



## Physical properties of carboxymethyl cellulose based nano-biocomposites with Graphene nano-platelets



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### ABSTRACT

Carboxymethyl cellulose (CMC) based bio-nanocomposite filled with graphene nano-platelets (GNPs) was prepared using casting technique. The morphology, thermal, light barrier, water vapor permeability (WVP), contact angle, moisture absorption and mechanical properties of the resulted bio-nanocomposites were investigated. The results indicated with addition of 0.5% w/w GNPs to polymer matrix, ultimate tensile strength (UTS) decreased from 7.74 MPa (in the pure film) to 5.69 MPa however, strain to break (SB) increased from 12.49% to 19.87%. The GNPs caused to reducing of light transmission and increasing of the water repelling nature of nano-biocomposites. However, it had not effect on melting point of CMC based nano-biocomposites.

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### 1. Introduction

Biodegradable packaging materials have recently got more attention, since synthetic packaging materials have caused environmental issues, because of their non-degradable and non-renewable nature. In addition, the enhancement of petroleum price is another reason for development of substitutes for synthetic plastic [1]. Biopolymers, such as polysaccharides [2–5], proteins [6–9], are considered the most respondent candidates for this intention and have potential for use as biodegradable packaging materials due to their biodegradability, plenty and stability [10]. Cellulose is the most abundant renewable resource, and its derivatives have superior film-forming properties [11,12]. CMC is a cellulose ether that shows thermal gelation and forming excellent films and it is extensively used in the pharmaceutical and food industries. CMC film is affective oxygen, carbon dioxide and lipid barrier however; it has weak water vapor barrier properties due to possessing a lot of hydrophil groups, such as OH and COOH, in its chemical structure [13]. Nevertheless, its water vapor barrier properties might be improved by adding hydrophobic materials and nanoparticles as reinforcing fillers to the biopolymer matrix. [14]. In recent years, the reinforcement properties of nano-fillers in polymer and

biopolymer matrixes have drawn increasing interest for obtaining high performance and lightweight biopolymeric materials which be suitable for packaging applications. “Graphene”, a molecular sheet of graphite, is an important nano-filler, has an ideal 2D structure with a monolayer of carbon atoms packed into a honeycomb crystal plane. Graphene oxide (GO), with oxygen functional groups such as hydroxyls and epoxides, is the product of chemical exfoliation of graphite. It has high water solubility due to presence of oxygen containing functional groups. The controlled reduction of graphite oxide yields graphene nano-platelets (GNPs) which their structures constituted from several layers of carbon atoms [15–18]. According to literature review, graphene with its unique physical properties is a multifunctional nanofiller that can improve electrical, thermal, mechanical, or gas barrier properties of polymer composites at very small loadings [19], several research works has been carried out on graphene oxide (GO) loaded biocomposites such as transparent and high gas barrier films based on poly (vinyl alcohol)/graphene oxide composite [20], the composite based on plasticized starch and graphene oxide/reduced graphene oxide [21], sodium alginate/graphene oxide composite films with enhanced thermal and mechanical properties [22]. However, according to our knowledge, no published reports are available in the literatures which evaluate the effects on of GNPs on the carboxymethyl cellulose based films. The main purpose of this work was to evaluate the influence of GNPs, as a reinforcing agent, on the most important physico-mechanical properties of the CMC based films.

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## 2. Materials and methods

### 2.1. Materials

Na-CMC powder used in this work (>97% and low density) was purchased from Sigma (USA). GNPs powder was used as a nano-filler (>99.5% and 2–18 nm thickness) purchased from us-nano (USA). Glycerol was used as a plasticizer (with average molecular weight (A.M.W.)=2.10 g/mol and 99.5%) was obtained from ARJ (South Korea). Calcium nitrate (>99.5% and  $M_W = 236.15$  g/mol) was purchased from LobaChemie (India). Potassium sulfate (>99%, pH=5.5–7.5 and  $M_W = 174.27$  g/mol) was supplied by RANKEM (India). Calcium sulfate (>99% and  $M_W = 172.17$ ) was supplied by CDH (India).

### 2.2. Preparation of films

#### 2.2.1. Preparation of CMC film

Amount of 1.5 g of CMC powder were mixed with 80 ml distilled water. Then transferred to a water bath at 80 °C for 10 min, and then 20 ml distilled water and 0.7 ml glycerol was added and agitated by a magnetic stirrer (600 rpm) at 80 °C for 20 min. After, the sample was sonicated for 30 min. Then 100 ml of sample was poured into a glass plate and dried at 55 °C for 18 h in an oven to cast the film.

#### 2.2.2. Preparation of CMC/GNPs film

1.5 g of Na-CMC powder were mixed with 80 ml distilled water. Then transferred to a water bath at 80 °C for 10 min, different GNPs concentrations (0.5, 1, 1.5 and 2% w/w CMC) were mixed with 20 ml distilled water and sonicated for 30 min. The CMC and GNPs concentrations and 0.7 ml glycerol were mixed together and agitated by a magnetic stirrer (600 rpm) at 80 °C for 20 min. After, samples were sonicated for 30 min to ensurement of suspension uniformity and creation of less agglomerates, and then 100 ml of samples was poured into glass plates and dried at 55 °C for 18 h in oven to cast the film.

### 2.3. Film thickness

Thickness of films was measured with a micrometer (Alton) to nearest 0.01 mm. A measurement was taken at three random places of the films. An average film thickness was 0.12 mm for films with GNPs and 0.11 mm for control films (without nano filler).

### 2.4. Mechanical properties

The ultimate tensile strength (UTS) and strain to break (SB) of the samples and stress-strain was determined by using a tensile machine (STM-1/SANTAM, Iran) according to the ASTM D882-91 [23]. First, the samples conditioned for 24 h at RH = 55%. Then, three film samples, 6 × 0.5 cm strips, were cut and mounted between the grips of the machine. The primary grip distance and cross-head speed were determinate to 50 mm and 5 mm/min, respectively.

### 2.5. Water vapor permeability (WVP)

WVP test was performed by ASTM method E96-95 [24]. A specific chalice with an average diameter of 2 cm and a depth of 4.5 cm were employed to determine WVP of films. The Film was broken into plates with a diameter slightly larger than the diameter of the chalice. After placing 3 g of anhydrous CaSO<sub>4</sub> in each cup, they were coated with films. Relative humidity (RH) of 0 was preserved using anhydrous CaSO<sub>4</sub> in the cup. Each cup was placed in a desiccator containing saturated K<sub>2</sub>SO<sub>4</sub> solution in a small cup at the bottom. A little content of solid K<sub>2</sub>SO<sub>4</sub> was kept at the bottom of the saturated solution to ensure that the solution remained saturated at all

times. Saturated K<sub>2</sub>SO<sub>4</sub> solution in the desiccator provides a relative RH of 97% at 25 °C. The desiccator maintained in an incubator at 25 ± 0.1 °C. The cup was weighted every 24 h and water vapor transport was determined by the weight gain of the cup. Changes in the weight of the cup were recorded as a function of time. Slopes were calculated by linear regression (weight change vs time). The water vapor transmission rate (WVTR) was defined as the slope (g/s) dried by the transfer area (m<sup>2</sup>). WVP (g/m/s/Pa) was calculated as:

$$WVP = \frac{WVTR}{P(R_1 - R_2)} X \quad (1)$$

where  $P$  is the saturation vapor pressure of water (Pa) at the test temperature (25 °C),  $R_1$  is the RH in the desiccator,  $R_2$  is the RH in the cup and  $X$  is the film thickness (m). Under this condition, the driving force [ $P(R_1 - R_2)$ ] is 3073.93 Pa. All measurements were carried out in three replicates.

### 2.6. Moisture absorption

To measure the moisture absorption Angles and Dufrense method was used [25]. The samples (24 mm × 24 mm) were conditioned using CaNO<sub>3</sub> at RH = 55% at 25 °C for 24 h. Then, samples maintained at desiccator containing CaSO<sub>4</sub> (RH = 0%) for 24 h. After primary weighing sample moved to a desiccator containing NaCl saturated solution with RH = 75% at 25 °C. To ensure the preservation of saturation, some NaCl sediment was created at the bottom of the desiccator. Then, the weight of the samples was measured at various times until a constant weight and the moisture absorption was calculated from the following equation:

$$\text{Moisture absorption (\%)} = \frac{W_t - W_0}{W_0} \times 100$$

where  $W_t$  is the sample weight after time  $t$  in RH = 75%, and  $W_0$  is the primary weight of the samples. This examination for each sample was repeated three times.

### 2.7. Contact angle measurement

To measure contact angle, sessile drop that is a conventional method of determining wettability features of solid surfaces was used. 9 μl of distilled water was dropped on the surface of samples. The photo was taken of drop and film contact after 60 s by the canon DIGITAL IXUS 80 IS camera with 5 times zoom. After, Adobe Acrobat 9 professional software was used for measurement of contact angle drop with the film's surface. Calculate the angle between the tangent to the drop at the point of contact and a line drawn along the surface of the film shows contact angle.

### 2.8. Optical properties

The amount of light transmission or transparency of films was carried out by ASTM method D1746 [26]. Sheets of 30 mm × 20 mm were first conditioned at RH = 55% (CaNO<sub>3</sub>) for 24 h. After, sample placed on one of the two bearing cells of Ultrospec 2000 UV-vis spectrophotometer. In another cell, the air was considered as a reference. The amount of light transmission was calculated in different parts of UV (wavelengths of 240 nm and 360 nm) and visible area (600 nm). This examination for each sample was repeated three times.

### 2.9. Thermal properties

The thermal properties of the films were determined by differential scanning calorimetry (DSC) (Perkin Elmer DSC jade, Netherland). The film samples (5 g ± 3 mg) were cut as small segments and were placed into a sample pan of DSC equipment. The

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