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Non-silicate nanoparticles for improved nanohybrid resin composites

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Abstract

Objectives: Zirconia and alumina nanoparticles were coated with a silica-rich layer (ALSI and ZRSI) and used to prepare experimental nanohybrid resin composites, which were characterized and compared to a control commercial resin composite (Filtek Z350 XT).

Methods: Silica nanoparticles with sizes compatible to ALSI (Aerosil 150) and ZRSI (Aerosil OX 50) were tested as references. The volume of nanoparticles was equivalent across the composites, which also had consistent content of glass microparticles. C=C conversion, viscosity, depth of cure, surface topography, hardness, opacity, radio-opacity, and edge chipping resistance (ReA) were tested after 24 h. Flexural strength (σ_f) and fracture toughness (K_{IC}) were also tested after 15K thermal cycles. Data were analyzed using one-way or two-way ANOVA and Tukey's test ($\alpha=0.05$).

Results: ALSI and ZRSI yielded resin composites with lower viscosity and more irregular nanoagglomerates compared to nanosilica-based composites. C=C conversion and depth of cure were lower for ZRSI composite, which had higher opacity, radio-opacity, and hardness. ReA was higher for ALSI composite. Composites with ALSI and ZRSI showed stable σ_f after aging, whereas the control and Aerosil 150 resin composites showed significant degradation. The commercial and nanosilica-based composites showed up to 42% reduction in K_{IC} after aging, whereas resin composites with ZRSI and ALSI showed a more stable K_{IC} .

Significance: ALSI and ZRSI generated nanohybrid resin composites with improved and/or more stable physical properties compared with nanosilica-based and commercial composites. This

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study suggests that changing the composition of nanofillers is a simple method to enhance the performance of nanohybrid composites.

Keywords

fillers; silica; methacrylates; nanotechnology; surface properties; mechanical stress

1. INTRODUCTION

Resin composites are major restorative materials in dentistry. In the past decades, alterations in their formulation were made to overcome shortcomings observed in the clinical service of restorations. These alterations included use of monomers with higher molecular mass and lower polymerization shrinkage, more reactive photoinitiator systems, increased filler loading, and reduced filler particle size [1-4]. Better adhesives and improved restorative techniques were developed concurrently. Today, micro/nanohybrid resin composites are considered the gold standard materials for direct restorations [5-8]. Since fractures are one of the most reported reasons for failure of restorations [5-7], it seems that there is still room for improvement in mechanical performance of dental resin composites.

The increase in filler loading and reduction in particle size were not accompanied by drastic changes in particle composition. Glass microparticles and/or silica nanoparticles are the filler types present in almost all commercial materials. Particles containing silica are highly reactive to organosilanes and allow simple, effective coupling with the resin phase. However, silica nanoparticles also have some limitations, including radiolucency and poor mechanical properties [9]. In a previous study, a method to coat crystalline, non-silicate ceramic nanoparticles with a silica-rich layer was described [10]. This layer was shown to allow effective silanization of the non-silicate nanoparticles and render stable reinforcement of a dimethacrylate polymeric matrix. However, the experimental resin composites tested in that study did not emulate commercial materials nor were compared with a proprietary resin composite. Therefore, a question was raised whether the use of non-silicate nanoparticles such as alumina or zirconia, in substitution of silica, would actually result in restorative materials with improved properties. Replacing silica with alumina or zirconia could increase fracture toughness, but also could be detrimental to optical properties of the resin composites.

The aim of this study was to coat the surface of zirconia and alumina nanoparticles with a silica-rich layer and use the coated nanoparticles to prepare experimental nanohybrid resin composites, which were characterized and compared with nanosilica-based correspondents and a commercial material. The hypothesis was that resin composites with non-silicate nanoparticles would have improved mechanical properties as compared with materials containing silica nanoparticles.

2. MATERIALS AND METHODS

2.1. Study design and nanoparticle surface functiona

In this *in vitro* study, five resin composites (four experimental, one commercial) were tested. Experimental nanohybrid resin composites were prepared. Table 1 presents characteristics of the inorganic particles tested. Alumina spherical nanoparticles (1020MR, gamma) and zirconia spherical nanoparticles (5931HT, monoclinic crystallographic structure) from Nanoamor (Houston, TX, USA) were coated with a silica-rich layer, generating silica-coated alumina nanoparticles (herein referred as ALSI) and silica-coated zirconia nanoparticles (herein referred as ZRSI). The sol-gel method used to coat the particles with an amorphous silica layer was reported by Kaizer et al. [10]. Tetraethyl orthosilicate (Sigma Aldrich, St. Louis, MO, USA) was used as silica precursor. Silica nanoparticles with sizes compatible to alumina and zirconia nanoparticles were tested as references: Aerosil 150 and Aerosil OX 50 (Evonik, Essen, Germany). All nanoparticles were coated with 10 mass% 3-(trimethoxysilyl)propyl methacrylate (Sigma-Aldrich) relative to filler mass [10]. Silanization of the powders was checked using Fourier Transform infrared (FTIR) spectroscopy, as detailed elsewhere [11]. Barium borosilicate glass microparticles, cr d b die manufacturer with 1 mass% silane relative to filler mass (Esstech Inc., Essington, PA USA), were used as received to obtain a hybrid filler system. A commercial nanofill resin composite, shade A2D, served as a control (Filtek Z350 XT; 3M ESPE, St. Paul, MN, USA.) This resin composite is composed by bisphenol-A glycidyl dimethacrylate (Bis-GMA), urethane dimethacrylate (UDMA), bisphenol-A ethoxylated dimethacrylate (Bis-EMA), and triethylene glycol dimethacrylate (TEGDMA), 78.5 mass% Zr/Si nanoparticles (20 nm in size) and nanoagglomerates (0.6 – 1.4 μm in size). This material was selected as a control because it is one of the most used and tested commercial resin composites.

2.2. Formulation of the experimental nanohybrid resin composites

The formulation of the experimental nanohybrid resin composites was defined based on several pilot analyses including handling characteristics (consistent with commercial restorative composites of medium viscosity) and degree of C=C conversion (above 50%). The resin composites were prepared containing a consistent 70% mass of microparticles, then equivalent volume fractions of nanoparticles (ALSI, ZRSI, Aerosil 150, or Aerosil OX 50) were added to the experimental materials. The definitive experimental resin composites had handling characteristics similar to regular direct restoratives. Since the nanoparticles tested had distinct surface areas and densities, the final mass of inorganic fillers in the resin composites (nano + micro) were slightly different: 75% (ALSI, ZRSI), 72.9% (Aerosil 150), and 72.5% (Aerosil OX 50). The monomers used for formulating the experimental resin composites were Bis-GMA, Bis-EMA6, UDMA, and TEGDMA (7:7:5:1 m/m) (Esstech) to emulate the resin phase composition of the commercial control material. Polymerization promoters were camphorquinone as photoinitiator (0.4 mass%) and ethyl 4-(dimethylamino)benzoate as co-initiator (0.8 mass%), from Sigma-Aldrich. The components were mechanically mixed with a centrifugal mixer (SpeedMixer DAC150; FlackTek, Landrum, SC, USA) to produce homogeneous pastes. The experimental nanohybrid resin composites containing non-silicate nanoparticles are herein referred as ALSI or ZRSI resin composites, the nanohybrid resin composite with silica nanoparticles are herein referred as

nanosilica-based resin composites. Physical/chemical tests, response-variables, and sample sizes involved in characterization of the five resin composites are presented as follows.

2.3. C=C conversion

Degree of C=C conversion ($n=6$) was evaluated by FTIR spectroscopy (Prestige-21; Shimadzu, Tokyo, Japan) with an attenuated total reflectance diamond device. The resin composite was placed into a silicone mold (thickness 2 mm, diameter 4 mm) with the center of the bottom surface of the resin composite in contact with the diamond cell. Spectrum of the unpolymerized material was acquired in absorbance mode using 24 co-added scans at 4 cm^{-1} resolution. Photoactivation was carried out from top surface for 40 s by using a LED curing unit with 1200 mW/cm^2 irradiance (Radii Cal; SDI, Bayswater, Victoria, Australia). This photoactivation time is consistent with opaque shades of commercial resin composites. Irradiance of the light-curing unit was confirmed with a power meter (MARC LC, BlueLight Analytics, Halifax, Canada). After photoactivation, another spectrum was immediately acquired (polymer), and C=C conversion (%) at the bottom of specimen was calculated. A baseline technique was used for calculating the difference in intensity of the aliphatic C=C stretching vibration (peak height) at 1635 cm^{-1} between the polymerized and unpolymerized states. The symmetric ring stretching vibration at 1608 cm^{-1} was an internal standard.

2.4. Viscosity and depth of cure

Viscosity was analyzed with an oscillatory rheometer (RS-CPS +; Brookfield, Middleboro, MA, USA). A standard 0.5 mL volume of resin composite was used and measurements ($n=3$) were performed on parallel plates using P25 spindle for 1 min, at a shear rate of 0 to 0.5 s^{-1} and 37°C temperature. The averaged viscosity curves were adjusted by curve fitting ($R^2 > 0.9$) using SigmaPlot v.12.0 (Systat Software Inc., San Jose, CA, USA). For depth of cure analysis, a 6-mm-deep metallic mold (diameter 4 mm) was filled with resin composite ($n=3$). The material was photoactivated from the top surface for 40 s and all unpolymerized material at the bottom was removed with a scalpel blade. The minimum thickness of the remaining polymerized resin composite was measured at the center or periphery of the specimen with a digital caliper accurate to 0.001 mm and divided by two, according to ISO 4049 specification [12].

2.5. Surface topography, elemental analysis, and hardness

Photopolymerized resin composite disks (2 mm diameter, 1 mm thickness) were embedded in epoxy resin ($n=3$) and wet-polished with 600, 1200, 1500, 2000, and 2500-grit SiC abrasive papers followed by polishing with diamond suspensions of 3 and $1\text{ }\mu\text{m}$ particle sizes. Environmental scanning electron microscopy (SEM) images were obtained by using secondary electron detector, 400 pA beam current, and 15 kV beam power (EVO 50; Carls Zeiss AG, Oberkochen, Germany). Elemental surface analysis was carried out using energy-dispersive X-ray spectroscopy (EDS). Disks with same dimensions were prepared and wet-polished with 600 and 1200-grit SiC papers for hardness readings ($n=3$). Five Knoop indentations, with at least $500\text{ }\mu\text{m}$ distance between each other, were performed on the top surface of each specimen with 50 gf applied for 15 s, by using a digital microhardness tester (FM-700; Future-Tech, Kawasaki, Japan). The average of five readings was the Knoop hardness (kgf/mm^2) recorded for each specimen.

2.6. Opacity and radio-opacity

A spectrophotometer (SP60; X-Rite, Grand Rapids, MI, USA) was used for determining opacity (n=5) by calculating the contrast ratios of resin composite disks (2 mm diameter, 1 mm thickness) photopolymerized as indicated in section 2.3. Readings were made in triplicate over a black background ($L=0.19$; $a=-0.1$; $b=-0.10$) and a white background ($L=94.2$; $a=-0.87$; $b=-0.42$). Contrast ratio was calculated by dividing the spectral reflectance of light on the black over the white background. Radio-opacity was measured according to ISO 4049 standard [12]. Radiographs of the same disks (n=5) were obtained using a digital phosphorus plate system (VistaScan; Dürr Dental, Bietigheim-Bissingen, Germany) with 70 kV, 8 mA, 0.2 s exposure, and 400 mm focal-film distance. An aluminum step wedge scale was radiographed with the specimens. Gray levels (pixel density) on each resin composite were measured in triplicate in the radiographs using Adobe Photoshop CS6 (Adobe, San Jose, CA, USA) and compared with the aluminum scale. Radiodensity was recorded in equivalence to millimeters of aluminum.

2.7. Edge chipping resistance (ReA)

Bar-shaped specimens (12 mm length 5×5 mm height $\times$ 2.8 mm width) were prepared and positioned at a digital micropositioned X–Y stage (resolution 0.001 mm) coupled to a universal testing machine (DL2000; EMIC, São José dos Pinhais, PR, Brazil). Photoactivation was carried out through the 2.8-mm-thick side of the bar using overlapping positionings of the light guide on both faces to avoid problems with depth of cure. A metal rod with a Vickers indenter was connected to the load cell (HBM U9B/2KN, Germany), as previously described [13]. A load was applied through the Vickers indenter at a crosshead speed of 1 mm/min until a chip fracture occurred; the peak load (N) was recorded. Calibration for indentation distance was performed prior testing each bar-shaped specimen by assessing different distances from the indenter tip to specimen edge (0.1 to 0.7 mm, with 0.1 mm increments). This was important to confirm a linear behavior between increased edge distance (d) and force (F) [13] for all experimental materials tested. For each resin composite, 15 chips were produced at a 0.5 mm distance from the specimen edge, which is considered a clinically relevant distance [14]. Indentations were placed at least 3 mm apart from each other and invalid chips were excluded from the study [13,15]. At least 6 bar-shaped specimens per group were used for generating the 15 chips for each group. Edge chipping resistance (ReA, N/mm) was calculated by the ratio between F (in N) and d (in mm).

2.8. Flexural strength and fracture toughness before and after aging

Flexural strength (σ_f) was measured in three-point bending mode (n=10). Bar-shaped specimens (25 mm $\times$ 2 mm $\times$ 2 mm) were prepared in accordance with ISO 4049 standard [12] and tested at a crosshead speed of 0.5 mm/min until failure in a mechanical testing machine (DL500; EMIC), with 20 mm span between supports. σ_f was calculated as previously detailed [10]. Fracture toughness (K_{IC}) was measured by the single-edge notched beam method [14]. For each material, 15 bars (25 mm long $\times$ 5 mm high $\times$ 2.8 mm wide) were fabricated by using a metallic mold with a V-shape notch at the center (2.5 mm in height, 0.5 mm in bottom width). Photoactivation was carried out through the 2.8-mm-thick

side of the bar using overlapping positionings of the light guide on both faces to avoid problems with depth of cure. The specimens were positioned in the supports (20 mm span) with the notch opposite to the load application and subjected to three-point bending at 0.5 mm/min until failure. K_{IC} (MPa $\sqrt{m}$) was calculated as previously described [16]. Flexural strength and fracture toughness tests were conducted after storing the specimens in distilled water at 37°C, for 24 h, and after subjecting another set of specimens to 15K thermal cycles in water at 5°C and 55°C, with 30 s dwell time and 2 s interval between baths (Termocycle; BIOPDI, São Carlos, SP, Brazil).

2.9. Statistical analysis

Statistical analysis was carried out with SigmaPlot 12.0 software. Normality (Shapiro-Wilk test) and equal variance of data were confirmed beforehand. Data for C=C conversion, depth of cure, hardness, opacity, radio-opacity, and ReA were subjected to one-way Analysis of Variance (ANOVA) followed by the Tukey *post hoc* test. Data for σ_f and K_{IC} were subjected to two-way ANOVA (material $\times$ storage time). Pairwise multiple comparison procedures were performed with the Tukey method. Significance level was set at $\alpha=0.05$. Power of all performed statistical tests was between 0.76 and 1.

3. RESULTS

Viscosity results are presented in Figure 1. The experimental resin composites showed a thixotropic behavior. Although all materials had handling characteristics consistent with commercial resin composites, the distinct nanoparticles led to appreciable differences in viscosity. ALSI and ZRSI nanoparticles yielded hybrid resin composites with lower viscosity compared with their silica nanoparticle references (ALSI vs. Aerosil 150; ZRSI vs. Aerosil OX 50). The lowest viscosity among all resin composites was observed for the ZRSI resin composite. Figure 2 presents SEM images of the resin composite polished surfaces. Nanoagglomerates were observed in all images, their composition was confirmed in the EDS analysis. The agglomerates were more clearly detected and appeared more closely bound for ALSI, ZRSI, and the commercial resin composites. The agglomerates in the commercial material were round and uniformly dispersed in the polymer matrix, whereas those in ALSI and ZRSI resin composites were more irregular in shape and dispersion.

As shown in Table 2, degree of C=C conversion ($p = 0.008$) and depth of cure ($p < 0.001$) were significantly lower for the ZRSI resin composites compared with almost all other experimental materials, which had improved C=C conversion as compared with the control ($p < 0.001$). The opacity of the ZRSI resin composite also was higher than all other materials ($p < 0.001$). Significantly improved hardness ($p = 0.025$) and radio-opacity ($p < 0.001$) were observed in the ZRSI resin composite relative to materials formulated with ALSI or silica nanoparticles. ReA was significantly higher when ALSI nanoparticles were used ($p < 0.001$), except compared to the commercial material ($p = 0.86$).

Figure 3 presents the results for σ_f . The statistical analysis showed that the factors material ($p < 0.001$) and storage time ($p = 0.048$) were significant, as well was their interaction ($p = 0.013$). σ_f varied between 64 MPa (ALSI) and 90 MPa (Aerosil 150) at 24 h, but the stability after aging was the most interesting finding. Whereas resin composites with ALSI

and ZRSI showed stable σ_f after aging, materials with Aerosil 150 and the commercial resin composite showed significant degradation in σ_f . A similar behavior was observed for K_{IC} (Figure 4), the statistical analysis revealed that both factors and their interaction were significant ($p=0.013$). Resin composites containing ALSI or ZRSI nanoparticles showed significantly higher K_{IC} before and after aging compared with all other resin composites tested ($p=0.013$), except ZRSI compared with OX 50 at 24 h ($p=0.962$). The stability in mechanical performance after aging again was the most distinctive finding. The commercial resin composite and those formulated with silica nanoparticles showed remarkable degradation in K_{IC} after 15K thermal cycles (between 24% and 42%), whereas the ALSI and ZRSI resin composites showed less degradation in K_{IC} (up to 17%).

4. DISCUSSION

Novel nanohybrid resin composites containing alumina and zirconia nanoparticles coated with a silica layer (ALSI and ZRSI) exhibited many different characteristics and properties as compared with materials containing traditional silica nanoparticles. Above all, ALSI and ZRSI resin composites showed improved and/or more stable mechanical properties as compared with nanosilica-based references. Thus, the hypothesis tested was accepted. These are interesting findings since composition of the filler system is perhaps one of the few aspects that may still have room for improvements in current methacrylate-based dental composite formulations.

Resin composites containing ALSI and ZRSI showed lower viscosity compared with nanosilica-based materials. This finding may be related to the more homogeneous dispersion and less clustering of silica nanoparticles within the resin phase than ALSI and ZRSI, as observed in the SEM/EDS analysis. The higher viscosity may be explained by the larger surface area occupied by discrete nanoparticles in the composite paste. It should be noted that all components in the resin composites were thoroughly mixed and their final handling characteristics were consistent with commercial materials. Optimizing the dispersion of nanoparticles was not a primary aim of the study as hybrid resin composites were tested, but these findings suggest that there exists room for enhancing the nanofiller distribution. A more effective dispersion would allow taking better advantage of the nanoparticles, but could also mean increasing the resin composite viscosity. Improved nanofiller dispersion could be accomplished by using methods such as high intensity ultrasonication, steric hindrance by using surfactants, and/or heating up the mixture [17].

The C=C conversion at the bottom of 2-mm-thick specimens was lower for resin composites with ZRSI. This finding is likely a result of the high degree of whiteness of zirconia, which resulted in higher opacity to the ZRSI resin composite. In fact, the depth of cure for this composite was below 2 mm, which explains the C=C conversion results. In addition to optical absorption, light transmission characteristics of composites are largely determined by the scattering of light from particle inclusions [18,19]. The commercial resin composite was the least opaque material, but it is worth noting that it does not have a hybrid filler system. This means more scattering centers in the experimental hybrids than in the commercial material due to the presence of particles with distinct sizes, volumes, morphologies, and refractive indices [18,19]. In addition, the commercial material is likely a result of strategic choice of

optical properties of the filler system leading to a good match with the polymer refractive index. When there is a good match of the refractive indices of resin phase and particles, light will scatter and bend less between the material interfaces, resulting in better light transmission [18]. The optical characteristics of the experimental nanohybrid resin composites could be improved, if needed, by tuning the polymer chemistry. Possibilities to overcome a lower C=C conversion could be using more reactive initiator systems or using ZRSI-based resin composite as an indirect material. This possibility was raised in a previous study [10] because it was observed that the silica layer deposited over the non-silicate nanoparticles may react to heat by fusing (and apparent particle growth), generating 3D porous structures. These 3D structures could function as scaffold networks for polymer-infiltrated, dual network composite blocks and used as indirect restoratives.

Hardness of the ALSI and ZRSI resin composites was significantly higher compared with the nanosilica references, and similar to the commercial material. This is an important finding because it provides evidence that the deposition of a silica-rich layer was not detrimental to the surface hardness of the non-silicate nanoparticles. In addition, it corroborates previous findings [10] showing effective silanization of silica-coated, alumina and zirconia nanoparticles and coupling with the polymer matrix in dental composites. There is evidence that non-bonded filler particles within a composite may reduce its hardness [20]. ReA was also significantly greater for the ALSI-based resin composite compared to its nanosilica reference, whereas ZRSI particles improved hardness but not ReA. The method to fracture a chip off the specimen involves load application through an indenter, leading to stress build up, crack growth and propagation, and energy dispersion [21,22]. The energy navigation within the material is affected by its microstructure and degree of mixing of the fillers, which varied largely across the resin composites tested here. This may explain why the ReA value of the ZRSI-based resin composite was not as high as the ReA value for the ALSI-based material. Other variables may include friction coefficient of indenter with the surface, polymer relaxation and crack growth velocity, and the strength of coupling between the polymer matrix and filler particles. ReA values did not exactly correlate with K_{IC} values, which is in agreement with previous studies [21,22].

The mechanical performance of ALSI and ZRSI composites after aging by thermal cycling (σ_f and K_{IC}) was generally more stable compared with the nanosilica-based references and even with the commercial resin composite. This finding reinforces that physical properties of current nanohybrid resin composites can be enhanced by simply changing the composition of nanofillers, provided that a strong, stable chemical interfacial bond with the polymer matrix is achieved [10]. Increasing σ_f and K_{IC} has long been regarded as a significant issue with restorative composites to extend their service life [23]. Explanation on why resin composites with ALSI or ZRSI nanoparticles suffered less degradation has to consider many aspects. First, it suggests that the novel resin composites are more resistant to crack initiation and/or propagation, despite previous evidences indicating that agglomerated and less uniformly dispersed nanoparticles may impair the mechanical properties of polymeric composites [24,25]. Second, differences in microstructure are likely involved. Damage by aging in water and cyclic thermal changes may occur by a combination of polymer and/or filler-interfacial deterioration, a process assisted by pre-existing voids, defective interfaces, and residual stresses [23]. The heterogeneous structure of composites may lead to areas of

localized stress concentration owing to the different mechanical properties and thermal expansion characteristics of the components. Thermal residual strain may be an important factor, because of the mismatch in shrinkage between the components, resulting in crack propagation [26]. Finally, differences in particle stiffness and filler-polymer interact) may modify the deformation rate of the polymeric matrix and microcrack deflection within the structure [26]. Interestingly, the results of this study confirm the anticipated improvement in mechanical performance for hybrid composites containing silica-coated alumina and zirconia nanoparticles raised in previous work [10].

5. CONCLUSIONS

The silanated, silica-coated zirconia and alumina nanoparticles generated nanohybrid resin composites with improved and/or more stable physical properties compared with the experimental nanosilica-based references and the commercial nanofill resin composite tested. The present study suggests that changing the composition of nanofillers is a simple method to enhance the performance of nanohybrid resin composites.

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HIGHLIGHTS

- Alumina and zirconia nanoparticles were coated with a silica layer (ALSI, ZRSI).
- ALSI, ZRSI, and silica nanoparticles were used to prepare nanohybrid composites.
- Distinct nanoparticles led to appreciable changes in physical/chemical properties.
- Mechanical performance of composites with ALSI or ZRSI was more stable after aging.
- Replacing silica nanofillers is a simple method to improve hybrid resin composites.

Figure 1. Viscosity of the experimental resin composites (n=3). Note that Y-axis has a logarithmic scale. The resin composites showed a thixotropic behavior. ALSI and ZRSI nanoparticles yielded hybrid resin composites with lower viscosity compared with their silica nanoparticle references (Aerosil 150 and Aerosil OX 50, respectively).

Figure 2.

SEM images of the resin composite polished surfaces (field width: 100 µm).

Nanoagglomerates were observed in all images (arrows), but were more clearly detected and appeared more closely bound for ALSI, ZRSI, and the commercial resin composite (Filtek Z350 XT). Composition of the agglomerates was confirmed in the EDS analysis. The agglomerates in the commercial material were round and uniformly dispersed in the polymer matrix, whereas those in ALSI and ZRSI were more irregular in shape and dispersion.

Figure 3.

Means + standard deviations for flexural strength (σ_f) at 24 h and after aging by 15K thermal cycles (n=10). Whereas ALSI and ZRSI showed stable σ_f after aging, Aerosil 150 and the commercial resin composite (Filtek Z350 XT) showed significant degradation.

Figure 4.

Means + standard deviations for fracture toughness (K_{IC}) at 24 h and after aging by 15K thermal cycles (n=15). Whereas the commercial resin composite (Filtek Z350 XT) and those formulated with silica nanoparticles (Aerosil 150 and Aerosil OX 50) showed remarkable degradation in K_{IC} after 15K thermal cycles, the resin composites prepared with ALSI and ZRSI showed less degradation.

Table 1.

Characteristics of inorganic particles tested

Particle type	Size, nm	Surface area, m ² /g	Composition
Alumina	10	180 ± 20	99.7% Al ₂ O ₃
ALSI	20	90 ± 10	78% Al, 6% Si
Zirconia	40	25 ± 5	>99.5% ZrO ₂
ZRSI	80	15 ± 5	85% Zr, 3% Si
Aerosil 150	14	150 ± 15	>99.8% SiO ₂
Aerosil OX 50	40	50 ± 15	>99.8% SiO ₂
Ba-B-Si glass	700	10	50% SiO ₂ , 33% BaO, 9% B ₂ O ₃

Data are averages ± standard deviations (when available) obtained from the suppliers or measured as reported by Kaizer et al. [10].

Table 2.

Means (standard deviations) for C=C conversion (n=6), depth of cure (n=3), Knoop hardness (n=3), opacity (n=5), radio-opacity (n=5), and edge chipping resistance (ReA, n=15)

Resin composite	C=C conversion, %	Depth of cure, mm	Hardness, kgf/mm ²	Opacity, %	Radio-opacity, mm Al	ReA, N/mm
ALSI	59 (4) ^{ab}	2.81 (0.02) ^b	104 (2) ^b	37 (2) ^c	3.1 (0.4) ^b	308 (68) ^a
Aerosil 150	56 (2) ^{bc}	2.99 (0.01) ^a	66 (1) ^c	40 (1) ^{bc}	3.3 (0.5) ^b	50 (7) ^c
ZRSI	52 (2) ^{cd}	1.79 (0.01) ^d	121 (5) ^a	57 (4) ^a	6.1 (0.6) ^a	178 (17) ^b
Aerosil OX 50	61 (1) ^a	2.99 (0.01) ^a	80 (1) ^{bc}	44 (4) ^b	3.6 (0.6) ^b	175 (35) ^b
Filetek Z350 XT (control)	47 (2) ^d	2.64 (0.03) ^c	118 (1) ^a	29 (2) ^d	2.7 (0.1) ^b	292 (69) ^a

In each column, distinct letters indicate significant differences between the resin composites ($p < 0.05$).