Characterization of green rHDPE biocomposites filled with natural filler: Rheological and thermal studies

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Abstract. Palm kernel shell filled recycled high density polyethylene (rHDPE/PKS) biocomposites were produced in order to reduce the waste product from palm oil production. The biocomposites at various filler loading were prepared by melt mixing at 180 °C. Ultra Plast TP01 was selected as coupling agent in rHDPE/PKS biocomposites, in order to modify the properties of biocomposites. It was found that the higher filler loading had reduced the melt flow index (MFI) values. However, with the increasing of testing temperature from 180 to 210 °C, the MFI values of the biocomposites were increased. The presence of Ultra Plast TP01was capable to increase MFI values of the biocomposites. The thermal studies showed that thermal stability of the biocomposites was affected by PKS loading and coupling agent. Though the thermal stability of biocomposites was reduced by PKS, it can be improved by Ultra Plast TP01. Hence, Ultra Plast TP01 can serve as an effective coupling agent for rHDPE/PKS.

1. Introduction

Currently, the increasing demand of polymeric materials in society is challenged by the decreasing resources. Thus, waste materials can serve as one of the alternatives to resolve this issue [1]. Many types of natural fillers such as kenaf [2], hemp [3], sisal [4] and chitosan [5] were chosen as fillers due to several advantages such as low cost, light weight, high availability and bio-degradable. The addition of natural bio-materials into biopolymer or synthetic polymer leads to the production of biocomposites [6]. These biocomposites help to reduce the consumption of non-degradable polymer.

In 2011, Malaysia had produced 18.91 million metric tonnes of crude palm oil [7]. In the production of palm oil, plenty of by-products were generated. Ng *et al*. [8] reported that about four kilogram of dry biomass was obtained in order to produce one kilogram of palm oil. Example of oil palm biomass includes empty fruit bunches, palm kernel shells (PKS), oil palm fronds, oil palm trunks, mesocarp fibre and palm oil mill effluent. PKS is the hard and stony endocarp that was obtained after the nut was separated from its kernel [9, 10]. Zwart [7] revealed that the amount of PKS generated annually was up to 4.0 million metric tonnes. Therefore, PKS can serve as a promising filler in polymeric materials to form biocomposites.

High density polyethylene is generally used to prepare milk jugs and plastic bottles which are served for single usage. Thus, there are massive post-consumer plastic been generated every year. Lei *et al.* [11] reported 19.2 million tonnes of plastic waste was collected in USA at 2001, in which 40 %

of it was HDPE. Therefore, recycling HDPE would help to reduce the municipal solid waste since HDPE is non-degradable. A comparative study between virgin and recycled HDPE filled with hemp fibre was carried out by Lu and co-workers [12]. They concluded that rHDPE were having comparable mechanical properties to virgin HDPE. At certain fibre loading, the rHDPE composites had even higher mechanical properties than those of virgin HDPE. Besides, there are other natural fillers such as wood flour and bagasse were also reported as filler in rHDPE [11, 13].

The incorporation of filler into polymeric matrix is aimed to reduce the usage of non-degradable petroleum based polymer. However, the non-compatible nature between the hydrophilic natural filler and hydrophobic polymer matrix tend to compromise the mechanical and thermal properties of biocomposites. In order to improve the interaction between filler and matrix, different chemical treatments can be conducted on natural fillers. Examples of chemical treatments include alkali treatment, silane coupling agents, maleated coupling agents, acetylation and so on [14, 15]. Generally, the application of different chemical treatments on the filler and matrix are beneficial to improve and enhance the properties of biocomposites [16, 17].

In this research, the rheological behaviour and thermal degradation properties of rHDPE/PKS biocomposites were studied by using melt flow indexer and thermogravimetric analysis. The composites were prepared at different filler loading. A coupling agent, Ultra Plus TP01 was added to enhance the properties of biocomposites.

2. Experimental

2.1. Materials

The polymer used in this study was recycled high density polyethylene (rHDPE). It was supplied by SLT Plastic Sdn. Bhd., Penang in pellet form with the density of 0.92 g/cm^3. The palm kernel shell (PKS) was supplied by DRPTS Manufacturing Sdn. Bhd., Melaka, in powder form. In order to obtain fine particles of PKS, it was sieved by using 75 μm sieve. Then, it was dried in oven for 20 hours at 80 ^{0}C. The coupling agent used in this project was Ultra Plast TP01 which obtained from Performance Additive Sdn. Bhd., Selangor. The formulation of rHDPE/PKS biocomposites with and without coupling agent is shown in Table 1.

Table 1. Formulation of rHDPE/PKS biocomposites with and without Ultra Plast TP01.

Materials	Without Coupling Agent	With Coupling Agent
rHDPE (php)	100	100
PKS (php)	0, 10, 20, 30, 40	10, 20, 30, 40
Ultra Plast TP01 (php)	-	1*

*1 wt% from the weight of rHDPE

2.1.1. Biocomposites preparation

Compounding of rHDPE/PKS biocomposites carried out using Z-Blade mixer at speed of 30 rpm at temperature 180 ^{0}C. rHDPE was inserted into mixing chamber for 10 minutes heating. Then, PKS was loaded and mixing was continued for 10 minutes. The whole mixing process was completed in 20 minutes. The rHDPE/PKS biocomposites were subjected to compression molding. The composites were preheated for 6 minutes followed by 8 minutes of compression to form a uniform and standard flat surface. Finally, the composite were cooled for 2 minutes. With molding process, it was desired to prepare sheet samples with 1 mm thickness.

2.1.2. Morphological study

The morphology of PKS powder was determined through Scanning Electron Microscopy (SEM) with the model of JOEL JSM6460LA. PKS powder was dispersed on the sticky conductive carbon tape that

was mounted on aluminium stub. Then a thin layer of palladium was sputtered by using the sputter coater to prevent electrostatic charging during testing.

2.1.3. Rheological study

The rhelogical behaviour of the rHDPE/PKS composite was determined by the means of MFI test that followed ASTM D 1238. Melt flow index (MFI) is the amount of polymer (in grams) that can be forced through a standard die in 10 minutes when subjected to a specified force at given temperature based on the standard procedure. First, biocomposite was loaded into melt flow indexer and allowed to preheat for 5 minutes. Then the melted biocomposites were extruded from the die with the applied load of 5 kg. Similar procedure was conducted at different testing temperature that varied from 180 to 210 °C. The following equation was used to measure MFI values:

$$\text{MFI} = \frac{m}{t} \times 600 \text{ s.min}^{-1} \quad (1)$$

Where,

m = average weight of extrudate (g)
t = time of extruded (s)

2.1.4. Thermal study

Thermogravimetric analysis (TGA) was accomplished by using Perkin Elmer Pyris Diamond TG-DTA. The weight of samples was approximately about 15-20 mg. The samples were heated at 20 ^{0}C/min within the temperature range of 30-650 ^{0}C and under nitrogen flow of 50 mL/min. The weight losses of samples at different percentage were obtained and tabulated.

3. Results and Discussion

3.1. Morphological study

The scanning electron microscope (SEM) was used to examine the microstructure of PKS as illustrated in Figure 1. It can be seen that the surface of these agro-waste particles are rough and irregular in shape. According to Okoroigwe [18], there were micro pores found on the surface of PKS. The micro pores were used to exchange fluid with the surrounding mesocraps. Therefore, PKS had tendency to absorb moisture. Therefore, PKS must be dried and free from moisture in order to avoid agglomeration and poor dispersion in rHDPE. The PKS particles were found to be smaller than 75 µm.

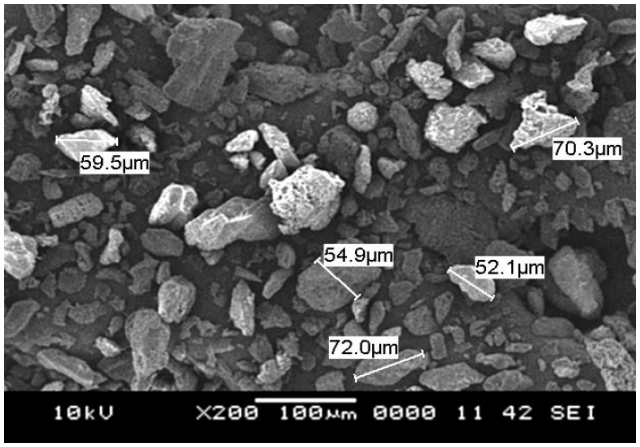

Figure 1: Scanning Electron Microscopy (SEM) of PKS at mgnification of 200X.

3.2. Rheological study

The rheological properties of rHDPE/PKS can be studied through melt flow index (MFI) test. Figure 2 shows the effect of filler loading on the MFI values of biocomposites. It can be seen that as the filler loading increased, MFI values of both rHDPE/PKS biocomposites with and without coupling agent were decreased. This phenomenon was due to the agglomeration of PKS and poor interfacial interaction between rHDPE and PKS. The flow of the polymer melts was caused by the sliding of polymer chains. In the presence of PKS as filler, it hindered the flow of rHDPE. Thus, the MFI values of the composites were decreased. To improve the interfacial interaction and speed up the flowability of biocomposites, the coupling agent was added to biocomposites. It can be seen that the presence of coupling agent increased the MFI values of rHDPE/PKS biosomposites significantly. The greatest MFI value was demonstrated by rHDPE/PKS 10 with more than 200 % increment. The addition of Ultra Plus TP01 as coupling agent had enhanced the flowability of rHPE/PKS biocomposites.

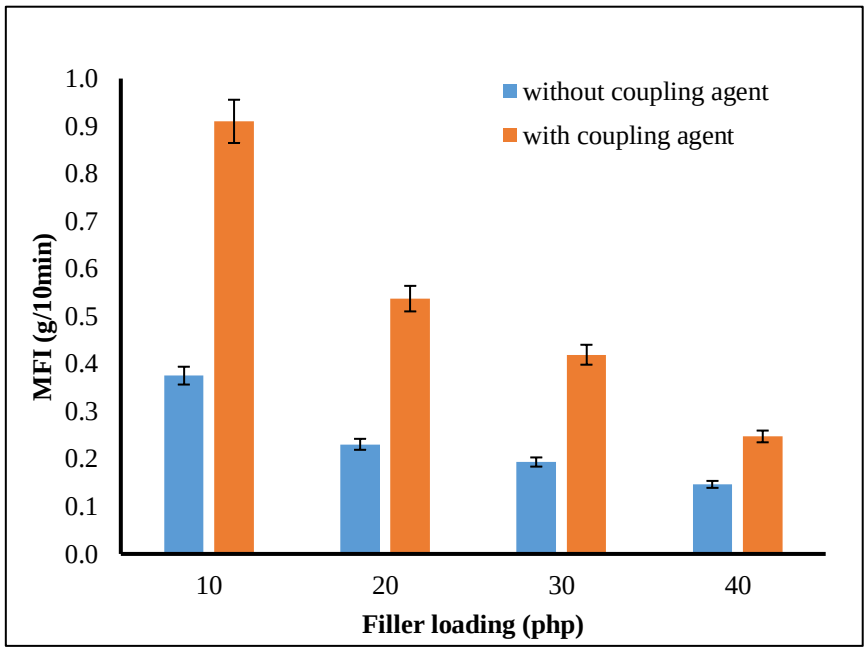

Figure 2: MFI values of rHDPE/PKS biocomposites at (a) different filler loading and (b) addition of coupling agent

Besides filler loading, temperature can also influenced the MFI values of rHDPE/PKS biocomposites. Figure 3 shows the rise of testing temperature for composites at similar filler loading had increased the MFI values linearly. In order to provide greater flowability of the biocomposites, the composite melts must possess sufficient thermal energy to make it mobile and allow it to move. High temperature that was applied on the biocomposites triggered the flowability of the material. This was due to larger free space in the molecular chain motion and weak intermolecular interaction at higher temperature [10].

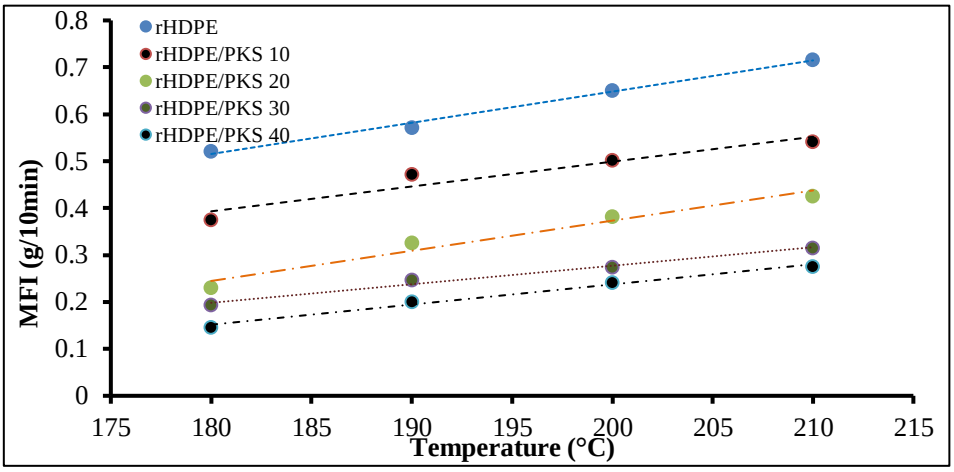

Figure 3: MFI values of rHDPE/PKS biocomposites with different filler loading on various testing temperature

3.3. Thermal study

The comparison of thermogravimetric analysis (TGA) curves of rHDPE/PKS biocomposites with different filler loading are shown in Figure 4 (a). The results showed that rHDPE, PKS, Ultra Plus TP01 and biocomposites were thermally stable up to 250 °C. Table 2 summarizes the weight loss of the samples up to 50 %. At similar weight loss percentage, it can be seen that the decomposition temperature of the rHDPE was reduced with the addition of PKS. As the PKS increased from 20 to 40 php, the decomposition temperature was further reduced. This indicated that the PKS had lower thermal stability. Figure 4 (b) illustrates the TGA curves of rHDPE/PKS biocomposites with and without coupling agent. The weight loss of biocomposites with coupling agent was delayed to higher temperature. It was believed that better interfacial bonding between PKS and rHDPE had established and the rHDPE had covered the PKS to slow down the thermal decomposition. As a result, the presence of coupling agent had enhanced the thermal stability of the biocomposites. This was in agreement to the results in author's previous work [19].

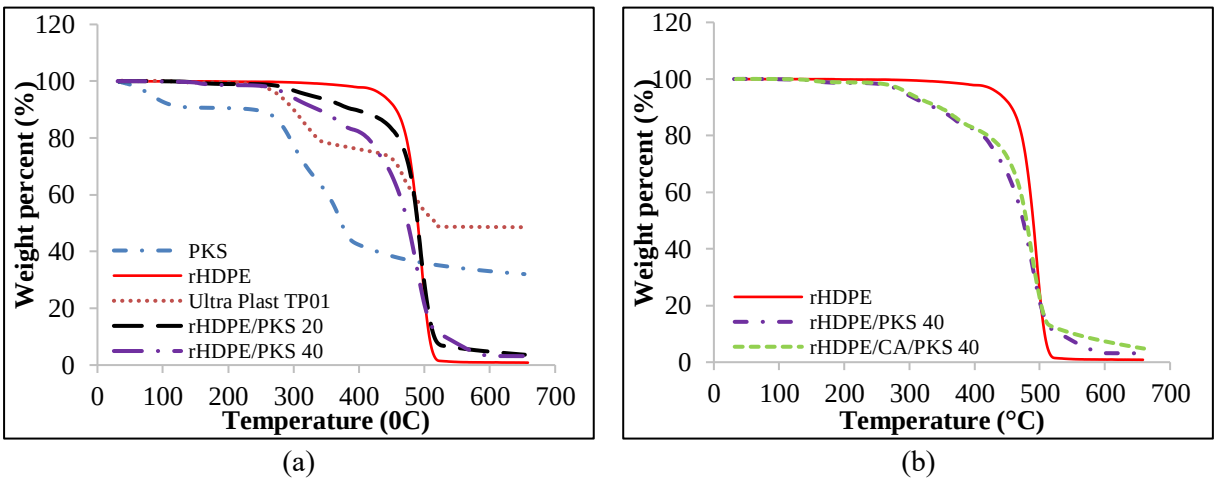

Figure 4: Comparison of thermogravimetric analysis curves of rHDPE/PKS biocomposites at (a) different filler loading and (b) addition of coupling agent

Table 2: Temperature for PKS, rHDPE and rHDPE/PKS biocomposites at different percentage of weight loss

Composite	Temperture (°C)				
	$T_{10\%}$*	$T_{20\%}$	$T_{30\%}$	$T_{40\%}$	$T_{50\%}$
Ultra Plast TP01	300	335	460	485	515
PKS	240	295	320	355	375
rHDPE	457	472	479	485	490
rHDPE/PKS 20	393	460	475	484	489
rHDPE/PKS 40	335	415	445	465	475
rHDPE/CA/PKS 40	345	420	455	470	479

*$T_{10\%}$ (^{0}C): temperature at 10 % weight loss

4. Conclusion

The rHDPE/PKS biocomposites was successfully prepared with the addition of Ultra Plus TP01 as coupling agent. The increase of filler loading on rHDPE/PKS biocomposites had lowered the MFI values and thermal stability. However, the addition of coupling agent on rHDPE/PKS biocomposites had increased MFI values and thermal stability compared to the biocomposites without coupling agent. The presence of coupling agent improved the interfacial interaction between matrix and filler as the rheological and thermal properties were enhanced.

5. Acknowledgement

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6. References

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