THE EFFECT OF TiO_2 AS ADDITIVES ON PROPERTIES OF COMPOSITE MgO FOR BONE REPAIR

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ABSTRACT

Magnesium oxide (MgO) is regarded as a biocompatible material. A composite material from MgO oxide prepared by mixing MgO powder with TiO_2 (rutile phase) (2, 5, 10)Wt.% using powder metallurgy technique. It is used to be bioceramic material. The compressed samples were dried and sintered at (1200) ^oC. porosity measurement showed that the porosity decreasing with increasing TiO_2% . X-ray showed the presence of Mg_2TiO_4 in the composite structure of MgO with (5, 10)%TiO_2 samples.

The mechanical study showed an increasing in compressive strength, hardness, wear resistance and biodegradation resistance with increasing TiO_2% content in the limit of used percentage. The prepared composite material didn't present antibacterial activity while previous researches showed opposite result because of using nanoscale particle size of MgO.

KEY WORDS: Magnesium ceramic oxide (MgO), Titanium Oxide (TiO_2), biodegradation ceramic oxide, composite bioceramic, bone repair

تأثير اضافة TiO_2 على خواص الماد المركبة من MgO لترميم العظم

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الخلاصة

يعتبر أوكسيد المغنيسيوم (MgO) مادة متوافقة حيويا. تم إعداد مادة مركبة من اوكسيد المغنيسيوم عن طريق خلط مسحوق MgO مع (2، 5، 10) ٪ TiO_2طورrutile باستخدام تقنية تكنولوجيا المساحيق لإنتاج مادة حياتية. تم تجفيف العينات المضغوطة وتلبيدها بدرجة حرارة 1200م .^{o}اظهرت قياسات المسامية انخفاض المسامية بزيادة نسبة TiO2 المضافة .وأكدت نتائج الأشعة السينية ظهور الطور (Mg_2TiO_4)في هيكل عينات MgO مع (5، 10)٪ TiO_2.
وأظهرت دراسة الخواص الميكانيكية زيادة في مقاومة الانضغاط، ،الصلادة ،مقاومة البلى و مقاومة التحلل مع زيادة محتوى TiO_2ضمن مدى الاضافة في البحث. ولم تظهر المادة المركبة نشاط مضاد للجراثيم في حين أظهرت الأبحاث السابقة نتيجة عكسية بسبب استخدام حجم الجسيمات النانوية من MgO .

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INTRODUCTION :

The recent bone substitutes consist of metals, ceramics, biological or synthetic polymers, and their composites, all either bioinert or bioactive and bioresorbable in nature. (Nabiyouni, 2014). The mean advantages of magnesium (Mg) over other non-resorbable biomaterials especially for orthopedic applications are represented by, it is biocompatible, non-toxic degradation product material, and encourage bone formation. MgO density is closed with natural bones compared with titanium alloys and stainless steels, resulting in reduce the stress shielding which represent a big problem with titanium alloys and stainless steels as they have higher density and elastic modulus than that of bone. Another advantage of Mg is having the ability to absorb energy in shock and vibration conditions that provide significant benefit in biomedical load-bearing applications (Tan et al., 2013, Kirkland, 2012). Magnesium-based bioceramics include a large collection of magnesium compounds e.g., oxides, phosphates and silicates, which used in orthopedic applications like bone cements, scaffolds for bone regeneration, tumor treatment, implant coating, and as DNA carriers.(Nabiyouni, 2014). It can be practical in non-permanent implant for orthopedic, e.g., bone screws (Frau et al., 2013), in addition Magnesium oxide (MgO) is a biocompatible material exhibiting strong antibacterial properties, and promising material for bone regeneration.(Hickey, 2014; Krishnamoorthy et al., 2012) . The drawback of using Mg is law elastic modulus and high degradation rate which means that there may be a greater chance of failure in high-load applications (Kirkland, 2012). However this fact is critical when considering degradable materials, as temporary implant with appropriate mechanical support is required during bioresorption and bone remodeling process. For this reason researches directed to customize and controlling the mechanical properties and degradation rate of Mg-based device. This paper reports on physical and some mechanical properties as well as the antibacterial effect of the MgO as biomaterial and evaluate the effect of different additions of TiO_2 (rutile phase) at different percentage as reinforcing material.

MATERIALS AND METHODS

Sample preparation and characterization

MgO powders from (New Rochelle, NewYork, 10801-USA) with mean particle size of (3.1)µm has been used with different adding percentages (2, 5, 10)Wt.% of rutile TiO_2 with mean particle size of (0.37)µm. Particle size for both oxides were characterized using Bettersize 2000 Laser particle size analyzer. Powders were mixed for 6 hr to get a homogenous distribution after that samples were prepared by powder metallurgy technique using hydraulic press technique. Cylinder samples with 13 mm diameter and 20mm high were dried at (100) ^oC for 24hr then sintering process have been done at (1200) ^oC and 5 ^oC/min heating rate. After sintering, samples were analyst using X-ray diffraction (Shimadzo, 6000) at room temperature with Cukα radiation (λ = 1.5405 Å), and a scanning speed of 5◦/min from 10◦ to 80◦ of 2Θ (Bragg angle) and 40 KV/30 mA an applied power to determine the phases present in the samples. The XRD peaks match with the standard JCPDS file no.(001-1235) for MgO , (021-1276) for TiO_2 and (025-1157) for Mg_2TiO_4. Apparent Porosity for the specimens were tested by Archimedes method using ASTM C373-88 (1988). The mechanical properties of the sintered specimens were estimated by compressive test, the test was made according to ASTM standard C-773-88(1999). Vickers Micro hardness was measured according to ASTM standard C1327-90(1990) , using digital microvickers hardness tester (TH-717) at 9.8 N for 15 sec and hardness (Hv.) was calculated using equation:

$Hv=1.854(p/d^2)$ (1)

The ability of samples to resist mechanical abrasion was tested using pin-on-disk apparatus according to ASTM G99 (Carter& Norton, 2007). The speed of disk was 200rpm, pin diameter was 4mm and applying load was 2 N. all above information have been chosen as a working conditions for all samples in order to evaluate wear resistance. Wear is commonly related with mechanical and chemical properties of material, it consider a limiting factor for long term performance (Black& Hasting, 1998). Biodegradation test was done in Tris-HCl buffer solution according to the ISO 10993-14: 2009 by evaluating weight loss of samples after immersion in solution at pH 7.4 and temperature 37^0C for different periods along 80hr. The amount of solution for each sample is counted by using solution volume / surface area (SV /SA) ratio= 0.5 ml/mm^2. At each time point the samples were taken out of the immersion medium, washed by distilled water and dried at 100°C, the weight change of samples was calculated after various time by following eq.(Wang et al., 2017):

$$\textbf{Weight loss} = \frac{\Delta W}{S.A} \quad (2)$$

Where : ΔW the weight loss of sample(g), S.A. the surface area (mm^2)

The antibacterial activity of MgO samples towards gram positive (E. coli) bacteria was estimated at a static state using a concentration of 8 mg/mL MgO and treatment for 24 hr in order to evaluate the performance of MgO and TiO_2 against bacteria.

RESULTS AND DISCUSSION

Characterization of the samples

Particle size analysis in Figure 1 and Figure 2 shows mean particle size is 0.37µ and 3.1µ for TiO_2 and MgO respectively. XRD patterns Figures 3 & 4 for raw materials revealed that MgO and TiO_2 used in this study did not contain any organic components or impurity. After preparation and sintering of samples, X-ray patterns for sintered samples Fig. 5 showed the presence of orthotitanates phase (Mg_2TiO_4)in the structure of MgO composite sample with(5, 10)% TiO_2 which confirmed by the phase diagram of MgO-TiO_2 binary system Figure 6 (Carter& Norton, 2007). Mg_2TiO_4 could probably be formed as a result of the high temperature due to the following reaction (White et al., 2013):

$TiO_2 + 2MgO \rightarrow Mg_2TiO_4$.

The presence of a secondary phase such as Mg_2TiO_4 illustrate that TiO_2 was involved in the MgO structure. Table 1 and Figure 7 shows the variation of porosity and shrinkage volume of samples with increasing TiO_2%. The porosity are relatively high for standard sample as well as for composite sample the reason of that may belong to use low pressing load during sample production process, this can be reduced by controlling on homogeneous mixing of powder and increasing pressing load during producing samples. It is clear that continuous adding of TiO_2% lead to decreasing porosity as a result of packing process due to using a wide range of particle size after powders mixing.

Mechanical properties:

Compressive Strength of prepared samples under uniaxial compression stress was done, Figure (8) showed increasing of compressive strength with increasing the TiO_2 addition. It can be observed that there is a significant improving in the mechanical properties with the additions of TiO_2 which agree with the results of other researchers used Mg-Ti composite (Esen et al., 2013). The compressive strength for MgO sample was 10.3 Mpa while for composite MgO+10% TiO_2 was 33Mpa

In present work the compressive strength values for all cases of TiO_2 additions are greater than those stated for human trabecular bone 2-12 MPa (Mozafari et al., 2010), but at the same time they less than compressive strength values for cortical bone 130-180 MPa (Mozafari et al., 2010). As expected Figure (9) shows increasing hardness of MgO from 112 MPa with increasing the TiO_2 additions until it reach to 621 MPa for MgO+10% TiO_2. The hardness value for MgO + 10% TiO_2 lies in the range of hardness values measured for dentine using Vickers test (Chun et al., 2014).

Wear resistance

Figure (10) shows decreasing weight loss of MgO composite samples with increasing TiO_2% that has been confirmed by increasing hardness as well as decreasing porosity with raising the TiO_2% content, due to reducing abrasive wear. Material hardness is frequently used as a guideline to the abrasive wear- resistance.

Biodegradation Test

It is clear from Figure 11 there was a significant difference in weight loss between MgO sample and the composite samples with different TiO_2%percentage. The weight loss for MgO sample after immersion for 106 hr in Tris-HCl buffer solution was 22% from starting weight while the weight loss for composite samples with (2, 5, 10)%TiO_2 were (3, 2, 4)% respectively from origin weight which give an indication that additions of TiO_2 reduce the degradation rate due to its inert natural in biological fluid.

Anti- bacterial activity of MgO

Figure (12) shows no anti-bacterial activity for MgO after 24 hr. even after additions of TiO_2 , the reason of this results may belong to using Macroscale particle size of MgO, other research proved that nanoscale MgO particle have antibacterial activity (Tang & Lv, 2014). (Hickey et al., 2014) mentioned that MgO reduced bacterial activity for orthopedic tissue engineering and other paper showed that antibacterial activity of MgO is inversely proportional with particle size and proved clear antibacterial activity for MgO nano particle towards Escherichia coli (E. coli)(Tang & Lv, 2014).

CONCLUSIONS:

1- It was found that additions of TiO_2 to MgO matrix in the range of (2, 5,10)% lead to decrease the porosity and increasing the strength and Vickers hardness significantly.

2- Improving hardness with increasing TiO_2 content lead to decrease weight loss of composite sample resulting from abrasion that mean improving wear resistance of MgO composite

3- Reduction in biodegradation rate of MgO with (2, 5, 10)%TiO_2 additions

4- Due to using MgO powder in microscale particle size, all samples didn't show antibacterial effect in static test.

Table 1 summarize the effect of TiO_2% on the porosity and volume shrinkage of MgO samples

TiO_2%	0%	2%	5%	10%
Porosity%	37.8	27.7	28	25.6
Volume Shrinkage%	39.63	48.27	51.13	48.22

Table 2 summarize the effect of TiO_2% on the hardness and of compressive strength of MgO samples

TiO_2%	0	2	5	10
HV(MPa)	111.73	281.935	384.06	621.205
Comp. strength(MPa)after sintering at 1200°C	10.3	20.1	22.5	33.1

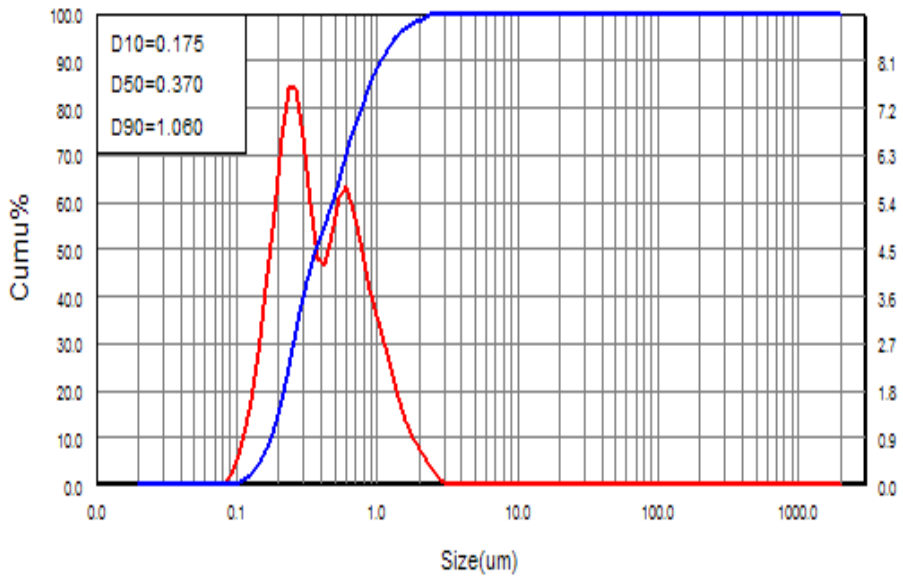

Fig. 1 , Particle size analysis for TiO_2

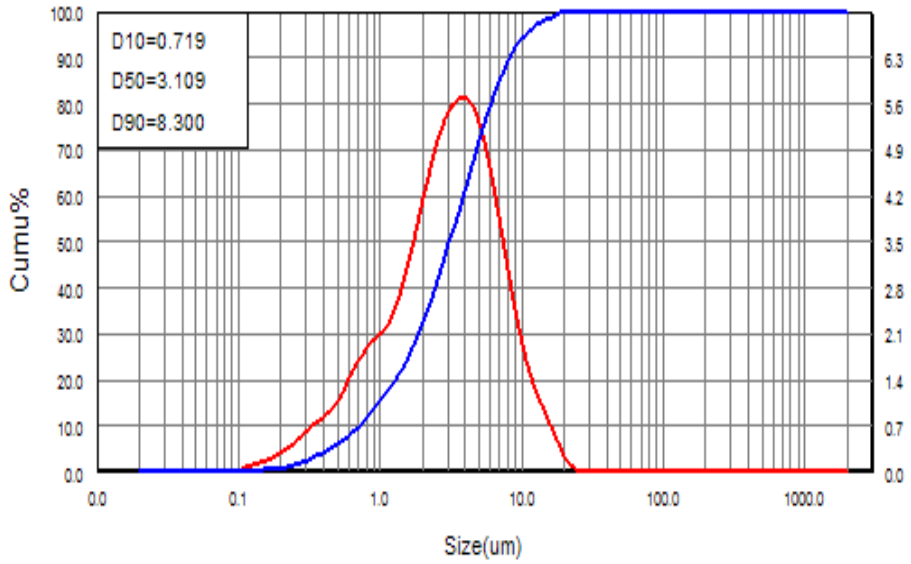

Fig. 2 , Particle size analysis for MgO

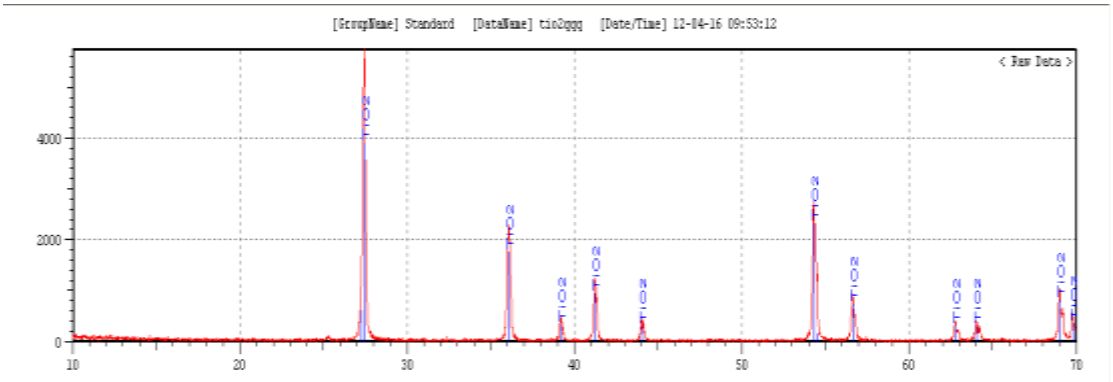

Fig.3. XRD analysis for raw TiO_2

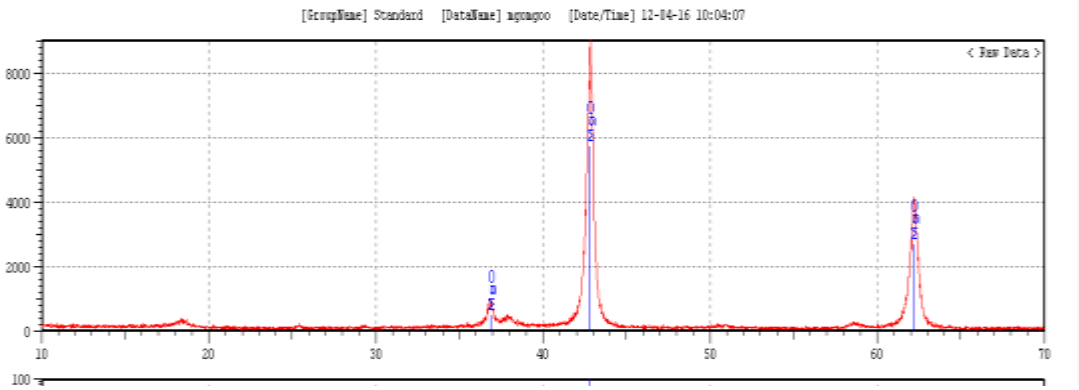

Fig. 4. XRD analysis for raw MgO

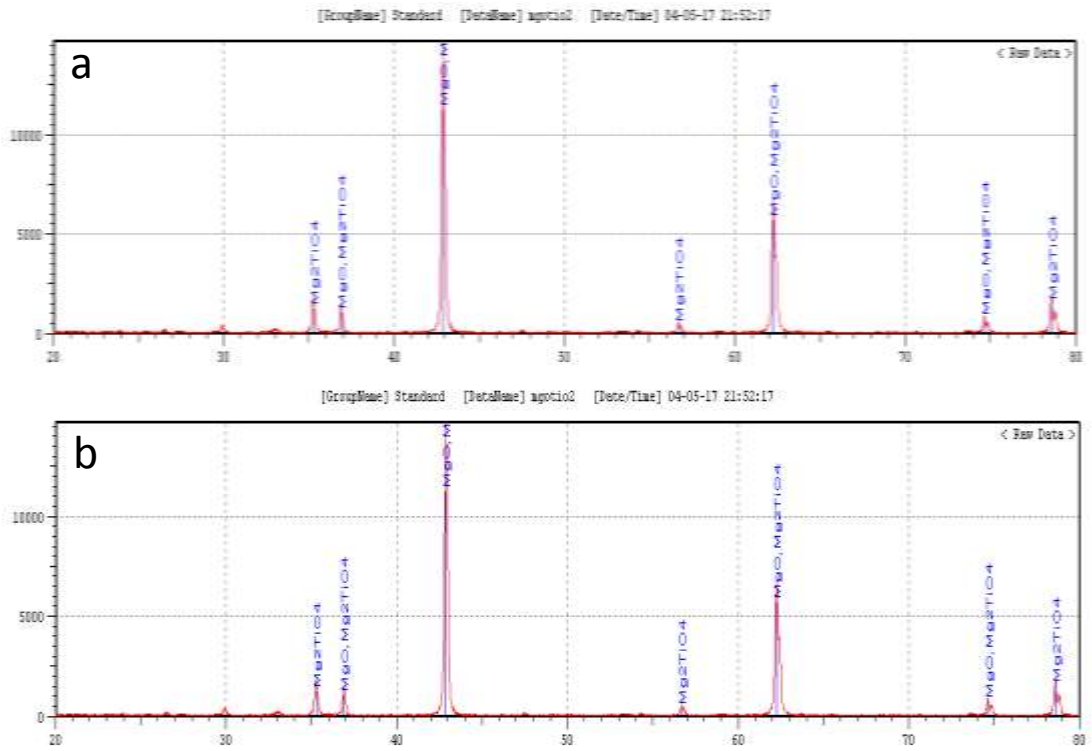

Fig. 5. XRD analysis for samples : a) MgO+5%TiO_2, b)MgO+10%TiO_2

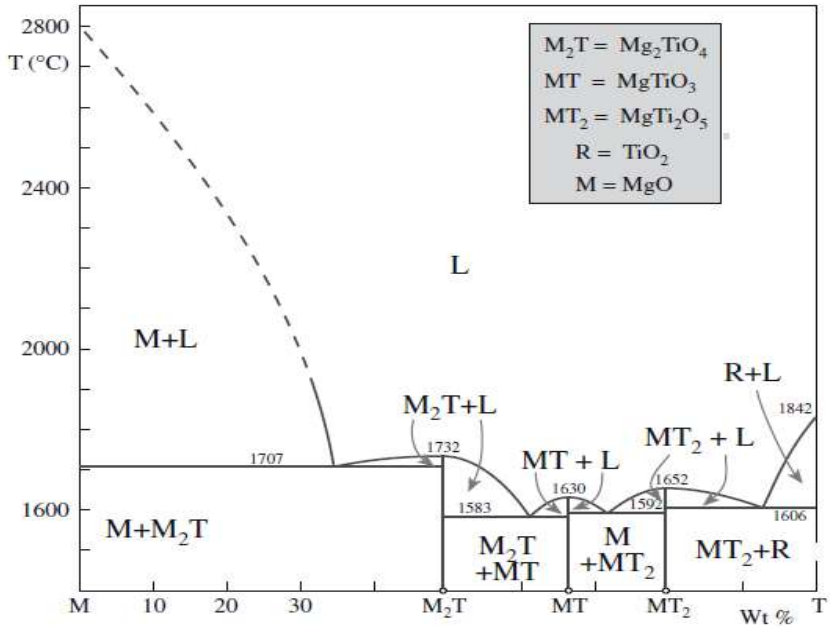

Fig. 6. phase diagram of the binary system MgO-TiO_2 (Carter& Norton, 2007)

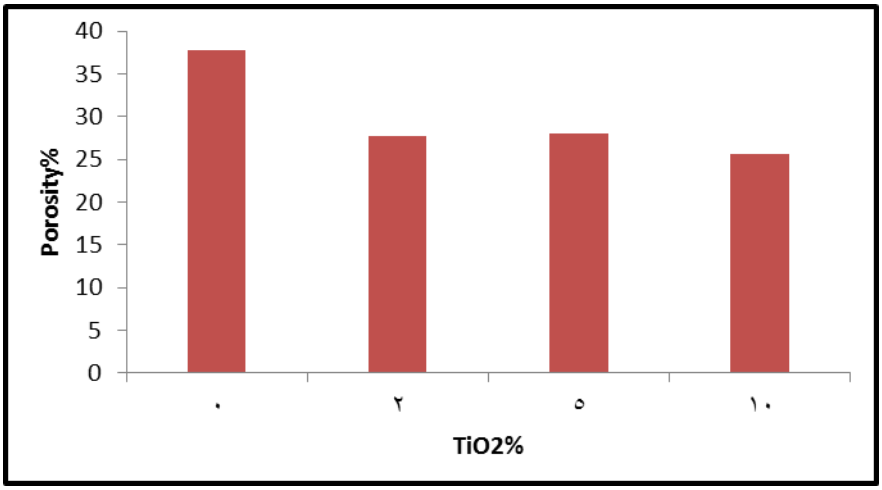

Fig. 7. Variation the apparent porosity of composite MgO with different percentages of TiO_2

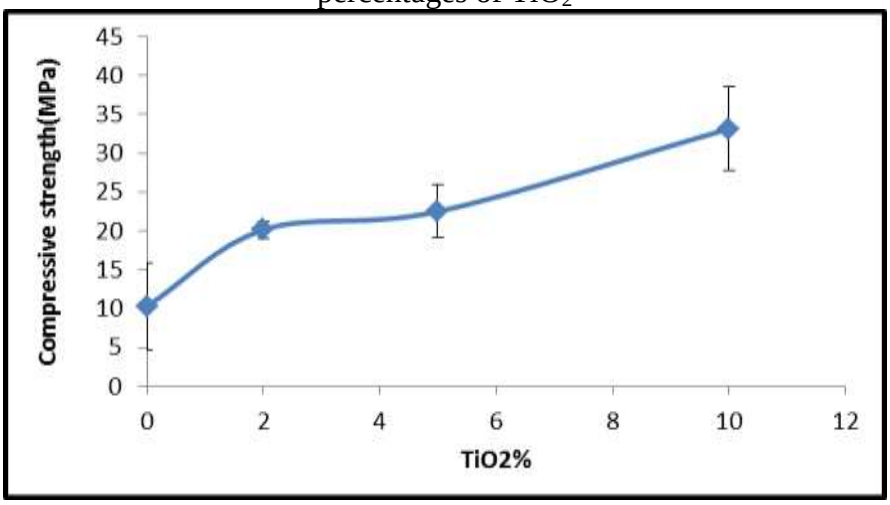

Fig.8 Variation the compressive strength of composite MgO with different percentages of TiO_2.

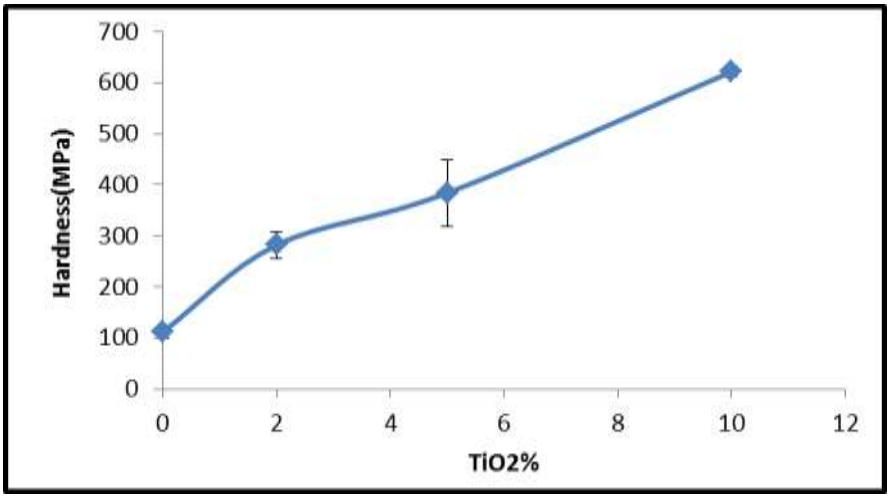

Fig.9 Variation the Hardness of composite MgO with different percentages of TiO_2

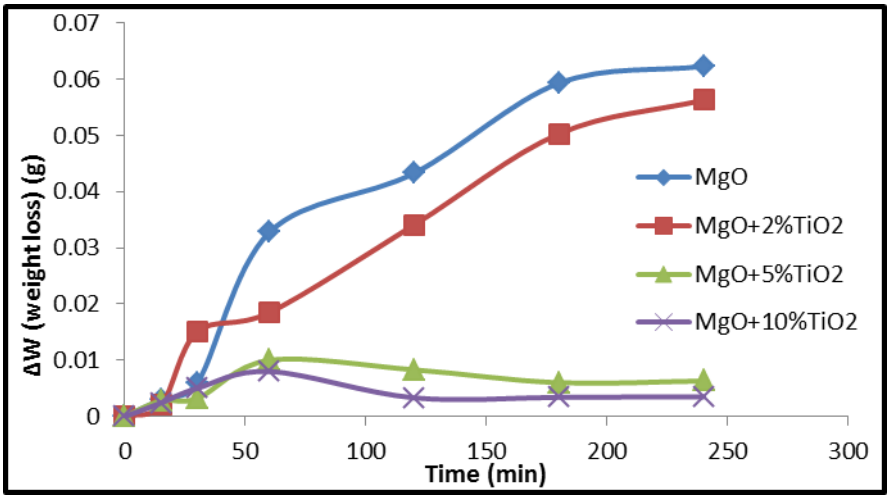

Fig.10 Variation the weight loss due to wear for composite MgO with different percentages of TiO_2

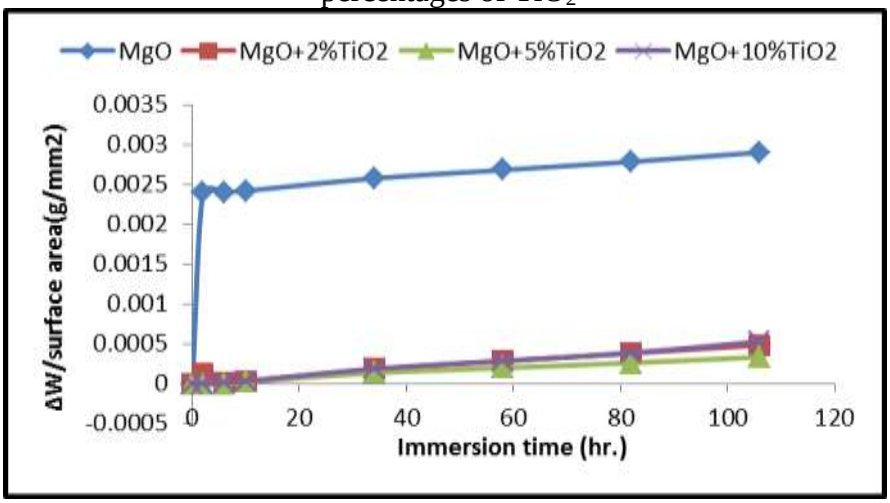

Fig.11 Variation of weight loss due to biodegradation for composite MgO with different percentages of TiO_2

Figure 12 anti-bacterial activity for MgO after 24 hr: 1) TiO_2 sample, 2)MgO sample, 3)MgO+2%TiO_2 sample, 4)MgO+5%TiO_2, sample 5)MgO+10%TiO_2 sample

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