



Fabrication and Characterization of Biodegradable Poly(vinyl alcohol)/Chitosan Blends

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Poly(vinyl alcohol)/chitosan (PVA/CS) blends were prepared by solution casting method using glutaraldehyde as a cross linking agent. Fourier transform infrared spectroscopy (FTIR) and microhardness technique were employed to study the intermolecular interactions between constituents of polymer blends and mechanical properties respectively. The degradation properties of PVA/CS films were studied by composting method. FTIR spectra of poly(vinyl alcohol) and PVA/CS blends showed some variations in the absorption bands which reflected interactions between the components of blends. The mechanical stiffness of PVA/CS blends was enhanced by chitosan upto 40 % loading and it was found optimum composition for the maximum enhancement of mechanical properties of the blend. The degradation rate of blends was found increased with the increase in chitosan content.

Keywords: Biodegradation, Chitosan blends, FTIR, Microhardness, Poly(vinyl alcohol).

INTRODUCTION

World-wide material industries are experiencing a revolutionary shift from petro-chemical materials to environmentally sustainable materials because of increasing environmental concerns and decreasing petro-chemical resources [1]. The development of biodegradable materials is the way to decrease the amount of plastic solid waste in the environment and generate new materials. The biodegradable polymers are divided into two main groups *viz.*, natural polymers such as cellulose, chitin, starch, protein *etc.* and synthetic polymers for example aliphatic polyesters, poly(vinyl alcohol) *etc.* [1-4].

Synthetic biodegradable polymers have excellent properties and it has exhibited high potential towards the replacement of the plastics extensively used in many applications [1]. Natural materials are relatively less expensive and they have been employed into several products for conventional applications [1]. Recently, chitosan-based biodegradable products have been used in a number of medical and industrial applications [5].

Chitosan (CS) is an amino polysaccharide which consists of 2-amino-2-deoxy- β -D-glucopyranose and 2-acetamido-2-deoxy- β -D-glucopyranose [6,7]. Its unique properties such as nontoxicity, biocompatibility biodegradability and bioactivity have attracted interest for its investigation and biomedical applications, including wound healing, homeostatic, immunity

enhancing, hypolipidemic, gene therapy, tissue engineering *etc.* [6-8].

Poly(vinyl alcohol) is a semicrystalline hydrophilic biodegradable synthetic polymer which is mainly composed of C-C bonds [1,9]. Poly(vinyl alcohol) is manufactured from poly(vinyl acetate) by the polymerization of vinyl acetate, followed by hydrolysis of poly(vinyl acetate) to poly(vinyl alcohol). The hydrolysis reaction is not complete that result in polymerization with a certain degree of hydrolysis [10]. Its properties mainly depend on the degree of hydrolysis [6]. Its non-toxicity, water-solubility, biocompatibility and biodegradability make it widely applicable in biomedical field [11-15].

The blending of two or more polymers is an important technique to improve the cost effectiveness of commercial products [8]. Chitosan films are brittle and not suitable for use in its dry state. To enhance the mechanical properties with degradability of chitosan films, poly(vinyl alcohol) was chosen to blend with chitosan using the solution casting method. Chitosan may potentially be miscible with poly(vinyl alcohol) due to the formation of hydrogen bonds [8,16,17]. Lewandowska [6] has reported the results of thermal and rheological properties and has shown that chitosan with poly(vinyl alcohol) are poorly miscible [6,18,19]. Jia *et al.* [11] explored the electrospun nanofibers of poly(vinyl alcohol)/chitosan (PVA/CS) blends and FTIR, DSC, XRD results proved that there were strong intermolecular hydrogen

bonds between poly(vinyl alcohol) and chitosan [1]. Chuang *et al.* [17] studied the PVA/CS blends by DSC, SEM and electron spectroscopy for chemical analysis (ESCA) and reported phase separation [18].

Different types of chemical and physical crosslinking agents are used to decrease the solubility (improve the stability) of PVA/CS blends [20]. Some chemical cross-linking agents used for poly(vinyl alcohol) and chitosan are formaldehyde [21,22], acetaldehyde [23], glutaraldehyde [24], epichlorohydrine [25], genipin [26], glyoxal [27], ascorbic acid [28], *etc.* and physical cross linking agents are methanol, ethanol, γ -radiation induced cross linking, γ -radiation followed by freeze-thawing [29,30] *etc.* In this work, glutaraldehyde was chosen as a cross-linking agent since it is less expensive, readily available and highly soluble in aqueous solution [31]. The aldehyde groups readily react with amino groups which form imine bonds (Schiff's base) and acetal bonds with hydroxyl groups [32], making glutaraldehyde more efficient on the cross-linking of chitosan and poly(vinyl alcohol) [11].

Although several researchers have studied PVA/CS blends in various aspects, the investigation of mechanical properties by microindentation technique and degradation properties of these blends is not reported. Therefore, PVA/CS films with various blend ratios were prepared using solution casting method and their structural correlation, mechanical properties and degradation properties were examined by Fourier transform infrared spectroscopy (FTIR), microhardness and compost burial method.

EXPERIMENTAL

Analytical grade glacial acetic acid, sodium hydroxide, sodium sulphate and glutaraldehyde were purchased from Fisher Scientific, India and were used without further purification. Chitosan (Fluka 48165, obtained from crab shells; degree of deacetylation; DD = 68.65 %) and poly(vinyl alcohol) (PVA) under the trade name of Mowiol® 18-88 were purchased from Sigma Aldrich Company, Germany. Poly(vinyl alcohol) has molecular weight (M_w) of 130,000 g/mol and average density of 1.27 g/cm³.

Preparation of poly(vinyl alcohol)/chitosan blends (PVA/CS): The poly(vinyl alcohol)/chitosan blends were prepared by dissolution method using glutaraldehyde (GA) as a cross-linking agent following the modified protocol of Bahrami *et al.* [33]. Chitosan solution of 2.1 % was prepared by dissolving chitosan in 1 % aqueous acetic acid solution with stirring for 24 h at room temperature.

The poly(vinyl alcohol) was dissolved in distilled water to make 3.2 % solution by stirring for 40 min at 95 °C. Glutaraldehyde at 0.57 wt % related to the total amount of polymer was added to the solution of polyvinyl alcohol and cooled to room temperature. Both polymer solutions were carefully mixed at various proportions. The mixed solution was poured into a Petri dish and evaporated to produce a cast film. The resulting film was immersed into 4 % NaOH and then in saturated Na₂SO₄ solution for 2 h to neutralize it and finally washed with deionized water to remove alkali and unreacted materials. The film was dried at 40 °C and kept in desiccators to avoid moisture absorption. The blends thus prepared are presented in Table-1.

TABLE-1
LIST OF PVA/CS BLENDS PREPARED BY
SOLUTION CASTING PROCESS

S. No.	Sample code	PVA (%)	CS (%)
1	PVA	100	0
2	PVA/5 % CS	95	5
3	PVA/10 % CS	90	10
4	PVA/20 % CS	80	20
5	PVA/40 % CS	60	40
6	PVA/60 % CS	40	60
7	PVA/100 % CS	0	100

FTIR spectroscopy: FTIR spectroscopy (Perkin Elmer FTIR-2000 with attenuated total reflectance (ATR) mode) was used to study the effect of different treatments on the properties of the samples. The FTIR spectra were recorded within the wave number range of 4000-500 cm⁻¹.

Microhardness measurement: Microhardness measurements were performed on Fischerscope® (Helmut Fischer, Germany) microhardness tester equipped with a pyramidal Vickers diamond indenter at ambient temperature. The samples film approximately 0.5 mm thick, 1 cm wide and 1 cm long, were penetrated by the indenter with the loading rate of 200 mN/20 s. The maximum load was 200 mN. Martens hardness (HM) and Indentation modulus (E_{IT}) were evaluated from the load-indentation depth curves.

Biodegradation: The biodegradation test was performed under compost burial conditions. It was carried out following the modified protocol of Azahari and his coworkers [34]. Two different pots were filled with vermicompost approximate capacity of 10 L. The specimens were cut into 1.5 cm × 2.0 cm in rectangular shape and each sample was enclosed in tea bags individually and made small holes in bags. The samples were buried in the compost at a depth of 10 cm and the moisture of the compost was maintained by sprinkling water at regular intervals of time [34].

The degradation of the samples was determined at regular intervals of 7 days by carefully removing the sample from the compost and washing it gently with ethanol to remove traces of compost from the film and dried in oven at 60 °C for 4 h and weight of the samples were taken on digital balance. Weight loss of the sample over time was used to indicate the degradation rate of compost burial test which is calculated by the eqn. 1 [34].

$$\text{Weight loss (\%)} = \frac{W_i - W_d}{W_i} \times 100 \quad (1)$$

where, W_i is the initial dry weight and W_d is the dry weight of the film after being washed with alcohol.

RESULTS AND DISCUSSION

Spectroscopic characterization of PVA/CS blends: The FTIR spectra of poly(vinyl alcohol), chitosan and its blends (PVA/20 % CS) have been compared in Fig. 1(a,b). It showed that the spectra of the corresponding blend *i.e.* the poly(vinyl alcohol) blend containing 20 wt % chitosan are different from that of the pure poly(vinyl alcohol) and chitosan. The FTIR spectra showed the absorption peaks of poly(vinyl alcohol) at about 3265 cm⁻¹ (-OH stretching) and at about 1084 and 1415

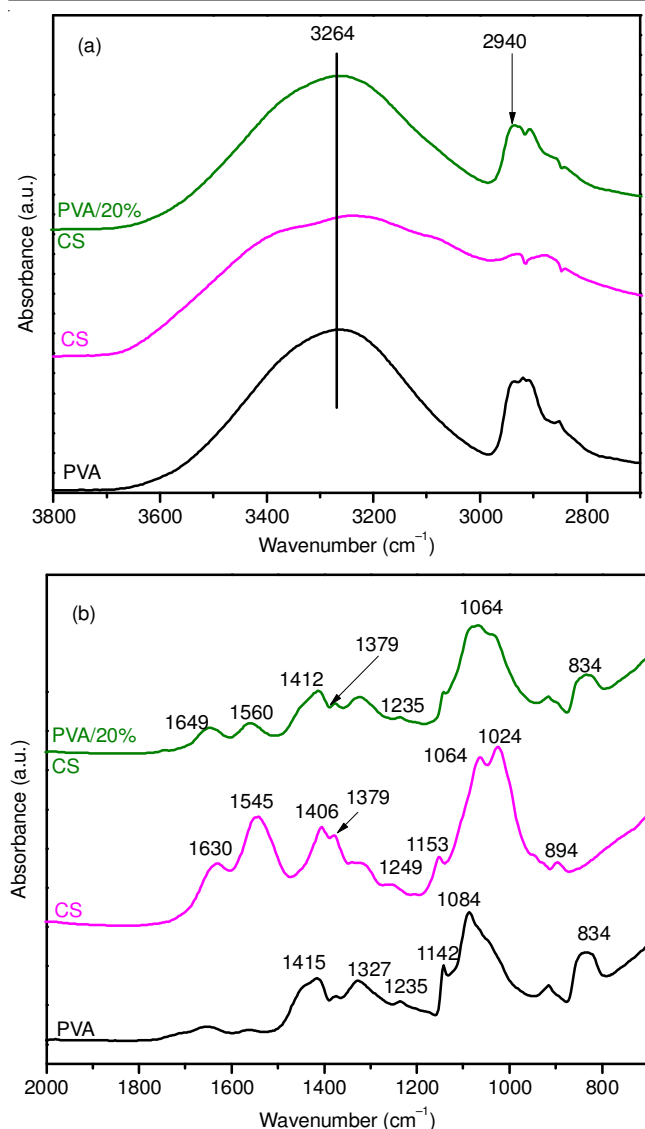


Fig. 1. FTIR spectra of pure components (poly(vinyl alcohol) and chitosan) compared with PVA/20 % CS blend within two spectral regions (a) 3600-700 cm^{-1} and (b) 2000-700 cm^{-1}

cm^{-1} for the $-\text{C}-\text{O}$ group [35]. The peak at 1142 cm^{-1} which is sensitive to poly(vinyl alcohol) crystallinity [36], disappeared in the spectra of blend (PVA/20 % CS) indicated that the compounding between poly(vinyl alcohol) and chitosan made the sample amorphous.

The characteristics band of chitosan at 1545 cm^{-1} which is assigned to the stretching vibration of amino group of chitosan [37], shifted to 1560 cm^{-1} . Bands appeared at 894 and 1024 cm^{-1} were mainly due to saccharide group [38]. In the spectra of film, amide band of chitosan shifted from 1630 to 1649 cm^{-1} indicated that cross linking were present in the blended compounds through H-bonding and covalent bond between

amino group of chitosan and glutaraldehyde [38] (Table-2). The band at 1249 cm^{-1} in chitosan (ω_{CH}) was found disappeared in PVA/CS blend suggesting the formation of H-bonding between poly(vinyl alcohol) and chitosan molecule [11]. This is due to the fact that when two or more polymers are mixed, change in characteristics spectral peaks reflected that the blends are the physical blends with chemical interactions [39]. The broad peak at 1024 cm^{-1} due to C-O stretching vibration in the spectrum of chitosan [37] was shifted to 1031 cm^{-1} in the blend (PVA/CS). The FTIR results revealed that the cross linking was present in the blended compounds through H-bonding and covalent bond between amine group of chitosan and glutaraldehyde.

Microhardness of PVA/CS blends: The microhardness of a polymer (resistance to the local deformation) is a property related to mechanical behaviour such as stiffness, elasticity, modulus and plasticity [40]. The high modulus and stiffness values correlate with higher degrees of microhardness [41]. Microhardness and elastic properties of the polyvinyl alcohol, chitosan and their blends were determined by recording micro-indentation measurement [41]. Indentation was performed in load control mode to a load as high as 200 mN . Evidently, no fracture was observed during loading.

Fig. 2 presents the Martens hardness (HM) and indentation modulus (E_{IT}) of PVA/CS blends as a function of weight fraction of chitosan (CS). In case of PVA/CS blends, a linear variation was observed in HM and E_{IT} values with increasing chitosan content upto $40 \text{ wt \%}$ of it (Fig. 2).

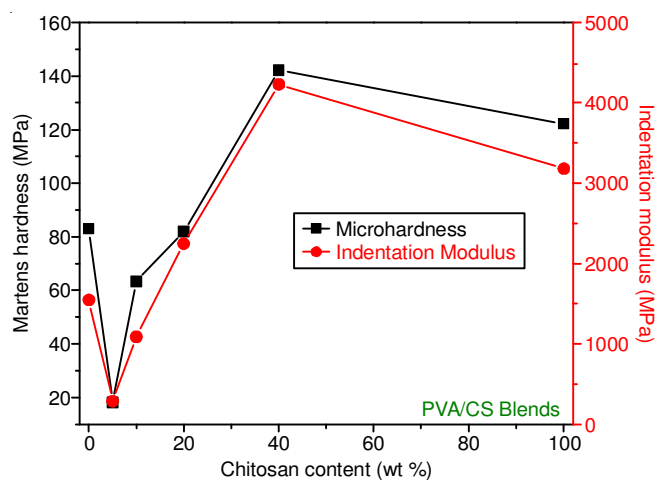


Fig. 2. Plot of Martens hardness (HM) and indentation modulus as a function of chitosan content in PVA/CS blends

Fabrication of chitosan to the poly(vinyl alcohol) decreased the microhardness and then gradually increased with the chitosan content upto $40 \text{ wt \%}$ of chitosan. Similar trend was found in the case of indentation modulus (E_{IT}). The drop in micro-

TABLE-2
CHARACTERISTIC FTIR BANDS OF PVA, CS AND PVA/20 % CS BLENDS

Assignment	Band centered (cm^{-1})								
	OH * NH	v(CH)	v(C=O) (amide band I)	v(NH) (amide band II)	-OH	$\omega(\text{CH})$	C-C (saccharine)	C-OH (1° alcohol)	C-C
PVA	3264	2940	-	-	1235	-	1142	1084	834
PVA/20 % CS	3264	2940	1649	1560	1235	-	-	1064	834
CS	3387, 3236*	2925	1630	1545	-	1249	1153	1064	894

hardness was due to weakness in the adhesion between poly(vinyl alcohol) and chitosan which was also explained for fly ash and nano clay epoxy composite [42]. The enhancement of mechanical properties of PVA/CS blends by comparison with neat poly(vinyl alcohol) resulted from the good adhesion at filler/matrix interface [42]. The hydrogen bonding between the -OH and -NH₂ group of chitosan and OH group of poly(vinyl alcohol) matrix led to improved adhesion between phases which resulted in improved mechanical properties [43]. In the high levels of filler content over 40 % chitosan content cause a weakness in the adhesion force between matrix (PVA) and filler (CS), fillers showed an agglomeration problem in higher loading chitosan content. Hence, a drop or weakness in the mechanical properties of the PVA/CS blends was observed which was also explored for epoxy composite [43]. It is also explained that increasing the filler ratio caused the increasing cluster in the nano-clay filled composite and a decrease in the hardness value of epoxy composites [44].

The Martens hardness value changed from an initial value of 83.08 MPa in the pure poly(vinyl alcohol) to a value of 142.18 MPa (highest value) in 40 % wt. of chitosan content. In addition, the lower values of HM and E_{IT} might be attributed to the reduction of crystallinity caused after the blending which was also supported by the results obtained from FTIR.

Thus it was concluded that the mechanical strength of PVA/CS blends was enhanced by chitosan upto 40 % loading and it was found optimum composition for the maximum enhancement of mechanical properties of blends.

Compost burial biodegradation: During the biodegradation process, the resistance and durability of polymeric materials are made weak by the action of microorganism or/and environmental abiotic factors [45]. The growth of microorganisms adhering to the polymer surface can provoke the formation of cracks, increase the size of pores and others defects, that may lead to the disintegration of a material into small fragments [46,47]. There are various methods for testing degradation of biodegradable polymers. The characteristics of biodegradation are loss of weight, change in surface properties, tensile strength, physicochemical properties, carbon dioxide production *etc.* [47]. In this study, biodegradation of prepared samples was analyzed by inspecting the weight loss as well as *via* physical appearance.

Weight loss method: Weight loss was measured at regular intervals of 7 days for 8 weeks using the eqn. 1 as mentioned in the materials and method section. It was used to indicate the degradation rate of the compost burial test. Weight loss of the poly(vinyl alcohol), chitosan and PVA/CS blends is shown in the Fig. 3.

All the films in compost degraded rapidly in the first 3 weeks (21 days). The rapid degradation was due to the composting process, which occurred in two main stages: an active composting stage and a curing period. In the first stage, the temperature raised and remained elevated as long as there was available oxygen, which resulted strong microbial activity. In the second stage, the temperature decreased but the film continued to compost at a slower rate [48]. After 21 days, the weight loss was slightly lower but the composting process did not stop at a particular point. Rather, it continued slowly until the last remaining nutrients were consumed by the remaining

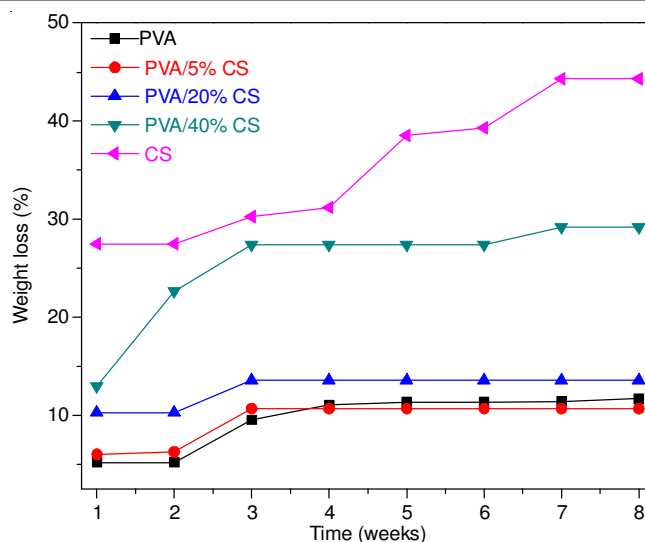


Fig. 3. Weight loss versus time of PVA, CS and PVA/CS blends of vermicompost burial biodegradation tests

microorganisms and almost all of the carbon had been converted into CO₂ [48]. The pure chitosan showed highest weight loss while pure poly(vinyl alcohol) showed the lowest weight loss and in PVA/CS blends weight loss increased with the increase of chitosan content. Thus weight loss results proved that loading of chitosan to poly(vinyl alcohol) increases the degradation properties.

Physical appearance: The change in physical appearance of different samples with burying time under the composting soil is also studied visual appearance clearly showed the degradation of PVA/CS blends. The pure poly(vinyl alcohol) film, PVA/CS film containing 0, 5, 20 % chitosan did not break down whereas higher weight percentage 40 and 100 % of chitosan containing poly(vinyl alcohol) blends broke down into very small fragments. Thus changes in physical appearances also confirmed the degradation of the samples.

Conclusion

Chitosan was successfully blended with poly(vinyl alcohol) using solution casting method to prepare thin film PVA/CS blends. FTIR spectra of PVA/CS blends exhibited the existence of relevant functional groups of both chitosan and poly(vinyl alcohol) with some shifting of absorption bands revealing some interactions between poly(vinyl alcohol) with chitosan. The microindentation results revealed that mechanical strength of blends was enhanced by chitosan upto 40 % loading of chitosan; it was optimum composition for the enhancement of mechanical properties of the blends. The best degradation among PVA/CS blends was shown by 40 wt % of chitosan in the blends. The biodegradation study proved that loading of chitosan to poly(vinyl alcohol) increased the degradation properties.

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