Effect of nanoclay filler on mechanical and morphological properties of Napier/ epoxy composites

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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. This is due to the establishment of environmental awareness, the tendency of renewable product, pollution issues and financial problem. Thus, many engineering composite applications are now adopting natural fibre resources instead of using synthetic fibres [1]. Although synthetic fibres have yield mechanical properties and better reinforcement in polymer composites, they are non-renewable, non-biodegradable and quite expensive resources. Therefore, a lot of industrial and structural applications such as aerospace, automotive, marine, construction and packaging are improving the utilisation of natural fibre reinforced composites due to their cost-effectiveness, high specific strength, toxic free, renewability, low density and biodegradable behaviour [2]. Moreover, some researchers have investigated on several kinds of natural fibre resources such as hemp, jute, bamboo, kenaf, oil palm, coconut seed, kapok and Raphia and its have contributed significantly on composite materials [3]. However, poor adhesion bonding between fibres and matrix, low durability, low fibres partition and poor thermal properties are still concerned issues to be addressed in reinforced composite applications. The mechanical properties, such as tensile, impact and flexural properties as well as the morphological behaviour of the natural fibres are still of research interest to be addressed [4].

Natural fibres reinforced composites are widely utilised in the structural applications due to their relatively high mechanical performance, low cost and environmentally friendly applications. Epoxy resins are commonly selected matrix used in fabrication natural fibres reinforced composites. They are one of the outstanding resins amongst the class of thermosetting resins. Epoxy resins are contributing to better mechanical, thermal, adhesive and electrical properties [5]. Their primary function is to enhance the adhesive structure when reinforcing with natural fibres. However,

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epoxy resins do have limitations when it comes to high-performance applications due to their inherent brittleness behaviour. Therefore, various studies of epoxy resin have been carried out to overcome the shortcomings, hence enhance their performance such as additional of nanoparticles, optimum fibre orientation, fibre weight fraction with matrix and surface modification [6].

In recent year, a new approach is employed to enhance the performance of the composite by adding nanoclay filler into the matrix system. Addition of nanoclay filler into matrix found to improve the mechanical properties such as flexural strength, interlaminar shear strength and tensile toughness behaviour [7]. Montmorillonite (MMT) is the common nanoclay which can be used to increase the mechanical properties of polymers. It contains 25−30 wt% trimethyl stearyl ammoniums that able to also improve the modulus and enhance chemical resistance. Also, montmorillonite clay can also reduce crack propagation and improve the flexural strength; consequently due to it consists of platelets with an inner octahedral layer inserted between two silicates tetrahedral [8]. The low density of nanoclay particles plays a significant role in minimising the overall weight of the resin matrix [9]. The surface modification also can be achieved efficiently for better dispersion and distribution in the resin phase by adding nanoclay filler. This proper dispersion in nanoscale makes altering in flexural strength properties and prevents crack propagation of composites.

2. Natural fibre

Natural fibre is a fibrous fibre; extracted from three subdivided classes such as plant fibres, animal fibres and mineral source fibres. The widely used of natural fibre are usually derived from the plant. Plant fibres consist of five basic types of natural fibre which include seed fibres, core fibres, bast fibres, leaf fibres, grass and reed fibres [10]. Table 6.1 shows that the types of natural fibres with particular examples. Recently, there are many investigations on several kinds of natural fibres, such as coconut, jute, flax, hemp kenaf, ramie, bamboo, Napier grass, reeds, banana, sisal, pineapple and kapok for uses in many applications especially as reinforcement in composite materials. Fig. 6.1 shows the more prevalently natural fibres which are widely utilised in particular industries. The natural fibres provide many significant

Table 6.1 Types of natural fibres with examples [10].

No.	Types of natural fibres	Examples
1.	Bast fibres	Jute, flax, hemp, ramie, kenaf
2.	Leaf fibres	Banana, sisal, agave, pineapple
3.	Seed fibres	Coir, cotton, kapok, coconut
4.	Core fibres	Kenaf, hemp, jute, bamboo, Napier
5.	Grass and stem fibres	Wheat, corn, rice

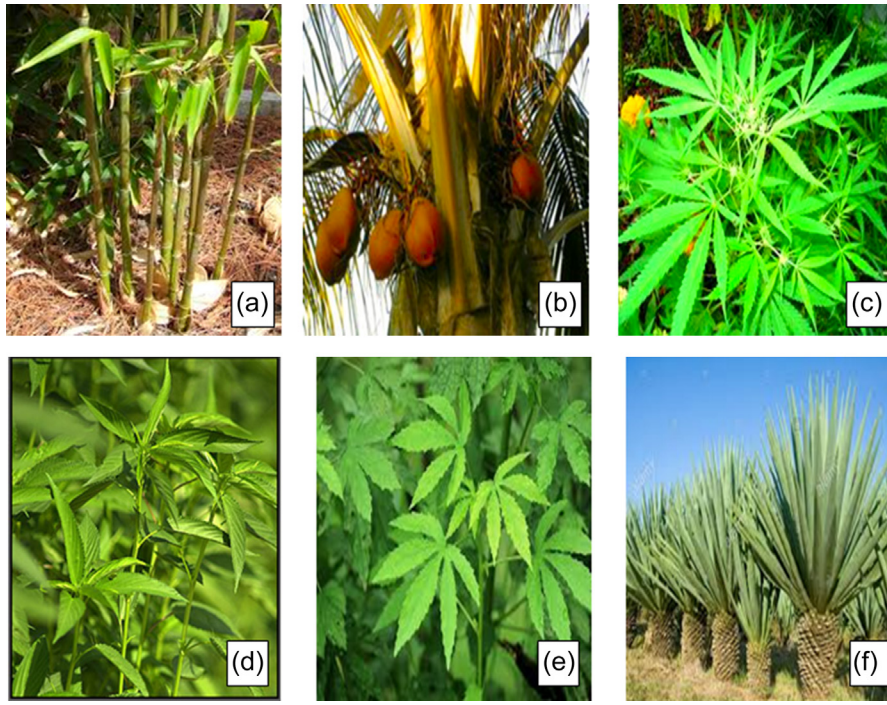


Fig. 6.1 Type of natural fibres: (A) Bamboo; (B) Coconut; (C) Hemp; (D) Jute; (E) Kenaf; (F) Sisal [12−17].

advantages and potentials such as low cost when compared to synthetic fibres, low density, lightweight, excellent mechanical properties, biodegradability, renewable source, high specific stiffness, acoustic insulation and non-toxicity [11]. Their excellent characteristics are utilised for use in aerospace, automotive, plastics and packaging industries.

From the 90s, natural fibres are in demand for many engineering applications as a response to the laws of environmental. This is because the growing uses of synthetic fibre which consequently produce non-biodegradable waste disposal that leads to serious pollution concerns [17]. Thus the needs for the substitution of synthetic fibres; e.g. glass or carbon to natural fibres for reinforcing of polymer composites is now more essential [18]. Liu et al. reported that high performance of flax fibre was able to replace carbon or glass fibres as reinforcement's materials for plastics. The author also mentioned about the superior properties of thermoplastic and thermosetting composites reinforced with flax fibre was obtained from a mixture of epoxy resin and soybean oil and generated "Green" composites from renewable materials or resources [19].

Natural fibres are seen as potential fibres for many engineering applications. However, there are still critical issues causing limitations; performance during service, long-term performance and fracture behaviour. Thus, it is essential to perform the necessary studies to improve their performance. Other factors, i.e., high moisture

sensitivity, poor wettability, low thermal degradation temperature and low chemical resistance are the critical disadvantages of natural fibres that need overcome. Thus, the natural fibres must be significantly examined methodically to investigate their physical, morphological, chemical, flexural and tensile performance [20]. Rao K et al. studied the chemical and physical compositions of natural fibres to determine their physical properties. They investigated their fibre structure, density cellulose content and cross-sectional shape [21].

Valadez et al. also reported that the application of chemical treatment on the surface of the fibre to improve the adhesion characteristics and bonding intensity of natural fibre reinforced composites. The author strongly stressed that there was an enhancement of the adhesion characteristics of natural fibre surfaces after going through chemical treatment [22]. Besides, there was a cost-effective way to enhance the fibre surface such as chemical treatment. This kind of treatment could remove all the existing impurities on the fibre surface like hemicelluloses, lignin or waxy substances to avoid the moisture absorption from the surrounding. Overall, it is necessary to continue the low-cost modification of natural fibres to fulfil the need of the today composites market.

3. Napier grass fibre

As a result of environmental awareness, much research in engineering applications are focused on natural fibres as substitution of synthetic fibres for fibre reinforced composites because of their unique characteristics and eco-friendly advantages. Advantages like lightweight, environmental sustainability, low material cost, low density, renewability and potential mechanical properties are playing a vital role in making composites nowadays [23].

In the recent review, a natural fibre extracted from Napier grass which is also known as '*Pennisetum purpureum'* or elephant grass was investigated. Napier grass is a native of Africa, and it was promoted to South America, Australia and Asia as food or provisions for animals. Napier grass is the core fibres type of which the fibres presence inside the bast fibres of the centre of the plant's stems. It is similar to bamboo, yellowish colour stem and highly sustainable throughout Malaysia. It could be harvested 4 to 6 times a year. Napier fibres are described by long narrow fibres with thick-cell wall on stems. Napier grass is natural to grow by underground stems, deeply rooted and densely clump plant; can grow up to 7.5 m tall. Moreover, it can be perennial grow and fast growing in the drought weather [24]. Napier grass especially when young is mainly providing good taste and highly nutritious of fodder crop for animals. It has been used widely before for biomass production due to its high sustainability. In addition, the mechanical properties of the grass, like tensile, impact and flexural strength have been reviewed by the earlier researchers [25] (Fig. 6.2).

After the conventional water retting process, a manual extraction is applied to extract the fibre from Napier stems in order to remove all the hemicelluloses, wax or impurities on the surface. Rao et al. studied the effect of extracting elephant grass

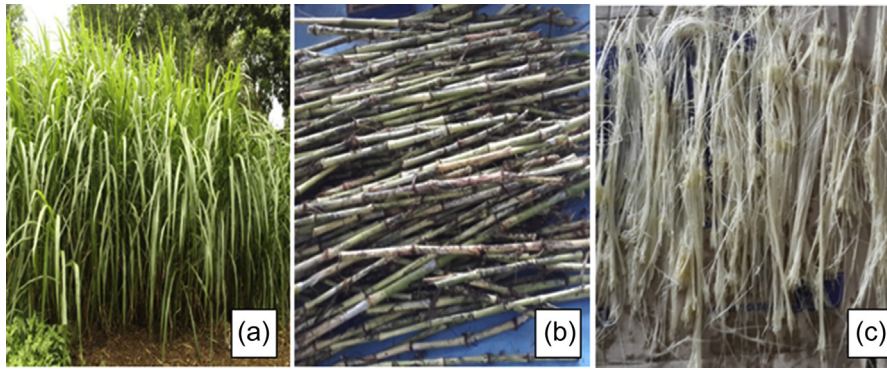


Fig. 6.2 Napier Grass Fibre: (A) Napier Grass; (B) Napier stem; (C) Napier fibre strand.

fibres via chemical and retting process on the tensile strength. They found that the retting process yielded superior tensile strength and elastic modulus of the fibres by almost 1.5 times greater than those chemically extracted fibres [26]. Ridzuan et al. reviewed the properties of P. purpureum fibres and found that it has high moisture substances due to their multi-cellular structures. The surface morphological was observed and emphatically proved that there is the existence of contamination on the surface of untreated P. purpureum fibres [27].

Moreover, research reported that the surface behaviour of the Napier fibres becomes uneven and rougher after alkali treatment and it has improved the structural, thermal, and tensile properties. The author also mentioned that Napier grass fibres are excellent raw material to strengthen in the fabrication of bio-composites [28]. Kommula et al. had also investigated the mechanical performances, water absorption, and chemical resistance of Napier grass fibre reinforced epoxy resin composites. They found that 20 wt% Napier fibre strands reinforcing composites was able to obtain optimum mechanical properties. Besides, short fibres strand-epoxy composites displayed poor mechanical performances compared to long linear fibre reinforced epoxy composites. There is also an improvement in interfacial bonding between matrix and fibre strand after undergoing alkali treatment on fibre strands [29].

M. Haameem et al. have studied and characterised the mechanical behaviours of Napier fibres reinforced polyester composites. The flexural and tensile strength of the untreated Napier fibre reinforced polyester composites are dependent on the volume fraction of fibres. The result showed that a 25% volume fraction of Napier fibre in the composite is enough to produce optimum tensile and flexural properties. Furthermore, the author also found that more than 80% improvement on the tensile strength of the alkaline-treated Napier fibres compared to the untreated fibres [30]. Furthermore, the tensile and flexural strength of Napier grass also has been investigated through the previous researches on fabricating of Napier fibre-reinforced polyester laminates. Subsequently, the results obtained proved that the Napier fibre-reinforced polyester laminates performing good properties compared to other natural fibre-based composites.

To conclude, the use of Napier grass has the potential to be promoted as a possible source for reinforcing materials in composites industries. This could positively contribute to many engineering applications today especially for reinforcement in composites.

4. Natural fibre reinforced epoxy composites

In the past decades, the creation of synthetic fibre reinforced polymer composites resulting in widespread use in various engineering industries. The wastage from the manufacturing and removal of composites structures are all non-biodegradable material. It is major concerns to the environment because there is still have not any perfect methods for the disposal of non-degradable synthetic fibre materials. In recent years, scientists and engineers have been actively exploring to search the elements as substitution of using synthetic fibres to overcome the pollution problems. The natural fibres successfully validated to be an alternative source for reinforcing composites.

Natural fibre composites have been gradually used for many engineering applications over recent years. For example, natural fibre composites have become attractive for structural applications such as construction, marine, aerospace and automobile industries. This is due to their low specific mass, high mechanical performance, biodegradable and low in cost [31]. There are still however poor characteristics of natural fibres in reinforced composites such as low thermal properties, poor fibre partition, low durability and poor interfacial strength between resin and fibres due to incompatibility issues to be addressed. Researchers have focussed on enhancing the mechanical properties and interfacial bonding intensity of natural fibre composites. Mohanty et al. studied the effect of different chemical surface treatments on mechanical properties of jute fibres composites. Alkali treatment and cyanoethylation surface modification result in improved tensile and bending strength [32]. Furthermore, Sreekumar et al. indicated that the damping factor, loss modulus and storage modulus of fibre-reinforced polyester composites could immensely change by fibres surface treatments at a wide range of temperatures [33].

Fahmi Idris found that the higher fibre volume fraction, the higher the peak load and energy absorption. Addition of Napier fibre improves the impact response of the epoxy composites. Besides, the higher the fibre volume fraction of the reinforced composite, the longer the time contact and energy absorption when the force applied on it which means that it has a low brittle fracture and more ductile [34]. Also, J.H. Song reported the effects of strain rate on sisal fibre reinforced polymer—matrix composites. The epoxy resin composite was reinforced by sisal fibre through the resin transfer moulding (RTM) method. The mechanical properties of composites were tested with different surface modification such as permanganate, silane and non-treated treatments. The results showed that untreated fibres composites yielded a stable fracture and deformation energy while permanganate-treated fibre reinforced composites had the highest tensile strength compared to other surface treatments [35].

Santosh et al. examined the difference in mechanical properties of banana fibres which reinforced with both epoxy and vinyl ester resin. The study found that banana fibres reinforced epoxy composites had a higher impact, flexural and tensile strength compared to banana fibres reinforced vinyl ester composites. Besides, the mechanical properties like impact, flexural and tensile strength of both banana fibres epoxy and vinyl ester composite can be enhanced by alkali treatment with 5% of NaOH [36]. Physical, mechanical and thermal properties of jute and bamboo fibre reinforced unidirectional epoxy composites had been investigated by Subhankar Biswas et al. The unidirectional composites were produced by using vacuum infusion technique and found that jute and Bamboo reinforced epoxy composites performed high flexure strength with arrangement transverse and longitudinal respectively. This study reviewed jute fibre reinforced epoxy composites had higher Young's modulus while Bamboo fibre reinforced epoxy performed stronger tensile strength [37].

Madhukiran et al. reviewed the hardness and tensile characteristics of reinforcing banana and pineapple fibres with epoxy composites. Both banana and pineapple fibres were extracted by water retting and manual cleaning process. The results showed that the tensile strength had increased gradually with the increase in fibre weight fraction. This revealed that hybridisation of reinforcement composites could obtain a better result than a single type of natural fibres [38]. On a similar note, the mechanical properties of jute fibre reinforced composites with polyester, and epoxy resin matrices were examined by Ajith Gopinath [39]. The research reported that jute epoxy composites obtained superior flexural and tensile properties compared to jute polyester composite. However, the processing time required for jute epoxy composite is much longer than jute polyester composite. The author also mentioned that jute epoxy composites are more suitable for fabricating automotive applications rather than jute polyester composites.

Overall, natural fibres reinforced composites can be great significance than metals and ceramics due to its high stiffness and stronger. Besides, natural fibres reinforced composites are very light in weight, thus the ratios of strength to weight and stiffness to weight is much stronger than aluminium and steel. It is also possible to achieve the mechanical properties of metals, ceramics polymer.

5. Nanoclay reinforced composites

In the past decade, fibre reinforced polymer composites have been used in large quantity for structural applications, for example, an automobile, marine and construction industries as a result of their superior mechanical properties. Besides, the high mechanical, thermal and electrical performance of the epoxy resins were also widely used as a matrix material in fibre reinforced polymer composites. There were some concerns about their limitation for many high-performance applications due to their low impact resistance and inherent brittleness properties. However, research then revealed that incorporation of nanoparticle into matrix composites would overcome some of the limitations of their composites properties. Over the recent years, carbon nanofillers have

been investigated for reinforcing fibres epoxy composites and found that addition of carbon nanofillers into epoxy resins can enhance the mechanical, functional, structural and adhesive properties [40].

Past research found that the nanofiller loadings range from 1 to 3 vol% was the maximum volume to improvise the mechanical properties of the epoxy composites. If the nanofiller loading volume is more than the mentioned range, a reduction could occur on both tensile strength and tensile modulus of the filled epoxy composites. Sandler et al. reported that adding 1 wt % of CNT with oriented randomly into the matrix was enough to obtain a better state of dispersion and mechanical properties improvement [41]. Martone et al. had examined the influences on the bending modulus of the composites by adding multi-walled carbon nanotube (MWCNT) into an epoxy system. The outcomes indicated that the MWCNT could maximise the reinforcement efficiency like aspect ratio and bending modulus with very low volume loading 0.05% w/w. This is because low filler loading could obtain better dispersion and optimise the interfacial bonding between fibre and matrix [42].

Furthermore, Mittal et al. investigated that graphene and carbon nanotube (CNT) has a great deal potential to improvise the properties of composites for several engineering applications because of their satisfied structural, functional properties and its suitability. The authors mentioned various factors that can optimize the functions of multi-walled carbon nanotube (MWCNT) or graphene nanoplatelet (GNP) reinforced epoxy composites such as quality of fillers, aspect ratio, amount of fillers loading, surface modification, state of dispersion of filler in matrix, the selection of matrix and as well as adhesion bonding between fillers and matrix [43]. In addition, Guo et al. reviewed the effects of on the mechanical performances and fracture morphologies of composites reinforced with multi-walled carbon nanotube filler (MWCNT). This study found that increasing the volume loading of MWCNT lead increasing in the tensile strength and fracture strain of composites, yet Young's modulus dropped at the same time. This is because of the addition of MWCNT could harden the composites and the outside layer of MWCNT damaged by oxidation after mixed-acid treatment [44]. To summary, nanofiller could be used to improve and modify the mechanical performance in composites. Nanofiller able to enhance the surface finishing on the composites while maintaining minimum health hazards.

6. Nanoclay filled Napier/epoxy composites

Nanoclay or nano-layered silicate are optimised-clay minerals with several enhancements properties and have become much popular as reinforcing fillers for composites amongst the various nanoparticles. This is due to their high aspect ratio, potentially exfoliation characteristics and better mechanical performance. It is like montmorillonite which the most commonly used in materials applications. Nanoclay consisted of approximately 1 nm thick alumina silicate layer surface and stacked with around 10 nm sized of multilayer stacks. Thus it has an excellent aspect ratio and specific surface area with approximately 657m^2/g. Many researchers found promising that

nanoclay filler enables to strengthen and altering the mechanical properties dramatically of fibre reinforced polymer when nanoclay was well dispersed in epoxy resin composites [45]. Moreover, few research studies have been carried out to test the effect of nanoclay filler on the mechanical properties of fibre reinforced polymer. The presence of nanoclay of less than 10% by weight of epoxy found to improve the mechanical properties; tensile strength and tensile modulus. The brittle behaviour was reported when a large amount of nanoclay loading into epoxy resin system. This was suspected of causing by agglomeration of nanoclay fillers in the epoxy resin.

Aidah et al. reported the effect of nanoclay filler on the mechanical properties of glass fibre reinforced polymer (GFRP). The morphological properties on specimen surface have been carried out through FESEM technique. Crack propagation was observed on the epoxy matrix due to the addition of a certain amount of nanoclays filler. Besides, there was a fracture surface occurred on the interface bonding between fibre and epoxy of the GFRP without nanoclay filler loading. This clearly showed that it has a weak adhesion bonding between fibre and matrix. This study highlighted that 5 wt% of nanoclay filler enable to optimised in the flexural properties of the GFRP composites. This was possibly caused by better interface bonding between the nanoclay filler, fibre and matrix, improvement in stiffness properties of the composites and well adhesion between fibre and matrix with the help of nanoclay filler [46]. Furthermore, a study also indicated that nanoclay particles could dramatically drop the whole weight of the resin matrix compared to other nanoparticles due to its lower density. This was a significant advantage and essential on fabricating a composite with a low weight ratio of nanoclay filler to reinforcement properties [47].

Montmorillonite (MMT) clay is one of the available forms of nanoclay known as layered silicate materials. It has been widely used as inorganic fillers in polymer applications due to the ability to increase and modify the mechanical properties of polymers significantly such as reduction in crack propagation and enhancement in flexural strength. It is low in cost consequently on using this kind of method for the improvement of the properties of polymers [48]. Yuanxin Zhou et al. investigated the effect of montmorillonite clay on mechanical and thermal properties of epoxy composites. The flexural tests have been carried out to assess the mechanical properties behaviour. The result displayed that 2.0 wt% of nanoclay loading in epoxy resin performance most significant improvement in flexural strength as compared to without nanoclay loading in epoxy resin. Addition of 2 wt% nanoclay has increased by 31.6% and 27% in flexural modulus and strength respectively [49].

The purpose of nanoclays fillers can be divided into two main reasons; to enhance the properties of the materials and bring down the cost of the component. Recently, nanoclay particles have been proved and widely used in many engineering applications for enhancement of the tensile toughness and flexural strength properties of epoxy composites as well as surface finishing. To conclude, adding nanoclay filler in the Napier fibres reinforced epoxy composites can increase the roughness of the surface and maximise in the contact area between the epoxy resins on the fibres. Thus, it may dramatically enhance in their interfacial bonding leading to improvise the mechanical and morphological properties of the composites when modifying by adding of nanoclay filler.

7. Fabrication and flexure test of nanoclay filled Napier/epoxy composites

First and foremost, the extracted raw Napier fibres were oven dried at 55°C for 30 min to remove excess moistures. The composite samples of Napier fibre reinforced epoxy resin was fabricated with 75% of epoxy resin and 25% of Napier fibre weight content (with ratio 3:l). Specimens from each subgroup were fabricated by using the vacuum infusion technique. The vacuum infusion technique is one of the effective methods for fabricating composite components, and it brought many advantages such as operates with low-cost tooling, unlimited setup time, high aspect ratio, consistent resin usage and wasted no resin. At the beginning of the vacuum infusion technique, the glass surface was polished by wax, and then the resin feed spiral was installed at one side of the glass plate. Few layers of Napier fibres were then positioned and oriented randomly on the glass surface. Next, the vacuum connector and resin feed spiral were connected. The infusion mesh was placed after the peel ply layer of the infusion was put. Moreover, the resin feed spiral and vacuum hose were sealed and positioned while the vacuum bag was then being taped. After that, the vacuum pump was connected and switched on to withdraw the air inside. The 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 a prepared resin trap. The process was continued run under room temperature for around 6 h to ensure the epoxy resin with nanoclay filler full covered onto the Napier fibres (Fig. 6.3). Lastly, the Napier fibre epoxy composite was done fabricating and stored for thoroughly dried and hardened. The same procedures were repeated with different amount of nanoclay filler volume fraction specimens [50].

Five different nanoclay filler[1] loading of Napier/epoxy composites such as neat, 2 wt%, 3 wt%, 4 wt% and 5 wt% were fabricated by vacuum infusion technique. There are some procedures, and precaution steps need to comply with to fabricate a satisfactory composite. The epoxy was first stirred by hand with nanoclay filler for 20 min at room temperature to get sound dispersion. Next, the epoxy hardener was added at a ratio of 3:1 by weight (epoxy: hardener) and then slowly stirred for another 20 min to remove small tiny air bubbles inside. After that, the mixtures were ready to be infused at room temperature until the Napier fibres fully covered by the epoxy matrix. The thickness of the composite was controlled by a Perspex moulding, and the thickness of composite fabricated was within ranges of 3−4 mm.

It was hard to fabricate Napier/epoxy composite with nanoclay filler beyond 5 wt% because of the nanoclay filler would make the epoxy mixture itself became very viscous and stagnant. As a result, the more the nanoclay filler loaded, the more viscous of the epoxy mixture. Consequently, the surface of the composites was full of voids and holes because of the epoxy matrix unable to adequately cover all the fibres (Fig. 6.3).

The three-point bending test was carried out by using INSTRON micro-tester. The cross-head speed should not set higher than 2 mm/min in order to get the compliance

[1] Nanoclay filler refers to Montmorillonite.

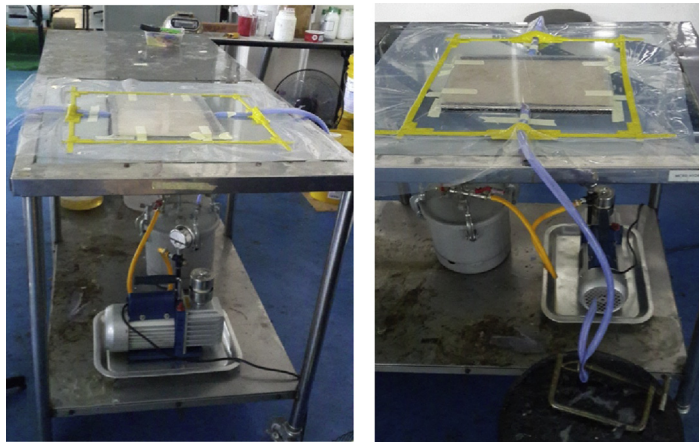


Fig. 6.3 Experimental setup for vacuum infusion process.

curve determination. Besides, the load applied to the centre of the specimen to get an accurate result as shown in Fig. 6.4(A, B). Eight specimens were tested for each type of composite, and the results were recorded. The results obtained; the load and extension data are being used to find the flexural strength and modulus, as well as the strain to failure.

The flexure stress shows the ability of the composites to withstand deformation under bending load. This stress can be obtained and calculated on the load-deflection curve by using the equation given;

$$\sigma_f = \frac{3pl}{2bd^2}$$

where σ_f = flexural strength (MPa);

p = maximum load (N);
l = support span (mm);
b = width of specimen (mm) and
d = thickness of specimen (mm).

Flexural strain illustrates the minimal changes in the length of the test specimen when undergoing deformation, where the maximum strain happens at midspan. It can also be calculated for any deflection using;

$$\varepsilon_f = \frac{6Dd}{l^2}$$

where ε_f = flexural strain(mm/mm).

D = maximum deflection of the centre of the beam (mm);
d = thickness of specimen (mm);
l = support span (mm).

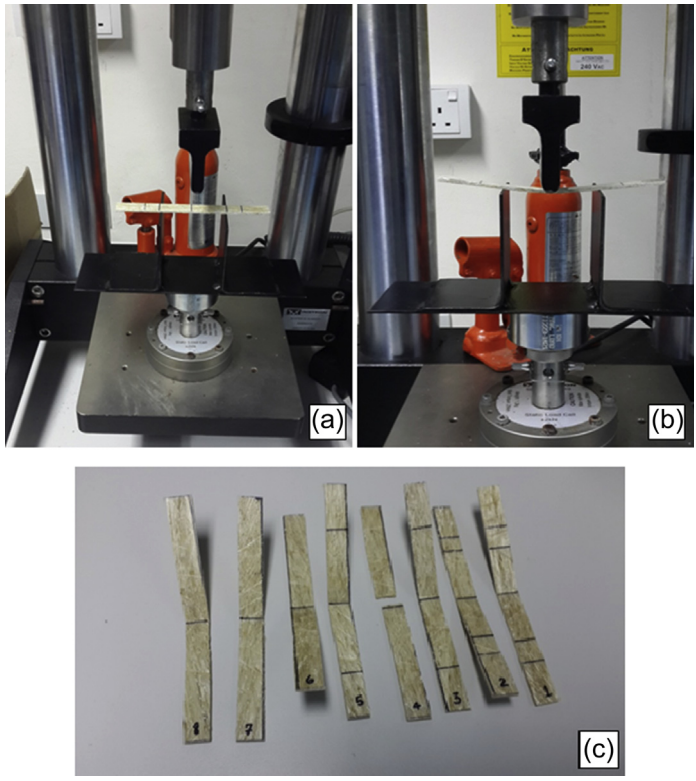


Fig. 6.4 (A) Before three-point bending testing, (B) During the three-point bending test, (C) Fractured specimen after the test.

Flexural modulus often called modulus elasticity which is used to demonstrate the bending stiffness of the composites. It can be calculated through mathematical calculation or by tangential of the initial straight line portion of the stress-strain curve.

$$E = \frac{ml^3}{4bd^3}$$

where E = flexural modulus (N/m^2) and.

m = initial slope of the load deflection (N/mm).

Finally, the morphology of the nanoclay filled Napier reinforced epoxy composites were observed by using field emission scanning electron microscope (FESEM). The images obtained used to evaluate the surface of the specimen and characterise their morphological properties. The microscope was acquired with 3−5 kV accelerating voltages, and the magnification was focused in a range of 50−200 times. Thus, the specimens were prepared with diameter 10 mm × 10 mm. Before scanning, the

specimens have to be consistently coated with a thin layer of platinum in order to prevent charging and caused a white spot on the scanned pictures.

8. Flexural strength and modulus of nanoclay filled Napier/epoxy composites

The flexural stress-strain trend of the neat, 2 wt%, 3 wt%, 4 wt% and 5 wt% nanoclay filled Napier/epoxy composite is illustrated in Fig. 6.5. It clearly shows that the composites undergo only an elastic region and no plastic deformation. In the beginning, the stress increases proportionally with the strain until reaching the elastic limit. According to Hooke's law, the flexural modulus of the composite is calculated at the initial flexural strain of 1% (0.01 mm/mm). Furthermore, the strain gradually increased beyond the elastic limit until it reached to the yield stress as the load was increased, where there is no more increment in load applied for further deformation of composite. After the yield strength point, the composite did not further undergo any plastic strain, and it suddenly decreased sharply, where the composite was broken at that time. Only neat Napier/epoxy composite that yields and then breaks before the 3.5% strain limit. On the other hand, the 2 wt%, 3 wt%, 4 wt% and 5 wt% nanoclay filled Napier/epoxy composite that breaks within strain limit of 2%−3% before yielding because no obvious yield point was found in the stress-strain curve. The trend of this stress-strain curve shows similar characteristics to those of brittle materials. Therefore, it reveals that the composites become more brittleness and stiffness as the nanoclay filler loading increases.

In addition, the presences of nanoclay filler enable to improve the flexural stress-strain response of the Napier/epoxy composite especially 3 wt% of nanoclay filler enhances the most. This is indicated by the area under the stress-strain curve of the nanoclay filled composites increases compared to neat Napier/epoxy composite.

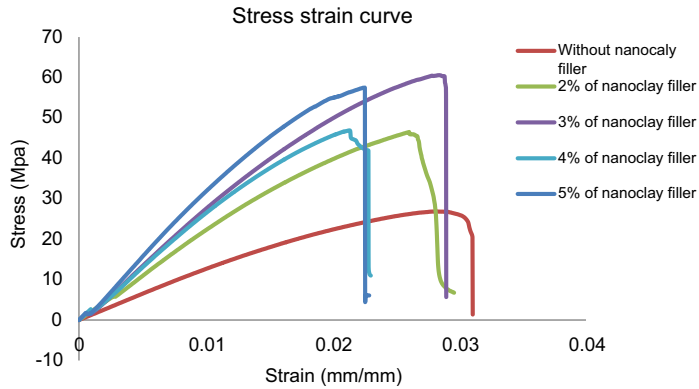


Fig. 6.5 Flexural stress-strain for various nanoclay-filled loading Napier/epoxy composites. Nanoclay filler refers to Montmorillonite.

It is due to the proper dispersion of nanoclay filler in the epoxy matrix where improving the fracture toughness of the material. There is no constant increment to the stress-strain curve may be due to the uncontrollable failure during the vacuum infusion process. During processing, the epoxy matrix can form small bubbles under high vacuum conditions. Consequently, the bubbles then trapped in the fabric and sometimes voids occurred after the epoxy resin solidifying. However, this is one of the reasons to affect the results on the mechanical properties.

Fig. 6.6 presents the strain to failure with the different nanoclay filler contents for Napier/epoxy composites. It is clearly shown from the above figure that the strain to failure values decreased with increases the amount of nanoclay filler content of the composites. This indicated that the nanoclay fillers cause the epoxy matrix to behave more brittle-like. The results show that the maximum strain to failure values was observed with neat Napier/epoxy composites at 3.08% while the least strain to failure seen with 5 wt% of nanoclay filled composite at 2.21%. Besides, the stain to failure value for 2 wt%, 3 wt% and 4 wt% of nanoclay filler slightly reduced with 3.0%, 2.98% and 2.73% respectively. The drop in strain to failure values of the nanoclay filled Napier/epoxy composite could be explained by the presence of the nanoclay filler in the epoxy matrix changes their properties from elastic behaviour to more brittle-like behaviour. This is because the nanoclay fillers limit the mobility and flexibility of the matrix, and thus the higher the amount for nanoclay filler content, the higher the brittleness of the composite.

The flexural strength of nanoclay filled Napier/epoxy composites from 2 wt% to 5 wt% is much better than neat Napier/epoxy composites as shown in Fig. 6.7. It was illustrated that the nanoclay fillers are 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 nanoclay filler loading from neat to 3 wt%, and there were slight decreases with further increase in filler loading. However, Table 4.3 shows that the addition of 3 wt% of nanoclay filler exhibits the highest flexural strength with

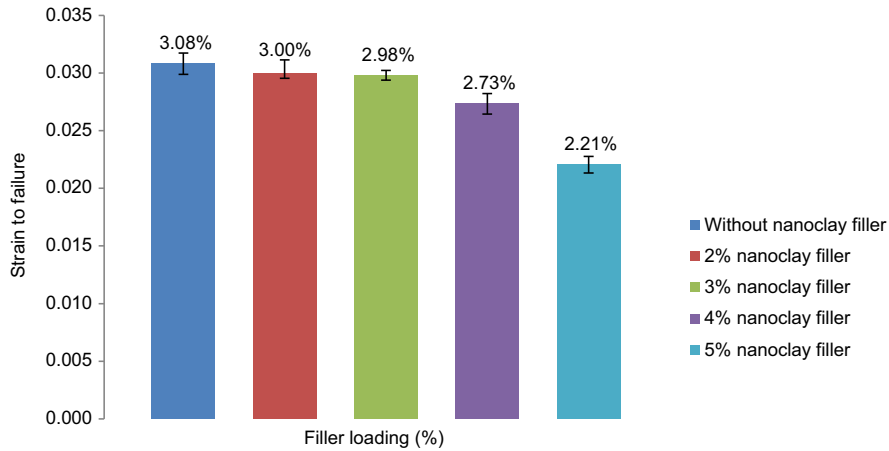


Fig. 6.6 Strain to failure for various nanoclay-filled loading Napier/epoxy composites. Nanoclay filler refers to Montmorillonite.

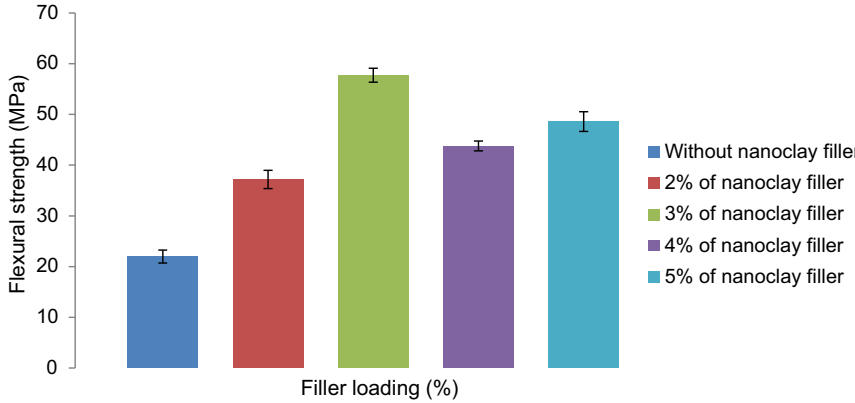


Fig. 6.7 Flexural strength for various nanoclay-filled loading Napier/epoxy composites. Nanoclay filler refers to Montmorillonite.

the value 57.72 MPa, followed by 5 wt%, 4 wt%, 2 wt% and last; without nanoclay filler respectively.

By comparing to the neat Napier/epoxy composites, the addition of 3 wt% of nanoclay filler had significantly increased the composite's flexural strength with an improvement of approximately 163%. The improvement is achieved due to the nanoclay filler plays an essential role in the curing of epoxy resin which could significantly improve the interface interaction and created exfoliated structure in the composite. Also, with a further increase in the filler loading of nanoclay to 4 wt% and 5 wt%, the flexural strength Napier/epoxy composite dropped to 43.77 MPa and 48.60 MPa respectively. In general, the flexural strength of 4 wt% of nanoclay filled Napier/epoxy composites are expected to be higher than 5 wt% of nanoclay filled yet experimental testing revealed unexpected results. The flexural strength of 4 wt% of nanoclay filled composites is found somewhat lower than the 5 wt% of nanoclay filled composites by almost 10%. This might be due to the poor dispersion of nanoclay filler in the epoxy composites.

Furthermore, the gradual decreased in the flexural strength with addition more than 3 wt% of nanoclay fillers are suspected due to the inappropriate dispersion of the nanoclay filler and formation of agglomeration in the epoxy resin. This causes the non-rich nanoclay of the epoxy resin to crack easily from the stress applied in the epoxy resin. This might be the critical reason that leads to crack propagation and reduction in flexural strength of the Napier/epoxy composite [52]. Therefore, excellent dispersion of nanoclay filler in the epoxy is vital in resulting flexural strength and physical properties of the composite materials. In Solhi et al.'s [53] and Zukas et al.' [54] investigation, results show that; increasing the % wt of nanoparticles exceeding a threshold point; the flexural strength experienced significant reduction. Furthermore, past research investigated the flexural strength of the nanoclay/E-glass epoxy composites, revealed that the highest flexural strength was observed at 3 wt% addition of nanoclay, beyond which it subsequently dropped. Nevertheless, the presence of higher amounts of nanoclay up to 5 wt% gradually decrease the flexural strength due to the agglomeration of the nanoclay fillers at higher ratios and consequently embrittlement of the matrix [51].

Similarly, Li et al. [55] and Adabo et al. [56] reported that increasing the amount of nanofiller could have a significant improvement on flexural strength, but then the strength dropped eventually by further increasing the amount nanofiller in the resin metric. As a result, the flexural strength will undergo significant reduction when the amount of nanoscale filler adding beyond the particular percentage. Moreover, the high viscosity of the epoxy resin phase will weaken the bonding between fibres and epoxy resin. Thus, the interfacial adhesion between the epoxy matrix and the Napier fibres deteriorated, resulting in the strength reduction.

Napier/epoxy composites ranked among the highest flexural modulus with approximately mean value of 3.2 GPa. There was over 180% of improvement compared to neat Napier/epoxy composites. This could be due to the formation of the exfoliated structure resulting in the strong interfacial interaction between the epoxy matrix and nanoclay filler [57]. Besides, the flexural modulus for 2 wt%, 3 wt% and 4 wt% of nanoclay filler also displayed significant enhancement with 42%, 132% and 130% respectively. The flexural modulus of 3 wt% and 4 wt% nanoclay filler loading showed no significant differences which, unexpected. This may be due to the agglomeration of clay and intercalated structure in the epoxy resin that contribute no increment in flexural modulus value.

The presence of nanoclay filler in the epoxy matrix contributed to 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 a consequence of the addition of nanoclay filler in the epoxy metric. Based on Chisholm et al.'s study, a significant enhancement was obtained in flexural modulus of epoxy by adding nanoparticles due to higher surface energy [58]. Besides, the highly dispersed of nanoclay filler could provide great bonding with epoxy matrix and thus the efficiency of stress transferring boosted up subsequently, leading to ameliorate the flexural modulus. Consequently, the neat Napier/epoxy composite was rated as the lowest in flexural modulus due to its weak interfacial bonding between the epoxy resin and Napier fibres and thus impaired their adhesion chains which can potentially hinder the flexural modulus.

Past researchers investigated that nanoclay fillers facilitate to build up strong interface bonding and adhesion to fibres and epoxy matrix and then enhance the mechanical properties. The rigid nanoclay fillers bonding expected to improve the flexural modulus, stiffness and toughness, however also resulting in an increase of its brittleness and reduction in strain to failure. Krushnamurty et al. mentioned that nanoclay filler could improve matrix toughness because of their rough fracture surface and as well as strong inter-filament bonding of the nanoclay filled glass/epoxy composites [51]. According to Siddiqui et al., the flexural modulus of epoxy composites naturally improve with the presence of the organo-clay and the increment of the flexural modulus was at the expense of a reduction in flexural strength [59]. Also, the high flexural modulus of the composites also attributes to the brilliant performance of the thermoset epoxy. This is because it has low viscosity and thus low processing temperature is needed for fabricating composites. It provides an advantage to facilitate the creation of a better fibre/matrix composite compared to the use of thermoplastic resins.

9. Morphology of nanoclay filled Napier reinforced epoxy composites

The fracture surface of Napier/epoxy composites with and without nanoclay filler through SEM are shown in Fig. 6.8. Fig. 6.8(A) shows the fractured surface of neat nanoclay filled composites; it is clear with a smooth surface. It can be observed that a large number of tiny white particles are inspected on the fracture surface of the composites. Composite fractured surface with 2 wt% of nanoclay filler indicates smaller areas and fewer nanoclay fillers as shown in Fig. 6.8(B), whereas for 5 wt% nanoclay filled composites, large areas with presence of nanoclay filler is observed as shown in Fig. 6.8(E). The increased loading of nanoclay filled Napier/epoxy composites, the tinier white particles found on the epoxy interface.

In order to achieve the better mechanical performance of the composites, the nanoclay filler should be well distributed in the epoxy matrix. Excellent and homogeneous dispersion of nanoclay filler indicates that the clay fillers are thoroughly dispersed and bounded by the epoxy. The insufficient nanoclay fillers in the composites can cause clay agglomeration due to a non-homogeneous mixture [60]. Thus, it could contribute to crack propagation and affect the flexural strength as well as its modulus. From Fig. 6.8(B) of 2 wt% of nanoclay filler, it shows that the nanoclay filler was poorly distributed in the epoxy matrix and aggregations were observed. Therefore, the mechanical performances were not as good as expected and the composites cracked under loading. Nonetheless, for the 3 wt% and 5 wt% of nanoclay loading, the SEM images displayed that the nanoclay fillers are well distributed throughout the composites without apparent agglomeration observed. Thus, it brings significant advantages to the flexural strength and modulus properties.

Fig. 6.9 shows the various loading of nanoclay filler displayed varying degrees of surface roughness. It can be seen that a relatively smooth fracture surface is displayed by the neat Napier/epoxy composites as shown in Fig. 6.9(A). Compared to the neat

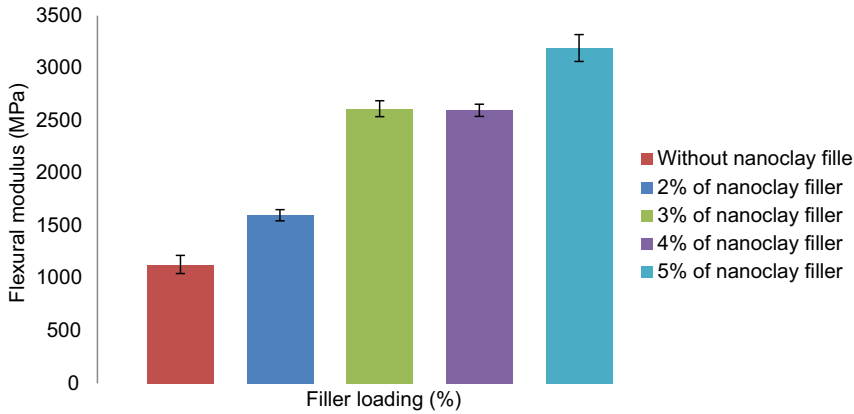


Fig. 6.8 Flexural modulus for various nanoclay-filled loading Napier/epoxy composites. Nanoclay filler refers to Montmorillonite.

Napier/epoxy composite, the fracture surface of the nanoclay filler composites exhibited a much rougher fracture surface as shown in Fig. 6.9(B−D). It is because of the presence of nanoclay fillers in the epoxy matrix influences the fracture path to be more complicated and very rough surface occurred. These rough surfaces could promote better interfacial bonding between the Napier fibres and the epoxy resin. It is

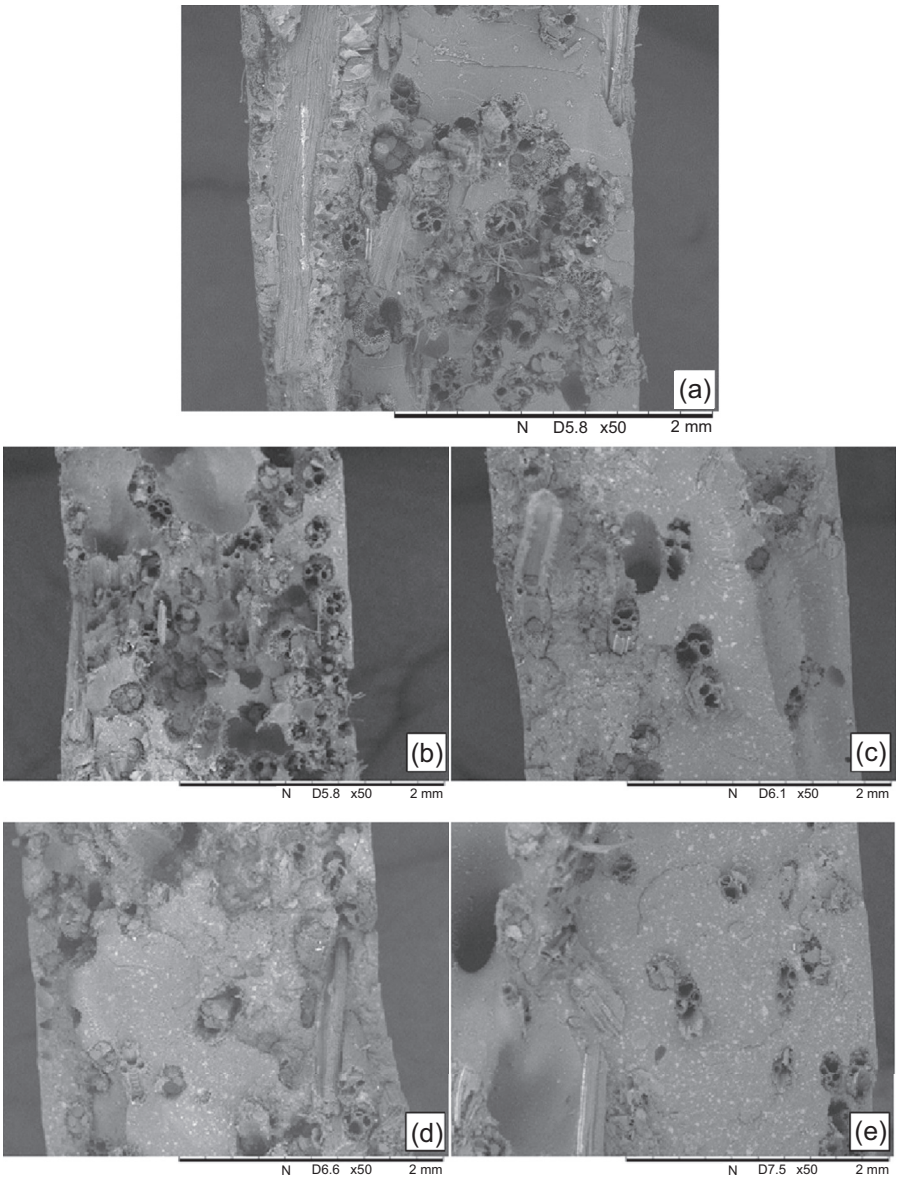


Fig. 6.9 SEM images of the fracture surface of the Napier/epoxy composites at various loadings of nanoclay. (A) Neat, (B) 2 wt%, (C) 3 wt%, (D) 4 wt%, (E) 5 wt% of nanoclay filler. Nanoclay filler refers to Montmorillonite.

illustrated that the addition of nanoclay filler into the Napier/epoxy composites results in improvement in toughness. This is supported by the increment in the flexural modulus as the nanoclay filler loading increases. Moreover, it can also be observed that the fractured surface of the nanoclay filled Napier/epoxy composites shows a textured surface compared with that of the neat Napier/epoxy composite. As a result, the composites become tougher in behaviour. By comparison, the surface of 5 wt% of nanoclay filler composites is rougher thus yield the highest flexural modulus. S. Parija et al. mentioned that the higher amount of nanoclay filler contents in the polymer matrix could provide high efficiency of stress transfer in the composites and created excellent flexural modulus [61]. Researchers also found that the nanoclay particles could create stress disturbance to the polymer composites and enable to enhance the toughening mechanism of the composites. In addition, the nanoclay fillers can act as additional reinforcement to the epoxy matrix and enhances the interface structures due to the smaller in size of nanoclay filler able to bundle between Napier fibres and epoxy matrix (Fig. 6.10). Consequently, this can improve the flexural strength and modulus where the mobility was reduced (Fig. 6.10).

Fig. 6.11 exhibits apparent agglomerates which were observed in SEM micrograph with 200 × magnifications. The agglomeration of the nanoclay filler in the composites

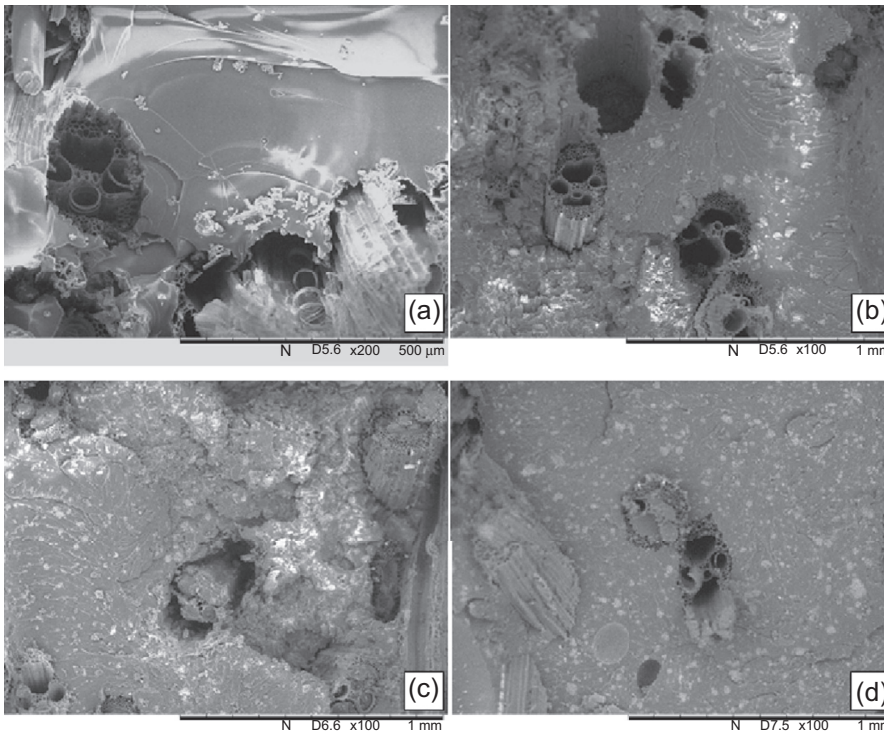


Fig. 6.10 SEM images of the roughness surface of the Napier/epoxy composites at various loading of nanoclay. (A) Neat, (B) 3 wt%, (C) 4 wt%, (D) 5 wt% of nanoclay filler. Nanoclay filler refers to Montmorillonite.

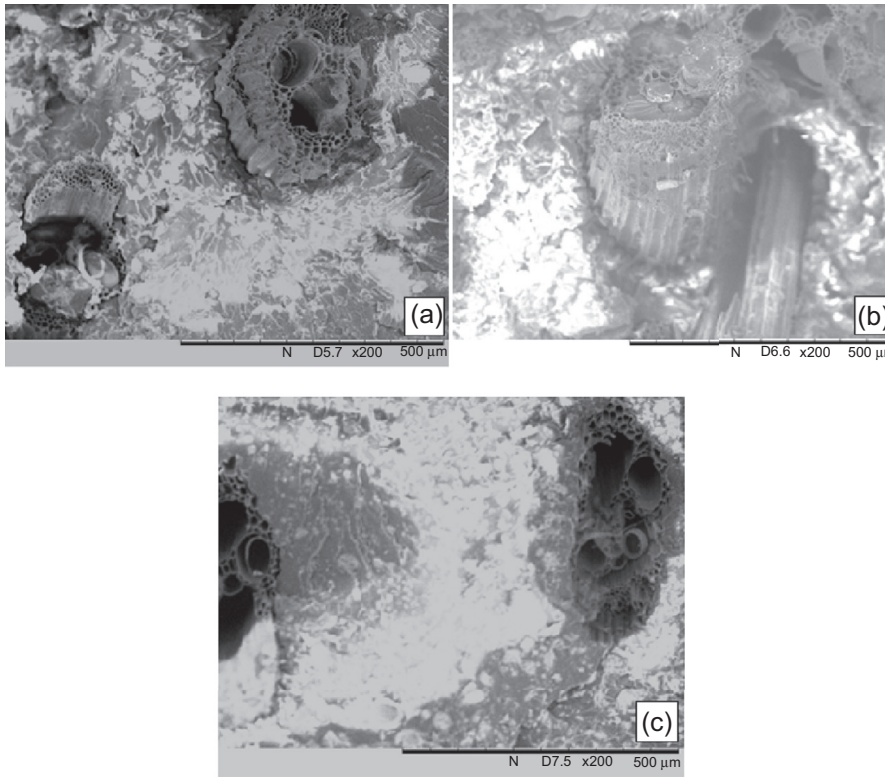


Fig. 6.11 SEM images of the agglomeration of nanoclay on the fracture surface of the Napier/epoxy composites at various loading of nanoclay. (A) 3 wt%, (B) 4 wt%, (C) 5 wt% of nanoclay filler.

causes the stress concentration and consequently crack propagation initiated. This reduces the flexural strength of the composites and yield brittle fracture behaviour. This appearance assures the stress concentrated on the particular points and causes the lesser rich area of nanoclay to cracks easily [62,63].

As shown in the SEM image of Fig. 6.12(A), the neat Napier/epoxy composite demonstrated that the fractures took place along the bonding interface between the epoxy resin and Napier fibres. The Napier fibres are completely separate from the fractured surface that proves poor interphase bonding between the Napier fibre and epoxy matrix and consequently, more Napier fibres pull out. In contrast, with the presence of nanoclay fillers in the composites, the fibres pull-out has been greatly reduced, of which the epoxy matrix is completely secured the Napier fibres at the surface of failure. As can be observed from the 5 wt% nanoclay fillers, lesser fibre pull-out observed under 100 × magnifications. As a result, it indicates an enhancement of adhesion capability between the Napier fibres and epoxy matrix with the presence of the nanoclay filler. The previous study reported similar findings; nanoclay filler improved the cohesion properties between the adjacent and the interlayer of composite layers [51].

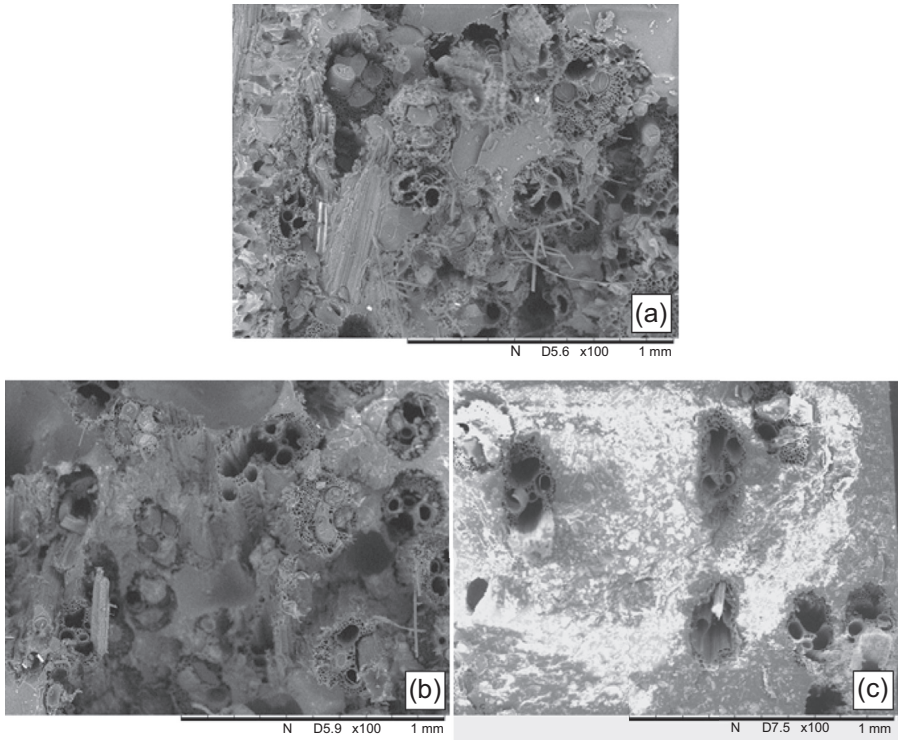


Fig. 6.12 SEM images of the fibre pull-out observed from the Napier/epoxy composites at various loading of nanoclay. (A) Neat, (B) 2 wt%, (C) 5 wt% of nanoclay filler.

However, this advantage can lead to increase of flexural strength and modulus of natural fibres reinforced composites. It can be concluded that better adhesion of nanoclay filled Napier/epoxy able to produce better stress transfer in the matrix, thus subsequently enhances their strength, toughness and modulus.

10. Conclusion

The effect of nanoclay filler loading on the mechanical and morphological properties of Napier/epoxy composites was investigated. The Napier/epoxy composites reinforced with nanoclay filler were successfully fabricated using vacuum infusion technique. Five different nanoclay filler loading of Napier/epoxy composites such as neat, 2 wt%, 3 wt%, 4 wt% and 5 wt% were fabricated. Three-point bending test was carried out according to ASTM 790 standard. Based on the experimental results, it can be concluded that the reinforcement of nanoclay fillers in Napier/epoxy composites has a significant impact on the flexural properties compared to neat Napier/epoxy composite. The fracture mode is no longer ductile with plastic deformation, but rather

becoming brittle-like behaviour. This was confirmed by the decreased in the strain to failure with the loading increase of nanoclay filler. In addition, the stress-strain curve shows similar characteristics to brittle materials. The findings can also be supported by the rougher surface on the fractured surface of the composites.

The incorporation of nanoclay filler had enhanced the flexural strength of Napier/epoxy composites. However, it was investigated that there was a maximum improvement limit. The highest tensile strength was achieved by 3 wt% of nanoclay filled composites at 57.72 MPa. However, there is a reduction in flexural strength with a further increase in nanoclay fillers. The high nanoclay filler contents affect the filler-filler interaction which consequently agglomeration occurred and thus caused a reduction in the flexural strength of the composites. From the observation under SEM, the nanoclay filler distribution was quite uniformly in the epoxy matrix although there is the problem of the agglomeration of the nanoclay filler at higher nanoclay filler ratios within the epoxy matrix. Therefore, the proper dispersion and distribution of nanoclay filler particles in the epoxy matrix act as an essential role in the mechanical properties of the composites. From this morphology, it was concluded that the fibres become roughened with the addition of nanoclay. By comparison, the fracture surface of 5 wt% of nanoclay 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 nanoclay 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 nanoclay filler was added. As a conclusion, the presence of nanoclay 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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