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Preparation and characterization of advanced biocomposite films from partially pregelatinized maize starch/polyvinyl alcohol

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Abstract: *This study intended to focus on the effect of partially pregelatinized maize starch (PMS)on the physico-mechanical, thermal and chemical characteristics of sorbitol plasticized and unplasticized PMS/PVA(Polyvinyl alcohol) biocomposite films. Boric acid (BA) was used as crosslinked agent. The tensile strength (TS), percentage of elongation at break (EB%), water solubility and moisture uptake of prepared biocomposites were investigated. The biocomposite films were investigated by FTIR,DSC and TGA respectively. It was observed that the TS increased with increasing PMS for both unplasticized and plasticized biocomposites, while EB (%)decreased. Both biocomposites exhibited the decreasing trend of water solubility with increasing PMS; however, it shown increasing trend of moisture absorbency.The FTIR result revealed that the hydrogen bonding takes place between PMS and PVA in biocomposite film and thus biocomposite film exhibited greater thermal stability than that of pure PMS and PVA films. Moreover, the recyclability nature of the biocomposites was also observed and found it recyclable. Hence, the sorbitol plasticized PMS/PVA based biocomposite can be used as a low cost eco-friendly advanced biodegradable material for industrial applications.*

Key words: *Biocomposite, partially pregelatinized maize starch (PMS), PVA.*

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1. Introduction

Over the decades, due to increase in solid waste accumulation of synthetic plastics and polymers derived from petroleum, the progress of bio based materials are of great consideration now a days. Several research groups have been giving their utmost efforts to improve sustainable biocomposite materials for green environment. Recently, the bio-blends from starch and poly vinyl alcohol have advanced significantly. Materials from renewable resources have grown much consideration during the last decades due to overall global necessity for alternatives to fossil resources[1]. Natural fiber fillers based polymer composite, also called eco-composites[2] have attracted the consideration of both scientific and industrial community[3-5]. Lately, carboxymethyl cellulose/PVA blends for biodegradable packaging materials has been reported[6]. PMS/PVA based biocomposite incorporation with boric acid can be another promising materials for green environment. Starch is a naturally abundant biopolymer with advantages such as low cost, available from renewable resources and capable to replace some synthetic polymers[7-9]. Though, the inherent disadvantages of starch (high water absorbency, low tensile property), have limited to extensive applications[10]. For developing its properties, starch is being usually blended with other thermoplastic polymers[11-16]. PVA has good mechanical and barrier properties and is very compatible with starch. It is a water-soluble, nontoxic, flexible and synthetic biodegradable polymer. Moreover, PVA exhibits the features of ease of preparation, good film formation, strong conglutination, high thermal stability, excellent chemical resistance, good durability, and adhesive properties[17]. PVA based biodegradable composites by the incorporation of natural polymers such as pea starch and cellulose have been repoted[11,18].

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Owing to the versatile characteristics of PVA, scientists have gained dedication on the research of bio-blend films incorporating PVA and starch[19]. Taking into consideration the environmental issues, boric acid (BA) was used due to its excellent crosslinking agent and has no adverse effect on the environment[20]. So far, no specific research works about sorbitol plasticized PMS/PVA based biocomposite has been reported yet. The aim of this article was to focus on the preparation of PMS/PVA based biocomposite incorporating of BA and to explore the physico-mechanical, chemical and thermal properties; as a low cost eco-friendly sustainable biodegradable packaging material for variety of applications.

2. Materials and Methods

2.1. Materials

White granular partially pregelatinized maize starch (PMS, pharma grade) having particle size between 75-125 µm containing 9% moisture was collected from Colorcon, USA. Polyvinyl alcohol (PVA) with a molecular weight of 115,000 was purchased from Merck (Schuchardt OHG 85662, Hohenbrum, Germany). Reagent grade sorbitol and boric acid (BA) were purchased from Merck (India).

2.2 Preparation of PMS/PVA based biocomposite films

The PMS/PVA based biocomposite films were prepared by solution casting[21-22].Various formulated films (PMS: PVA: 2:7, 3:6, 4:5, 5:4, 6:3, 7:2) were prepared with and without sorbitol. The colloidal suspension of PMS in deionized water was prepared by continuous stirring with a magnetic hot plate at about 70 °C for 1h. PVA was dissolved in deionized water by continuous stirring with a magnetic hot plate through heating at about 90 °C for 2h. The colloidal suspension of PMS, PVA and BA were blended for 2h through heating at about 85-90 °C by continuous stirring until the homogeneous mixture obtained. 10% boric acid as crosslinked agent and sorbitol as plasticizing agent were incorporated in the mixture respectively. Finally, the biocomposite films were obtained by solution casting on a silicon paper coated glass plate, dried with the relative humidity (RH) at approximately 50% in the room temperature and removed from the plate for characterization.

2.3 Experimental

2.3.1 Mechanical properties (Tensile strength and percentage of Elongation at break)

The tensile properties such as, tensile strength (TS) and percentage of elongation at break (EB%) of the biocomposite films were measured with a universal testing machine (Hounsfield, model H50 ks 0404, UK) by ASTM D 882-80a (1995a)[23].

2.3.2 Water Solubility measurement

The water solubility of the biocomposite films was measured by using a modified reported method[24]. Various films having dimension 30×30 mm^2 were dried at 60 °C for 24h in a vacuum oven. The dried films were kept in a desiccators containing silica gel for about half an hour. The conditioned specimens were immersed in 100 mL deionized water kept in a beaker for 24 h. Each of the films (with an initial weight)was weighed and recorded. After 24 h soaking in water, each of the films was removed, oven dried and final dried specimens were weighed and recorded.

2.3.3 Moisture uptake

The moisture uptake of the biocomposite films was measured reported method by Cao & Chen et.al[25]. The films having dimension 30×30 mm^2 were dried at 60 °C overnight in a vacuum oven. The dried specimens were kept in a desiccator containing silica gel for 6 hours (0% of RH). Each of the samples was weighed initially and recorded. After taking initial weight, each of the specimens was conditioned at room temperature in a desiccator of 98%

RH (conditioned by saturated $CuSO_4.5H_2O$ solution) for seven days. Later, the specimens were removed from desiccator, weighed and recorded. The moisture uptake was determined as the percentage increase in weight after being conditioned for 7 days at 98% of RH. The determinations were performed in triplicate.

2.3.4 Fourier Transform Infrared (FTIR) spectroscopy.

FTIR spectra of the biocomposite film samples were recorded on a PerkinElmer spectrophotometer. The spectrophotometer was equipped with an attenuated total reflectance (ATR) accessory with a germanium crystal. The spectral resolution was 4 cm^{-1} with a scanning range from 4000-400 cm^{-1}.

2.3.5 Differential Scanning Calorimetry (DSC)

DSC analysis was performed using a PerkinElmer DSC-7 system under nitrogen atmosphere. The measurements were performed while heating the samples (5-10 mg) at a rate of 10 °C/min within the temperature range of 0-400 °C.

2.3.6 Thermogravimetric Analysis (TGA)

TGA analysis was performed using a Thermogravimetric analyzer (model TGA-50, Shimadzu, Japan) under nitrogen atmosphere. The measurement was performed while heating the samples inside a closed crucible at a rate of 10 °C/min within the temperature range of 30-600 °C. Nitrogen was used as a purging gas.

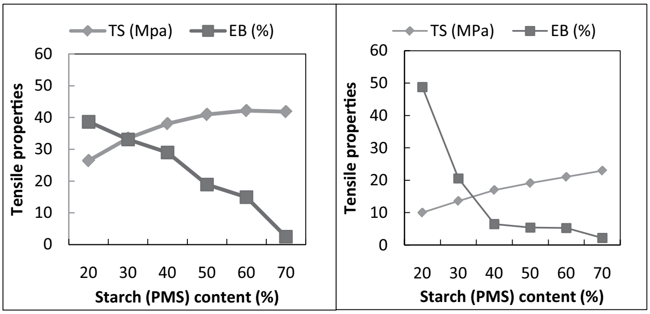
2.3.7 Recycling test

The recycling test of the biocomposite samples were done by simply boiling method. The samples were immersed in distilled water kept in a beaker and heated up to boiling the water. The recycling result of the samples were observed visually.

3. Results and discussion

3.1. Tensile properties (Tensile Strength and percentage of Elongation at Break)

Thetensile properties ofbiocomposites depend on cross linking agents and plasticizers used. Generally, the tensile strength increased and the elongation at break decreased as the percentage of cross linking agent increased. The results are often opposite when plasticizers are increased[26]. Fig 4a. shows the tensile strength (TS) and percentage of elongation at break (EB%) of unplasticized PMS/PVA based biocomposites containing 10% of BA. It has been observed that, the tensile strength showed an upward trend with increasing PMS. The reason can be attributed to the hydrogen bonds that were taking place between the PMS and PVA. For elongation, the opposite scenario was found, as EB (%) decreased with increasing PMS.



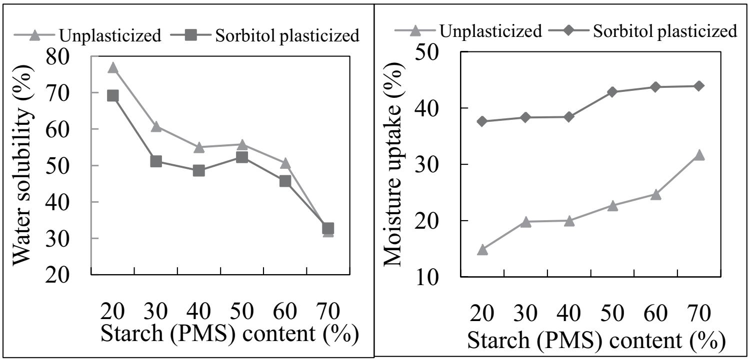
1a *1b*

Fig 1. *Tensile strength (TS) and percentage of elongation at break (EB %) of unplasticized (1a) and plasticized (1b) PMS/PVA biocomposite as a function of PMS content*

The TS value was observed 26.4, 33.5, 38.1, 40.95, 42.2, and 41.86 MPa; while EB (%) was 38.65, 33.09, 28.99, 18.89, 14.93 and 2.48 for unplasticized (Fig1a) biocomposites respectively.Fig 1b shows the tensile strength (TS) and percentage of elongation at break (EB%) of sorbitol plasticized PMS/PVA based biocomposites.It has been also observed that, the tensile strength increased with increasing PMS in presence of sorbitol, while percentage of EB kept falling off. TS was observed to be 10.05, 13.64, 17.0, 19.14, 21.05 and 22.98 MPa; while percentage of EB was found to be 48.78, 20.59, 6.49, 5.43, 5.29 and 2.21 for sorbitol plasticized biocomposite respectively. These result may be attributed due to hydrogen bonding took place between PMS and PVA.

3.2. Water solubility

The water solubility of different biocomposites is shown in figure 2a. It was observed that the water solubility of both unplasticized and sorbitol plasticized PMS/PVA based biocomposites decreased with increasing PMS content.The decreasing trend of solubility may be due to hydrogen bonding took place between PMS and PVA. Thus the more PMS content more the hydrogen bonding.



2a *2b*

Fig. 2 *The water solubility (2a) and moisture uptake (2b) of unplasticized and plasticized PMS/PVA biocomposite as a function of PMS content*

This finding is similar to citric acid where carboxyl groups formed strong hydrogen bonds with the hydroxyl groups on starch, thus improving the interaction between the molecules and decreasing the water sensitivity[27].

3.3. Moisture uptake

The strong hydrophilic nature of starch molecules, high starch content films showed higher water absorbency. Cross linking of starch macromolecules reinforces the intermolecular binding by introducing covalent bonds that supplement natural intermolecular hydrogen bonds so as to improve the water resistibility[28]. Since pure PVA and PMS is highly sensitive to moisture, changing in moisture sensitivity for the biocomposites is very significant. From the figure 2b, for both sorbitol plasticized and unplasticized biocomposites samples, the moisture uptake increased with increasing the amount of PMS. This result might be the high moisture sensitivity of PMS. Plasticized samples also showed more moisture uptake than their unplasticized counterparts. Since sorbitol acts as an excellent hygroscopic excipient, introducing it in the composites samples boosted water uptake greatly. The slowly increasing trend of moisture uptake might be due to the hydrogen bonding took place between PMS and PVA in presence of BA. Thus, the moisture sensitivity nature of PMS/PVA biocomposite greatly improved by incorporation of BA.

3.4. FTIR analysis

The FTIR spectra of pure starch (PMS), PVA and selected biocomposites samples are shown in figure 3. The main characteristics peaks in the spectrum of PMS, PVA and several biocomposites are listed in table 1. In the FTIR spectrum of the pure PMS, due to the presence of intermolecular and intramolecular hydrogen bonded –OH groups; a characteristic broad band was observed at 3344 cm^{-1}. A band was observed at 2924 cm^{-1}; indicating the presence of aliphatic C-H stretching vibrations. Another medium band observed at 1641 cm^{-1} indicated bending vibration of the hydrogen bonded -OH group of starch. The band was found at 1413 cm^{-1}; which was attributed to the vibrations associated with the CH_2 group. The stretching vibration of C-O bond in C-O-H and C-O-C group in the anhydrous glucose ring appeared at 1147 and 1002 cm^{-1} respectively. The FTIR spectrum of the pure PVA, due to the presence of hydrogen bonded –OH groups; a characteristic broad band was observed at 3292 cm^{-1}. A sharp band was observed at 2935 cm^{-1}; indicating the presence of aliphatic C-H stretching vibrations.

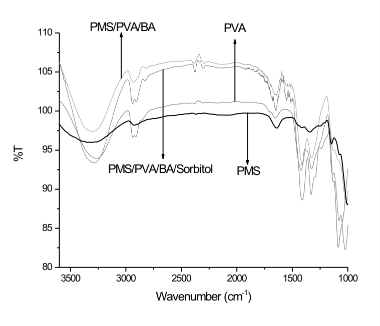


Fig 3. *FTIR spectra of purestarch (PMS), PVA and selected PMS/PVA/BA based biocomposites*

Another medium band observed at 1653 cm^{-1} indicated bending vibration of the bound water of PVA. Two sharp peaks were observed at 1415 cm^{-1} indicated –C-C-C- bending with C-H combination and at 1325 cm^{-1} which was attributed to the combination frequencies of –CH and –OH. Another two strong absorption peaks observed at 1130 and 1080 cm^{-1} (between 1060-1150 cm^{-1}) were assigned to the C-O-H and C-O-C stretching mode of PVA respectively[29]. In the FTIR spectrum of the sorbitol plasticized PMS/PVA/BA based biocomposite, a characteristic broad band was observed at 3275 cm^{-1}; due to the presence of intermolecular and intramolecular hydrogen-bonded –OH groups. The hydrogen bonded –OH absorption peaks of PMS (3344 cm^{-1}) and PVA (3292 cm^{-1}) significantly decreased to 3275 cm^{-1} in bio composite; which indicated that hydrogen bonding took place between PMS and PVA.

Table 1: Summary of the FTIR results

Functional group	PMS (cm^{-1})	PVA (cm^{-1})	PMS/PVA/ BA (cm^{-1})	PMS/PVA/BA/ Sorbitol (cm^{-1})
OH stretching	3344	3292	3311	3275
C-H stretching	2924	2935	2941	2933
Bound water	1641	1653	1647	1647
Vibrations associated to CH_2 group	1413/1340	-	1410/1325	1415/1330
C-O stretching of C-O-C	1002	1080	1010	1080/1023
C-O stretching of C-O-H	1147	1130	1135	1141

A sharp band was observed at 2933 cm^{-1}; indicating the presence of aliphatic C-H stretching vibrations that more or less similar with PMS and PVA. Another peak was found at 1647 cm^{-1}; indicating bending vibration of the hydrogen bonding -OH group that of similar with starch. Another two peaks were found at 1415 and 1330 cm^{-1}; which was attributed to the combination frequencies of –CH and –OH. Another two strong absorption peaks of -CO observed at 1141 and 1080 cm^{-1} (between 1060-1150 cm^{-1}) were assigned to the C-O-H and C-O-C stretching mode respectively. The FTIR spectrum of others biocomposite are listed in table 1.

3.5. Differential Scanning Calorimetry (DSC) Analysis

The DSC thermograms of the PMS, PVA, unplasticized PMS/PVA/BA and sorbitol plasticized PMS/PVA/BA based biocomposite exhibit sharp endothermic peaks (typically of a semi crystalline polymeric system in fig 4).

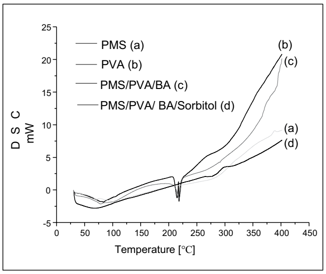


Figure 4. *DSC thermograms of starch (PMS), PVA and selected PMS/PVA/BA based biocomposites*

These endothermic peaks have been associated with the melting of crystalline starch and PVA domains reorganization. The main thermal parameters of PMS, PVA and biocomposites are shown in table 2. The DSC thermograms of PMS showed a broad endothermic peak at 84 °C. This temperature indicated the T_g of starch; as well as the crystallization transition. Another strong and narrow endothermic peak was observed at 218.26 °C; which represented the melting temperature T_m. For pure PVA, a broad endothermic peak at around 77 °C was found on the thermograms indicated the T_g of PVA; as well as the crystallization transition. Another strong and narrow endothermic peak was observed at 210 °C; which represented the melting temperature T_m. In the DSC thermograms of PMS/PVA/BA based biocomposite, a broad peak at around 75 °C was found on the thermograms that indicated the T_g of bio composite. For sorbitol plasticized PMS/PVA/BA based bio composite, a broad peak at around 70 °C was found on the thermograms obviously indicated the T_g of bio composite; as well as the crystallization transition.

Table 2: T_g and T_m of PMS, PVA and selected PMS/PVA based biocomposite

Sample	T_g	T_m
PMS	84	218.26
PVA	77	210
PMS/PVA/ BA	75	None
Sorbitol plasticized PMS/PVA/ BA	70	None

By introducing boric acid (BA) as a crosslinking agent to the PMS/PVA composite, it is found that T_g decreased and absent of clear T_m. This may be due to the loss of –OH groups that exist in PMS and PVA because of crosslinking.Crosslinked composites prepared by containing sorbitol as a plasticizer exhibited lower T_g. Plasticizers reduce the T_g value of polymers and provide their flow by improving flexibility and processability. These results were consistent with the effect of plasticizers in different polymer blend composites by investigating the degree of changes in T_g[30, 31].

3.6. Thermogravimetric Analysis (TGA)

The TGA thermograms of pure starch (PMS), PVA and selected biocomposites shown in Fig 5. In the TGA thermograms of pure starch (PMS), only three weight loss steps were observed. The initial weight loss (11.47%) occurred within the temperature range 40.0–201.12 °C; due to the elimination of moisture and water. Steps 2 and 3 were the degradation step. The maximum degradation (50.28%) was observed on step 2 in the temperature range 201.12–402.95 °C; with most prominent degradation at 310 °C due to the characteristic decomposition of starch (cracking of starch)[32]. Some gases such as CO_2, CO, H_2O and other small volatiles are released during this stage along with carbonaceous residue formation[27,33]. The last stage took place between 488.42 - 599.62 °C and corresponds to decomposition of the previously formed residue[32]. In the TGA thermograms of pure PVA, three weight loss steps were observed. The initial weight loss (10.43%) within the temperature range 50.0–288.83 °C was associated with the elimination of moisture and water. Steps 2 and 3 were the degradation step. In step 2, the maximum degradation (74.91%) was observed in the temperature range 288.83–525.00 °C and was due to the characteristic decomposition of PVA. In degradation step 3, from 525to 599.34 °C a slow degradation of 13.41% was observed, due to the characteristic decomposition of PVA (cracking of PVA). Afterwards, the curve becomes flat which indicated that only the inorganic residues were left[32]. In the TGA thermograms of unplasticized and sorbitol plasticized PMS/PVA/BA based biocomposite, three weight loss steps were also observed. The initial weight loss (approximately 16%) within the temperature range 30–280 °C was associated with the elimination of moisture and water. Steps 2 and 3 were the degradation step. In step 2, the maximum degradation (approximately 50%) was observed in the temperature range from 280.9–425 °C and was due to the characteristic decomposition of the polymer. In degradation step 3, temperature range from 425 to 600 °C a slow degradation was observed, due to the moderately strong bond breaking of the polymer backbone.

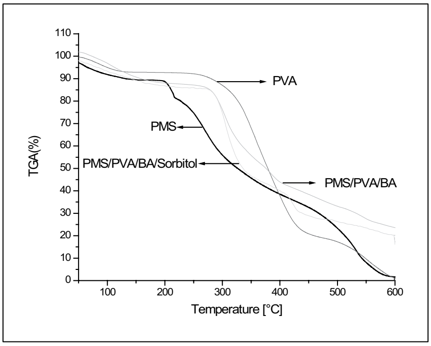


Fig 5. TGA thermograms of starch (PMS), PVA and selected PMS/PVA/BA based biocomposite

Afterwards, the curve becomes flat which indicated that only the inorganic residues were left. It was observed that both sorbitol plasticized and unplasticized PMS/PVA/BA biocomposite samples showed similar weight loss in different steps of degradation, and neither completely resembled PMS or PVA; although the unplasticized sample maintained its weight for longer temperature range. However, the PMS/PVA/BA based biocomposites experienced the overall lowest thermal degradation; therefore, more thermally stability; due to the crosslinking through hydrogen bonding between PMS and PVA in presences of BA. This result again proved that the resemblance found by FTIR and DSC analysis.

3.7. Recycling

It was observed that all kinds of biocomposites were completely dispersed in boiling water within 10 minutes. In addition, the suspended dispersion materials were again used to prepare bio composite film by solution casting.Therefore, the biocomposites described in this article can be considered as reversible and recycling materials.

4. Conclusion

Starch (PMS) based biocomposite materials with advanced properties have been developed and characterized the physico-mechanical, chemical and thermal properties along with recycling nature of PMS/PVA based biocomposite films. It was observed that the TS increased with increasing PMS for both unplasticized and sorbitol plasticized biocomposites, while EB (%)decreased. Furthermore, the unplasticized biocomposite films was very hard and brittle and showed the higher TS value; however, sorbitol plasticized biocomposites showed flexible film and reasonable TS value. Based on this result, 40% PMS containing biocomposite was considered as optimized biocomposite for further development. On the other hand, both unplasticized and sorbitol plasticized biocomposites were the experience of decreasing trend of water solubility with increasing PMS and thus exhibited increasing trend of moisture absorbency. The FTIR, DSC and TGA results revealed that the hydrogen bonding takes place between PMS and PVA with the incorporation of BA and thus the biocomposite exhibited greater thermal stability than that of pure PMS and PVA. Moreover, the recyclability nature of the biocomposites was also observed and found it recyclable.So far, no specific research works about sorbitol plasticized PMS/PVA based biocomposite has been reported yet. Hence, the sorbitol plasticized PMS/PVA based biocomposite can be used as promising eco-friendly recyclable advanced material for green environment.

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