



# Flammability, Biodegradability and Mechanical Properties of Bio-Composites Waste Polypropylene/Kenaf Fiber Containing Nano CaCO<sub>3</sub> with Diammonium Phosphate

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## Abstract

Bio-composites base on waste polypropylene (rPP) and kenaf fibre (KF) using coupling agent acrylic acid (AA), and crosslinker divinylbenzene (DVB) containing nano CaCO<sub>3</sub> (nCC) with and without DAP as a mixture fire retardant (FR) was successfully processed in melt. Flammability of bio-composite was horizontally burning tested, according to ASTM D635. To study the nature of its biodegradability, the bio-composites were technically buried in garbage dump land. The tensile strength properties of bio-composites were measured according to ASTM D638 type V. Effect of 20% total weight flame-retardant [nCC+DAP] ratio 7:13 can effectively reduce the burning rate (BR) up to 54% compared to bio-composites without any fire retardant. Biodegradability of bio-composite rPP/DVB/AA/KF/[nCC+DAP] was examined by burying the bio-composite specimens in the garbage soil during four months. The biodegradability of bio-composite was measured by the losing weight (LW) of bio-composite specimens after burying in the soil for four months, it was found up to 11.82%. However, the present of [nCC+DAP] in the bio-composites can marginally decreasing the tensile strength (TS), compared to that of without FR.

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*Keywords:* Bio-composite, waste polypropylene, biodegradability, flammability, burning rate.

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## 1. Introduction

Chemical products that are based on renewable resources are important issue to sustainable development [1]. The utilization of renewable resources such as KF filler into PP matrix is being actively

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pursued due to improvement in material properties as well as biodegradability [2-4]. Plastics, especially PP which is widely used in automotive, household, and any other industrial applications such as in mineral water packaging [5] contributes a large percentage to household waste and polluting the environment. This is because PP is non-degradable. However, PP waste can be transformed to other useful product such as bio-composite by adding natural fiber, which have higher economic value and saving the environment from pollution.

PP waste (referred as recycled PP, rPP), which has non-polar reactive methine functional group, is capable to react with cellulose of KF by using coupling agent acrylic acid (AA) [6,7]. To improve binding efficiency, DVB was used as compatibilizer [8]. In this work, KF was used either as filler or enforcement in rPP/AA/KF bio-composites. The demand for composites in various applications such as components of building materials, and automotive industry is increasing due to the environmental and economical matter [9]. Flame retardant of the bio-composite materials has become more important in order to comply with the safety requirements of products. Burning process is depended on 3 conditions, such as: oxygen, fuel and heat. Flame retardant can be achieved by the disruption of the burning process at any of these stages that can be lead to the termination of the process before actual ignition occurs. The most expeditious method used to acquire flame retardant is the incorporation of flame-retardants that can interfere with the combustion during a particular stage of the process so that the resulting system shows satisfactory flame retardant [10].

The bio-composites made with natural fiber filler material can be improved inhibitory ability of the flame with the addition of flame inhibiting compounds. Tesoro [11] reported one class of flame inhibiting compound is an inorganic acid and its salts, eg ammonium salts of sulfate and phosphate. Another study conducted by Liodaks and Antonopoulos [12] by comparing the flame inhibiting compound diammonium phosphate, ammonium sulfate, and magnesium carbonate to the ability of the flame on natural fibers, resulting in a conclusion that the diammonium phosphate and ammonium sulfate is an effective flame inhibitors. Robenson and Paul [13] gives an account of the nanocomposite, in which nano-geopolymer has been used as material for nanocomposite that has the ability flame inhibitors. Research conducted by Patra *et al.* [14] added  $\text{CaCO}_3$  nanoparticles to produce a nanocomposite that has the ability to inhibit the flame is higher than the starting material. Tang *et al.* [15] make a mixture of montmorillonite and polypropylene with  $\text{CaCO}_3$ , which owns the flame of good inhibitory ability, the study also reported that better mechanical properties demonstrated by the addition of compound materials with nano-sized particles. Making a material with the ability to inhibit the flame is also done by Xu *et al.* [16] by adding  $\text{SnO}_2$  coated  $\text{CaCO}_3$  on polyvinyl chloride (PVC) that provide inhibitory ability of the flame better than PVC or  $\text{PVC/SnO}_2$  or  $\text{PVC/CaCO}_3$ .

A flame barrier system must be able to produce a gas that can reduce the concentration of  $\text{O}_2$  which supports combustion, reduce the heat propagation in polymers are burned, and produces charcoal to block the view of polymer interactions  $\text{O}_2$  [11]. Levan and Winandy [17] concluded that the phosphoric acid most effective in reducing the concentration of flammable gases and increase the formation of soot to prevent burning, followed by diammonium phosphate and monoammonium phosphate. The study also reported that during the burning of diammonium phosphate (DAP) can be decomposed into  $\text{NH}_3$  gas and phosphoric acid [17]. To improve the performance of the DAP as fire retardant made by combining the DAP with  $\text{CaCO}_3$ . Phosphoric acid from the DAP formed during combustion will react with the  $\text{CaCO}_3$  produces  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Gaseous  $\text{NH}_3$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  can inhibit combustion.  $\text{NH}_3$  gas can reduce the concentration of  $\text{O}_2$  that support combustion [14], while the  $\text{CO}_2$  gas is heavier than  $\text{O}_2$ , The  $\text{CO}_2$  will going down and wrapped the burning object. Replacement  $\text{O}_2$  by  $\text{CO}_2$  and  $\text{NH}_3$  gases cause the  $\text{O}_2$  concentration in the supporting combustion is reduced so that the combustion process is inhibited. Water vapor will cool the system and lower the temperature which will inhibit combustion. Patra *et al.* [14] states that a compound with nano particles were added for the specific purpose of making a

nanocomposite will further enhance the mechanical properties or the ability to inhibit flame. Therefore, the use of nano particle size  $\text{CaCO}_3$  (nCC) in the composite becomes more evenly distributed. The large surface area possess these nanofillers promotes better interfacial interactions with the polymer matrix, leading to better property enhancement [18,19].

The previous work reported [14] combination ammonium polyphosphate (APP) and  $\text{CaCO}_3$  can reduce the flammability of PP. In this study APP compound is replaced with sodium polyphosphate (NaPP) or diammonium phosphate (DAP) which can also serve as a flame extinguishing compound. In addition there are two types of  $\text{CaCO}_3$  compounds used in this work i.e. (1) natural  $\text{CaCO}_3$ , (2)  $\text{CaCO}_3$  pro-analysis grade in nanoparticles. The objective of this paper is to study the effect of mixture fire retardant [nano $\text{CaCO}_3$ +DAP] or [nano $\text{CaCO}_3$ +NaPP] on the flammability, biodegradability and mechanical properties of rPP/DVB/AA/KF bio-composites.

## 2. Experiment

### 2.1. Materials and sample preparation

All chemicals as starting compounds are in pro-analysis grade and used without any further purification. The rPP was obtained from waste drinking water cup. The rPP samples were prepared by washing the waste drinking cups with ethanol, and chopped in  $2 \times 2 \text{ mm}^2$ . The Kenaf Fibre (KF) used was first cleaned with ethanol, dried in oven at  $40^\circ\text{C}$  and ground into 100 mesh particle size.

The synthesis of rPP/DVB/AA/KF/nCC/DAP bio-composite was reactively processed in melt using apparatus Laboplastomill Merk Toyoseiki model 30R150 with starting materials of rPP, KF, AA, DVB containing fire retardant mixture of nCC with DAP or NaPP. The formulation of bio-composites synthesis can be seen in Table 1. Our earlier investigation (unpublished data) showed that the coupling agent AA and crosslinker DVB provides better mechanical properties for the natural fibre filled rPP at optimum loading of 20% and hence is used for this study.

Table 1. Formulation of rPP/DVB/AA/KF/[CC+DAP] or [CC+NaPP] bio-composites

Ingredients (phr)	Bio-composites							
	C1	C2	C3	C4	C5	C6	C7	C8
rPP	100	80	65	65	65	65	65	65
KF	-	20	15	15	15	15	15	15
CCnat	-	-	7	-	7	7	-	-
nanoCC	-	-	-	7	-	-	7	7
DAP	-	-	-	-	13	-	13	-
NaPP	-	-	-	-	-	13	-	13

The flammability of the bio-composites produced by formula F1-F7 was tested in accordance to ASTM D635 in order to determine their time to ignition (TTI), burning rate (BR) and heat release (HR). Flammability test reveals the TTI. When the burning reaches  $L = 25 \text{ mm}$ , the burning time (sec.) is started to be counted and finished when reaches length  $L = 100 \text{ mm}$ . Thus, BR can be calculated by using the following the equation  $\text{BR (mm/min)} = 60L/t$

The highest TTI and the lowest BR show that the material has poor flammability. The HR is the ability of a material to release heat after burning is extinguished at a certain period of time. Thus, the percentage of heat released during that period of time can be measured by using the equation  $\text{HR (\%)} = \{(1 - T_1/T_0) \times 100\}$ , where,  $T_1$  is the material's temperature after the period has elapsed, and  $T_0$  is combustion temperature.

Biodegradation tests were conducted by burying bio-composites in garbage soil for four months, and then measured the lost of weight (*LW*) of the composites after bio-degradation process.

## 2.2. Characterization

Characterization of starting materials as well as new material produced were performed using (1) Atlas Melt Flow Indexer (MFI) in order to determine the melt flow index of bio-composite in accordance with ASTM 1238; (2) Paul Weber Maschinen-u-Aparatbau D-7064 Rhemshalden-Brunbach hot press was utilized to prepare specimens; (3) Tensometry (MPG SC-2 DE) was used to determine tensile strength, TS, in accordance with ASTM D638; (4) Horizontal burning method to perform flammability test in accordance with ASTM D635; and (5) Burial method in cellulolytic bacteria enriched garbage soil for four months to perform biodegradability test.

## 3. Results and Discussion

### 3.1. Flammability of the composite

Figure 1 show the flammability of the polypropylene and filled composites (formulas C1 – C8) measured by horizontal burning test. The TTI of starting materials C1 (rPP) and C2 bio-composites are 1.6 and 2.16 seconds respectively. The bio-composites rPP/DVB/AA/KF containing 20 phr mixture of fire retardant [nCC+NaPP] with ratio of 7:13 (C8) inhibited TTI to 129% of bio-composite without fire retardant (C2). When the bio-composites rPP/DVB/AA/KF containing 20 phr mixture of fire retardant [nCC+DAP] with ratio of 7:13 (C8) inhibited TTI to 149% of bio-composite C2. The burning rate (BR) of rPP and C2 are 2.15 and 1.09 mm/min respectively. The BR of C8 and C7 decrease to 49% and 54% respectively compared to that bio-composites without fire retardant (C2). The percentages HR of rPP and C2 are 73 and 76% respectively. The percentages HR of C8 and C7, increase to 11 and 15 % respectively compared to that bio-composites without fire retardant (C2). Phosphoric acid from the DAP formed during combustion will react with the  $\text{CaCO}_3$  produces  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Gaseous  $\text{NH}_3$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  can inhibit combustion [14,20].

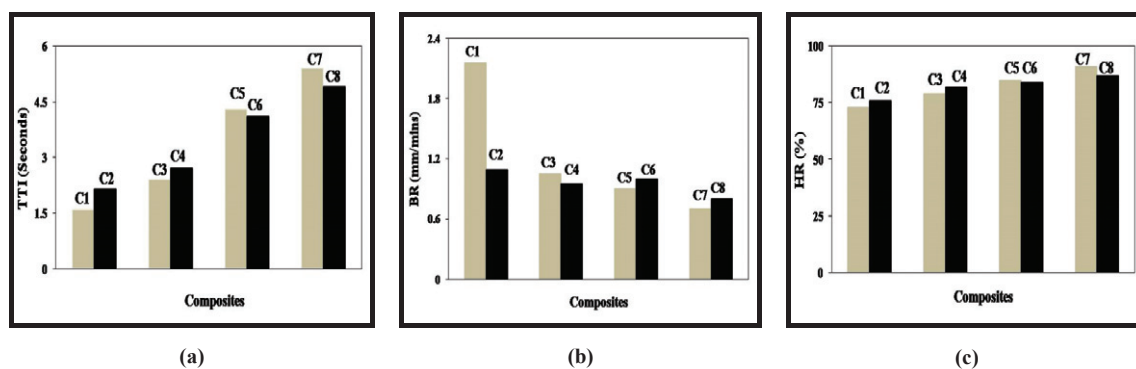


Fig. 1. Results of flammability test of bio-composites: (a) time to ignition, (b) burning rate, and (c) heat release

### 3.2. Biodegradation and mechanical characterizations

Results of biodegradability examination can be seen in Figure 2. Water Absorption (WA) of rPP and C2 are 0 and 1.65 respectively. The WA of bio-composites C8 and C7 can increase up to 1.88% and 1.92%, respectively compared to C2. The Losing Weight (LW) of rPP and C2 are 0 and 5.75% respectively. The LW of bio-composites C7 is higher by approximately 11.82% of biocomposites C2 without fire retardant. This occurs because the cellulose of KF inside composite rPP/DVB/AA/KF in the moist waste ground containing cellulolytic bacteria performed self-biodegradation. This result is supported by the previous work that plastic composites containing natural fiber can absorb water and thus will degrade after being buried in soil [6,7]. The presence of  $\text{CaCO}_3$  in bio-composites are also able to absorb water so it helps in the biodegradation process, this is supported by WA data of bio-composite C8 and C7 reached 1.88% and 19.2% respectively.

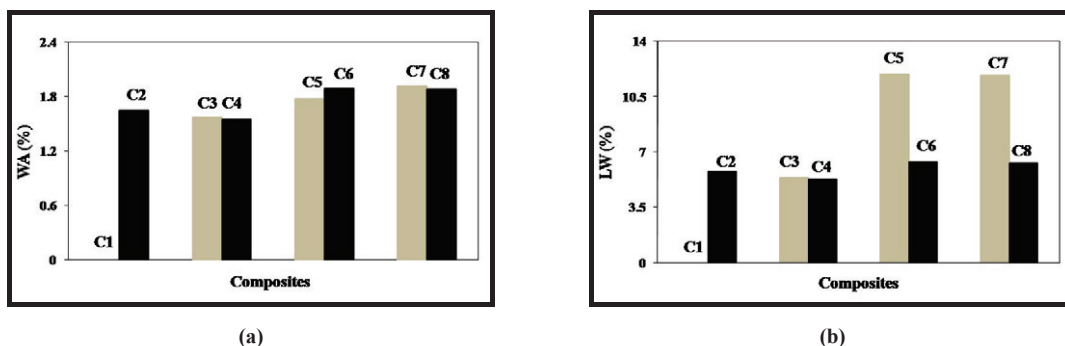


Fig. 2. Results of biodegradability test of bio-composites: (a) water absorption and (b) lost of weight

Mechanical properties examination results of bio-composites as presented in Figure 3 are as follows: The MFI of rPP and C2 are 15.6 and 9.8 g/10 min respectively. The MFI of C8 and C7 decrease up to 33 and 28% respectively compared to bio-composite C2 without fire retardant. The Tensile Strength (TS) of rPP and C2 are 24.8 and 32.4 MPa respectively. The TS of C8 and C7 were lower by 33% and 28%, respectively compared to bio-composite C2. The presence of fire retardant [nCC+NaPP] or [nCC+DAP] in the composites resulting the decrease in TS due to reduction of its elasticity. Similar results have been reported in previous work that in the presence 20%  $\text{Mg}(\text{OH})_2$  fire retardant, the mechanical properties of composite rPP/wood or rice husk fiber were decreased [10].

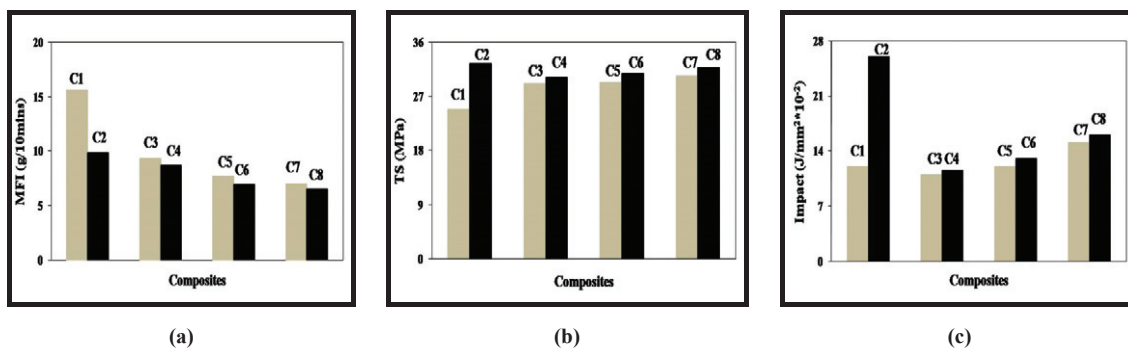


Figure 3. Results of Mechanical Properties of Bio-composites: (a) MFI, (b) TS, and (c) Impact

#### 4. Conclusion

Bio-composites rPP/DVB/AA/KF containing fire retardant mixtures of [nCC+NaPP] or [nCC+DAP] were studied for their structure interactions, flammability, biodegradability and mechanical properties. The bio-composite rPP/DVB/AA/KF containing 20 phr of mixture [nCC+NaPP] with ratio of 7:13 (C8) can effectively increase TTI to 129% and in the same time reduce burning rate to 49% and heat release to 18% compared to bio-composites without any addition of fire retardant. The biodegradability (LW) of bio-composite C7 was 7%. The bio-composite rPP/DVB/AA/KF containing 20 phr of mixture [nCC+DAP] with ratio of 7:13 (C7) can effectively increase TTI to 149% and in the same time reduce burning rate to 54% and increase heat release to 15% compared to bio-composites without any addition of fire retardant. The biodegradability (LW) of bio-composite C7 was 11.82%. However, TS of bio-composites in the presence of fire retardant mixture was slightly decreased. At the same time, better properties than rPP was obtained.

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