Chitosan/graphene oxide biocomposite film from pencil rod

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Abstract. Graphene Oxide (GO) has been successfully synthesized using Hummber method from graphite powder of pencil rod. The excellent solubility of graphene oxide (GO) in water imparts its feasibility as a new filler for reinforcement hydrophilic biopolymers. In this research, the biocomposite film was fabricated from chitosan/graphene oxide. The characteristics of graphene oxide were investigated using Fourier Transform Infrared (FT-IR) and X-ray Diffraction (XRD). The results of the XRD showed graphene structure in 2θ, appeared at 9.0715° with interlayer spacing was about 9.74063 Å. Preparation films with several variations of chitosan/graphene oxide was done by casting method and characterized by mechanical and morphological analysis. The mechanical properties of the tensile test in the film show that the film CS/GO (85:15)% has the optimum Young's modulus size of 2.9 GPa compared to other variations of CS/GO film. Morphological analysis film CS/GO (85:15)% by Scanning Electron Microscopy (SEM), the obtained biocomposites film showed fine dispersion of GO in the CS matrix and could mix each other homogeneously.

1. Introduction

Graphene, as an unique material, provides several interesting characteristics because of its structure which has hexagonal structure forming planar sheet of all-$sp^2$ as size as an atom [1]. The most interesting characteristic, the mechanical strength of graphene is higher than steel due to its structure indicating this material can be used as reinforcement in fabricating composite. However, in utilizing it as reinforcement in biocompatible composite, it is more suitable to combine the graphene oxide (GO) than graphene due to the higher presence of oxygen functional groups particularly hydroxyls and epoxides. Chemically speaking, the existence of these two characteristics – either the structure and functional groups --, provides higher possibility of intercalation of various molecules so it can be functioned in fabricating composite. Therefore, in this paper we present the utilization of graphene oxide as filler to enhance the mechanical strength of chitosan.

S Synthesizing graphene has invited many scientists. Graphene is considered as a material which has unique properties either in mechanical and electrical. It has two-dimensional structure with $sp^2$ hexagonally packed in density and it was predicted in 1940 from graphite theoretically[2]. Sixty years after predicting, single graphene sheets had been prepared by Novoselov and Geim of the University of Manchester[3]. Many studies have reported that graphene’s properties for either in academic or industrial field. It is potentially to be designed for supercapacitor[4]; coated in composite with conductive properties[5]; and as catalyst[6].
Graphene is a monolayer graphitic carbon which is formed inside the graphite. This deposition then can be separated by performing the two steps which are Brodie oxidation and Hummers method. In synthesizing the graphene, the preparation of graphene oxide must be conducted in form of dispersions in water and other solvents[7]. However, the graphene oxide (GO) membranes and the precursor of graphite oxide generated significance differences in hydration and solvation properties [8]. Therefore, intercalation process can be occurred exactly the same either in water or alcohol condition depending on the numbers of monolayers which are corresponded, but the solvents’ volume are varied as the temperature and pressure conditions [9].

The preparation of graphene oxide (GO) widely used is exfoliation by performing Hummers method. The reaction involves the intercalation process which is essential in obtaining the quantities of graphene oxide. Subsequently, the preparation must be conducted in electrochemical reaction so the reduction from graphite to graphite oxide is proceeded properly[10]. Thus, the graphene oxide can be derived from graphite oxide by instrument test throughout the presence of functional groups.

Chitosan is a derivative of chitin compounds which is produced by de-acetylation involving high concentrate of base solution. This material is classified as organic material as the chemical composition is composed of linear polysaccharide with glucosamine[11]. The linearity of chemical structure produces interesting properties, such as good flocculants and chelating properties. While in the physical form, chitosan is hard and commonly found as skeleton of invertebrate, such as Arthropod Sp, but the most resources of chitosan can be found in Crustacean Sp. Surprisingly, chitosan comprises two hydroxyl group functions and one free amino group indicating the material is occasionally dissolved in neutral pH of water[12]. And more importantly, chitosan is an organic material with reactive functional groups particularly in the amino compounds so it is non-toxic or biocompatible.

The preparation of chitosan and graphene oxide are respectively prepared from Blankasand pencil’s graphite. The fabrication of composite is performed by using casting method with certain percentage of compositions. The bio-composite that has been prepared therefore is investigated to understand the morphological properties with Scanning Electron Microscope (SEM). In addition to understand the mechanical properties, we performed mechanical test including tensile test and analyze the data with software OriginPro 2016 (32-bit) b9.3.226.

2. Materials and methods

2.1. Materials and Instruments
AnalyticalBalance, Oven (Carbolite), Mechanical Stirrer, Universal pH, A thermometer, A hot plate, magnetic Stirrer, Ice bath, Cuvette, Bottles of distilled water, A spatula, Sentrifugator VS-GOOCFi, Ultrasonication instruments, a set of SEM JSM- 35C Shumandju, Equipment tensile Gotech AL 7000 M, a set of XRD Shimadzu XRD-6100, a set of FTIR Shimadzu IR prestige-21, chitosan solid powder graphite of pencil rod, Distilled water (H2O), H2SO4 98%, KMnO4, NaNO3, H2O2 30%, CH3COOH 2%.

2.2. Preparation of grapehene oxide
As many as 2 grams of graphite were putted in beaker glass and then those were added with 1 gram of Sodium Nitrate (NaNO3), then the mixture powder was poured with 46 ml of sulphate acid (H2SO4) 98%. During the reaction, the solution was in exotermic condition so it must be stirred in the ice-bath to maintain temperature while the KMnO4 was added after the temperature being controlled by the ice bath to 20°C. The solution then was moved from the ice-bath and it was heated on temperature of 35°C for twenty hours. Afterward, the solution then was poured with 92 ml of distilled water gradually while at the same time it was stirred for 15 minute to achieve neutral conditions. Hence, the solution was added with hydrogen peroxide (H2O2 30%) before being centrifuged by centrifuge with angular velocity for 7200 rpm for 10 minutes. After being centrifuged the solution was comprised by solution and precipitate. Then, the precipitate was washed with warm distillate water to increase the pH near 7.
The obtained yellow-brown powder was re-dispersed into distillate water while at the same time stirred until homogeneous, followed by treatment using mild ultrasound for 30 min. Graphene oxide powder was obtained after dried at 105°C of the suspension.

2.3. Preparation of chitosan/graphene oxide biocomposite film

As many as 2 grams of chitosan were dissolved into 200 ml of aqueous acetic acid 2% to prepare chitosan solution. The mixture was stirred continuously at room temperature. The graphene oxide powder (0.2 g) was dispersed into 20 ml of distilled water. Thus, the graphene oxide was added in chitosan solution under stirring at room temperature for 1 hour followed by sonication for 1 hour with 50/60 Hz to ensure a homogeneous dispersion of chitosan/graphene oxide in solution. The mixed solution was cast on glass plate and then dried in water at a temperature 50°C for 8 hour. The films containing 0, 5, 10, 15, 20, 25 % GO were removed from the glass plate and cut.

2.4. Characterization

The Fourier Transform Infrared (FT-IR) spectra for graphite of pencil rod, graphene oxide, chitosan, and chitosan/graphene oxide biocomposite film were recorded on a Shimadzu IR prestige 21. FT-IR spectra were measured in the range 4000-500 cm⁻¹. Powder samples were mixed with KBr and pressed it into a thin pellet used for analysis.

To clarify the crystal structure of fine graphite, graphite of pencil rod, graphene oxide, wide-angle X-ray Diffraction (XRD) measurements were recorded using Shimadzu XRD-6100. The Cu-Kα was used as the source (wavelength \( \lambda = 0.1542 \)), the recorded region of 20 was 5-45°.

The tensile properties of cast sample were measured using a Gotech AI 7000 M at room temperature. A 1 kN load cell was used and the strain rate was 5.0 mm/min. To ensure data accuracy and repeatability, at least 3 measurements were carried out for each biocomposite film.

The morphology of biocomposite films was observed using Scanning Electron Microscopy (SEM), JSM-35 C Shumandju. The films were frozen in liquid nitrogen, and immediately snapped and then sputtered with gold before observation.

3. Result and discussion

Chitosan and graphene oxide can be well mixed and form homogeneously aqueous solution, and the obtained mixture is stable at the room temperature. After mixing, the solutions of chitosan or chitosan/graphene oxide were casted onto substrates, there formed the films. FTIR studies confirmed the successful oxidation from graphite extracted from pencil rod to graphite oxide. The FT-IR spectrum of graphite of pencil rod which is displayed in figure 1 depicts strong OH peak at 3410.15 cm⁻¹ and C=O group at 1620.1 cm⁻¹ while the spectrum also shows a C-C peak at 1056.99 cm⁻¹. The FT-IR spectrum of graphene oxide depicts a strong OH peak at 3394 cm⁻¹ and the other functional groups of C–O including COOH (1720 cm⁻¹), C–OH (1388 cm⁻¹), and C–O–C (1087 cm⁻¹) which are clearly visible. The spectrum also shows a C=C aromatic peak at 1580 cm⁻¹ while, for chitosan, the peak at 3425.58 cm⁻¹ which both of them are corresponding to N–H stretching vibration of amino group. The vibrations related with N-H bending and N-H deformation are at 1566 cm⁻¹ and 1404.18 cm⁻¹, respectively. According to the FTIR’s result, the peak of 1404.18 cm-1 indicates the presence of vibration mode C-OH. The peaks characteristics absorption in the curve of CS/graphene oxide are approximately similar with the curve of fine chitosan as shown in Fig. 1. The FT-IR spectrum of the CS/graphene oxide compound shows a combination of characteristics which is similar to that of fine chitosan and graphene oxide which includes the broad absorption of band is located at 3425.58 cm⁻¹, assigned to the mixture of the amine stretch from the chitosan to the OH groups in graphene oxide. The peak at 1620.21 cm⁻¹ illustrates the presence of the COOH groups from graphene oxide and is downshifted due to hydrogen bonding between the graphene oxide and hexatomic ring of the chitosan.
On the other hand, the peak at 1566.2 cm\(^{-1}\) presents the C=C groups from graphene oxide and it also indicates the presence of N-H bonding that is resulted from chitosan. The spectrum of the N-H deformation from chitosan represented at 1411.89 cm\(^{-1}\). The peak in the region about 1080.14 cm\(^{-1}\) is the indication of C–O–C stretching from the graphene oxide layers. The FT-IR results indicate the existence of the interaction between chitosan and graphene oxide.

![Figure 1. FT-IR spectrum from graphite of pencil rod, chitosan, graphene oxide, and chitosan/graphene oxide film](image)

The XRD patterns of graphite of pencil rod, graphite powder, and graphene oxide are depicted in figure 2 performed in the range of 5°-70°. The diffraction angles of the graphite of pencil rod forms peak 26.369° with d-spacing 3.7721 Å. On the other side, the commercial graphite forms peak 26.6025° with d-spacing 3.34810 Å. That is proves that the graphite of pencil rod compound have a lot of percentage of graphite. Graphene oxide form a new peak is 9.0715° with d-spacing 9.74063Å. The change of angle XRD patterns are shifted toward the left shows the occurrence of a material change to the nature of crystallinity. Graphene oxide is reduced (Taufantri, et al. 2016). Widening the distance between the layers of graphite pencils of 3.34810 Å into Graphene oxide at 9.74063Å. It occurs due to the formation phenol group, an epoxy group, ketone group, carboxyl group, and a carbonyl group. The addition of HmoleculesO\(_2\) and clusters of oxygen also causes graphene oxide has a d-spacing wider. (Taufantri, et al, 2016).
In this research, we performed tensile test to understand the mechanical strength of chitosan film and its variation based on the composition of the graphene oxide as the filler. The tensile test performed 2000 Kgf of force with speed approximately 5 mm for every minutes in condition of room temperature. The average film thickness of the film CS and CS / GO is 0.1 to 0.11 mm. The tensile strength of the film and the film biocomposite CS CS / GO can be seen in Table 1.

Table 1. Data Testing Mechanical properties of Graphene Oxide Film of Chitosan and CS/GO

| No. | Variations of biocomposite films | Maximum strain (MPa) | Modulus Young's (GPa) |
|-----|---------------------------------|----------------------|----------------------|
| 1   | CS                              | 5.83                 | 1.0                  |
| 2   | CS/ GO 95: 5%                   | 7.75                 | 0.9                  |
| 3   | CS/ GO 90: 10%                  | 10                   | 2.0                  |
| 4   | CS/ GO 85: 15%                  | 10.5                 | 2.9                  |
| 5   | CS/ GO 80: 20%                  | 5.68                 | 0.9                  |
| 6   | CS/ GO 75: 25%                  | 4.56                 | 1.6                  |

Table1 shows the addition of fillers on biocomposite ranging from weight variation of 5% increases the tensile strength of biocomposites CS/ GO ranging from 5.83MPa to 7.75MPa. The maximum tensile strength occurs in variations CS/ GO 85: 15% is equal to 10.5MPa while the minimum properties shown in variations of 75:25%. However, the tensile strength decreased with the addition of Graphene oxide by 20% and so on. The exact properties are also shown on the graph the stress-strain of chitosan films and films biocomposite CS/ GO displayed on Fig.3. The Modulus Young's of pure chitosan equals to 1.0 GPa. With the addition of fillers that graphene oxide film inbiocomposite CS/ GO increases the Modulus Young drastically in the variation of CS/ GO 85: 15%, around 2.9 GPa.
Figure 3. Graph Stress-Strain of Film and Film Chitosan Chitosan / Graphene Oxide

According to the Fig.3, the presence of graphene oxide as the reinforcement increases the stress-strain. But more importantly, the quantities of GO within the biocomposites are associated to the mechanical properties, in particular the tensile strength. The composition of CS/GO with variation of 85/15% affects the tensile properties in maximum numbers. The increase in tensile strength of the resulting biocomposite films may be due to the strength of hydrogen chain attached to the chitosan and graphene oxide and homogeneous distribution of chitosan and a high compatibility between graphene oxide layer and matrix assisted by a high interfacial surface area. However, the increase in weight gain by 20% Graphene oxide effects tensile test for impairment and Young's modulus. This may be caused by the large value of viscosity.

The results of SEM analysis of the film provide direct information about the interaction interface of the film that can be seen in Figure 8, showing the surface of the film CS and CS/GO. In figure 4a, it can be seen the film’s surface is clear without the presence of Graphene Oxide, while it also appears that the film does not have pores implying of high density caused by the dissolved in acetic acid 2%. In figure 4b, the surface of biocomposite CS/GO with variation ratio of 85:15% is illustrated mixed homogenously implying the uniformity and homogeneity in the distribution of Graphene oxide on the film. And the cross-linking and physical chain chitosan structure in the CS/GO (85:15) % is denser than the film CS, which predicts an increasing in the mechanical strength.

Figure 4. (a) SEM on the film CS, and (b) SEM CS / GO 85: 15%
4. Conclusion
The graphene oxide was successfully synthesized from pencils rod by using Hummer method, however, the quantities of the graphene oxide that has been extracted is small. Comparing from previous research, the graphene oxide synthesized from pencils rod is smaller than those which from natural graphite significantly. Furthermore, the crystallinity of both graphite and graphene synthesized from pencils rod are similar to those which are synthesized from natural graphite. The mechanical properties of film biocomposite is influenced by the presence of graphene oxide as reinforcement. Based on the tensile test, the optimum composition of chitosan and graphene oxide is 85:15%, which contributed for 10.5 Mpa and 2.9 GPa of Modulus Young. While the minimum numbers of tensile test and modulus Young is contributed by the composition of 75:25%, accounted for 4.56 and 1.6, respectively.

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6. References

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