The synthesis, modification, and application of nanosilica in polymethyl methacrylate denture base

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This study aimed to investigate amount of γ -methacryloxypropyltrimethoxysilane (MPS) silanized on experimental nanosilica particles (NPs), amount of NP and amount of MPS silanized NP on flexural strength (FS), flexural modulus (FM), and fracture toughness (FT) of NP reinforced polymethyl methacrylate (PMMA). The chemisorbed amount of MPS was determined using elemental analysis. Six groups ($n=8$) were prepared with chemisorbed amount and mixed with PMMA-monomer to make 0.25, 0.5, 1, 5, 10 and 15% (w/w) of NP reinforced PMMA. PMMA without NP served as control. Seven groups ($n=8$) were prepared with 1% of NP silanized with 0, 0.061, 0.123, 0.246, 0.493, 0.987, and 1.974 gMPS/g_{silica} and mixed with PMMA-monomer to make NP reinforced PMMA. FS, FM, and FT were determined using 3-point bending test. One-way ANOVA and multiple comparisons showed that 0.246 gMPS/g_{silica} of 1% amount of silanized NP group was significantly highest in FS, FM, and FT compared to the others ($p<0.05$).

Keywords: Flexural properties, Modification, Nanosilica, Silane coupling agent, Synthesis

INTRODUCTION

Nanotechnology is based on the use of matter at dimensions between 1–100 nanometers (nm). Nanoparticles have a very high surface area to volume ratio, resulting in increased molecular interaction between the polymer and nanoparticles in a composite nanomaterial¹⁾. At the nanoscale, the inorganic nanoparticles are used to reinforce the polymer matrix. However, the effect of nanoparticle enhancement depends on particle size and degree of dispersion²⁾.

Nanosilica particles (NPs) are frequently used as fillers to improve a material's properties, such as abrasion resistance, mechanical properties, and refractive index. The small size and homogeneous distribution of the nanoparticles in the matrix are essential for optical transparency and optimal mechanical properties³⁾. The Stöber method was developed to produce uniform-size NPs using ammonia catalyzed hydrolysis and condensation using low molecular-weight alcohol as a solvent⁴⁾. The size and dispersion of these particles are controlled by the concentration of tetraethyorthosilicate, water, and ammonia^{5–8)}. However, inorganic particles cannot be dispersed in a nonpolar organic polymer unless a dispersing agent is used. Silane coupling agents are often used as a dispersing agent to form stable chemical bonds between the inorganic particles and organic polymer material. Moreover, silanization improved the dispersive stability of the particles in a polymer and enhanced the mechanical properties of polymer based composite materials⁹⁾. The high viscosity of organic polymers makes it difficult to disperse nanoparticles

in the polymer matrix. Low dispersion limits the effect of the nanoparticles on improving polymer mechanical properties. Thus, predispersing the nanoparticles in the monomer or pre-polymer before preparation of the nanocomposites is recommended²⁾.

γ -methacryloxypropyltrimethoxysilane (MPS) is the silane coupling agent most commonly used in dentistry to modify the silica surface⁹⁾. An important factor is the amount of MPS needed to form a monolayer on the NP surface. Theoretical calculations generated two estimated MPS amounts, depending on the MPS molecule orientation¹⁰⁾. If the MPS molecule is oriented perpendicular to the surface, it is estimated that 6.9 μmol of MPS is needed to create a monolayer covering 1.0 m^2 of the particle surface. If the MPS molecule is oriented parallel to the surface, resulting in hydrogen bonding between the MPS carbonyl group and Si-OH on NP surface also siloxane bond between Si-OH of MPS and Si-OH on NP surface, only 3.0 μmol of MPS is needed for a monolayer covering 1.0 m^2 of the particle surface¹⁰⁾. These calculations were based on a computer simulation. However, the calculated amount of MPS required monolayer coverage on the particle surface by Arkles's equation¹¹⁾ was 12.82 $\mu\text{mol}/\text{m}^2$. Posthumus *et al.*¹²⁾ reported that the actual values can deviate from both Arkles's equation and Posthumus *et al.*'s calculation due to incomplete coverage and increased MPS molecular weight due to homocondensation. The homocondensed molecule is too large to react with the silica surface, resulting in multilayer formation. Söderholm and Shang¹³⁾ found that the amount of MPS needed to form a monolayer on the silica surface was 1.59 $\mu\text{mol}/\text{m}^2$. This amount was approximately 8 times lower than that based on Arkles's equation (12.82 $\mu\text{mol}/\text{m}^2$). However, the actual amounts

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of MPS used in silanization were lower than the amount needed for complete monolayer coverage^{12,13}, based on both computer simulation and Arkles's equation. The optimal amount MPS required for NP silanization is still unknown.

Polymethyl methacrylate (PMMA) has been commonly used since the 1940's to fabricate denture base¹⁴. The advantages of PMMA are low cost, simple fabrication process, light weight, satisfactory esthetics, color matching ability, and easy to finish and polish¹⁵. However, some disadvantages exist, including low strength and toughness. Many studies have been performed to improve the mechanical properties of denture base materials by adding fillers to the PMMA denture base^{16,17}. It was reported that alumina with a chemisorbed MPS monolayer adequately improved the mechanical properties of PMMA denture base¹⁷. However, there are no studies concerning the effect of the amount of MPS on NPs on the mechanical properties of NP reinforced PMMA. In this study, NPs with a chemisorbed silane monolayer were predispersed in PMMA liquid monomer to obtain a homogenous suspension, which was subsequently mixed with PMMA polymer powder. It was hypothesized that this process would generate a homogenous material that improved the mechanical properties of PMMA denture base.

Therefore, the objectives of this study were to investigate the chemisorbed amounts of silanized on NPs and to investigate the effect of various amount of NPs and various amount of MPS silanized on the NPs on mechanical properties of NPs reinforced PMMA denture base. The null hypotheses were that there would be no differences in the mechanical properties of PMMA denture base reinforced with various amount of NPs and amount of MPS silanized on the NPs.

MATERIALS AND METHODS

Precursor, silane coupling agent, and solutions

The precursor, silane coupling agent, and solutions used in this study, and their manufacturer, are shown in Table 1. The chemicals were used as received.

NPs synthesis and modification

Spherical NPs were prepared by hydrolysing tetraethoxysilane (TEOS) in ethanol (ETH), distilled water (H₂O), and ammonium hydroxide (NH₄OH). The particle size was controlled by the concentrations of TEOS, H₂O, and NH₄OH in ETH, as previously described⁵. In this study, 36 nm-size NPs were synthesized from the concentrations of TEOS, H₂O and NH₄OH equal to 0.322, 1 and 0.233 mol/L, respectively. Eight milliliters of TEOS was added to 100 mL of absolute ETH and magnetically stirred at room temperature (RT) (23±2°C) for 10 min. Next, 2 mL of H₂O was added drop by dropping into the reaction media to facilitate TEOS hydrolysis. After 90 min, 1 mL of NH₄OH (catalyst) was added to the reaction mixture. The reaction continued for 7 days to obtain monodispersed NPs.

The amount of MPS used for NP silanization was calculated using the modified Posthumus's equation¹²) as follows:

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

where, X is the amount of silane (g), m_{silica} is the amount of silica (g), MW_{MPS} is the molecular weight of MPS (248.35 g/mol), M_{MPS} is the amount of required chemisorbed MPS (6.9 μmol/m²), and BET_{silica} is the NP surface area (576 m²/g).

The NPs were silanized with 0, 0.061, 0.123, 0.246, 0.493, 0.987, and 1.974 g_{MPS}/g_{silica} MPS. The MPS was pre-hydrolyzed in 80% ETH at RT for 1 h. The hydrolyzed MPS was added to the NP suspension

Table 1 Precursor, silane coupling agent and solutions used in the present study

Name	Concentration (%)	Code	Brand	Mfg.	Lot No.
Precursor					
Tetraethoxysilane	98	TEOS	SIGMA-ALDRICH®	SIGMA-ALDRICH®, St. Louis, MO, USA	WXBC1471V
Silane coupling agent					
γ-methacryloxy propyltrimethoxysilane	99	MPS	SIGMA-ALDRICH®	SIGMA-ALDRICH®	SHBD3265V
Solutions					
Ethanol	99.90	ETH	EMSURE®	Merck, Darmstadt, Germany	K47648083610
Ammonium hydroxide	28–30	NH ₄ OH	J.T.Baker	Avantor Performance Materials, Center Valley, PA, USA	101273
Isopropanol	99.50	ISP	UNIVAR	Ajax Finechem, NSW, Australia	1506196057

and stirred using a magnetic stirrer at 200 rpm for 2 h at RT, and then refluxed at 70°C for 4 h. At the end of the reaction, the mixture was allowed to cool and divided into two parts for analysis. The first part was dried by evaporating the solvent in an oven (Mettler, Schwabach, Germany) at 50±5°C. This process resulted in a mixture of silanized NP, unreacted MPS, and homocondensated MPS, which is referred to as the dried sample. The other part was diluted with isopropanol at a 3:1(v/v) ratio to improve the solubility of the homocondensated MPS. This sample was centrifuged using high speed centrifugation (Avanti® J-E, Beckman Coulter, Indianapolis, IN, USA) at 20,000 rpm for 2 h at RT¹²⁾. The clear supernatant, which contained the homocondensated MPS and unreacted MPS, was decanted from the sediment. This sediment was composed of NPs silanized with MPS. This sediment is referred to as the centrifuged sample. The dried and centrifuged samples were dried at 50±5°C in an oven for at least 16 h.

NPs characterization

1. Transmission electron microscopy (TEM)

The morphology and distribution of the experimental NPs in solution were observed using a TEM (JEM-2100, JEOL, Tokyo, Japan) at an acceleration voltage of 80 kV. One drop of the NP suspension was evaporated on a carbon-coated copper grid. The morphology and distribution of NPs are shown in Fig. 1.

The morphology and distribution of the NPs in the NP reinforced PMMA denture base were evaluated using a TEM operated at an acceleration voltage of 120 kV. Thin sections, approximately 200 nm thick, were prepared using an ultramicrotome (Leica EM UC7, Leica Microsystems, Vienna, Austria) equipped with a diamond knife at RT without chemical etching.

2. Dynamic light-scattering evaluation (DLS)

The size and distribution of the NPs were determined using a Zetasizer with dynamic light-scattering and Stokes-Einstein autocorrelation function (Zetasizer, Malvern Instrument, Malvern, UK).

3. Automatic physisorption analysis

The surface area of the NPs were measured by using an automatic physisorption analyzer (Micromeritics ASAP 2000, Micromeritics Instrument, Norcross, GA, USA) with adsorption-desorption of nitrogen isotherm at 77 K.

4. Fourier transform infrared spectrophotometry (FTIR)

The silanized MPS was characterized using FTIR measurements with a narrow bandpass mercury-cadmium-telluride (MCT) detector. The dried and centrifuged specimens of silanized NP as described above were analyzed using FTIR spectrophotometer (PerkinElmer 2000, PerkinElmer, Waltham, MA, USA). Each IR spectra was collected from 400–4,000 cm⁻¹ under the nitrogen purge. Prior to the measurement, 100 mg of the dried or centrifuged sample were mixed with 1 g of KBr powder and IR spectra were taken on a

Fig. 1 TEM images of NP size and distribution. A: 20k magnification, B: 40k magnification.

PerkinElmer 2000 spectrometer.

5. Organic element analysis

The carbon content on the silanized NP surface was analyzed to determine the amount of chemisorbed MPS on the NP surface using an organic element analyzer (Thermo FLASH 2000, Thermo Fisher Scientific, Waltham, MA, USA). The amount of carbon on the NP surface was calculated to determine the MPS content. The MPS content was determined using the number of carbon atoms in each MPS molecule; one molecule of MPS contains 7 carbon atoms. Surface coverage (C) was calculated, as follows¹⁸⁾:

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

where, C is surface coverage (molecule/nm²), M_{MPS} is the amount of MPS on the NP surface (μmol/m²=μmol×10⁻¹⁸/nm²), and N_A is Avogadro's number (6.02×10²³ molecules/mol).

Flexural strength (FS) and flexural modulus (FM) evaluation of NPs reinforced PMMA denture base

1. Effect of the amount of NPs

The elemental analysis and FTIR results indicated that 0.246 g_{MPS}/g_{silica} MPS created a chemisorbed monolayer on the NPs. Therefore, 0.246 g_{MPS}/g_{silica} silanized NPs were used. The silanized NPs were divided into 7 groups ($n=8$): 0 (control), 0.25, 0.5, 1, 5, 10, and 15% (w/w) silanized NPs. Heat-polymerized PMMA (Triplex hot, Ivoclar Vivadent, Schaan, Liechtenstein) was used in this study. Each silanized NP group was mixed with the PMMA monomer using a rotor stator mixer at 3,000 rpm for 10 min to form a homogeneous suspension. This is referred to as the modified monomer. The PMMA powder and modified monomer of each group was mixed at a ratio of 23.4 g powder to 10 mL modified monomer. After the dough stage, the mixture was placed in a flask, pressed, and heat-polymerized with heat up to 100°C and boiled for 45 min. After the flask cooled to RT, the specimens were deflasked.

2. Effect of the amount of MPS

Based on the FS and FM results of the 0.246 g_{MPS}/g_{silica} of 0–15% silanized NPs groups, 1% of silanized NPs was selected when determining the effect of the amount of

MPS. The specimens were divided into 7 groups ($n=8$): 0, 0.061, 0.123, 0.246, 0.493, 0.987, and 1.974 g_{MPS}/g_{silica} MPS. The FS and FM values of the control and 0.246 g_{MPS}/g_{silica} of 1% of silanized NPs groups from the section above were used in analyzing the effect of the amount of MPS results. The specimens in these groups were fabricated as described above and evaluated for FS and FM.

FS and FM test

FS and FM were determined using a three-point bending test according to ISO 20795-1:2013¹⁹. Bar-shaped specimens, 10 mm-wide, 64 mm-long, and 3.3 mm-thick, were fabricated as described above and polished with #500, #1000, and #1200 wet silicon carbide paper using a polishing machine (Nano2000, PACE Technologies, Tucson, AZ, USA) to achieve the required dimensions of 10.0±0.2×64.0×3.2±0.2 mm. The width and thickness of each specimen were measured with a digital micrometer (Mitutoyo IP65, Mitutoyo, Kanagawa, Japan). To minimize edge failure in the specimens during flexural testing, an edge chamfer was prepared with #1000 wet silicon carbide paper using a polishing machine. The specimens were immersed in 37°C deionized water for 50±2 h prior to the three-point bending test. A three-point bending test, with a support span of 50 mm, a cross-head speed of 5 mm/min, and 500 N load cell, was conducted at RT using a universal testing machine (EX-S500N, Shimadzu, Kyoto, Japan). The FS and FM were calculated using Trapezium II software (Shimadzu). FS (σ) and FM (E) were calculated using the following equations:

$$\sigma = 3FL/2bh^2$$

$$E = FL^3/4bh^3d$$

where, F is the maximum load during the flexural test (N), L is the span distance (50.0 mm), b is the specimen width, h is the specimen height, and d is the deflection (mm)

Fracture toughness (FT) of NPs reinforced PMMA denture base

The specimens were prepared as described in the effect of the MPS amount section above.

FT test

FT was determined using a three-point bending test according to ISO 20795-1:2013¹⁹. The bar-shaped specimens, 8 mm-height, 39 mm-long, 4 mm-width, were fabricated following a conventional compressive process and polished with # 500, #1000, #1200 wet silicon carbide paper using a polishing machine (Nano2000, PACE Technologies) to achieve the required dimensions of 8.0±0.2×39.0×4.0±0.2 mm. Pre-crack was created to the depth of 3.0±0.2 mm using low speed cutting machine (IsoMet 1000, Buehler, Lake Bluff, IL, USA). The razor blade (Feather-Cut, FEATHER Safety Razor, Gifu, Japan) was set of the bottom of the pre-crack and the crack length was cut with hand in a back and forth sliding motion to depth 0.1–0.4 mm. The specimens were immersed in 37°C deionized water for 7 days±2 h prior

to the three-point bending test. This test was conducted with a support span of 32 mm, a cross-head speed of 1 mm/min, and 500 N load cells at RT, using a universal testing machine. The test was considered finished when the load dropped 1.0±0.2 N from the maximum load. The maximum load was recorded in N. An optical microscope with a micrometer scale was used to measure the length of the crack. FT (K_{max}) was calculated from the following equation:

$$K_{max} = f P_{max} l_t \sqrt{10^{-3}} / (b_l h_l^{3/2})$$

where, f is a geometrical function dependent on x :

$$f(x) = 3x^{1/2} [1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)] / [2(1+2x)(1-x)^{3/2}]$$

where, $x = a/h_l$, P_{max} is the maximum specimen load (N), l_t is the span distance (32 mm), b_l is the specimen width, h_l is the specimen height, and a is the total crack length.

Scanning electron microscopy (SEM)

The fractured surfaces of the pure PMMA, 0, 0.061, 0.123, 0.493, 0.987, and 1.974 g_{MPS}/g_{silica} of 1% silanized NP specimens after the three-point bending FT test were observed using a field emission scanning electron microscope (JEOL JSM7800F, JEOL). After the FT test, the fractured surfaces of specimens were carbon coated. The primary electron beam energy was operated at 5 kV for each specimen. Backscattered electrons were used to create backscatter diffraction images.

Color measurement

A spectrophotometer (Ultrascan XE, Hunter Lab, Reston, VA, USA) was used to measure the color changes using the CIE $L^*a^*b^*$ color system. This system is based on three parameters for defining color: L^* , a^* , and b^* . L^* represents lightness, a^* represents red-green, and b^* represents yellow-blue. The ΔE was calculated based on the L^* , a^* , and b^* values obtained on a black background between the control and experimental group using the following equation:

$$\Delta E = [(L^*_1 - L^*_2)^2 + (a^*_1 - a^*_2)^2 + (b^*_1 - b^*_2)^2]^{1/2}$$

where, the subscripts 1 and 2 refer to the color coordinates of the control and experimental groups, respectively. A high ΔE value indicates a large color difference. Three measurements were made on each specimen, and the average value was recorded.

Statistical analysis

The FS, FM, and ΔE of 0.246 g_{MPS}/g_{silica} of 0–15% amount of silanized NP groups and the FS, FM, FT and ΔE of the 0–1.974 g_{MPS}/g_{silica} of 1% amount of silanized NP groups were analyzed using One-way ANOVA and Tukey's *post-hoc* comparison (SPSS version.20, IBM, Armonk, NY, USA). The significance level was set at $\alpha=0.05$.

RESULTS

The TEM images revealed NPs of similar size that were evenly distributed in ETH with low aggregation and agglomeration (Fig. 1). The DLS analysis demonstrated 36-nm particles with homogeneous distribution (Fig. 2). The specific surface area determined by the automatic

physisorption analyzer of the experimental NPs was 576 m²/g.

The FTIR spectra of the dried samples demonstrated absorption peaks at 3,434, 2,986, 1,702, 1,631, 1,091, and 462 cm⁻¹ representing hydrogen bonds, hydrocarbon chains, carbonyl groups, vinyl group, Si-O-Si (symmetrical stretch), and Si-O-Si (rocking), respectively (Fig. 3A)^{10,20}. In contrast, hydrocarbon chains, carbonyl groups, and vinyl groups were not detected on the untreated NPs. The intensity of the absorption peak at 2,986, 1,702, and 1,631 cm⁻¹ of the dried samples concentration dependently increased in the 0.061–1.974 g_{MPS}/g_{silica} groups. The absorption peaks of centrifuged sample were the same as dried sample with intensity of absorption peaks at 2,986, 1,702, and 1,631 cm⁻¹ and reached the plateau at 0.246 g_{MPS}/g_{silica} group (Fig. 3B).

The amount of MPS adsorbed on the NP surface based on elemental carbon analysis in the dried groups ranged from 0.43–8.39 μmol/m², while those of the centrifuged groups ranged from 0.49–3.11 μmol/m² (Fig. 4). The number of MPS molecules chemisorbed on the NP surface ranged from 0.26–5.05 molecule/nm² in the dried groups and 0.30–1.87 molecule/nm² in the centrifuged groups (Fig. 4).

The FS of the 0.246 g_{MPS}/g_{silica} of 0–15% amount of silanized NP groups ranged from 84.3–105.8 MPa (Table 2). The FM of these groups ranged from 2.4–3.1 GPa (Table 2). One-way ANOVA of the FS and FM revealed significant differences between the groups. The Tukey-HSD test indicated that the FS and FM of the 0.246 g_{MPS}/g_{silica} of 1% amount of silanized NP group was significantly higher than those of the other groups. The FS of the 0–1.974 g_{MPS}/g_{silica} of 1% amount of silanized NP groups ranged from 80.3–105.8 MPa (Table 3). The FM of these groups ranged from 2.4–3.0 GPa (Table 3).

Fig. 2 NPs size and distribution of NPs determined by DLS (average size of experimental NPs is 36 nm).

One-way ANOVA of the FS and FM of the 0–1.974 g_{MPS}/g_{silica} of 1% amount of silanized NP groups demonstrated significant differences between groups. The Tukey-HSD test showed that the FS and FM of the 0.246 g_{MPS}/g_{silica} of 1% amount silanized NP group was significantly higher than those of the other groups.

The FT of the 0–1.974 g_{MPS}/g_{silica} of 1% amount of silanized NP groups ranged from 1.6–2.4 MPa·m^{1/2} (Table 3). One-way ANOVA found significant differences between groups and the Tukey-HSD indicated that the

Fig. 3 FTIR spectra of A: dried samples showing absorption peaks at 3,434, 2,986, 1,702, 1,631, 1,091, and 462 cm⁻¹ representing hydrogen bonds, hydrocarbon chains, carbonyl groups, vinyl group, Si-O-Si (symmetrical stretch), and Si-O-Si (rocking), respectively. B: The FTIR spectra of centrifuged samples shows that the absorption peaks at 3,434, 2,986, 1,702, 1,631, 1,091, and 462 cm⁻¹ reached plateau in the 0.246 g_{MPS}/g_{silica} group.

Fig. 4 Amount of MPS on the NP surface and number of molecules of MPS on the NP surface as determined by elemental analysis in the dried groups and centrifuged groups.

FT of the 0.246 g_{MPS}/g_{silica} of 1% amount of silanized NP group was significantly higher than those of the other groups.

The ΔE of the 0.246 g_{MPS}/g_{silica} of 0.25–15% amount of silanized NP groups ranged from 0.7–1.8 (Table 2). One-way ANOVA revealed significant differences in ΔE between groups and the Tukey-HSD indicated that the ΔE of the 0.246 g_{MPS}/g_{silica} of 15% amount of silanized NP group was significantly higher than those of the other groups. The ΔE of the 0–1.974 g_{MPS}/g_{silica} of 1% amount of silanized NP groups ranged from 0.6–0.8 (Table 3). One-way ANOVA revealed no significant differences between groups.

DISCUSSION

This study was to investigate the chemisorbed amounts of silanized on NPs and to investigate the effect of

Table 2 Flexural strength, flexural modulus, and ΔE of 0.246 g_{MPS}/g_{silica} with different amount of NP groups

Conditions	Flexural strength	Flexural modulus	ΔE
	(MPa)	(GPa)	
control (no filler)	85.2 (3.8) ^a	2.4 (0.1) ^a	—
0.25% NP	93.4 (4.2) ^b	2.7 (0.1) ^b	0.8 (0.2) ^a
0.5% NP	94.5 (3.1) ^b	2.7 (0.0) ^b	0.7 (0.1) ^a
1% NP	105.8 (3.4) ^c	3.0 (0.0) ^c	0.8 (0.1) ^a
5% NP	97.0 (2.5) ^b	2.9 (0.1) ^c	1.4 (0.1) ^b
10% NP	89.3 (3.6) ^{a,b}	3.1 (0.1) ^c	1.6 (0.1) ^{b,c}
15% NP	84.3 (3.6) ^a	3.1 (0.1) ^c	1.8 (0.2) ^c

% (w/w)

Mean values ($n=8$) and standard deviations in parentheses.

For each property, values denoted with same letters are not significantly different ($p>0.05$).

Table 3 Flexural strength, flexural modulus, fracture toughness, and ΔE of 1% amount of NP with different amount of MPS groups

Conditions	Flexural strength	Flexural modulus	Fracture toughness	ΔE
	(MPa)	(GPa)	(MPa · m ^{1/2})	
control (no filler)	85.2 (3.8) ^a	2.4 (0.1) ^a	1.9 (0.2) ^{a,b}	—
0.000 (unsilanized)	81.0 (5.0) ^a	2.6 (0.1) ^a	1.6 (0.4) ^a	0.6 (0.1) ^a
0.061	80.3 (5.4) ^a	2.4 (0.0) ^a	1.9 (0.3) ^{a,b}	0.7 (0.1) ^a
0.123	97.1 (1.6) ^b	2.7 (0.1) ^b	2.0 (0.3) ^b	0.6 (0.1) ^a
0.246	105.8 (3.4) ^c	3.0 (0.0) ^c	2.4 (0.3) ^c	0.8 (0.1) ^a
0.493	98.2 (3.3) ^b	2.6 (0.0) ^b	2.0 (0.3) ^b	0.8 (0.2) ^a
0.987	93.9 (3.6) ^b	2.6 (0.0) ^b	1.9 (0.2) ^{a,b}	0.7 (0.1) ^a
1.974	84.6 (4.0) ^a	2.3 (0.1) ^a	1.6 (0.2) ^a	0.6 (0.1) ^a

Amount of MPS (g_{MPS}/g_{silica})

Mean values ($n=8$) and standard deviations in parentheses.

For each property, values denoted with same letters are not significantly different ($p>0.05$).

various amounts of NPs and various amounts of MPS silanized on the NPs on mechanical properties of NPs reinforced PMMA denture base.

FTIR results indicated that the silanization process used in this study was effective. The FTIR spectra in the dried NP groups as a function of MPS amount demonstrated 2,986, 1,702, and 1,631 cm^{-1} peak intensities corresponding to the chemisorbed and physisorbed MPS, which gradually increased from the 0.061 to 1.974 $\text{g}_{\text{MPS}}/\text{g}_{\text{silica}}$ groups. In the centrifuged groups, the adsorption peak intensity reached the plateau at the 0.246 $\text{g}_{\text{MPS}}/\text{g}_{\text{silica}}$ groups. The spectra of the >0.246 $\text{g}_{\text{MPS}}/\text{g}_{\text{silica}}$ centrifuged groups indicated the complete removal of physisorbed MPS by isopropanol and centrifugation at 20,000 rpm.

The elemental analysis results indicated that the amount of MPS required to form a chemisorbed monolayer on the NP surface was $1.77 \mu\text{mol}/\text{m}^2$ corresponded to approximately 1.07 MPS molecules on 1 nm^2 of the NP surface. The plateauing of the amount of MPS in the chemisorbed monolayer probably occurred because of the steric hindrance of the organic groups of the MPS molecule¹⁸. Silica has 3 or 4 Si-OH groups per nm^2 of the NP surface²¹; therefore, unreacted Si-OH groups on the NP still remained. The amount of chemisorbed MPS in this study was 7 times lower than that theoretically calculated by Arkles ($12.82 \mu\text{mol}/\text{m}^2$)¹¹. In contrast to the study of Arksornnukit *et al.*²², they reported that $12.88 \mu\text{mol}/\text{m}^2$ was required for monolayer coverage and 7.7 MPS molecules per nm^2 of silica based on Arkles's equation. This difference is probably due to the difference in the size of the silica particles between the two studies. Larger silica particles provide adequate space for silane oligomer adsorption. Therefore, higher molecular weight molecules would also be chemisorbed on the silica surface.

The orientation of the MPS molecule on the NPs can be parallel or perpendicular. The parallel orientation results in one MPS molecule reacting with two Si-OH molecules on the NP surface, generating a hydrogen bond between C=O of MPS and Si-OH on the NP surface and a siloxane bond between Si-OH of MPS and Si-OH on the NP surface. The perpendicular orientation results in one MPS molecule reacting with one Si-OH molecule, generating a siloxane bond between Si-OH of MPS and Si-OH on the NP surface¹⁸. The behavior of the C=O band in MPS molecule indicates that the orientation behavior of MPS depends upon the number of chemisorbed MPS molecules on 1 nm^2 NP surface. The result of this study also showed that the parallel orientation of MPS adsorption was between 0.61–1.07 molecule on 1 nm^2 which showed C=O band at $1,702 \text{ cm}^{-1}$ representing hydrogen bond C=O group with Si-OH groups. While, the groups which exceeded 1.07 molecule on 1 nm^2 , a new C=O band at $1,720 \text{ cm}^{-1}$ appeared due to the free C=O (Fig. 5)^{10,13}. This results indicated that MPS molecules oriented perpendicular to the NP surface. MPS molecules can be further forced chemisorption to the NP beyond the plateau phase which was demonstrated in Fig. 4. Excess amount of MPS will likely transform

Fig. 5 The 1,800–1,600 cm^{-1} interval showing the location of the C=O peak at $1,702 \text{ cm}^{-1}$. This peak reached plateau at 0.246 $\text{g}_{\text{MPS}}/\text{g}_{\text{silica}}$. Above this MPS amount, a peak at $1,720 \text{ cm}^{-1}$ is observed. The height of this peaked increases as the MPS amount increases.

the direction of adsorbed MPS molecules at NP surface from parallel to perpendicular. As a result, the amount of MPS per surface area of NP increased from 1.07 to 1.87 molecule/ nm^2 .

The FS and FM results showed differences based on the amount of silanized NPs incorporated into the PMMA. Therefore, the null hypothesis that there would be no differences in the FS and FM of PMMA denture base reinforced with different amounts of silanized NPs was rejected. The FS and FM of the PMMA containing 0.246 $\text{g}_{\text{MPS}}/\text{g}_{\text{silica}}$ silanized NP steadily increased in the 0.25–1% groups. The increasing amounts of silanized NP resulted in more covalent linkages at the interface between the NPs and the PMMA matrix. However, when the NP amount exceeded 1%, the interparticle spacing decreased, allowing for increased agglomeration of silanized NPs (Fig. 6). This agglomeration generated stress concentration at the agglomerated particles and

Fig. 6 Representative TEM images (9.6k magnification) of PMMA containing 0.246 g_{MPS}/g_{silica} silanized NP. A: The highly agglomerated of NP of 15%, B: 10% (w/w) PMMA, C: The slightly agglomerated of NP of 5% (w/w) of PMMA, D: The homogeneous dispersion of silanized NP 1% (w/w) of PMMA.

decreased the mechanical properties of the PMMA matrix^{23–25}. Thus, the FS in the groups containing >1% silanized NPs was reduced, however, there was no significant differences in FM between these groups. The results of the present study indicated that the optimum loading amounts of 36-nm NPs was 1%, which generated a homogeneous dispersion of the silanized NPs in the PMMA matrix, resulting in the highest FS and FM (Fig. 6).

The FS, FM, and FT results were different based on the amount of MPS on the NPs. Therefore, the null hypotheses that there would be no differences in the FS, FM, or FT of PMMA denture base reinforced with NPs with various amounts of silanization were rejected. PMMA containing 0.246 g_{MPS}/g_{silica} silanized NPs showed the highest FS, FM, and FT. The results from elemental analysis showed that a chemisorbed monolayer was presented in the 0.246 g_{MPS}/g_{silica} group. The chemisorbed monolayer of MPS creates covalent linkages between the nanoparticles and the polymer matrix^{2,9,10}. The covalent bond between the NPs and PMMA *via* MPS molecule provide adequate stress transfer from the matrix to the NPs^{17,26}. In PMMA containing unsilanized NPs, the bonding at the interface between the inorganic silica and the organic polymer matrix is poor². When a force is placed, stress will be concentrated at the interface between the filler and the matrix. The stress cannot be effectively transferred; therefore, it will cause cracks, and finally induces material failure, which explains the lowest FS, FM, and FT values observed in the PMMA

containing unsilanized NPs groups. However, the amount of MPS is also an important factor. The FS, FM, and FT of the 0.061 and 0.123 g_{MPS}/g_{silica} groups were lower than that of the 0.246 g_{MPS}/g_{silica} group. This can be attributed to incomplete NP surface coverage by the MPS molecules. The remaining Si-OH on the silica surface cannot react with PMMA, creating a weak interface between the PMMA and silica surface. Moreover, the 0.493, 0.987, and 1.974 g_{MPS}/g_{silica} groups, which have a physisorbed layer on the NP surface as demonstrated by the elemental analysis, also showed lower FS, FM, and FT values compared with the 0.246 g_{MPS}/g_{silica} group. This resulted from the physisorbed layer, which contains weak Van der Waal's forces and hydrogen bonds.

The SEM images can explain the cause, location of failure, and the mechanism of particle reinforcement of composites (Fig. 7). The fractured surface for the pure PMMA matrix revealed a brittle behavior characterized by a large smooth area. Higher magnification showed that the cracks propagated as river lines (Fig. 7A)²⁷. This indicates a weak resistance to crack propagation, and minimal energy was required to fracture the specimen. The 1% unsilanized NP reinforced PMMA denture base showed a smooth fractured surface with agglomeration and uncovered NP, indicating that there were no chemical bonds between the inorganic silica and the organic resin matrix (Fig. 7B)²³. The fractured surface of the 0.061 and 0.123 g_{MPS}/g_{silica} MPS groups showed rougher fractured surfaces and fractured surface cavitation. This indicated that the material was tough (Fig. 7C and D). The PMMA containing 0.246 g_{MPS}/g_{silica} of 1% amounts of NPs revealed a tougher behavior characterized by the roughest fractured surface, out of the plane cracking, fractured surface cavitation, and NP debonding/pullout (Fig. 7E). This behavior requires additional energy to fracture the materials, resulting in increased FS and FT. However, the PMMA containing 0.493, 0.987, and 1.974 g_{MPS}/g_{silica} of 1% amount of NP groups revealed ductile behavior characterized by large fracture surface cavitation. The over adsorbed amount of MPS of these groups created a physisorbed layer on nanosilica surface resulted in crack propagation along physisorbed layer (Fig. 7F–H). The chemisorbed MPS monolayer/nanoparticle interface is an important factor in the toughening mechanism of nanocomposite materials. Cracks encounter particles as obstacles, which deviate and branch the crack front. In addition, a large amount of energy is consumed at the particle/matrix interface under strong bonding conditions^{16,28}.

This study synthesized monodispersed NP and silanized with MPS in monodisperse suspension that allowed chemisorbed monolayer formation. One percent (w/w) of NP incorporated into PMMA increased FS, FM and FT of PMMA denture base. This higher fracture resistance would be beneficial in terms of preventing fracture at the thin denture base area such as midline in complete denture and area around attachment housing in implant retained overdenture. The lesser amount of nano-sized silica created reinforcement of PMMA in this study helped in reducing cost of material, compared to

Fig. 7 Representative SEM images the fractured FT specimen surfaces.

A: Pure PMMA, A1: The smooth fractured surface, A2: White arrow showed the river lines, B: 1% (w/w) unsilanized NP, B1: The smooth fractured surface, B2: White arrow showed agglomeration and uncoverage of NP, C: 1% (w/w) 0.061 MPS amount, D: 1% (w/w) 0.123 MPS amount, C1, C2, D1, D2: The rougher fractured surface. White arrows showed cavitation on fractured surface. E: 1% (w/w) 0.246 MPS amount, E1: The roughest fractured surface, E2: Black arrow showed the NP pullout and white arrow showed cavitation on fractured surface, F: 1% (w/w) 0.493 MPS amount, G: 1% (w/w) 0.987 MPS amount, H: 1% (w/w) 1.974 MPS amount, F–H: White arrows showed large cavitation and black arrows showed crack propagation along physisorbed layer of silanized NP. 1: 4k magnification, 2: 20k magnification.

the previous study which advocated 5% (w/w)²⁹. This difference is probably due to the difference in level of dispersion. The reinforcement mechanism resulted from molecular interaction between particle and matrix. In contrast to the monodisperse NP in the present study, the agglomeration of particles in the higher amount of nano-sized filler, resulted in the reduction of surface area to volume ratio. Therefore, it required more amounts of particles to improve mechanical properties²⁹.

ΔE between the groups were measured using the perceptibility threshold (PT) and acceptability threshold (AT). Several studies used $\Delta E=1.0$ as the threshold at which 50% of observers can distinguish a ΔE between 2 objects (PT) and $\Delta E=3.7$ as the threshold at which 50%

of observers accepted a ΔE (AT)^{30–32}. The ΔE of this study indicated that the increasing amounts of silanized NP and amount of MPS silanized on NPs in PMMA denture base affected the color of the material; however, the difference from pure PMMA was within the AT. This is likely due to the refractive index of NP (1.45) which is very close to those of MPS and PMMA denture base³³.

CONCLUSIONS

Within the limitations of this study, it was concluded that the amount of MPS in a chemisorbed monolayer on the 36-nm spherical NPs was 1.77 $\mu\text{mol}/\text{m}^2$ and the number of MPS molecules in the chemisorbed monolayer was

1.07 molecule/nm². Arkles's equation is not applicable in calculating the chemisorbed amount of silane on NPs. The PMMA denture base reinforced with 0.246 g_{MPS}/g_{silica} of 1% amount of silanized NPs provided the highest FS, FM, and FT with a clinically acceptable ΔE .

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