

Structure–Property Relation in Polyvinyl Alcohol/Starch Composites

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ABSTRACT: A series of polyvinyl alcohol (PVA)/starch films were cast by the solvent method. Mechanical, optical, wide-angle X-ray scattering (WAXS), and biodegradation studies of starch-filled PVA films were carried out. With the addition of starch there was an increase in haze and diffusion of light, whereas there was only slight change associated with tensile behavior and burst strength of the PVA film. Microstructural parameters, such as crystal size ($\langle N \rangle$) and lattice distortion (g , in %) were estimated using one-

dimensional Hosemann's paracrystalline model along with WAXS data. These parameters quantify the changes in the PVA/starch systems, which resulted in the observed physical properties. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 630–635, 2004

Key words: polyvinyl alcohol; films; mechanical properties; microstructure; biodegradable

INTRODUCTION

Polyvinyl alcohol (PVA) is a material with technological potential as a water-processable polymer. Commercially produced PVA is approximately atactic. It is made from the hydrolysis of polyvinyl acetate, and is found to be 53% syndiotactic. Many investigators have reported the model for the crystal structure of PVA.^{1–6} Isotactic PVA has a high melting point ($T_m = 230^\circ\text{C}$) compared with that of polyethylene ($T_m = 117\text{--}135^\circ\text{C}$) as a result of the high level of hydrogen bonding in the crystals (there are hydrogen bonding opportunities for every second carbon atom). Dissolution must involve the replacement of polymer–polymer hydrogen bonds with polymer–water hydrogen bonds.

Development of ecofriendly packaging materials is a continuing area of challenge for packaging technologists. The excellent chemical resistance, optical and physical properties of PVA resins have resulted in its broad industrial uses. PVA is often modified by combination with other polymers or fillers to enhance its performance and barrier properties. Incorporation of naturally occurring polymers or fillers like starch into other polymeric materials enhances the ecofriendliness.^{7,8} Starch is a naturally occurring polymer, cost effective, and easy to handle. Both PVA and starch are polar polymers; thus a composite of PVA and starch is

likely to produce a material having excellent mechanical properties and barrier behavior. Incorporation of starch into the PVA matrix changes the physicochemical properties of the material and thus modifies the polymer structure at both the molecular and the morphological levels.^{9–12} Crystal imperfection or crystal lattice distortion may occur during incorporation of fillers and these morphological changes have an effect on the properties of films. In continuation of previous work,⁷ this study reports on the effect of starch content on the properties of PVA films, such as mechanical, optical, and microstructural parameters. These studies were carried out to assess their potential uses as packaging films. For the first time the changes in properties attributed to addition of starch in PVA have been quantified in terms of crystal imperfection parameters. Such a contribution to this well-studied PVA/starch composite is very rare.

EXPERIMENTAL

Materials

PVA [degree of polymerization: 17,000–18,000; and hydrolyzed between 99.0 and 99.8% from poly(vinyl acetate) used in this study] was obtained from M/s. Loba Chem (India) and cornstarch was obtained from M/s. Riddhi Siddhi Chemicals (I) Ltd. (India).

Procedure

Blends of PVA/starch of different compositions were prepared by using water as the common solvent. A

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series of PVA/starch blends were prepared with different starch content from 1 to 10% and PVA/starch films were cast. The solid content of polymer was optimized at 2% in water and the system was made into a homogeneous solution by constant stirring at a temperature of 90–100°C. Later the solution was filtered through cotton onto a glass-plate mold lined with metallized polyester sheet. After drying the solution at room temperature, the films were allowed to dry in a hot-air oven for 8–9 h at 60°C and the dried PVA/starch films were removed from the mold. Films (size 35 × 25 cm; thickness 150 ± 10 gauge) were cast and stored in polyethylene bags at 4°C before use in further studies.

Methods

Mechanical properties such as tensile behavior and burst strength were measured using an Instron universal testing machine (model 4302) according to ASTM D-882 and ASTM D-77 methods, respectively. All measurements were performed for at least six samples in each case and an average value is reported. All tests were performed at ambient temperature. The optical properties such as total transmittance of light, total diffuse and haze values of films were measured using a Sugatest hazemeter (model 206) (Japan) according to ASTM D-1003.

Wide-angle X-ray scattering (WAXS) studies

Equatorial reflections of all the PVA/starch samples were collected by transmission mode using a curved position-sensitive detector (CPSD) attached to a Stoe diffractometer with 25 mA and 30 kV specifications. Intensity data were collected using Bragg–Brentano geometry (fine focus setting) with germanium monochromated Cu–K α ($\lambda = 1.5402 \text{ \AA}$) radiation at intervals of 0.02° in the 2θ range 5–55°. The pattern recorded from the PVA/starch composite was corrected for Lorentz polarization and also for instrumental broadening (using the Stokes deconvolution method).

Crystal imperfection parameters such as crystal size ($\langle N \rangle$) and lattice strain (g , in %) were determined by use of the Fourier method of Warren and Hosemann's one-dimensional paracrystalline model in which the simulated intensity profile was matched with the experimental one.^{13–16} The following equations were used to simulate the wide-angle X-ray profile:

$$I(s) = \sum_{n=-\infty}^{\infty} A(n) \cos[2\pi n d(s - s_0)] \quad (1)$$

where $A(n)$ is the product of size coefficient as (n) and lattice distortion (strain coefficient) $A_d(n)$. The expres-

sion and explanation of the various notations are given in our earlier study.⁷ Using Hosemann's one-dimensional paracrystalline model we have the following relationship:

$$I(s) = I_{N-1}(s) + I_N^1(s) \quad (2)$$

Here $s = (2\pi \sin \theta/\lambda)$ and (N) is the number of unit cells causing Bragg reflections. $I_N(s)$ is computed as:

$$I_N(s) = 2 \times \text{Re} \left[\frac{1 - I^{N+1}}{1 - I} + \frac{Iv}{d(1 - I)^2} \right] \times \{I^N(N(1 - I) + 1) - 1\}^{-1} \quad (3)$$

where $v = 2ia^2s + d$; $I = I_1(s) = \exp(-a^2s^2 + ids)$; $a^2 = \omega^2/2$; and $D = Nd$. Also

$$I_N^1(s) = \frac{2a_N}{D(\pi)^{1/2}} \exp(iDs) [1 - a_N s \{D(a_N s) + i(\pi)^{1/2} \exp(-a_N^2 s^2)\}] \quad (4)$$

where, $a_N^2 = N\omega^2/2$, ω is the standard deviation of the nearest-neighbor probability function, $D(a_N s)$ is the Dawson's integral or the error function with complex argument and can be computed. $\langle N \rangle$ is the number of unit cells counted in a direction perpendicular to the (hkl) Bragg plane, d is the spacing of the (hkl) planes, "Re" refers to the real part of the expression, s is $\sin \theta/\lambda$, λ is the wavelength of X-rays used, a is related to the standard deviation, g is the lattice distortion function, and D is the crystal size ($=\langle N \rangle d_{\text{hkl}}$). $I_N^1(s)$ is the modified intensity for the probability peak centered at D .

Here, we compute $\Delta^2 = [I_{\text{cal}} - (I_{\text{exp}} + \text{BG})]^2$ /number of points, where BG is the error in the background point estimation. The background level is assumed to be constant over the range of s used and estimated as the intensity at the limits of s . The effect of background on the parameters estimated has been thoroughly studied and incorporated in the standard deviation estimation. According to the Hosemann model, one can define a parameter α^* ($=N^{1/2}g$) called enthalpy, which is a measure of the phase stability in polymers, although it is only an empirical definition.

Biodegradation

The biodegradability of different PVA/starch films was determined by exposing the samples to compost mud (soil containing manure). In this study, the degradation of plastic was evaluated by measuring its weight loss, which refers to the erosion of molecules from the solid phase into the aqueous phase, although the value does not always indicate complete degradation or mineralization of the molecules. However, the

TABLE I
Mechanical Properties of PVA/Starch Composites

Starch in PVA film (%)	Tensile strength (kg/cm ²) [$\pm 2\%$]	Percentage elongation at break [$\pm 2\%$]	Burst strength (kg/cm ²) [$\pm 0.5\%$ for 100 gauge]
0.0	268	200	0.90
1.0	270	204	0.70
2.5	265	220	0.70
5.0	270	208	0.79
7.5	266	212	0.88
10.0	279	230	0.85

molecules released from PVA/starch films might be theoretically starch and/or PVA-metabolites such as low-molecular organic acids and ketonic compounds.¹⁷ These dissolved components are not recalcitrant and would be easily degraded by microorganisms in a natural environment. Therefore, the evaluation of its degradation based on weight loss seems practical.

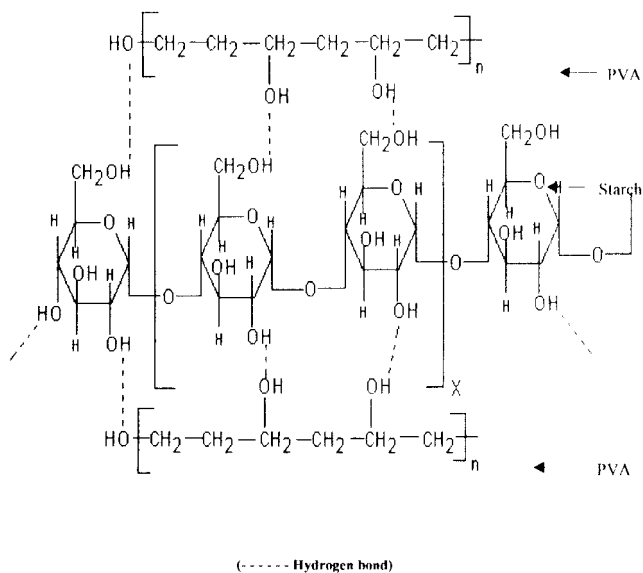
RESULTS AND DISCUSSION

Mechanical properties

The calculated mechanical properties such as tensile strength and percentage elongation at break of the PVA and PVA/starch films are given in Table I. The tensile strength, which is a measure of the resistance to direct pull, is important in machinability and packaging applications. It was observed that there was a slight variation in the tensile strength for all the compositions of PVA/starch compared with the tensile strength of plain PVA film. The tensile strength values for PVA/starch films are in the range 272 ± 7 kg/cm². The percentage elongation at break of PVA/starch is in the range 204–230, whereas for plain PVA film it is 200. From Table I, it may also be observed that there was a slight reduction in burst strength after incorporation of starch into PVA. A slight improvement in the tensile behavior of PVA/starch may be attributed to the formation of hydrogen bonds or chemical interaction between the –OH group of PVA and the –OH group of starch. The probability of formation of hydrogen bonds between PVA and starch is shown in Scheme 1.

Optical properties

The measured percentage transmission of light (at 480 nm), total diffuse and haze values of PVA/starch films are presented in Table II. Light transmittance decreases from 92 to 72% with an increase in starch content from 0 to 10%. This is attributed to the incor-



Scheme 1 Hydrogen bond formation between PVA and starch in PVA/starch blends.

poration of starch into PVA film, which scatters more light and increases the haze value. These results clearly indicate that PVA/starch blends are partially miscible blends, whereas haze values increase from 6 to 34.2 with increase in starch content in PVA blends, attributed to the incorporation of starch. Starch in the PVA system scatters the light and increases the haze value.

WAXS studies

WAXS recordings for pure PVA and its blends with different starch content are shown in Figure 1. From the figure, one observes only two reflections, which are well separated, at 2θ values of 9.3 and 19.18. The matching of simulated and experimental X-ray intensities was carried out as explained in our earlier study⁷ and the crystal imperfection parameters obtained from these computations are given in Table III. We carried out the computation for two Bragg reflections (2θ at 9.3 and 19.18°) and these do provide insight into

TABLE II
Optical Properties of PVA/Starch Composites

Starch in PVA (%)	Haze	Total transmittance	Diffusivity (%)
0	6.0	92	6
1	7.0	90	6
2.5	13.3	90	10
5	21.0	82	14
7.5	23.0	75	10
10	34.2	72	13

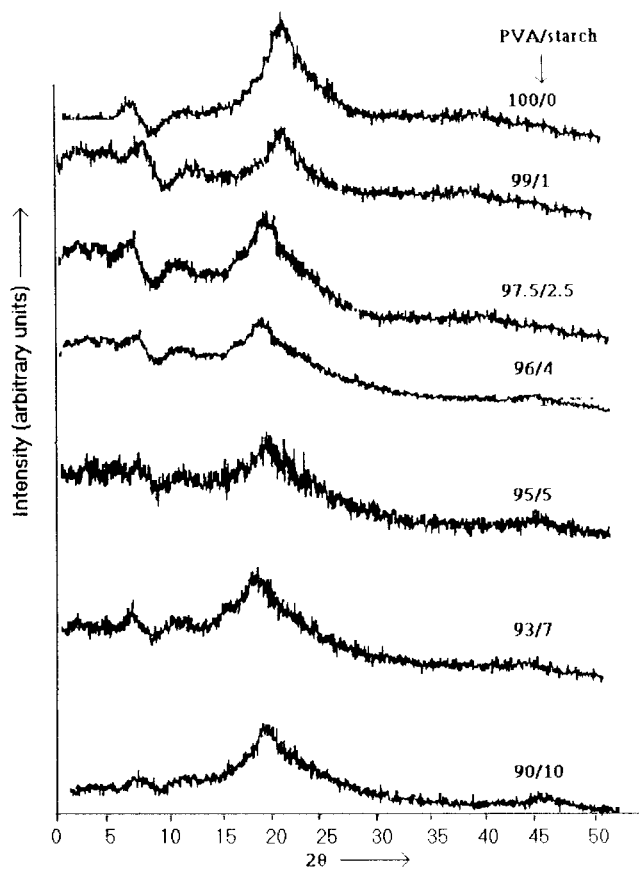


Figure 1 Wide-angle X-ray scattering patterns for PVA and blends of PVA with different starch contents.

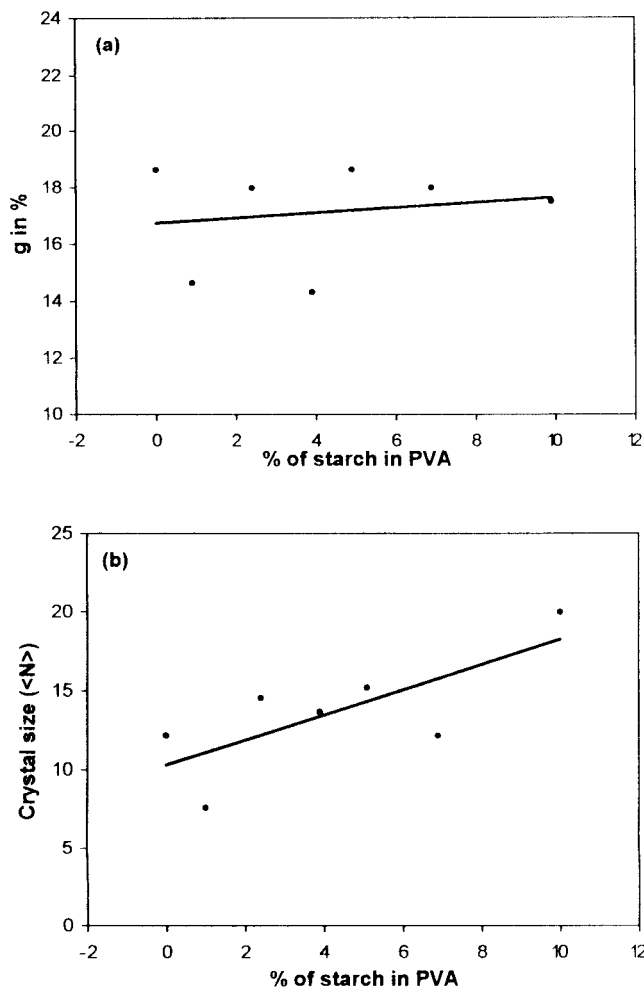


Figure 2 (a) Variation of crystal size (211) reflection with composition of PVA/starch. (b) Variation of lattice strain (g in %) (211) reflection with composition of PVA/starch.

changes in PVA/starch composites at the microlevel. A careful observation of Table III indicates that the values of α^* for the second Bragg reflection are greater than 0.4 and according to Hosemann,¹⁵ we are measuring the correlation length of the specimen here. The correlation lengths increase with increase in percentage of starch in the PVA matrix. These results justify the insignificant changes in physical properties, given

that the crystal region is not affected by the addition of starch. The percentage of deviation between simulated and experimental profiles was less than 2% in all the samples and for all the reflections. These results are

TABLE III
Microstructural Parameters of PVA/Starch Composites Obtained from WAXS^{a,b}

Sample	$d = 9.546 \text{ \AA}$					$d = 4.627 \text{ \AA}$				
	N	g (%)	Deviation (%)	D_{surf} (Å)	α^*	N	g (%)	Deviation (%)	D_{surf} (Å)	α^*
Pure PVA films	13.7 (3)	9.5 (2)	2.3	131.25	0.35	12.2 (3)	18.5 (2)	0.6	56.64	0.63
PVA + 1% starch	5.2 (1)	8.9 (1)	1.5	50.12	0.20	7.4 (1)	14.4 (1)	0.9	34.40	0.39
PVA + 2.5% starch	5.3 (1)	13.9 (1)	1.4	51.26	0.30	14.5 (1)	18.1 (1)	1.0	67.01	0.68
PVA + 4% starch	5.4 (1)	13.9 (1)	1.2	51.93	0.32	13.9 (1)	14.3 (1)	0.8	62.56	0.53
PVA + 5% starch	5.6 (2)	13.3 (1)	1.6	51.93	0.31	15.4 (2)	18.5 (1)	1.0	71.03	0.73
PVA + 7.5% starch	—	Insufficient data		—	—	12.5 (1)	18.0 (1)	0.8	57.98	0.64
PVA + 10% starch	—	Insufficient data		—	—	19.6 (1)	17.7 (1)	0.6	90.60	0.76

^a Value of errors are given in parenthesis.

^bStandard fit is the rms value of the deviation of the data from the fitted function in user unit. A reduced χ^2 much larger than 1.0 may be the result of incorrect function; here it is linearity.

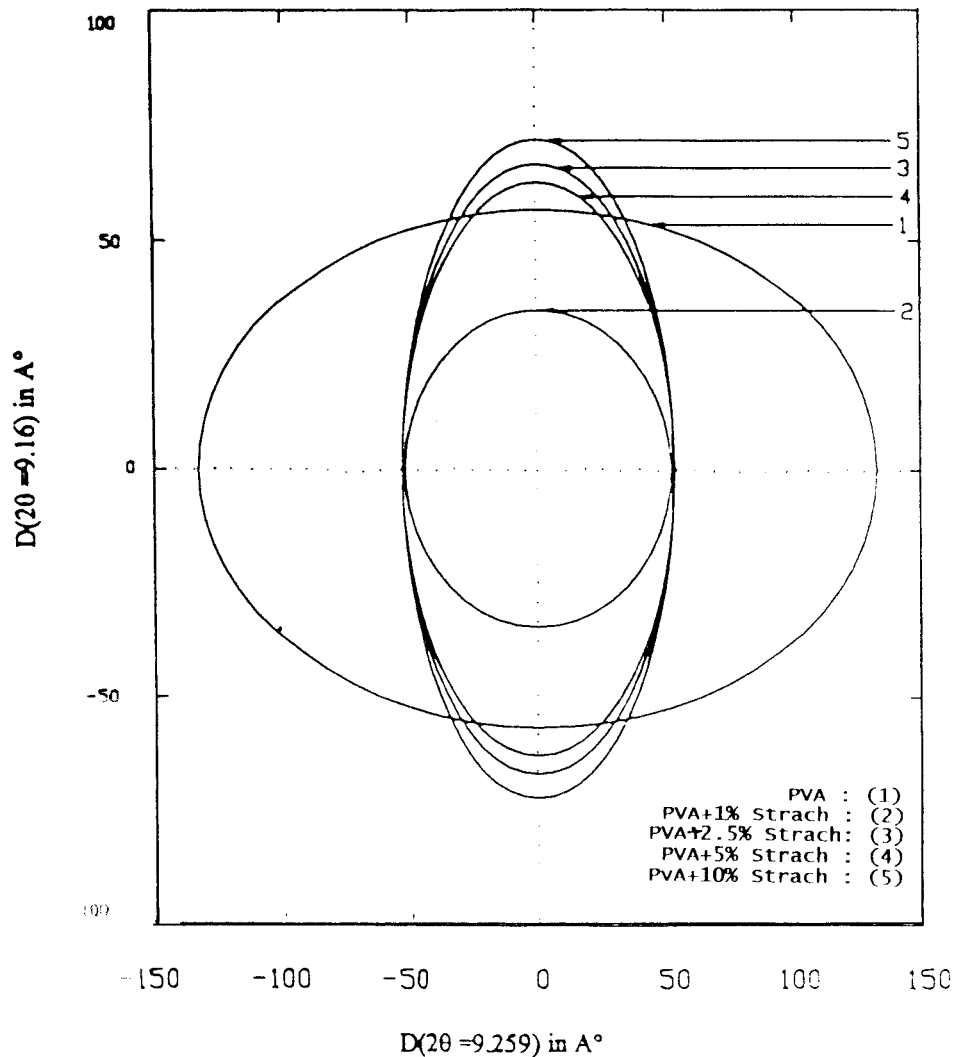


Figure 3 Variation in crystallite shape ellipsoid with percentage of starch in PVA films.

further justified by the behavior of microstructural quantities such as crystal size or correlation length ($\langle N \rangle$) and lattice strain (g) at the microscopic level as shown in Table III. In fact, if one looks at the effects of concentration of starch in PVA on structural parameters, we observe that there is an approximate linear change in microcrystalline parameters, as shown in Figure 2(a) and (b).

The statistical parameters for a linear fit give a standard fit value of 2.8, and a reduced χ^2 value of 7.87, which clearly shows the linear function and so is only an approximation. Here the standard fit value constitutes the rms values of the deviation of the data from the fitted function in user units (the number of unit cells). It is evident from Table III that for the first Bragg reflection, α^* values are less than 0.4 and thus the parameter $\langle N \rangle$ corresponds to the crystal size (Hosemann).¹⁵ Also, α^* remains constant for all the PVA/starch films, indicating that the

energy measured for the formation of polymer network does not vary with the percentage of starch. The crystal size value increases as observed for the reflection, $d = 4.627 \text{ \AA}$, with an increase in starch, which is compensated by the variation of lattice strain, resulting in insignificant changes in mechanical properties of the composites except for the haze. This may be attributable to the increase in degree of hydrogen bonding in the presence of starch, which leads to the reorientation of the polymer network in the blends. This is quantified in terms of crystal imperfection parameters such as lattice strain (g , in %) and crystal size ($\langle N \rangle$). To put these results in a better perspective we projected these results to a common x - y plane using the following equation and fitted the crystal size values of PVA/starch blends into a shape ellipsoid with one D_{surf} ($2\theta = 9.3$) in \AA along the x -axis and the other D_{surf} ($2\theta = 19.18$) along the y -axis.

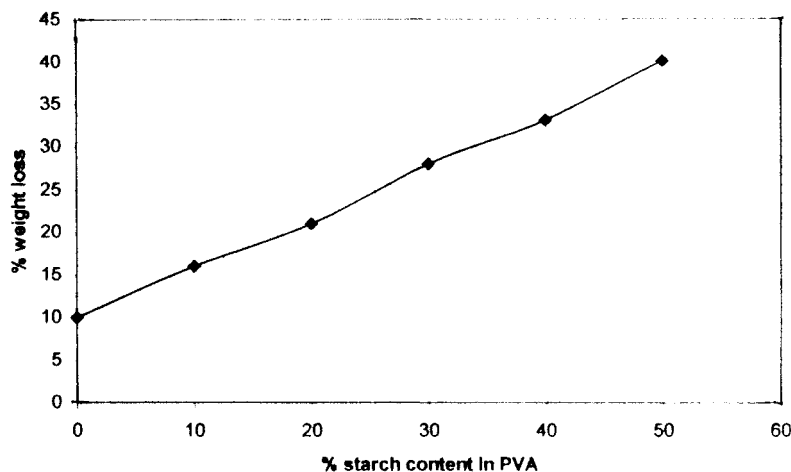


Figure 4 Weight loss during the biodegradation of PVA/starch films in compost mud (60 days).

$$\left(\frac{2}{N_{hkl}}\right)^2 = \left(\frac{\cos \theta}{y}\right)^2 + \left(\frac{\sin \theta}{x}\right)^2 \quad (5)$$

Here 2θ is the angle between the two (hkl) planes and D_{surf} is the crystal size corresponding to the particular (hkl) reflection. Figure 3 shows the comparison of the shape ellipsoid of crystallites of PVA/starch blends. According to Hosemann's model, these changes in crystal size values as well as shape ellipsoids are attributed to the interplay between the strain present in the polymer network and also the number of the unit cells coherently contributing to the X-ray reflection. This concept has been quantified in terms of the parameter α^* , called enthalpy.¹⁵ The average value of α^* is very low, which is in agreement with Hosemann's observation on polymer, and the value represents the amount of energy needed for the formation of the polymer network. The phase stabilization in PVA/starch composites has been quantified in terms of parameters α^* .

Biodegradation

The rate of biodegradation of PVA/starch blends is graphically shown in Figure 4. From the figure, it may be observed that the rate of biodegradation increases with an increase in starch content in the PVA matrix. There was about 40% weight loss in 50/50 PVA/starch film for 60 days and breakage of the film did not occur even after 3 months under optimized conditions. The ultimate weight loss did not exceed 40%, and thus this PVA/starch blend plastic film may not be easily degraded in natural conditions.

CONCLUSIONS

Increasing the percentage of starch content in the PVA matrix retains the mechanical properties such as ten-

sile strength (270 kg/cm²), percentage elongation at break (200%), and burst strength (0.70–0.88). These results support the formation of a hydrogen bond between the –OH group of PVA and the –OH of starch networks. PVA/starch film may not easily degrade in natural conditions. The extent of changes in the amorphous/crystalline regions has been quantified in the form of lattice strain (g) and crystal size ($\langle N \rangle$) values. The study establishes the structure-dependent physical properties of starch-modified PVA films.

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