

Structure Property Relations in Polyethylene Oxide /Starch Blended Films Using WAXS Techniques

Rampura. S. Jagadish,¹ Baldev Raj,¹ Puttanna Parameswara,² Rudrappa Somashekar²

¹Department of Food Packaging Technology, Central Food Technological Research Institute, Mysore 570020, Karnataka, India

²Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore 570006, Karnataka, India

Correspondence to: B. Raj (E-mail: baldev1564@yahoo.com)

ABSTRACT: A series of polyethylene oxide (PEO)/starch blends were prepared by extrusion and their films were prepared by compression molding. It was observed that the presence of characteristic peaks of PEO and starch at 845 and 1643.7 cm^{-1} , respectively, in FTIR spectra of PEO/starch blends favors the blending of PEO/starch. The physicochemical and optical properties of PEO/starch-blended films were measured. The tensile strength of the blended films decreased, whereas the haze values increased with an enhanced starch concentration in PEO/starch blends. The results obtained were correlated with microstructural parameters such as, crystallite size and lattice strain determined using wide angle X-ray scattering (WAXS) data. The X-ray line profile analysis shows that the crystallite shape area is maximum in PEO and decreases with the addition of starch. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: PEO; starch; mechanical properties; crystallite size; microstructural parameters; WAXS

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INTRODUCTION

In view of the modern society's over dependence on plastics, which has reached a stage where its over use has become detrimental for the survival of future generations. It is therefore natural that a growing public concern over diminishing landfill space and accumulation of surface litter has necessitated the development of degradable plastics. In this regard, blending of polymers is an effective way for the development of novel polymeric materials with desired properties, low cost, less time consuming, and easy process ability. The blends between biopolymer and synthetic polymers are of particular significance, because they can combine biocompatibility with good process ability and mechanical resistance and also can be used as biomaterials. In view of the recent thrust on eco-friendly packaging materials for food products, one such interesting blend could be polyethylene oxide (PEO)/starch blend.^{1,2}

Polyethylene oxide has been widely used in biomedical field because of its excellent hydrophilic nature, high viscosity, ability to form hydrogen bonds with ether oxygen, and biocompatibility. It also finds applications in different aspects of industry including cosmetics.^{3,4} Studies by Kondo and Sawatari⁵ have established that the primary hydroxyl group on cellulose and methyl celluloses can form hydrogen bond together with oxygen

in PEO. Caykara et al. have reported hydroxyl groups on sodium alginate, which can also form a hydrogen bond to the ether oxygen in PEO. Similarly, hydroxyl group on starch can also form a hydrogen bond to the ether oxygen in PEO. Therefore, PEO as a suitable polymer blended with starch was consequently selected for these studies.

Starch is next to cellulose, one of the most abundant and naturally occurring polymer, it is also a chief reserve polysaccharide of grains consisting of cereals, millets, and pulses. It has linear amylose, α -(1-4)-*D*-glucan (water soluble) and branched α -(1-4) (1-6)-amylopectin (water insoluble) components, its granules vary in size from 2 to 100 μm and may be round, oval, or irregular in shape. They are birefringent in general and show characteristic "maltese cross" pattern under polarizing microscope. They are also semicrystalline in nature and exhibit a well-defined X-ray diffraction patterns.^{7,8} Today, starch which is of low cost and with its versatile properties, such as aqueous dispersion, bonding ability, formation of films, etc., has become the most important hydrocolloid for various uses.^{9,10} Incorporation of starch into the PEO matrix changes the physicochemical properties of the material which modifies the polymer structure both at the molecular and the morphological levels. In view of this, the wide angle X-ray (XRD) analysis was carried

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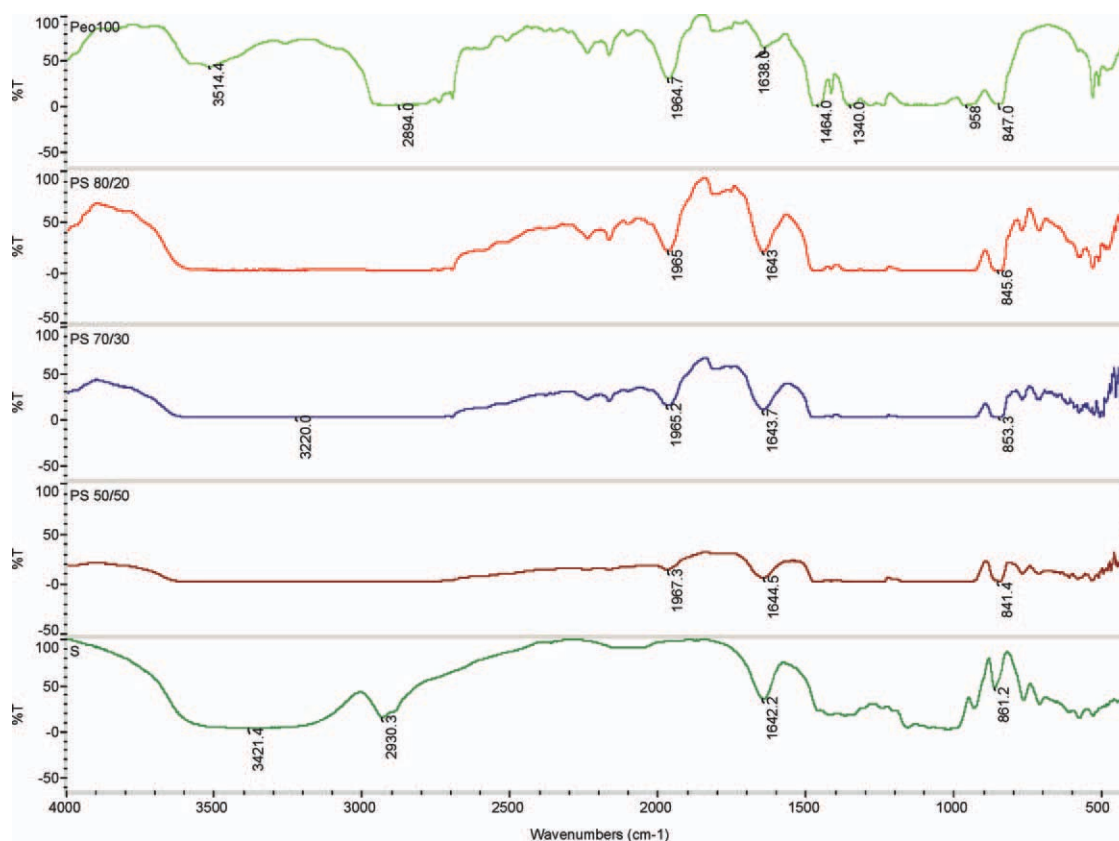


Figure 1. FTIR characteristics of PEO/starch-blended films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

out to determine microstructural parameters, such as crystal size and lattice strain. These microstructural parameters are correlated with measured values of physicomechanical and an optical property of PEO/starch blends. In fact, the shelf life of food products is determined by the physical properties of these specific blends.

EXPERIMENTAL

Materials

Polyethylene oxide (PEO) of molecular weight (~ 200 kDa) was procured from Sigma-Aldrich, St. Louis, MO, and corn starch was obtained from M/S Riddhi Siddhi, Gluco Bio Ltd. Gokak,

Karnataka, India. All other chemicals were of analytical grade and obtained from M/s SD Fine Chemicals, Bangalore, Karnataka, India.

Methods

Extrusion Process for PEO/Starch Films. A series of PEO/starch blends, namely 100/0, 90/10, 80/20, 70/30, and 60/40 were extruded, using mixing extruder (LE-075, Custom scientific instrument). Rotor and header temperature were maintained at 80 and 100°C, respectively, after standardization. The screw rotation was set at 60 rpm. Once, the set temperatures of rotor and header were attained, and then several compositions

Table I. Physicomechanical and Optical Properties of PEO/Starch-Blended Films

PEO/starch films (wt %)	Tensile strength (MPa)	Percent elongation	Heat seal strength (MPa)	Haze
PS-100/0	3.47 \pm 0.071 ^a	17.10 \pm 0.363 ^a	2.7 \pm 0.114 ^a	82.2 \pm 0.560 ^a
PS-95/05	3.22 \pm 0.065 ^b	13.5 \pm 0.243 ^b	2.51 \pm 0.081 ^b	83.7 \pm 0.346 ^b
PS-90/10	3.07 \pm 0.138 ^b	10.3 \pm 0.139 ^c	2.43 \pm 0.162 ^b	84.7 \pm 0.337 ^c
PS-85/15	2.89 \pm 0.090 ^c	9.15 \pm 0.185 ^d	2.31 \pm 0.147 ^b	85.4 \pm 0.785 ^c
PS-80/20	2.76 \pm 0.055 ^d	8.20 \pm 0.259 ^e	2.27 \pm 0.051 ^b	86.5 \pm 0.176 ^d
PS-75/25	2.49 \pm 0.119 ^e	7.69 \pm 0.276 ^f	2.09 \pm 0.048 ^c	87.1 \pm 0.157 ^e
PS-70/30	2.26 \pm 0.202 ^e	7.30 \pm 0.244 ^g	1.79 \pm 0.085 ^d	87.4 \pm 0.640 ^e
PS-60/40	1.94 \pm 0.126 ^f	5.90 \pm 0.142 ^h	1.52 \pm 0.108 ^e	88.1 \pm 0.748 ^e

The data with different superscripts (a, b, c, d, e, f, g, and h) differ significantly at the probability level $P \leq 0.05$. The data with same superscripts does not differ significantly. Thickness of the film = 25 μm .

Table II. Microstructural Parameters of PEO/Starch-Blended Films Using WAXS Data and Exponential Distribution Function

Sample	$d_{hkl} = 4.63\text{\AA}$				$d_{hkl} = 3.80\text{\AA}$				Crystallite area (nm ²)
	$\langle N \rangle$	g (%)	Δ (%)	$D_S = \langle N \rangle_{dhkl}$	$\langle N \rangle$	g (%)	Δ (%)	$D_S = \langle N \rangle_{dhkl}$	
PS-100/0	36.49	0.1	4.71	168.95	29.47	0.1	4.11	111.98	189.19
PS-95/05	35.35	0.1	5.75	163.67	26.98	0.1	5.72	102.52	167.79
PS-90/10	33.92	0.1	3.92	157.05	28.07	0.1	3.87	106.66	167.50
PS-85/15	33.99	0.1	5.61	157.37	27.61	0.2	5.75	104.92	165.11
PS-80/20	33.14	0.2	5.68	153.44	27.50	0.2	5.92	104.50	160.34
PS-75/25	30.73	0.1	4.77	142.28	28.81	0.1	4.78	109.48	155.76
PS-70/30	31.20	0.1	4.11	144.45	27.41	0.2	5.81	104.16	150.45
PS-60/40	46.54	0.1	4.49	215.48	29.20	0.1	4.52	110.96	239.09

$\langle N \rangle$, average number of unit cells in the direction perpendicular to Bragg's plane; g , lattice strain parameter; $D_S = \langle N \rangle_{dhkl} \rightarrow$ surface weight crystallite size; Δ = standard deviation of the parameters.

of physically blended PEO/starch samples were fed separately through the feed hopper into the feed section of the barrel. As a result, continuous strands of PEO/starch blends emerged through the die. These strands were then passed through the pelletizer to obtain pellets. The prepared pellets of different compositions of PEO/starch blends were used for processing films by thermo-press technique at 80–90°C at 100 kg/cm² pressure and were cooled slowly. The processed films with 25–30 μm were collected and then stored in sealed aluminum foil-based pouches at 4°C to prevent any interaction with atmospheric moisture.

FTIR Spectral Studies. Thin films of PEO/starch with uniform thickness were used for obtaining the IR spectra using FTIR-RAMAN Nicolet 5700 instrument. All measurements were carried out at 20°C in anhydrous conditions with air as the background. For each sample, 32 scans at a 2 cm⁻¹ resolution were collected in the range of 4000–400 cm⁻¹. The spectra were then analyzed with a curve-resolving technique based on a linear least squares analysis to fit in a combination of Lorentzian and Gaussian curve shapes.^{11,12}

Mechanical Properties. Tensile strength (TS) and percentage elongation (% ε) at break for the series of PEO/starch-blended films were measured as per ASTM-D-882 method using Lloyd's universal testing (LLOYDS-50K, London, UK) instrument at an ambient temperature of 25 ± 2°C and an average of five measurements was noted.

Heat seal strength (HSS) is the measure of the force required to pull apart the pieces of film that were sealed together. The test was carried out for the series of PEO/starch-blended films as per ASTM-D-1876 using LLOYD's universal testing (LLOYD's-50K, London, UK) instrument. Two strips of the same plastic films (6.25 cm × 2.5 cm) were then sealed together using a HP impulse sealer (Sunray Industries, Mysore, India) at 8.4 kgf/cm² pressure for 6 s to obtain a standard seal width of 10 mm. Free ends of the sample were mounted on two grips of the tensile testing machine and the movable jaw was driven at a constant rate of 100 mm/min breaking the sealed area apart. The load required to break the seal of the sample was noted. Seal strength

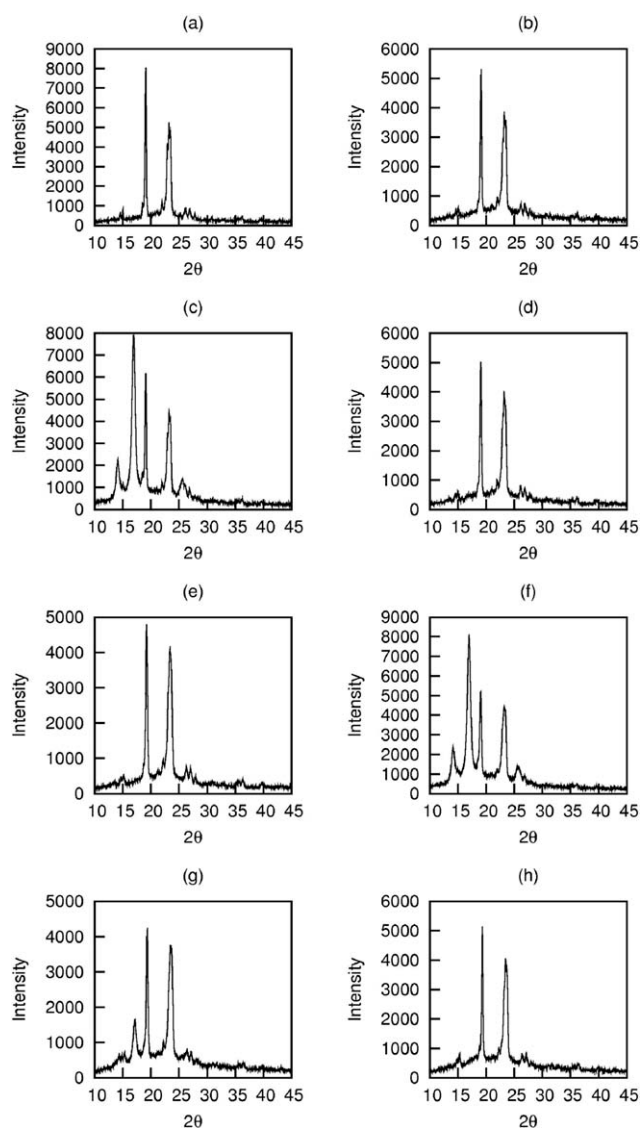


Figure 2. X-ray diffraction patterns for, PEO, starch, and PEO/starch-blended films. (a) PS100/0, (b) PS95/05, (c) PS90/10, (d) PS85/15, (e) PS80/20, (f) PS75/25, (g) PS70/30, (h) PS60/40.

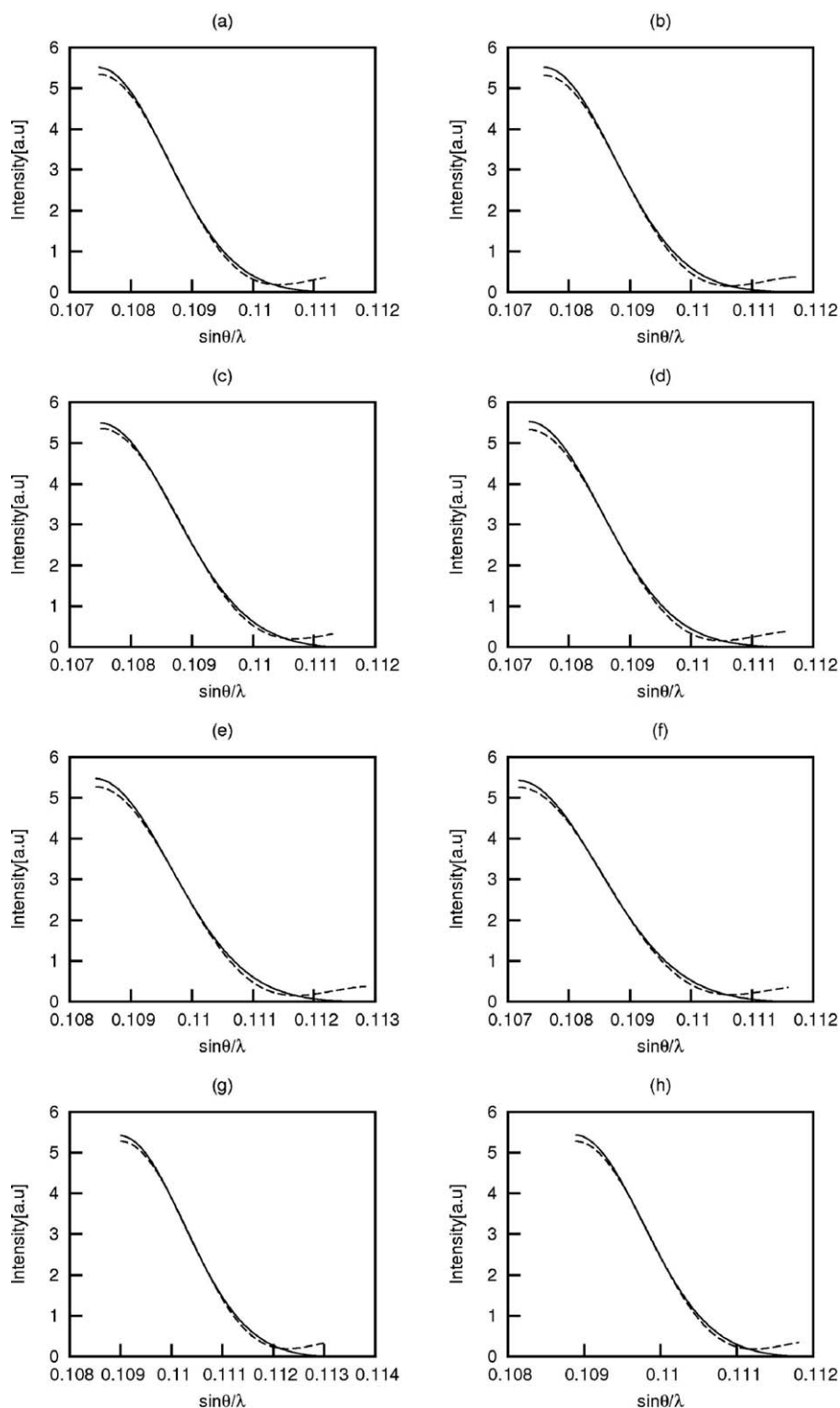


Figure 3. Experimental and simulated profiles for, PEO, starch, and PEO/starch-blended films using exponential size distribution function for 2θ – 19° . (a) PS100/0, (b) PS 95/05, (c) PS 90/10, (d) PS 85/15, (e) PS 80/20, (f) PS75/25, (g) PS70/30, (h) PS60/40.

was calculated by dividing the load at break by the seal width. An average of five measurements was noted.

Optical Properties. Optical properties of the series of PEO/starch-blended films were measured by a Suga test using Digital

Haze meter (model HGM-2DP, Japan). The haze behavior of dust- and grease-free films was recorded as per ASTM-D-1003-61 method.

X-ray Diffraction Patterns. The XRD patterns of the PEO/starch blends were recorded using Rigaku Miniflex II

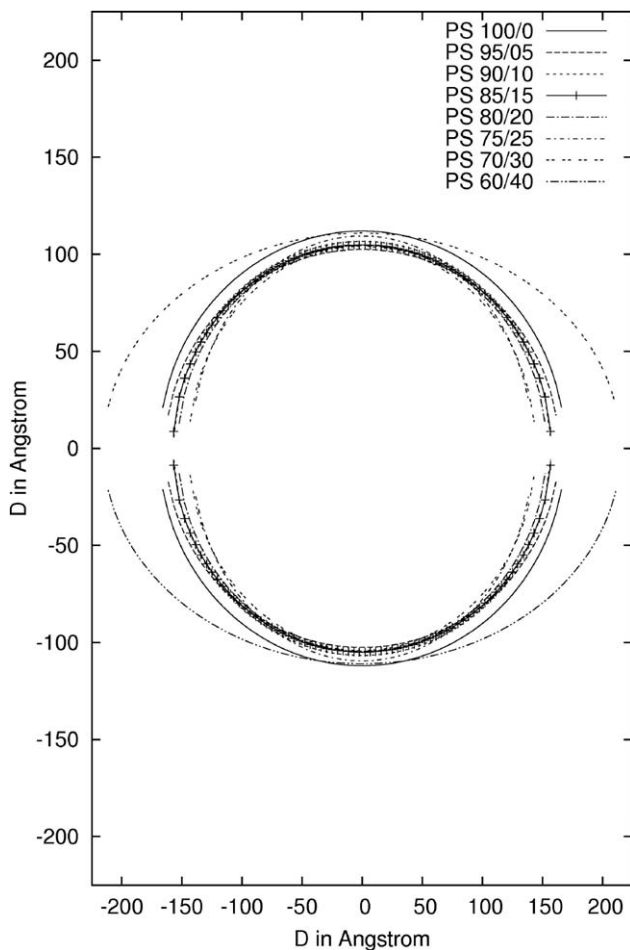


Figure 4. Ellipticity of crystallites observed in PEO and PEO/starch-blended films.

Diffractometer with Cu-K α radiation of wavelength 1.5406 Å. The samples were scanned in the two-theta range 10–45°. Obtained XRD patterns were used for X-ray line profile analysis (LPA) to determine microstructural parameters.

Theory of Line Profile Analysis. The scans of X-ray diffraction profile obtained from pure and blended film samples were used for the estimation of microstructural parameters such as crystal size and lattice strain/distortion using line profile analysis. For the line profile analysis, we have used Fourier method of Warren and Averbach,¹³ wherein an analytical expression for the crystallite size distribution has been used. This method is also referred as single-order method.

The crystallite size $D (=Nd_{hkl})$ and lattice distortion ' g ' (in %) are related through the Fourier coefficients $A(n)$ of the X-ray profile intensity $I(s)$ given by^{13–15}

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

Also, Fourier coefficients can be factorized into size $A_s(n)$ and disorder $A_d(n)$ coefficients.

$$A(n) = A_s(n) \cdot A_d(n) \quad (2)$$

Various analytical forms for the distribution of crystallite sizes have been investigated by Hall and Somashekar.¹⁶ Using asymmetric exponential distribution function, one can arrive at the following expression^{17,18}:

$$A_s(n) = A(0)(1 - n/\langle N \rangle); \quad n \leq p, \quad (3)$$

$$A_s(n) = A(0)(\exp\{-\alpha(n - p)\}/\alpha\langle N \rangle); \quad n \geq p. \quad (4)$$

Here ' p ' is the smallest crystal size.

$$A_d(n) = \exp(-2\pi^2 m^2 n g^2) \quad (5)$$

$A_d(n)$ is the disorder coefficient for a paracrystal having a Gaussian distribution of standard deviation σ , ' m ' is the order of reflection, and ' g ' is the paracrystallinity parameter of lattice distortion. Essentially, an intensity profile I versus 2θ , is converted into I versus $\sin(\theta)/\lambda$ and hence used to compute Fourier coefficient. Initial values of $\langle N \rangle$ and ' g ' were obtained using the method of Nandi et al.¹⁹ Using these values in the above-mentioned equations, the corresponding values for the distribution function are obtained. The reliability of this method was also analyzed in the recently concluded round robin test by IUCr.²⁰

Statistical Analysis. The significant differences between means of samples were determined by t -test using Microsoft Excel. Significance of differences was defined at $P \leq 0.05$.

RESULTS AND DISCUSSION

Chemical Characterization by FTIR Spectroscopy

FTIR analysis of blended films was carried out to detect any peak shift that could be attributed to weak interactions between two polymers. The FTIR spectra of PEO, starch, and PEO/starch-blended films in the wave number range of 4000–400 cm^{-1} were depicted in Figure 1. In the spectrum of PEO, the characteristic band of PEO was observed at 847 cm^{-1} due to C—O—C bonding along with (—O—H) stretching at 3514.4 cm^{-1} , (—C—H) stretching of methylene groups at 2894 cm^{-1} , and —C—H stretching, bending, and rocking vibrations at 1464, 1340, and 958 cm^{-1} were observed, respectively. On the other

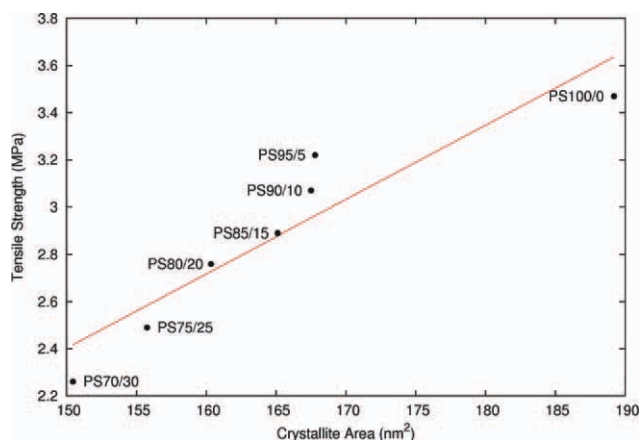


Figure 5. Variation of tensile strength with crystallite area for different percentage of starch in PEO films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

hand in the spectrum of starch, strong absorption owing to (—O—H) stretching vibration appeared at 3421.4 cm^{-1} . It is typical of the polymeric absorption of hydroxyl groups. —C—H stretching at 2930.3 cm^{-1} and the peak at 1642.2 cm^{-1} attributed to deformation of O—H were observed. In the blends of PEO/starch, it was observed that the presence of characteristic peaks of PEO and starch at 845 and 1643.7 cm^{-1} , respectively, favors the blending of PEO/starch. Further, broadening of 3421 and 1642 cm^{-1} can be attributed to the intermolecular hydrogen bonding between PEO/starch that favors blending.^{6,21–23}

Mechanical Properties

The physicochemical properties of PEO/starch-blended films are presented in Table I. Tensile strength values decreased from 3.47 MPa for 100/0 PEO/starch film to 1.94 MPa for 60/40 PEO/starch films. Tensile strength of 95/5 and 90/10 PEO/starch-blended films were similar to the TS of pure PEO films. However, with 20% or more starch in the blend, the TS of the films decreased relatively to the starch fraction. Compared with the TS values of widely used LDPE film of 4.14 MPa for 25- μm thickness, 90/10 PEO/starch films retained good tensile strength. Similar to TS, Percent elongation (% ϵ), and Heat seal strength (HSS) values were decreased from 17.1 and 2.7 MPa for 100/0 PEO/starch films to 5.90 and 1.52 MPa for 60/40 PEO/starch films, respectively. The reduction in TS, (% ϵ), and HSS of PEO/starch-blended films due to the formation of hydrogen bonds between PEO and starch, leads to the formation polymer network favoring increase in amorphous content in the blends. These results were in accordance with the reported literatures.^{7,22}

Optical Properties

The optical properties viz., haze for the PEO/starch-blended films are reported in Table I. The haze values increased from 82.2 to 88.1 as the starch content enhanced from 0% to 40% in PEO/starch-blended films as observed in Table II. The increase in haze after incorporation of starch into the PEO matrix could be due to the scattering or diffusion of light radiation by starch.^{7,22,24}

Microstructural Parameters Using WAXS Data of the Blends

X-ray diffraction patterns of PEO/starch blends of different weight ratios are as shown in Figure 2. Presence of sharp (crystalline) and broad (amorphous) peaks in all the samples confirms two phase morphology. As seen from the patterns, PEO/starch blends consists of two major crystalline peaks at $2\theta = 19^\circ$ ($d = 4.63\text{ \AA}$) and $2\theta = 23.39^\circ$ ($d = 3.80\text{ \AA}$). These peaks are used for line profile analysis to determine microstructural parameters, such as crystallite size ($\langle N \rangle$), lattice strain (g , in %), and crystallite area in blended films. The experimental and simulated intensity profiles are as shown in Figure 3. Microstructural parameters calculated are given in Table II. For a better perspective of the results given in table, we have projected crystallite size along two directions on to a two dimension space and the corresponding crystallite shapes for various blends studied here are given in Figure 4. It is observed that the pure synthetic polymer (PEO) showed higher crystallite size and crystallite area. This is in conformity with the high value of tensile strength observed here for PEO. These microstructural parameters decrease in blended films with the addition of starch. Here, PEO being more crystalline, the variation in crystallite area in the blends is mainly due

to variation in crystallite area of synthetic polymer. The decrease in crystallite area of the films is in consistence with the mechanical properties (Figure 5). Tensile strength of PEO alone is higher compared with that of starch-added films. This kind of decrease in crystallite area and hence the mechanical properties is due to formation of bulky groups, which leads to an increase of amorphous content in the blends. Similar behaviors with starch/synthetic polymers are reported by Ramkumar et al.²⁵ However, the crystallite area increases after 30% of starch loading probably due to the phase separation between PEO and starch. This phase separation at higher dosage of starch may be due to the immiscible nature of blends. Moreover, at higher loading, starch agglomerated and was confined in between PEO chains.²²

CONCLUSION

The tensile strength and percent elongation decrease gradually with the addition of starch to PEO. The X-ray line profile analysis also shows that the crystallite shape area is maximum in PEO and decreases gradually with the addition of starch, due to the formation of hydrogen bonds between PEO and starch, which leads to a formation of polymer network favoring amorphous component. However, the haze values increased with an increase in starch concentration in PEO–starch-blended films. There are several food products whose shelf life depends on the reduced amount of light, which may act as a reduced catalytic factor in the nondegradation of food products. The earlier studies indicate the characteristic nature of PEO/starch blends for appropriate applications in industries.

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