

The effect of grafted caged silica (polyhedral oligomeric silsesquioxanes) on the properties of dental composites and adhesives

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Abstract—With the emergence of commercial grafted caged silica (Polyhedral Oligomeric Silsesquioxanes, POSS) having a three-dimensional (3D) morphology with peripheral functionality, new opportunities have been created for formulating dental adhesives and composites with enhanced mechanical and physical properties. The objective of the present study was to investigate the properties obtained by incorporating grafted caged silica into acrylate based dental composite and adhesive systems. Two commercial POSS materials (methacrylated and octaphenyl grafted) were added to dental restorative-glass-filled pre-polymers, based on BisGMA (bis-phenol A-glycidylmethacrylate), HEMA (2-hydroxyethylmethacrylate) and TEGDMA (tetraethylglycidylmethacrylate). The nanostructured organic/inorganic hybrid compounds exhibited enhanced mechanical and thermal properties in cases where the POSS added was in concentrations up to 2 wt%. Beyond this threshold concentration, properties decreased due to agglomeration. In the case of the acrylated POSS, the T_g increased by 5 °C, the composite compressive strength by 7%, and the bond shear strength by 36% and the shrinkage was reduced by 28% compared with neat dental composites and adhesives. Furthermore, in the case of octaphenyl grafted POSS, the compressive strength was reduced by 20%, the adhesive shear bond strength decreased by 49% and the shrinkage was reduced by 67%. It was concluded that the type of the grafted functional group of the caged silica was the dominant factor in nano-tailoring of improved dental composites and adhesives.

Keywords: Dental composites; adhesives; POSS; nanotechnology; polymers.

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1. INTRODUCTION

Polyhedral oligomeric silsesquioxanes (POSS) are nanostructured organic/inorganic hybrid compounds that have been used as reactive nanofillers to form nanocomposites. Silsesquioxanes are a class of compounds with the empirical formula $\text{RSiO}_{1.5}$. The caged silica may possess a variety of functional groups (R group) that can potentially react with the host matrix. A significant effort has been made to systemize the chemistry of POSS systems [1–22].

POSS molecules can be dispersed in the polymer matrix at the level of individual molecules, which are much smaller in size (dimension 1.5 nm) than the average dimension of conventional fillers.

The synthesis techniques for modification of a POSS molecule allow for the generation of a variety of functionalized substitutes on the POSS cage [5, 12, 17], such as epoxy group [20], methacrylates [21], octaaminophenyl [22], etc. These possibilities offer alternatives for tailoring the interactions between POSS molecules and polymer chains and, consequently, to control the mechanical and thermal properties of nanocomposites. POSS materials have high thermal stabilities and they are highly soluble in common organic solvents, such as tetrahydrofuran (THF), toluene, chloroform and hexane [13].

Extensive studies have established that the introduction of the nanostructured POSS monomers into a polymer leads to increased thermal stability, higher glass transition temperatures, better flame and heat resistance and enhancements in modulus and melt strength [8, 15], increased oxygen permeability [14], increased fluid elasticity, improved oxidation resistance [15], yet retaining the polymer's processability. Importantly, these property enhancements occur at low POSS contents (<10 mol%) [8].

POSS materials have been incorporated into epoxy [3, 15–17], high-density polyethylene [9], triblock copolymers based on polymethacrylate/POSS and poly(*n*-butyl acrylate) [19], styrene [6], vinyl ester [3, 6], methyl methacrylate resins, cyanate ester, phenolic, styrene-divinylbenzene, polydicyclopentadiene [3] and polyurethane [7, 14].

Dodiuk *et al.* [16] examined the thermal properties, and shear and peel strengths of epoxy/POSS for adhesive applications. Results showed that only small amounts of POSS (<5 wt%) were needed to enhance the shear and peel strengths. They concluded that the type of the functional group (reactive or non-reactive) of the POSS was the dominant factor in the formation of the molecular network.

Fong *et al.* [23] used methacrylated POSS monomers for dental resins and their advantages were demonstrated in terms of reduced shrinkage.

Composite materials that contain metal oxides and silica nanoparticles in polymeric matrices are commonly used for dental fillings as a replacement for amalgam. Strong adhesion accompanied by minimal shrinkage is essential in dental applications. Dental matrices are composed of acrylate or methacrylate-based monomers that can be photo-polymerized, chemically polymerized, or dual-cured [24, 25].

Dodiuk-Kenig *et al.* [26] have used hyperbranched dendritic derivatives in order to increase adhesion and compression and reduce shrinkage successfully.

The objective of the current study was to investigate the effect of POSS functional group and content on mechanical, thermal, morphological and adhesion properties of methacrylate/POSS dental nanocomposite adhesives.

2. EXPERIMENTAL

Two types of POSS materials were included in this study: dimethylsilyloxypropyl methacrylate-POSS (C₄₄H₈₀O₁₅Si₉), a reactive type, and octaphenylpentacycloocta-siloxaneoctaphenyl-POSS (C₄₈H₄₀O₁₂Si₈), a non-reactive one.

The formulated nanocomposites were studied with respect to their compressive strength, linear shrinkage and adhesion to dental tissues (dentin and enamel). The bond strength was tested using shear bond strength (SBS) specimens. Furthermore, the effect of POSS on the glass transition temperature (T_g) of various dental compositions was evaluated, using differential scanning calorimetry (DSC). Finally, atomic force microscopy (AFM) was used to examine the surface morphology of the resultant nanocomposites.

The two POSS types were incorporated into the acrylate-based composites in concentrations between 1 and 4 wt% and to the adhesives in concentrations between 0.5 and 5 wt%. These concentrations were chosen based on previous studies using POSS for epoxy [16].

Table 1 summarizes the types of raw materials used in the base formulations.

The basic dental composite formulation is presented in Table 2. On the basis of this formulation, POSS dental composite formulations were prepared. The dental composite is a highly filled material consisting of two parts: base and catalyst, polymerizing chemically by oxidation-reduction reaction when mixed in equal amounts [3].

Table 1.

Raw materials used

Component	Chemical composition
Organic matrix	Acrylic mono- or multifunctional monomers and oligomers
Inorganic filler	Silica glass containing strontium, barium, quartz, colloidal silica
Accelerator for polymerization	Phosphonate
Photosensitizers for the light curing process	Camphorquinone (CQ) and ethyl-4-dimethylaminobenzoate (EDB)
Initiators for polymerization	Tertiary amine and benzoyl peroxide
Dendritic component	Hyperbranched polyesteramide

Table 2.

Basic dental composite formulation

Sample	Base		Catalyst	
	Material	Amount (wt%)	Material	Amount (wt%)
1	Bis-GMA	13.97	Bis-GMA	13.1
2	HEMA	15	TEGDMA	13.08
3	DHEPT	0.4	BPO	0.4
4	Filler	70.583	Filler	73.1
5	BHT	0.017	BHT	0.02
6	Hyperbranched polyesteramide	0.3	Hyperbranched polyesteramide	0.3
Total		100		100

Filler (for both parts of the model composition) contained silanized glass (97 wt%) and colloidal silica (3 wt%). Bis-GMA, bisphenylglycidylmethacrylate; TEGDMA, tetraethylglycidylmethacrylate; HEMA, 2-hydroxyethylmethacrylate; DHEPT, N,N-dihydroxyethyl-*p*-toluidine; BHT, 2,6-di-*tert*-butyl-4-methylphenol; BPO, benzoyl peroxide.

Table 3.

Basic dental adhesive formulation

Sample	Component	Amount (wt%)
1	HEMA	4.1
2	Acetone	51.65
3	Ethanol	8.91
4	Sodium salt of toluenesulfonic acid	0.09
5	Glutaraldehyde	0.9
6	PENTA	1.8
7	Urethane-di-methacrylate oligomer	19
8	TEGDMA	9.5
9	MEK	1.0
10	Diethylphosphite	2.0
11	Morpholinoethylmethacrylate	0.8
12	Camphorquinone	0.25
Total		100

HEMA, 2-hydroxyethylmethacrylate; PENTA, 2, 3, 4, 5, 6-pentachlorophenol; TEGDMA, tetraethylglycidylmethacrylate; MEK, methyl ethyl ketone.

The basic dental adhesive formulation is shown in Table 3. On the basis of this formulation the adhesive formulations containing both types of POSS were prepared.

The compressive strength was determined using a Lloyd Mechanical Tester LR10K in accordance with ISO 9917. The cross-head speed was 0.5 mm/min and 10 specimens were prepared for each formulation.

For compressive strength determination cylindrical specimens 4.0 ± 0.1 mm in diameter and 8.0 ± 0.1 mm in length were prepared ($n = 10$). All specimens were

kept at room temperature for 30 min and then immersed in water at 37°C for 24 h prior to measurements.

For the linear shrinkage measurements, glass test tubes of 4.15 mm diameter were filled with composite material and self-polymerized by free-radical mechanism. 10 specimens were prepared for each formulation.

The length (height of the polymerized specimen) was measured using an optical microscope with an intrinsic scale accurate to 0.1 mm. The measurements were carried out during the polymerization process after 5, 10 and 30 min from the beginning of the polymerization.

The shear bond strength (SBS) of light-cured adhesive formulations to dentin was determined using a mechanical tester. Ground and polished (to expose the dentin) bovine teeth were used. The dentin surface was rinsed with water for 24 h. The excess moisture was removed from the surface by blotting followed by application of the primer. After 20 s the surface was air-dried for 5 s. The adhesive was applied by a micro-brush. After 20 s the surface was air-dried for 5 s and then light-cured for 20 s. A second application of the adhesive was carried out followed by air drying after 20 s for 5 s.

A gelatin capsule technique [26] was used for preparation of composite specimens (4.5 mm in diameter). The composite was loaded in the capsule approximately 2/3 full and then cured for 1 min. Additional composite was added to slightly overfill the capsule. The specimens were, additionally, cured for 40 s and after 2 min for another minute. Then, the composite resin cylinders were bonded to the tooth surface. After bonding and curing the sample, specimens were left at room temperature for 1 h and then were placed in water at 37°C for 24 h prior to measurements.

The differential scanning calorimetry (DSC, Perkin Elmer 7) was carried out to characterize the T_g values of the various dental composite systems. The specimen preparation technique was identical to that used for compressive strength determination.

The AFM was used to characterize the three-dimensional topography for the various dental adhesive systems. Samples were prepared by casting adhesives of different formulations on a polyester film, the adhesive was then covered by another layer of the film and was light cured for 5 min on each side.

The experimental results were analyzed statistically (10 specimens) by ANOVA (two-factor with replication ($P < 0.05$); Software, Office Excel 2003).

3. RESULTS AND DISCUSSION

The effect of POSS concentration on the glass transition temperature (T_g) of the dental compositions formulated is shown in Table 4.

As can be seen for both POSS types the T_g increases with the increase of POSS concentration until 2% and beyond this level the T_g decreases.

The effect of POSS concentration on the compressive strength of dental composites is summarized in Table 5.

Table 4.The T_g of dental composite – POSS formulations

POSS (wt%)	T_g (°C)	
	POSS-methacrylate	POSS-octaphenyl
0	127.6	127.6
1	134.2	129.7
2	135.5	132.7
3	133.2	131.4

Table 5.

Compressive strengths (MPa) of dental composite–POSS formulations

POSS (wt%)	POSS-methacrylate	POSS-octaphenyl
0	249.7	249.7
1	233.2	203.6
2	268.3	200.8
4	169.9	215.8

Standard deviation is $\pm 10\%$.**Table 6.**

Linear shrinkage (%) of dental composite–POSS systems

POSS (wt%)	POSS-methacrylate	POSS-octaphenyl
0	0.56	0.56
1	0.40	0.18
2	0.65	0.40
4	0.60	0.29

Standard deviation is $\pm 10\%$.

It can be concluded that an increase in compressive strength is obtained with the addition of 2 wt% POSS-methacrylate. Upon increase of POSS-methacrylate concentration above 2 wt%, a decrease in compressive strength is observed. Moreover, the addition of POSS-octaphenyl resulted in a noticeable decrease in compressive strength. The T_g results are in agreement with these results. Comparing the results in Tables 4 and 5 the maximum recorded T_g was for the case of 2 wt% POSS-methacrylate. In the case of POSS-octaphenyl the low compressive strengths are accompanied by low T_g values. The T_g results show that the maximum T_g value coincides with the maximum compressive strength.

The influence of POSS addition on the linear shrinkage property of the composites is shown for the dental composite–POSS systems in Table 6.

The 1 wt% dental composite/POSS-methacrylate system exhibited a significant decrease in the linear shrinkage. The POSS-octaphenyl showed a very low linear

Table 7.

Shear bond strength (MPa) of dental adhesive–POSS formulations

POSS (wt%)	POSS-methacrylate	POSS-octaphenyl
0	25.0	25.0
0.5	—	21.5
1	26.4	14.5
2	39.2	12.7
3	—	21.1
5	33.7	14.5

Standard deviation is $\pm 10\%$.

shrinkage at the same concentration. The largest decrease (about 67%) in linear shrinkage was observed with the incorporation of 1 wt% POSS-octaphenyl. This can be attributed to the phenyl groups that cause a reduction in shrinkage due to decrease of free volume as reflected also in the T_g increase.

The effect of POSS nano-particles on adhesion to dentin was studied using the adhesive formulation described in Table 3. The shear bond strength (SBS) results for the dental adhesive/POSS-methacrylate and POSS-octaphenyl formulations are given in Table 7.

It can be seen that the adhesive composition with POSS-methacrylate addition demonstrates enhanced bonding to dentin. Above 2 wt%, a decrease in shear strength was observed. In contrast, POSS-octaphenyl addition reduces significantly the SBS compared to the neat formulation. In general, the shear bond strength of the acrylate dental adhesives correlates well with the compressive strength of the acrylate dental composites. The interaction of POSS-methacrylate with the base acrylate resin results in high values of both shear bond strength and compressive strength with the incorporation of 2 wt% of nano-particles. In the case of the non-reactive POSS-octaphenyl, the decrease in adhesive shear bond strength correlates with reduced composite compressive strength. These results are supported by Lücke and Stoppek-Langner [2], who studied the effect of POSS-methacrylate on dental resins. They concluded that POSS-methacrylate could be combined with methacrylated resins in order to produce materials with improved properties.

AFM was used to study and correlate the macro-properties of the resultant POSS containing nano-composite adhesives as well as the nano-structure. Figures 1–5 present surface nanotopography results. A summary of surface roughness values following cryogenic fracture is given in Table 8.

It can be seen from the AFM results that the finest topography is obtained in the case of 2 wt% POSS-methacrylate (surface roughness of 156 nm). This fine nanostructure correlates with the highest shear bond strength of the dental adhesives, highest compressive strength of the dental composites and the highest T_g exhibited by the POSS-methacrylate system at 2 wt% level. As the concentration of the nano-particles increases, agglomeration is evident by the increase of roughness to more

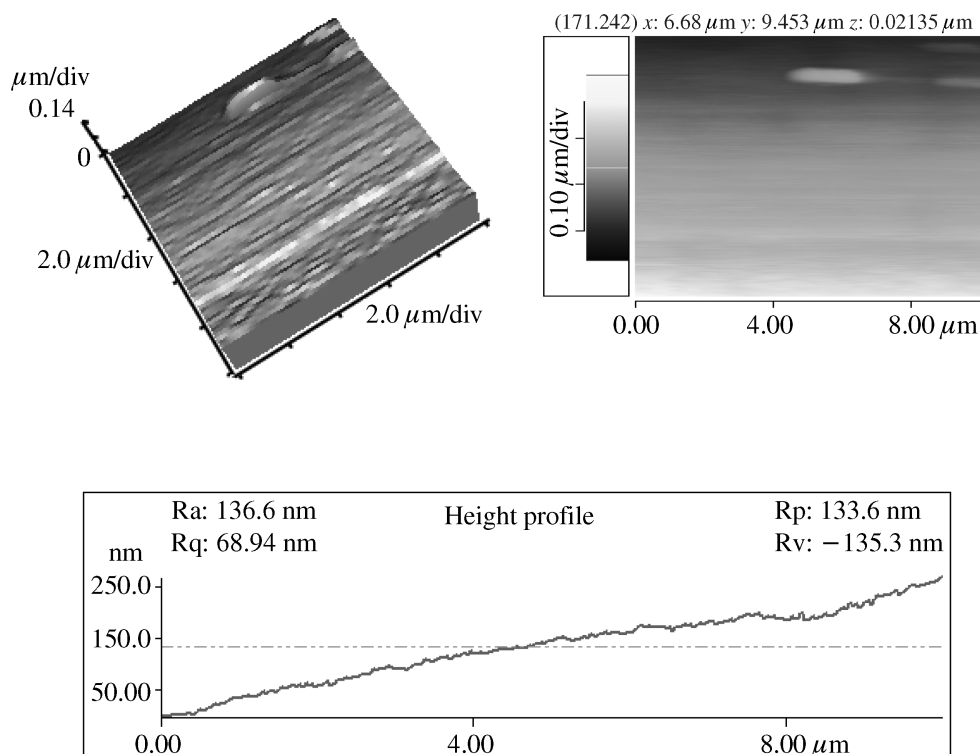


Figure 1. Neat resin. Upper left: nano-topography. Upper right: nano-surface from above. Lower part: roughness profile (horizontal axis scan length).

Table 8.

AFM roughness results

POSS additive	POSS (wt%)	Roughness (nm)
POSS-methacrylate	2	156
POSS-methacrylate	4	703
POSS-octaphenyl	2	508
POSS-octaphenyl	4	587

than 700 nm and simultaneously the mechanical, as well as the thermal properties decrease. In the case of the non-reactive POSS-octaphenyl the roughness is in the range of 500 to 600 nm, leading to lower mechanical and thermal properties.

4. CONCLUSIONS

The incorporation of POSS into dental adhesives and composites is highly effective. In the case of the reactive POSS-methacrylate, the acrylate-based resins demonstrated improved mechanical, as well as thermal properties. This is sup-

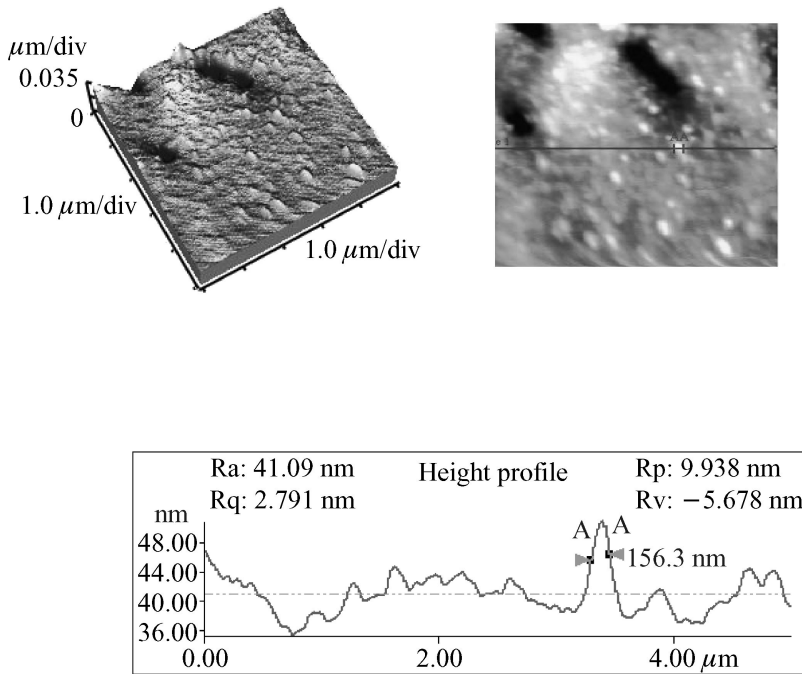


Figure 2. 2 wt% POSS-methacrylate. Upper left: nano-topography. Upper right: nano-surface from above. Lower part: roughness profile (horizontal axis scan length).

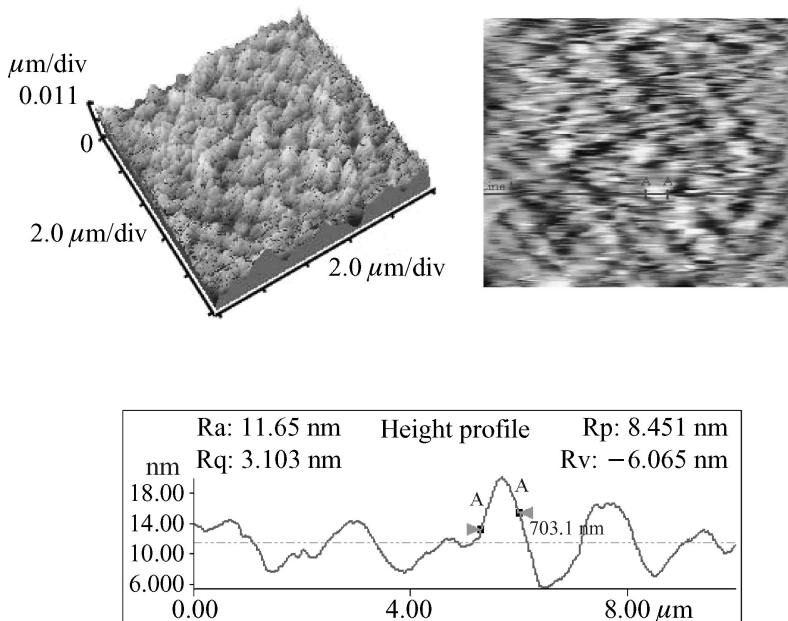


Figure 3. 4 wt% POSS-methacrylate. Upper left: nano-topography. Upper right: nano-surface from above. Lower part: roughness profile (horizontal axis scan length).

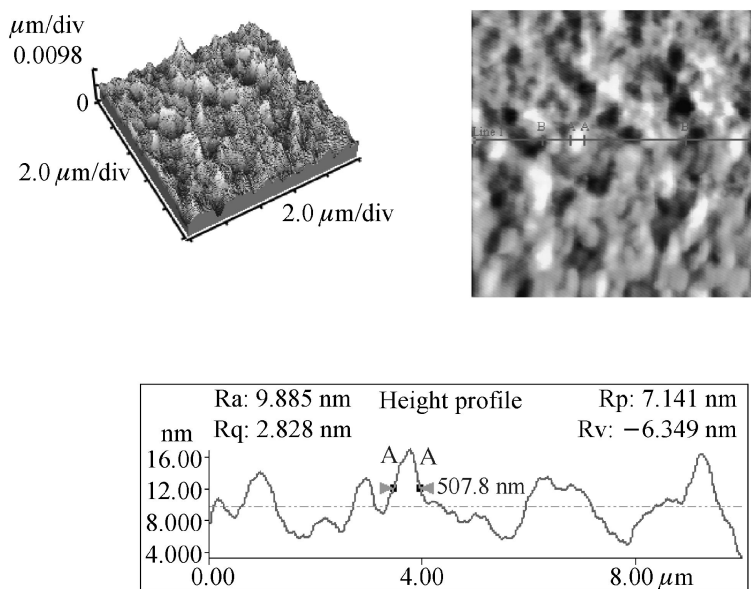


Figure 4. 2 wt% POSS-octaphenyl. Upper left: nano-topography. Upper right: nano-surface from above. Lower part: roughness profile (horizontal axis scan length).

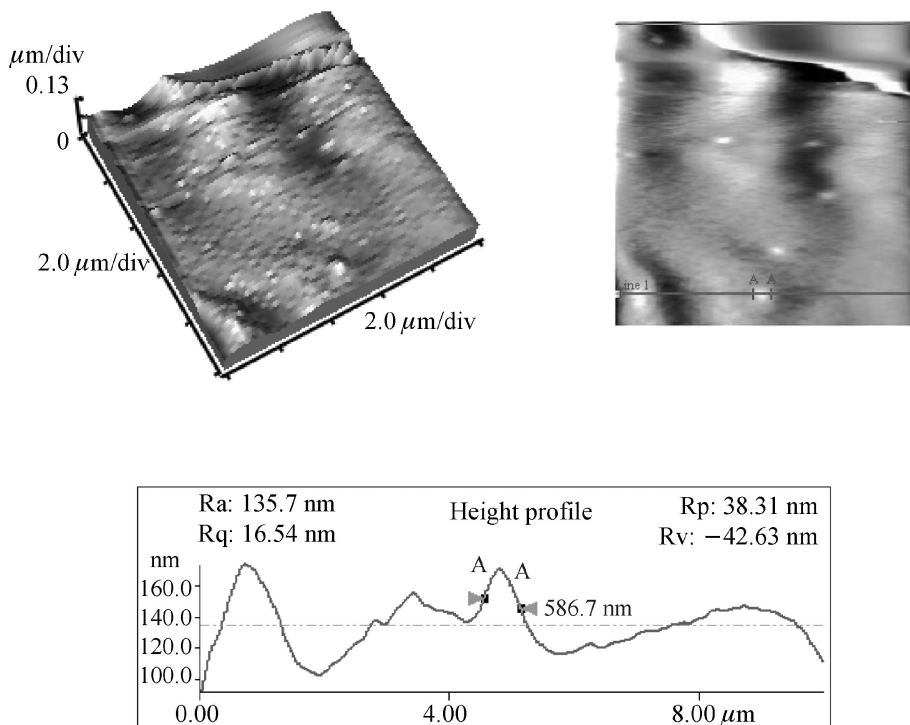


Figure 5. 4 wt% POSS-octaphenyl roughness. Upper left: nano-topography. Upper right: nano-surface from above. Lower part: roughness profile (horizontal axis scan length).

ported by the fine nanostructure that was observed using AFM. Above 2 wt% addition of the reactive POSS, agglomeration occurs and the nano-effect is diminished. Consequently, the mechanical and thermal properties decrease. The combination of POSS-methacrylate and acrylate-based resin does not reduce significantly the shrinkage, although a minimum in shrinkage was observed at 2 wt% POSS level. The non-reactive POSS-octaphenyl affected the acrylate based dental adhesive and dental resin differently. In this case the POSS-octaphenyl acts as a filler, reducing both the dental adhesive shear strength and dental composite compressive strength. Due to its bulkiness the POSS-octaphenyl reduced the shrinkage of the acrylate system upon polymerization.

Since an enhancement of both adhesion and compressive strengths in conjunction with reduced shrinkage is the objectives of advanced dental adhesives and composites, incorporation of both functionalized reactive and non-reactive POSS compounds requires further investigations.

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