Synthesis, characterization and evaluation of biodegradable properties polyvinyl alcohol/maize starch blend films

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ARTICLE INFORMATION

ABSTRACT

In this study various ratios of polyvinyl alcohol (PVOH) and maize starch (MS) were casted on petri dishes. Then biodegradability of the polymer films prepared was investigated based on their ability to absorb polar solvent (water) and non-polar solvents benzene and xylene. The absorption test revealed that the polymer films of MS blend and PVOH/MS blend ratios of 4:6 permitted more diffusion rate of water to saturation at every time interval of 1 hour giving rise to their increased sizes; whereas in benzene and xylene media the polymer film ratios showed less diffusion rate and absorption. In polar solvent, the unblended PVOH and the blended 6:4 ratio in the polymer films exhibited less diffusion rate and absorption. The polymer films with 4:6 ratios show greater strength against disintegration in polar solvent. The probability coefficients P>0.05 were obtained from ANOVA test $F_{(4,20)} = 0.733$, $P = 0.580$; $F_{(4,20)} = 2.79$, $P = 0.540$; and $F_{(4,20)} = 2.46$, $P = 0.790$ for polymer films immersed in water, benzene and xylene respectively. This implies that there were significant differences in mean data distributions for the polymer film ratios on diffusion and absorption of the various solvents used. This study also revealed that MS can be blended into a synthetic polymer like polyvinyl alcohol to produce packing material with biodegradable potentials.

1. Introduction

The synthetic polymer materials produced from past scientific and technological methods takes many years to degrade, and as such these synthetic polymer materials cause significant environmental problems [1]. Hence it is necessary to give attention to the development of various biodegradable polymer materials. The biodegradable polymer can be classified into two categories based on the raw materials used: degradable synthetic polymers and renewable natural polymers [1, 2]. Synthetic degradable polymers are more plastics, polyesters, polyethylene and nylon whereas the renewable natural polymers include starch, cellulose, and chitosan. Polyvinyl acetate (PVA) is compatible with starch and blends to have good film properties, which degrade in various microbial environments [3]. The uses of PVA with starch improve the mechanical properties of the blends [4]. PVA/MS blends are one of the most popular biodegradable plastics widely used in packing and agricultural applications [5]. Starch is a mixture of amylase and

amylopectin, the amylase is a linear polymer of α-δ-glycopyranosyl units containing both 1, 4-α-δ-glycosidid linear linkages and 1, 6-α-δ-glycosidic linkages at the branch points. The α-amylase is the main enzyme involved in the hydrolysis of 1, 4-α-δ-glycosidic linkage in starch. As the natural biodegradable polymer hydrolysis, α-amylase readily catalyses and degrade the hydrolysed starch [6]. PVA is a synthetic polymer with a backbone that consists primarily of –OH bonds which makes it absolutely biodegradable; and being water-soluble polymer it has a broad range of application in medicinal, agricultural and food industries [2,6,7,8,9]. In the material industry biodegradability of PVA depends largely on its molecular weight which forms excellent film, strong adherence and high thermal stability on being mixed with starch [10, 12]. Based on these studies, the aim of this paper to examine the effect of solvents absorption and rate of diffusion on biodegradable PVA/MS blend films.

2. Materials and Method

2.1. Material Collection

The materials used were bought from chemical stores, maize starch was made by Loba Chemic Lab reagents, and the PVOH was of research grade from Aldrich Chemical Inc. and had average M.W $9x10^3$-$1x10^4$, pH 4.5-7, density 1.3g/cm^3, 80% hydrolysis rate and as such provide a polymer that can degrade rapidly. Glycerol was produced by BDH re-packed in Nigeria by NAAFCO. Paraffin was made by Sigma-Aldrich (M) solution, BDH. Solvents used were de-ionized water, benzene was produced by Qualikems, M.W 78.11, Xylene (sulphur free) was made by BDH Chemical Ltd, M.W 106.17. Ohaus AR2130 Adventurer electronic laboratory balance, USA.

2.2. Preparation of Samples

Sample cast blending method was used to produce the polymer film casted [11, 12], the ratio of 10:00, 08:02, 06:04, 04:06 and 0:10 by weight of PVOH and MS were measured and blended in each round conical flask, deionised water was added to the mixture and stirred with a high speed stirrer in a constant temperature water bath at 80^{0}C for 30 minutes. Then plasticiser, glycerol and paraffin oil were added to each mixture, stirred for 10 minutes until a smooth polymer film was obtained. Thereafter, the various mixtures were casted onto petri dishes, dried in desiccators for 24 hours. The polymer films obtained were further cured in oven below 30^{0}C for 30 minutes. The polymer films were finally peeled off from the petri-dishes. These steps were repeated for all samples.

3. Results and Discussion

3.1. Result
3.1.1. Kinetic Studies and Solvent Adsorption Test Methods
Three sets of different samples of the dried polymer blends were cut into rectangular shapes size. Dried weight of polymer films were recorded before immersion separately into distilled water, benzene, and xylene at 25$^°$C. Readings were taken after every 60 minutes for both polar solvent non-polar solvents until the films reached equilibrium weight. The moisture on the surface films

was removed and the weights of the films were measured. The solvent content (S_θ) absorbed by each polymer film was calculated from the dry weight of the swelled film (W_0) and after absorption (W_θ), using 1 and presented as %S_θ.

$$\% S_\theta = \frac{W_\theta - W_0}{W_0} \times 100 \qquad 1$$

W_θ = weight of wet film and W_0 = weight of dry film obtained from films were used to calculate the diffusion coefficient or diffusivity (D) applying 2.

$$D = \frac{L^2}{6(\sqrt{t})^2} \times \left(\frac{W_\theta - W_0}{W_{max}}\right)^2 \qquad 2$$

Where W_{max} is the maximum solvent content in take and L is the thickness of the sample film, it was assumed that absorption process was linear at an early stage of immersion, the t is the time taken at the beginning of absorption process so that weight change (W_θ - W_0) was expected to vary linearly with the square root of time [2, 13, 14].

Table 1: Absorption and Diffusion of water by PVA/MS with time

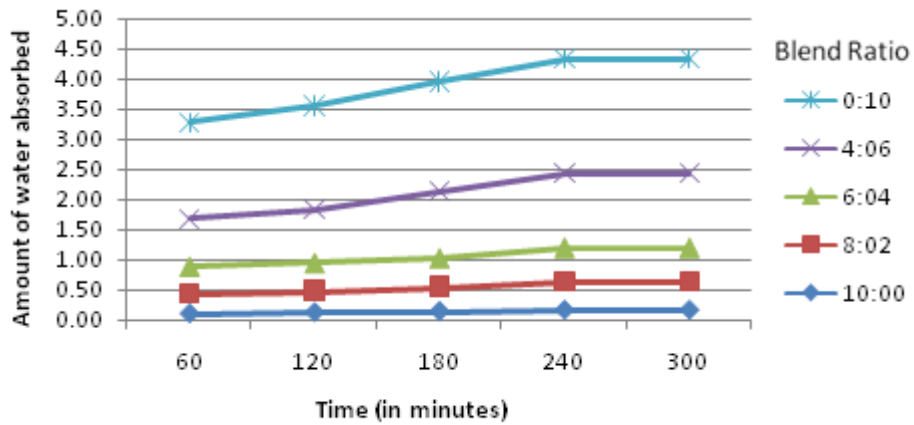| PVA/MS Blend Ratio	t	60mins	120mins	180mins	240mins	300mins
				Wet Weight (g)		
	S_θ	0.10	0.12	0.14	0.16	0.16
10:00	(Dx10^{-9} m^2/s)	0.33	0.31	0.32	0.28	0.21
	S_θ	0.33	0.35	0.40	0.46	0.46
8:02	(Dx10^{-9} m^2/s)	0.43	0.32	0.32	0.28	0.21
	S_θ	0.45	0.47	0.48	0.57	0.57
6:04	(Dx10^{-9} m^2/s)	0.52	0.38	0.30	0.28	0.21
	S_θ	0.81	0.90	1.12	1.24	1.24
4:06	(Dx10^{-9} m^2/s)	0.36	0.29	0.34	0.28	0.21
	S_θ	1.60	1.72	1.83	1.91	1.91
0:10	(Dx10^{-9} m^2/s)	0.59	0.45	0.38	0.28	0.21

Fig. 1a. Absorption of Water by PVA/MS Blend Ratio with Time

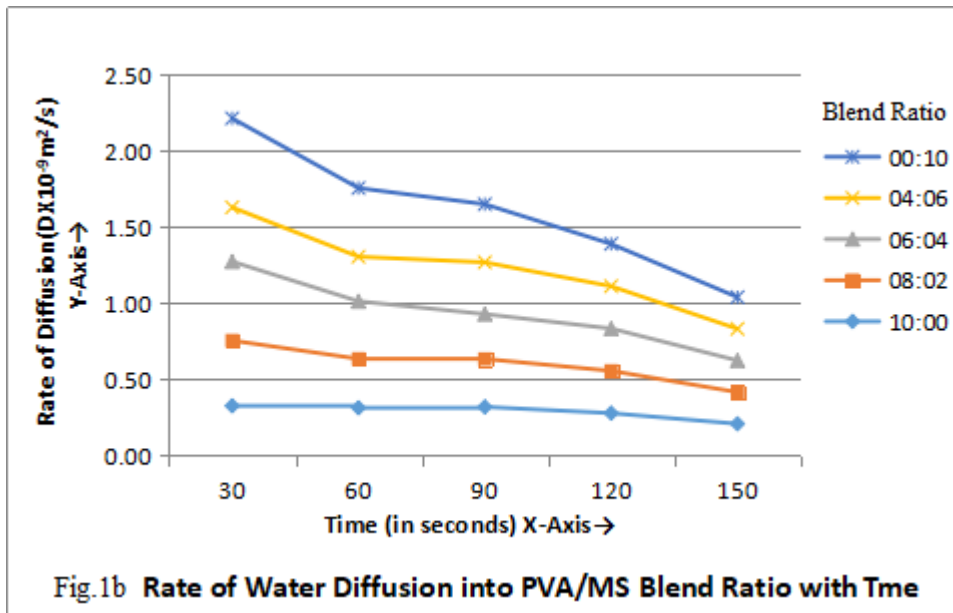Fig.1b Rate of Water Diffusion into PVA/MS Blend Ratio with Tme

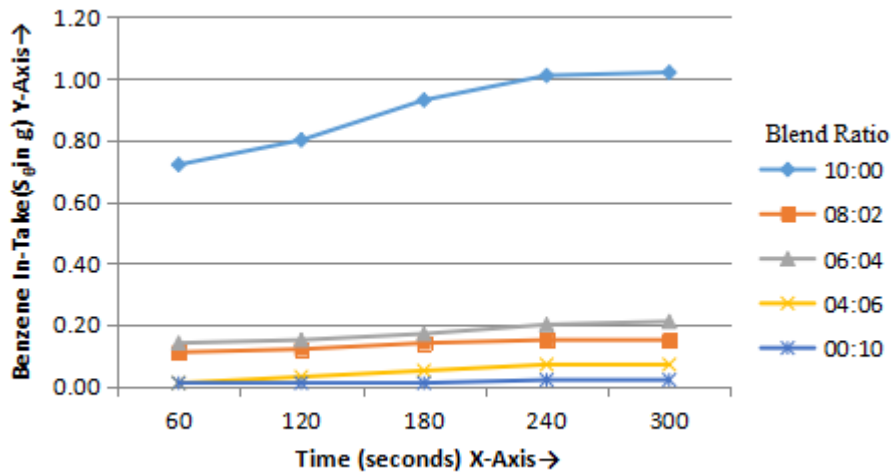| Table 2. Absorption and Diffusion of benzene by PVOH/MS with time						
PVOH/MS Blend Ratio		Wet Weight (g)				
		60mins	120mins	180mins	240mins	300mins
10:00	S_θ	0.72	0.8	0.93	1.01	1.02
	$(Dx10^{-9}\ m^2/s)$	0.210	0.128	0.115	0.102	0.083
08:02	S_θ	0.11	0.12	0.14	0.15	0.15
	$(Dx10^{-9}\ m^2/s)$	0.224	0.133	0.121	0.104	0.083
06:04	S_θ	0.14	0.15	0.17	0.20	0.21
	$(Dx10^{-9}\ m^2/s)$	0.185	0.160	0.091	0.095	0.083
04:06	S_θ	0.01	0.03	0.05	0.07	0.07
	$(Dx10^{-9}\ m^2/s)$	0.009	0.038	0.071	0.104	0.083
00:10	S_θ	0.01	0.01	0.01	0.02	0.02
	$(Dx10^{-9}\ m^2/s)$	0.104	0.052	0.035	0.104	0.083

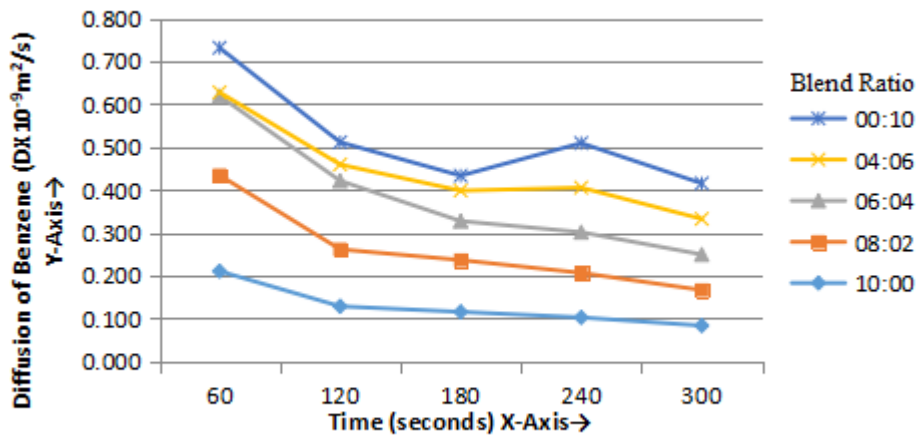Fig. 2a   Absorption of benzene by PVA/MS Blend Ratio with Time

Fig. 2b   Diffusion of Benzene into PVA/MS Blend Ratio with Time

Table 3: Absorption and Diffusion of xylene by PVOH/MS with time

| PVOH/MS Blend Ratio		Wet Weight (g)				
		60mins	120mins	180mins	240mins	300mins
10:00	S_θ	0.83	0.90	1.01	1.03	1.04
	$(Dx10^{-9}\ m^2/s)$	0.265	0.156	0.131	0.102	0.083
08:02	S_θ	0.24	0.25	0.26	0.27	0.27
	$(Dx10^{-9}\ m^2/s)$	0.329	0.179	0.129	0.104	0.083
06:04	S_θ	0.11	0.12	0.13	0.14	0.14
	$(Dx10^{-9}\ m^2/s)$	0.257	0.153	0.120	0.104	0.083
04:06	S_θ	0.03	0.04	0.06	0.07	0.07
	$(Dx10^{-9}\ m^2/s)$	0.077	0.068	0.102	0.104	0.083
00:10	S_θ	0.01	0.02	0.03	0.05	0.05
	$(Dx10^{-9}\ m^2/s)$	0.017	0.033	0.050	0.104	0.083
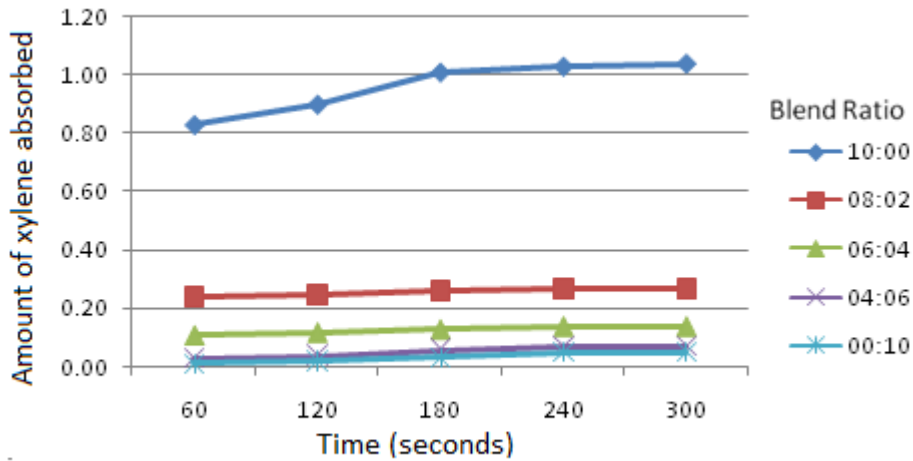
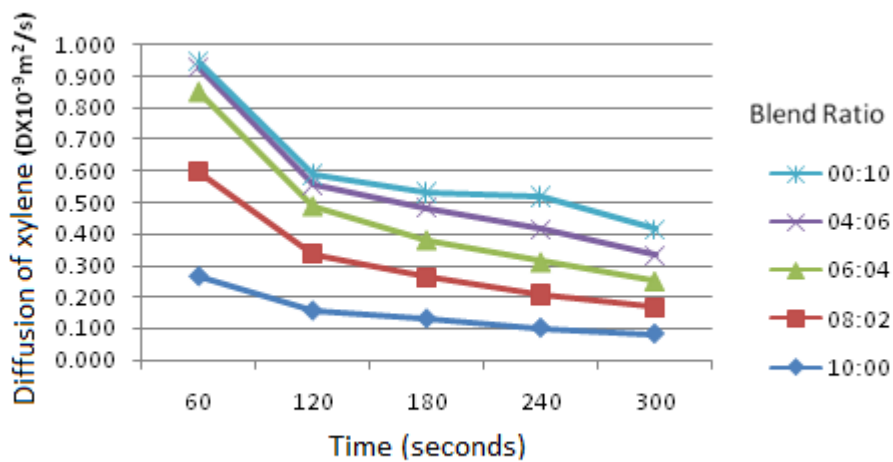Fig.3a. Absorption of xylene by PVA/MS Blend Ratio with Time

Fig.3b Rate of Diffusion of xylene by PVA/MS Blend Ratio with Time

Table 4:   ANOVA Test

	M(SD)	F	Sign	df
Water absorption	0.14(±0.03)	168.43*	0.00	4,20
Water diffusion	0.29(±0.05)	0.73**	0.58	4,20
Benzene absorption	0.90(±0.13)	171.98*	0.00	4,20
Benzene diffusion	0.13(±0.05)	2.79**	0.54	4,20
Xylene absorption	0.10(±0.09)	392.95*	0.00	4,20
Xylene diffusion	0.15(±0.07)	2.46**	0.79	4,20

Key M(SD) = Mean(Standard deviation) F = Factorial, Sign = Significant /Probability (P), df = degree of freedom. *P<0.05 and **P>0.05 significant level.

3.2. Discussion

In Table 1, curve of water up-take by PVOH-MS films showed that as the concentration by weight of PVOH decreases with increasing concentration by weight of MS that is 8:2, 6:4, and 4:6, the absorption of water increases; whereas the ratio of 10:0 PVOH-MS had the least water up-take. Maximum water up-take was exhibited by the 0:10 ratio of PVOH-MS concentration by weight, it was also observed that this polymer films blend disintegrated at saturation level compared to the reverse process in which 10:0 ratios of PVOH-MS do not easily disintegrate in water. The ratios of 6:4 and 4:6 PVOH-MS polymer films exhibited more stable and resistant to dispersion in water. In Table 2 and 3, the ratio 10:0 PVOH/MS (i.e. pure PVOH) films showed high absorption of benzene and xylene and the diffusion rate of these solvents decreased on saturation; PVOH had selective absorption properties for non-polar solvents, it was shown that when MS were used in various blend ratios with PVOH, the polymer films had very little increase in amount of benzene and xylene but decreased faster as the rate of diffusion of solvents reached saturation.

As in Table 2 and 3, the curves of benzene and xylene up-take by PVOH-MS polymer films showed reverse process compared to that in Tab.1, in which the 0:10 ratios of PVOH-MS had the least absorption of the organic solvents and disintegrate at saturation level in therir respective organic solvents; but the 10:0 ratios of PVS-MS absorbed more of the solvents and dispersed at saturation level. The pure PVOH films demonstrated higher benzene and xylene uptake than the PVOH/MS films, this solvents absorption were due to affinity of the organic component of the PVOH composites for non-polar solvents.

In Fig.1(a-b), the PVOH films that contained starch showed higher water uptake than the pure PVOH films, this water absorption is due to hydrophilic nature of MS in the composites. Therefore a higher MS content led to a higher amount of water being absorbed. The concentration ratio of 8:2, 6:4 in water diffusion rate by pure MS polymer blend do not show similar trend as pure PVOH films, the pure MS films showed high water up-take than benzene and xylene.

As concentration of MS decreases in the PVOH-MS ratio films that is from 6:4 to 4:6 respectively, absorption and rate of diffusion of solvents into the polymer film decreases, and the tendency of polymer film to disperse in solvent medium decreases.

Figures 2 and 3(a-b) showed that the PVOH-MS films behaved differently as the ratios increases from 6:4 to 4:6. Absorption of benzene and xylene were more pronounced as PVOH concentration in the PVOH-MS films increases; hence, 8:2 ratio of polymer films absorbed more solvents than 6:4 ratio of polymer films; 4:6 ratio of polymer films showed the least absorption at saturation level. Therefore 6:4 and 4:6 ratio of the PVOH-MS polymer films were more stable and resistant to disintegration in water, benzene and xylene.

The figures 1a-3b are graphs with linear curves and the relationship between absorption (S_θ) and square root of time take ($\sqrt{t}$) were observed to be linear as they were terminated at saturation level, The trends in solvents uptake among group samples of pure PVOH, MS, and PVOH/MS polymer blends varied greatly from one another, and difference in results obtained as shown in Tables 1-4 depend largely on the bond strengths within samples' cavities.

In Table 4, the ANOVA's F-test showed that the polymer blended films on absorption generally had M(SD) = 0.14($\pm$0.03), F = 168.43 for water absorbed; P = 0.00; M(SD) 0.90($\pm$0.13), F = 171.98, P = 0.00 for benzene absorbed; and M(SD) 0.10($\pm$0.09), F =392.953, P = 0.00 for xylene

absorbed; their P values less than 0.05, showed that the polymer films within groups had not shown any significant differences in their mean data distributions on absorption of the solvents. These results depicted that the materials formulated in their respective ratios had selective absorption properties, and their tendencies to exhibit these characteristic properties formed the good material strength at 4:6 and 6:4 ratios.

The ANOVA test (Table.4) also revealed that water, benzene, and xylene diffusion rate into the films among groups have significant differences in their rate of diffusion mean data spread, since all P values are greater than 0.05; F-test recorded M(SD) = 0.29($\pm$0.05), F = 0.73, P = 0.58 for water diffusion rate; M(SD) = 0.13($\pm$0.05) F = 2.79, P = 0.54 for benzene diffusion rate; and M(SD) = 0.15($\pm$0.07), F = 2.400, P = 0.79 for xylene diffusion rate .

4. Conclusion

As absorption increases with time, the saturation of the polymer film increases faster and the rate of diffusion tend to decrease. At saturation the blend films of PVOH and MS in 6:4 and 4:6 ratios respectively gave better molecular bond strength, large enough to resist dispersion.

The 6:4 and 4:6 ratio of the PVOH-MS polymer films have the most suitable formulation for blending PVOH-MS polymer films, these compositions formed the suitable polymer films with rigid, plastic and large intra-molecules that wedged penetration of large amount of water, benzene, and xylene; thereby reduced the tendency of the polymer films towards dispersion in the media and can be seen suitable for packing materials.

5. Acknowledgement

6. Conflict of Interest

There is no conflict of interest associated with this work.

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