Thermal Degradation Behaviour and Tensile Properties of OPEFB Fiber Filled HDPE/Clay Nanocomposites

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ABSTRACT

The effect of clay/HDPE nanocomposites on mechanical and thermal properties of OPEFB fibers filled polymer nanocomposites was investigated. OPEFB/MAPE/clay/HDPE nanocomposites were prepared by melt compounding containing 68 wt% of high density polyethylene, 30 wt% of OPEFB fibers, 2 wt% of maleic anhydride graft polyethylene (MAPE) and four different of clay loading (3, 5, 7 and 10 per hundred of HDPE). Tensile test were conducted on an Instron 8032 Digital Control testing machine according to ASTM D638. The result indicates that the particle size distribution is between 500 to 600 μm at the maximum peak. The tendencies of agglomerate will of course opposed by shear forces and the presence of the agglomerates may depend upon processing conditions. Tensile properties of the reinforcement between OPEFB fibers and clay/HDPE nanocomposites reported that the tensile strength and tensile modulus are slightly higher and the results was supported by the FESEM analysis when the fracture surface at 7 phr which was preferred as the highest value in tensile strength that clear show the interfacial region between filler and matrix was continuous and indicates some good interaction. There is a large increment in tensile modulus with the presence of OPEFB fiber and MAPE as a coupling agent. The thermal degradation behavior shows the char formation increased with the increasing of clay/HDPE nanocomposites but in presence of OPEFB fibers, the char formation was increased and decreased as clay loading increased. The presence of clay may not affect the crystal structure of the HDPE matrix. It was only shows that the XRD patterns slightly changed when the clay loading increased. From the research works, it can be conclude that the best and good properties between four different of clay/HDPE nanocomposites was at 7 phr representing for both types which is with and without presence of filler and coupling agent.

INTRODUCTION

Polymer/nanoclay composite has been growing interest in recent years due to their outstanding properties at low loading levels as compared with the conventional composites. Clay acts as the importance in enhancement of the physical, mechanical, and thermal properties because could produce an affected in polymer nanocomposites by adding some quantity of clay. Melt compounding is a technique of processing methods for preparing nanocomposites, where has been applied well in industrial and its practical applications are well known. Short fibers are often used as reinforcing materials for compounding with thermoplastics polymers to improve their thermal or mechanical properties. The clay particles and polymer molecules are the same size in polymer nanocomposites which allows to be closely mixing and chemically bonded to each other [8]. High density polyethylene (HDPE) composite is a commonly used thermoplastic with the high degree of crystalline structure [6]. PE such as low stiffness and tensile strength, owning its inherent chemical nature, this polymer need to be improved to extent its engineering applications. Maleic anhydride grafted polyethylene (MAPE) was regularly introduced to promote interaction between PE chains and the organically modified montmorillonite (OMT) because of difficulty to fabricate PE based on nanocomposites [12]. HDPE possess higher tensile strength attributed to its crystalline structure compared to other types of PEs. Kutcha et al. [11] has combined PE with an organically-modified clay in a twin screw extruder and claim the formation of a nanocomposite.
Many experimental studies have been conducted and results reported for investigating the mechanical and thermal properties of OPEFB filled nanocomposites recently. The objective of this research paper is to determine the thermal degradation behavior and mechanical properties of OPEFB fiber reinforce clay/HDPE nanocomposites at varied clay loading with the addition of coupling agent.

MATERIALS AND METHODS

Materials:
Oil palm fruit bunch was supplied by Poly Region Sdn Bhd. High density polyethylene (HDPE) was manufactured by Lotte Chemical Titan Holding Sdn. Bhd. (melt flow index = 2.16, density = 0.946 g/cm³, melting temperature = 120 - 130 °C, processing temperature = 185 °C). Polyethylene nanoclay (PE nanoclay) pellets were provided by Nanocor Inc. in the form of master batch which ready for injection molding. Meanwhile maleic anhydride graft polyethylene (MAPE) was used as a coupling agent in this study.

Preparation of Nanocomposites:
OPEFB fibers obtained in the form of short fibers were sieved to separate the particles to get the range size of between 300 µm to 355 µm. The formulations consist of 68 wt% of high density polyethylene, 30 wt% of OPEFB fibers be prepared based on the equipment capability; 2 wt% of maleic anhydride graft polyethylene (MAPE) and four different of clay loading (3, 5, 7 and 10 per hundred of clay/HDPE nanocomposites). Before the OPEFB fiber been processing, the fibers must be washed first with distilled water to remove impurities and dried at oven at 80°C for about 8 hours to constant weight before making the composites. The quantities of HDPE composite, OPEFB fibers and MAPE had been fixed during preparation. The compounding of MAPE/clay/HDPE nanocomposites was performed in a dispersion mixer at 185ºC and a rotor speed of 50 rpm for 30 minutes. After the compound was thoroughly mixed, OPEFB fibers were added and the compounding was continued for the next 30 minutes. The compound was removed from the mixer and allowed to cool at room temperature. The total mixing time is approximately 1 hour. The composites were fabricated using injection moulding techniques into flat dog-bone shape after the compounded material was crushed into granules.

Tensile Properties Characterization:
Tensile test were conducted on an Instron 8032 Digital Control testing machine. The familiar dog-bone of the molded samples was utilized in the testing procedure. This type I sample is the preferred sample and be used where material having a thickness of 7 mm or less. Tensile strength was determined at a crosshead speed of 5 mm/min according to standard of ASTM D638 and five samples were used in each case. The test was performed until the tensile failure occurred.

Material Characterization:
X-Ray diffraction (XRD) patterns were obtained by Rigaku Geiger Flex, 2-circle powder diffractometer equipped with Cu radiation with (λ = 0.15406 nm) at room temperature. The diffractograms were scanned in 2θ ranges from 5 to 60° at a rate of 1.5°/min. X-ray diffraction analysis was used in order to identify the unknown compound or element. All types of specimens were analyzed at the cross-section of specimens. Thermal gravimetric analysis (TGA) was performed to understand the thermal degradation characteristics of the specimens by TGA Q500 series thermogravimetric analyzer (Perkin Elmer thermal analyzer). The investigated range of temperature was 0 to 600 °C at a constant heating rate of 10 °C/min. All the measurement was made by a nitrogen flow (10 ml/min). TGA continuously measured the weight of a sample as function of time and temperature. Specimens were in the form of granules after the compounding process with the between mass from 17 to 20 mg for each analysis. The test was carried out in nitrogen atmosphere. During the research worked, weight loss and heating rate were continuously recorded.

Morphology Study:
The morphology of the samples was examined using a Hitachi field emission scanning electron microscope (FESEM). The samples were cut first at the failure occurred using a cutter machine and then sputter coated with
a thin layer of gold to minimize electrostatic charging during observations. The operating voltage was fixed at the lowest possible voltage (5kV) in order to prevent polymer damage and maintain high resolution images.

RESULTS AND DISCUSSIONS

Particle Size Distribution:

Fig. 2 indicates the particle size distribution of OPEFB fiber. For higher volume fraction of fiber, the agglomeration of OPEFB particles is easily occurred. The particle size distribution is between 500 to 600 μm at the maximum peak. The tendencies of agglomerate will of course opposed by shear forces and the presence of the agglomerates may depend upon processing conditions (sieving). Over-energetic sieving due to attrition of the particles and changed the particle size distribution, while insufficient energy fails to break down of loose agglomerate [10]. The FESEM micrograph provides clearly observation for OPEFB fibers at 355 μm in Fig. 3. The observation indicates the agglomeration of OPEFB particles tend to exhibit the irregular shape compared to cylindrical shape. It is assumed that these uneven porous surfaces are responsible for the mechanical bonding between the fiber surface and the matrix polymer.

![Particle Size Distribution of OPEFB fibers](image)

**Fig. 2**: Particle Size Distribution of OPEFB fibers.

**Fig. 3**: OPEFB fibers size at 355 μm.

X-Ray Diffraction (XRD):

Fig. 4 shows the XRD of HDPE, clay/HDPE and OPEFB/MAPE/clay/HDPE nanocomposites. The crystal structure of the HDPE matrix may not affected with presence of clay in this case of varied PE nanoclay loading. It was only shows that the XRD patterns slightly changed when the clay loading increased. From the results, it indicates that the pure HDPE composite do not had the characteristic peak at the beginning, which shows the exfoliation of the layered silicate [14]. The starting of diffraction peak for the pure HDPE composite is approximately 21.53°, which corresponds to a (110) spacing. When the clay was diluted with pure HDPE to create HDPE/PE nanoclay composite, the diffraction peak was found to start around 7.68° at 3 phr, indicating the increase in d-spacing of galleries of the organoclay and further increased as clay loading increased. This improvement in the dispersion was due to the processing conditions for the fabrication of nanocomposites [18].
Fig. 4: XRD patterns of HDPE, clay/HDPE, and OPEFB/MAPE/clay/HDPE nanocomposites.

The starting of the diffraction peak was around 14.14° at 3 phr for 355 μm. The two peaks became weaker at 2θ around 53.09° and 54.84° are corresponding to reflection planes (410) and (311), respectively meaning that exfoliation or disordering of the clay may have occurred [19]. The weak crystalline peaks remained unchanged at the same position of the original structure of HDPE matrix regardless of the clay loading. However, diffraction peaks did not turn to change much as expected with addition of OPEFB fibers and MAPE as coupling agent since the presence of the fibers in the polymer creates further complexities in the morphology of the system. This behavior is also causes the polar interactions between the maleic anhydride groups in the HDPE and the OH groups of clay and coupling agent and help polymer chains to penetrate the galleries of the organoclay easily [5,8,4]. The presence of lower angle peak in PE nanoclay composites suggests the larger clay d-spacing formed in clay reinforced PE nanocomposite, which helps the mobility of PE chains during crystallization.

**Thermal Gravimetric Analysis (TGA):**

TGA of three different types of specimens were studied as shown in Fig. 5. The TG curves showed significant changes of decomposition with and without OPEFB fiber. This can be explained with two different typical of TG curves where in single and three stages of decomposition. From the result again, TG curves clearly indicates that the temperature where moisture started to liberate was higher for HDPE composite due to higher weight loss was around 84%. This condition can be described on the changes occurring in the structure and morphology of HDPE composite. Thus, the heating been decreased due to liberate of moisture absorption where moisture strongly held within a packed structure and causes to a higher finished temperature [15]. The decomposition temperature of the clay/HDPE nanocomposites occurs between range of 410 °C and 530 °C meanwhile the OPEFB fiber occurs below 200 °C at the first stage, between range of 200 °C and 400 °C at the second stage [7] and the rest of HDPE composite completely finished at 500 °C. Mostly in the amorphous regions, the initial decomposition of the cellulose constituents had taken place [13]. At the last stage of OPEFB/clay/HDPE nanocomposites curves was noticed that the decomposition increased caused by charred layers that assist to insulate the lignocelluloses from further thermal degradation [16]. The char formation increased with the increasing of PE nanoclay loading but in presence of OPEFB fiber, the char formation was increased and decreased as clay loading increased.

Fig. 5: TGA curves of HDPE, clay/HDPE, and OPEFB/MAPE/clay/HDPE nanocomposites.
**Tensile Properties:**

The tensile properties of clay/HDPE nanocomposites were compared with OPEFB/MAPE/clay/HDPE nanocomposites. The results of the tensile tests performed of the pure HDPE, clay/HDPE nanocomposites, and OPEFB/MAPE/clay/HDPE nanocomposites are shown in the Fig. 6. As reported in the result, the presence of filler as reinforcement with the matrix indicates the enhancement of composites compared without the filler. The important role in determining the mechanical properties of fiber filled thermoplastics composites is filler. The enhancement for tensile strength of OPEFB/MAPE/clay/HDPE nanocomposites up to 7 phr was supposed to continue to increase, but it decreased at 10 phr which is believed because of the poor adhesion of filler and matrix. From other research studies that have investigated, the increment of tensile strength of a composite may not affect the thermoplastic matrix[2]. Furthermore, the presence of flaws created by fiber ends causes a reduction in tensile strength. Therefore, the stress concentrations occurred from the flaws cause the bond between fibers and matrix to break [17]. The level of the interfacial bond developed between the filler and matrix is the main factor on the tensile strength of filled compositions. The effectiveness of the coupling agent of the polymer affected the interfacial bond strength [2].

![Fig. 6: Tensile Strength of HDPE, clay/HDPE, and OPEFB/MAPE/clay/HDPE nanocomposites.](image)

Fig. 6 shows the tensile modulus of clay/HDPE and OPEFB/MAPE/clay/HDPE nanocomposites. The result indicates there is a large increment in tensile modulus with the presence of OPEFB fibers and MAPE as a coupling agent. The Young’s modulus or elastic modulus is a parameter related to the rigidity of the polymer. This large increment is attributed to the reinforcement impact prepared by the fibers that allows uniform distribution of the tension applied to the continuous polymer matrix to the dispersed phase, which are fibers [1]. In the presence of MAPE, better moduli was observed for the composites system containing clay/HDPE and OPEFB/MAPE/clay/HDPE nanocomposites compared with the corresponding of pure HDPE composite. Besides, both of nanocomposites types shows the consistency when the clay loading increased. The enhancement in tensile modulus with varied of clay loading obviously reveals the ability of OPEFB fibers to impart greater stiffness into HDPE composite [9].

![Fig. 7: Tensile Modulus of HDPE, clay/HDPE, and OPEFB/MAPE/clay/HDPE nanocomposites.](image)
**Morphological Study:**

Fig. 8 shows the observation on the fractures surface of HDPE, clay/HDPE and OPEFB/MAPE/clay/HDPE nanocomposites for tensile test at varied clay loading. Interestingly, in Fig. 8 (a) - (c) there is no much difference in the fracture surface can be envisage for pure HDPE and varied clay loading reinforced clay/HDPE nanocomposites since the tensile strength values approximately same. Reinforcement clay is uniformly distributes in the matrix and does not give an indication of aggregation. Uniform dispersion is important because if the matrix consists of aggregates of particles, the stress field in the vicinity of the aggregate will be high resulting in easier crack initiation and propagation, and consequent premature failure [3]. However, the matrix was seems like pulled out at the surface for pure HDPE composite in Fig. 8 (a). Meanwhile, by the presence of the coupling agent increased the mechanical properties that gave the better bonding between OPEFB fibers and HDPE matrix. Fig. 8 (d) observed that the OPEFB fibers nicely embedded in the matrix and was supported with fracture surface at 7 phr which was preferred as the highest value in tensile strength. The interfacial region between filler and matrix was showing clearly continuous and indicates some good interaction. Fig. 8 (e) show that OPEFB fibers are disengaged or pull out caused of poor adhesion between filler and the matrix. Moreover, debonded fibers leave empty holes where larger flaws be created and hence aggravate the fracture resistance capability.

![Fig. 8: Fractures surface of tensile test for clay/HDPE nanocomposites of a) HDPE b) 7 phr c) 10 phr d) 355 μm, 7 phr e) 355 μm, 10 phr](image)

**Conclusion:**

The influence of OPEFB fibers and MAPE as a coupling agent reported as the good mechanical performance and environmental advantages. The presence of filler as reinforcement with the matrix indicates the enhancement of composites compared without the filler. The tensile strength and tensile modulus are slightly higher and the results was supported by the FESEM analysis when the fracture surface at 7 phr which was preferred as the highest value in tensile strength clear show that the interfacial region between filler and matrix was continuous and indicates some good interaction. In the presence of MAPE, better moduli was observed for the composites system containing clay/HDPE and OPEFB/MAPE/clay/HDPE nanocomposites compared with the corresponding of pure HDPE composite. Besides, both of nanocomposites types shows the consistency when the clay loading increased. In TG curves, the char formation increased with the increasing of clay/HDPE nanocomposites but in presence of OPEFB fibers, the char formation was increased and decreased as clay loading increased. The crystal structure of HDPE matrix does not affect with the addition of clay. From the research works, it can be conclude that the best and good properties between four different of clay/HDPE nanocomposites was at 7 phr representing for both types which is with and without presence of filler and coupling agent.

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