Fabrication of Graphene Oxide/Calcium Carbonate/Chitosan Nanocomposite Film with Enhanced Mechanical Properties

M Handayani1,*, E Sulistiyono1, F Rokhmanto1, N Darsono1, P L Fransisca1, A Erryani1 and J T Wardono1
1Research Center of Metallurgy and Materials, Indonesian Institute of Sciences
*E-mail: murni.handayani@lipi.go.id

Abstract. Nanocomposites are an attractive field of materials providing novel performance owing to their remarkable properties at low filler loading. Currently, they are being increasingly used by industry whilst displacing the use of conventional filler materials. A lot of nanoscale fillers are capable to enhance mechanical and thermal properties of nanocomposites. Graphene, a single layer of carbon atoms in a hexagonal lattice, has recently attracted much attention due to their novel electronic and mechanical properties. Graphene and graphene oxide show very high mechanical properties with well biocompatibility, and they have potential application as biomaterials. Therefore, 2D graphene or graphene oxide sheets are expected to offer promising nanoscale filler for the next generation of nanocomposite materials. Here, Graphene Oxide/Calcium Carbonate/Chitosan (GO/CaCO3/CS) Nanocomposite Film has been fabricated by the blending aqueous solution. The graphene oxide used in this study was synthesized by chemical way using modified hummer’s technique. The graphene oxide resulted from hummer’s method was characterized by IR, XRD and SEM-EDX. The measurement result of the mechanical properties of the nanocomposite film showed that with adding GO content in the composite enhanced the tensile strength and peaks at the content of GO 5 % due to good dispersion of the graphene oxide as nano-scale fillers.

1. Introduction
Nanocomposites are an attractive field of materials providing novel performance owing to their remarkable properties at low filler loading. Recently, they are being increasingly used by industry whilst displacing the use of conventional filler materials. A lot of nanoscale fillers are able to enhance mechanical and thermal properties of nanocomposites [1].

Graphene is one atomic layer sheet of carbon atoms with sp2 hybridized two dimensional honeycomb structure, has recently attracted much attention due to their fascinating physical, chemical, optics and mechanical properties. It’s a single atomic layer of the graphite with each carbon atom bonded with strong covalent bonds [2]. The potential applications of this unique nanostructure hold novel promises for various industrial and professional fields such as nanoelectronics, sensor applications, composite materials, energy storage, and hydrogen storage [3]. Besides that, graphene and graphene oxide exhibit very high mechanical properties with well biocompatibility, and very promising as functional biomaterials [4]. 2D graphene or graphene oxide sheets are expected to offer very potential nanoscale reinforcements for the next generation of nanocomposite materials [5]. Nevertheless, the neat graphene does not have functional groups which restricts the dispersibility in the matrix and limits the applications of graphene as nanoscale filler in nanocomposite materials.
Graphene oxide is more appropriate than the neat graphene owing to the higher contents of oxygen functional groups such as hydroxyl and epoxides [6].

Chitosan is a natural polymer found in the exoskeleton of crustaceans, produced by de-acetylation of chitin, composed mainly of b-(1,4)-linked 2-deoxy-2-amino-D-glucopyranose units. Chitosan is one of the most abundant natural biopolymer which is an antibacterial, biocompatible, non-toxic, edible biodegradable polymer with good mechanical properties and it is widely used for food packaging, biosensor, water treatment, biomedicine, drug delivery and as a matrix of biomaterial for bone tissue engineering [1,5].

Calcium carbonate, a natural mineral with great biocompatibility, is one of the most common and inexpensive inorganic filler that has been widely used in industry, technology, and many other fields. Along with technological developments, the use of calcium carbonate, especially with particle size in nanoscale, is not only for fillers but also for biocompatible materials with has advantage that is easily adaptable in human body [5,7,8].

In this work, we reported the facile preparation of graphene oxide and used as nano-fillers material of graphene oxide/calcium carbonate/chitosan nanocomposites by blending and casting method. The effect of the loading of graphene oxide contents to the mechanical properties of the nanocomposites was investigated.

2. Experimental
2.1. Materials
Graphene oxide (GO) was synthesized by modified hummer’s method using graphite powder which was purchased from Merck. The other chemical such as KMnO₄, NaNO₃, 98% H₂SO₄, NaOH, Hac and 30 % H₂O₂ are analytical grade chemical. Chitosan (CH) was purchased from Merck. Calcium carbonate (CaCO₃) nanoparticles with average of size around 100 nm was obtained from natural limestone which was synthesized using ultrasonic method reported in the previous study [7, 8].

2.2. Experiment
2.2.1. Preparation of Graphene Oxide
Graphene oxide was synthesized by well known modified Hummer’s method. 1 g natural graphite powder was added into a 250 mL beaker, then 0.5 g NaNO₃ and 23 mL H₂SO₄ were added into it under stirring in an ice-bath. 5 gr KMnO₄ was added slowly into the beaker with stirring and the temperature was controlled under 20 °C. After maintaining the mixture stirred below 20 °C for 2 hours, increase the temperature to 35-40 °C and the reaction was kept for around 14 hours. Next step, add hydrogen peroxide and distilled water into the brown paste mixture and stir for 30 mins. Then, add some amount of distilled water into the mixture to neutralize the pH and dilute the mixture. After that, 1 M HCl was added and followed by adding distilled water to neutralized the solution. The result was filtered and dried in oven at 80 °C. To exfoliate the graphite oxide become graphene oxide, we applied the ultrasonication for around 30 minutes and then centrifugation.

2.2.2. Preparation of Graphene Oxide/Calcium Carbonate/Chitosan
Desired concentration of oxidized graphene oxide powder from natural graphite obtained from the above synthesis was dispersed in distilled water and sonicated for around 30 minutes. After that, 0.4 g powder of nano calcium carbonate precipitates was added and followed with adding by 100 ml of ultrapure water. The solution was then sonicated for 90 minutes then stirred for one night at room temperature. After that, 1 ml acetic acid glassial (HAc) was added to the solution and 1.5 g chitosan were added into the suspension under stirring for 60 minutes. The mixture solution was cast on the glass plate and it was kept at room temperature and then dried at 50 °C. The dry nanocomposite films were then immersed in 0.1 NaOH and followed by washing the film with water and dried at room temperature for 24 hours. Finally the nanocomposites films were dried in oven at 50 °C. We prepared 4 samples nanocomposites films as follows : Chitosan film without adding the reinforcement of graphene oxide and calcium carbonate (CH), calcium carbonate/chitosan films with content of
graphene oxide is 1% (GO1/CAL/CH), graphene oxide/calcium carbonate/chitosan with content of graphene oxide is 5% (GO5/CAL/CH) and graphene oxide/calcium carbonate/chitosan with content of graphene oxide is 10% (GO10/CAL/CH).

2.2.3. Characterization
The characterization of the crystal structure of graphene oxide was done by X-Ray Diffraction (XRD). The morphology and elemental analysis of graphene oxide were performed by SEM-EDX JEOL with Type JSM-6390A. The mechanical properties of nanocomposite films such as tensile properties, young’s modulus and break elongation were characterized by using Tinius Olsen, 300 SL, Super L-60.

3. Results and Discussion
3.1. Analysis of graphene oxide using Fourier Transform Infrared (FT-IR)
The results of the analysis using FT-IR for graphene oxide is depicted in Figure 1. FT-IR technique is used in this analysis to investigate the functional group which can confirm the bond interaction of graphene oxide. A strong and broad band at 3425.58 cm\(^{-1}\) is indicated the O-H stretching vibration. The peak at in the range 1630 cm\(^{-1}\) to 1650 cm\(^{-1}\) show the C=C bond. Peak at 1620 cm\(^{-1}\) is attributed to C=O stretching vibrations, and the peak at 1057 cm\(^{-1}\) is attributed to C-O-C bond which is appropriate with the previous report [9].

![Figure 1. FT-IR spectra of graphene oxide.](image)

3.2. Analysis of graphene oxide by X-Ray Diffraction (XRD)
The X-ray Diffraction Analysis / XRD is the most common used technique to characterize crystalline material. The average spacing’s between layer or row of atoms can be measured by this technique. Besides that, XRD can be applied to determine the orientation of a single crystal. The analysis of graphene oxide synthesized by hummer’s method is demonstrated in Figure 2.
It is known that the diffraction peak of pure graphite is at 2θ around 26° due to the interlayer distance of 0.335 nm \([9,10]\). Here we confirm that graphene oxide demonstrate a typical diffraction peak at 2θ around 9.9° with d-spacing = 0.89 nm which is indicated to the typical peak of GO. The disappearance of the peak at 26° proves that the compound result is completely oxidized after treatment of the oxidation and exfoliation of graphite resulted the formation of oxygen-containing functional groups.

3.3. Analisys of graphene oxide by scanning electron microscopy-Energy-dispersive X-ray spectroscopy (EDX)

![Figure 2. XRD Analysis result of graphene oxide.](image)

![Figure 3. (Left) SEM analysis result of the graphene oxide produced by hummer’s method, (Right): EDX analysis result of the graphene oxide.](image)
The result of SEM analysis for graphene oxide is shown in figure 3. The magnification of the image was taken at 25,000 x. The result indicates that the typical surface morphology of the graphene oxide have well observed and show a porous interlinked three dimensional graphene layer. The elemental analysis result obtained from EDX analysis shows that the majority of the content of the compound is carbon (with 62.93% of mass) and following with oxygen (with 35.44% of mass) which proves the existence of graphene oxide. The existence of sulfur element even though it is a very small content (1.63 % of mass) indicated that the neutralization of the sample is not performed completely.

3.4. Mechanical properties of nanocomposites films
We investigate the mechanical properties of the nanocomposites films to observe the effect of adding the different of the content of graphene oxide in the nanocomposites. We compared also to the adding the chitosan matrix with calcium carbonate only without adding the graphene oxide. The results of the mechanical properties of the nanocomposites such as tensile strength, young’s modulus, and elongation at break are shown in Table 1.

| Sample Code      | Ultimate Force (N) | Tensile Strength (Mpa) | Young's Modulus (Gpa) | Elongation (%) |
|------------------|--------------------|------------------------|-----------------------|----------------|
| CH               | 19.8               | 16.5                   | 4.52                  | 4.3            |
| GO1/CAL/CH       | 85.2               | 71                     | 3.45                  | 9.8            |
| GO5/CAL/CH       | 102                | 85.2                   | 5.68                  | 14.8           |
| GO10/CAL/CH      | 88.5               | 73.8                   | 6.21                  | 4.19           |

The tensile strength of chitosan without adding the nanoscale filler give the result of 16.5 Mpa and increase to 71 Mpa with adding the fillers nanoparticles. The result demonstrate that the nanoscale filler can increase the tensile strength significantly compared to the pure chitosan. The calcium carbonate supports the graphene oxide filler to the chitosan matrix so that increases the tensile strength significantly. Note that we use the same weight of the calcium carbonate and the results show that the increasing of the tensile strength of the nanocomposites is mainly due to the content of GO addition on the nanocomposites films. The detail graphic of the mechanical properties of the nanocomposites films was shown in Figure 4.

Increasing the percentage of GO on the nanocomposite make the tensile strength higher with the maximum tensile strength is 85.2 Mpa with the loading of the GO content of 5%. This means that increasing GO content enhances the tensile strength due to the good dispersibility of the nanofiller into matrix and resulting the higher reinforcement effect. However, when the content of GO is increased further to 10%, the tensile strength is decreasing to 73.8 % as a result of the agglomeration of the GO particles at higher contents and give rise the dispersion the fillers in the matrix is not homogenous.
Figure 4. Measurement results of the mechanical properties of nanocomposite films.

The addition of the nanoscale fillers on the nanocomposite film causes the young modulus increases gradually with the maximum 6.21 GPa by adding of 10% GO in the nanocomposites films. Besides, the elongation at the break point is increasing gradually until the maximum at the addition of 5% GO content and then drastically reduces after the addition of GO content 10%. The result can be attributed to the interaction between higher content of GO with the matrix which restrict the movement of the chitosan chain.

4. Conclusion
The graphene oxide was successfully synthesized by hummer’s method and the result was confirmed by FT-IR, XRD and SEM-EDX. The obtained graphene oxide was used as nanoscale reinforcement materials in the nanocomposites films. The mechanical properties of the nanocomposites were affected by the addition of the graphene oxide as reinforcement. Based on the result of tensile strength measurement, the tensile strength of the nanocomposite increased significantly and reached the maximum with value is 85.2 Mpa with the addition of 5% GO due to good dispersion of graphene oxide in the nanocomposites. The young modulus increases gradually with the maximum 6.21 GPa by adding of 10% GO in the nanocomposites films. Besides, the elongation is increasing gradually until the maximum at the addition of 5% GO content and then drastically reduces after the addition of GO content 10%.

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