RESEARCH

The Effect of Titanium Dioxide Nanoparticles On Microhardness and SEM-EDS Analysis of Glass Ionomer Cement and Amalgomer

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ABSTRACT

The Effect of Titanium Dioxide Nanoparticles On Microhardness and SEM-EDS Analysis of Glass Ionomer Cement and Amalgomer

Background: The aim of this study was to examine the effect of the addition of titanium dioxide (TiO_2) nanoparticles on elemental composition and micro hardness of a conventional glass-ionomer and an amalgomer.

Methods: A conventional glass ionomer cement (GICs) and an amalgomer were used in this study. Seventeen samples were prepared from each material using teflon molds (8 x 2) and determined as the control group. Each material was then blended with 3 % (w/w) TiO_2 nanoparticles (anatase phase, 17 nm particle size) and seventeen samples were prepared to form experimental groups. Characterization of TiO_2 nanoparticles, surface morphology evaluation and elemental composition analysis of the specimens were performed by Scanning Electron Microscope (SEM) and Energy Distribution Spectrometry (SEM-EDS). Specimens were submitted to the Vickers micro hardness test for 10 seconds at a load of 100gf. Data were analyzed with Shapiro-Wilk, Kruskal-Wallis and Bonferroni post-hoc tests ($p=0.05$).

Results: EDS mapping showed the presence of elements typical for (GICs) in the composition of the control and experimental groups and a high proportion of titanium in the composition of experimental groups. Micro hardness data showed a small insignificant increase for the experimental groups compared with the control groups ($p>0.05$). While the highest mean microhardness value was recorded in Amalgomer (experimental) (84.34 ± 4.33), Ionofil (control) exhibited the lowest mean micro hardness value (58.62 ± 6.90).

Conclusion: Within the limitations of this study, it can be concluded that the addition of 3% $Ti0_2$ nanoparticles improves the surface microhardness of the tested materials, although statistically insignificant, compared to unmodified GICs and amalgomer.

KEYWORDS

Glass ionomer, Hardness tests, Nanoparticles, Titanium dioxide

ÖZ

Titanyum dioksit nanopartiküllerin cam iyonomer siman ve amalgomerin SEM-EDS analizi ve mikrosertliği üzerine etkisinin değerlendirilmesi

Amaç: Bu çalışmanın amacı, titanyum dioksit (TiO_2) nanopartikül ilavesinin, bir geleneksel cam-iyonomer ve bir amalgomerin elementel kompozisyonu ve mikro sertliği üzerine etkisini incelemektir.

Gereç ve Yöntemler: Bu çalışmada, bir geleneksel cam iyonomer siman ve bir amalgomer kullanıldı. Her bir materyalden teflon kalıplar (8x2) kullanılarak 17 adet disk şeklinde örnek hazırlandı ve kontrol grubu olarak belirlendi. Daha sonra her bir materyal, anataz fazında, partikül büyüklüğü 17 nm olan ağırlıkça % 3 oranında TiO_2 nanopartiküller ile karıştırıldı. TiO_2 nanopartikül ihtiva eden her bir materyalden de 17 adet örnek hazırlanarak deney grupları oluşturuldu. TiO_2 nanopartiküllerinin karakterizasyonu, gruplara ait örneklerin yüzey morfolojisinin değerlendirilmesi ve elemental kompozisyonlarının analizi, Taramalı Elektron Mikroskobu (SEM) ve Enerji Dağılım Spektrometresi (SEM-EDS) ile gerçekleştirildi. Örnekler, 100 g yükte 10 sn boyunca Vickers mikro sertlik testine tabi tutuldu. Veriler, Shapiro-Wilk, Kruskal-Wallis ve Bonferroni post-hoc testleri ile analiz edildi ($p=0.05$).

Bulgular: EDS haritalaması, kontrol ve deney gruplarının bileşiminde, geleneksel cam iyonomerler için tipik olan elementlerin varlığını ve deney gruplarının bileşiminde yüksek oranda titanium varlığı gösterdi. Mikro sertlik verileri, kontrol grubuna kıyasla deney gruplarında istatistiksel olarak anlamsız küçük bir artış gösterdi ($p>0.05$). En yüksek ortalama mikro sertlik değeri Amalgomer'de (deney grubu) (84.34 ± 4.33) kaydedilirken, İonofil (kontrol grubu) en düşük ortalama mikro sertlik değerini (58.62 ± 6.90) gösterdi.

Sonuç: Bu çalışmanın sınırları dahilinde, modifiye edilmemiş GIC'lere ve amalgomere kıyasla, % 3 $Ti0_2$ nanopartikül ilavesinin test edilen materyallerin yüzey mikro sertliğini, istatistiksel olarak önemsiz olmasına rağmen, arttırdığı sonucuna varılabilir.

ANAHTAR KELİMELER

Cam iyonomer, Nanopartikül, Sertlik testleri, Titanyum dioksit

Nanotechnology has become one of the most popular research areas and has developed in multiple disciplines. Due to peculiar chemical and physical properties of nanoparticles in regards to size, size distribution, morphology, polymorphic nature, biocompatibility, biodegradability, and aggregation propensity; nanomaterials always remain a center of interest for researchers.[1,2] Currently, there are wide variety of nanomaterial's applications in different fields of dentistry.[3,4] With the great development of these nanophased materials, much attention is directed towards the use of Titanium dioxide (TiO_2) nanoparticles. It has been suggested to use TiO_2 nanoparticles as reinforcing fillers. TiO_2 nanoparticles have also several favourable properties such as chemical stability, biocompatibility, and antibacterial effect by

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photocatalystic properties. All of these properties make them suitable additives for resin materials.[3-5]

In recent years, nanotechnology has been applied in the production of many dental materials, which has led to a significant improvement for restorative materials.[1] Researchers have been focused in improving the physical, mechanical and antibacterial properties of the materials by using nanoparticles.[3,6] One of the materials utilized in this development is glass ionomer cement. Glass ionomer cements (GICs) are used in a wide variety of applications owing to their unique properties such as biocompatibility, fluoride release, anticariogenic effect, elasticity similar to dentin, low thermal expansion coefficient and chemical adhesion to dental tissues.[6-8] Regardless of these favorable attributes, GICs have some limitations such as brittleness, susceptibility to dehydration, poor mechanical (low compressive strength and wear resistance) and physical (high solubility and slow setting rate) properties restricting the use of GICs in clinical conditions.[4,7,8] Therefore, these materials have undergone some variations to deal with the poor mechanical properties. And, a new ceramic-reinforced glass ionomer (Amalgomer CR) has been introduced to the dental market. It is affirmed by the manufacturer that this material combines the high strength of a metallic restorative and the other advantages of glass ionomers. The product includes a particulate ceramic component with the aim of increasing the strength. It has been defined that zirconia is the major part of the additive of this product. And it is stated that zirconia is an excellent material for strengthening and hardening in certain composite contexts in consequence of its unique character of a phase transformation from tetragonal to monoclinics under stres.[9,10] Additionally, various materials have been incorporated into GICs, such as fibers, strontium oxide, silica particles, hydroxyapatite, glass fiber, amino acids, zirconia and bioactiveglass to enhance the mechanical and physical properties of GICs.[7,8]

In the last few years, nanoparticles (NPs) such as titanium dioxide, hydroxyapatite, and fluoroapatite have been incorporated into glass-ionomers with the aim to increase their mechanical strength.[4,5,11,12] In studies, TiO_2 NPs are especially preferred as an additive in dental materials to comply with the optical properties of natural teeth, improve physical and mechanical properties and enhance antibacterial properties.[13,14] In a previous study, it has been reported that TiO_2 NPs incorporated in glass ionomers increased the compressive strength. This result was linked to their small size and the effect of better packaging of particles in the cement matrix.[5] In another study, the authors concluded that GICs were stronger in compression than those without additional nanoparticles.[6] Furthermore, dental resin composites reinforced with $Ti0_2$ NPs have also been found to have improved microhardness and flexural strength.[13]

When selecting a restorative material, one of the main considerations is its mechanical properties. Surface hardness testing is widely used method to assess the mechanical properties of restorative materials because hardness ensures resistance of plastic modifications, and affects the success of clinical durability of restorative materials.[15-17] And these mechanical properties are claimed to also show the relationship between the content of the filler, the size of the filler and the silane. Vickers hardness test is used to measure the surface hardness using a pyramidal indentation with a specific load and application time.[18]

Although, there are studies available evaluating microhardness of conventional GIC and amalgomer[16,19,20], there is lack of research regarding the surface microhardness of the materials reinforced with TiO_2 nanoparticles. Therefore, the aim of this study was to evaluate the effect of the addition of titanium dioxide nanoparticles on the elemental composition and microhardness of a conventional glass ionomer cement and an amalgomer.

MATERIALS AND METHODS

Two restorative materials; a conventional glass ionomer cement and an amalgomer were used in the study. The compositions and manufacturers of the materials were listed in Table 1.

Table 1.

Restorative materials used in the study

Classification	Material	Manufacturer	Composition	Batch no
Conventional glass ionomer cement	Ionofil U	Voco, Cuxhaven Germany	Powder: Calcium-alumino-fluorosilicate glass Liquid: Polyacrylic acid, tartaric acid, water	1910352
Amalgomer	Amalgomer CR	Advanced Healthcare Ltd., Tonbridge, UK	Powder: Fluoro-aluminosilicate glass, polyacrylic acid powder, tartaric acid powder and ceramic reinforcing powder Liquid: Polyacrylic acid, distilled water	011519-82

Seventeen disc shaped specimens (8 mm diameter, 2 mm height) were prepared from each material using teflon molds according to the manufacturers' instructions and determined as the control groups of the materials (n=17). The molds were filled by the materials and covered with two matrix strips and glass slides. A slight pressure was applied to form a uniformly flat surface. Materials were allowed to set for

the time recommended by the manufacturer. Then, to prepare the materials modified with TiO_2 NPs, the powder of each material was blended with TiO_2 NPs in anatase phase and in 17 nm particle size at 3 % (w/w) (Nanografi, ODTÜ Teknokent, Ankara, Turkey). TiO_2 nanoparticles were weighed on a 0.0001 precision analytical balance (Precisa XB 205A SCS, Zürich, Switzerland) and mixed with the restorative powder by spatulation. Seventeen specimens were prepared from each material containing TiO_2 NPs with the same method as described above and served as experimental groups of the materials (n=17).

TiO_2 NPs were characterized by a scanning electron microscope (SEM, Quanta Feg 250, FEI, The Netherlands) with low vacuum, high voltage technique at 15.00 kV and 11.0-12.0 mm working distance at 10.000x, 20.000x, and 50.000x magnifications and an energy dispersive X-ray spectroscopy (EDS, Quanta Feg 250, FEI, The Netherlands) at an accelerating voltage of 20 kV.

Three specimens out of 17 specimens prepared for each group were firstly used for surface morphology evaluation by SEM and also elemental composition analysis by EDS. The surfaces of specimens belonging to control and experimental groups were examined under SEM with low vacuum, high voltage technique at 10.00 kV and 10.0-11.0 mm working distance at 1000x, 2000x magnifications. Elemental analysis of specimens belonging to control and experimental groups was determined with an EDS at an accelerating voltage of 20 kV.

All of the specimens of each groups were stored in distilled water at 37º C in an incubator for 24 hours prior to microhardness evaluation. The microhardness test was carried out with a digital Vickers microhardness tester (TTS Matsuzawa HWMMT-X3, Tokyo, Japan) using a diamond indenter with 100 g load and a dwell time of 10 s. Three Vickers tests were carried out for each specimen and the mean value was calculated and determined as Vickers hardness number (VHN).

Statistical test

The Vickers microhardness datasets were checked for their normality with Shapiro-Wilk test. Since not all of them were normally distributed, then non-parametric independent Kruskal-Wallis H test was used to compare the pairs. The post-hoc adjustment was made using Bonferroni correction. For the multiple comparisons, we used 95 % confidence interval with p=0.05.

RESULTS

The SEM image of the TiO_2 NPs demonstrated that the nanoparticles were granular in form and uniformly distributed (Figure 1).

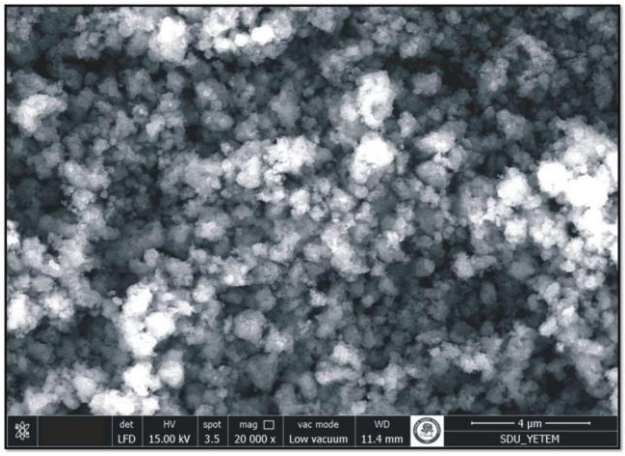

Figure 1

SEM image of TiO_2 NPs at 20000x magnification

And the presence of high amounts of titanium and oxygen elements was displayed in EDS mapping (Figure 2).

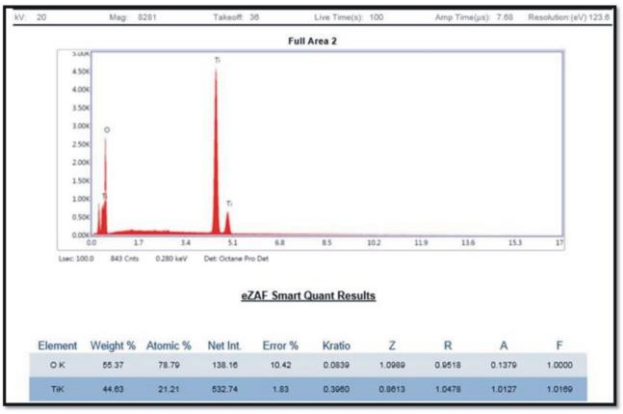

Figure 2

EDS analysis of TiO_2 NPs

The surface morphology of the experimental groups exhibited a higher degree of integrity and the nanoparticles were uniformly distributed throughout the matrices (Figures 3-4). Nanoparticle clusters that are likely to be seen due to the tendency of nanoparticles to come together were not encountered. However, surface cracks were observed in both groups of GIC, along with more intense in the experimental group (Figure 3). In addition, SEM micrographs were also provided evidence of air voids along the all groups (Figures 3-4). But in experimental group of amalgomer, occurrence of the air voids was diminished compared to control group (Figure 4).

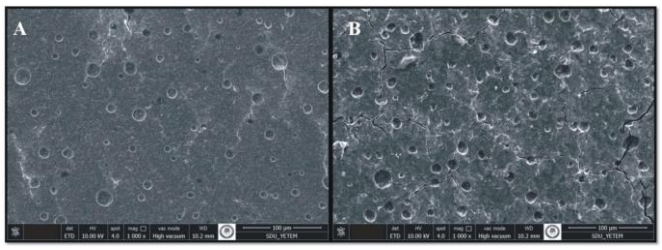

Figure 3

SEM images of surfaces of the groups at 1000x magnification (A) GICs-control (B) GICs-experimental

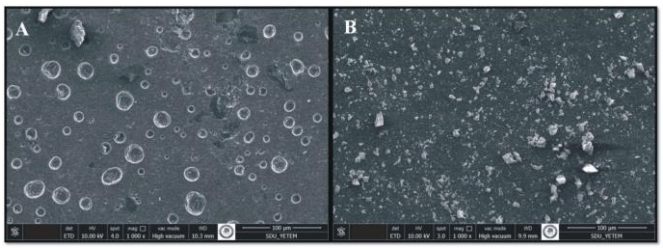

Figure 4

SEM images of surfaces of the groups at 1000x magnification (A) Amalgomer-control (B) Amalgomer-experimental

The EDS spectra confirm the presence of Al, Sr, Ca, Si, Na elements in the composition of the control and experimental groups. However, a high proportion of titanium was also detected in the composition of experimental group materials by incorporating the TiO_2 nanoparticles, while the concentration of oxygen increased (Figures 5-6).

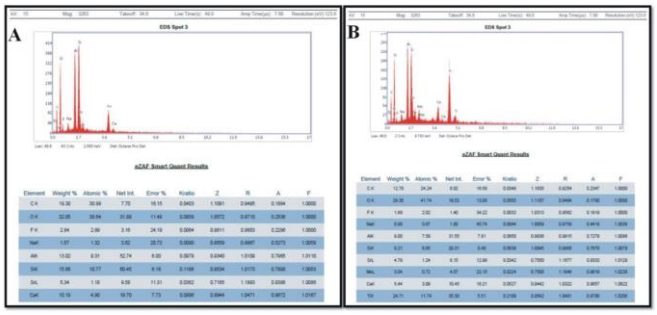

Figure 5

EDS analysis of the groups (A) GICs-control (B) GICs-experimental

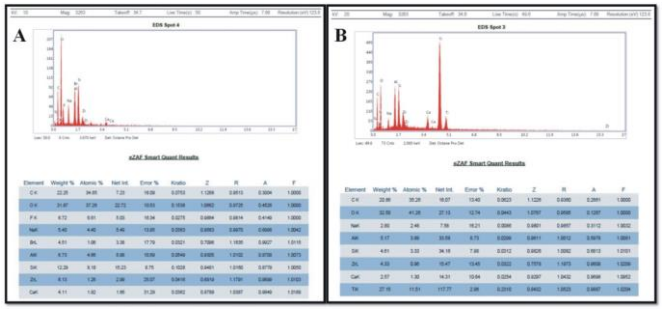

Figure 6

EDS analysis of of the groups (A) Amalgomer-control (B) Amalgomer-experimental

The Vickers hardness values for the experimental and control groups were presented in Table 2.

Table 2.

Microhardness (VHN) values of groups

Varibles	Amalgomer control	Ionofill control	Amalgomer experimental	Ionofill experimental
Mean ±SD	79.65±7.35	58.62±6.90	84.34±4.33	63.80±2.97
Mean Rank	48.00	12.86	53.94	24.00
p	<0.001*		<0.001*	

** Only the differences between Vickers micro hardness values of each control groups and each experimental groups were statistically significant.*

According to the test results, while the highest mean micro hardness value was recorded in Amalgomer (experimental group) (84.34±4.33), Ionofil (control group) exhibited the lowest mean Vickers micro hardness value among the materials (58.62±6.90). These results indicated that microhardness of experimental gorups of materials increased due to incorporation of 3 wt % of TiO_2. However, this increase in microhardness values was not statistically significant ($p > 0.05$). As a result of comparing the control groups of the materials with each other and the experimental groups with each other, the difference between the groups was statistically significant ($p < 0.05$).

DISCUSSION

One of the requirements of an ideal restorative material is exhibiting an ability to withstand the traumas of occlusion.[8] GICs are widely used materials in restorative dentistry, but unfortunately they usually cannot withstand the forces occurred in the posterior area because of their low mechanical properties. Therefore, many researchers have attempted to enhance the mechanical properties of GICs by changing the chemical structure of ionomer glass or polyalkenoic acid.[8] This is because increasing these properties contributes to the service and life of restorative materials, since the forces can withstand more effectively.[7]

In present study, it was revealed that the significant difference between microhardness values of GICs and amalgomer, which are observed when the material groups were compared with each other, might be material dependant. Amalgomer is a product of recent efforts to improve GICs by adding ceramic to the content. It can be considered that the coarse ceramic particles reinforced in Amalgomer contribute to its high microhardness values. It has been claimed that the phase transformation of zirconia from tetragonal to monoclinic produced a volume change of 4% which creates a local compression stress, and thereby increasing the fracture resistance of the material by preventing crack propagation.[10] In addition, it has been claimed that the ceramic filler might have partially

reacted with the matrix, which might have produced some bonding and possibly a modified polysalt matrix.[9] Moreover, it was concluded that there are other factors that might be in charge of the difference of surface micro-hardness values among the different tested materials involving morphology, distribution and density of filler particles, monomer type and ratio, the degree of conversion; which all vary greatly between the different products present in the market.[21]

The use of nanoparticles has become an important research area in dentistry.[22] It has been recently stated that the addition of nanoparticles could lead to an increased filler loading and increased surface area, and so this may enable to improve the mechanical properties.[7] TiO_2 can be considered to be the most preferable nanoparticles in the development of restorative materials in dentistry due to their high biocompatibility and appropriate color.[5,13,14] In present study TiO_2 NPs caused an increase in microhardness values of both materials, though statistically insignificant. These results are consistent with previous studies.[5,22] And it may be attributed to the high surface area of nanoparticles and their succesful mechanical interlocking with the polymer matrix. So, the contact between liquid and powder particles may be increased by nanoparticulate structure, which in turn increases the hardness. It is well-documented that the size of filler particles as well as distribution of filler particles has a positive effect on the different physical and mechanical properties of the restorative materials, such as surface hardness.[21] Generally, smaller particle size and higher filler density increase the compressive strength and microhardness of GICs, while large particles can cause higher wear resistance.[7] A previous study reported that the increase in surface hardness of GIC-containing 3% (w/w) TiO_2 nanoparticles, whilst not statistically significant, could be also explained by the presence of fewer glass particles at the surface of GIC, which resulted in higher amount of acid to react with the nanoparticles.[5] In an another study evaluating the effect of the addition of 3% TiO_2 nanoparticles to GIC in terms of compressive strength, it has been reported that the improved compressive strength of GIC could be attributed to the small sizes of TiO_2 particles included in glass powder. It was stated that nanoparticles filled the voids between large glass particles in GIC and also served as additional bonding sites for the polyacrylic polymer. Thus, TiO_2 NPs serve as fillers between GIC powder particles.[4] In present study, only 3 % TiO_2 nanoparticles was used. With the use of different percentages of nanoparticles, results that may lead to statistically significant values on microhardness values can also be obtained or adverse effects on microhardness values can be resulted between the modified materials.

One possible explanation for the difference between the microhardness values of the experimental and control groups may be air voids in cement matrices of control groups. The presence of these voids, which are formed by the inclusion of air during mixing, may be a possible reason for the low micro hardness of the control groups. As previously mentioned, the number and size of voids incorporated during mixing and placement of restorative materials affect their mechanical characteristics.[23] After the material has dried, these voids are kept in the cement, where they perpetuate their function as stress concentrations, thereby developing mechanical weakness points.[5] And some authors defended that a dense and uniform distribution of all type of particles within the matrix was a key factor for enhancing mechanical properties.[7]

CONCLUSION

Within the limitations of this study, it can be concluded that the addition of 3% TiO_2 nanoparticles improves the surface micro hardness of the tested materials, although statistically insignificant, compared to the unmodified GICs and amalgomer. In addition, it is still not clear how the physicochemical mechanisms between nanoparticles and cements are realized, and further studies must be carried out.

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