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Investigating Some of the Mechanical Properties of Glass-Ionomers Cements Modified with ZnO and TiO2 Nanoparticles

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Abstract

Glass-ionomer cement (GIC) is one of the common restorative materials, but they exhibit relatively low mechanical properties. The aim of this study is the improvement of the properties of glass ionomer cement by incorporation of (1, 3 and 5wt.%) of different types of ZnO and TiO2 nanoparticles. Two conventional types of GIC Luting Cement were used (Ketac Cem radiopaque and Polyalkenoate Cement). Flexural strength and diametral tensile strength were calculated after 24 hr. and 3 weeks according to ISO4049. The results show a slight increase in flexural strength of glass ionomer cement, after adding 1 wt.% of both ZnO/NPs and TiO2/NPs, while the increase in flexural strength was significant at 3wt.% which reached 14% and 15.71% for ZnO/NPs and TiO2/NPs respectively for Ketac Cem radiopaque and reached 4.79% and 8.59% for Polyalkenoate Cement at the same ratio. Also, the flexural strength value increased after 3 weeks for all incorporation weight percentages. The modified tested cement also exhibited higher diametral tensile strength after 3 weeks, than that recorded in 24 hr for all concentrations (1, 3 and 5wt.%) of ZnO and TiO2 nanoparticles, in addition to the increase in diametral tensile strength after the incorporation of nanoparticles with glass ionomer cement. Within the limits of this study, a considerable increase in flexural strength and diametral tensile strength was observed with ZnO and TiO2 nanoparticles incorporations in 3wt% by weight. Furthermore, an increase in these properties after 3-week storage in distilled water was noticed.

Keywords: Mechanical properties, Glass ionomer cement, ZnO nanoparticles, TiO2 nanoparticles, Diametral tensile strength, Flexural Strength.

دراسة بعض الخصائص الميكانيكية لأسمنت الأيونومر الزجاجي المطورة بجسيمات اوكسيد الزنك واكسيد التاتونيوم النانوية

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الخلاصة

أسمنت الأيونومر الزجاجي هو عبارة عن مادة مرممة تستخدم في طب الأسنان كمادة حشو وأسمنت لصق، وخصائصه الميكانيكية منخفضة نسبيًا. الهدف من الدراسة تحسين الخصائص الميكانيكية لأسمنت الأيونومر الزجاجي من خلال اضافة جسيمات ZnO و TiO_2 النانوية بنسب وزنية مختلفة (1 ، 3 و 5 % Wt). تم استخدام نوعين من أنواع GIC Luting Cement المتوفرة في الاسواق (Ketac Cem radiopaque و Polyalkenoate Cement). تم قياس قوة الانثناء وقوة الشد المحوري للاسمنت المحضر بعد 24 ساعة و 3 أسابيع ، وفقًا للمواصفة ISO 4049. تظهر النتائج زيادة طفيفة في قوة الانثناء في أسمنت الأيونومر الزجاجي المطور مع إضافة 1% لكل من ZnO / NPs و TiO_2 / NPs ، ويزداد بشكل كبير عند النسبة 3% حيث تصل هذه الزيادة الى 14% إلى 15.71% ، على التوالي بالنسبة للمواد النانوية المستخدمة في Ketac Cem radiopaque كذلك تزداد النسبة لتصل الى 4.79% إلى 8.59% لـ Polyalkenoate Cement . أيضا، تم زيادة قيمة قوة الانثناء بعد غمرها بالماء المقطر 3 أسابيع لجميع المواد المستخدمة. كذلك أظهر الأسمنت المعدل ارتفاع في قيمة قوة الشد المحوري بعد 24 ساعة و 3 أسابيع من غمرها بالماء لكل تركيز (1 و 3 و 5%) من جسيمات ZnO و TiO_2 النانوية، وخصوصا بالنسبة الوزنية 3% للإسمنت الأيونومر الزجاجي المعدل. اظهرت النتائج زيادة كبيرة في قوة الانثناء وقوة الشد المحوري مع دمج جسيمات ZnO و TiO_2 النانوية بنسبة 3% بالوزن. علاوة على ذلك ، فقد لوحظ زيادة في قيم هذه الخصائص بعد تخزينها 3 أسابيع في الماء المقطر.

الكلمات المفتاحية: الخصائص الميكانيكية، الاسمنت الزجاجي، اوكسيد الزنك النانوي، اوكسيد التيتانيوم النانوي، قوة الشد المحوري، قوة الانثناء.

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Introduction

Glass ionomer cement (GIC) is a type of biomaterial of common use in modern dentistry [1]. These kinds of materials have become widely used since their inception 40 years ago because of their great advantages such as fluoride release (and ability to absorb it from external sources such as toothpaste, recharge of fluoride content) [2], as well as GICs other positive properties like, translucent, adhesion to tooth structure, low value of thermal expansion coefficient, being tooth colored and stability in an aqueous environment [3-6]. However, the most significant disadvantages are their brittle nature and relatively weak mechanical properties [7 and 8]. To overcome the problem, efforts have been made to improve the mechanical properties of GIC by addition of a variety of fillers such as metals, fibers, and hydroxyapatite powders. Also, the incorporation of nanoparticles into GIC may improve some properties without compromising the biological characteristics.

This has met with some success, as resulting cement was found to be stronger in comparison to those with no added nanoparticles. GICs can be developed by combining them with nanoparticles because the small loading of these nanoparticles can greatly enhance the mechanical properties of the resulting compounds, as well as maintenance of the biological compatibility and aesthetic properties of the primary cement [9 and 10]. Titanium dioxide particles are usually preferred additive in dentistry due to their pleasing color, so TiO_2 is applied as a pigment, chemically stable, high biocompatibility and non-toxic [11 and 12], also TiO_2 powder has good physical properties (due to high surface energy, high hardness, high refractive index) and low cost. ZnO nanoparticles are believed to be nontoxic, biosafety and biocompatible and have been also used as drug carriers, cosmetics, and fillings in medical materials [13]. Furthermore, recent studies have shown that ZnO nanoparticles have an antibacterial activity greater than microscopic particles [14 and 15]. In spite of the fact that ZnO and TiO_2 are widely used ingredients in dermatological preparations and sunscreens and many other products, only two reports have focused on the effects of these nanoparticles on human germ cells [16]. The aim of this study is to investigate the effects of adding two types of ZnO and TiO_2 nanoparticles with ratio (1, 3 and 5wt.%), into conventional glass ionomer cement on mechanical properties such as flexural strength, their modulus and diametral tensile strength, and also to study the effect of these incorporations after 3 weeks.

Material and Methods

Two commercial types of GIC Luting Cement (powder/liquid) were used, as shown in table 1. Experimental GICs were prepared by incorporating TiO_2 nanoparticles (TiO_2/NPs) size < 25nm (Sigma-Aldrich, Louis, USA) and ZnO nanoparticles (ZnO/NPs) (average particle size of 20 nm with hexagonal crystal structure and 99.8% purity) (Nano parts Espadana, Isfahan, Iran) into the powder of control GIC at concentrations 1, 3 and 5wt.%.

Table 1. Materials used in this study

Material	Group	Batch No.	Manufacturer	P/L ratio
Polyalkenoate Cement (Medicem)	PCM	1140129	Promedica Neumünster Germany	1.5
Ketac Cem radiopaque	KCR	596393	3M ESPE Deutschland GmbH, Neuss-Germany	1.7

Flexural strength (FS) and modulus

Each concentration of nanoparticles (ZnO/NPs and TiO_2/NPs) specimens was tested for flexural strength according to ISO 4049. The specimen formed were prepared in a split stainless-steel precision mold (25×2×2 mm) (n=4) as shown in figure 1.

The mold was placed on a glass slab and freshly mixed cement was applied until the mold was slightly overfilled and allowed to set for 30 min and immersed in distilled water at 37°C until tested. Three-point flexural strength tests were carried out on the test bar at a span of 20 mm and a constant crosshead speed of 1 mm / min using a universal testing machine (Zwick 1435, Ulm, Germany).

FS (MPa) was calculated according to the following formula [17]:

$$FS = \frac{3FL}{2bd^2}$$

Where F is the maximum force (N), L is the distance between the layers (mm), b is the width of the specimen (mm) and d is the height of the specimen (mm). Flexural modulus FM (MPa) was calculated using the following formula [17]:

$$FM = \frac{3PL^3}{4bd^3D}$$

Where P is the load at fracture (N), L is the distance between the supporting wedges (mm), b and d are the width (mm) and thickness (mm) of the specimen respectively and D is the deformation of the specimen at P. The flexural strengths and flexural modulus of the modified GIC were determined at 24 hr and 3 weeks.

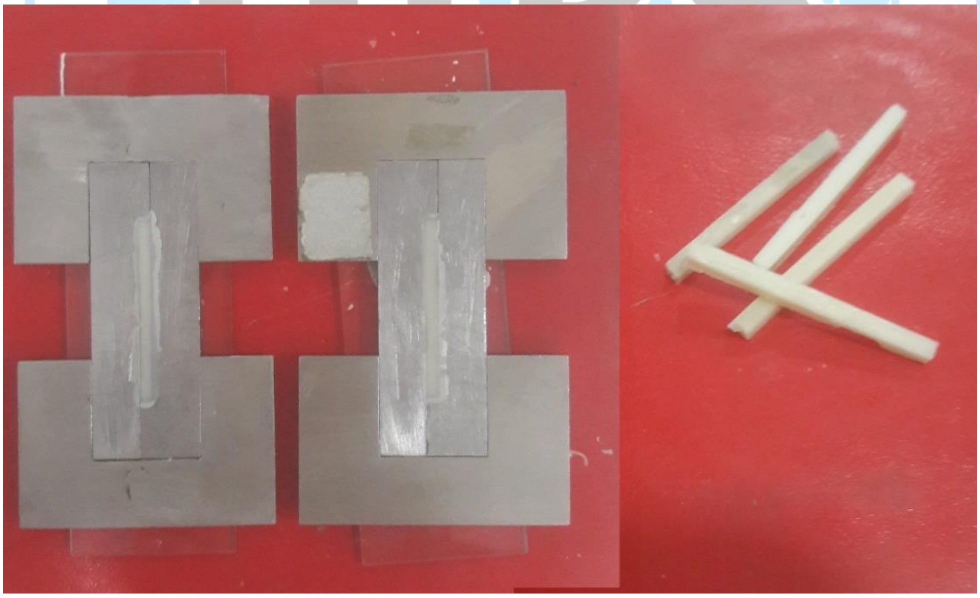

Figure 1: Specimen preparation for flexural strength test

Diametral tensile strength (DTS)

Diametral tensile strength (DTS) test was performed adopting the procedure of ANSI/ADA specification No. 27.4 specimens (of each concentration). Cylindrical specimens (6×3 mm) were prepared using a stainless-steel mold figure 2. The mold was placed on a glass slab and freshly mixed cement was applied until the mold was slightly overfilled and allowed to set for 30 min and immersed in distilled water at 37°C until tested.

The DTS (MPa) was then calculated according to the following equation [17]:

$$DTS = \frac{2p}{\pi dL}$$

Where P is the load at fracture (N), and d (mm) and L (mm) are the diameter and thickness of the cylindrical specimen, respectively. The DTS of the modified GIC were determined at 24hr and 3 weeks.

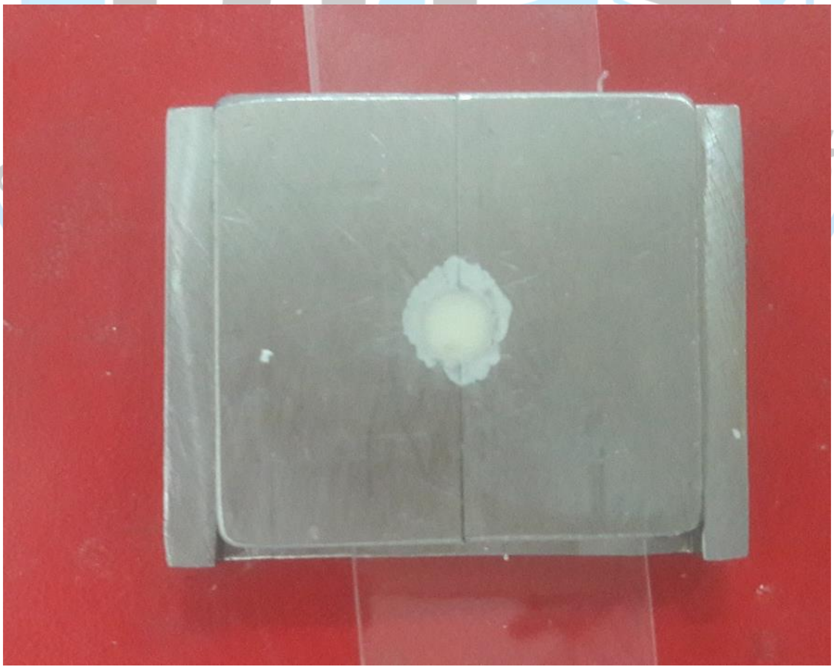

Figure 2: Split stainless-steel mold used to prepare specimens for mold for DTS test

Results

Flexural Strength and modulus

The result of the of flexural strength (FS) of PCM and KCR groups modified GIC are shown in figures (3 and 4) by various ZnO/NPs and TiO_2/NPs concentrations and measured after 24hr and 3Weeks. The modified GIC increased in flexural strength when ZnO/NPs and TiO_2/NPs concentrations increased in 1 and 3wt%. The maximum observed mean values after 24hr were 12.055 ±0.593 (KCR TiO_2/NPs), 11.877±0.789 (KCR ZnO/NPs), 19.841±0.467 (PCM TiO_2/NPs) and 19.147±0.708 (PCM ZnO/NPs). Comparison of the results of the 24hr and 3weeks specimens shows that the FS mean value increases with ZnO/NPs and TiO_2/NPs, on the other hand; it decreases at 5wt.% but still higher than the mean value of control for KCR and PCM groups modified.

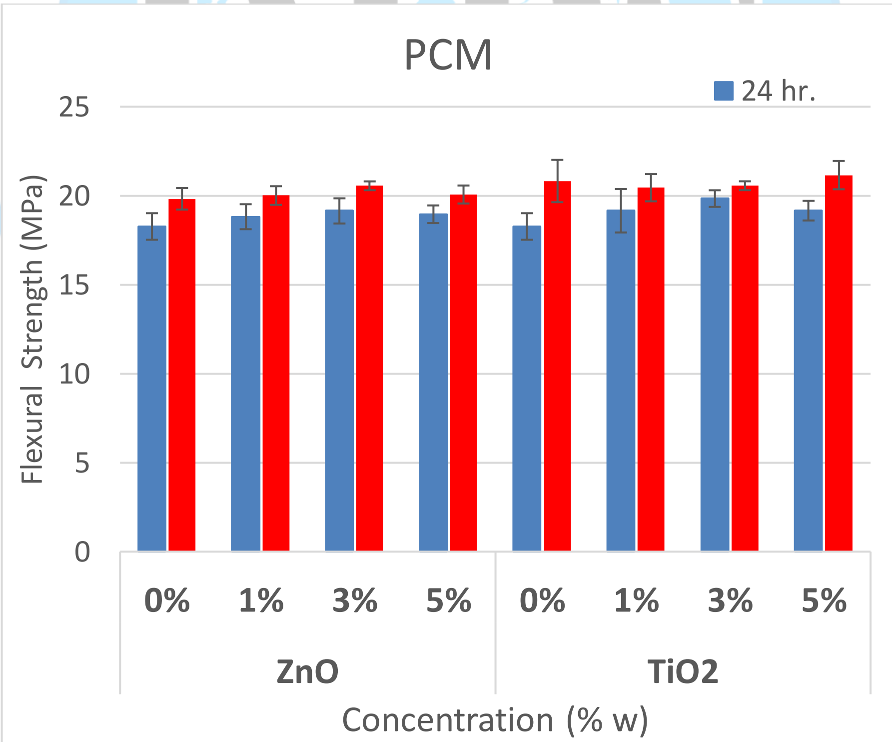

Figure 3: The mean value of flexural strength of PCM group

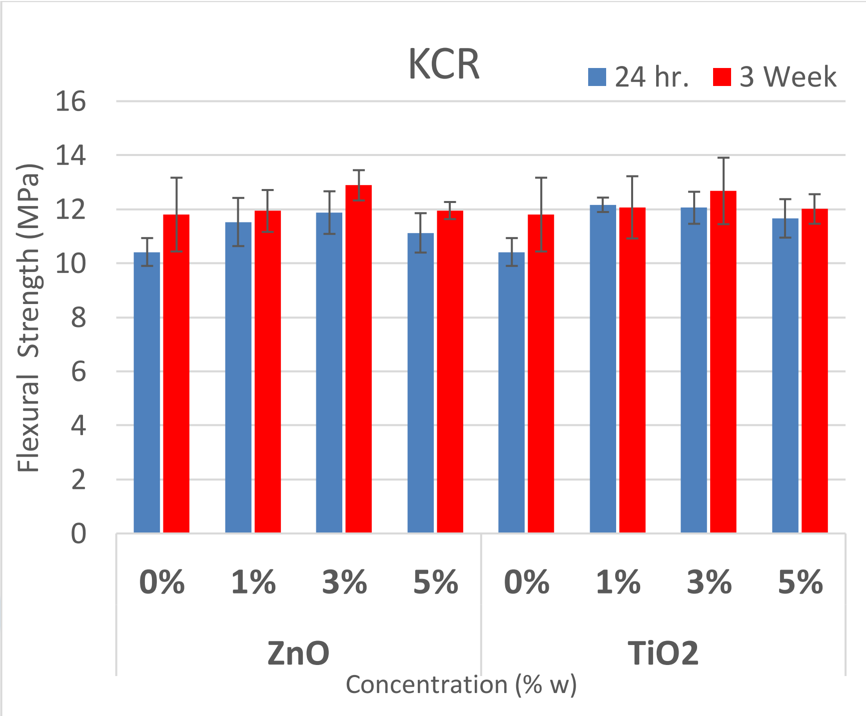

Figure 4. The mean value of flexural strength of KCR group

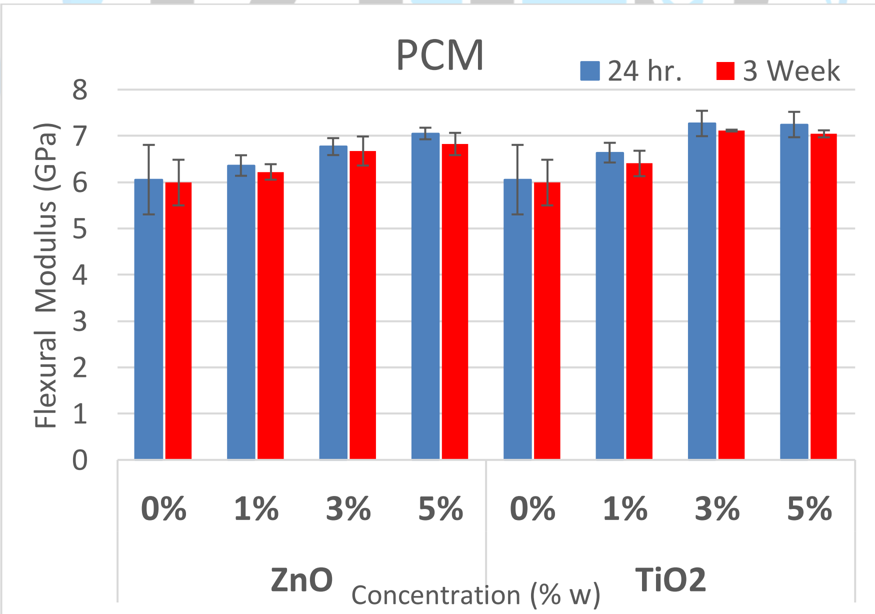

Figure 5: The mean value of flexural modulus of PCM group

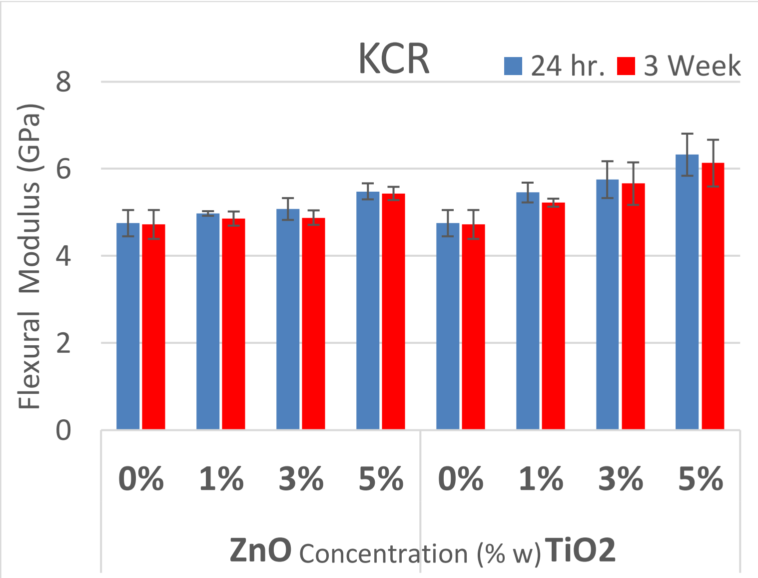

Figure 6: The mean value of flexural modulus of KCR group

Figures 5 and 6 show the mean value and standard deviation of the flexural modulus of modified GICs and demonstrates the effects of incorporation of nanoparticles, the increases in the flexural modulus for all ratio of incorporation compared with the control (0%), for KCR group the value ranged from 5.456±0.227GPa for 1%wt. to 6.325±0.483GPa at 5% for TiO_2/NPs and to ZnO/NPs the flexural modulus recorded 4.975±0.053 to 5.483±0.184GPa for 1 and 5wt%. respectively. Also, for PCM group the flexural modulus increases from 6.055 ±0.750GPa for control to 7.052±0.125GPa for incorporation ratio 5% ZnO/NPs and 7.269±0.274GPa for 3% TiO_2/NPs.

Diametral tensile strength (DTS)

The mean values (standard deviation) of DTS, by various ZnO/NPs and TiO_2/NPs concentrations, are shown in figures 7 and 8. The results of the DTS measurement showed that the modified GIC containing 3 wt.% ZnO/NPs and TiO_2/NPs have the highest value as compared to other samples, modified GIC KCR group has been recorded between 26.16±0.67MPa for ZnO/NPs and 26.46±0.97MPa to TiO_2/NPs, while PCM group has recorded

26.93±0.33 and 27.00±0.22MPa to ZnO/NPs and TiO_2/NPs respectively. Furthermore, at 3 weeks the mean values of DTS of KCR and PCM modified GIC increases.

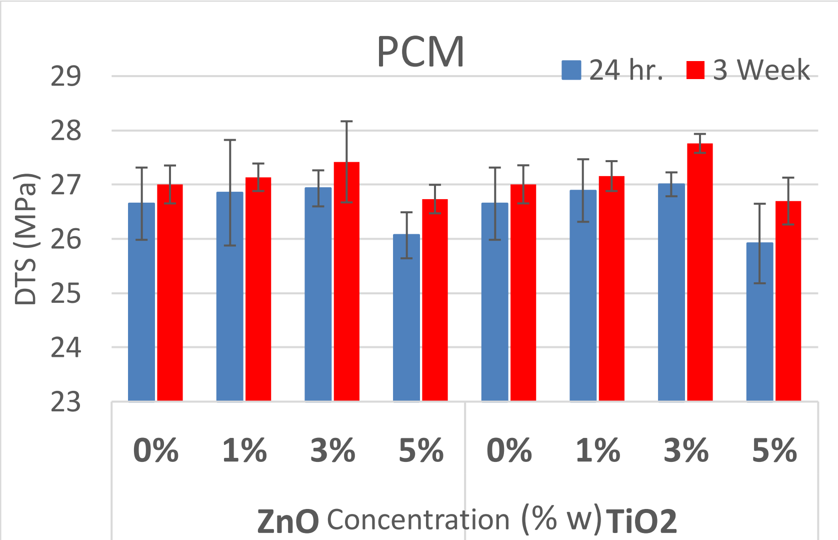

Figure 7: The mean value of DTS of GIC PCM group

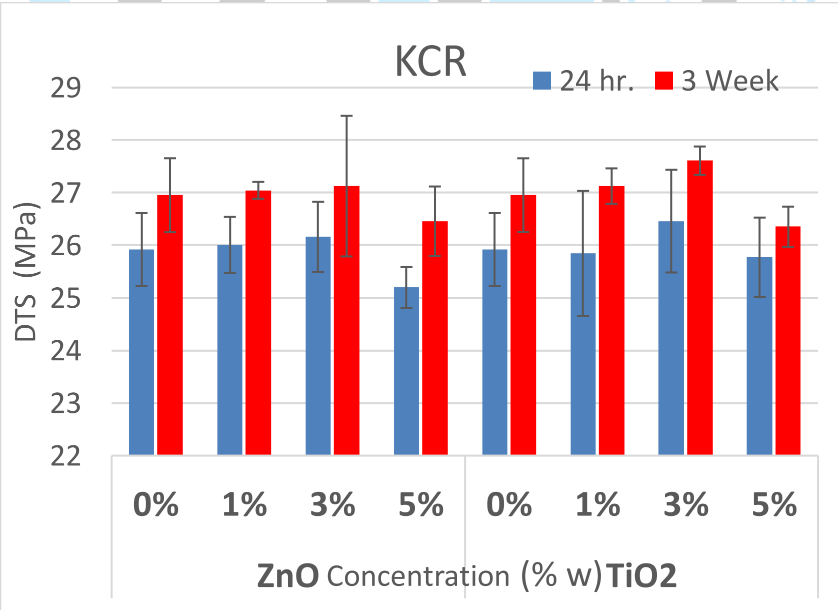

Figure 8: The mean value of DTS of GIC KCR group

Discussion

The main factor which affects the longevity and durability of dental restorations is secondary caries [18]. GICs effects on cariogenic bacteria are known, probably resulting from the release of fluoride, but this information is unreliable.[19 and 20]. We selected TiO_2 and ZnO because many materials containing TiO_2 or ZnO have antimicrobial effects and used in various ways [21-23].

In general, GIC has some weak mechanical properties, which is an obstacle to its use as a posterior restorative material despite the rest of its wonderful properties such as biocompatibility, bioactivity, remineralization of the carious. The strength of the GIC was assessed by flexural test because it was considered to be the most convenient test for this kind of material [24]. Figures 3 and 4 showed that the modified GIC with ZnO/NPs and TiO_2/NPs had a much higher value of flexural strength.

This is attributed to the small size of nanoparticles that leads to wider particle size distribution occupying the empty spaces between the GIC particles which result in higher mechanical properties and act as a reinforcing material in the composition of the GIC. In addition, ZnO/NPs and TiO_2/NPs have a crystalline structure that causes in low concentration (< 3wt.%) the formation of crystalline phases at the amorphous matrix of the GIC and increases FS. However, in concentration > 5wt.% this slight increase causes the agglomerate of nanoparticles.

The agglomerated compounds can act as stress concentrating centers which lead to high crystalline phases that leads to fragility in the amorphous matrix of GIC, which results towards adversely affect in mechanical properties of GIC, on the other hand, increasing the nanoparticles concentration leads to a large surface area which may cause increase in water uptake and resultant degradation of GIC.

All samples, when stored in water 3 weeks, showed a general increase in FS range from 13.29% to 3% for group KCR and from 10.43% to 3.63% for PCM group. In addition, figures 7 and 8 showed an increase in DTS after 3 weeks 5% to 3.39% for KCR group and from 3% to 1.33% for PCM group. The results of our study revealed a small increase in FS and DTS of modified GIC for ZnO/NPs and TiO_2/NPS after 3 weeks. This result indicated that water has an important effect on flexural properties of GIC [25].

Conclusions

ZnO and TiO_2 nanoparticles can be employed for manufacturing GIC to improve mechanical properties. Modified GIC, which has lower concentrations (<3wt.%) of ZnO or TiO_2 nanoparticles, increases the mechanical properties at high concentration (>5 wt.%), which in turn leads to devolution of mechanical properties of GIC. However, the overall effects from the addition of ZnO and TiO_2 nanoparticles on the mechanical of GIC were more impressive. Also, the result has shown that the GICs became stronger and higher in mechanical properties after 21 days of storage in distilled water at 37°C.

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