Effect of incorporating different types of Sentang tree waste particle on the thermal stability of Wood Polymer Composite (WPC)

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Abstract. This article presents the potential use of tree waste materials such as the leaves (L), branches (B) and trunks (T) of Azadirachta excelsa (Sentang) tree in the production of wood polymer composite (WPC). The WPC was fabricated from high-density polyethylene (HDPE) as bonding matrix, maleic anhydride (MA) as coupling agent, and Sentang tree waste particles (L, B and T) as filler, prepared using twin-screw extruder followed by injection moulding machine. The effects of incorporating these types of Sentang tree waste particle (at 35% and 45% particles loading by weight) on the thermal stability of WPC were reported. The chemical compositions of L, B and T were also determined and their influences on the thermal stability of WPC were discussed. The thermal behaviour was determined by using thermogravimetric analysis (TGA), whereas the chemical analysis using Technical Association of the Pulp and Paper Industry (TAPPI) methods. The addition of these tree waste particles as filler has increased the thermal stability of WPC compared to virgin HDPE (without any particle incorporation). The highest mass loss was experienced by virgin HDPE. It was also observed that chemical compositions of the particles played vital role in influencing the thermal stability of WPC.

1. Introduction
The interests worldwide towards eco-friendly materials have been due to concerns towards the subsequent impacts on the environment such as waste disposal, global warming, air pollution, water pollution and climate change. Wood plastic composite (WPC) is eco-friendly material that is composed of plant-based materials or lignocellulosic materials with thermoplastics as the bonding matrix. The plant-based materials are sustainable and when properly managed, therefore the use, reuse, recycle and processing will have minimal impact on the environment. The plant-based materials such as wood particles and other natural fibers (examples are rice husk, oil palm, corn stalk, coconut coir, kenaf and date palm fibers) are also in abundance, recyclable, low cost, renewable and easy to decompose (biodegradable) compared to glass fibers. Glass fibers are made of synthetic fibers that have high strength in terms of mechanical strength but possesses some weakness such as non-biodegradable, cannot be recycled, insufficient supply from petroleum resources, the manufacture of composites is energy intensive process which require high heat and pressure and this makes them as non-environmentally friendly materials [1][2][3][4]. WPC has a lot of advantages such as low density, lightweight, good thermal insulation properties, recyclable, biodegradable, relatively low price, and low
abrasiveness. It contributes significantly to carbon dioxide sequestration (reducing the amount of carbon dioxide in the atmosphere) [5] when the resources are sustainable. The presence of wood particles or lignocellulosic materials accelerates the decomposition rate of WPC compared to virgin polymers composed of 100% plastics such as virgin polyethylene (vPE), virgin polypropylene (vPP) and others. There are various methods in the fabrication of WPC such as extrusion process, injection molding and compression molding. In addition, the recent advance in making WPC is by additive manufacturing processes which includes the fused layer modeling and laser sintering. Owing to the fact that WPC advancement has gaining interest throughout the world, there are various applications that had been introduced such as construction materials, automotive paneling (door panel and dashboard), packaging, household items, electrical casings and materials in aerospace components [6][7].

In this research, the WPC is composed of waste particle of Sentang (Azadirachta excelsa) tree leaves, branches and trunks mixed with HDPE as bonding matrix and maleic anhydride (MA) as coupling agent. The waste particle filler loading by weight were 35% and 45% combined with 2% of MA (also by weight). The aim of this study was to determine the thermal stability of HDPE composites mixed with Sentang tree waste particle using thermogravimetric analysis (TGA) in relation to the chemical constituents and types of waste particle fillers (leaves, branches and trunks).

2. Materials and methods

2.1. Materials

Sentang (Azadirachta excelsa) tree particles were from the leaves, branches and trunks, which were waste materials from tree felling. The waste particles were used as filler in the production of the WPC. The leaves, branches and trunks were first reduced to fine particles using a laboratory grinder and sieved through a 50-mesh vibrating screen. The waste particles were then oven-dried at 105 ± 2°C for 24 hours and stored in sealed plastic bags before the compounding process. The HDPE was locally supplied in the form of pellets of 0.95 g/cm³ density with melt flow index (MFI) of 18.0g/10min, and melting point of 190°C. The maleic anhydride (MA) was also locally supplied in the form of powder of a melting point of 52 to 54°C, density of 1.48 g/cm³ and melt flow index (MFI) of 1.9 g/10 min.

2.2. Manufacture of WPC

The waste particles (leaf, branch and trunk separately) were used as filler in the HDPE composites. The compositions of the composites were weighed according to the required ratios of waste particle/HDPE/MA (35:63:2, and 45:53:2) respectively. The barrel temperature of extruder was set at 190°C with twin-screw speed set at 4 rpm. HDPE was added into the barrel until it totally melted, then followed by MA and waste flour. The compounding of polymer matrix, coupling agent and flour took about 30 to 40 minutes to mixed thoroughly. The compound was transformed into pellets using a crusher machine. After that, the pellets were fed into an injection molder set at 190°C. Molten pellets in the molder were forced out into a mold under high pressure. The molten material filled the cavity in the mold and solidifies as it cools to form the test samples. Finally, the molded test samples were conditioned at a temperature of 23 ± 2°C with a relative humidity of 50 ± 5%, as stated in ASTM D 618. The same steps were repeated to produce all the WPC test samples. The compositions of WPC were shown in Table 1.

2.3. Chemical compositions of waste particle

The chemical compositions of waste particles of Sentang tree leaf, branch and trunk were determined according to the TAPPI standard methods. Five chemical constituents were determined in this study. These constituents were the extractive (hot-water soluble extractive and alcohol extractive), holocellulose, alpha cellulose, lignin and ash contents.
2.3.1. **Hot-water extractive content.** 13 g of waste particle samples (leaf, branch and trunk of Sentang tree) were added into an extraction thimble. The samples were heated using Soxhlet apparatus over 200 ml of distilled water and boiled for 6 hours. The residue from the extraction was cooled in a fume hood for 24 hours and subsequently oven-dried at 105±2°C for 48 hours.

2.3.2. **Alcohol extractive content.** The residues from hot-water extraction were boiled for 6 hours using Soxhlet apparatus over a 200 ml ethanol-toluene. The ratio of ethanol to toluene used in this research was 1:2. Next, the residue was cooled in a fume hood for 6 hours and oven-dried at 105±2°C for 48 hours.

2.3.3. **Holocellulose content.** 2 g of the oven-dried residues were mixed with 0.75 g sodium chloride, 0.25 g acetic acid and 80 ml distilled water inside the 250 ml Erlenmeyer flask. The flask was heated using the water bath at 80°C and shaken for 3 hours. The same amount of sodium chloride, acetic acid and distilled water were added constantly for each hour in between. Then, the mixture was left to cool, filtered and the residues were washed with 100 ml distilled water followed by 25 ml acetic acid. The filtered samples were oven-dried at 105±2°C for 48 hours.

2.3.4. **Alpha cellulose content.** The extracted residues from the holocellulose extraction was used for alpha-cellulose extraction. 75 ml sodium chloride were transferred into a 100 ml Erlenmeyer flask along with extracted residues at room temperature for 2 hours. The mixture was shaken every 15 minutes. After that, it was filtered and washed consecutively using 25 ml sodium chloride, 150 ml distilled water, 25 ml acetic acid and 25 ml acetone. Finally, the filtered samples were oven-dried at 105±2°C for 48 hours.

2.3.5. **Lignin content.** 5 g of the extracted alpha cellulose samples were mixed with 15 ml of 72% sulfuric acid and stirred for 2 hours inside a beaker. Then, the mixture was diluted using 200 ml of distilled water and boiled for 4 hours. The residue was filtered and washed using hot distilled water. The filtered residue was oven-dried at a temperature of 105±2°C for 48 hours.

2.3.6. **Ash content.** 2 g of the extracted lignin free alpha cellulose sample was placed in porcelain crucible and heated over a low flame of Bunsen burner to carbonize the sample without flaming (char). After that, it was placed in a furnace at 525 ± 25°C for 4 to 5 hours. The sample was left to cool overnight and transferred into a desiccator at room temperature.

2.4. **Thermogravimetric analysis (TGA)** The Perkin Elmer TGA-6000 thermal analyser was used in performing the thermogravimetric analysis (TGA) test. The samples were weighed approximately 10 mg and heated in the temperature range of 0 to 600 °C at a heating rate of 10 °C/min under flowing nitrogen at a rate of 10 ml/min.

| Formulation | Filler Type | Filler (%) | HDPE (%) | MA (%) | Code |
|-------------|-------------|------------|-----------|--------|------|
| Virgin HDPE (vHDPE) | - | 0 | 100 | 0 | vHDPE |
| WPC | Leaf | 35 | 63 | 2 | L35 |
| 35% Leaf, 63% HDPE, 2% MA | 45 | 53 | 2 | L45 |
| Branch | 35 | 63 | 2 | B35 |
| Branch | 45 | 53 | 2 | B45 |
| 35% Branch, 63% HDPE, 2% MA | 35 | 63 | 2 | T35 |
| Trunk | 45 | 53 | 2 | T45 |

Table 1. The compositions of WPC.
3. Results and discussion

3.1. Chemical compositions of Sentang tree waste particle

The chemical compositions of Sentang tree waste particle as presented in Table 2 consisted of hot-water soluble extractive, alcohol soluble extractive, holocellulose, alpha cellulose, lignin and ash contents. The determination of chemical attributes of the waste particle were used to identify the differences in thermal properties of WPC filled with leaf, branch and trunk particles. Based on the results in Table 2, the highest extractive contents were from the leaves followed by branches and trunks. The presence of a lot of colouring agents and sugars in the leaves can be the factors that contributed to the high extractive contents in the leaf compared to branch and trunk [8,9]. The green colour of chlorophyll pigments plays important roles in absorbing sunlight, store energy by converting carbon dioxide and water into glucose through the process of photosynthesis and the exchange of gaseous in the presence of chlorophyll. However, the extractive in branch and trunk was lower than the leaf. The extractives in the branch and trunk are organic substances that accumulate around the woody element of the branch and trunk that produce gum, resin, odour and colour. The extractives in wood contributes to the strength and durability of the wood in terms of mechanical, physical and thermal strength [10]. As the functions of the extractive in the leaves were mostly different as compared to those in the branch and trunk, the quantities and chemical structures were different. The trunk of Sentang tree had the highest holocellulose, alpha cellulose and lignin contents compared to branch and leaf. This is due to the quantity and structure of cells present in the trunk which consist of these chemical constituents. The main components of holocellulose are cellulose and hemicellulose followed by its minor components composed of sugars such as starch and pectin. In the trunks, as secondary growth occurs, the cell division inside it accelerates and corresponds to the increases of trunk diameter. This led to the cells inside the trunk to be highly packed and denser compared to leaves [11]. The ash contents inside the leaf were higher than the branch and trunk.

| Composition (%)       | Leaf  | Branch | Trunk |
|-----------------------|-------|--------|-------|
| Hot-water extractive  | 25.5  | 11.7   | 9.9   |
| Alcohol extractive    | 3.3   | 2.9    | 2.3   |
| Holocellulose         | 70.5  | 83.5   | 85.5  |
| Alpha-cellulose       | 22.5  | 39.0   | 40.0  |
| Lignin                | 26.6  | 26.8   | 49.6  |
| Ash content           | 6.5   | 1.0    | 1.5   |

3.2. Thermogravimetric analysis (TGA)

Table 3 summarizes the thermal properties of the vHDPE and WPC filled with leaf, branch and trunk particles at different filler loadings, whereas Figure 1 shows the TGA curves of the investigated samples. The TGA curves provides important information about the thermal properties and degradation behaviors of the materials [12]. The results showed that vHDPE had different degradation trends compared with WPC filled with waste particles (L25, L35, B35, B45, T35 and T45) because of their differences in chemical constituents and molecular structures. From Figure 1, the TGA curves of vHDPE is observed as single stage decomposition because it is a long linear polymer that has a high degree of crystallinity and low branching of molecule whereas WPC filled with waste particles undergoes multistage decompositions due to the presence of cellulose, hemicellulose, lignin and small amount of extractives and inorganic elements [13]. Five possible decompositions phenomenon that takes place in this research are; (1) the evaporation of water and extractives of lower molar mass, (2) degradation of hemicelluloses, (3) degradation of celluloses, (4) degradation of HDPE matrix and MA, and (5) the degradation of high molar mass fraction of lignin. Based on the results, the decomposition temperature of WPC filled with
tree waste particles occurred at the interval of 150°C to 560°C. The decomposition of hemicellulose, cellulose and lignin takes place at the temperature of 190 – 380°C, 250 – 380°C and 150 – 900°C respectively as mentioned by the previous studies [13]. From the results obtained in this research, there were two decomposition stages during the pyrolysis of WPC of different tree waste particles filler loadings (L25, L35, B35, B45, T35 and T45). Previous research by [14,15] agrees that the degradation of the wood flour component primarily occurs at the first stage. The first stage was due to the decomposition of waste flour such as leaf (L), branch (B) and trunk (T) at the temperature of 150°C to 400°C, followed by further degradation of HDPE. HDPE will degrade after the degradation of waste flour as the temperature reaches above 390.1°C. Recent studies also found that the HDPE began to soften above 135.4°C and this causes the HDPE to encase the waste flour (leaf, branch and trunk) particles, thus it prevents the release of combustible volatiles [13]. The second stage (350 – 561°C) was the result from the degradation of combination of this encased waste flour and HDPE units. The results indicated that the addition of tree waste particle into the HDPE initiates the degradation of HDPE due to the presence of free radicals, carbonyl and carboxyl from tree waste particles during the first stage of degradation. Thus, the rising of temperature and decreasing of the rate of decomposition of WPC were resulted from the increasing of filler content of tree waste particles. This principle is equivalent to the studies made by [16–18].

For WPC, at the first stage of degradation, B45 had the highest mass loss with 27.68% and L45 has the lowest mass loss with 7.75%. The highest mass loss of B45 indicated that the hemicellulose, cellulose and lignin began to decompose at temperatures of 175.84°C to 390.29°C. L45 that comprised of leaf particle had the lowest mass loss because leaf has low molecular weight and the cells inside it is not highly packed compare to branch and trunk. The vHDPE had the highest mass loss at 66.03% whereas WPC of L45 had the lowest mass loss at the second stage of degradation. At this stage, the degradation was mainly on the polymer matrix (HDPE). The high mass loss of vHDPE was because vHDPE contains 100% plastic (polymer). However, for WPC, the formation of char residues slowed down the heat transfer of polymer matrix to the tree waste particle that hindering the degradation process, and this suggests for the low mass loss of WPC. Recent studies from [18] found that WPC filled with poplar wood flour had the better thermal stability compared to poly(propylene) carbonate (PPC). Thus, this study is in a good agreement with the previous studies, as WPC filled with tree waste particle had better thermal stability compared to vHDPE.

**Table 3.** Thermal degradation temperature and mass loss of vHDPE and WPC filled with leaf (L), branch (B) and trunk (T) particles (WPCL, WPCB and WPCT) at different filler loading.

| Sample | First stage | Second stage | Residue (%) at 600°C |
|--------|-------------|--------------|----------------------|
|        | T_i (°C)   | T_f (°C)     | Mass loss (%)        | T_i (°C) | T_f (°C) | Mass loss (%) |
| vHDPE  | -          | -            | -                    | 390.1    | 561.0    | 66.03         | 33.78       |
| L35    | 94.31      | 354.98       | 8.71                 | 358.54   | 545.51   | 57.22         | 36.01       |
| L45    | 83.54      | 361.55       | 7.75                 | 361.55   | 547.75   | 34.19         | 60.82       |
| B35    | 171.62     | 392.71       | 13.03                | 398.06   | 542.26   | 45.41         | 43.83       |
| B45    | 175.84     | 390.29       | 27.68                | 393.91   | 533.93   | 55.89         | 18.00       |
| T35    | 196.96     | 413.72       | 23.01                | 415.63   | 508.05   | 63.63         | 15.51       |
| T45    | 148.11     | 413.26       | 17.75                | 417.09   | 559.54   | 36.49         | 47.41       |

T_i: Initial temperature  
T_f: Final temperature
4. Conclusions
The effects of incorporating different types of Sentang (Azadirachta excelsa) tree waste particle on the thermal stability of wood polymer composite (WPC) were determined in this study. The influences of chemical composition of the particles (from leaf, branch and trunk of the tree) on the thermal stability of WPC were also discussed. Trunk had the highest compositions of holocellulose, alpha cellulose and lignin contents, followed by leaf that had the highest content of extractives and inorganic elements. The TGA analysis showed that the addition of these tree waste particles as filler increased the thermal stability of WPC compared to virgin HDPE (without any particle incorporation). The highest mass loss was experienced by virgin HDPE because of its molecular structure as it is composed of 100% plastics. From the study, it was observed that the determination of chemical compositions of the particles played vital role in the thermal stability of the WPC. Overall, the use of tree waste particle from leaf, branch and trunk as fillers in WPC production is favorable in accordance to the environmental advantages and good thermal properties of the composite with unique chemical compositions.

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