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Effect of SiO_2 particles on the biodegradability of starch/PVA blends

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Abstract

The present work aimed to study the SiO_2µPs, and NPs effect on the biodegradability of St/PVA blends. The samples were prepared by casting method as PVA, St/PVA blends with different concentrations (30, 40, 50, and 60 %). FTIR test was carried out for the samples preparation. The results proved some changes which might be related to changing in crystallinity of St/PVA matrix as well as physical incorporation of SiO_2 µPs, and NPs addition. The enzymatic test and water uptake results proved that increase in weight loss with increases of starch ratio. The lowest weight loss was PVA; the highest weight loss is 60% St/PVA whereas the lowest weight loss is 30%St/PVA for blends involved. SiO_2µPs (753.7 nm), and NPs (263.1 nm) were added at different concentrations (1.5, 2, and 2.5 %). 1.5% SiO_2 µPs, and NPs were the lowest weight loss then it was increased by SiO_2µPs, and NPs addition. The samples were investigated with optical microscope. It was concluded that the samples involved could be used as packaging materials for medical application and its degradation could be controlled by SiO_2µPs, and NPs addition.

Key words
PVA, corn starch, SiO_2, biodegradability, α-amylase.

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تأثير دقائق SiO_2 على التفكك الاحيائي لخلائط Starch /PVA

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الخلاصة

يهدف هذا البحث الى دراسه تاثير NPs و SiO_2µPs على التفكك الاحيائي لخلائط St/PVA. حضرت النماذج بطريقه الاذابه كنماذج منPVA وخلائط St/PVA بمختلف التراكيز (30, 40, 50, 60 %). اجري فحص FTIR على النماذج مدار البحث. اظهرت النتائج بعض التغيرات ذات العلاقة بتغير البلوريه في اساس starch/PVA اضافه الى المساهمه الفيزياويه الناجمه عن اضافه NPs و SiO_2µPs. اظهرت نتائج الفحوصات الانزيميه و الامتصاصية زياده في الامتصاصيه و الفقدان بالوزن بزيادة نسبه النشا. ان اقل امتصاصيه وفقدان بالوزن كانت ل PVA، في حين اعلى امتصاصيه و فقدان بالوزن كانت ل 60%St/PVA و اقل امتصاصيه و فقدان بالوزن كانت ل 30%St/PVA بالنسبه الخلائط مدار البحث. تم اضافت NPs (263.1 nm) و SiO_2µPs (753.7 nm) بمختلف التراكيز (1.5, 2, 2.5 %). حيث ان NPs وSiO_2µPs 1.5 اعطى اقل امتصاصيه و فقدان بالوزن ثم ازداد بزيادة نسبة NPs و SiO_2µPs. فسرت النتائج باستخدام المجهر الضوئي. نستنتج بان نتائج مدار البحث يمكن استخدامها كمواد تعبئه وتغليف للتطبيقات الزراعيه و الطبيه ويمكن السيطره على التفكك من خلال اضافه NPs و SiO_2µPs.

Introduction

Biodegradable polymers are interesting material because of their probability to save the environment through reducing non-biodegradable synthetic plastic waste [1-3]. It is very important to develop several materials that can biologically degrade to reduce the pollution. These materials are not only suitable for daily life but also reducing the environmental pollution. Biodegradation include enzymatic and chemical degradation via living microorganisms [4, 5]. PVA is a polymer consists of many hydroxyl groups, with very good properties, such as poor permeability, water soluble, good water absorption capability, and used in various industrial [6-9]. Starch is a semi-crystalline polymer stocked in granules as corn, rice, and potato. It is composed of amylose and amylopectin. The amounts of amylose and amylopectin depend on the source of plant. Corn starch granules generally consist of (70 %) amylopectin and (30 %) amylose [10, 11]. Both of them are easily degradates by enzymes. Enzyme of α-amylase is derived fundamentally from (Bacillus licheniformis), (Bacillus amyloliquefaciens), and (Aspergillus oryzae). The studies indicate that the addition of SiO_2 particles can improved the performance of PVA/Starch blend. The blends of starch/ PVA showed excellent compatibility [12, 13]. These blends are one of the most common biodegradable materials. It's widely used in agricultural and packaging applications [14]. Zainab Waheed and et al [15] investigated the polymer blend and polymer nano composite that based on (PVA) and studies the Structural properties, barrier, mechanical, and thermal properties, as well as biodegradation of these material. Mohammad Taghi T. and Zahra A. [16] studies PVA/Starch blend and hydrolyzed it by α- amylase at two temperatures 25 ^oC and 37 ^oC for 72h and found that after 72h the losing mass is nearly neglected. Harith I. J. and et al. [17] prepared a blend of PVA/Starch at different concentration of PVA show that with increase in PVA ratio the weight loss decreased, and by increase the immersion in enzyme, water, and soil time; the weight loss increase.

Experimental part

Material

The materials that used in this research were a white powder of poly vinyl alcohol (PVA), from Barcelona Espana (Didactic) with purity of (99.9 %). A white powder of corn starch (St) from spain (panreac), a white powder of SiO_2 µPs (753.7 nm), and NPs (263.1 nm) from china, distil water to dissolve the PVA, And a beige powder of alpha amylase source (Aspergillus oryzae) from England.

Sample preparation

Purified polymer (PVA) (10 g) was dissolved in (100 ml) of distilled water in water bath. The solution was mixed by using magnetic stirrer. The stirring process was done for 1 hour, raising the temperature gradually from room temperature (20) ^oC to (90) ^oC and then cooling the solution gradually to room temperature with stirring. Then the solution was curing on glass plate for 24 hour, after that it can be removed using tong or needle. In order for St/PVA blend films, the (PVA) was dissolved as previous step and starch was added in different ratio (30, 40, 50, and 60 %) at (90) ^oC, then cooling the solution to the room temperature with stirring till get homogeneous solution. Curing process was obtained by pour the solution on glass plate to curing for 48 hour. Solution of (30:70) St/PVA ratio was mixed with silicon dioxide (SiO_2) powder at (90) ^oC for preparing SiO_2/St/PVA films then cooling to room temperature. Silicon dioxide was adding in two particle size micro particle (SiO_2 µPs), and nano particle (SiO_2 NPs) in different ratio (1.5, 2, and 2.5), to study the effect of particle size on the blend.

Testing technique

Absorption test

This test was applied on a square sample 3x3 cm. Samples were weighted using four digital balances 10^{-4}, to obtained the dry weight (Wdry), then it immerged in a distilled water for 1to 10 min, after immersion, the samples removed from water to take its wet weight (W wet). Weight gain of samples was calculated using equation below:

$$\text{Weight gain \%} = (W_{wet} - W_{dry}) / W_{dry} \times 100 \qquad (1)$$

Enzymatic test

This test was applied on a samples with a dimension of 3x3 cm, and then the weight was done using four digital balances 10^{-4} (dry weight). The enzyme was prepared by mixing α-amylase from (Aspergillus oryzae) in distilled water in a ratio (1mg/1ml). With enzyme activity 1750 U/g, and PH value 7. The samples and mixture were immersed in a beaker then put in a magnetic stirrer were stirred at low speed in room temperatures for 10 min. Then the samples removed from the mixture and washed by water, then dried at 90 ^{o}C for 1 hour and weight (wet weight). The enzymatic degradation calculated from equation:

$$\text{Weight loss (\%)} = (W_{dry} - W_{wet}) / W_{dry} \times 100 \qquad (2)$$

Fourier Transform Infra-Red (FTIR) spectroscopy

It is a technique used the vibration action of molecules when exposed to infrared IR radiation. The use of IR spectroscopy comes from light with specific molecular vibrations interaction. FTIR analysis was carried out using "SHMADZU-8400S" FTIR spectrometer (Japan) in the range of (400-4000 cm^{-1}). The sample was place on a private FTIR holder so that the reconstructed beam is directed through the samples and fixated onto the detector. The resulting diagram give a curve explain the relationship between the wave number in the x-axis, and transmission % in y-axis.

Optical microscope

Optical microscopes are widely used for sample texture examination because of its low price, easy sample preparation and simply use the device. It is used to study cracks, air bubbles and deformation in samples surface. The morphology of PVA, St/PVA blend, µPs, and NPs SiO_2/St/PVA films were studied by using Optical microscope from Carl Zeiss Company, with magnification X100 (100 times magnified).

Results and discussion

Uptake water study

Figs. 1 to 3 show the starch content effect on the water absorption of starch/PVA films at different concentration (30, 40, 50, and 60) %, and SiO_2 µPs, and NPs effect on 30 % St/PVA blends films at different concentration (1.5, 2, and 2.5) %. The results proved that (dissolving time) of St/PVA blend films decrease with starch ratio increase; that was attributed to the (hydroxyl groups) of PVA [18, 19]. However; the intermolecular and intra-molecular hydrogen bonds in hydroxyl groups of PVA, and starch enhanced the solubility process of St/PVA in water. The films immerged in water caused in hydrogen bond break and increased its solubility in water; the result was in a good agreement with D Yu [20]. The films solubility increases with (citric acid contents) in blends. In general, the film solubility was attributed to components of interaction energy, dispersion force, acid base component, as well as hydrogen bonding characteristic that was in a good agreement with thawied and comyn, [21, 22]. The polymer solubility in solution depends on many factors molecular weight, material addition that is in a good an agreement with Schmaljohas and Jamel [23, 24]. The water absorption capacity and degradability of most important in biodegradation materials; the starch is sensitive material to the water and thermo plastic material so this property effected in mechanical properties of the blends involved. Fig. 1 show the typical marine; it begin weight gain, steady absorption; the slowly water absorption. St/PVA is not suitable to make blend because of high hydro philicity, and improvement in water resistance is necessity. Therefore; SiO_2 µPs, and NPs were used at different concentration to improve the properties of St/PVA blend films. The results showed maximum water absorption for 60% St/PVA (681 %); whereas for 30% St/PVA was (407 %); 30% St/PVA blend films was modified with µPs, and NPs SiO_2 addition; it was found that 1.5 % SiO_2 (µPs, and NPs) give the lowest water absorption at about (250 %), and (220 %) irrespectively. SiO_2 µPs and NPs participate in intermolecular bond interactions with starch and PVA, molecules which reduce the water absorption by St/PVA blends films [25].

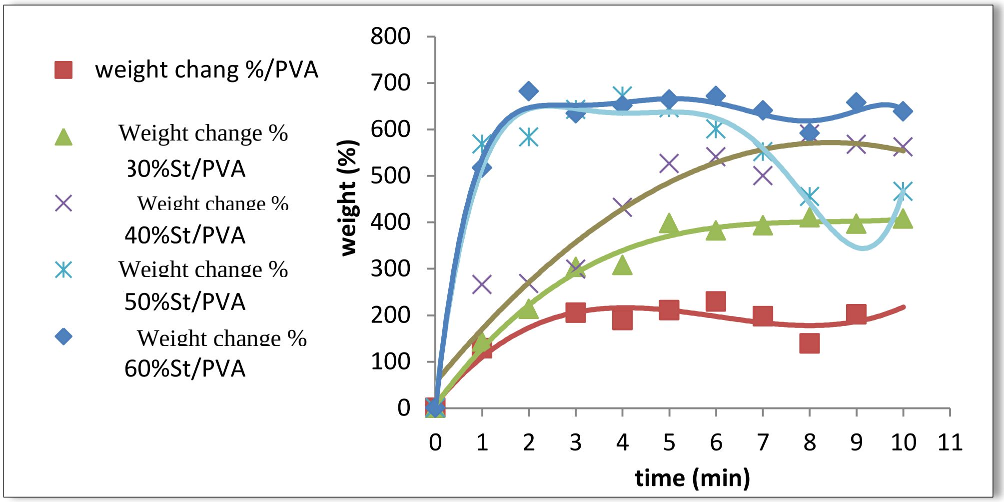


Fig. 1: Water absorption of St /PVA blend film.

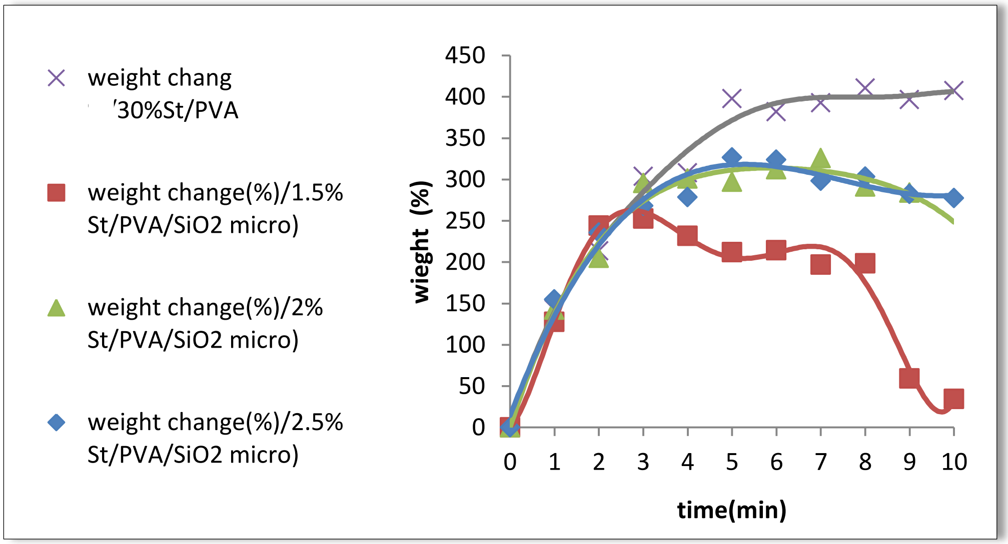


Fig. 2: Water absorption of micro SiO_2/St/PVA blend film.

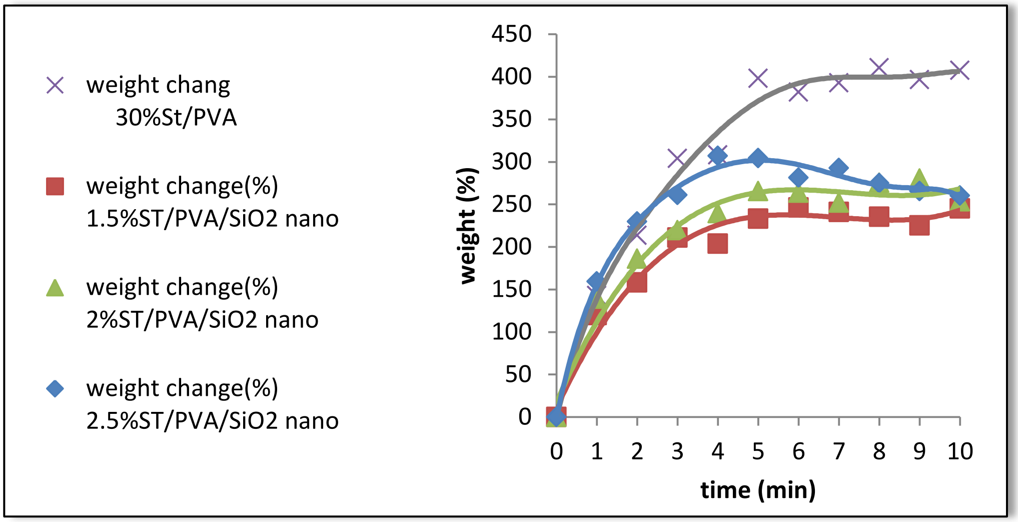


Fig. 3: Water absorption of nano SiO_2/St/PVA blend film.

Enzymatic degradation study

It was seen that the degradation rate of pure (PVA) was lower than (St/PVA) blend films at different concentration (30-60 %); this was attributed to (St/PVA) films absorbing more of amylase solution than the pure (PVA). The excess of (-OH) group in starch, which suffered the penetration of α-amylase into St/PVA blend films which enhanced the amylase attack on the starch; so the films will absorb more of enzymatic solution at starch content increased [17, 26].

Fig. 4 was done for 30% St/PVA blends, which modified by (SiO_2) µPs, and NPs with different concentration (1.5, 2, and 2.5 %). The results proved that (SiO_2) µPs, and NPs addition modified the enzymatic degradation rates of (St/PVA) blend films and lower it; so it would be more compact [25]. SiO_2 µPs and NPs from a dense structure between starch and (PVA) as a result (SiO2 /St/PVA) would be more compact; then the diffusion of α-amylase in the blend was reduced [25]. It was found that 1.5 % SiO_2 µPs, and NPs addition have the lower biodegradation rates; which attributed to decrease in crystanility by increase SiO_2 ratio and lower the composite compact [27], Figs. 5-7.

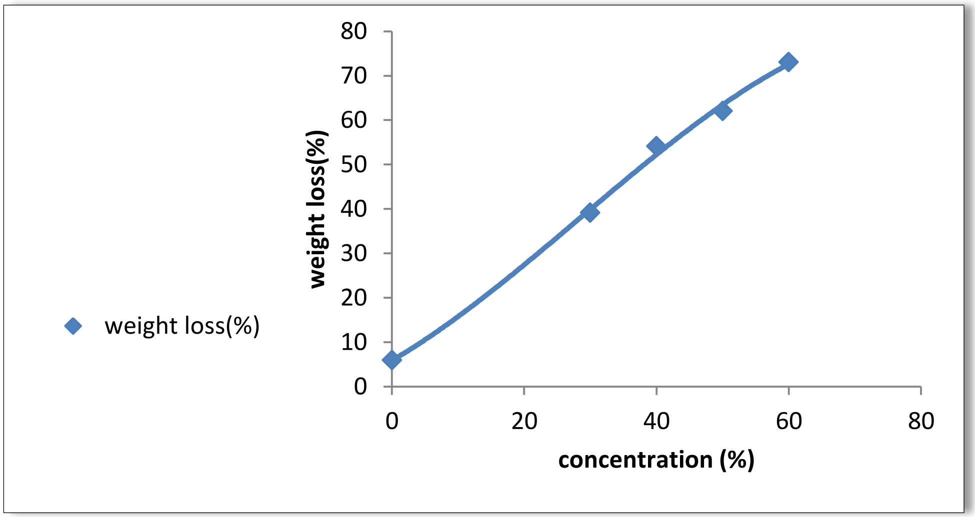


Fig. 4: Enzymatic degradation of starch/PVA blend films

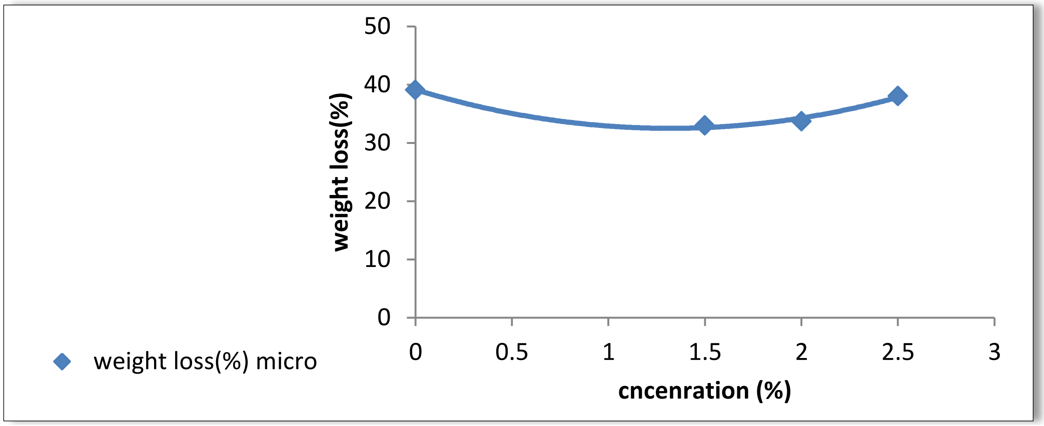


Fig. 5: Enzymatic degradation of micro SiO_2/St/PVA blend films.

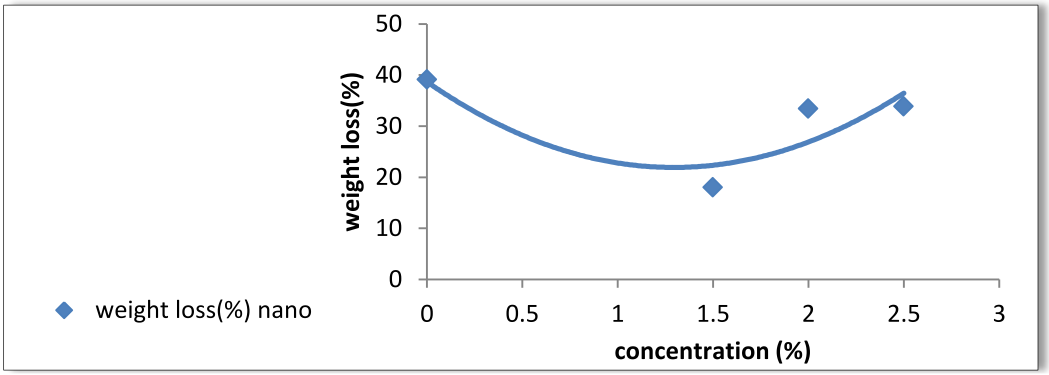


Fig. 6: Enzymatic degradation of nano SiO_2/St/PVA blend films.

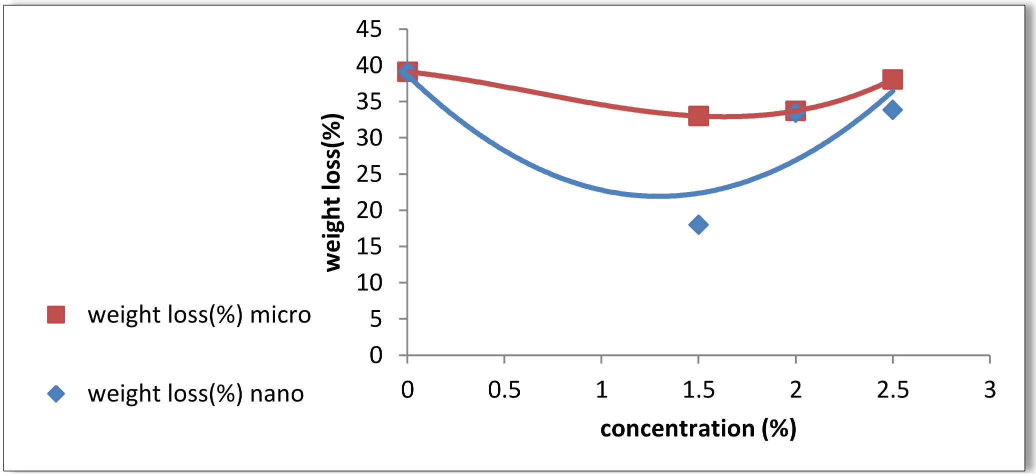


Fig. 7: Enzymatic degradation of SiO_2/St/PVA blend films.

FTIR Analysis

There were five main regions in FTIR spectra:-

a) Stretching- vibration of (OH) groups between (3100-3600 cm^{-1}).

b) Stretching- vibration of (C=O) between (1550-1750 cm^{-1}).

c) Stretching- vibration of (C=C) within range of (1550-1610 cm^{-1}).

d) Stretching- vibration of (C-O)at about of (880-1259 cm^{-1}).

e) Stretching- vibration of (C-H) at about of (1429-1465 cm^{-1}).

The broad band in the region of (3390-3400 cm^{-1}) was due to the hydroxyl stretching and the band in the region of (2929 cm^{-1}) was due to (CH_2) asymmetric and symmetric stretching vibration and the band (1429-

1465 cm^{-1}) was associated to (CH_2) bending vibration [16, 28]. The PVA FTIR spectrum shows appearance of bands at (611.43 cm^{-1}), and (850.61 cm^{-1}) were due to (C-H) out of phase bending; the band at (1093.54 cm^{-1}) was attributed to (C-O) bond stretching and band at (1435.04 cm^{-1}) corresponded to bending vibration of ($CH-CH_2$) which certified basic carbon skelton of PVA [29]. The appearance of the bands at (1375.25 cm^{-1}) was attributed to (CH_2) bending and the bands at (1735.93cm^{-1}) was due to (C=O) stretching [30, 25]. It was found bands at (2939.52 cm^{-1}) which was attributed to (C-H) elephatic stretching; and bands at (3388.93 cm^{1}) was due to hydroxyl groups stretching [31]. Starch spectrum proved bands within range to (574.79-1082.07 cm^{-1}) corresponded to (C-O) bond stretching. The band at (1641.42 cm^{-1}) was the feature of lightly bond water in starch. The appearance of the bands at (2927.94 cm^{-1}) was due to bending vibration of (C-H), and the bands at (3390.86 cm^{-1}) were attributed to hydroxyl group stretching [32]. Fig. 8 shows the FTIR spectra of St/PVA blends at different concentration (30-60 %). It was seen the physical mixing and chemical reactions caused change in FTIR characterizes; it was seen new bands within range of (1649-1718 cm^{-1}). Were attributed to starch addition and caused by (C=O) stretching; the results proved bands shifting toward the longer (wave numbers). These results proved that the mixing process was carried out successfully, that was in a good agreement with Elisabeta and Esraa [33, 34]. After starch addition; it was seen a broad band at (3415.93 cm^{-1}) which was attributed to hydroxyl group stretching; and bands at (1085.92 cm^{-1}), and (1259.52 cm^{-1}) of attributed to (C-O) stretching (C-O-H). The appearance of the bands at (848.68 cm^{-1}) was also attributed to the starch addition, the results in a good agreement with [34, 35]. Fig. 9 and 10 show the FTIR spectra after SiO_2 µps, and Nps addition at different concentration (1.5, 2, and 2.5 %) the results proved some changes which might be related to changing in crystallinity of the St/PVA matrix as well as physical incorporation of SiO_2 µps, and Nps addition. It was found appearance of bands around (556-579 cm^{-1}) for spectra of St/PVA films contains SiO_2 µPs, and NPs; which was attributed to possible interaction between SiO_2 and St/PVA blend though hydrogen bonding [36]. The blends (1653-1718 cm^{-1}) indicated to the bond water in starch that formed hydrogen bonds. The bands located at (1429.25-1486.26 cm^{-1}) and (842.89 cm^{-1}) were assigned to vibration associated with the (CH_2) group. The band at (1020-1027 cm^{-1}) was related to (C-O) bond stretching of (C-O-C) group in a hydrogelocose ring. The (C-O) band stretching of (C-O-H) group. It was seen at (1151.5 cm^{-1}) in 60% St/PVA that was in a good agreement with Ahmet [29]. Table 1 shows the FTIR-characteristic.

Hydrogen 3100-3600	C-H Stretch Aromatic 2800-3060	C-H Stretch Alphatic 2800-3000	C=O Stretch 1550-1750	CH2 Bended 1300-1380	C-O Stretch 880 - 1259	Si-O-C Stretching 570-970

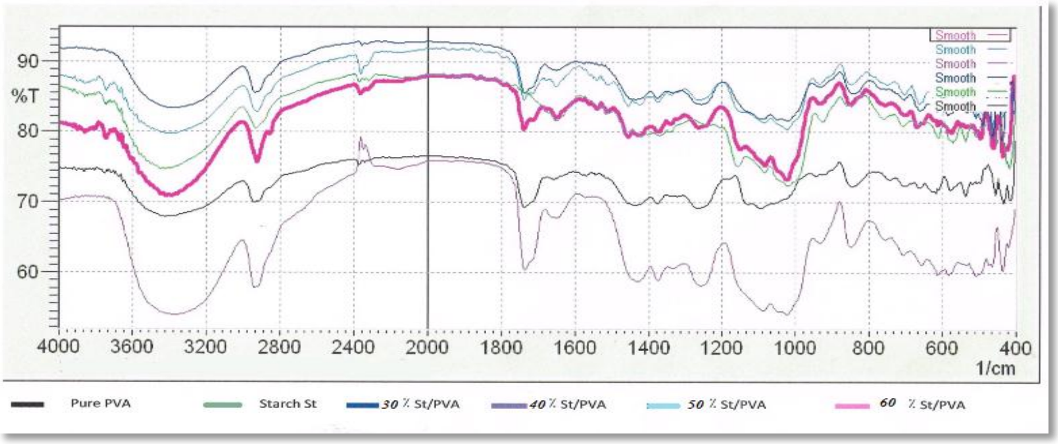


Fig. 8: FTIR spectra of St/PVA blend films.

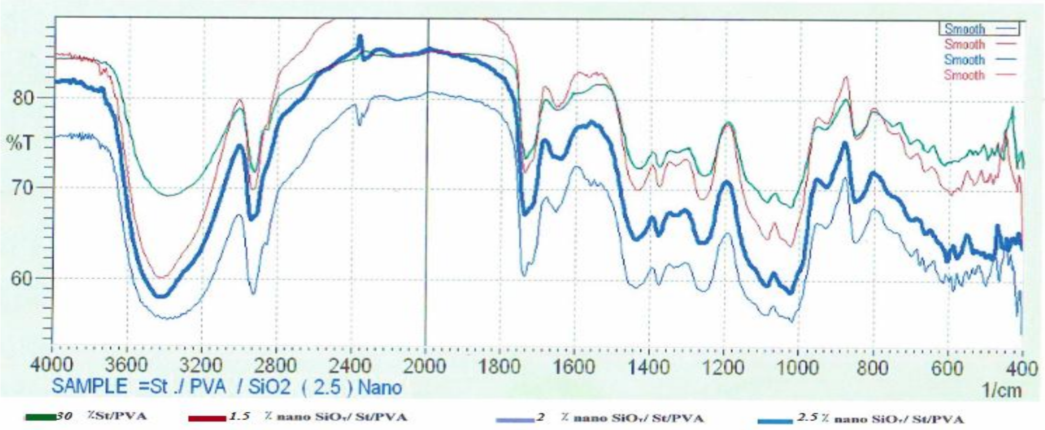


Fig. 9: FTIR spectra of micro SiO_2/ St/PVA films.

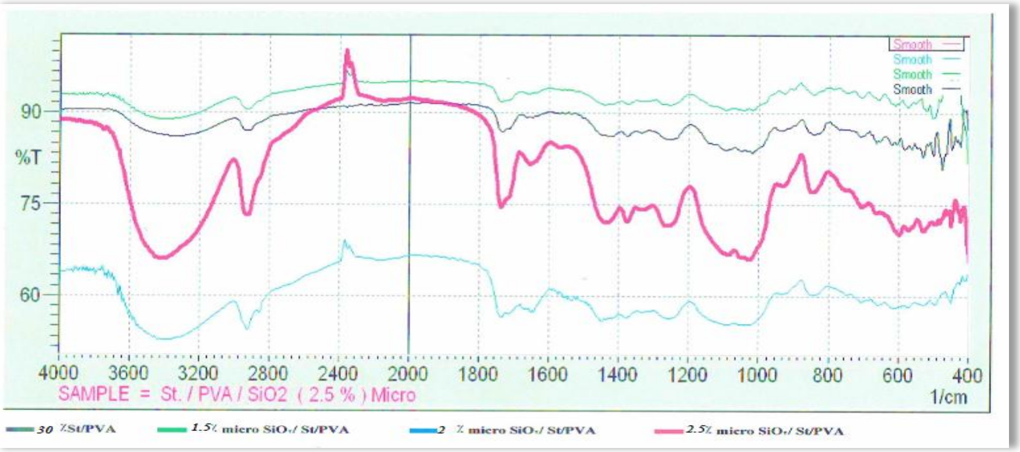
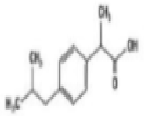
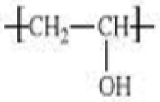


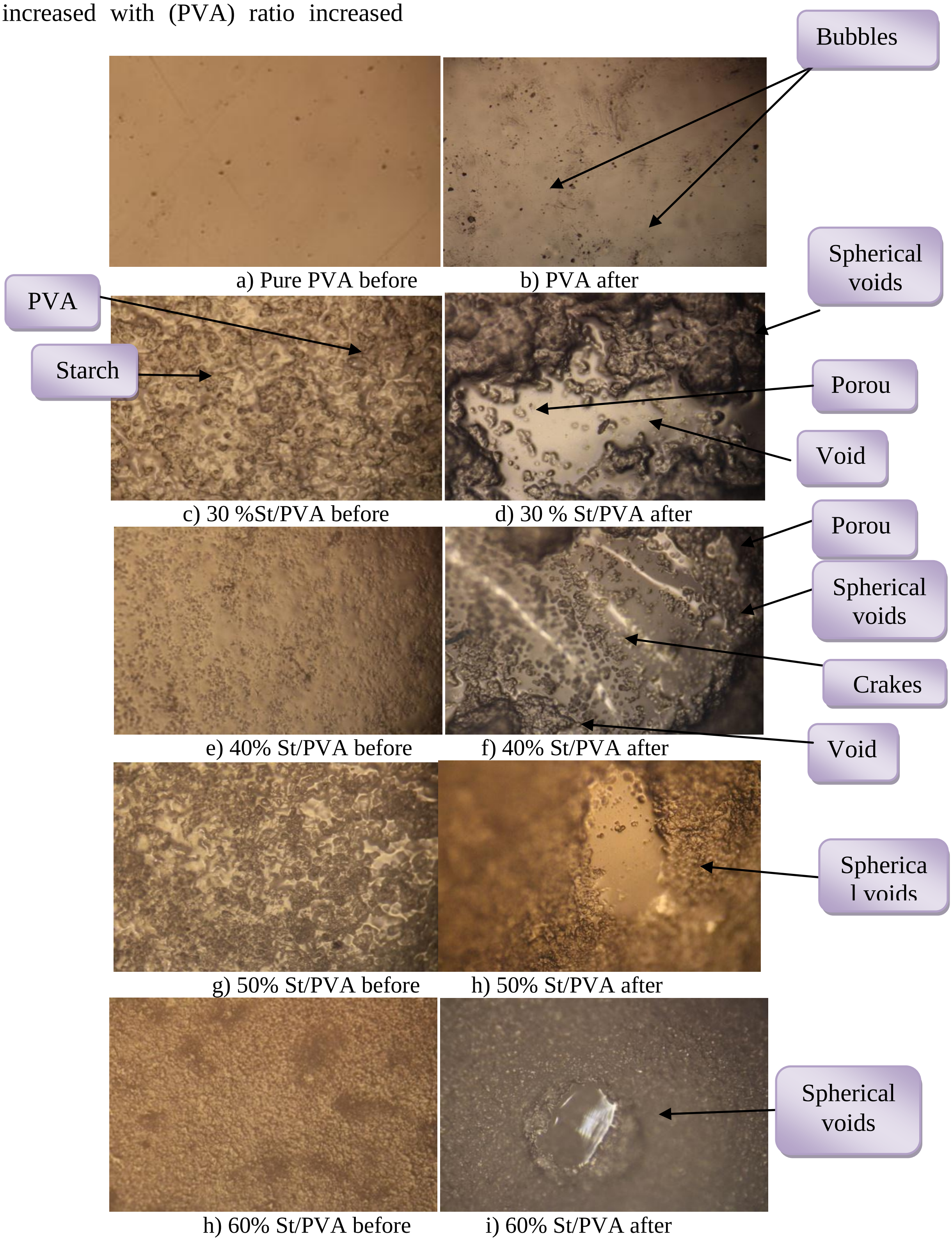
Fig. 10: FTIR spectra of nano SiO_2/ St/PVA films.

Table 1: show FTIR-characteristic peaks.

Polymer system	*Si-O-C Stretching 570-970*	*C-O Stretch 880 - 1259*	*CH2 Bended 1300-1380*	*C=O Stretch 1550-1750*	*C-H Stretch Alphatic 2800-3000*	*C-H Stretch Aromatic 2800-3060*	*Hydrogen 3100-3600*
 PVA	611.43-850.61	1093.64-850.61	1375.25	1735.93	2939.52	2939.52	3388.93
 $-\!\!\left[CH_2-\underset{\displaystyle OH}{\underset{\vert}{CH}}\right]\!\!-$ St	574.79	1157.29-1018.41	1371.39	1641.42	2927.94	-------------	3390.86
30% St/PVA	605.65-848.68	1259.52-1029.99	1375.25	1649.14	2929.87	2929.87	3415.93
40% St/PVA	578.64	1253.73-1026.13	1375.25	1649.14-1732.08	2927.94	2927.94	3398.57
50% St/PVA	576.72	1259.52-1026.13	1375.25	1656.85-1737.86	2926.01	2926.01	3398.57
60% St/PVA	578.64	1251.80-1026.13	1375.25	1649.14-1730.15	2931.80	2931.80	3400.50
1.5 %SiO_2/St/PVA NPs	574.79	1257.59-1022.27	1375.25	1737.68-1653.00	2924.09-2854.65	2924.09-2854.65	3388.93
2% SiO_2/St/PVA NPs	842.89-574.79	1255.66-1020.34	1375.25	1735.39-1718.58	2939.52	2939.52	3327.21
2.5% SiO_2/St/PVA NPs	576.72	1257.59-1024.20	1375.25	1735.93	2924.09	2924.09	3390.86
1.5% SiO_2/St/PVA µPs	605.65	1085.92-1026.13	1375.25	1730.15	2937.59	2937.59	3394.72
2% SiO_2/St/PVA µPs	574.79	1259.52-1026.13	1375.25	1735.93	2939.52	2939.52	3327.21
2.5% SiO_2/St/PVA µPs	576.72	1120.64-1026.13	------------	1737.86	2924.09-2854.65	2924.09-2854.65	3369.64

Optical microscope study

Fig. 11 shows the optical micrographs of (PVA) and starch/PVA blends at different concentration (30-60 %) and before and after α- amylase immersion for (10 min). The results proved that the blend compatibility increased with starch ratio concentration. That was in a good agreement with Mohammad [37]. By starch addition; the dispersed phase (starch) would be miscible in (PVA); as a results of that the blends would be miscible blends and of homogenous morphology; it was attributed to the (PVA) characteristic (hydrophilic); that property caused hydrogen linking increase and result in an adhesion strength between the starch chain. This results in a good agreement with azhar [38]. It was seen that the porous were increased with (PVA) ratio increased which was attributed to the blend miscibility this was in a good agreement with Esraa [34].



a) Pure PVA before b) PVA after

c) 30 %St/PVA before d) 30 % St/PVA after

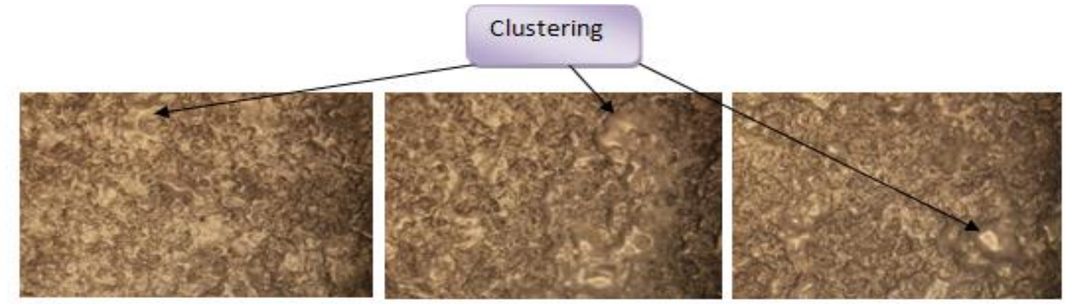
e) 40% St/PVA before f) 40% St/PVA after

g) 50% St/PVA before h) 50% St/PVA after

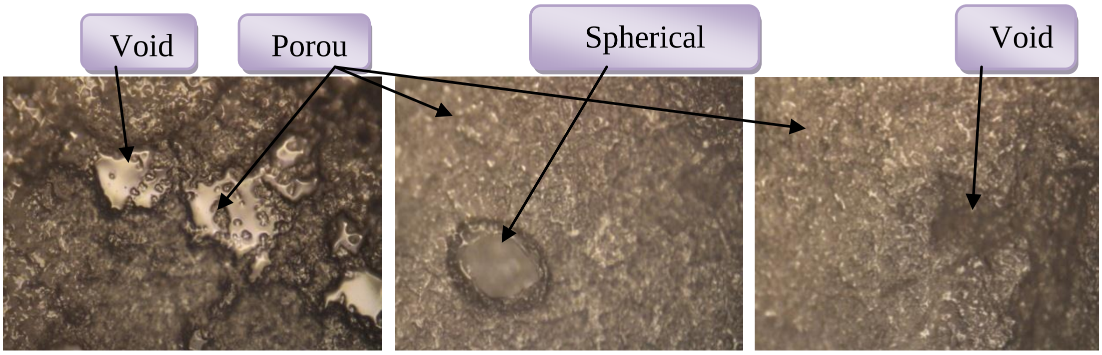
h) 60% St/PVA before i) 60% St/PVA after

Fig. 11: The optical micrographs of (PVA) and St/PVA blends before and after α-amylase immersion.

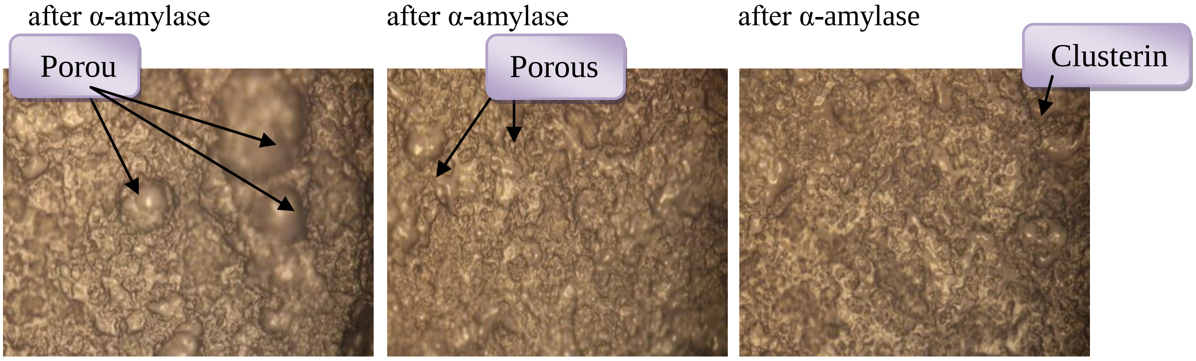
SiO_2 μPs and NPs were added at different concentration (1.5, 2, and 2.5 %). The blend compatibility decreased with SiO_2 μPs addition [37] as shown in Fig. 12 for NPs SiO_2/St/PVA at different concentration that the (SiO_2) NPs films was compact that suggested the miscibility and compatibility of samples were improved. Because the surface of NPs SiO_2 had plenty of unsaturated residual bonds, and different hydroxyl group bonding stats; it was ease to form a strong hydrogen bond with starch and (PVA). The Strong chemical bond (C-O-Si) was also formed in NPs SiO_2 /St/PVA) hybrid materials, such that the strong interfacial binding force took place in NPs SiO_2 and St/PVA, and the films surface showed compact and smooth ultra-structure [39]. The optical microscopic results proved that the samples of more starch ratio were more affected by α-amylase. It was found spherical holes that were attributed to the samples attack by α-amylase. It was seen that the biodegradation of St/PVA blends was higher than that of (PVA) that was attributed to high hydrolysis stability of starch; this results was enhanced with weight loss results; and that was proved with porous as spherical holes shown in micrographic results [34, 40].



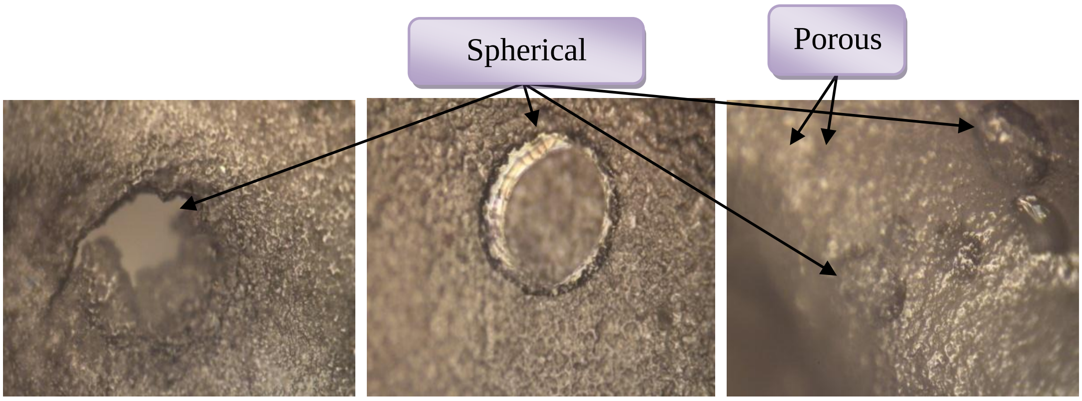
a) 1.5% μPs SiO_2/St/PVA before b) 2 % μPs SiO_2/St/PVA before c) 2.5% μPs SiO_2/St/PVA before



d) 1.5% μPs SiO_2/St/PVA after α-amylase e) 2% μPs SiO_2/St/PVA after α-amylase f) 2.5% μPs SiO_2/St/PVA after α-amylase



g) 1.5% NPs SiO_2/St/PVA before h) 2% NPs SiO_2/St/PVA before i) 2.5% NPs SiO_2/St/PVA before



j) 1.5 % NPs SiO_2/St/PVA after α-amylase   k) 2% NPs SiO_2/St/PVA after α-amylase   l) 2.5% NPs SiO_2/St/PVA after α-amylase

Fig. 12: SiO_2 µPs and NPs before and after α-amylase immersion.

Conclusions

It was concluded that the samples evolved could be used as packaging materials for medical application and its degradation could be controlled by SiO_2µPs, and NPs addition.

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