Influence of MWCNTs addition on mechanical and thermal behaviour of epoxy/kenaf multi-scale nanocomposite

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Abstract. This research was conducted to develop kenaf reinforced epoxy/MWCNTs multi-scale composite using kenaf fibre and MWCNTs as the reinforcement in epoxy as the hosted matrix. The composites were produced by using a combination of hand lay-up and vacuum bagging process. The selection of optimum composition of epoxy-MWCNTs is based on the MWCNTs loading and the resulted mixture viscosity. Lower resin viscosity is required to allow good wetting and interaction between matrix and filler, which will yielded superior final performance of the fabricated composites. Therefore, different loading of MWCNTs (0.0 wt. %,
0.5 wt. %, 1.0 wt. %, 3.0 wt. %, 5.0 wt. %, 7.0 wt. %) were used to investigate the mechanical and thermal properties of the composites. As a result, the epoxy/kenaf/MWCNTs multi-scale composite at 1.0 wt. % of MWCNTs addition had yielded substantial improvement by 15.54 % in tensile strength and 90.54 % in fracture toughness. Besides, the fracture surface morphology of the selected samples were analysed via scanning electron microscopy (SEM) observation to further support the reinforcement characteristic of epoxy/kenaf/MWCNTs multi-scale composite.

1. Introduction

The processing technique are improving by the development of technology beginning from macro, micro and current trend to nanoscale inclusion. Theoretically, a dimension that have at least one dimension in the range of 1 to 100 nm are classified as nanoscale inclusion. In the prospectus of the properties produced by the addition of nanofiller, a composite's properties promised a positive tendency to increase but it also depend on the content added in the system. Furthermore, the interfacial interaction between the polymer matrix and reinforcement is also an important parameter which affect the properties of polymer matrix nanocomposite. Thus, a good dispersion between matrix and reinforcement must be thoughtfully considered when producing a nanocomposite [1].

Among all matrix resin that are available in the industries, epoxy resin has its own potential for many high performance application. Epoxy is one of the resin from thermoset family that commonly used as matrix for composite application. In addition, epoxy can be produced from reacting epichlorohydrin with bisphenol [2]. When compared to other polymer, epoxy offers astonishing properties of epoxy such as high corrosion resistance, high mechanical properties and low shrinkage properties [3]. This make epoxy as one of the favorable choice in high performance application especially in aircraft and aerospace industries [4].

However, the extraordinary properties of epoxy discredited by the brittleness behavior of the material in nature of the cross linked molecular structure. Epoxy resin also has low toughness that resulted in weak resistance to crack. Therefore, addition of fine particle is introduced to enhance the properties of epoxy resin [5]. Considering into that the incorporation of nano-size reinforcement of functional filler is advisable to compensate with the limitation of epoxy resin. Functional nanofiller like carbon nanotubes, carbon nanofibre, or graphene were able to modify and improvise the mechanical and thermal properties of polymer matrix resin, like epoxy. In this work, MWCNTs were used as nanofiller in the epoxy matrix.

Carbon nanotubes are outstanding filler for polymer composites. Carbon nanotubes can broadly enhance the electrical, thermal and mechanical properties of the resulting nanocomposites. The Young's modulus of CNTs is nearly to 1 TPa but dependent to the type and diameter of carbon nanotubes. Moreover, the theoretical strength of carbon nanotubes is 100 times higher than steel [6]. Recent advanced in CNTs research, specifically on the synthesis technology and surface modification had allow this nanofiller become compatible with another materials. Therefore, MWCNTs were dispersed in water [7], and due to that the MWCNTs are expected to easily be dispersed in the polymer matrix.

Instead of nanofiller alone, natural fibre also can be used as the reinforcement. According to Akil et al. (2011) [8], natural fibres are commonly used as filler to produce a green composite because it is cheaper, have low density compared to others synthesis fibre and the strength is higher than glass fibre. It is more preferable to produce low cost and high strength composite from many prospective of interest. Among many established natural fibres that were widely exploited for their promising properties, kenaf fibre is one of the kind that capture many interest. In addition, Huda et al. (2006) [9], pointed that kenaf fibre is effectively reinforced the thermoset and thermoplastic composites. By times, kenaf fibre is slowly replacing synthesis material as kenaf fibre has many better properties to offer. In this work, kenaf fibre was used in a non-woven pattern as the natural reinforcement agent for epoxy matrix. The natural fibre based epoxy composite system was further reinforced by multi scaling the epoxy resin by MWCNTs incorporation. It is expected that by hybridizing the MWCNTs nanofiller with kenaf natural fibre through epoxy resin as nanocomposite matrix, the benefit of nanoreinforcement by CNTs will be amplified the potential of kenaf fibre as natural reinforcement agent, for high performance composite application.

2. Experimental

2.1. Materials
The neat epoxy resin used in this work was a standard diglycidylether of bisphenol A (DGEBA) coded CP 360 Part A with an epoxy equivalent viscosity of 8500 mPa.s and the curing agent was amine hardener coded CP 360 Part B that were supplied by Terra Techno Engineering, Malaysia. The multi- walled carbon nanotubes (MWCNTs, Flo Tub 9000 Series, CNano Technology Limited, China) was purchased from CNano Technology Limited, China and were used as it is. The kenaf fiber mat supplied from Lembaga Kenaf & Tembakau Negara (LKTN), Malaysia was conditioned in-house and used as it is.

2.2. Preparation of composites
There are six categories of multi-scale kenaf-MWCNTs/epoxy plate with different MWCNTs loading at 0.00 wt. %, 0.50 wt.%, 1.00 wt.%, 3.00 wt.%, 5.00 wt.% and 7.00 wt. % were prepared by using hand lay-up and vacuum bagging methods. The mixture of epoxy and MWCNTs then stirred by using mechanical overhead stirrer at a speed of 1000 rpm for 60 minutes. Later, the hardener agent CP 360B were poured into the mixture and stirred for 5 minutes prior to integration with kenaf fiber mat.

Meanwhile, a set-up for vacuum bagging was prepared by placing a sheet of plastic on the flat surface before layering with the non-woven kenaf fiber above it. Next, the prepared mixture of

epoxy/MWCNTs was poured onto the kenaf fibre mat and spread uniformly on the surface of kenaf mat by hand lay-up process. Then, the sample is attach with plastic bagging by using sealant tape around the mould edge. A spherical tube is then install to suck out the excessive resin and bubbles throughout the vacuum bagging process. Finally, the multi-scale kenaf-MWCNTs/epoxy composits were left to cure at room temperature for 24 hours. The resulted composites were fabricated into 300 mm x 300 mm. The after-cured samples were then cut into specific dimension fulfilling the requirements for the tensile, flexural and fracture toughness tests, in accordance to the standard methods of ASTM D3039, ASTM D790 and ASTM D5045, respectively.

2.3. Mechanical properties evaluation

2.3.1. Tensile properties. The tensile properties of the samples were measured by using an Instron 5969 Universal Testing Machine (UTM) equipped with maximum 50 kN load cell. The tensile test was performed at the crosshead speed rate of 2.00 mm/min and gauge length of 60 mm, according to ASTM D3039M-14. The specimens were cut to nominal dimensions of 100 mm x 18 mm and each mix were prepared for three times repetition.

2.3.2. Fracture toughness properties. The fracture toughness evaluation on the multi-scale epoxy/kenaf-MWCNTs composites were performed in accordance to ASTM D5045-14 Standard Test Method for Fracture Toughness and Strain Energy Release Rate of Plastic Materials by closely referred to Bakar et al. (2012) work. A span of 80 mm was specified with crosshead speed of 2 mm/min performed on Autograph UTM 50 kN, Shimadzu, Japan. The fracture toughness was calculated by the formula in Equation 1 and Equation 2 as denoted as below where P is the maximum load, S is the span length, a is the notch length, B is the sample thickness, W is the sample width and y is the geometry correction factor. Three samples were prepared from each category and conditioned at room temperature where the average value were considered as the results.

$$K_{IC} = \left(\frac{\overline{PS}}{BW^{\frac{3}{2}}} \right) x(y) \tag{1}$$

$$Y = 3(a/w)^{1/2} x \left(\frac{1.99 - \left(\frac{a}{w}\right)\left[1 - \left(\frac{a}{w}\right)\right]\left[2.15 - 3.93 \left(\frac{a}{w}\right) + 2.7 \left(\frac{a}{w}\right)^2\right]}{2\left[1 + 2\left(\frac{a}{w}\right)\right]\left[1 - \left(\frac{a}{w}\right)\right]^{\frac{3}{2}}} \right) \tag{2}$$

2.4. Thermal analysis

2.4.1. Dynamic Mechanical Analysis (DMA). Dynamic mechanical analysis (DMA) is commonly used to measure temperature dependence properties, such as the storage modulus, E', loss modulus, E'', and damping factor, tan σ [11]. The loss modulus, E'', was used to determine the glass transition temperature (T_g) of the unfilled epoxy and multi-scale epoxy/MWCNTs-kenaf composites. A Pyris Diamond DMA (Perkin Elmer) with a dual cantilever was used to perform the DMA measurements. Specimens with dimensions of *l x w x t*(40 x 10 x 1) mm were prepared according to ASTM D5418-15. The specimens were evaluated over a temperature range of 30 °C to 180 °C, using a heating rate of 2 °C/min and a fixed frequency of 1.0 Hz.

2.5. Scanning electron microscopy
Morphological structures of the samples were investigated using scanning electron microscope (SEM, Zeiss EVO-50 FESEM) by applying an accelerating voltage of 20 kV. Fractured surfaces from tensile testing were analyzed. All samples were sputter-coated with gold to eliminate electron charging.

3. Results and discussions

3.1. Tensile properties analysis

Figure 1 depicted the ultimate tensile strength of the fabricated composites incorporated with a series of specified content of MWCNTs. It is clearly shows that the ultimate tensile strength were found increases with the increase in the content of MWCNTs inclusion, up to an optimum point at 1.00 wt. %, before drastically dropped after addition of MWCNTs at higher loading. The largest increase of ultimate tensile strength is 25.06 MPa occurred at 1.00 wt. % of MWCNTs with 15.54 % increment from epoxy/kenaf composite acted as control sample for this study. The ultimate tensile strength of the control sample is 21.69 MPa.
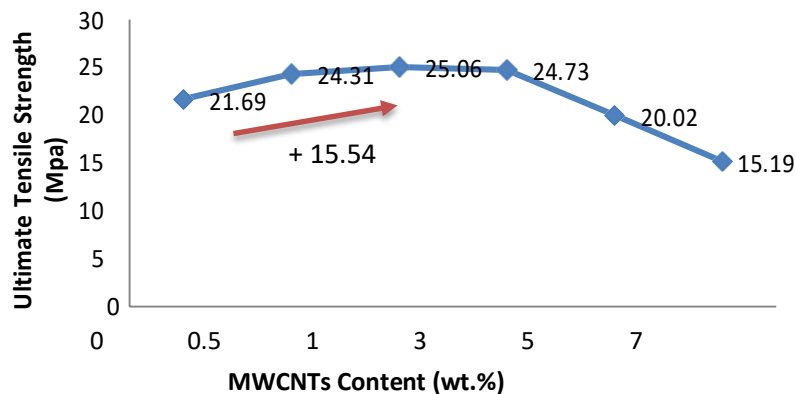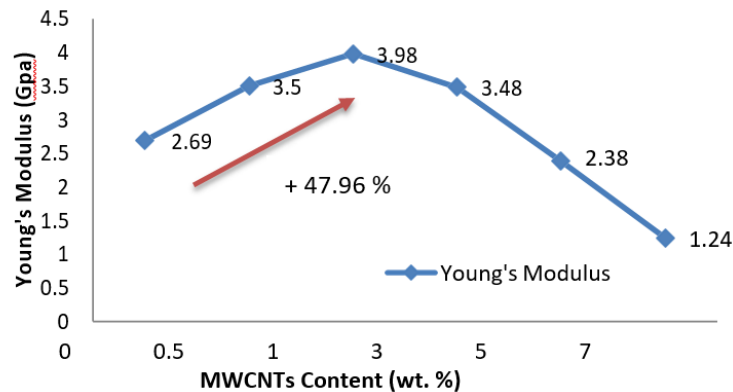

Figure 1. The effect of MWCNTs content on ultimate tensile strength of MWCNTs-kenaf/epoxy multi-scale composite system

An increase in the tensile strength and tensile modulus for multi-scaled hybrid composite system as compared than common micro composites system can be partially explained on the basis of the interaction between the filler and the matrix. It has been found that a greater adhesion between the matrix and nano inclusion had caused less matrix-filler debonding when a stress is been applied. Hence, the elastic modulus and strength are greatly improved due to this beneficial interaction [1]. However, further increased in the percentages of MWCNTs were significantly diminish the strength of produced multi- scale composites. From 1.00 wt. % to 7.00 wt. % addition of MWCNTs added to composite, it was found that the strength was decreases from 25.06 MP to 15.19 MPa which is around 39.39% of reduction. This is because the strength of the nano-reinforcement adhesives begin to degrade due to the agglomeration phenomena that caused by the filler-filler interaction [12]. Furthermore, there is a sharp decreased in the ultimate tensile strength when 7.00 wt. % MWCNTs is added, which is about 24.11 %. This is because the viscosity of epoxy-MWCNTs matrix is getting too high was resulted in a bad dispersion of the nano-reinforcement.

Figure 2 depicts the Young's modulus results of multi-scaled epoxy/kenaf hybrid composites reinforced with MWCNTs nanofiller. The plotted graph shows the effects of various loading system of MWCNTs toward the resulted composites. The addition of MWCNTs yielded an improvement in the Young's modulus up to 1.00 wt. % inclusion, before eventually decrease with more involvement of MWCNTs nanofiller. The trend was similar with the ultimate tensile strength attribute as in Figure 1. The highest Young's modulus of 3.98 GPa was obtained at 1.00 wt. % of MWCNTs loading

system. This favourable trend of 48.00 % improvement in MWCNTs-kenaf/epoxy multi-scale composite was noticed when compared to the control sample. The lowest Young's modulus was detected from the sample with the addition of 7.00 wt. % of MWCNTs which is 1.24 GPa. There is almost 53.9 % reduction as compared to the neat epoxy kenaf fibre multi scale composite. The properties dropped might be due to the improper dispersion of MWCNTs at higher concentration which closely related with the agglomeration phenomena.

Figure 2. The effect of MWCNTs content on Young's modulus of MWCNT kenaf/epoxy multi- scale composite system.

Figure 3 shows the percentage of elongation at break for the multi-scale composites versus percentages of MWCNTs content. By comparing the graph of Young's modulus and percentage of elongation at break, it can be seen that the elongation attributes was inversely proportional to the Young's modulus results. This is because the stiffer the sample, the lower the percentages of elongation at break of the tested specimen of that particular epoxy system. The percentage of elongation at break was further decreased when the MWCNTs loadings were increased up to 1.00 wt. % of MWCNTs addition. After that, the percentage of elongation at break was unexpectedly increased with the increase of MWCNTs loadings. At 1.00 wt. % of MWCNTs inclusion, the fabricated multi-scaled composite possessed the smallest amount of elongation characteristic which is 1.82 %. This is due to the factor of having good interfacial interaction between the epoxy matrix and hybrid reinforcement. Therefore, the sample is getting stiffer and brittle as representing by the lower percentages of the elongation at break. In contrast, the specimen of 7.00 wt. % of MWCNTs produced the highest percentages of break, which is 3.10 %. The further addition of MWCNTs in the composite caused the viscosity of epoxy-MWCNTs to increase significantly. Thus, serious agglomerations of MWCNTs prevent proper interaction between epoxy resin and hardener. This improper mixing had caused premature curing of the epoxy matrix. As a result, the outer surface of the sample was improperly cured while the internal region was partially uncured. The sample tends to break at the specific region which later caused the testing machine unable to detect the definite elongation properties.
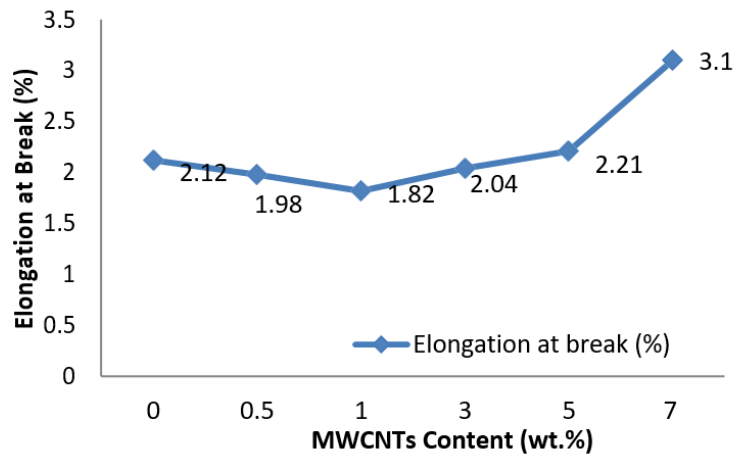
Figure 3. The effect of MWCNTs content on elongation at break (%) of MWCNTs-kenaf/epoxy multi-scale composite system

3.2. Fracture toughness analysis

According to Chandrasekaran et al. [13], the fracture toughness of composite started to decrease beyond certain weight fraction of filler addition which is in parallel with the results found in this work. This phenomenon is due to the MWCNTs fibre that was being pulled out during the impact loading and therefore contributed to the high toughness of produced multi-scaled composites. Figure 4 shows that the fracture toughness was increased when the MWCNTs content increased. The positive increment were noticed to linearly increase up to 1.00 wt. % of MWCNTs addition and later decreased as the content of the nanofiller increased. The maximum fracture toughness is showed by the sample of 1.00 wt. % of MWCNTs content with 90.52 % improvement compared to the unfilled epoxy/kenaf system. At 3.00 wt. % of MWCNTs content, the fracture toughness of the composites are started to diminish by
4.19 % compared to 1.00 wt. MWCNTs-kenaf/epoxy system. This is because when the MWCNTs content increased, the MWCNTs prone to agglomerate and degrade the quality of the resulted composites [12]. All the small fracture were started around the agglomeration area of MWCNTs which later propagate throughout the sample that resulting in fracture or failure of the done hybrid composites [13].
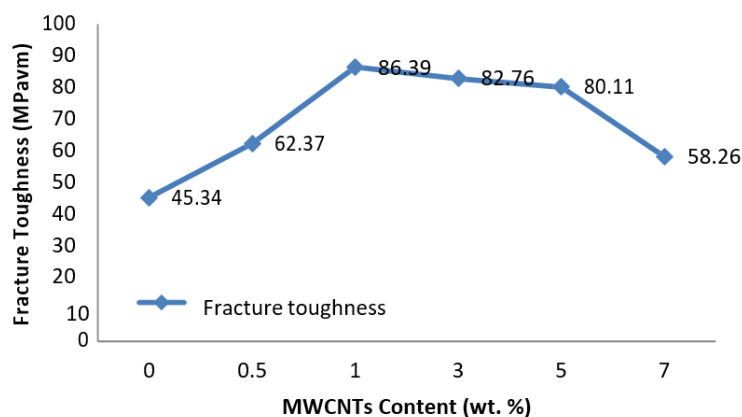

Figure 4. The effect of MWCNTs content on fracture toughness of MWCNTs-kenaf/epoxy multi-scale composite.

3.3. Thermo-mechanical properties evaluation by DMA

Figure 5 shows the storage modulus of multi-scaled hybrid composites with different loading of MWCNTs additions. The graph shows the composition of 1.00 wt. %-MWCNTs addition has the highest storage modulus value of 1700 MPa and decreased with more addition of MWCNTs. This finding proved that the presence of 1.00 wt. %-MWCNTs in the sample introduced a good interfacial bonding between the fibre and matrix. Therefore, the load applied can be transferred efficiently even at the exposure of heat. However, at 0.5 wt. %-MWCNTs addition, the storage modulus was lower than 1.0 wt. %-MWCNTs sample. This is because the small amount of MWCNTs only acted as notches instead of giving reinforcement effect which reducing the load transfer efficiency [14]. While, at 7.0 wt. %- MWCNTs content, the storage modulus are much lower because the higher content of MWCNTs given higher tendency of being affected by agglomeration factor. Thus, the interfacial bonding became weak and load cannot transferred effectively.
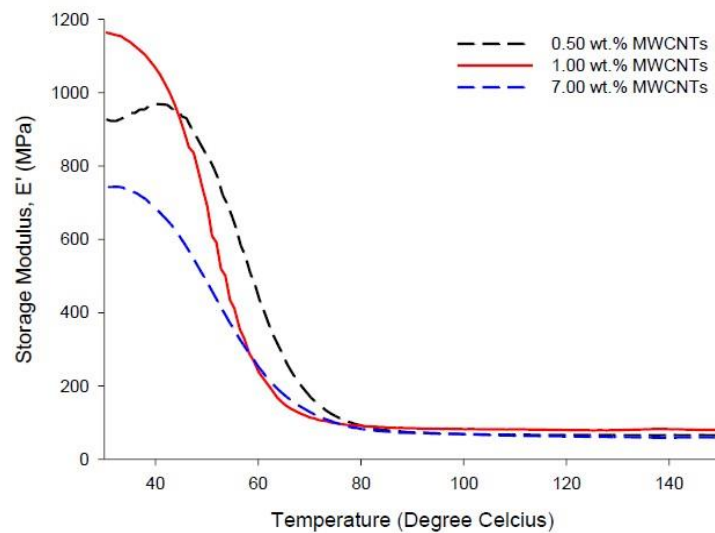
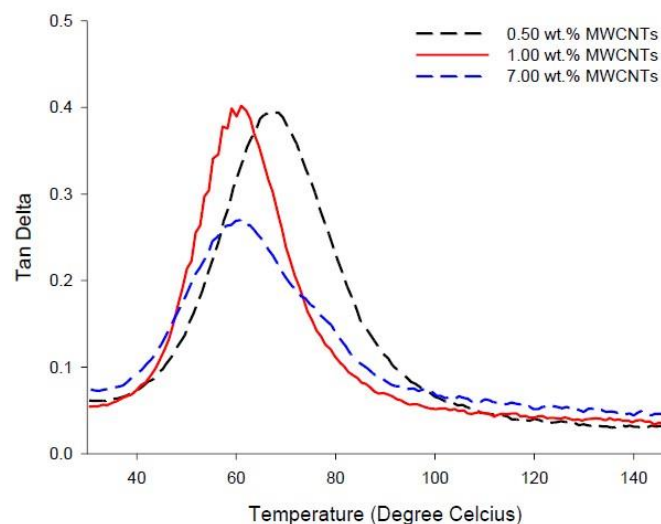**Figure 5.** The effect of different MWCNTs addition on storage modulus (E") of epoxy/kenaf multi-scaled composites

Figure 6 depicts the loss modulus of epoxy/kenaf multi-scaled composites with different MWCNTs loading. The loss modulus (E') presented in this work is in parallel with the storage modulus (E") trend as in Figure 6. At 1.0 wt. %-MWCNTs addition, the loss modulus is 150 MPa which is higher than the composition of 0.5 wt. %-MWCNTs composite and 7.0 wt. %-MWCNTs composite. At low addition of MWCNTs, the loss modulus is lower because the energy losses caused by the rearrangement of the molecules and MWCNTs as well as the internal friction between the fibres and epoxy matrix. From the graph, 1.0 wt. %-MWCNTs composite has higher loss modulus showing that the composite has higher potential of decapitated energy as heat. At high addition of MWCNTs, the loss modulus is the lowest because the over-filler-interaction leads to bad dispersion and produced worst agglomeration site. Later, this event caused the bad energy dissipation and affect the mechanical properties.
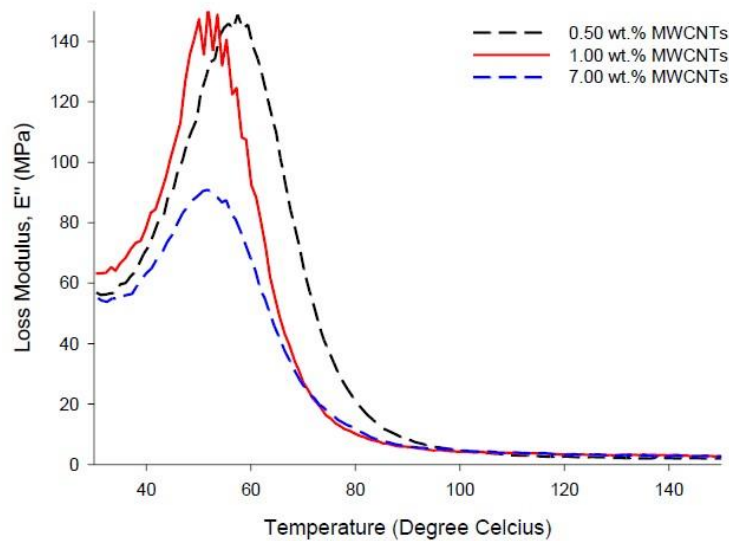
Figure 6. The effect of different MWCNTs addition on loss modulus (E') of epoxy/kenaf multi-scaled composites

Tan delta is the ratio of loss modulus to storage modulus which also known as the damping factor of the produced composites. The increase in tan delta notified that more potential of energy dissipation while a decrease in tan delta means the composite have more elastic properties [14]. At 1.0 wt. %- MWCNTs addition, the sample has the highest damping factor as compared than others. This indicated that the sample with 1.0 wt. % of MWCNTs content has higher potential to dissipate heat and produced a tougher composites system. In contrast, 7.0 wt. %-MWCNTs composite presented the lowest damping factor which is believed due to the decrement of the mobility of polymer molecules chains as hindered by the MWCNTs agglomeration [15].


Figure 7. The effect of different MWCNTs addition on tan delta of epoxy/kenaf multi-scaled composites

3.4. Fractured surface observation via SEM
Micrograph at figure 8 shows the fracture surface at the fractured samples with different MWCNTs filler loadings which are 0 wt. % of MWCNTs, 1.00 wt. % of MWCNTs and 7.00 wt. % MWCNTs.

According to Garg et al. [16], the higher the MWCNTs filler loading, the higher the tendency of agglomeration of MWCNTs bundles formation due to the increased of epoxy matrix viscosity. Figure 8

(a) shows the micrograph of 0.0 wt. % of MWCNTs sample. From the micrograph, it was clearly shows that some fibres were being pulled out from the matrix. This is due to the poor interface interaction between the epoxy matrix and the kenaf fibre with the presence of MWCNTs nanofiller. The weak interface was resulting lower strength of the produced hybrid composites. Other than that, there are some internal pores and voids were detected in the kenaf fibres. Those the pores and voids were acted as stress concentration point that becoming a weak point which lowering the resulted strength of the fabricated samples. Micrograph 8 (b) shows that the fibre were break into two rather than pulled out from the epoxy matrix. This proves that the matrix-filler interface are stronger which promoting a better resulted strength. Other than that, a good dispersion of MWCNTs in epoxy was found tends to reduce the stress concentration which further enhanced the uniformity of the stress distribution of the produced hybrid multi-scaled composites [17]. The fracture micrograph is depicted in Figure 8 (c) shows the fibre breakage with non-homogeneous matrix wetting, whereby the agglomeration of MWCNTs was limits the wetting of epoxy to the kenaf fibre surface. Other than that, the micrograph of Figure 8 (c) also shows the poor interfacial of matrix and the kenaf fibre. This totally reduced the strength of produced composites. According to Rahmanian et al. [18], too much of MWCNTs added could lead into a reduction of the resulted strength and modulus of the multi-scaled composites due to the worst agglomeration factor. This is because agglomeration will becoming as a source of crack initiation and propagation [17].
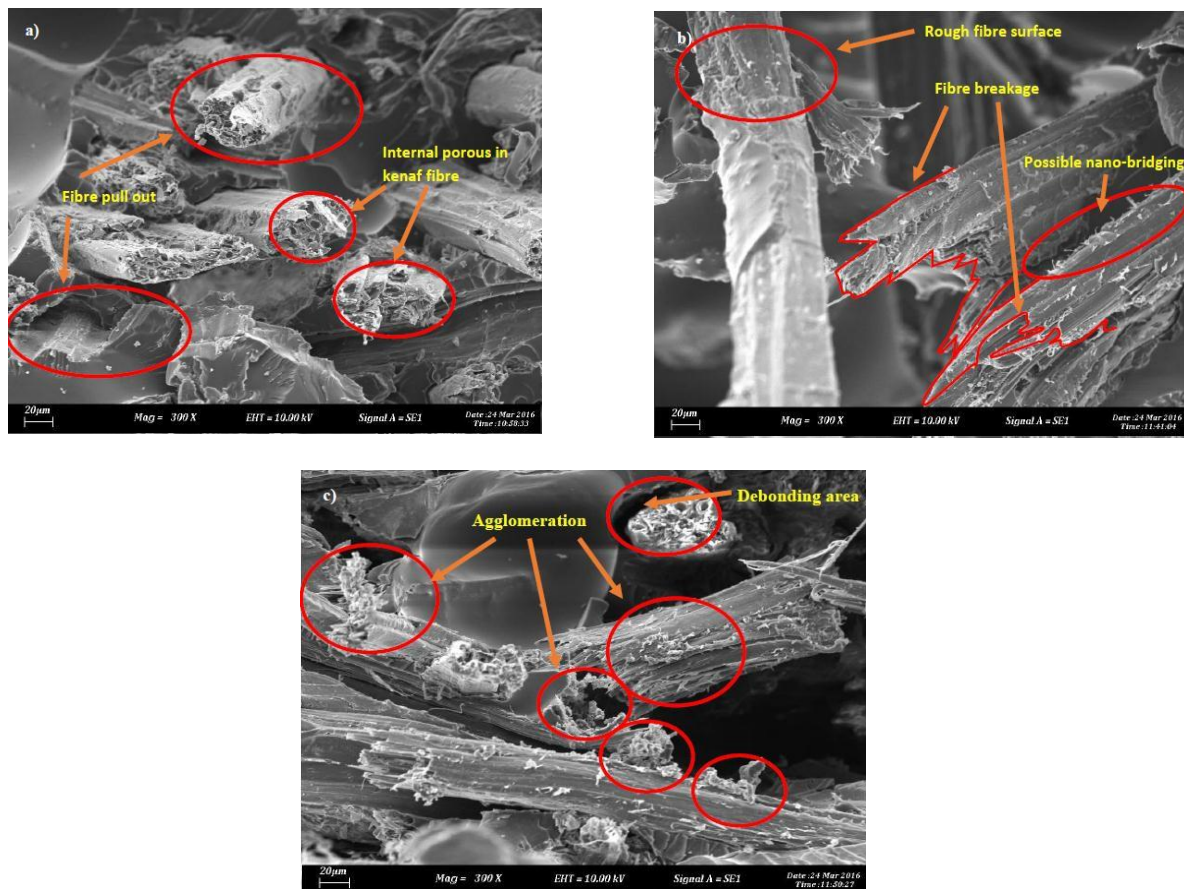
Figure 8. (a) Micrograph of neat epoxy kenaf composite, (b) micrograph of 1.0 wt. % MWCNTs epoxy/kenaf nanocomposite and (c) micrograph of 7.0 wt. % MWCNTs epoxy/kenaf multi-scale composites.

4. Conclusion

Kenaf fibre reinforced epoxy/MWCNTs multi-scaled hybrid composites were successfully produced by using the simplified vacuum bagging technique. The results of tensile, fracture toughness and thermo- mechanical tests showed that at composition of 1.0 wt. % MWCNTs in epoxy/kenaf multi-scaled hybrid composite possess the best tensile, fracture toughness and viscoelastic properties. Fracture surface analysis showed less fibres pulled out for resulted epoxy/kenaf/1.0 wt. % MWCNTs multi-scaled composite.

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