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Pretreatment Studies and Characterization of Bio-Degradable and 3D-Printable Filaments from Coconut Waste

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ABSTRACT

Natural fiber based filaments are economic, environmental friendly and sustainable which enable them to be applied in the production of novel composite materials. This research aims to produce 3D printed filaments composed of Poly lactic acid (PLA) reinforced with 5 wt%, 10 wt% and 15wt% of coconut fiber (CF) and coconut shell powder (CSP). These fillers were alkaline and silane treated in order to enhance the thermal properties. These fillers were characterized by FTIR, SEM and TGA analysis. The SEM images show that there are structural changes in the fillers after successive treatments. TGA results shows enhancement of thermal stability for CF by 10 °C whereas decreased by 10 °C for CSP. These fillers are melt blended with PLA as a polymer matrix and extruded as filaments. The filament which is reinforced with CSP holds good for 3D printing whereas, the filaments reinforced with CF clogged during the process of 3D printing due to the large diameter of the filaments.

Keywords: 3D printed natural fiber composite, bio-degradable composite, coconut waste, natural fibers

1. INTRODUCTION

Production of filaments made of natural fibers and its composites for Additive Manufacturing (AM) is becoming a trend. This is because; filaments made of natural fiber composites are cost effective, sustainable and cause less environmental impacts. PLA, Polyethylene terephthalate, Acrylonitrile butadiene styrene, Polyvinyl alcohol, Polyamide and Polyhydroxyalkanoates are some of the commonly used polymers in the field of AM. Out of all, PLA is the most preferred and trending polymer because of its bio-degradability [1]. Some of the natural fibers that are used as fillers along with PLA in AM filaments are fibers from wood, bamboo, hemp, harakeke, flax, sugarcane and pine [2]. In the modern era, natural fibers and its composites seeks greater attention almost in all applications as they have wide range of advantages [3]. Plant based natural fibers such as coconut fibers are abundantly available and considered as agricultural waste in Malaysia [4]. Additionally, these fibers have low thermal conductivity and low bulk density to produce cost-effective and lightweight composite products. However, the major drawback of these composites is the presence of strong polarized hydroxyl groups in the natural fibers which affects the formation of strong interfacial bonding with the non-polar polymer matrix [5]. These phenomena lead to the poor interfacial adhesion between polymer matrix and natural fibers which can be overcome by surface modification [6]. Alkaline treatment is targeted to separate the lignin content in the fiber, thus more cellulose can be exposed for binding process as it helps to enhance the interfacial adhesion in the composite.

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However, Silane coupling agent has bi-functional groups which can respectively react with the two phases thereby forming a bridge in between polar fibers and non-polar polymer matrix [7]. Thus, in this research, the fillers were subjected to alkaline and silane treatments successively which are melt blended with PLA as a polymer matrix and then extruded as filaments. Feasibility test for 3D printing was conducted using the produced filaments.

2. MATERIAL AND METHODS

2.1 Materials

Poly (lactic Acid) pellets are purchased from Nature Works Corporation. Coconut fibers (CF) and Coconut Shells are obtained from local markets. 3 glycidoxypropyltrimethoxysilane (GPTMS) is purchased from Sigma Aldrich Sdn Bhd. Sodium hydroxide (NaOH) pellets; ethanol (95% purity) and acetic acid (98% purity) were purchased from Merck Milipore Sdn Bhd.

2.2 Surface Modification of Fillers

2.2.1 Sample Preparation

The coconut shells were broken into smaller pieces using a hammer and later ball milled into coconut shell powder (CSP) and sieved to less than 500 μm . While, the coconut husk was subjected to sun drying for 24 hours and the strands from the coconut husk are shredded manually. The shells and coconut fibers were cleaned with distilled water and sun dried for a day followed by oven drying for 2 hours at 60 $^{\circ}\text{C}$ to minimise the moisture content. Coconut fibers were cut to the length of $\sim 1 - 3$ mm.

2.2.2 Pre-Treatment

The fillers are then subjected to alkaline treatment to reduce the lignin and hemicellulose content from the surface of the fibers. The fillers were soaked in 5 wt% NaOH solution for 6 hours [8]. Later, the fibers were washed with distilled water till pH of 7 was obtained. The fillers were dried in oven for 48 hours at 60 $^{\circ}\text{C}$. A Half batch of fillers from the alkaline treatment was subjected to GPTMS coupling agent treatment. 3 wt% of GPTMS coupling agent was hydrolysed in 80:20 w/w (water: ethanol) solution. Before the addition of the GPTMS, the water ethanol mixture was adjusted to pH 3.5 using 1M acetic acid solution. The soaking time was fixed for an hour followed by oven drying for 48 hours at 80 $^{\circ}\text{C}$. The fillers were thus coated with the GPTMS solution.

2.3 Melt Blending

The first stage of the composite preparation was the internal mixing of the CSP and CF fibers with PLA as a polymer matrix. The equipment utilized was Brabender Plastograph® EC. Mixing conditions were 180 $^{\circ}\text{C}$ with the rotor speed of 50 rpm as reported by [7]. The solid PLA resins were added into the internal mixer and melted for 1 minute followed by the fillers which provides undisturbed mixing for 8 minutes. During this initial mixing process, the hopper and weigh ram was slotted in back for continuous force. At the last 2 minutes of mixing, the hopper and the weigh ram were detached to give space for the bubbles to escape. It was highlighted that fiber moisture can significantly affect the fiber dispersion and also have an effect on bubble formation during the mixing [9]. Therefore, the fillers were dried 2 hours prior to mixing. A total of 19 different samples were prepared using internal mixer. The sample summary is shown in Table 1 below:

Note: Accepted manuscripts are articles that have been peer-reviewed and accepted for publication by the Editorial Board. These articles have not yet been copyedited and/or formatted in the journal house style.

Table 1 Composite Lump obtained from Internal Mixer.

Code	Treatment	Batch
Pure PLA	None	PLA
5CF95PLA	None	5wt% Untreated PLA reinforced coconut fiber composite (UPCFC)
5CF95PLA	Alkali	5wt% Alkaline treated PCFC
5CF95PLA	Alkali+ GPTMS	5wt% GPTMS treated PCFC
10CF90PLA	None	10wt% Untreated PCFC
10CF90PLA	Alkali	10wt% Alkaline treated PCFC
10CF90PLA	Alkali+ GPTMS	10wt% GPTMS treated PCFC
15CF85PLA	None	15wt% Untreated PCFC
15CF85PLA	Alkali	15wt% Alkaline treated PCFC
15CF85PLA	Alkali+ GPTMS	15wt% GPTMS treated PCFC
5CSP95PLA	None	5wt% Untreated PCSPC
5CSP95PLA	Alkali	5wt% Alkaline treated PCSPC
5CSP95PLA	Alkali + GPTMS	5wt% GPTMS treated PCSPC
10CSP90PLA	None	10wt% Untreated PCSPC
10CSP90PLA	Alkali	10wt% Alkaline treated PCSPC
10CSP90PLA	Alkali + GPTMS	10wt% GPTMS treated PCSPC
15CSP85PLA	None	15wt% Untreated PCSPC
15CSP85PLA	Alkali	15wt% Alkaline treated PCSPC
15CSP85PLA	Alkali + GPTMS	15wt% GPTMS treated PCSPC

2.4 Hot Pressing and Crushing

The collected composite lumps were then hot pressed into 1 mm thickness composite sheets. The temperature used was similar to the mixing process. The composite was placed inside a stainless steel mould and preheated for 7 minutes. Then, the melted composite was completely compressed for 1 minute by 5 tons of hydraulic pressure. At last, the mould was cooled for 5 minutes and the composite sheet was removed from the mould as shown in Figure 1(a). The sheets are then manually crushed into smaller pieces as shown in Figure 1(b).

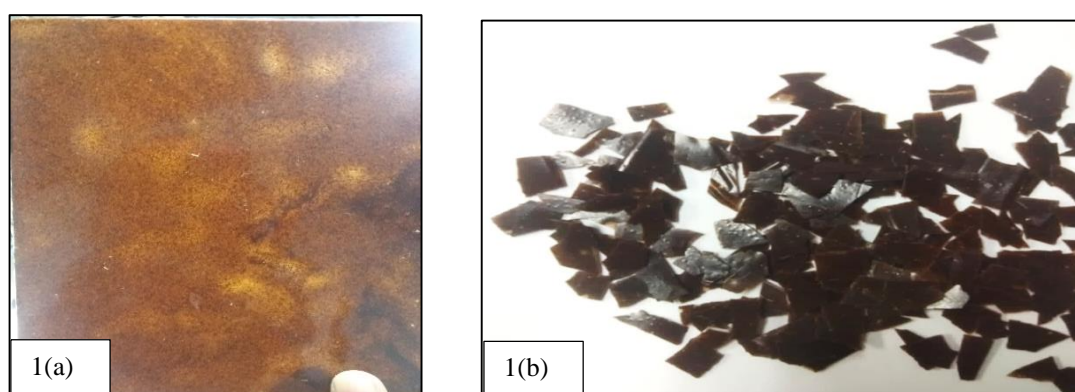


Figure .1(a) Hot pressed composite sheet (b) Composite crushed into smaller pieces.

2.5 Extrusion of Bio-Degradable Filaments

The crushed composites were then dried in the oven for 1 hour at 90 °C to remove any moisture present during manual cutting and also to avoid any bubble formation during extrusion. The single screw extruder used was the Wellzoom Desktop Extruder. Pure PLA was added into the hopper before the addition of the prepared composite in order to stabilize and to get consistent extrusion. Thus, the crushed composite pellets were added gradually into the hopper for the extrusion. The main setting for this extrusion is the barrel temperature and extrusion die temperature together with the screw rotating speed. The extrusion temperature has experimented in the range of 170 °C to 190 °C based on the pure PLA melting temperature [10]. Trials along with the extrusion temperature and speed are tabulated in Table 2.

Table 2 Trial Procedure for the Single Screw Extrusion

Trial	Single Screw Extruder Part		Screw Rotating Speed, RPM
	Barrel Temperature	Extrusion Die Temperature	
1	175°C	180°C	25-30
2	180°C	185°C	25-30
3	185°C	190°C	25-30

2.6 Characterization Techniques

2.6.1 Chemical Analysis

FTIR analysis was carried out using Perking Elmer ATR Spectrum 100. The attenuated total reflectance (ATR) method was used. Each sample underwent 16 scans in the frequency range 4000-550 cm^{-1} at a resolution of 4 cm^{-1} . This FTIR analysis helps to understand the changes before and after the pre-treatments. A background check is necessary to eliminate the effects of air and other possible disturbances. A small amount of the sample around 1 mg to 2 mg is enough to cover the crystal in the FTIR. The samples then pressed with a nob for further analysis.

2.6.2 Morphological Examination

The untreated, alkaline and GPTMS treated CSP and CF fibers were examined by SEC Desktop Mini-SEM SNE-3000M from SEC Co. Ltd, Suwon, Korea. The samples were sputter coated with a thin layer of gold and analysed at an accelerating voltage of 30 kV with a magnification factor ranging from 100 x to 3000 x.

2.6.3 Thermal Analysis

Thermal analysis was carried out using a Pyris Diamond TGA 8000 from PerkinElmer. The samples (5±1 mg) were performed for thermal scanning from 30 °C to 600 °C at the heating rate of 10°C/min under a nitrogen atmosphere. The nitrogen flow rate was 20.0 ml/min.

3. RESULTS AND DISCUSSION

3.1 Chemical Analysis

The FTIR spectra of untreated CSP, CF (UCSP, UCF) and alkaline treated CSP, CF (ATCSP, ATCF) are shown in Figure 2, 3 and the silane treated CSP and CF (STCSP, STCF) are shown in Figure 4, 5.

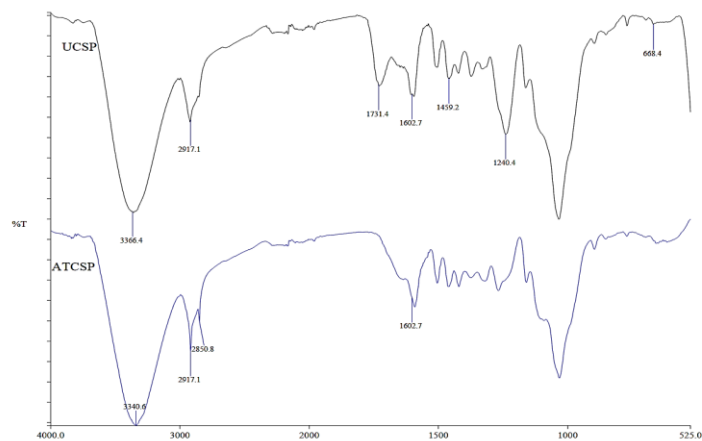


Figure 2. (Left) FTIR Spectra of UCSP, 5wt% alkaline solution (NaOH) treated CSP (ATCSP).

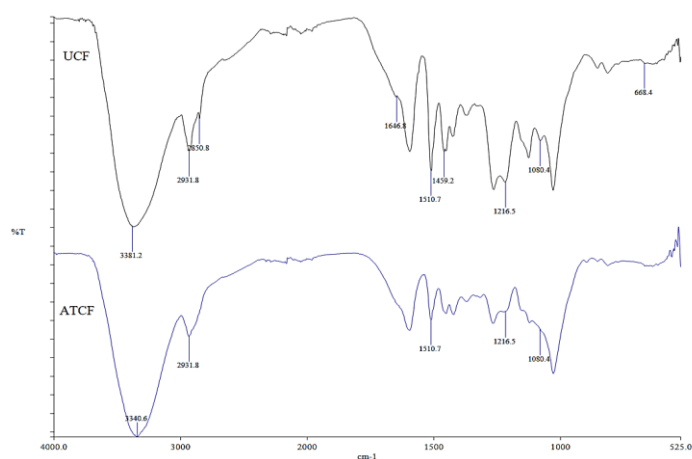


Figure 3. (Right) FTIR Spectra of UCF, 5wt% alkaline solution (NaOH) treated CF (ATCF).

The broad absorption band ($3100\text{--}3500\text{ cm}^{-1}$) reflects the presence of alcoholic groups (O-H stretching vibrations) [11]. The peaks in the range of $2900\text{--}3000\text{ cm}^{-1}$ attribute to the C-H stretching vibrations from chlorophylls. The carbonyl peak (C=O stretching vibration) which attributes to the hemicellulose content was present in both UCSP and UCF fiber at 1731.4 cm^{-1} and 1646.5 cm^{-1} . The lignin peak in UCSP was present at range of 1595.3 to 1602.7 cm^{-1} and 1236.7 cm^{-1} while in UCF was at 1510.7 cm^{-1} and 1216.5 cm^{-1} . The COOH bending peaks at 668.4 cm^{-1} and CH_2 symmetric bending peaks at 1461.1 cm^{-1} were present in both the fillers. These differences among the untreated fibers prove the different characteristics of the fibers. The alkaline treatment on CSP and CF was targeted to remove waxes, hemicellulose, pectin and lignin from the fiber surface to improve the surface roughness. Lignin and hemicellulose removal results in increasing the numbers of reactive hydroxyl groups on the surface for better chemical bonding during reinforcement in polymer matrices. From Figure 2 and Figure 3, the peak at 1731.4 cm^{-1} is attributed to the C=O stretching vibration of the acetyl and ester group of hemicellulose or waxes which was removed after alkaline treatment. In addition, the peak intensity at 1236.7 cm^{-1} and 1204.4 cm^{-1} for UCSP and UCF have reduced after the alkaline treatment. This peak attributed to C=O stretch of the acetyl group of lignin and the reduction proves the removal of the lignin from the surface yet the small shift in peak concludes very minute amount of lignin present after the treatment process [12].

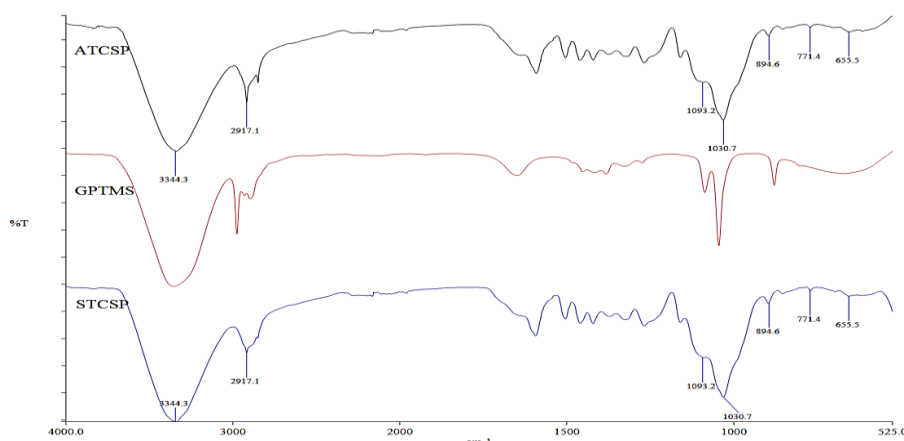


Figure 4. FTIR Spectra of ATCSP, 3wt% silane solution (GPTMS), STCSP

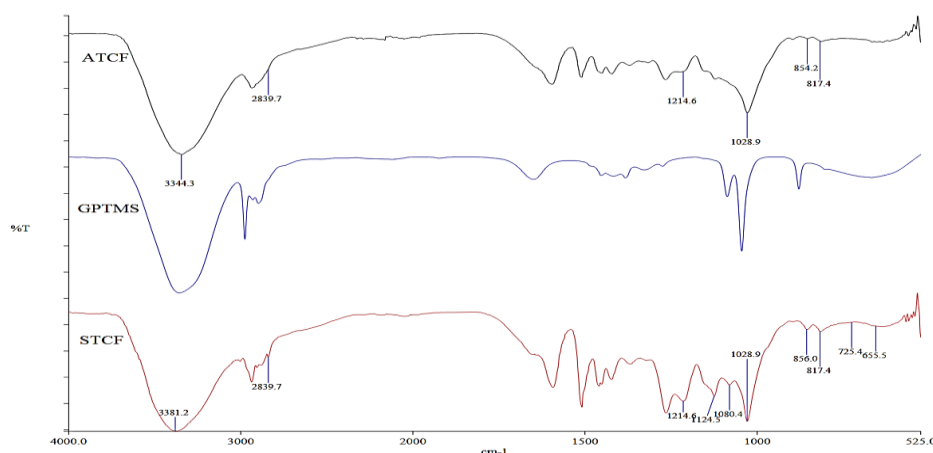


Figure 5. (Right) FTIR Spectra of UCF, 3wt% silane solution (3-GPTMS), STCF.

The FTIR spectra shown in Figure 4 and 5, shows the effect of 3-GPTMS treatment on ATCSP and ATCF fiber. The peak at 3344.3 cm^{-1} in ATCF and 3340.6 cm^{-1} in ATCSP attributes to the OH group of the fibers. 3-GPTMS treatment roots the increase in the intensity for both the fibers and the peak shift from 3344.3 cm^{-1} to 3377.5 cm^{-1} for STCF. This shift of the peak the evidences the interaction between the hydroxyl group of fibers and the polar group of 3-GPTMS. The band range from 1000 to 1200 cm^{-1} attributes to Si-O-Si or Si-O-Cellulose stretching vibrations of methoxy groups directly bonded to silicon and the cellulose. These linkages were found in Figure 4 at the peak 1093.2 cm^{-1} for STCSP and in Figure 5 at the peak 1124.5 cm^{-1} and 1080.4 cm^{-1} for STCF. The peak at 1124.5 cm^{-1} for STCF is more obvious because of the Si-O-Si bond overlapped with the C-O stretching from the cellulose structure of CF. The intensity of peak at 894.6 cm^{-1} for STCSP and 856.0 cm^{-1} for STCF increased. These peeks attributed to the stretching vibration of Si-OH, silanol groups produced in the silane hydrolysis. The peak at 771.4 cm^{-1} for STCSP attributes the existence of symmetric stretching of Si-C bond of 3-GPTMS. There should be a peak appearance at 700 cm^{-1} for STCF due to the asymmetric Si-O-C bending in 3-GPTMS.

3.2 Morphological Examination

It was observed that the outer layer of both the UCSP and UCF showed rigid structure [Figure 6(a,d)]. On the contrary, alkaline and silane treated surfaces [Figure 6(b,c,e,f)] demonstrated

smooth and porous structure. The untreated surfaces showed flaky appearance which could be due to the presence of impurities such as waxes and lignin which was subsequently reduced after the NaOH and Silane treatment.

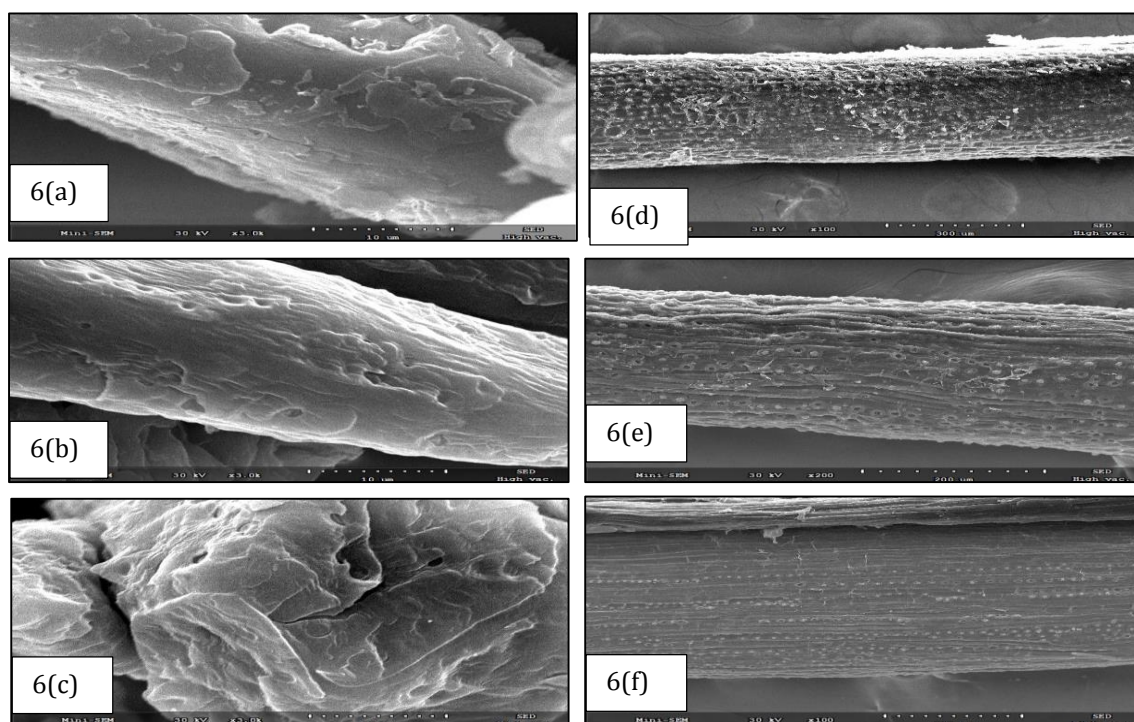


Figure 6. SEM images of fillers (a) Untreated CSP (UCSP) (b) Alkaline treated CSP (ATCSP), (c) Silane Treated CSP (STCSP), (d) Untreated CF (UCF), (e) Alkaline treated CF (ATCF), (f) Silane Treated CF (STCF)

3.3 Thermal Analysis of Fillers

The TGA results for untreated, alkaline treated, silane treated CSP and CF are shown in Figure 7 and 8. The decomposition profile of CSP and CF fibers takes place in three distinct stages. The first stage of the fiber weight loss about 6-9% occurred from 30°C to 190°C. The initial weight loss at the peak of 80 °C (CSP) and 100 °C (CF) attributes to the moisture loss. The second and last stages were observed at 190 to 360 °C and 360 to 500 °C. This distinct stages approximately similar as previously reported for coconut pith [13].

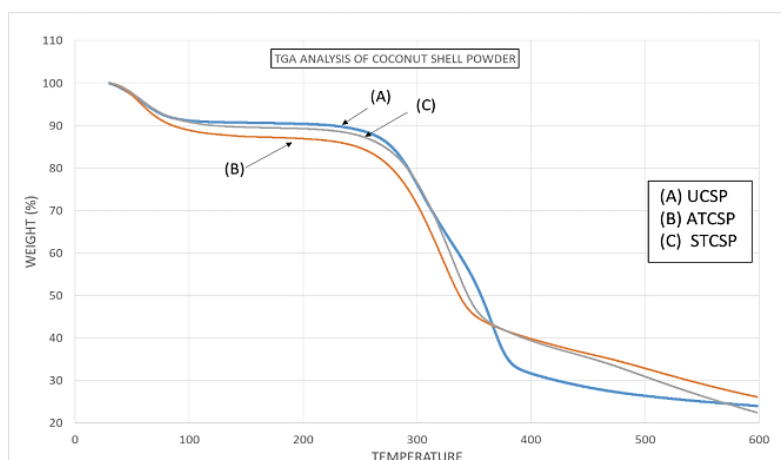


Figure 7. (Left) TGA curves of coconut shell powder

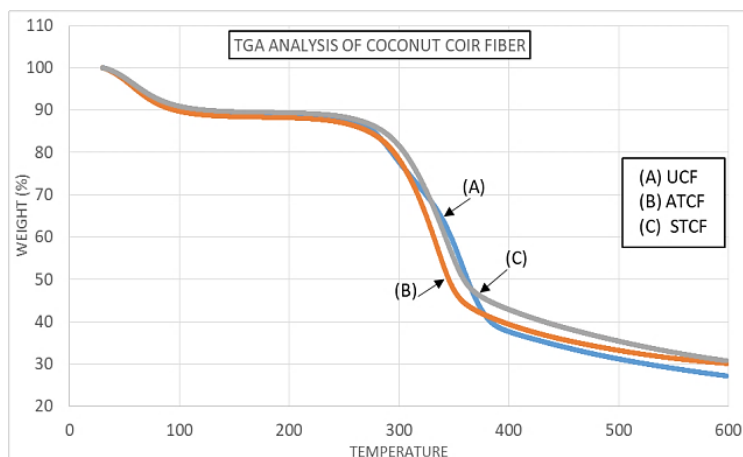


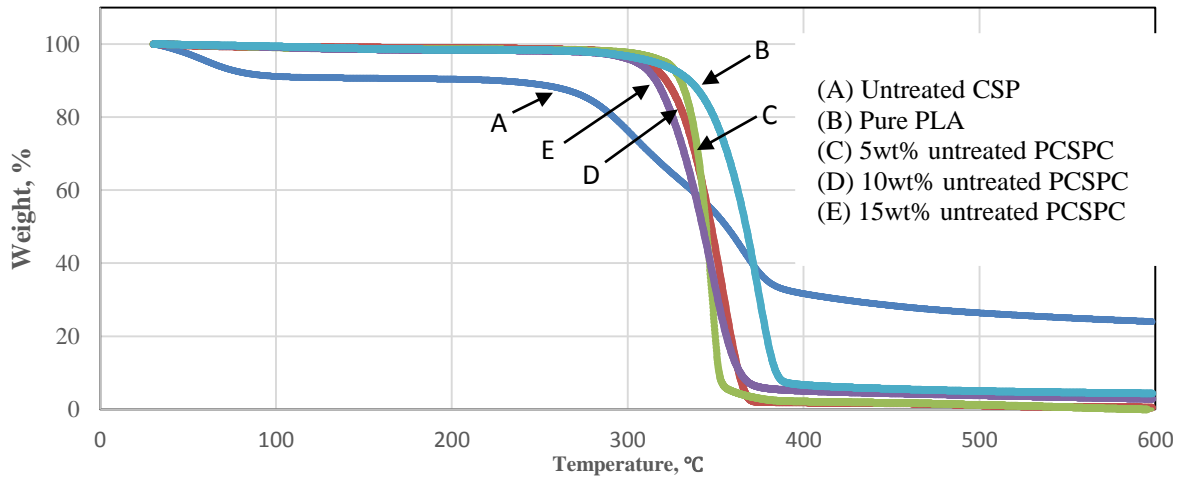
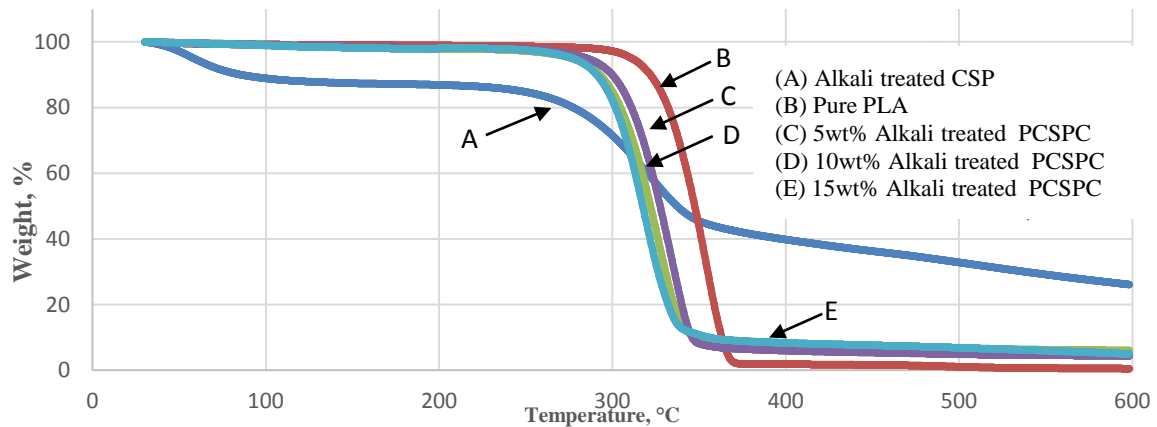
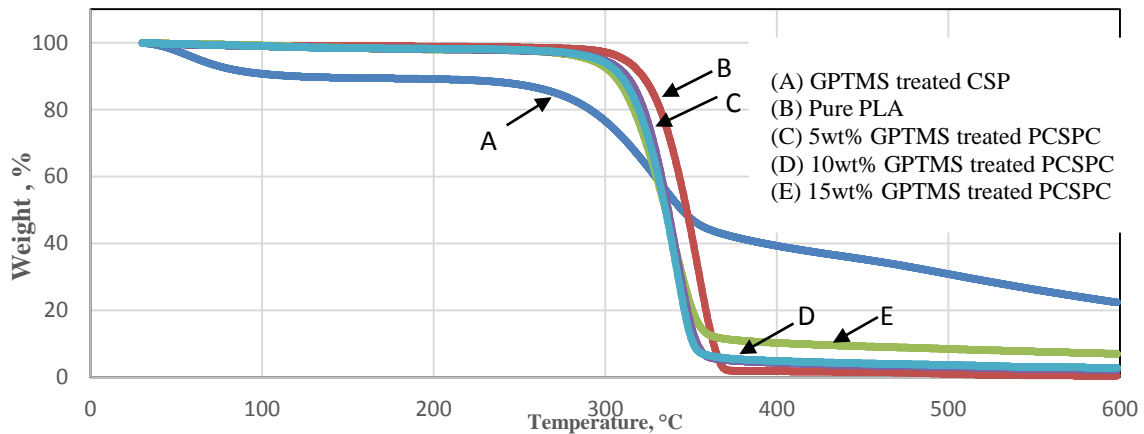
Figure 8. (Right) TGA curves of coconut fiber.

The second stage involves the degradation of hemicellulose, lignin, and cellulose in the fibers. For UCSP the weight loss before 235°C was slow while the rapid weight loss occurred from 250°C to 360°C. The degradation peak was found to be at 285°C with 55% mass loss. Alkaline treated CSP, ATCSP showed a smooth decline in the second stage as the treatment have removed significant amount of hemicellulose, lignin and other easily hydrolysed substances. For ATCSP, the degradation peak appeared at 260°C but after the CSP subjected to silane treatment the peak has shifted to higher temperature at 275°C. Evidently, the alkaline treatment causes a decrease in thermal stability but it can be improved via following silane treatment as the GPTMS solution works as a coating for the fibers to improve the hydrophobicity of the fiber as proved via SEM morphology.

Based on Figure 8, for UCF the main degradation (second stage degradation) was observed in the range of 270°C to 360°C which results in 60% of CF weight loss. The degradation peak was observed at 275°C which shifted to 285°C after alkaline treatment and further to 295°C after silane treatment. The silane treated CF shows a higher degradation temperature compared to untreated CF as silane treatment provides a hydrophobic coating to the CF surface by grafting the alkyl chain in the silyl part to CF. CSP and CF fibers undergo the last stage of degradation starting from 350°C to 500°C. At this stage the weight loss of the fibers are slow and treated CSP and CF has a higher amount of residual compared to untreated fiber. Higher residual prove the enhancement in the thermal stability with the GPTMS treatment compared to alkaline treated fibers.

3.4 Thermal Analysis of Composites

Thermo gravimetric analysis of Untreated CSP (UCSP), PLA, and Untreated PLA reinforced coconut shell powder composite (UPCSPC) are shown in Figure 9 and the thermal stability of alkali treated CSP, PLA, and alkaline treated PCSPC are shown in Figure 10 while GPTMS treated CSP, PLA, and GPTMS treated PCSPC are shown in Figure 11.

TGA ANALYSIS OF UNTREATED CSP AND COMPOSITE**Figure 9.** Thermal properties of untreated CSP, PLA, Untreated PCSPC.**TGA ANALYSIS OF ALKALI TREATED CSP AND COMPOSITES****Figure 10.** Thermal properties of alkali treated CSP, PLA, alkali treated PCSPC.**TGA ANALYSIS OF GPTMS TREATED CSP AND COMPOSITES****Figure 11.** Thermal properties of GPTMS treated CSP, PLA, GPTMS treated PCSPC.

As observed in Figure 9, Figure 10 and Figure 11, the pure PLA starts to degrade around 300°C and the fastest weight loss took place at the peak of temperature around 354°C. The untreated, alkaline treated, and GPTMS treated PCSPC shows the thermal stability in between the pure PLA and CSP. The thermal degradation of the composites increases with increasing CSP content. However, above 350°C, thermal degradation decreases with increasing CSP content. The same trend observed in Figure 10 and Figure 11. As a result, the CSP reinforcement in PLA matrix enhanced the thermal stability. Moreover, the total weight loss at 600°C has decreased with increasing filler content which proves the enhancement of thermal stability of the composite. This enhancement attributes to fiber-matrix interface. Comparing Figure 10 to Figure 11, the GPTMS treated CSP/PLA composites shows increment in peak temperatures and the weight loss at 600°C have decreased compared to alkaline treated PCSPC. This result has a similar trend to the result reported for durian fiber -reinforced PLA composites [14]. This can be due to the fact that GPTMS treatment enables a strong filler-matrix interaction and leads to better dispersion of CSP in the PLA matrix. This provides better thermal protection to the composite [7].

3.5 Extruded Filaments

Production of filaments was mainly based on controlling the barrel and extrusion die temperature. This is because; the filaments are extruded with proper flow only when the barrel and extrusion die temperature is equivalent to the melting temperature of pure PLA. If the barrel and extrusion die temperature is kept lesser than the melting temperature of PLA, then the extrusion of filament failed. If the barrel and extrusion die temperature is kept higher than the melting temperature of PLA, then there was the faster ejection of filaments. Trial 1 failed to extrude filaments as the temperature was not enough to melt the PLA composite. On the contrary, trial 3 exhibits too fast ejection with uncontrollable diameter. Only trial 2 can successfully eject filament but, with uneven diameter. Hence, considering the parameters of the trial 2, a total of 19 batches of filaments were tried and only 13 batches were successfully extruded. Table 3 shows the results of the extrusion process.

Table 3 Results of the Extrusion Process

Code	Ejection	Diameter range
Pure PLA	Successful	1.75-1.78
5CF95PLA	Successful	1.60 - 2.10
5CF95PLA	Successful	1.50 - 2.00
5CF95PLA	Successful	1.60 - 2.06
10CF90PLA	Failed	Nil
10CF90PLA	Failed	Nil
10CF90PLA	Failed	Nil
15CF85PLA	Failed	Nil
15CF85PLA	Failed	Nil
15CF85PLA	Failed	Nil
5CSP95PLA	Successful	1.70 - 1.95
5CSP95PLA	Successful	1.60 - 1.85
5CSP95PLA	Successful	1.65 - 1.75
10CSP90PLA	Successful	1.52 - 1.85
10CSP90PLA	Successful	1.50 - 1.95
10CSP90PLA	Successful	1.54 - 1.85
15CSP85PLA	Successful	1.32 - 1.95
15CSP85PLA	Successful	1.35 - 1.81
15CSP85PLA	Successful	1.40 - 1.76

Filaments which are clogged in the die and the filaments which are successfully extruded were shown in Figure 12.



Figure 12. (Left) Flushed fibers after the degradation out of extrusion die and (Right) Successful extrusion of 5wt% Untreated PCSPC (bottom) and PCFC (top) composite filament.

3.6 3D Printing of Extruded Filaments

The successfully extruded filaments are fed into the 3D printer (Raisen 3D N2 Plus) which uses the Fused Deposition Modelling (FDM) technology. The diameter of the nozzle was at 1 mm and the temperature was set at 200°C. The velocity of the feedstock was set at 30 mm/min according to the standard parameters. Only 5 wt% PCFC and 5 wt% PCSPC filaments were selected for 3D printing because only 5% of fillers provided successful extrusion in both the cases (CF and CSP). PCSPC filaments were successfully printed as shown in Figure 13 (Left) whereas, PCFC clogged shown in Figure 13 (Right) due to their increased level of filament diameter when compared to PCSPC. TGA results obtained for the composite will also be applicable for the filament and 3D printed parts since, the temperature of the extrusion and 3D printing's process was within the limits of degradation temperature of the composite.

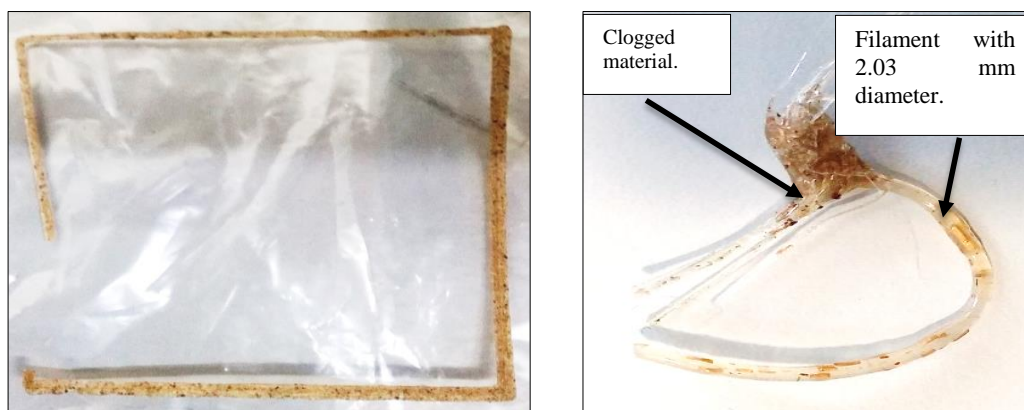


Figure 13. (Left) Successful ejection of material for 5wt% untreated PCSPC, 13(Right) Clogged material for 5wt% Untreated PCFC.

4. CONCLUSION

The fillers were successfully pre-treated using 5 wt% alkaline solutions and 3 wt% GPTMS solution. The results conclude that alkaline treatment had similar effect on both the CSP and CF while the silane treatment on CSP seems more effective compared to CF. Pre-treatment also enhanced the thermal stability of the CF by 10 °C while decreased by 10 °C for CSP. Further, GPTMS treated PCSPC shows increment in peak temperatures. The weight loss at 600°C has decreased compared to alkaline treated PCSPC which proves the better thermal stability. SEM analysis also confirmed the structural changes from rough to smooth after the successive

treatments, which could be due to the removal of lignin and impurities as confirmed by FTIR studies. For detailed characterisation on structural and morphological changes, the size and elemental composition of the untreated and treated filler will be incorporated in future studies. Thus, the PCSPC filaments were successfully 3D printed. However, these natural material based composites are vulnerable to microbial attacks. This limitation is slowing down the use of natural materials like coconut waste in real world applications which can be overcome by mixing additives in the composites.

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