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# Efficient methods of surface functionalization of lignocellulosic waste toward surface clickability enhancement

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## ABSTRACT

This work targets the development of a pioneering synthetic strategy to modify the surface of lignocellulosic/natural filler material abundant in date palm pedicels by incorporating azide and alkyne moieties with the aid of microwave as a heating source. The novelty of this work is originated from the fact that functionalization was achieved, in both cases, using shorter modification path within short time. The developed technique takes into consideration the environmental regulations by endorsing the use of green chemistry toward fast and simple materials synthesize that can be widely used industrially. The functionalized material can be utilized as an intermediate product for several modern applications such as click chemistry and bio-composite production. The modified materials were characterized using Fourier transform infrared, solid-state 13C nuclear magnetic resonance (ssNMR), x-ray diffraction (XRD), and thermo-gravimetric analysis (TGA). Characterization techniques provide evidence that the functional groups were successfully incorporated in the natural filler which depicts that the used functionalization technique is effective in providing a trouble-free route toward natural filler modification. Thereby, the findings of this work provide a new opportunity for using click chemistry approach to fabricate cost-effective and sustainable bio-composite materials.
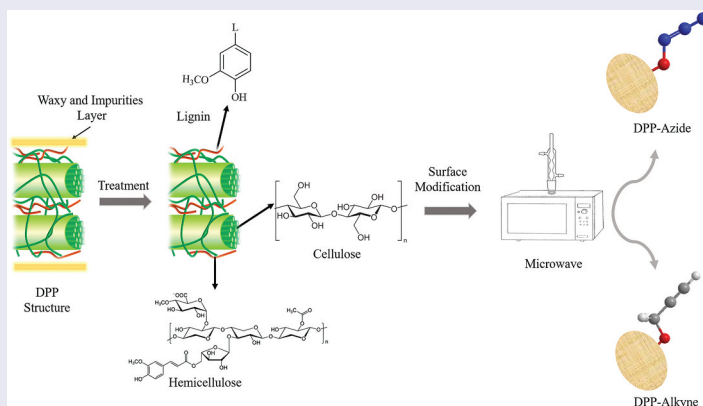
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## Introduction

In the last few decades, plant fiber/filler-reinforced composites were progressively developed to replace regular commercial composites where synthetic fibers are usually used. Their cost-effective production, low environmental impact, and acceptable mechanical properties, once compared to those of glass fibers, encourage industrial sectors to invest in this area [1,2]. The composite properties are significantly dependent on morphology, bonding, reactivity, and other characteristics of the interfacial region [3]. A strongly bonded interface will firmly contribute to better material performance which can be accomplished by physical or chemical crosslinking [4,5]. In specific, chemical bonding is an effective option to achieve a strong adhesion at interface manifested by an enhanced compatibility between composite ingredients [6]. This will allow for a smooth load transfer among components through the interface and thus enhance the mechanical properties of produced composites [7].

One of the drawbacks of natural filler reinforced polymer composites is the weakening of their mechanical properties due to incompatibility between hydrophobic polymer and hydrophilic natural filler. One way to alleviate such problem is by enhancing surface properties of the natural filler making it more suitable for specific applications using chemical, physical or biological treatment methods [8,9]. For example, grafting coupling agents such as maleic anhydride and 3-isopropenyl-α, α-dimethylbenzyl isocyanate onto the polymer surface has been used. This incorporation allows reaction between the modified polymer surface and the functional groups available on the natural filler surface [10,11]. Natural fillers such as polysaccharides and lignocellulosic biomass are by far the most abundant renewable natural polymers. Thus, the potential to prepare different functionalized and grafted bio-based polymers is of great interest for industrial and medical applications [12]. The hydroxyl functional groups at the natural polymer surface are the most vital groups which can be chemically altered to produce modified bio-composites with tailored properties that can be used for applications related to advanced and high-valued biomaterials. A growing number of cellulosic-based materials have been recognized for the use in several industrial applications such as flexible substrates synthesis, high surface area and nanostructured materials preparation, and molecular scaffolds [13].

Agricultural wastes such as date palm and coir fibers are mainly composed of cellulose (33–45%), hemicellulose (60–75%) and lignin (14–27%) [14]. Of the total number of about 100 million date palm trees in the world, nearly 62 million trees are located in the Middle East and North Africa. The world production of date palm agro-residues accounted for 4,200 thousand tons per year. Date palm tree waste can be found in the form of bunches, petioles, palm trunks and leaves [15]. Currently, due to their high durability and strength characteristics, palm fibers are used to make a variety of by-products such as mattresses, sofas, marine ropes, sacks, and traditional raincoats. However, these applications only utilize a small percentage of the total material produced, and the majority of the material is discarded directly as waste [16]. As a result, bulk amount of date palm waste can be used as sustainable natural source that can be used to extract natural fillers. Nowadays, enormous use of date palm fibers has been identified in the wood composite industry [17].

The use of renewable resources, the improvement of reaction conditions, and the development of less-toxic and more biodegradable compounds are the main leading motives toward advancement in materials science and polymer chemistry synthesis [18]. Modified lignocellulosic and cellulosic materials are considered as attractive compounds in the field of sustainable chemistry, therefore, creation of new synthesis/modifications path using advanced chemistry applications can significantly broaden the diversity of bio-polymers as the method is capable of yielding compounds, which are not accessible via the most commonly applied production methods [19]. Several investigations, to look for new synthesis routes to expand the range of applications of natural fillers while retaining its prominent properties, have been reported. Functionalization of bio-fillers and tailoring their properties to achieve desired physiochemical properties is a crucial field of research that has a wide range of applications [20]. In contrast to the physical blending treatment, covalent linking through chemical reaction between lignocellulosic biomass and polymeric matrix can positively provide a stronger interfacial bonding and better compatibility [21,22]. For example, cellulose is used as a reinforcing agent in plastic composites. This has created a need for the control of its properties, such as hydrophobicity and adhesion forces [23]. Hence, considerable efforts have been directed toward the development of modified cellulose materials that incorporate several chemical groups using different synthesis route such as click chemistry approach [24]. Lee et al. [25] concluded that click chemistry enhances the storage modulus of the cross-linked gels, prepared via click chemistry route, once compared to the non-cross-linked gels. Moreover, Hu et al. [26] found that the crosslinking densities of the prepared materials based on click reaction gradually increased, together with simultaneous enhancement of tensile properties.

Azides and alkynes are useful intermediates in organic synthesis, because they can be used for the preparation of a variety of compounds that has attractive applications mainly in click reactions. Therefore, considerable attention in synthetic polymer chemistry, were given to click reactions, owing to their high specificity, high tolerance of functional groups, and high quantitative reaction yields [27]. Click reaction promotes the use of organic reactions which include the linking of two molecular building blocks in a facile, selective and high-yielding reaction under mild reaction conditions with no byproducts [28]. Actually, azides are very versatile due to the fact that they can be easily converted into other functional groups, such as amines, nitrenes, imines, iminophosphoranes, amides, triazoles, tetrazoles, aziridines, or triazenes [29]. On the other hand, alkyne compounds have been introduced and used intensively as powerful precursors to many surface reactions such as azide-alkyne cycloaddition, cyclotrimerization and homo-coupling [30]. Several investigations on azido or alkyno-grafted cellulose has been reported and widely applied for further functionalization using click chemistry [31]. Nevertheless, azide and alkyne functionalization reactions cannot usually be heated since the product has hazardous nature in general. Hence, many reactions have been accelerated by the use of microwave. However, microwave heating for reactions involving azide and alkyne is still limited. Methods such as microwave irradiation, ultrasonic and plasma are recommended to be used to accelerate the reactions between the precursors, hence reducing reaction time, and improve the yield. Microwave technology has become recognized that many chemical reactions, which require heating are likely to proceed more rapidly using this form of heating [32,33].

To the best of authors' knowledge, there are no works that report the use of microwave heating to integrate azide and alkyne moieties onto natural fillers. This motivated us to perform a systematic study in which microwave heating was used to develop chemical modification techniques where azide and alkyne functional groups were chemically incorporated onto the date palm powder (DPP) extracted from agro-waste. During the study, microwave power and duration of heating were carefully analysed and selected in order to achieve the optimal conditions. To confirm the successful incorporation of the functional groups onto DPP surface, the synthesized materials were characterized using FTIR, $^{13}$C ssNMR, XPS, TGA, XRD and SEM.

## Methods

### Chemicals and materials

Propargyl alcohol (ALc, 99%, Sigma-Aldrich Company, USA). Acetyl chloride (99%, Sigma-Aldrich Company, USA). Sodium azide (NaN$_3$, Fisher chemical, UK). N, N-dimethylformamide (DMF 99%, Sigma-Aldrich Company, USA). Thionyl chloride (SOCl$_2$, Sigma-Aldrich Company, USA). All chemicals were used without further modification.

### Experimental

### Microwave setup

The microwave chemical reactor is used to accelerate the functionalization methods. It is equipped with a magnetic stirrer tray and the output power was controllable from 0 to 900 Watt with a frequency of 2450 MHz ± 50 Hz. To control temperature within the cavity of the microwave oven, a thermocouple is used. Besides to precise temperature control, the microwave has a magnetic stirring, and a digital display of temperature and stirring speed. The microwave heating parameters were selected and optimized based on published researches that used microwave energy for chemical synthesis [28,34]. Hence, microwave power was set at 450 Watt for all reactions as such value is moderate and effective within an acceptable energy limit. The temperature was kept constant during the reaction and set in accordance with boiling point of solvent or catalyst to prevent rapid evaporation. The reaction time was monitored based on FTIR observations, the samples were tested per 5 minutes until the targeted peaks are clearly determined.

### DPP preparation

Date palm pedicel agro-residues (0.5–2 m length) were collected from a local farm. Then, the branches were cut into small pieces using electrical sawing machine, followed by sieving to an average particle size of 150 $\mu$m using Cryogenic Ball Milling machine. In order to obtain the optimal utilization of the hydroxyl group available in DPP surface, a new treatment method was implemented as reported in [35]. This is due to capability of the treatment method to remove the outer surface of the DPP cell wall containing wax and impurities. Those substances work as barriers around the hydroxyl group at the biomass surface (hemicellulose, lignin and cellulose). Table 1 lists the chemical

composition of the untreated and treated DPP as was obtained via an extractive method as reported in [36–38].

### DPP-Az production

DPP powder (2 g) is carefully and slowly immersed in thionyl chloride ($SOCl_2$) and stirred in microwave (450 Watt, 70°C, 5 min). It is worth mentioning that vigorous reaction takes place, following this step, where HCl and $SO_2$ are produced as reaction by-products. Then, the chlorinated DPP is added to DMF solvent containing $NaN_3$ (2 g) and stirred in microwave (450 Watt, 100°C, 15 min) as described in Scheme 1. The product (DPP-Az) was washed with distilled water to remove the excess $NaN_3$.

### DPP-Alkyne production

The synthesis was carried out as per procedures reported in the literature [39] with modification in the heat source and the reaction time. Briefly, a mixture of propargyl alcohol (20 ml) with acetyl chloride (5 drops) as catalyst was mixed in microwave (450 Watt, 50°C, 10 min). After that, 4 g of DPP is added to the mixture and stirred in microwave (450 Watt, 60°C, 20 min). Later, the product (DPP-Alkyne) was filtered and washed several times with distilled water to remove impurities. Scheme. 2. shows the schematic representation for DPP-Alkyne production.

### Characterization

### Fourier transform infrared (FTIR) spectroscopy

FTIR is used to obtain an infrared spectrum corresponding to the chemical functional groups available at the surface of the synthesized bio-composites. FTIR spectrometer simultaneously collects high spectral resolution data over a wide spectral range. FTIR data of the materials were collected using Cary 630 FTIR spectrophotometer from Agilent Technologies. The instrument was employed in the spectral range from 650 to 4000 $cm^{-1}$ with a resolution of 16 $cm^{-1}$ and 64 scans for the analysis.

**Table 1.** Chemical composition (%) of untreated and treated DPP.

|  | Untreated | Treated |
|---|---|---|
| Wax | 5.40 ± 0.28 | NA |
| Water soluble matters | 2.27 ± 0.02 | NA |
| Pectin | 4.95 ± 0.69 | NA |
| Hemicellulose | 16.57 ± 0.44 | 10.77 ± 0.30 |
| Lignin | 25.02 ± 0.61 | 24.34 ± 1.43 |
| Cellulose | 45.79 ± 0.86 | 64.89 ± 1.29 |
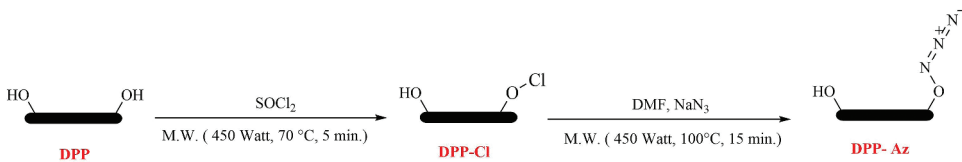


**Scheme. 1.** Schematic representation for DPP-Az preparation.

### Solid-state $^{13}$C nuclear magnetic resonance (ssNMR)

Due to the inability of natural filler (DPP) dissolving, ssNMR was the only available NMR instrument for process evaluation. The samples were analysed with a JEOL ECX-400 (JEOL, Japan) high resolution multinuclear FT-NMR spectrometer at NMR Research Centre (SIF) in Indian Institute of Science (IISc). All chemical shifts are stated in ppm.

### X-ray photoelectron spectroscopy (XPS)

XPS is used to acquire qualitative information on the chemical species present on the surface of the tested material. Samples were analysed using (Omicron Nanotechnology, Germany) with a monochromatic Al-K$_\alpha$ X-ray source (1486.6 eV) operated at 20-mA emission current and a 15-kV anode potential. The data acquisitioned in a fixed analyser transmission mode, with a pass energy of 50 eV for wide scans and 20 eV for high-resolution scans. The base pressure in the analysis chamber was maintained at $10^{-10}$ mbar. Sample charging was prevented by using a charge neutralizer. During the experiment, all the tested samples were flooded with electrons to remunerate for surface charging during XPS measurements. Data analysis was carried out using CASAXPS software.

### Thermo-gravimetric analysis (TGA) and derivative thermogravimetry (DTG)

Thermal gravimetric analysis (TGA) and Derivative Thermogravimetry (DTG) were conducted on the treated and functionalized date palm fibers. The thermograms of samples were recorded by using a Thermo-Gravimetric Analyzer (TGA Q 500 TA Instrument, USA). The samples were placed in an alumina pan at temperatures of 25–600°C and heating rate of 20°C/min under inert atmosphere of $N_2$ at a flow rate of 50 ml/min.

### X-ray diffraction (XRD)

To investigate the crystallinity degree of the modified DPP, samples were analysed at ambient temperature by step scanning on an X-ray powder diffractometer (Rigaku Corporation, Japan). The measurements were carried out at 40 kV and 20 mA with a detector placed on a goniometer scanning the range from 5° to 70°, at a scan speed of 2° min$^{-1}$ using monochromatic CuKα radiation (λ = 0.15406 nm). The crystallinity degree of the materials was then calculated from the area of crystalline and non-crystalline peaks.

### Morphological characteristics

The morphological features and surface appearance on the DPP fibers were evaluated using a Scanning Electron Microscope (SEM) Model (JSM-7800 F JEOL, Japan) at
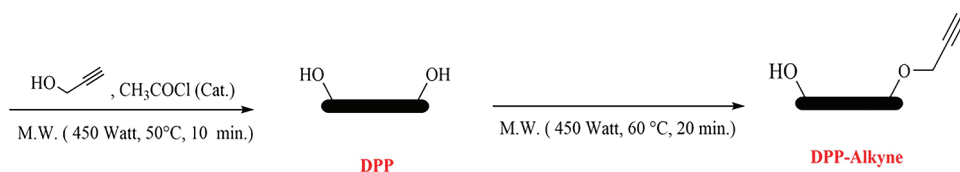


**Scheme. 2.** Schematic representation for DPP-Alkyne preparation.

magnification range of 100–500x. The samples were gold coated prior to SEM examination.

# Results and discussion

## Reaction time

The state of art in the advanced synthesis is to modify the material surface using greener, simpler and faster methods where minimal steps and less expensive chemicals are required to attach the functional group onto the surface. However, the reported methods in the literature as listed in Table 2, are expensive and require long preparation time. Moreover, those methods were normally performed at room temperature or used conventional heating methods known for their time-consuming. Therefore, this work satisfies the stringent needs, in term of obtaining the functionalization using fewer materials for a short period of time. Compared to other reported methods in the literature, it is clearly observed that the steps involved in this study and/or time to accomplish the reaction can be reduced dramatically as summarized in Table 2. A few other modification techniques require the use of limited, highly toxic, and expensive chemicals for prolonged processing time, in days, rather than hours. The proposed method, in this work, use sodium azide for grafting azide group on the DPP surface as it is available and not expensive. In addition to that, sodium azide was found to be the most popular group for click chemistry synthesis [40]. Evidently, the developed methods, presented in this article, are very promising technique for many applications where time and cost reduction along with satisfactory performance are sought. Moreover, current methods are not only applicable for the date palm but can also be applied for a wide variety of materials where the hydroxyl groups can be found naturally or grafted onto.
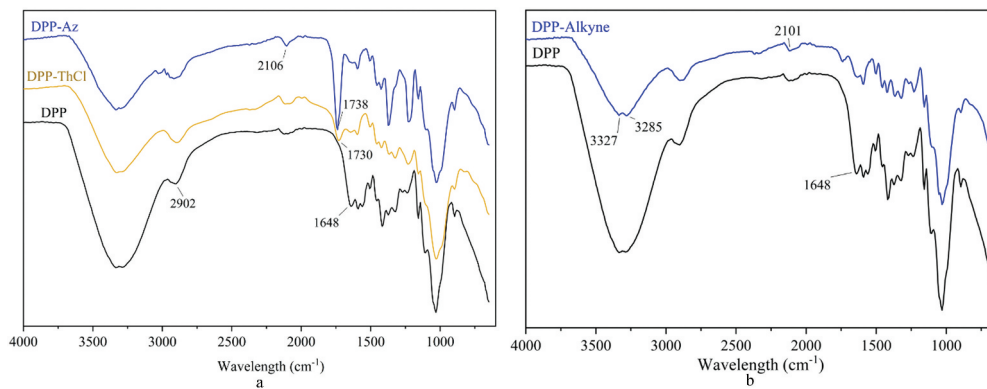
## FTIR

The FTIR spectra of the treated DPP, DPP-Az, and DPP-Alkyne are depicted in Figure 1 (a) and (b). The FTIR spectra of the three samples confirms the presence of water revealed by the peak between 3300 and 3400 $cm^{-1}$ that is assigned to stretching of hydrogen bonding (O-H) of water molecules that was absorbed onto the samples [41]. In addition, the three samples displayed the band observed around 2902 $cm^{-1}$ which is attributed to asymmetric C–H bands in methyl and methylene groups in the DPP [42]. These absorption bands are normally associated with the presence of cellulose, hemicellulose, and lignin.

Major findings are clearly observed in the range between 1600 and 2200 $cm^{-1}$. The observed peak at absorbance band 2106 $cm^{-1}$, for DPP-Az are assigned to ($-N_3$) anti-symmetric [43]. On the other hand, for DPP-Alkyne sample, the bands 2101 $cm^{-1}$ correspond to the stretching vibration of alkyne group due to functionalization procedures. Another characteristic peak appears at 3285 $cm^{-1}$ due to CH stretching mode of the propargyl moiety as can be seen in Figure 1 (b). However, this peak is not very sharp, presumably overlapping with a broad peak due to stretching of hydrogen bonding (O-H) of water molecules within the same region. The sharp peak appeared at 1738 $cm^{-1}$, for the functionalized samples, may be attributed to carbonyl C = O stretching of the acetyl

**Table 2.** The required time for natural polymer alkynation and azidation methods.

|  | Material | Time (h) | Ref. |
|---|---|---|---|
| Alkyne | DPP | 0.3 | *Current work* |
|  | Cellulose | 5–12 | [56] |
|  |  | 5 | [21] |
|  |  | 6 | [23] |
|  |  | 6 | [57] |
|  |  | 24 | [31] |
|  |  | 25 | [58] |
|  |  | 26 | [59] |
|  |  | 48 | [60] |
|  |  | 96 | [49] |
|  |  | 96 | [61] |
|  |  | 96 | [12] |
|  | Lignin | 2 | [62] |
|  | Kapok fiber | 12 | [48] |
| Azide | DPP | 0.5 | *Current work* |
|  | Cellulose | 25 | [63] |
|  |  | 48 | [60] |
|  |  | 48 | [19] |
|  |  | 72 | [61] |
|  | Chitosan | 48 | [49] |
|  | Lignin | 36 | [24] |
|  | Kapok fiber | 72 | [48] |

group of hemicelluloses or the carboxylic groups of hemicellulose [44]. Another major observation at 1648 cm$^{-1}$ is associated with the (O-H) bending vibration of the adsorbed water into DPP. All other peaks are associated with original biomass including cellulose, hemicellulose, and lignin. The bands between 1500 and 1400 cm$^{-1}$ might be assigned to C–C stretching of the aromatic ring while bands around 1380 cm$^{-1}$ and 1000 cm$^{-1}$ might be due to C–H stretching of cellulose and C–O stretching vibration of cellulose and hemicellulose, respectively [44,45]. Moreover, DPP-Az sample exhibited a small peak at around 1034 cm$^{-1}$ which is due to the stretching vibration of C–N groups which further support the incorporation of azide molecule in the chains of the cellulose of the DPP [42,43]. Finally, the bands between 850 and 550 cm$^{-1}$ can be assigned to C–Cl or C–H stretching vibrations of cellulose. Therefore, based on the FTIR finding, it is confirmed



**Figure 1.** FTIR spectra of a) DPP-Az, b) DPP-Alkyne.

that substantial parts of azide and alkyne groups are successfully added to the DPP surface.

### NMR

The occurrence of DPP-Az and DPP-Alkyne were further investigated by ssNMR spectroscopy, as shown in Figures 2 and 3. The obtained ssNMR data were compared to raw fiber, reported by [46,47] where common functional groups appear at 105, 88, 83, 74, 73, 65, 56 ppm for cellulose and 21, 33, 153 ppm for hemicellulose and lignin of the raw fiber, DPP-Az and DPP-alkyne. New peaks appear in the DPP-Az and DPP-Alkyne sample confirming the successful incorporation of the azide and alkyne groups on the natural fiber surface. Specifically, Figure 2 represents the ssNMR spectra of DPP-Az which exhibits a peak at 64.31 ppm confirming the incorporation of the C$-$N$_3$ group [48]. Moreover, Figure 3 for the DPP-Alkyne sample displays a peak at 72.85 ppm for CH, and 82.71 ppm for C, respectively, indicating the successful introduction of the alkyne [49]. Moreover, based on the FTIR and ssNMR analysis, the incorporation of the functional groups was not at the surface only, it is believed that the functional groups were introduced deeply inside the particle surface [50,51].

### XPS analysis

XPS analysis was conducted on DPP before and after functionalization. Figure 4 shows the survey spectra of non-functionalized and the functionalized DPP samples. In general, cellulose contains four different types of carbon bonds which are: C1 that represents carbons attached to other carbons or hydrogen, C2 which involve carbon bounded to one oxygen atoms, C3 that include carbons attached to two oxygen atoms and C4 carbon from carboxyl group which is confirmed by FTIR analysis. For DPP sample, characteristic peaks of (C 1s) at 285 eV and (O 1s) at 532 eV can only be found. Moreover, XPS spectrum of the DPP-Az sample reveal a new peak at 401 eV that is assigned to the binding energy of (N 1s) related to triazole structure from azide molecule. This peak, for N element, confirms the grafting of azide onto the cellulose chains of the DPP. In this work, no high-resolution XPS was conducted but XPS results support the FTIR findings providing strong evidence confirming the successful introduction of azide and alkyne group onto the cellulose chains of the DPP.

### XRD analysis

The XRD patterns for DPP, DPP-Az and DPP-Alkyne are presented in Figure 5. The crystalline plane (002) corresponds to the intense broad peak at $2\theta = 22°$ is attributed to cellulose. In general, the broad peak, shown for all samples, represents the poor crystallinity and the amorphous nature of the biomass content. It is observed that the surface functionalization of DPP is potentially affecting the pattern peaks, especially in case of DPP-Alkyne which depicts new crystalline peak around $2\theta = 20°$ and new peaks around 32° and 44°. These changes are believed to be due to the incorporation of alkyne on the powder microstructure and molecules arrangement. It is found that the crystallinity degree of the DPP-Alkyne is increased to 62.4% over the DPP which is 58.7%.
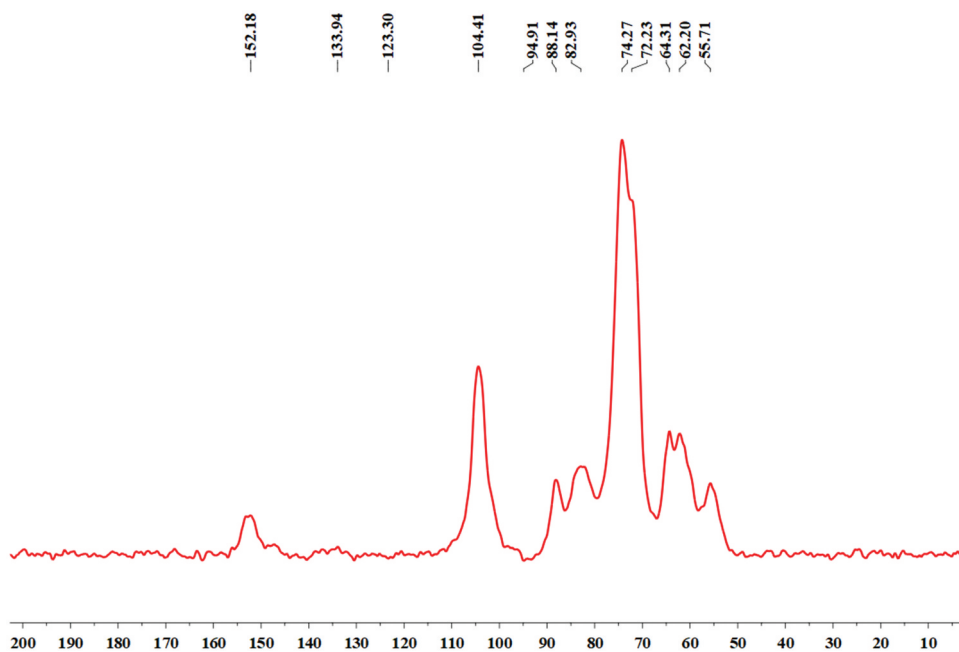
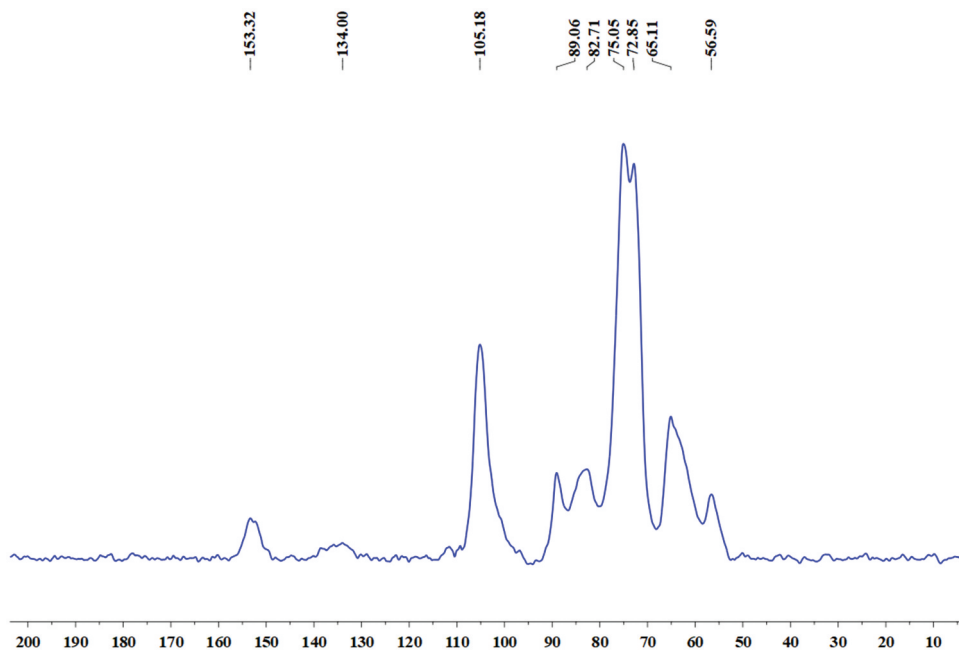**Figure 2.** $^{13}$C-ssNMR spectra of DPP-Az.



**Figure 3.** $^{13}$C-ssNMR spectra of DPP-Alkyne.

Meanwhile, the azide group reduces the crystallinity of DPP to 49.4% as a result of the crystalline biomass extraction due to azide reaction involving thionyl chloride as
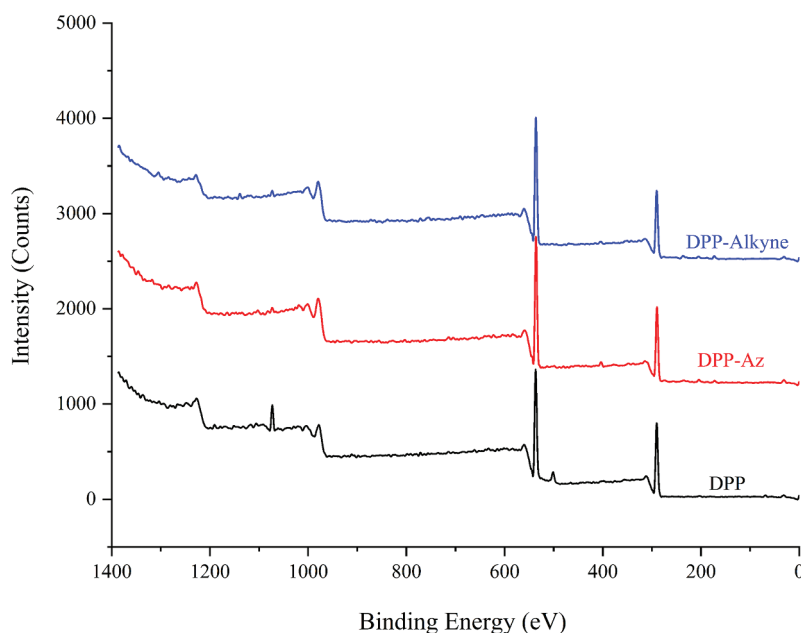
**Figure 4.** XPS spectra of DPP, DPP-Az and DPP-Alkyne.

exhibited by a change in colour of DPP from brown to lighter brown. Therefore, it is expected that azide reaction may altered the chemical structure causing removal of some functional groups resulting in decreasing the degree of crystallinity as confirmed by the XRD.

### *Thermogravimetric analysis (TGA)*

TGA is used to investigate the thermal stability of DPP, DPP-Az and DPP-Alkyne specimens under an inert atmosphere. Cellulose, the main component of the DPP, decomposition under an inert atmosphere is normally endothermic process where cellulose resistant against thermal degradation will be high due to the crystallinity nature of cellulose and the degradation will be due to the presence of free radicals [52,53]. To obtain further understanding about the degradation mechanism, derivative thermogravimetry, DTG, analysis for the three samples was implemented and distinct degradation stages were observed. The first decomposition zone (under 150°C) displayed a mass loss of 7–13% for all samples. This loss is normally associated with the removal of adsorbed and bounded water [54]. Upon increasing temperature, DPP undergoes two further degradation steps; the first zone (in the range between 150°C and 400°C) includes a major mass loss indicating overlapping simultaneous degradation of holocellulose (cellulose and hemicellulose) and lignin, while the second zone in the range between 400°C and 470°C is attributed to lignin degradation. It is important to mention that lignin degradation proceeds gradually over a wider temperature range than cellulose and hemicellulose. However, DPP-Az starts to decompose at a temperature around 180°C and exhibited two different zones between 150°C and 250°C attributed for the
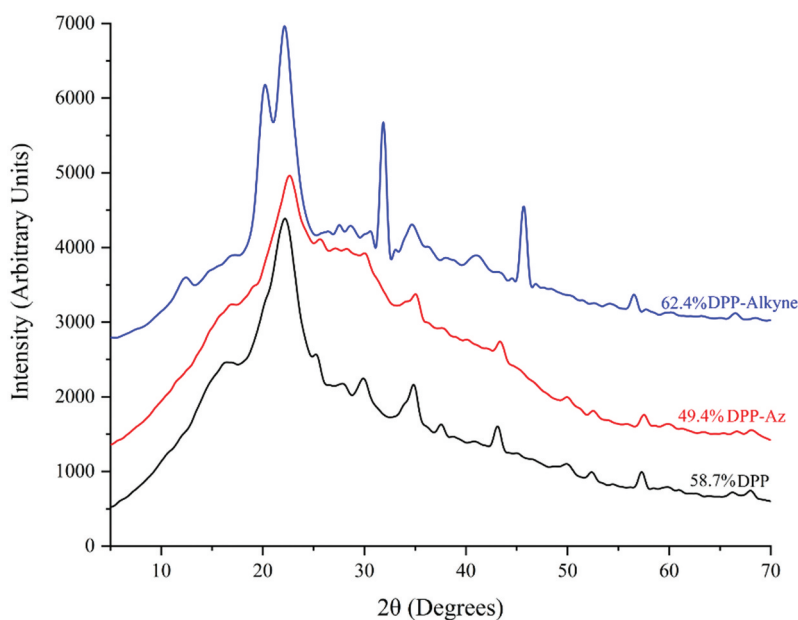
**Figure 5.** XRD curves of DPP, DPP-Az and DPP-Alkyne.

degradation of hemicellulose and between 250°C and 400°C for the simultaneous degradation of cellulose and lignin. For DPP-Alkyne, three degradation zones were observed in the range between (150°C–250°C, 250°C–300°C and 300°C–400°C) that are attributed to hemicellulose, simultaneous degradation of hemicellulose, cellulose and lignin, and simultaneous degradation of cellulose and lignin, respectively. Results of weight loss as depicted in Figure 6 reveal an evident change in thermal degradation process of the modified DPP because of the addition of the functional groups. The incorporation of the azide and alkyne groups contributed positively to the thermal stability of the original DPP by introducing new molecules with double and triple bonds which foster intermolecular interactions. Moreover, this shift to the right confirms the fact that the incorporated functional were not only added to the surface of the DPP but were also introduced deeply inside the backbone of the cellulose as evident by ssNMR analysis. A distinct peak for lignin is not clearly captured in the case of functionalized DPP once compared to DPP reflecting the overlapping of the DTG curves of hemicellulose, cellulose and lignin which can be due to the complexity of the polymeric material well reported in the literature. Overall, enhanced thermal characteristics of the functionalized DPP confirm its potential use as a stable filler for advanced synthesis of natural fiber composite materials even at high temperatures [55].

### SEM

The morphology of original and modified DPP is analysed by SEM as shown in Figure 7. It is clearly observed that the functionalized surface of date palm powder is affected by addition of azide or alkyne group. Indeed, rough surface of natural filler is desired in bio-
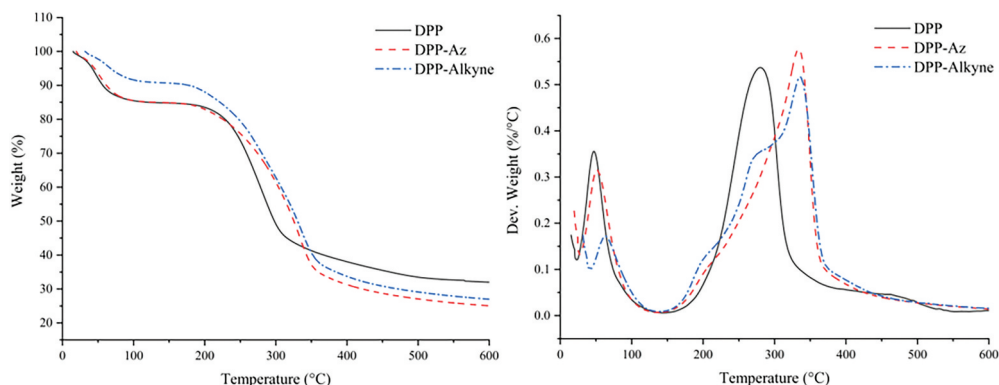
**Figure 6.** TGA/DTG curves of DPP, DPP-Az and DPP-Alkyne.

composites fabrication to enhance the polymer matrix penetration into the filler surface which is significant for mechanical interlocking improvement. Figure 7 confirms that DPP-Az produces rougher surface in comparison to DPP-Alkyne. It may be an attribute of filler biomass extraction and breaking structure due to the partial collapse of DPP after solvent removal and the mechanism of DPP modification, whereas the alkynation structure looks more stable with clear voids on the surface. Hence, this structure improves the polymer/filler mechanical interlocking which is an added advantage to the surface modification.

## Conclusion

A successful surface modification of DPP for advanced chemical synthesis using efficient schemes is achieved using azide and alkyne functional groups. The two schemes show significant capability to functionalize DPP lignocellulosic material in a short time and safe manner. Experimental characterization of functionalized DPP as conducted by FTIR, ssNMR and XPS tools have shown evidence that the DPP surface was successfully modified. TGA analysis has affirmed that azide and alkyne bonds are capable of improving the thermal stability of DPP. Furthermore, XRD test was performed to acquire better grasp of DPP physical behaviour after it was chemically modified. Crystallinity degree changes of DPP-Az and DPP-Alkyne have been analysed which showed that functionalization also affects the microstructure crystallinity. SEM revealed that current surface modification is not only achieved by the addition of azide and alkyne functional groups but also by improving the surface roughness triggering mechanical interlocking which is needed in several applications. Hence, chemical crosslinking and mechanical interlocking boost the sustainability of processing which are crucial characteristics for industrial implementation.

Even though the presented methods aim mainly to enhance the DPP surface reactivity to be used in high-performance bio-composites, they are also applicable to other similar polymers which contains hydroxyl groups on the surfaces such as polysaccharides. Further application on functionalization of polymers to graft azide and alkyne groups is underway. To synthesis pioneer bio-composites, the functionalized DPP powder and the functionalized polymer will be interlocked using the corresponding click reaction.
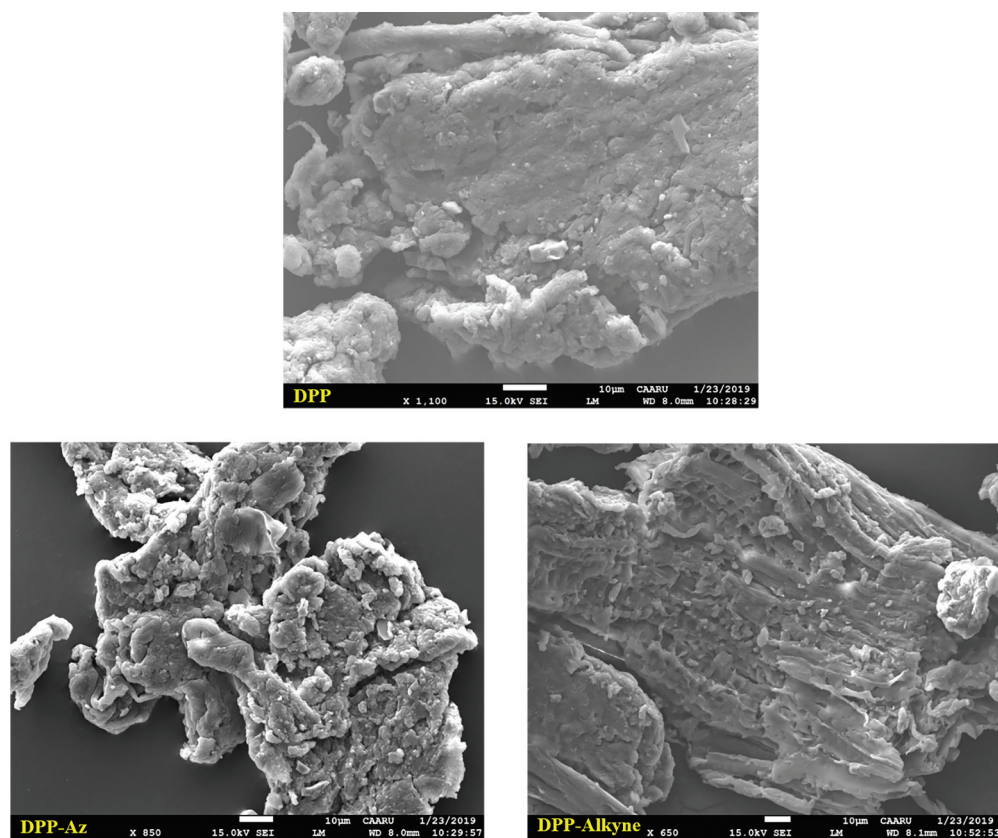
**Figure 7.** SEM photography of (a) DPP, (b) DPP-Az, and (c) DPP-Alkyne.

The formation of new functional materials with improved strength and performance will create new opportunities for product design.

## Disclosure statement

No potential conflict of interest was reported by the authors.

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