



Macromolecular Nanotechnology

Synthesis of click-coupled graphene sheet with chitosan: Effective exfoliation and enhanced properties of their nanocomposites



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ABSTRACT

Graphene sheet (GS) is functionalized with chitosan via a click coupling between azide-functionalized chitosan and alkynyl-decorated graphene oxide. The coupling is confirmed by Fourier transform infrared and X-ray photoelectron spectroscopy, and the complete exfoliation of GS in the chitosan matrix is confirmed by X-ray diffraction measurements. With the addition of a small amount of the click coupled GS-f-CS (2 wt%) in the chitosan matrix, the breaking stress and tensile modulus of a chitosan composite film is increased by more than 200%. In addition, the click coupled GS-f-CS shows higher antimicrobial activity than pure chitosan. The click coupling approach used for graphene sheet may be very effective for enhancing both the functional and mechanical properties of composites by employing a suitable target polymer.

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1. Introduction

Recently, more awareness has been paid to natural polymers for sustainable development and environment protection [1]. Chitosan, a polysaccharide composed of β -(1-4)-linked-2-deoxy-2-amino-D-glucopyranose units, is generally obtained by alkaline deacetylation of chitin [2,3], which is one of the most abundant natural polymers on earth [4]. Owing to its good biocompatibility, biodegradability, low immunogenicity, antibacterial properties [5], and bearing amino and hydroxyl groups, chitosan has been widely used in applications such as controlled drug release [6], biosensors [7], biological engineering [8], catalysts [9], pervaporation [10], packaging materials [11], and membrane separation [12]. Moreover, chitosan has been extensively investigated for several decades to prepare high-performance chitosan-based materials for meeting this wide range of applications.

However, the mechanical properties of pure chitosan are not good enough to meet the criteria for these applica-

tions. Thus, owing to the requirement of achieving high mechanical strength for chitosan, a lot of research has been focused on improving its mechanical properties [13,14]. Nanocomposite fabrication by introducing nanofillers such as clay, inorganic nanoparticles, and carbon nanotubes has been proved to be an effective approach for improving the mechanical properties of a chitosan matrix [15–17]. In the past few years, one-dimensional carbon nanotubes have been considered to be an ideal reinforcing agent for polymer matrices because of their unique structure and properties [18–21]. However, the expensive multistep methods used to prepare and purify carbon nanotubes as well as their intrinsic bundling limit their applications on an industrial scale.

On the other hand, sp^2 -bonded graphene in the form of two-dimensional (2D) single layer or few layers has attracted a great deal of interest in recent years owing to its low cost, unique structure, and extraordinary electronic and mechanical properties [22–25]. As in the case of carbon nanotubes, the processing and dispersion of graphene nanomaterials in polymer matrices are the main challenges preventing the implementation of high-performance graphene-based nanocomposites. The intrinsic van der

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Waals interactions between graphene layers easily result in agglomeration. Such agglomerations inexorably lower the reinforcement effectiveness of nanofillers, because the maximal load transfer and lowest filler loading can only be attained when the nanofillers are dispersed on the molecular scale and interact with the polymer matrix by chemical bonding. These chemical functionalizations have been found to be a feasible and effective way for improving the dispersion and effective exfoliation of graphene materials in polymer matrices [26,27]. Graphene oxide (GO) is densely loaded with oxygen-containing functional groups on its basal planes and edges; this makes GO suitable for covalent functionalization with polymeric molecules via etherification, amidation, atom transfer radical polymerization (ATRP), etc [28,29]. However, these approaches for covalent functionalization of polymers on graphene sheets (GSs) involve complex procedures with low efficiency.

After its inventions by Sharpless and coworkers, the “click chemistry” technique has received significant attention from researchers in the field of materials chemistry [30]. The Cu(I)-catalyzed [3 + 2] Huisgen cycloaddition reaction is the most successful variant between azide and alkynyl moieties, forming a high yield of 1,4-substituted 1,2,3-triazole with an enormously high tolerance of functional groups and often proceeds better in water than in an organic solvent and the products require no or minimal purification [31,32]. There have been a few reports on graphene based chitosan composite with enhanced mechanical properties but these studies involved simple physical mixing of two components [13,33,34]. To the best of our knowledge, the covalent functionalization of chitosan with GO achieved by employing click chemistry reactions has not been reported yet.

In this present study, a click chemistry approach has been utilized for realizing the covalent attachment of alkynyl-functionalized graphene oxide with azide-moiety-containing chitosan with superior mechanical and highly enhanced antimicrobial properties. It is believed that these highly functionalized graphene materials with biocompatible chitosan can be safely investigated to take advantage of their unique physicochemical processes for industrial and biomedical applications.

2. Methods

2.1. Materials

Medium molecular-weight chitosan (85% deacetylated), graphite, N,N'-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), epichlorohydrin, propargyl amine, ascorbic acid, copper sulfate pentahydrate, and sodium azide were purchased from Sigma-Aldrich, Korea. Epichlorohydrin was purchased from Tokyo Chemical Industry Co., Ltd. All other reagents and solvents were of analytical grade and used without further purification.

2.2. Synthesis of GO decorated with alkynyl moieties (GO-alkynyl)

GO was decorated with alkynyl groups via the reaction of GO with propargyl amine in the presence of DCC and DMAP

in dry DMF. In a typical reaction, GO (0.3 g) was dispersed in 100 mL of DMF for 1 h using a bath sonicator. Propargyl amine (0.536 g, 5.46 mmol) was then added into the GO suspension and dissolved by stirring. DCC (8 g, 41.74 mmol) and DMAP (0.6 g, 4.92 mmol) were gradually added into the flask for about 30 min. The reaction mixture was stirred for 16 h at room temperature. After completion of the reaction, 100 mL of DMF was added to the reaction mixture and the reaction product was filtered using a 0.2- μ m PTFE membrane. The final product was washed with a generous amount of DMF and then dried under vacuum for 24 h.

2.3. Azidation of epichlorohydrin

Sodium azide (12.8 g, 0.20 mol) was dissolved in 40 mL of water containing 0.16 g (0.55 mol) tetrabutylammonium bromide as a phase transfer catalyst in a round-bottom flask. Then, 18.5 g (0.20 mol) of epichlorohydrin was added, covered by foil to protected from light and stirred overnight at room temperature of 25 °C. After completion of the reaction, dichloromethane was added and the non-aqueous layer that formed was separated using a separating funnel and dried over anhydrous sodium sulfate. Dichloromethane was then removed under reduced pressure to yield 85% azidated product.

2.4. Azidation of chitosan (CS-N₃)

Chitosan (1.5 g) was dissolved in 55 mL of 5% acetic acid and 6 mL of 5% hydrochloric acid, and 8 g of azidated epichlorohydrin was added to this solution. The solution was protected from light and stirred with a magnetic stirrer at 25 °C for 24 h. The reaction product was precipitated by pouring to a 40% ammonia solution in methanol. The precipitate was then filtered, washed several times with methanol, once with water, and finally with acetone. The product (CS-N₃) was dried under reduced pressure at room temperature and was kept in a desiccator in the dark until use.

2.5. Click coupling between azidated chitosan (CS-N₃) and GO-alkynyl

Cu(I)-catalyzed click chemistry was utilized for the coupling of CS-N₃ with alkynated GO (Scheme 1). In a 100-mL round-bottom flask, GO-alkynyl (20 mg) was dispersed in DCM by bath sonication for 10 min. A 10 mL aqueous solution of copper sulfate pentahydrate (10.4 mg) and sodium L-ascorbate (17 mg) was added into the reaction flask. CS-N₃ (0.32 g) dissolved in 40 mL of 5% acetic acid was also successively added into this mixture. The reaction mixture was then stirred for 48 h at room temperature under a nitrogen flow. The obtained product was precipitated by pouring into a 40% ammonia solution in methanol. The precipitate was filtered through a 0.2- μ m PTFE membrane, washed several times with methanol, once with water, and finally with acetone. The final product, chitosan functionalized graphene (GS-f-CS) was dried for 48 h under vacuum.

2.6. Preparation of chitosan film reinforced with GS-f-CS

Nanocomposite films were fabricated by incorporating 0.25, 0.5, 1.0, and 2.0 wt% of GS-f-CS to a pure chitosan

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