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Synthesis and characterization of graphene oxide/carboxymethylcellulose/alginate composite blend films

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ABSTRACT

In this work, graphene oxide/carboxymethylcellulose/alginate (GO/CMC/Alg) composite blends were prepared by a simple solution mixing-evaporation method. The resulting structure, thermal stability, and mechanical properties of the blends were investigated by wide-angle X-ray diffractometry, Fourier transform infrared spectroscopy, Raman spectroscopy, scanning electron microscopy, thermogravimetric analysis, and mechanical testing. The obtained findings revealed that CMC, Alg, and graphene oxide were able to form a homogeneous mixture. When compared to a CMC/Alg blend, the incorporation of 1 wt% graphene oxide improved the tensile strength and Young's modulus by 40% and 1128%, respectively. In addition, the GO/CMC/Alg composite blend film showed a higher storage modulus than the CMC/Alg blend.

1. Introduction

Polymeric blends are physical mixtures of structurally different polymers or copolymers that interact via secondary forces with no covalent bonding. Such interactions include hydrogen bonding, dipole–dipole forces, and the formation of charge transfer complexes for homopolymer mixtures (Tuncer, Serkan, Mehmet, & Olgun, 2005). Blend materials from either synthetic or natural polymers alone are not always able to satisfy the complex demands of biomaterials. The success of synthetic polymers as biomaterials may be attributed to their wide range of mechanical properties and the development of transformation processes that allow a variety of different shapes to be easily obtained at a low production cost. Biological polymers present good biocompatibility, but their mechanical properties are often poor. Therefore, biologically important polymeric materials based on blends of synthetic and natural polymers have been studied (Preeti & Jathi, 2010). Alginate (Alg) is a natural biopolymer derived from brown seaweed (Mohan & Nair, 2005). It is hydrophilic, biocompatible, and relatively economical. Alg has been widely used in the medical field for wound dressings, scaffolds for hepatocyte culture, and as a surgical or dental impression material, even if an allergic reaction has occurred on the skin (Ng & Cheng, 2007; Patel, 1993). Carboxymethylcellulose (CMC) is a water-soluble anionic linear polysaccharide and semi-synthetic derivative of cellulose that is produced by the partial substitution of the 2, 3, and 6 hydroxyl groups of cellulose by carboxymethyl groups. CMC polymers are made up of linear β-(1 → 4)-linked glycanes that exhibit polyelectrolyte characteristics due to the presence of weakly acidic groups (Chakraborty, Chakraborty, & Ghosh, 2006; Tong, Xiao, & Lim, 2008). In terms of applications, CMC is an important industrial polymer that has been employed in flocculation, drug reduction, detergents, textiles, paper, foods, and drug formulations (Biswal & Singh, 2004). Researchers have also reported that the addition of CMC produces separate smaller-sized micro fibrils during the growth of Gluconacetobacter. Xylinus (Chen, Chen, Huang, & Lin, 2011; Haigler, Brown, & Benziman, 1980; Hirai, Tsuji, Yamamoto, & Horii, 1998). CMC is primarily used because it has a high viscosity and is both non-toxic and non-allergenic. The numerous hydroxyl and carboxylic groups in CMC enable water binding and moisture sorption properties. Consequently, CMC hydrogels exhibit a high water content and good biodegradability which, when combined with the low cost of the material, has facilitated their use in a wide range of applications (Nie, Liu, Zhan, & Guo, 2004). Generally, the occurrence of specific intermolecular interactions through hydrogen bonding between two or more polymers is responsible for the observed mixing behavior and properties of blends prepared from aqueous solutions (Gaisford, Beezer, Bishop, Walker, & Parsons, 2009). The properties of the resulting blends can be studied so as to expand their range of application in biomedical

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and pharmaceutical devices. Because both Alg and CMC are water-soluble polymers, they are compatible due to the formation of hydrogen bonds. Numerous reports have been published on the material properties of individual pullulan, alginate, and CMC films (Kawahara et al., 2003; Lee, Chan, Dolzhenko, & Heng, 2006). In addition, blended CMC/Alg films have been investigated as potential composites (Sayeda, Kariman, & Salmawi, 2013). However, no significant improvement was observed in the tensile strength of CMC/Alg films when compared that of the individual component films. Thus, the physical properties of CMC/Alg blend film must be improved to satisfy the demands of specific applications.

The approach of using nano-fillers such as carbon nanotubes, clay, and silica has proven to be effective way to enhance the mechanical, electrical, and thermal properties of polymers (Azeez, Rhee, Park, & Hui, 2013; Azeez, Rhee, Park, Kim, & Jung, 2013; Ha, Rhee, Park, & Lee, 2010; Liu, Phang, Shen, Chow, & Zhang, 2004; Park & Jana, 2003; Park, Kim, Yoo, Rhee, & Lee, 2010; Shaffer & Windle, 1999; Yang et al., 2006). Recently, the application of graphene oxide (GO) as a nano-filler in polymer matrices to prepare polymer nanocomposites has been reported (Yadav, Rhee, Jung, & Park, 2013; Yadav, Jung, et al., 2013; Yadav, Yoo, & Cho, 2013; Yang, Pan, Huang, & Li, 2010; Yu, Ramesh, Itkis, Bekyarova, & Haddon, 2007). Graphene, a single sheet of graphite, has an ideal 2D structure with a monolayer of carbon atoms packed into a honeycomb crystal plane. Using both experimental and theoretical methods, researchers (Geim & Novoselov, 2007; Rao, Sood, Subrahmanyam, & Govindaraj, 2009; Stankovich et al., 2006) have demonstrated the advantages of graphene in the field of materials science. Due to its sp^2 hybrid carbon network and extraordinary mechanical, electronic, and thermal properties, graphene has opened new pathways for the development of a wide range of novel functional materials. Perfect graphene does not exist naturally, but bulk and solution-processable functionalized graphene materials, including GO, can now be prepared (Hao, Qian, Zhang, & Hou, 2008; Li & Kaner, 2008; Park, Jeevananda, Kim, Kim, & Lee, 2008; Park, An, et al., 2008). The large surface area of GO has a number of functional groups (e.g., —OH, —COOH, —O—, and C=O) that make the material hydrophilic and readily dispersible in water as well as some organic solvents (Paredes, Villar-Rodil, Martinez-Alonso, & Tascon, 2008). As a result, graphene-based materials may be easily fabricated by solution casting. Due to its numerous oxygen-containing functional groups and good dispersibility in water, GO is able to interact with the —OH groups of CMC and Alg via hydrogen bonding in an aqueous system. Thus, GO may be viewed as a physical cross-linking agent to obtain interacting polymers, as it can promote miscibility between CMC and Alg molecules, resulting in a compatible blend with enhanced properties. In this work, we report on a simple and environmentally friendly solution mixing-evaporation method for the preparation of blended GO/CMC/Alg composite films. The effects of GO loading on the structure and properties of the blended composites were subsequently investigated.

2. Experimental method

2.1. Materials and methods

Sodium carboxymethyl cellulose (CMC, chemical grade, average molecular weight 250,000 g/mol), sodium alginate (NaAlg, chemical grade, MW 14,000–132,000 g/mol), potassium permanganate (analytical grade), sodium nitrate, and graphite with an average particle size of <20 μm were purchased from Sigma–Aldrich (Korea). Hydrogen peroxide was supplied by the Daejung Chemicals and Metals Company, Ltd. (South Korea), while hydrochloric acid was purchased from Fluka. Sulfuric acid (98%) was purchased from the Junsei Chemical Company (Japan). The water used in this work was distilled and deionized.

2.2. Synthesis of graphene oxide

Graphene oxide (GO) was synthesized from natural graphite flakes (mean particles size of <20 μm) using the Hummers method (Hummers & Offeman, 1958; Ramanathan et al., 2008) with some modification. Briefly, 2 g of graphite and 1 g of $NaNO_3$ were dissolved in 46 mL of concentrated H_2SO_4 in an ice bath. After about 15 min of stirring, 6 g of $KMnO_4$ was gradually added to the suspension under slow stirring in order to hold the reaction temperature below 20 °C. The suspension was stirred for 2 h and then maintained at 35 °C for 30 min. Next, 92 mL of deionized water was slowly poured into the suspension. While the addition of water resulted in a quick increase in temperature, the conditions were controlled such that the temperature remained less than 98 °C. After 15 min, the suspension was further diluted to approximately 280 mL with warm deionized water, after which 20 mL of 30% H_2O_2 was added to remove residual $KMnO_4$ and MnO_2. At this point, the suspension took on a luminous yellow color. The suspension was filtered and washed with a warm 5% HCl aqueous solution and deionized water, respectively, until no sulfates were detected. The pH of the filtrate was subsequently adjusted to 7. The graphene oxide was dried under vacuum at 50 °C to a constant weight and then milled to an ideal particle size. The average size of graphene flakes are 500–5000 nm.

2.3. Preparation of blended GO/CMC/Alg composite films

CMC/Alg composite films containing GO were prepared by a simple solution mixing-evaporation method (Wang, Shen, Zhang, & Tong, 2005). Briefly, 0.01 g of GO was first dissolved in 50 mL of water and sonicated in an ultrasonic bath (Kum Sung Ultrasonic, Korea) for 15 min. Next, a solution containing 0.25 g of CMC, 0.75 g of sodium alginate (Alg), and 49 mL of deionized water was stirred for 5 h using a magnetic stirrer so as to dissolve the CMC and Alg. The GO solution was then added to the CMC/Alg solution, followed by stirring for 5 h. The solution was subsequently degassed for 30 min to remove bubbles, and then poured onto a glass plate at 80 °C under vacuum until dry. Specifics regarding the degassing and curing cycles were determined on the basis of trial and error. Lastly, the dried GO/CMC/Alg composite thin films with an average thickness of 0.04 mm were carefully removed from the glass plate.

The procedure for preparing blended CMC/Alg films was similar to that used for the fabrication of GO/CMC/Alg films, except that no GO was added.

2.4. Characterization

Wide-angle XRD patterns of the composite films were recorded with a Rigaku Rotaflex (RU-200B) X-ray diffractometer using Cu Kα radiation with a Ni filter. The tube current and voltage were 300 mA and 40 kV, respectively, and data from the 2θ angular regions between 5 and 80° were collected. The tensile properties of the composite films were measured at room temperature with a universal test device (Instron 8871), while the surface morphology of the films was analyzed by field emission scanning electron microscopy (FE-SEM, LEO SUPRA 55, Carl Zeiss, Germany). The thermal stability of the films was investigated using a thermogravimetric analysis (TA) instrument (SDT Q600) from 30 °C to 900 °C under a nitrogen atmosphere at a heating rate of 10 °C/min. Dynamic mechanical analysis (DMA) of the nanocomposites was conducted with a dynamic mechanical analyzer (DMA, Q800, TA Company) using tension membrane clamps at a frequency of 1 Hz and a heating rate of 2 °C/min. Raman analysis of the composites