Effect of nano-clay fillers on mechanical and morphological properties of Napier/epoxy Composites

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Abstract. The effect of nano clay filler on the mechanical and morphological properties of Napier/epoxy composites was investigated. Neat, 2 wt%, 3 wt%, 4 wt% and 5 wt% of Montmorillonite (MMT) nano clay filled Napier/epoxy composites were fabricated by vacuum infusion technique. These specimens were tested in the three points bending according to the ASTM D790. The flexural stress-strain curve, flexural strength, flexural modulus and strain to failure were then discovered based on the flexural test results. The results revealed that flexural strength and flexural modulus increased when a particular amount of nano clay was added to the epoxy matrix. 3 wt% of nano clay filler yielded the highest flexural strength with an improvement of 163% when compared to the neat Napier/epoxy composites. Moreover, a maximum of 180% increases in flexural modulus was registered at 5 wt% of nano clay filler. The enhanced properties of nano clay filled composites were highly achieved due to better dispersion and distribution of nano clay in the epoxy resin as well as an increase on the interfacial bonding. Using Scanning Electron Microscopy (SEM), morphological analysis was conducted to observe the fracture surfaces of the specimens after the flexural test. Overall, the presence of nano clay filler loading with a range of 3 wt% to 5 wt% in the Napier/epoxy composites shows the significant improvement in mechanical and morphological properties.

1. Introduction
Over the past decade, the adoption of natural fibres is gradually increasing as reinforcing resources in particular applications for composites structural industries all over the world. A lot of industrial and structural applications such as aerospace, automotive, marine, construction and packaging are raising utilisation of natural fibre reinforced composites due to their cost-effective, particularly high specific strength, toxic free, renewability, low density and biodegradable behaviour [1]. Currently, some research study on extracting fibres from Napier grass which also known as ‘Pennisetum purpureum’ or elephant grass. It is looking like bamboo, yellowish colour stem and highly sustainable in Malaysia. Napier grass fibres have been successfully proved that it has potential to use as alternative resources in reinforcement composite materials [2-6]. Epoxy resins are commonly selected in fabrication natural fibres reinforced composites as matrix materials. They are one of the outstanding resins amongst the class of thermosetting resins. Their primary function is to enhance the structural adhesion when reinforcing together in natural fibres and composite materials [7]. In recent year, a new interest is generated to improve the performance of the composite by adding nano clay filler into the matrix system. Montmorillonite (MMT) clay contains 25-30 wt. % trimethyl stearyl ammonium that able to improve flexural strength and modulus, reduce crack propagation and achieve better surface modification [8-10]. Consequently, this study aims to determine the effect of nano clay filler on
mechanical and morphological properties of Napier fibres reinforced epoxy composites. The various amounts of nano clay filler are added to an epoxy resin to improve the mechanical behaviour and morphological performance of the Napier epoxy composites. Moreover, Napier epoxy composites are going to fabricate using vacuum infusion technique to generate superior performance of composites. Overall, the flexural test is going to carry out in this paper to investigate the effect of nano clay filler on mechanical performance of Napier reinforced epoxy composites. Also, the fracture behaviour obtained on the surface of specimens is achieved through FESEM observations.

2. Materials and Methods

2.1 Extraction of fibres

The Napier grass stems were obtained from Kodiang, Perlis, in northern peninsular Malaysia. The Napier grass fibres were being extracted by using a simple manual after few weeks of water retting process. In the beginning, the Napier stems were cleaned to remove the impurities on its surface and then the leaves, thorn node and root portion were cut off since only the stem part was required. Next, the stems were crushed with a hammer between the stem internodes to crack the thick and harder stem wall and enable water to diffuse into the inner stem. The stems then were chopped into the small portions with 2 or 3 segments between stems. The cracked-stems were submerged in water tanks filled with water for four weeks and monitored daily. After that, the soaked Napier fibres were extracted manually and made sure all the impurities such as hemicelluloses, lignin or waxy component removing from the surface of the fibres. Lastly, the extracted raw fibres were going to put under the sun for drying process for few days to eliminate the excess moisture inside.

2.2 Preparation of nano clay-epoxy mixture

The various amounts of nano clay filler such as 2 wt%, 3 wt%, 4 wt% and 5 wt% were prepared for fabricating Napier/epoxy composites. Firstly, the nano-clay filler was directly added into epoxy resin. Manual hand mixing method was used for half an hour to reduce the nano-clay filler agglomeration and improvise their dispersion. After that, the epoxy hardener at a ratio of 3:1 by weight (epoxy: hardener) was then slowly added to the nano-clay filled epoxy resin and stirred until it becomes a bit gelling.

2.3 Composite fabrication

Neat, 2 wt%, 3 wt%, 4 wt% and 5 wt% nano clay filled Napier/epoxy composites were fabricated through vacuum infusion technique. First and foremost, the extracted raw Napier fibres were oven dried at 55 °c for 30 min to remove excess moisture. The composite samples were fabricated with 75% of nano clay-epoxy resin and 25% of Napier fibre weight content (with ratio 3: 1). Next, the glass surface was being polished by wax. Few-layer of Napier fibres were prepared and then positioned on the glass surface. The black enka channel was then put and taped at the two end sides of the Napier fibres. The Napier fibres were then surrounded by adhesive clay as the area for infusion purpose. After that, the resin feed spiral and vacuum hose were sealed and positioned at the two centre sides by using a sealant tape. The transparent Perspex was covered and taped on the Napier fibres which acted as a mould for fabricating composite. The vacuum bag was being taped and sealed on the area surrounding by a sealant tape. The vacuum pump was then connected and switched on to withdraw the air inside for around half an hour. Then the epoxy resin and hardener was mixed and prepared. Furthermore, the prepared resin was then infused and flow slowly onto the surface of Napier fibres. While the resin was distributed until the end of the edge, the excess resin flowed into an installed resin trap. The process was continued run at room temperature for around 6 hours to ensure the epoxy resin with nano clay filler full covered onto the Napier fibres. Lastly, the Napier fibre epoxy composite was done fabricating and stored for fully dried and hardened.

2.4 Flexural testing
Three-point bending test was carried out by using INSTRON micro-tester according to ASTM D-790 standards at a constant crosshead speed of 1 mm/min. The specimens were cut into dimensions of rectangular shape (12.7 cm x 1.27 cm x 0.3 cm) by using hand Dremel. Eight specimens were tested for each type of composites of different filler contents. The flexural stress-strain curve, flexural strength and modulus, as well as the strain to failure were determined. In a three-point bending test, the flexural stress was given by $\sigma_f = (3PL)/(2bd^2)$ where P is maximum load (N), L is a support span length (mm), b is the width of the specimen (mm), and d is the thickness of specimen (mm), respectively. While flexural strain was calculated by $\epsilon_f = (6Dd)/(L^2)$ where D is a maximum deflection of the centre of the beam (mm). Besides, the modulus was given by $E = (mL^3)/(4bd^3)$ where m is the initial slope of the load-deflection (N/mm) and could also be determined using the stress-strain curve.

2.5 Morphological testing
The morphology properties of the Napier fibre epoxy composited is observed by using scanning electron microscope (SEM). It was used to investigate the fracture surface of the specimens, the distribution of nano clay filler within the epoxy matrix, agglomeration of nano clay filler and fibre pull-out failure. The microscope was acquired with 5-15 kV accelerating voltages, and the magnification was focused in a range of 50 to 200 times. Thus, the specimens must cut into a small size with diameter 10mm x 10mm. Before scanning, the specimens have to be consistently coated with thin layer of platinum to prevent charging and caused a white spot on the scanned pictures.

3. Results and Discussion

3.1 Flexural Test properties
Table 3.1 shows the mean value of the ultimate flexural load and maximum extension of different loading of 2%, 3%, 4% and 5% of nano clay filled Napier/epoxy composites. Throughout, the results for neat Napier/epoxy composite are included for comparison. It can be seen that 3% of nano clay-filled Napier/epoxy composite showed most improved ultimate load capacity than other nano-clay filled composite. There is an increase of over 125.33%. The 2 wt%, 4 wt% and 5 wt% of nano clay filler displayed the ultimate load of 46.30N, 66.34N and 78.83N respectively. This indicates that nano clay filler further acts as a load bearing reinforcement in the Napier/epoxy composites. Besides, 5% of nano clay-filled Napier/epoxy composite has the smallest deflection with the value of 3.78mm only which is a reduction of 64% compared to pure Napier/epoxy composite. However, 2 wt%, 3 wt% and 4 wt% of nano clay filler exhibited maximum extension of 8.85mm, 6.07 and 4.43mm respectively. This suggested that the addition of nano clay filler might reduce the elasticity and flexibility of the composites due to the agglomeration of nano clay and thus attributed to the weak intercalated structure in the Napier/epoxy composites.

| wt% of Nanoclay in Epoxy | Ultimate Load (N) | Max. Extension (mm) |
|--------------------------|-------------------|---------------------|
| Neat                     | 38.13             | 10.56               |
| 2%                       | 46.30             | 8.85                |
| 3%                       | 85.92             | 6.07                |
| 4%                       | 66.34             | 4.43                |
| 5%                       | 78.83             | 3.78                |

The flexural stress-strain trend of the neat, 2 wt%, 3 wt%, 4 wt% and 5 wt% Nano clay filled Napier/epoxy composite is illustrated in Figure 3.1(a). It clearly showed that the composites undergo elastic region and plastic deformation before fracture. After the yield point, the composite did experience slight plastic strain, before it decreased sharply and fractures. Neat Napier/epoxy composites, shows distinct yielding before fractures at 3.5% strain while the 2 wt%, 3 wt%, 4 wt% and 5 wt% nano clay filled Napier/epoxy composite indicate lower strain to failure at ranges 2% to 3%.
The trend of this stress-strain curve shows similar characteristics to those of brittle materials. Therefore, the results suggest that the composites become stiffer and more brittleness like as the nano-clay filler contents increases.

The flexural strength of nano clay filled Napier/epoxy composites with 2 wt% to 5 wt% filler contents exhibited significant improvement than that of neat Napier/epoxy composites as shown in Figure 3.1(b). It is suggested that the presence of nano-clay filler is creating strong bonding between Napier fibres and epoxy resin. Thus, it resulted in increases the capability of the epoxy composite to sustain the stress during bending test. The flexural strength of filled epoxy composite increases with a rise in nano clay contents from neat (0 wt%) to 3 wt% before went slightly decreases with further increase in filler loading. The addition of 3 wt% of nano clay filler exhibits the highest flexural strength with the value 57.72 MPa and with an improvement of approximately 163% comparing to the neat Napier/epoxy composites, followed by 5 wt%, 4 wt%, and 2 wt% and without nano clay filler respectively. The improvement was achieved due to the interface interaction and created exfoliated structure in the composite with the addition of nano clay filler. Also, with a further increase in the filler loading of nano clay to 4 wt% and 5 wt%, the flexural strength Napier/epoxy composite dropped to 43.77 MPa and 48.599 MPa respectively. In Solhi et al.’s [11] and Zukas et al. [12] studies, results showed that by increasing the number of nanoparticles to more than a particular point, the flexural strength faced a significant reduction. Nevertheless, the presence of higher amounts of nano clay up to 5 wt% gradually decreased the flexural strength due to the agglomeration of the nano clay fillers at higher ratios and consequently embrittlement of the matrix [13].

Figure 3.1(c) showed the flexural modulus for various nano clay-filled loading Napier/Epoxy composite. There was an increment in the flexural modulus as the nano-clay filler loading increases. The flexural modulus of 5 wt% nano clay filled Napier/epoxy composites ranked the highest flexural modulus of approximately mean value of 3.2GPa. There was over 180% of improvement compared to neat Napier/epoxy composites with the value of 1.12GPa. It ranked as the highest flexural modulus due to the formation of exfoliated structure where strong interfacial interaction between the epoxy matrix and nano clay filler [14]. Besides, the flexural modulus for 2 wt%, 3 wt% and 4 wt% of nano clay filler also displayed significant enhancement with 42%, 132% and 130% respectively. The presence of nano clay filler in the epoxy matrix contributed in stronger the bonding via rearranging the chain structure of the epoxy, and it enables to tighten the chain for preventing the chain free to move. Thus, it significantly improves the flexural modulus as consequence of the addition of nano clay filler in the epoxy matrix. Based on Chisholm et al.’s study, a significant enhancement was investigated in flexural modulus of epoxy matrix by adding nanoparticles due to it able provided higher surface energy [15]. Besides, the highly dispersed of nano clay filler could provide well bonding with epoxy matrix and thus the efficiency of stress transferring boosted up subsequently, leading to ameliorate the flexural modulus.

Figure 3.1(d) presented the strain to failure with the different nano clay filler content for Napier/epoxy composites. The figure showed that the strain to failure values decreased with increases the amount of nano clay filler content of the composites. This suggested that addition of nano clay filler seem to change the epoxy matrix to be more brittle behaviour, which was reflected by minimised strain to failure values of the composites. The results show that the maximum strain to failure values occurred at neat Napier/epoxy composite at 3.08% while the minimum strain to failure values happened to 5 wt% of nano clay filled composite at 2.21% strain. Besides, the strain-to-failure for 2 wt%, 3 wt% and 4 wt% of nano clay filler contents yield reduced strain at 3.0%, 2.98% and 2.73% respectively. The drop in strain to failure values of the nano clay filled Napier/epoxy composite could be described as the presence of the nano clay filler in the epoxy matrix would change their properties from elastic behaviour to brittle behaviour.
3.2 Morphological Properties on Fracture Surface

The fracture surface observation of Napier/epoxy composites with and without nano clay filler through SEM are shown in Figure 3.2. It revealed that the fracture surface of composites without nano clay filler is clear and with a smooth surface. It can be observed that there are a large number of tiny white particles inspected on the fracture surface of the composites. The increased nano clay filler contents in the reinforced Napier/epoxy composites can be evident from the increased of the tiny white spot on within the epoxy matrix. In order to achieve the better mechanical performance of the composites, the nano-clay filler should be well distributed in the epoxy matrix. Moreover, for the 3 wt% and 5 wt% of nano clay loading, the SEM image displayed that the nano-clay filler is quite well distributed throughout the Napier fibres and epoxy matrix and also distributed equally without any agglomeration observed. Thus, it brings significant advantages to the flexural strength and modulus properties.

Figure 3.1. (a) Graph of Flexural Stress-Strain, (b) Histogram of Flexural Strength, (c) Histogram of Flexural Modulus, (d) Histogram of Strain to Failure for Various Nanoclay-filled Loading Napier/Epoxy Composite.
Figure 3.2. SEM image of the fracture surface of the Napier/epoxy composites, (a) Without nano clay fillers, (b) With nano clay fillers.

From Figure 3.3 shows the various loading of nano clay filler displayed varying degrees of surface roughness. It can be clearly seen that a relatively smooth fracture surface is demonstrated by the neat Napier/epoxy composites shown in Figure 3.3(a). Compared to the neat Napier/epoxy composite sample, the fracture surface of the nano clay filled composites exhibited a rougher fracture surface as shown in Figure 3.3(b). The presence of nano clay filler in the epoxy matrix influences the fracture path to be more complex and thus the rough surface. These rough surfaces could promote better interfacial bonding between the fibres and the epoxy resin. It is illustrated that addition of nano clay filler into the Napier/epoxy composite interphases resulted in an improvement in toughness [16].

Figure 3.3. SEM image of the roughness surface of the Napier/epoxy composites, (a) Without nano clay fillers, (b) With nano clay filler.

Besides, Figure 3.4 exhibited that a huge number of agglomerates which was observed in SEM micrograph with 200 x magnifications. This kind of observation can justify the reduction of mechanical properties at nano clay loading of beyond 3 wt%. However, the accumulation of the nano clay filler in the composites causes the stress concentration and consequently crack propagation occurred. Therefore, higher agglomeration clay can be the critical reason for crack propagation, and it affects to the reduction in flexural strength as well as matrix fracture. [17-18].
Figure 3.4. SEM image of the agglomeration of nano clay on the fracture surface of the Napier/epoxy composites at a various wt% of nano clay contents.

As shown in the SEM image of Figure 3.5(a), the neat Napier/epoxy composite demonstrates the fracture took place along the bonding interface between the epoxy resin and Napier fibres. The Napier fibres are completely separate from the fracture surface that proves the poor bonding between the Napier fibre and epoxy matrix and consequently, more Napier fibres pull out. In contrast, with the presence of nano clay filler reinforced composites, the Napier fibres pull-out the phenomenon has been significantly reduced, and thus improve the consolidation between the epoxy matrix and the Napier fibres as shown in figure 3.5(b). The 5 wt% nano clay filled composites were observed with the least fibres pull-out under 100 x magnifications. As a result, it suggests an enhancement of adhesion capability between the Napier fibres and epoxy matrix with the presence of the nano clay filler. Some research mentioned that nano clay filler could improvise the cohesion properties between the adjacent and the interlayer of composite layers [13].

Figure 3.5. SEM image of the fibre pull-out on the fracture surface of the Napier/epoxy composites, (a) Without nano clay fillers, (b) With nano clay fillers.

4. Conclusion
The effect of nano clay filler loading on mechanical and morphological properties of Napier/epoxy composites was investigated. Based on the experimental results, it can be figured out that the reinforcement of nano clay filler in Napier/epoxy composites has a significant impact on the flexural properties compared to neat Napier/epoxy composite. However, for the fracture mode, it is no longer ductile with plastic deformation, but showing becoming brittleness like behaviour. The highest tensile strength was ranked by 3 wt% of nano clay filler with the value 57.72 GPa. However, there is a reduction in flexural strength for further increase of nano clay filler loading. It was attributed to the intercalated structure in the Napier/epoxy composite with above 3 wt% of nano clay filler was loaded. This study demonstrates that the flexural modulus is improved with increasing of the nano clay filler content up to 5 wt%. This is due to the formation of exfoliated structure where strong interfacial
interaction between the epoxy matrix and nano clay filler. From the observation under SEM, the better intercalation of nano clay in the epoxy composites was examined in the specimen with 3 wt% and 5 wt% of nano clay filler loadings. By comparison, the fracture surface of 5 wt% of nano clay filler composite is rougher, and it ranked as the highest in flexural modulus. Also, fibre pull-out failure was observed on the flexural fracture surfaces of the neat Napier/epoxy composite. With the addition of nano clay filler, it could help to reduce the fibre pull-out failure problem due to the enhancement of adhesion capability between the Napier fibres and epoxy matrix. Overall, the SEM shows an improvement in interfacial bonding between the Napier fibres and epoxy matrix upon the nano-clay filler was added \[19\]. As concluded, the presence of nano clay filler loading with a range of 3 wt% to 5 wt% in the Napier/epoxy composites shows the significant improvement in mechanical and morphological properties.

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6. References
[1] D. H. H. Cheung, M. P. Ho, K. T. Lau and F. Cardona: ‘Natural fibre-reinforced composites for bioengineering and environmental engineering applications’, Compos. Part B Eng., vol. 40(7), pp. 655–663, 2009.
[2] Koviier K, “Fiber reinforced concrete”. The Cement and Concrete institute, Midrand, 2001.
[3] M.J.M. Ridzuan, M.S. Abdul Majid*, M. Afendi, S.N. Aqmariah Kanafiah, J.M. Zahri, and A.G. Gibson, “Characterisation of natural cellulosic fibre from Pennisetum purpureum stem as potential reinforcement of polymer composites,” Mater. Des., vol. 89, pp. 839–847, Jan. 2016.
[4] M. Haameem J.A., M.S. Abdul Majid, M. Afendi, H.F.A. Marzuki, I. Fahmi, and A.G. Gibson, “Mechanical properties of Napier grass fibre/polyester composites,” Compos. Struct., vol. 136, pp. 1–10, Feb. 2016.
[5] M. Haameem J.A., M.S. Abdul Majid*, M. Afendi, H.F.A. Marzuki, E.A. Hilmi, I. Fahmi, and A.G. Gibson, “Effects of water absorption on Napier grass fibre/polyester composites,” Compos. Struct., vol. 144, pp. 138–146, Jun. 2016.
[6] M.J.M. Ridzuan, M.S. Abdul Majid*, M. Afendi, K. Azduwin, N.A.M. Amin, J.M. Zahri, and A.G. Gibson, “Moisture absorption and mechanical degradation of hybrid Pennisetum purpureum/glass–epoxy composites,” Compos. Struct., vol. 141, pp. 110–116, May 2016.
[7] Amir, W.W., Jumahat, A. and Kalam, A., Characterization of Nanoclay-Modified Epoxy Polymers Using X-Ray Diffraction Analysis. Applied Mechanics and Materials, 2015, pp. 175-180.
[8] Mousavinasab SM, Atai M, Alavi B., “To Compare the Microleakage Among Experimental Adhesives Containing Nanoclay Fillers after the Storages of 24 Hours and 6 Month,” Open Dent J, vol. 5, pp. 52-7, 2011.
[9] Paul DR, Robeson LM. Polymer nanotechnology: Nanocomposites. Polymer (Guildf), 2008, pp. 3187-3391.
[10] M.S. Fartini, M.S. Abdul Majid*, M.J.M. Ridzuan · N.A.M. Amin, Geoff Gibson, Compressive properties of Napier (Pennisetum Purpureum) filled polyester composites. Plastics, Rubber and Composites: Macromolecular Engineering, Plast. Rubber Compos., vol. 45, no. 3, pp. 136-146, April 2016.
[11] Solhi L, Atai M, Nodehi A, Imani M, “A novel dentin bonding system containing poly (methacrylic acid) grafted nanoclay: synthesis, characterization and properties,” Dent Mater, vol. 28, pp. 1041-1050, 2012.
[12] Zukas T, Jankauskaitė V, Žukienė K, “The Influence of Nanofillers on the Mechanical Properties of Carbon Fibre Reinforced Methyl Methacrylate Composite,” Mater Scienc, vol. 18, pp. 250-255, 2012.
[13] K. Krushnamurty, I. Srikanth, B. Rangababu, S. K. Majee, R. Bauri, Ch. Subrahmanyam, “Effect of nanoclay on the toughness of epoxy and mechanical, impact properties of E-glass-epoxy composites,” Advanced Materials, vol. 6, pp. 684-689, March 2015.

[14] S. S. Ray and M. Okamoto, “Polymer/layered silicate nanocomposites: a review from preparation to processing,” Progress in Polymer Science, vol. 28, no. 11, pp. 1539–1641, 2003.

[15] Chisholm N, Mahfuz H, Rangari VK, Ashfaq A, Jeelani S, “Fabrication and mechanical characterization of carbon/ SiC-epoxy nanocomposites,” Composite Structural, vol. 67, pp. 115-139, 2005.

[16] Kusmono and Zainal ArifinMohd Ishak, “Effect of Clay Addition on Mechanical Properties of Unsaturated Polyester/Glass Fiber Composites,” International Journal of Polymer Science, Oct 2013.

[17] Ikejima I, Nomoto R, McCabe JF, “Shear punch strength and flexural strength of model composites with varying filler volume fraction, particle size and silanation,” Dent Mater, vol. 19, pp. 206-211, 2003.

[18] Nunes MF, Swift EJ, Perdigão J, “Effects of adhesive composition on microtensile bond strength to human dentin,” Am J Dent, vol. 14, pp. 340-343, 2001.

[19] Mohammad Hossein Pol, G.H. Liaghat, “Studies on the Mechanical Properties of Composites Reinforced with Nanoparticles,” Polymer Composites, vol.10, pp. 206-211, 2017.