Mechanical Properties Optimization of Cellulose Nanofiber/Graphene Oxide Nanocomposite Produced by Mixing Method

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Abstract. This research implemented a green route to multifunctional nanocomposite materials composed by cellulose nanofiber (CNF) and graphene oxide (GO). Aqueous solutions with different ratio of GO (prepared with LiCl/DMAc 8%($^{w}/_{v}$)) were mixed with cellulose nanofiber by using magnetic stirrer at the temperature of 70 ^{o}C for 30 minutes. The mixture obtained was dried in room temperature for 24 hours. The nanocomposite were characterized with several analysis such as; Fourier Transform Infrared (FTIR), mechanical properties testing, Transmission Electron Microscope (TEM), and Scanning Electron Microscope (SEM) analysis. The characteristic of cellulose nanofiber functional groups was exhibited through FTIR spectra. The CNF/GO with 0.06wt% indicated a higher mechanical properties compared to the CNF. Its tensile strength increased drastically from 26.36 MPa to 49.69 MPa while its young's modulus also showed an extreme increase from 1.379381 GPa to 6.973478 GPa respectively. Moreover, cellulose nanofiber diameter had been examined through TEM and its morphology was analyzed with SEM. Finally, it can be concluded that the celulose nanofiber mechanical properties can be optimized by graphene oxide through the mixing process.

Keywords: Cellulose Nanofiber, Graphene Oxide, Nanocomposites, Mechanical Properties, Mixing Method.

1 Introduction

Oil palm empty fruit bunches (OPEFB)is by-product of steam sterilization process of oil palm plantations (PKS)(Or, Putra and Selamat, 2017), which can be used as a source of cellulosic fibers., while cellulose nanofibers or cellulose nanofibrils (CNFs) are obtained from OPEFB (Ferrer et al., 2012), which has at least one dimension in nanometer range and low thermal expansion, high specific area, good mechanical, optical properties are had them(Feng et al., 2018), obtained from the steam explosive method. Steam explosive method in alkali medium followed by hydrochloric acid treatment and high shear homogenization is an effective method to be used in the separation of cellulose nanofiber from lignin and hemicellulose (Saelee et al., 2016),(Kaushik and Singh, 2011).

Thus, the development of nanocomposites based on CNF is widely used in various regions as reinforcement and CNF has the ability to absorb more energy than synthetic fibers (Kalia et al., 2011)and usually be applied for sensors, cosmetics and biomedicine (Feng et al.,

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2018).One of the method in reinforcing CNF by reinforcement agents, such as graphene oxide (GO) (Wang, Wu and Huang, 2018).

Graphene oxide (GO) is a material where the electronegative oxygen atom is bound to the graphite structure(Lu, Ocola and Chen, 2009). GO can be generated by the Hummers method. The Hummers method is one of the methods used to oxidize strongly graphite using K2Cr2O7 or KMnO4(Sitko et al., 2013)-(Alam, Sharma and Kumar, 2017). The electrical, mechanical, and thermal properties of polymeric material could be improved by GO(Amaturrahim et al., 2018).

Improvement transitional behavior of mechanical and thermal properties of material composite using blending method with modify cellulose in solvent. Enhancing properties of cellulose can be greatly enhanced by inorganic fillers(Zhang et al., 2012). Nanocomposite materials based on renewable and natural polymer which was fabricated from fuctional graphene is importance. The comparing of filler and polymer matrix can lead to enhance functional properties and can be used potentially wide-ranging applications(Phiri et al., 2018).

In this studying, GO was fabricated from strong oxidation of graphite which was blended with LiCl/DMAc 8% via ultrasonicator resulting GO activated of LiCl/DMAc. The purpose of this research is to make regenerated films from cellulose nanofiber/graphene oxide nanocomposites in the solvent LiCl/DMAc 8% and evaluated its mechanical properties. Functional groups spectra, dimension of CNF, morphology and mechanical properties (tensile strength) were characterized in this work as well.

2 Materials And Methods

2.1 Materials

Oil palm empty fruit bunches (OPEFB) as raw material was collected from PTPN IV Adolina, Serdang Berdagai, Indonesia. Sodium hydroxide (NaOH), sodium hypochloride (NaOCl), hydrogen peroxide (H2O2) 30%, hydrochloric acid (HCl) 37%, aceton, lithium chloride (LiCl), N,N dimethyl acetamide (DMAc) were purchased from Sigma Aldrich Singapore. Graphene oxide was prepared via a modified Hummers Method through an acid oxidation towards the graphite.

2.2 Isolation of α-Cellulose from Oil Palm Empty Fruit Bunches (OPEFB)

OPEFB was cutted into 3 cm length and washed with tap water to clean up the dirt. After being cleaned, it was soaked into water overnight and oven dried at 80°C. About 75 gr of dried OPEFB treated with 1 L of 2% NaOH and stirred for 4 hours at 50°C to remove the major part of the lignin and hemicellulose(Julie Chandra, George and Narayanankutty, 2016) . Next, they were prepared by steam explosion in autoclave and NaOH 2% at 130 ^{0}C and the pressure was 180 kPa for 2 hours. Then, fibers were washed with distilled water until the neutral pH was reached(Saelee *et al.*, 2016),(Salehudin *et al.*, 2014). After that, bleaching process was conducted using sodium hypochloride solution with 6-14% of concentration (Salehudin *et al.*, 2014).

To separate α-cellulose from β and γ-cellulose, a dried bleached OPEFB was soaked into 17.5% NaOH at 70 °C for 2 hours. This mixture was then filtered, washed with distilled water until its pH was neutral. The bleaching process was performed one more time with 10%

$H_2O_2$for 2 hours at 70 °C to remove the remaining lignin and hemicellulose. Finally, it was dried in an oven at 50°C and after that was kept in vacuum desicator (Kaushik and Singh, 2011)(Ohwoavworhua and Adelakun, 2005),(Sinaga *et al.*, 2018).

2.3 Treatment for Isolating Cellulose Nanofibers (CNFs)

Theα-cellulose that had dried was hydrolized with 10% hydrochloric acid ($^w/_v$) via ultrasonication for 3 hours and washed with distilled water until its pH reached neutral. After that, it was homogenized with high shear homogenizer at 8000 rpm for 4 hours and the resulted suspension was filtered and dried in an oven at 50 ^{0}C (Feng *et al.*, 2018),(Julie Chandra, George and Narayanankutty, 2016),(Lee *et al.*, 2009).

2.4 Synthesis of Graphene Oxides from Commercial Graphite

As much as 2 g of graphite were putted into a beaker glass. Then, an amount of 2 g of $NaNO_3$ and 150 ml of H_2SO_4(c) were added while the mixtured was stirred for 2 hours in ice bath. Then, 10 grams of $KMnO_4$ (s) was gradually added and stirred for 4 hours at 20 ^{0}C. After that, it was transferred from ice bath and stirred for 20 hours at 35 ^{0}C. Then, 200 mL 5% H_2SO_4 and 10 mL 30% H_2O_2 were added and stirred for 1 hour. The centrifugation was conducted at 7200 rpm for 10 minutes until the supernatant and sediment were clearly separated. The sediment obtained was washed with warm distilled water until the pH approached 7. Then, it was ultrasound at 5060 Hz for 5 hours. The centrifugation was conducted again at 7200 rpm for 10 minutes to obtain sediment. Then, the precipitate was dried in an oven at a temperature of 105^{0}C to obtain graphene oxide powder. Graphene oxide powder was characterized by XRD and FTIR(Song *et al.*, 2014).

2.5 Fabrication of CNF/GO Nanocomposites

Firstly, cellulose nanofibers (CNFs) were activated while stirred using distilled water, acetone and DMAc each for 1 hour and filtered. The activated sample was put into 8% LiCl/DMAc ($^w/_v$) solution. The solution was heated at 70^{0}C for 30 mins until it formed the gel. Transparent solution was obtained after 24 hours. Colloid of graphene oxide (GO)in 8% LiCl/DMAc ($^w/_v$) was prepared by adding 20 mg GO into 40 ml 8% LiCl/DMAc ($^w/_v$) solution with mild ultrasound sonication for 24 hours. The CNF/GO composites were prepared by putting the obtained two solutions together according to mass ratios of CNF to GO: 100/0 (RC), 99,8/0,2 (RC0,2), 99,6/0,4 (RC0,4), 99,4/0,6 (RC),6). The mixture solutions were stirred at 70^{0}C for 30 minutes and then spread over a glass plate. The glass plate covered with the mixed solution was coagulated in the air and the film was detached in distilled water. The detached film was soaked in running water for overnight. The mixture film was finally dried and stored. The CNF/GO nanocomposite films were characterized by mechanical properties testing and scanning electron microscope (SEM) analysis(Zhang *et al.*, 2012)

2.6 Characterization

The CNF/GO nanocomposites characterized by Fourier transform infrared (FTIR) spectroscopy of cellulose nanofiber (CNF) were recorded with Shimadzu IR Prestige-21 spectrometer using KBr pellet. All FTIR spectra were recorded in the wave number with range of 4000-500 cm^{-1}. The dimension of CNF were observed under high resolution TEM using a

JEM-1400 electron microscope with an accelerating of 100 V. Mechanical properties of CNF/GO nanocomposites were measured by Instron 5567 testing machine at 1 mm/min of speed at room temperature. The rectangular specimen (50 mm x 15 mm x 0.4 mm). The morphology of CNF/GO nanocomposites were exhibited by scanning electron microscope (SEM) HITACHI S3400N Japan and operated at 10.0 kV). Samples were recorded at a magnification between 200 to 1000x. All measurements were performed for at least three samples and the average value was recorded.

3 Result And Discussion

3.1 FTIR Analysis

The FTIR spectrum of cellulose nanofiber is shown in Figure 1. The peak in area of 3387 cm^{-1} shows -OH stretching band, that is, due to vibrations hydrogen bonded hydroxyl group in the cellulose structure. The peak at 2916 cm^{-1} corresponds to the aliphatic saturated C-H stretching vibration of cellulose and hemicellulose(Kaushik and Singh, 2011). The sharp peak at 1627 cm^{-1} shows thedeformation vibration of the OH band on the intercalated water molecule. The peak at 1427 cm^{-1}indicates the curve of the HCH and O-CH bonds. The peaks at 1165, 1111, 1056 cm^{-1} show the asymmetric bridge streching of C_1-O-C_4,C_2-O_2H, and C_1-O-C_5 pyranose ring skeletal streching and C_6H_2-O_6H respectively(Amaturrahim *et al.*, 2018).

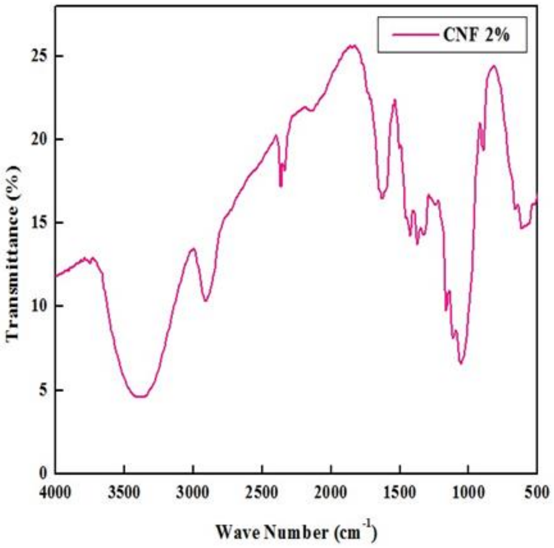

Figure.1.FTIR spectrum of 2% cellulose nanofiber (CNF).

3.2 Mechanical Properties of CNF Nanocomposites

To evaluate the reinforcing effect of graphene oxide in CNF/GO nanocomposites, tensile strength test of pure cellulose nanofiber and three CNF/BC films with a graphene oxide content of 0.02, 0.04, 0.06 wt%, respectively was conducted. The representative stress-strain curves are shown in Figure 2 and mechanical properties of the film are summarized in Tabel 1. Tensile strength of cellulose nanofiber from mixing method was drastically increased comparing without graphene oxide.

Mechanical properties of the CNF/GO nanocomposite films are not depend on fibril modulus but also interaction between cellulose nanofiber and graphene oxide. Mechanical properties of CNF/GO nanocomposites have improved with the increasing of graphene oxide loadings. Incorporation of 0.06 wt%, graphene oxide significantly improved the mechanical properties of cellulose nanofiber (Amaturrahim *et al.*, 2018). For example, the Young modulus of nanocomposite film with 0.06 wt% of graphene oxide was 6.97 Gpa,corresponding to an increase of 505.55% compared to 1.37 GPa of pure cellulose nanofiber film. The tensile strength was increased to 49.69 MPa, corresponding to an increase of 188.5% compared to 26.36 MPa of pure cellulose nanofiber film. The elongation at break changed much with addition graphene oxide(Zhang et al., 2012), indicating that dispersion of graphene oxide nanosheet on the molecular scale in cellulose nanofiber matrix and also the interaction between cellulose nanofiber and graphene oxide made a great contribution to the mechanical enhancement. The oxygen containing groups on graphene oxide can interact with OH on cellulose nanofiber through hydrogen bonding both intra and intermoleculary. The elongation at break decreased from 20.92% (cellulose nanofiber) to 3% (cellulose nanofiber/0.06) due to the brittle nature of graphene oxide nanosheet(Amaturrahim et al., 2018).

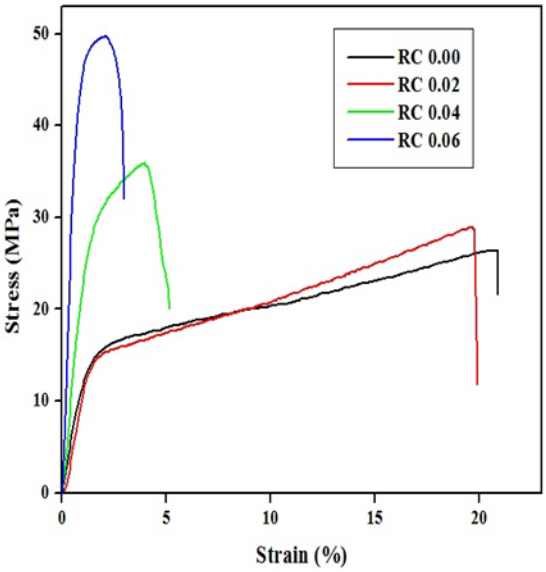

Figure 2. Stress-strain of curves of cellulose nanofiber/graphene oxide (CNF/GO) nanocomposite films with graphene oxide content of 0.00, 0.02, 0.04 and 0.06 ($^{w}/_{v}$) %

Table 1. Mechanical properties of cellulose nanofiber/graphene oxide (CNF/GO) nanocomposite films with different graphene oxide contents.

Sample	Young Modulus (GPa)	Tensile Strength (MPa)	Elongation at break (%)
RC 0.00 wt%	1.379381	26.36	20.92308
RC 0.02 wt%	1.2911	28.89	19.88676
RC 0.04 wt%	2.747574	35.86	5.19988
RC 0.06 wt%	6.973478	49.69	3.00000

3.3Morphology of CNF/GO Nanocomposites

Tranmission electron microscope (TEM) was used to investigate the diameter distribution diameter of cellulose nanofiber. Figure 3 shows TEM image of distribution of nano-fiber diameter of cellulose nanofiber. The average fiber diameters is found in the range 20-60 nm. A tendency of agglomeration could also be observed from TEM. The particle was found least diameter at 25.612 nm and the biggest diameter at 58.82 nm(Kaushik and Singh, 2011).

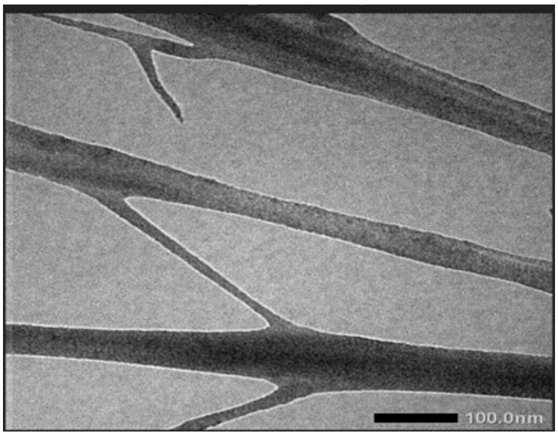

Figure.3.TEM image of cellulose nanofiber (CNF)

In the other hand, scanning electron microscope (SEM) was used to investigate microstructure of the CNF/GO nanocomposite films. Fig.4. shown SEM image of the surface morphology of RC 0.00 and RC 0.06 with magnification 1000x. It indicated that graphene oxide nanosheet weredispersed within the cellulose nanofiber matrix(Amaturrahim *et al.*, 2018)(Zhang *et al.*, 2012). The strong adhesion between cellulose nanofiber fibers and graphene oxide nanosheet was beneficial to improve the mechanical properties of CNF/GO nanocomposites (Amaturrahim *et al.*, 2018).

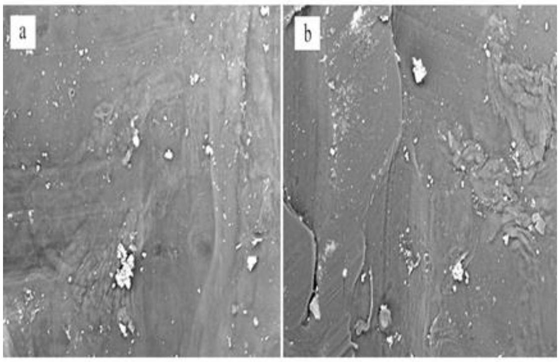

Figure. 4.SEM image of CNF/GO nanocomposite films (a) RC 0.00 GO wt%, (b) RC 0.06 GO wt%

4 Conclusions

In this work, cellulose nanofiber/graphene oxide (CNF/GO) nanocomposite was successfully prepared by mixing method. During mixing process, cellulose nanofiber has very strong interaction with graphene oxide and made graphene oxide well dispered into cellulose nanofiber matrix. The cellulose nanofiber/graphene oxide nanocomposite films exhibited a significant improvement on mechanical properties. With these enhancements, the cellulose nanofiber/graphene oxide nanocomposite films may find applications in the future.

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