Original Article

Effects of Adding TiO_2 Nanoparticles on Flexural Strength and Hardness of Two New Commercial Flowable Dental Composites

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Abstract

Introduction The present study aimed to investigate the effect of adding TiO_2 nanoparticles on the flexural strength and hardness of two dental composites. **Methods:** TiO_2 nanoparticles were prepared and added to two flowable dental composites (Beautifil Flow Plus and Clearfil AP-X Flow) at 0, 0.2, 0.5, and 1% (w/w) which was confirmed by SEM and TEM analysis. Mixing was manually performed using Lentulo Spiral Paste Carrier. The specimens were divided into 8 groups of 10 according to the type of composites and different concentrations of TiO_2 nanoparticles. Bar-shaped specimens (2×2×25 mm) were fabricated in a half-split stainless steel mold and cured for 40 s by an LED curing system. Flexural strength was evaluated using a universal testing machine. Surface microhardness was also measured by the Vickers microhardness tester. **Results:** For the two tested composites, flexural strength increased by 0.5% TiO_2 nanoparticles concentration. The flexural strength of Clearfil AP-X Flow combined with 0.2, 0.5 and 1% TiO_2 nanoparticles were 112.54±12.87 ($P>0.05$), 114.62±8.14 ($P>0.05$), and 99.92±6.23 ($P<0.05$), respectively. Also, for Beautifil Flow combined with 0.2, 0.5 and 1% TiO_2 nanoparticles were, 92.21±4.26 ($P<0.05$), 94.05±5.36 ($P<0.05$) and 74.17±9.43 ($P<0.05$), respectively. **Conclusion:** Adding TiO_2 nanoparticles to Clearfil AP-X Flow composite decreased the hardness; however, adding TiO_2 nanoparticles by 1% concentration increased the surface hardness of Beautifil Flow and reached its maximum value. Also, TiO_2 nanoparticles at very low concentrations enhance the flexural strength of dental flowable composites.

Keywords: Flowable Composite, Nanoparticles, Surface Hardness, Titanium Dioxide

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Introduction

The consistency of most dental composite resins is desirable for clinical conditions; however, some cases require a type of composite resin with lower viscosity for better adaptability with the cavity walls. Therefore, a new category of "flowable composite resins" was introduced in late 1996. These flowable composites were created using the same size of small particles by reducing filler contents to about 40-50% (volume percent) compared to 55%-75% of conventional hybrid composites which can modify the viscosity of these materials (2, 3). Despite the fact that these types of dental composites provide a wide range of various benefits to practitioners, our literature review revealed a paucity in studies evaluating the characteristics and application techniques of these new materials (1, 4, 5). Several authors have suggested that the three-point flexural strength test is better than other test methods due to less complexity (6).

Some previous studies have focused on the pretreatment of inorganic monomers and fillers to improve the properties of flowable resin composites (7). These research studies have shown that fibers and microparticles may also be used to reinforce dental resin composites. It has been shown that combining small amounts of networked and/or short fibers into the composites can lead to increased strength (8, 9).

Using nanoparticles in dentistry has become a significant area of research (10, 11). Among these inorganic fillers,

TiO_2 has a highly efficient photocatalytic effect and is chemically stable (9).

Previous studies using TiO_2 nanoparticles in epoxy resins revealed that they can enhance toughness, stiffness, and strength (12). TiO_2 nanoparticles have many promising properties as an inorganic additive in resin composites. The nanoparticles were combined with cold-curing resin composites to achieve opalescence (13). In recent studies, dental resin composites and glass-ionomer cement with TiO_2 nanoparticles demonstrated superior mechanical properties (14). Some nanoparticles have been applied in attempt to add antimicrobial properties to dental materials (11). TiO2 nanoparticles have been used as additives to many biomaterials due to their antimicrobial properties (15). Interactions between nanoparticles and cells have been extensively studied owing to their nanoscale size. The cytotoxicity of different nanoparticles and dental materials that have been investigated in recent studies revealed different results (16, 17).

Therefore, the present study aimed to evaluate the effect of TiO_2 nanoparticles on the flexural strength and hardness of two commercial dental flowable composites.

Materials and Methods

Preparation and characterization of TiO_2 nanoparticles

Titanium isopropoxide 97% (Sigma Aldrich, Saint Louis, MO, USA) was diluted in isopropyl alcohol (Merck) as the initial solution. Precipitation of TiO_2 nanoparticles occurred by adding alkaline (pH 8) distilled water. Distilled water was then used for washing the precipitate. Then the as-prepared precipitate was centrifuged and heated. Morphological analysis and measuring the size of the TiO_2 nanoparticles were performed using scanning electron microscopy (SEM) (XL30, Philips, Netherlands) and transmission electron microscopy (TEM) (JEOL, JEM-1011; Japan), respectively. X-ray diffraction (XRD) was used as a technique to determine the structure by analyzing the diffraction peaks (18). XRD pattern of the TiO_2 nanoparticles was obtained by a DX-1000 X-ray powder diffractometer (Dandong Fangyuan, Dandong, China).

Specimen preparation

TiO_2 nanoparticles were added to the Beautifil Flow (Shofu, Kyoto, Japan) and Clearfil AP-X Flow (Kuraray, Kyoto, Japan) composites. Initially, mixing was manually performed by spatulating TiO_2 nanoparticles in the flowable composite and then using a Lentulo Spiral Paste Carrier (19, 20). The Lentulo Spiral was inserted into the mixture of composite resin and nanoparticles and poured into a pre-darkened syringe tube. After mixing for 15 min, the drill/grinder was extracted with attached Lentulo; a syringe plunger was inserted into the syringe tube and 80 bar-shaped specimens (2×2×25 mm) were fabricated in a half-split stainless steel mold (ISO 4049) and then cured by LED (Monitex, GT1200) with a power of 800 MW/Cm^2. The light guide was placed at the center of the specimen and against the glass slide and then the specimen was irradiated for a polymerization time of 20 s (as recommended by the manufacturer). After photoactivating the center of the specimen, the light guide was placed at the other section next to the center that overlaps the previous section; the same procedure applies to the other side of the center; both sides were irradiated as recommended by the manufacturer. Finally, the specimens were kept in distilled water at 37ºC for 24 h before testing.

The specimens were divided into 8 groups of 10 according to the type of composites and different concentrations of TiO_2 nanoparticles (0%, 0.2%, 0.5%, and 1% w/w).

Flexural strength

The specimens were subjected to a three-point-bend test using a universal testing machine (Zwick Roell, Z020) at a crosshead speed of 0.5 mm/min to measure flexural strength. Flexural strength (in MPa) is determined using the following formula:

$$\text{Flexural Strength} = \frac{3FL}{2BH^2}$$

Where F is the failure load (Newtons), B is the specimen width (mm), L is the distance between the supports (mm), and H is the specimen height (mm).

Hardness

Ten samples of the respective composites were placed inside a stainless steel mold (8 mm in diameter and 2 mm thickness) for measuring the Vicker’s microhardness of the composites, while a dark opaque paper background covered with a polyester matrix strip was used. This arrangement reduced the possibility of obtaining higher artificial hardness in that area. The mold was filled with the flowable resin composite and another polyester matrix strip was adjusted on the surface of the filled mold. A glass slide was pressed against the top layer of the polyester film to form a flat surface of composites and to extrude the excess composite resin. The composite material was then light-cured from the top for 20 s by an LED (Monitex, GT1200) with a power of 800 MW/Cm^2. The microhardness was calculated by applying a load of 200 g for 15 s using a microindenter (MHV-1000Z, China), and the indentation size was recorded 15 s later. A total of 5 square indentations were produced in each specimen, and this process was repeated 3 times. Finally, the average indentation size was used to determine the Vickers hardness number (VHN) using the following formula (21).

$$\mathrm{HV} = \frac{1854 \times F(g)}{D^2(\mu m)}$$

F is the load (g), HV is the microhardness value, and D is the dimension of the indentation (mm).

Statistical analysis

Data analysis was performed using SPSS software (version 16). The results of the study were analyzed using one-way ANOVA test. A p-value ≤ 0.05 was considered statistically significant.

Results

SEM, TEM, and XRD analysis

SEM and TEM (Figure 1) were used to investigate the size and morphology of particles. The SEM and TEM images indicate that the TiO_2 particles are spherical with an average diameter of 30 nm. A typical XRD pattern of the as-prepared TiO_2 nanoparticles is shown in Figure 2. XRD pattern of pure TiO_2 shows five primary peaks at 27, 36, 39, 41, 44, 54, 57, 63, 64, 69, and 70, which can be attributed to different diffraction planes.

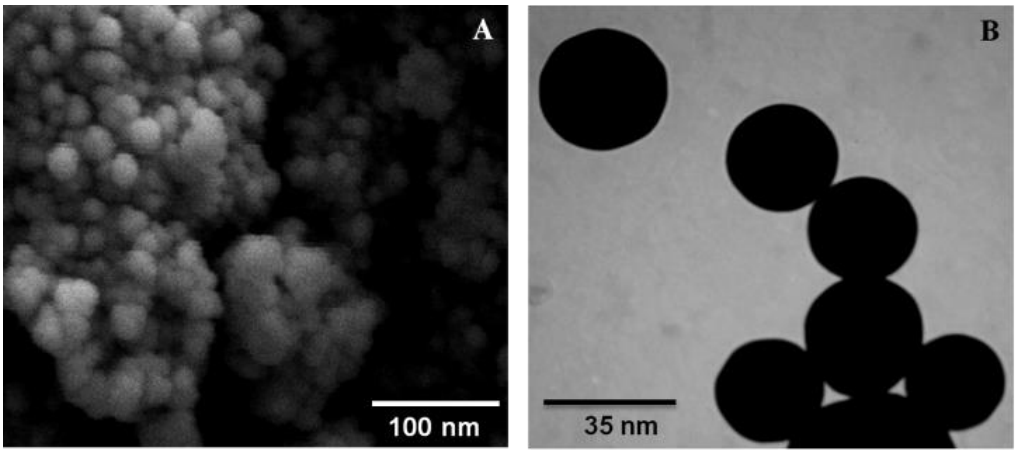

Figure 1. (A) SEM photography of TiO2 nanoparticles, (B) TEM photography of TiO_2 nanoparticles

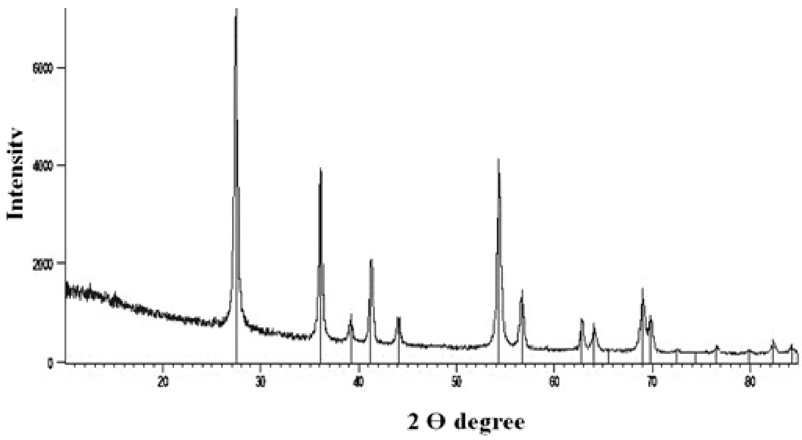

Figure 2. XRD report of TiO_2 nanoparticles

Scanning electron microscope

Figure 3 indicates the distribution of a 0.5% concentration of TiO_2 nanoparticles in composite resins. SEM indicated that TiO_2 nanoparticles had a homogeneous distribution in Clearfil AP-X Flow and Beautifil Flow.

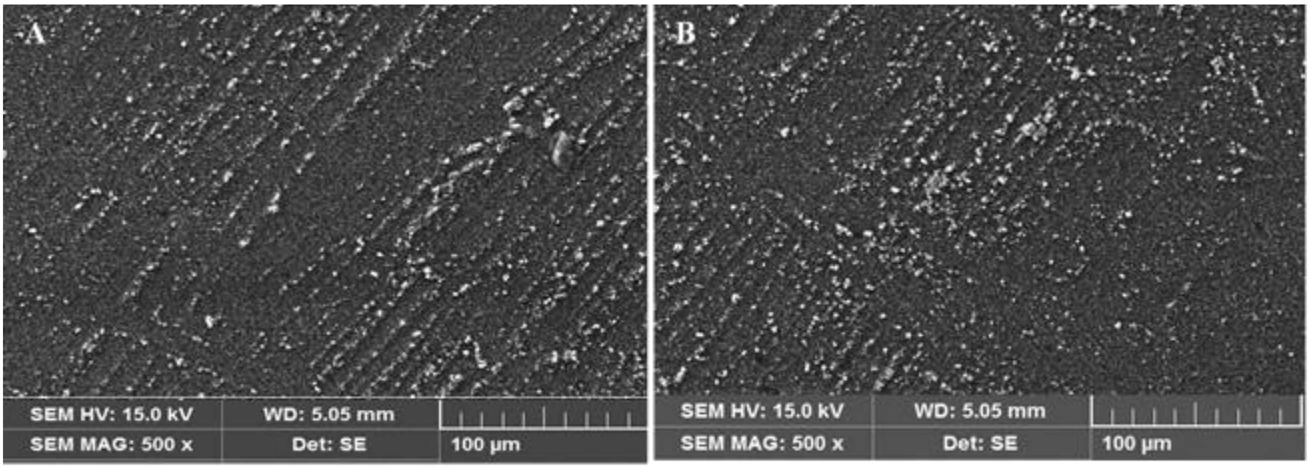

Figure 3. SEM images taken from cross-section of (A) Beautifil Flow with 0.5% TiO_2 nanoparticles and (B) Clearfil AP-X Flow with 0.5% TiO_2 nanoparticles 0.5 wt%

Flexural strength and Hardness

ANOVA test showed a significant difference in flexural strength of Clearfil AP-X Flow with 1% TiO_2 nanoparticles and Beautifil Flow with 0.2, 0.5, and 1% TiO_2 nanoparticles. The flexural strength of Clearfil AP-X Flow with 0.2, 0.5, and 1% TiO_2 nanoparticles were 112.54±12.87 (P>0.05), 114.62±8.14 (P>0.05), and 99.92±6.23 (P<0.05), respectively. Also, the flexural strength of Beautifil Flow combined with 0.2, 0.5, and 1% TiO_2 nanoparticles were 92.21±4.26 (P<0.05), 94.05±5.36 (P<0.01), and 74.17±9.43 (P<0.05), respectively. Flexural strength increased by 0.5% TiO_2 nanoparticles concentration and decreased by 1% for the two tested composites. The increase of flexural strength in Clearfil AP-X Flow is lower than that of the Beautifil Flow.

ANOVA test revealed a significant difference in hardness of Clearfil AP-X Flow with 0.5 and 1% TiO_2 nanoparticles and Beautifil Flow combined with 1% nanoparticles. The hardness of Clearfil AP-X Flow with 0.2, 0.5, and 1% TiO_2 nanoparticles were 86.22±1.69 (P>0.05), 78.08±3.02 (P<0.05), and 60.80±3.27 (P<0.01), respectively. Also, for Beautifil Flow combined with 0.2, 0.5 and 1% TiO_2 nanoparticles were 38.35±0.75 (P>0.05), 39.45±0.93 (P>0.05) and 41.41±3.24 (P<0.05), respectively. Results clearly indicated that the addition of TiO_2 nanoparticles to Clearfil AP-X Flow decreased the hardness of specimens. Adding TiO_2 nanoparticles with the concentration of 1% w/w to Beautifil Flow composites, increased surface hardness to its maximum value. The average values of flexural strength and hardness at different TiO_2 concentrations are displayed in Table I.

Table I. Mean flexural strength, standard deviations of each group (MPa), mean hardness, and standard deviations of each group

		TiO_2 concentration				Significance
		0% w/w (A)	0.2% w/w (B)	0.5% w/w (C)	1% w/w (D)	*P<0.05 **P<0.01
Flexural Strength	Clearfil AP-X Flow	111.12±5.86	112.54±12.87	114.62±8.14	99.92±6.23	A,D* B,D*C,D**
	Beautifil Flow	81.62±4.82	92.21±4.26	94.05±5.36	74.17±9.43	A,B* A,C**A,D* B,D** C,D**
Hardness	Clearfil AP-X Flow	89.26±4.30	86.22±1.69	78.08±3.02	60.80±3.27	A,C* A,D** B,C* B,D**
	Beautifil Flow	37.05±2.97	38.35±0.75	39.45±0.93	41.41±3.24	A,D* B,D*

Discussion

SEM and TEM images indicate that TiO_2 particles are spherical with an average diameter of 30 nm. In the present study, TiO_2 nanoparticles had a homogeneous distribution in Clearfil AP-X Flow and Beautifil Flow composites. Flexural strength increased by 0.5% TiO_2 nanoparticles concentration for the two tested composites. Results revealed that adding TiO_2 nanoparticles to Clearfil AP-X Flow decreased the hardness of specimens. For Beautifil Flow, adding TiO_2 nanoparticles at a concentration of 1% w/w increased surface hardness to its maximum value.

Scientists have conducted extensive research in aims of improving inorganic fillers in different types of dental resin composites. The current tendency is to reduce the size of filler particles from micrometer to nanometer scales (22). Using nanoscale fillers in resin composites seems to affect their biological and mechanical properties (23). TiO2 nanoparticles are optimal for application in dentistry due to their high biocompatibility and satisfactory color (24). TiO_2 is considered a chemically stable and inexpensive nanoparticle that has been used for a wide range of environmental applications (15).

Clearfil AP-X Flow is a flowable and restorative composite resin. The inorganic filler particles of this composite are treated with a novel technology of surface coating. This treatment leads to a reinforced resin matrix with a high filler loading of 81 wt% which is similar to universal composite resins. Beautifil Flow is another flowable restorative composite that consists of filler content of about 50 wt%. This lower filler content may result in less optimal mechanical properties. Bending the bar specimen occurred when the load was applied under the flexural condition.

Compressive stresses are mostly directed at the top surface of the sample; whereas tensile forces mainly affect the more inferior surfaces. The main advantage of flexural modulus for polymeric composites is that it describes the combined effects of tensile and compressive deformation (15). Based on the obtained flexural strength values, increasing the concentration of TiO_2 nanoparticles up to 0.5% w/w increased the flexural strength while adding a further amount of TiO_2 nanoparticles decreased flexural strength. Another important reason is a phenomenon called agglomeration in which fine nanoparticles accumulate around each other or other particles and create nanoclusters that weaken mechanical properties. An increase in TiO_2 content, causes agglomeration of these particles. Some structural defects such as micro-pores and micro-cracks may develop due to the agglomeration of TiO_2 nanoparticles at high percentages. Shirkavand and Moslehifard (25) evaluated the tensile strength of dental acrylic resins using TiO_2 nanoparticles. They demonstrated that a significant increase was observed in tensile strength using TiO_2 nanoparticle reinforcement agents up to 1% w/w; however, the opposite was noticed when a greater increase in TiO_2 nanoparticles was applied. The difference in the results may be attributed to different test methods and dental materials.

The measured hardness for Beautifil Flow increased by about 1.11 times compared to the control group by adding 1% w/w of TiO_2 nanoparticles. Nevertheless, the measured hardness the Clearfil AP-X Flow decreased to about one-third of the control group. However, the hardness of Clearfil AP-X Flow in all concentrations was higher than that of other flowable composites. In this context, a study was conducted by Yang Xia et al. in 2008 in which a group of samples was produced with TiO_2 nanoparticles whose surface was coated with a binding agent, and another group produced without a binding agent. They found that the specimens produced from TiO_2-coated with the binding agent increased in hardness (12). One of the possible reasons for obtaining better hardness in Beautifil Flow is related to its lower filler content. This lower concentration allows TiO_2 nanoparticles to be distributed in a more homogeneous mixture pattern. The filler content of Clearfil AP-X Flow was about 81% and as a result, inadequate space was available to distribute a homogeneous mixture of TiO_2 nanoparticles. Also, the type of fillers in each composite might affect the results. Clearfil AP-X Flow composite contains silanated fillers. Optimized silane content provided composites with the highest resistance against hydrolytic degradation. The silane treatment of fillers generally improved the flexural strength of the composites. The silane treatment of fillers improves the physical properties of the resultant composites and their resistance to hydrolytic degradation.

Moreover, this *in vitro* implementation requires long-term *in vitro* and *in vivo* studies with larger sample sizes, using various resin composites, adhesive systems, and different depths of dentin or different cavity preparations, since these factors may affect dentin bonding.

Conclusion

Due to the limitations of the present study, adding TiO_2 nanoparticles at very low concentrations up to 0.5% w/w positively affects the flexural strength of both Beautifil Flow and Clearfil AP-X Flow dental flowable composites. The hardness of Beautifil Flow with low or moderate filler content increased by adding TiO_2 nanoparticles; however, the opposite results were observed in Clearfil AP-X Flow.

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Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of the present study.

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