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Physical and mechanical properties of polyvinyl alcohol/starch/ carboxy methyl cellulose/montmorillonite nanocomposite films

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ABSTRACT

Polyvinyl alcohol (PVA) / starch (S) /Carboxy methyl cellulose (CMC) / MMT (Montmorillonite) bionanocomposite films were prepared from PVA, MMT, CMC and soluble starch aqueous suspensions by casting method in the presence of a plasticizer that contained glycerol. The clay dispersion in the films was analyzed by XRD (X-ray diffraction). XRD test showed that the clay nanolayers formed an exfoliated structure. The effect of MMT loading on the morphology, thermal behavior and mechanical properties of the films were investigated by means of SEM (Scanning electron microscopy), DSC (Differential scanning calorimetry) and tensile testing. SEM photographs demonstrated a homogeneous dispersion of MMT within the PVA/S/CMC matrix as well as a strong interfacial adherence between matrix and fillers, which led to an increase of glass transition temperature. With the addition of 1% nanoclay, there was an increase in the tensile strength. The addition of MMT improved the thermal resistance of biocomposites.

KEYWORDS

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

INTRODUCTION

In order to solve problems generated by plastic waste, lots of effort had been made to obtain an environmental friendly material. Most of the research investigation is focused on substituting petro-based plastics by biodegradable materials with similar properties in a low cost and effective manner. Starch is a biodegradable polymer produced in abundance from many renewable resources. As a consequence, it is easily available and very cheap. Being the end product of photosynthesis, starch is the major form of stored carbohydrate in plants[1-3]. The thermoplastic starch or plasticized starch is obtained after disruption and plasticization of native starch, by temperature and in presence of water and another plasticizer, such as glycerol. However, the thermoplastic starch has some limitations: it is mostly water-soluble and has poor resistance and low strength. The resistance to water may be improved by adding certain synthetic polymers[4], such as polyvinyl alcohol and natural polymers[5], such as lignin or carboxy methyl cellulose. PVA has been used previously in extruded thermoplastic starch to improve properties such as elongation and process ability (predominantly through improving melt strength)[6-8]. Carboxy methyl cellulose is cellulose ether which exhibits thermal gelation and forms excellent films. Because of its polymeric structure and high molecular weight, it can be used as filler in biocomposite film production. Carboxy methyl cellulose can improve the mechanical and barrier properties of starch-based films[9]. In addition, it is possible to improve the mechanical properties of this polymer by adding fillers. These composites could be used in packaging where good barrier and thermal properties are required[2,3,10]. Development of the polymer/clay nanocomposites is one of the latest revolutionary steps of the polymer technology. Preparations of blends or nanocomposites using inorganic or natural fibers are among the routes to improve some of the properties of biodegradable polymers. The nanocomposites obtained from adding a low percentage of clay to polymers showed improvement in the properties such as barrier, thermal and oxidative when compared with traditional composites. Clay minerals are aluminum silicates of a layered type classified as phyllosilicates. Montmorillonite is among the most commonly used layered silicates because it is environmentally friendly and readily available in large quantities with relatively low cost. MMT crystal lattice consists of 1nm thin layers with an octahedral alumina sheet sandwiched between two tetrahedral silica sheets. The aspect ratio is about 100. The stacking of the platelets leads to a Van der Waals gap or gallery between the layers. The layers are negatively charged and this charge is balanced by alkali cations such as Na^+, Li^+ or Ca^{2+} in the gallery between the aluminosilicate layers. The Na-MMT clay is hydrophilic with a high surface area[11,12]. The improvement in the polymer properties was reached when the clay was exfoliated and the major problem in preparing the composites was to separate the layers of the clay because they had been initially agglomerated. Therefore, it is possible to improve the properties of starch by the adding small amounts of environmentally friendly filler, to use the starch in more special or severe situations[11,13,14]. This research aims at investigating the mechanical, morphological and thermal properties of glycerol plasticized PVA/S/CMC/MMT bionanocomposites.

MATERIALS AND METHODS

Materials

Soluble starch (ST) was provided by Merck company, and polyvinyl alcohol with M_n=72000 and glycerol (M_n= 92/10, grade of pure 78%) purchased from Merck company. Carboxy methyl cellulose sodium salt, with an average molecular weight of M_n=295225 was purchased from Fluka company. Sodium montmorillonite (Cloisite Na^+) with a cation exchange capacity (CEC) of 92.6 mequiv. /100 g clay was supplied by Nanocor Inc. (Arlington Heights, IL).

Preparation of films

Films were obtained by casting method[15]. 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). Then, glycerol (40 cc/100 g starch) was 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. On the other hand, the montmorillonite (MMT) was dispersed in 35 cc distilled water by sonication for 10 min at room temperature. The clay ratios were 0, 1, 3 and 5 (w/w), relative to dry blend. Then, PVA, starch, CMC and MMT solutions were mixed together and stirred with by 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 resulting in films with 0.08±0.01 mm thickness, measured with an Alton M820-25 hand-held micrometer with a sensitivity of 0.01 mm and then dried at 60°C in oven to cast the films.

X-ray diffraction (XRD)

X-ray diffraction (XRD) studies of the samples were carried out using a Bruker D8 Advance X-ray diffractometer (Karlsruhe, Germany) operating at CuKα wavelength of 0.1539 nm. The samples were exposed to the X-ray beam with the X-ray generator running at 40 kV and 40 mA. Scattered radiation was detected at ambient temperature in the angular region (2θ) of 1–20° at a rate of 1°/min and a step size of 0.05°.

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[16]. Film specimens were kept in a desiccator containing dry calcium sulphate till they reached constant weight. Afterwards, 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:

$$\%TSM = [(\text{initial dry } W_t - \text{final dry } W_t) / \text{initial dry } W_t] \times 100 \qquad (1)$$

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[17]. In brief; a preweighed dried piece of a blend sample (0.1 g) was immersed in doubly 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:

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

Mechanical properties

Ultimate tensile strength (UTS) and strain to break (SB) the films was determined at 21°C±1°C using a tensile tester (Zwick/Roell model FR010 Germany) according to ASTM standard method D882-91[18]. Three dumbbelly forms films (8 cm×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 property of the films was determined by differential scanning calorimetry (DSC) (Model F3 200 DSC Netzsch, Germany). The film samples (5 mg±3 mg) were cut in 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 was measured at a heating scan rate of 10°C/min from 0°C to 300°C and 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 (Netherland). The films were covered with pure metallic Au. The laying down of Au was carried out by evaporating the metal under a high vacuum, to reach a thickness of around 100 °A.

RESULTS AND DISCUSSION

X-ray diffraction

In order to investigate the dispersion of the MMT layers in polymer matrix, X-ray diffraction analyses were performed on the nanocomposites. Figure 1 shows the XRD patterns of the pristine and ultrasonically treated MMT, the PVA/S/CMC/MMT bionanocomposites. PVA/S/CMC/MMT shows no peak in the study range while MMT exhibits a single 001 diffraction peak around 7.3º. The XRD patterns revealed that when MMT was treated by ultrasonic, there was no any sharp 001 peak. As we know, starch is a linear molecule consisting of ring-like monomer with size of about 0.55nm[19] (that is equal to d-spacing difference of pristine clay). Some researchers reported that, starch chains can be exfoliated completely in the starch–unmodified MMT[20-23].

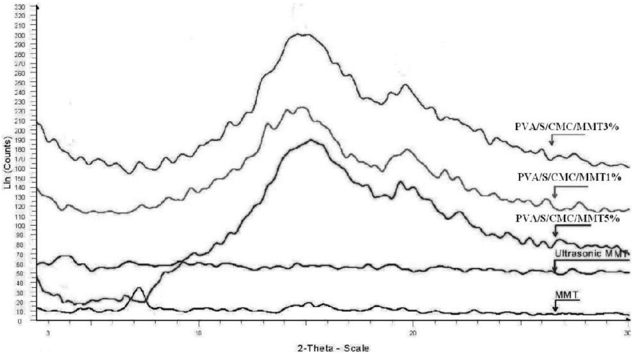

Figure 1 : XRD patterns for the pristine MMT, ultrasonically treated MMT, PVA/S/CMC/MMT bionanocomposites

As shown in Figure 1, there was no any sharp 001 peak in XRD pattern of PVA/S/CMC/MMT nanocomposite. This result confirms the extensive diffusion of polymer chains inside galleries of nanoclay and starch, CMC and PVA chains exfoliated completely in the PVA/S/CMC/MMT nanocomposites.

Solubility in water

The water solubility of the PVA/S/CMC/MMT films as a function of MMT content is shown in Figure 2. In all concentrations, the addition of MMT decreased the water solubility of starch films. The %TSM was 46.27% for the samples without MMT, which decreased to 43.72%, 40.21% and 35.28% for the films containing 1, 3 and 5% W/W MMT, respectively. This finding confirms the author[24] who investigated the effect of MMT on the solubility thermoplastic starch/CMC/MMT in the water and found that when filler content increased, the solubility in water values decreased gradually.

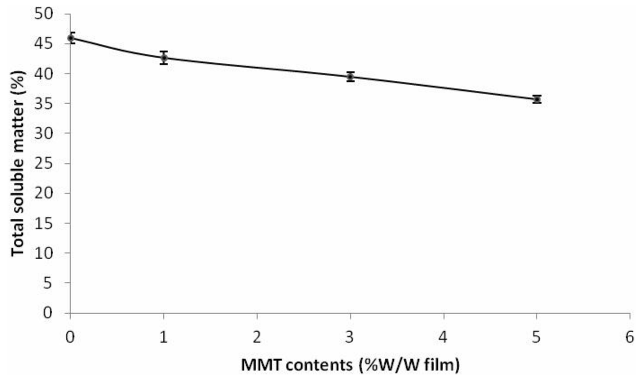

Figure 2 : Water solubility of the PVA/S/CMC/MMT films as a function of MMT content

The hydroxyl groups of MMT can form strong hydrogen bonds with the hydroxyl groups on PVA, starch and the hydroxyl and carboxyl groups on CMC; thus, improving the interactions between the molecules, the cohesiveness of biopolymer matrix and decreasing the water sensitivity.

Swelling studies

Water sensitivity of starch-based material is a key challenge towards the substitution of traditional plastics for commodity, most precisely, for packaging applications. TABLE 1 shows the swelling ratio of the bionanocomposites as a function of the MMT content. The addition of MMT, in all concentrations, decreased the SR of PVA/S/CMC/MMT films. This finding confirms the author[24] who investigated the effect of MMT on the swelling ratio of the starch/CMC/MMT and reported that when filler content increased, the swelling ratio values decreased gradually.

It was observed that the swelling ratio of PVA/S/CMC biocomposites was higher than that of PVA/S/CMC/MMT bionanocomposites. As water molecules can easily diffuse to H bonds with OH-groups of glucosyl units along the polymer chains. Approximately 19.74% reduction in total swelling ratio was achieved by a 1% MMT addition in the film, and it was further reduced to more than 31.98% when the MMT content reached 3%. At the level of 5% MMT, the films showed the highest swelling ratio values. These results indicated that the addition of MMT improved the water resistance of the PVA/S/CMC matrix. The reason could be that the PVA, starch and CMC are able to form hydrogen bonds with the hydroxyl groups of the MMT layers and this strong structure could reduce the diffusion of water molecules in the material. The equilibrium water uptake value depends on hydrophilic character as well as morphology (macro-voids, free volume, crystal size and degree of crystallinity). The clay produces a tortuous path-way and also a diminution of the length of free way for water uptake. Similar results have been obtained by other authors who observed a diminution in the water absorbed by nanocomposites made with MMT or kaolin compared with the native starch[13,25-27].

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

PVA%/starch%/ CMC%	MMT (% W/W blend)	PH	Temperature (^{0}C)	Swelling ratio
50%/30%/20%	0%	6.8	25	16.56±1.72
50%/30%/20%	1%	6.8	25	12.76±0.63
50%/30%/20%	3%	6.8	25	11.96±0.19
50%/30%/20%	5%	6.8	25	12.09±0.44

Mechanical properties

Mechanical properties of the PVA/S/CMC/MMT films resulted from the tensile test are shown in Figures 3-5 and TABLE 2. The curves reported in Figure 3 show an improvement of the mechanical strength with the increase of MMT content.

The UTS and SB as the function of MMT concentration are shown in Figures 4, 5 and TABLE 2. An increase in the UTS was observed when 1- 5% (w/w) of MMT was added to the PVA/S/CMC. With the increase of the MMT concentration from 0 to 5%, the UTS increased 5 from 18.36 to 20.38 MPa, however, the SB decreased noticeably from 35.56 to 5.22%. A similar behavior was also observed in the UTS increment by other authors[13,21,23,24,28] in plasticized starch/clay and starch/CMC/clay systems. This behavior was expected and was attributed to the resistance exerted by the clay itself and to the orientation and aspect ratio of the intercalated silicate layers. In addition, the stretching resistance of the oriented backbone of the polymer chain in the gallery bonded by hydrogen interaction also contributed to enhance the tensile strength. The layered silicate acts as a mechanical reinforcement of starch reducing the flexibility of the polymer. The main reason for this improvement in the mechanical properties is the stronger interfacial interaction between the matrix and layered silicate due to the vast surface exposed of the clay layers. During the processing and drying of the composites, the original hydrogen bonds formed between the starch molecules were replaced by the new hydrogen bonds formed between the hydroxyl groups in PVA and starch molecules, the hydroxyl and carboxyl groups in CMC and the hydroxyl groups in MMT. The existence of these new hydrogen bonds would improve the mechanical properties.

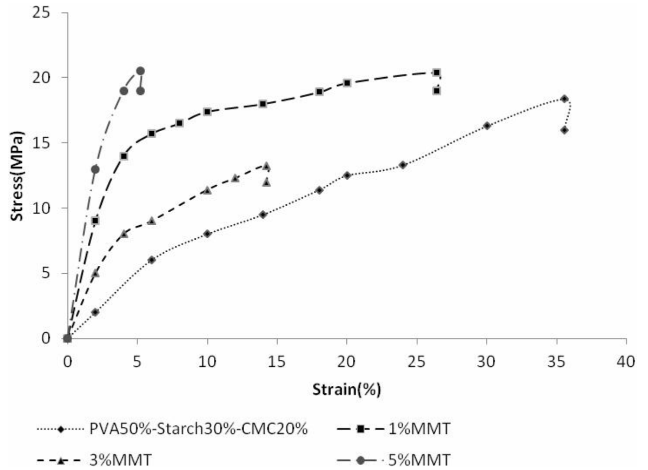

Figure 3 : Stress vs. strain for PVA/S/CMC/MMT films as a function of MMT content.

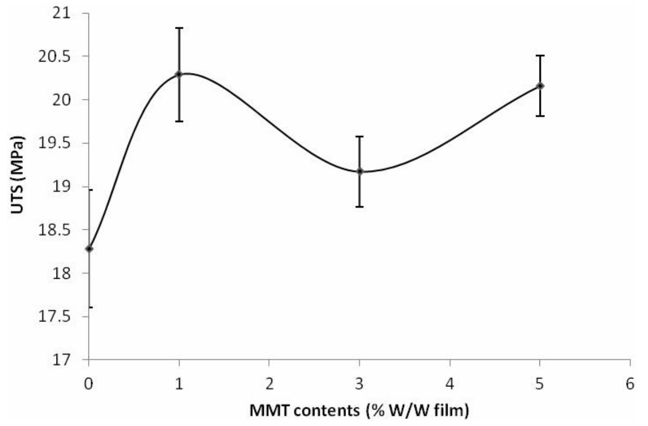

Figure 4 : The ultimate tensile strength (UTS) of the PVA/S/CMC/MMT films as a function of MMT content.

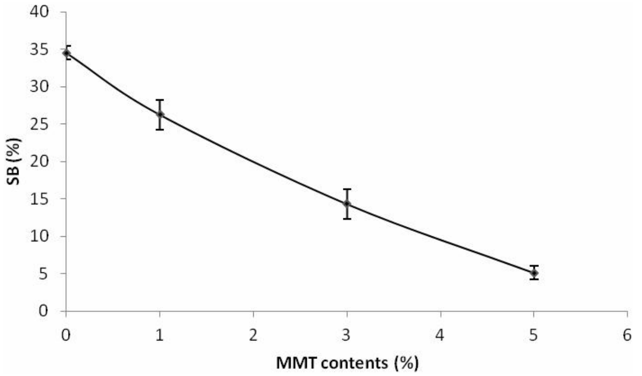

Figure 5 : The strain to break (SB) of the PVA/S/CMC/MMT films as a function of MMT content.

TABLE 2 : The ultimate tensile strength (UTS) and strain to break (SB) of PVA/S/CMC/MMT films as a function of MMT content.

PVA%/S%/ CMC%	MMT (%w/w film)	UTS (MPa)	SB (%)
50%/30%/20%	0%	18.28±0.68	34.50±0.93
50%/30%/20%	1%	20.29±0.54	26.25±1.99
50%/30%/20%	3%	19.17±0.41	14.32±2.01
50%/30%/20%	5%	20.16±0.35	5.12±0.86

Thermal properties

The DSC thermograms of the PVA/S/CMC and PVA/S/CMC/MMT bionanocomposites films exhibited sharp endothermic peaks (typical of a semi-crystalline polymeric system) at the range of 230°C to 250 °C. These endothermic peaks have been associated with the melting of crystalline starch, CMC and PVA domains. The melting peak of PVA/S/CMC was around 241.1 °C. As shown in Figure 6, melting peak of PVA/S/CMC/MMT bionanocomposites was higher than PVA/S/CMC biocomposite and it was raised by increasing MMT contents. The temperature position of the melting peak increased from 241.1 to 247.3 °C as MMT content increased from 1 to 3% (w/w) blend. But temperature position of the melting peak decreased from 247.3 to 238.2 °C as MMT content increased from 3 to 5% (w/w) blend. The change in the position of this peak indicates that MMT contents favor the formation of larger crystal domains and lower the mobility of the biopolymer chains. These results indicate exfoliation of MMT layers within the starch chains in amorphous regions, and this induces well ordered arrangement and good organization of chains in amorphous regions which in turn increases the degree of crystallinity. Therefore, by reducing amorphous regions and forming compact crystalline sections caused by MMT incorporation, the melting temperature increased. Hence, MMT is able to increase the PVA/S/CMC matrix cohesiveness.

Scanning electronic microscopy (SEM)

Figure 7 shows the morphology of PVA/S/CMC and their nanocomposites with MMT. The addition of MMT did not significantly change the morphology of PVA/S/CMC composite. Blends PVA/S/CMC and PVA/S/CMC/MMT had a uniform morphology, with no evidence of phase separation. Homogeneous distributions of the MMT in the PVA/S/CMC matrix were observed in all nanocomposite 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 fillers and matrix. Such an even and uniform distribution of the fillers in the matrix could play an important role in improving the mechanical performance of the resulting nanocomposite films.

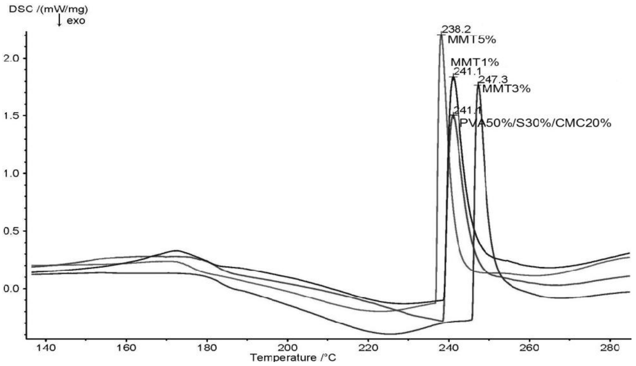

Figure 6 : Thermogram of the PVA/S/CMC/MMT films containing different amount of MMT.

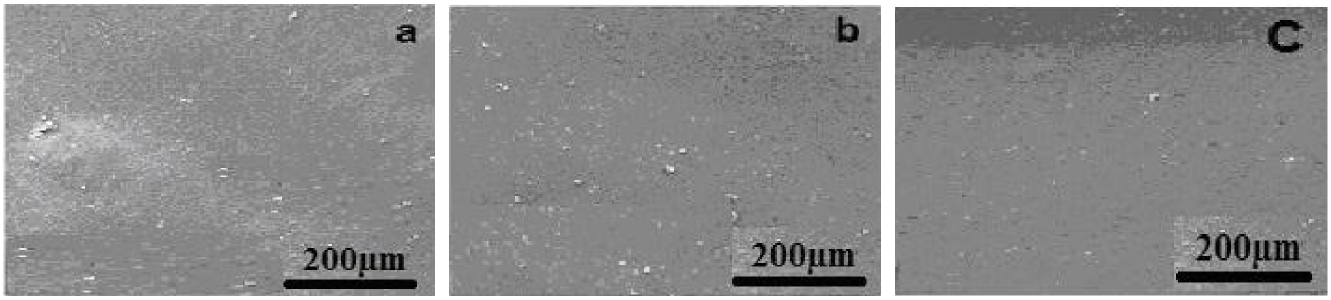

Figure 7 : SEM micrograph of the composites of PVA/S/CMC (a) PVA/ S/CMC/MMT (1%W/W film) (b) PVA/ S/CMC/MMT (3%W/W film) (c)

CONCLUSIONS

The present study shows the role of MMT on the physicmechanical properties of PVA/S/CMC films. The addition of MMT to PVA/starch/CMC blends improved the mechanical properties of the resulted starch based composites. MMT (0-5% W/W film) could increase the UTS of PVA/S/CMC/MMT nanocomposite films compared to the PVA/S/CMC films, and decrease SB of PVA/S/CMC/MMT nanocomposite films compared to the PVA/S/CMC films.

Solubility of the films decreased from 46.24% to 35.28%. By addition of 1 and 3% MMT (W/W film), T_m increased from 241.1 to 247.3^{0}C. In addition, by increasing MMT content, external properties of the composite films improved appreciably. Based on these results, the PVA/S/CMC/MMT bionanocomposite films show better physicomechanical properties than PVA/S/CMC films and they can be potentially replaced of PVA/S/CMC films.

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