

Preparation and Characterization (Mechanical and Water Absorption Properties) of CMC/PVA/Clay Nanocomposite Films

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ABSTRACT: The aim of this study was to produce Carboxy Methyl Cellulose (CMC) and Poly Vinyl Alcohol (PVA) films and to enhance their properties by reinforcing them with nanoclay particles. Thus, nanocomposite films were prepared with blending of CMC and PVA, as a matrix and several filler loadings of nanoclay particles. The various formulations of nanocomposite films obtained with casting method and their different characterizations were studied. The mechanical and water absorption properties of these films are discussed in this article. Results showed that with increasing filler loading, Tensile Stress (TS), elongation at break (E), and Modulus Of Elasticity (MOE) of the CMC/PVA/nanoclay composites raised, decreased, and enhanced, respectively. In addition, water absorption of films decreased as more filler was incorporated in the composite. X-Ray Diffraction (XRD) patterns showed that films containing 3% clay have proper mixing and exhibited the best dispersion in the CMC/PVA matrix.

KEYWORDS: Carboxymethyl cellulose (CMC); Mechanical properties; Nanoclay; Poly vinyl alcohol (PVA); Water absorption; X-ray diffraction (XRD).

INTRODUCTION

The incorporation of natural polymers as a filler/reinforcing component for preparing bio- and nano-composites has obtained important placement in the packaging industry due to environmental problems of synthetic polymers. They have received more attention particularly for reducing the cost and high volume applications. Fillers play important roles to modify

the desirable properties of composites [1-2].

In fact, nanocomposites are new class of composites in which fillers are in the nanometer range at least in one dimension [3, 4-5]. The interest in new nanoscale fillers has grown rapidly in the last years, day to day. This interest arises from the fact that when these nano fillers are used instead of conventional reinforcing materials,

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the nanocomposites exhibit better performances such as mechanical, thermal stability, dimensional stability, flame retardant, gas barrier properties, and etc. at relatively small loadings [5-6]. In general, preparation of nanocomposites using inorganic or natural fibers/particles plays important role to improve the polymers properties. Development of the polymer/clay nanocomposites is one of the revolutionary steps in the polymers technology. In fact, nanocomposites exhibit improved or even new properties when compared to micro- and macro-composites. Strong interfacial interactions between the dispersed clay layers and the polymer matrix lead to enhanced mechanical, thermal and barrier properties of the main polymer. The nature and properties of components as well as preparation methodology and conditions affect on the final properties of polymer/clay nanocomposite. The aim of clay minerals addition to the polymers is to improve the polymer properties and to produce the polymer/clay nanocomposites with demand characteristics for desired applications such as packaging fields. The performance of polymer/clay nanocomposites strongly depends on the breaking up of clay particles in the polymer matrix [7-8].

The dispersion of nanofillers is rather poor due to their incompatibility with polymers. Therefore, organic surfactant and compatibilizer additions are required to improve the dispersion of these nanofillers in polymeric matrices. In order to obtain good interfacial adhesions and mechanical properties, the hydrophilic clay needs to be modified prior to introduce in most polymer matrices [5, 9]. For instance, in study of the two different sizes of silica particles (micro-silica and nano-silica) influence on mechanical properties of sulfur and plasticized sulfur-silica composite, sulfur was plasticized using dicyclopentadiene (DCPD) and methyl styrene (MSt) [10].

Montmorillonite (MMT) is a layered aluminum silicate with exchangeable cations and reactive -OH groups on the surface. It is one of the most generally used layered silicates because of its lamellar elements that exhibit high properties such as high aspect ratio. In addition, clays can provide dramatic and adjustable improved properties at very lower loadings due to its low price, availability as well as desirable nanostructure and interfacial interactions [7-8, 11, 12-13].

Carboxy Methyl Cellulose (CMC) is cellulose ether which forms excellent films. Because of its polymeric

structure and high molecular weight, it can be used in the biocomposite films production. For example, CMC can improve the mechanical and barrier properties of starch-based films [14, 15-16]. Some researches [7, 17-18] have proved potential of organoclays for starch-based polymer nanocomposites to improve the long-term mechanical properties over the unfilled formulations.

The resistance to water may be improved by adding certain synthetic polymers, such as Polyvinyl Alcohol (PVA) and natural polymers [15], 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) [15, 19-20]. PVA, as a water-soluble polymer, has been widely used as a matrix for the preparation of nanocomposites. The main reason is owing to its easy processability, high optical clarity and biocompatibility [21].

Glycerol is one of the most accepted plasticizers used in the organization of edible films and coatings because of its stability and compatibility with the hydrophilic nature of the biopolymer chains. The main benefits of this plasticizer are a high boiling point, lack of odor, water solubility, and miscibility with those components [22, 23-24].

Therefore, a nanocomposite film was produced based on nano clay particles in this research. Carboxy Methyl Cellulose (CMC) and Poly Vinyl Alcohol (PVA) were used as matrices. Glycerol also was applied as plasticizer. The objective of this paper is to investigate the effect of different clay filler loadings (0.5, 1, 3%) on the mechanical and water absorption properties of CMC/PVA nanocomposite films.

EXPERIMENTAL SECTION

Materials

CMC with an average molecular weight of 41,000 (practical grade) and PVA were purchased from Tetrachem agency (Tehran, Iran). Nanoclay particles, MMT or modified montmorillonite (Cloisite Na⁺) was prepared from Southern Clay (Gonzales, TX, USA). Glycerol was purchased from Merck company agency (Tehran, Iran).

Nanocomposites Preparation

CMC/PVA/clay nanocomposite films were prepared via casting technique (film-forming solutions). All materials



Fig. 1: Prepared CMC/PVA composite films based on different loadings of nanoclay.

were weighted by digital scale 0.0001 (with an accuracy of 0.1 mg, Japan). Distilled water was used as solvent. Nanoclay particles (MMT) in concentrations of 0.5, 1 and 3 wt% (based on the weight of CMC) were used. 10% v of CMC and PVA were dissolved in the 60mL of distilled water by heating at 90°C, for 40 min separately. Different percentages of nanoclay dispersed in 100mL of distilled water, followed by ultrasonication in a water bath for 20 minutes. Ultrasound can modify the properties of the films. MMT solution was mixed in solution contains CMC and PVA for 30min, under vigorous magnetic stirring at room temperature with 2mL glycerol (40 mL for 100 g CMC). To control film thickness, the specified amount of each film-forming solution poured onto a plate (Petri dishes) on a soft and uniform surface. The solutions were dried for 18 hours at lab conditions (almost $25 \pm 1^\circ\text{C}$ and $40 \pm 2\%$ relative humidity). After this time the dried film solutions were easy to cast out. The dried films were peeled off and used for different testing. The obtained CMC/PVA films with different nanoclay loadings are given in Fig. 1.

The thickness of films was measured with a micrometer (Insize, Japan). Five thickness measurements were taken of each film, one in the centre and four around the perimeter. Thus, an average thickness value was used in the calculations.

Mechanical Tests

Mechanical test of prepared films was performed according to the modified method ASTM D0882-02 [25]. This test was done by an Instron universal testing machine (Model Zwick material testing, England) at the Tarbiat Modares University (Tehran, Iran) in laboratory conditions (temperature 25°C and 50% relative

humidity). The cross-head speed was set at 60 mm/minute. The specimens were placed vertically in the grips of the testing machine. Data was processed with computerized Instron software and then Tensile Stress (TS), elongation at break (E), and modulus of elasticity (MOE) of the CMC/PVA/nanoclay composites were calculated.

Water Absorption

Water absorption uses to determine the amount of water absorbed under specified conditions. Thus, prepared films with dimensions of $0.3 \times 23 \times 23\text{mm}$ were placed in the desiccators containing calcium sulfate for 24 hours. After that, the films were weighed and kept over saturated solution of sodium chloride in small desiccators at $20\text{--}25^\circ\text{C}$ to achieve constant weight at 75% relative humidity [26]. Moisture absorption calculates using the following equation:

$$\text{Water absorption (\%)} = [(W_t - W_0)/W_0] \times 100$$

W_0 = Samples initial mass

W_t = Samples final mass

X-Ray Diffraction (XRD)

Xray diffractometer (Model Xpert-philips, Pw 3040/60, MI, USA) was applied to obtain the information on the clay particles inside the matrix.

RESULTS AND DISCUSSION

Mechanical Testing

The mechanical behavior of CMC/PVA/MMT composites was analyzed as well as pure CMC/PVA samples. The mechanical properties of specimens are shown in Table 1 and Figs. 2, 3, 4.

Table 1: Tensile properties of films.

Films	Tensile strength (MPa)	Elongation at break (%)	Modulus (MPa)
CMC/PVA	11.54 ± 1.96^A	24.55 ± 0.82^A	36.2 ± 5.48^A
CMC/PVA/0.5%Clay	14 ± 0.3^{AB}	17.87 ± 0.54^B	96.14 ± 3.44^B
CMC/PVA/1%Clay	20.36 ± 0.75^{BC}	11.92 ± 0.33^C	124.66 ± 9.22^C
CMC/PVA/3%Clay	25.01 ± 2.49^C	6.85 ± 2.36^C	184.14 ± 6.19^D

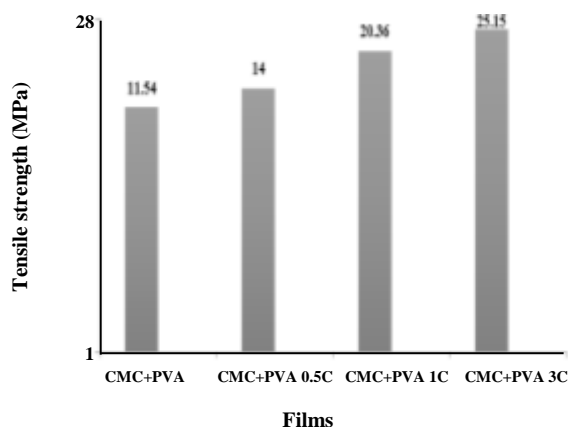


Fig. 2: Tensile strength of Films.

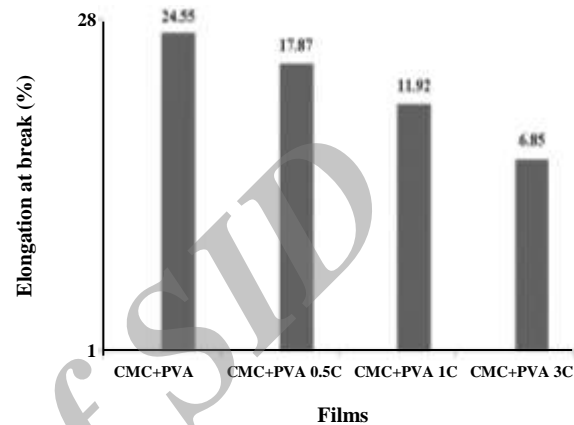


Fig. 3: Elongation at break of Films.

As it is shown in Fig. 2, when the clay concentration increase from 0 to 3%, Tensile Strength (TS) of the films improve significantly from 11.54 to 25.01 MPa ($P < 0.05$). This finding is consistent with those of *Sinha Ray et al.* [27] who found the same result. The significantly increase in the TS of polymer/clay nanocomposites as increasing of clay particles is ascribed to the uniform distribution of clay particles in the polymer structure and create interfacial bonding between the molecules and the formation of ionic bonds between clay and polymer compounds, in comparison with the pure polymer matrix. However, *Muller et al.* Produced Thermoplastic Starch (TPS) films by reinforcing them with hydrophilic and hydrophobic nanoclays. They stated that the hydrophobic nanoclays increased the rigidity of the films but did not alter the tensile strength [28].

Fig. 3 shows that the elongation at break property significantly ($P < 0.05$) decrease from 24.55 to 6.85% with increasing in the clay content (from 0 to 3%) in the nanocomposite formulation. This result seems to be in agreement with the results obtained from the research by *Rhim & Ng* [29] who added some type of modified clay to achieve a reduction in the percent of elongation.

The ratio of stress to strain in the linear region, elastic modulus increases from 36.2 to 184.14 MPa with increasing in the clay content, Fig. 4.

Water Absorption

Moisture absorption of nanocomposites containing nanoparticles is shown in Table 2 and Fig. 5. It is 22.03 percent for CMC/PVA composites that decreased by adding 0.5, 1 and 3 percent nano clay to 20.75, 19.04 and 16.95%, respectively. It means there is 1.27, 2.99 and 5.07 percent reduction in the absorption of water, respectively. This result is the same finding of *Abolghasemi Fakhri et al.* [30] who observed that addition of 3, 5 and 7% MMT to the formulation films based on cellulose, resulted in 5.8, 12.1, and 14.74% reduction in the moisture absorption, respectively. *Muller et al.* also concluded that the blending of nanoclays with thermoplastic starch modifies the WVP properties, and these changes are strongly associated with the dispersion of nanoclay in the polymer matrix [28]. In fact, the reasons for this conclusion can be attributed to be existent of more coherent structure with high cohesion and free space in the polymer which fill due to the addition of

Table 2: Water absorption of films.

Films	Water absorption
CMC/PVA	0.84 ^A ±22.03
CMC/PVA/0.5%Clay	2 ^{AB} ±20.75
CMC/PVA/1%Clay	3.14 ^{AB} ±19.04
CMC/PVA/3%Clay	2.5 ^B ±16.95

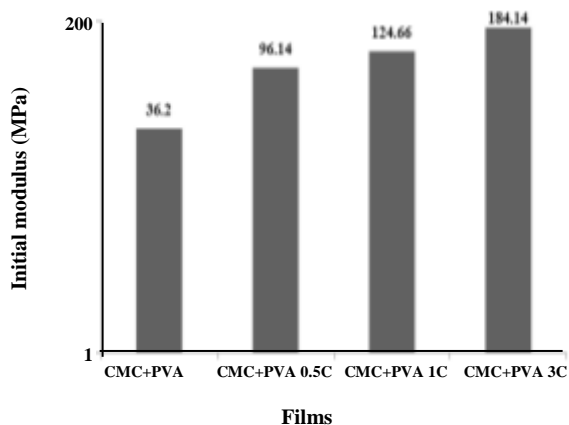


Fig. 4: Initial modulus of Films.

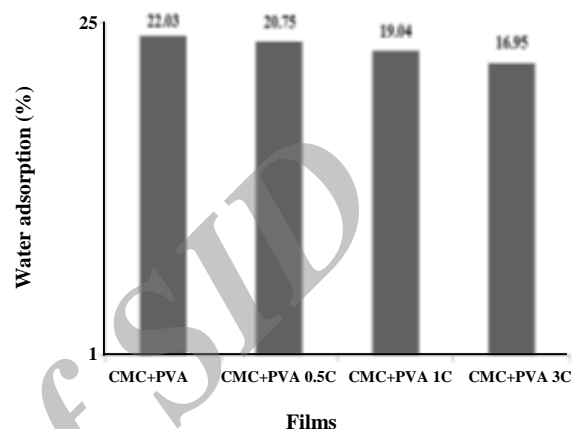


Fig. 5: Water adsorption of films.

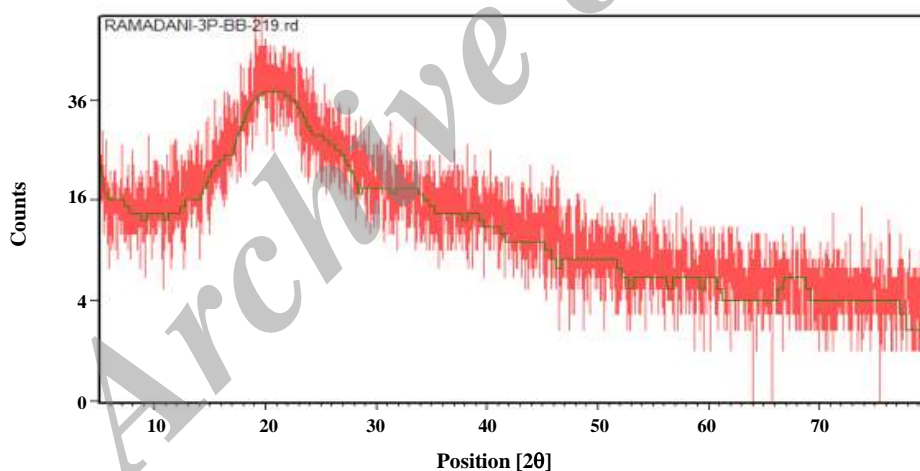


Fig. 6: CMC/PVA/3%nanoclay film XRD pattern.

nanoparticles. In the other hand, clay fillers are less hydrophilic than that of the matrix in resulted the reduction of permeability of the films.

XRD analysis

The X-Ray Diffraction (XRD) is an important laboratory technique to quality control of micro- and

nano- composites structure [31]. Thus XRD patterns were used to examine the dispersion of clay nanoparticles in the polymer matrix. The results showed that the diffraction peak is not observed for the clay (Fig. 6). No peak, indicating that the incorporation of CMC/PVA and nanoclay in the film is a kind of layered. This result is in agreement with the results of Ray *et al.* [32]. In fact,

CMC/PVA polymer chains can enter in the space between the layers of clay nano-layers and distribute throughout the matrix.

CONCLUSIONS

Owing to environment pollution and lack of adequate resources for the continued using petroleum derivatives, application of natural polymers allows for huge changes in the packaging industry. Therefore, nanocomposite materials were obtained from CMC/PVA as a matrix and nanoclay particles as a reinforcing material. The results of mechanical properties of CMC/PVA/nanoclay composites showed that with increasing clay loading in the specimens, the TS, elongation percent, and modulus characteristics increase, decrease, and increase, respectively. In addition, water absorption of nanocomposite was reduced with increasing of clay content in the samples. However, disappeared clay peak of the XRD result is the fact that nano-clay layers are distributed throughout the matrix.

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