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Research Article

Structural Properties of Nanoparticles TiO2/PVA Polymeric Films

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Abstract

In this research, X-ray diffraction of the powder (PVA polymer, titanium dioxide with two particle sizes) and (TiO_2 (15.7 nm)/PVA and TiO_2 (45.7 nm)/PVA) films have been studied, the amount of polymer is (0.5) g and (0.01)g from each particle sizes of nanoparticles will be used. Casting method is used to prepare homogeneous films on glass petri dishes. All parameters accounted for the X-ray diffraction; full width half maximum (FWHM), Miller indices (hkl), size of crystalline (D), Specific Surface Area (S) and Dislocation Density (δ). The nature of the structural of materials and films will be investigated. The XRD pattern of PVA polymer has semi-crystalline nature and the titanium dioxide with two particle sizes have crystalline structure; anatase type. While the mixture between these materials led to appearing some crystalline peaks into XRD pattern of PVA polymer.

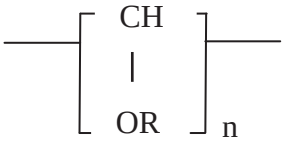
Keywords: Nanoparticle doped polymer**,** PolyVinyl Alcohol (PVA), Titanium dioxide (TiO_2), Structure Properties, X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM).

الخلاصة

في هذا البحث, تم دراسة حيود الاشعة السينية لمساحيق (بوليمر PVA ، ثنائي أوكسيد التيتانيوم ذو الحجمين الحبيبين) واغشية (TiO_2 (15.7 nm)/PVA and TiO_2 (45.7 nm)/PVA)، وقد أستخدم نسبة (0.5) غم من البوليمر و (0.01) غم من كلا الحجمين الحبيبين للمادة النانوية. استخدمت طريقة الصب لتحضير اغشية متجانسة على أطباق زجاجية. تم حساب كل معاملات حيود الاشعة السينية ، أقصى منتصف لعرض الحزمة ، معاملات ميلر، الحجم البلوري ، المساحة السطحية المحددة وكثافة الانخلاع. وتم بحث الطبيعة التركيبية للمواد والاغشية. وبينت النتائج أن حيود الاشعة السينية لبوليمر PVA هو ذو تركيب شبة بلوري وأن ثنائي أوكسيد التيتانيوم ذو الحجمين الحبيبين لها تراكيب بلورية; نوع (anatase). بينما المزيج بين هذه المواد أدى الى ظهور بعض الحزم البلورية في نموذج حيود الاشعة السينية لبوليمر PVA.

Introduction

The general chemical structure of PolyVinyl Alcohol (PVA) is shown in Fig. (1)[1].



Where R= H or$COCH_3$

Figure (1): Chemical structure of PVA polymer [1].

PVA is a polymer of great interest because of its Biomedical applications [2]. It has been applied in the industrial, commercial, medical, and food sectors and has been used to produce many end products, such as lacquers, resins, surgical threads, and food packaging materials that are often in contact with food [3]. PolyVinyl alcohol for food use is an odorless and tasteless, translucent, white or cream colored granular powder. It is most important soluble in water, Dimethyl Sulfoxide (DMSO), Ethylene Glycol (EG), and N-Methyl Pyrrolidone (NMP) [4]. Titanium dioxide belongs to the family of transition metal oxides. There are four commonly known polymorphs of TiO_2 found in nature: anatase (tetragonal), brookite (orthorhombic), rutile (tetragonal), and TiO_2 (B) (monoclinic). Besides these polymorphs,

two additional high-pressure forms have been synthesized from the rutile phase. These are TiO_2 (II) with the α-PbO_2 structure, TiO_2 (H) with hollandite, baddelleyite with ZrO_2, Cotunnite with $PdCl_2$ [5]. Among these unique properties, nanosized organic and inorganic particles are being producing for use in medical properties. Titanium dioxide (TiO_2) also known as titanium oxide or titanium IV oxide or Titania, is the naturally occurring oxide of titanium. It is a versatile transition-metal oxide and a useful material in various present / future applications related to catalysis, electronics, photonics, sensing, medicine, and controlled drug release [6]. Used chemical spry pyrolysis technique to prepare thin films of titanium dioxide TiO_2 pure and TiO_2: PVA polymer on glass substrate preheated at (350 ˚C) for TiO_2pure and at (160 ˚C) for TiO_2: PVA. With spray rate 3Sec. /1min, and thickness (250 nm). The investigation of (XRD) indicates that the structure of TiO_2 pure and TiO_2: PVA thin films are polycrystalline, and XRD investigation is anatase titanium dioxide. Where intensity of (101) is more than the intensity of (000), (200) and (105) for TiO_2 and TiO_2: PVA thin films. The optical properties measurement explains the effect of adding PVA on transmittance, absorbance, refractive index, absorption coefficient and electronic transitions of prepared thin films, their results observe that the filling of PVA generally increase optical properties [7]. Explained the effect of TiO_2 (5, 10 and 15 mg) nano-particles on optical, electrical and mechanical properties of poly (vinyl alcohol) (PVA) films. The un-doped (PVA) films show high transmittance in the visible region, and decrease with the increasing of TiO_2 [8]. Studied polyvinyl alcohol (PVA) doped with titanium dioxide nanoparticles at different weight percentage (1.25, 2.5, 5, 7.5, 10 TiO_2/PVA) are prepared using the sonification and casting techniques. The structural properties of those samples are examined by XRD, FTIR, and UV-Visible. The XRD pattern reveals that the amorphous domain in PVA polymer matrix increases with the raising of the TiO_2 content. The complexation of the dopant with the polymer is examined by FTIR studies. The absorption spectra of UV-Visible light shows irregular changes of the absorption for high doping samples in UV range (7.5, 10 TiO_2 /PVA). Absorbance, transmittance and reflectance spectra are used for the determination of the optical constants. The results indicate that the optical band gap is decreased with the increase of TiO_2 content, while the refractive index increases to high value for the composites of high dopant [9].

The aim of this work is to investigate the nature of the structural characteristics of PVA polymer, TiO_2 nanoparticles with two particle sizes (15.7 and 45.7) nm, TiO_2 (15.7 nm)/PVA and TiO_2 (45.7 nm)/PVA films that done by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) measurement.

Materials and Methods

Pure PVA and TiO_2 nanoparticles doped PVA films have been prepared by employing solution casting method. Hot distilled water (~55°C) (10 ml) was used to dissolve (0.5 g) from PVA is a granular powder with molecular weight (M_w=14000 g/mole) obtained from (BHD Chemicals Ltd). This solution was magnetically stirred continuously for (3 hrs.) until mixture became homogeneous viscous solution. Then it poured into glass petri dish with diameter (8 cm) and keeps under room temperature (~30°C) for (7 days) to evaporate all solvent slowly. In order to prepare TiO_2 nanoparticles/PVA composite films with two particle sizes for TiO_2 nanoparticles; (15.7 and 45.7 nm) obtained from (Intelligent Materials Pvt. Ltd. United States) and (HIMEDIA), respectively. The amount of powder for each particle size as used (0.01 g) with (10 ml) hot distilled water. (6 ml) of this TiO_2 nanoparticles solution was added to PVA solution to get 15.7 nm TiO_2/PVA an and 45.7 nm TiO_2/PVA films. X-Ray Diffraction (XRD) instrument is from type (SHIMADZU XRD – 6000) made in Japan, with following specifications are Target is CuK_α, wavelength is 1.5406 A, Current is 30 (mA) and Voltage is (40 KV) and Scanning Electron Microscopy (SEM) type (INSPECTS50) made in Holland. Mathematical definitions

The particle size is calculating by equation (1). The average grain size of all the samples was estimated from X-ray line broadening analysis by Scherer's formula [10]:

$$\boldsymbol{D = \frac{K\lambda}{\beta Cos\Theta}} \qquad (1)$$

Where (K) represents a Scherer's factor, normally taken as (0.94). λ is the X-ray wavelength, β is the value of the FWHM in degree unit and transform to radian by multiplying (π/180), θ is the Bragg's angle. Specific Surface Area (S) or (SSA) is the Surface Area (SA) per mass. Mathematically, SSA can be calculated using formula (2) [11]:

$$S=(6x10^3)/(D_p.\rho) \quad (2)$$

Where SSA & S are the specific surface area, D_p is the size (spherical shaped), and ρ is the density of TiO_2 (3.9 g/cm^3) and (4.23 g/cm^3) particle sizes (15.7 and 45.7) nm, respectively.

The dislocation density is the length of dislocation lines per unit volume of the crystal [12]. The dislocation density (δ) in the sample has been determined using equation (3) [13]:

$$\delta=1/D^2 \quad (3)$$

Results and Discussion

The X-ray diffraction of pure PVApowder is shown in Figure (2). The observation of the maximum intensity diffraction peak (331) at 2θ = 19.7167º corresponding d-spacing 4.49908 Å to the (110) reflection a plane which contains the extended planar zig-zag chain direction of the crystallites. That is indicate PVA has semi-crystalline nature [14]. Firstly; the peaks at 2θ less than (20º) are due to crystalline nature which may be attributed to intermolecular interaction of hydrogen bonding for PVA chains. Secondly; two small peaks at 2θ = 23.2148º, 17.3494º corresponding d-spacing 3.82848 Å 5.10727 Å, with intensities (73) and (54), respectively. These results are matching with results obtained from [7] and [9]. The value of particle size is calculated by equation (1) nearly (3.0543 nm). Table (1) illustrated some structural properties for pure PVA powder.

Table 1: XRD Parameters for Pure PVA Powder.

2θ(deg)	FWHM (deg)	Intensity (counts)	d (Å)
11.5143	1.45000	19	7.67902
14.5363	0.52000	11	6.08869
15.8327	1.30660	28	5.59294
16.4911	0.0000	41	5.37110
17.3494	0.0000	54	5.10727
19.7167	1.954	331	4.49908
23.2146	1.4934	73	3.82848
40.6984	1.9900	42	2.21516
42.3323	1.1200	17	2.13336

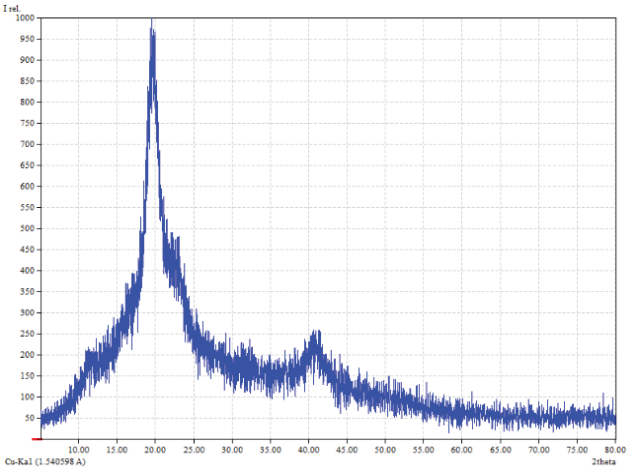


Figure (2): XRD pattern for pure PVA powder.

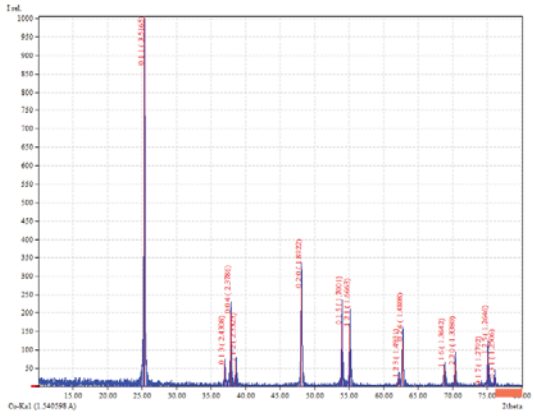
Table (2a): XRD Parameters for Pure TiO_2 (15.7 nm) Powder.

2θ(deg)	FWHM (deg)	Intensity (counts)	d (Å)	hkl	D(nm)	Sx10^6 (m^2. g^{-1})	□x10^6 (m^{-2})
25.3424	0.54100	285	3.51165	011	15.1	0.1018	4.385
36.9362	0.28000	16	2.43168	013	30.4	0.0505	1.082
37.8804	0.67000	50	2.37321	004	12.6	0.1220	6.298
38.7148	0.50000	12	2.32396	112	16.9	0.0910	3.501
48.0716	0.59500	77	1.89120	020	14.7	0.1046	4.627
53.9815	0.75000	39	1.69727	015	11.9	0.1292	7.061
55.0311	0.73000	39	1.66735	121	12.2	0.1260	6.718

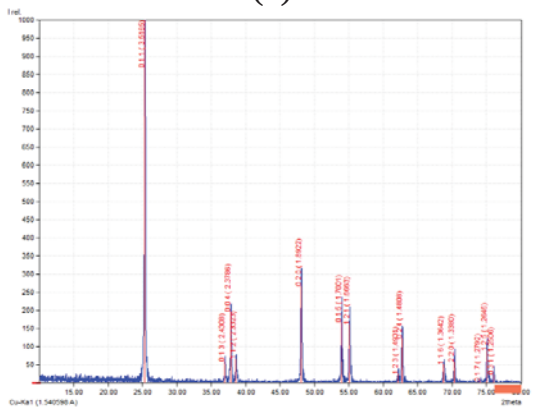
62.0836	**0.40000**	**12**	**1.49380**	**123**	**23.4**	**0.0657**	**1.826**
62.7034	**0.76000**	**28**	**1.48052**	**024**	**12.3**	**0.1250**	**6.609**
68.8616	**0.76000**	**10**	**1.36237**	**116**	**12.7**	**0.1211**	**6.200**
70.3212	**0.64000**	**12**	**1.33763**	**220**	**15.2**	**0.1011**	**4.328**
75.0799	**0.84000**	**16**	**1.26421**	**125**	**11.9**	**0.1292**	**7.061**

Table (2b): XRD Parameters for Pure TiO_2 (45.7 nm) Powder.

2θ(deg)	**FWHM (deg)**	**Intensity (counts)**	**d (Å)**	**hkl**	**D(nm)**	**Sx10^6 ($m^2 . g^{-1}$)**	**□x10^5 (m^{-2})**
25.3712	**0.21100**	**759**	**3.50773**	**011**	**39.5**	**0.0358**	**6.409**
37.0077	**0.19670**	**46**	**2.42715**	**013**	**43.0**	**0.0329**	**5.408**
37.8515	**0.2010□0**	**172**	**2.37496**	**004**	**41.9**	**0.0338**	**5.696**
38.6286	**0.18750**	**48**	**2.32895**	**112**	**45.9**	**0.0308**	**4.746**
48.0967	**0.19930**	**253**	**1.89027**	**020**	**44.6**	**0.0317**	**5.0272**
53.9434	**0.20180**	**159**	**1.69838**	**015**	**44.4**	**0.0319**	**5.0726**
55.1201	**0.21570**	**147**	**1.66487**	**121**	**42.2**	**0.0336**	**5.6153**
62.1691	**0.17900**	**25**	**1.49196**	**123**	**52.2**	**0.0271**	**3.6699**
62.7443	**0.20810**	**119**	**1.47965**	**024**	**45.1**	**0.0314**	**4.9163**
68.8009	**0.21860**	**45**	**1.36343**	**116**	**44.2**	**0.0320**	**5.1186**
70.3422	**0.19800**	**55**	**1.33728**	**220**	**49.9**	**0.0284**	**4.0160**
75.0910	**0.214200**	**85**	**1.26405**	**125**	**47.3**	**0.0299**	**4.4696**
76.0766	**0.186000**	**25**	**1.25011**	**031**	**55.0**	**0.0257**	**3.3057**



(a)



(b)

Figure (3): XRD Pattern for Pure TiO_2 nanoparticles powder with two particles sizes a-(15.7 nm) b-(45.7 nm).

The X-ray diffraction pattern of pure TiO_2 nanoparticles powder with two particles sizes are shown in Figure (3) (a) (b), respectively. Strong diffraction peaks at 25º, 48º and 37º indicating TiO_2 in the anatase phase, the intensities of XRD peaks of the sample reflects that the formed nanoparticles are crystalline [7,9]. The intensity is increased with decreasing the Particle size, the particle size is nearly (15.7 nm) for Figure 3a and (45.7 nm) for Figure 3-b. Table 2 (a) (b) illustrated some structural properties for pure TiO_2 nanoparticles with two particle sizes, respectively.

We conclude from table (2 A, B) the specific surface area (S) and dislocation density (□) are decreased with increasing the particle size of TiO_2 nanoparticles.

The X-ray diffraction pattern for (6 ml) TiO_2 (for two particles sizes (15.7 nm) and (45.7 nm))/PVA films are shown in Figure (4) (a)(b), respectively. From these figs., the effect of TiO_2 nanoparticles with two particles sizes on PVA structure still amorphous behavior with appear-

ing some crystalline peak with addition TiO_2 nanoparticles [7, 9]. The intensity is increase with increasing the particle size of TiO_2 nanoparticles and the particle size found by eq. (1) are nearly (17.0261, 79.4998) nm for TiO_2 (15.7, 45.7) nm/PVA, respectively. Table (4-5) (a) (b) which it emerged adding PVA polymer enhanced the structural properties of TiO_2 thin film.

Table (3a): XRD Parameters for TiO_2 (15.7 nm)/PVA Film.

2θ (deg)	FWHM (deg)	Intensity (counts)	d (Å)	D (nm)
13.3140	0.62800	98	6.64479	12.838
14.5000	1.00000	15	6.10385	8.0610
16.1722	0.66200	396	5.47629	12.269
19.1800	2.00000	143	4.62374	39.758
24.8216	0.82330	48	3.58413	9.974
43.7905	0.44760	81	2.06564	19.257

Table (3b): XRD Parameters for TiO_2 (45.7 nm)/PVA Film.

2θ (deg)	FWHM (deg)	Intensity (counts)	d (Å)	D (nm)
13.2065	0.61890	172	6.69864	127.53
16.0854	0.61950	595	5.50564	127.81
19.7000	0.00000	53	4.50285	0.0000
20.4000	1.30000	28	4.34989	6.2286
24.8025	0.75500	71	3.58685	10.8405
43.7164	0.41290	85	2.06897	204.59

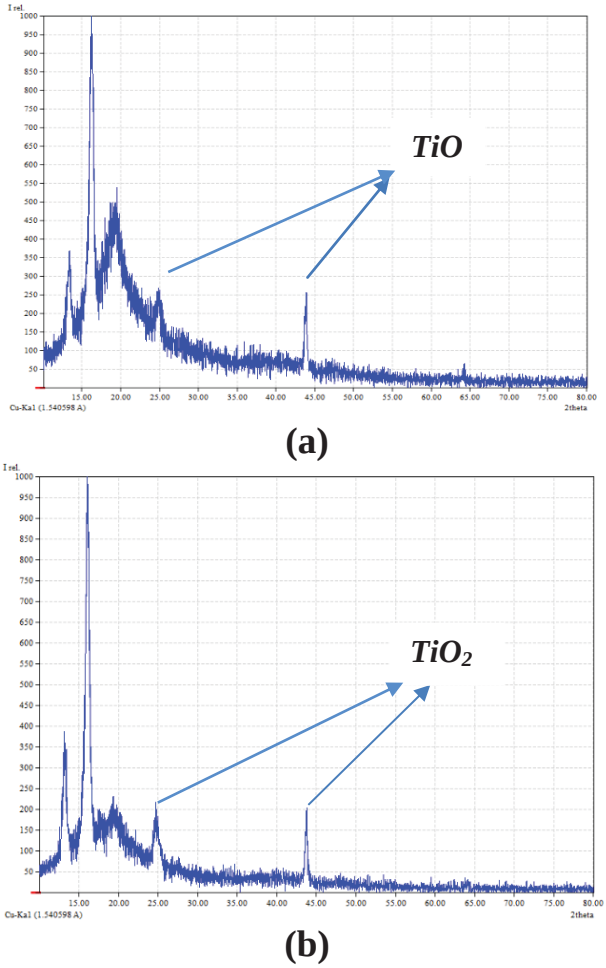
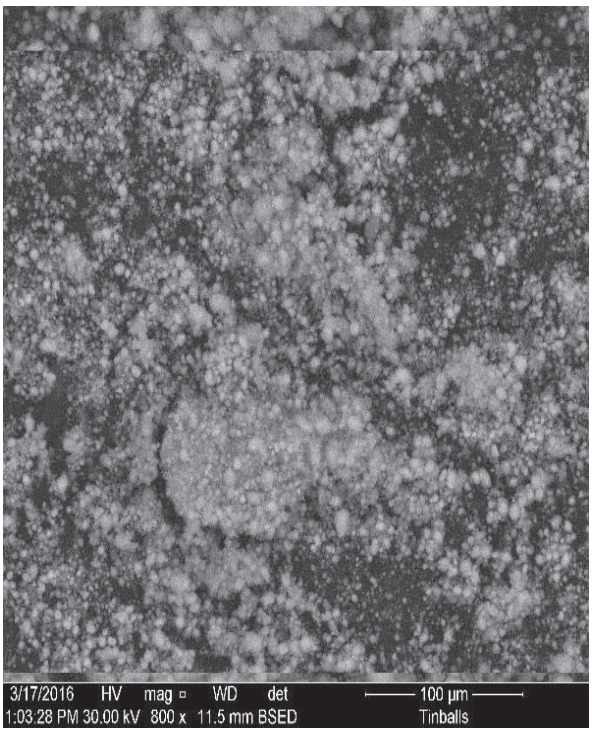


Figure (4): XRD Pattern for a- TiO_2 (15.7 nm)/PVA and b- TiO_2 (45.7 nm)/PVA Films.

The SEM images of TiO_2 at different magnification are shown in Figure (5) for TiO_2 (15.7 nm) and Figure (6) for TiO_2 (45.7 nm) which confirms that the TiO_2 nanoparticles are pseudo spherical in shape. It has been observed that TiO_2 nanoparticles are agglomerated to from clusters. The effect of increasing particle size of TiO_2 leads to form big agglomerated. This result is matching with [15].

Figures (7, 8) show micrographs of (6ml) TiO_2 nanoparticles with two particles sizes (15.7, 45.7) nm doped with PVA films, respectively. It can be seen that TiO_2 nanoparticles cover the surface of PVA films and emerge PVA particles to form white granule scattered randomly. The SEM image of TiO_2/PVA films shows the rough

surface with some gathering of TiO_2 nanoparticles in PVA, this result is matching with [8].



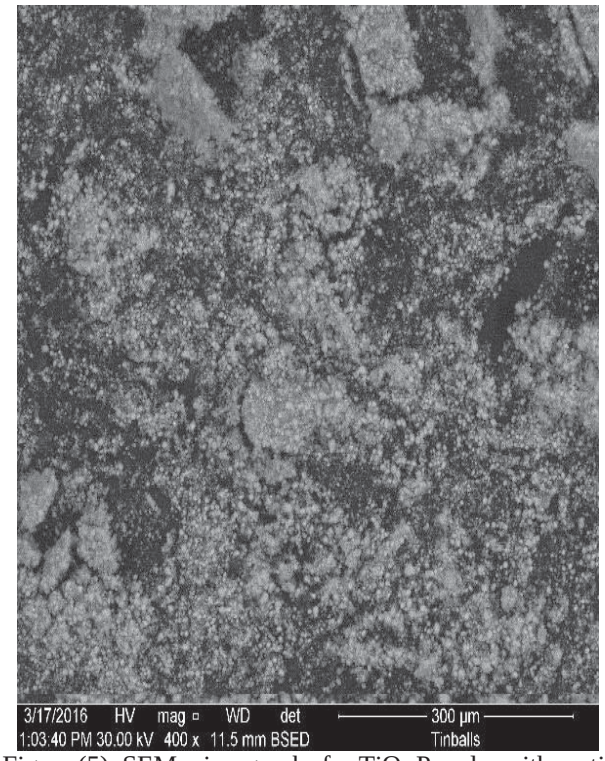


Figure (5): SEM micrographs for TiO_2 Powder with particle size (15.7 nm).

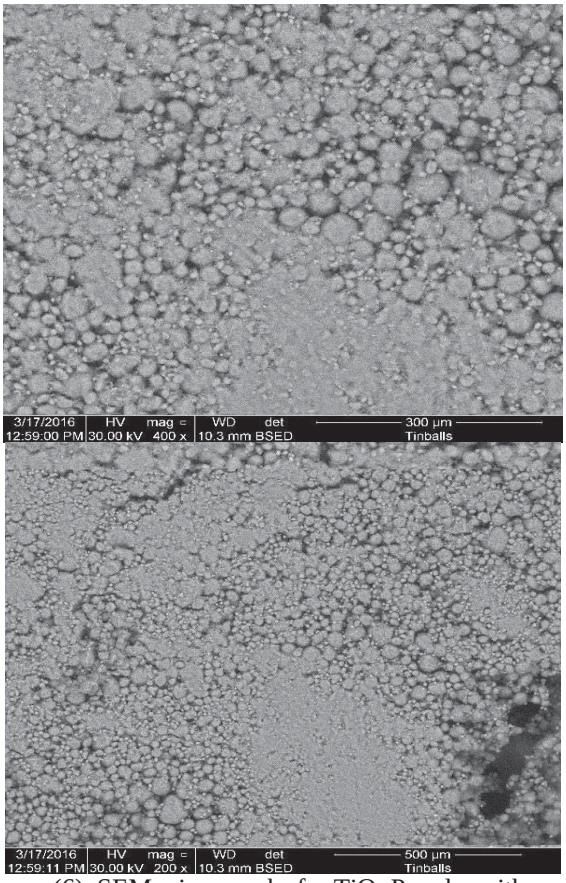


Figure (6): SEM micrographs for TiO_2 Powder with particle size (45.7 nm).

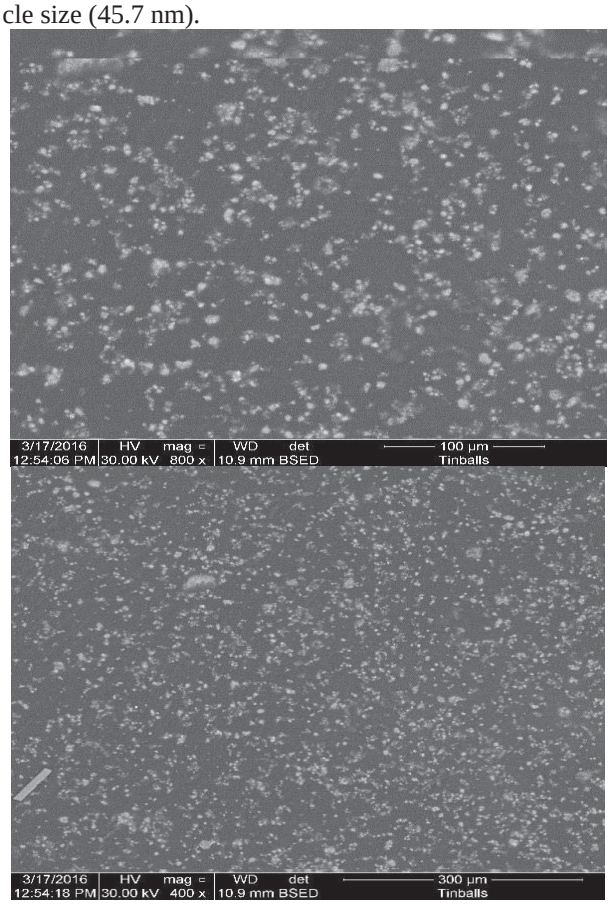


Figure (7): SEM micrographs for TiO_2 (15.7 nm)/PVA Films.

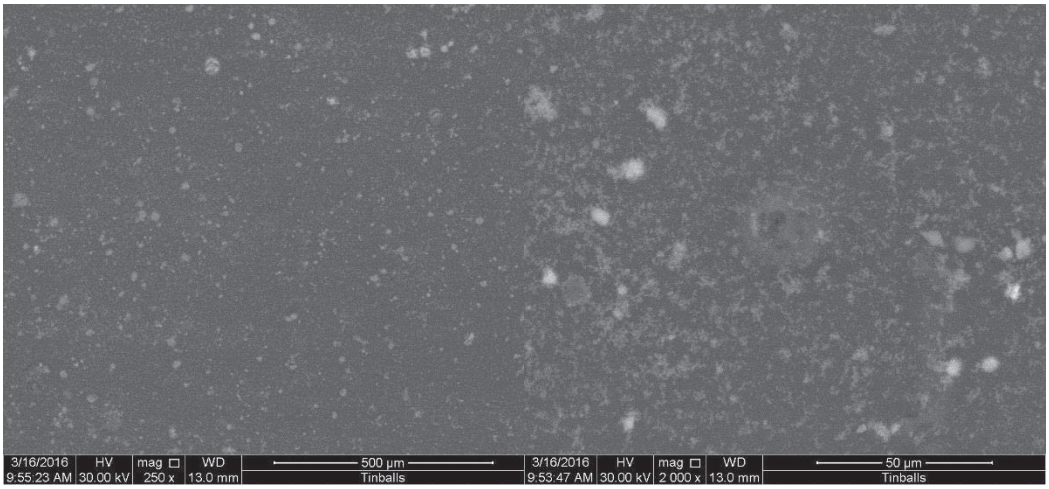


Figure (8): SEM micrographs for TiO_2 (45.7 nm)/PVA Films.

Conclusions

XRD parameters of materials and films calculated and have known the nature of the structural of materials and films. In spite of crystalline materials TiO_2 nanoparticles, the polymer still amorphous behavior with appearing some crystalline peak from these materials in it, the specific surface area (S) and dislocation density (□) are decreased with increasing the particle size of TiO_2 nanoparticles. The SEM showed crystalline structure of TiO_2 nanoparticles and matching with XRD results, The SEM image of TiO_2 /PVA films showed rough surface with some gathering of PVA polymer.

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