Effect of Silica Bodies on Oil Palm Fibre-Polyethylene Composites

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The influence of natural protrusion, also known as silica bodies, was studied in relationship to sliding resistance reinforcement in an oil palm fibre-polyethylene composites. Experimental work on oil palm fibres-LLDPE composites (using fibres with and without protrusions) was conducted, which included x-ray microtomography (µ-CT scan), scanning electron microscopy, and degree of grafting analyses. A finite element micromechanical model was then developed using information from the experimental results to simulate fibre pull-out from the matrix. Microscopic observation after mechanical tests of the composites showed crater marks due to silica bodies in contact with the matrix, whereas fibres were uniformly distributed inside the matrix from the µ-CT scan. Likewise, the degree of grafting analysis showed a positive influence of silica bodies as an additional reinforcement to the composites. These were further supported by the modelling results of fibre pull-out, which showed a clear difference between models with and without silica bodies.

Keywords: Composites; Reinforcement; Modelling; Simulation

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INTRODUCTION

Utilisation of natural fibres in composites applications offers the advantages of being biodegradable, low cost, renewable, sustainable, as well as having low density (Wei and McDonald 2016). However, the main challenge of commercialising these natural fibres as filler in composites is their lack of filler-matrix compatibility (González-López *et al*. 2018). For example, the hydrophobic nature of polymer and hydrophilic nature of natural fibres leads to inferior filler-matrix interfacial behaviour (Sahari *et al*. 2013). Efforts were made to modify the fibre surface to improve the chemical affinity between polymer and natural fibres, such as incorporating particles of ceramic minerals on the polymeric matrices reinforced with fibres (Silva *et al*. 2012). On the other hand, it is interesting to note that oil palm fibres surface have naturally contained protrusions, also known as silica bodies, which are partly embedded on the outer surface of the fibres (Omar *et al*. 2016). These natural protrusions are a result from silica depositions from soil to the plant leaves and stem, which provide mechanical strength, rigidity, and shield from pest and microbial attack (Neethirajan *et al*. 2009). Omar *et al*. (2014, 2016) reported no significant effect of the protrusions towards fibres integrity from both simple representative and micromechanics finite element modelling results. However, in composites applications involving the fibres as filler, it is not clear from any experimental work the influence of

silica bodies towards providing sliding resistance to the filler-matrix interface. Hanipah *et al.* (2016) for example showed that silica bodies provided reinforcement by restricting sliding between filler-matrix through the finite element model. Nascimento *et al.* (2012) also discussed that silica bodies improved the fibre-matrix interface by preventing sliding (for piassava fibres). In contrast, Karuppuchamy *et al.* (2015) reported that silica bodies need to be removed *via* pre-treatment to increase fibre-matrix interface. In response, Xiang *et al*. (2015) showed that pre-treatment will alter/reduce the mechanical strength of the fibres by weakening the cellulose-hemicellulose-lignin natural interaction within the fibres. Therefore, we believe that the best fibres to be used for composites are those with silica bodies still intact. However, the fibres need to be chemically modified to enhance the filler-matrix contact, therefore improving filler-matrix sliding/damage. This will be the aim of this work, which is a continuation from the work by Omar *et al.* (2016) and Hanipah *et al.* (2016) on oil palm fibres and their composites, respectively. Experimental work on the oil palm fibres-LLDPE composites is conducted, which includes x-ray microtomography (µ-CT scan), scanning electron microscopy (SEM), and degree of grafting analysis. This is then followed with the development of a micromechanical finite element model using information from microscopy and the µ-CT scan to simulate fibre pull-out from matrix.

EXPERIMENTAL

Materials and Methods

The filler used was oil palm mesocarp fibres (OPMF) obtained from Besout Palm Oil Mill (Sungkai, Perak, Malaysia), which were kept in a controlled environmental of -20 °C. The fibres were washed to remove oil residues and dried at 105 °C for 24 h until moisture content reached below 5% (Xiang *et al.* 2015). Regarding the treated sample used in degree of grafting (DOG) analysis, OPMF were treated with 500 mL of sodium hydroxide solution (NaOH) at constant concentrations of 5% (w/v) of fibre to (NaOH) ratio of 1:10 (g/mL), as described by Xiang *et al.* (2015). OPMF were soaked in NaOH solution for 30 min at room temperature and then autoclaved at 121°C, 15 psi for 5 min. Note that Xiang *et al.* (2015) reported removal of silica bodies using this treatment method.

Linear low-density polyethylene (LLDPE) (COTENE ™ 3901, density 0.905 g/cm^3, melt flow index 4.0 (g/10 min); melting temperature 160 °C) was used as the matrix. Itaconic anhydride (Sigma Aldrich) with a melting temperature of 68 °C was selected as the reactive monomer, whereas di-tert-butyl peroxide (Fluka, Sigma-Aldrich) density 0.794 g/mL was used as an initiator. In these experiments, the monomer and initiator were kept constant to 5 wt% of the total polymer and 2 wt% of the monomer, respectively (Mohamad-Jani *et al.* 2007). The fibres were added at 10 wt% of increment until 60 wt%. The reaction was carried out in the Brabender internal mixer using a constant temperature of 170 °C and a rotor blade speed 30 rpm at 10 min. Moulded dumbbell shaped samples with 3 mm thickness were prepared at 170 °C and 100 kg/cm^3 pressure according to ASTM D638 standard. Chemical titration of the polymer was performed to measure the degree of grafting, following the work by Verbeek and Hanipah (2009). The morphology of composites was analysed using a scanning electron microscope (SEM) (model E-1010, Hitachi, Japan) at acceleration voltage ranges of 5 kV. Internal structure and volume of the composites were obtained *via* µ-CT scanner (Skyscan 1172, Kontich, Belgium). The total height of the sample was approximately 7.50 mm, which was scanned at a spatial resolution of 1.5 µm.

The finite element model was then developed to simulate fibre pull-out. Firstly, boundary coordinates of the fibre µ-CT scan image were obtained using Matlab written codes, and coordinates were then imported into Abaqus software through Python-written script to enable regeneration of the slice geometry. The 2D geometry generated was then extruded to 100 µm height to generate a 3D geometry, where from the results in µ-CT analysis by Omar *et al.* (2016), changes of cell wall area fraction across this height were minimal. One-hundred thirty three protrusions representing silica bodies (spheres with a diameter of 12 µm) were added randomly on the outer surface of the virtual fibres (partly embedded, strong silica bodies cohesion contact with the fibres and 11% silica bodies area fraction). To improve convergence during finite element processing, both fibres and silica bodies were combined as an entity. The µ-CT finite element model images are shown in Fig. 1a.

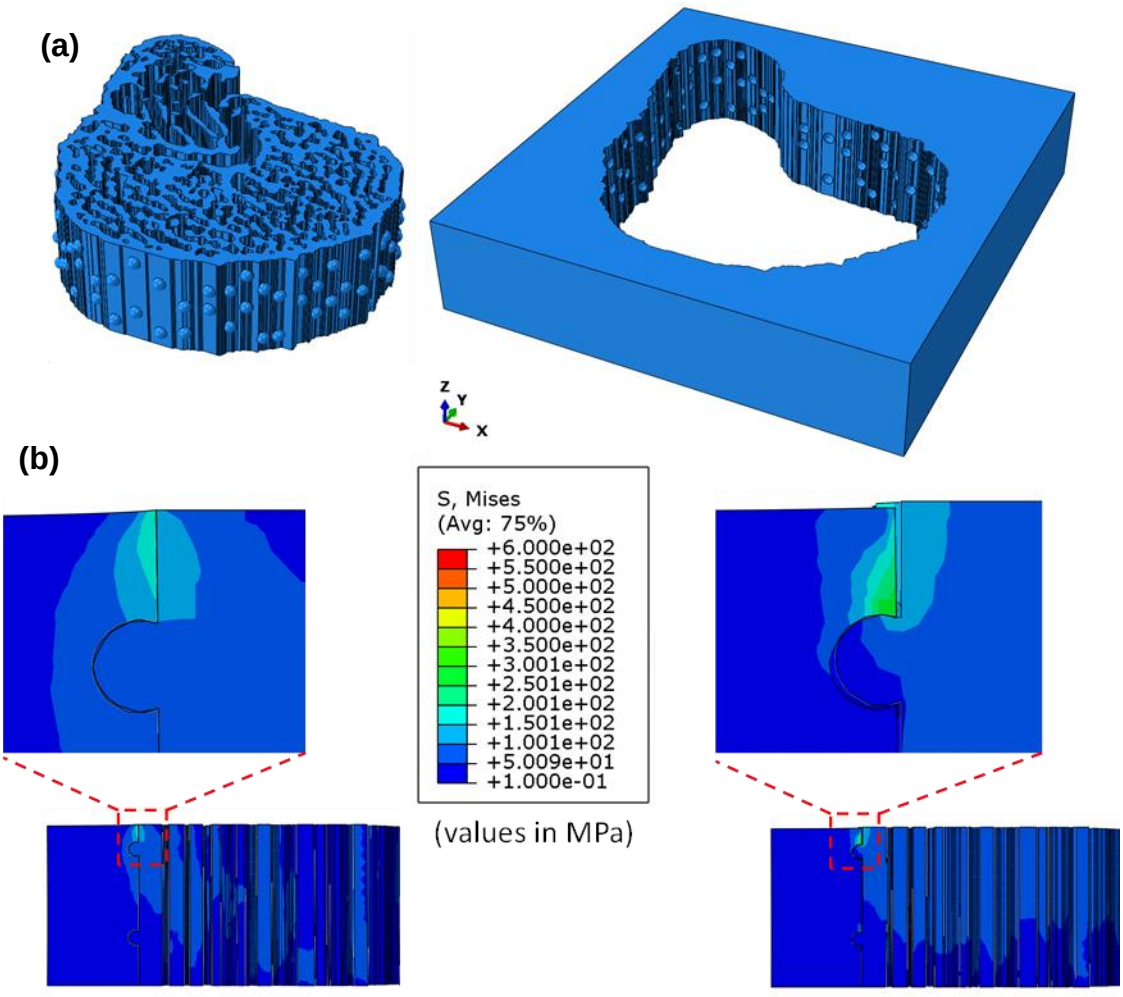

Fig. 1. (a) Micromechanics model development; (b) Comparison between model with strong and weak fibre-matrix interface.

The outer boundary geometry of the fibre was then used as the basis to develop the matrix to ensure both the fibre and matrix matched each other for contact interaction model later, as shown in Fig. 1(a). The meshes were refined until the results converged to less than 5% difference. For the boundary conditions, the base of the model were fixed in all directions (*x*, *y*, and *z* axes in Fig. 1(a)), and deformation was applied in the *z* (tension)

direction on the top surface of the fibre (at constant speed of 1 µm/s). The fibre-matrix interaction was set to be either tie-constraint (strong contact) or frictionless (weak contact). The tie-constraint interaction refers to strong contact between fibre and matrix without any slippage allowed. In contrast, slippage was allowed freely for the frictionless interaction but no element interpenetration was allowed. The van der Waals hyperelastic and Prony series viscoelastic model was used for the fibre, similar to those reported by Hanipah *et al*. (2016), with the parameters shown in Table 1. A lower shear modulus (μ= 1 GPa) was set for the matrix to improve convergence of the model.

Table 1. Material Properties used for Oil Palm Fibres

Materials constant	Value
μ	2.2 (fibre) 1.0 (matrix)
a	1.6 (fibre and matrix)
λ_m	20 (fibre and matrix)
g_i (at ξ_i = 0.1, 1, 10, 100, 1000, and ∞ s)	0.6, 0.08, 0.06, 0.05, 0.005, 0.205 (fibre)

RESULTS AND DISCUSSION

Microscopic observation after tensile tests of the composites from SEM is shown in Fig. 2, which shows crater marks on the matrix in contact with the filler. Occurrence of silica bodies on the fibre itself provide additional reinforcement to the sliding of filler-matrix during deformation.

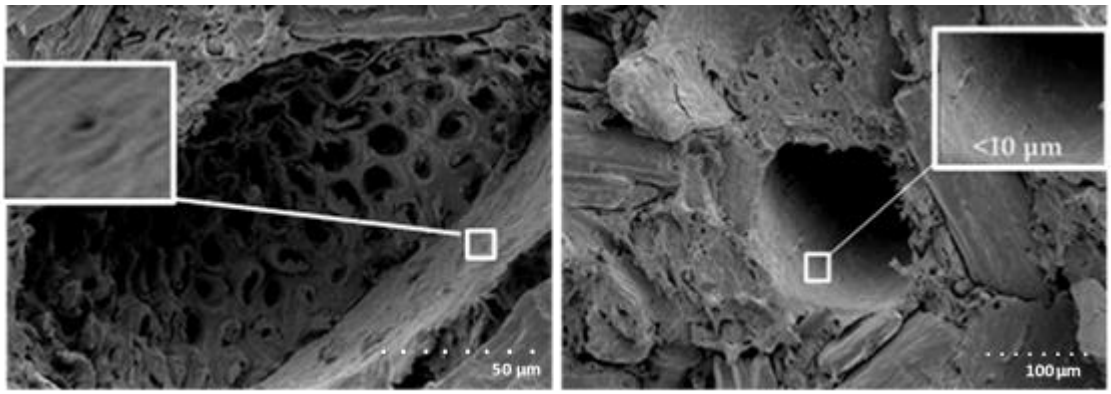

Fig. 2. SEM images showing craters formed on matrix after the tensile test

X-ray microtomography or µ-CT scan was then performed to observe fibre distribution in the matrix, which is a non-destructive method. A sample with 7.5 mm x 8.0 mm x 3.0 mm (height x length x wide) was used, where the test was conducted at the lowest spatial resolution of 1.5 µm. Overall, image slices of the sample at different heights in Fig. 3(a)-(d) shows random distribution of fibre within the matrix (polymer).

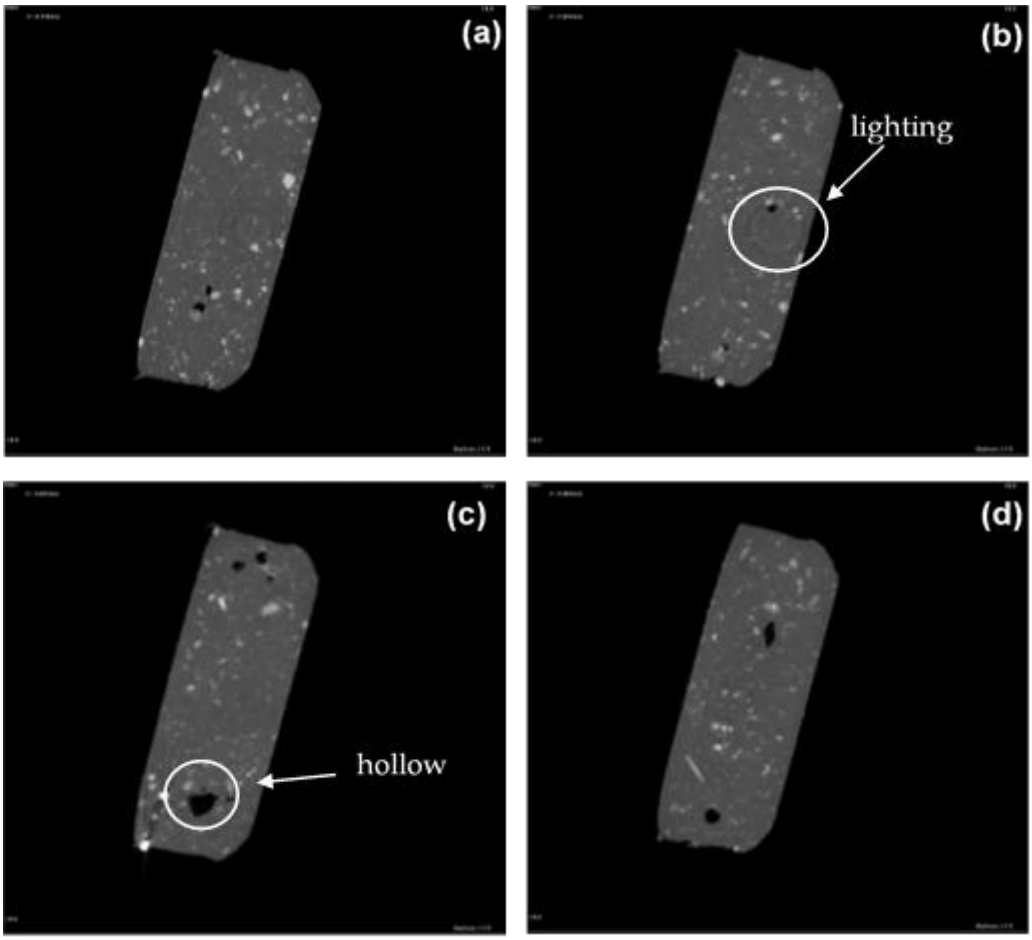

Fig. 3. Images of µ-CTslices with 10 wt% OPMF loading at (a) 0 mm height, (b) 2.5 mm height, (c) 5.0 mm height and (d) 7.5 mm height

The images obtained from different height of the sample can be used to analyse the area fraction distribution of the composites across different height. To conduct this, the images was converted into black and white images (binary), before the difference between black and white area was analysed using ImageJ (Rasband 2012). The results using 100 images at different height of the sample are shown in Fig. 4, which shows area fraction ranges of 9-12% (average of ~10%). On the other hand, radial lighting shadow is observed in Fig. 3(a) and 3(b), which can be due inconsistence shape of the sample causing inconsistent scanning. It is worth noting that a flat square or round shape of sample is preferred for the µ-CT scan. Likewise, Fig. 3(c) shows hollow (void) within the sample due to processing of the composites, which highlighted the advantage µ-CT scan to investigate irregularities during processing of composites. It should be noted that due to the limitation of the µ-CT scanner, clear images of the filler (fibre) interface cannot be obtained, even though the test was conducted at the lowest spatial resolution (1.5 µm). It is suggested that a more advanced scanner such as x-ray nanotomography (Diaz *et al.* 2011) to be used in the future investigate the interface of the fibre-matrix.

Degree of grafting (DOG) test was conducted to measure the efficiency of grafting reaction between anhydride, LLDPE and OPMF through chemical titration process. Higher DOG values will lead to a better mechanical properties as it indicates formation of new bonds between anhydride, LLDPE and OPMF (Wei and McDonald 2016).

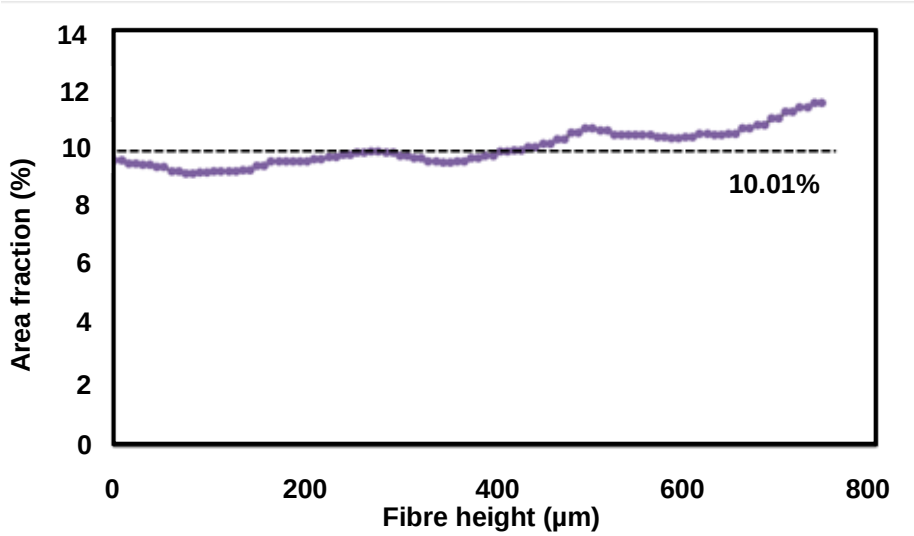

Fig. 4. Area fraction of fibre loading at difference sample heights

Figure 5(a) shows DOG of untreated and treated OPMF. It can be seen that the highest DOG for both treated and untreated samples were recorded at 30 wt% of OPMF. The analyses showed the presence of hydroxyl (OH) bonds between both fibre and silica bodies with the anhydrate filled matrix, suggesting that strong contact can be obtained by retaining the silica bodies. Modelling results of fibre pull-out simulations is shown in Fig. 1(b). In particular, when frictionless contact interaction was defined between the filler-matrix interfaces, the model with silica bodies is shown to restrict filler sliding (higher stress at the proximity of silica body-matrix area). This is consistent to the work by Nascimento *et al.* (2012), who reported that protrusion (silica bodies) was found to be responsible for the reinforcement of the piassava composites. Figure 5(b) shows a clear difference for the composite model results with and without silica bodies (frictionless contact was defined between the interface in this case). If strong contact is defined between filler and matrix, only then both models (with and without silica bodies) show similar force-displacement results. It should be noted that parallel experimental work (*i.e.* tensile tests) of the fibres (with and without silica bodies) need to be conducted to investigate the effect of silica bodies towards stress-strain results of the composites. However, one of the issue with parallel experimental work of oil palm fibres is the large variation of stress-strain results (as highlighted by Hanipah *et al.* (2017)), which can be due to multiple failures and complexility of the fibres (see recent work by Ahmad *et al.* (2019)). This hampers the effort to obtain a clear difference between fibres with and without silica bodies. Thus, it is suggested that the best approach to investigate the difference is through finite element modeling, as well as microscopic observation, as reported here. In addition, the fibres used in the future should be obtained directly from the plantation farm rather than from a processing mill, since the fibres obtained from the mill went through milling, washing, and drying processes, which changed the structural behaviour of the oil palm fibres (causing variation of the mechanical behaviour of the fibres). Further, the chemical treatment performed to remove silica bodies can also influence the structural behaviour of the fibres, as highlighted by Xiang *et al*. (2015). Consistent fibres can assist in obtaining uniform and

precise composites, which can be used in high value added application such as 3D printing filament.

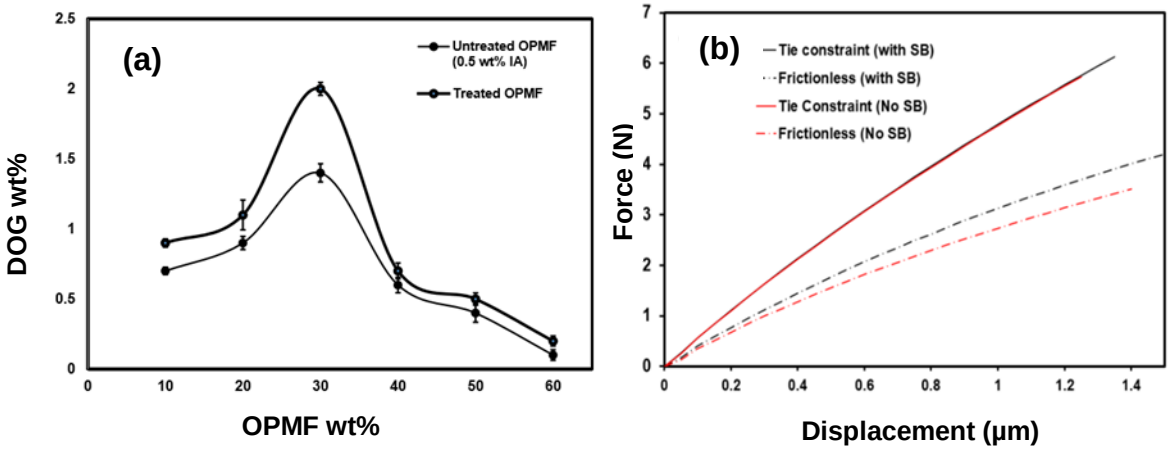

Fig. 5. (a) Degree of grafting of treated and untreated OPMF, (b) Modelling results (SB refers to silica bodies)

CONCLUSIONS

1. Microscopy, x-ray microtomography, and degree of grafting of oil palm composites showed a positive influence of the natural protrusion (silica bodies) towards resistance to sliding and towards structural integrity of oil palm fibres composites.
2. The experimental results were further supported by a micromechanics model consisting of a 'virtual' fibre containing silica bodies in contact with a matrix to simulate fibre pull-out resistance.

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