Natural and synthetics nanomaterials: comparative study on their mechanical and thermal properties as nanofiller in polymer composite

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Abstract. In this research, natural nanomaterials including cellulose nanocrystal (CNC) and nanofiber cellulose (NFC) and synthetic nanomaterials such as carbon nanofiber (CNF) and carbon nanotube (CNT) with different structures, sizes and surface areas were produced and analyzed. CNC and NFC were fabricated by use of acid hydrolysing and mechanical methods, respectively and synthetics nanomaterials were produced by chemical vapor deposition method (CVD). Here, in order to evaluate the effect of these nanomaterials on the mechanical and thermal properties of the polymer, use them as nanofiller in the polymer matrix. The most important challenge in this study is to evaluate and compare these nanofibers based on the effects of their structures and compositions on the mechanical and thermal properties. The characteristics of these nanofibers such as morphology, structure, and composition and also the properties of these nanomaterials including thermal stability and mechanical strength were investigated, comprehensively. Based on the results, CNT with high thermal stability and strong structure has the best filler for using in polymer composite.

1. Introduction
Synthetics nanomaterials including carbon nanomaterials has many applications in industries and sciences. Carbon nanomaterials such as CNT and CNF are made from sp² carbon atoms with one-dimension (1D) structures. The structure of pure CNT can be visualized as a single sheet of graphite rolled to form a tube. Besides, CNFs have cylindrical nanostructures with different stacking arrangements of graphene sheets, such as stacked platelet, ribbon or herringbone [1]. CNF and CNT with low-density and high aspect ratio, as well as extraordinary mechanical, thermal, electrical and electrochemical properties have produced a huge amount of activity in most areas of science and engineering [2]. There are many techniques to synthesis carbon nanomaterials but chemical vapor deposition as the most effective method has been employed to fabricate carbon nanomaterials [3,4]. Besides, in order to obtain different types of carbon nanomaterials with different structures, some parameters such as temperature, time, flow rate of carrier gas and carbon source amount should be changed [5,6].

To prepare natural nanomaterials there are many natural sources. Kenaf is a natural tropical plant that has been grown commercially to generate a secondary source of income for developing countries including Malaysia. Its high cellulose content, ranging between 44 and 63.5% in kenaf, [7] has generated interest in exploiting the material as nanofillers in composites. The cellulose nanocrystals (CNC) and
nanofibers (NFC) can be obtained via acid hydrolysis and mechanical treatment, respectively. CNC and NFC have been used in many applications such as filler in polymer composite to make a wide range of other functional materials [8-11].

In this research we produced natural and synthetics nanomaterials and analyzing their properties based on their characterization. Besides, the produced nanomaterials were used as nanofiller in polymer matrix to evaluate the effects of these nanomaterials on the thermal and mechanical properties of different composites and compare together.

2. Experimental Part

2.1. Synthesis of synthetic and natural fibers

In this part the nickel nitrate hexahydrate powder (Ni(NO$_3$)$_2$.6H$_2$O; Sigma-Aldrich), as Ni precursors, was put in a quartz crucible locate in the CVD reactor and dried in the reactor at 150°C to remove water for 1 h and then increased the temperature to 400°C for 1h to remove nitrate. The reaction temperature was set at 650°C and 800°C to produce high quality CNF and CNT, respectively. The process was done by the decomposition of the acetylene at 50 standard cubic centimeters per minute (sccm) flow rate on the Ni particles at 100/100sccm H$_2$/N$_2$ flow rates for 30min.

Here, CNC and NFC were produced by use of acid hydrolysing and mechanical methods, respectively. For Preparation of CNC, firstly, acid hydrolysis was conducted under mechanical stirring using 65wt% H$_2$SO$_4$ (pre-heated) for 45 min. Then the suspension dilute with cold distilled water to stop the reaction. The suspension then centrifuge for 10 min at 10,000 rpm. The aqueous suspension subsequently dialyzes against distilled water until a constant pH attain. The resulting suspension was subsequently dried and stored in the refrigerator.

For fabricating NFC, firstly, Kenaf bast fibers retted in water was cut and then cooked in a rotatory digester contains 25wt% NaOH and 0.1 wt% anthraquinone solution (liquor to fiber ratio was 7:1) at 160°C for 2 h. After that, AQ was added to the solution to not only increase the delignification rate but also protect the fibers from alkali degradation called end-wise degradation of cellulosic chains. Extraction of nanofibers were done by further mechanical destruction using super-masscolloider. Aqueous suspensions with the concentration of 3 wt% was prepared and prepared and blend until formation of a homogeneous mixture. To some up, the produced suspensions were fed into the grinder and the process repeated until a gel was formed. And then it was dried and formed into the powder shape.

2.2. Preparing of polymer composite

Initially, 5 wt.% nanomaterials was added into the polypropylene matrix in to the melting mixing machine at 200°C of screw temperature and 60 rpm of screw rotation for 5 min. Then, the produced composite was cooled to 25°C in a mold. After that, it was pressed by Hot Press Machine at a 200°C under 150kg/cm$^2$ pressure for 10 min and then cooled.

2.3. Characterization of the composite

The prepared polymer composite was cut into the dog-bone shape based on the ASTM D638 standard. To fulfill a tensile test, an Intron Universal Testing Machine was used at room temperature to analysis the modulus of elasticity and the strength of PP, CNC/PP, NFC/PP, CNT/PP and CNF/PP. Moreover, to determine the thermal resistance and stability of the produced nanocomposites, a thermal gravimetric analysis (TGA) test was employed. Here, TGA was fulfilled on a Mettle Stare SW 9.10 thermal gravimetric analyzer.

3. Results and Discussion

The FESEM images of the produced nanocellulose were shown in Figure 1. CNCs present a simple needle-like structure with an average length of 200nm, a diameter of 20nm. NFCs exhibit a complex, highly entangled, web-like structure. Twisted/untwisted, curled/straight, and entangled/separate nano-
fibrils and their bundles with diameters ranging from 50 to 200 nm in diameter can be identified from the micrograph.

Figure 1. SEM/TEM images of (a) CNC, (b) NFC, (c) CNF and (d) CNT

The TGA curves in Figure 2 illustrate the degradation process of different nanocomposite filled with natural and synthetics nanofibers based on the weight loss (wt.%) versus temperature (°C). The curves related to CNC/PP and NFC/PP reveal that the initial weight loss related to the evaporation of moisture. Further loss in weight may be attributable to pyrolysis of NFC/PP and CNC/PP decomposed at 300°C–400°C and 250°C–370°C, respectively. The lower degradation temperature of CNC/PP could be due to the smaller dimensions compared to the NFC/PP, which leads to higher specific surface area.

On the other hand, it is obvious that the decomposition temperature of the CNF/PP was started about 400°C and complete at 550°C and for CNT/PP, the decomposition temperature of sample was increased to about 500° C and completed at 610° C. since the composition of CNT/PP and CNF/PP is same, therefore, the thermal stability of CNT is more than CNF due to its structure and morphology. Briefly, the thermal analysis showed that the thermal degradation phenomenon of natural nanofibers (CNC and CNF) is much lower than synthetics nanofibers (CNF and CNT).
Figure 2. TGA curves of PP, CNC/PP, NFC/PP, CNF/PP and CNT/PP

According to Table 1, presence of nanofibers enhanced the mechanical properties of the composite. Comparison of the elasticity and strength of them illustrates a significant difference in the tensile modulus that related to the different nanofillers. The tensile modulus and strength of synthetics fiber are significantly more than natural nanomaterials related to the hard structures and bigger length of carbon nanomaterials.

| Sample   | Tensile modulus (GPa) | Tensile strength (GPa) |
|----------|-----------------------|------------------------|
| PP       | 1.5                   | 0.02                   |
| CNC/PP   | 620                   | 19                     |
| NFC/PP   | 405                   | 10                     |
| CNF/PP   | 650                   | 21                     |
| CNT/PP   | 780                   | 27                     |

4. Conclusion
The most important contribution of this research is related to apply the CNC and NFC as natural fibers with CNT and CNF as synthetics fibers in order to apply in polypropylene matrix and analysis the thermal and mechanical properties of them. In order to evaluate the effects of the types of nanofillers on the polymer matrix in terms of thermal and mechanical properties, the TGA and tensile test were performed on the produced nanocomposites. Since the CNT has highest thermals stability and strongest structure, the thermal stability, tensile stress and Young's modulus of this composite are higher than others.

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