Flexural and thermal properties of biocomposites from *Cerbera manghas* L. and polypropylene

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Abstract. *Cerbera manghas* L., sea mango (SM) was used as filler in polymer biocomposites. The hot melt internal mixing technology for blending SM as filler in polypropylene (PP) matrix is demonstrated. Different weight percentages (5 wt% - 25 wt%) of SM was added into the PP matrix. Results indicated that biocomposite with 10wt% of SM showed improvement in the flexural strength, and stiffness of the biocomposites was increased as the SM content increased. Further enhancement of biocomposites flexural properties, thermal stability and degree of crystallinity showed positive results when compatibilizer such as polypropylene-grafted-maleic anhydride copolymer (PP-g-MA) was incorporated in the biocomposite system. SM has played an important role in providing excellent thermal stability to the biocomposites, which increasing the thermal degradation temperature up to 25 °C at low filler content. The PP-g-MA compatibilizer improved the wettability between SM and PP with the presence of esterification bonding that bridged together both polymer matrix and natural filler.

1. Introduction

Biocomposites for use in furniture making or interior panelling of track vehicles have already been explored. Biodegradable polymers are blended with fillers to form such biocomposites. The use of natural fillers for polymer blending are gaining more interests when considering a sustainable environment. The noted advantages of using natural fillers are low density, high specific properties, low cost, and relatively no abrasiveness. Since natural fillers can be obtained from waste materials, environmental pollution can also be lessened. Commodity plastics such as polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC) are compounded with natural fillers that are derived from wood, hemp, kenaf, flax, and palm oil to form biocomposites [1–3].

Polypropylene (PP) is a commercially available essential thermoplastic material having a broad range of applications in diverse fields because of its excellent chemical and mechanical properties [4]. However, polypropylene is a petroleum-based polymer which is non-biodegradable in nature. A
thermoplastic material blended with natural fillers to form biocomposites offers potential alternative for such non-biodegradable polymer [5]. But biocomposites has a drawback of not being compatible with hydrophobic polymers due to the hydrophilic nature of natural fibers. Such incompatibility will lead to poor dispersion making the reinforcement insufficient that will result to poor mechanical properties. The interactions between the fiber and polymer matrix materials depend on the chemical feature and composition of the surface layer of fiber and matrix. Natural fibers are susceptible to modification due to the hydroxyl group from cellulose and lignin. The hydroxyl group cause the polar nature of the fiber by the formation of hydrogen bonding within the cellulose molecules, thus reducing the reactivity towards the non-polar polymer matrix. Chemical modification or compatibilizer can be used to change the surface tension and polarity of the surface of fibers [2].

Several studies have been performed in determining the effect of compatibilizers on the mechanical and thermal properties of PP biocomposites [1,4–6]. Compatibilizers including polypropylene grafted with maleic anhydride (PP-g-MA) is used to enhance the interfacial properties between the polar side of the fiber and the non-polar side of the polymer matrix. Polypropylene grafted maleic anhydride (PP-g-MA) possessing two functional groups such as polar anhydride and non-polar hydrocarbon groups. The polar group will react with the hydroxyl group of cellulose fiber, whereas the non-polar group will react with the functional group of the polymer matrix. After adding the compatibilizer, the surface energy of fiber is increased to a level, which closer to the surface energy of the matrix. This will result to a better wettability and higher interfacial adhesion of the fiber to the matrix [7].

Considering the kinds of natural fillers used in general, there is no study yet reported on using sea mango (SM) as natural filler incorporated in polypropylene matrix to produce biocomposite materials. Thus, this study is aimed to investigate the effect of sea mango content and PP-g-MA as a compatibilizer on flexural properties, morphological characteristics, crystallinity, and thermal behaviours of the PP/SM biocomposites.

2. Materials and method
2.1. Materials
Polypropylene matrix with density of 0.915 g cm$^{-3}$ was supplied by Lotte Chemical Titan (M) Sdn. Bhd. Sea mango (SM) fillers were collected at the School of Environmental Engineering, UniMAP, Perlis, Malaysia. Polypropylene-grafted-maleic anhydride (PP-g-MA) with melting point of 156 °C and 8–10% of maleic anhydride content was supplied by Sigma-Aldrich. Sodium hydroxide (NaOH) was obtained from HmbG Chemicals.

2.2. Alkali treatment
The collected sea mango fibers were first washed several times with hot water (50 °C) to eliminate the dirt, soil, and other impurities. After washing with hot water, the fibers were sundried then 195 grams of dried fibers were soaked in 0.041M sodium hydroxide (NaOH) solution at room temperature for 3 hours. After treatment, the fibers were rinsed with distilled water several times until pH of distilled water reached 7.0. The treated fibers were then dried in an oven at 40 °C for 48 hr.

2.3. Biocomposites compounding
Prior to compounding, the sea mango fibers were ground into small particle size then sieved into 75µm size. These biocomposite materials were prepared by using Z-blade mixer at 180°C for 15 minutes with rotor speed of 50 rpm. Polypropylene (PP) and PP-g-MA were placed into the chamber for 5 minutes until completely melted. The sea mango fillers were then added and mixed continuously for another 10 mins such that the total mixing time for each formulation is 15 mins. Different weight % of fillers (5, 10, 15, 20, 25%) were tested to determine which percentage can bring out the highest flexural properties. The blend of biocomposites were then formed into a sheet using a laboratory mill at 1.0 mm nip setting. The compounded biocomposite were then placed in a desiccator to maintain its stability before hot press. Compression was done by using a compression moulding machine model GT-7014-H30C at 180°C. The specimens were preheated for 8 minutes followed by full compression for 2 minutes to produce a
homogenous flat sheet surface. The specimens were immediately cooled for 5 minutes. The moulded sheets were then placed in desiccator. The obtained sheet samples were then cut into rectangular shape following the required dimensions referred to in ASTM D790 for flexural test.

2.4. Flexural test and morphological determination
Flexural tests of all the composites sample were done according to ASTM D790 by Instron 5567 with dimensions of 3.2mm x 12.7mm x 125mm. The crosshead speed used was 3 mm min\(^{-1}\). Flexural strength and flexural modulus were determined. Five composite samples from each formulation were tested and the average values were reported.

Scanning electron microscope (SEM) model JEOL JSM 6460LA was used to observe the tensile fractured surface of the samples. The specimen was coated with a thin layer of palladium before observing the surface. SEM was carried out to study the morphology of the tensile fractures’ surfaces PP/SM biocomposite, with and without PP-g-MA.

2.5. Evaluation of thermal properties
The thermal gravimetric analysis (TGA) following ASTM E 1131 standard was used to measure the weight percentage change as a function of temperature in a controlled nitrogen. The thermal stability of the biocomposites was analysed in the range of 25 - 800°C under the inert nitrogen in order to prevent unwanted oxidation. The heating rate was set at 10°C/min.

The ASTM D3418. DSC standard was used for analyzing the thermal behaviour of biocomposite materials and was carried out using DSC-Q10 using 15 mg for each formulation. Each specimen was scanned from 25°C to 250°C at a heating rate and cooling rate of 10°C/min under nitrogen. The specimen’s percentage crystallinity (%) is calculated based on the Equation 1.

\[
\text{Percentage of crystallinity (\%)} = \frac{\Delta H_f}{\Delta H_f^0} \times 100\%
\]

where \(\Delta H_f\) is the heat fusion of the PP/SM biocomposite, \(\Delta H_f^0\) is the heat fusion for 100% crystalline PP, which is 209 Jg\(^{-1}\) [8].

3. Results and discussion
3.1. Flexural test and morphological studies
Figure 1 illustrates the flexural strength and modulus of PP/SM biocomposites with and without PP-g-MA. PP biocomposite. The 10 wt% SM content showed the highest flexural strength of 27.42 MPa and with the addition of PP-g-MA, the flexural strength of PP is further increased. This indicates that the incorporation of PP-g-MA enhanced the interfacial bonding between SM filler and PP matrix. The good bonding is affected by the surface activity of filler, filler-matrix interaction, and particle size [9]. Moreover, flexural modulus also increases with the filler content for both with and without PP-g-MA (Figure 1(b)). Improvements of modulus with the increasing amount of filler can be due to the higher stiffness of sea mango filler compared with neat PP [6]. The PP-g-MA compatibilizer has also contributed in enhancing the flexural modulus of PP biocomposites.

Figure 2 displays the SEM micrograph of fracture surface of neat PP and its biocomposites with 10 wt% and 25 wt% of SM. The fractured surface of neat PP has a relatively smooth surface with some prominent terraced markings, which shows that the neat PP has weak resistance to crack propagation [3]. In PP biocomposite without compatibilizer, it can be seen that number of holes of biocomposite with 25 wt% of SM content (Figure 2(d)) is higher than the biocomposite with 10 wt% of SM content (Figure 2(b)), and large amount of voids due to detachment of SM filler can be seen in Figure 2(d). This is due to the poor bonded interfacial area between matrix and filler causes brittle deformation of the composites [10]. Figures 2© and 2(e) show fractured surface of PP biocomposites with PP-g-MA
compatibilizer. Lesser voids in Figure 2(c) is found compared to Figure 2(e) indicating that PP-g-MA compatibilizer helps the matrix to encapsulate filler by introducing interfacial bond between the two elements [11]. This result supported higher flexural strength of compatibilised PP biocomposite with SM, which has been discussed earlier.

![Figure 1](image1.png)

**Figure 1.** Flexural strength (a) and flexural modulus (b) of PP/SM biocomposites.

![Figure 2](image2.png)

**Figure 2.** SEM micrographs of fracture surfaces of PP/SM biocomposites: (a) Neat PP; (b) PP/10wt%SM biocomposites without PP-g-MA; (c) PP/10wt%SM biocomposites with PP-g-MA. (d) PP/25wt%SM biocomposites without PP-g-MA. (e) PP/25wt%SM with PP-g-MA.

3.2 Thermal properties of PP/SM biocomposites
Thermal stability of the SM is significant to predict its integration into PP matrix. Figure 3 shows the thermal behavior of the biocomposites using TGA. Generally, neat PP and its biocomposites possess a single-step thermal decomposition. In uncompatibilized biocomposites system, 10wt% SM in PP has the highest thermal stability (Table 1). Sea mango filler has significantly enhanced the thermal stability of the biocomposite by increasing the initial degradation temperature ($T_{\text{onset}}$) of 28°C as comparing to neat
PP. Thermal stability decreases at higher SM content due to poor adhesion between the sea mango filler and polypropylene. It validates that the biocomposite has less stable structure towards heat [10].

In addition, biocomposites with the presence of PP-g-MA show remarkable thermal stability than the other composites tested in this study. This indicates good adhesion of the hydrogen bonds and covalent linkages between the hydroxyl group of SM and the maleated anhydride group of PP-g-MA [12]. Table 2 shows the differential scanning calorimetry (DSC) measurements of neat PP and its biocomposites with compatibilizers containing 5 – 25 wt% of SM content. The melting point (T<sub>m</sub>) and crystallization temperature (T<sub>c</sub>) were obtained from the main peak of the endothermic and exothermic curves, respectively. From Table 1, it can be seen that the melting point decreased with the addition of SM content, which reported similar results in his study of flax, hemp and sisal fibers filled polypropylene composites [13]. Whereas, the heat of fusion (ΔH<sub>f</sub>) and crystallization temperature (T<sub>c</sub>) of biocomposites are higher than neat PP. The higher the T<sub>c</sub> and ΔH<sub>f</sub> of the biocomposites indicating that the crystallization of the PP matrix is favoured in the presence of SM fillers. It can be due to the nucleation effect of the SM fillers whereby the fillers act as sites for heterogeneous nucleation that in turn inducing the crystallization of the PP matrix [14]. Furthermore, impregnation of PP-g-MA compatibilizer into PP/SM biocomposites showed higher heat of fusion and crystallinity (X<sub>c</sub>). This is due to the chemical bond formed between the SM filler and PP matrix which does not physically constrain the mobilization of the polymer chain. Hence, the addition of MA group from PP-g-MA compatibilizer improved the chemical bond between filler and matrix by enhanced the interfacial adhesion SM to the PP matrix [15].

**Figure 3.** (a) TG thermogram and (b) DTG curves of PP/SM biocomposites with and without PP-g-MA.

**Table 1.** Thermogravimetric analysis of the PP/SM biocomposites.

| Specimens            | T<sub>onset</sub> (°C) | T<sub>degradation</sub> (°C) |
|----------------------|------------------------|-----------------------------|
| Neat PP              | 229.11                 | 403.10                      |
| 5wt% SM              | 243.78                 | 438.72                      |
| 5wt% SM/PP-g-MA      | 265.21                 | 438.80                      |
| 10wt% SM             | 256.85                 | 438.83                      |
| 10wt% SM/PP-g-MA     | 278.20                 | 439.57                      |
| 25wt% SM             | 227.21                 | 418.40                      |
| 25wt% SM/PP-g-MA     | 230.42                 | 438.98                      |
Table 2. Summary of $T_m$, $T_c$, $\Delta H_f$ and degree of crystallinity ($X_c$) of PP and biocomposites.

| Specimens             | $T_m$ (°C) | $T_c$ (°C) | $\Delta H_f$ (Jg$^{-1}$) | $X_c$ (%) |
|-----------------------|------------|------------|--------------------------|-----------|
| Neat PP               | 168.01     | 139.41     | 54.85                    | 26.24     |
| 5wt% SM               | 167.59     | 140.39     | 70.61                    | 33.78     |
| 5wt% SM/PP-g-MA       | 167.82     | 142.13     | 75.89                    | 36.31     |
| 10wt% SM              | 166.26     | 141.19     | 95.91                    | 45.89     |
| 10wt% SM/PP-g-MA      | 166.58     | 141.99     | 103.50                   | 49.52     |
| 25wt% SM              | 165.42     | 140.23     | 84.35                    | 40.36     |
| 25wt% SM/PP-g-MA      | 165.11     | 140.81     | 91.02                    | 43.55     |

4. Conclusions

Sea mango (SM) filler can be a good reinforcement and nucleating agent for PP matrix, which shows increased in flexural strength and degree of crystallinity. The utilization of PP-g-MA as compatibilizer has further improved the flexural and thermal properties of PP/SM biocomposites. The compatibilizing effect helps to promote good interfacial adhesion existed between the PP matrix and SM filler. Sea mango filler has remarkably increased the thermal stability of the biocomposites (up to 20 °C). This is due to the ability of fillers to absorb the heat generated and reduced overall degradation process. The addition of PP-g-MA into biocomposites, which contains carboxyl group has induced the compatibility between the PP and SM filler resulting better thermal properties of biocomposites. Finally, compatibilized biocomposite with 10 wt% of SM possess the best flexural and thermal properties.

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