



Effect of carboxymethyl cellulose and montmorillonite addition on the physicochemical and thermal properties of basil seed mucilage-based biodegradable film

Marzieh Qomi-Marzdashti¹, Younes Zahedi^{2*}

1- MSc graduated, Department of Food Science & Technology, University of Mohaghegh Ardabili, Ardabil, Iran.

2- Associate professor, Department of Food Science & Technology, University of Mohaghegh Ardabili, Ardabil, Iran.

ABSTRACT

The aim of this study was optimization and improvement of the physicochemical characteristics films based on basil seed mucilage (BSM) and carboxymethyl cellulose (CMC) (100, 162.5 and 225% w/w the mucilage) using montmorillonite (MMT) (0 and 8% w/w the mucilage) by casting method. The produced films properties were evaluated for thickness, moisture content, density, mechanical properties, Fourier Transform Infrared Spectrometer (FTIR), and thermogravimetric analysis (TGA). Results indicated that thickness and density of the films were not significantly influenced by CMC and MMT addition ($p > 0.05$), but the moisture content of nanocomposites decreased with increasing CMC content ($p < 0.05$). Presence of CMC and MMT in the film matrix caused to enhancement of ultimate tensile strength (UTS) and elongation at break (EB) in nanocomposites; the maximum of UTS and EB with the values of 27.9 MPa and 41%, respectively, were obtained for the nanocomposite made by 225% CMC and 8% MMT. FTIR spectra revealed no new compounds resultant from the chemical interactions, and only some shifts were observed for some peaks, and also slightly weakening or intensifying in several peaks. TGA plots showed that incorporation of CMC and MMT led to improvement of thermal properties. In conclusion, simultaneous loading of nanoclay and CMC generated the improved nanocomposites, and the treatment loaded with both MMT and the maximum level of CMC (T7) is advised as the best film for employing in the food packaging.

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*Corresponding Author E-Mail:
younes.zahedi@gmail.com,
Y_zahedi@uma.ac.ir

1- Introduction

Today, packaging is used to maintain the quality of food and ensure consumer health safety. The packaging protect the food products against physical (crushing, abrasion and impact), chemical (UV) and biological (microorganisms) damage, and helps to safely handling, transportation and store of them. In the past decades, petroleum-based plastic materials have been used in the food industry due to their attractive properties such as flexibility, safety, versatility and low cost. Among the advantages of biodegradable films, considering the applications in food packaging, it can be mentioned the preventing from transfer of moisture, oxygen, and flavors, and as a result, increasing the shelf life of food products. Plant-based polysaccharides and proteins have attracted a lot of attention as raw materials for the preparation of bionanocomposite films, which can be due to their availability and low cost [1]. Basil seed mucilage (BSM) is an acidic polysaccharide with uronic acid content of approximately 7%. Compared to other polysaccharides, BSM has attractive advantages such as low production cost, biocompatibility, biodegradability, and good rheological properties, which enable it to have great potential as a film-forming agent [2].

BSM has wide applications due to its cheapness, non-irritability and non-toxicity. It offers significant physical and chemical properties such as high water absorption capacity, high viscosity, heat resistance, non-Newtonian pseudoplastic behavior, absorption, emulsifying and stabilizing properties [3]. It is also reported that BSM can produce films with good appearance and satisfactory mechanical properties [4, 5]. In a effort, the use of BSM as an edible film ingredient and the effect of adding glycerol as a plasticizer were investigated; The results showed that the addition of glycerol significantly

increased the water vapor permeability and the solubility of BSM film, and increasing the concentration of glycerol from 25 to 50% increased the elongation at break and decreased the tensile strength [2]. In another research, a film with antibacterial and antioxidant properties was produced by adding oregano essential oil to BSM, which increased the shelf life of fresh apricot slices and reduced fruit spoilage, resulting in better preservation of apricots [6].

Carboxymethyl cellulose (CMC) is a cellulose derivative and is widely used in the production of edible and biodegradable films; Studies have shown that the films prepared from CMC have moderate mechanical resistance, oil proof, transparent, odorless and tasteless [7]. Investigations have shown that although the permeability and sensitivity to moisture of the films from CMC and other cellulose derivatives are less in comparison with other hydrophilic biopolymer ones, they are still higher in comparison with the synthetic films [8]. Due to the low flexibility and brittleness of CMC films, plasticizers are used to increase their flexibility. In recent years, many studies have been conducted on improving the functional properties of biopolymeric films by producing alloy films (blended films) by means of the mixing a biodegradable polymer with other biopolymers [9].

The main problems of biocomposites are relatively weak mechanical properties and low resistance against moisture and gases, which have limited their applications. One of the strategies to improve the properties of biopolymer films is to use the fillers with special characteristics. Various inorganic materials such as layered solid materials, synthetic nanofibers, carbon nanotubes, and cellulose nanofibers can be added as fillers to the polymer to prepare nanocomposites [10]. Polymeric nanocomposites, especially silicate nanocomposites, provide better

mechanical, optical, thermal, and physico-chemical properties compared to pure polymeric film or common composites due to the presence of nano-sized particles dispersed in the polymer matrix. Also, they have other advantages such as low permeability, low density, transparency and good surface properties, and their biodegradability is still maintained by remaining the inorganic materials and natural mineral after decomposition [11]. Montmorillonite (MMT) or nanoclay is one of the inorganic clay fillers, which has a crystalline and layered structure consisting of stacked silicate sheets with a high aspect ratio. A high aspect ratio plays an important role in increasing the mechanical and physical properties of composite materials. Normally, the diameter of silicate plates is in the range of 10 to 1000 nm. Employing of MMT has received much attention due to its natural origin, high elastic modulus and improved mechanical properties [12]. Due to these outstanding features, nanoclay has been widely used in the packaging industry to strengthen the biopolymers, and very favorable outputs have been attained; Researchers have reported that the addition of MMT to starch-CMC film increased the tensile strength by more than three times compared to starch-CMC biocomposites. Also, nanocomposites loaded with 7% MMT showed the least water solubility [13]. In another research that focused on the improvement of CMC film properties using MMT, the results showed that CMC presented the best film-forming properties compared to other biopolymers that were tested, and its barrier and physical properties was greatly improved in the presence of nanoclay [14]. The review literatures showed that no research had used the simultaneous combination of BSM with CMC and nanoclay to prepare a biodegradable film. Therefore, the aim of this research was to prepare a blended film based on BSM with different concentrations of CMC to measure the effect of adding CMC on net BSM film.

Next, nanoclay in a low and optimal concentration, obtained from the articles was incorporated to the filmogenic solutions to reduce the possible negative effects from CMC, and the properties of the resulting nanocomposite films were re-determined.

2. Materials and methods

2.1. Materials

Basil seeds was purchased from a local grocery in Ardabil, Iran, glycerol, calcium nitrate tetrahydrate from Merck (Darmstadt, Germany), sodium montmorillonite (Cloisite® Na+) from Nanocor Inc., and carboxymethyl cellulose sodium salt (CMC, 400–800 cP, 2% in H₂O (25 °C)) from Sigma-Aldrich (Schnelldorf, Germany).

2.2. Methods

Basil seeds mucilage was extracted by method of Razavi et al. [15] (temperature of distilled water = 50 °C, pH = 7, soaking time = 20 min, and water to seed ratio of 50 : 1). The extracted mucilage was poured into the polypropylene molds, dried at 50 °C for 48 h. Dried mucilage was peeled from the mold, powdered and maintained in zip pack bags up to film making.

2.3. Film preparation

2.3.1. Preparation of nanoclay solution

To prepare MMT nanodispersion, 0.032 gr MMT NPs (8% w/w mucilage) was dispersed in 25 ml distilled water, stirred for 30 min in 1200 rpm, and then sonicated in an ultrasonic bath (Backer vCLEAN, 6 L, Iran) under 35 kHz frequency for 30 min. To prevent MMT precipitation, the solution was gradually added to the filmogenic solution immediately after sonication.

2.3.2. Making net BSM film, BSM-CMC blend films and nanocomposites

In order to fabrication of net BSM film, first, 0.4 gr (100% w/w mucilage) glycerol as plasticizer was weighted and then, mixed with distilled water. The solution was heated to 80 °C, then, the mucilage powder was gradually added under stirring, mixed at 1200 rpm for 10 min. The beaker was sealed with Al foil, kept for 24 h at ambient temperature for complete hydration of mucilage, poured into the polystyrene mold as control film

sample. To making T2 to T4 films (Table 1), the beaker containing mucilage was heated to 80 °C under stirring with 900 rpm, then CMC was gradually added, mixed at 1200 rpm for 40 min. The solution was maintained at ambient temperature to cooling and removing air bubbles, casted on polystyrene molds. In order to prepare nanocomposite films (T5

to T7), the MMT sonicated solutions were added drop wise into the BSM-CMC film solution, mixed for a further 15 min at 1200 rpm without heating. Finally, the solutions were then cooled at room temperature, and the filmogenic solutions were cast onto polystyrene molds. The films were dried at 50 °C for 36 h in an oven.

Table 1 Formulations of basil seed mucilage based films* .

Film composition (treatment)	BSM (g/100 ml water)	CMC (g/100 ml water)	MMT (g/100 ml water)
T1 = BSM	0.40	0	0
100%+BSM T2 = CMC	0.40	0.40	0
162.5%+BSM T3 = CMC	0.40	0.65	0
225%+BSM T4 = CMC	0.40	0.90	0
100%+BSM %8+CMC T5 = MMT	0.40	0.40	0.032
T6 = MMT%8+CMC162.5%+BSM	0.40	0.65	0.032
T7 = MMT%8+CMC225%+BSM	0.40	0.90	0.032

* BSM = basil seed mucilage, CMC= carboxymethyl cellulose, MMT= montmorillonite.

2.4. Film conditioning and thickness measurements

The dried films were gently peeled off from molds and transferred into the zip packaging for storage. All of the films were equilibrated at 23 ± 1 °C and 50 ± 2% RH, inside a chamber containing saturated solution of calcium nitrate tetrahydrate for 48 h before mechanical properties, density and moisture content tests. Film thickness was measured with an electronic micrometer (QLR digit-IP54, China) at several positions of the films and the mean measurements were used to calculate the properties of the films.

2.5. Moisture content

The moisture content (MC) of the film samples was determined by measuring the weight loss of two grams of each films

before and after drying in oven at 105 °C until constant weight. MC was calculated with Eq. (1) in triplicate.

$$(\%)MC = \frac{(W_f - W_0)}{W_0} \times 100$$

(1)

Where W_0 was initial weight of specimen and W_f was weight of specimen after oven drying.

2.6. Density

The film density (ρ_s) was evaluated instantly after the conditioning, weighting, and thickness measuring according to the Eq. (2):

$$\rho_s = \frac{\text{weight (g)}}{\text{thickness (cm)} \times \text{area (cm}^2\text{)}}$$

(2)

where A is the film area (2 × 2 cm²), δ is the film thickness (cm), m is the film mass (g) and ρ_s is the density of the film

(g/cm³). The tests were measured in three replicates for each type of film.

2.7. Mechanical properties

The ultimate tensile strength (UTS) and elongation at break (EB) of the films (10×80 mm²) were determined using a STM-20 Universal Testing Machine (SANTAM, ENG. DESIGN CO. LTD) equipped with a 25 Kg load cell according to the ASTM D882-02 (ASTM, 2002) method. Initial grip separation and crosshead speed were 50 mm and 50 mm/min, respectively. The tests were measured in five replicates for each type of film and mean of the measurements were used.

2.8. FT-IR spectroscopy

Fourier transform infrared (FT-IR) spectra of the nanocomposite films were recorded using a FT-IR spectrophotometer (model Spectrum RXI, Perkin Elmer, UK). The spectrum was taken in the wavelength range of 4000–400 cm⁻¹ and a resolution of 1 cm⁻¹ on film samples.

2.9. Thermogravimetric analysis (TGA)

Thermal stability of the film samples was distinguished using a thermogravimetric analyzer (TGA) (Linseis STA PT 1000, Selb, Germany) under a nitrogen atmosphere, a heating rate of 10 °C/min, and a temperature range of 25 to 550 °C.

2.11. Statistical analysis

Statistical analyses, on a completely randomized design, were performed by the analysis of variance (ANOVA) procedure in Minitab. Duncan's multiple range test ($p \leq 0.05$) was used to detect differences among the mean values of the films properties.

3. Results and discussion

3.1. Film thickness

Changes in the ratio of carboxymethyl cellulose (CMC) and nanoclay (MMT) did not make a significant difference in the

BSM films thickness ($p > 0.05$). However, as shown in Table 2, the pure BSM film had the lowest thickness (67 μm) and the film with the highest percentage of CMC and MMT had the highest thickness (88 μm). In fact, the pure BSM film had the lowest thickness due to the lowest amount of solid matter, and vice versa, the film containing the highest amount of CMC and MMT with the highest amount of solid matter had the maximum thickness. In some previous researches, it has been found that decreasing the percentage of BSM or increasing the percentage of CMC in the structure of the film prepared from BSM and thymol essence [17] and cassava starch and CMC [18] has increased the thickness of the films.

3.2. Film density

As it is clear in Table 2, the changes of CMC and MMT ratio in the nanocomposite structure did not make a significant difference among the density of the films ($p > 0.05$); However, the pure BSM film had the lowest density (1.17 g/cm³) and the T5 film had the highest density (1.40 g/cm³). On the one hand, with the addition of CMC (density = 1.6 g/cm³) and MMT (density = 2-3 g/cm³) to the film formulation, it was expected that the density would increase due to the high density of these materials. But on the other hand, the presence of these materials caused a decrease in water loss during drying (and a decrease in the measured moisture content (Table 3)) due to their ability to absorb water, and because water has a lower density than CMC and MMT, remaining more water in the body of the films neutralized the effect of density increasing caused by these two substances. And as the data shows, the density of blend and nanocomposite films slightly increased.

Table 2 Effect of CMC and MMT addition on the thickness and density of BSM-based composite films*

Treatment	Thickness (μm)	Density (g/cm ³)
T1	67 ± 15.3	1.17 ± 0.17

T2	81 ± 13.6	1.40 ± 0.10
T3	67 ± 10.8	1.17 ± 0.18
T4	75 ± 2.0	1.37 ± 0.07
T5	80 ± 18.8	1.40 ± 0.05
T6	72 ± 25.2	1.29 ± 0.06
T7	88 ± 7.3	1.30 ± 0.12

*: T1: BSM, T2: BSM + 100% CMC, T3: BSM + 162.5% CMC, T4 :BSM + 225% CMC, T5: BSM +100% CMC + 8% MMT, T6: BSM +162.5% CMC + 8% MMT, T7: BSM +225% CMC + 8% MMT.

3.3. Moisture content

Fig. 1 shows the effect of changes in the ratio of CMC and MMT nanoclay in the composite structure on the moisture content of the films. As it is known, the pure BSM film has the highest moisture content, and the film moisture content decreased significantly ($p < 0.05$) with

increasing CMC content. Due to the presence of a large number of hydroxyl groups on CMC, some of the free water in the film matrix will be bonded with these groups, thereby reducing the water evaporation during drying [17, 18 and 19]. Loading MMT did not change moisture content of the films maybe due to trace amount ($p > 0.05$).

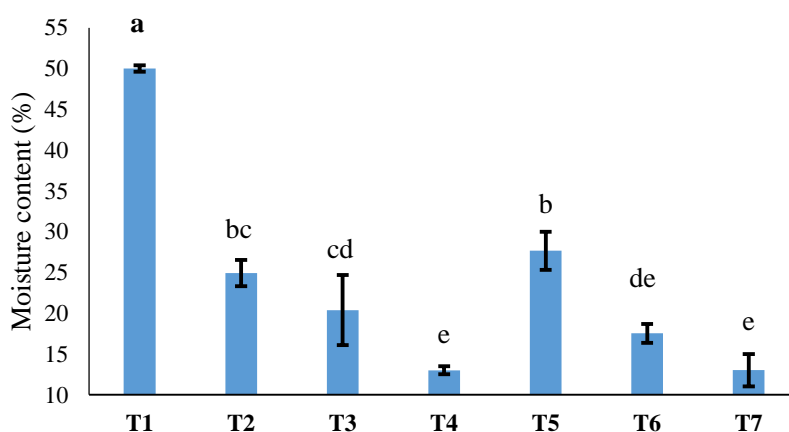


Fig. 1 Effect of CMC and MMT addition on moisture content of BSM-based composite films (T1: BSM, T2: BSM + 100% CMC, T3: BSM + 162.5% CMC, T4 :BSM + 225% CMC, T5: BSM +100% CMC + 8% MMT, T6: BSM +162.5% CMC + 8% MMT, T7: BSM +225% CMC + 8% MMT). Different lowercases on the top of bars indicate significant differences ($p < 0.05$) among treatments.

3.4. Ultimate tensile strength (UTS)

Mechanical properties of composite polymers depend on the proliferation of interface interactions of the compounds. In general, the establishment of appropriate interactions among different compounds causes an important improvement in the mechanical properties of films. Fig. 2 shows the effects of different proportions

of CMC and MMT on the UTS of nanocomposite films. As seen, the increase in CMC and MMT increased the UTS of the films, but UTS changes of treatments compared to the control are not significant except for the treatment containing highest percentage of CMC and MMT. The increase in UTS with the increase of CMC is probably due to strong intermolecular interactions between CMC and BSM macromolecules, leading to strengthening

the biopolymer network and thereby improving UTS of the films [20]. By reducing CMC level, the softening property of BSM prevails and as a result UTS of the film decreases. In fact, presence of BSM in CMC chains space inhibit the formation of strong CMC intermolecular bonds, thereby diminishing UTS and increasing the films flexibility [21 and 22]. Increasing CMC concentration resulted in strong connections between macromolecules and enhancing the film continuity and diminishing the films flexibility [23]. In a research conducted by Hazirah et al. [24] on the effect of adding xanthan gum on the properties of CMC-gelatin film, the negative effect of adding the gum was

revealed on both UTS and EB. Wang et al. [25] reported that the addition of *Dioscorea opposita* mucilage to CMC film decreased the UTS and increased EB of the films. The mechanical changes of the films by MMT incorporation can be attributed to the fact that the high aspect ratio of the silicate layers provides a large surface area for strong interactions between CMC and MMT which leads to strengthening the UTS and reducing the EB of the films [13, 26 and 27]. In line with the findings of this study, there are many reports on the increase of UTS and decrease of EB of the nanocomposites as a result of adding small amounts of nanoclay [28 and 29].

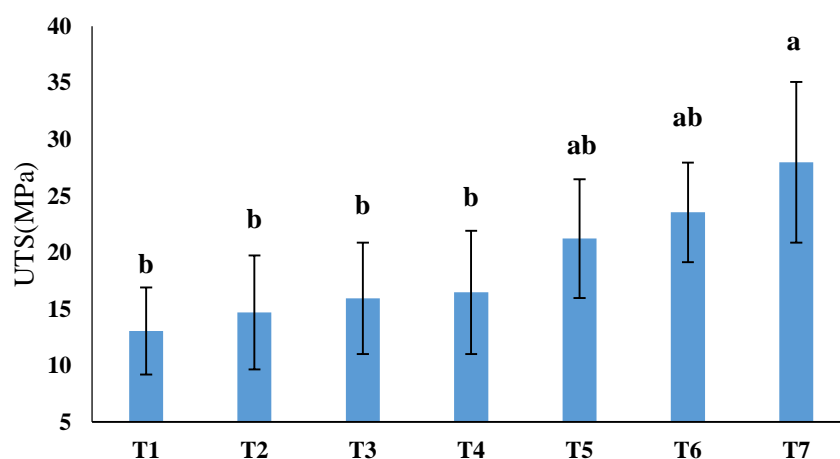


Fig. 2 Effect of CMC and MMT addition on ultimate tensile strength (UTS) of BSM-based composite films (T1: BSM, T2: BSM + 100% CMC, T3: BSM + 162.5% CMC, T4 :BSM + 225% CMC, T5: BSM +100% CMC + 8% MMT, T6: BSM +162.5% CMC + 8% MMT, T7: BSM +225% CMC + 8% MMT). Different lowercases on the top of bars indicate significant differences ($p < 0.05$) among treatments.

3.5. Elongation at break (EB)

Elongation at break refers to the film ability against changes in shape without tearing. The EB is desirable for edible films because it improves the film efficiency for wrapping and surrounding food [30]. The effects of different levels of CMC and MMT on the EB of nanocomposite films are presented in Fig. 3. As seen, with increasing CMC and MMT amount, the %EB of the films has increased too. It has been reported in

several researches that polysaccharidic films show high flexibility, and by increasing their ratio in film formulation, the film acquires elasticity. Since the moisture content of polysaccharide-based films changes with the relative humidity of the surrounding atmosphere, it is very important that the films are equilibrated in ambient with a relative humidity and temperature similar to the environmental conditions for their application, and their mechanical properties be determined under these conditions. In fact, the water content of layers changes with relative humidity,

and water acts as a plasticizer for polysaccharide-based layers, thus affecting its mechanical properties and making the film flexible [31 and 32]. It has been reported that the loading MMT into the edible films led to brittleness and fragility of the films, and the EB of films decreases with the increase of MMT [13, 16 and 33]. However, it seems that dedicated elasticity by hydrophilic BSM and CMC neutralized the brittleness effect of MMT, and the

obtained films show a suitable EB in spite of high UTS. Also, in a project focused on the effect of MMT on the mechanical properties of BSM, the EB of films increased with the increase of MMT, which can indicate the fact that the interaction between MMT and BSM can be different from other polysaccharides, and the combination of these materials gives a strong and flexible structure to the edible film [34].

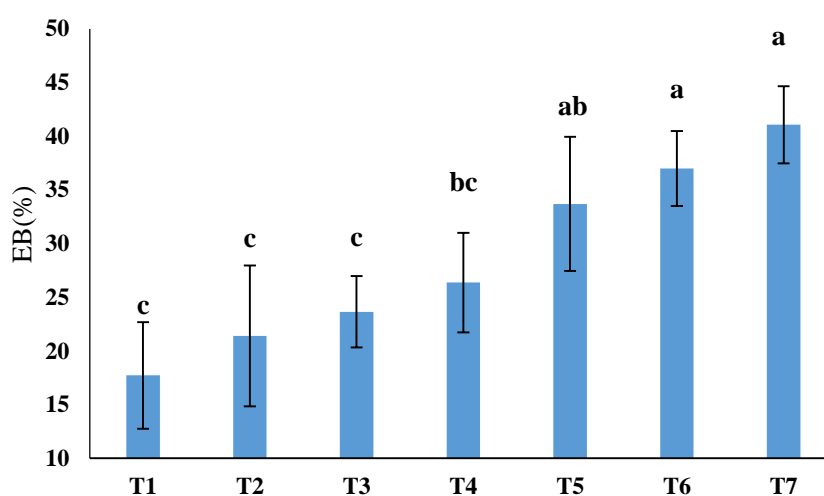


Fig. 3 Effect of CMC and MMT addition on elongation at break (EB) of BSM-based composite films (T1: BSM, T2: BSM + 100% CMC, T3: BSM + 162.5% CMC, T4 :BSM + 225% CMC, T5: BSM +100% CMC + 8% MMT, T6: BSM +162.5% CMC + 8% MMT, T7: BSM +225% CMC + 8% MMT). Different lowercases on the top of bars indicate significant differences ($p < 0.05$) among treatments.

3.6. FTIR

FTIR spectroscopy results of nanocomposite films are presented in Fig. 4. On the pure BSM spectrum, the peaks appeared at 3500 to 3000 cm^{-1} are related to -OH stretch caused by inter- and intramolecular hydrogen bonds, including the stretching of free -OH groups as well as -OH bonding groups of carboxylic acid and -OH stretching of alcohol [3]. The peaks between 2800-3000 cm^{-1} show C—H stretching and CH, CH₂ and CH₃ bending, the peaks in the region of 1600-1700 cm^{-1} indicate the stretching of the amide -I group of C=O and C—N, while the N—H bending of the amide-II group is in the range of 1500-1600 cm^{-1} [35]. The

peaks at 1600-1630 cm^{-1} are from free carboxylate groups, the peaks between 1400 to 1600 cm^{-1} show symmetric and asymmetric C—O stretching which confirms the presence of uronic acid, and the peaks appeared in the range of 1130-1160 cm^{-1} are due to C—O and C—O—C stretching. The peak at 1008 cm^{-1} shows the C=O stretching of alcohol, and the peak at 863 cm^{-1} is due to the aromatic C—H bond [19]. It is found from the other spectra, the addition of CMC and MMT did not change the general trend and shape of the pure BSM spectrum, and only the intensity and weakness of the absorption peaks changed to some extent, and in some cases, the absorption peaks have slightly shifted.

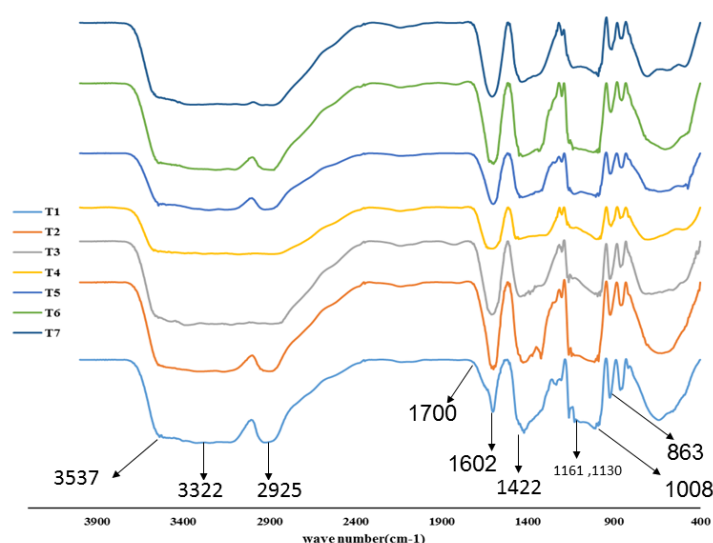


Fig. 4 The FTIR spectra of BSM-based composite films (T1: BSM, T2: BSM + 100% CMC, T3: BSM + 162.5% CMC, T4: BSM + 225% CMC, T5: BSM + 100% CMC + 8% MMT, T6: BSM + 162.5% CMC + 8% MMT, T7: BSM + 225% CMC + 8% MMT).

3.7. TGA

The use of film in food packaging is influenced by its thermal stability. Figs. 5 and 6 show the thermogravimetric (TGA) curves of nanocomposite films. According to these Figs, four stages of thermal degradation can be recognized in the curves. The first stage, between 35 and 100 °C, is related to moisture evaporation [36]. The second stage, at a temperature of 120-210 °C, was created due to the thermal degradation of glycerol in the sponge [37]. The third stage, at a temperature of 255 to 320 °C, was due to the thermal degradation of glucomannan, xylan and other polysaccharides in hemicellulose in BSM molecules [2]. The fourth stage, at a temperature of 460-410 °C, was due to the thermal decomposition of cellulose and lignin in BSM [38]. The thermal properties of the films have increased with the increase of CMC in the nanocomposite films, especially in the third and fourth stages. The reason for such a phenomenon can be due to the placement of BSM between CMC chains, and as a result, the moisture content of composite films is lower than that of pure BSM film. The

lower weight loss of the composite films in the second stage can be attributed to the better thermal properties of CMC, which have a higher temperature tolerance than the pure BSM film [9]. The reason for the weight loss of the pure BSM film compared to the composite films can be attributed to the evaporation or destruction of a part of volatile substances of the mucilage and antioxidants with low stability [39]. The lower weight loss of the composite films compared to the pure BSM film in the third stage is probably due to the placement of stable and mineral mucilage compounds around and between the CMC chains, which act as layers or protective networks and increase the thermal stability of the film. Among the mineral and metal compounds isolated and identified in mucilage, which can be attributed to the increase in thermal stability, calcium, fluorine, chlorine, silica, sulfur, sodium, potassium, magnesium, manganese, iron, zinc and other mineral compounds can make nanocomposites more stable by creating a larger and more complex ionic network or by acting as fillers in the CMC used in this study [40]. The much lower weight loss of composite films compared to the pure BSM film in

the fourth stage can be related to the presence of aromatic substances in BSM in such a way that with the increase of the CMC in the films, the amount of volatile aromatic substances decreases and the content of non-volatile dry matter increases. The addition of MMT has improved the properties of composite films to some extent. MMT has a high thermal resistance due to its inorganic nature, and increases the temperature at which thermal decomposition of films begins [41]. On the other hand, nanoparticles increase thermal stability by limiting the movements of CMC-BSM molecules and reducing the free volume for the folding of polymer chains [42]. The dominant mechanism of thermal decomposition of CMC-BSM composite film is its chain breakage [43]. Chain breakage is the result of release of free radicals and volatile products resulting from thermal decomposition through polymer chains [44]. Therefore, the behavior of nanocomposites at the beginning of thermal decomposition can be described in terms of the ability to release free radicals in the polymer matrix. Polymer chains with low mobility create a physical barrier for the release of free radicals, and

thus delay the degradation of the polymer [43]. On the other hand, nano-sized silicate layers properly dispersed in the polymer act as a shield against oxygen, and also prevent the penetration of volatile products produced during decomposition in the matrix and leaving the nanocomposite structure [45]. Thus, the presence of silicate on the surface of the sample increases the thermal stability of nanocomposites by creating a protective coating on the polymer and acting as a thermal insulator and mass transfer barrier. The way of dispersion of nanoparticles and the morphology of nanocomposites play an important role in reducing the rate of thermal decomposition of the polymer matrix. More interfacial interaction between nanoparticles and polymer chains will cause more restrictions for the movement of the chains, and thus the breaking of the polymer chains will be more difficult and their decomposition temperature will increase [46].

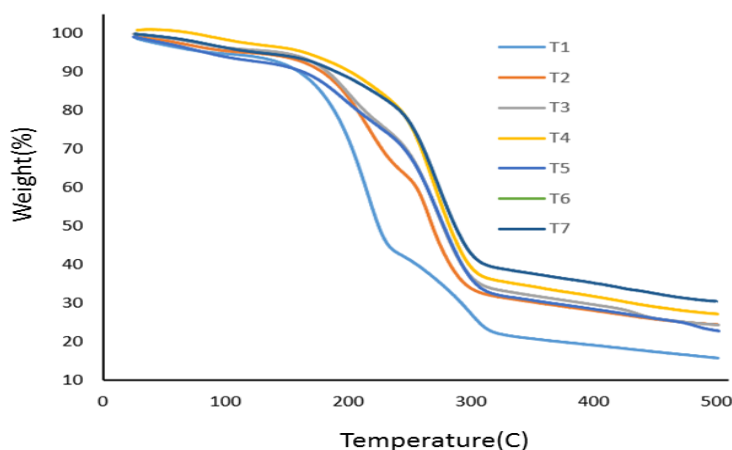


Fig. 5 TGA graphs of BSM-based composite films (T1: BSM, T2: BSM + 100% CMC, T3: BSM + 162.5% CMC, T4 :BSM + 225% CMC, T5: BSM +100% CMC + 8% MMT, T6: BSM +162.5% CMC + 8% MMT, T7: BSM +225% CMC + 8% MMT).

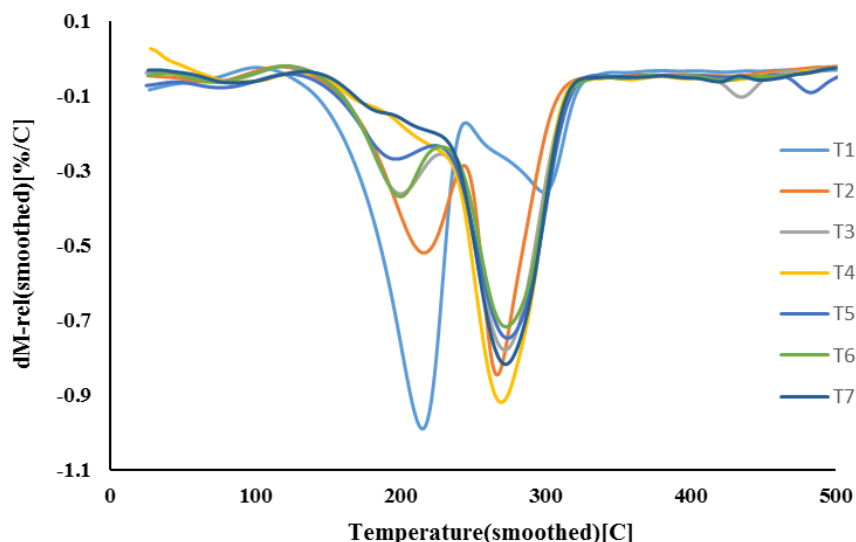


Fig. 6 DTG graphs of BSM-based composite films (T1: BSM, T2: BSM + 100% CMC, T3: BSM + 162.5% CMC, T4: BSM + 225% CMC, T5: BSM + 100% CMC + 8% MMT, T6: BSM + 162.5% CMC + 8% MMT, T7: BSM + 225% CMC + 8% MMT).

4. Conclusion

The addition of CMC and MMT improved the mechanical properties of the resulting nanocomposites by more than two times in the films containing the maximum concentration of these two substances, without exceeding the thickness of the films from suitable limit. Also, the thermal stability of the films increased as a result of CMC and MMT incorporation without any specific chemical interaction being observed on the FTIR spectra. In general, T7 treatment can be recommended as the best treatment for use in the primary packaging of food.

References

[1] Ghanbarzadeh, B, Almasi, H. & Zahedi, Y. 2009. [Biodegradable edible biopolymers in food and drug packaging](#). Tehran, Amir Kabir

University of technology publication, 526 pages (In Persian).

- [2] Khazaei, N., Esmaili, M., Djomeh, Z. E., Ghasemlou, M., & Jouki, M. 2014. Characterization of new biodegradable edible film made from basil seed (*Ocimum basilicum L.*) gum. *Carbohydrate polymers*, 102: 199-206.
- [3] Maqsood, H., Uroos, M., Muazzam, R., Naz, S., & Muhammad, N. 2020. Extraction of basil seed mucilage using ionic liquid and preparation of AuNps/mucilage nanocomposite for catalytic degradation of dye. *International Journal of Biological Macromolecules*, 164: 1847-1857.
- [4] Allafchian, A., Jalali, S. A. H., Hosseini, F., & Massoud, M. 2017. *Ocimum basilicum* mucilage as a new green polymer support for silver in magnetic nanocomposites: production and characterization. *Journal of environmental chemical engineering*, 5(6): 5912-5920.
- [5] Zahedi, Y. 2019. Edible/Biodegradable Films and Coatings from Natural Hydrocolloids (chapter 23), In: *Emerging Natural Hydrocolloids: Rheology and Functions*, First Edition. Ed. by S. M.A. Razavi., John Wiley & Sons Ltd.
- [6] Hashemi, S. M. B., Khaneghah, A. M., Ghahfarrokhi, M. G., & Eş, I. 2017. Basil-seed gum containing *Origanum vulgare subsp. viride* essential oil as edible coating for fresh cut apricots. *Postharvest Biology and Technology*, 125: 26-34.
- [7] Azzaoui, K., Mejdoubi, E., Lamhamdi, A., Jodeh, S., Hamed, O., Berrabah, M. & Zougagh, M. 2017. Preparation and characterization of biodegradable nanocomposites derived from carboxymethyl cellulose and

- hydroxyapatite. Carbohydrate polymers, 167: 59-69.
- [8] Torabi, A., Mohebbi, M., Tabatabaei-Yazdi, F., Shahidi, F., Khalilian-Movahhed, M. & Zahedi Y. 2020. Application of different carbohydrates to produce squash puree based edible sheet. Journal of Food Science and Technology, 57(2):673-682.
- [9] Oun, A. A., & Rhim, J. W. 2015. Preparation and characterization of sodium carboxymethyl cellulose/cotton linter cellulose nanofibril composite films. Carbohydrate polymers, 127: 101-109.
- [10] Abulyazied, D. E., & Ene, A. 2021. An investigative study on the progress of nanoclay-reinforced polymers: Preparation, properties, and applications: A review. Polymers, 13(24): 4401-4409.
- [11] Oliver-Ortega, H., Tresserras, J., Julian, F., Alcalà, M., Bala, A., Espinach, F. X., & Méndez, J. A. 2021a. Nanocomposites materials of PLA Reinforced with nanoclays using a masterbatch technology: A study of the mechanical performance and its sustainability. Polymers, 13(13): 2133-2140.
- [12] Oliver-Ortega, H., Vandemoortele, V., Bala, A., Julian, F., Méndez, J. A., & Espinach, F. X. 2021b. Nanoclay effect into the biodegradation and processability of poly (lactic acid) nanocomposites for food packaging. Polymers, 13(16), 2741-2749.
- [13] Almasi, H., Ghanbarzadeh, B., & Entezami, A. A. 2010. Physicochemical properties of starch-CMC-nanoclay biodegradable films. International journal of biological macromolecules, 46(1): 1-5.
- [14] Shin, S. H., Kim, S. J., Lee, S. H., Park, K. M., & Han, J. 2014. Apple peel and carboxymethylcellulose-based nanocomposite films containing different nanoclays. Journal of food science, 79(3): E342-E353.
- [15] Razavi, S. M., Mortazavi, S. A., Matia-Merino, L., Hosseini-Parvar, S. H., Motamedzadegan, A., & Khanipour, E. 2009. Optimisation study of gum extraction from Basil seeds (*Ocimum basilicum L.*). International journal of food Science & Technology, 44(9): 1755-1762.
- [16] Zahedi, Y., Fathi-Achachlouei, B., & Yousefi, A. R. 2018. Physical and mechanical properties of hybrid montmorillonite/zinc oxide reinforced carboxymethyl cellulose nanocomposites. International journal of biological macromolecules, 108: 863-873.
- [17] Khazaei, N., Esmaili, M., & Emam-Djomeh, Z. 2017. Application of active edible coatings made from basil seed gum and thymol for quality maintenance of shrimp during cold storage. Journal of the Science of Food and Agriculture, 97(6): 1837-1845.
- [18] Lin, L., Peng, S., Shi, C., Li, C., Hua, Z., & Cui, H. 2022. Preparation and characterization of cassava starch/sodium carboxymethyl cellulose edible film incorporating apple polyphenols. International Journal of Biological Macromolecules, 212: 155-164.
- [19] Hashemi-Gahruei, H., Eskandari, M. H., Van der Meer, P., & Hosseini, S. M. H. 2019. Study on hydrophobic modification of basil seed gum-based (BSG) films by octenyl succinate anhydride (OSA). Carbohydrate polymers, 219: 155-161.
- [20] Ghanbarzadeh, B., Almasi, H., & Entezami, A. A. 2010. Physical properties of edible modified starch/carboxymethyl cellulose films. Innovative food science & emerging technologies, 11(4): 697-702.
- [21] Rezaie, A., Rezaei, M., & Alboofetileh, M. 2021. Preparation of biodegradable carboxymethyl cellulose-Arabic gum composite film and evaluation of its physical, mechanical and thermal properties. Iranian Food Science and Technology Research Journal, 17(2): 287-297 (In Persian).
- [22] Tongdeesoontorn, W., Mauer, L. J., Wongruong, S., & Rachtanapun, P. 2009. Water vapour permeability and sorption isotherms of cassava starch based films blended with gelatin and carboxymethyl cellulose. Asian Journal of Food and Agro-Industry, 2(4): 501-514.
- [23] Ballesteros, L. F., Cerqueira, M. A., Teixeira, J. A., & Mussatto, S. I. 2018. Production and physicochemical properties of carboxymethyl cellulose films enriched with spent coffee grounds polysaccharides. International journal of biological macromolecules, 106: 647-655.
- [24] Hazirah, M. N., Isa, M. I. N., & Sarbon, N. M. 2016. Effect of xanthan gum on the physical and mechanical properties of gelatin-carboxymethyl cellulose film blends. Food Packaging and Shelf Life, 9:55-63.
- [25] Wang, R., Li, X., Ren, Z., Xie, S., Wu, Y., Chen, W. & Liu, X. 2020. Characterization and antibacterial properties of biodegradable films based on CMC, mucilage from *Dioscorea opposita Thunb.* and Ag nanoparticles. International Journal of Biological Macromolecules, 163: 2189-2198.
- [26] Fathi-Achachlouei, B. & Zahedi, Y. 2018. Fabrication and evaluation of properties of carboxymethyl cellulose-based hybrid nanocomposites reinforced with titanium dioxide and montmorillonite. Food Science and Technology. 15(81): 35-47 (In Persian).
- [27] Gutiérrez, M. Q., Echeverría, I., Ihl, M., Bifani, V., & Mauri, A. N. 2012. Carboxymethylcellulose-montmorillonite nanocomposite films activated with murta (*Ugni molinae Turcz*) leaves extract. Carbohydrate polymers, 87(2): 1495-1502.

- [28] Ghanbarzadeh, B., Almasi, H., & Oleyaei, S. A. 2014. A novel modified starch/carboxymethyl cellulose/montmorillonite bionanocomposite film: structural and physical properties. *International Journal of Food Engineering*, 10(1): 121-130.
- [29] Taghizadeh, M. T., Sabouri, N., & Ghanbarzadeh, B. 2013. Polyvinyl alcohol: starch: carboxymethyl cellulose containing sodium montmorillonite clay blends; mechanical properties and biodegradation behavior. *SpringerPlus*, 2(1): 1-8.
- [30] Moghimi, R., Aliahmadi, A., & Rafati, H. 2017. Antibacterial hydroxypropyl methyl cellulose edible films containing nanoemulsions of *Thymus daenensis* essential oil for food packaging. *Carbohydrate polymers*, 175: 241-248.
- [32] Ma, X., Chang, P. R., & Yu, J. (2008). Properties of biodegradable thermoplastic pea starch/carboxymethyl cellulose and pea starch/microcrystalline cellulose composites. *Carbohydrate Polymers*, 72(3), 369-375.
- [31] Donhowe, I. G., & Fennema, O. (1993). The effects of solution composition and drying temperature on crystallinity, permeability and mechanical properties of methylcellulose films. *Journal of Food Processing and Preservation*, 17(4), 231-246.
- [32] Ma, X., Chang, P. R., & Yu, J. 2008. Properties of biodegradable thermoplastic pea starch/carboxymethyl cellulose and pea starch/microcrystalline cellulose composites. *Carbohydrate Polymers*, 72(3): 369-375.
- [33] Slavutsky A. M., María A. Bertuzzi, Margarita A., María G., Nelio A. 2014. Preparation and characterization of montmorillonite/brea gum nanocomposites films. *Food Hydrocolloids*, 35: 27-278.
- [34] Rohini, B., Padma Ishwarya, S., Ram, R. & Arun Kuma, V. 2020. *Ocimum basilicum* seed mucilage reinforced with montmorillonite for preparation of bionanocomposite film for food packaging applications. *Polymer Testing*, 87: 48-55.
- [35] Kang, J., Cui, S. W., Chen, J., Phillips, G. O., Wu, Y., & Wang, Q. 2011. New studies on gum ghatti (*Anogeissus latifolia*) part I. Fractionation, chemical and physical characterization of the gum. *Food hydrocolloids*, 25(8): 1984-1990.
- [36] Thessrimuang, N., & Prachayawarakorn, J. 2019. Development, modification and characterization of new biodegradable film from basil seed (*Ocimum basilicum L.*) mucilage. *Journal of the Science of Food and Agriculture*, 99(12): 5508-5515.
- [37] Tantiwatcharothai, S., & Prachayawarakorn, J. 2019. Characterization of an antibacterial wound dressing from basil seed (*Ocimum basilicum L.*) mucilage-ZnO nanocomposite. *International journal of biological macromolecules*, 135: 133-140.
- [38] Azwa, Z.N., Yousif, A. C., & Karunasena M. W. 2013. A review on the degradability of polymeric composites based on natural fibre. *Materials & Design*, 47: 424-442.
- [39] De Dicastillo, C. L., Bustos, F., Guarda, A., & Galotto, M. J. 2016. Cross-linked methyl cellulose films with murta fruit extract for antioxidant and antimicrobial active food packaging. *Food Hydrocolloids*, 60: 335-344.
- [40] Haque M. M. & Alsareii S. A. 2015. A review of the therapeutic effects of using miswak (*Salvadora Persica*) on oral health. *Saudi medical journal*, 36 (5): 530-543.
- [41] Ma, C. C. M., Chen, Y. J., & Kuan, H. C. 2006. Polystyrene nanocomposite materials preparation, mechanical, electrical and thermal properties, and morphology. *Journal of applied polymer science*, 100(1): 508-515.
- [42] Mohanty, S., & Nayak, S. K. 2007. Melt blended polystyrene/layered silicate nanocomposites: effect of clay modification on the mechanical, thermal, morphological and viscoelastic behavior. *Journal of Thermoplastic Composite Materials*, 20(2): 175-193.
- [43] Pandey, J. K., Reddy, K. R., Kumar, A. P., & Singh, R. P. 2005. An overview on the degradability of polymer nanocomposites. *Polymer degradation and stability*, 88(2), 234-250
- [44] Lee, J. Y., Liao, Y., Nagahata, R., & Horiuchi, S. 2006. Effect of metal nanoparticles on thermal stabilization of polymer/metal nanocomposites prepared by a one-step dry process. *Polymer*, 47(23): 7970-7979.
- [45] Zanetti, M., & Costa, L. 2004. Preparation and combustion behaviour of polymer/layered silicate nanocomposites based upon PE and EVA. *Polymer*, 45(13): 4367-4373.
- [46] Vaziri, H. S., Omaraei, I. A., Abadyan, M., Mortezaei, M., & Yousefi, N. 2011. Thermophysical and rheological behavior of polystyrene/silica nanocomposites: Investigation of nanoparticle content. *Materials & Design*, 32(8-9): 4537-4542.



مقاله علمی-پژوهشی

تأثیر افزودن کربوکسی متیل سلولز و مونت موریلونیت بر خواص فیزیکی-شیمیایی و حرارتی فیلم زیست تخریب پذیر موسیلاژ دانه ریحان

مرضیه قمی مرزدشتی^۱ و یونس زاهدی^{۲*}

۱- مرضیه قمی مرزدشتی، دانش آموخته کارشناسی ارشد علوم و مهندسی صنایع غذایی، دانشگاه محقق اردبیلی، اردبیل، ایران.

۲- یونس زاهدی (مسئول مکاتبات)، دانشیار گروه علوم و مهندسی صنایع غذایی، دانشگاه محقق اردبیلی، اردبیل، ایران.

اطلاعات مقاله	چکیده
تاریخ های مقاله : تاریخ دریافت: ۱۴۰۲/۳/۳۰ تاریخ پذیرش: ۱۴۰۲/۹/۴	هدف از این مطالعه بهینه سازی و بهبود خواص بیوپلیمر بر پایه موسیلاژ دانه ریحان و کربوکسی متیل سلولز (۱۰۰، ۱۶۲/۵ و ۲۲۵٪ وزنی موسیلاژ) با استفاده از نانو رس (صفر و ۸٪ وزنی موسیلاژ) و با بهره گیری از روش تولید قالب گیری بود. پس از تهیه ضخامت، رطوبت، دانسیته، خواص مکانیکی، طیف سنجی مادون قرمز تبدیل فوریه (FTIR) و وزن سنجی حرارتی (TGA) در فیلم ها اندازه گیری شد. نتایج نشان داد که ضخامت و دانسیته فیلم خالص BSM بصورت معنی داری تحت تأثیر اضافه شدن CMC و MMT قرار نگرفتند ($p > 0.05$) ولی مقدار رطوبت با افزایش غلظت CMC روند کاهشی به خود گرفت ($p < 0.05$) در حالیکه حضور MMT روی این پارامتر بی تأثیر بود. استفاده از CMC و MMT باعث افزایش مقاومت به کشش نهایی و همچنین ازدیاد طول تا نقطه پارگی نانوکامپوزیت ها شد به گونه ای که بیشترین مقاومت کششی و ازدیاد طول در نقطه پارگی به ترتیب به میزان ۲۷/۹ MPa و ۴۱٪ برای نانوکامپوزیت حاوی ۸٪ MMT و ۲۲۵٪ CMC حاصل شد. نتایج FTIR حاکی از این بود که فعل و انفعالات شیمیایی خاصی که منجر به تولید ترکیبات جدید شود اتفاق نیفتاده است و فقط شدت و ضعف پیک های جذبی تا حدی تغییر کرده و در مواردی نیز طول موج های پیک های جذبی بصورت جزئی تغییر مکان داده اند. نتایج TGA نشان داد افزودن CMC و MMT سبب بهبود مقاومت حرارتی فیلم ها می شود. در مجموع، نتایج اندازه گیری ها حاکی از تأثیر مثبت CMC و MMT روی فیلم BSM بود و تیمار حاوی MMT و بیشینه غلظت CMC را می توان به عنوان فیلمی با ویژگی های بهتر برای استفاده در بسته بندی توصیه نمود.
کلمات کلیدی: بسته بندی مواد غذایی، زیست تخریب پذیری، نانوکامپوزیت.	
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* مسئول مکاتبات: younes.zahedi@gmail.com Y_zahedi@uma.ac.ir	