STRUCTURE DEVELOPMENT AND PROPERTIES OF PLASTICIZED PVA-STARCH-PADDY STRAW COMPOSITES

PRATIK PANDIT POTDAR,^{*} PREETINDER KAUR,^{*} MANPREET SINGH,^{*} MALHARI B. KULKARNI^{**} and SUBRAMANIAM RADHAKRISHNAN^{**}

 *College of Agricultural Engineering and Technology, Punjab Agricultural University, Ludhiana 141004, India
 **Polymer Engineering, MIT World Peace University S124, Paud Road Kothrud, Pune 411038, India
 © Corresponding author: S. Radhakrishnan, radhakrishnan.s@mitpune.edu.in

Received June 8, 2023

Paddy straw is often burnt in the fields or disposed of in ways that cause extensive environmental pollution. The present study focused on using paddy straw in bio-compostable composites fabricated with polyvinyl alcohol (PVA) and thermoplastic starch blends as a matrix. Locally available paddy straw was chopped, cleaned and treated with 15% NaOH solution for four hours. The alkali treatment produced changes in the crystal structure and surface morphology of the paddy straw. Then, it was dispersed in blends of PVA and starch solutions containing polyethylene glycol (PEG200) as plasticizer. The PEG200 acted as both plasticizer and compatibilizer, as evidenced by the single glass transition peak and the lower melting point of the film cast from these blends. These composite films had higher thermal stability, increased tensile strength, but also flexibility. These properties were associated with structure development with strong hydrogen bonding interaction between the paddy straw and PVA-starch blends, which was supported by results of characterization studies.

Keywords: composite, bio-polymer, PVA, paddy straw, starch, crystal structure, morphology

INTRODUCTION

Conventional plastics have been used extensively for flexible and rigid packaging due to their excellent barrier properties, optical clarity, mechanical properties, sealability etc. However, these have become a major source of pollution largely because of the use-and-throw habits of people. Packaging materials constitute almost 42% of plastic waste in the environment.¹ Hence, extensive efforts have been made in recent years packaging substitute plastics with to polymers.2-4 biodegradable/biocompostable Researchers are looking at natural resources, such as starch, cellulose, oil extracts etc. for developing such eco-friendly materials.5-7

At the same time, there is ever-growing farm waste being generated due to increasing production. Farmers face a number of difficulties for proper disposal of this waste and many of them take to burning the residues after harvesting the crop. As an example, paddy straw or stubble is not properly disposed of in many states of India. In order to mitigate this problem, it is essential to make a value-added product out of such waste.

Starch based composites using paddy straw appear to be an attractive route to properly utilize this natural resource. Polyvinyl alcohol (PVA) blended with starch has been explored by many research groups, including the authors of the present work, for the synthesis of biocompostable films.⁸⁻¹¹ Starch is considered as an attractive biodegradable filler due to its low cost, low density, non-abrasive nature and biodegradability characteristics. Starch is composed of amylose, a linear polymer of a-1,4-linked glucose units and amylopectin, a highly branched polymer of a-1,4linked chains interlinked with 1,6-linkages.¹²⁻¹⁴ However, native starch exists in granular state owing to hydrogen bonding between the adjacent molecules. This leads to improper dispersion within the plastic matrix, thereby leading to poor composite properties.

Plasticization of starch with a suitable amount of water and plasticizers to convert it into *Cellulose Chem. Technol.*, **57** (9-10), 1073-1085 (2023) thermoplastic starch (TPS) to improve processability has been reported by a number of authors.¹⁵⁻¹⁷ A number of plasticizers, such as glycerol, sorbitol, polyethylene glycol (PEG), urea etc. have been studied in the past.¹⁸⁻²⁰ Polyvinyl alcohol (PVA) is readily mixed with starch in aqueous medium and few reports are available on solvent cast blends of PVA and starch. However, PVA is also crystalline polymer, which cannot be easily processed by melt extrusion techniques.²¹ The effects of plasticizer on PVA have not been reported extensively. The previous studies²² have revealed that the structure of PVA/cassava starch was greatly affected by the plasticizer used and the heat treatment given during the film preparation. Incorporation of natural fibers into polymer blends can lead to considerable improvement in the mechanical, as well as barrier properties.^{23,24}

incorporated PVA-starch blends with nanocellulose have been reported²⁵ to exhibit improved mechanical performance. The fibers used in making polymer composites usually have to be pretreated, so as to increase interfacial bonding. To improve the interfacial adhesion between natural straw and the polymer, some technologies are used to modify the surface structure of the straw, including physical methods (such as gamma radiation or corona),^{26,27} as well as chemical methods,^{28,29} such as pretreatment of straw surfaces by coupling agents, such as silanes and isocyanates, and/or modification of the matrix by grafting with reactive moieties, such as acrylic acid, maleic anhydride, etc. In our earlier studies, banana fibers treated with alkali exhibited higher strength tensile in polypropylene hybrid composites.³⁰ In the present investigations, the paddy straw was also pretreated before use. The effect of alkali treatment on the structure development has also been investigated. The present studies are mainly focused on the effect of incorporating paddy straw on the structure development and properties of PVA-starch blends.³¹⁻³⁴ These results are expected to lead to optimizing the composition and processing for

improving the properties of composites made from PVA starch and paddy straw. All the materials are readily available and eco-friendly, while the process for making the composites is easily adaptable to the farm environment, and thus, our study is expected to provide a solution to the existing problem of paddy straw disposal.

EXPERIMENTAL

Materials

Paddy straw obtained from the fields of Punjab Agricultural University, Ludhiana, India, was first chopped, then washed with copious amounts of water and dried in an air circulating oven. This was used for further experimentation. PVA of M.W. 14000 and degree of hydrolyzation of 86-89 mole%, was supplied by Thomas, India. Corn starch was supplied by Ridhi Sidhi Co., India. Polyethylene glycol (PEG 200), NaOH and other chemicals were procured from Loba Chemie, and were used as such. Deionised water was used for making blends and casting films.

Preparation of formulations

The cut and dried paddy straw was first treated with alkali at different concentrations (Table 1) at 55 °C for 4 h. This mass was filtered and then dried thoroughly at 55 °C in an air circulating oven as before. The process flow chart for the preparation of the PVA-starch composite with paddy straw is given in Scheme 1.

In 200 mL of water, 10% of starch (w/w basis) was added, mixed with a stirrer and heated to constant temperature of 60 °C, followed by continuous stirring for 4 hours to obtain a clear solution. The PVA solution was prepared separately by addition of 10% of PVA powder to 200 mL of water (w/w basis) under continuous stirring and heated to constant temperature of 60 °C. This was further stirred thoroughly for 4 hours to obtain a clear solution free from turbidity. The two solutions were then mixed in different proportions, as given in Table 2. The treated paddy straw was first ground, then dispersed in the solution containing PVA (14000 MW) and corn starch in different proportions with plasticizer (polyethylene glycol PEG200) (see Table 2), mixed thoroughly and cast in flat plastic trays. The plasticizer concentration was kept at 20% with respect to solid for all compositions. These were dried at 55 °C for four hours.

Table 1Rice straw alkali treatment process

Sample no.	NaOH concentration (%)	Temperature (°C)	Time (min)
1	5	55	240
2	10	55	240
3	15	55	240



Scheme 1: Process flow chart for sample preparation

Sample	Starch	PVA	Paddy straw	PEG
code	(% total)	(% total)	(% total)	(%)
0	3 (40%)	4 (53.3)	0	0.5
1g UT	3 (35.3%)	4 (47.06%)	1 (11.75%)	0.5
2g UT	3 (31.57%)	4 (42.10%)	2 (21.05%)	0.5
3g UT	3 (28.57%)	4 (38.09%)	3 (28.57%)	0.5
4g UT	3 (26.08%)	4 (34.78%)	4 (34.78%)	0.5
1g T	3 (35.3%)	4 (47.06%)	1 (11.75%)	0.5
2g T	3 (31.57%)	4 (42.10%)	2 (21.05%)	0.5
3g T	3 (28.57%)	4 (38.09%)	3 (28.57%)	0.5
4g T	3 (26.08%)	4 (34.78%)	4 (34.78%)	0.5

Table 2 Film casting formulations

Note: UT = untreated paddy straw powder, T = alkali treated paddy straw powder

The thickness of every composite film was calculated by using a digital micrometer (model QLR digit-IP54, Qinghai, China) to the nearest 0.0001 mm. Measurements were taken at ten random places of the films. Thus, the average thickness of each film was determined. The sheets were peeled off, cut to size, characterized and tested for different mechanical and thermal properties.

Physico-chemical and mechanical characterization Wide angle X-ray diffraction (WAXD)

Wide angle X-ray diffraction (XRD) analysis was carried out using an X-ray diffractometer (Philips X'Pert MPD, Japan), which had a graphite monochromatic beam, and a Cu Ka radiation source operated at 40 kv and 30 mA. The basal spacing or d 001 reflection of the samples was calculated from Bragg's equation by monitoring the diffraction angle 2θ from 5° to 50°.

Scanning electron microscopy

The morphology of PVA-starch-paddy straw composite films was analyzed by using a JEOL JSM-6360LA scanning electron microscope (JEOL Ltd., Tokyo, Japan). Both treated and untreated paddy straw particles were dispersed on the stub, followed by sputter coating. The composite films were also observed and micrographs were recorded at magnifications from 350 to 1000X.

Fourier-transform infrared spectroscopy

Fourier-transform infrared spectroscopy (FTIR) spectra were examined in attenuated total reflection mode (ATR) and the data were converted internally in transmittance (T, %). Spectrograms of all the samples

were recorded from 400 to 4000 cm⁻¹, with 32 scans at a resolution of about 8 cm⁻¹ on an Alpha FTIR spectrometer (Bruker UK Ltd.).

Thermal properties

The melting, crystallization and thermal stability of PVA-starch-paddy straw composites were studied using differential scanning calorimetry (DSC 7020 Ibaraki, Japan) and thermogravimetric Hitachi, (STA7200 Ibaraki. analysis Hitachi, Japan), respectively. The samples for DSC analysis (5–10 mg) were initially scanned from 30 °C to 200 °C under nitrogen atmosphere, at a heating rate of 10 °C/min, to erase the previous thermal history. Subsequently, the sample was held at 200 °C for 1 minute, cooled to 30 °C and rescanned from 30 °C to 200 °C. The corresponding glass transition temperature, melting temperature, heat of fusion and crystallization temperature were recorded. The thermal stability of the PVA-starch-paddy straw composites was determined using TGA with samples of 5 mg weight, scanned from 30 °C to 700 °C, at a heating rate of 10 °C/min in nitrogen atmosphere. The onset and final degradation temperature and the corresponding percentage weight loss for the samples were noted. Differential thermogravimetry (DTG) as well as differential thermal analysis curves were also recorded for determining the exact transition and peak temperatures.

Mechanical characterization

The tensile strength and elongation at break of the PVA-starch-paddy straw composite films were assessed by utilizing a double column texture analyzer (Stable Micro Systems, Model: TA.TXT Plus). The tension test was employed to ascertain the tensile strength of the composite films. The strain value was set at 50 per cent and grip separation was set at 50 mm, with a cross-head speed of 20 m/min. The tensile strength and elongation at break were estimated according to standard procedures. Three test specimens were used and the average value was determined.

Water vapour transmission rate (WVTR)

WVTR is a film barrier property, and it was assessed by using the desiccant method ASTM E96. A desiccant (anhydrous CaCl₂) was put in a Petri dish and the film was placed over the opening of the Petri dish and the dish was sealed with the help of silicon grease. The initial weight of the Petri dish was measured at room temperature and afterwards, it was put in a desiccator carrying saturated sodium chloride solution at the bottom, thereby maintaining a relative humidity of 90%. Subsequently, the desiccator was put inside an incubator at 38 ± 1 °C for 7 h. The gain/loss in weight was checked at regular intervals, which was due to the absorption of the moisture that permeated through the film. WVTR was determined by using the formula WVTR = 24 x (Mg/tA), where Mg is the mass gain/loss in g, t is the time in h, and A is the surface

area in m^2 , which was estimated from the diameter – in this case, it was 0.09 m.

RESULTS AND DISCUSSION XRD analysis

The alkali treatment of paddy straw resulted in the removal of lignin and the colour changed from brown to pale yellow. There was also an increase in the fluffy nature of the straw powder. The structural changes in the straw due to the treatment were investigated. The XRD diffractograms of untreated and alkali treated paddy straw are compared in Figure 1. It is seen that the untreated (UT curve) exhibits two major peaks, but after the alkali treatment, the peak at 16.2 degrees is considerably suppressed (curve TR). The overall intensity of the main peak at 22.5 is also reduced, suggesting that the crystallinity is reduced after the alkali treatment. There are several crystalline forms of cellulose (cellulose I, II, III and IV), having different lattice parameters.^{35,36} The peaks can be assigned to the crystal forms of cellulose, which is the main constituent of straw and stubble. The crystal form I of cellulose is the most common and dominant in nature. The three peaks observed at 16, 22 and 25 degrees in untreated paddy straw can be assigned to reflections from (0-11), (002) and (004) planes respectively. The small sharp peaks superposed near 25 degrees are due to impurities/silicates. After the alkali treatment, the peak at 16 degrees is considerably suppressed. In fact, this is a composite peak, with reflection from Ia as well as I β forms.³⁷ It may be pointed out that the alkali concentration used of 10% and the temperature of 50 °C caused penetration of the alkali inside the straw matrix, leading to breakage bonds. especially of hydrogen in the hemicellulose regions. This led to removal of lignin and hemicelluloses, yielding a purer cellulose product.

The XRD diffractograms of the PVA-starch with different concentrations of paddy straw are compiled in Figure 2. In this system, both starch and cellulose are crystalline and polymorphic. With the addition of paddy straw (cellulose II), the crystal form of starch changes from Va to Vh +B type. The main diffraction peaks of the composite films were observed at 15° and 22.5°, representing the crystalline polymorph I cellulose, which is the dominant form of cellulose in nature.³⁸ The XRD diffractograms for the PVA-starch-paddy composite films containing 60% PVA, 40% starch with 12% PEG and different

amount of paddy straw (PS) indicated as 1gT, 2gT, 3gT and 4gT corresponding to 11.75%, 21.05%, 28.57% and 34.78% of total, respectively. It is seen that there are mainly two major peaks at 2 θ of 20.2 and 22.5 degrees, with additional small peaks at 9.8, 13.4, 16.5 or 17.2 and 41.1 degrees. It is seen that the peaks in the range from 7 to 16 degrees decrease in intensity,



Figure 1: XRD diffractograms of paddy straw before (UT) and after treatment (TR)

Scanning electron microscopy

The surface structure of the untreated and treated paddy straw was observed under FE-SEM. Figure 3 (A and B) shows the SEM images of untreated and alkali treated paddy, respectively. There is considerable surface roughening and modification by the alkali treatment. This leads to better coverage of the straw by the polymer, as seen in Figure 3D, as compared to the polymer on the untreated straw (Fig. 3C). This can lead to further nucleation effects in the treated paddy straw containing composite. Better straw-polymer matrix interaction can lead to improvement in mechanical properties. These aspects are discussed below in the paper.

FTIR analysis of films

The effect of alkali treatment on the chemical structure modification of the paddy straw is seen in the FTIR spectra depicted in Figure 4. It is seen that with increasing alkali concentration in the treatment, the absorption bands at 1010, 1220, 1620 and 1680 cm⁻¹ decrease considerably, while the band at 998-987 cm⁻¹ becomes more pronounced. The broad band at 3300-3400 cm⁻¹ corresponding to –OH decreases after the alkali treatment. These changes can be attributed to the removal of the lignin and surface modification with partial replacement of the –OH groups of cellulose by –ONa.

while those at 20.2 and 22.5 increase in intensity with the addition of paddy straw. There is a slight shift of the peaks in the presence of paddy straw. These changes suggest that the crystalline structure of starch gets modified in the presence of paddy straw. The increase of certain reflections indicates that there may be nucleation effects, which are discussed later in this paper.



Figure 2: XRD of paddy straw-PVA-starch composites containing different concentrations of treated paddy straw (legend as per Table 2)

Figure 5 (A and B) shows the FTIR spectra of various film samples containing different concentrations of paddy straw with and without treatment, respectively. The FTIR spectra of the composite film displayed characteristic peaks within the range of 3550–674 cm⁻¹. The peak at about 3307–3240 cm⁻¹ is due to hydroxyl group (O–H) stretching, which is affected by hydrogen bonding. The various peaks noted in the FTIR spectra are listed and assigned in Table 3. The peak at 1640 cm⁻¹ is associated to O–H stretching, which gives another confirmation of nucleation. The characteristic absorption peaks at 995–1123 cm⁻¹ indicated C–O-C stretching in the film due to starch bonding (Table 3).

Figure 6 depicts the FTIR spectra of the paddy straw filled PVA-starch films in the carbonyl region, where (A) is for the untreated and (B) is for the treated straw containing samples. The absorption band in this region has three components, which indicates the hydrogen bonding present, wherein the lower frequency component (1644 cm⁻¹) is due to intermolecular hydrogen bonding, while the higher frequency (1732 cm⁻¹) component is due to intramolecular hydrogen bonding and the central peak is from the unbonded group.^{39,40} It is further seen that the intramolecular hydrogen bonding component becomes higher for the treated straw, which indicates these samples contain a higher number



of active sites on the surface.

Figure 3: SEM images of (A) untreated and (B) treated paddy straw, and of PVA-starch composites containing (C) untreated and (D) treated paddy straw



Figure 4: FTIR spectra of paddy straw alone with and without treatment (UT) – numbers indicate the concentration of alkali used for treatment



Figure 5: FTIR spectra of composite films with (A) untreated straw, (B) treated straw (legend as per Table 2)

Peak wavenumber (cm ⁻¹)		Assignment	Remarks	
Untreated	Treated	Assignment	ixellial KS	
	3307	-OH	PVA	
3242	3240	-OH	H bond	
2902	2950	-CH2	Starch	
	2840	-CH2	Cellulose II	
2353	2347		Starch	
2302	2304		Starch	
1714	1746	-COONa	Alkali treat	
1691	1694	-C=O	Bound	
1641	1640	-OH	Bound water	
1508	1530	C-O	Starch	
1447	1440	-CH	Cellulose II	
1229	1231		Starch	
	1123	C-O-C	Cellulose II	
1059	1053	C-OH	Starch	
1008/977	995	C-O-C	Starch	
	830		Starch	
774	789		Starch	
671	674		Starch	

 Table 3

 Analysis of FTIR spectra and assignment of different bands



Figure 6: FTIR spectra of paddy straw filled samples in the carbonyl region 1600-1800 cm⁻¹ (A) for untreated, and (B) treated paddy straw

Differential scanning calorimetry analysis

The differential scanning calorimetry (DSC) scans for the first heating cycle of PVA-starch samples containing treated paddy straw are shown in Figure 7. The DSC scans for the same samples after final melting, followed by the second heating cycle are shown in Figure 8.

In Figure 7, there is a broad endotherm near 110 °C, which is affected by the entrapped moisture in the films and hence, it is broad near the glass transition temperature of PVA. In the second heating cycle, after melting (180-200 °C) of PVA and starch, the broad peak disappears (see Fig. 8) and the glass transition (Tg) of the main matrix without moisture becomes evident as a step near 55 °C. Since the samples contain PEG as compatibilizer and plasticizer for the PVA-starch matrix, there is lowering of Tg from its

original value of 67 °C for PVA.41 It is interesting to see that the Tg in the composite shifts from 55 °C to a higher temperature (63.7 °C) with the increase of paddy straw concentration. Also, the melting peak is sharp, appearing at 195 °C in the second heating cycle. The melting point is lower than that of pure PVA or starch due to the plasticizing effect of PEG.⁴² Also, it is seen that there is a single melting peak, which suggests that PEG is also a good compatibilizer for this blend. The shift in Tg is more clearly seen in Figure 9, which presents the DSC scan of the second heating in PVA-starch-paddy straw composites in the Tg region (40-65 °C). The incorporation of paddy straw leads to a high level of hydrogen bonding, giving rise to virtual cross-linking, stiffening and tight entanglement of the fibers with the polymer, which leads to a shift in Tg to

higher temperature with the increasing paddy straw concentration.

The cooling curves for the PVA-starch-paddy straw composites are shown in Figure 10. It is interesting to see that the crystallization peak, which is single, suggests that there is no phase separation in the polymer matrix. This also supports the plasticization and compatibilizing effect of PEG added to the matrix. Further, the



PVA-Starch-Straw

Figure 7: DSC first heating scan for paddy straw-PVAstarch composite Tg PVA-Starch-Straw



Figure 9: DSC scan in the Tg region for paddy straw-PVA-starch composite

Thermal characterization Thermogravimetric analysis (TGA)

Thermal stability plays a vital role in biopolymer-based packaging material. The typical thermograms are presented in Figure 11. The addition of straw clearly increases the thermal stability in the starch-PVA blend. The degradation crystallization peak temperature shifts from 165 °C to 172.3 °C, which is indicative of the nucleating effect for polymer crystallization, which is observed in other fiber filled polymers as well.⁴³⁻⁴⁵ This is also associated with the good coverage of the paddy straw surface by the polymer and hydrogen bonding between the two components.

PVA-Starch-Straw 2nd



Figure 8: DSC second heating scan for paddy straw-PVA-starch composite Tc PVA-Strach-Straw



Figure 10: DSC cooling scans showing shift in the crystallization peak (Tc)

temperature shifts by almost 20 °C for 28% straw addition. The temperature of the biocomposite films was compared at 10 and 50% weight loss (maximum weight loss), as presented in Table 4. The results revealed a remarkable thermal behavior of the biocomposite films, which required higher temperature for an initial 10% weight loss. The onset of degradation shifts from 267 to 272 °C, while the peak degradation temperature increases from 310 °C to 329 °C with the addition of paddy straw. The higher thermal in the PVA-starch-paddy stability straw composite can also be associated with the strong bonding and tight matrix formation due to the adhesive effect of the polymer used. The thermal degradation behavior is exemplified in the DTG curves shown in Figure 12. It is evident that the weight loss takes place in three steps, first is due to the evaporation of moisture and low molecular weight plasticizer evolution, the second due to the degradation of the polymer matrix and the third is due to the degradation of the cellulose/starch component. The major peak in DTG is seen to shift to higher temperature with the addition of paddy straw, which is in agreement with the observations made above.

Differential thermal analysis (DTA)

The thermal transitions taking place during heating of the PVA-starch paddy straw composite films are seen in the differential thermal analysis (DTA) curves shown in Figure 13. It is interesting to note that the DTA curves give all thermodynamic transitions with and without weight loss. Hence, the transitions near 100 °C and below 200 °C are due to glass transition and melting of the polymer matrix, while those above 200 °C, occurring at 300 -320 °C and 400 °C, are due to breakage of chains in the matrix and the fiber.



Temperature (°C)

Figure 13: DTA curves of paddy straw-PVA-starch composites

Sample	Degradation temperature (°C)
0.0	310.4
1.0 (1gT)	322.7
2.0 (2gT)	335.2
3.0 (3gT)	330.0
4.0 (4gT)	329.2
4.0 (4gT)	329.2

 Table 4

 TGA data: composite films and their degradation temperature

It is interesting to note that the latter show a shift to higher temperatures by the addition of paddy straw to the PVA-starch matrix. It may be pointed out that higher thermal energy is required for the degradation of the paddy straw composite than for the PVA-starch matrix alone, as there is an upward shift of these curves in the former case with respect to latter.^{46,47}

Mechanical properties of PVA-starch-paddy straw composites

The mechanical response of these composite thin sheets is depicted in Figure 14 (A and B), for the samples containing untreated and treated paddy straw. It is seen that, in both cases, the tensile strength increases, while the elongation (or displacement) decreases with the addition of paddy straw. These changes are more pronounced in the treated paddy straw containing composites. The values of tensile strength and elongation derived from these graphs are tabulated in Table 5.

The mean value of the tensile strength of PVA-starch-paddy composite increased, while the elongation decreased with the addition of paddy

straw. As indicated earlier, the treatment of paddy straw creates surface medication and more coverage by the polymer matrix with greater interaction/binding of the straw fibers. It may be mentioned here that, in the present case, PEG has been incorporated as plasticizer, which can assist in improving the elongation, as compared to pure starch or PVA matrix. These two components in the polymer matrix are known to be stiff, with very low elongation at break.^{12,22,45} J. Liu et al.⁴⁸ reported studies on rice straw-starch composites, in which they found that the flexural strength was in the range of 1.5 to 3.5MPa for starch content of 10 to 12%. The moisture absorption was almost 10% within 24 h. J. Guzman et al.⁴⁹ have reported the properties of thermoplastic corn starch reinforced with barley straw using glycerol as plasticizer. They found the tensile strength to increase from 4 MPa to 7 MPa for barley straw concentration of 15%. However, the moisture absorption was very high >100% in 24 h. M. Ramirez et al.⁵⁰ have investigated cassava starch composite with eucalyptus wood particles using 30% glycerol as plasticizer.



Figure 14: Mechanical response of PVA-starch composite sheets containing (A) untreated and (B) treated paddy straw (numbers in the legend indicate the weight of paddy added)

Sample	Tensile strength	Elongation
Sample	(MPa)	(%)
PVA-starch-PEG	0.89	24.8
Treated 1g	1.7	26.8
Treated 2g	1.86	26.0
Treated 3g	4.01	9.6
Treated 4g	3.99	9.2
Untreated 1g	0.83	29
Untreated 2g	2.29	21
Untreated 3g	3.69	7.5
Untreated 4g	3.85	5.5

 Table 5

 Mechanical properties of PVA-starch-paddy composites

Tabl	e 6	

WVTR of PVA-starch-paddy composite films

Sample	WVTR
Sample	$(g/m^2/day)$
Control	117.32
Treated 1g	62.12
Treated 2g	75.33
Treated 3g	65.44
Treated 4g	52.68
Untreated 1g	50.17
Untreated 2g	38.57
Untreated 3g	46.23
Untreated 4g	54.57

They obtained the tensile strength between 1.9 MPa and 4.5 MPa for compression molded sheets. The moisture absorption was 7% after 24 h. Our findings are more or less similar to these reports, except that the elongation at break is superior in the present case (26%) to those reported by these authors (9.6%). Since PEG is a good plasticizer as well as compatibilizer, which has been discussed in earlier sections, more flexibility is imparted in the present samples.

Water vapor transmission rate (WVTR)

The WVTR plays an important role in packaging applications, as well as in the biodegradability of materials. The values of WCTR for the present samples are shown in Table 6. It is seen that the incorporation of paddy straw decreased the WVTR considerably, as compared to the control films, *i.e.* plasticized PVA-starch films. The reduction in the WVTR of PVA-starch-paddy straw composite films can be attributed to the increase in the tortuous path for the water molecules due to the intermeshing of the straw fibers, leading to less diffusivity. This is similar to the reduction of WVTR reported in nanofiber or nanoclay composites.^{51,52} It can be

noted that the WVTR in the case of untreated paddy straw containing samples is slightly lower than in that of the treated paddy straw samples. Since the untreated straw contained lignin, as well as some waxy surface, this led to its hydrophobic nature, causing repulsion of water vapor. Nonetheless, the PVA-starch-paddy straw exhibited composite films lower **WVTR** compared to other biopolymers, such as PLA (WVTR = 177)⁵³ but not so low as that of $17).^{53}$ polyethylene (WVTR = This is advantageous in retaining freshness of green vegetables stored in packs made from PVAstarch-paddy straw (average WVTR = 60).

CONCLUSION

The findings of the present study on the development of PVA-starch-paddy straw composites bring out the possibilities of effectively utilizing paddy straw in an ecofriendly manner. The internal structure development in the straw after its treatment and then, within the polymer matrix, are discussed in this paper. The changes in the crystalline phase, plasticization and the compatibilizing effect of PEG yielded a good material, with flexibility, toughness and low water permeation. The thermal stability considerably improved by the addition of paddy straw to the PVA-starch matrix. There is also improvement in mechanical properties and lowering of WVTR. Moreover, sufficient diffusivity was observed to label the materials as "breathing", which is needed for storage of green produce. All these properties are very appropriate for bio-compostable packaging materials. It may be noted that the materials used are easily available on the farm and no complex machinery is needed to make the sheets. It is planned to make large sheets and hand mold items like trays, boxes, bowls etc. using these materials with the help of farm labour, so as to demonstrate the applications in an agricultural environment. Further studies are underway to explore these applications in the near future.

ACKNOWLEDGEMENTS: The authors wish to acknowledge the ICMR for the financial support provided to Mr. Pratik Potdar, PAU, and Prof. Dr. Vishwanath Karad, founder president of MIT World Peace University (MIT-WPU), for the facilities provided to carry out the project.

REFERENCES

B. Stijn and R. T. Scott, ACS Macro. Lett., 9, 1376 (2020), https://doi.org/10.1021/acsmacrolett.0c00437 D. M. Nguyen, T. V. Do, A. C. Grillet, H. H. Thuc and C. N. H.Thuc, Int. Biodeter. Biodegrad., 115, 257 (2016), https://doi.org/10.1016/j.ibiod.2016.09.004 M. Guimaraes, V. R. Botaro, K. M. Novack, F. G. Teixeira and G. H. G.Tonoli, J. Polym. Res., 22, 192 (2015), https://doi.org/10.1007/s10965-015-0834-z Y. Jost, Express Polym. Lett., 12, 429 (2018), https://doi.org/10.3144/expresspolymlett.2018.36 P. Lu, Y. Yang, R. Liu, X. Lui, J. Ma et al., Carbohyd. Polym., 249, 116831 (2020),https://doi.org/10.1016/j.carbpol.2020.116831 ⁶ D. Hermawan, T. K. Lai, S. Jafarzadeh, D. A. Gopakumar, M. Hasan et al., Bioresources, 14, 3389 (2019), https://doi.org/10.15376/biores.14.2.3389-3410 K. Hazrati, S. Sapuan, M. Zuhri and R. Jumaidin, J. Mater. Res. Technol., 15, 1342 (2021),https://doi.org/10.1016/j.jmrt.2021.09.003 ⁸ B. R. Siddaramiah and R. Somashekar, J. Appl. Polym. Sci., 91. 630 (2004).https://doi.org/10.1002/app.13194 K. Yao, J. Cai, M. Liu, Y. Yu, H. Xiong et al., Carbohyd. Polym., 86. 1784 (2011), https://doi.org/10.1016/j.carbpol.2011.07.008 ¹⁰ H. Ismail and N. F. Zaaba, *Polym. Plast. Technol.* (2011), Eng., 50, 1214 https://doi.org/10.1080/03602559.2011.566241

¹¹ J. Girones, J. P. Lopez, P. Mutje, A. J. F. Carvalho and F. Vilaseca, Compos. Sci. Technol., 72, 858 (2012),https://doi.org/10.1016/j.compscitech.2012.02.019 ¹² J. N. BeMiller and R. L. Whistler, in "Starch: Chemistry and Technology", edited by R. L. Whistler, Academic Press, 2009 A. G. Lopez, M. A. Rodriguez, J. A. Saja, F. S. Bellucci and M. Adranuy, Polimeros: Ciênc. Tecnol., 36 24. (2014),https://doi.org/10.4322/polimeros.2014.053 ¹⁴ J. J. Soest, S. H. Hulleman, D. Wit and J. F. Vliegenthart, Ind. Crop. Prod., 5, 11 (1996), https://doi.org/10.1016/0926-6690(95)00048-8 ¹⁵ P. A. Sreekumar, M. A. Al- Harthi and S. K. De, J. Appl. Polym. Sci., 123, 135 (2012),https://doi.org/10.1002/app.34465 ¹⁶ F. Yu, K. Prashantha, J. Soulestin, M. F. Lacrampe and P. Krawczak, Carbohyd. Polym., 91, 253 (2013), https://doi.org/10.1016/j.carbpol.2012.08.008 ¹⁷ X. F. Ma, J. G. Yu and J. J. Wan, Carbohyd. Polvm.. 64. (2006).267 https://doi.org/10.1016/j.carbpol.2005.11.042 ¹⁸ H. Li and M. A. Huneault, J. Appl. Polym. Sci., 2439 119. (2011),https://doi.org/10.1016/j.carbpol.2005.11.042 ¹⁹ L. Natta and N. Athapol, *Starch/Starke*, 56, 348 (2004), https://doi.org/10.1002/star.200300249 ²⁰ M. L. Sanyang, S. M. Sapuan, M. Jawaid, M. R. Ishak and J. Sahari, J. Food Sci. Technol., 53, 326 (2015), https://doi.org/10.1007/s13197-015-2009-7 ²¹ X. Jiang, T. Jiang, X. Zhang, H. Dai and X. Zhang, Polym. Eng. Sci., 52, 2245 (2012),https://doi.org/10.1002/pen.23166 ²² S. Radhakrishnan, S. Thorat, A. Khare and M.B. Kulkarni, in "Natural Polymers: Green Approach", edited by S. Thomas, Apple Acad Press CRC, 2021, chapter 11 ²³ Q. Chen, Y. Shi, G. Chen and M. Cai, *Int. J. Biol.* Macromol.. 142. (2019), 846 https://doi.org/10.1016/j.ijbiomac.2019.10.024 ²⁴ A. Kaushik, M. Singh and G. Verma, *Carbohyd*. 337 Polvm.. (2010),82. https://doi.org/10.1016/j.carbpol.2010.04.063 J. Zanela, A. P. Blick, M. Casagrande, M. V. Grossman and F. Yamashita, Starch, 70, 7 (2018), https://doi.org/10.1002/star.201700248 ²⁶ J. Jane, J. Macromol. Sci., **32**, 751 (1995), http://dx.doi.org/10.1080/10601329508010286 ²⁷ T. P. Tran, J. C. Benezet and A. Bergeret, Ind. (2014), Crop. Prod., 58. 111 https://doi.org/10.1016/j.indcrop.2014.04.012 ²⁸ S. Nigam, A. K. Das and M. K. Patidar, *Environ*. Challenges, 100280 (2021),5, https://doi.org/10.1016/j.envc.2021.100280 ²⁹ S. Yokota, A. Nishimoto and T. Kondo, J. Wood. Sci., 68, 14 (2022), https://doi.org/10.1186/s10086-022-02022-9

³⁰ K. Jõgi and R. Bhat, Sustain. Chem. Pharm., 1, 100326 (2020),

https://doi.org/10.1016/j.scp.2020.100326

³¹ Y. Srisuwan and Y. Baimark, Carbohyd. Polym., 119155 283. (2022),https://doi.org/10.1016/j.carbpol.2022.119155

³² A. Shafqat, A. Tahir, K. W. Ullah, A. Mahmood, G. H. Abbasi et al., Cellulose Chem. Technol., 55, 867 https://doi.org/10.35812/ (2021),CelluloseChemTechnol.2021.55.73

³³ E. Ghasemi, H. R. Ghorbani, M. Khorvash, M. R. Emami and K. Karimi, Animal, 7, 1106 (2013), https://doi.org/10.1017/S1751731113000256

³⁴ M. B. Kulkarni, S. Radhakrishnan, N. Samarth and P. A. Mahanwar, Mater. Res. Express., 6, 075318 (2019), https://doi.org/10.1088/2053-1591/ab12a3

³⁵ S. P. Gautam, P. S. Bundela, A. K. Pandey, M. K. Jamaluddin, S. Awasthi et al., J. Appl. Natur. Sci., 2, 330 (2010), https://doi.org/10.31018/jans.v2i2.143

³⁶ N. Terinte, R. Ibbett and K. C. Schuster, *Lenzing*. Ber., 89. 118 (2011),https://www.lenzing.com/download-center/filter1/ research-and-developement

³⁷ H. Suryanto, E. Marsyahyo, Y. S. Iarawan and R. Soenoko, Key Eng. Mater., 594, 720 (2015), https://doi.org/10.4028/www.scientific.net/KEM.594-595.720

³⁸ S. W. Kuo, J. Polym. Res., **15**, 459 (2008), https://doi.org/10.1007/s10965-008-9192-4

³⁹ L. Guo, H. Sato, T. Hashimoto and Y. Ozaki, 3897 Macromolecules. 43. (2010),https://doi.org/10.1021/ma100307m

⁴⁰ F. Lin, W. Wu, H. Sun and A. Xiang, J. Polym. Mat., 28, 577 (2011)

⁴¹ B. Ayana, S. Suin and B. B. Khatua, *Carbohyd*. (2014). Polym., 110, 430 https://doi.org/10.1016/j.carbpol.2014.04.024

⁴² C. Saujanya, R. Tangarilla and S. Radhakrishnan, Mater. Eng., 287, 272 Macromol. (2002),https://doi.org/10.1002/1439-2054(20020401)287:4% 3C272:: AID-MAME272%3E3.0.CO;2-J

43 K. Shi, G. Liu, H. Sun, B. Yang and Y. Weng, Polymers, 4305 14, (2022),https://doi.org/10.3390/polym14204305

⁴⁴ T. Hatakeyama and F. X. Quinn, in "Thermal Analysis Fundamentals and Applications to Polymer Science Termogravimetry", 2nd ed., John Wiley & Sons, 1999, p. 63 https://doi.org/10.1021/ja945128t

⁴⁵ M. E. Brown, in "Introduction to Thermal Analysis: Techniques and Applications", 1st ed., Springer, 2007 p. 181

⁴⁶ K. S. Chan, H. B. Senin and I. Naimah, AIP Conf. Procs., 1136, 366 (2009),https://doi.org/10.1063/1.3160165

⁴⁷ J. Liu, C. Jia and C. He, *AASRI Proc.*, **3**, 83 (2012), https://doi.org/10.1016/j.aasri.2012.11.015

⁴⁸ J. A. Guzman, R. R. Anda, F. J. Talavera, R. M. Gonzalez and M. G. L Ramirez, Fiber. Polym., 9, 1970 (2018), https://doi.org/10.1007/s12221-018-8023-4

⁴⁹ M. G. Lomeli, A. J. Guzman, S. G. Enriquez, J. J. Rivera and R. M. Gonzalez, Bioresources, 9, 2960 (2014),http://dx.doi.org/10.15376/biores.9.2.2960-2974

⁵⁰ S. Hemsri, K. Puttiwanit, K. Saeaung and P. Satung, IOP Conf. Ser. Mater. Sci. Eng., 965, 01 (2020),http://dx.doi.org/10.1088/1757-899X/965/1/012020

⁵¹ H. Y. Yu, H. Zhang, M. L. Song, Y. Zhou, J. Yao et al., Appl. Mater. Interfaces., 9, 43930 (2017), https://doi.org/10.1021/acsami.7b09102

⁵² R. Shogren, J. Environ. Polym. Degrad., 5, 91 (1997), https://doi.org/10.1007/BF02763592

⁵³ M. D. Steven and J. H. Hotchkiss, Packag. Technol. 17 Sci., 15. (2002).https://doi.org/10.1002/pts.562