

Article

Abrasive Wear Behavior of CNT-Filled Unidirectional Kenaf–Epoxy Composites

Napisah Sapiai ¹, Aidah Jumahat ^{1,2,*}, Mohammad Jawaid ^{3,*} and Carlo Santulli ^{4,*}

- ¹ Faculty of Mechanical Engineering, Universiti Teknologi MARA (UiTM), Shah Alam, Selangor 40450, Malaysia; napisah@uitm.edu.my
- ² Institute for Infrastructure Engineering Sustainable and Management (IIESM), Universiti Teknologi MARA, Shah Alam, Selangor 40450, Malaysia
- ³ Department of Biocomposite Technology, Institute of Tropical Forestry and Forest Products, Universiti Putra Malaysia, UPM Serdang, Selangor 43400, Malaysia
- ⁴ Geology Division (SST), School of Science and Technology (SST), Università degli Studi di Camerino, Via Gentile III da Varano 7, 62032 Camerino, Italy
- * Correspondence: aidahjumahat@uitm.edu.my (A.J.); jawaid@upm.edu.my (M.J.); carlo.santulli@unicam.it (C.S.); Tel.: +60-122-290890 (A.J.); +39-380-6522232 (C.S.)

Abstract: Kenaf (*Hibiscus Cannabinus*) fibers have received significant attention for replacing the usage of synthetic fibers, especially glass fiber, in the fabrication of fiber-reinforced polymer (FRP) composites. The aim of this research was to study the change in wear behavior of kenaf–epoxy fiber composites by filling them with multiwall carbon nanotubes (MWCNT). In particular, the effect of untreated MWCNT (PMWCNT), acid-treated MWCNT (AMWCNT), and silane-treated MWCNT (SMWCNT) was studied, using three different MWCNT loadings, i.e., 0.5, 0.75, and 1 wt.%. The abrasive wear test was conducted to measure the wear properties of the composites. A thermal infrared camera was also used to measure the punctual contact temperature during the abrasive wear test, while the abraded surfaces were analyzed using the stereomicroscope. Starting from the considerable reduction of wear rate with the introduction of kenaf fibers, it was observed that PMWCNT provided some further, yet modest, reduction of wear rate only at the higher loadings. In contrast, the inclusion of AMWCNT proved to increase the specific wear rate of the epoxy–kenaf composites, an effect worsened at higher loadings. This may be due to the weakened interfacial bonding between the AMWCNT and epoxy. On the other hand, the presence of SMWCNT improved the interfacial bonding between CNT and epoxy, as shown by an increase in contact temperature. However, the increase in bonding strength was stipulated to have caused the rougher worn debris, thus inducing a three-body abrasive wear effect.

Keywords: kenaf composites; multiwall carbon nanotubes (MWCNT); acid treated; silane treated; abrasive wear

Citation: Sapiai, N.; Jumahat, A.; Jawaid, M.; Santulli, C. Abrasive Wear Behaviour of CNTs Filled Unidirectional Kenaf Epoxy Composites. *Processes* **2021**, *9*, 128. <https://doi.org/10.3390/pr9010128>

Received: 5 December 2020

Accepted: 5 January 2021

Published: 8 January 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Wear is defined as the loss of materials when being exposed to another moving object. Wear is one of the principal objectives of tribology, i.e., the study of the surface behavior of a material when interacting with another moving body, among others like friction and lubrication. The potential of polymer matrix composite (PMC), when used as a substitute in wear applications for existing materials has been explored quite extensively throughout the years. PMCs provide many advantages, such as being relatively cheap, having a high strength-to-weight ratio, and, especially if the reinforcement is formed by plant fibers, a higher environmental friendliness compared to non-renewable sources like metals. It is noteworthy that the latter also consume a significant amount of energy in order to be produced. However, in order for the polymer to have the properties at par to

metals, some enhancements need to be done. Therefore, various types of fibers and reinforcement particles are being incorporated into the polymer matrix to improve the properties of polymers [1–7].

In particular, several studies have explored the prospective of kenaf fiber as the reinforcement in composites for wear applications [1–3]. It has been found out that when kenaf was added into the matrix, the interfacial strength between the polymer matrix and kenaf fiber reduced the adhesive wear effect. On the other hand, by adding kenaf into the matrix, the thermal effect caused by the friction during sliding could be reduced. In addition, the bond strength between kenaf fiber and the polymer matrix also reduces the chance of softened matrix to be removed in a large amount during sliding. Kenaf fiber was stated as being more difficult to be pulverized amongst other natural fibers, which made it an ideal reinforcement in wear-resistant applications [1–3].

A significant effort has been made to improve the wear properties of polymers. The test parameter used during wear testing is one of the factors that may contribute to the wear behavior of a material [8–11]. Usually, applied load, sliding speed, and sliding distance are the test parameters that affect the wear behavior. A higher sliding speed and load does result in a higher friction exerted on the surface, thus generating heat which will eventually induce a thermal effect, where the softening of the polymer matrix occurs. This effect may induce wear since the softening of the matrix eventually leads to the fiber pull-out and also a large amount of matrix being removed at once [10]. Longer sliding distance also results in higher mass loss, thus affecting the wear rate of the materials [8,9].

Currently, the focus on a nanoparticle-type of reinforcement has increased tremendously due to its vast potential [4–7,12–14]. Compared to micro-sized particles, nano-sized particles have a larger surface area, which promotes higher bonding strength with the matrix. Higher adhesion strength leads to better wear-resistant composites. Nano-sized particles also produce smaller and smoother debris than micro-particles, which helps in the formation of a tribo-protective layer during sliding. This layer lowers the friction between the contacting bodies and eventually decreases the wearing rate and mass loss of the materials [6,7,12–14].

Multiwall carbon nanotubes (MWCNT) are well known due to their high-end properties. Such properties could help to significantly improve the mechanical properties of PMC, though they tend to agglomerate easily [7,14–16]. The agglomeration of MWCNT could have a degrading effect on the wear properties of the composites since the agglomerated part of MWCNT induces larger chunks of materials being removed from the surface, thus causing the increase in wear rate [7]. Therefore, treatments like acid and silane are introduced in order to help in easing the dispersion of MWCNT in the matrix phase [15–17]. The acid used during the treatment aids in removing any impurities in the MWCNT and improves the dispersion. However, the acid has been found to be interfering with the functional groups of the MWCNT, which leads to the reduction of crosslinking density. It would also implicate in the reduction of glass transition temperature as well as the electrical conductivity of the matrix [7,15]. On the other hand, silane modification has proven to have helped in enhancing dispersion, thermal stability, adhesion between MWCNT and matrix, and mechanical properties of the composites [16]. Silane molecules induce the formation of covalent bonds, thus producing a higher crosslinking density network of the composites, though they may reduce the electrical conductivity of the MWCNT [15–17].

Common mechanisms of wear in polymer matrix composites include breakage of matrix or fiber, pulling out of fiber, fiber–matrix debonding, and peeling of resin [18]. However, these mechanisms are usually related to higher load and speed as well as more destructive wear test such as the pin on disk wear test. For the abrasive wear test, the load and speed used are much lower, and it gives a smaller scale of destruction compared to other wear tests. The mechanisms which are usually associated with abrasive wear are micro-cracking, micro-cutting, micro-fatigue, and micro-ploughing [19–21]. Micro-ploughing could be observed when materials are being displaced by an abrasive counter

face and it could be identified by the presence of ridges and grooves. On the other hand, micro-cutting could be observed when the particles are being detached from the surface when swept by the abrasive counter face. Micro-cracking usually occurs on brittle material such as ceramics which is caused by high-stress concentration imposed on the surface of the material by the abrasive particles. Finally, micro-fatigue could be observed when the abraded surface of the material shows a rough worn surface due to the repeated sliding action by the abrasive counter body [19].

Therefore, the main objective of this paper is to investigate the effect of incorporating varying amounts of untreated or pristine MWCNT (PMWCNT), acid-treated MWCNT (AMWCNT), and silane-treated MWCNT (SMWCNT) on the abrasive wear behavior of epoxy–kenaf composites.

2. Materials and Methods

2.1. Materials

Epoxy Miracast 1517 A/B used as a matrix was supplied by Miracon Sdn. Bhd., Malaysia. The reinforcing material, namely yarn kenaf fibers with an average diameter of 1.54 mm, was supplied by Innovative Pultrusion Sdn. Bhd., Malaysia. The MWCNT, Flo Tub 9000 Series used as nanofiller was bought from CNano Technology (Beijing) Ltd., China. The sulfuric acid (95%), nitric acid (62–65%), acetone (99.5%), and ethanol (99.5%) used as reagents in acid treatment were supplied by 99.5%, R&M Chemicals, Chandigarh, India. The 3-aminopropyltriethoxysilane (99%) supplied by Sigma Aldrich, USA was used as a silane functionalization agent.

As for the acid treatment process, 3 g of as-received/pristine MWCNT (PMWCNT) was weighed and dispersed in 300 mL of acid solution at 80 °C, and refluxed for 4 h. The acid solution was a combination of H₂SO₄ and HNO₃ with ratio 3:1. Then, distilled water was added to the solution, which was continuously stirred for another 6 h. After that, the solution was added with distilled water and acetone until it reached pH of 6–7. The oxidized MWCNT was then dried in the oven at 80 °C for 24 h and was ground to get AMWCNT powder. For the silane treatment process, AMWCNT powder was dispersed in 300 mL of 2 wt.% 3-aminopropyltriethoxysilane–ethanol–water solution. The solution was then stirred for 4 h at 70 °C before being filtered and dried in the oven at 80 °C for 12 h. The dried SMWCNT was also ground to attain a fine powder of SMWCNT.

2.2. Fabrication of MWCNT–Epoxy–Kenaf Composites

Initially, varying amounts of PMWCNT at 0.5, 0.75, and 1 wt.% were mixed together with epoxy using a mechanical stirrer for 1 h. Before being mixed with epoxy resin, the PMWCNT was dispersed in ethanol solution to enhance the degree of dispersion inside epoxy resin. Next, the mixtures of PMWCNT–epoxy were degassed under a high vacuum machine for 1 h, followed by the addition of a hardening agent at a 100:30 (epoxy: hardener) ratio. The degasification process was essential for removing any entrapped air during the fabrication process. This process was then repeated using the same amount series of AMWCNT and SMWCNT.

The epoxy–kenaf composites were produced using dry filament winding and impregnation of kenaf fibers into epoxy, which had been initially incorporated with MWCNT. Kenaf fibers were wound on a 430 × 300 mm frame in one direction. Then, the composites were left at room temperature for 24 h for curing process. Finally, the plates of composites were cut into disc shapes for abrasive wear test standard. Table 1 describes the formulation of MWCNT–epoxy–kenaf composites.

Table 1. The formulation of multiwall carbon nanotube (MWCNT)–epoxy–kenaf composites.

| Varieties of MWCNT–Epoxy–Kenaf Composites | Surface Treatment of MWCNT | MWCNT (wt.%) | Density (g/cm ³) |
|-------------------------------------------|----------------------------|--------------|------------------------------|
| Epoxy–kenaf | - | - | 1.1424 |
| 0.5 wt.% PMWCNT–epoxy–kenaf | as received/pristine | 0.5 | 1.1451 |
| 0.75 wt.% PMWCNT–epoxy–kenaf | as-received/pristine | 0.75 | 1.1460 |
| 1 wt.% PMWCNT–epoxy–kenaf | as-received/pristine | 1 | 1.1462 |
| 0.5 wt.% AMWCNT–epoxy–kenaf | acid treatment | 0.5 | 1.1320 |
| 0.75 wt.% AMWCNT–epoxy–kenaf | acid treatment | 0.75 | 1.1325 |
| 1 wt.% AMWCNT–epoxy–kenaf | acid treatment | 1 | 1.1328 |
| 0.5 wt.% SMWCNT–epoxy–kenaf | silane treatment | 0.5 | 1.1254 |
| 0.75 wt.% SMWCNT–epoxy–kenaf | silane treatment | 0.75 | 1.1275 |
| 1 wt.% SMWCNT–epoxy–kenaf | silane treatment | 1 | 1.1305 |

2.3. Suspension Stability Test

The suspension stability of untreated and treated MWCNT was compared in order to evaluate the effectiveness of the surface modification. This test was done using the ultrasonication process. Next, 0.1 mg of PMWCNT was diluted in 30 mL ethanol and ultrasonicated for 30 min. The mixture was then left to rest for 72 h (3 days). The same procedure was repeated for AMWCNT and SMWCNT. The PMWCNT, AMWCNT, and SMWCNT dispersion was evaluated in every 30 min, 12, 24, and 72 h.

2.4. Volume Fraction of Epoxy–Kenaf Composites

The Alicona 3D Surface Metrology System software was used to determine the volume fraction of the fibers. This technique requires the use of metallographic specimen preparation. The small section of kenaf composites were cut and mounted perpendicularly to the fibers axis. The specimens were then ground with abrasive papers and polished with 1 μ diamond paste. The surface of the polished specimen should display a clear delineation of fibers and matrix in order to get clear images. The best images were used to calculate the volume fraction by using resident software in image analyzer. At least 5 samples for each system were observed to calculate the volume fraction.

2.5. Abrasive Wear Test

The wear test for MWCNT–epoxy–kenaf composites was tested using TR 600 abrasive wear tester (Figure 1a) in accordance with ASTM D3389 test standard. The specimen was in a disc shape with a 123-mm diameter and thickness of 5 to 6 mm. The test was conducted at a speed setting of 2.5 m/s and applied load of 10 N. The mass of the specimen was weighed using precision balance with readabilities up to 0.1 mg. The mass loss was determined using the mass of specimens before and after the wear test and recorded at every 2000 m interval for 20,000 m sliding distance. In between each interval, the rollers were scrubbed and dusted to ensure the abrasive roller's surface was in good condition. During the fifth cycle, which represented the 10,000 m sliding distance, thermal images were taken using the infrared thermal camera as shown in Figure 1b at a constant distance from the specimen.

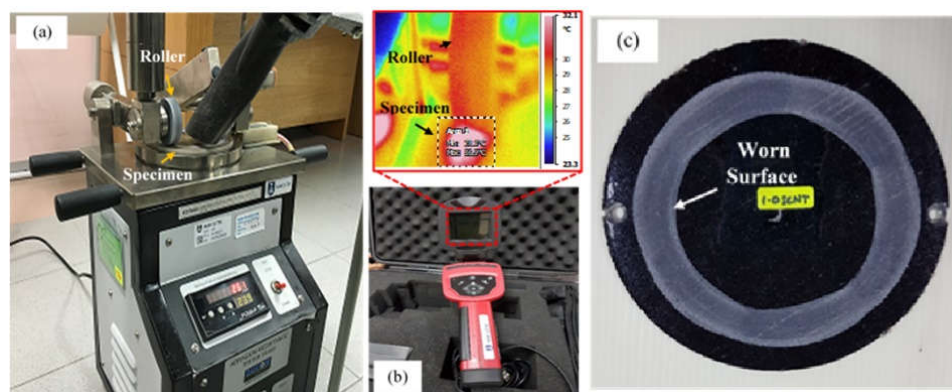


Figure 1. (a) The experiment set-up for the abrasion wear test, (b) infrared thermal image camera, and (c) composite specimen (diameter: 123 mm, thickness: 5 mm) after wear test.

The specific wear rate of the composite was calculated using Equation (1).

$$W_s = \frac{\Delta m}{L\rho F} \quad (1)$$

where the specific wear rate (W_s) is described as the function of mass loss Δm (expressed in g) over the multiplication of the sliding distance L (in m), the density ρ (in g/mm^3), and applied load F (in N) with the expressed unit of mm^3/Nm [2]. Lastly, the abraded test specimens (Figure 1a) were further analyzed using the stereomicroscope with $10\times$ magnification for observing the worn surface conditions. At least 5 specimens for each composite system were tested to determine the wear properties.

3. Results and Discussion

3.1. Suspension Stability Analysis

The suspension stability of the PMWCNT, AMWCNT, and SMWCNT in aqueous ethanol solution was compared in order to evaluate the effectiveness of treatment on the MWCNT surfaces. Even though this method cannot quantify the dispersion quality, it still provided useful information for the comparative study. It should be noted that, in this study, MWCNT was first dispersed in ethanol solution before being mixed with epoxy resin. This was an important step to segregate MWCNT from each other and later gave homogeneous dispersion in the epoxy matrix. Figure 2 shows the digital images of PMWCNT, AMWCNT, and SMWCNT in aqueous ethanol solution, left for 30 min, 12 h, 24 h, and 72 h after sonication process. It can be seen clearly that highly dispersed PMWCNT, AMWCNT, and SMWCNT were visually observed as a black solution without precipitation right after the sonication process. The pristine CNT started to sediment after 30 minutes' sonication processes and completed sedimentation after being left for 24 h. It was believed that PMWCNT's relatively easy sedimentation was due to agglomerated structures of PMWCNT, whereas AMWCNT and SMWCNT were more stabled and had maintained their dispersion in ethanol even after 72 h. This suggests that the structure of PMWCNT was slightly altered after acid and silane treatments. The changes of MWCNT's structure can be explained in terms of the existence of functional groups as revealed by FTIR and supported by TEM images from a previous study [16].

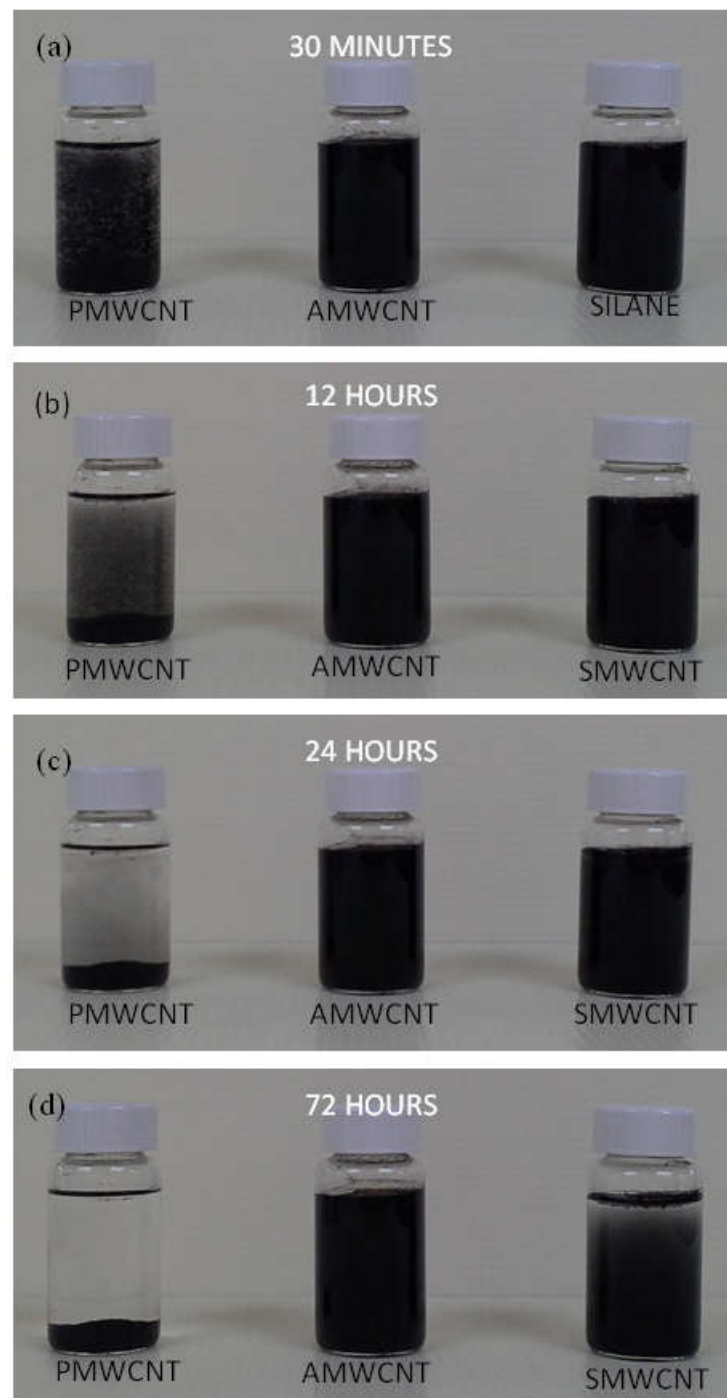


Figure 2. Digital images of MWCNT dispersion in ethanol after: (a) 30 min, (b) 12 h, (c) 24 h, and (d) 72 h.

3.2. Epoxy–Kenaf Composites Volume Fraction

The image analysis technique was used to determine the volume fraction of epoxy–kenaf composites. Figure 3 shows the grayscale optical image, which was used to calculate the total frame area and total kenaf fibers' field area. The volume fraction was calculated by dividing the total kenaf fibers' field area to the total frame area. The volume percentage of kenaf fibers recorded was an average of 17.9 ± 2.3 vol.%.



Figure 3. Optical micrograph of cross section of epoxy–kenaf composite for measurement of fibers' volume fraction with magnification of 5x.

3.3. Abrasive Wear Properties

3.3.1. Effect of PMWCNT Inclusion into Epoxy–Kenaf Composites on the Specific Wear Rates

When kenaf fiber was incorporated into epoxy resin, an increase in wear resistance, i.e., reduction in wear rate, was expected, resulting in turn in an improved thermal stability and no pull-out of fibers [1]. Therefore, when the temperature started to rise due to the contact between the surfaces, the kenaf prevented the progressive sliding of epoxy resin, thus lowering the amount of material removed. In other words, the interface adhesion between the epoxy and kenaf helped to reduce the adhesive wear, reducing also the ploughing of the surface, since kenaf was difficult to be pulverized especially when the fiber was in a normal orientation to the abrasive roller [20].

Figure 4 illustrates the specific wear rates of PMWCNT-filled epoxy–kenaf composites, as compared with the epoxy and epoxy–kenaf composites. When compared to the neat epoxy, the wear rates of all these composites showed decrement. During the early state stage, which spanned from 2000 to 4000 m, the wear rates were decreasing for all composite specimens. This occurrence was due to the difference in the surface roughness of the samples' surface and the counter face. A similar report also was found by Chauhan et al., which stated that the difference in initial surface roughness allowed for a strong interlocking process to occur, thus leading to a larger amount of material to be removed which explained the higher wear rate in the beginning [10]. After a longer exposition to the abrasive counter face, the surface topography of composites was deemed to become more and more similar to the counter face, thus the wear rate started to be in a steadier state and continue until lower rates were attained.

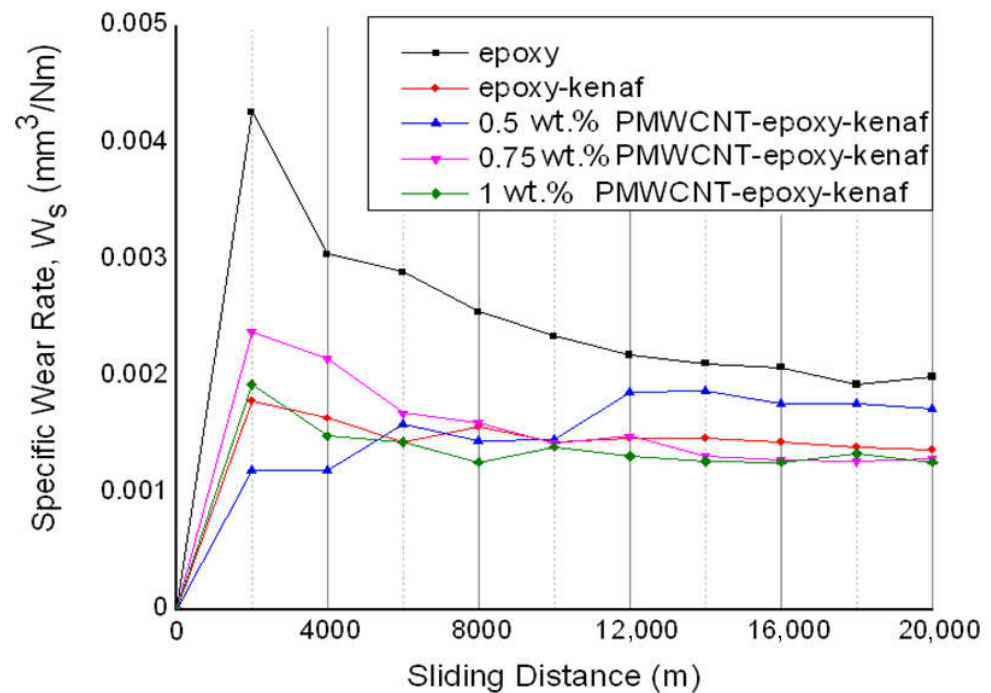


Figure 4. Specific wear rates of untreated MWCNT (PMWCNT)-filled epoxy–kenaf composites.

Fluctuating wear rates were measured in the 0.5 wt.% PMWCNT–epoxy–kenaf composite. This behavior could be attributed to the MWCNT not being distributed properly inside the epoxy matrix, since the MWCNT tended to easily agglomerate if untreated [7,22].

The incorporation of 0.75 and 1% wt.% of PMWCNT showed similar wear rate compared to the epoxy–kenaf composite. Although the 1 wt.% PMWCNT–epoxy–kenaf composite showed a slight improvement in the wear resistance of the composite as compared to kenaf composites, the changes could not be regarded as significant. It was speculated that untreated MWCNT would improve the wear properties of the composites; however, there might be several reasons why the MWCNT had not been performing as expected. Firstly, the MWCNT may not have been dispersed well inside the epoxy matrix. The agglomeration of MWCNT may result in large chunks of MWCNT being removed during the test, thus inhibiting the MWCNT to perform well [7]. Furthermore, the abrasive wear could be caused by four different mechanisms, which were micro-cutting, micro-ploughing, micro-cracking, and micro-fatigue [19]. By considering the type of material, the former two mechanisms would be more dominant compared to the latter two. Therefore, when MWCNT was incorporated into the composite, the epoxy layer became more ductile or softer per se due to the MWCNT, thus making it easier to be cut through, i.e., the micro-cutting mechanism was induced, which promoted higher wear.

In between each cycle, the abrasive rollers were scrubbed and dusted. MWCNT was expected to wear, producing small-sized debris, which would then form the tribo-protective layer. This protective layer was expected to prevent the three-body abrasive wear effect that may have resulted in poorer wear resistance of materials [14,23]. The action of scrubbing and dusting the counter face might have removed the protective layer, which would constrain the significant improvement of the wear rates. Overall, the composite with 1 wt.% of PMWCNT showed the most promising wear resistance compared to the epoxy–kenaf composite without any PMWCNT filling.

3.3.2. Effect of Acid and Silane Treatment on the MWCNT on the Wear Rates of the Epoxy–Kenaf Composites

The wear rates for the AMWCNT-filled epoxy–kenaf composites are shown in Figure 5. The wear properties did not improve regardless of the acid treatment. For every amount of MWCNT included into the epoxy–kenaf composites, the wear rates seemed to increase when the MWCNT was treated with acid. The biggest difference of wear rates was observed between 1 wt.% AMWCNT–epoxy–kenaf and 1 wt.% PMWCNT–epoxy–kenaf. On the other hand, a similar increment was observed for 0.5 and 0.75 wt.% AMWCNT and PMWCNT epoxy–kenaf composites. Although it is speculated that the acid treatment procedures would help in improving the dispersion of the MWCNT inside the epoxy resin, it was also reported that the side effect of the MWCNT with acid treatment can be the reduction of crosslinking density due to the interference in the functional group [15]. As a fair assumption, it can be said that the acid treatment may have reduced the crosslinking density of the epoxy resin, thus decreasing the bond strength between the MWCNT and epoxy, an effect obviously much more evident at larger AMWCNT loadings. This led eventually to higher wear rates due to the increment of the adhesive wear. The higher amount of MWCNT may have linearly increased the wear effect, increasing the possibility of interference with the functional group of epoxies likely to happen [15,20].

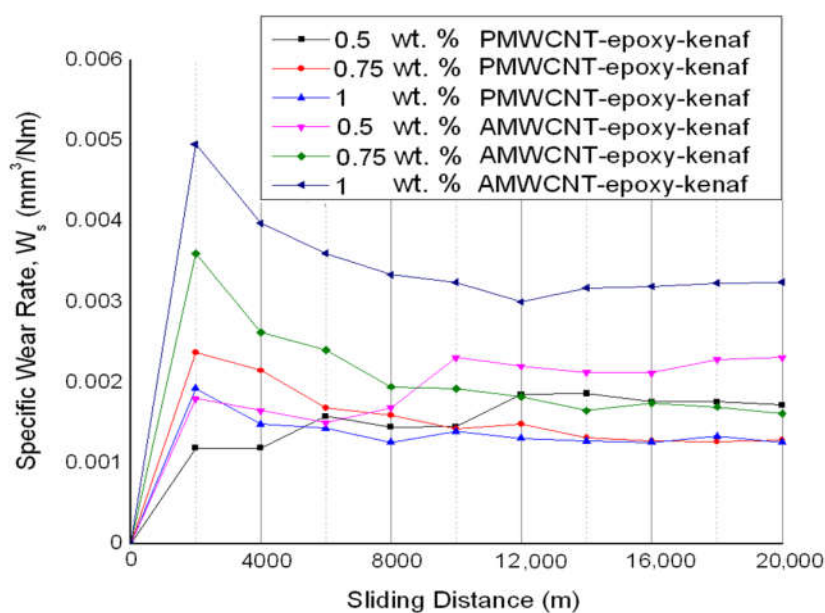


Figure 5. Specific wear rates of PMWCNT- and acid-treated MWCNT (AMWCNT)-filled epoxy–kenaf composites.

In Figure 6, the effect of silane treatment on the wear rates of the SMWCNT-filled epoxy–kenaf composites is depicted. No improvements were observed with all the percentages of SMWCNT incorporated into the epoxy–kenaf composites with respect to the introduction of PMWCNT. In addition, the increase of wear rates was even larger than that observed with AMWCNT-filled epoxy–kenaf composites. It was supported by various studies that silane treatment would strengthen the interfacial bonding between MWCNT and epoxy. However, the wear rates observed for SMWCNT-filled composites showed no improvement, despite the increased bond strength [15–17]. It could be postulated that when the bonding strength between MWCNT and epoxy had increased, this resulted in the three-body abrasive wear effect with the rough epoxy surface finished. Since the three-body abrasive wear effect could inflict more severe effect on the wear rate compared to adhesive wear effect, the wear rates for SMWCNT-filled composites were observed to be higher compared to AMWCNT-filled composites.

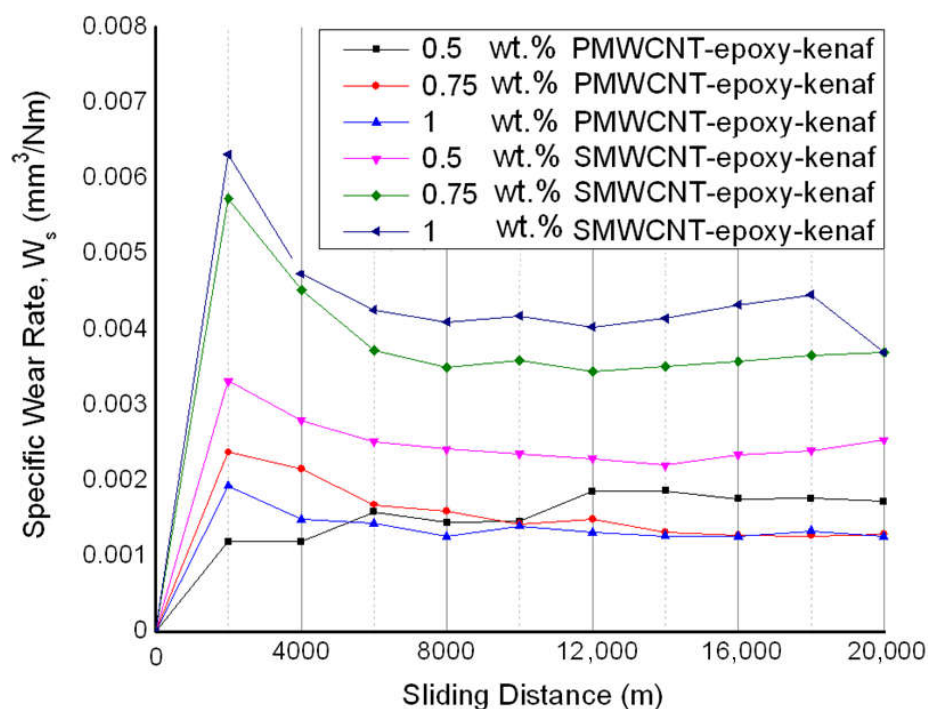


Figure 6. Specific wear rates of PMWCNT- and silane-treated MWCNT (SMWCNT)-filled epoxy–kenaf composites.

3.4. Characterisation of MWCNT-Filled Epoxy–Kenaf Composites During and After Subjected to Wear Test

3.4.1. Thermal Behavior and Abraded Surface Evaluation of PMWCNT-Filled Epoxy–Kenaf Composite Compared with Epoxy and Epoxy–Kenaf Composites

Thermal images taken of the composites are illustrated in Figure 7. It was observed that the contact temperature dropped significantly for epoxy–kenaf composites, as depicted in Figure 7b, as compared against the pure epoxy resin, whose image is represented in Figure 7a. The maximum temperatures remained lower than 35 °C for the PMWCNT–epoxy–kenaf composites, whereas for the epoxy resin, the maximum contact temperature recorded was around 40 °C. This suggests that by incorporating PMWCNT into the epoxy–kenaf composites, the temperature differences appeared minimal, observing values for area 1 for 0.5 wt.% PMWCNT–epoxy–kenaf (Figure 7c), 0.75 wt.% PMWCNT–epoxy–kenaf (Figure 7d), and 1 wt.% PMWCNT–epoxy–kenaf (Figure 7e) composites. This can demonstrate that at this level of introduction for PMWCNT, which is sufficient to the substantial improvement of wear rates, no increase in temperature that could create problems to the thermal stability of the resin was revealed. The absolute temperature measurements could of course be affected by the difference in emissivity of the different materials forming the composite. However, the differences in emissivity between kenaf–epoxy composites [24] and multiwall carbon nanotubes (MWCNT) [25] were found to be minimal, i.e., to be both approximated to 0.92 e.g., in the referenced studies. It appears to the authors that reasoning as if the difference in emissivity between the aforementioned materials could be negligible would lead to a minimal error in temperature measurement, also considering that the objective of the study was to observe a more general thermal stability of the composite. In addition, the inclusion of PMWCNT into the composites may have contributed to producing smaller-sized debris, which would then form a thin transfer film, creating a barrier between the counter face and the sample surface, thus reducing the friction between the surfaces of the samples and counter face. The decrease in friction resulted in the reduction of the contact temperature and wear rates [6,7,10].

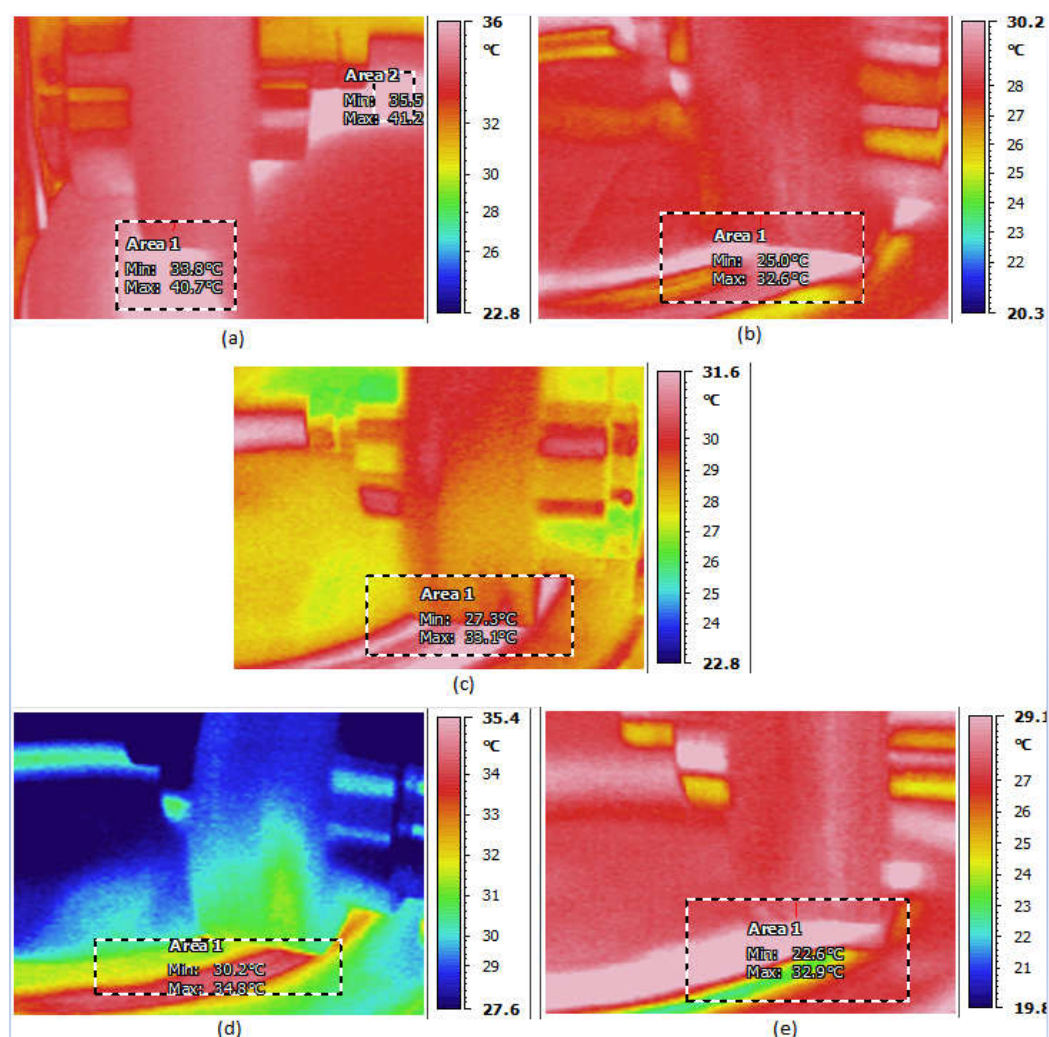


Figure 7. Thermal images for (a) epoxy, (b) epoxy-kenaf, (c) 0.5 wt.% PMWCNT-epoxy-kenaf, (d) 0.75 wt.% PMWCNT-epoxy-kenaf, and (e) 1 wt.% PMWCNT-epoxy-kenaf composites.

Figure 8 illustrates the surface images of the abraded surface obtained from the stereomicroscope. The black arrows indicate the sliding directions of the sample. It can be seen in Figure 8a that the abraded surface of epoxy resin appeared to be rougher than in the other cases. The rough abrasion may be due to larger debris formed during wearing. Larger-sized debris could lead to three-body abrasive wear, which would further enhance the wearing rate [22]. The rough worn surface also indicated that apart from the apparent micro-cutting and micro-ploughing, the specimen was also being exposed to micro-fatigue abrasive wear, which is also the basic mechanism of abrasive wear [7,19]. On the other hand, Figure 8b shows the kenaf composite's abraded surface. The abraded surface seemed to appear smoother compared to the pure epoxy. The smoother surface suggested that smaller-sized debris had been produced, thus reducing the effect of three-body abrasive wear which led to decreasing wear rate and increasing wear resistance [22]. The smaller-sized debris was generated since the effect of the adhesive wear had been reduced.

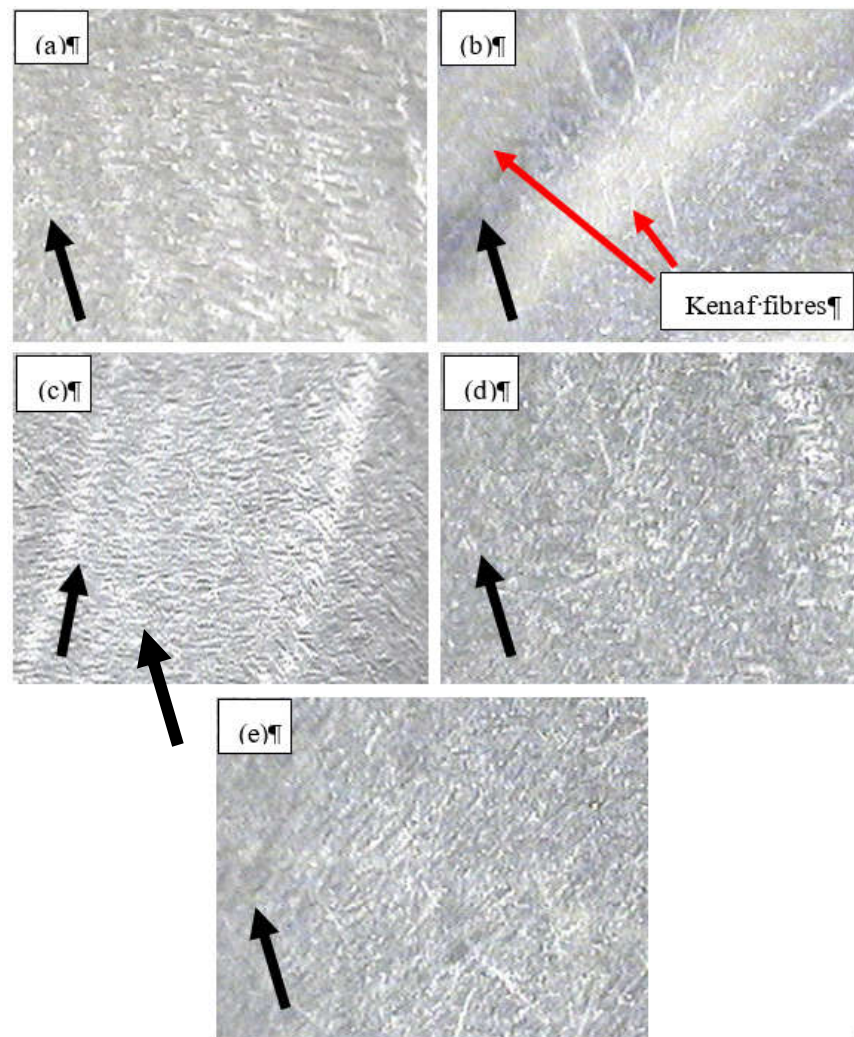


Figure 8. Images of the abraded surfaces for: (a) Epoxy, (b) epoxy–kenaf, (c) 0.5 wt.% PMWCNT–epoxy–kenaf, (d) 0.75 wt.% PMWCNT–epoxy–kenaf, and (e) 1 wt.% PMWCNT–epoxy–kenaf composites (magnification of 10x).

The abraded surfaces of the PMWCNT-filled kenaf composites are shown in Figure 8. It could be seen from 0.5 wt.% PMWCNT–epoxy–kenaf (Figure 8c), followed by 0.75 wt.% PMWCNT–epoxy–kenaf (Figure 8d), and 1 wt.% PMWCNT–epoxy–kenaf (Figure 8e) that the surface roughness had indeed improved. It seemed to be smoother in accordance with the increasing amount of PMWCNT. It was noticed that the surface profile of the PMWCNT-filled composites seemed to be rougher than the kenaf composites. This may be due to the agglomeration of the PMWCNT inside the composites, which led to bigger-sized debris being produced, resulting in rougher worn surfaces caused by the three-body abrasive effect and the micro-fatigue abrasive worn mechanism [7,19,22].

3.4.2. Thermal Behavior and Abraded Surface Evaluation of AMWCNT- and SMWCNT-Filled Epoxy–Kenaf Composite

Figure 9 displays thermal images of AMWCNT and SMWCNT–epoxy–kenaf composites. Small increments of contact temperature were exhibited by SMWCNT–epoxy–kenaf composites, as compared against the AMWCNT–epoxy–kenaf composites. The temperature had also increased with respect to untreated MWCNT-filled kenaf composites. However, the contact temperatures for these composites remained under 38 °C, which was still lower compared to pure epoxy resin. The increments of temperatures were ascribed to the reduction in the interfacial strength between the epoxy and the treated MWCNT. The acid

treatment process may have destroyed the functional group of the resin which resulted in weaker bond strength. The decrease in adhesion strength would eventually lead to an increase in adhesive wear, thus causing more materials to be removed, hence an increment in friction [1,4,8,20].

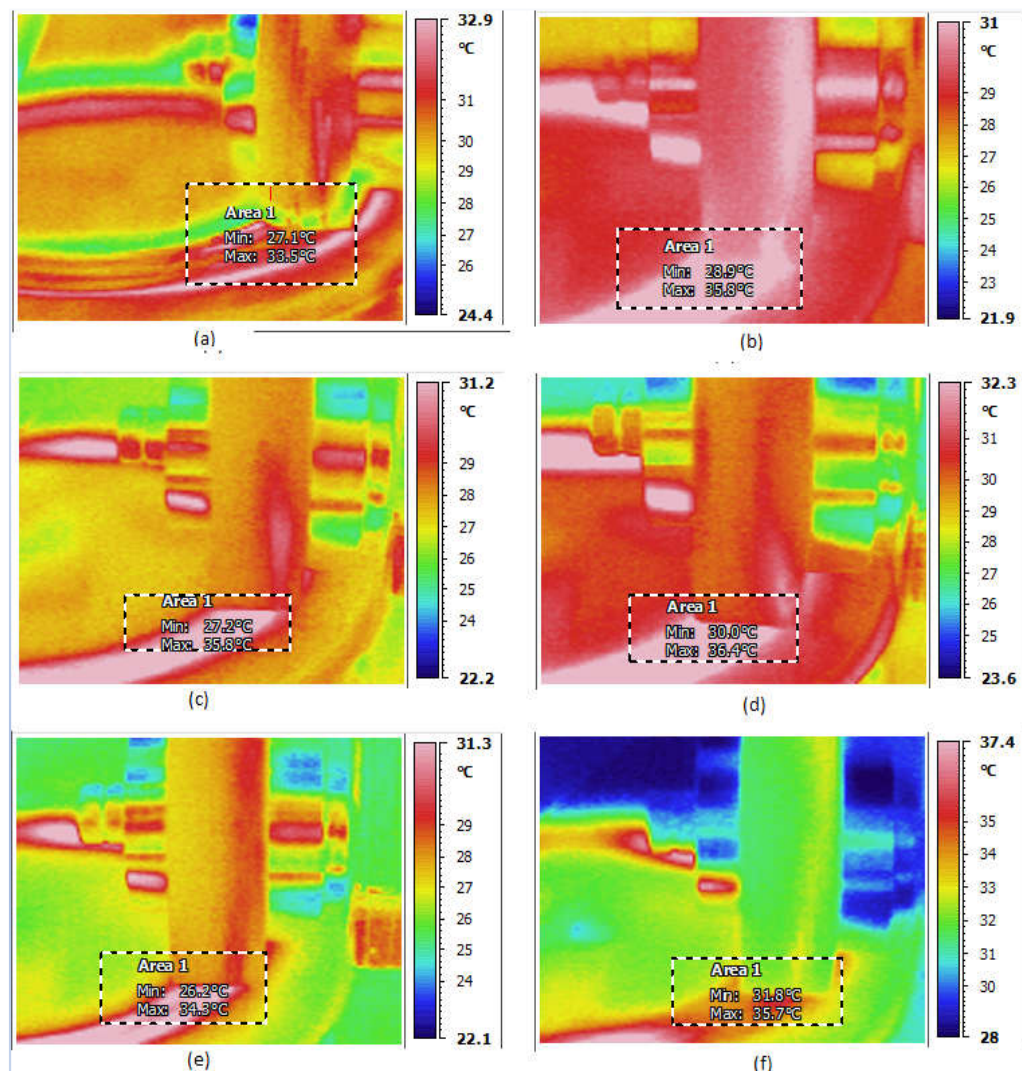


Figure 9. Thermal images captured for different composites: (a) 0.5 wt.% AMWCNT-epoxy-kenaf, (b) 0.5 wt.% SMCNT-epoxy-kenaf, (c) 0.75 wt.% AMWCNT-epoxy-kenaf, (d) 0.75 wt.% SMCNT-epoxy-kenaf, (e) 1 wt.% AMWCNT-epoxy-kenaf, and (f) 1 wt.% SMCNT-epoxy-kenaf.

The wear rate was observed to worsen for the SMCNT-epoxy-kenaf composites. Although the silane treatment is known to help in improving the bonding strength between MWCNT and epoxy, as reported, e.g., in [26], this attribute, beneficial in other mechanical properties of the composites, may have not been desirable for the wear properties. This is because, when the bond strength increased, rougher-shaped debris was produced as a result of the substantially intact surface contact between epoxy and MWCNT. The rough-shaped debris would eventually induce the three-body abrasive wear effect. Since the temperature for the SMCNT-filled composites seemed to be the highest compared to PMWCNT- and AMWCNT-filled composites, this may suggest that rough-shaped debris may have been inducing the increase in friction, thus increasing the temperatures as well as the wear rates.

Figure 10 exhibits the surface profiles for the AMWCNT- and SMCNT-filled epoxy-kenaf composites. The surface profiles of AMWCNT- and SMCNT-filled epoxy-

kenaf composites seemed rougher compared to PMWCNT-filled epoxy–kenaf composites, comparing back with Figure 8. This behavior may suggest that the weakened MWCNT bond strength was due to the acid treatment, resulting in the increment of the adhesive wear. The increase in adhesive wear resulted in an increasing amount of material being worn out, thus resulting in a rougher abraded surface produced. Nevertheless, the silane treatment had previously suggested the improvement of bonding strength between MWCNT and epoxy [15–17]. However, the improvement on interfacial bonding may have not been very favorable for reducing the wear rates of the composites. The intense bonding strength was believed to have kept the epoxy and MWCNT still intact when abraded, thus producing rough debris. The rough-shaped debris may have induced the three-body abrasive wear affect. The surface profiles of SMWCNT-filled composites could have been because of the three-body abrasive wear effect, since rough abraded surfaces were observed.

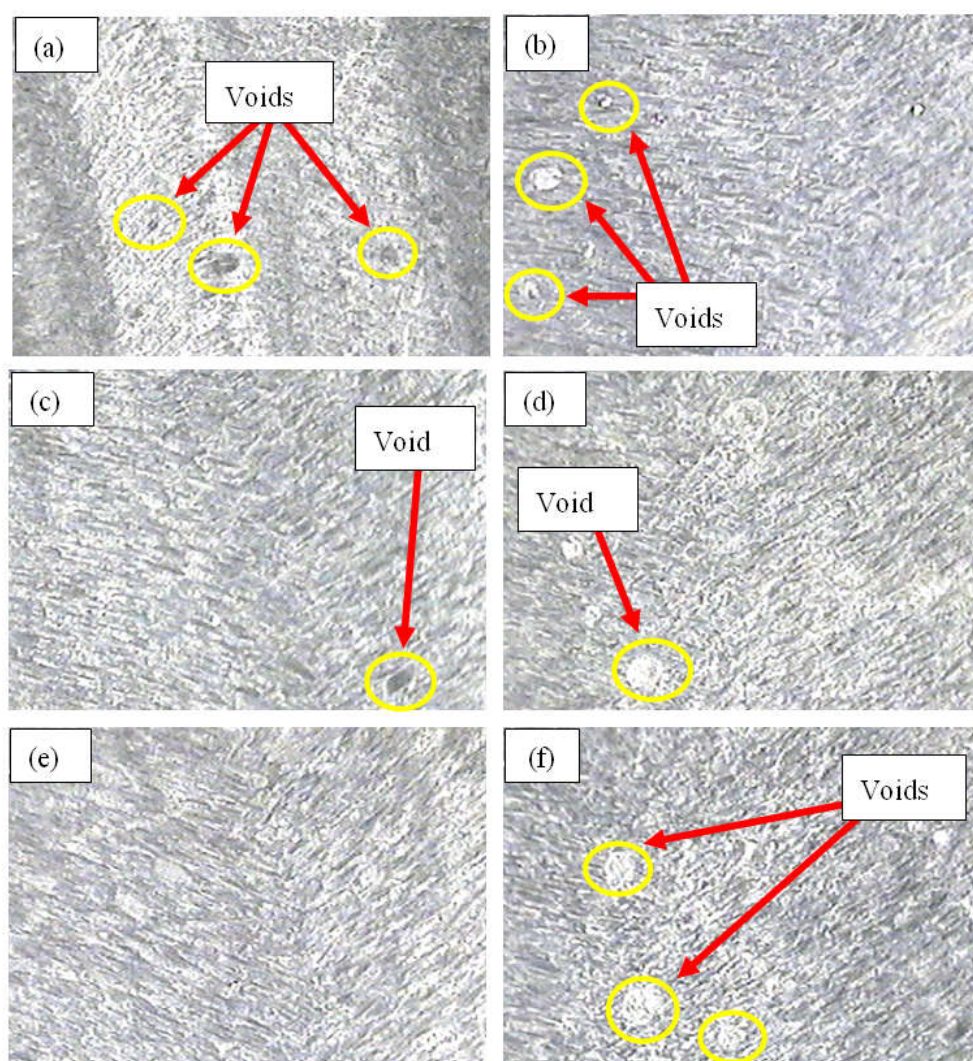


Figure 10. Surface profiles for different composites: (a) 0.5 wt.% AMWCNT–epoxy–kenaf, (b) 0.5 wt.% SMWCNT–epoxy–kenaf, (c) 0.75 wt.% AMWCNT–epoxy–kenaf (d) 0.75 wt.% SMWCNT–epoxy–kenaf (e) 1 wt.% AMWCNT–epoxy–kenaf, and (f) 1 wt.% SMWCNT–epoxy–kenaf (magnification of 10x).

Additionally, voids and unscratched spots were also present on the evaluated surfaces. As discussed earlier, the existence of voids might have improved the interlocking effect, thus leading to a higher amount of material being dug out during contact [10,22]. Another possible observation from Figure 10 is that, as the content of the AMWCNT and

SMWCNT increased passing from 0.5 to 1 wt. %, the abraded surface became rougher accordingly, so that larger and rougher debris would be generated when the surface was being abraded, as the stereomicroscope images indicate.

4. Conclusions

The effects of incorporating untreated CNT (PMWCNT), acid-treated CNT (AMWCNT), and silane-treated CNT (SMWCNT) on the wear properties of kenaf composites were investigated. When kenaf was added into the epoxy resin, the thermal stability of epoxy increased and the good bonding strength between kenaf and epoxy reduced the fatigue and adhesive wear of the epoxy, thus improving the wear resistance. The inclusion of the PMWCNT into the composites showed improvement in the wear rates, though not in a consistent way, probably due to uneven distribution of the reinforcement, though the situation slightly improved with higher loadings. When the MWCNT was treated with acid and silane, the wear rates unexpectedly increased. It was speculated that the acid treatment may have caused the interference in the functional group and the reduction of the crosslinking density. In addition, the silane treatment induced the production of rougher-shaped debris, thus leading to the three-body abrasive wear effect which would eventually increase the wear rates. Overall, the findings showed the trade-off property between wear and other mechanical properties, which suggested the interest for the introduction of MWCNT in kenaf–epoxy composites.

Author Contributions: Conceptualization, N.S. and A.J.; methodology, N.S.; validation, A.J. and M.J.; formal analysis and investigation, N.S. and A.J.; writing—original draft preparation, N.S.; writing—review and editing, C.S., A.J., and M.J.; supervision and project administration, A.J.; funding acquisition, A.J. and M.J. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Fundamental Research Grant Scheme (FRGS), grant number no: 600-IRMI/FRGS 5/3 (336/2019) and the APC was funded by Universiti Putra Malaysia.

Institutional Review Board Statement: Not applicable

Informed Consent Statement: Not applicable

Data Availability Statement: Data is contained within the article

Acknowledgments: The authors would like to thank the Faculty of Mechanical Engineering, Universiti Teknologi Mara (UiTM), Shah Alam, and the Ministry of Higher Education, Malaysia for the research support.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Chin, C.W.; Yousif, B.F. Potential of kenaf fibres as reinforcement for tribological applications. *Wear* **2009**, *267*, 1550–1557.
2. Nordin, N.A.; Yussof, F.M.; Kasolang, S.; Salleh, Z.; Ahmad, M.A. Wear Rate of Natural Fibre: Long Kenaf Composite. *Procedia Eng.* **2013**, *68*, 145–151.
3. Nayak, S.; Mohanty, J. Erosion wear behavior of benzoyl chloride modified areca sheath fiber reinforced polymer composites. *Compos. Commun.* **2020**, *18*, 19–25.
4. Friedrich, K.; Zhang, Z.; Schlarb, A.K. Effects of various fillers on the sliding wear of polymer composites. *Compos. Sci. Technol.* **2005**, *65*, 2329–2343.
5. Jumahat, A.; Talib, A.A.A.; Abdullah, A. Wear Properties of Nanoclay Filled Epoxy Polymers and Fiber Reinforced Hybrid Composites, Chap. 11. In *Nanoclay Reinforced Polymer Composites: Nanocomposites and Bionanocomposites*; Jawaid, M., Qaiss, A.K., Bouhfid, R., Eds.; Springer: Singapore, 2016; pp. 247–260.
6. Jumahat, A.; Kasolang, S.; Bahari, M.T. Wear properties of nanosilica filled epoxy polymers and FRP composites. *J. Tribol.* **2015**, *6*, 24–36.
7. Yan, L.; Wang, H.; Wang, C.; Sun, L.; Liu, D.; Zhu, Y. Friction and wear properties of aligned carbon nanotubes reinforced epoxy composites under water lubricated condition. *Wear* **2013**, *308*, 105–112.
8. Agrawal, S.; Singh, K.K.; Sarkar, P.K. A comparative study of wear and friction characteristics of glass fibre reinforced epoxy resin, sliding under dry, oil-lubricated and inert gas environments. *Tribol. Int.* **2016**, *96*, 217–224.

9. Manakari, V.; Parande, G.; Doddamani, M.; Gaitonde, V.N.; Siddhalingeswar, I.G.; Kishore; Shunmugasamy, V.C.; Gupta, N. Dry sliding wear of epoxy/cenosphere syntactic foams. *Tribol. Int.* **2015**, *92*, 425–438.
10. Chauhan, S.R.; Thakur, S. Effects of particle size, particle loading and sliding distance on the friction and wear properties of cenosphere particulate filled vinylester composites, *Mater. Des.* **2013**, *51*, 398–408.
11. Dhieb, H.; Bujinsters, J.G.; Elleuch, K.; Celis, J.P. Effect of relative humidity and full immersion in water on friction, wear and debonding of unidirectional carbon fiber reinforced epoxy under reciprocating sliding. *Compos. Part. B* **2016**, *88*, 240–252.
12. Sharma, S.; Bijwe, J.; Panier, S.; Sharma, M. Abrasive wear performance of SiC-UHMWPE nano-composites—Influence of amount and size. *Wear* **2015**, 332–333, 863–871.
13. Österle, W.; Dmitriev, A.L.; Wetzels, B.; Zhang, G.; Hausler, I.; Jim, B.C. The role of carbon fibers and silica nanoparticles on friction and wear reduction of an advanced polymer matrix composite. *Mater. Des.* **2016**, *93*, 474–484.
14. Parikh, H.H.; Gohil, P.P. Sliding wear experimental investigation and prediction using response surface method: Fillers filled fiber reinforced composites. *Mater. Today Proc.* **2019**, *8*, 5388–5393.
15. Bose, S.; Khare, R.A.; Moldenaers, P. Assessing the strengths and weaknesses of various types of pre-treatments of carbon nanotubes on the properties of polymer/carbon nanotubes composites: A critical review. *Polymer* **2010**, *51*, 975–993.
16. Sapiai, N.; Jumahat, A.; Mahmud, J. Mechanical properties of functionalised CNT filled kenaf reinforced epoxy composites. *Mater. Res. Express* **2018**, *5*, 045034.
17. Lee, J.H.; Rhee, K.Y.; Park, S.J. Silane modification of carbon nanotubes and its effects on the material properties of carbon/CNT/epoxy three-phase composites. *Compos. Part. A* **2011**, *42*, 478–483.
18. Cirino, M.; Friedrich, K.; Pipes, R.N. The effect of fibre orientation on the abrasive wear behavior of polymer composite materials. *Wear* **1988**, *121*, 127–141.
19. Morioka, Y.; Tsuchiya, Y.; Shioya, M. Correlations between the abrasive wear, fatigue, and tensile properties of filler-dispersed polyamide 6. *Wear* **2015**, 338–339, 297–306.
20. Basavarajappa, S.; Ellangovan, S. Dry sliding wear characteristics of glass–epoxy composite filled with silicon carbide and graphite particles. *Wear* **2012**, *296*, 491–496.
21. Sapiai, N.; Jumahat, A.; Mahmud, J. Wear properties of acid and silane modified CNT filled hybrid glass/kenaf epoxy composites. Chap. 6. In *Synthesis and Tribological Application of Hybrid. Materials*; Sukumaran, J., Jawaid, M., Nagarajan, R., De Baets, P., Eds.; Wiley-Vch: Weinheim, Germany, 2018; pp. 97–114.
22. Sapiai, N.; Jumahat, A.; Jawaid, M.; Khan, A. Effect of MWCNT surface functionalisation and distribution on compressive properties of kenaf and hybrid kenaf/glass fibres reinforced polymer composites. *Polymers* **2020**, *12*, 2522.
23. Ruckdäschel, H.; Sandler, J.K.W.; Altstädt, V. On the friction and wear of carbon nano fiber reinforced PEEK-based polymer composites. *Tribol. Interface Eng. Ser.* **2008**, *55*, 149–208.
24. Suriani, M.J.; Ali, A.; Khalina, A.; Sapuan, S.M.; Abdullah, S. Detection of Defects in Kenaf/Epoxy using Infrared Thermal Imaging Technique. *Procedia Chem.* **2012**, *4*, 172–178.
25. Huang, S.; Wang, N.; Bao, J.; Ye, H.; Zhang, D.; Yue, W.; Fu, Y.; Ye, L.; Jeppson, K.; Liu, J. Infrared Emissivity Measurement for Vertically Aligned Multiwall Carbon Nanotubes (CNTs) Based Heat Spreader Applied in High Power Electronics Packaging. In Proceedings of the 6th Electronic System-Integration Technology Conference (ESTC), Grenoble, France, 13–15 September 2016; IEEE: New York, NY, USA, 2016; doi:10.1109/ESTC.2016.7764696.
26. Wu, S.Y.; Yuen, S.-M.; Ma, C.-C.M.; Chiang, C.-L.; Huang, Y.-L.; Wu, H.-H.; Teng, C.-C.; Yang, C.-C.; Wei, M.-H. Preparation, morphology, and properties of silane-modified MWCNT/epoxy composites, *J. Appl. Polym. Sci.* **2010**, *115*, 3481–3488.