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Preparation and characterization of rice husk derived cellulose and polyvinyl alcohol blended heat sealable packaging film

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A greener route for efficient extraction of chemically modified cellulose (CMC) from rice husk has been demonstrates. The extracted CMC is solution blended with polyvinyl alcohol (PVA) under optimized conditions to prepare CMC blended polyvinyl alcohol (CMC-b-PVA) packaging film. Further, the developed film has been characterized by Fourier transform infrared spectrophotometer, shore D, optical microscope, universal testing machine and soil burial test. The obtained results disclose the significant improvements in the mechanical properties by 1.49 times and reduced water vapor transmission rate by 33.33 % than PVA film due to reinforcement effect of CMC in PVA matrix. Furthermore, a heat sealed packet from the developed CMC-b-PVA film has been developed, which exhibits the comparable properties to commercially used flexible polyvinyl chloride films in packaging of edible packets along with optimized water barrier and biodegradable nature.

Keywords: Heat sealability, Physical mechanical properties, PVA/Cellulose film, Rice husk, Water barrier

Innovations in packaging materials is an integral step for industrial and social developments in ensuring the supply of edible and non-edible products along with quality control[1], although, packaging is a natural process to preserve and protect the quality of different agricultural and animal products. However, in the current era the commercial exploitation of packaging from different resources but most of them are non-biodegradable synthetic polymer and their composites. The popular polymers used in the application of packaging are i.e polyethene, polyvinyl chloride, and polypropylene. Thus, the huge consumption of non-biodegradable polymers has created several detrimental environmental problems like animal choking, blockage of water channels, pollution of air, water and soils[2]. Therefore, it is essential to develop biodegradable packaging materials with advantageous features like gas barrier and mechanical properties to substitute of existing non-biodegradable packaging materials[3]. In this, context several biopolymers like alginate, polylactic acid, chitosan, cellulose to explore with chemical modification like grafting, composite and blending in packaging applications with certain limitation[4-5]. Some of the representative biodegradable packaging materials are listed in Table 1 along with their properties and applications.

In this regards, cellulose based composite has been also reported as a promising material due to biodegradability, edible nature, cheap availability and good mechanical properties. Although cellulose is naturally used packaging materials as bark, husk and coating of seed, fruits and other part of plants in combination other components. But, its processability, plasticity and mixibility are inherent limitations of cellulose to extensive use in packaging commercial materials[15]. In this regards, the current innovations of materials science like extraction, functionalization, size confinements, derivatization, grafting and making composites have been added several features in cellulose to use as packaging materials[16,17]. Furthermore, PVA is a widely used synthetic biodegradable polymer prepared from non-petroleum route a long with some inherent problem i.e mechanical strength, slow biodegradability and processability. Thus, the improvement in these properties makes it more suitable for use in advanced packaging materials[18]. It is reported that, the reinforcing of different fillers including cellulose is a promising step to improve the properties like strength and biodegradability to use PVA as packaging film. In this regard, Zhu *et al.* has reported improvement in mechanical, stability and gas barrier of PVA after blending with chemical derivatization of cellulose[19]. However, the concept of heat seal ability is not reported as per our observation, while it is very important aspects in commercialization of packaging

Table 1 — Representative biopolymer-based packaging materials.

S.No.	Composition	Properties	Applications	Ref.
1	ZnO/ Sodium Caseinate	Improved mechanical and barrier properties	Food Packaging	6
2	PCL/Ag-Kaolinite Nanocomposites	Improved barrier and antibacterial properties.	Food packaging	7
3.	Poly(vinyl alcohol) and sago pith waste	Optimized mechanical and water barrier	--------------	8
4.	PLA/ Bixin	UV barrier	Active packaging	9
5.	Furcellaran/gelatin hydrolysate/rosemary extract	Improved UV barrier and tensile	Intelligent packaging	10
6.	Ca^{2+} crosslinking konjac glucomannan/gellan gum	Improved mechanical and antimicrobial properties	Packaging	11
7	Gelatine/Chitosan	Uvbarrier , transparency and antimicrobial	Active packaging	12
8.	Starch and lauroylarginate	Flexible and antimicrobial	Active packaging	13
9	Chitosan, clay, PVA and Lactate	Enhanced and barrier	Active food packaging	14
10	Cellulose/PVA	Heat sealabilityand improved properties	Wide range	Present work

materials[20]. In the context above developments, the present paper reports the preparation of blends of cellulose extracted from rice husk with PVA having heat sealability. The, effect of cellulose on mechanical properties of PVA are discussed in the light of their use in packaging applications.

Experimental Section

Materials

Poly vinyl alcohol, NaOH (98%), Hydrogen peroxide (30%) and H_2SO_4(95%) were purchased from M/s Loba chemicals, India and used without any further purification. Rice husk was procured from local market of Delhi, India, while the double distilled water and AR grade solvents were used in entire investigation.

Extraction of cellulose

The cellulose was extracted using hot alkali treatment methods[21]. Initially, 10 g finely grounded rice husk was washed with distilled and then dried in hot air oven at 60 °C for 6 hours. Later, it was treated with 20 mL solution of 10% NaOH for 6 h at 80 °C on a magnetic stirrer. Thus, the produced filtrate and precipitates were separated after filtering with a whatman no 1 filter paper. The precipitate was washed and then treated with hydrogen peroxide along with constant stirring at magnetic. Finally, a white puff type precipitate was obtained, which was further treated with acid to reduce the size. The resultant precipitate was collected after centrifugation followed by drying in hot air oven.

Preparation of PVA/Cellulose blends

Initially, solutions of cellulose and PVA were prepared after dispersing 200 mg cellulose in 10 mL distilled water and 2 g PVA in 20 mL distilled water in two beakers after stirring on magnetic stirrer. Finally, both solutions were mixed and further stirred for 60 mins and finally a white colour suspension like solution was obtained. The solution was poured in glass petri dish to cast a film. The film was peeled out with the help of forceps and dried in a hot air oven at 65 °C for 6 h. For comparison, a similar film was also prepared using commercial cellulose using similar procedure.

Characterization

Structural characterization

The i.rspectra were recorded in ATR mode using Bruker Alpha model infra-red spectrometer. The spectra were recorded at resolution of 2 cm^{-1} in the range of 4000–500 cm^{-1}. However, the surface morphology of film was evaluated on OLYMPUS CH20 optical microscope at magnification of one thousand.

Water vapour transmission rate

The water vapour transmission rate (WVTR) of film was measure by the standard ASTM method[22]. Initially, the prepared films with diameter of 2 cm and thickness ~0.25 mm were cut and conditioned at 25 °C and 50% humidity for 48 h in glass chamber. Further, a 20 mL Schott Duran laboratory bottles were taken and a hole was made in their caps with help of a drilling machine. The preconditioned films were placed on the mouth between bottle containing 5 mL distilled water and caped properly. Further, the bottles were placed in an atmosphere-controlled chamber having 50% RH and temperature 25°C. The regular weight loss through bottles were monitored at interval of 120 min for 168 h using a Sartorius electronic balance with least count 0.1 mg. The WVTR and percentage water vapor permeability(WVP) were calculated using Eqn. 1 and Eqn. 2.

$$\text{WVTR} = \frac{x}{t \times A} \quad \ldots (1)$$

$$WVP\% = \frac{WVTR \times l}{\Delta RH} \quad \ldots (2)$$

The x is change weight of bottle, t is time, A is area, l is thickness of film and ΔRH is change humidity across the film at the test temperatures.

Mechanical testing

Stress strain curve of films were recorded with STS-348-star universal tensile machine having 5000kg capacity. The test conditions were used as per ASTM D882 for tensile testing of thin plastic. The initial gauge separation and cross-speed were set to 50mm with 25 mm/min, respectively. The test specimens were equilibrated in a atmosphere controlled chamber (temperature 25°C and 50% RH) for 24hr before testing. However, all these tests were conducted at ambient temperature and an average value of three repeated test was taken for each material and mean is reported.

The shore hardness of film was evaluated by JSE testing machine Model no. 6711. The hardness of the films for determining against its resistance to intended force applied by a specific type of indenter. The test was carried at five places and mean is reported.

Biodegradation experiments

Biodegradability was estimated out by standard soil burial test at ambient temperature under moisture-controlled conditions. Specimens of each film were placed in a series of perforated boxes containing moisturized soil with requisite amount SSSS of compost. The specimens (40 × 10mm) were buried 150mm beneath the surface of soil, specimens were also regularly moistened with distilled water. They were further taken out after predetermined time period, washed with water several times in order to ensure the stop of degradation, dried at room temperature to a constant weight, and then was stored in darkness until testing. The specimens were weighed on the analytical balance. The weight loss was evaluated by Eq. 3 for evaluation bio-degradability.

$$\text{Weight loss} = \frac{(w_0 - w_t)}{w_0} \times 100 \quad \ldots (3)$$

where, w_o =initial mass and w_t = remaining mass at any given time.

Preparation and testing of heat-sealed packet

The packets of developed film with volume of 200 cc were made by heat sealing the film on a heat-sealing instrument after applying standard mechanical pressure and requisite temperature. The change in thickness under pressure after storage in packets were measured for distilled water.

Results and Discussion

FT-IR Spectroscopy

The FT-IR spectra of prepared hybrid films and PVA are shown in Fig. 1, while the peak positions along with respective groups are in Table 2. The comparison of peaks of pure PVA film with its cellulose blends are indicating some spectral shifted due to interaction between cellulose and PVA matrix. The hydroxyl peak observed in pure PVA at 3250.33 cm^{-1} shifted in extracted cellulose, commercial

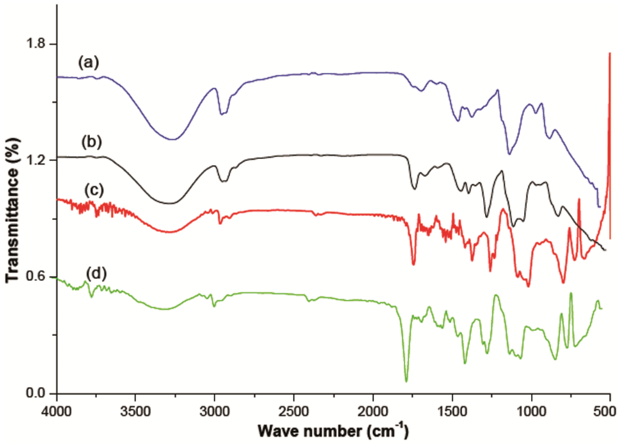

Fig. 1 — FTIR spectra of a) pure PVA; b) PVA+ cellulose; c) PVA+ Extracted cellulose and d) PVA+ CMC

Table 2 — IR peaks of composite film

Groups	PVA (cm^{-1})	PVA + Cellulose(cm^{-1})	PVA+ Extracted cellulose (cm^{-1})	PVA + CMC (cm^{-1})
ν_{OH}	3250.33	3278.62	3273.79	3280.35
ν_{C-H}	-	-	2967.82	2964.20
$\nu_{C=O}$	1652.88	1716.36	1743.10	1743.68
V_{C-O}	1086.35	1089.59	1087.94	1085.27
ν_{C-C}	2938.22	2940.22	2967.82	3010.27
$\nu_{C=C}$	-	1651.41	1652.45	1647.59

cellulose and CMC reinforced PVA films at 3279 cm^{-1}, 3273 cm^{-1} and 3280 cm^{-1} respectively[23,24]. Among all, the CMC reinforce film shows more spectral shift indicating better interaction between cellulose and PVA matrix.

The shift of spectra towards lower wave number is supporting in revealing the improvement in mechanical strength and stability of materials. The additional peak appearing at 640 -700 Cm-1 is revealing the sulphonation of cellulose during treatment with sulphuric acid[24].

Optical photograph

The optical micrograph of different films is shown in Fig. 2. The photograph is indicating that the morphology of PVA and modified CMCs is most regularly distributed in PVA matrix, while others having irregular morphology.

Mechanical properties

Stress strain curve of pure PVA film and its cellulose blended films are shown in Fig. 3. The result reveals the tensile strength and load bearing capacity of PVA film is significantly improved in blend of PVA and cellulose[25]. The properties of CMC reinforced PVA is bests than extracted cellulose and commercial cellulose. It may be due to better reinforcing of CMC due to smaller size and sulphonation of cellulose, which creates better interaction and dispersion in pristine PVA matrix (Table 3).

The shore hardness of PVA and cellulose blended PVA films are given in Table 4, which revealed that the best hardness is in PVA and CMC film due to

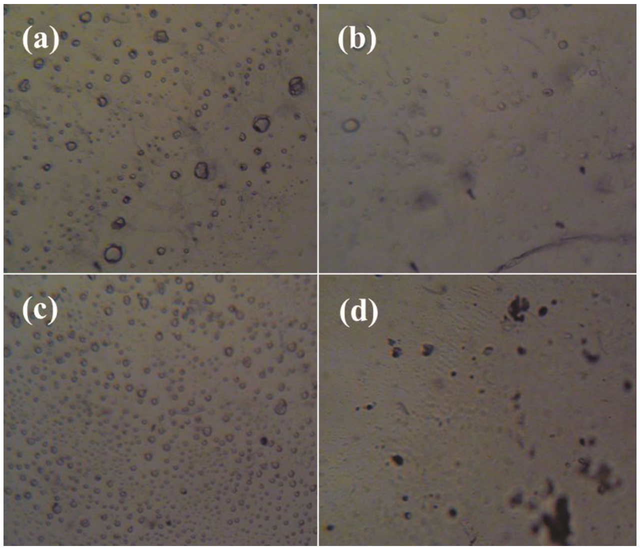

Fig. 2 — Optical photograph of a) pure PVA; b) PVA+Commercial cellulose; (c) PVA+ CMC and (d) PVA+ Extracted cellulose.

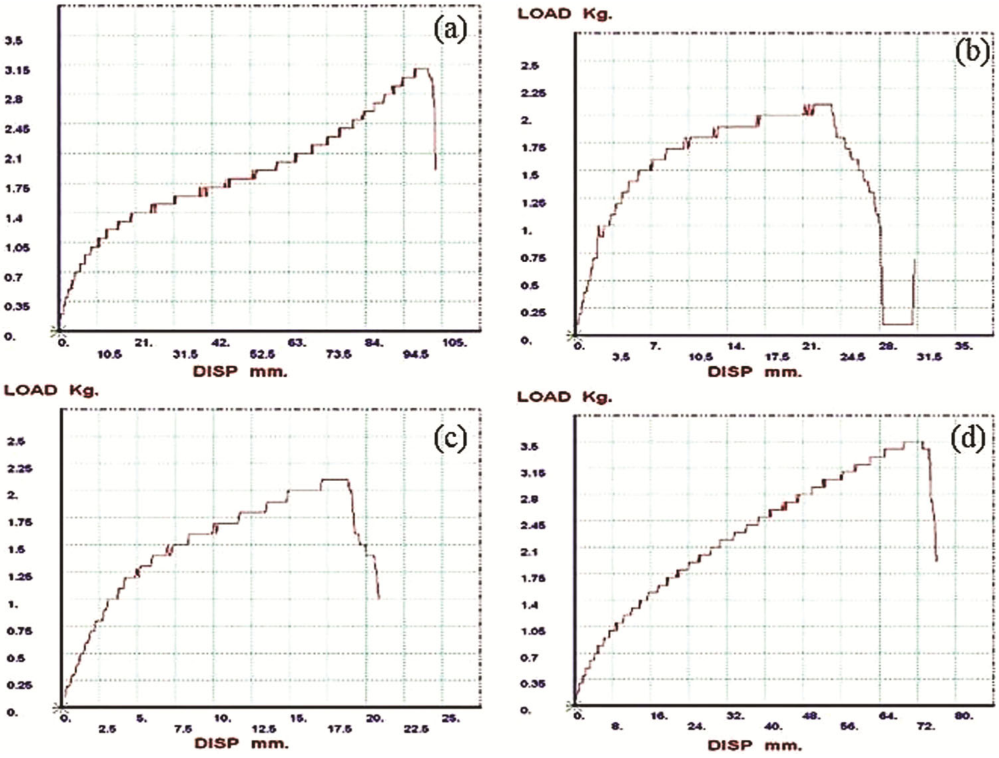

Fig. 3 — Stress strain curve of: a) Pure PVA; b) PVA+ Commercial Cellulose; (c) PVA + Extracted Cellulose and (d) PVA + CMC.

Table 3 — Mechanical properties of film.

Composite films	Pure PVA	PVA + MCC	PVA + Modified MCC	PVA + Extracted Cellulose
Tensile strength (kg/mm^2)	3.66	2.08	1.06	2.88
Break elongation percentage	171.883	47.00	34.66	126.5
Load of cell (kg)	100	100	100	100
Temperature (° C)	25	25	25	25
Speed (mm/min.)	50	50	50	50
Gauge length (mm)	60	60	60	60
Peak load (kg)	3.1	2.1	2.1	3.5
Peak elongation (%)	168.833	39.333	31.333	121.667
Break Load (kg)	1.90	0.80	1.00	1.90
Cross-sectional area (mm^2)	0.8456	1.012	10.980	1.2156
Peak time & Break time (sec.)	116. 5	27.10	21.60	84.10
	118.50	32.40	23.90	87.40

the uniform dispersibility of cellulose particles into PVA matrix since the cellulose reinforcement possesses smaller size.

Water vapour transmission rate

PVA is highly hydrophilic polymer due to the presence of the hydroxyl groups on its chain, which allows the easy water transmission through PVA film. However, the WVTR is drastically changed after reinforcement of cellulose in PVA matrix (Table 5).The trends is indicating lowest WVTR in film containing CMC. It may be because during treatment of sulphuric acid produces cellulose with smaller size with presence of sulphate groups. This change in WVTR is depends on the relative hydrophilicity and hydrophobicity. The presence of cellulose in PVA modifies the ratio of hydrophilicity and hydrophobicity and resultant, the extent of water permeability change as well as making it more suitability for long term packaging applications[26]. This chemical modification allows better interactions with PVA groups. The better interaction develops better cross linking as well as resistance to water permeation and thermal stability.

Biodegradability test

The observed extent of weight loss of film with time during soil burial test is confirming the improved biodegradability of developed cellulose blended PVA film than pristine PVA film. In general the biodegradability is depends on active state period for working of microbes, which performs the enzymatic degradation during compositing process of soil burial test[27]. Here, the weight loss is indicating the active state period for blend film is four weeks. In the period the pristine PVA indicates degradation by 5.12 % in four week, while blend is showing the degradation of 24.52 % in four week. The lesser percentage of PVA is due to hydrolytic stability of PVA chain than cellulose. Further, the higher porosity of blended film is also supportive for arial migration and water retaining capacity for better degradation of PVA and cellulose blended film.

Table 4 — Shore hardness results

S. No.	Film	Hardness (Mhos)
1	Commercial cellulose/ PVA	5.35
3	CMC /PVA	7.33
4	Pure PVA	4.9

Table 5 — Water vapour transmission rate of developed film

S. No.	Composite films	WVTR (g/hm^2)
1	PVA + MCC	6.19
2	PVA + Modified MCC	6.41
3	PVA + Extracted cellulose	6.63
4	Pure PVA	9.95

Sealability test

The basic properties of heat sealed materials are quick melting and solidification of materials. In this regards, the cellulose in not heat sealable due crystalline nature and PVA is heat sealable but degrade due lack of strength. However, the basic improved synergised above discussed properties are indicating their sealability along with strength. In this regards, Figure 4 is showing the physical appearance of heat-sealed packet developed from cellulose/PVA film.

The essential commercial properties of the developed packet were determined and compared with a commercial heat-sealed packet of polyethene in Table 6. The results are comparable

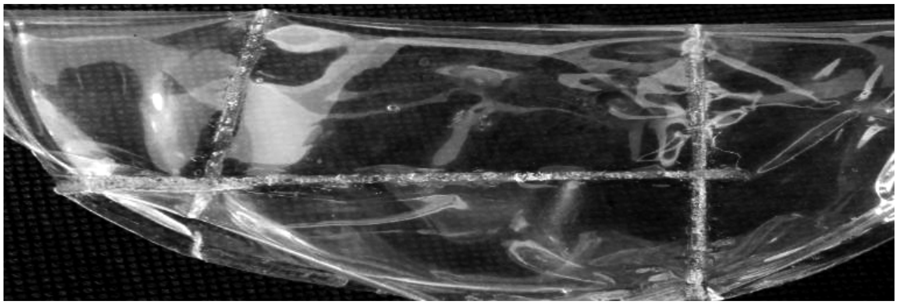

Fig. 4 — Heat sealed packet from cellulose/PVA film.

Table 6 — Properties of sealed packets.

Sample	Water leakage	Change in thickness		Change in hardness	
		After 1 day	After 5 days	After 1 day	After 5 days
Cellulose/PVA	Comparable to PVC	No change	dec. by 0.65	No change	dec. by 0.125
Commercial	Standard	No change	dec. by 0.50%	No change	No change

to commercial film and hence confirming the suitability of materials for bulk packaging of different products.

Furthermore, the sealability is combined effect of thermal and mechanical properties of both constituent polymers. Generally, PVA is heat sealable with water permeation but cellulose is not sealable due to lack of plasticity. However, the reinforcing of cellulose in PVA reduce WVTR along with plasticity for heat sealablity in blend. The presence of cellulose also improves the strength of PVA due to alignment of strength in the orientation of crystallinity of cellulose. Thus, the finding reveals the synergism between plasticity, strength and water vapour transmission rate to develop biodegradability packaging film as replacement of existing non degradable plastic like poly-vinyl chloride and polyethene.

Conclusion

The biodegradable composites of rice derived chemically modified cellulose reinforced PVA film was prepared using through solvent casting method. The structural, morphological, physical and mechanical properties of prepared composite revealed its suitability for packaging application with optimized mechanical and reduced water vapour transmission rate. Finally, the heat-sealed packet of composite was demonstrated for the use in packaging film due to synergistic effect of constituent polymers with comparable properties to commercial polyvinyl alcohol.

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