Thermal properties of pineapple leaf/kenaf fibre reinforced vinyl ester hybrid composites

A A Mazlan¹, M T H Sultan¹,²,³, A U M Shah¹,² and S N A Safri²

¹Department of Aerospace Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor Darul Ehsan, Malaysia
²Laboratory of Biocomposite Technology, Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia, 43400 UPM Serdang, Selangor Darul Ehsan, Malaysia
³Aerospace Malaysia Innovation Centre (944751-A), Prime Minister’s Department, MIGHT Partnership Hub, Jalan Impact, 63000 Cyberjaya, Selangor Darul Ehsan, Malaysia

*Corresponding author: thariq@upm.edu.my

Abstract. In this modern technology era, the usage of natural fibres has been widely used in various field of applications such as aerospace, maritime, military, automotive as well as structural building. This is due to the reason that they are lightweight, cheap, good sustainability and biodegradable. Only a small amount of research work being conducted on the hybridization of pineapple leaf and kenaf fibres reinforced with vinyl ester (PALF/KF/VE) hybrid composites. Thus, in this present work, the PALF/KF/VE hybrid composites are presented. The thermal properties of PALF, KF, VE as well as hybrid composites were investigated based on their structural components. PALF was in long fibre form while kenaf fibre was in woven form fabricated to form hybrid composites by using the hand lay-up and hot compression moulding. TGA testing was conducted to determine their respective thermal properties. From the experimental testing, the results showed that the thermal stability of hybrid composites enhanced rather than fibres themselves. The thermal degradation of PALF and KF occurred at the range temperature of 250–370 °C while neat VE, PALF/VE and PALF/KF/VE occurred at 300–450 °C. Thus, these composites can be used for various application such as automotive, aerospace, structural and others.

1. Introduction
Recently, natural fibres become one of hot topic issues discussed in the composite’s application [1]. The research work on the natural fibres have been attracted the researchers to explore them. This is due to the reason that they have more advantages over the synthetic fibres such as biodegradable, lightweight, cheap in cost and high availability [2]. The natural fibres can be used as a reinforcement but only in the low-stress application. Pineapple, ananas comosus is one of the largest tropical fruits in Malaysia. Several research works had been conducted to study the properties of pineapple leaf fibre (PALF), mechanically, thermally and chemically [3], [4], [5]. TGA dan DSC testing being worked by the researchers to investigated the thermal properties of PALF [6]. Another study showed that PALF composites recorded the onset temperature approximately at 270 °C for thermal degradation [7].

Kenaf is well known as a hardy plant with a fibrous stalk which resistant to insect and ability to grow under climatic condition that required less water, pesticides and fertilizers. Globally, kenaf is one of the suitable biological resources that can replace the fossil fuels because of its physical properties. A lot of research work being conducted on the kenaf fibres (KF) and its composites [8], [9], [10], [11]. Besides,
the thermal degradation behaviour of kenaf/PALF hybrid composites were investigated [12] with respect to the fibre content and length. Vinyl ester (VE) resin is a thermosetting polymer that produced by the mixture of epoxy and unsaturated polyester resin. VE has high toughness, strength and chemical resistance. Therefore, VE possessed high thermal and electrical insulation properties. A lot of research works being worked on to investigate the properties of VE [13], [14]. A research work conducted on the properties of betel nut husk reinforced with VE composites [15]. Since there is no previous research work that examined the thermal properties of PALF/KF/VE hybrid composites, the present research work examined the thermal properties of PALF, kenaf fibre, neat VE, PALF/VE and PALF/KF/VE hybrid composites. The discussion is done based on the component of the composites. The hybridization of PALF with KF enhanced the thermal stability of composites.

2. Materials and Methodology

2.1 Materials
PALF, in the roving form of a thin yarn, with the average thickness of 1 mm, was used as reinforcement material. Prior to reinforcement, the PALF was chopped into 30 mm length, by using a chopper gun. Woven KF was used to be hybridized with PALF. In this study, the resin used was MFE-11, a premium standard Bisphenol-A type epoxy VE resin supplied by Sino Polymer Co., LTD. The hardener that was used was methyl ethyl ketone peroxide (MEKP).

2.2 Methodology
In this study, PALF, kenaf fibres, neat VE, PALF/VE and PALF/KF/VE hybrid composites were fabricated. The woven kenaf fibre were used as addition to the present research work which focusing on the hybridization of PALF and kenaf fibre. The hand lay-up and hot compress method was used to prepare the composites. The ratio used for fibres to matrix resin was 30:70. The temperature used for the 40 tonnes hot compression machine was 70°C at 3 minutes. After that, the composites were left for 3 hours before it is hardened completely. Thermal behaviours composites were examined using a thermogravimetric analyser (TGA DTA; Universal V3.9 TA instruments) in the Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia (UPM). The heating rate of the sample has been set to 10°C/min.

3. Results and Discussion
Thermogravimetric analysis or thermal gravimetric analysis (TGA) were studied to determine the thermal properties of the PALF, kenaf fibre, VE resin and PALF/KF/VE hybrid composites.

Figure 1. TGA curve of PALF, KF, Neat VE, PALF/VE and PALF/KF/VE hybrid composites.
Based on Figure 1, it can be observed that the thermal degradation of PALF and KF occurred at early stage. There were several steps of degradation of the composites and their respective components [16]. From 50 °C to 250 °C, both of the fibres started to degrade slowly at the first stage. The first stage indicated the weight losses due to the evaporation or vaporisation of water molecules in the composites [17]. This is due to the facts that PALF and KF are the natural resources that obviously have high content of moisture. However, in the range of temperature of 250-370 °C, as the temperature increase, there was major weight loss occurred in the stage due to the decomposition of hemicellulose of the PALF [18]. The final stage of degradation of PALF and KF can be observed at temperature range from 370-580 °C because of the decomposition of lignin, ash and cellulose content in the fibres [19], [20]. The percentage of weight of PALF, KF, neat VE, PALF/VE and PALF/KF/VE hybrid composites were illustrated as in table 1.

| Sample       | Weight Loss (%) |
|--------------|-----------------|
|              | $T_{60^\circ C}$ | $T_{100^\circ C}$ | $T_{180^\circ C}$ | $T_{260^\circ C}$ | $T_{300^\circ C}$ | $T_{370^\circ C}$ | $T_{450^\circ C}$ | $T_{530^\circ C}$ | $T_{570^\circ C}$ |
| PALF         | 4.18            | 5.3             | 6.18             | 9.16             | 20.53            | 70.11             | 76.71             | 78.84             | 79.31             |
| KF           | 5.87            | 7.43            | 8.46             | 12.52            | 21.75            | 66.13             | 78.14             | 83.71             | 86.12             |
| Neat VE      | 0.03            | 0.4             | 4.07             | 4.55             | 5.04             | 11.31             | 94.36             | 95.46             | 96.51             |
| PALF/VE      | 0.51            | 1.17            | 4.77             | 5.49             | 6.51             | 16.08             | 92.21             | 94.06             | 94.68             |
| PALF/KF/VE   | 0.6             | 0.78            | 3.41             | 4.3              | 5.99             | 14.68             | 94.27             | 95.42             | 95.63             |

The neat VE, PALF/VE and PALF/KF/VE hybrid composites losses its water at first stage (100-300 °C). As the temperature increase from 300 to 450 °C, these composites loss their weight significantly as degradation of hemicellulose occurred. Last but not least, at the final stage of thermal degradation, the degradation of lignin, ash and cellulose occurred [21], [22], [23]. In the case of composites, the thermal degradation of neat VE, PALF/VE and hybrid composites showed difference to each other. The thermal degradation of neat VE and PALF/VE and hybrid composites illustrated almost the same trend to each other while for the thermal degradation of PALF/VE, the trend differed. The neat VE showed better thermal stability because VE is one of the synthetic thermoset matrixes which expected to produce better thermal stability. The reinforcement of natural fibres with VE enhanced the performance of the fibre composites. It can be observed from the figure 1 that showed that the degradation of PALF/VE occurred faster compared to the neat VE and hybrid composites. From 100 °C to 300 °C, the PALF/KF/VE hybrid composites presented lower degradation compared to PALF/VE composites. This is due to the fact that the hybrid composites composed of PALF and KF rather than the composites that composed of PALF only. The hybrid composites will always show better performance than an individual fibre composite. The lower degradation that occurred explained that the hybrid composites has better thermal stability compared to PALF/VE composites. When the rapid degradation occurred from 300 °C to 450 °C, the graph still showed that hybrid composites possessed lower degradation compared to PALF/VE composites due to the components existed in the composites. However, as the temperature continued to increase, the residue of PALF/VE was higher than PALF/VE hybrid composites.
Figure 2 showed the DTG of PALF, KF, neat VE, PALF/VE and PALF/KF/VE hybrid composites. The graph presented the rate of percentage of weight loss as the temperature keeps increasing. From the figure 2, in comparing the fibres with the composites, the degradation of weight of PALF and KF occurred earlier than the composites. From 300 °C to 390 °C, PALF showed higher weight loss compared to KF. For the case of neat VE, PALF/VE and PALF/KF/VE hybrid composites, the rate of degradation of these composites showed higher compared to the PALF’s and KF’s. The rapid degradation started to occur from 300 °C to 390 °C. Among these three composites, neat VE and hybrid composites illustrated almost the same rate of degradation while the PALF/VE composites showed lower rate of degradation. After 450 °C, the rate of degradation of these composites started to show almost the same trend to each other. Based on the analysis that has been done, it can be concluded that the hybridization of PALF and KF improved the thermal stability of the composites. PALF/KF/VE hybrid composites showed better thermal stability compared to PALF/VE composites due to the extra component added to the composites which is KF.

The TGA and DTG graph clearly depicts the thermal stability of the PALF/KF/VE hybrid composites, revealing that the hybrid composite is a highly resistant material, even without hybridizing it with other synthetic materials. This statement is in strong agreement with other established findings, reporting that the hemicellulose is responsible for the thermal degradation of fibres, while the existence of lignin in the lignocellulose fibres improves the thermal stability [24].

4. Conclusion
From the TGA testing, it can be noticed that the degradation of PALF and KF occurred at 250-370 °C while the degradation of neat VE, PALF/VE and PALF/KF hybrid composites occurred at 300-450 °C due to the properties of VE. In the DTG graph, the rate of degradation of neat VE, PALF/VE and hybrid composites is higher compared to the PALF and KF and rapid degradation occurred between 300 to 390 °C. In comparing the PALF/VE and PALF/KF/VE hybrid composites, it shows that the hybridization of PALF and KF improved the thermal stability compared to PALF/VE composites. The thermal degradation of PALF and KF showed a good potential to be used as a reinforcement in the various application such as automotive, aerospace, structural and others.

Acknowledgement
This work is supported by UPM under HiCoE grant, 6369107 and Newton Fund, 6300896. The authors would like to express their gratitude and sincere appreciation to the Department of Aerospace Engineering, Faculty of Engineering, Universiti Putra Malaysia and Laboratory of Biocomposite Technology, Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia (HiCOE) for the close collaboration in this research.
References

[1] Shah A U M, Sultan M T H, Cardona F, Jawaid M, Talib A R A and Yidris N 2017 Thermal analysis of bamboo fibre and its composites BioRes. 12 2394-2406.

[2] Nor A F, Sultan M T H, Jawaid M, Azmi A M and Shah A U M 2019 Analysing impact properties of CNT filled bamboo/glass hybrid nanocomposites through drop-weight impact testing, UWPI and compression-after-impact behaviour Compos. Part B Eng. 168 166–174.

[3] Mohamed A R and Khalina A 2014 Mechanical and thermal properties of josapine pineapple leaf fiber (PALF) and PALF-reinforced vinyl ester composites Fiber Polym. 15 1035–1041.

[4] Siregar J P, Salit M S, Ab Rahman M Z and Mohd Dahlan K Z H 2011 Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) analysis of pineapple leaf fibre (PALF) reinforced high impact polystyrene (HIPS) composites Pertanika J. Sci. Technol. 19 161–170.

[5] Siakeng R, Jawaid M, Ariffin H and Sapuan S M 2018 Thermal properties of coir and pineapple leaf fibre reinforced polylactic acid hybrid composites IOP Conf. Ser. Mater. Sci. Eng. 368.

[6] Wan Nadirah W O, Jawaid M, Al Masri A A, Abdul Khalil H P S, Suhailly S S and Mohamed A R 2012 Cell wall morphology, chemical and thermal analysis of cultivated pineapple leaf fibres for industrial applications J. Polym. Environ. 20 404–411.

[7] Oliveira G et al. 2014 Effect of surface treatment on performance of pineapple leaf fibre-poly carbonate composites Polym. Test. 5 628–632.

[8] Salman S D, Leman Z, Sultan M T H, Ishak M R and Cardona F 2017 Effect of kenaf fibers on trauma penetration depth and ballistic impact resistance for laminated composites Text. Res. J. 87 2051-2065.

[9] Salman S D, Sharba M J, Leman Z, Sultan M T H, Ishak M R and Cardona F 2016 Tension-compression fatigue behavior of plain woven kenaf/kevlar hybrid composites BioResources 11 3575-3586.

[10] Salman S D, Leman Z, Sultan M T H, Ishak M R and Cardona F 2016 Influence of fiber content on mechanical and morphological properties of woven kenaf reinforced PVB film produced using a hot press technique Int. J. Polym. Sci. 2016 1-11

[11] Pang C, Shanks R A and Daver F 2015 Characterization of kenaf fiber composites prepared with tributyl citrate plasticized cellulose acetate Compos. Part A Appl. Sci. Manuf. 70 52–58.

[12] Aji I S, Zainudin E S, Khalina A, Sapuan S M and Khairul M D 2012 Thermal property determination of hybridized kenaf/PALF reinforced HDPE composite by thermogravimetric analysis J. Therm. Anal. Calorim. 109 893–900.

[13] Jofre-reche A, Su J C and Alia C 2018 Characterization of the structure of vinyl ester resin in a climate chamber under different conditions of degradation Polym. Degrad. And Stab. 153 88–99.

[14] Alhuthali A, Low I M and Dong C 2012 Characterisation of the water absorption, mechanical and thermal properties of recycled cellulose fibre reinforced vinyl-ester eco-nanocomposites Compos. Part B Eng. 43 2772–2781.

[15] Yusriah L and Sapuan S M 2018 Properties of betel nut husk reinforced vinyl ester composites. Elsevier Ltd.

[16] Jumaidin R, Sapuan S M, Jawaid M, Ishak M R and Sahari J 2017 Thermal, mechanical, and physical properties of seaweed/sugar palm fibre reinforced thermoplastic sugar palm Starch/Agar hybrid composites Int. J. Biol. Macromol. 97 606–615.

[17] Sanyang M L, Sapuan S M, Jawaid M, Ishak M R and Sahari J 2016 Effect of plasticizer type and concentration on physical properties of biodegradable films based on sugar palm (arenga pinnata) starch for food packaging J. Food Sci. Technol. 53 326–336.

[18] Asim M et al. 2018 Thermal, physical properties and flammability of silane treated kenaf/pineapple leaf fibres phenolic hybrid composites Compos. Struct. 202 1330-1338.

[19] Fung K L, Xing X S, Li R K Y, Tjong S C and Mai Y W 2003 An investigation on the processing of sisal fibre reinforced polypropylene composites Compos. Sci. Technol. 63, 1255–1258.
[20] El-Shekeil Y A, Sapuan S M, Zainudin E S and Khalina A 2011 Optimizing processing parameters and fiber size for kenaf fiber reinforced thermoplastic polyurethane composite Key Eng. Mater. 471–472, 297–302.

[21] Elkhaoulani A, Arrakhiz F Z, Benmoussa K, Bouhfid R and Qaiss A 2013 Mechanical and thermal properties of polymer composite based on natural fibers: Moroccan hemp fibers/polypropylene Mater. Des. 49 203–208.

[22] El-Shekeil Y A, Sapuan S M, Jawaid M and Al-Shuja’a O M 2014 Influence of fiber content on mechanical, morphological and thermal properties of kenaf fibers reinforced poly(vinyl chloride)/thermoplastic polyurethane poly-blend composites Mater. Des. 58, 130–135.

[23] Abdel Hakim A A, Nassar M and Sultan M 2011 Preparation and characterization of rigid polyurethane foam prepared from sugar-cane bagasse polyol Mater. Chem. Phys. 129, 301–307.

[24] Manfredi L B, Rodríguez E S, Wladyka-Przybylak M and Vázquez A 2006 Thermal degradation and fire resistance of unsaturated polyester, modified acrylic resins and their composites with natural fibres Polym. Degrad. Stab. 91 255–261.