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Preparation and evalution water resistance, mechanical and morpholgical characteristics of PVA/SiO_2 nanocomposites for food industry applications

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Thin films prepared from Poly vinyl alcohol (PVA) and silica nanoparticles(SiO_2) by using solvent casting method have been studied as potential packaging materials. PVA/ SiO_2 nanocomposites were characterized by Fourier transform infrared (FT-IR), Scanning electron microscopy (SEM), Differential scanning calorimetry, atomic force microscopy (AFM), Water contact angle, Water absorption capacity **,**Water solubility ,and mechanical properties. The results showed that the mechanical properties such as (tensile strength, elongation at break ,modulus) increased with increasing nanoparticle content to7wt. % compared with pure PVA, while the mechanical properties decreasing with increasing SiO_2 content to 9 wt. % , but it remains higher than the matrix material, also an increase in the crystallinity with addition 7wt. % from SiO_2 which interpreted and supported the improvement of results of mechanical properties for nanocomposites PVA/SiO_2, but Crystallinity decreased to 0.012 with increase SiO_2 to 9 wt. %. The result of water contact angle showed the surface of nanocomposite films less hydrophilic. Result of FTIR showed that it does not create chemical bond between PVA and nanoparticles but only physical interaction. AFM measurements indicated a reduced the surface roughness with increase nanoparticles and was less roughness at percent 7wt. % SiO_2 .However, the roughness is increased at 9 wt. % due to agglomerate the nanoparticles. The SEM results showed the good desperation between PVA and nanoparticles.

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Keywords: Thin Film, Nanoparticle, PVA, Food packaging

1. Introduction

Food packaging is an important part of food industry, materials of food packaging must have adequate biodegradability, mechanical strength, antioxidant and antibacterial properties, these are properties are necessary for food safety and extending the shelf life of packaged foods . Presently, the materials used in food packaging are controlled by petroleum based plastic materials produced from fossil fuels because they are relatively cheap and suitable for use with good processing ability and durability [1].

The properties of the packaging materials have been improved using nanotechnology .Since the properties that important for food packaging application include barrier, mechanical, and thermal properties, a lot of research effort has been done within this area [2–8].Similarly, among others, active (antimicrobial/antioxidant) [9–11], antifouling [12,13],encapsulation [14], and sensing [15–17] .

In recent years, polyvinyl alcohol combined with nanofillers has received much attention due to the excellent properties of the nanoparticles. The thermal and mechanical properties of the nanocomposites were improved, due to the structure of nanoscale , the interactions between PVA matrix and nanoparticles, and surface properties of nanofillers.[18,19].Nano fillers such as (zinc oxide , titanium dioxide, silicate, nanocellulose, silver nanoparticles etc.) incorporated with biopolymers accelarate functions such as antimicrobial activity, oxygen scavenging and bio sensing properties and also improves mechanical and barrier properties [20]

Advance of antifouling or antimicrobial polymers indicates the antimicrobial effect and arrangement of biofilm.these materials either repel organisms (antifouling) or destroy microbes (antimicrobial) present near the surface.[21]

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Recently, the shelf life of the food has been increased through antimicrobial food packaging systems by destroying external pathogenic microorganisms Bio-nanocomposites that have antimicrobial activity are usually favorite due to high surface to volume ratio and increased surface reactivity of the nano-sized antimicrobial agents, this enables them to inactivate more microorganisms compared to bulk materials.[20]

(Jia et al.) used radical copolymerization of vinyl silica nanoparticles and vinylacetate to prepare nanocomposite from PVA and nano-SiO_2.The result show that improved thermal and mechanical properties compared to the pure PVA, due to strong interactions between nanoparticale and the matrix by covalent bonding. [22]

(Khankrua et al.) prepared nanocomposites from, PBS, PLA and PHBV with silica using twin-screw extrusion, the resulting show improvement in the mechanical at low silica content (0.1–0.5 wt%), while at high content, deteriorated of the mechanical properties due to agglomeration of the silica. [23]

(Mohaddeseh Kariminejad et al.) prepared the composite films from gelatin and polyvinyl alcohol and studied effects nano-SiO_2 on the structural and physicochemical properties of this films, the result showed the use of nano-SiO_2 led to improve properties film and the films can be made more effective as food packaging[24]

In this study silicon dioxide was chosen due to important applicability in both biological and synthetic materials, and it has an extremely large specific surface area, that leads to an enhanced reaction between the filler and polymer matrix in composites ,also the purpose of this study is prepare PVA/SiO_2 nanocomposite with better mechanical, morphological properties for food packaging application.

2. Experimental

2.1 Materials and Prepartion of The Nanocomposite

Polyvinylalcohol was obtained from Amir Kabir Company, Iran, and Nanoparticles of silica (Sio_2) that acquired from the Sinopharm Chemical Reagent Company,chain.

Thin film from polyvinylalcohol and nano-SiO_2 fabricated by solvent casting method, at first dissolved 10 grams from PVA in (100 ml) from distilled water, and stirrer by magnetic stirrer for 1 hr. with heating at 90 °C. Nano silica was dispersed in distilled water using ultrasonic device at 30% for 10 min and 40ºC. Then 10 grams of PVA is mixed with different proportions of nano silica(0, 5, 7, 9) wt.% and the solutions were stirred at 25°C for 1hr. , finally the resulting mixture poured onto glass plates (25 x25) cm and kept for 48 hr. to dry at 25ºC, the film peeled out from the plate to obtain a dried film.

3. Results and discussion

3.1. Water Absorption Capacity Test (Wa)

The study of (Wa) is necessry for food packaging applications.Water absorption capacity tests have been performed according to (ASTM standard D570-98). samples of all materials were cutting in size of 1.5× 1.5 cm2 ,pre-dried this samples in vacuum oven at 50◦C for 24 hr, and cooled to room temperature, then weighing to measure initial dry weight (Wo). The amount of water absorbed was calculated Where a known weight was taken from the dry polymer and immersed in distilled water at room temperature for 24 hours ,to make sure it reaches a state of equilibrium. Wet polymer filtered and Calculate the percentage of the amount of water absorbed using the following relationship:

$$W_a\,(\%) = \frac{W_t - W_o}{W_o} \times 100\% \qquad (1)$$

The value of (Wa) for pure PVA and PVA/ SiO_2 nanocomposite as shown in figure 1, the adding nano-fillers greatly reduced the dimensions of the films and reduced Wa ,this reduction in Wa attributed to incorporation SiO_2 created tortuous paths to prevent diffusion the water and interaction between the nanofillers and the matrix resulted in a reduced number of hydroxyl groups in the nanocomposite films.

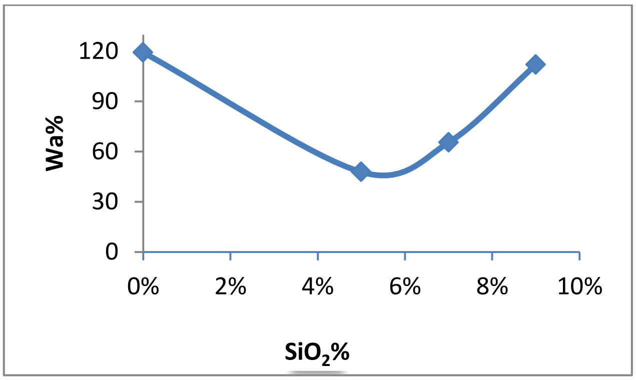


Fig. 1. Water Absorption (Wa)of pure PVA and PVA/ SiO_2 nanocomposite.

3.2. Water Solubility Test (w_s)

To determine the water solubility, all samples taken from the water absorption tests were used. Samples were dried in a vacuum oven for 24 hour at 65 °C, then cooled to room temperature and samples were weighed to obtain dry weight after immersion (Wd). Then, determine the percentage of solubility in water using the relationship:

$$W_s\,(\%) = \frac{W_o - W_d}{W_o} \times 100\% \qquad (2)$$

The value of (w_s) for pure PVA and PVA/ SiO_2 nanocomposite as shown in figure 2. Also, as in Water Absorption, the Water Solubility (W_S) decreases with the addition of nano-silica, this reduction in (w_s) due to SiO_2 is exhaustion free hydroxyl groups of matrix to form strong hydrogen bonds and reduced the number of free hydroxyl groups that react with water molecules .This result agreement with Zainab Waheed Abdullah[25].

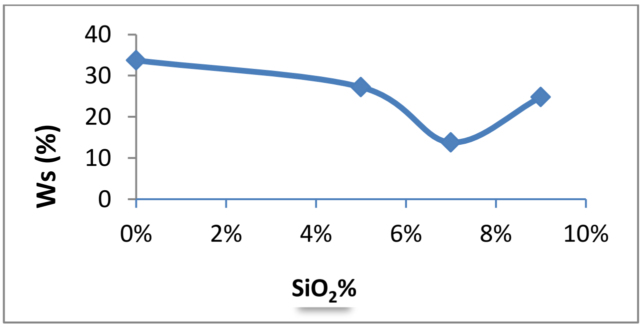


Fig. 2. Solubility of water for pure PVA and PVA/ SiO_2 nanocomposite.

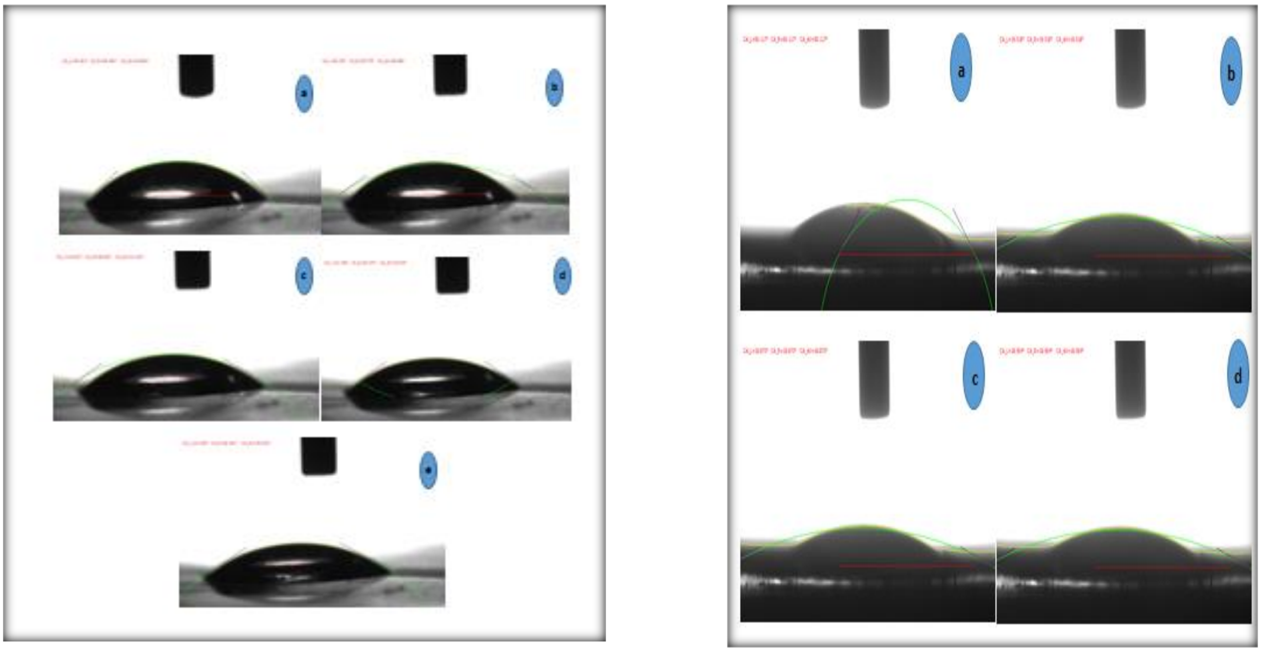
3.3. Contact Angle Test

Figure 3 shows an image of water contact angle measurements of pure PVA film and nanocomposite films, from figure 3 and table 1, there is an increase in the contact angles with water for nanocomposite films from 39.401° to 41.743° with increase SiO_2 percent from 0 to 9 wt. %,due to the presence of nanofillers led to the use of hydroxyl groups to form a hydrogen bond with the matrix with low number of hydroxyl groups , which leads to making the surface of the nanocomposite less hydrophilic. This increased in contact angles with water for nanocomposite films have been related with decrease in Wa and Ws.

The contact angle of nanocomposite decrease with increase time as show in table 1 such as at 7% SiO_2 the contact angle is (74.247°,60.122°,68.832°,58.699°,52.561°) at the time(0,15,30,45,60) sec respectively, while the contact angle for pure PVA is (39.401°, 30.341°, 33.627°, 31.795°, 31.764°) at the same time.

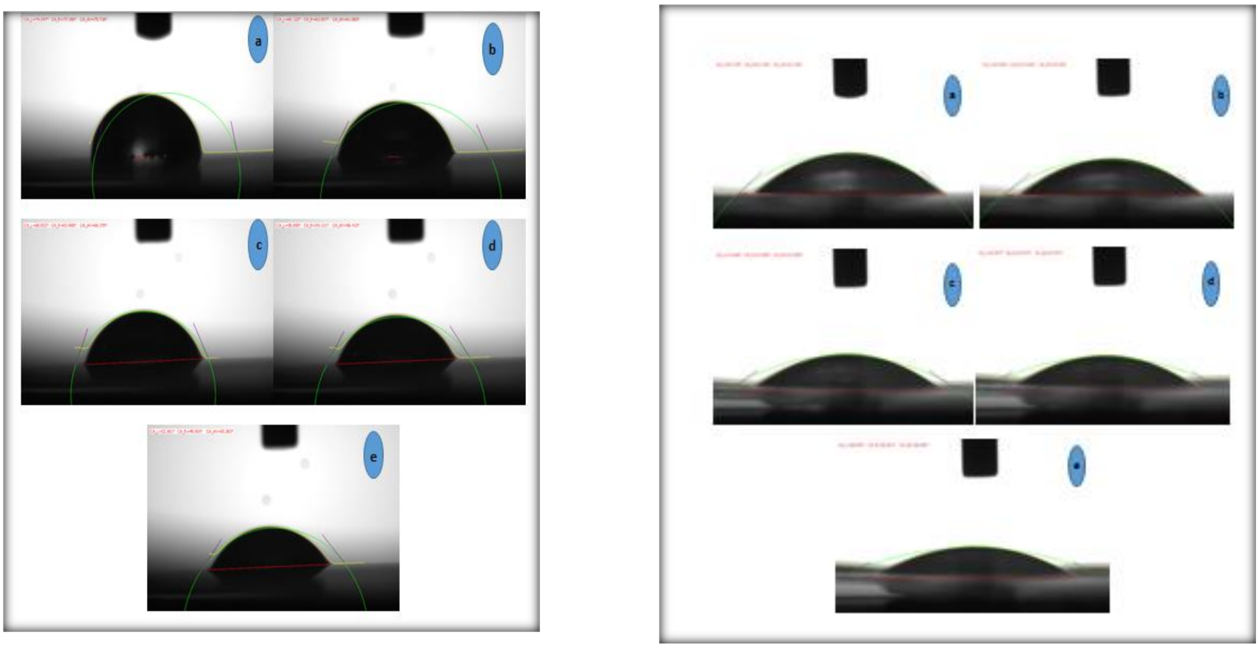
Table 1. Water Contact Angle For Pure PVA and Nanocomposite at Different Time

Time**(sec)**	Contact angle(°)			
	PVA	PVA/ 5% SiO_2	PVA/ 7% SiO_2	PVA/ 9% SiO_2
0	39.401°	50.117°	74.247°	41.743°
15	30.341°	19.518°	60.122°	37.025°
30	33.627°	18.873°	68.832°	31.650°
45	31.795°	18.504°	58.699°	27.977°
60	31.764°	0°	52.561°	26.061°



Pure PVA

PVA/5% SiO_2



PVA/7% SiO_2

PVA/9% SiO_2

Fig. 3. Contact angle Images of pure PVA and nanocomposite with different SiO_2*loading at time a) zero sec b) 15 sec c) 30 sec d) 45 sec e) 60 sec*

3.4. Uv-Vis Spectra Test

The light transmittance (T%) is one of the important features in food packaging , ultraviolet-visible (UV-vis) spectrometer was used to measure light transmittance of all samples in the range (190-1100) nm. Light transmittance curves for pure PVA, PVA /SiO_2 nanocomposites as shown in figure 4.

Pure PVA has a T% in the range 60-70%, while the addition of SiO_2 lead to decrease in T% due to the nanofiller resulting in an increase in light dispersion sites ,this decrease in T% is an advantage for food packaging applications because the enhanced UV-spectra results in protection of food from lipid oxidation and decolonization.

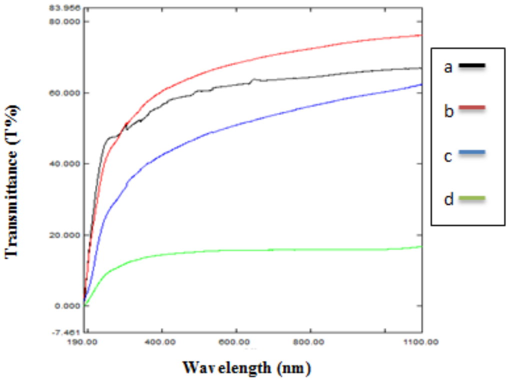


Fig. 4. UV-vis spectra of (a) pure PVA (b) PVA/ 5% SiO_2 *(c) PVA/ 7%* SiO_2 *(d) PVA/9%* SiO_2

3.5. Tensile test

In current study, the mechanical properties and behavior are studied by using tensile test. The tensile strength, elongation at break, and elastic modulus were measured according to ASTM (D882-09). The films were cut to strips with dimensions (50 mm x1 mm).moreover, the value of each property is the average of tested five samples [26].

Figures (5) and (6) show the tensile strength and elastic modulus for nanocomposite of PVA reinforced with different weight fraction of silica SiO_2. The results referred there are increase in tensile strength and elastic modulus with increased the percent of nano silica and reached to 80 and 143 MPa at (5 and 7) % SiO_2 respectively due to good adherent and bonding between PVA and SiO_2 nanoparticles. This result agreement with Xiangmin Xu. [27]. But, the tensile strength decreased at 9% SiO_2 due to the agglomeration of SiO_2, showing that The PVA do not stimulate to form silicon dioxide, which correspond with (Cheng et al., 2010; Chrissafis et al., 2008; Tang, et al., 2008) [28,29,30].

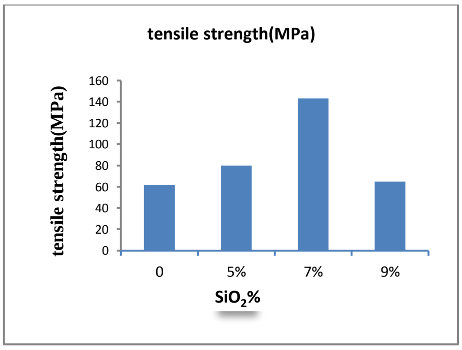


Fig. 5. The Tensile Strength of Nanocomposite of PVA as a Function SiO_2*%*

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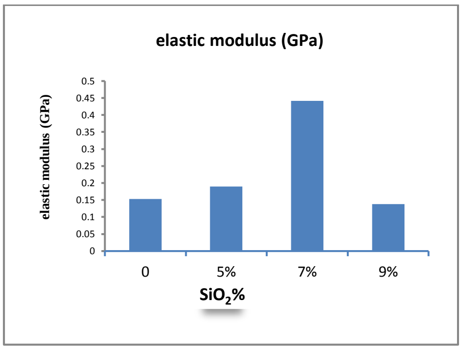


Fig.6. The Elastic Modulus of Nanocomposite of PVA as a Function SiO_2%.

the elongation of the nanocomposite increased in with increase the percent SiO_2% as shown in Figure 7 and the highest value of elongation is (1391%) at 7% SiO_2 due to good bonding, the physical adsorption and interactions of hydroxyl group between PVA and SiO_2 that support the transfer the force from matrix to nanoparticles [31]. While at 9% SiO_2, the elongation decreases due agglomerate which represent a defect restricted the elongation. [18]

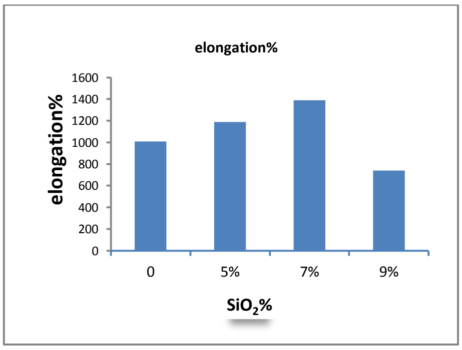


Fig. 7. The Elongation of Nanocomposite of PVA as a Function SiO_2%.

3.6. Hardness Test

The hardness increased with increased the weight fraction of SiO2% as revealed in figure (8) that can be attributed to enhance the strength and stiffness due to form the hydrogen bonding between PVA and SiO_2 [18], Moreover, the nanosilica was dispersed between the chains of polymer and obstructed the movement of chains thus the resistant of penetration and hardness was increased [32].

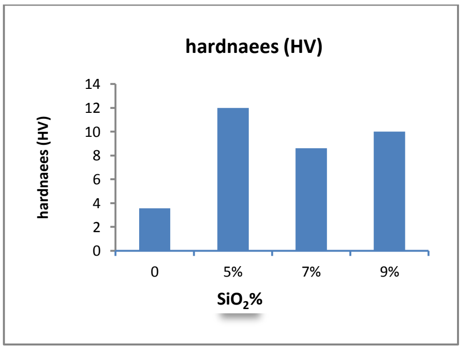


Fig. 8. The Hardness of Nanocomposite of PVA as a Function SiO_2%.

3.7. Differential Scanning Calorimeter (DSC)

DSC measurement was performed under an inert gas atmosphere ,weighted samples (8-10)± 0.5 mg mounted on aluminum vats and heated from (25 to 250 °C) at heating rate of (10 °C/min).

The degree of crystallinity was calculated in equation (3):

$$C\ (\%) = (\Delta H_f / \Delta H^\circ_f)*100\% \tag{3}$$

where:

ΔH_f : Melting Enthalpy of polyvinyl alcohol.

ΔH°_f : Melting Enthalpy of polyvinyl alcohol is 168 J/g at 100% crystallization.

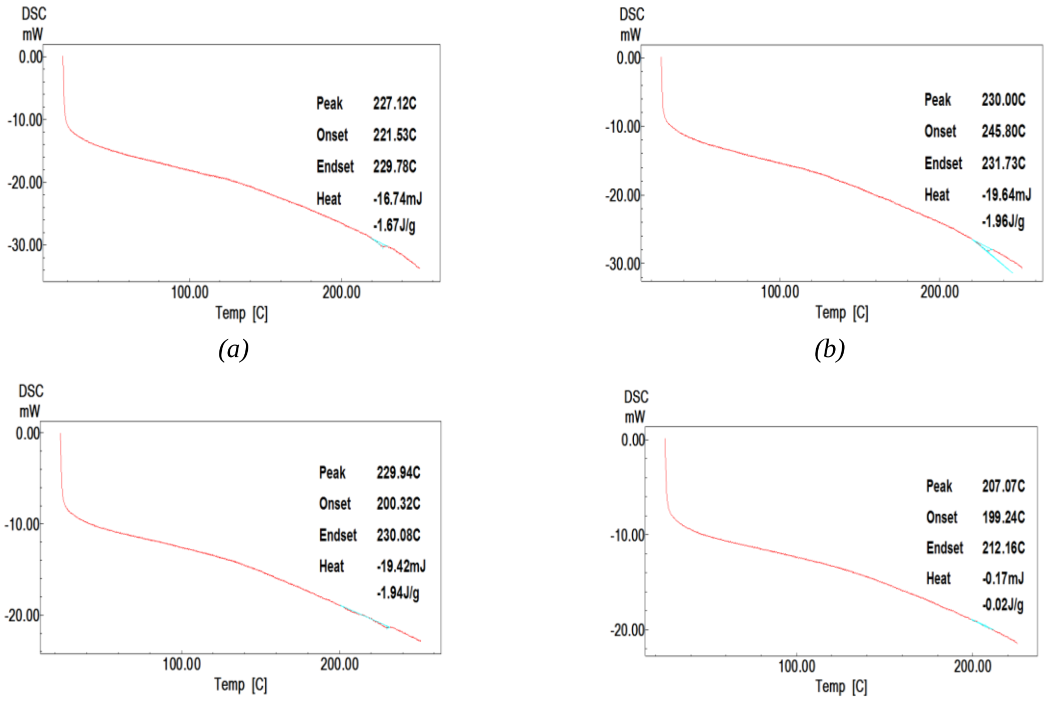
The degree of crystallinity and the melting temperature (T_m) for each samples shown in Table 2, these factors are used to study the effect of SiO_2 the thermal properties and crystallization degree of nanocomposite (PVA/SiO_2).

The Figure (9) referred that the melting temperature increased with increased the percent of SiO_2 due to good distribution of Nano silica that bind the chains of PVA which increased the resistance to melt. But, at 9% of SiO_2 the melting temperature is decreased due to agglomerate.

The degree of crystallinity increased with increased the weight fraction of SiO_2 due to uniform distribution of SiO_2 that don't restricted the motion of chains, which interpreted and supported the improvement of results of mechanical properties for nanocomposites PVA/SiO_2. While at 9% SiO_2 the degree of crystalline decreased due to agglomerate that prevent or restricted the folding of PVA chains.

Table 2. Melting Temperature, Enthalpy of melting and Degree of Crystallinity for nanocomposite as a function of SiO_2.

Samples	T_m (°C)	ΔH(J/g)	C %
PVA	227.12	-1.67	0.97
PVA +0.05 SiO_2	230	-1.96	1.16
PVA+0.07 SiO_2	229.94	-1.94	1.154
PVA+0.09 SiO_2	207.07	-0.02	0.012



(a) *(b)*

(c) *(d)*

Fig. 9. DSC Measurements for a. Neat PVA, b. PVA/ 5% SiO_2, c. PVA/7%SiO_2, d. PVA/9%SiO_2.

3.8. FTIR Analysis

Figure (10) show the FTIR spectrum for neat PVA and nanocomposite (PVA/5% SiO_2). The Table 3. Listed the most important bands of neat PVA and nanocomposite (PVA/5% SiO_2) that driven from Figure 6.and compare with the bands that mention in reference [34], It note the CH_2 stretching bands at 2767.80 cm^{-1} ,OH stretching at 3540 cm^{-1}, CH_2 bending band at 1565.27 cm^{-1}, and C=O stretching bands at 1665.5 cm^{-1}, moreover the bands are shifted toward left side at the spectrum of nanocomposite (PVA/5% SiO_2) and observed bands at 1047 cm^{-1} and 918 cm^{-1} for Si—Si bonds because the peaks were belonged to the Si–O–Si stretching vibration [33].

From the results, it can have concluded the are no create chemical bond between polymer and nanoparticles but only physical interaction. The shifting in bands indicated to good distribution of SiO2 within matrix (PVA)

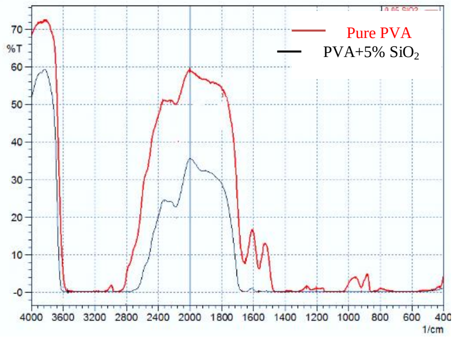


Fig. 10. FTIR spectrum for Neat PVA and PVA/5%SiO_2.

Table 3. the Transmission bands of the FTIR spectrum for Neat PVA and PVA/5%SiO_2.

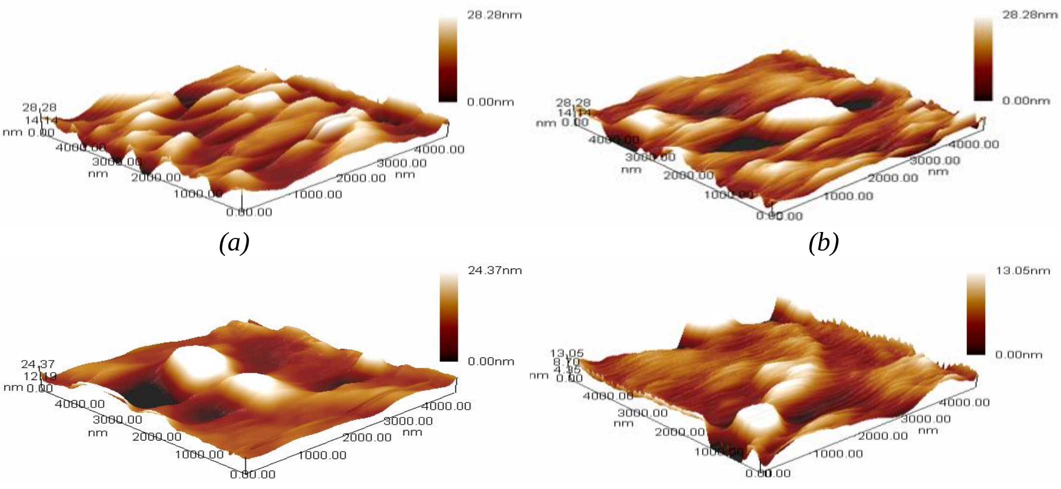
Types of bond	Standard PVA [Alireza Kharazmi,et.al][34]	Exp. PVA	PVA+ Sio_2
CH_2 stretching	2917	2767.80	2899
OH stretching	3280	3540	3534
CH_2 bending	1425	1565.27	1561.41
C=O	1690	1665.5	1653.92
Si–O–Si	_____	______	1047 918

3.9. Atomic Force Microscopy (AFM)

Figure 11. revealed the 3D topography for the surface of nanocomposite (PVA/SiO_2) that prepared with different weight fraction of SiO_2 (0,5,7 and 9) %. It shown that good distribution of SiO_2 within matrix and also the highest hills that have white color are good distributed and decreased with increased the weight fraction of SiO_2 due to good dispersed the nanoparticles, it fills the spaces between chains of polymer and indicate to interaction and wettability the Sio_2 within matrix. therefore, the surface roughness is decreased and the lower roughness at percent 7%. However, the roughness is increased at 9 wt. % due to agglomerate the nanoparticles.

Table 4. Roughness Average, Root Mean Square for Neat PVA and Nanocomposite.

Samples	Sa (Roughness average)	Sq. (Root Mean Square)
PVA	5.01	6.50
PVA/ 5% SiO_2	5.31	6.58
PVA/ 7% SiO_2	2.31	2.77
PVA/9% SiO_2	4.06	5.53



(a) (b)

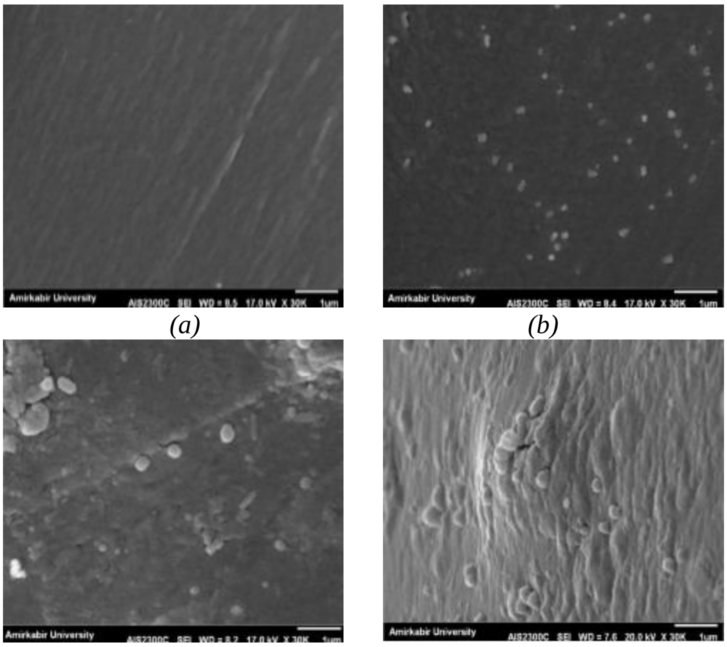
(c) (d)

Fig.11. AFM Topography of (a) Neat PVA (b) PVA/5%wt. SiO_2 (c) PVA/7 %wt. SiO_2 (d) PVA/9 %wt. SiO_2.

3.10. Scanning Electron Microscope (SEM)

The scanning electron microscopy can be used as a tool to study the microstructural of PVA and the changes that accrue at reinforce with different percent of Nano SiO_2

From Figure 12. The microstructure of Neat PVA shown in **a** which referred to smooth surface and free from any defect and voids, moreover, the microstructure of nanocomposite that shown a good distribution and adherent of SiO_2 by PVA which enhanced the transfer of load from matrix to nanoparticles and support the results of mechanical properties that shown above. However, when reinforced with 9% SiO_2 there are agglomerates of nanoparticles observe in **d** which explain why the mechanical properties are decreased at this percent.



(a) (b)

(c) (d)

Fig. 12. Scanning Electron Microscopy Images of (a)Neat PVA, (b)) PVA/5% SiO_2 ,(c) PVA/ 7% SiO_2, (d) PVA/ 9% SiO_2

4. Conclusions

Thin films from PVA and different concentration (0,5,7,9) wt % nano-SiO_2 were prepared using solvent casting method. The tensile properties such as tensile strength and elongation at break and modulus of the PVA/ SiO_2 nanocomposite increase with increasing nanoparticles percent to7 wt. % . The tensile strength value increases from 62 MPa of neat PVA to 143 MPa at 7 wt % nano-SiO_2, but the mechanical properties of the films decrease with increasing nano-SiO_2 to 9 wt. %.

The AFM shown that the surface roughness is decreased with addition nano-SiO_2.The degree of crystallinity increased with increased nano-SiO_2 content to 7wt. %, While at 9% SiO_2 the degree of crystalline decreased due to agglomerate.the microstructure of nanocomposite that shown a good distribution and adherent of SiO_2 by PVA which enhanced the transfer of load from matrix to nanoparticles and support the results of mechanical properties. The water contact angle increased with increased SiO_2 content which make the surface of nanocomposite films are less hydrophilic, this increase in the water contact angle is related with reduction in Wa and Ws.

From the results of this study, adding a low content from Silica nanoparticles improve the thermal and mechanical properties of polyvinylalcohol, these properties of the film enable it to be used in food packaging applications.

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