The study on physical and mechanical properties of latex/graphene oxide composite film

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Abstract. This study examined the effects of the addition of Graphene Oxide (GO) to the physical and mechanical properties of latex. GO was synthesized from the graphite of the pencil rod using the modified Hummer method. The composite was made by using stirrer and printed with casting method. Several tests were conducted in order to examine the properties. The swelling index was performed to examine the physical properties, tensile strength test to test the mechanical properties seen by tensile test, and lastly Scanning Electron Microscopy (SEM) to identify the morphology. The results show that the swelling index value changed with the addition of GO to the latex. The mechanical properties were increasing with optimum value of tensile strength with the quantity of GO as much as 4 phr, ie 3.72 MPa. Moreover, the morphology indicates the interaction that occurs between curative materials with the GO, causing the surface tighter and denser. It leads to the increasing of the tensile strength.

1. Introduction

Recently, natural rubber has begun to become the center of attention in the industrial world. This is due to the increasing number of consumer demand for goods from rubber raw materials. Industries that will absorb rubber marketing are the tire industry, automotive, asphalt, and others. Natural rubber has low physical properties when compared to those that have been given additional ingredients such as fillers. Therefore, it is necessary to add certain ingredients that can improve the characteristics so that this natural rubber can be produced into more useful products. Filling materials are added to natural rubber latex formulations to improve the physical properties of natural rubber latex so that high and can be used for the production of latex raw materials.

Fillers added to natural rubber latex can increase vulcanization of natural rubber so that its tensile strength and other mechanical properties will be increased [1]. Each type of filling material provides certain properties as a result of its specific chemical surface. The filler material with nanoparticle size is able to increase the value of polymer reinforcement compared to a large filler material [2]. Carbon black, silica, clays, boehmite, carbon nanotubes and etc., have been utilized as reinforcing fillers in the rubber industry.

One of the fillers that are being developed is graphene. Graphene has an arrangement of hexagonal-shaped atoms that resemble honeycomb and forms a sheet as thin as one atom [3]. One of the most
interesting characteristics of graphene is its highly ordered and almost perfect arrangement of atoms. graphene can be used as a filler in composite materials and more favored than other fillers, due to high surface area, aspect ratio, tensile strength, electrical and thermal conductivity, flexibility, ability to resist electromagnetic waves, transparency, and low thermal expansion coefficient [4].

But in the synthesis process, graphene requires a high cost. As one of the derivatives, graphene oxide can be an alternative [5]. Graphene oxide or commonly called graphite oxide or graphitic acid, is a compound of a mixture of carbon, hydrogen, and oxygen obtained through a strong oxidation process of graphite having a layered structure such as graphite, just the position of carbon atoms in graphene oxide plus the presence of groups of oxygen atoms which not only extends the distance between layers but also makes the atomic layer thick and hydrophilic. As a result, oxidation of this layer can interact with water under ultrasonification treatment [3,6].

2. Materials and Method
2.1. Materials
Graphite flakes were obtained from pencil rod 5B. Natural rubber (NR) latex with a total solid content of 60%. The ingredients including sulfur (S), zinc oxide (ZnO), Potassium hydroxide (KOH) and TMTD (Tetramethylthiuram disulfide). The reagent including concentrated sulfuric acid (H2SO4), potassium permanganate (KMnO4), Sodium nitrate (NaNO3), hydrogen peroxide (H2O2) were purchased from Merck.

2.2. Synthesis process of graphene oxide (GO)
Graphite oxide was synthesized from pencil rod 5B flakes according to a modified Hummers’ method. Briefly, as many as 2 g of pencil rod 5B flakes were added to 1 g of NaNO3 and 46 mL of H2SO4 and they were mixed by stirring process. Then, an amount of 6 g KMnO4 was added slowly. The system was kept in the ice-bath to keep the temperature low at 20 °C. Next, the mixture was heated at 35 °C for 20 hours, and slowly added with 92 mL distilled water and stirred for 15 minutes. After that, the mixture were added with H2O2 30% to reduce KMnO4 which losing the vapors and bubbles. The mixture was neutralized using the centrifugation at 7200 rpm in 10 minutes until its pH was 7, then it was treated by ultrasonicator at 50/60 Hz for 30 minutes. Finally, the GO powder was dried in oven at a temperature of 105 °C.

2.3. Preparation of NR/GO composite
The GO powder was dispersed in distilled water at 2mg/mL for 4 h and putted in ultrasonicator to produce a homogeneous suspension. Then, it was mixed with the natural rubber and the curative agent with stirring with magnetic stirrer for 2 h. The mixture was casted to plates glass and maturated for overnight at room temperature. Then, it was dried overnight at 70 °C, and continued by heating them at 100 °C for 15 mins for further drying to solve the cross-linking process. The formulation of the mixture was exhibited on the table below.

| Table 1. The formulation of the mixture |
|---------------------------------------|
|     Ingredients   | Phr |
|-------------------|-----|
|       NR          | 100 |
|    50% Sulfur     | 0.5 |
| 50% ZnO          | 0.25|
|     50% TMTD     | 0.75|
|        10% KOH   | 0.5 |
|       GO         | 1,2,3,4,5|

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2.4. Characterization
The film morphology was characterized using scanning electron microscope (SEM) (ZEISS). The film mechanical properties were conducted on a universal testing machine (RTF-1500) at room temperature with cross-head speed of 500 mm/min. The samples were prepared by cutting of 40 mm long and 10 mm wide whereas the thickness was measured each other. The distance between the jaws was 20 mm. The swelling test was carried out according to ASTM D 3616. The test pieces weight about 0.2 g. The sample was soaked in toluene for 24 hours.

3. Result and Discussion
3.1. Swelling index of NR/GO film
The Result of swelling index was shown in Table 2. The addition of graphene oxide as a filler in NR latex films has decreased the value of swelling index. Without addition the swelling index is 8.33 and it was changed with addition GO. From the result, the film has moderately vulcanized state.

| Sample          | Swelling Index |
|-----------------|----------------|
| NR              | 8.33           |
| NR/GO 1 phr     | 7.00           |
| NR/GO 2phr      | 6.70           |
| NR/GO 3phr      | 6.64           |
| NR/GO 4phr      | 6.35           |
| NR/GO 5phr      | 6.16           |

3.2. Morphology of NR/GO film
The morphology of NR/GO film was characterized by SEM, and displayed in Fig. 1. It shows the surface of latex film, where the curative materials has been distributed on the surface of latex. Fig. 1 (b) shows the film surface of latex/ graphene oxide film with 1 phr of graphene oxide. Graphene oxide has begun to form physical interactions with curative materials but still not formed a solid surface. In Figure 1.c shows the film surface of latex / graphene oxide film with 4 phr of graphene oxide. Graphene oxide formed physical interaction with curative materials and latex components to form composites that are more dense and evenly distributed. This also causes an increase in the tensile strength value of the latex / graphene oxide composite.
3.3. Tensile properties
The stress-strain curves of natural rubber and latex/graphene oxide film was given in Fig. 2. This figure showed significant improvement on tensile strength of latex and latex_GO films. With the addition of filler at latex from 1 phr variation can increase tensile strength of latex from 1.17 MPa to 2.77 MPa. This continued to increase to a maximum of 4 phr up to 255% and decreases with the addition of 5 phr. It is shown in Table 2. This sharp increase in stress was caused by strain-induced crystallization during the rapid stretching phase [7].

From the previous study, Chunmei et al. (2017) [7], obtained an increased tensile strength with the addition of 5% graphene oxide. Malas et al. (2012) [8], revealed a strong increase in Pull value with the addition of 3% graphite. From these results, it appears that GO has a stronger reinforcement effect on the increase in tensile strength of latex.

4. Conclusion
Graphene oxide as a reinforce agent for latex was prepared by mixing and casting method. The tensile strength was proven to be increased with the addition GO. The swelling index is also changed. Moreover, the morphology analysis revealed the interaction between GO and the curative agent in latex.

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6. References

[1] William J H 2008 *J. Waste Manag.* **29**(4) 797

[2] Leblanc J L 2002 *Prog. Polym. Sci.* **27** 627

[3] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorevia I V and Firsov A A 2004 *Science* **306**(5696) 666

[4] Dreyer D R, Park S, Bielawski C W and Ruoff R S *Chem. Soc. Rev.* **39** 228

[5] Amaturrahim S A, Gea S, Nasution D Y and Hutapea Y A 2018 *Asian J. Chem* **30**(7) 1564

[6] Gea S, Sari J N, Bulan R, Piliang A, Amaturrahim S A, Hutapea Y A 2018 *Journal of Physics: Conf. Series* **970** 012006

[7] Zhang C, Zhai T, Dan Y, Turng L S 2016 *Polym. Composite* **38**(1) 1

[8] Malas A, Das C K, Das A, Heinrich G 2012 *Mater. Des.* **39** 410