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Effect of TiO_2 Nanoparticles on Water absorption and shrinkage of the PVA/CS Blend and PVA/CS nanocomposites thick Films

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Abstract

In this paper the effect ofaddition 0.2,0.4,0.6,0.8,1gof Titanium oxide (TiO_2) Nanoparticles inwater absorption, dimensions change and thickness for Polyvinyl alcohol (PVA)/Corn Starch(CS)10g/10g blend and PVA/CS/TiO_2 thick films have been studied. Films were prepared using solution casting method. Films were immersing in water for 60 days. The results show that, the water absorption and dimensions change decrease with increasing nanoparticles content, but thickness increase with increasing nanoparticles after immersion, also weightlosing, dimensions change and thickness were found after drying. The results show that the weightlosing, dimensions change decrease with increasing nanoparticles, reducing in thickness increase with increasing nanoparticles

Keyword: Biodegradation, absorption, shrinkage, blend, film.

CS: Corn Starch
PVA: Polyvinyl alcohol
TiO_2: Titanium oxide
WAC: water absorption capability.

تاثيرالجزيئات النانوية لاوكسيد التيتانيوم على امتصاصية الماء والتقلص لخلائط بولي نشا الذرة المدعمة بالجسيمات / نشا الذرة واغشية بولي فينيل الكحول/فينيل الكحول النانوية

الخلاصة

في هذا البحث تم دراسةتاثيراضافة الجزيئات النانوية لاوكسيد التيتانيوم باوزان مختلفة 0.2,0.4,0.6,0.8,1gعلى امتصاصية الماء والتغيربالابعاد والسمك لرقائق النشا مع البولي فينيل الكحول 10g/10g ورقائق النشا مع البولي فينيل الكحول والتيتانيوم اوكسايد.تم تحضيرالرقائق بطريقة الصب اليدوي. كما تم غمر الافلام المصنعة بالماء لمدة 60يوما. واظهرت النتائج ان امتصاصية الماء والتغيربالابعاد للرقائق تقل مع زيادة محتوى الجزيئات النانويةلكن السمك يزداد بزيادتها بعدالغمر، وايضا تم دراسة فقدان الوزن والتغير بالابعاد والسمك بعدالتجفيف،ووجد ان فقدان الوزن والتغير بالابعاد يقل بزيادة الجزيئات النانوية ولكن النقصان بالسمك يزداد بزيادة هذه الجزيئات.

الكلمات المرشدة : تحلل بايلوجي ،امتصاص،تقلص،خليط،غشاء،نشا الذرة،بولي فينيل الكحول،اوكسيد التيتانيوم ،قابلية امتصاص الماء.

INTRODUCTION

Biodegradable polymers have been a subject of interest for many years because of their potential to protect the environment by reducing non-biodegradable synthetic plastic waste [1]. It is quite important to develop some materials that can biodegrade to minimize the pollution. These materials not only provide the convenience for daily life but also minimize the impact to the environment after being used[2]. In the long run, these materials will decompose into small environmentally friendly molecules and be handled in properly controlled environment [3].Starch has been considered as a suitable source material because of its inherent biodegradability, ready availability, and relatively low cost[4].However, the poor mechanical properties and relatively high hydrophilic nature of starch prevent its use in widespread applications, for this reason, blends of starch with other biodegradable synthetic polymeric have been investigated for numerous packaging applications. Blends of starch with synthetic polymer(e.g. polyvinyl alcohol, aliphatic polyesters, etc)are prepared to achieve the desired performance for different applications PVA chosen because CS/PVA blends have demonstrated excellent compatibility the water solubility of PVA because it contains many hydroxyl groups make it easy it mix with the starch PVA, others excellent properties of its low permeability, and are found in wide industrial and agricultural application. Water absorption and the degradability is the most important factor and properties for the biodegradable materials TiO_2 nanoparticles were used to improve the properties of PVA/CS blend[5].

Experimental

This part presents raw materials and preparation method used to prepare PVA/CS blend and PVA/CS nanocomposites thick films.

Samples were prepared for biodegradation tests under the influence of water immersion anddrying**.**

Raw Materials

The raw materials used to prepare the films were; Corn Starch (CS)powder, supplied by Changchun Jincheng Corn Development Co. Ltd., Da Cheng Group (China), Polyvinyl alcohol (PVA) water-soluble powder of average molecular weight (MW14000) and purity 99.9%, supplied by Merck Schuchardt OHG. Hohenbrunn, Germany. TiO_2 nanoparticles supplied by MTI Corporation, with particle size 50 nm, surface area 200 mm^2/gm. Purity 99.9%. Formaldehyde and glycerine. Distilled water was used.

Film preparation Method

Two groups of PVA/CS based biodegradable polymer films were prepared using solutions casting method. The preparing steps for the first group can be summarized as following[6]:

Mixing 200 mL of deionized water and 10g of PVA at temperature 80°C and waiting for PVA to dissolves.30 mL of water was added to 10 g of starch to dissolves and the mixture was added to PVA solution to make the PVA/CS blend, then it was added3mL of glycerinas a plasticizerandraising the temperatureto 85 °C. 5mL of buotanol and 15mL of formaldehyde were added to the mixture. The temperature of the mixture was raised to 95°C during the mixing stage for three hours. When prepared the second group, As the method above but TiO_2nanoparticles with

0.2,0.4,0.6,0.8,1g were added with the 10 g of PVA to make PVA/CS/TiO_2 nanocomposites thick films. It was used a mixer type 500 rpm to receiving good homogenous distribution.
The product mixture was poured on glass plates of dimensions 10cm×10cm×0.45mm. Finally the sheets were pulled from the molds after drying and cutting into the shapes according to the required test using a scissor.

Water Absorption Measurements

The major mechanism that role the water penetration into the composite is diffusion; this mechanism involves direct diffusion of water molecules into matrix. The surface damage and cracks produced as a result of the entry of water [7]. The water absorption capability (WAC)was calculated with the following equation:

$$WAC\% = \frac{\mathrm{Wwet} - \mathrm{W}dry}{\mathrm{Wdry}} \times 100. \quad \ldots(1)$$

Where:
W_{wet} represent weight after immersion, W_{dry} represent weight before immersion. Water absorption of the immersed films was determined based on data obtained from simple immersion test using the following procedure, the dried samples were cut into the dimensionsof1cm×1cm×different thicknesses as shown in fig.1.The films were immersed in water for about 2 month and dried, then to be measure the differences.

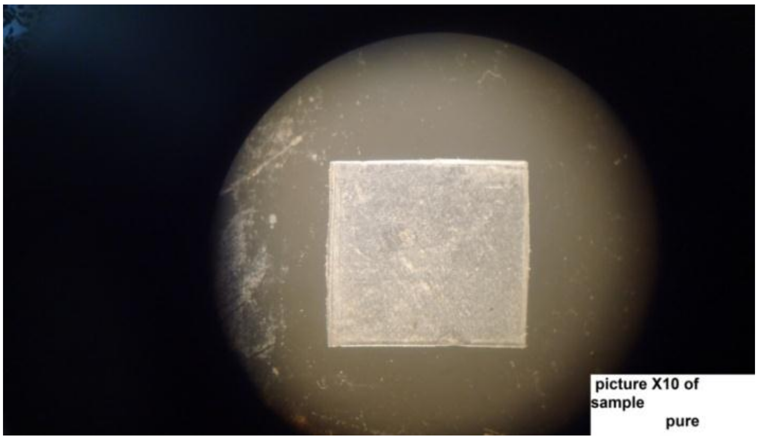

Figure (1) PVA/starch blend

Losing Mass

Indicate the decrease in volume, thickness, weight because of water exit after immersion carrying somedissolved materials, and it increase with time. mass loss was calculated by the equation below:

$$\mathrm{Loss}\% = \mathrm{Wwet} - \mathrm{Wdry}'/\mathrm{Wdry}' \times 100\% \quad \ldots(2)$$

Where;
the W_{wet} represent weight after immersion, W_{dry}' represent weight after shrinkage.

Results and discussion

Table 1shows the values of dimensions, thickness, weight for PVA/CS blend and PVA/CS/TiO_2 nanocomposites thick films before immersion in water, table 2 shows The values of dimensions, thickness and weight for PVA/CS blend and PVA/CS/TiO_2 nanocomposites thick films after immersion in water, table3shows the percentage values for WAC% for dimensions, thickness and weight for PVA/CS blend and PVA/CS/TiO_2 nanocomposites thick films after immersion in water. The results showed that there were dimensions, thickness and weight change for films. For PVA/CS blend, there are molecules for CS and PVA, there molecules bonding together to form large chains, which distribution randomly. The chains have intra molecules force (bonds) form by polarity. The polarity effected on the water molecules and the activity causes to diffuse inside the structure, so that the water was located between these chains making swelling and dimensions change. The addition of TiO_2 nanoparticles were located between these chains, and separated it, so that the polarity affected was reduced and diffusion presses was decreased. Also when nanoparticles were located between chains, the movement of water molecules was decreased and the water content was decreased. The increasing in thickness compare to PVA/CS blend is due to presence of TiO_2 nanoparticles between the chains.

Table (1) List values of dimensions, thickness and weight of films before water immersion

Sample	Average Length After Immersion $(dry)_{mm}$	Average Width After Immersion $(dry)_{mm}$	Thickness After Immersion $(dry)_{mm}$	Weight After Immersion $(dry)_g$
PVA/CS	16.23333	10.53333	0.762	0.1659
PVA/CS/0.2 g TiO_2	16.06667	9.96667	0.635	0.1192
PVA/CS/0.4 g TiO_2	14.63333	10.13333	0.7366	0.1257
PVA/CS/0.6 g TiO_2	11.6	11.23333	0.762	0.1336
PVA/CS/0.8 g TiO_2	15.6	11.1	1.143	0.1928
PVA/CS/1g TiO_2	14.8	9.73333	0.9652	0.1699

Table (2) List values of dimensions, thickness and weight of films after water immersion

Sample	Average Length Before Immersion $(dry)_{mm}$	Average Width Before Immersion $(dry)_{mm}$	Thickness Before Immersion $(dry)_{mm}$	Weight Before Immersion $(dry)_{g}$
PVA/CS	10.96667	7.4	0.4826	0.0495
PVA/CS/0.2g TiO_2	10.43333	6.56667	0.4064	0.0330
PVA/CS/0.4g TiO_2	10.8	7.63333	0.5969	0.0464
PVA/CS/0.6g TiO_2	9.03333	7.63333	0.6096	0.0426
PVA/CS/0.8g TiO_2	10.7	10.23333	0.8382	0.0479
PVA/CS/1g TiO_2	10.43333	7	0.635	0.0472

Table (3) List percentage values for Average WAC% for dimensions, thickness and weight of films after water immersion.

Sample	Average WAC% For Length After $Immersion(dry)_{mm}$	Average WAC% For Width After $Immersion(dry)_{mm}$	WAC% For Thickness After $Immersion(dry)_{mm}$	WAC% For Weight After $Immersion(dry)_{g}$
PVA/CS	48.024	42.035	57.895	235.152
PVA/CS/0.2 g TiO_2	53.978	51.867	56.945	261.212
PVA/CS/0.4 g TiO_2	35.494	32.751	23.404	170.905
PVA/CS/0.6 g TiO_2	28.413	47.167	25	213.615
PVA/CS/0.8 g TiO_2	45.794	8.469	36.364	302.505
PVA/CS/1g TiO_2	41.853	39.048	52	259.958

Fig.2 to 7 show the films after immersion in water for about 60 days dimensions change this due to accumulation for water with time,holes and cavities was appeared.

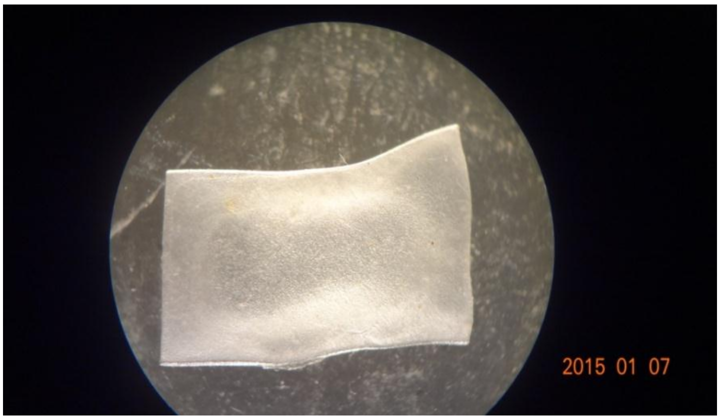

Figure (2) PVA/CS blend

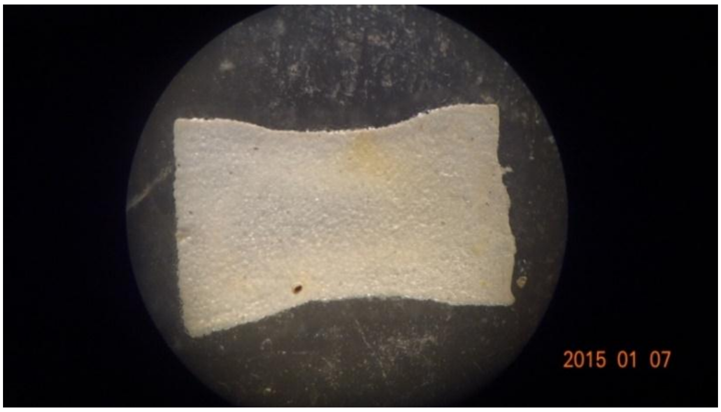

Figure (3)PVA/CS/0.2gTiO_2film.

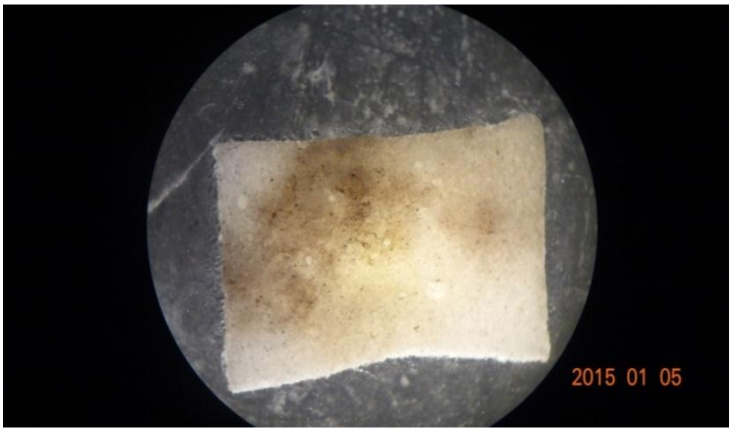

Figure (4) PVA/CS/ 0.4g TiO_2 film.

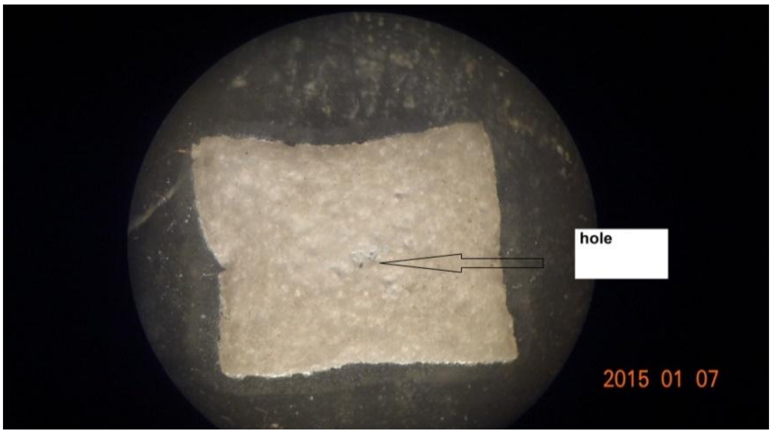

Figure (5)PVA/CS/0.6g TiO_2 film.

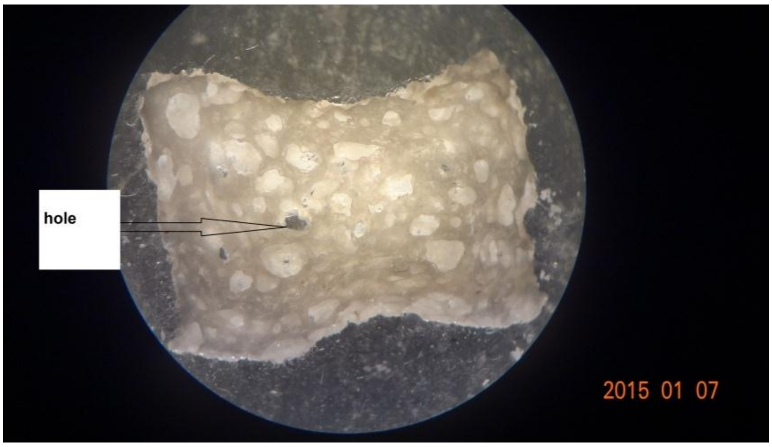

Figure (6)PVA/CS/0.8g TiO_2 film.

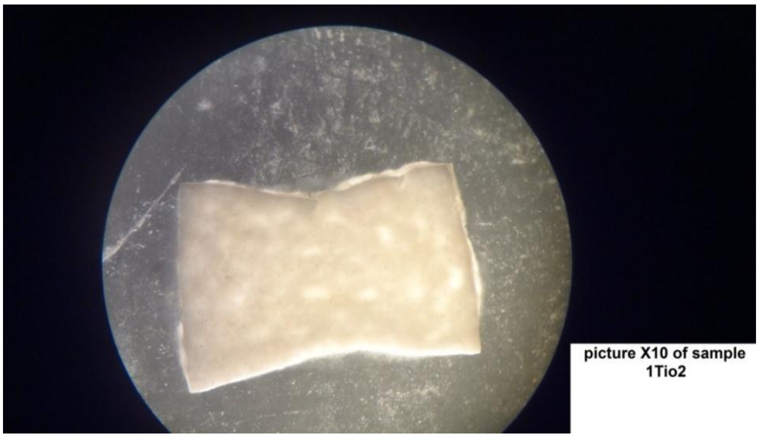

Figure (7) PVA/CS/ 1g TiO_2 film

After immersion the films for 2 months, the films were taken out and left 2 months. Table 4 shows value for dimensions, thickness and weight for PVA/CS blend and TiO_2 nanocomposite thick films after shrinkage, table 5 shows percentage value for Loss% in dimensions,thickness and weight for PVA/CS blend and TiO_2 nanocomposite thick films after shrinkage.

For PVA/CS blend, the water evaporated outside the structure (through three dimension), so that the molecules for blend affected and moved their position. Addition TiO_2 nanoparticles encourage water molecules to diffusion in any path which had low distribution of TiO_2.So that the chains was expanded and moved to stable position making shrinkage**,**when the water molecules diffuse inside structure the water molecules was located between chains, addition TiO_2 nanoparticles was located the spaces between there chains and the water was located in interface region between particles and blend.

After leaving the samples in the air about 2 months, the water was diffuse out of the structure.The reduction in weight and thickness were due to the some materials for starch or PVA was dissolved in water after immersion.

Table (4) List values of dimensions, thickness and weight of films after shrinkage.

Sample	Average Length After Shrinkage(dry)$_{mm}$	Average Width After Shrinkage (dry)$_{mm}$	Thickness After Shrinkage (dry)$_{mm}$	Weight After Shrinkage (dry)$_g$
PVA/CS	11.63333	7.46667	0.4318	0.0347
PVA/CS/0.2 g TiO_2	12.73333	6.53333	0.3048	0.0197
PVA/CS/0.4 g TiO_2	11	6.83333	0.4826	0.0349
PVA/CS/0.6 g TiO_2	9.66667	7.76667	0.5842	0.0260
PVA/CS/0.8 g TiO_2	11.8	8	0.635	0.0300
PVA/CS/1g TiO_2	9.8	6.06667	0.5842	0.0346

Table (5) List percentage values of the Loss% in dimensions, thickness and weight of films after shrinkage.

Sample	Average Loss% in Length After Shrinkage $(dry)_{mm}$	Average Loss% in Width After Shrinkage$(dry)_{mm}$	Loss% in Thickness After Shrinkage $(dry)_{mm}$	Loss% in Weight After Shrinkage $(dry)_g$
PVA/CS	-460	-306.667	-33.02	-13.12
PVA/CS/0.2g TiO_2	-333.334	-343.33	-33.02	-9.95
PVA/CS/0.4g TiO_2	-363.333	-330	-25.4	-9.08
PVA/CS/0.6g TiO_2	-193.333	-3.46667	-17.78	-10.76
PVA/CS/0.8g TiO_2	-380	-310	-50.8	-16.28
PVA/CS/1g TiO_2	-500	-366.666	-38.1	-13.53

Fig.8.to13show the films after Shrinkage 2 month the shape was changed, and when addition and increasing TiO_2 nanoparticles, holes and cavities was appeared.

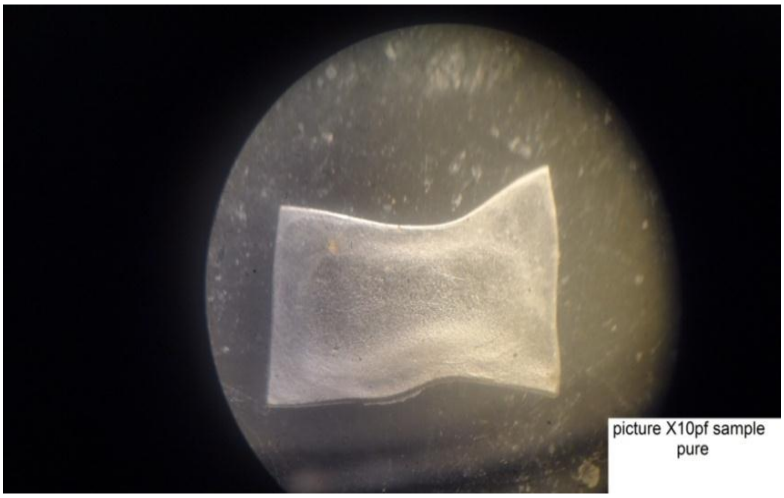

Figure (8) PVA/CS blend.

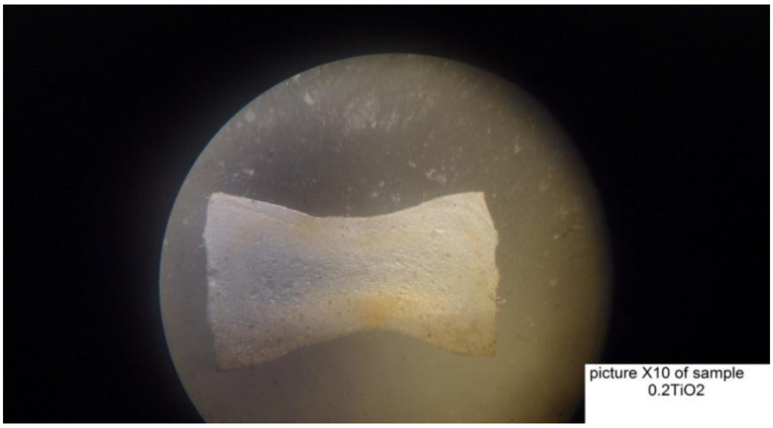

Figure (9) PVA/CS/0.2g TiO_2 thick film.

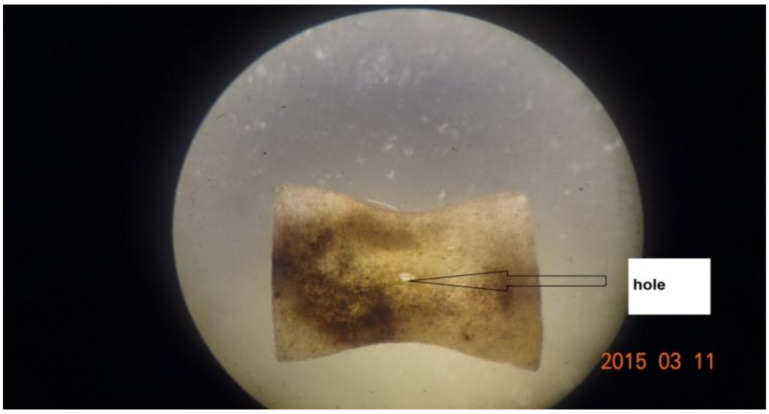

Figure (10)PVA/CS/0.4g TiO_2 thick film.

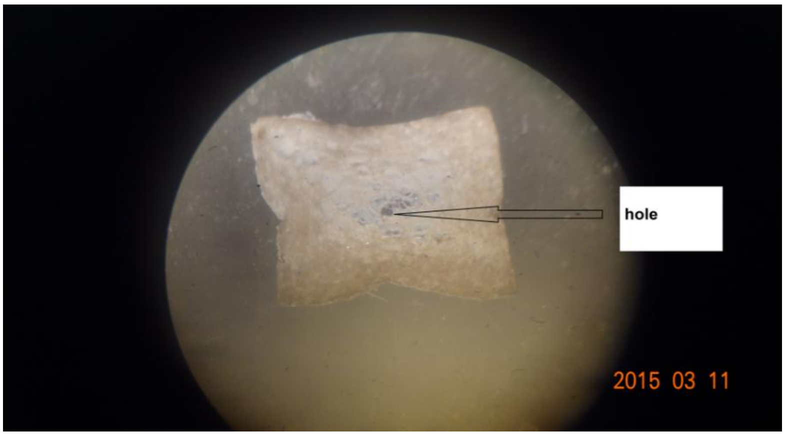

Figure (11)PVA/CS/0.6g TiO_2 thick film.

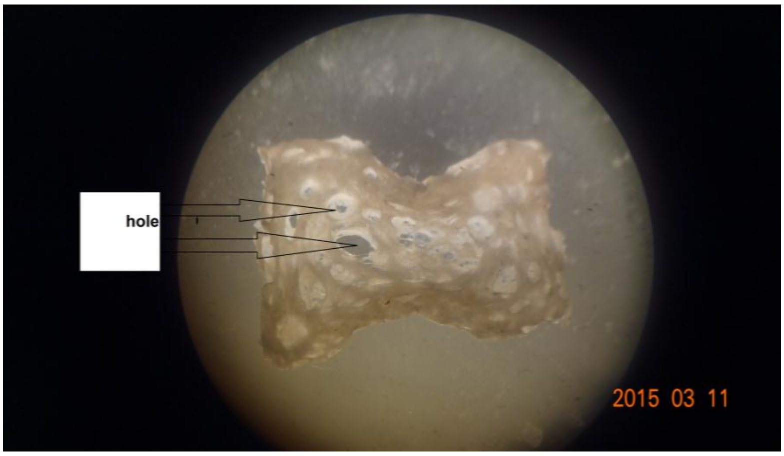

Figure (12)PVA/CS/0.8g TiO_2 thick film.

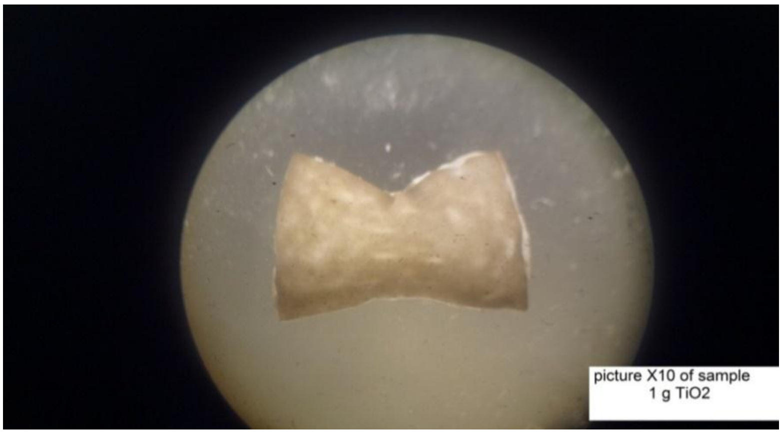

Figure (13) PVA/CS/1 gTiO_2 thick film

Conclusions

The results obtained out of this work lead to the following conclusions:

1.Addition of TiO_2 nanoparticles affected on the biodegradation behavior for the films by reducing weight loss for all films except PVA/CS/0.2, PVA/CS/0.8 PVA/CS/1g TiO_2 nanocomposites thick films, changing in dimensions and thickness for all films during the immersion in water, reducing weight loss for all films except PVA/CS/0.8g, PVA/CS/1g TiO_2 nanocomposites thick films, changing in dimensions and thickness for all films during the drying.

2.Addition of TiO_2 nanoparticles lead to form bulges and holes on the surface for films after immersion in water and drying.

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