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Mechanical, thermal and morphological properties of polyvinyl alcohol/starch/carboxy methyl cellulose biodegradable blends

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ABSTRACT

Polyvinyl alcohol (PVA) / starch (S) /Carboxy methyl cellulose (CMC) composite films were prepared from PVA, three different loading of CMC and soluble starch aqueous suspensions by casting method in the presence of plasticizer containing glycerol. The effects of the CMC addition on the some physical properties of the resulted blend films were investigated. Reactive hydroxyl groups were exposed on the CMC surface, which could establish new hydrogen bonds with polyvinyl alcohol and starch. Tensile tests demonstrated positive results from mechanochemical treatment. With the addition of 20% CMC was an increase in the tensile strength and percentage elongation at break. A decrease in the thermal resistance of polyvinyl alcohol/starch composite with the addition of CMC was also observed by means of DSC (Differential scanning calorimetry) analysis. The SEM (Scanning electron microscopy) indicates morphological structure of the polyvinyl alcohol/starch films in the different percent of CMC.

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KEYWORDS

Starch;
Polyvinyl alcohol;
Carboxy methyl cellulose;
Biocomposites;
Physical properties.

INTRODUCTION

The severe environmental problems, including the increasing difficulties of waste disposal and the deepening threat of global warming (due to carbon dioxide release during incineration) caused by the nonbiodegradability of a number of polymers (used in packaging and agriculture field) have raised concerns all over the world^[1]. In order to solve the problems generated by plastic waste, many efforts have been done to obtain an environmental friendly material. Most of the researches are focused on substitu-

tion of the petro-based plastics by biodegradable materials with similar properties and low in cost^[2-4]. Among the natural polymers, starch has been considered as one of the most promising candidates for this regard because of its attractive combination of price, abundance and thermoplastic behavior, in addition to biodegradability. The main disadvantage of biodegradable starch-based films is their hydrophilic character, which leads to low stability when these materials are submitted to different environmental conditions^[5]. In addition, starch-based materials have poor mechanical properties and particularly poor elongation at am-

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bient conditions. Thus, the incorporation of a plasticizer is required to overcome the brittleness of these materials. Plasticizers reduced intermolecular forces and increase the mobility of polymer chains, decreasing the glass transition temperature and increasing permeability^[6]. One approach to improve the functional properties of starch films is to blend starch with other polymers (natural and synthetic). Biodegradable starch-based plastics such as starch/cellulose and starch/PVA have recently been investigated for their great potential marketability in agricultural foils, garbage and composting bags, and food packaging, in the fast food industry, and in biomedical fields^[7-10]. PVA is a versatile polymer with many industrial applications, and it may be the only synthesized polymer whose backbone is mainly composed of C-C bonds that is absolutely biodegradable. PVA is the most readily biodegradable of vinyl polymers. It is readily degraded in wastewater activated sludge. The microbial degradation of PVA has been studied, as well as its enzymatic degradation by secondary alcohol peroxidases isolated from soil bacteria of pseudomonas strain. The excellent chemical resistance, optical and physical properties of PVA resins, has resulted in its broad industrial uses^[11-13]. Carboxy methyl cellulose is cellulose ether forms excellent films. Because of its polymeric structure and high molecular weight, it is capable to use as filler in biocomposite films production. Carboxy methyl cellulose is able to improve the mechanical and barrier properties of starch-based films^[14]. PVA, carboxy methyl cellulose and starch are polar polymers; thus a composite of PVA, carboxy methyl cellulose and starch is likely to produce a material having excellent mechanical properties^[15]. This study reports on the effect of carboxy methyl cellulose content, on the properties of PVA/starch films, such as mechanical, thermal and morphological parameters. These studies were carried out to assess their potential uses as packaging films.

EXPERIMENTAL

Materials

Starch (ST) was provided by Merck company, and polyvinyl alcohol (PVA) with $M_n=72000$ and glycerol

($M_n=92/10$, 78% purity) purchased from Merck company. Carboxy methyl cellulose sodium salt, with an average molecular weight of $M_n=295225$ was purchased from Fluka company.

Methods

Preparation of films

Films were obtained by the casting method^[16]. First, PVA (2.5 g) was solubilized in 50 cc of distilled water at 75°C for 15 min and starch (2.5, 2, 1.5 g) was mixed (25°C for 10 min) with distilled water (15 cc) and glycerol (40 cc/100 g starch) then added to 20cc of boiling water to obtain a clear solution. Carboxy methyl cellulose (0, 0.5, 1g) was solubilized in 75 cc of distilled water at 75°C for 15 min. Then, PVA, starch and CMC solutions were mixed together and stirred with using a magnetic bar at 75°C for 90 min with a reflux condenser. Then, about 70cc of the sample was poured into a Teflon casting tray and then dried at 60°C in oven to cast the films. The thickness of the films was 0.08±0.01 mm. The thickness of the films measured with an Alton M820-25 hand-held micrometer having a sensitivity of 0.01 mm.

Solubility in water

Solubility in water was defined as the percentage of the dry matter of film which is solubilized after 24 h immersion in water^[17].

Film specimens were kept in a desiccator containing dry calcium sulphate till they reached constant weight. Afterward, about 500 mg of each film were immersed in beakers containing 50 ml of distilled water at 23 °C for 24 h with periodical gentle manual agitation. The Films were removed from the water and were placed back in the desiccator until they reached a constant weight to obtain the final dry weight of the film. The percentage of the total soluble matter (%TSM) of the films was calculated using the following equation:

$$\%TSM = \frac{[(\text{initial dry } W_i - \text{final dry } W_f)]}{\text{initial dry } W_i} \times 100 \quad (1)$$

TSM tests for each type of film were carried out in three replicates.

Swelling studies

The extent of swelling was determined by a conventional gravimetric procedure^[18]. In brief; a

preweighed dried piece of a blend sample (0.1 g) was immersed in distilled water, and allowed to swell. By recording the weights of the swollen blends at desired time intervals, it was possible to monitor the extent of swelling. The swelling process was expressed in terms of the swelling ratio, as follows:

$$\text{Swelling ratio (SR)} = \frac{\text{Weight of swollen blend/}}{\text{Weight of dry blend}} \quad (2)$$

Mechanical properties

Ultimate tensile strength (UTS) and strain to break (SB) of the films were determined at $21^{\circ}\text{C} \pm 1^{\circ}\text{C}$ using a tensile tester (Zwick/Roell model FR010, Germany) according to ASTM standard method D882-91^[19]. Three dumbbelloid forms films (8 cm \times 0.5 cm) were cut from each of samples and were mounted between the grips of the machine. The initial grip separation and cross-head speed were set to 50 mm and 5 mm/min, respectively.

Thermal properties

The thermal properties of the films were determined by differential scanning calorimetry (DSC) (Model F3 200 DSC Netzsch, Germany). The film samples (5 mg \pm 3 mg) were cut as small pieces and were placed into a sample pan of DSC equipment. The reference was an empty pan. The glass transition temperature (T_g) of the different films were measured at a heating scan rate of $10^{\circ}\text{C}/\text{min}$ from 0°C to 300°C and they were identified as the midpoint temperature of a step-down shift in baseline due to change in heat capacity upon glass transition. Also the melting point (T_m) of the films was determined. The T_g and T_m of the each film was determined in duplicate and the results were averaged.

Scanning electronic microscopy (SEM)

The morphology of the surface of the films was investigated using a scanning electronic microscope of XL30 type (Netherlands). The films were covered with pure metallic Au. The laying down of Au was carried out using evaporation of the metal under a high vacuum, to give a thickness of around 100 \AA .

Fourier transformed infrared spectroscopy (FTIR)

Infrared spectra with a resolution of 4 cm^{-1} of the samples as KBr pellets were recorded by Shimadzu FT-IR RF50 spectrometer.

RESULTS AND DISCUSSION

Solubility in water

The water solubility of the PVA/S/CMC films as a function of CMC content is shown in Figure 1. Addition of CMC, in all concentrations, increased the water solubility of films. The %TSM was 27.41% for the samples without CMC, which increased to 33.77%, 43.71% and 46.27% for the films containing 5, 10 and 20% W/W CMC, respectively. This is in agreement with^[20] that investigated the effect of CMC on the solubility in water of the thermoplastic starch/CMC and reported that when filler content increased, the solubility in water values increased gradually. The observed results may be explained by the fact that an increased CMC content in the blend renders the network more hydrophilic and henceforth, the degree of water sorption increases, which, in turn, increases the solubility in water.

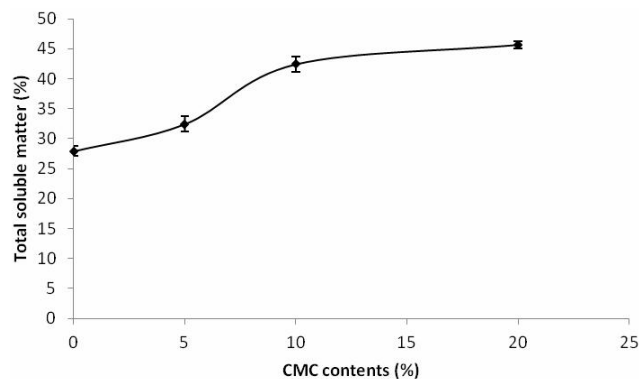


Figure 1 : Water solubility of the PVA/S/CMC films as a function of CMC content

Swelling studies

The swelling ratio of the PVA/S/CMC films as a function of CMC content is shown in TABLE 1. Addition of CMC, in all concentrations, increased the SR of PVA/S/CMC films. This is in agreement with^[20] that investigated the effect of CMC on the swelling ratio of the thermoplastic starch/CMC and reported that when filler content increased, the swelling ratio values increased gradually. Carboxymethyl cellulose (CMC), being a modified natural water-soluble polymer, contains hydroxy and carboxyl groups which impart hydrophilicity to the molecule. When the weight fraction of CMC is increased in the reaction mixture of the blend, the swelling ratio is found to increase substantially. The

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observed results may be explained by the fact that an increased CMC content in the blend renders the network more hydrophilic and henceforth, the degree of water sorption increases, which, in turn, increases the swelling ratio. Another plausible explanation rests upon the possibility that as the content of CMC increases in the blend matrix, there may be an increase in the mutual repulsion between the carboxylate groups of the CMC molecules, which relaxes the network chains of the blend and widens the mesh sizes of the blend. This ultimately results in enhanced swelling of the system.

TABLE 1 : The swelling ratio of the PVA/S/CMC films as a function of CMC content

PVA%/S%/CMC%	PH	Temperature	Swelling ratio
50%/50%/0%	6.8	25	3.96 ± 0.69
50%/45%/5%	6.8	25	5.94 ± 1.16
50%/40%/10%	6.8	25	7.96 ± 1.31
50%/30%/20%	6.8	25	16.56 ± 1.72

Mechanical properties

Figures 2-4 show the relationships between CMC content and the tensile properties of the PVA/S/CMC films. The curves reported in Figure 2 show an improvement of the mechanical strength with the increase of CMC content. This is in agreement with^[14] who reported a significant improvement mechanical property of starch films is achieved by adding relatively small amounts of CMC (till 10%). The UTS and SB as the function of CMC concentration are shown in Figures 3 and 4, respectively. It was observed an important increase of fourfold in the UTS when 5% W/W of CMC was added to the PVA/starch, but with increasing CMC concentration from 5% to 20%, the UTS decreased from 27.88 MPa to 18.36 MPa. Therefore, with increasing CMC concentration from 0% to 20%, the UTS increased significantly from 6.38 MPa to 18.36 MPa. This was probably due to the interfacial interaction between the matrix and filler due to the chemical similarity (polysaccharide structure) of starch and CMC. It was interesting that with increasing CMC concentration (from 0% to 20%), the UTS increased significantly. It was observed an important decrease of sixfold in the SB when 5% W/W of CMC was added to the PVA/starch, but with increasing CMC concentration from 5% to 20%, the SB increased from 4.03% to 35.56%.

Therefore, with increasing CMC concentration from 0% to 20%, the SB increased significantly from 23.86% to 35.56%. It seems CMC could improve the films strength without depressing effect on flexibility.

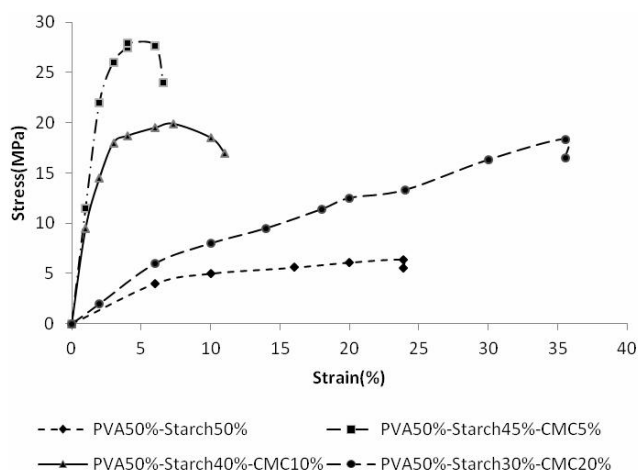


Figure 2 : Stress vs. strain for PVA/S/CMC films as a function of CMC content.

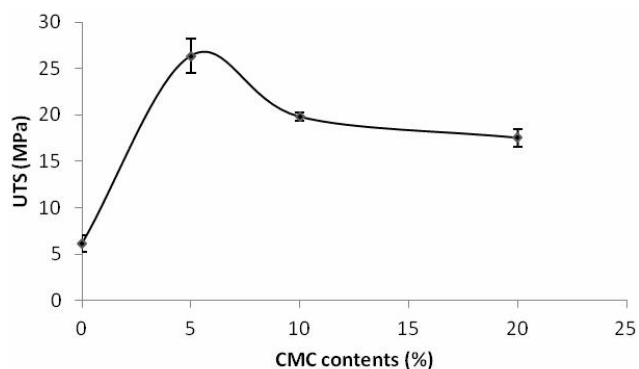


Figure 3 : The ultimate tensile strength (UTS) of the PVA/S/CMC films as a function of CMC content.

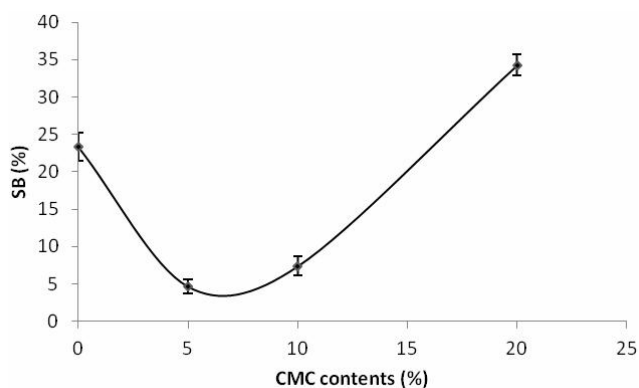


Figure 4 : The strain to break (SB) of the PVA/S/CMC films as a function of CMC content.

Thermal properties

Three characteristic thermal transitions may exist for semi crystalline polymers such as starch: a glass tran-

sition for the amorphous fraction, a melting transition for the crystalline fraction and a transition due to crystallization. The DSC thermograms of the PVA/starch, PVA/S/CMC films (Figure 5) exhibited sharp endothermic peaks (typical of a semi-crystalline polymeric system) at the range of 220 °C to 280 °C. These endothermic peaks have been associated with the melting of crystalline starch, PVA and CMC domains reorganized during the retrogradation. The melting peak of PVA/starch was around 263.8 °C. For PVA/S/CMC polymer blend films, the temperature position of the melting peak decreased from 263.8 °C to 241.1 °C as CMC content increased from 0 to 20% W/W film.

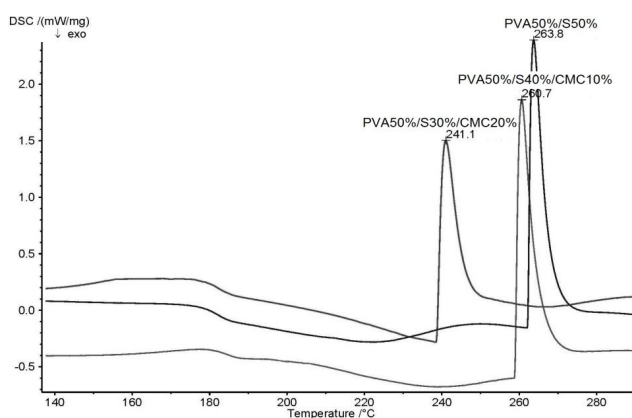


Figure 5 : Thermogram of the PVA/S/CMC films containing different amount of CMC.

Glass transition temperatures were observed in PVA/S/CMC polymer blend films at the range of 150 °C to 200 °C depend on CMC content. It could also be seen in the DSC curves of the PVA/S/CMC films (Figure 5) that the T_g decreased when the CMC content increased from 0 to 20% W/W film, respectively. The change in the position of the glass transition indicates that higher CMC contents might be act as lubricant agent and decreased intermolecular interaction and association in PVA/Starch film matrix which in turn decreases degree of crystallinity.

Scanning electronic microscopy (SEM)

Figure 6 shows the morphology of PVA/S/CMC films with different contents of starch and CMC. The addition of CMC significantly changes the morphology of PVA/S/CMC composite. Blends PVA/starch and PVA/S/CMC had a uniform morphology, with no evidence of phase separation. Homogeneous distributions of the CMC in the PVA/S/CMC matrix were observed

in all composite films, implying good adhesion between fillers and matrix. This is attributed to the good compatibility resulting from the chemical similarities between starch and carboxy methyl cellulose and the hydrogen bonding interactions existing in the interface between PVA, starch and CMC. Such an event and uniform distribution of the fillers in the matrix could play an important role in improving the mechanical performance of the resulting composite films.

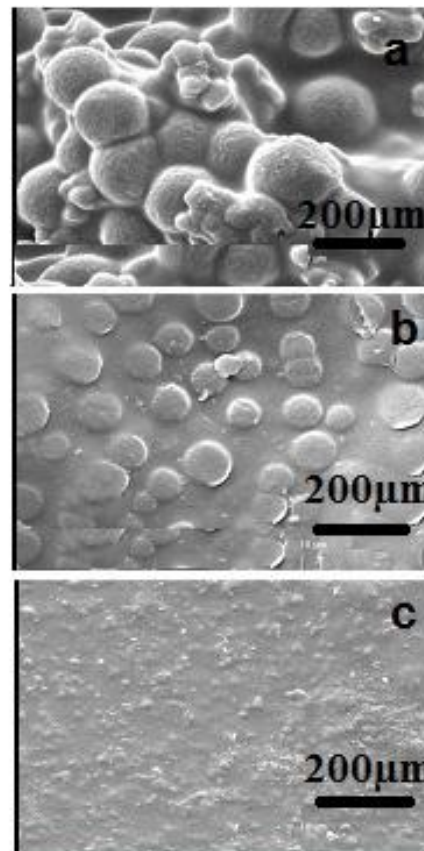


Figure 6 : SEM micrograph of the composites of PVA50%/S50% (a) PVA50%/S45%/CMC5% (b) and PVA50%/S30%/CMC20% (c)

Fourier transform infrared spectroscopy (FTIR)

Numerous characteristic peaks were identified from the FTIR spectra of the PVA/S/CMC composite samples are shown in Figure 7. In the neat starch samples characteristics peaks at 3447.3 cm^{-1} were due to both water present in the system and the hydroxyl groups of the sugar units^[21,22]. The PVA50%/Starch50% had some similar bands with O–H stretching at 3437 cm^{-1} ^[23]. The improvement in elongation at break reported for PVA/S/CMC (observed in tensile tests reported in this paper) could be explained

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by the disruption of the crystallinity (or retrogradation) of the starch due to the disruption of intermolecular H-bonding of the starch molecules themselves and the introduction of H bonding between PVA, starch and CMC chains. This interaction was confirmed via FTIR in which the -OH stretch from the glucose ring at 3447.3 cm^{-1} for the starch shifted to a lower wavenumber (3427.4 cm^{-1}) upon the addition of 20 wt% CMC. This downward shift in wavenumber is consistent with previous literature in which H-bonding has been shown to decrease the wavenumber of the hydroxy stretch due to a lower bond force from electron delocalization^[24]. Thus the primary interaction between starch, CMC and PVOH was through the -OH groups with a possibility of interaction at the O-5 ring oxygen^[25].

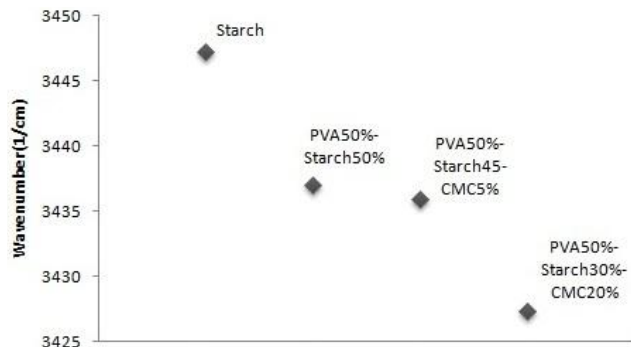


Figure 7 : Hydroxy stretch differences from FTIR spectra due to interactions with water, PVA, S and CMC.

CONCLUSIONS

The present study shows the role of CMC on the physicomechanical properties of PVA/starch films. The addition of CMC to PVA/starch blends improved the mechanical properties of the resulted starch based composites. CMC (20% W/W film) could increase the UTS and SB of starch based composite films by more than 35% and 67% compared to the PVA/starch film respectively. Solubility of the films increased from 27.14% to 46.27%. By addition of 10 and 20% CMC (W/W film), T_m decreased from 263.8 to 241.1 °C. In addition, by increasing of CMC content, outward properties of the composite films improved appreciably. With considering these results, it seems that the PVA/S/CMC biocomposit films show better physicomechanical properties than PVA/starch films and can be potentially re-

placed of PVA/starch films.

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