STUDY ON PERMEABILITY OF BIONANOCOMPOSITE FILM BASED ON TRAGACANTH GUM - CHITOSAN - GRAPHENE OXIDE

Talaei Saman and *Kiani Abolfazl
Department of Polymer Engineering, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran
**Author for Correspondence*

ABSTRACT

Tragacanth gum and chitosan, as two important naturally-occurring polymers show high water absorption but low mechanical properties. In this study, films were prepared via solution casting of these two biopolymers with incorporation of graphene oxide in order to obtain nanobiocomposite structure. Prepared nanobiocomposites enjoy appropriate biodegradability and biocompatibility. The permeability of the films against vapor and CO_2 is decreased by adding nanoparticles. The prepared films can be used in packaging industry regarding their biodegradability, lower permeability and better physical and mechanical properties.

Keywords: *Tragacanth Gum, Chitosan, Graphene Oxide, Nanobiocomposite*

INTRODUCTION

Since 1970, the topic of biodegradable polymers became critical as a result of worsening waste landfills worldwide. Over 30 percent of plastics are aimed at consuming products which only 2 percent is recycled, wherein biodegradable polymers is essential as appropriate replacement for common plastics (Chandra, 1998).

Tragacanth gum is a biopolymer with herbal resource which is a dried gummy exudate obtained from the stems of the Astragalus species. This valuable gum is specific to Iran which has been known as Persian Tragancanth from the past. It has medicinal and antimicrobial properties. Now, it is mainly used as emulsifier, thickener, and Musilage agent in pharmaceutical Industry (Balaghi, 2011). Nevertheless, Tragacanth gum does not provide desirable mechanical properties that might be resolved by mixing it with other polymers. Tragacanth gum is a complex, anionic polysaccharide with relatively special structural stability against heat, acidity, and aging (Gralen and Karrholm, 1950). Tragacanth gum is a mixture of two polysaccharides, an insoluble but swellable component called bassorin and the soluble part called Tragacanthin. This biodegradable and biocompatible polymer is non-allergic, and non-carcinogenic and it does not create any unpleasant poisonous effect in people (Anderson, 1989). Some new applications of Tragacanth gum include green fabrication of silver nanoparticles (Kora, 2012) wound healing adhesives, hydrogel membranes (Kiani *et al.,* 2012) superabsorbent hydrogels (Khoylou and Naimian, 2009), and carriers of controlled drug release (Siahi *et al.*, 2005). Safari *et al.,* (2013) used Tragacanth gum to improve textural properties of microcapsules. Mohebi *et al.,* (2012) prepared coatings for mushroom packaging and showed that these coatings increased mushroom durability and freshness. Tavakoli *et al.,* (2014) prepared Tragacanth-based hydrogels and used them in biomedical applications. Kiani *et al.,* (2012) prepared Tragacanth-based hydrogel membrane (GT). They announced that synthesized hydrogel membranes have diverse swelling properties. Films of this biopolymer had been crosslinked through reactions with glycerin, ethylene glycol, triethylene glycol, glutaraldehyde, as well as heat alone. The effects of crosslinking agent concentration, reaction temperature of crosslinker, and reaction time (2-24 hours) on equilibrium swelling of each of synthesized hydrogels were studied.

Chitosan, as a natural amino polysaccharide with unique properties, is extensively used in medicine industry. One of its outstanding characteristics is high biocompatibility, acceptable biodegradability with low poisonousness, and antibacterial and anti-allergy properties (Jayakumar, 2007). Most polysaccharides are acidic while Chitosan is basic in nature. Such unique property enables it to form links with fats, Cholesterol, proteins, DNA, RNA, and metal ions. Chitosan is derived from Chitin. The number of acetyl groups on the chain differentiates these two polymers. Tripathi *et al.,* (2009) (Rinaudo, 2008) studied bioactivity and physicochemical properties of crosslinked Chitosan-Polyvinyl alcohol for food packaging applications. They used Chitosan and Polyvinyl alcohol crosslinked with glutaraldehyde and showed that obtained film can be promising for food-packaging applications. Han *et al.*, (2011) produced composite film from chitosan and graphene oxide with increased mechanical strength in humid condition. Graphene oxide was produced from graphite through Hummers method. They realized that tensile strength of films had considerably increased by adding graphene oxide. Young's modulus of the composite films had noticeably risen compared to pure Chitosan. Zuo *et al.*, (2013) produced nanocomposites from graphene oxide (GO) and Chitosan by two methods and compared their properties with pure chitosan film. In the first method nanocomposite was obtained through physical mixture of graphene oxide and Chitosan (GO/Chitosan) while in other method it was prepared through graphene oxide dispersion in Chitosan matrix and formation of amid links among them (GO-Chitosan). They found out that tensile strength of GO-Chitosan film had increased by 2.5 times compared with pure Chitosan film; however, Go/Chitosan tensile strength had risen by 1.4 times. It was also observed that adding graphene oxide had reduced elongation at break which was referred to interaction between graphene oxide and polymer matrix that limited regular movements of the chitosan chains.

In this study, bionanocomposite films made up of chitosan and tragacanth gum were prepared by incorporation of graphene oxide nanoplatelets into the structure of composing biopolymers. In this way, we could take advantage of different natures of biopolymers and stregthening effect of nanoparticle. The films were also crosslinked using glutaraldehyde to diminish their water sensitivity. Morphology of the films as well as their CO_2 and water vapor permeabilities was determined.

MATERIALS AND METHODS

Materials

Tragacanth gum was the best Persian quality (with density of 1.27 g/cm^3, moisture content of 11.2%, and 3.5% ash) collected from Khuzestan province region. Chitosan was purchased from Sigma-Aldrich with medium molecular weight, acetylation degree of 75-85% and viscosity of 200-800 cPs. Acetic acid, 98% sulfuric acid, sodium hydroxide, glycerin, glutaraldehyde and 25% hydrochloric acid were all purchased from Merck Company, Germany. Graphite was purchased from Merck, Germany with density of 2.2 g/cm^3.

Preparation of Chitosan- Tragacanth Alloy

First, Tragacanth flakes were converted in to microparticles by four blades rotating mill. They are passed through 200-micrometer mesh in order to give uniform particles. To prepare the solution, 8g Tragacanth powder is solved in 1600ml water at 60rpm for 2h and then 90rpm for 8h in order to obtain uniform solution.

After degassing, 0.5 wt% Tragacanth solution was ready. To prepare 2 wt% Chitosan solution, 32g Chitosan powder was added to 1600ml 1M acetic acid solution and mixed with the aid of internal mixer at 60rpm for 5h in order to reach uniformity.

Chitosan/Tragacanth alloy (80/20) was prepared by mixing the solutions with an internal mixer and adding 1M NAOH solution. Then, 98% sulfuric acid was added as acetalization catalyst followed by glutaraldehyd addition and the mixture was stirred till to obtain a uniform solution. Sulfuric acid was set at 1 wt% of pure Chitosan and glutaraldehyde at 1 wt% of total polymer. Finally, solution was poured into petri dish and allowed to stand for 4 days in atmosphere until all the solvent evaporated and film made up of Chitosan and Tragacanth gum was obtained. Prepared films were fragile using this method, therefore, glycerin was added as plasticizer at 20 wt% of total polymer weight.

Preparation of Nano Composite Film

Graphene oxide synthesis was done through Hummers method (Pan, 2011) .

2 wt% graphene oxide was added to the solution made up of Tragacanth and Chitosan in the same condition of preparation of Chitosan/Tragacanth solution. To have better distribution of nanoparticles, the solution was placed in Ultrasound machine for 360 minutes. Pure Chitosan and Tragacanth film and alloy film were used as control. Prepared films had a thickness of 70µm.

Test Methods

Composite films with and without nanoparticles were evaluated by CO_2 and water vapor permeability as well as FTIR, XRD and SEM.

Fourier Transform Infrared Spectroscopy (FTIR)

To study chemical structures of synthesized composite films and to compare them with pure samples FTIR spectroscopy was performed using Spectrum RX1 FTIR on KBR tablets of the samples. The spectrum was obtained in the wavelength range of 400-4000 cm^{-1} as an average of 16 scans with accuracy of 4 cm^{-1}.

X-ray Diffraction (XRD)

X-ray diffraction was done by PANanlytical device model X’Pert Pro MPD made in Netherland. Device voltage was 40kV and the current was 40mA, tube Cu K_α and wavelength was 1.54 °A. 2Ө was recorded between 3 to 80 degree with speed of 0.02 degree/s at temperature of 25 ˚C.

CO_2 Permeability Test

Composite and nanocomposite films (70µm thickness) were prepared in accordance with ASTM D 1434-8 and the permeability against CO_2 at 24°C and 1bar was measured. Diameter of tube and condensation temperature was 3.3 ˚A and 304 K, respectively.

Time-delay method was used to study the CO_2 permeability which is the most common method for gas permeability measurements in polymer films.

The pressure was kept constant during the measurements, i.e. downstream pressure was atmospheric and changes in volume of the gas passing the films were recorded.

Water Vapor Permeability Test

E96 ASTM standard method was utilized. To conduct this experiment, silica gel was poured inside cell covered by prepared film samples.

Cells were placed inside desiccator containing distilled water. Water creates humidity of 100% at 25 °C changes in cell weights versus time were measured by a digital weigher with accuracy of 0.0001g.

In all samples, graphs of cell weight changes versus time were straight lines (R^2>0.98). Cell weights have been measured at 0, 24, 48, and 72 hours after being placed in desiccator.

Field Emission-SEM

To study and compare fracture surface of the samples, SEM images of composite films with and without nanoparticles were obtained using Mira3-XMU with various enlargements.

Samples were broken in liquid nitrogen and covered by gold coating. Then SEM photographs were taken in vacuum.

RESULTS AND DISCUSSION

Figure 1 shows FTIR spectra of Tragacanth gum, Chitosan, their composite and nanocomposite films. As one can see, from the peaks in the range 1751 – 1565 cm^{-1} for tragacanth gum and chitosan individual films and their displacement in composite films, a favorable interaction between COOH group of tragacanth and NH_2 groups of chitosan could be understood.

Figure 2 shows X-ray diffraction pattern of nanoparticle and composite and nanocomposite films. The peak at 10 degree in graphene oxide showed the increased distance of layers compared to graphite. In Nano-composite samples, the peak intensity of graphene oxide had substantially decreased around 10 degrees indicating appropriate distribution of nanoparticles in nanocomposite film with no accumulation.

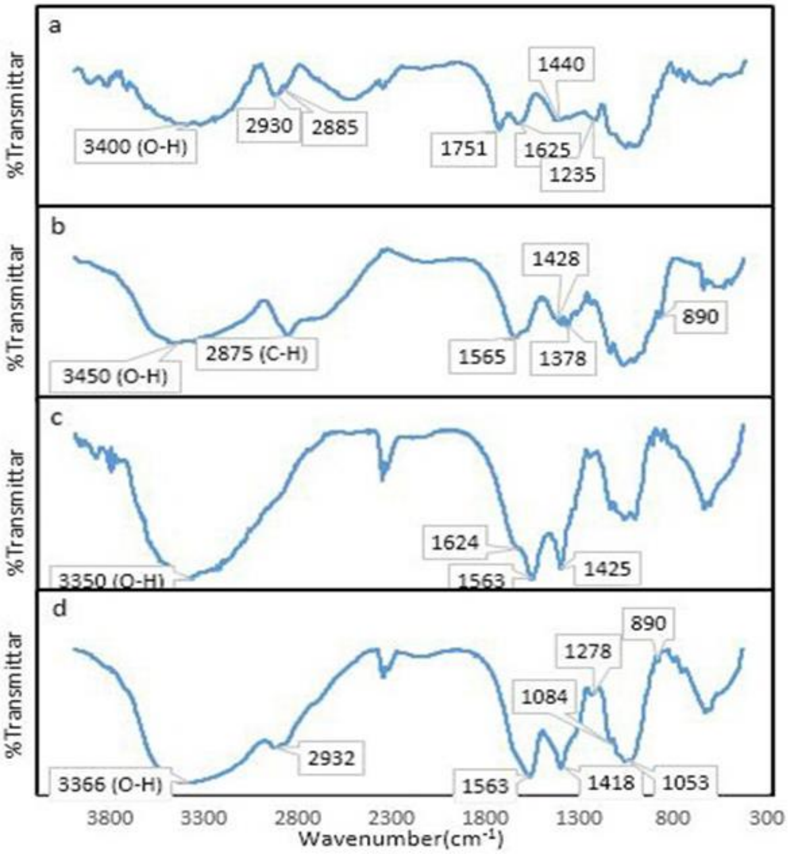

Figure 1: FTIR (a) Tragacanth gum (b) Chitosan (c) Tragacanth gum-Chitosan composite film (d) nanocomposite film containing 2 wt% graphene oxide

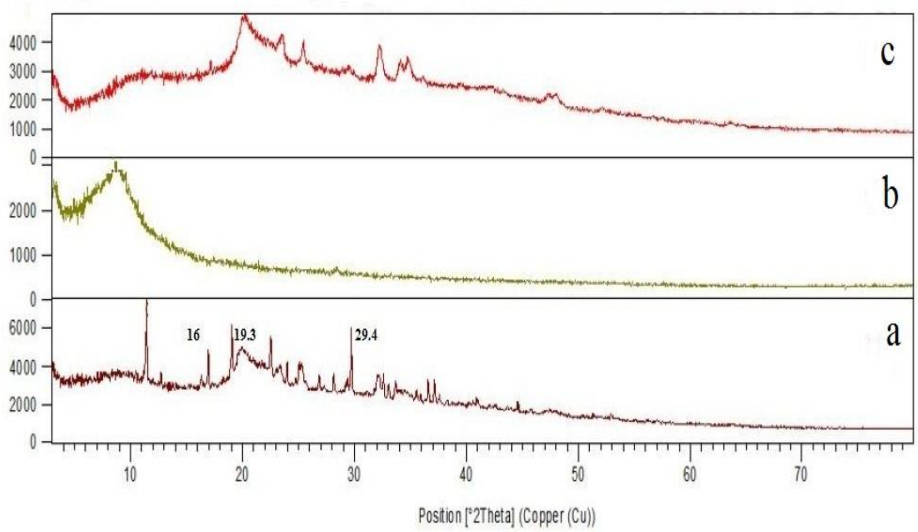

Figure 2: X-ray diffraction pattern of Chitosan- Tragacanth gum composite film (a) graphene oxide (b) and nanocomposite of Chitosan- Tragacanth gum- graphene oxide (c)

Figure 3 shows changes of cell weights covered by Chitosan-Tragacanth gum composite and Chitosan-Tragacanth gum-graphene oxide nanocomposite films in water vapor permeability test. As it can be observed, with appropriate approximation ($R^2 > 0.98$), permeability graphs for both samples were linear.

Water vapor permeability was decreased by adding graphene oxide to Chitosan-Tragacanth gum composite film, as graphene oxide layers acted as barrier for permeation.

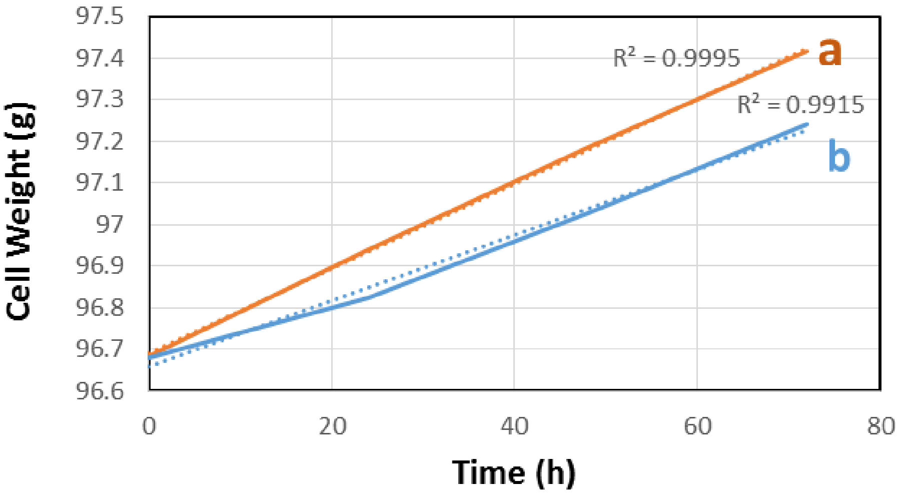

Figure 3: Changes of cell weight versus time for Chitosan- Tragacanth gum composite (a) and Chitosan- Tragacanth gum-graphene oxide nanocomposite (b)

Figure 4 shows CO_2 permeability from composite and nanocomposite films. As it can be found, adding 2wt% graphene oxide to Chitosan-Tragacanth gum film led to 43% reduction in permeability of the film against CO_2 which could be attributed to presence of graphene oxide layers in polymer bed which acted as barrier.

Figure 4: Permeability of Chitosan – Tragacanth gum composite (a) and Chitosan – tragacanth gum – graphene oxide nanocomposite (b)

Figure 5 shows SEM images of surface (5a) and fracture surface (5b) of Chitosan-Tragacanth gum composite film. The fracture surface of this sample, containing glycerol and aldehyde, was uniform with no sign of phase separation showing good compatibility of these two biopolymers. Further, surface of this sample was completely flat and uniform indicating the appropriate interaction between the components.

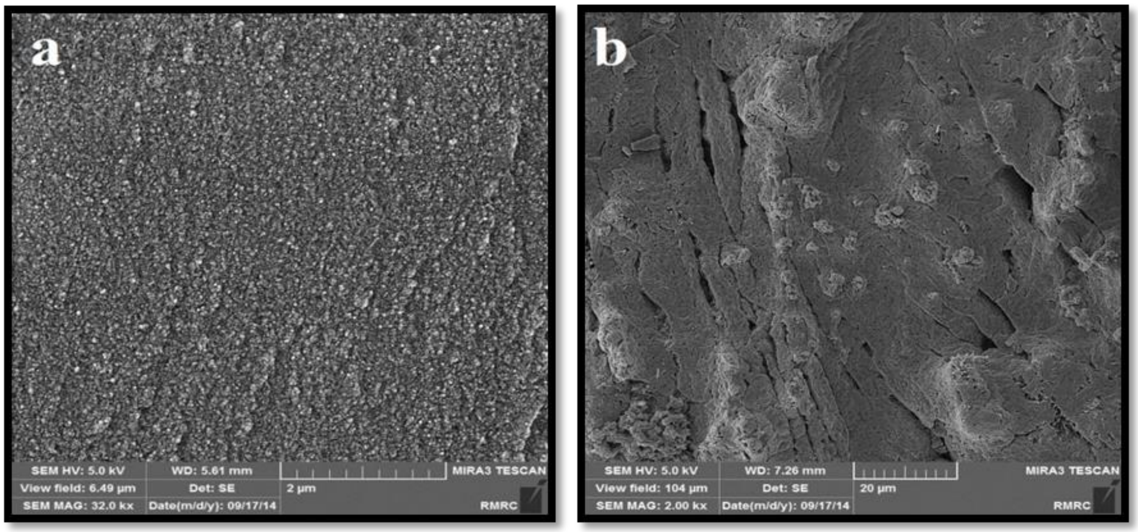

Figure 5: SEM images of external surface (a) and fracture surface (b) of composite sample made up of Chitosan and Tragacanth gum

Figure 6 shows SEM images of fracture cross section of nanocomposite film. Nanoparticles can be observed well in polymer matrix and lack of nanoparticle aggregation was found. The size of graphene oxide nanoparticles was estimated almost 29 nm which was good enough to be considered as a nanocomposite system.

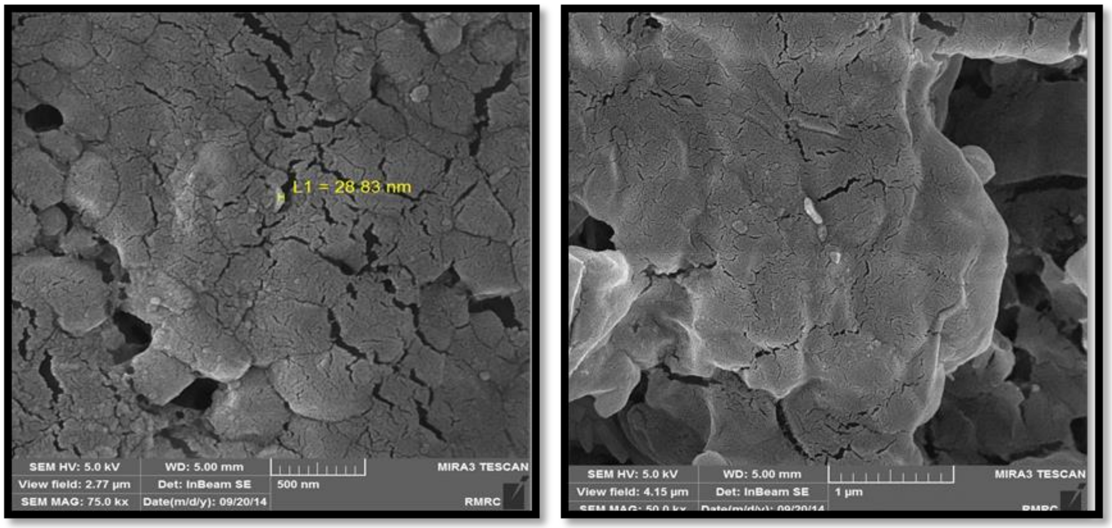

Figure 6: SEM images of nanocomposite films fracture surface with different enlargements

Conclusion

A nanobiocomposite film made up of two biopolymers, i.e. Chitosan and Tragacanth gum, and graphene oxide nanoparticles was successfully prepared.

SEM photographs as well as XRD patterns proved the dispersion of nanoparticles in biopolymer mixture.

The favorable interactions between acidic Tragacanth gum and basic Chitosan were obvious in FTIR spectra.

Permeability of prepared films against water vapor and CO_2 was decreased by adding graphene oxide to Chitosan-Tragacanth gum composites.

The results showed that prepared bionanocomposite is promising for food-packaging industry.

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