

Modified Cocoa Pod Husk-Filled Polypropylene Composites by Using Methacrylic Acid

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The effect of filler modification using methacrylic acid (MAA) on polypropylene (PP)/cocoa pod husk (CPH) composites was studied. The performances of unmodified and modified PP/CPH composites were analyzed for torque development, tensile properties, and thermal properties. The presence of MAA increased the stabilization torque of the PP/CPH composites. The tensile strength and modulus of the modified PP/CPH composites were improved compared to unmodified PP/CPH composites, but the elongation at break was reduced. The crystallinity and thermal stability of the PP/CPH composites increased after modification with MAA. All the composite property changes were due to the improvement in filler-matrix adhesion and this was confirmed by scanning electron microscopy (SEM).

Keywords: Cocoa Pod Husk; Polypropylene; Composites; Methacrylic Acid

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INTRODUCTION

Natural filler-based composite materials, which are often called biocomposites, have garnered interest among researchers and industries due to today's ecological problems and economic factors including the accumulation of agricultural waste and cost of products. Nowadays, there are numerous green and eco-friendly products made from natural filler and thermoplastic materials that have been successfully produced and marketed. Recently, natural filler has become a popular choice of filler in thermoplastic materials. This is due to the fact that natural fillers exhibit some excellent properties compared to conventional fillers. Natural fillers are inexpensive, are obtained from renewable resources, present a minimal health hazard, have low density, are less abrasive to processing machinery, and are eco-friendly (Chun *et al.* 2012; Salmah *et al.* 2012a; Chun *et al.* 2013b). The most well-known example of such a material is IKEA injection-moulded furniture, which is produced from polypropylene (PP)/wood flour biocomposites (Niskanen 2011). In Malaysia, Melsom Biodegradable Enterprise has produced a series of eco-friendly tableware from rice husk-filled thermoplastic biocomposites (Chun *et al.* 2013a).

Many natural fillers found in Malaysia are obtained from crop residues and by-products of the agricultural industry, such as the coconut shell (Chun *et al.* 2012; Salmah *et al.* 2012a; Chun *et al.* 2013a,b), palm kernel shell (Salmah *et al.* 2013; Salmah *et al.* 2012b), oil palm empty fruit bunch (Hassan *et al.* 2010), corn cob (Chun and Husseinsyah 2013; Yeng *et al.* 2013), and rice husk (Premala Hattotuwa *et al.* 2003). Cocoa (*Theobroma cacao*) is an important agricultural crop in several tropical countries, including Malaysia (Lucia *et al.* 2012). Cocoa pod husk (CPH) is a non-food part of the cocoa pod, and it usually accounts for 52 to 76% of the cocoa pod wet weight.

In the cocoa industry, every ton of dry cocoa bean produced will generate ten tons of cocoa pod husks as waste (Lucia *et al.* 2001). The CPH is readily abundant but does not have any marketable value; therefore, the utilizations of CPH as natural filler in thermo-plastic materials will provide a new application route for CPH into useful resources for the thermoplastic industry. Meanwhile, the utilization of CPH can bring economic benefit and reduce the ecological impact.

In general, compounding natural filler in thermoplastic materials would not produce good composite properties due to the weak interfacial adhesion between the hydrophilic natural filler and the hydrophobic matrix. Filler modification is one of the methods used to modify the hydrophilic properties of natural filler. Thus, the filler dispersion, wettability, and filler-matrix interaction can be enhanced *via* filler modification. In previous studies it was reported that natural filler modified with silane coupling agent (Chun *et al.* 2012; Xie *et al.* 2010), acrylic acid (Salmah *et al.* 2012a), maleic acid (Chun *et al.* 2013b), sodium dodecyl sulphate (Chun *et al.* 2013a), and modified fatty acid (Chun and Husseinsyah 2013) significantly improved the properties of the composite. In the present work, PP/CPH composites were developed and methacrylic acid (MAA) was used to modify CPH to enhance the properties of the PP/CPH composites. The effects of MAA on the torque development, tensile properties, thermal properties, and morphology of the PP/CPH composites were studied.

EXPERIMENTAL

Materials

Cocoa pod husk (CPH) was collected from cocoa plantations, Perak. The CPH was first dried in an oven at 80 °C for 24 h. The dried CPH was crushed into small pieces and further ground into fine powder. The CPH powder was sieved, and the average particle size of the CPH powder was 22 µm, measured using a Malvern Particle Size Analyzer Instrument.

Polypropylene (PP) type co-polymer, grade SM 340 was used as the matrix and was supplied by Titan Petchem (M) Sdn. Bhd. Methacrylic acid (MAA) and ethanol were obtained from Sigma Aldrich, Penang.

Table 1. Formulation of PP/CPH Composites

Materials	PP (phr)	CPH (phr)	MAA (%)
Unmodified PP/CPH	100	0, 10, 20, 30, 40	-
Modified PP/CPH	100	10, 20, 30, 40	3*

phr = part per hundred resin
* 3% from weight of CPH

Filler Modification

The MAA solution was prepared by dissolving 3% MAA into ethanol. CPH was added slowly into MAA solution and stirred continuously for 1 h. The CPH was soaked in MAA solution and left overnight (12 h). The soaked CPH was filtered and dried in an oven at 80 °C for 24 h.

Melt Compounding and Moulding Procedures

The unmodified and modified PP/CPH composites listed in Table 1 were compounded using a Brabender[®] Plastograph intermixer, Model EC PLUS in counter-rotating mode at 180 °C and a rotor speed of 50 rpm. The mixing procedures involved were as follows: i) the PP was transferred into the mixing chamber for 3 min until it melted homogeneously; ii) the unmodified or modified CPH was added to the melted PP and continuously mixed for 5 min. The total time for compounding was 8 min. All the compounds were moulded into 1 mm-thick sheets using a hotpress, model GT 7014A at 180 °C. The compression sequences involved were as follows: i) preheat the compound for 4 min; ii) compress the compound under a pressure of 100 kgf/cm² for 1 min; iii) cooling under the same pressure for 5 min. The PP/CPH composite sheets were cut into tensile bars using a dumbbell cutter with dimensions according to ASTM D638 type IV.

Processing Torque Measurement

The processing torque was measured during the compounding of the PP/CPH composites using a Brabender[®] Plastograph internal mixer. The torque changes of the composites with time were recorded and the torque versus time curves were plotted. The torque values at the end of processing time were taken as stabilization torque.

Tensile Testing

Tensile testing was carried out using an Instron Universal Testing Machine, model 5569. The load cell selected was 50 kN and the cross-head speed was 30 mm/min. The test was performed at 25 ± 3 °C.

Morphology Analysis

The tensile fracture surfaces of the PP/CPH composites were analysed using a scanning electron microscope (SEM), model JEOL JSM-6460 LA. The samples were coated with a thin layer of palladium for conductive purposes and analysed at 5 keV.

Fourier Transmission Infra-Red (FTIR) Spectroscopy

PerkinElmer Paragon 1000 FTIR spectrometer was used to characterize chemical groups in pure MAA, virgin PP, unmodified and modified CPH, and PP/CPH composites. The Attenuated Total Reflectance (ATR) method was selected. The sample was recorded with 4 scans in the frequency range 4000-600 cm⁻¹ with a resolution of 4 cm⁻¹.

Differential Scanning Calorimetry (DSC) Analysis

DSC analysis was evaluated using a DSC Q10, Research Instrument. The samples were cut into small pieces and placed into a closed aluminum pan with sample weights in the range of 7 ± 2 mg. The specimens were heated from 30 °C to 200 °C with a heating rate of 10 °C/min under a nitrogen atmosphere. The nitrogen gas flow rate was 50 mL/min. The degree of crystallinity of the composites (X_c) can be evaluated from DSC data using following equation,

$$X_c = (\Delta H_f / \Delta H_f^0) \times 100 \quad (1)$$

where ΔH_f is the heat of fusion of the PP/CPH composites, and ΔH_f^0 is the heat of fusion for 100% crystalline PP ($\Delta H_{100} = 209$ J/g).

Thermogravimetric Analysis (TGA)

TGA analysis was carried out using a TGA Pyris Diamond PerkinElmer apparatus. The samples were about 7 ± 2 mg in weight and were placed into a platinum crucible. The samples were then heated from 30 °C to 700 °C at a heating rate of 10 °C/min under a nitrogen atmosphere with a nitrogen flow rate of 50 mL/min.

RESULTS AND DISCUSSION

Torque Development

The torque-time curves of the neat PP, unmodified, and modified PP/CPH composites with different CPH contents are shown in Fig. 1. Generally, once the PP pellets were transferred into the mixing chamber, the torque rose rapidly due to the resistance exerted on the rotors by unmelt PP pellets. The torque decreased gradually with time as the PP pellets melted, which subjected them to the shearing reaction at high temperature. The torque in the PP/CPH composites increased again just after 3 min. This was due to the addition of CPH into the melted PP. The torque gradually decreased and achieved stabilization torque as the PP and CPH were compounded homogeneously. Similar trends of torque development have also been reported by many researchers (Shaari Balakrishana *et al.* 2012; Osman *et al.* 2012).

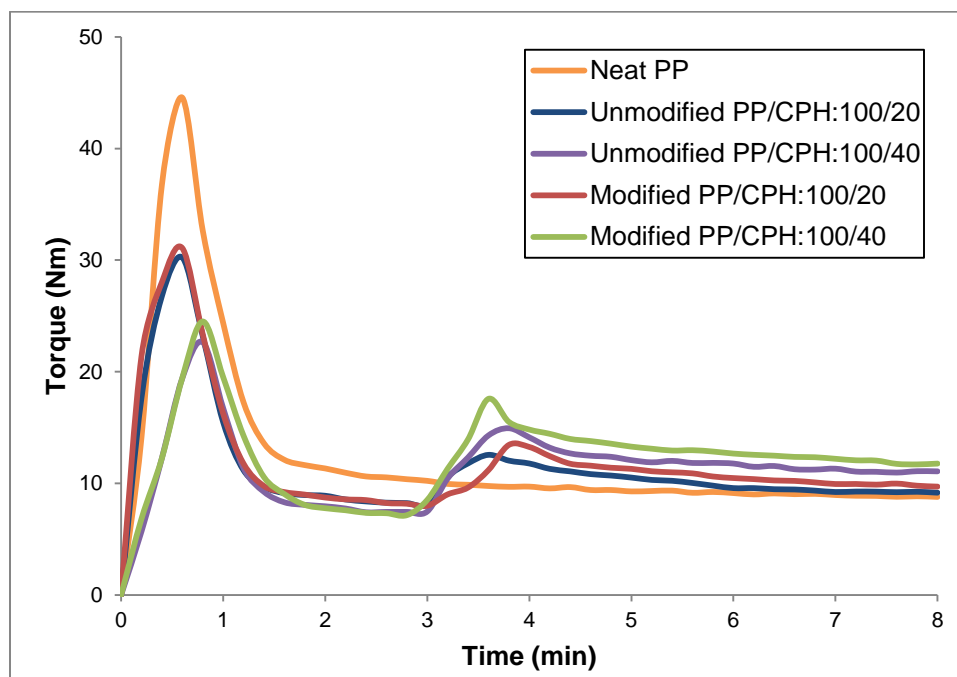


Fig. 1. The torque-time curves of neat PP and unmodified and modified PP/CPH composites

Figure 2 illustrates the stabilization torque *vs.* filler content for the unmodified and modified PP/CPH composites. As shown, both PP/CPH composites' stabilization torque increased with increasing CPH content. This result indicated that the dispersed CPH particles in the melted PP hindered the polymer chain mobility. The disperse resistance from the CPH led to an increase in stabilization torque at a higher CPH content. Meanwhile, the modified PP/CPH biocomposites had a higher stabilization torque than

the unmodified PP/CPH biocomposites. This is attributed to the modified CPH with MAA having better dispersion and filler-matrix interactions compared to unmodified CPH in the PP matrix; therefore, modified CPH yields a higher viscosity of PP/CPH biocomposites.

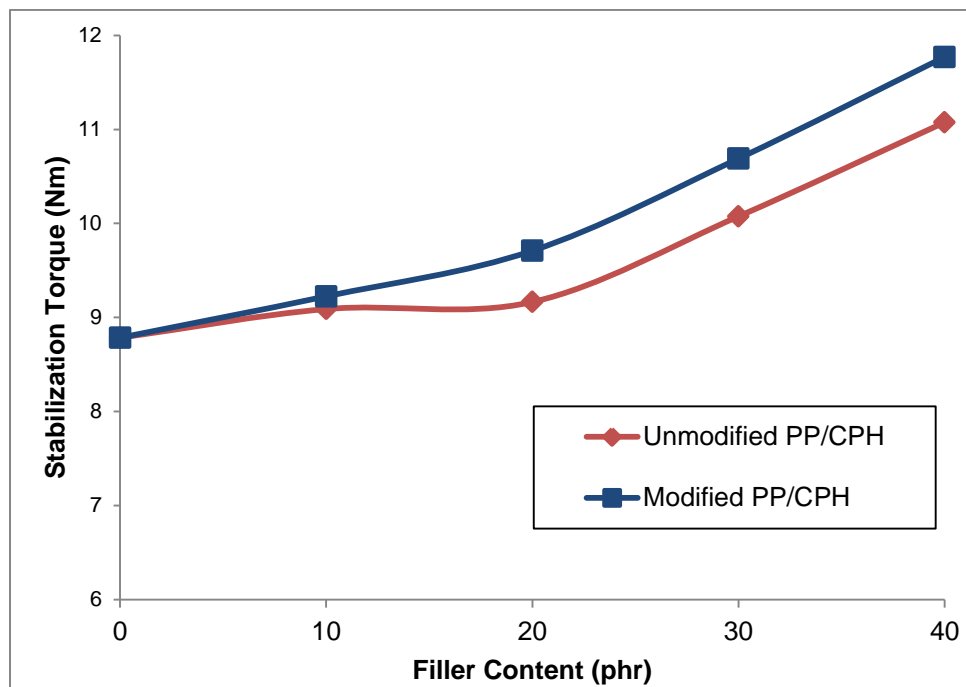


Fig. 2. The stabilization torque of unmodified and modified PP/CPH composites

Tensile Properties

Figure 3 illustrates the effect of CPH content and MAA modification on the tensile strength of the PP/CPH composites. The increase in CPH content reduced the tensile strength of the unmodified and modified PP/CPH composites. This was a common observation for the particular natural filler-containing thermoplastic composites; similar results were also found in previous studies (Chun *et al.* 2013a; Salmah *et al.* 2012c; Chun and Husseinsyah 2013). This particular form of natural filler usually has a low aspect ratio, and its ability to transfer stress from the matrix was poor; therefore, the addition of CPH decreased the tensile strength of the PP matrix.

Another reason for the decrease in tensile strength was poor wettability between the hydrophilic CPH and the hydrophobic PP matrix. The poor wettability contributed to poor filler dispersion and poor interfacial bonding. The poor interfacial adhesion between the filler and the matrix caused poor stress transfer and also allowed initial crack propagation. This finding is also supported by the presence of filler agglomeration. The modified PP/CPH composites, however, showed higher tensile strength than the unmodified PP/CPH composites.

The MAA modification increased the filler-matrix interaction by reacting with hydroxyl groups on the CPH surface *via* esterification. As a result, the modified CPH had better wettability in the PP matrix, which improved the filler dispersion and filler-matrix adhesion. Chun *et al.* (2013b) and Salmah *et al.* (2012a) reported that modifying coconut shell powder with maleic acid and acrylic acid improved the tensile strength of the resulting composites.

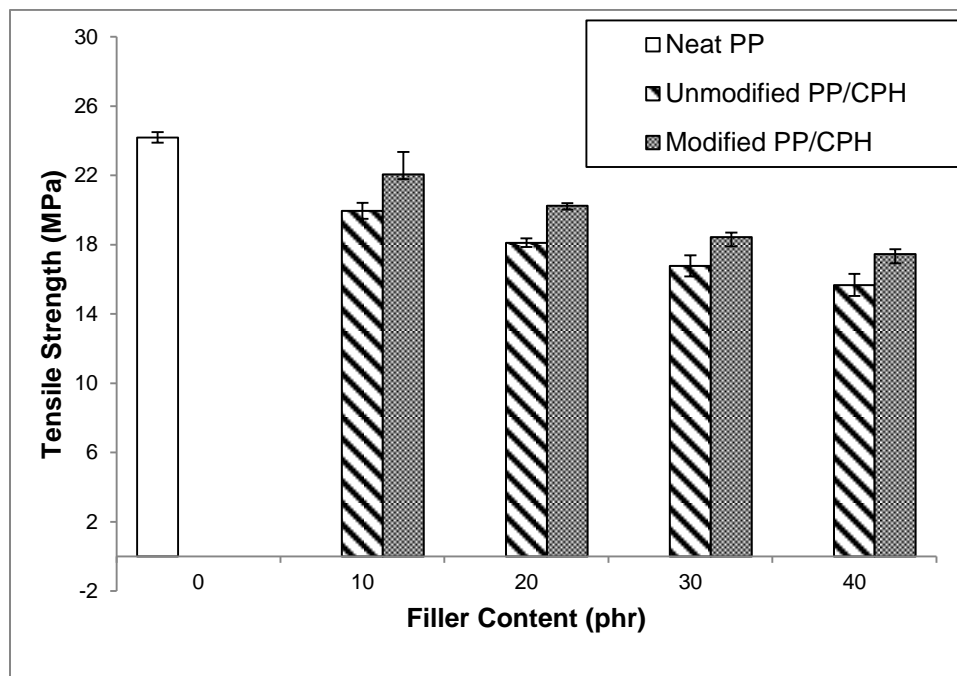


Fig. 3. Effect of filler content on tensile strength of unmodified and modified PP/CPH composites

The elongation at break of the unmodified and modified PP/CPH composites is shown in Fig. 4. The results indicate that the elongation at break of both composites had decreasing trends as the CPH content increased. The decrease in elongation at break was probably caused by the presence of rigid CPH particles, which inhibit the PP chain mobility, resulting in more brittle composites. This is a general trend that has also been reported by other researchers (Shaari Balakrishana *et al.* 2012; Osman *et al.* 2012; Salmah and Ismail 2008). Nevertheless, modified PP/CPH with MAA showed lower elongation at break values compared to unmodified PP/CPH composites. The addition of MAA chemically altered the CPH surface, making it more hydrophobic, leading to enhanced filler-matrix interfacial bonding; therefore, the ductility of the PP/CPH composites was reduced by the enhanced interfacial bonding. Salmah *et al.* (2011a) also found a similar effect of modified chitosan with acrylic acid on the elongation at break of PP/chitosan composites.

Contrary to the negative effect on the elongation at break, the incorporation of unmodified and modified CPH yielded PP/CPH composites with an increase in tensile modulus (as shown in Fig. 5). It is possible that the friction between the CPH particles and the PP matrix generated a rigid interface, which induced the flexibility of the PP matrix. This led to more rigid and stiffer composites. A similar observation was also reported by Faisal *et al.* (2013). Consequently, modification of PP/CPH composites with MAA increased the tensile modulus. It can be seen that modified CPH had better filler dispersion and interfacial interaction with the PP matrix. The improvement in filler dispersion increased the surface area of the filler-matrix interaction and it, along with the enhanced interfacial bonding, yielded a stiffening effect on the PP/CPH composites. Additionally, the MAA modification also enhanced the nucleating effect of CPH on the PP matrix and it increased the stiffness of the composites as the crystallinity increased. According to Farsi (2010), the tensile modulus of PP/wood flour composites was

improved by acrylic acid treatment; the presence of acrylic acid increased the bonding strength between the wood flour and the PP matrix.

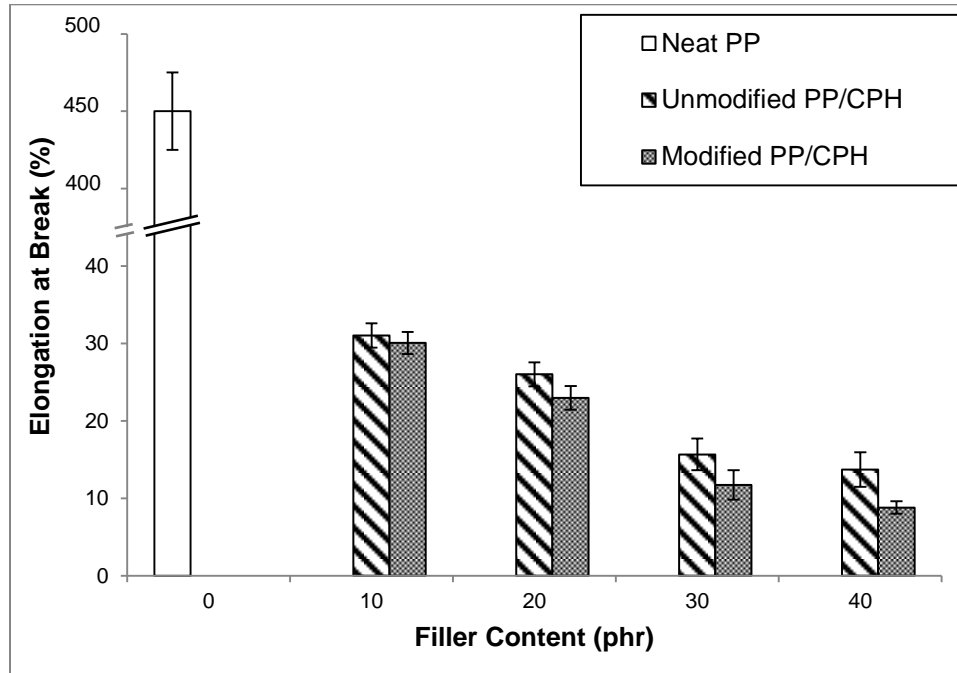


Fig. 4. Effect of filler content on elongation at break of unmodified and modified PP/CPH composites

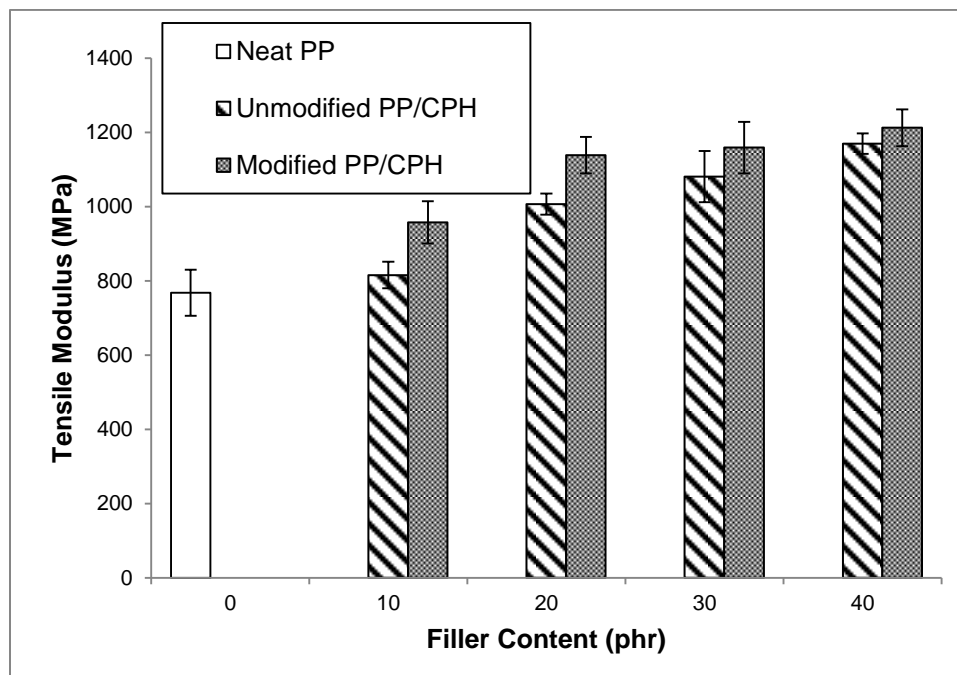


Fig. 5. Effect of filler content on tensile modulus of unmodified and modified PP/CPH composites

Morphology Study

SEM micrographs of the tensile fracture surface of the unmodified PP/CPH composites at 20 and 40 php of CPH content are displayed in Figs. 6 (a) and (b). The SEM micrographs show that the CPH particles were poorly dispersed in the PP matrix and the poor interfacial adhesion between the CPH particle and the PP matrix. This observation was demonstrated by the presence of holes due to the filler pull-out and detached CPH particles. In contrast, modified PP/CPH composites exhibit a more brittle fracture surface compared to unmodified PP/CPH composites (as shown in Figs. 6 (c) and (d)). Other than that, the modified CPH particles were well dispersed and embedded in the PP matrix. This indicates that modified CPH has better wettability with the hydrophobic PP matrix. The less filler pull-out evidenced the better filler-matrix adhesion between the modified CPH and the PP matrix.

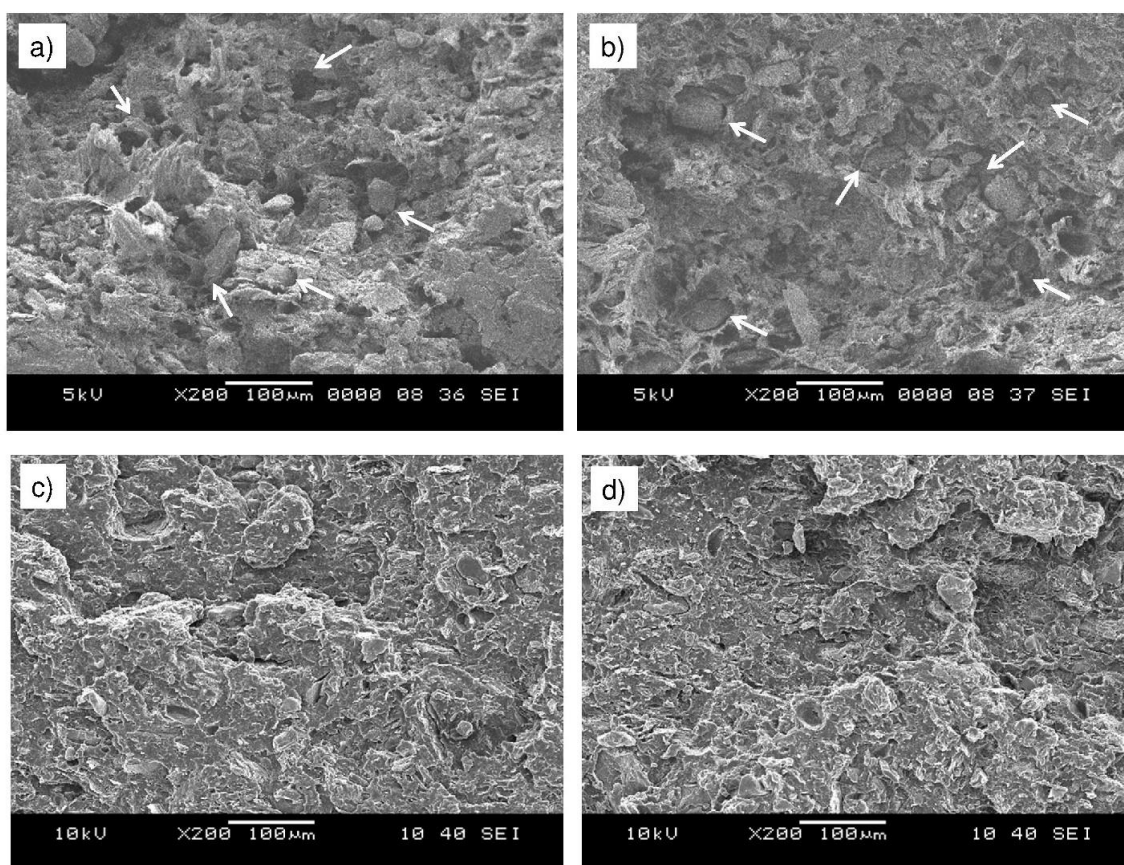


Fig. 6. SEM Micrographs of fracture surface: (a) unmodified PP/CPH:100/20; (b) unmodified PP/CPH:100/40; (c) modified PP/CPH:100/20; (d) modified PP/CPH:100/40.

Fourier Transform Infra-Red (FTIR) Analysis

The FTIR spectra of pure MAA, the unmodified CPH, and CPH modified with MAA are shown in Fig. 7. The main characteristic peak of pure MAA, CPH, and neat PP are summarized in Table 2. Figure 8 shows the FTIR spectra of neat PP, unmodified PP/CPH composites, and modified PP/CPH composites.

The broad peak at 3291 cm^{-1} was assigned to the $-\text{OH}$ groups on the CPH surface and it also reflected the hydrophilicity of CPH. The addition of CPH into PP matrix was also attributed to the $-\text{OH}$ group peak at 3300 cm^{-1} . The hydrophilicity of CPH was

significantly reduced after modification with MAA, as the intensity of -OH groups absorptions band decreased compared to unmodified CPH. Peaks at 1601 cm^{-1} and 1043 cm^{-1} were found in PP/CPH composites. The peaks were assigned to the $\text{C}=\text{C}$ stretching from hemicellulose, C-O-C and C-O groups of cellulose and lignin from CPH.

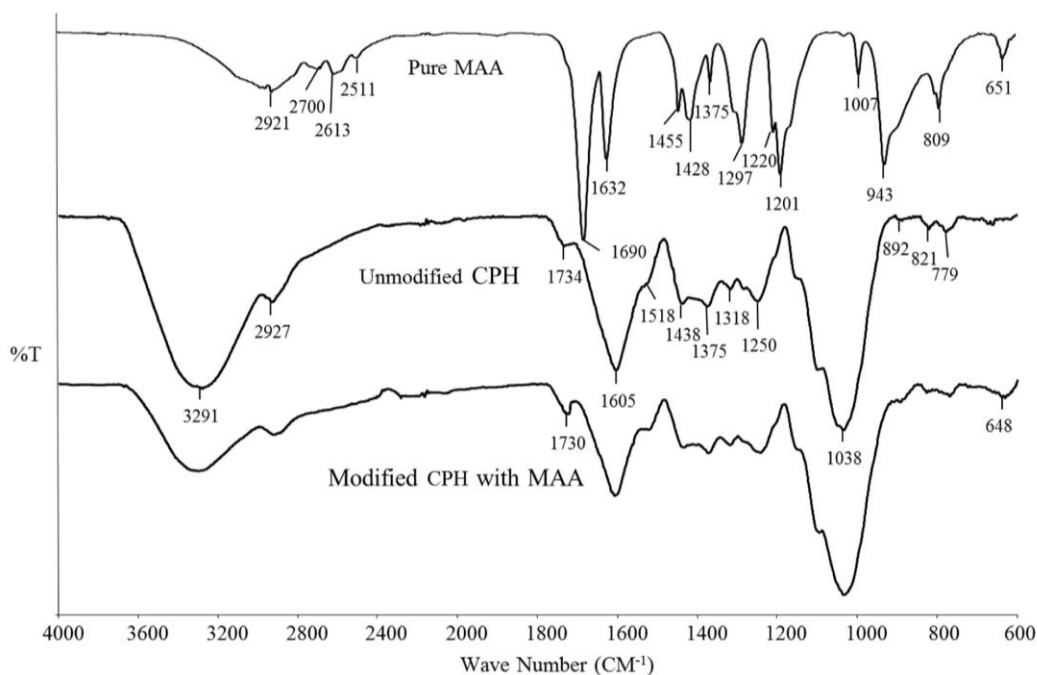


Fig. 7. FTIR spectra of pure MAA, unmodified, and modified CPH

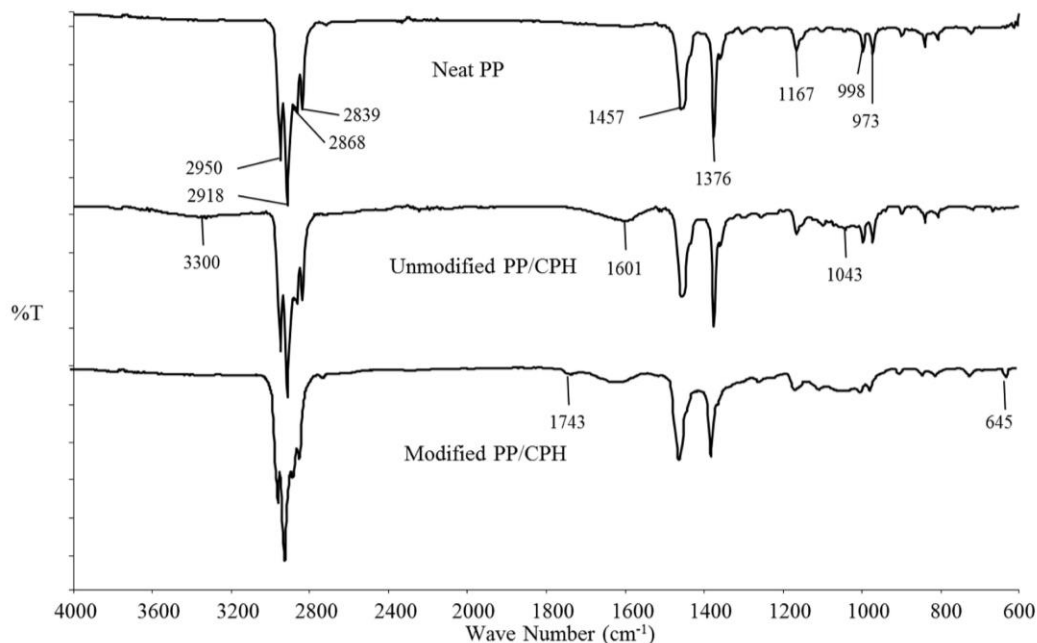


Fig. 8. FTIR spectra of neat PP, unmodified, and modified PP/CPH composites

Table 2. Functional Groups of Pure MAA, CPH, and neat PP

Methacrylic acid	
Wave number (cm ⁻¹)	Functional group
3000-2850	C-H stretching vibration
2700, 2613, 2511	-OH stretching vibration of carboxylic acid
1690	C=O stretching vibration of carboxylic acid
1632	C=C stretching vibration
1455	C-H bending vibration
1428	O-H bending vibration of carboxylic acid
1375	-CH ₃ bending vibration
1320-1000	C-O stretching vibration of carboxylic acid
943	O-H bending vibration of carboxylic acid
809, 651	=C-H bending vibration
Cocoa Pod Husk	
Wave number (cm ⁻¹)	Functional group
3800-3000	Hydroxyl group (-OH) of CPH and absorbed moisture
2927	C-H stretching vibration
1734	Carboxyl (C=O) group from hemicellulose
1605	C=C stretching from hemicellulose
1518	Ring conjugated C=C stretching of lignin
1438	CH ₂ groups deformation from cellulose or C-H deformation in lignin
1375	C-H groups deformation in cellulose and hemicellulose
1318	C-H groups vibration in cellulose
1250	C-O groups from acetyl group in lignin
1000-1150	C-O-C and C-O groups from main carbohydrates of cellulose and lignin
700-900	C-H vibration in lignin
Neat Polypropylene	
Wave number (cm ⁻¹)	Functional group
3000-2800	C-H stretching vibration
1457	-CH ₂ bending vibration
1376	-CH ₃ bending vibration
1167	-CH ₃ symmetric deformation vibration
998	-CH ₃ rocking vibration
973	-CH ₂ rocking vibration

The increased peak intensity at 1730 cm^{-1} on modified CPH and the presence of a new peak at 1743 cm^{-1} on modified PP/CPH evidenced the existence of an ester bond between MAA and CPH. The new peak at 648 cm^{-1} appeared in modified CPH (Fig. 7), and a peak at 645 cm^{-1} for modified PP/CPH (Fig. 8) indicated $=\text{C}-\text{H}$ bending vibration of bonded MAA on CPH surface. However, other characteristic peaks of MAA could not be observed in modified CPH. This might be due to the overlapping of characteristic peaks between MAA and CPH. The schematic reaction of MAA, CPH, and PP matrix is illustrated in Fig. 9.

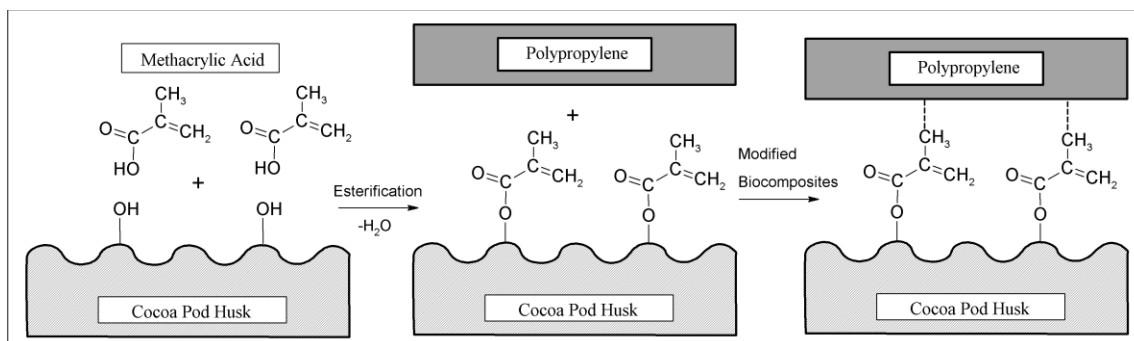


Fig. 9. Schematic reaction between MAA, CPH, and the PP matrix

Differential Scanning Calorimetry (DSC)

The DSC curves of neat PP and the unmodified and modified PP/CPH composites are displayed in Fig. 10. All the DSC data are summarized in Table 3. The melting temperature (T_m) of neat PP was $165\text{ }^\circ\text{C}$ with a crystallinity of 27%. From Table 2, the crystallinity of the PP/CPH composites increased with increasing CPH content. This result is due to the nucleating effect of the CPH. This result was consistent with a previous study (Chun *et al.* 2012; Salmah *et al.* 2012a; Chun *et al.* 2013a,b; Chun and Salmah 2013).

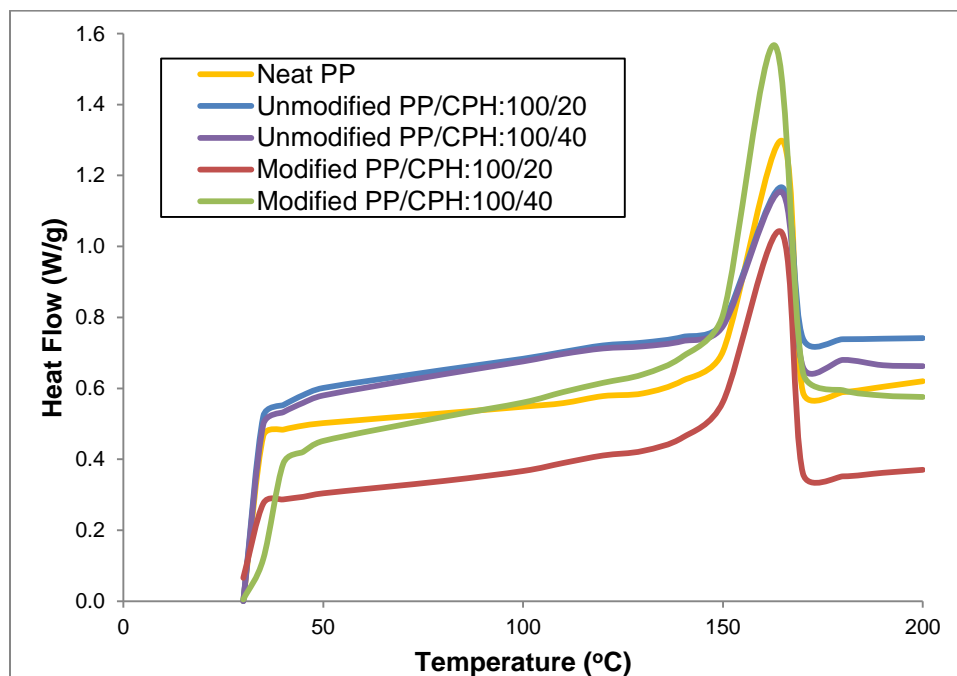


Fig. 10. DSC curves of neat PP and unmodified and modified PP/CPH composites

Furthermore, the modified PP/CPH composites showed higher crystallinity compared to the unmodified PP/CPH composites. This can be explained by the presence of MAA promoting the migration and diffusion of PP chains to form a transcrystalline structure on the filler surface.

Most findings have shown that for PP/natural filler composites, the filler modification can enhance the nucleating effect of natural filler and it increases the crystallinity of the composite (Salmah and Ismail 2008; Salmah *et al.* 2011a; Salmah *et al.* 2011b, 2012c). The T_m of PP/CPH biocomposites showed no significant change from the CPH content and MAA modification.

Table 3. DSC Data of Unmodified and Modified PP/CPH Biocomposites

Materials	T_m ($^{\circ}\text{C}$)	X_c (%)
Neat PP	165	27
Unmodified PP/CPH:100/20	165	28
Unmodified PP/CPH:100/40	165	31
Modified PP/CPH:100/20	165	30
Modified PP/CPH:100/40	164	43

Thermogravimetric Analysis (TGA)

Derivative thermogravimetric (DTG) and TGA curves of neat PP and CPH, as well as unmodified and modified PP/CPH composites are shown in Figs. 11 and 12, respectively. All the data from the DTG and TGA curves are summarized in Table 4.

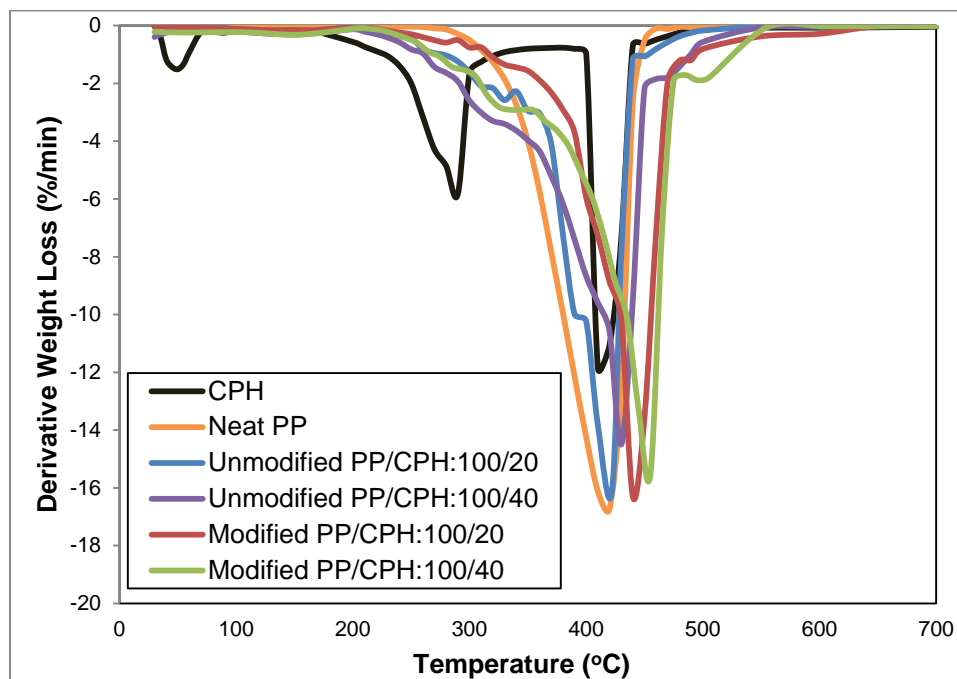


Fig. 11. DTG curves of CPH, neat PP, and unmodified and modified PP/CPH composites

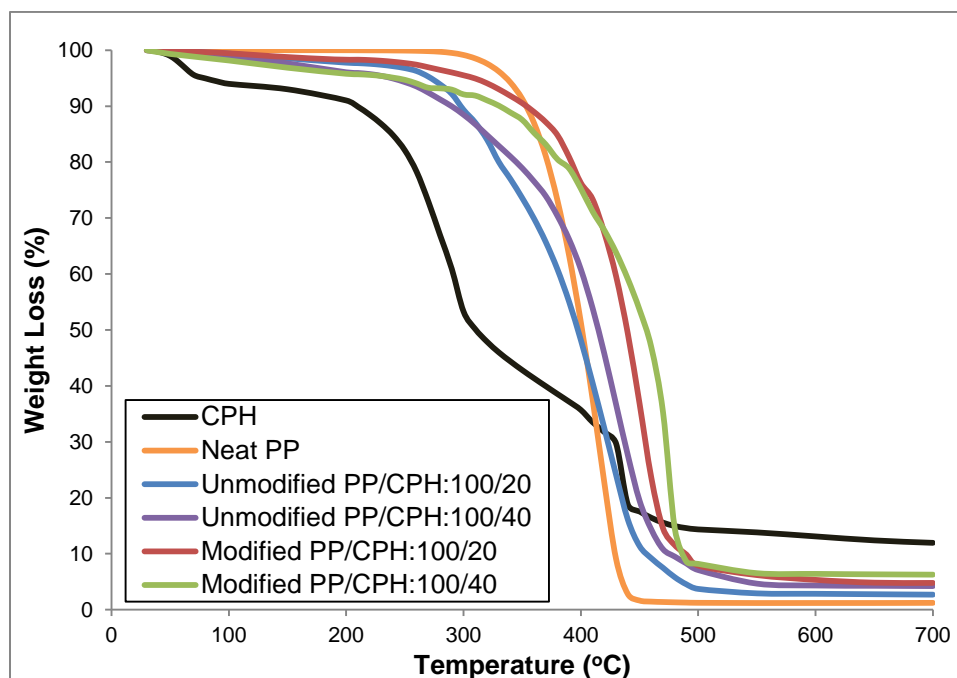


Fig. 12. TGA curves of CPH, neat PP, and unmodified and modified PP/CPH composites

According to the DTG curve, the CPH decomposed in 3 steps: i) evaporation of moisture in CPH at a temperature of 30 to 100 °C; ii) decomposition of hemicellulose at 200 to 350 °C; and iii) decomposition of lignin and cellulose at a temperature above 350 °C. The neat PP decomposed in single step above 300 °C (as shown in Fig. 11), and the decomposition temperature at maximum rate (T_{dmax}) was 418 °C. According to Table 4, unmodified and modified PP/CPH composites had undergone an early thermal degradation as evidenced from the temperature at 5% weight loss ($T_{d5\%}$).

Table 4. TGA Data of Unmodified and Modified PP/CPH Composites

Sample	$T_{d5\%}$ (°C)	T_{dmax} (°C)	Residue at 700 °C (%)
Neat PP	336	418	1.22
Unmodified PP/CPH:100/20	272	422	2.69
Unmodified PP/CPH:100/40	246	432	4.22
Modified PP/CPH:100/20	292	439	4.79
Modified PP/CPH:100/40	249	455	6.27

An increase in CPH content decreased the $T_{d5\%}$ of both composites. Alternately, the T_{dmax} of the PP/CPH composites was higher at a higher CPH content. This indicated that the addition of more CPH increased the thermal stability of the PP/CPH composites at high decomposition temperatures. The early thermal decomposition of the composites was assigned by the loss of moisture and decomposition of hemicellulose in the CPH; however, a high thermal stability pyrolysis material was generated from the thermal decomposition of hemicellulose. Thus, the pyrolysis material was providing a shielding effect on the composites and delayed the thermal decomposition process (Chun *et al.* 2012; Salmah *et al.* 2012a; Chun *et al.* 2013a,b). Shih and Huang (2011) reported that

increasing the banana fiber content increased the formation of pyrolysis material and inhibited the thermal decomposition of the composite. In addition, the thermal stability of the PP/CPH composites increased, as seen from the increase in $T_{d5\%}$ and T_{dmax} . The improvement in thermal stability was also supported by the higher residual content at 700 °C as compared to the unmodified PP/CPH composites. This was because the MAA modification enhanced the filler dispersion and the filler-matrix interaction. According to Araujo *et al.* (2008) and Arbelaiz *et al.* (2006), modified curaua fiber and flax fiber provides better thermal stability for the composites tested in their studies.

CONCLUSIONS

1. The utilization of CPH as filler in PP composites reduced the waste from cocoa plantations. The developments of PP/CPH biocomposites have potential to replace forest product, such as wooden fitting, fixtures, decking, and furniture.
2. The addition of the CPH in the PP/CPH composites reduced the tensile strength and elongation at break, but it increased the tensile modulus. The reduction in strength was due to poor filler-matrix interaction, which can be observed through the SEM micrographs.
3. The incorporation of CPH resulted in an early thermal decomposition of the PP/CPH composites; however, an increased CPH content raised the thermal stability of the composites for higher temperatures. The crystallinity of the PP/CPH composites also increased with CPH content.
4. The modification of CPH with MAA improved the tensile strength and tensile modulus of the PP/CPH composites. It also increased the thermal stability and crystallinity of the PP/CPH composites. Those improvements were due to the enhanced filler-matrix interaction. The FTIR results show that the presence of ester bonding between MAA and CPH in modified CPH and modified PP/CPH composites.

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