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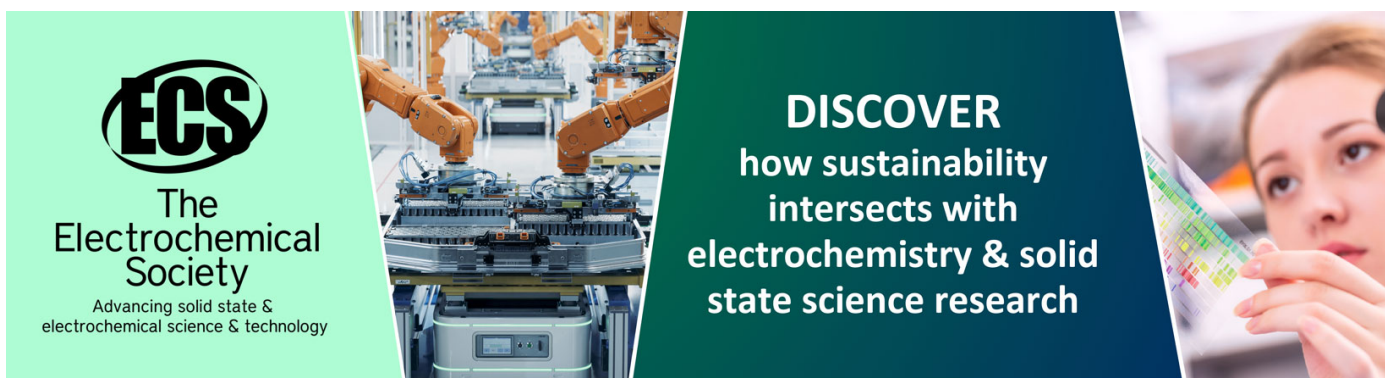
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The Influence of Graphene Oxide and Cristobalite Phase of Silica Precipitate on Chitosan – Based Nanocomposites

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Abstract. Nanocomposites are commonly used as fillers with size at the nanoscale and have low loading, have the potential to match or significantly improve performance to supply conventional composites. Graphene oxide (GO), an oxidative exfoliating product of natural graphite, has attracted much attention due to its excellent strengthening effect on polymers. Young modifications of the GO sheet and the strong interaction interface between GO and the matrix polymer. Therefore, graphene oxide is expected to offer a promising nanoscale for the next generation of nanocomposite materials. Besides that, silica precipitate a critical materials used in many applications worldwide. Silica Precipitates have become key fillers in nanocomposites due to their properties which can improve mechanical properties. In this study, Chitosan-based Nanocomposite Films have been made by casting methods. The effect of graphene oxide and silica precipitates on the chitosan film and their properties were investigated. Graphene oxide used in this study was synthesized with chemicals from pure graphite using the Hummer Method. Graphene oxide produced from the hummer method was characterized by X-Ray Diffraction and Scanning Electron Microscope. Silica precipitates in this study uses cristobalite phase of silica. The measurement results of the mechanical properties of nanocomposite films show that adding cristobalite phase of silica precipitate content in composites increases the tensile strength of 21.3 Mpa and higher than addition of GO in the chitosan films. Meanwhile, addition of GO in chitosan film increases the young modulus up to 2.73 Gpa.

1. Introduction

Graphene oxide (GO) is a potential nanocarbon-based material with attractive in many applications, including nanocomposites, electronics, sensor, and functional biomaterial [1-2]. Graphene oxide has superior properties, such as high conductivity, high mechanical strength, a high aspect ratio and unique graphitized plane structure. [1] GO is obtained by the controlled oxidation of graphite. GO consists of covalently attached oxygen groups such as hydroxyl, epoxy, carbonyl and carboxyl groups. Hence, GO is hydrophilic and readily swell and disperse in water. The polar functional groups attached on the basal planes and at the edges of GO sheets can change their remarkable properties. GO can be dispersed through functionalization, or chemically revamp to make various graphene-based nanocomposites with superior mechanical and thermal properties [2-3].



Chitosan (CS) has attracted great interest of researchers owing to its superior biocompatibility, hypotoxicity, antimicrobial activities and biodegradability. [4] Chitosan is one of the most abundant natural polysaccharides on earth, it is widely used for biosensors, food packaging, water treatment, separation membrane, artificial skin, tissue engineering and drug delivery system. Chitosan a (1-4)-linked 2-amino-2-deoxy- β -D-glucopyranose, is derived from chitin, a (1-4)-linked 2-acetamido-2-deoxy- β -D-glucopyranose [5]. Nevertheless, biofilms made only from chitosan shows poor water resistance, low mechanical properties and thermal stability, which limit them from wide-ranging applications. On the other hand, nanocomposite technology using nanofillers such as clay, silica, carbon nanotubes and graphene has already demonstrated to be an effective way to enhance the electrical, mechanical and thermal properties of nanocomposites [5-6].

Silica (SiO_2) represent many functions and it has already been widely utilized in many applications such as for the glass, ceramic, cement, sandblasting industries, as well as supporting materials for the metal casting, oil and mining industries, and refractory bricks [7]. SiO_2 has hydroxyl groups on its surface, which facilitates the formation of hydrogen-bonding interaction between SiO_2 and polymers. It has been demonstrated that SiO_2 can be used as a reinforcement nanofiller to enhance the mechanical properties of composite materials. The reinforcement mechanisms are attributed to the good stiffness of SiO_2 and the chain-like structure of aggregated SiO_2 nanoparticles as well as the hydrogen-bonding interaction between SiO_2 and polymers [8].

In this study, chitosan based-nanocomposites was prepared by blending and casting technique. The affect of graphene oxide and cristobalite phase of silica precipitate for the properties of nanocomposites was investigated.

2. Experimental

2.1. Materials

Graphene oxide (GO) was prepared by modified hummer's technique using graphite powder which was purchased from Merck. The other chemical such as KMnO_4 , NaNO_3 , 98% H_2SO_4 , NaOH , Hac and 30 % H_2O_2 are analytical grade chemical. Chitosan (CS) was purchased from Merck. Cristobalite Phase of Silica Precipitate is obtained from PT. Lautan Luas Tbk.

2.2. Preparation of Graphene Oxide

Graphene oxide was synthesized by modified Hummer's method as presented in our previous studies [9-10].

2.3. Preparation of Nanocomposites Film

3 mg of Graphene Oxide was added with 50 mL of distilled water and then sonicated. After sonication, 50 mL ethanol and 1.5 ml glacial acetic acid was added to the solution followed with stirring the mixture and then 1 gram of chitosan was added and stirred for 60 minutes. The mixture was poured into a petri dish and allowed to stand until dry and oven at $<50^\circ\text{C}$. After drying, a biocomposite film GO / Chitosan was obtained. We prepared 3 samples of nanocomposite films as follows: graphene oxide / chitosan film without adding silica precipitate (GCS), silica precipitate / chitosan film without adding graphene oxide (SCS), and graphene oxide / silica precipitate / chitosan film (GSCS) with each weight of graphene oxide and silica precipitate is 3 mg respectively, each dissolved in 25 mL of distilled water.

2.4. Characterization

The characterization of the graphene oxide resulted from the synthesis was conducted by X-Ray Diffraction (XRD). The morphology and elemental analysis of graphene oxide and Nanocomposites were performed by Scanning Electron Microscopy (SEM)- Energy-dispersive X-ray spectroscopy (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.

2.5. Methanol Uptake Test of Nanocomposite Film

Methanol uptake is done by measuring the difference in membrane weight before and after immersion in methanol. Dry weight (W_d) was measured from the membrane which was dried for 24 hours at room temperature. Wet weight (W_w) was measured from a membrane immersed in 5 M of methanol for 24 hours.

3. Experimental Result

3.1. Analysis of Graphene Oxide

Crystal structure analysis of Graphene oxide was performed using XRD. The results are shown in Figure 1. The successful result of graphite oxidation is indicated by the absence of the diffraction peaks of pure graphite, due to the introduction of the oxygen function to the basal carbon plane. It was found that the sharp diffraction peaks were observed at $2\theta = 10.66^\circ$ with an interlayer distance of 0.82 nm and no diffraction peak of pure graphite were found at $2\theta = 26$ which indicated that Graphene Oxide has been successfully synthesized [11-13].

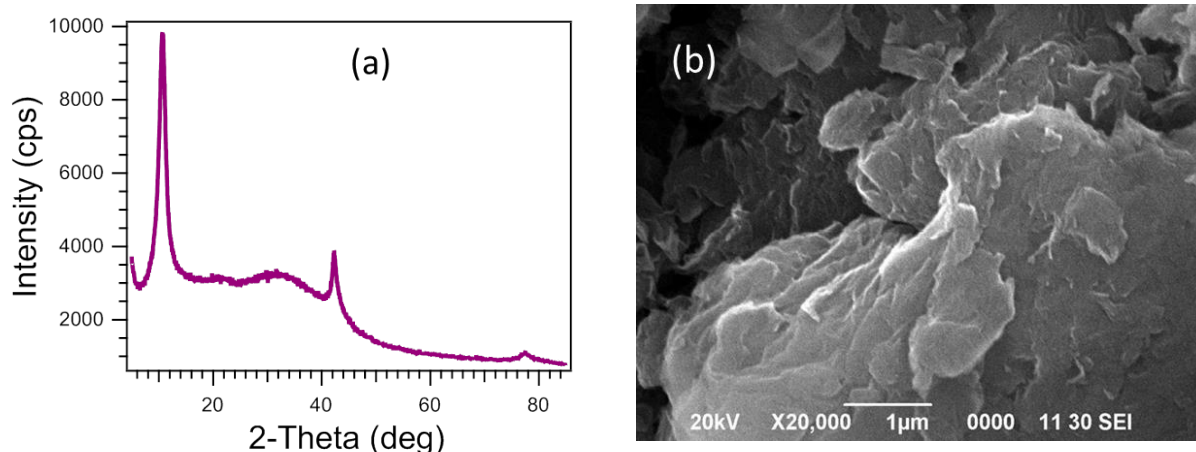


Figure 1. Analysis Result of Graphene oxide by (a) XRD and (b) SEM with 20.000x magnification

SEM measurement was carried out to determine the morphological structure of the surface of Graphene Oxide. Figure 1.b is a surface morphological image using SEM analysis at a magnification of 20.000x of the GO after sonication treatment. The SEM analysis shows that the exfoliation of the graphite layers surface forming the porous three-dimensional layer of graphene. The exfoliation of the layers indicates fairly fine sheets with almost the same for size distribution. The sheets and wrinkled areas in the SEM results show the characteristics of GO which are consistent with the results of our previous studies [9,12].

3.2. Analysis result of Nanocomposites

Biocomposite film characterization was carried out using SEM aims to determine the morphology of a nanocomposites and by using EDX to obtain the chemical composition contained in the nanocomposites. We choose the biocomposite film of GSCS for the observation by SEM-EDX due to the complete composition of graphene oxide, cristobalite phase of silica precipitate and chitosan. The SEM-EDX results obtained are as follows:

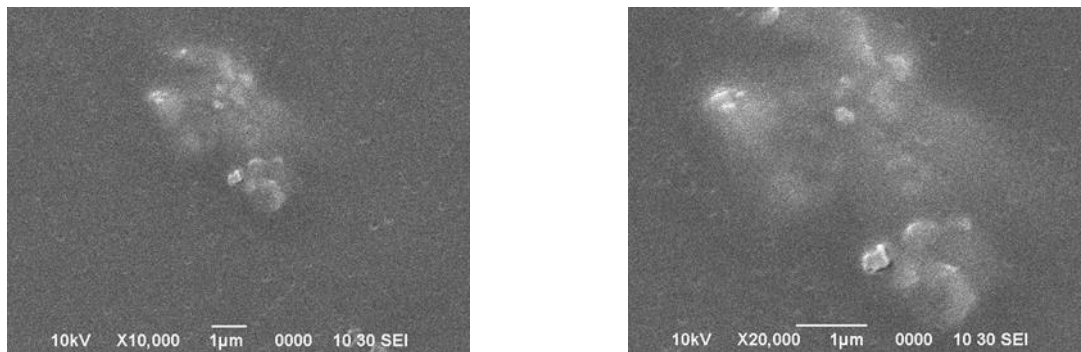


Figure 2. Results of SEM Mapping of nanocomposites GSCS at : a).Magnification of 10.000x, b) Magnification of 20.000x

The morphology of GSCS Biocomposite Film can be seen from SEM characterization in figure 2. Smooth morphology indicates that graphene oxide is well dispersed. In addition, the surface of the composite film shows good homogeneity, showing the incorporation of chitosan and graphene oxide in the composite. However, there are several areas with SiO_2 particles still clump together and form small agglomerates in the composite matrix. This means that the dispersion of SiO_2 in the biocomposite film needs to be increased. The EDX observation for GSCS composite is shown in figure 3 below. The composite contents of carbon, oxygen and silica, with the mass percentage of the element for carbon, oxygen and silica is 67.21 %, 27.37% and 5.42 % , respectively. The element of carbon and oxygen indicates the content of graphene oxide and chitosan in the composite , while silica content of 5.42% indicates the cristobalite phase of silica precipitate dispersion in nanocomposite film.

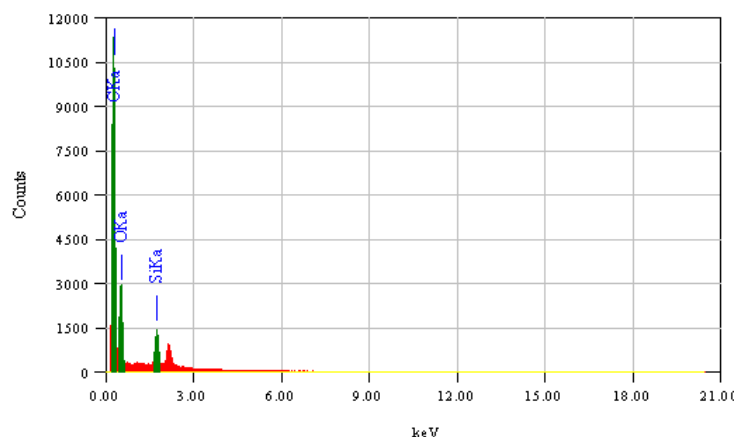


Figure 3. Results of EDX observation of GSCS composite

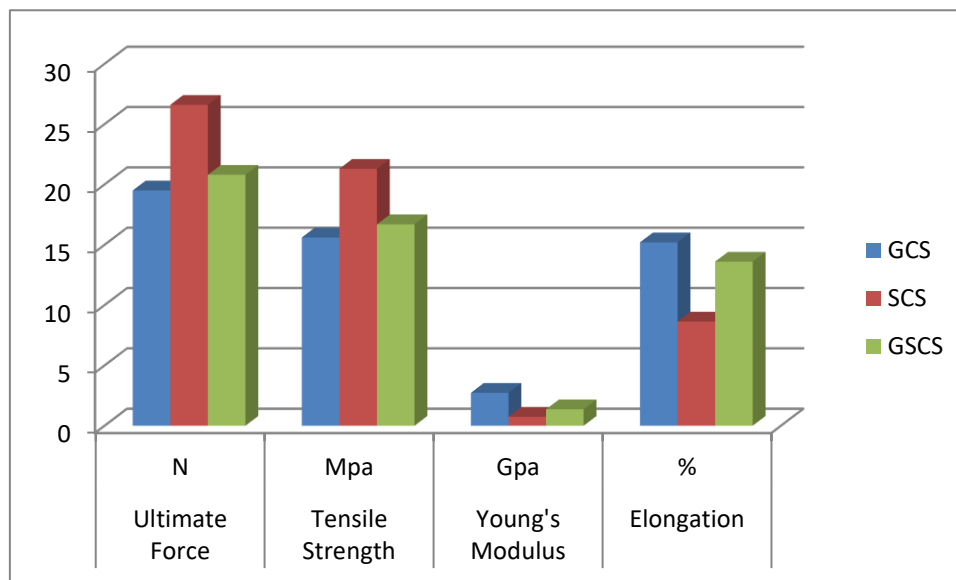
3.3. Mechanical Properties of Nanocomposites

Characterization of mechanical properties is used to determine the strength of the composite membrane against forces coming from outside that can damage the membrane. The mechanical properties of the biocomposite film were observed for the addition of graphene oxide and cristobalite phase of silica precipitate to the chitosan-based biocomposites . The results of the mechanical properties of the nanocomposite films such as tensile strength, Young's modulus, and elongation are shown in Table 1.

Table 1. The results of mechanical properties for GCS, SCS and GSCS nanocomposites

Sample code	Ultimate Force	Tensile Strength	Young's Modulus	Elongation
	N	Mpa	Gpa	%
GCS	19.5	15.6	2.73	15.2
SCS	26.6	21.3	0.75	8.64
GSCS	20.8	16.7	1.36	13.6

The tensile strength of the nanocomposites are shown in table 1 indicating that cristobalite phase of silica precipitate-chitosan composite (SCS) gives the highest tensile strength compared to the other composites, with the value of the tensile strength of the SCS is 21.3 Mpa. The result demonstrates that the silica precipitate is effective as a filler of nanocomposite which increases the tensile strength significantly. The detail bar chart of the mechanical properties of the nanocomposites films are shown in figure 4 below.

**Figure 4.** Bar chart of the mechanical properties of nanocomposites.

However, the addition of the silica precipitates give rise to the lowest young's modulus and the elongation of break point for the SCS nanocomposites. Meanwhile, the addition of graphene oxide to the chitosan matrix increase the young modulus and elongation at break. It is depicted for the nanocomposites of GCS and GSCS which the value of young modulus are 2.73 Gpa and 1.36 Gpa, respectively. Furthermore, the elongation at break point for GCS and GSCS is higher compared with SCS. The value of elongation at break point of GCS and GSCS are 15.2% and 13.6%, respectively. The enhancement of young modulus and elongation by the addition of graphene oxide as nanoreinforcement in the chitosan matrix indicate that interfacial adhesion improved owing to the compatibility of graphene oxide to the matrix composite [14-15]. The homogeneity and the excellent dispersion of graphene oxide as a filler in the matrix is also important to affect the young modulus and elongation which match well with the result of morphological image of the nanocomposites [4], where the silica precipitate is found agglomerated in several areas from the SEM investigation. Such agglomerations give rise to lower the effectiveness of nanofillers for the function of reinforcement.

The maximal load transfer will be achieved if the nanofillers are well dispersed at molecular level in the matrix [16].

3.4. Methanol Uptake Test of Nanocomposites Film

Methanol permeability is the passage of methanol into a nanocomposite membrane. The percentage of methanol uptake shows the ability of the nanocomposite membrane to absorb methanol, the permeability value of methanol in a membrane can be predicted. The nanocomposite membrane characterization for methanol uptake as described as follows. The weight of wet membrane was recorded, and then, the liquid in the membrane and the liquid droplets on the surface of the membrane were removed. After that, the moist membrane was dried at temperature of 120 °C for at least 24 h. The weight of the membrane in the dry state were also recorded. Using equation 1, methanol uptake (%) was determined.

$$\% \text{ Methanol Uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \dots (1)$$

The result of methanol uptake is shown in Table 2 below.

Table 2. Methanol uptake for GCS, SCS and GSCS nanocomposites

Sample code	Methanol Uptake %
GCS	0 %
SCS	0 %
GSCS	88.9 %

The methanol uptake of the GCS, SCS and GSCS nanocomposite membrane is shown in Table 2. For GCS and SCS nanocomposite membrane, there are no methanol uptakes occurring in nanocomposites, meanwhile the methanol uptake for GSCS increase significantly up to 88.9 %. This result indicates that synergistic effect of the nanofillers of graphene oxide and silica precipitate for methanol uptake of nanocomposites is observed [8].

4. Conclusion

Chitosan based-nanocomposites was prepared successfully by blending and casting technique. Graphene oxide as nanofiller was synthesized from pure graphite and characterization was done by XRD and SEM. The characterization result showed that Graphene Oxide has been successfully synthesized. The characterization of nanocomposite was performed by SEM-EDX analysis. The surface of the composite film shows good homogeneity, showing the incorporation of chitosan and graphene oxide in the composite. However, there are several areas with SiO₂ particles still clump together and form small agglomerates in the composite matrix. The affect cristobalite phase of silica precipitate for the mechanical properties indicated that the silica precipitate is effective as a filler of nanocomposite which increases the tensile strength significantly. However, the addition of the silica precipitates give rise to the lowest young's modulus and the elongation of break point for the SCS nanocomposites. Meanwhile, the addition of graphene oxide to the chitosan matrix increase the young modulus and elongation at break. The enhancement of young modulus and elongation by the addition of graphene oxide as nanoreinforcement in the chitosan matrix indicates that interfacial adhesion improved owing to the compatibility of graphene oxide to the matrix composite. The result of methanol uptake of nanocomposite indicates that synergistic effect of the nanofillers of graphene oxide and silica precipitate is observed.

Acknowledgment

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References

- [1] N. Shaari, S. K. Kamarudin, S. Basri, L. K. Shyuan, M. S. Masdar, and D. Nordin, "Enhanced Proton Conductivity and Methanol Permeability Reduction via Sodium Alginate Electrolyte-Sulfonated Graphene Oxide Bio-membrane," *Nanoscale Res. Lett.*, vol. 13, 2018.
- [2] P. P. Zuo *et al.*, "Fabrication of biocompatible and mechanically reinforced graphene oxide-chitosan nanocomposite films," *Chem. Cent. J.*, vol. 7, no. 1, pp. 1–11, 2013.
- [3] D. Han, L. Yan, W. Chen, and W. Li, "Preparation of chitosan/graphene oxide composite film with enhanced mechanical strength in the wet state," *Carbohydr. Polym.*, vol. 83, no. 2, pp. 653–658, 2011, [Online]. Available: <http://dx.doi.org/10.1016/j.carbpol.2010.08.038>.
- [4] L. Shao, X. Chang, Y. Zhang, Y. Huang, Y. Yao, and Z. Guo, "Graphene oxide cross-linked chitosan nanocomposite membrane," *Appl. Surf. Sci.*, vol. 280, pp. 989–992, 2013.
- [5] J. Ma, C. Liu, R. Li, and J. Wang, "Properties and structural characterization of chitosan/poly(vinyl alcohol)/graphene oxide nano composites," *E-Polymers*, no. 033, pp. 1–13, 2012.
- [6] J. Ahmed, M. Mulla, Y. A. Arfat, and L. A. Thai T, "Mechanical, thermal, structural and barrier properties of crab shell chitosan/graphene oxide composite films," *Food Hydrocoll.*, vol. 71, no. September, pp. 141–148, 2017, [Online]. Available: <http://dx.doi.org/10.1016/j.foodhyd.2017.05.013>.
- [7] E. Febriana *et al.*, "Dissolution of quartz sand in sodium hydroxide solution for producing amorphous precipitated silica," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 858, no. 1, 2020.
- [8] X. L. Xu, X. F. Wang, J. Le Li, J. H. Yang, Y. Wang, and Z. W. Zhou, "Preparation of hybrid graphene oxide/nano-silica nanofillers and their application in poly(vinyl alcohol) composites," *Polym. Compos.*, vol. 38, pp. E89–E97, 2017.
- [9] N. M. Latiff, X. Fu, D. K. Mohamed, A. Veksha, M. Handayani, and G. Lisak, "Carbon based copper(II) phthalocyanine catalysts for electrochemical CO₂ reduction: Effect of carbon support on electrocatalytic activity," *Carbon N. Y.*, vol. 168, pp. 245–253, 2020.
- [10] M. Handayani *et al.*, "Synthesis of graphene oxide from used electrode graphite with controlled oxidation process," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 541, no. 1, 2019.
- [11] M. Handayani *et al.*, "Fabrication of Graphene Oxide/Calcium Carbonate/Chitosan Nanocomposite Film with Enhanced Mechanical Properties," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 578, no. 1, 2019.
- [12] Y. K. Krisnandi, I. Abdullah, I. B. G. Prabawanta, and M. Handayani, "In-situ hydrothermal synthesis of nickel nanoparticle/reduced graphene oxides as catalyst on CO₂ methanation," *AIP Conf. Proc.*, vol. 2242, no. June, 2020.
- [13] I. Larraza *et al.*, "Influence of process parameters in graphene oxide obtention on the properties of mechanically strong alginate nanocomposites," *Materials (Basel)*, vol. 13, no. 5, 2020.
- [14] D. Ege, A. R. Kamali, and A. R. Boccaccini, "Graphene Oxide/Polymer-Based Biomaterials," *Adv. Eng. Mater.*, vol. 19, no. 12, pp. 16–34, 2017.
- [15] S. I. Abdullah and M. N. M. Ansari, "Mechanical properties of graphene oxide (GO)/epoxy composites," *HBRC J.*, vol. 11, no. 2, pp. 151–156, 2015, [Online]. Available: <http://dx.doi.org/10.1016/j.hbrj.2014.06.001>.
- [16] J. Liang *et al.*, "Molecular-level dispersion of graphene into poly(vinyl alcohol) and effective reinforcement of their nanocomposites," *Adv. Funct. Mater.*, vol. 19, no. 14, pp. 2297–2302, 2009.