system (Sessile Drop, Kruss G10, and Germany). The

contact angle was defined as the angle at which the liquid interface met the solid surface of the composite disc at four points on each sample. The surface of the drop was constantly monitored, and the contact angle was measured just after 20 s, when the droplet was stabilized. The mean of the four points was recorded as the water contact angle of each sample.

Data were statistically analyzed by the SPSS software (Version 11, SPSS Inc., Chicago, USA) and two-way ANOVA followed by the Tukey-HSD tests and independent t-test. Level of significance was set at 0.05.

RESULTS

Means and SDs of the water contact angle of the composite resins are summarized in Table 1.

Two-way ANOVA for the water contact angle of the control and test groups indicated that the addition of nano-particles reduced the contact angle ($P=0.000$), and the difference was dependent on the type of the nano-particle ($P=0.000$) and its concentration ($P=0.011$). The interaction of the type and concentration of the nano-particle on the reduction of the water contact angle was also significant ($P=0.000$).

Tukey HSD test indicated that the water contact angle varied by addition of metallic nano-particles to composite resins (Table 2). Independent t-test showed that the water contact angle depended on concentration of metallic nano-particles ($P=0.028$).

Groups	Groups	P-value *
Control	0.5% ZnO	0.000
Control	1% ZnO	0.000
Control	0.5% Ag	0.000
Control	1% Ag	0.000
0.5% Ag	1% Ag	0.008
0.5% ZnO	1% ZnO	0.000

*Tukey HSD tests

Table 1- Mean and SD for water contact angle of composite resins

Groups	Number	Mean	SD	Min	Max
Control	12	87.53	7.77	78.60	96.50
0.5% Ag	12	78.10	10.84	67.30	89.90
1% Ag	12	81.35	7.69	74.10	92.50
0.5% ZnO	12	72.63	2.15	69.40	75.50
1% ZnO	12	66.18	1.05	64.50	75.50

DISCUSSION

Nanotechnology is developing in various fields, including dentistry. In this technique the size of the particles change into nanometer dimensions to achieve different characteristics.^(12,13) Application of nanoparticles of silver and zinc oxide is increasingly growing in medicine and industry for their antibacterial properties.⁽¹²⁻¹⁵⁾ The level of sorption of microorganisms by composite resins is higher than other restorative materials,^(16,17) which can be the cause of plaque accumulation and recurrent caries in composite resin restorations. Therefore, addition of antibacterial materials to composite resins can increase the longevity of these restorative materials.

The lower the surface wetting and water sorption of the composite resin, the less its staining.⁽¹¹⁾ Surface roughness is one of the most important contributing factors in bacterial adhesion.^(18,19)

In the present study, the influence of surface roughness was eliminated by polishing all the specimens to a level of clinically acceptable surface smoothness (about 1 μm). In order to have the same physical properties in the whole mass of the composite resin, the nano-particles should be distributed uniformly in it. To collect data on this matter, we observed the broken surfaces of composite resin samples for the surface elements by SEM-EDX.

Addition of both nano-silver and nano-zinc oxide particles resulted in an increase in the

water contact angle of composite resins. Contrary to the results of the present study, Burger et al¹¹ reported greater hydrophobicity upon addition of silver to composite resins. The characteristics of the filler within the composition of the composite resin have an important role in the amount of its water sorption.⁽²⁰⁾ The amount of water sorption of composite resin depends on the hydrophilicity of the polymer matrix and also the composition of the filler. In addition, there is a relationship between the amount of filler and water sorption.⁽²⁰⁾ Metallic particles of silver and inorganic materials like ZnO are of greater surface energy compared to composite resins. Therefore, addition of these particles to hydrophobic materials such as composite resins results in an increase in surface free energy and reduction in contact angle.^(21,22) Since ZnO has a higher free surface energy,⁽²¹⁾ it caused a greater reduction in contact angle of composite resins compared to silver nano-particles in this study.

The results of the present study also indicated that depending on the type of the metallic nano-particles, addition of different concentrations resulted in different amounts of water contact angle ($P=0.000$).

The studied composite resins exhibited higher contact angles by increasing the concentration of nano-silver from 0.5% to 1% by weight while it was still lower than the control group. The increase in concentration of nano-zinc oxide particles from 0.5–1% by weight resulted in a lower

contact angle in composite resins. In addition to surface free energy, water contact angle depends on the size of the particles incorporated into composite resins. Cohesion followed by agglomeration easily occurs among ZnO nano-particles due to their huge specific surface area and high intrinsic surface energy.^(21,23) The decrease in contact angle of nano-zinc oxide-loaded composite resins by increasing nano-particle concentration can be explained by this fact. It has been reported that nano-ZnO particles have higher contact angles than micro-particles of ZnO;⁽²⁴⁾ therefore, wettability of ZnO particles is enhanced with an increase in the size.

Considering the fact that antibacterial properties of these nano-particles are previously reported in the literature, it can be supposed that the measurement of water contact angle is not a definite criterion for selection of the suitable material with the potential to decrease the bacterial plaque accumulation in the oral cavity. Further studies are required to determine the optimum amount of silver and zinc oxide nano-particles for a change in contact angle and antibacterial effects of restorative materials.

CONCLUSIONS

Within the limitations of the present study, it was concluded that:

1. Addition of nano-silver and nano-zinc oxide to composite resin caused a reduction in the water contact angle of the composite resin.

2. An increase in the concentration of nano-silver from 0.5% to 1% by weight resulted in an increase in water contact angle of composite resin, although it was still lower than the contact angle of the control group.
3. An increase in the concentration of nano-zinc oxide from 0.5% to 1% by weight resulted in further decrease in the contact angle of composite resin.

REFERENCES

1. Bagis YH, Baltacioglu IH, Kahyaogullari S. Comparing microleakage and the layering methods of silorane-based resin composite in wide Class II MOD cavities. *Oper Dent* 2009; 34:578-85.
2. Weinmann W, Thalacker C, Guggenberger R. Siloranes in dental composites. *Dent Mater* 2005; 21:68-74.
3. Leprince J, Palin WM, Mullier T, Devaux J, Vreven J, Leloup G. Investigating filler morphology and mechanical properties of new low-shrinkage resin composite types. *J Oral Rehabil* 2010; 37:364-76.
4. Klautau EB, Carneiro KK, Lobato MF, Machado SM, Silva e Souza MH Jr. Low shrinkage composite resins: influence on sealing ability in unfavorable C-factor cavities. *Braz Oral Res* 2011; 25:5-12.
5. Ilie N, Jelen E, Clementino-Luedemann T, Hickel R. Low-shrinkage composite for dental application. *Dent Mater J* 2007; 26:149-55.
6. Cruz AD, Cogo K, Bergamaschi Cde C, Bóscolo FN, Groppo FC, Almeida SM. Oral streptococci growth on aging and non-aging esthetic restorations after radiotherapy. *Braz Dent J* 2010; 21:346-50.
7. Montanaro L, Campoccia D, Rizzi S, Donati ME, Breschi L, Prati C, Arciola CR. Evaluation of bacterial adhesion of *Streptococcus mutans* on dental restorative materials. *Biomaterials* 2004; 25:4457-63.
8. Spacciapoli P, Buxton D, Rothstein D, Friden P. Antimicrobial activity of silver nitrate against periodontal pathogens. *J Periodontol Res* 2001; 36:108-13.
9. Balazs DJ, Triandafillu K, Wood P, Chevotot Y, van Delden C, Harms H, Hollenstein C, Mathieu HJ. Inhibition of bacterial adhesion on PVC endotracheal tubes by RF-oxygen glow discharge, sodium hydroxide and silver nitrate treatments. *Biomaterials* 2004; 25:2139-51.
10. Sheng J, Nguyen PT, Marquis RE. Multi-target antimicrobial actions of zinc against oral anaerobes. *Arch Oral Biol* 2005; 50:747-57.
11. Kondo Y, Takagaki T, Okuda M, Ikeda M, Kadoma Y, Yamauchi J, Okada K, Sadr A, Nikaido T, Tagami J. Effect of PMMA filler particles addition on the physical properties of resin composite. *Dent Mater J* 2010; 29:596-601.
12. Sahoo SK, Parveen S, Panda JJ. The present and future of nanotechnology in human health care. *Nanomedicine* 2007; 3:20-31.
13. Rai M, Yadav A, Gade A. Silver nanoparticles as a new generation of antimicrobials. *Biotechnol Adv* 2009; 27:76-83.
14. Li LH, Deng JC, Deng HR, Liu ZL, Xin L. Synthesis and characterization of chitosan/ZnO nanoparticle composite membranes. *Carbohydr Res* 2010; 345:994-8.
15. Kumar R, Münstedt H. Silver ion release from antimicrobial polyamide/silver composites. *Biomaterials* 2005; 26:2081-8.
16. Papagiannoulis L, Kakaboura A, Eliades G. In vivo vs in vitro anticariogenic behavior of glass-ionomer and resin composite restorative materials. *Dent Mater* 2002; 18:561-9.

17. Svanberg M, Mjör IA, Orstavik D. Mutans streptococci in plaque from margins of amalgam, composite, and glass-ionomer restorations. *J Dent Res* 1990; 69:861-4.
18. Burgers R, Eidt A, Frankenberger R, Rosentritt M, Schweikl H, Handel G, Hahnel S. The anti-adherence activity and bactericidal effect of microparticulate silver additives in composite resin materials. *Arch Oral Biol* 2009; 54:595-601.
19. Teughels W, Van Assche N, Sliepen I, Quirynen M. Effect of material characteristics and/or surface topography on biofilm development. *Clin Oral Implants Res* 2006; 2:68-81.
20. Berger SB, Palialol AR, Cavalli V, Giannini M. Characterization of water sorption, solubility and filler particles of light-cured composite resins. *Braz Dent J* 2009; 20:314-8.
21. Torchinsky I, Rosenman G. Wettability modification of nanomaterials by low-energy electron flux. *Nanoscale ResLett* 2009; 4:1209-17.
22. Kasraei S, Azarsina M. Addition of silver nanoparticles reduces the wettability of methacrylate and silorane-based composites. *Braz Oral Res* 2012; 26:505-10.
23. Liu Y, He L, Mustapha A, Li H, Hu ZQ, Lin M. Antibacterial activities of zinc oxide nanoparticles against *Escherichia coli* O157:H7. *J Appl Microbiol* 2009; 107:1193-201.
24. Zhang J, Huang W, Han Y. Wettability of zinc oxide surfaces with controllable structures. *Langmuir* 2006; 22:2946-50.