Original Article

Thermal properties of treated sugar palm yarn/glass fiber reinforced unsaturated polyester hybrid composites

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ABSTRACT

In this work, the effects of alkaline treatment and hybridization on the thermal properties of sugar palm yarn/glass fiber were investigated. The sugar palm fiber was treated with 1% of sodium hydroxide (NaOH) solution for 1 h and the ratio of between matrix and reinforcement was 70/30 wt.% and 60/40 wt.%, respectively, while the ratio of reinforcement between sugar palm yarn fiber and glass fiber was 70/30 wt.%, 60/40 wt.% and 50/50 wt.%, respectively. The thermal properties of the hybrid composites were analyzed using a dynamic mechanical analyzer (DMA) and Thermogravimetric analysis (TGA). The storage modulus (\(E^\prime\)), loss modulus (\(E^\prime\prime\)) and damping factor (\(\tan \delta\)) were evaluated as a function of the alkaline treatment and different percentages of fiber loading. Also, the peak high was investigated for the tan \(\delta\) curves. In the glassy state area, a higher glass fiber loading hybridized with treated sugar palm fiber exhibited the highest storage modulus, loss modulus and the lowest damping factor. TGA demonstrated that the percentage of residue decreased as the glass fiber loading increased. Overall, the hybridization of glass fiber with treated sugar palm fiber enhances the thermal properties of the hybrid composites for structural applications.

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1. Introduction

The demand for environmental awareness, preserving nature and to be beneficial for societal economics has attracted the attention of many researchers to examine the potential usage of natural fibers [1]. The largest advantages of using natural fibers in composites are the lower cost of materials, their sustainability and density [2,3]. Natural fibers can cost as little as $0.50/kg, and can be grown in just a few months [4]. They are also easy to grow and have the potential to be a cash crop for local farmers. Natural fibers are also significantly lighter than glass, with a density of 1.15–1.50 g/cm\(^3\) versus 2.4 g/cm\(^3\) for E-glass [5]. As a result, an expansion of the usage of natural fibers to replace and reduce the dependency on the...
synthetic fibers has been seen in various applications, mainly in building, automotive parts, construction etc. [6–9]. There are numerous names for natural fibers as recognized around the world but the type which is the subject of this research is sugar palm fiber, or by its scientific name Arenga pinnata [10,11]. Generally, this fiber has similar properties as other natural fibers. Nevertheless, sugar palm fibers are found to have a high percentage of cellulose content that provides strength and stiffness that greatly validates its usage in various industrial applications and nanomaterial products [12,13].

Two major factors have been highlighted by previous researchers [14] currently limit the large scale production of natural fiber composites. First is the strength of natural fiber composites being very low compared to glass fiber composites. This is often a result of the incompatibility between the fiber and the resin matrix. The wettability of the fibers is greatly reduced compared to glass and this constitutes a challenge for scaled up production. However, when comparing specific strengths, natural fibers are not much less than glass fiber composites. The second factor in limiting large scale production of natural fiber composites is the hydrophilic properties of natural fibers. Natural fibers absorb water from the air and direct contact with the environment. This absorption deforms the surface of the composites by swelling and creating voids. The result of these deformations is lower strength and an increase in mass. Additionally, with water absorption rates as high as 20 wt. % the light weight advantage is often nullified.

The treatment of fibers is currently an area of research receiving significant attention. Chemical treatment such as alkali treatment, bleaching, acetylation, benzoylation, vinyl grafting, peroxide treatment and treatment with various coupling agents may improve the level of interfacial adhesion between the natural fiber and the matrix and enhance the mechanical properties of the fiber [15,16]. Comparing the chemical treatments listed, the alkali treatment is the most standard chemical treatment used which is a low cost and very effective surface modification and improves the mechanical properties of the natural fibers [17]. The alkali treatment removes a certain amount of hemicellulose, lignin, wax and oils that cover the external surface of the fiber cell wall. As a result, this gives the fiber rougher surfaces for better fiber interlocking for matrix penetration and greater contact area between the fiber and the matrix [18]. Alkali treatment also leads to a fibrillation effect after the removal of partial parts of the hemicellulose. Initially, untreated fibers are packed together as in a bundle. After the fiber treatment, the packed alignments of the fiber are broken into smaller groups (fibrillation effect) through the dissolution of hemicellulose and other amorphous parts. This facilitates the rearrangement of the fiber bundles into fibrils along the direction of tensile deformation, hence resulting in higher mechanical properties and better thermal stability [19,20].

By hybridization the behavior of hybrid composites appears to be simply a weighted sum of the individual components in which there is a more favorable balance between the advantages and disadvantages inherent in any composite material [21]. As a result, a balance of mechanical, thermal and cost reduction for engineering applications can be achieved [22]. In addition, through hybridization, it is possible to achieve a balance and more attractive performance properties with a reduced cost of the composites, which could not be obtained with a single kind of reinforcement. It is generally accepted that the properties of hybrid composites are controlled by factors such as the nature of the matrix, the nature of the chemical composition of the fibers, fiber length and the relative composition of the reinforcements, the fibre-matrix interface and the hybrid design. In other words, by careful selection of reinforcements and processing techniques, it is possible to engineer the material to better suit various practical requirements with economic benefits [23,24]. Among the hybrid composites that combine natural fibers with a glass fiber reinforced thermosetting polymer are sugar palm [25,26], kenaf [27–29], sisal [29–31], banana [32,33], jute [34–36], basalt [37,38], flax [29,39,40], coir [41–43], oil palm fiber empty fruit bunch (EFB) [44,45] and pineapple leaf fiber [46].

Several studies have revealed that through the hybridization of natural fiber and synthetic fiber this has improved the thermal properties of the composites. Researcher [47] developed a bamboo/glass fiber reinforced polyester hybrid composite that indicated that the storage modulus decreased with the addition of bamboo fiber. The damping factor was lowered when a greater loading of bamboo fiber was substituted. Also, studies of the dynamic mechanical properties of pineapple hybridized with glass fiber reinforced unsaturated polyester showed the storage modulus and damping factor were enhanced with increasing glass fiber loading [48]. Researcher [49] studied the effect of hybridization of coir/glass fiber reinforced unsaturated polyester composite which revealed that the storage modulus was greater and the damping factor reduced as compared to coir fiber reinforced unsaturated polyester composites. In this study, the thermal properties of the hybrid fibers which were treated by using an alkaline solution and different fiber reinforcement were highlighted. The method to produce composite samples was achieved by a simple fabrication method and the utilization of modified sugar palm yarn fiber which may attract further interest from researchers and industry.

2. Experimental

2.1. Materials

In this research, the main material used as reinforcement was sugar palm fiber which was purchased from Hafiz Adha Enterprise at Kampung Kuala Jempol, Negeri Sembilan, Malaysia. A woven E-glass fiber (210gsm) was supplied by Sky Tech Malaysia Sdn. Bhd. Unsaturated polyester resin (RTM grade, 40% styrene content, density of 1.025 g/cm³) was purchased from CCP Composites Resins Malaysia Sdn. Bhd, methyl ethyl ketone peroxide (MEKP) (Butanox-M50) as a curing initiator was purchased from AkzoNobel China and cobalt (II) naphthanate as a reaction accelerator was purchased from SIGMA ALDRICH (M) Sdn. Bhd. Sodium hydroxide (NaOH) pellets were purchased from MERCK (M) Sdn Bhd. Table 1 shows the mechanical properties of sugar palm fiber and unsaturated polyester composite.
Table 1 – The mechanical properties of sugar palm fiber and unsaturated polyester composites.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Untreated Sugar palm fiber</th>
<th>Treated sugar palm fiber</th>
<th>Unsaturated polyester</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>1.292</td>
<td>1.193</td>
<td>1.212</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>156.96</td>
<td>332.28</td>
<td>44.40</td>
</tr>
<tr>
<td>Tensile modulus (GPa)</td>
<td>4.96</td>
<td>17.27</td>
<td>3.54</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>7.98</td>
<td>5.3</td>
<td>2.15</td>
</tr>
<tr>
<td>Reference</td>
<td>[1]</td>
<td></td>
<td>[2]</td>
</tr>
</tbody>
</table>

Fig. 1 – (a) Sugar palm tree, (b) a bundle of sugar palm fibers, (c) combed sugar palm fibers, (d) soaked sugar palm fibers in 1% of NaOH solution, (e) yarning process and (f) yarn sugar palm fiber [52,53].

Table 2 – Chemical compositions of untreated and treated sugar palm fiber.

<table>
<thead>
<tr>
<th>Chemical constituents</th>
<th>Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Untreated fiber</td>
</tr>
<tr>
<td>Cellulose</td>
<td>47.74</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>5.96</td>
</tr>
<tr>
<td>Lignin</td>
<td>37.68</td>
</tr>
</tbody>
</table>

2.2. Alkaline treatment

The bundles of sugar palm fiber were soaked (Fig. 1d) in a 1% NaOH solution or 0.25 M for 1 h. The treated sugar palm fibers were then washed several times with distilled water until pH 7 was obtained. Subsequently, the fibers were dried in an oven at 60 °C for 24 h. Furthermore, the chemical compositions (Table 2) of the untreated and treated sugar palm fiber were analysed according to the following standard methods: ethyl-benzene extractive (TAPPI T 204 CM-97), lignin (TAPPI T 222 OM-98), holocellulose [51] and alfa-cellulose (TAPPI T 203 CM-99).

2.3. Yarning process of sugar palm fiber

Firstly, the raw sugar palm fiber in bundle form (Fig. 1b) was combed (Fig. 1c) in order to align the fibers and remove a portion of the shortest fibers. For each piece of 2500 tex of sugar palm yarn fiber, the sugar palm fiber was constantly weighed using a weighing balance and aligned at 0.5 g/0.2 m. The tex of the sugar palm yarn fiber was measured using Eq. 1 in accordance with ASTM D1907.

\[
\text{Lineardensity(Tex) = w × K / l}
\]  

(1)

where, w is an average weight of yarn (g), K is a constant value (1000 m/g) for tex and l is the length of the yarn in meters (m) unit. Then, a manual hand spinning machine from SDL ATLAS (Fig. 1e) with a speed of 1000 rpm/pc of sugar palm fiber was used to make a yarn fiber with a Z-twist direction (Fig. 1f).

2.4. Preparation of composites

A mould was prepared by spraying with silicon mould release agent to avoid any sticking with the composites. As per
the results obtained from a previous study, the mechanical properties increased linearly from 10 to 40 wt.% [50]. For the fabrication of hybrid composites, the ratio between the matrix and the reinforcement was selected at 70/30 wt.% and 60/40 wt.%, respectively. The ratio of reinforcement between the sugar palm yarn fiber and glass fiber was selected at 70/30 wt.%, 60/40 wt.% and 50/50 wt.%, respectively (Table 3). A certain ratio of glass fiber was placed inside the mould, following a planing of all ratios of sugar palm fiber and finally the rest of the glass fiber ratio. On each placement, a small amount of mixed unsaturated polyester resin was poured over the fiber in order to improve the absorption of resin and to minimize the formation of voids and finally compressed using a hot press machine at 70 °C and 80 bar for 30 min [20]. Fig. 2 shows the schematic diagram of layout segmentation and reinforcement layout.

2.5. Characterizations

DMA Q800 from TA Instruments was used for the evaluation of the dynamic mechanical thermal behaviors of the composites. Rectangular specimens having size 60 mm × 10 mm × 3 mm were used for the DMA under three-point bending mode at an oscillation frequency of 1 Hz. The temperature was ramped from 30 to 150 °C under a controlled sinusoidal strain with a heating rate of 5 °C/min. TGA was performed via a TGA Q500 from TA Instruments and was conducted under ramp mode from 30 to 600 °C under a nitrogen atmosphere at a flow rate of 50 mL/min. The heating rate utilized was 20 °C/min. A sample of 5–10 mg of the materials was heated in the sample pan. The temperature was raised. The determination of the percentage of weight loss versus temperature was analyzed from the TGA curve.

3. Results and discussion

3.1. Dynamic mechanical analysis properties

3.1.1. Storage modulus

The storage modulus curve provides information regarding stiffness, fiber/matrix adhesion and the rigidity of the composites. It demonstrates that the storage modulus of both untreated and treated fiber reinforced composites is higher than that of the neat unsaturated polyester composites (2130 MPa) at a temperature of 30 °C, which is due to the effect of reinforcement of the polymer matrix by the sugar palm yarn fiber and the glass fiber. From Fig. 3, the storage modulus has three areas such as rigid, glass transition and a rubbery area. In the first area, the material is tightly packed and stiff in nature because of the rigid polymeric chain. The second area shows that the storage modulus decreases when the temperature rises above the glass transition temperature (Tg) due to the increase in mobility of the polymeric chain [54]. Polymeric chain movement decreases the fiber-matrix adhesion as well as the stiffness of the composites. For the third rubbery plateau area, the higher temperature accelerates the
material mobility and there no significant change in storage modulus is observed. It is clear in Fig. 3 where the increase in temperature caused a decline in the stiffness and rigidity of the hybrid composites. Moreover, the overlapping of the storage modulus curves in the rubber plateau area has proven that at higher temperature there is no significant change in storage modulus due to hybridization or an increase of the glass fiber ratio and alkaline treatment.

Variation in storage modulus occurs due to the effect of incorporation of glass fiber and effect of alkaline treatment.

Fig. 3 – Storage modulus of (a) neat unsaturated polyester composites, (b) untreated and (c) treated sugar palm yarn fiber hybrid composites.
of the sugar palm yarn fiber. It is clear that the storage values of the treated fiber composites are higher compared to the untreated fiber composites. Overall, the storage modulus increases with temperature which is prominent with the increase in glass fiber ratio. In the case of the optimized glass fiber ratio, it is found that the storage modulus for the 40 wt.% (8400 MPa) of fiber with a 50/50 wt.% fiber ratio is 22% higher than for the 30 wt.% (6700 MPa) of fiber with a 50/50 wt.% fiber ratio. This is because of the additional percentage ratio of stiffer and higher modulus glass fibers (70 GPa) rather than sugar palm fibers (4.96–17.27 GPa) in the composite system [55,56]. Interestingly from the analysis, it is evident that replacing the glass fiber ratio with sugar palm yarn fiber by a balance ratio (50/50 wt.%) increased the storage modulus or in other words, improved the stiffness of the composites. This could be attributed to the fact that an effective layering design of balance (50/50 wt.%) between the outer layer of the skin of the composite is governed by the woven glass fiber and the sugar palm yarn fiber acted as a core or tendon for the composite structure. In addition, an optimized matrix acts as a binder of the fibers, transferring the cycling load to the fibers and providing rigidity and shape to the structure. This contributes to the improvement of the dynamic mechanical properties of the composites under the influence of temperature.

Furthermore, the incorporation of 40 wt.% treated sugar palm yarn with a 50/50 wt.% fiber ratio showed a 3% increase in the storage modulus from 8200 to 8450 MPa. This indicates that the incorporation of treated sugar palm yarn fibers imparts greater stiffness to the composite material whereby a similar trend is observed in the static flexural modulus in a previous study [50]. It was reported by Keusch et al. [55] that the storage modulus is directly proportional to the interfacial adhesion. An increase in the storage modulus from the treated fiber composites was exhibited by the better compatibility and balance ratio of the pack arrangement between the sugar palm yarn fiber and glass fiber with the matrix. This is due to better compatibility leading to better interfacial bonding and an effective stress transfer between the fiber and the matrix that takes place in the composite systems during the cyclic load application [57]. Improved interfacial bonding due to the hydrophobicity of the glass fiber with the matrix also contributed to the improvement in the storage modulus. In addition, the improvement in the compatibility is also due to the reduction in the hydrophilicity of the sugar palm fiber after the alkaline treatment by the removal of 16% of hemicellulose content (Table 2). The reduction in the hydrophilic nature makes the fiber more compatible by improving the adhesion with the hydrophobic glass fiber and unsaturated polyester matrix [58].

### 3.1.3. Loss modulus

Loss modulus (E) is a measure of the energy dissipated or lost as heat per cycle of sinusoidal deformation, when different systems are compared at the same strain deformation. It is in fact the viscous response of the material that is more sensitive to the molecular motions of the polymer chain. Fig. 4 illustrates the loss modulus of the hybrid sugar palm yarn/glass fiber reinforced unsaturated polyester composites as a function of temperature. It can be seen from the figure that the loss modulus peak value increases with an increase of fiber load-

from 30 to 40 wt.%, an increasing ratio of glass fiber from 70/30 to 50/50 wt.% and also on the effect after the alkaline treatment of the sugar palm fiber. Overall, the loss modulus increases and then decreases after passing the maximum point of the peak (glass transition area) as a function of temperature for all the composite samples. The 40 wt.% treated sugar palm yarn with a 50/50 wt.% fiber ratio achieved the highest loss modulus of about 700 MPa and 1184 MPa at around the glassy area and at the glass transition area, respectively.

The shifting of Tg towards a higher temperature is correlated with the reduced movement of the unsaturated polyester chains, which indicates enhanced interfacial adhesion between the reinforcement with the matrix due to the effect of the alkaline treatment. It has been shown that the Tg from the loss modulus increases from 61.20 to 73.84 °C. According to researcher [59] the high values of Tg could be associated with the decrease in mobility of the matrix chain caused by the addition of fiber and indicates a good interaction between the fiber and matrix, which is observed from the results obtained by the increase in fiber loading from 30 to 40 wt.% of fiber reinforcement. Moreover, the highest loss modulus achieved as the fiber loading increased caused an increase in the internal friction and improved the energy dissipation [60]. The results that are obtained are also in line with the findings of other researchers [61]. Similar to the storage modulus curve after the glass transition area, all curves are overlapping with each other which indicates that at higher temperature there is no significant change in loss modulus due to the increasing fiber loading, glass fiber ratio and alkaline treatment.

### 3.1.3. Tan delta (tan δ)

Tan delta or the damping factor is the ratio between the loss modulus and the storage modulus. Tan δ can be correlated to the impact toughness of the material. The Tg of a composite is the peak of either the storage modulus or the tan δ curve. However, the peak maximum in the tan δ plot is preferred to calculate Tg because the apex of the peak is more definite than the uncertain placement of tangents [62]. Compared to other plots, it represents a longer-range cooperative molecular motion which is consistent with rubbery flow, permanent deformation or both depending on the molecular structure. Fig. 5 delineates the tan δ for hybrid sugar palm yarn/glass fiber reinforced unsaturated polyester composites. The presence of the fiber reinforcement can be detected by the height of the tan δ curve. The higher the fiber loading, the lower the value of tan δ, as may be noted comparing values for the neat unsaturated polyester composites (Fig. 3a) and the 40 wt.% treated sugar palm yarn with 50/50 wt.% fiber ratio (0.9678–0.3550).

Table 4 shows the summary peak of the tan δ (damping factor) value and Tg obtained from Fig. 5 of different fiber loadings and the effect of an alkaline treatment. The tan δ is the minimum for the treated fiber hybrid composites to indicate that the efficiency of the stress transfer between the matrix fibers is increased and the fiber-matrix interfacial bonding is increased. The lower tan δ value in the graph indicates good interfacial adhesion between the reinforcement and the matrix [63]. The composites with a higher damping factor exhibited lower fiber/matrix adhesion [47]. From Table 4 it is clear that 40 wt.% treated sugar palm yarn with
50/50 wt.% fiber ratio showed a lower tan δ value (0.3555) which is attributed to the higher load carrying capacity of sugar palm yarn and glass fiber. In addition, the increases in the damping factor as the glass fiber ratio increases are attributed to the matrix and the interface degradation of the material system. The synthetic materials used in the research are glass fiber and unsaturated polyester. The glass fiber is regarded as an elastic material, which can store energy and avoid energy dissipation, while unsaturated polyester is considered to be a visco-elastic material as it has both viscosity and elasticity. When the unsaturated polyester is deformed, one part of the energy may be stored in the form of heat energy. It is reasonable to anticipate that the increase in the glass fiber ratio with a sufficient and effective loading of unsaturated polyester is caused by the energy dissipation of the matrix.

Researcher [57] found that the material which possesses a lower damping value associated with Tg has shown better load bearing properties due to improved interfacial adhesion. It has been reported that improved interfacial adhesion restricts the intermolecular movement of the polymeric chain which leads to a reduction in the damping factor. This improvement agrees with the previous study that examined the mechanical properties of the morphology of hybrid composites of 40 wt.% treated sugar palm yarn/glass fiber [53]. A similar report by [64], indi-

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Fig. 4 – Loss modulus of (a) untreated and (b) treated sugar palm yarn fiber hybrid composites.
Fig. 5 – Tan δ of (a) untreated and (b) treated sugar palm yarn fiber hybrid composites.

<table>
<thead>
<tr>
<th>Designation of fibers</th>
<th>Fiber ratio (wt.%)</th>
<th>Peak height from Tan δ</th>
<th>Tg from Tan δ (°C)</th>
<th>Tg from loss modulus (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat unsaturated polyester</td>
<td>–</td>
<td>0.9678</td>
<td>88.75</td>
<td>60.35</td>
</tr>
<tr>
<td>30 wt.% -</td>
<td>70/30</td>
<td>0.5378</td>
<td>73.20</td>
<td>61.20</td>
</tr>
<tr>
<td></td>
<td>60/40</td>
<td>0.5492</td>
<td>71.50</td>
<td>62.60</td>
</tr>
<tr>
<td>Untreated</td>
<td>50/50</td>
<td>0.4080</td>
<td>72.50</td>
<td>64.43</td>
</tr>
<tr>
<td>40 wt.% -</td>
<td>70/30</td>
<td>0.4375</td>
<td>81.50</td>
<td>72.92</td>
</tr>
<tr>
<td></td>
<td>60/40</td>
<td>0.4255</td>
<td>78.30</td>
<td>71.83</td>
</tr>
<tr>
<td>Untreated</td>
<td>50/50</td>
<td>0.3922</td>
<td>79.50</td>
<td>72.02</td>
</tr>
<tr>
<td>30 wt.% -</td>
<td>70/30</td>
<td>0.3900</td>
<td>73.00</td>
<td>61.27</td>
</tr>
<tr>
<td></td>
<td>60/40</td>
<td>0.4000</td>
<td>71.50</td>
<td>62.73</td>
</tr>
<tr>
<td>Treated</td>
<td>50/50</td>
<td>0.3680</td>
<td>73.52</td>
<td>70.10</td>
</tr>
<tr>
<td>40 wt.% -</td>
<td>70/30</td>
<td>0.4235</td>
<td>82.20</td>
<td>73.84</td>
</tr>
<tr>
<td></td>
<td>60/40</td>
<td>0.3680</td>
<td>81.57</td>
<td>73.00</td>
</tr>
<tr>
<td>Treated</td>
<td>50/50</td>
<td>0.3550</td>
<td>82.50</td>
<td>73.11</td>
</tr>
</tbody>
</table>
icates that the incorporation of stiff fibers reduces the tan δ peak by restricting the movement of the polymer molecules and gives greater damping resistance in the composite system. The T_g of the composites ranges from 71.50 to 82.50 °C. It is observed that there is a shift of T_g values to a higher temperature as a result of the impact of high fiber loading that restricts the chain mobility of the unsaturated polyester and also the effect of the alkaline treatment that improved the interfacial adhesion of sugar palm yarn fiber with glass fiber and the matrix. However, from Fig. 3(a), the T_g of the neat unsaturated polyester composites is 88.75 °C, which is higher than the T_g of the reinforced fiber composites. This is due to the impact of the reduced thermal stability of materials which is contributed by the sugar palm yarn fiber. However, upon the increase of the glass fiber ratio and the effect of the alkaline treatment, the T_g increased from 73.20 to 82.50 °C which resulted in interfacial adhesion and increased the thermal stability of the composites.

3.2. Thermogravimetric analysis properties

The determination of the thermal property characterization of the polymeric materials is crucial because it determines the thermal stability of the materials in the temperature range over which the materials can be used to the point of noticeable degradation [65]. From a previous study [50], a major degradation step is observed for neat unsaturated polyester composites by statistical chain rupture, in which styrene is the primary product in the range of 360 to 400 °C. Almost similar results have also been reported by other researchers [66], where the peak showing the temperature of the maximum degradation rate appears at around 350–400 °C for neat unsaturated polyester composites (Aropol FS 6912). From the result obtained in Table 5, it may be concluded that the addition of sugar palm fibers to the composite decreases the unsaturated polyester degradation onset that occurs with temperature, and the maximum thermal decomposition. This arises due to some portions of the unsaturated polyester matrix being replaced with the less thermally stable sugar palm fibers, which then reduces the thermal stability of the polymer matrix system as a whole [67]. The tremendous thermal stability decreases upon an increase in the sugar palm fiber that is also contributed to by the fiber-fiber interaction. This particular fiber-fiber interaction is strongest at higher sugar palm fibers loadings than that of the fiber-unsaturated polyester interaction. This may further reduce the decomposition temperature due to non-limited mobility [68].

The degradation temperature for natural fiber-based composites regularly occurs between the decomposition temperature of the reinforcement and that of the polymer matrix [69]. There is a small but noticeable step in the first stage of degradation temperature at around 80–130 °C from both untreated and treated sugar palm fiber composites due to the presence of water in the sugar palm fibers. The addition of glass fiber to the composite increases the onset temperature. This is due to the high thermal stability of the glass fiber, which resists degradation and absorbs heat in the matrix and prolongs the degradation. These factors affect the onset of decomposition and the percentage of residues, and improves the resistance to heat [70]. Fig. 6 displays the schematic thermal degradation pathway of hybrid sugar palm/glass fiber/unsaturated polyester composites.

At a 50/50 wt.% ratio of 30 wt.% and 40 wt.% from the untreated and treated sugar palm fiber, a small decrease in structural destabilization can be observed. This could be attributed to the balanced ratio between the sugar palm fibers that are less thermally stable and the glass fibers which tend to be more thermally stable in the composite structures. The effect of the balance ratio caused the sugar palm fiber, which is less thermally stable, to absorb most of the heat earlier upon the temperature increase compared to the glass fiber. From Table 5 at up to 600 °C the residues gradually decrease because the composites become more thermally stable and resistant to heat due to the increase in glass fiber loadings from ratios of 30 wt.%, 40 wt.% and 50 wt.%. Degradation of composites with a higher level of glass fiber would be a result of the higher silica content above 400 °C and the residual composite residue of about 20% due to silica determined at the end of the heating. It has also been proven that the residue left is higher for the 40 wt.% glass fiber content compared to different fiber loadings between the glass and sugar palm fibers.

The higher onset temperature for the 70/30 wt.% ratio at 30 wt.% and 40 wt.% of fiber loading as compared to the other loadings may be due to the contribution of the fiber-fiber interaction of the sugar palm fibers. This particular fiber-fiber interaction is stronger at higher sugar palm fiber loadings than that of the fiber-matrix interaction. This may further reduce the decomposition temperature due to non-limited mobility [68]. Furthermore, the improvement in thermal stability at the onset decomposition temperature clearly showed that the decomposition improved at each of 10%, 25% and 50% of weight loss (Table 5). The slight shift of temperature to higher values indicated that the structural properties of the hybrid composites are able to shield the structure from the absorption of heat at the low temperature of decomposition as the glass fiber ratio increased. This occurred due to some portions of the matrix being replaced with highly thermally stable glass fiber and some ratio of less thermally stable sugar palm fibers, which then increase the thermal stability of the polymer matrix system as a whole [67]. However, the thermal stability of both untreated and treated reinforced fiber composites still shows below the onset and T10% of the degradation temperature. In addition, the T25% degradation temperature for both the untreated and treated fiber reinforced composites is higher than the neat unsaturated polyester composites. This is due to the chain rupture of the styrene structure that maintains the thermal characteristic of unsaturated polyester in the range of 360 to 400 °C. Hence, above that temperature, the thermal stability of the composites is influenced by the compositions of cellulose, lignin and the silica that remains in the composite systems.

In addition, referring to Table 5, it would appear that the treated sugar palm fiber hybrid composites display higher thermal stability values than the untreated sugar palm fiber hybrid composites. As the alkaline treatment removes the wax on the fiber surface, the alkaline treatment also causes a reduction of hemicellulose and lignin content. Since the cellulose is highly crystalline and relatively more thermally stable than hemicellulose (amorphous), the improvement of the crystalline structure might cause an addition of hydro-
Table 5 – The characteristic temperatures of the thermal properties of neat unsaturated polyester composites [1], untreated and treated sugar palm hybrid composites.

<table>
<thead>
<tr>
<th>Designation of fibers</th>
<th>Fiber ratio (wt.%)</th>
<th>$T_{\text{onset}}$ (°C)</th>
<th>$T_{\text{max}}$ (°C)</th>
<th>$T_{10%}$ (°C)</th>
<th>$T_{25%}$ (°C)</th>
<th>$T_{50%}$ (°C)</th>
<th>Residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat unsaturated polyester</td>
<td>-</td>
<td>340.53</td>
<td>380.42</td>
<td>282.90</td>
<td>312.53</td>
<td>360.94</td>
<td>0.42</td>
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Fig. 6 – Thermal degradation pathway of hybrid sugar palm/glass fiber/unsaturated polyester composites.

gen binding instead of hydroxyl structure after the alkaline treatment by the removal of the hydroxyl group. From that, better thermal energy is distributed over many bonds through improved hydrogen bonding [71].

As the ordered region increases, the crystalline structure of cellulose increases the mobility of the cellulose chains and this could strain and strengthen the existing hydrogen bonding, thus increasing stability [59]. Furthermore, the improvement in the thermal stability of the treated sugar palm hybrid composites compared to the untreated sugar palm hybrid composites can also be due to the improvement of the hydrophobicity of sugar palm, which enhances the possibility to adhere to the glass fiber and the matrix.

4. Conclusions

The thermal properties of the treated hybrid composite derived from sugar palm fiber, glass fiber and unsaturated polyester matrix have been successfully evaluated.

1 The storage modulus and loss modulus are higher for the 40 wt.% treated sugar palm yarn with a 50/50 wt.% fiber ratio compared to other hybrid composites. The 50/50 wt.% fiber ratio of the 40 wt.% treated sugar palm yarn fiber showing good fiber interactions resulting in compatibility between
fiber and matrix that reduces the damping factor of the composites. 
2 The DMA depicted the highest $T_g$ of 82.50°C that is also recorded by the 40 wt.% treated sugar palm yarn with a 50/50 wt.% fiber ratio composite. 
3 The result obtained reveals that the thermal stability, char residue and decomposition temperature improved as the sugar palm and glass fiber ratio increased up to 50/50 for both 30 wt.% and 40 wt.% of fiber loading.

**Conflict of interest**

The authors declare no conflicts of interest.

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**References**


