Study of starch, sugar blending effect on the biodegradability of (PVA) for packaging applications

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Abstract

PVA, Starch/PVA, and Starch/PVA/sugar samples of different concentrations (10, 20, 30 and 40 % wt/wt) were prepared by casting method. DSC analysis was carried; the results showed only one glass transition temperature (T_g) for the samples involved, which suggest that starch/PVA and starch/PVA/sugar blends are miscible. The miscibility is attributed to the hydrogen bonds between PVA and starch. This is in a good agreement with (FTIR) results. T_g and T_m decrease with starch and sugar content compared with that for (PVA). Systematic decrease in ultimate strength, due to starch and sugar ratio increase, is attributed to (PVA), which has more hydroxyl groups that made its ultimate strength higher than that for starch/PVA, and starch/PVA/sugar blends. It is observed from water uptake tests that the solubility time decreases with starch ratio; it is attributed to decrease in hydroxyl groups caused by PVA ratio decrease. The inter- and inter-molecular bonds of the hydroxyl groups enhanced the solubility process of the starch/PVA blends in water. The water immersion causes hydrogen bonds (inter and intermolecular bonds) to decompose, that increases the film solubility. Water absorption and capacity of degradability are most important in biodegradable materials. The results suggest the samples that have undergone investigation, can be used for shopping, and food packaging.

The study of soil burial for the sample at (3cm) depth, and at (13cm) depth has exhibited weight loss increase with soil burial time. The biodegradability rapidly increases at the first (6-7) weeks; it is found that the weight loss at (3cm) depth is greater than that at (13cm) that was attributed to the differences in the availability of oxygen ratio. It is found that PVA undergoes lowest weight loss, the weight loss changes with starch, and sugar content. In dry soil, the weight loss is lower. The results proved that the biodegradation decreases with soil burial time after seven weeks of burial. It is concluded that the samples involved are biodegradable material that can be used for packaging applications and biologically friendly synthetic polymer blends to solve the solid waste accumulation problem.

Key words

PVA, starch/PVA, starch/PVA/sugar blends, biodegradable material, water uptake, weight loss.

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دراسة تأثير خلط النشا والسكر على القابلية على التفكك الإحيائي للبولي فينيل الكحول (PVA)

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الخلاصة

حضرت نماذج من PVA و خلائط Starch/PVA و Starch/PVA/sugar ولمختلف التراكيز (10,20,30,40%wt/wt) بطريقة الاذابة. اجري فحص DSC للنماذج واظهرت النتائج وجود (T_g) واحدة لجميع الخلائط Starch/PVA و Starch/PVA/sugar مما يدل ان الخلائط قابلة للامتزاج. تعزى القابلية على للامتزاج الى الاواصر الهدروجينية مابين PVA و starch وذلك يتفق مع نتائج (FTIR) التي تبين قابلية على الامتزاج للخلائط تعتمد على النسب. تقل T_g و T_m بزيادة محتوى النشا starch و sugar عن تلك الخاصة PVA. وجد تناقص نظامي في المتانة ultimate strength بازدياد نسبة starchوsugar. يعزى ذلك الى ان PVA يمتلك مجاميع من الهدروكسيل hydroxyl groups اكثر من خلائط Starch/PVA و Starch/PVA/sugar.. اظهرت فحوصات الامتصاص للماء water uptake tests بان زمن الذوبان يقل بازدياد نسبة النشا starch. وقد اعزي ذلك الى تناقص في مجاميع الهدروكسيل نتيجة لتناقص نسبة PVA. ان الاواصر مابين الجزيئات ومابين الذرات أي داخل الجزيئات لمجاميع الهيدروكسيل inter and intermolecular bonds عززت عملية الذوبان لخلائط starch/PVA في الماء. ان امتصاص الماء والقدرة على التفكك الاحيائي من العوامل الاكثر اهمية في المواد المتفككة احيائيا. اظهرت النتائج بانه يمكن استخدام النماذج لاغراض التعبئة للتسويق والمواد الغذائية shopping, and food packages. اظهرت نتائج طمر النماذج في التربة على عمق (3cm) و (13cm) ازدياد في فقدان الوزن بزيادة مدة الطمر. ازدادت القابلية على التفكك الاحياثي عند weeks (6-7) الاولى: كما وجد ان فقدان الوزن عند عمق (3cm) اكبر من (13cm) وقد اعزي ذلك الى وفرة الاوكسجين. تغير فقدان الوزن مع محتوى starch و sugar. يكون فقدان الوزن في التربة الجافة اقل (كما هو في بحثنا الحالي). اظهرت النتائج ان التفكك الاحياثي يقل ما بعد الاسبوع السابع للطمر. نستنتج بان النماذج مدار البحث تعتبر مواد قابلة للتفكك الاحيائي ويمكن استخدامها لاغراض التعبئة والتغليف وانها تمثل خلائط بوليميرية صديقة للبيئة لحل مشكلة تراكم النفايات الصلبة.

Introduction

During the past twenty years, the production of food packaging plastic products, such as poly-olefin, increased, which was not associated with any increase in the amount of plastic solid wastes. These products are characterized with excellent mechanical properties, as well as, chemical weathering and biodegradable resistance [1-3]. The biodegradable polymers were used as packaging materials to solve the problem of solid waste accumulation [3]. Polyvinyl alcohol (PVA) is well known as a biologically-friendly synthetic polymer; it is water soluble, non-toxic, biocompatible, high optical clarity, and on the basis of these characteristics it is used in biomedical applications [4].

The starch is available as a low cost raw material, which was used in biomaterial fields. The packaging films, which are starch content lack strength and rigidity. It withstands application of any stress to which any packaging may be exposed. The starch/PVA blend is also a biodegradable material, with good forming, strong conglutination, and high thermal stability [1]. Starch is a carbohydrate, which consists of a large number of glucose units joined by glycoside bonds; it is composed of two types of molecules, the linear and helical amylase, and branched amyl pectin. The starch acts as filler in thermoplastics that is attributed to its biodegradability-renew ability and its low cost [5-7]. Pure starch lacks strength, water resistibility, and thermal stability [8-10]. Guilbent, et al., worked on biodegradable packaging material and its surface treatment; other groups used various blends and cross-linked them to produce film for food packaging [11, 12]. Shangwen, et al. studied biodegradable starch/PVA blends before and after nano particles of SiO_2 addition at different ratio.The results proved increase in tensile strength at 5% SiO_2, and increase in water absorption resistance [13]. Najim, et al. studied starch/PVA blends by using acetic acid. The results showed that the physical, thermal, and biodegradability properties were changed by the blend ratio. The biodegradation increased with starch ratio [14].

Experimental part

Starch/PVA, and Starch/PVA/Sugar blends were prepared at different concentrations (10wt%, 20wt%, 30wt%, and 40 wt %). Starch/PVA blends were blended in hot water at 80°C, and shaken by using magnetic stirrer for one hour till a homogenous solution is obtained. Solution of several formulations was prepared with various concentrations. The solution was cast using flat glass plate and left till it dries. Starch/PVA/Sugar blends were prepared by the addition of sugar of different concentrations (10wt%, 20wt%, 30wt%, and 40 wt%); the same procedure employed above was repeated to cast the (Starch/PVA/Sugar) blend films. The prepared samples were tested in order to measure their mechanical properties including the tensile strength and elongation at break by using tensile machine of (LARYEE-50kN, China), with the crosshead speed of (5mm/min). Water uptake for the samples involved was tested. The water uptake ($(W_a-W_0)/W_0\%$), where W_a, and W_0 are the sample weight after and before soaking with water respectively. The degradation of sample in soil involved was studied by determining the percentage of weight loss in soil by using (%weight loss=($W_0-W_a)/W_0\%$)), where W_0, and W_a are the sample weight before and after soil burial treatment respectively. Further tests included FTIR, DSC, and optical microscopicy.

Results and discussion

Figs.1 and 2 show the FTIR spectra of (PVA), starch/PVA, starch/PVA/sugar blends; For (PVA) spectrum, it was found some bands at (828.34 cm^{-1}), and (916.8 cm^{-1}), which was attributed to (C-H)bending, and (C-O)stretching irrespectively. There were some bands at (1324 cm^{-1}), and (1376 cm^{-1}) due to ($-CH_2$) bending; The bands at (1578.89 cm^{-1}) was attributed to ($-CH_2$) wagging, and (C=O) stretching; the appearance of some bands at (1578.89 cm^{-1}), (1655.79cm^{-1}), and (1708.5 cm^{-1}) was due to (C=O) stretching; The bands at (1708.5 cm^{-1}) was attributed to Acetate groups produced through(PVA) fabrication process. The bands at (2935.7 cm^{-1}) was attributed to (OH) stretching [15]. For the starch /PVA blends , it was found that the physical mixing induced changes in FTIR spectra, e.g, some bands disappeared within range of (626-970 cm^{-1}), which was attributed to (C-H) bending, and (C-O) stretching irrespectively. The appearance of new band at (2853.64 cm^{-1}) was due to the (C-H) stretching for aromatic bond. The disappearance of some bands within range of (1550-1610 cm^{-1}), which was attributed to ($-CH_2$), and (C=C) stretching. The bands within range of (3100-3400cm^{-1}) was attributed to (OH) stretching. The FTIR spectra proved that the starch and (PVA) were successfully mixed, and in a good agreement with [16]. The appearance of bands at (1070.49 cm^{-1}), and (1240.58 cm^{-1}) were due to (C-O) stretching of (C-O-H) groups, and to (C-O) stretching of (C-O-C) groups of glucose in starch [15].

Starch/PVA/Sugar spectra showed disappearance in some bands within range of (1550-1750 cm^{-1}), and (2800-3060 cm^{-1}) due to (C=O) stretching; and (C-H) stretching of aromatic bonds irrespectively; It was seen broaden in bands within range of (3100-3400 cm^{-1}), that was related with (OH) wagging of semi crystalline starch, and sugar. That indicates to the presence of hydrogen bond (H-bond). The shift in some bonds was attributed to (CH_2) bending, and the broaden in some bands at (1240.58 cm^{-1}), and (1663.31cm^{-1}), which suggested of hydrogen bond presence [17, 18].

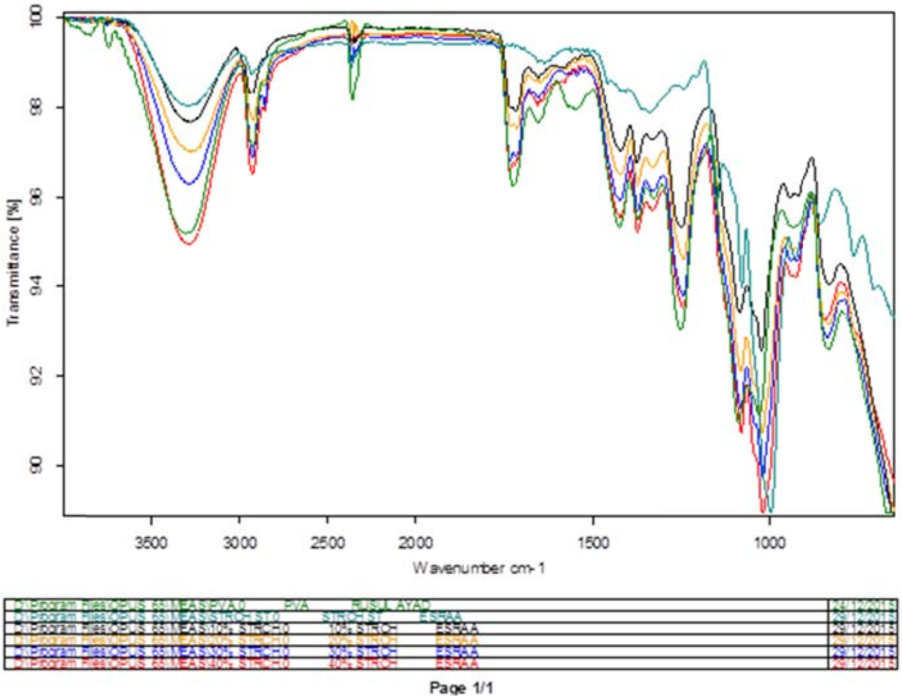


Fig.1: The FTIR spectra for of PVA, starch, and Starch/PVA at different ratio.

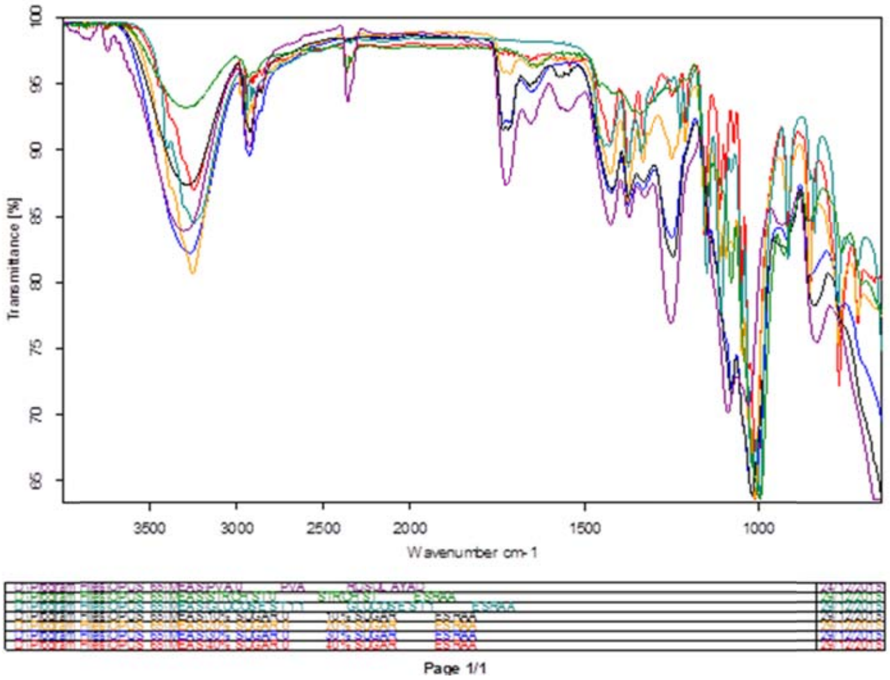


Fig. 2: The FTIR spectra for of PVA, starch, sugar, and Starch/PVA/sugar at different ratio.

Table 1: The main characteristics of FTIR spectra for the samples involved.

Polymer system	C-H out phase bending 625-970	C-O Stretch 880-1000	CH$_2$ Bending 1300-1380	CH$_2$wagging C=C Stretch 1550-1610	C=O Stretch 1550-1750	C-H Stretch aliphatic 2800-3000	C-H Stretch aromatic 2800-3060	Hydroxyl 3400=3600
PVA	**828.34 916.28**	**912.28**	**1324 1376**	**1578.89**	**1578.89 1655.79 1708.51**	**2935.72**	**-------------**	**3266.08**
STARCH	**704.55 762.55 856.97 926.26**	**926.26 996.45**	**1339.62**	**1602.87**	**1602.87 1602.87 1636. 1669.73 1697.7 1734.29**	**-----------**	**2925.52**	**3279.55 3588.83**
SUGAR	**715.79 772.45 838.14 915.4**	**915.4 996.21**	**1338.23 1372.92**	**-----------**	**----------**	**2880.98 2913.29 2944.67**	**---------**	**3241.73**
10% STARCH/PVA	**830.71 919.35 943.12**	**919.35 943.12**	**1333.56 1374.9**	**-----------**	**1652.2 1718.61**	**----------**	**2922.17**	**3277.22**
20% STARCH/PVA	**831.99 920.13**	**920.13**	**1329.25 1373.62**	**-------------**	**1648.76 1714.32**	**-------------**	**2919.31**	**3282.29**
30% STARCH/PVA	**834.65 921.63**	**921.63**	**1328.24 1373.75**	**--------------**	**1652.61 1731.95**	**------------**	**28.53.64 2923.39**	**3279.9**
40% STARCH/PVA	**840.59 924.9**	**924.9**	**1330.45 1373.99**	**------------**	**1666.34 1734.43**	**-----------**	**2922.04**	**3279.29**
10% STARCH/PVA /10%SUGAR	**837.19 920.41**	**920.41**	**1330.63 1374.44**	**1571.09**	**1571.09 1656.19 1734.33**	**2919.2**	**-----------**	**3281.6**
20% STARCH/PVA /20%SUGAR	**715.56 770.24 852.32 916.04**	**916.04**	**1331.21 1374.6**	**-----------**	**1647.92 1712.57**	**2902 2936.34**	**-------------**	**3251.91**
30% STARCH/PVA /30%SUGAR	**851.44 917.67**	**917.67**	**1373.88**	**------------**	**1648.64 1733.6**	**2922.13**	**---------------**	**3264.48**
40% STARCH/PVA /40%SUGAR	**715.27 769.41 851.68 914.97**	**914.97**	**1330.55 1373.45**	**------------**	**1653.71**	**2936.92 2971.81**	**-------------**	**3248.71**

Differential Scanning Calorimetric test (DSC)

Using (DSC) Technique: the results showed only one (T_g) for the sample involved, which suggested that starch/PVA, starch/PVA/sugar blends were miscible), the miscibility was attributed to the hydrogen bonds between PVA, and starch Figs.3 and 4. That was in a good agreement with (FTIR) results, which showed the blend miscibility associated with hydrogen bond reaction between (OH) groups of (PVA), and starch. It was plasticizer content dependent. T_g, and T_m decreased with starch and sugar content than that for (PVA) [17]. (PVA) is composed of two phases crystalline, and amorphous phases: so, it has complex behavior during heating process. The results showed that (T_g) of (PVA) was (85.5°C), which was due to relaxation process induced by micro Brownian motion of main chain backbone of (PVA). The results proved that there was no (T_g) for starch, which was attributed to segment mobility of amorphous (PVA) phase, which was increased by starch, and sugar addition. There was no trend degradation for the sample involved up to 250°C [16-17]. The intermolecular interaction was attributed to the hydrogen bonds between (PVA), and starch. The crystalline region decreased with starch content; which did not need high energy to break. The crystalline differences was attributed to the high crystallinitity of the starch/PVA/sugar blends during cooling [17] Table 2.

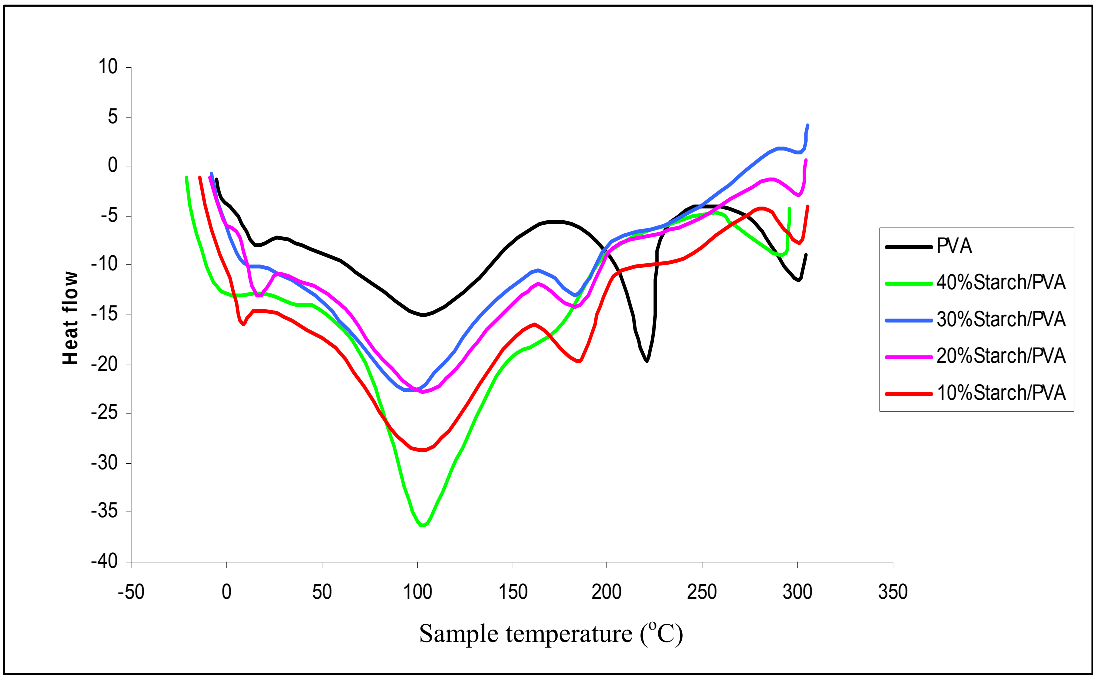


Fig. 3: DSC analysis of PVA, and Starch/PVA at different ratio.

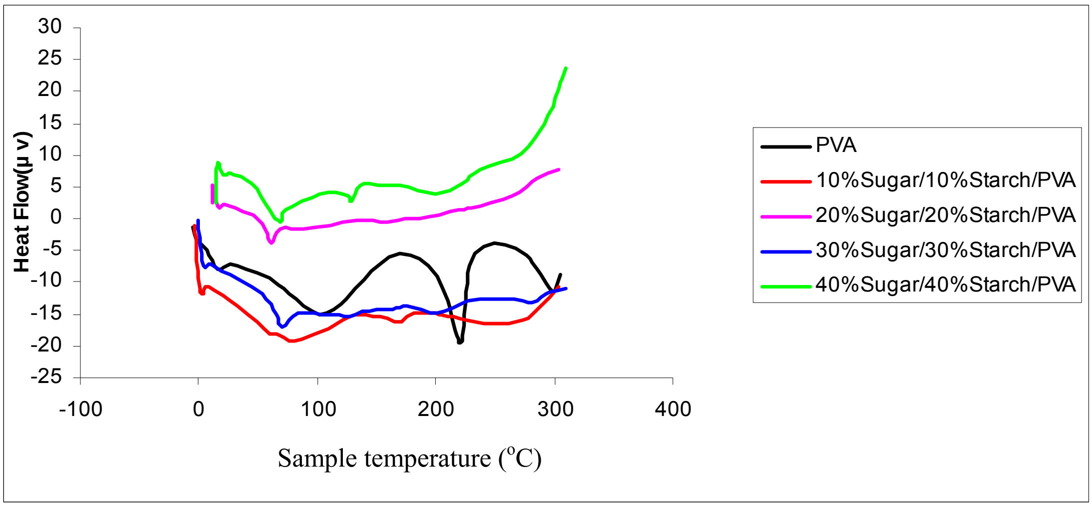


Fig. 4: DSC analysis of PVA, and Starch/PVA/Sugar at different ratio.

Table 2: T_g, T_m for the prepared samples.

Polymer systems	T_g°C	T_m°C
PVA	**85.5**	**224**
10% Starch/PVA	**65**	**194**
20% Starch/PVA	**66**	**194**
30% Starch/PVA	**65**	**194**
40% Starch/PVA	**62.5**	**210**
10%Starch/PVA/10%Sugar	**42**	**180**
20%Starch/PVA/20%Sugar	**47**	**174**
30%Starch/PVA/30%Sugar	**44**	**206**
40%Starch/PVA/40%Sugar	**45.5**	**206**

Tensile test results

Figs. 5 and 6 depict the stress-strain curves for the PVA, starch/PVA, starch/PVA/sugar blends of different ratios. Systematic decrease was observed in ultimate strength by starch, and increase of sugar ratio Fig. 7; this was attributed to (PVA), which has more hydroxyl groups, providing ultimate strength higher than that of starch/PVA, and starch/PVA/sugar blends. In other words, starch has (-OH) groups, that have decreased by acetylating process that caused decrease in ultimate strength [3, 17, 19]. For starch/PVA/sugar blends, its ultimate strength was seen to decrease with sugar ratio; but it was higher than that for starch/PVA, especially at 10% sugar, that was due to plasticizing effect (elongation) for blend films, and decrease in starch ratio Fig. 8 [19].

These results were enhanced by optical morphology. It was seen that clear PVA micrograph without bubbles were obtained; whereas for the prepared blends it was seen that the compatibility increased with starch and sugar contents; this confirmed the systematic changes in the mechanical properties Figs. 9 and 10 [16-18].

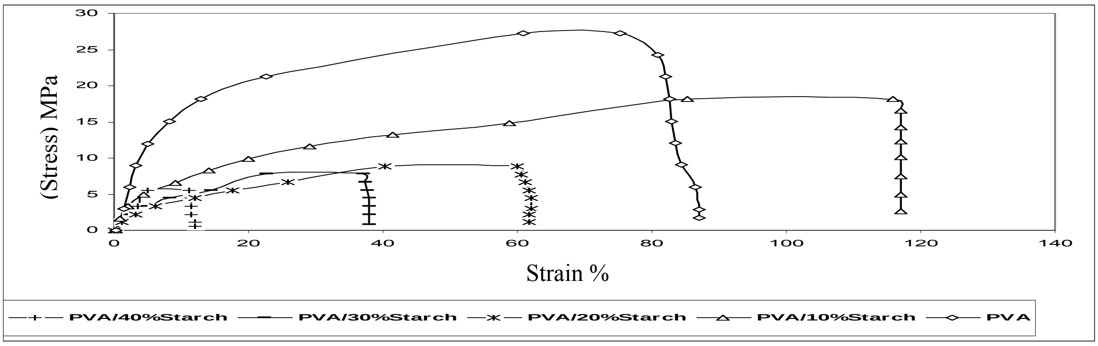


Fig. 5: The stress strain curves of PVA ,and Starch/PVA at different ratio.

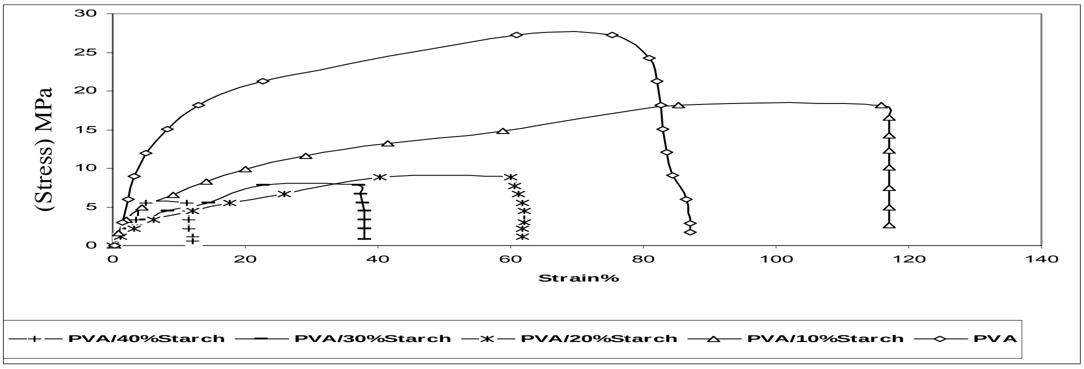


Fig.6: The stress strain curves of PVA, and Starch/PVA/sugar at different ratio.

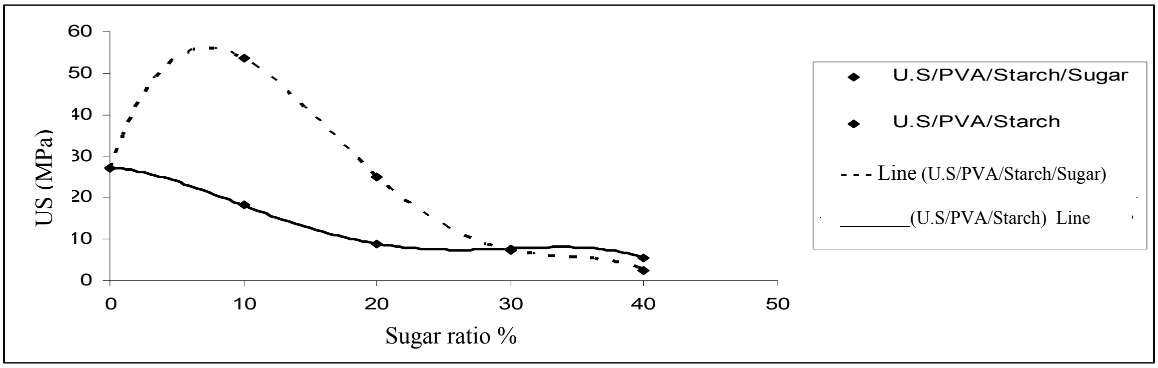


Fig.7: The ultimate strength against the starch, and sugar ratio.

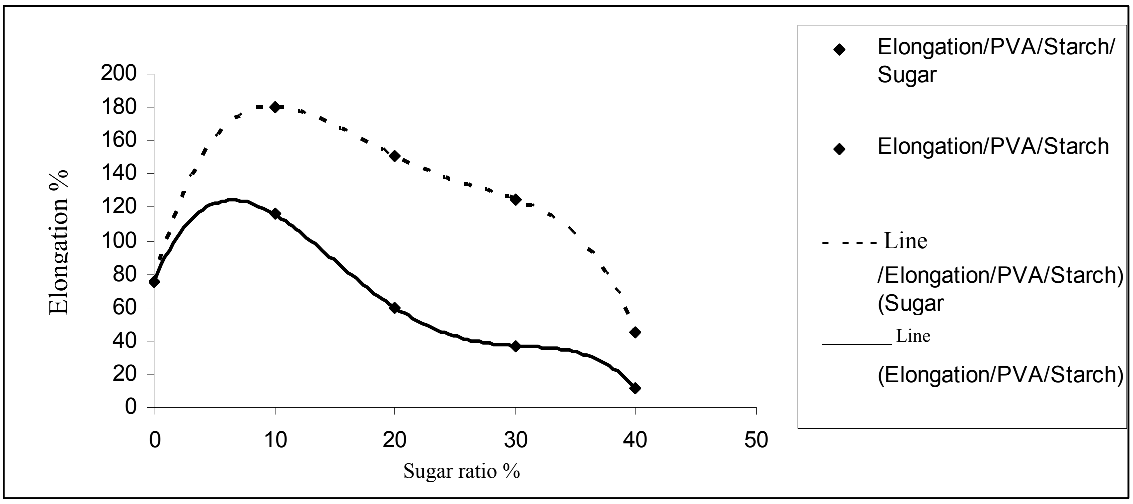
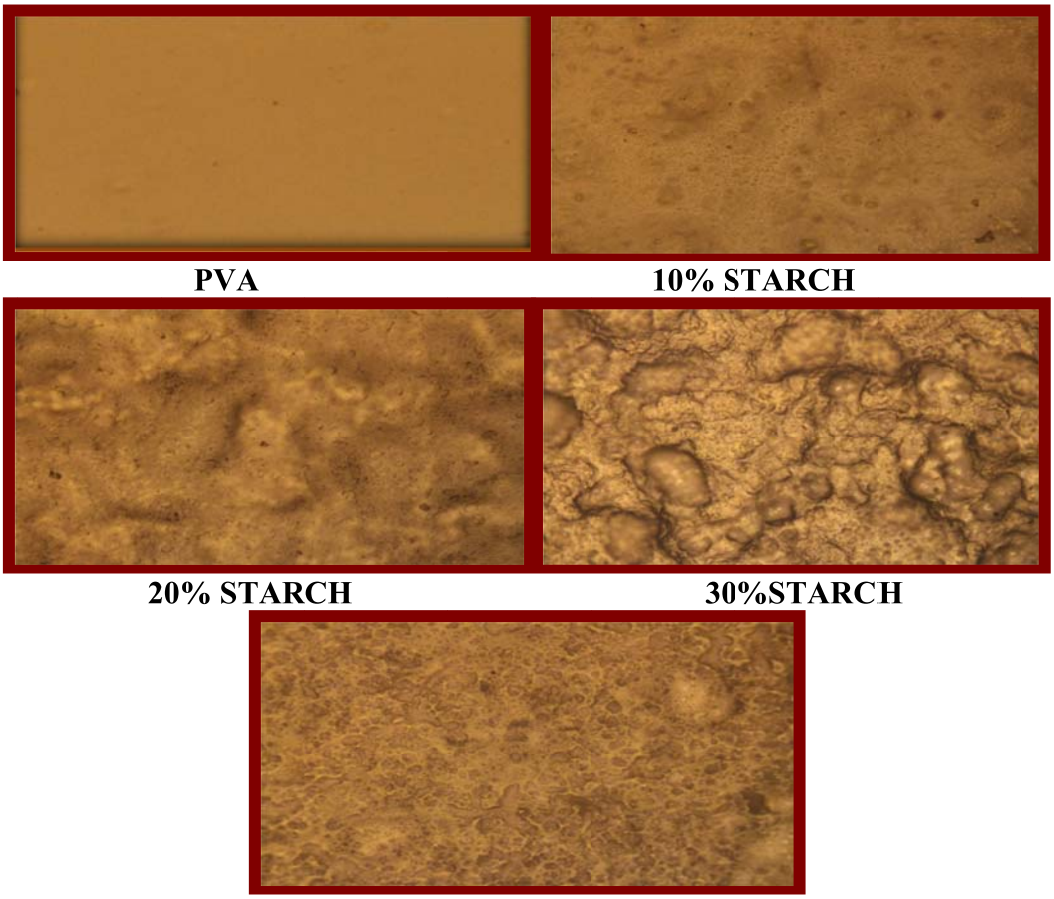


Fig. 8: The Elongation against the starch, and sugar ratio.

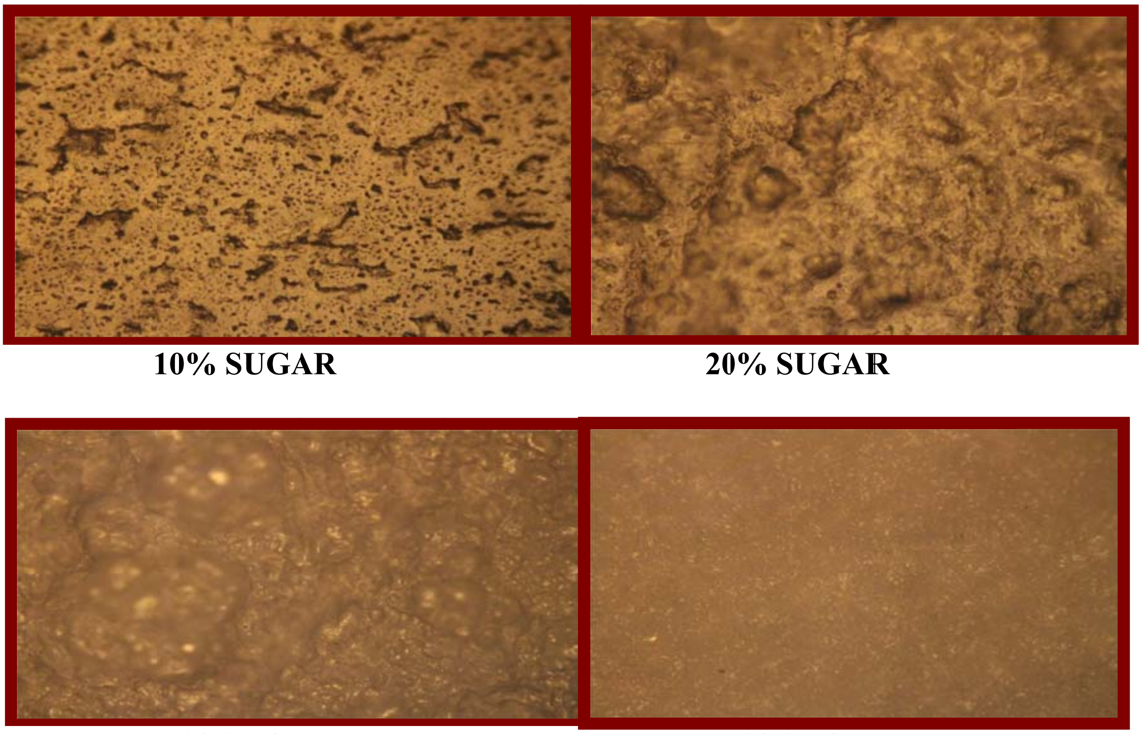


PVA **10% STARCH**

20% STARCH **30%STARCH**

40%STARCH

Fig.9: The optical micrographs of PVA, and Starch/PVA at different ratio.



10% SUGAR **20% SUGAR**

30% SUGAR **40% SUGAR**

Fig.10: The optical micrographs of PVA, and Starch/PVA/sugar at different ratio.

Water Uptake

Figs.11 and 12 illustrate the water uptake percentage against the soaking time for the samples involved. It was seen that the solubility time decreased with starch ratio; this is attributed to decrease in hydroxyl groups caused by PVA ratio decrease [20, 14]. The inter- and inter-molecular bonds of the hydroxyl groups enhanced the solubility process of the starch/PVA blends in water. The water immersion caused hydrogen bonds (inter and intermolecular bonds) by decomposition, that increased the film solubility [21]. Water absorption and capacity of degradability are most important in biodegradable materials. It was seen that there was typical behavior for the blends involved. Initially, weight gain rapidly increased followed by steady absorption region, and finally water absorption would be lower. The water absorption is enhanced by hydrogen bonding in hydrocarbons, PVA, starch, and sugar [21]. The results suggested that the samples involved can be used for shopping, and food packages [11, 12].

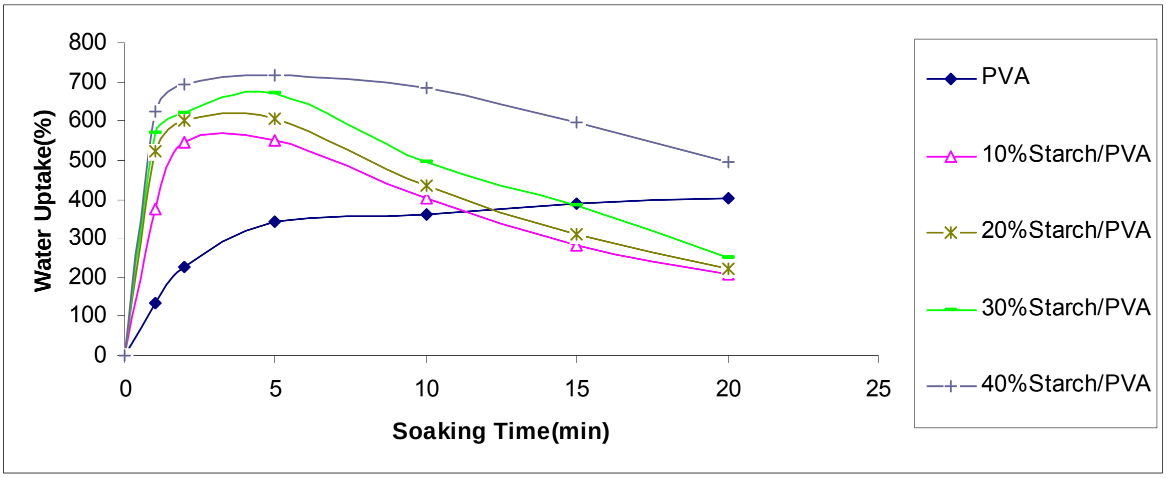


Fig.11: The water uptake relationship with soaking time in water for of PVA, and Starch/PVA at different ratio.

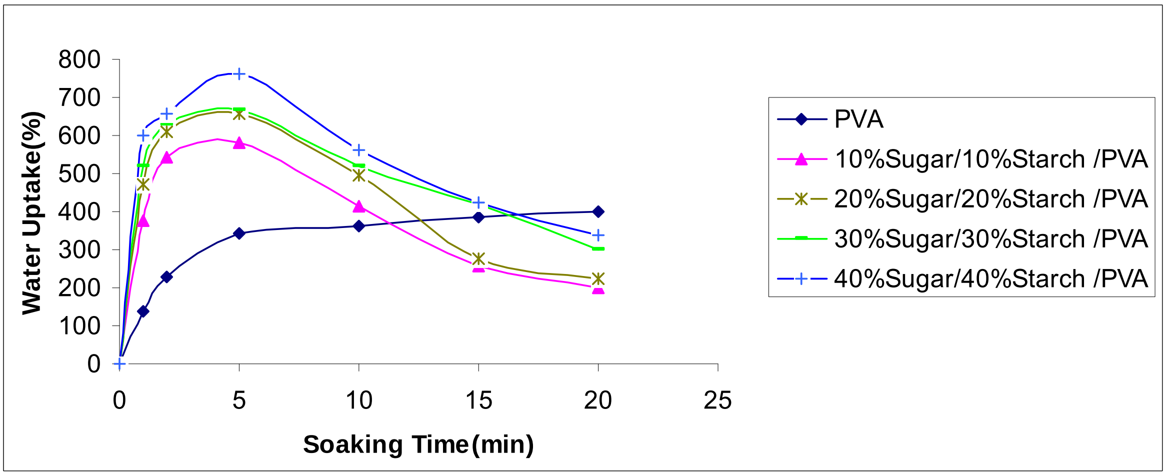


Fig.12: The water uptake relationship with soaking time in water for of PVA, and Starch/PVA/sugar at different ratio.

Soil burial study

The soil burial study for the sample involved is shown in Fig.13 and Fig.14 at 3cm depth, and Fig.15 and Fig.16 at (13cm) depth. The biodegradability has shown rapid increase at first (6-7) weeks. It was found that the weight loss at 3cm depth is higher than that at 13cm that was attributed to the difference in the oxygen ratio [22]. It was found that PVA has shown lowest weight loss. The weight loss depends on the blend type, microorganism type, and soil type (dry or moist). The weight loss changed with starch, and sugar content [14]. In dry soil, the weight loss would be lower than that for moist soil (as in the present work).The results proved that the biodegradation decreased with soil burial time after six weeks of burial [22, 23]. In the first stage (at first 6-7 weeks), the biodegradation was rabidly increasing. The biodegradability increased by starch and sugar ratio. Spherical holes were observed being created in the sample involved due to organism colonization attack. The organism would attack the starch, sugar, and the amorphous part of PVA. The PVA degraded with lower rate than the starch and sugar [22]. The results verified the increase in weight loss with soil burial time, and decrease in the increasing PVA ratio. The biodegradation of the blends involved was attributed to the high hydrolysability of starch and sugar. So, the weight would be more in the first (6-7) weeks of burial time then it would be slower till the residual nutrient of microorganism was consumed followed. In this process the carbon will converted to carbon oxide [23].

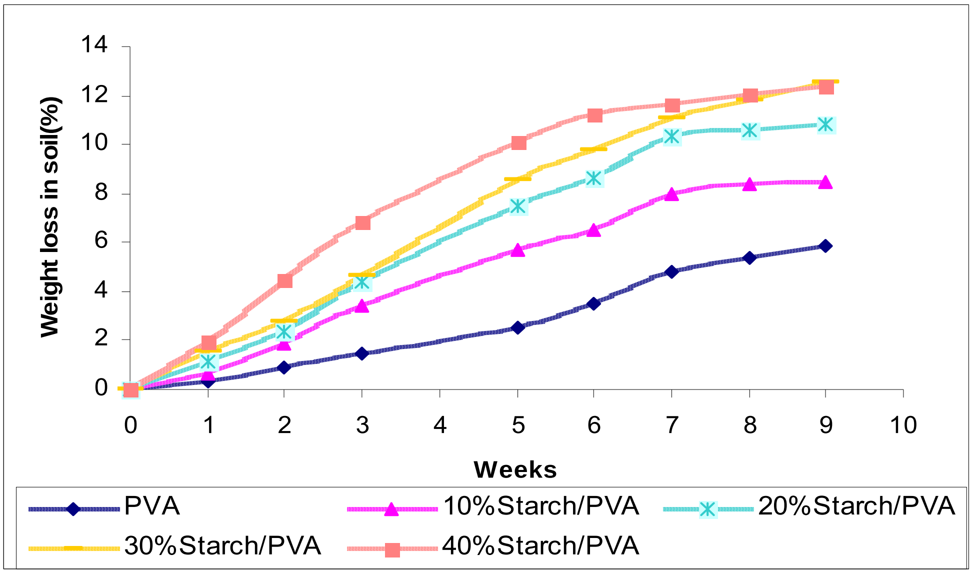


Fig. 13: The weight loss with the soil burial time at 3cm depth for the of PVA, and Starch/PVA at different ratio.

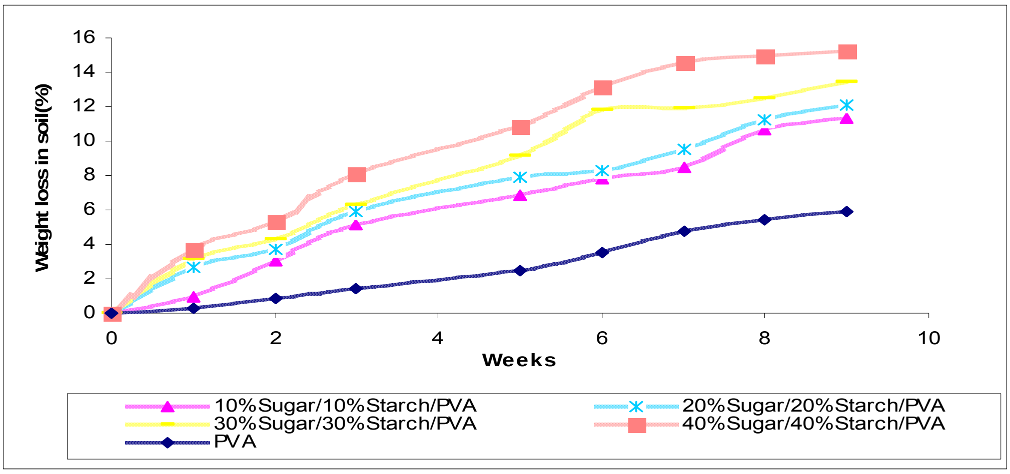


Fig. 14: The weight loss with the soil burial time at 3cm depth for the of PVA, and Starch/PVA/sugar at different ratio.

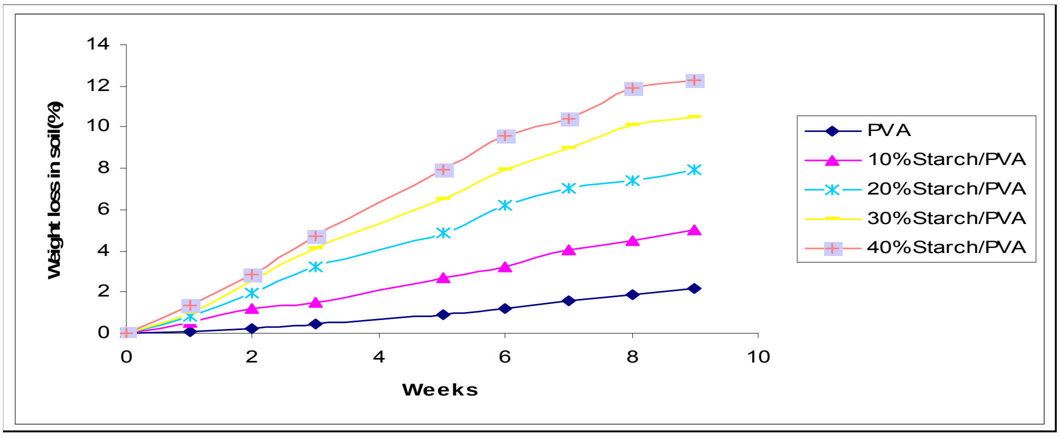


Fig. 15: The weight loss with the soil burial time at 13cm depth for the of PVA, and Starch/PVA at different ratio.

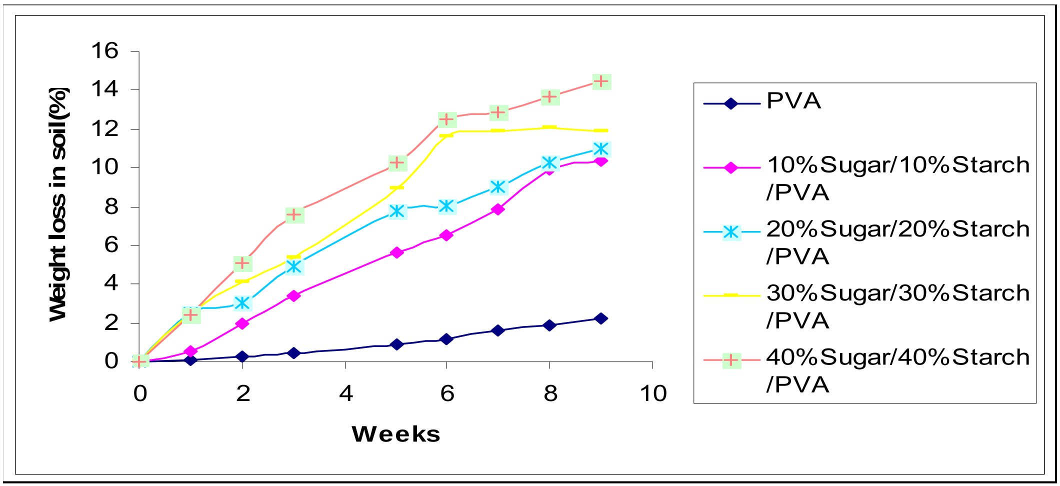


Fig. 16: The weight loss with the soil burial time at 13cm depth for the of PVA, and Starch/PVA/sugar at different ratio.

Conclusions

- The results show only one (Tg) for the sample involved, which suggest that starch/PVA, starch/PVA/sugar blends are miscible, the miscibility is attributed to the hydrogen bonds between PVA and starch. These findings are in good agreement with the (FTIR) results.
- Systematic decrease is found in ultimate strength by starch, and sugar ratio increase that is attributed to (PVA), which has more hydroxyl groups that made its ultimate strength higher than that of starch/PVA and starch/PVA/sugar blends.
- It is seen that the solubility time decreased with starch ratio. It is attributed to decrease in hydroxyl groups caused by PVA ratio decrease. The inter and intermolecular bonds of the hydroxyl groups enhanced the solubility process of the starch/PVA blends in water.
- It is found that the weight loss at (3cm) depth is higher than that at (13cm) that was attributed to the difference in oxygen ratio. It is found that PVA is of lowest weight loss. The weight loss is seen to change with starch and sugar content.
- The results proved that the biodegradation decreases with soil burial time, after a period of seven weeks, but the samples involved are biodegradable material that can be used for packaging applications and biologically friendly synthetic polymer blends.

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