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INVESTIGATION ON CHAR RESIDUES AND MEAN REACTIVITY OF COMPRESSION MOLDED RICE AND COFFEE HUSKS BIO-CHAR REINFORCED POLYPROPYLENE

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ABSTRACT

Fiber-reinforced plastics have gained utilization in recent years for many applications because they are a cheaper alternative to the ordinary petroleum-derived materials. On the other hand, considerable amounts of agricultural wastes still lack enough utilization. In this study, bio-chars of husks from two rice and two coffee varieties in Uganda were utilized as fillers to reinforce polypropylene (PP) and thus develop fiber-reinforced plastics. Bio-char filler material was varied between 0 % and 20 %. The plastics were prepared via melt mixing followed by compression molding. Effects of bio-char content on the thermal stability of the developed plastics were studied by use of an Eltra Thermostep Thermogravimetric analyzer. Thermogravimetric analysis (TGA) results showed that inclusion of bio-char improved the thermal stability of the developed fiber-reinforced plastics. Maximum rate of weight loss ranged from -0.0414 %/min (for 15 % unmodified *Wita*-9 rice bio-char) to 0.0023 %/min (for pure PP), corresponding to respective peak temperatures of 680.8 °C and 604 °C respectively. Peak temperatures generally increased with increase in filler loading. It was found out by this study that incorporation of bio-char fiber material resulted in increased char residues. These residues tended to hinder combustion. The highest char residues (17.4 %) were obtained when PP was loaded with 15 % neutral *Wita-9* rice husks bio-char. The highest mean reactivity attained was 6.1×10^{-5} %/minute/°C obtained when 10 % unmodified *Pussa* rice husks bio-char was used to reinforce PP.

KEY WORDS: Bio-char, coffee husks, fiber-reinforced plastics, rice husks, TGA.

1. INTRODUCTION

Fillers from various origins and sources have been incorporated in polypropylene as means of achieving enhanced material properties and/or as a means of cost saving. Fillers may be inorganic or organic [1]. Organic fillers based on agricultural origin are composed mainly of cellulose, lignin, and hemicellulose [2]. Their dominance as reinforcing fillers in the production of fiber-reinforced plastics roots from their inexpensiveness, renewable nature, non-abrasiveness and minimal environmental pollution [1,3,4]. Two examples of organic fillers based on agricultural origin are rice husks and coffee husks. Much as there are some challenges and limitations exhibited by use of agricultural fillers in their raw form, a few treatments have been noted to significantly enhance their properties. One such treatments is carbonization. Carbonization forms bio-char. Biochar is a carbon-rich solid residue obtained upon heating biomass material under oxygen-deficient conditions [5]. Fiber-reinforced plastics based on uncarbonized rice husks and coffee husks have cited numerous pros to society because of their good mechanical properties. Some examples include:

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Yiga et al., (2019) used rice husks and coffee husks as filler material in the production of fiber-reinforced PP. Tensile strengths and percentage elongations varied high above 27.4 MPa and 2.4 % - 70.3 % respectively. High impact strengths and Young's moduli were achieved [2]. Tan et al., (2017) developed biocomposites based on coffee waste and HDPE. Tensile strengths and moduli increased (10 MPa - 20 MPa) with increasing filler treatment time but decreased with increase in filler loading [6]. Reis et al., (2015) manufactured biocomposites based on coffee husks waste with Polyhydroxybutyrate. Tensile strengths, Young's moduli and Izod strength of the composites increased significantly at higher coffee parchment filling ratios [7].

Chen et al., (2018) manufactured composites from rice husk recycled HDPE and polyethylene terephthalate (PET). Composites' flexural properties showed linear increases with filler content [8]. Yaacab et al., (2016) developed paddy straw powder reinforced polylactic acid (PLA). Up to 15 wt. % of filler, tensile strengths of the biocomposites were above 30 MPa whereas elongations at break ranged between 2 % - 3 %. Young's modulus increased with increase in filler material [9]. Chen et al., (2015) showed that tensile strengths and Young's modulus improved for unmodified rice husk flour reinforcements in a recycled polymer blend of HDPE and PET. Increased filler reduced elongations at break but alkali treatment enhanced these and the impact strengths [10]. Atuanya et al., (2013) developed composites based on rice husks and recycled low density polyethylene (PE) mixed with pure PE. Mechanical properties increased with increasing filler contents [11]. Fávaro et al., (2010) manufactured composites from post-consumer high-density PE with rice husk fillers. Increasing filler contents increased composites' flexural moduli, tensile and Izod impact strength [12].

Yussuf et al., (2010) developed composites based on PLA/Kenaf and PLA/Rice husk. Addition of rice husks filler material led to increased flexural modulus of PLA from 3.4 GPa to 4 GPa [13]. Rosa et al., (2009) manufactured rice husk flour-PP by melt extrusion. Tensile strengths decreased with filler loading but coupling agent improved this property. Unlike elongations at break, Young's moduli increased with increase in filler loading [14]. Yang et al. (2007) used rice husks as filler material and observed that tensile strengths of rice husks polymer composites decreased with increasing filler loading but increased with compatibilization [4]. Premalal et al., (2002) showed that apart from elongations, rice husk powder-filled PP had lower mechanical properties than talc-filled PP [1].

A major disadvantage related to fiber-reinforced plastics based on uncarbonized rice and coffee husks material however, is their high flammability [15, 16]. Recently, flammability properties of fiber-reinforced plastics have been enhanced by incorporation of fire retardant additives, such as boron compounds [17], magnesium hydroxide [18], phosphorous-based compounds [16,19,20] and halogen [21]. To a great extent, these additives retard flammability, but have outlier disadvantages like production of dense smoke and corrosive combustion by-products during production. These have a negative impact on the environment [22]. Bio-char burns with little or no smoke because of its low volatile matter content [5].

The problem of high flammability of fiber-reinforced plastics developed with agricultural fillers in their raw form can be countered by use of bio-char from these materials as filler to transfer load. Additionally, bio-char has the ability to enhance mechanical properties like tensile strength and Young's modulus of fiber-reinforced plastics due to its hydrophobic nature [16,23,24]. This study therefore focused on developing fiber-reinforced plastics using compression molding with PP as matrix and modified, neutral and unmodified rice and coffee husks bio-chars as filler materials. Pre-treatment of the bio-chars was onset by use of NaOH. Thermal properties of the developed fiber-reinforced PP were determined using an Eltra Thermostep Thermogravimetric analyzer.

2. MATERIALS AND METHODS

2.1 Materials

Polypropylene (grade PP H032 TF) with a melt flow index of 3.0 g/10 min and density of 0.9 g/cm^3, supplied by Somochem Uganda Ltd, Kampala, Uganda. Distilled water and NaOH pellets (product code 211687) with a solubility of 1090 g/l in water at 20 °C were supplied by Lab Access Uganda Limited, Kampala, Uganda. Both *Pussa* and *Wita-9* rice husks were supplied by Kibimba Limited in Uganda. *Arabica* and *Robusta* coffee husks were obtained from Buginyanya Zonal Agricultural Research and Development Institute, Mbale District, and Mukono Zonal Agricultural Research and Development Institute, Mukono District, respectively.

2.2 Preparation

The raw material rice husks and coffee husks were first sun-dried to reduce their initial moisture content to less than 13 %. After sun-drying, a carbonization process was employed to form bio-char. During the carbonization process, holes on the carbonizer drum were covered with mud/clay to limit the amount of air available for complete combustion of husks in the carbonizer [5]. After carbonization, bio-char was divided into three series: One part was used as is. This constituted the unmodified filler material. The second part was modified by immersion in a distilled water for 3 hours, followed by drying at room temperature for 48 hours and sun-drying for 6 days. This constituted the neutral filler material. The third part was modified by immersion in a NaOH solution of liquor ratio 15:1 for 3 hours, after which drying at room temperature for 48hours and sun-drying for 6 days was effected. The resultant bio-chars were centrifuged and washed in multiple cycles with reverse osmosis water until a neutral pH was attained. This constituted the modified filler material. The bio-chars were then milled to <0.5 mm sizes before being used as filler material in composite processing. This treatment was carried out for both rice and coffee husks bio-chars.

Polypropylene was melted with various ratios (0 %, 5 %, 10 %, 15 % and 20 % by mass) of different rice and coffee bio-chars in a compression molding machine to obtain circular boards of 250 mm diameter. Uniform mixing between the filler and matrix materials was achieved by a motor attached to the compression rig. The residence time for bio-composite preparation at 195 °C during compression molding was 10 min. Compression was effected by use of a hand-screw jerk for 10 minutes under about 7 MPa loading. The boards developed were then air-cooled and stored before thermal characterization.

2.3 Characterization

Thermogravimetric analysis (TGA) was carried out on an Eltra Thermostep thermogravimetric analyzer under nitrogen atmosphere at a heating rate of 20 °C/min and a temperature range from room temperature to 1000 °C. This analysis provided thermal explanations in terms of the burning rates, weight losses, peak temperatures, char residues, reactivity and Differential Thermogravimetry. Burning rates and mean reactivities were calculated using Equations (1) and (2) respectively.

$$B_R = \frac{(W_i - W_0)}{t_i} \quad (\%/\mathrm{min}) \tag{1}$$

Where B_R is Burning rate, W_i is Weight at time i, W_0 is initial weight and t_i is the time it takes for the initial weight to reach W_i.

$$M_R = \frac{\mathrm{DTG_{min}}}{T_{\mathrm{peak}}} \ (\%/\mathrm{min}/^{\mathrm{o}}\mathrm{C}) \tag{2}$$

Where M_R is Mean reactivity, $\mathrm{DTG_{min}}$ is the maximum decomposition rate of change in weight and T_{peak} is peak temperature.

3. RESULTS AND DISCUSSION

3.1 Burning rate

Burning rates of the developed bio-char fiber-reinforced PP are shown in Figure 1. The highest burning rates reached with increasing time were 0.0425 %/min, 0.0397 %/min, 0.0375 %/min and 0.0349 %/min for 10 % unmodified *Pussa* rice husks bio-char reinforced PP, 15 % unmodified *Wita-9* rice husks bio-char reinforced PP, 20 % unmodified *Arabica* coffee husks bio-char reinforced PP and 10 % unmodified *Robusta* coffee husks bio-char reinforced PP respectively. In fact, because unmodified rice husks bio-char reinforced PP have highest burning rates reached, these particular plastics made with them undergo the greatest changes in weight per minute when temperatures reach 680.8 °C and 662.4 °C for 10 % unmodified *Pussa* rice husks bio-char, 15 % unmodified *Wita-9* rice husks bio-char respectively (see Figures 2b and 2d). A closer observation of Figure 1 shows that in the first four minutes, burning rates for the developed fiber-reinforced PP steadily increase, attributed to the addition of igniter gas to the TG analyzer, before decelerating in the next two minutes to reach plateau. In the accelerating phase at this time, rice husks caused a steeper rise compared to coffee husks. This could be attributed to the fact that rice husks have less moisture contents compared to coffee husks as reported in Yiga et al., (2019) [2]. Low moisture contents have a positive correlation with combustion [25,26].

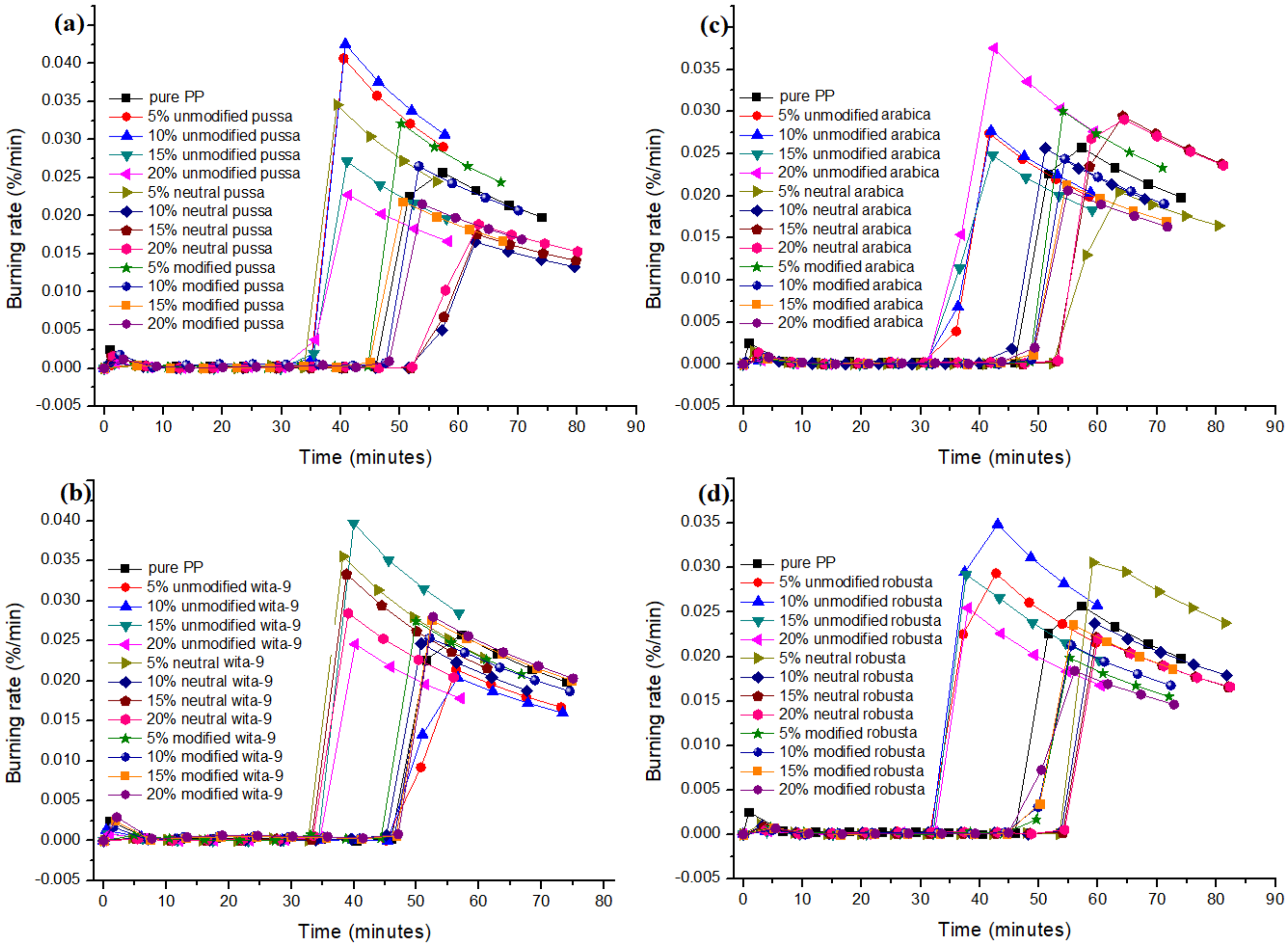

Fig. 1: Burning acceleration for bio-char reinforced PP a) Pussa rice b) Wita-9 rice c) Arabica coffee d) Robusta coffee

For most developed fiber-reinforced PP, plateau lasts up to about between 25 and 49 minutes, owing to the decomposition of hemicellulose [27]. The plateau phase of burning acceleration is generally shorter for unmodified bio-char reinforced PP because unmodified bio-char residues have lower hemicellulose compared to modified bio-char residues [2]. As time increased, the burning rates were reduced, owing to a fully developed bonded char structure, reducing the volatile products drastically, leading to thermal and flame protection of the matrix (PP) material [28]. One major note should be to the effect that the modification process leads to a reduction in burning rates of the developed fiber-reinforced PP. The reduction is attributed to the increasing lignin levels when these fillers are pre-treated with NaOH [2]. Lignin plays a major role in char-formation which reduces flammability [29].

3.2 Weight Loss and DTG

Figures 2 and 3 show representations (thermograms) of changes in weight of the developed bio-char reinforced PP with increasing temperatures as well as the first derivative of the weight loss curve. All the developed fiber-reinforced plastics showed an initial increase in weight from about 26 °C to 106 °C owing to addition of igniter gas to the thermogravimetric analyzer. Pure PP starts degrading at 455 °C, associated with the degradation of hemicelluloses while inclusion of filler material shifts the onset of degradation to up to 580 °C, depending on the specific fiber material and ratio loading [30]. After this temperature, thermal-degradation begins due to the rupture of the C-C bonds of the main chain [31]. Between 455 °C and 604 °C, celluloses are degraded from the plastic while lignins degrade at much higher temperatures between 604 °C and 916 °C. Among all components of polymers, hemicellulose is the most reactive and as a result, the temperature range of devolatilization is very narrow compared to that of lignin which occurs in a wider range [32]. It has been noted that composites made with natural fibers degraded at lower temperatures than glass and glass fiber composites but the carbonization process in this study tends to increase the temperatures at which composites made with rice and coffee husks bio-chars degrades [33].

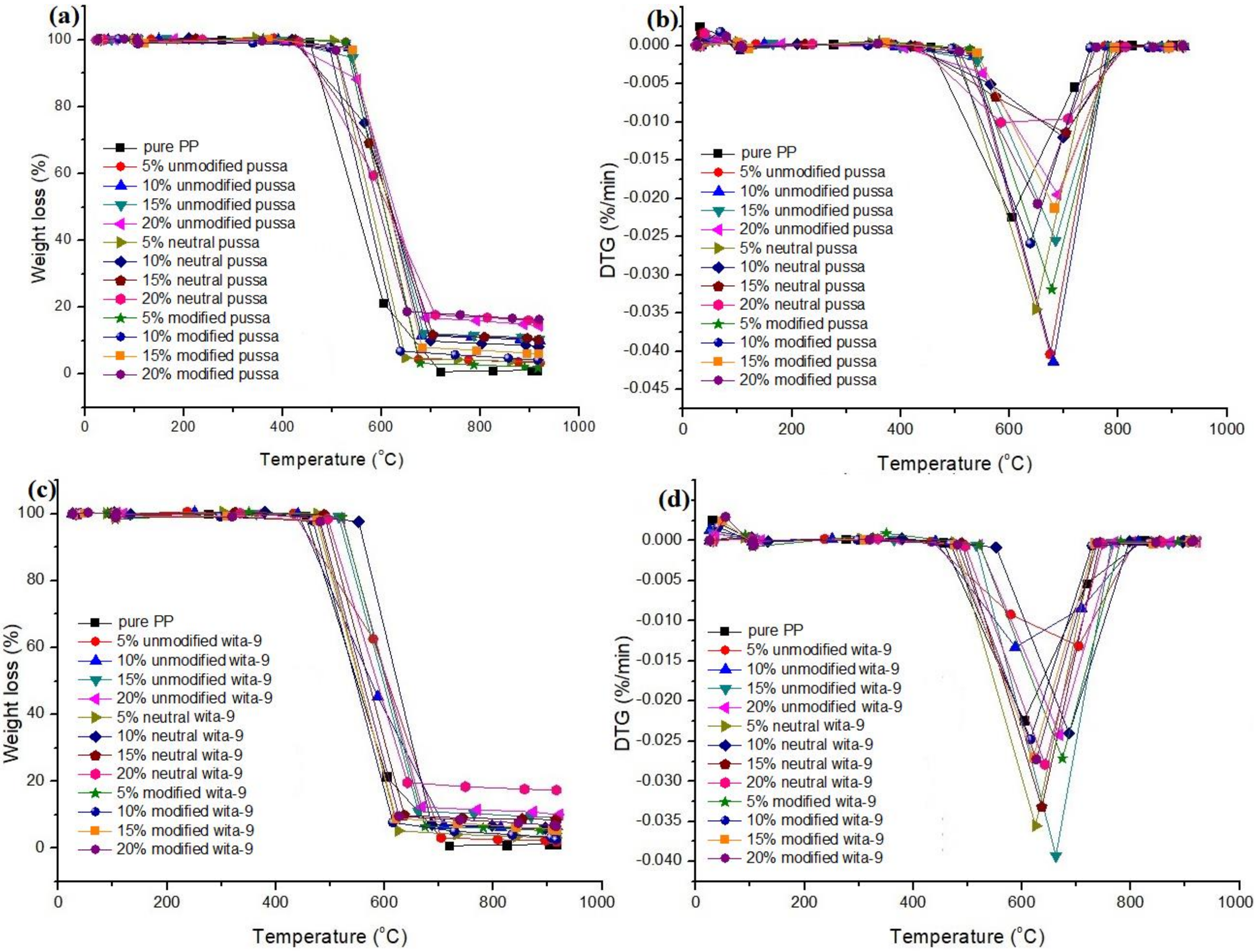

Fig. 2: Weight loss (a, c) and DTG (b, d) for bio-char reinforced PP; (a, b) Pussa (c, d) Wita-9

The thermograms for the developed fiber-reinforced PP showed a one-stage degradation process similar to that of pure PP. Similar to what was obtained by other researchers, mass losses for all the developed fiber-reinforced PP became constant over about 600 °C, indicating the formation of stable carbonaceous residues [34,35]. Aside from the filler material being made of bio-char, combustion at higher temperatures produces more char, which acts as an insulating layer against further thermal degradation [36]. In fact, char formation improves the thermal resistance of the developed fiber-reinforced PP as it cuts down release of combustible volatiles and acts as a barrier to the combustible gases generated by the polymer matrix degradation. This in turn hinders the access of oxygen to the surface of the polymer matrix [34].

The derivative of the mass loss per unit time as a function of temperature was studied to investigate the thermal degradation due to the different filler loadings and treatment means. DTG thermograms show the decomposition maximums in single peaks owing to the degradation of cellulose [30]. Figures 2b, 2d, 3b and 3d clearly illustrate that the derivative for the maximum rate of decomposition is much lower for fiber-reinforced PP compared to that of pure PP. This means that is its far harder to combust fiber reinforced PP as compared to pure PP. It is also clear from the thermographs that increase in filler loading and fiber treatment tends to produce a right-hand shift in the temperature (from the 604 °C obtained in pure PP) at which maximum degradation of the plastics occurs. This shows that thermal stability improves with increase in fiber loading as well as with alkali pre-treatment of the bio-chars. Wang et al., (2018), Saba et al., (2018) and Rahman et al., (2019) obtained similar results [27, 35, 37]. Such results signify that these plastics can be used in production of electrical appliances like cable housings due to high currents that they transmit.

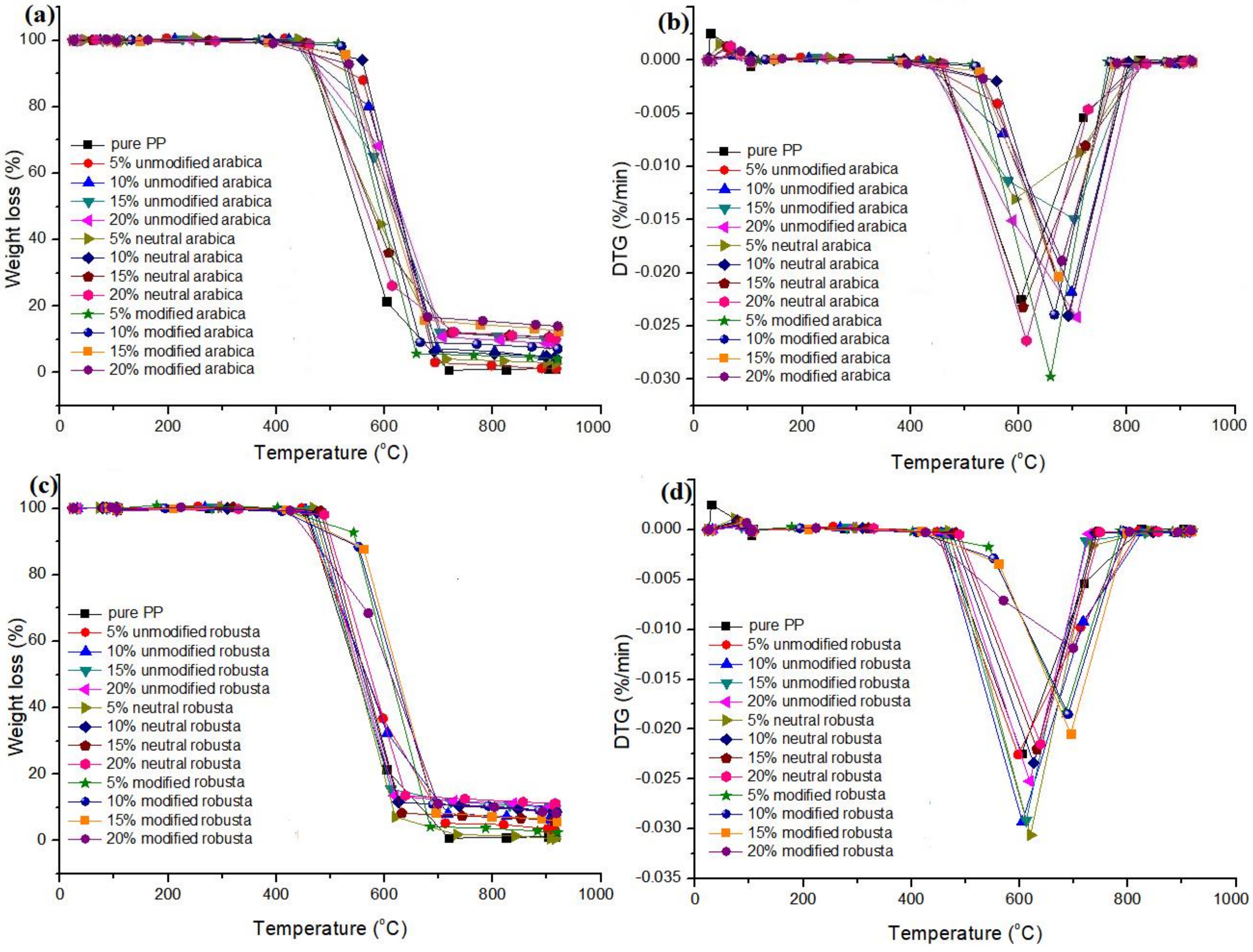

Fig. 3: Weight loss (a, c) and DTG (b, d) for bio-char reinforced PP; (a, b) Arabica (c, d) Robusta

3.3 Peak Temperatures

Results for temperatures at maximum weight loss (peak temperatures) for the developed fiber-reinforced PP are shown in Figure 4. This peak temperature is considered a measure of the reactivity of a sample [38]. Peak temperatures generally increased with increase in fiber loading. This is attributable to the fact that filler material increases char residues in the plastics which tends to hinder combustion. Similar results were obtained by Saba et al., (2017) [35]. In fact, increase in bio-char fiber material in the PP matrix led to a more sluggish rate of weight loss (see Figures 2 and 3), thus reaching maximum values of weight loss at higher temperatures. Similar results were achieved by Das et al., (2016) with the use of waste derived bio-chars [30]. The increase in peak temperatures with increase in fiber loading is also attributable to a reduction in the amount of meltable matrix (PP) which raises the temperatures at maximum weight losses.

When filler material was pre-treated, it was observed that apart from use of *Arabica* bio-char, there was a general reduction in peak temperatures. This means that the alkali pre-treatment process reduces the temperature at which maximum rate of change in weight occurs. This is attributable to the fact that upon alkali pre-treatment, the fiber material became more hydrophobic and thus increased the possibility to adhere with the matrix. Similar results were achieved by Lin et al., (2018) when alkali pre-treatment was effected on bamboo fibers [39].

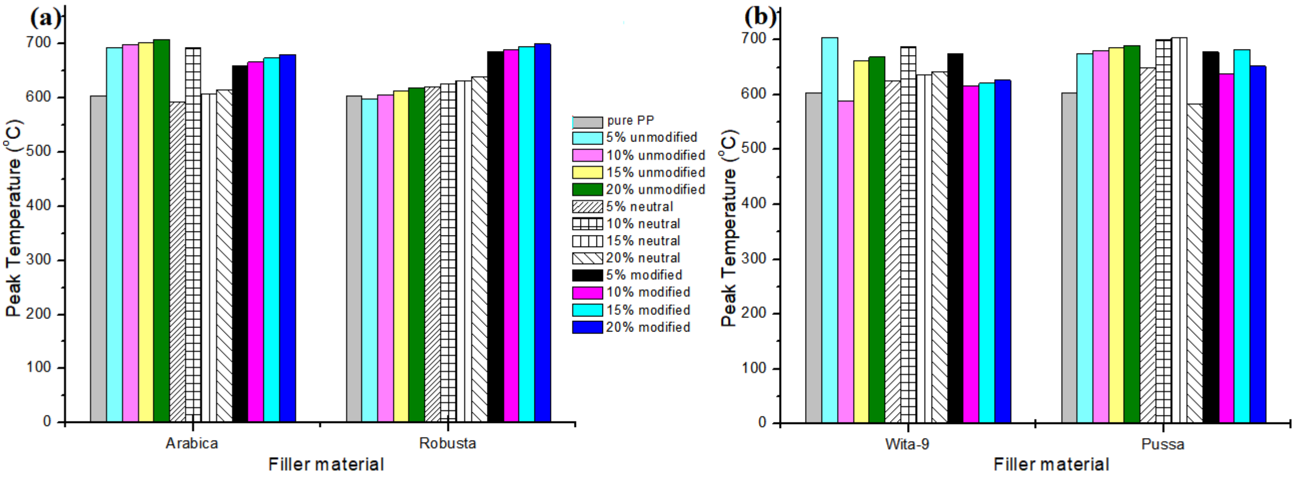

Fig. 4: Peak Temperatures obtained during bio-char reinforced PP combustion a) coffee husks b) rice husks

3.4 Char residues

Char residues are material left out after the completion of the combustion process during thermogravimetric analysis. Results for the remaining char residues at the maximum combustion temperatures for the developed fiber-reinforced PP are shown in Figures 5-7. The highest char residues (17.4 %) were obtained when PP was loaded with 15 % of neutral *Wita-9* rice husks bio-char. Incorporation of bio-char fiber material resulted in increased char residues. This is because the fiber material exerted a strong barrier effect on thermal degradation, thereby delaying weight loss for thermal degradation products as well as providing an insulative layer for the PP matrix [40, 41]. This is what improves the thermal stability of a fiber-reinforced plastic. Similar results were obtained by Molaba et al., (2018), Feng et al., (2013), Jacob et al., (2010) and Kabir et al., (2012) [16,42-44].

For *Arabica* coffee husks biochar reinforced PP, fiber alkali pre-treatment led to an increase in the char residues after combustion while for *Robusta* coffee husks biochar reinforced PP, a decrease was observed when alkali pre-treatment was effected (see Figures 5b, 6b and 7b). For *Wita-9* rice husks biochar reinforced PP, at 5 % filler loading, a 62 % increase in char residues was observed as a result of alkali pre-treatment, thereafter, the effect of alkali pre-treatment was a reduction in the char residues obtained after combustion. For *Pussa* rice husks bio-char reinforced PP, alkali pre-treatment decreased char residue formation till the 20 % filler loading when it reached 16.4 % compared to 14.5 % obtained when *Pussa* rice husks bio-char was unmodified (see Figures 5a, 6a and 7a). The reduction in char residues of the developed plastics due to alkali pre-treatment of *Robusta* coffee, *Wita-9* and *Pussa* rice bio-char was attributed to the fact that alkali pre-treatment removed all impurities from the fiber material, making it remain mainly with hemicellulose, lignin and cellulose material in its structure [45,46]. The char residues obtained in the current study are higher than those obtained in previous works which were based on investigating the effect of uncarbonized rice and coffee husk fillers in PP matrix material [2]. This is attributable to the fact that use of bio-char provides double advantages as it is an inherent insulating layer which becomes even more insulative at temperatures above 600 °C [47]. One common finding is that 3 % alkali pre-treatment leads to a reduction in the amount of residues after combustion of the developed fiber-reinforced PP [2].

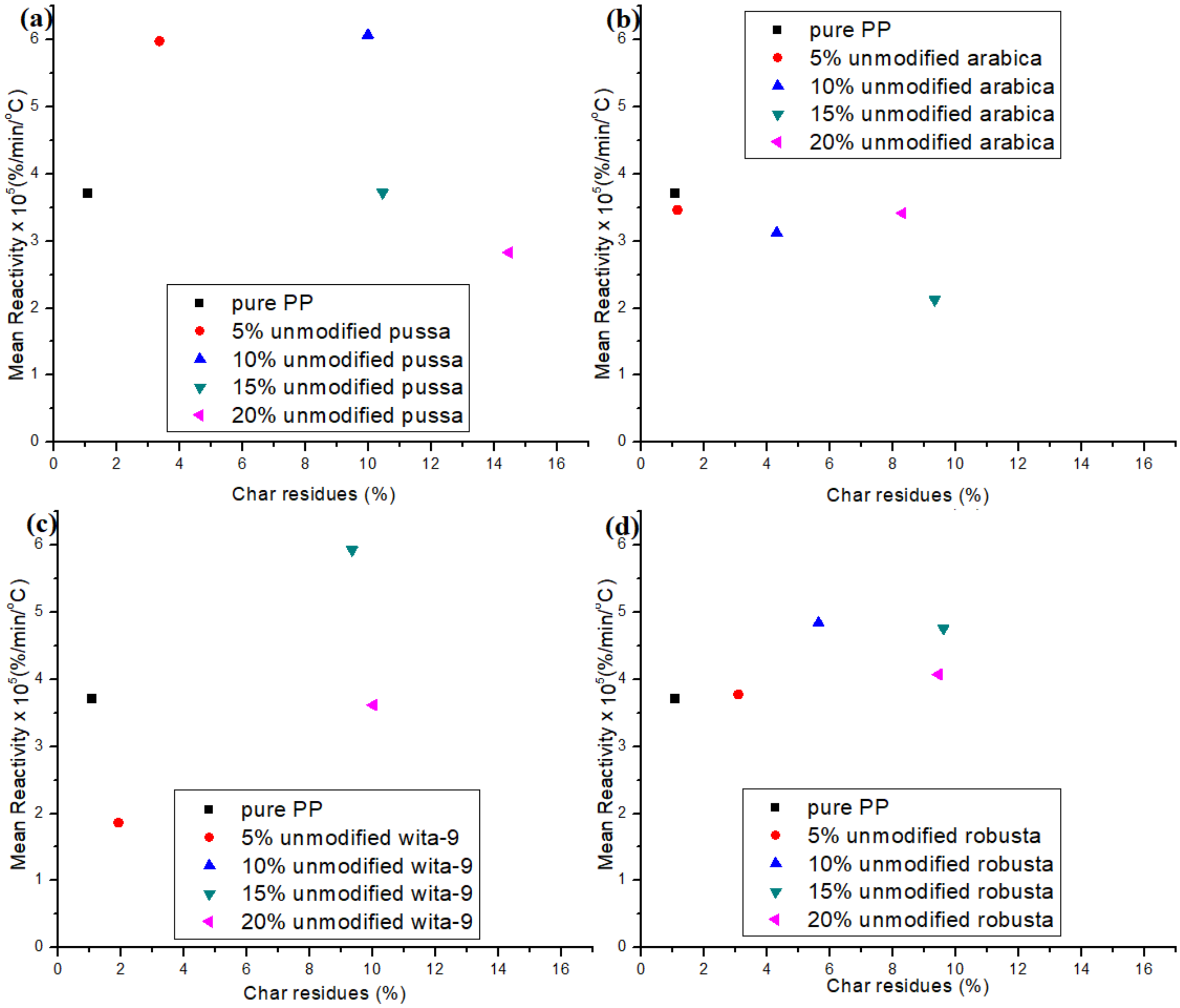

Fig. 5: Mean reactivity vs char residues for unmodified bio-char reinforced PP a) Pussa rice b) Arabica coffee c) Wita-9 rice d) Robusta coffee

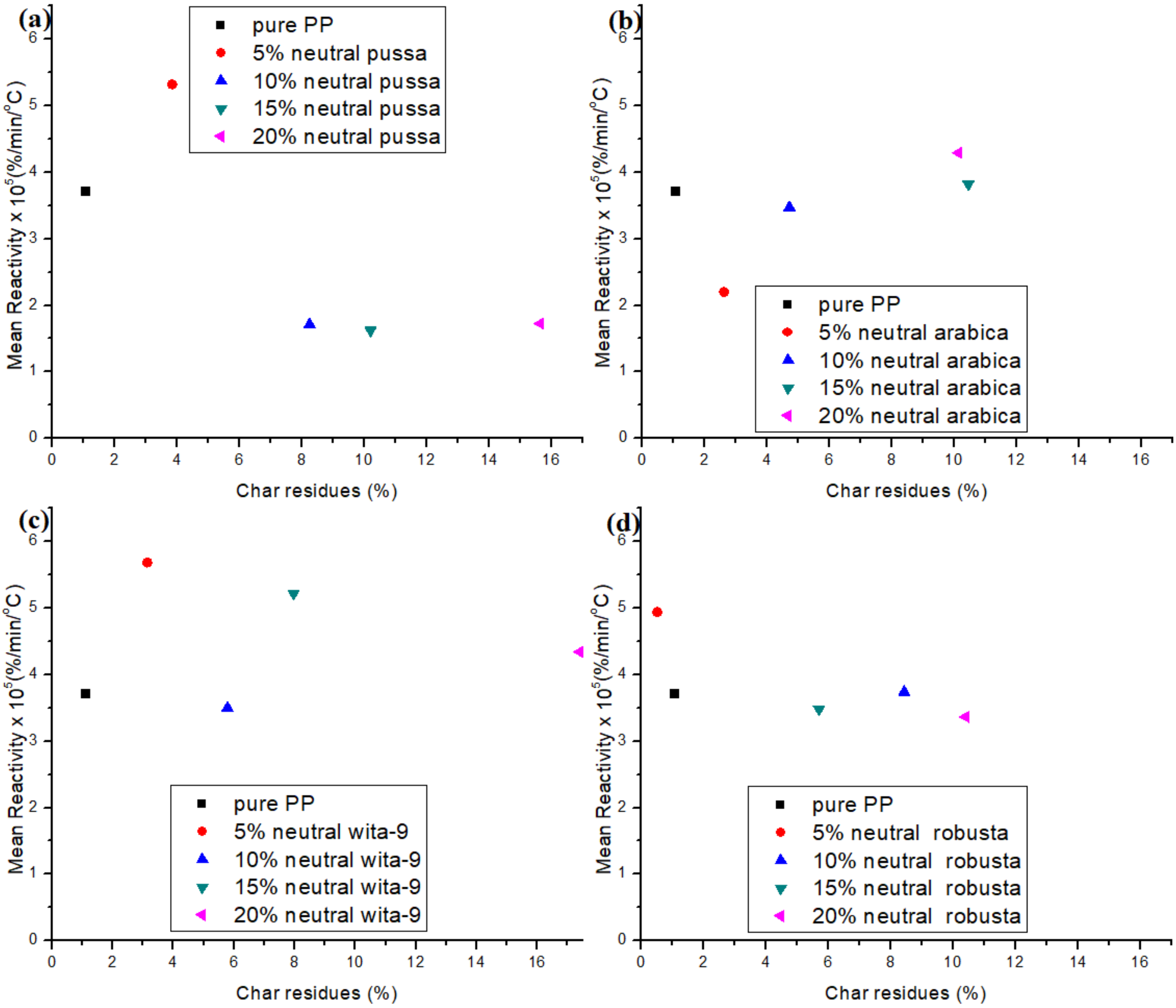

Fig. 6: Mean reactivity vs char residues for neutral bio-char reinforced PP a) Pussa rice b) Arabica coffee c) Wita-9 rice d) Robusta coffee

3.5 Reactivity

Reactivity analysis of the developed fiber-reinforced PP samples was obtained by the Ghetti method [48]. The results for the obtained mean reactivities at maximum weight loss are shown in Figures 5-7. The highest mean reactivity attained was 6.1×10^{-5} %/minute/°C obtained when 10 % unmodified *Pussa* rice husks bio-char was used to reinforce PP (see Figure 5a). For coffee husks, the highest mean reactivity attained was 5.0×10^{-5} %/minute/°C obtained when 5 % neutral *Robusta* coffee husks bio-char was used to reinforce PP (see Figure 6d). A clear trend is hard to note but, increase in filler loading leads to a reduction in mean reactivities for fiber-reinforced PP loaded with modified and unmodified *Arabica* coffee, neutral and modified *Robusta* coffee material as well as modified *Pussa* rice bio-char material.

The reductions in mean reactivities with increasing filler loadings are attributable to the fact that inclusion filler material reduces the amount of meltable matrix in the fiber-reinforced PP [2]. Another reason for this reduction could be high char conversion time which provides multiple insulative layers in the fiber-reinforced PP [49].

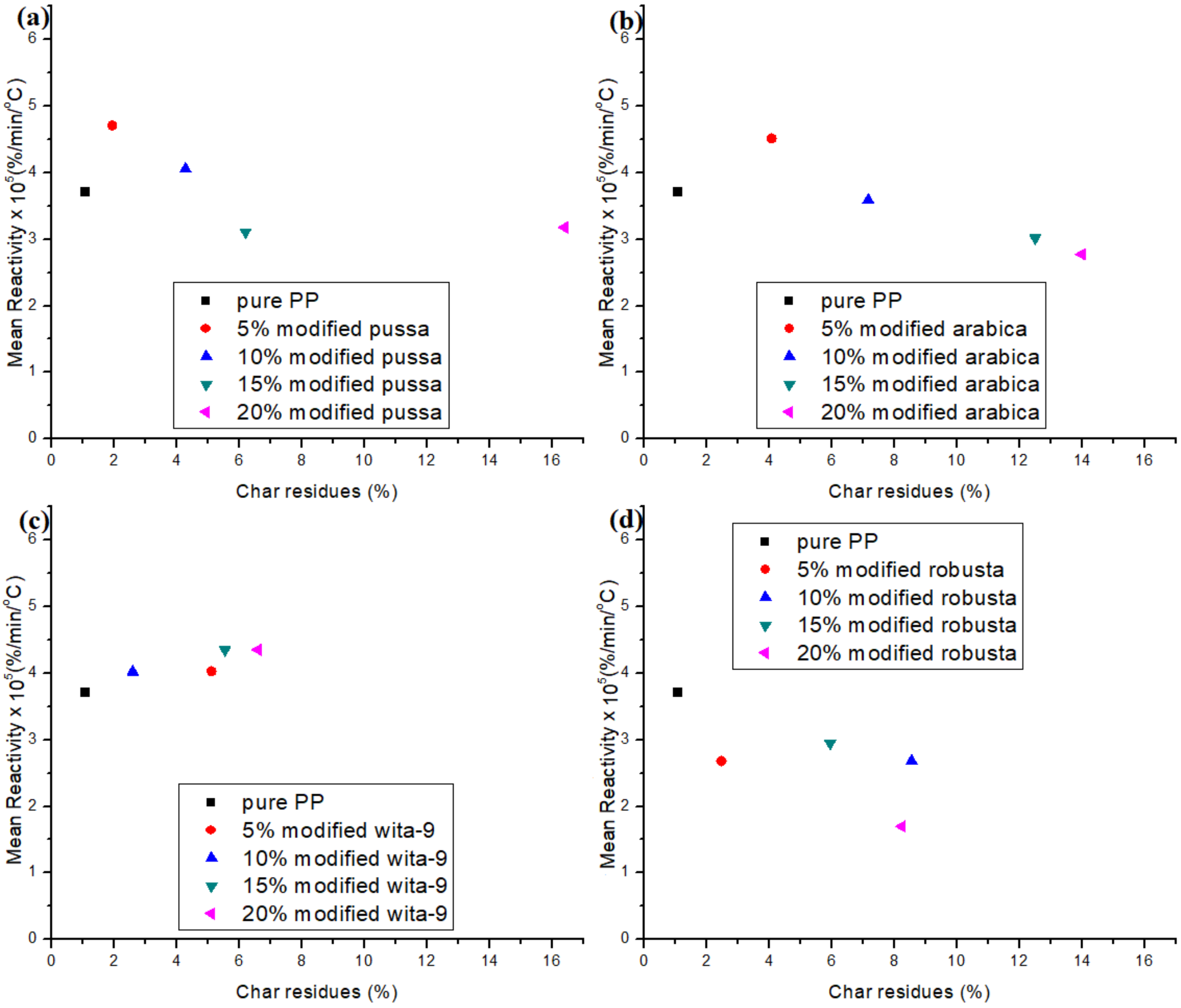

Fig. 7: Mean reactivity vs char residues for modified bio-char reinforced PP a) Pussa rice b) Arabica coffee c) Wita-9 rice d) Robusta coffee

Mean reactivity versus char residues plots gives an understanding of the time at which the peak temperature is reached during combustion of the fiber-reinforced plastics (see Figures 5-8). Basically, it shows the ratio of peak temperature to time at which the peak temperature is reached. Generally, for bio-char reinforced PP, it can be seen that this ratio increases with increasing filler loading. The trend is noticed clearly in unmodified *Robusta* coffee, neutral *Arabica* coffee and modified *Wita-9* rice husks bio-char reinforced PP. This therefore reflects that higher temperatures are required to reach peak decompositions of the developed plastics. This is because inclusion of rice and coffee husks bio-char filler material reduces the meltable matrix [2].

It should be noted that this ratio has a relationship with the mechanical properties of fiber-reinforced plastics. A higher ratio signifies good mechanical properties (higher tensile strength and Young's modulus as well as lower elongations at break) because fiber in the fiber-reinforced plastic takes longer to generate volatiles, resulting in porosity [50]. Additionally, pre-treatment has been noted to increase decomposition temperatures (and therefore ratio of the mean reactivity to char residues) of fiber material because the treatment removes natural and artificial impurities which renders fibers more hydrophobic and thus increases adhesion properties with the polymer matrix, which enhance mechanical properties [16].

Another explanation the ratio could bring about is that of activation energy. This is the energy required to start a combustion reaction. This follows that a higher ratio is synonymous with higher activation energy and therefore low reaction index with oxygen/air [51]. This is so because in conditions where the reaction with oxygen/air is low, the peak temperature reached during combustion of fiber-reinforced plastics is always at maximum. Inclusion of bio-char filler material therefore leads to an increasing ratio and therefore higher activation energy is required to onset degradation of the fiber-reinforced plastic. It is such plastics that are desired in applications that require high flame retardancy properties.

Figure 8 shows the ratio of mean reactivity to char residues on a filler loading aspect. In Figure 8a, it is seen that the ratios are low as shown by the dense appearance of data points on the left hand side of the figure, compared to the ratios in Figure 8d. It is obvious that increase in filler loading causes an increasing trend in the ratio of mean reactivity to char residues. This increasing ratio is observed by the right-hand shift of points as filler loading increases. This follows that as filler loading increases, the fiber-reinforced plastic increasingly reaches higher peak temperatures in a given thermal decomposition time and therefore this signifies improving thermal properties. This is because of increasing char and volatile matter formation levels as mean reactivity increases [52].

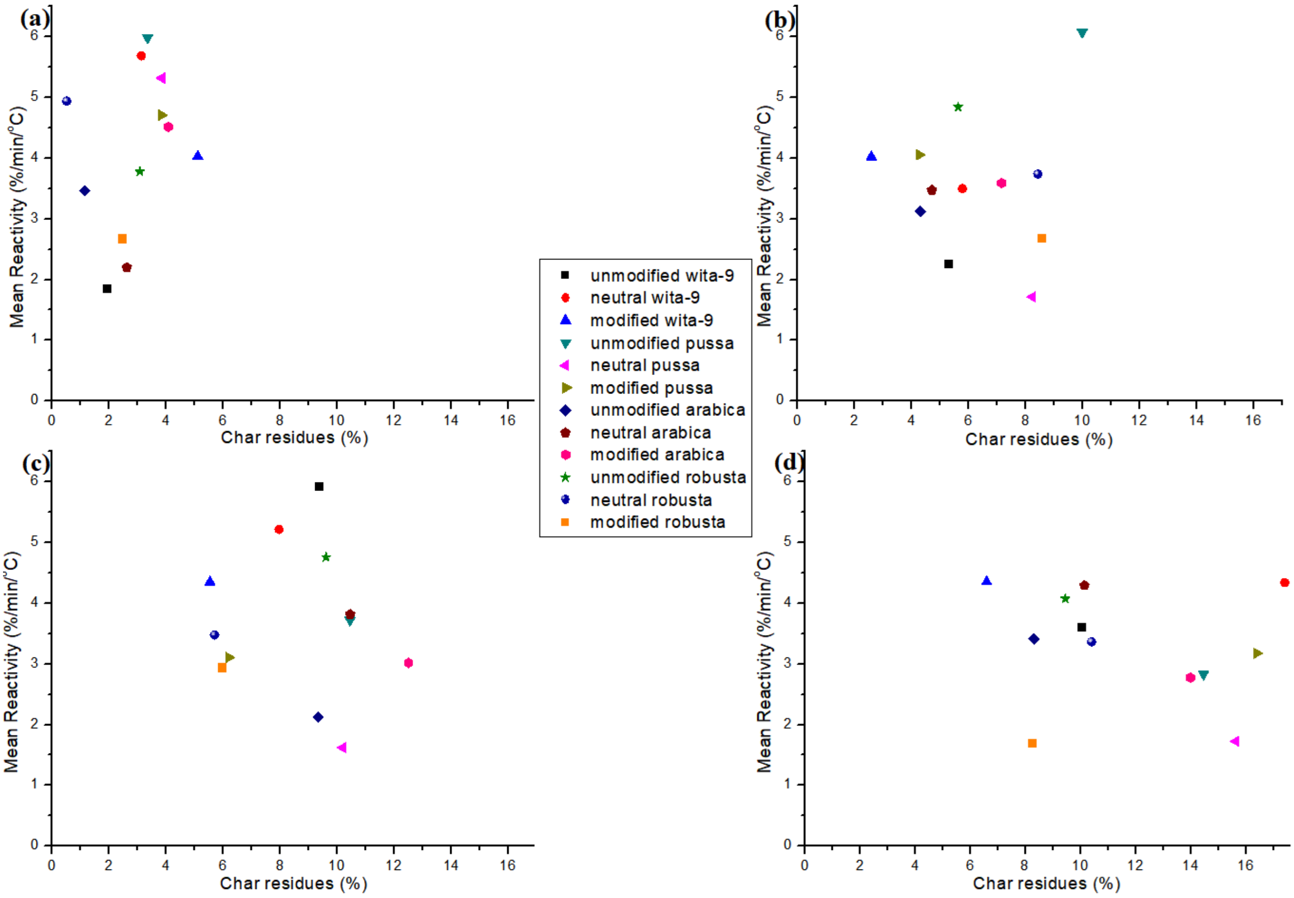

Fig. 8: Mean reactivity vs char residues for developed bio-char reinforced PP with various filler loadings a) 5% b) 10% c) 15% d) 20**%**

4. CONCLUSIONS

In this work, melt mixing coupled with compression molding was used to produce fiber-reinforced plastics. With this preparation method, a homogeneous composite material was obtained. Thermogravimetric analysis of fiber-reinforced PP made with bio-chars of *Arabica* and *Robusta* coffee husks as well as *Puss*a and *Wita-9* rice husks was carried. Thermogravimetry was carried out on an Eltra Thermostep thermogravimetric analyzer under nitrogen atmosphere at a heating rate of 20 °C/min. It was found that rate of weight loss for pure PP was faster than those of fiber-reinforced PP. Consequently, char residues obtained after combustion were found to be high in the latter. From DTG, the maximum rate of decomposition was found to be much lower for fiber-reinforced PP compared to that of pure PP. Peak temperatures generally increased with increase in filler loading. Mean reactivities ranged between 1.6×10^{-5} %/minute/°C - 6.1×10^{-5} %/minute/°C, 1.9×10^{-5} %/minute/ºC - 5.9×10^{-5} %/minute/°C, 2.1×10^{-5} %/minute/°C - 4.5×10^{-5} %/minute/°C, 1.7×10^{-5} %/minute/°C - 4.9×10^{-5} %/minute/°C for *Pussa* rice, *Wita-9* rice, *Arabica* coffee and *Robusta* coffee respectively. Increase in filler content in the fiber-reinforced PP led to an increase in the ratio of peak temperature to time taken to reach the peak temperature, signalling improving mechanical and thermal properties. The alkali pre-treatment process caused the fibers to swell and it removed the artificial and natural impurities from the fiber surface. In short, due to the improvement in thermal stability with the inclusion of bio-chars in PP, application in Electrical appliances is highly recommended.

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