

A Study of Flexural Properties of Polymethyl Methacrylate Reinforced with Various Amount of Silanized Nano Alumina

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Received: September 9, 2020 • Revised: December 21, 2020 • Accepted: December 29, 2020

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Abstract

Methods: Concentrations of silane coupling agent were calculated and analyzed by organic element analysis. The concentration was used for silanization of nano-alumina particles and silanized nano-alumina particles were mixed with acrylic resin at 0.25, 0.5, 0.75, 1, 3 and 5% w/w, producing the experimental groups. The control group was acrylic resin without nano-alumina. The specimens were 10 mm in width, 64 mm in length and 3.3 mm in thickness. Flexural strength and modulus of elasticity were investigated for all groups and were analyzed using one-way ANOVA at 95% confidence intervals.

Results: The concentration of silane coupling agent that forms monolayer on nano-alumina particles was 0.118 g for nano-alumina particles 1 g. The average flexural strength ranged between 75.86-100.63 MPa. The average modulus of elasticity ranged between 3.06-3.92 GPa.

Conclusions: The highest average flexural strength was found in the 0.25% w/w silanized nano-alumina group (100.63±14.05 MPa) and was significantly different from control group. The highest average modulus of elasticity was found in the 0.5% w/w silanized nano-alumina group (3.92±0.81 GPa) and was significantly different from control group.

Keywords: flexural strength, methyl methacrylate, modulus of elasticity, nano-alumina particles, silane coupling agents

Introduction

Restoring of worn dentition and vertical dimension loss needs the increase of vertical dimension back to normal proportion. Apart from fixed prosthesis, overlay removable partial dentures can be restored and used as interim protheses before restoring with permanent ones. Or, in case of patients with financial or health limitation, preventing them from using fixed full mouth protheses, using of overlay removable partial dentures is also an option for restoration.⁽¹⁾

Acrylic resin or polymethyl methacrylate is extensively used to fabricate various forms of denture including overlay removable partial dentures at denture bases and occlusal surfaces because it can be effectively formed, and it is easy to fabricate and repair. It is efficient for mounting with denture bases without harming cavity tissues, and can easily be reshaped with light weight and at low cost.⁽²⁾ Polymethyl methacrylate has low mechanical strength and at the same time accumulates functional stress, which can cause deformation of the material when interacting with

external force. This case occurs from occlusal loads which easily lead to fracture and cracking.⁽³⁾ Thus, mechanical properties reinforcement of acrylic resin needs to be done in order to increase the quality of dentures. Resistance to compressive strength is one of mechanical properties that can help the material resist to the loads in the oral cavity and show its performance. Katheng *et al.*⁽⁴⁾ found that using surface modified nano-alumina particles with silane coupling agent at 1% w/w can significantly increase the resistance value of compressive strength.

Apart from the compressive strength property of acrylic resin, flexural strength is another essential property. As when occlusal force is transferred on opposing abutment teeth, some stress is distributed on the incline of cusp. This creates shear force and tension force that cause dental fractures. Therefore, the mechanical properties as mentioned have to be improved. Flexural strength can be used to estimate the strength of material, especially for dentures with long span structure⁽⁵⁾, such as bridge and overlay removable partial denture. The flexural strength shows the value of resistance to the loads causing cracking from bent material. In addition, another mechanical property involved in denture endurance is modulus of elasticity which has the value of stress against 3-point bending test. It is used to indicate the level of material bending without damage by active force.

Currently, several researches on mechanical properties reinforcement of acrylic resin, such as nano-alumina particles mixing in acrylic resin, are conducted because nano-alumina particles are cheap, highly solid, highly chemically stable and highly resistant to acid and base. According to the study of Kundie *et al.*⁽⁶⁾, nano-alumina particles increased significant fracture toughness and modulus of elasticity. The result of the study done with surface modification functionalized with silane coupling agent was satisfying. According to the study of Guo *et al.*⁽⁷⁾, when nano-alumina particles went through surface modification with a coupling agent, it was found to be covalently bound between silane coupling agent and the nanoparticles. And, when it was added with a vinyl-ester resin, it has effects on modulus of elasticity and flexural strength increasing. The finding correlates with the study of Caglar *et al.*⁽⁵⁾ which was done by mixing surface modified nano-alumina particles with silane coupling agent, and thereby mixed into poly methyl methacrylate at 5% w/w. The result showed that flexural strength

and modulus of elasticity increased significantly. Moreover, Ellakwa *et al.*⁽⁸⁾ studied the property of polymethyl methacrylate thermal diffusivity of heat of denture base material with increasing nano-alumina particles. It was found that the rate of polymethyl methacrylate thermal diffusivity of heat correlatively increased with the amount of increasing nano-alumina particles. According to Chaijareenont *et al.*⁽⁹⁾, it was found that adding nano-alumina filler silanized with MPS resulted in an improvement of the flexural strength and wear resistance of polymethyl methacrylate.

Vojdani *et al.*⁽¹⁰⁾ did a comparative study on the flexural strength, surface hardness, and roughness of heat-polymerized acrylic resin reinforced with nano-alumina particles. It was found that polymethyl methacrylate reinforced with nano-alumina particles at 2.5% w/w had significantly higher flexural strength than polymethyl methacrylate without reinforcement with nano-alumina particles. The increased amounts of nano-alumina particles did not make denture base rough. In Jasim and Ismail's⁽¹¹⁾ study, acrylic resin denture base was reinforced with nano-alumina particles. It was found that the value of surface hardness increased in all experimental groups, and the value of flexural strength significantly augmented when nano-alumina particles were added at 1% and 2% w/w. Ash *et al.*⁽¹²⁾ reported that there was no direct adhesion between methyl methacrylate and nano-alumina particles. Therefore, the surface of filler has to be modified before using. Arksornnukit *et al.*⁽¹³⁾ found that when the surface of silane coupling agents was modified, the filler helped reinforce flexural properties towards polymethyl methacrylate.

Proper concentration of silane coupling agents should be proportionated in order to develop monolayer or chemisorbed layer when the coupling agents are bound to the surface as the process occurs on the surface of the particles that function as filler to reinforce the siloxane bond at the highest rate⁽¹⁴⁾ that was deemed to be covalent bond. Development of thicker layer has weak bonding due to Van der Waals force and hydrogen bond, called the physisorbed layers, which are easy to be washed away with chemical solvent⁽⁹⁾ such as tetrahydrofuran. Jiangkongkho *et al.*⁽¹⁵⁾ studied the use of fundamental equation of Posthumus⁽¹⁶⁾ to investigate proper concentration of silane coupling agents before being silanized on nanosilica particles, to analyze suitable amount of silane coupling

agent concentration that forms monolayer, and thereafter, to silanize nanosilica particles in order to determine the amount of filler that creates the highest flexural strength while the study of Chaijareenont *et al.*⁽⁹⁾ used the formation of monolayer by washing silanized nano-alumina particles with tetrahydrofuran. This includes the study of Katheng *et al.*⁽⁴⁾ that used Arkle's equation to calculate the amount of silane coupling agents before washing silanized nano-alumina particles with tetrahydrofuran where the formation of monolayer was not confirmed. These former studies show that there were no studies on precise concentration of silane coupling agents that form monolayer before reinforcing nano-alumina particles with silane coupling agent that forms monolayer and where the agents were used as filler in heat-polymerized poly methyl methacrylate. Thus, the purpose of this study is to investigate the concentration of silane coupling agents that form monolayer on nano-alumina particles and the effects of various amounts of silanized nano-alumina particles mixed in polymethyl methacrylate on two properties: flexural property and modulus of elasticity. The hypothesis of the study was the amount of silanized nano-alumina particles does not affect flexural properties of polymethyl methacrylate.

Materials and Methods

Step 1: Proper amount of silane coupling agent investigation

Nano-alumina particles with 20 nanometer in diameter (US Research Nano., Houston, TX, USA) and trimethoxysilane (3-methacryloxypropyl) or (MPS, Sigma-Aldrich[®], St. Louis, MO, USA) were used. The calculation began with Posthumus equation by using the surface value of nano-alumina indicated by manufacturer:

$$X = m_{\text{alumina}} \times MW_{\text{MPS}} \times M_{\text{MPS}} \times A_{\text{alumina}} \times 10^{-6}$$

X stands for silane coupling agent concentration in $\text{gram}_{\text{mps}}/\text{gram}_{\text{alumina}}$. M_{alumina} is the amount of nano-alumina particles in gram. MW_{MPS} is the weight of MPS silane molecule which equals to 248.35 gram/mole. M_{MPS} is the amount of MPS silane required to form chemisorbed layer. MPS has the value of $6.9 \mu\text{mol}/\text{m}^2$. And A_{alumina} is the surface value of nano-alumina particle in use, which is $138 \text{ m}^2/\text{gram}$. The result of calculation is the concentration

of silane coupling agent at $0.236 \text{ gram}_{\text{MPS}}/\text{gram}_{\text{alumina}}$.

Next, silane coupling agents per nano-alumina particles were prepared to test for the proper concentration that forms monolayer. To investigate silanization of nano-alumina particles, nine ranges of concentration were set: 0.01475, 0.0295, 0.059, 0.118, 0.236, 0.472, 0.944, 1.416 and $1.888 \text{ gram}_{\text{MPS}}/\text{gram}_{\text{alumina}}$ at the value of 1/32, 1/16, 1/8, 1/4, 1/2, 1, 2, 4, 6 and 8 times, calculated according to Posthumus equation. Preparation of silane coupling agents was done in ethanol solution with 99.8% by volume (ethanol, Carlo erba, Milano, Italy) in polyethylene bottle and mixed with nine bottles of deionized water to get concentration of ethanol solution at 70% by volume. Then, acetic acid (96% acetic acid, Carlo erba, Milano, Italy) was dripped to acquire (pH) at 4.5.⁽¹⁷⁾ Next, 1 gram of nano-alumina particle was added and taken to mix together in magnetic stirrer (Intllab[™], Shenzhen, China). Mixing process took 2 hours. Then, the substance was immediately put in the incubator machine (Memmert, Schwabach, Germany) at 70 degree Celsius for 4 hours. After that, it was left for cooling process at room temperature. Next, each range of concentration was divided into two portions. The first portion was taken to be dried in the incubator machine at 50 ± 5 degree Celsius until complete dry. The group was called dried group. The other portion was added with isopropanol solution (RCI labscan, Bangkok, Thailand) at 3:1 by volume and put into centrifuged machine (Hettich[®] 460R centrifuge, St. Louis, MO, USA) at 20,000 rounds per minute for 2 hours. Then, pipette was used to take out surfacing liquid. Nano-alumina particles were left at the bottom and taken to drying process at 50 ± 5 degree Celsius for 16 hours. This group is called centrifuged group.

All 18 groups of both dried group and centrifuged group of silanized nano-alumina particle specimens were taken to investigate with organic element analysis machine (Thermo Fisher Scientific, Waltham, MA, USA) to verify the number of Carbon on silane coupling agent surface and to calculate for proper concentration that form monolayer by using the equation⁽¹⁸⁾

$$C = M_{\text{MPS}} \times N_{\text{A}} \times 10^{-18}$$

C stands for the amount of silane coupling agent found on the surface of nano-alumina particle with molecule/square nanometer. M_{MPS} stands for amount

of silane coupling agent found on the surface of nano-alumina particle with $\mu\text{mol}/\text{m}^2$. The silane coupling agent using molecule consisted of 7 atoms of carbon, which has atomic number equals to 12. The molecule weight of MPS silane coupling agent was 248.35 gram/mole. Surface of nano-alumina particles was $138 \text{ m}^2/\text{gram}$. And, N_A stands for Avogadro's number with the value of 6.02×10^{23} molecule/mole.

Calculated concentration of silane coupling agent was taken to apply with surface modification of nano-alumina particles for further experiment.

Step 2: Specimen preparation for flexural properties experiment

Plastic prototype was fabricated by lowering its marginal ridge all around and making the inferior border at the base be wider than the superior one: 66 millimeters long, 50 millimeters wide and 3.5 millimeters thick. The mold for specimen fabrication was made of mixing stone plaster. Then, it was poured into brass dental flask until the lower part was fully filled. When the mixture was completely hardened, the piece was brushed and finished with water sandpaper. Then, the piece was applied with intermediate agent. Next, the prepared plastic prototype was put on the stone plasters by setting the smaller sized surface up and having equal interval from the border of dental flask recipient. After, the upper part of dental flask was taken on that of lower part. Then, stone plaster was fully poured into it. When the piece was completely hardened, plastic mold was taken out and the intermediate agent was applied on both upper and lower part of dental flask.

Salinized nano-alumina particles, calculated by using nano-alumina particle at 0.25, 0.5, 0.75, 1.3 and 5% w/w according to the studies of Katheng *et al.*⁽⁴⁾ and Jiangkongko *et al.*⁽¹⁵⁾ were mixed with powder of heat-polymerized methyl methacrylate (Major D-4f, Major, Moncalieri, Italy) in cubic mixer (Uniquetools, Chachoengsao, Thailand). The control group was acrylic resin without nano-alumina. All groups were taken to be mixed with monomer liquid by using 2.5 grams of powder per 1 milliliter of monomer. When the mixture went on dough stage, it was poured into the mold and left to set in hot water at 80 degree Celsius for 90 minutes. After that, the water was heated up to boiling and left in boiling stage for another 30 minutes. Then, it was left at room temperature until

reaching cooling stage and the specimen was taken out.

Polymethacrylate plate was polished until it became smooth and gained the size of 3.3 ± 0.2 millimeters with polish machine (MoPao160E, Shangdong, China) at the speed of 600 rounds per minute for 10 seconds. The range number of water sandpaper used were 200, 400, 600, 800 and 1,000 consecutively. Then, the specimens were cut by laser machine (laser CNC machine, T-BROs engineering, China) to get 10 ± 0.2 millimeters wide and 64 ± 0.01 millimeters long in accordance with the ISO 20795-1(2013)⁽¹⁹⁾ standard of flexural strength testing specimen. The size of specimen was verified with digital vernier caliper (Mitutoyo, Kanagawa, Japan).

Step 3: Flexural strength and modulus of elasticity testing

Flexural properties testing was conducted with all 7 groups. As shown in table 1, 12 specimens of each group were prepared and soaked in water at room temperature for 24 hours before experiment.

Table 1: Experimental groups and the component in each group.

Group	Nano-alumina particle quantity mixed in polymethyl methacrylate (percentages by weight: wt%)
1	0
2	0.25
3	0.5
4	0.75
5	1
6	3
7	5

Twelve pieces of specimens were taken to 3-point flexural properties test with universal testing machine (Instron[®]5566, Canton, USA) by setting the space between the base at 50 ± 0.1 millimeters. 1,000 newton load cell size was selected at the speed of 5 ± 0.1 millimeters per second. The load cell was put at right angle to the surface at the center of the specimen. Then, force emission was started until the specimens were cracked in accordance with ISO 20795-1(2013), followed by the calculation of flexural strength and modulus of elasticity values. Then, two specimens of each groups were randomly selected to check on fractured areas with scanning electron microscope (JSM 6335F, InTouchScope[™], Tokyo, Japan) in

order to investigate the agglomeration of nano-alumina particles, bonding and gap that occur between nano-alumina particles and resin matrix around them.

Data were analyzed with inferential statistics called one-way ANOVA to investigate the differences of average value of flexural strength in each experimental group, and to test with Tukey HSD' test to compare multiple variances in each experimental group with the confident level at 95% ($p < 0.05$) with SPSS program version 24, IBM, Armonk, NY, USA).

Results

Step 1: Test results of silane coupling agent amount on nano-alumina particles

At the concentration of 0.118 grams. for nano-alumina particles 1 grams., it was found that both dried group and centrifuged group had the most equal amount of Carbon at nano-alumina particle surface before the difference occurred between both groups at higher concentration (Figure 1). This indicates that at the concentration higher than 0.118 grams. for nano-alumina particles 1 grams. (including at the concentration at 0.236 grams. for nano-alumina particles 1 grams. from Posthumus equa-

tion calculation), centrifuged physisorbed layer occurred. Therefore, concentration value of silane coupling agents selected was 0.118 grams. for nano-alumina particles 1 grams. in order to test for flexural properties.

Step 2: Testing result of flexural strength and modulus of elasticity

Average flexural strength of each group was shown in Table 2 where the control group equals 76.37 ± 11.74 MPa. The highest average flexural strength of acrylic resin was found in the 0.25% w/w silanized nano-alumina group (100.63 ± 14.05 MPa) and was significantly different from control group whereas the lowest average flexural strength was found in the 5% w/w nano-alumina group (75.86 ± 8.85 MPa) and was not significantly different from control group.

Average modulus of elasticity of each group was shown in Table 2 where the control group equals 3.46 ± 0.41 GPa. The highest average modulus of elasticity of acrylic resin was found in the 0.5% w/w silanized nano-alumina group (3.92 ± 0.81 GPa) whereas the lowest average modulus of elasticity of acrylic resin was found in the 5% w/w nano-alumina group (3.06 ± 0.33 GPa). There was no significant difference between all experimental groups and control group.

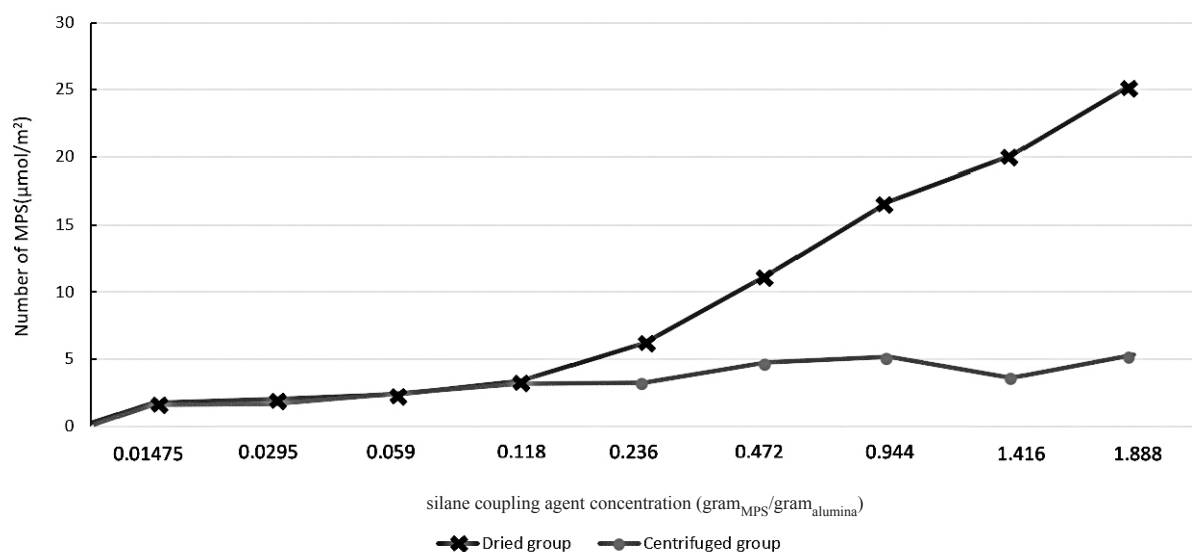


Figure 1: Number of silane coupling agent at surface of nano-alumina particle ($\mu\text{mol}/\text{m}^2$) by each silane coupling agent concentration ($\text{gram}_{\text{MPS}}/\text{gram}_{\text{alumina}}$).

Table 2: Average of flexural strength and modulus of elasticity of control group and each experimental group. The characters differ to demonstrate the difference was statistically significant ($p < 0.05$).

Group	Flexural strength (MPa)	Modulus of elasticity (GPa)
1	76.37±11.74 ^b	3.46±0.41 ^A
2	100.63±14.05 ^a	3.45±0.87 ^A
3	96.93±18.54 ^a	3.92±0.81 ^A
4	92.47±13.62 ^{ab}	3.84±0.83 ^A
5	90.82±17.37 ^{ab}	3.33±0.92 ^A
6	86.08±21.38 ^{ab}	3.33±0.92 ^A
7	75.86±8.85 ^b	3.06±0.33 ^A

The study showed that flexural strength tended to clearly decrease in accordance with the increased amount of alumina. This occurred when the 5% w/w silanized nano-alumina particle group had significantly lower average flexural strength than the 0.25 and 0.5% w/w silanized nano-alumina particle group while modulus of elasticity tended to slightly but unclearly decrease in accordance with the increased amount of alumina.

The pictures of nanoalumina particles at the fracture parts of the specimens by scanning electron microscope were shown in Figure 2,3 and 4

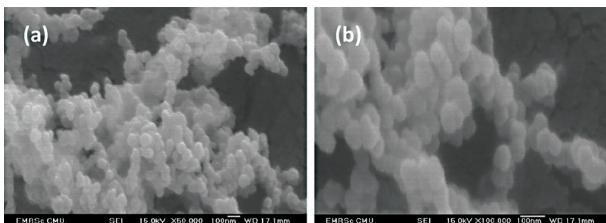


Figure 2: (a) Scanning electron micrography shown agglomeration of nano-alumina particles in the 5% w/w silanized group at 50,000 magnification. (b) Showed agglomeration of nano-alumina particles in the 5% w/w silanized group at 100,000 magnification.

Discussion

This study disapproves the hypothesis saying that the amount of silanized nano-alumina particles does not affect flexural strength of acrylic resin, and approves the hypothesis saying that the amount of silanized nano-alumina particles does not affect modulus of elasticity of acrylic resin.

The experiment was done to investigate the proper concentration of silane coupling agents for surface modification of nano-alumina particles that will form

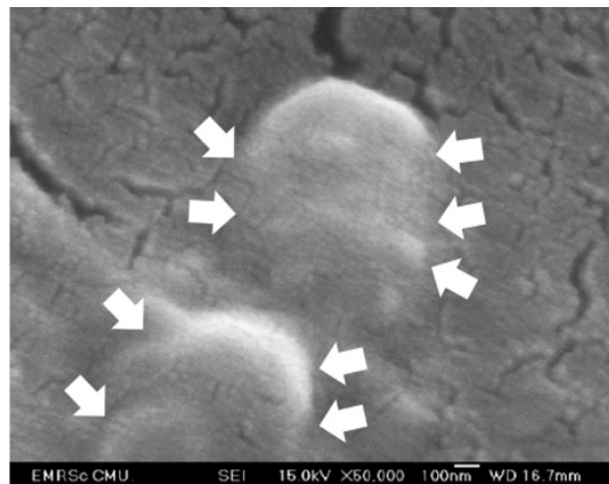


Figure 3: Scanning electron micrography shown silanized nano-alumina particle in matrix of resin acrylic in 3% w/w group. Bonding between nano-alumina particle and matrix of resin acrylic indicated by white arrows at 50,000 magnification.

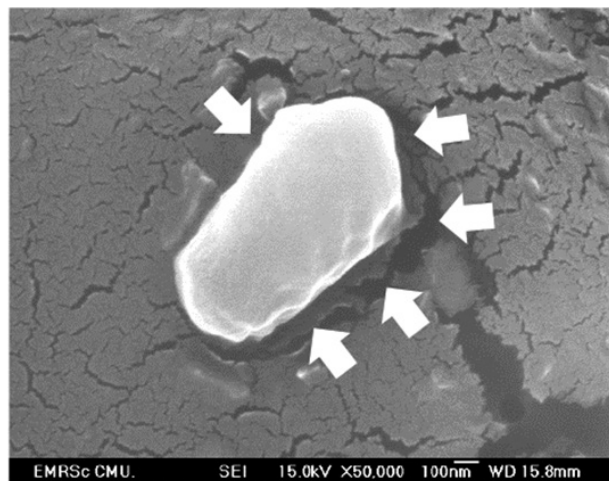


Figure 4: Scanning electron micrography shown non-silanized nano-alumina particle in matrix of resin acrylic in 3% w/w group. The gap between nano-alumina particle and matrix of resin acrylic indicated by white arrows at 50,000 magnification.

monolayer coverage which creates the highest strength.⁽¹⁴⁾ Katheng *et al.*⁽⁴⁾ prepared the afore mentioned substances along with MPS silane coupling agent at 0.46 $\text{gram}_{\text{MPS}}/\text{gram}_{\text{alumina}}$ according to Arkle equation before washing them with tetrahydrofuran. However, this study was based on Posthumus equation and was done with organic element analysis machine and found the silane coupling agent concentration at 0.118 $\text{gram}_{\text{MPS}}/\text{gram}_{\text{alumina}}$ ($3.15 \mu\text{mol}/\text{m}^2$ in centrifuged group or $3.4 \mu\text{mol}/\text{m}^2$ in dried group). This number is relevant to the

study of Chaijareenont *et al.* that was done on the 0.1% w/w silanizing nano-alumina particles. This increased the flexural properties of acrylic resin. On the contrary, at the concentration of less than 0.118gram_{MPS}/gram_{alumina}, the increasing level of silane coupling agents on nano-alumina particle surface had no difference in both dried group and centrifuged group. Only small amount of silane coupling agent on nano-alumina particles surface increased.

The concentration of silane coupling agent in this study was half amount of the result of Posthumus equation (0.236gram_{MPS}/gram_{alumina}). The finding corresponded to the study of Jiankongkho *et al.*⁽¹⁵⁾ The study used one-fourth less concentration of silane coupling agent that causes monolayer on nano-silica than the amount calculated from Posthumus equation. Posthumus *et al.*⁽¹⁶⁾ found that the concentration value decreased by 30% from the starting equation. Miller *et al.*⁽²⁰⁾ found that the formation of monolayer on nano-silica particles, which depends on the rod alignment of silane coupling agent molecule on perpendicular alignment, occurred when 6.9 $\mu\text{mol}/\text{m}^2$ silane coupling agents were used whereas on the parallel alignment of silane coupling agent, only 3 $\mu\text{mol}/\text{m}^2$ were needed in order to develop the formation of monolayer. However, when it was compared to oxide particle of other metal, the number of active oxide bond needs to be taken into account. Nano-alumina particle has single bond ready to react with silane coupling agent⁽²¹⁾ because there are three atoms of oxygen in alumina oxide for one molecule (Al_2O_3) while the bond of the active oxide of silica particle is more effective to create the bond with silane coupling agent from one molecule of silica oxide.⁽²²⁾

According to the study of Katheng *et al.*⁽⁴⁾, Chaijareenont *et al.*'s method of surface modification of nano-alumina⁽⁹⁾ was used by spinning silane coupling agent with nano-alumina particles until it was dried at room temperature. Then, it was washed with tetrahydrofuran. This process was repeated until it was unable to wash further and develop monolayer coverage. This experiment used the preparation method of Jiangkongkho *et al.*⁽¹⁵⁾ that used the centrifuge method with isopropanol instead. The advantage of this method was it reduced homocondensation of the molecule⁽¹⁶⁾ of silane coupling agent while there was no bonding with inorganic particles like nano-alumina particle. The molecule of monolayer silanized particles of silane coupling agent will not produce this condensation. The process was done before

using the mentioned method to analyze the concentration of silane coupling agent that required the monolayer surface modification of the particle. Thus, it should produce a more precise result. The experiment result of the study was in accordance with the study result of Katheng *et al.*⁽⁴⁾ in the case where the experimental group mixed with the lowest concentration of silanized nano-alumina particles produced the highest average of compressive strength endurance and significantly differed from control group. This was because nano-alumina particles were well dispersed and produced complete texture without pore or gap between nano-alumina particles and matrix of polymer (Figure 3).

The study showed that flexural strength of the 0.25% w/w silanized nano-alumina particle increased significantly in the control group. Acrylic resin group mixed with the 0.25% silanized nano-alumina particles had the highest average flexural strength (100.63 Mpa) which was 24.26Mpa (or 31.77%) higher than the average flexural strength of the control group. The findings corresponded with the study done by Ahmed *et al.*⁽²³⁾ which found that using silanized nano-alumina before mixing in acrylic resin helped increase flexural strength.

The preliminary experiment of this study was done with non-silanized nano-alumina particles mixed with acrylic resin (0.25, 0.5, 0.75, 1, 3 and 5% w/w). It was found that average flexural strength did not significantly increase compared to control group. The result matched with the study of Alhareb *et al.*⁽²⁴⁾ showing that adding non-silanized nano-alumina particles did not improve mechanical properties of acrylic resin. However, the finding showed the slight increase of flexural strength in non-silanized nano-alumina group. Alhareb *et al.*⁽²⁵⁾ explained that increasing mechanical properties in acrylic resin mixed with nano-alumina particle even without silanization, due to good dispersion of nano-alumina particles in the matrix of acrylic resin, led to absorption of compressive force and reduction of crack propagation. Furthermore, the finding corresponded to the study of Ahmed *et al.*⁽²³⁾ explained that mechanical properties of non-silanized filler were better because those fillers also had possibilities to create Van der Waals chemical bond and matrix of polymer.

The flexural strength from 3-point bending force test had three basic sources: compressive force, tensile force and shear force. The results of 3-point bending test will

come from combination of those three forces.⁽²⁶⁾ Katheng *et al.*⁽⁴⁾ did the test on compressive force endurance of nano-alumina particle and silane coupling agent of the same kind in the present experiment. The result showed that the group of acrylic resin mixed with the 1% w/w silanized nano-alumina particles produced the highest compressive strength, which was also significantly higher when comparing to control group and the group mixed with the 1% w/w non-silanized nano-alumina particles. In contrast to the present study, it was found that the group mixed with 1% w/w silanized nano-alumina particles did not have significant difference in flexural strength. This was because the test was based on 3-point bending force. Therefore, tensile and shear forces were taken into account. As a result, average flexural strength in this study tended to be different from that of the study of Katheng *et al.*⁽⁴⁾

From the acquired result shown that flexural strength tended to decrease when silane coupling agent was used with increasing number of nano-alumina particle, this effect was observed during the preparation of experimental specimens using silanized nano-alumina particles. When the amount of nano-alumina particles was at 5%, disposition of nano-alumina decreased⁽⁶⁾ as shown in Figure 2 and finally reduced the flexural strength. The finding corresponded to the study done by Kumar *et al.*⁽²⁷⁾ indicating that flexural strength of acrylic resin tended to decrease when the amount of the 1, 2 and 3% w/w silanized nano-alumina particles in experimental group was increased.

Non-silanized particles have high surface energy.⁽²⁸⁾ This facilitates moisture absorption. And, as the size of particle surface was at nanometer, these factors encouraged development of agglomeration.⁽⁶⁾ While surface modification with silane coupling agent improved surface condition of nano-alumina to be more suitable for particle disposition and better reduce surface energy and agglomeration⁽²⁹⁾, the disposition rate decreased in parallel with increasing amount of alumina. This also caused more agglomeration among one another and widened the interfacial between nano-alumina particles and acrylic resin matrix, which led to microcracks and breakings more easily. This result corresponded to the experiment of Kundie *et al.*⁽⁶⁾ Their study was done to test flexural strength by increasing the amount of silanized nano-alumina particle in acrylic resin. The study showed

that flexural strength decreased consecutively that can be explained by the agglomeration that can occur in both silanized and non-silanized particles. This corresponded to the study of Zhang *et al.*⁽³⁰⁾ explaining that agglomeration and gapping of increasing fillers made it more possible to agglomerate among themselves rather than happening between the fillers and acrylic resin matrix, especially during preparation of mixing nano-alumina particles with poly methacrylate powders in order to create the piece of work. The amount of filler also affected the ratio between poly methacrylate powders and monomers that led to the increase of residual monomer and affected the degree of conversion⁽⁶⁾ of carbon from double bond to single bond and flexural strength of acrylic resin in the end.

For the value result of modulus of elasticity, preliminary study result showed that the number of all groups applied with non-silanized nano-alumina particles was significantly lower than the number of control group and the group applied with silanized nano-alumina particles. This showed that when the fillers were not pre-silanized, the ability to resist to the force that permanently deformed the material of acrylic resin became lower than that of acrylic resin in control group and in silanized nano-alumina particle group. Observation from electron microscope found that when non-silanized nano-alumina particles were added, no adhesion between interfacial of fillers and matrix was found as shown in Figure 3, and this lowered the strength because there were increasing strains accumulated in the areas of fillers and led to the decrease of modulus of elasticity. The finding corresponded to the study done by Ellakwa *et al.*⁽⁸⁾ and Omrani *et al.*⁽³¹⁾ While the group added with nano-alumina particle was silanized, adhesion of interfacial between fillers and matrix was found as shown in Figure 4. And, it was possibly because the adhesion between acrylic resin and non-silanized nano-alumina particles was less than the adhesion between acrylic resin and silanized nano-alumina particles, the adhesion between nano-alumina particles and matrix of acrylic resin in the first group occurred by Van der Waals force, and there were gaps between particles and matrix of acrylic resin while the adhesion of latter group occurred with covalent bond which had more strength.

The results of this study showed decreasing tendency of flexural strength and average of modulus of elasticity whereas the amount of silanized nano-alumina particles became higher. The finding corresponded to

the study done by Kumar *et al.*⁽²⁷⁾ revealed that flexural strength tended to decrease, and to the study done by Hassan *et al.*⁽³²⁾ revealed that average modulus of elasticity reduced when the amount of silanized nano-alumina particles increased accordingly. However, these findings were in contrast to the study done by Aydin *et al.*⁽⁵⁾ This was because the present study was done with alumina particles at nano scale while the study of Aydin *et al.*⁽⁵⁾ used them at micro scale.

The present study was done in laboratory. When the result of the study is applied in real cavity conditions, there will be other factors affecting flexural strength and modulus of elasticity. Therefore, thermal cycling test and other mechanical properties study, such as wear resistance can better help to simulate the closest cavity conditions and do further studies.

Conclusions

Within the limit of this study, it can be concluded that:

1. Concentration of MPS silane coupling agent that produced monolayer coverage on nano-alumina particles was $0.118 \text{ gram}_{\text{MPS}}/\text{gram}_{\text{alumina}}$.
2. Flexural strength in acrylic resin group with 0.25% w/w heat-polymerized and silanized nano-alumina particles had the highest average and was significantly different from the control group.
3. Modulus of elasticity in acrylic resin group with heat-polymerized and silanized nano-alumina particles of all experimental groups was not significantly different from control group.

Acknowledgements

This work was supported by a research grant from Faculty of Dentistry, Chiang Mai University. We would like to express special thanks to Research Center, Faculty of Dentistry, Chiang Mai University, Science and Technology Service Center, Faculty of Science, Chiang Mai University, for the support of research tools and equipment, and to Dr. Thanapat Sastraruji for the statistical analysis advice in this research.

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