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Effects of Different Silane Coupling Agent Monomers on Flexural Strength of an Experimental Filled Resin Composite

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Abstract

The hydrolytic stability of various silane combinations and their effects on biomechanical properties and water sorption of an experimental dental composite made of *bis*-GMA and TEGDMA and silane-treated fillers were evaluated. Four silane coupling agents and their blends with a cross-linker silane were used as coupling agents for the 0.7-µm $BaSiO_3$ fillers. The silanization was carried out in toluene containing 1% (v/v) of one of the four following organofunctional silane coupling agents: 3-acryloxypropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, 3-styrylethyltrimethoxysilane, and 3-isocyanatopropyltriethoxysilane. Blends of these functional silanes with 1% (v/v) of a cross-linker silane, 1,2-bis-(triethoxysilyl)ethane were also used for silanization. Composites were prepared by mixing 5.00 g Ba-glass filler with 2.00 g of a resin mixture consisting of *bis*-GMA (58.8 wt-%) and TEGDMA (39.2 wt-%) in a high-speed mixer. Three-point bending test specimens (2.0 mm x 2.0 mm x 25.0 mm) were fabricated (n = 8) in a mould and photo-polymerized. The degree of conversion was measured with FTIR. Biomechanical testing was carried out according to the ISO 10477 standard. Specimens were tested (flexural strength) after 30 days of water storage (37 ºC, distilled water). Water sorption and solubility (in wt-%) were also measured on 1, 2, 3, 5, 7, 14, 21, and 30 days in water storage. Statistical analysis with ANOVA showed that the highest flexural strength was obtained when 3-acryloxypropyltrimethoxysilane + 1,2-*bis*-(triethoxysilyl)ethane (100.5 MPa; SD, 25.7 MPa) was used in the silanization step, and the lowest was obtained when 3-isocyanatopropyltriethoxysilane + 1,2-*bis*-(triethoxysilyl)ethane (28.9 MPa; SD, 8.8 MPa) was used. The three-point bending strength was significantly affected by the functionality of the main silane tested (p < 0.05), but not by the addition of the cross-

linker silane (p > 0.05). The composite that had been silanized with 3-isocyanatopropyltriethoxysilane had the greatest amount of water uptake (1.75%), and the composite silanized with 3-methacryloxypropyltrimethoxysilane + 1,2-*bis*-(triethoxysilyl)ethane had the least (1.08%). In conclusion, selection of the functional silane monomer can be a significant factor in developing filled resin composites in dentistry.

1. Introduction

Silver amalgam is probably the oldest composite material used in dentistry: it has served as a convenient and durable direct restorative material for more than 160 years. However, amalgam is dark and thus not an esthetic material in the anterior region. Substantial efforts in the design and development of tooth-like materials have yielded silicate cement and glass ionomer cement. One of the main advances in dentistry in the 1960s was the use of unfilled polymer resin-based restoratives, and subsequently filled resins (resin composites) and related adhesive cements [1].

The poor wear resistance of early unfilled resins in dentistry owing to mechanical and physical problems was addressed through the incorporation of fillers, leading to a composite structure and thus reinforcement. Filled resins or resin composites are now indispensable in contemporary dentistry. Clinical applications include direct restorations with filling composites and indirect restorations with luting cements, as in the cementation of crowns, bridges, inlays, and onlays [2].

Water sorption is an unavoidable property of restoratives, and means to minimize water sorption are continually sought. A range of observed chemical, physical, and biomechanical deficiencies have also necessitated the development of new dental composites with superior biomechanical properties and durability. One conclusion is that there is no ideal solution to the problem and several compromises are usually involved [3]. Currently, fillers are used in nearly all composite structures in dentistry. E-glass fibers are also being increasingly used for reinforcement in modern dental biomaterials [4] that use blue light to initiate the setting reactions [5].

Reinforcements in the composite types mentioned always need silane coupling agents to enhance the adhesion of glass fillers (and E-glass fibers) to the polymer matrix [6-9]. It is widely accepted that adhesion between the glassy filler surface and

4

silane is based on two main types of bonding: hydrogen bonds (such as -OH⋯O=) and covalent siloxane bonds (≡Si-O-Si≡) at the glass-polymer matrix interface [10]. To turn silane alkoxy groups (≡Si-O-R) into labile, reactive silanol groups (≡Si-OH), trialkoxysilane coupling agents with an organofunctional terminal group containing carbon-carbon double bonds >C=C< are activated in alcohol-water solutions with a suitable catalyst [11]. They can also be activated in non-aqueous systems for special applications that require a water-free environment [12]. -

The methacrylate group is the most usually applied due to its reactivity and chemical compatibility with most resin systems, such as those based on *bis*-phenol-A-diglycidyldimethacrylate (*bis*-GMA), triethyleneglycoldimethacrylate (TEGDMA), and methylmethacrylate (MMA) [13-14]. These resin systems form an organic matrix by free radical polymerization of dimethacrylates, *e.g. bis*-GMA. Very recently, some less studied silane monomers have been reported to produce significantly higher shear bond strength results, suggesting that they could be useful for adhesion promotion [15-17].

The reported literature on the adhesion promotion behavior of trialkoxysilane monomers is scant, other than for 3-methacryloxypropyltrimethoxysilane in dental resin composites with spherical fillers. 3-Styrylethyltrimethoxysilane has previously been evaluated as a coupling agent for fillers in experimental nanocomposites [18]. Some less studied silanes have been evaluated as adhesion promoters in dentistry and have been reported to alter flexural strength and modulus of E-glass fibers in resin-based composites [4]. Moreover, the addition of a cross-linker silane to a silane blend (a novel silane system) enhanced these biomechanical properties [17].

The present study aimed to assess the *in vitro* biomechanical properties of an experimental filled resin composite constituted of *bis*-GMA and TEGDMA matrix

and Ba-glass filler, after coupling using four organofunctional silane monomers, with or without a cross-linking silane monomer in an anhydrous medium, toluene. The hypothesis was that silane blends should result in higher flexural strength and lower water sorption than functional silanes only. Accordingly, the zero-hypothesis was that silanes alone or their blends promoted adhesion in experimental composites to the same degree and neither system lowered water sorption.

2. Materials and Methods

2.1. Silane Monomers and Filler Silanization

The silanes used for filler silanization were as follows: 3-methacryloxypropyltrimethoxysilane (purity 98%, Sigma-Aldrich Chemie GmbH, Steinheim, Germany; Lot S01603-022); 3-acryloxypropyltrimethoxysilane (95%, Gelest, Morrisville, PA, USA; Lot 5C-6412); 3-styrylethyltrimethoxysilane (92%, ABCR, Karlsruhe, Germany; Lot 7D-10467-S); and 3-isocyanatopropyltriethoxysilane (95%, Gelest, Morrisville, PA, USA; Lot 5I-7514). These silane monomers were also blended in a 1:1 ratio with a cross-linker silane, 1,2-*bis*-(triethoxysilyl)ethane (Gelest, Morrisville, PA, USA; Lot 5L-7926). Silanes were used as received, without further purification by distillation (Figure 1).

Next, 5.00 g of Ba-glass filler (SP345; Specialty Glass, Oldsmar, FL, USA; Lot 0726031-79) with a diameter of 0.7 μm was added to a glass bowl containing a magnetic stirrer and 65 mL of water-free toluene (Sigma Aldrich, Steinheim, Germany). A 0.250-mL aliquot of silane monomer (or 0.250 mL of functional silane + 0.250 mL cross-linker silane) was added to the bowl, and the contents were stirred for 23 h at room temperature. The toluene was decanted and the filler mixture was

washed with *n*-hexane, decanted again, and allowed to dry in an oven at 60°C for 24 h [19]. The filler was then used to prepare the experimental composite specimens.

2.2. The Resin System

The experimental resin consisted of 58.8 wt-% *bis*-phenol-A diglycidyldimethacrylate, *bis*-GMA (Röhm, Darmstadt, Germany), 39.2 wt-% triethyleneglycoldimethacrylate, TEGDMA (Sigma-Aldrich, Steinheim, Germany), 1.0 wt-% 2-(dimethylamino)ethylmethacrylate, DMAEMA (Sigma-Aldrich, Steinheim, Germany) and 1.0 wt-% camphorquinone (Fluka, Buchs, Switzerland). The resin was prepared in a polypropylene syringe covered with aluminum foil, and the syringe containing the resin was allowed to stabilize in the dark for 48 h before the next experimental step [4, 15-17].

2.3. Experimental Composite Specimens

A batch of filled resin composite mass was prepared by mixing 5.00 g of silanized filler and 2.00 g of resin matrix (60% [w/w] bis-GMA, 40% [w/w] TEGDMA) in a high-speed mixer (SpeedMixer DAC 150 FVZ-K; Hauschild, Hamm, Germany) at 1700 rpm in two successive mixing periods of 30 s, according to the manufacturer's instructions. The composite mass was protected from the light and stored in a refrigerator. The specimens were fabricated from this batch by placing an ample amount of composite into a stainless steel split mold with a brass frame and carefully filling the mold (total volume, 2.0 mm x 2.0 mm x 25.0 mm, *i.e.* 100 mm^3). Both the bottom and top of the mold were covered with a polyethylene foil (Transparent foil; Ivoclar, Schaan, Liechtenstein) [4, 17] to avoid any leakage of non-polymerized resin blend, according to the ISO Standard 10477:1992. There were 8 test specimens in

each group, and each sample had a filler content of 71.4 mass-%. A separate batch was used to fabricate one test group.

The experimental composite was light-polymerized with a halogen lamp hand-curing unit (Model 100 Optilux; SDS Kerr, Danbury, CT, USA), with an average light intensity of 930 mW cm^{-2} in the wavelength range of 400-505 nm and with a tip radius of 10 mm. The light intensity was measured by the curing radiometer that was incorporated in the curing unit . The specimens were irradiated for 3 x 40 s on both sides to ensure complete polymerization [4, 17]. The degree of conversion of each composite sample was measured by Fourier transform infrared (FTIR) spectroscopy.

2.4. Degree of Conversion

The degree of conversion was measured with a Perkin Elmer Spectrum One FTIR-spectrometer (Perkin-Elmer Ltd., Beaconsfield, UK) with an attenuated total reflectance (ATR) sampling accessory. The composite specimen was light-cured from the top. The measurements were made over a period of 15 min and specimens were scanned every 30 s, with a resolution of 4.00 cm^{-1}. Three measurements were made for each group. The degree of conversion, DC%, was calculated using the following formula [20]:

$$DC\% = \left[1 - \frac{C_{aliphatic}/C_{aromatic}}{U_{aliphatic}/U_{aromatic}} \right] \times 100 \qquad (1)$$

In formula (1), C = aliphatic to aromatic peak ratio from the light-cured specimen and U = aliphatic to aromatic peak ratio from uncured specimen.

2.5. Storage Conditions (Aging) and Sorption Measurement

Eight specimens were prepared from each resin-filler mixture. The specimens were then randomly divided into subgroups for different storage conditions: (a) storage at 37ºC ± 1ºC for 30 days, (b) water sorption group, and (c) solubility group. For group (b), each specimen's dry weight was measured and the specimens were stored in water for 1, 2, 3, 6, 7, 14, 21, 31 days (37ºC, distilled water) and reweighed. For group (c), specimens were weighed and stored in water for up to 30 days (37ºC, distilled water). At the storage time (in days) used for group (b), specimens were dried in an oven and weighed until their masses became constant.

2.6. Flexural testing

The flexural strength of the composite blocks was determined with the three-point bending strength test, performed according to the ISO 10477 standard. The composite specimens were also tested with a three-point loading test. The span between the supports was 20.0 mm and the crosshead speed during testing was 1.0 mm min^{-1}. The load was applied with a universal testing machine (Lloyd LRX; Lloyd Instruments Ltd., Fareham, England) to the center-point of the test specimens (Figure 2). The deflection and load were recorded using Lloyd Nexygen 2.0 software program (Lloyd Instruments Ltd). The load at fracture of the test specimen was used to calculate the ultimate flexural strength (ε_F) and flexural modulus (E_F), using the following formulas [20]:

$$\varepsilon_F = 3F_mI/2bh^2 \tag{2}$$

$$E_F = SI^3/4bh^3 \tag{3}$$

In formula (2), F_m is the applied load (N) at the highest point of load-deflection curve, I is the span length (20.0 mm), b is the width of the test specimen (mm) and h is the thickness of the test specimen (mm). In formula (3), S is the stiffness (N/m), and S =

F/d where d is the deflection (mm) corresponding to load F (N) at a point in the straight-line portion of the trace.

2.7. Statistical analysis of the results

The flexural strength data and water uptake and solubility data were statistically analyzed using a three-way analysis of variance (ANOVA), using SPSS software, version 11.0 (Statistical Package for Statistical Science Inc., Chicago, IL, USA). The flexural strength was the dependent variable and the type of silane and the storage conditions were the independent factors. The level of statistical significance was set at p = 0.05, in other words *p* values less than 0.05 were considered to be statistically significant in all tests (Figure 3).

2.8. Scanning electron microscopy

After flexural strength measurements, scanning electron microscopy (JSM 5500; JEOL, Tokyo, Japan) was used at a magnification of 1000x to examine the fractured surfaces of experimental composite specimens. An acceleration voltage of 14-18 kV in vacuum was used, at a working distance of 20 mm. The specimens were mounted on aluminum stubs and sputtered with gold (Unit E500; Polaron Equipment, Watford, UK) (Figure 4).

3. Results

Statistical analysis with ANOVA showed that the highest flexural strength was obtained when the 3-acryloxypropyltrimethoxysilane + 1,2-*bis*-(triethoxysilyl)ethane blend (100.5 MPa; SD, 25.7 MPa) was used in the silanization step. The lowest flexural strength was obtained when the 3-isocyanatopropyltriethoxysilane + 1,2-*bis*-

(triethoxysilyl)ethane blend (28.9 MPa; SD, 8.8 MPa) was used The three-point bending strength was significantly affected by the functionality of the main silane tested ($p < 0.05$), but not by the addition of the cross-linker silane ($p > 0.05$) (Table 1).

The composite that had been silanized with 3-isocyanatopropyltriethoxysilane had the greatest amount of water uptake (1.75%), whereas the sample silanized with 3-methacryloxypropyltrimethoxysilane + 1,2-*bis*-(triethoxysilyl)ethane (1.08%) had the least. The solubility was the lowest for 3-styrylethyltrimethoxysilane (0.19 mg/mm^3, and highest for 3-isocyanatopropyltriethoxysilane + 1,2-*bis*-(triethoxysilyl)ethane (0.57 mg/mm^3) (Table 2).

The degree of conversion, measured after taking three parallel FTIR measurements on samples, was found for experimental resin composite to be $59.6\% \pm 2.4\%$.

4. Discussion

The silane monomers were selected for this pilot study on the basis of some encouraging previous results, *i.e.* enhanced adhesion promotion, obtained for 3-isocyanatopropyltriethoxysilane [21], 3-styrylethyltrimethoxysilane [18], and 3-acryloxypropyltrimethoxysilane [15]. A silane blend system of a functional silane combined with a cross-linker silane has been reported to promote adhesion and protect against hydrolytic degradation in applications in production technology [22,23]. Recently in dental materials research, this blend has shown to promote adhesion of dimethacrylate resins onto silica-coated Ti [24] or zirconia [25], and to reinforce experimental E-glass fiber composite [4, 17]. Thus, the expectation was that

significantly higher changes would be observed after silanization with the blend than for silanization with 3-methacryloxypropyltrimethoxysilane alone, which is considered to be the gold standard [10, 11]. The use of the cross-linking silane 1,2-*bis*-(triethoxysilyl)ethane was also based on reported successful experiments [22-25]; however, this study was limited by the constant concentrations of the functional silane and the silanes in the blend.

Flexural strength, one of the key biomechanical properties of dental biomaterials, such as resin composites, is conventionally measured using a three-point bending test [20]. The maximum stress that is measured in the test is called the flexural strength. Statistical analysis showed that the highest flexural strength was obtained when 3-acryloxypropyltrimethoxysilane + 1,2-*bis*-(triethoxysilyl)ethane (100.5 MPa; SD, 25.7 MPa) was used (Table 1). Attention should also be given to the specimens silanized with 3-methacryloxypropyltrimethoxysilane and 3-styrylethyltrimethoxysilane, which produced the highest numerical values. It should be noted that the addition of the cross-linker silane did not produce significant differences. Surprisingly, the use of 3-isocyanatopropyltriethoxysilane led to the lowest results in the study. This is contrary to results of a previous study in which silica-coated Ti was silanized with 1.0 vol% solutions of 3-isocyanatopropyltriethoxysilane and 3-methacryloxypropyltrimethoxysilane [21]; in that study dimethacrylate resin adhesion was significantly better after thermo-cycling, *i.e.* after the specimens had been subjected to thermal stress between + 5 °C and 55 °C for 6000 cycles.

In general, water sorption should be low for resin composites, at 26 to 30 $\mu g/mm^3$, and the composite solubility should be between 0.25 and 2.5 mg/mm^3 [26]. Because excessive water sorption has a detrimental effect on both color stability (not

included in this research) and wear resistance (to be measured in the near future) [1], water sorption and composite solubility should be minimized. The results obtained concur well with specific values found in the literature. In this study, the results suggest that an addition of a cross-linker silane significantly reduces water uptake, but at the same time increases solubility (Figure 3, Table 2). So far, there have been no reports on resin composites of fillers silanized with silane blends, but elsewhere, silane blends have shown enhanced hydrolytic stability *e.g.* silanization pretreatment of galvanized steel [22, 23].

There was no statistically significant difference in solubility (*i.e.* the solubility of resin matrix) when the fillers were silanized with the silane blend or with the functional silane alone. Treatment with 3-isocyanatopropyltriethoxysilane gave distinctively different results from the other treatments, producing the lowest results, which suggests that the silanized fillers were not bonded strongly to the resin matrix and instead had been loosened out of the resinous monomer matrix. Interestingly, dental resin composite manufacturers do not reveal which silane coupling agent they have used in filler silanization. Yet, the stability and quality of the silane coupling agent (silane monomer) significantly affects solubility and water sorption [1, 26]; hence, silane selection can be crucial. The use of a resin matrix is typical in dental materials because it exhibits lower polymerization shrinkage and more rapid polymerization than methylmethacrylate. Resin matrix is thus widely used in photo-polymerizable resin systems [1, 5], with 2-(dimethylamino)ethylmethacrylate as a plasticizer. In this study, we used the conventional *bis*-GMA/TEGDMA system. When compared with some other dimethacrylate systems, such as UEDMA (urethaneethyldimethacrylate) in combination with *bis*-EMA (an ethoxylated *bis*-GMA), TEGDMA has been found to have the best plasticizing effect on *bis*-GMA

[27]. The glass filler type used in this study also reflects typical practice. It is known to have adequate X-ray opacity due to its Ba and Si content [1, 11, 26]. Filler silanization needs to take place in conditions that avoid extra humidity, such as in anhydrous, non-polar media [12]. For this reason, we selected toluene as the medium [19].

3-Styrylethyltrimethoxysilane has been recently reported to result in moderate improvement in flexural modulus compared with 3-methacryloxypropyltrimethoxysilane and blends of the mentioned silanes [18]. Numerically, those results correspond with ours. The degree of conversion was typical of those usually observed for this type of *bis*-GMA/TEGDMA resin system composite [1, 26]. In this study, we did not determine the linear coefficient of thermal expansion (α). It is known to be 25 to 38 x 10^{-6} $°C^{-1}$ for multipurpose dental composites with a particle diameter of 0.2-3.0 µm and a filler volume of 60%-70%, increasing with the percentage of filler content [26]. We did not select any particular dental product as a resin composite control because there is a plethora of available potential products for which the literature gives comprehensive data.

5. Conclusions.

The results obtained suggest the following:

1. The hypothesis that silane blends should produce higher flexural strength and lower water sorption compared with functional silanes only was found to be valid.

2. Silanes alone and their blends do not promote adhesion to equal extents in the experimental composites and neither one lowers water sorption.

3.   Addition of a cross-linker silane to the filler silanization reduces water uptake for all silanes, but not significantly for all the silane blends.

4.   Addition of a cross-linker silane during filler silanization enhances the solubility of resin composite.

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Table 1.

Silane(s) used and corresponding flexural strength and flexural modulus after the

solubility test (30 days, the maximum storage time) of the experimental resin. Key:

SD = standard deviation; ACPS = Silanization with 3-

acryloxypropyltrimethoxysilane; ACPS + BTSE = 3-acryloxypropyltrimethoxysilane

+ 1,2-*bis*-(triethoxysilyl)ethane; MPS = 3-methacryloxypropyltrimethoxysilane;

MPS + BTSE = 3-methacryloxypropyltrimethoxysilane + 1,2-*bis*-

(triethoxysilyl)ethane; STYRX = 3-styrylethyltrimethoxysilane;

STYRX + BTSE = 3-styrylethyltrimethoxysilane + 1,2-*bis*-(triethoxysilyl)ethane; ICS

= 3-isocyanatopropyltriethoxysilane; ICS + BTSE = 3-

isocyanatopropyltriethoxysilane + 1,2-*bis*-(triethoxysilyl)ethane.

Silane used	Flexural Strength / MPa	SD / MPa	Flexural Modulus / GPa	SD / GPa
ACPS	56.5	33.6	5.9	2.52
ACPS + BTSE	100.5	25.7	10.3	2.64
MPS	83.2	23.7	6.4	1.14
MPS + BTSE	67.3	23.7	5.2	0.88
STYRX	83.1	11.9	6.1	0.55
STYRX + BTSE	80.6	16.3	5.2	0.54
ICS	38.0	6.9	5.3	0.60
ICS + BTSE	28.9	8.8	4.1	0.76

Table 2.

Silane(s) used and corresponding water uptake and solubility for the experimental resin. Key: SD = standard deviation; m(soluble) = mass that was dissolved. *see also* Table 1

Silane used	Water uptake / %	SD %	m(water uptake) / g	SD / g	Solubility / %	SD %	m(soluble) / g	SD /g	Solubility mg/mm^3	SD mg/mm^3
ACPS	1.27 a	0.04	0.089 a	0.004	0.28	0.03	0.020	0.002	0.20	0.02
ACPS + BTSE	1.09 b	0.08	0.076 b	0.006	0.41	0.04	0.029	0.002	0.29	0.02
MPS	1.24 a	0.06	0.087 a	0.005	0.32	0.05	0.022	0.003	0.22	0.03
MPS + BTSE	1.08 b	0.09	0.076 b	0.007	0.38	0.04	0.027	0.003	0.27	0.03
STYRX	1.22 a	0.06	0.085 a	0.005	0.27	0.03	0.019	0.002	0.19	0.02
STYRX + BTSE	1.12 a	0.08	0.078 a	0.006	0.32	0.04	0.022	0.003	0.22	0.03
ICS	1.75	0.10	0.122	0.012	0.71	0.05	0.050	0.004	0.50	0.04
ICS + BTSE	1.54	0.10	0.108	0.011	0.82	0.05	0.057	0.003	0.57	0.03

a, b = groups do not differ statistically significantly. m(soluble) = mass that was dissolved
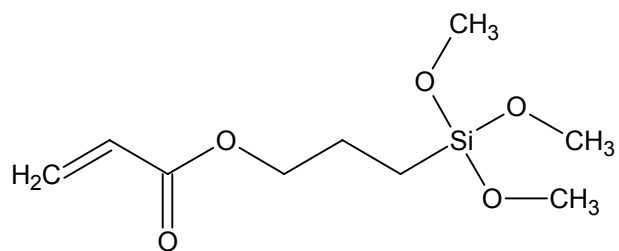
a)
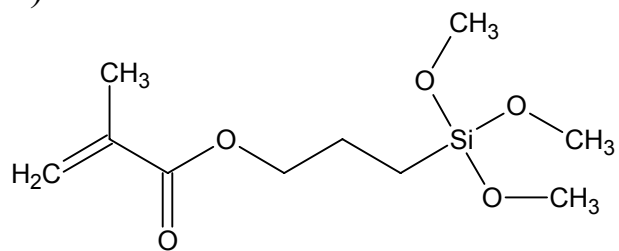
b)
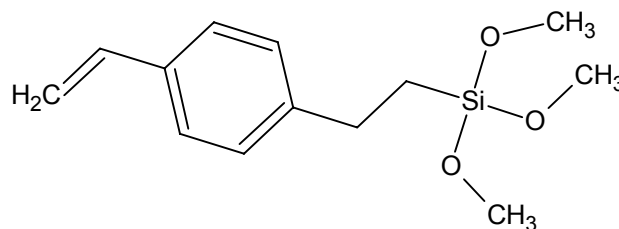
c)
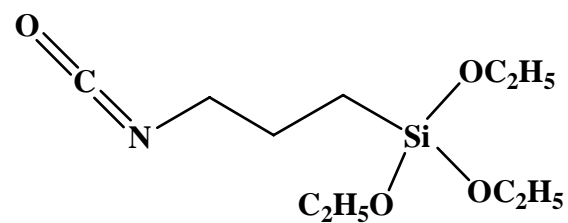
d)
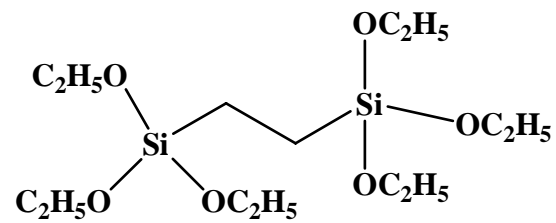
e)

Figure 1. Structures of silanes used in the experimental composites: a) 3-Acryloxypropyltrimethoxysilane, b) 3-Methacryloxypropyltrimethoxysilane, c) 3-Styrylethyltrimethoxysilane, d) 3-Isocyanatopropyltriethoxysilane, e) 1,2-*bis*-(Triethoxysilyl)ethane (the cross-linker silane).
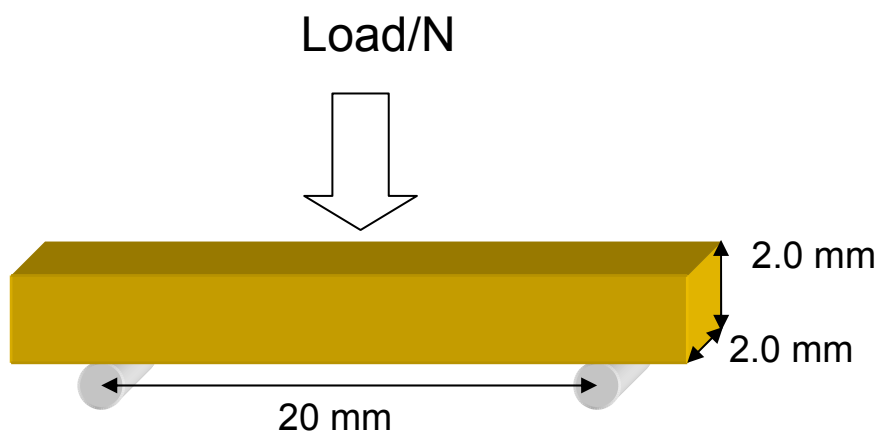

Figure 2. Schematic illustration of the set-up for the three-point flexural test with a rectangular resin composite test specimen.
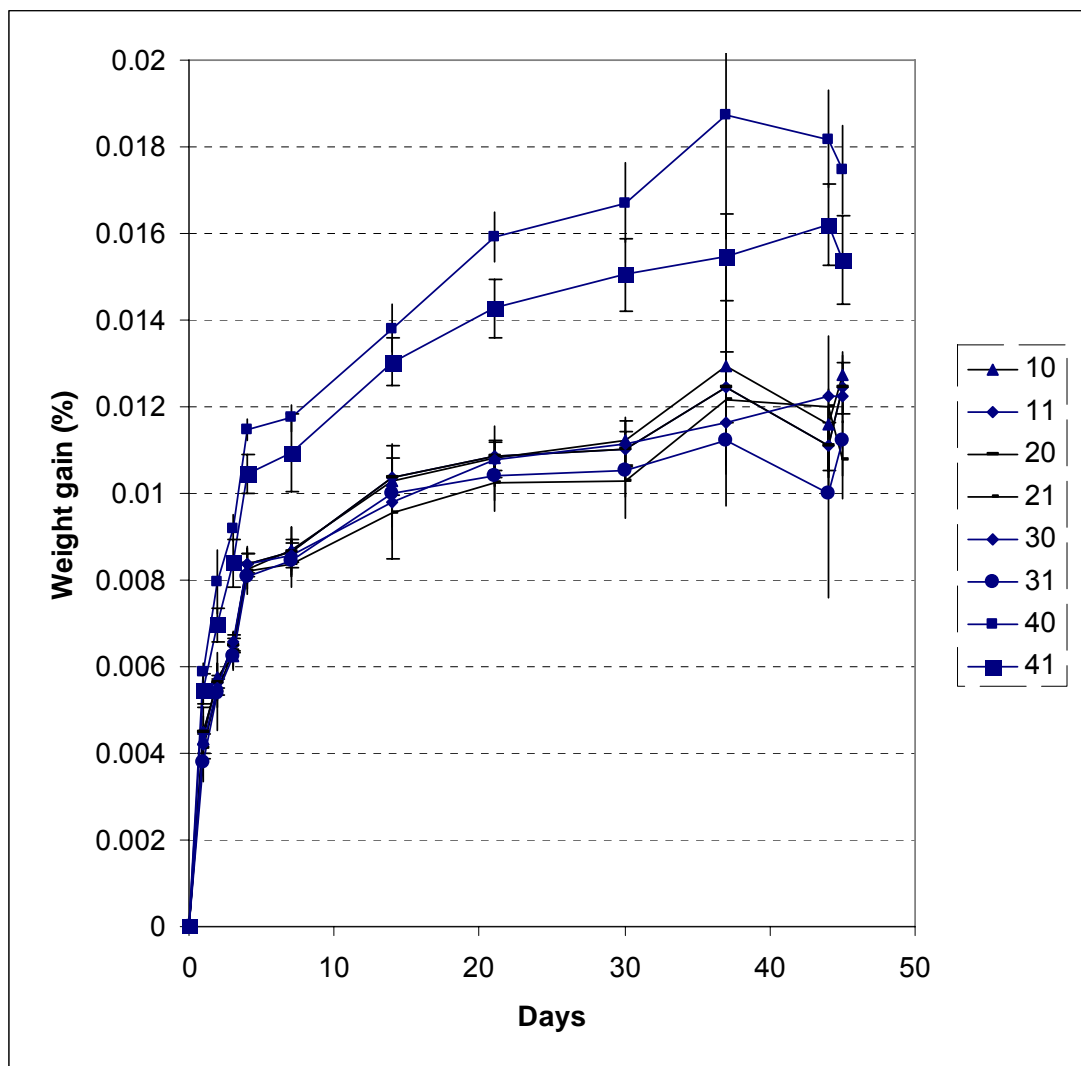
Figure 3. Water sorption of the experimental composite with different silanizations of the fillers. Key: 10 = Silanization with 3-acryloxypropyltrimethoxysilane,

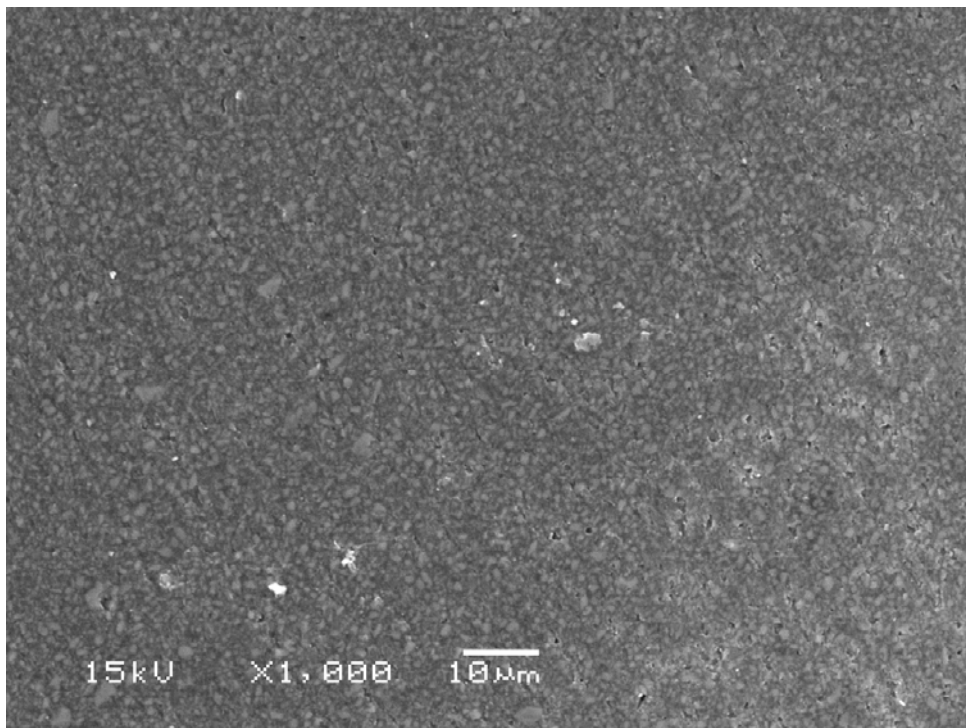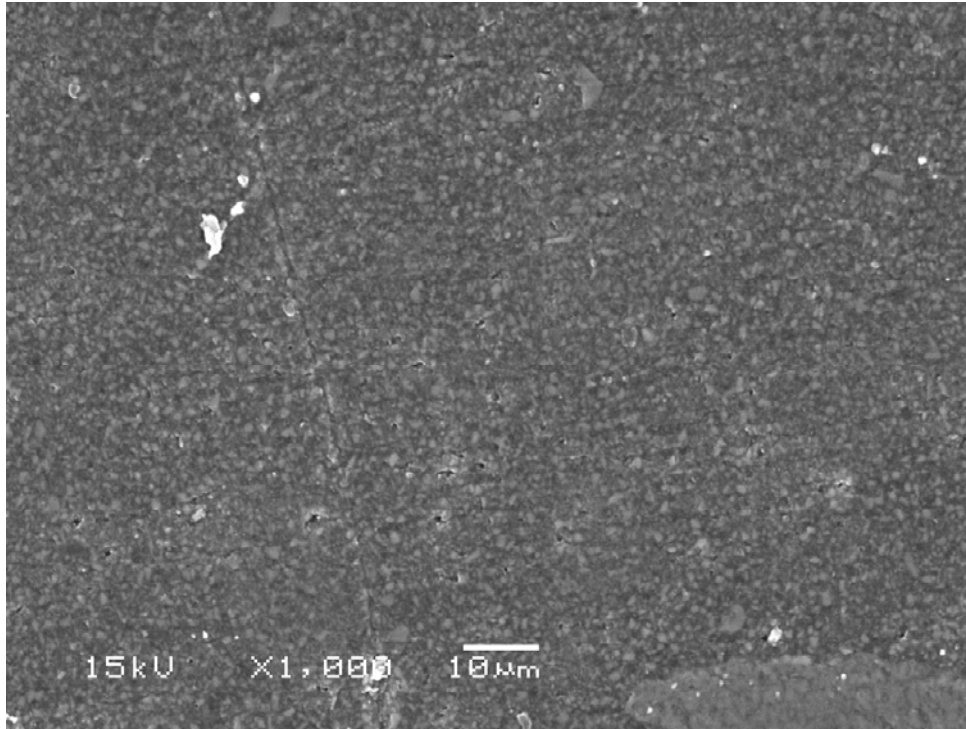11 = Silanization with 3-acryloxypropyltrimethoxysilane + 1,2-*bis*-(triethoxysilyl)ethane,

20 = Silanization with 3-methacryloxypropyltrimethoxysilane,

21 = Silanization with 3-methacryloxypropyltrimethoxysilane + 1,2-*bis*-(triethoxysilyl)ethane,

30 = Silanization with 3-styrylethyltrimethoxysilane,

31 = Silanization with 3-styrylethyltrimethoxysilane + 1,2-*bis*-(triethoxysilyl)ethane,

40 = Silanization with 3-isocyanatopropyltriethoxysilane and

41 = Silanization with 3-isocyanatopropyltriethoxysilane + 1,2-*bis*-(triethoxysilyl)ethane.
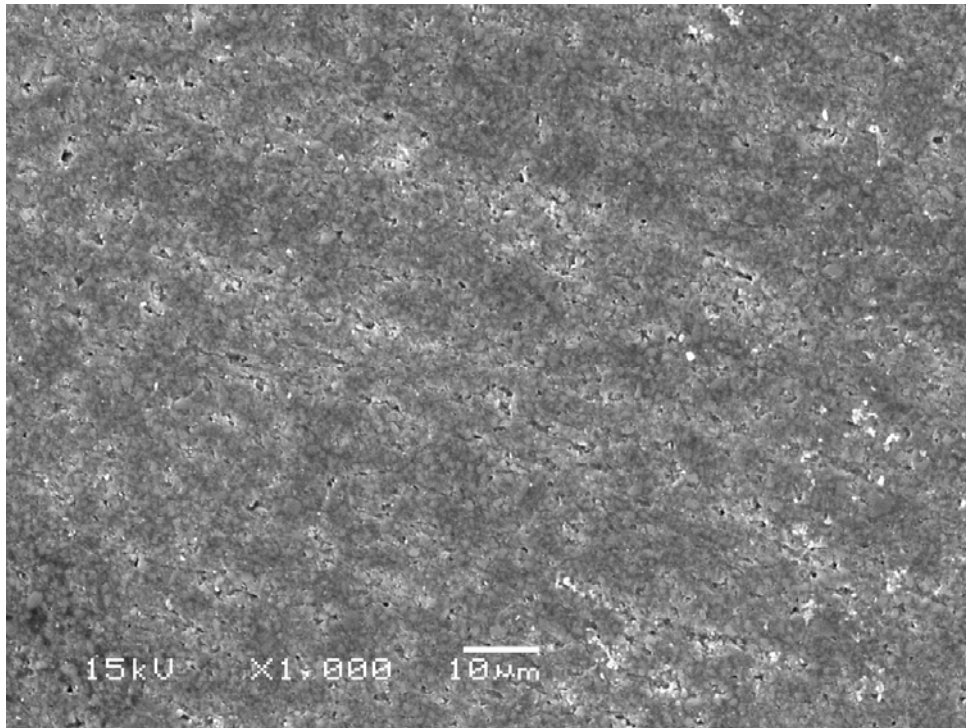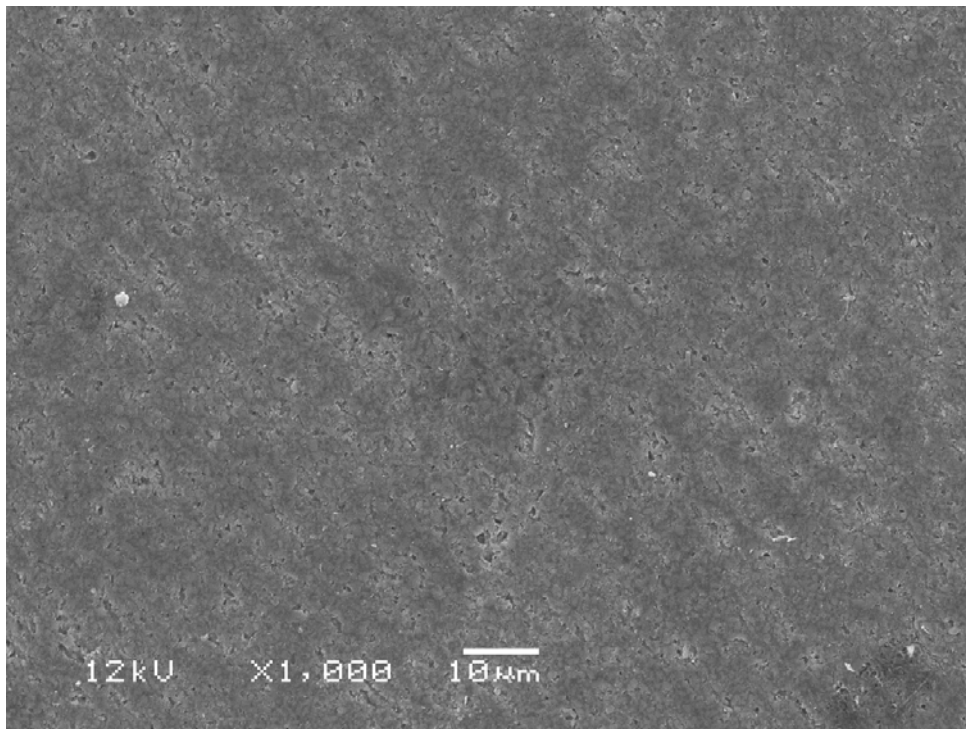
Figure 4: Composite specimens after water absorption and testing. a) Experimental composite with fillers silanized with 3-acryloxypropyltrimethoxysilane, (magnification 1000 x).
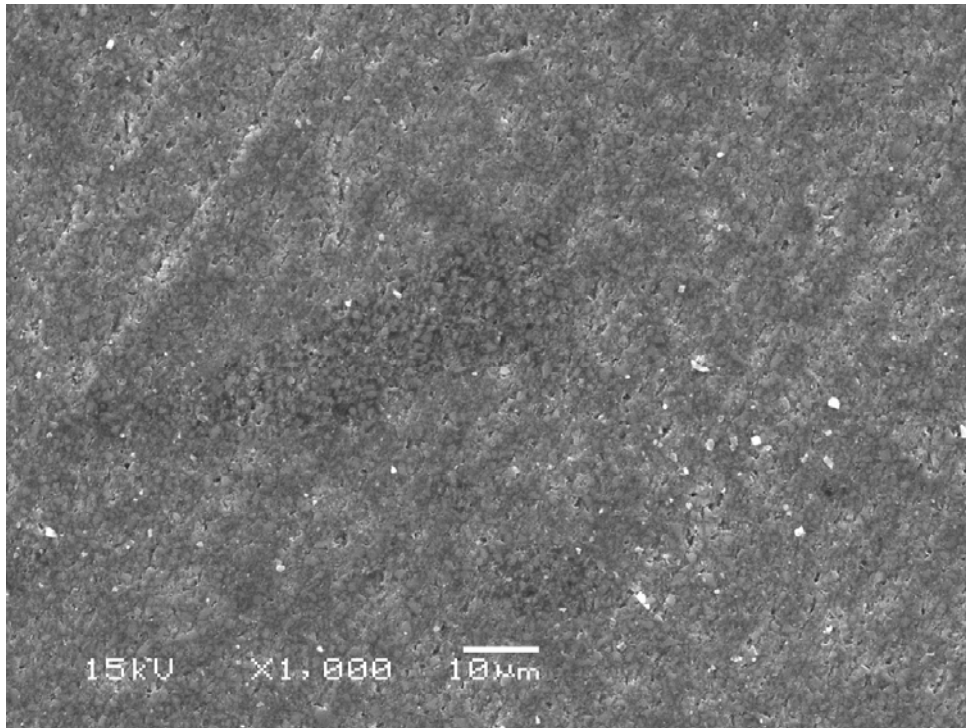

b) Experimental composite with fillers silanized with a blend of 3-acryloxypropyltrimethoxysilane and 1,2-*bis*-(triethoxysilyl)ethane (magnification 1000 x).
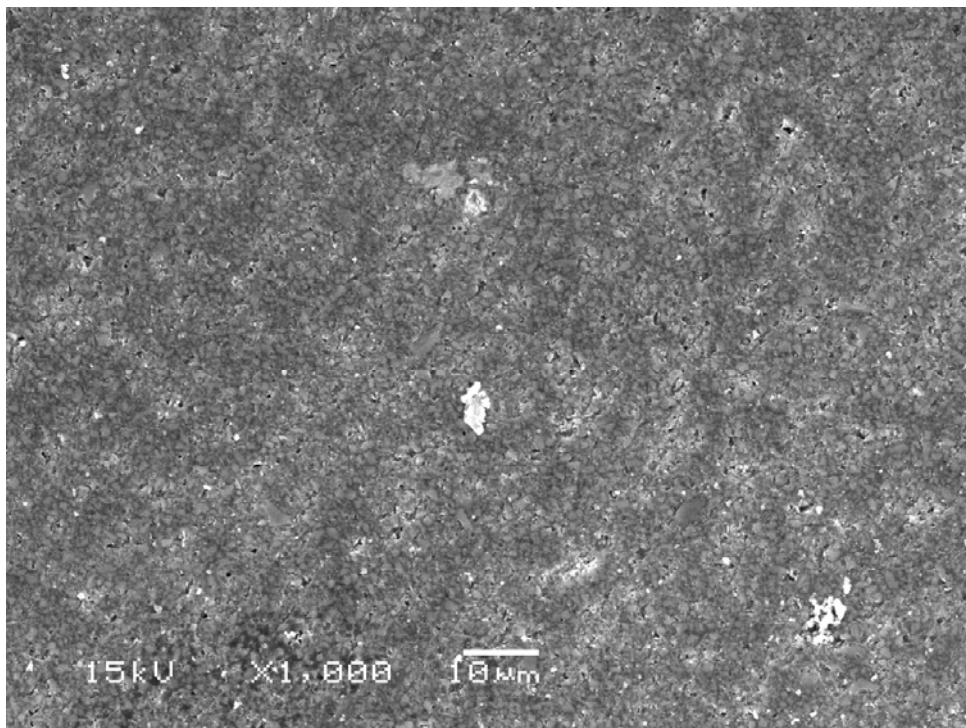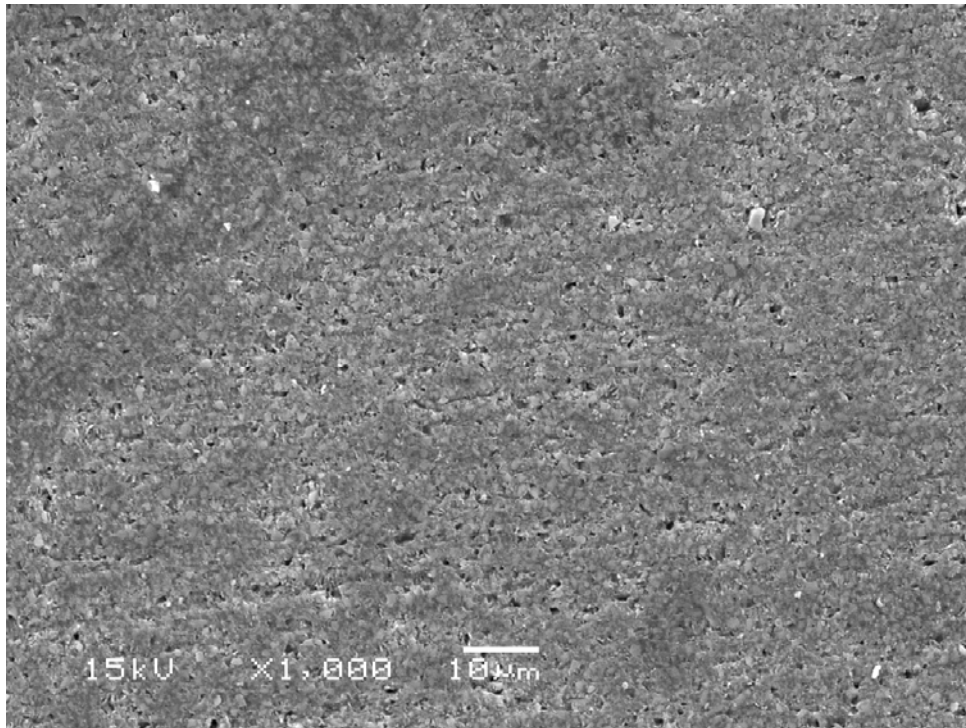
c) Experimental composite with fillers silanized with 3-methacryloxypropyltrimethoxysilane, (magnification 1000 x).

d) Experimental composite with fillers silanized with a blend of 3-methacryloxypropyltrimethoxysilane and 1,2-*bis*-(triethoxysilyl)ethane (magnification 1000 x).
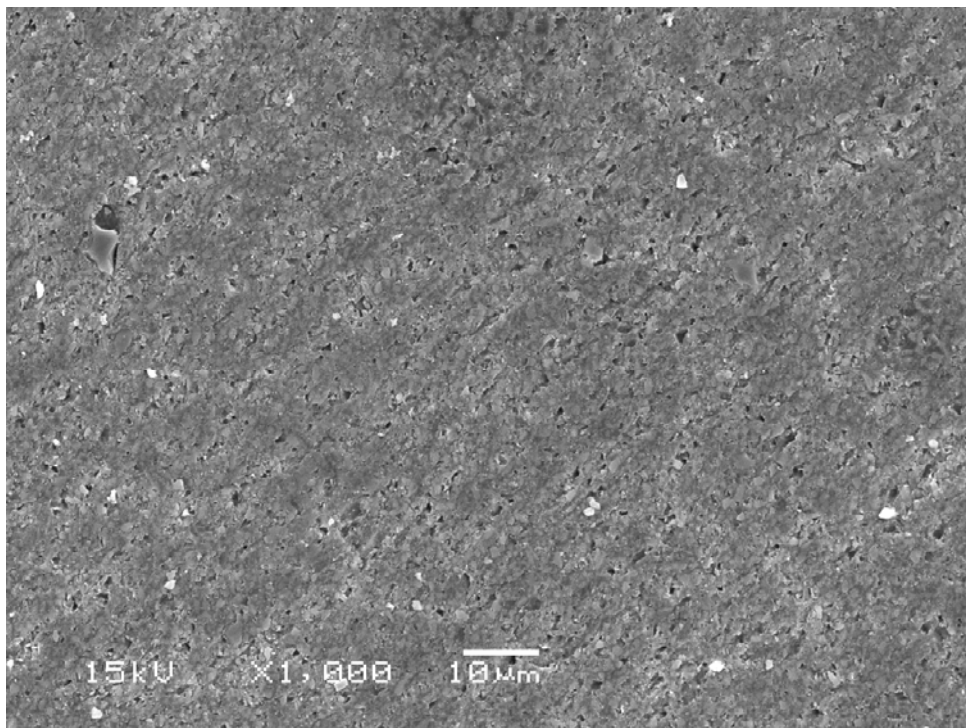
e) Experimental composite with fillers silanized with 3-styrylethyltrimethoxysilane (magnification 1000 x).

f) Experimental composite with fillers silanized with a blend of 3-styrylethyltrimethoxysilane and 1,2-*bis*-(triethoxysilyl)ethane (magnification 1000 x).

g) Experimental composite with fillers silanized with 3-
isocyanatopropyltriethoxysilane (magnification 1000 x).

h) Experimental composite with fillers silanized with a blend of 3-
isocyanatopropyltriethoxysilane and 1,2-*bis*-(triethoxysilyl)ethane (magnification
1000 x).