Preliminary Study of Palm Oil Based Coupling Agent for Polypropylene/Cocoa Pod Husk Composites

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INTRODUCTION

Cocoa (Theobroma Cacao) is one of the important crops among tropical countries including Malaysia. Cocoa pod husk (CPH) - a non-food part of cocoa fruit and is main waste material in cocoa industry [2,3,4]. In the cocoa industry estimate of cocoa pod husk generated as waste is around 40 million tons annually. Meanwhile, the CP does not have economic value and it burned as the way to dispose the CPH waste by farmer. Thus, the plenty of CPH not only the challenge for waste management and also increased the environmental impact. Consequently, the present work is developed to explore utilize of CPH as filler in thermoplastic materials. Additionally, the utilization of CPH will bring economic benefit and decreased the environmental impact. On the other hand, the abundance of hydrophilic hydroxyl groups of natural filler due to poor mechanical properties and poor water resistivity to a composite [9,20,21]. Many of literatures reported composites with neat natural filler show poor tensile strength and filler-matrix adhesion [1,4,16,17,18]. Therefore, there are numerous kind of coupling agent (such silane treatment [4,12,13,15], use of maleated polymer [6,10,1], fatty acid and its derivative [5,16,3,9,10,14,15] had been use to alter the hydrophilic natural filler in order to improve adhesion between natural filler and matrix.

To date, a new palm oil based coupling agent (POCA) had been initially developed in our laboratory. The POCA is type of glycidyl fatty acid ester, which consist of a reactive site (oxirane group) and organophilic site (fatty acid chains). In ideal, the POCA can effectively bond on filler surface by reacting with hydroxyl groups. At the same time, the chemical bonded POCA will change the properties of natural filler surface from hydrophilic to organophilic. In result, the treated natural filler with POCA had better filler dispersion and adhesion with PP matrix. Conclusion: From the results, the POCA show a potential as an effective coupling agent on PP/CPH composites, as the POCA had able to enhanced the tensile properties and interfacial properties.

Methodology:

Materials:

Polypropylene (PP, type co-polymer) used as matrix was supplied by Titan Petchem (M) Sdn. Bhd. The cocoa pod husk (CPH) use in this research was collected from cocoa plantation (Perak, Malaysia). The collected...
CPH was dried in oven at 80°C for 24 hours. The dried CPH was ground into fine powder and sieved to obtain average particle size of 22µm, which analyzed by Malvem Particle Size Analyzer Instrument. The palm oil based coupling agent (POCA) was prepared by reacting glycidyl chloride and sodium fatty acid derived from palm oil (as shown in Figure 1). The chemical used in this experimental was supplied by Sigma Aldrich.

**Fig. 1:** Schematic reaction of gycidyl chloride and sodium fatty acid from palm oil to produce palm oil based coupling agent.

**Filler Treatment:**
Firstly, the POCA-ethanol solution with 1, 3 and 5 wt% concentrations were prepared. The filler treatment was carried out by immersing the CPH in POCA-ethanol solution under constant stirring for 1 hour. Next, the CPH was left in the solution for 12 hours. The treated CPH was filtered and dried in oven at 80°C for a day.

**Preparation of PP/CPH Composites:**
The PP/CPH composites were prepared using a BrabenderPlastrographintermixer (Model EC PLUS). The PP and CPH were compound at 180°C for 8 minutes and a rotor speed of 50 rpm (counter rotating mode). The formulation of composite was shown in Table 1. Then, the composite compounds was moulded into sheet form (1mm thickness) at 180°C using a Hotpress (model GT 7014A). Composite sheets were cut into dumbbell shape with dimension according to ASTM D 638 Type IV.

<table>
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<tr>
<th>Table 1: Formulation of PP/CPH composites.</th>
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<tr>
<td>Materials</td>
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<td>PP/CPH composites</td>
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<td>phr = part per hundred resin</td>
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* based on weight of CPH

**Tensile Test:**
All composites tested for tensile properties by using an Instron Testing Machine (Model 5569). A cross-head speed of 30 mm/min was used and the load cell used was 50kN. A minimum of 5 specimens were measured for each composites.

**Morphological Analysis:**
The tensile fracture surface of composites was examined for morphological properties using scanning electron microscope (SEM, Model JEOL JSM-6460 LA). The specimen was coated with a thin layer of palladium before put into the SEM chamber.

**Fourier Transmission Infra-red (FTIR) Analysis:**
The treated CPH with different POCA content was characterized for chemical functional groups by Perkin Elmer Paragon 1000 FTIR spectrometer. The Attenuated Total Reflectance (ATR) method was selected. The sample was recorded with 8 scans in the frequency range 4000-600 cm⁻¹ with a resolution of 4 cm⁻¹.

**RESULTS AND DISCUSSION**

**Characterization of Treated CPH:**
Figure 2 illustrated the FTIR spectrums of untreated and treated CPH with difference POCA content. The broad peak found at 3291 cm⁻¹ was attributed to the hydroxyl (-OH) a group on the CPH and the peak at 2927 cm⁻¹ was assigned to C-H stretching. The peak indicated C=O and C=C stretching of hemicellulose was detected at 1732 cm⁻¹ and 1604 cm⁻¹, respectively. A small peak at 1518 cm⁻¹ was related to conjugate C-O group from aromatic skeletal in lignin. The peak at 1434 cm⁻¹ was assigned to the –CH₂ deformations vibration from cellulose. The peak at 1372 cm⁻¹ and 1038 cm⁻¹ was referring to C-H groups in cellulose and hemicellulose. Another peak at 1247 cm⁻¹ was corresponding to C-O groups from acetyl group in lignin. Besides, other peak at range of 700-900 cm⁻¹ was assigned as C-H vibration of lignin. The treated CPH show an
increase of peak intensity at 2923 cm\(^{-1}\), 2853 cm\(^{-1}\) and 1734 cm\(^{-1}\) compared to untreated CPH. The change of peak at 1734 cm\(^{-1}\) indicated the POCA had chemically bonded on CPH via ester linkage. Additionally, the peaks at 2923 cm\(^{-1}\) and 2853 cm\(^{-1}\) were related to fatty acid chains from POCA, which attached on CPH surface. Therefore, the intensity of related peaks is increased as the POCA content increased. Figure 3 displayed a schematic reaction between POCA and CPH.

![Schematic reaction between POCA and CPH](image)

**Fig. 2:** FTIR spectrums of untreated CPH and treated CPH with (a) 1 wt%, (b) 3 wt% and (c) 5 wt% of POCA content.

**Fig 3:** Schematic reaction between cocoa pod husk and POCA.

**Tensile Properties:**

The tensile strength and tensile modulus of PP/CPH composites increased with more POCA content (as shown in Figure 4). The composites with treated CPH with 3 wt% of POCA content show 18% higher tensile strength and 17% higher tensile modulus then the composites with untreated CPH. In previous research also found that the used of 3 wt% fatty acid based coupling agent (such as sodium dodecyl sulphate and ethylene diaminedilaurate) had shown a remarkable increase of tensile strength and tensile modulus on composites [3,16]. Nevertheless, the tensile strength and tensile modulus of composites initially to dropped as the treated CPH with 5 wt% of POCA. This can be explained by the treated CPH with 1 and 3 wt% of POCA exhibited a small surface coverage of POCA on CPH surface, which lead to a good filler dispersion and better wetting of CPH surface by PP matrix. As a result, the filler-matrix adhesion was enhanced that cause the tensile strength and tensile modulus increased. Alternatively, a larger surface coverage of POCA was found in treated CPH with 5 wt% of POCA. This might due to tightly packed coupling agent layer form on CPH surface, which lead to the difficulty of CPH wetting by PP matrix. Thus, a decreased of tensile strength and tensile modulus due to the weak interfacial adhesion can be observed. A similar observation was also reported by Danyadi [10] and Demjen [11].

Figure 4 also demonstrated the elongation at break of PP/CPH composites was slight decreased with increase of POCA content from 1 to 3 wt%. Then, elongation at break of composites increased at 5 wt% of POCA content. As discussion before, treated CPH with 3 wt% of POCA content exhibited a good adhesion with PP matrix. Therefore, the decrement of elongation at break was due to the strong interfacial adhesion that
restricted the chains mobility of PP matrix. However, increased of elongation at break was probably because of lubricating effect as the treated CPH with 5 wt% POCA. The similar results trend was also reported by Demjen [11].

**Fig. 4:** Effect of POCA content on tensile strength (▲), tensile modulus (◆) and elongation at break (■) of PP/CPH composites.

**Morphological Properties:**

Figures 5 (a) and (b) show the SEM micrographs on tensile fracture surface of PP/CPH composites with untreated CPH and treated CPH with 3 wt% of POCA. Figure 5 (a) illustrated that the untreated CPH was poor dispersed in PP matrix. Moreover, some holes corresponded to filler pull out and detached filler also observed which evidence the poor adhesion between untreated CPH and PP matrix. However, treated CPH in composites was well coated and embedded in PP matrix (as showed in Figure 5 (b)). This indicated the good filler-matrix adhesion.

**Fig. 5:** Tensile fracture surface of PP/CPH composites with (a) untreated CPH and (b) treated CPH with 3 wt% POCA content.

**Conclusion:**

The PP/CPH composite with 3 wt% of POCA exhibited highest tensile strength and tensile modulus which along with the decreased of elongation at break. This indicated 3 wt% of POCA was the optimum content for PP/CPH composites to obtain maximum improvement. However, the tensile strength and tensile modulus of PP/CPH dropped after this concentration. The good interfacial adhesion between treated CPH and PP matrix was also confirmed by SEM micrograph.

**REFERENCES**


