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Mechanical Properties and Flame Retardancy of Sawdust/Recycled High Density Polyethylene Composites: Effects of Alkali Treatment and Flame Retardant

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Abstract

Sawdust/recycled high density polyethylene (rHDPE) composites were prepared at a sawdust content of 30 wt% using a twin screw extruder. Effects of alkali treatment and flame retardants; ammonium polyphosphate (APP), aluminum trihydrate (ATH) and zinc borate (ZB) on mechanical, flame retarding and morphological properties of the rHDPE composites were investigated. The alkali treatment led to enhanced mechanical properties and flame retardancy of the composite. Tensile strength, elongation at break and impact strength of the composites were decreased with the addition of flame retardants while tensile modulus and flame retarding properties were increased. Among the flame retardants, APP exhibited the most effective improvement of flame retardancy of the composite. Moreover, the mechanical and flame retarding properties of the composite were improved in the presence of maleic anhydride grafted polyethylene.

Keywords: Recycled HDPE, sawdust, flame retardants, alkali treatment, compatibility

Introduction

Lignocellulosic fillers have received much attention for being used as reinforcing materials due to their biodegradability, renewable resources, low cost and light weight. Sawdust, a by-product from the wood industry, is one of the most used lignocellulosic fillers for preparing lignocellulosic fillers/polymer composites. Using sawdust in producing the lignocellulosic fillers/polymer composites benefits the environment and also adds value to the sawdust.

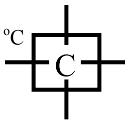
Because of a considerable increase in plastic consumption and plastic waste generation, plastic recycling offers an alternative solution for handling plastic waste. High density polyethylene (HDPE) is one of the most commonly used thermoplastics and constitutes a large portion of the post-consumer household wastes. Moreover, HDPE is easy to separate from the post-consumer household wastes and offers many advantages such as high toughness and good chemical resistance.

Sawdust/recycled high density polyethylene (rHDPE) composites have become popular because they offer interesting combinations of cost and properties [1]. However, the major drawback of the sawdust/rHDPE composites is poor interfacial adhesion between hydrophobic rHDPE and hydrophilic sawdust resulting in poor mechanical properties of the composites [2]. The interfacial adhesion between the sawdust and the rHDPE can be improved by filler surface treatment, matrix modification and adding a compatibilizer. Alkali treatment is one of the most used filler surface treatments because it offers high efficiency, low health hazards, low cost and is easy to handle. This treatment removes lignin, hemicellulose, pectin and impurities covering the surface of filler. Consequently, the effective filler surface area available for interaction with the matrix would increase [3].

Another limitation of sawdust/rHDPE composites is their high flammability [4]. In general, flame retardants have to be introduced into the materials to improve their fire resistance. Due to environmental concerns about the use of halogen compound flame retardants, halogen free flame retardants have become increasing popular. Ammonium polyphosphate (APP) is a very efficient flame retardant mainly used in polymers. APP is nontoxic and it does not generate additional quantities of smoke [5]. At about 250 °C, APP decomposes to yield polyphosphoric acid and ammonia.

$$(NH_4PO_3)_n \xrightarrow{250\,^{\circ}C} (HPO_3)_n + nNH_3 \quad (1)$$

Between 360 and 420 °C, the polyphosphoric acid reacts with the carbonaceous compound to form the char as an insulating protective layer which prevents further flame spread.

$(HPO_3)_n$ + Carbon source $\xrightarrow{360\text{-}420\,^{\circ}C}$  + H_3PO_4 (2)

Abu Baker *et al*. [6] found that APP could effectively reduce flammability of wood flour/polypropylene composites by achieving V-0 UL-94 classification. The limiting oxygen index (LOI) of the composites also increased with adding APP.

Aluminum trihydrate (ATH) is a wildly used flame retardant for polymers. The benefits of ATH include low health hazard, cost effectiveness and smoke suppressant [7]. ATH decomposes endothermically and releases water at about 200 °C. Moreover, aluminium oxide formed during the decomposition acts as a protective layer [8].

$$2Al(OH)_3 \xrightarrow{200\,^{\circ}C} Al_2O_3 + 3H_2O \quad (3)$$

Gracia *et al*. [9] reported that with the addition of ATH into wood fiber/HDPE composites, the composites extinguished after the flame was removed.

Additionally, zinc borate (ZB) is a boron based inorganic compound which is used as a flame retardant in many polymers. It can be used as smoke suppressant, afterglow suppressant, char promoter and flame retardant synergist. Normally, ZB is used in combination with other flame retardants. At about 320 °C, it decomposes endothermically and releases water [5]. Moreover, a char protective layer is formed which separates polymers from oxygen and fire [7].

$$2ZnO.3B_2O_3.3H_2O \xrightarrow{320\,^{\circ}C} 2ZnO.3B_2O_3 + 3H_2O \quad (4)$$

Gao and Zhang [10] showed that ZB improved the flame retardant property and thermal stability of polystyrene (PS). LOI of PS was enhanced when zinc borate was incorporated.

In order to increase the compatibility between flame retardants and rHDPE, maleic anhydride grated polyethylene (MAPE) was added into the composite. Ayrilmis [11] found that mechanical properties of wood flour/HDPE composite containing boron compounds was improved with increasing MAPE content.

The objective of this study was to investigate the influence of alkali treatment on mechanical, flame retarding and morphological properties of sawdust/rHDPE composites. The effect of 3 types of flame retardants; APP, ATH and ZB on the properties of the alkali treated sawdust/rHDPE composites was also examined. In addition, the properties of the composites with and without MAPE as a compatibilizer were studied.

Materials and methods

rHDPE was obtained from pasteurized milk bottles. Sawdust (*Albizia lebbeck Benth*) was supplied from Huathalae Sawmill, Nakhon Ratchasima, Thailand. Sodium hydroxide (NaOH, RPE-ACS, Carlo Erba) was purchased from Italmar (Thailand) Co., Ltd. APP (Exolit AP 765, Clariant, average diameter of 8 µm), ATH (APYRAL® 40CD, Nabaltec, average diameter of 1.3 µm) and ZB (Firebrake® ZB, Rio Tinto Mineral, average diameter of 9 µm) were used as flame retardants. Maleic anhydride grafted polyethylene (MAPE, maleic anhydride content of 0.9 wt%, Fusabond®E MB100D, DuPont) was obtained from Chemical Innovation, Co., Ltd and used as a compatibilizer.

Sawdust preparation

Sawdust was sieved using a 40 mesh screen and later dried in an oven at 60 °C for 24 h. This sawdust was called untreated sawdust (UT). Some sawdust was treated with 2 %wt/v sodium hydroxide solution for 30 min at room temperature. The sawdust was tested for neutralization using a pH meter to maintain a pH of 7. Then the sawdust was dried in an oven for 24 h. This sawdust was called alkali treated sawdust (AT).

Composite preparation

rHDPE composites were prepared at a sawdust content of 30 wt%. APP, ATH and ZB contents were 30 phr. MAPE content was 5 phr. The composites were mixed using a twin screw extruder (Brabender, DSE 35/17D). The temperatures of the processing zones were 175, 180, 185 and 190 °C. The screw speed was 20 rpm. The test specimens were processed by a compression molding machine (Labtech, LP20-B) at 190 °C under a constant pressure of 120 psi for 10 min.

Mechanical testing

Tensile properties of rHDPE and rHDPE composites were examined according to ASTM D638 using a universal testing machine (Instron, 5565) with a load cell of 5 kN and a crosshead speed of 50 mm/min. At least 5 specimens were tested.

Notched izod impact strength of rHDPE and rHDPE composites was performed according to ASTM D256 using an impact testing machine (CEAST 9050) with impact energy of 2.7 J. At least 5 specimens were tested.

Flammability testing

The flammability of rHDPE and rHDPE composites was investigated by a horizontal burning test according to ASTM D635. At least 5 specimens were tested. The specimen was held horizontally and flame was applied to one end of the specimen. The time for the flame to reach from the first reference mark (25 mm from the end) to the second reference mark which was 100 mm from the end was measured. Then, the burning rate of the specimen was calculated using the following equation.

$$V = 60L/t \tag{5}$$

where V is the burning rate (mm/min), L is the burned length (mm), t is the time (s) of burning.

Morphological analysis

Morphologies of the tensile fractured surface of rHDPE composites were examined using a scanning electron microscope (SEM, JEOL JCM-6010) at 10 keV. The samples were coated with gold before examination.

Results and discussion

Tensile properties of rHDPE and rHDPE composites are presented in **Table 1**. Tensile strength and tensile modulus of rHDPE were increased but elongation at break was decreased with adding untreated sawdust. This suggested that sawdust acted as reinforcing filler in the system [12]. Impact strength of the UT/rHDPE composite was lower than that of rHDPE because the addition of sawdust created stress concentration that required less energy to initiate cracking [13]. However, tensile properties and impact strength of AT/rHDPE composite were slightly higher than those of the UT/rHDPE composite due to the improvement of interfacial adhesion between the sawdust and rHDPE matrix. Alkali treatment increased the filler surface roughness by removing hemicellulose, lignin, and impurities on the filler surface resulting in better mechanical interlocking between sawdust and rHDPE matrix.

Table 1 Mechanical properties and burning rate of rHDPE and rHDPE composites.

Sample name	**Tensile strength (MPa)**	**Elongation at break (%)**	**Tensile modulus (GPa)**	**Impact strength (kJ/m^2)**	**Horizontal burning rate (mm/min)**
rHDPE	5.46±0.03	227.53±0.12	0.50±0.01	13.34±0.23	16.70±0.14
UT/rHDPE	20.14±1.20	2.02±0.15	1.45±0.04	5.76±0.10	21.58±0.61
AT/rHDPE	21.37±1.31	2.32±0.20	1.57±0.02	6.52±0.56	17.19±0.50
APP/AT/rHDPE	16.07±0.51	1.06±0.02	2.17±0.17	3.41±0.25	11.50±0.65
ATH/AT/rHDPE	17.97±1.75	1.39±0.04	2.12±0.07	3.53±0.11	12.14±0.06
ZB/AT/rHDPE	18.92±0.10	1.64±0.19	1.80±0.11	3.65±0.12	14.18±0.07
APP/AT/rHDPE/MAPE	25.04±0.63	4.28±0.24	2.07±0.02	3.79±0.32	No burning

The burning rate of rHDPE and rHDPE composites is listed in **Table 1**. Sawdust/rHDPE composites had a higher burning rate than rHDPE. This indicted that the composites had high sensitivity to flames [14]. The AT/rHDPE composite showed a lower burning rate than the UT/rHDPE composite. This may be due to an increase in char residue of the composite by alkali treatment. When the char layer built up it may separate the composite from heat and oxygen [15].

SEM micrographs of tensile fractured surface of the UT/rHDPE and AT/rHDPE composites are shown **Figure 1**. As shown in **Figure 1(a)**, the gap between rHDPE and sawdust was seen due to poor compatibility of sawdust and rHDPE matrix. From **Figure 1(b)**, the alkali treatment enhanced the compatibility between the sawdust and matrix resulting in an increase in the mechanical properties of the composite.

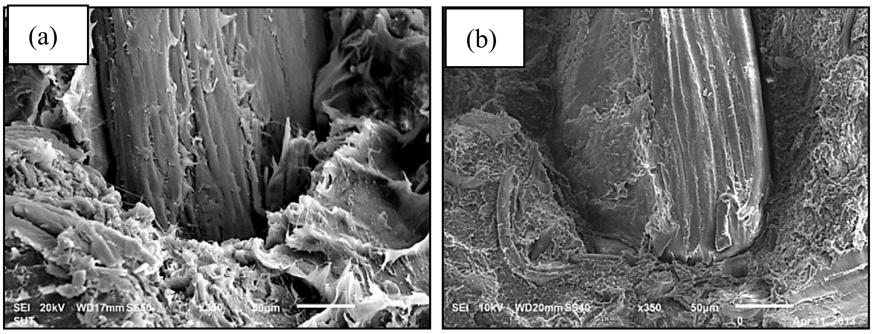


Figure 1 SEM micrographs of tensile fractured surface of rHDPE composites (a) UT/rHDPE and (b) AT//rHDPE (350×).

According to the mechanical and flame retarding properties, the AT/rHDPE composite was selected to investigate the effect of flame retardant type on the properties of the composites. From **Table 1**, with the incorporation of flame retardants, i.e. APP, ATH and ZB into the composites, the reduction of tensile strength, elongation at break and impact strength of the composites was found due to the poor interfacial adhesion between the flame retardants and the rHDPE matrix [16]. The composite with ZB showed higher tensile strength, elongation at break and impact strength when compared to the composite with APP or ATH because ZB had a rougher surface than APP and ATH as confirmed by SEM micrographs (**Figure 2**). This may promote mechanical interlocking between ZB and the polymer matrix. Tensile modulus of all composites with flame retardants were higher than that of the AT/rHDPE composite because the flame retardants were a rigid particle leading to enhanced stiffness of the composites [17].

Flame retardancy of the AT/rHDPE composite was improved by incorporating flame retardants. Among the composites containing the flame retardants, the APP/AT/rHDPE composite exhibited the lowest burning rate. APP produced a char protective layer separating the composite from heat and oxygen [5]. The composites with ATH or ZB also showed a lower burning rate than AT/rHDPE composite. This was because ATH and ZB released water and produced a char protective layer during the combustion [5,8]. However, AT/rHDPE/ZB composite had a higher burning rate than the AT/rHDPE/ATH composite. This indicated that ZB was a poor flame retardant for the AT/rHDPE composite when compared with the other flame retardants. From the results, APP was an effective flame retardant for the composites based upon the burning rate.

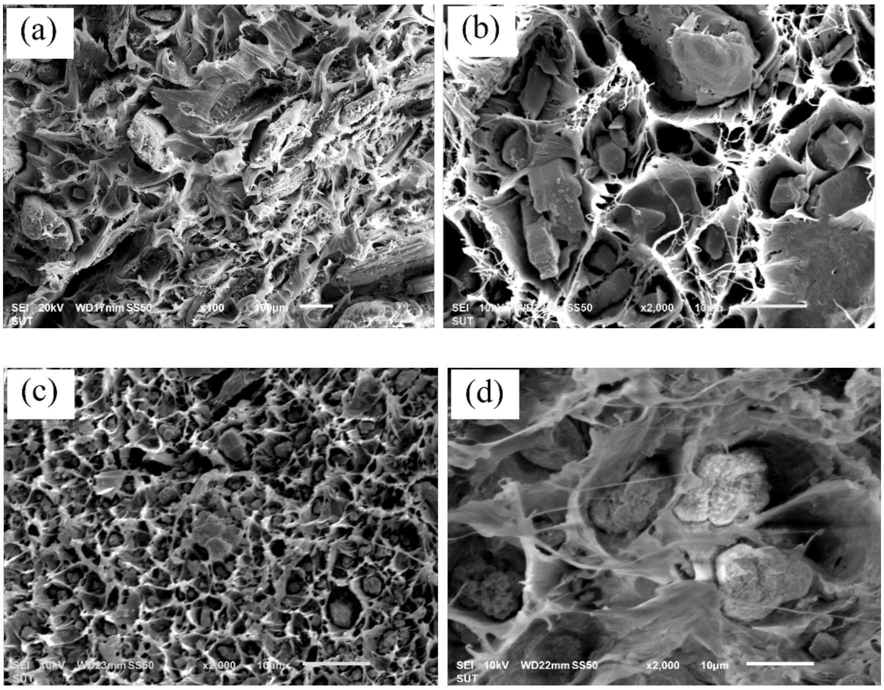


Figure 2 SEM micrographs of tensile fractured surface of rHDPE composites (a) AT/rHDPE (100×), (b) APP/AT/rHDPE (2000×), (c) ATH/AT/rHDPE (2000×) and (d) ZB/AT/rHDPE (2000×).

From **Figures 2(b) - 2(d)**, the poor interfacial adhesion between the flame retardants and the rHDPE matrix was observed. This caused a reduction in tensile strength, elongation at break and impact strength of the composites. However, from **Figure 2(d)**, it can be seen that ZB had rougher surface than APP or ATH which may promote mechanical interlocking between ZB and polymer matrix.

From the mechanical and flame retarding properties, the APP/AT/rHDPE composite was chosen to study the influence of MAPE as a compatibilizer on the properties of the composite. From **Table 1**, it can be seen that the mechanical and flame retarding properties of compatibilized rHDPE composite were better than that of uncompatibilized rHDPE composite. This was because MAPE improved the interfacial adhesion between PE and APP and the sawdust [14] as illustrated in **Figure 3(b)**. This result corresponded well with the properties of the composites.

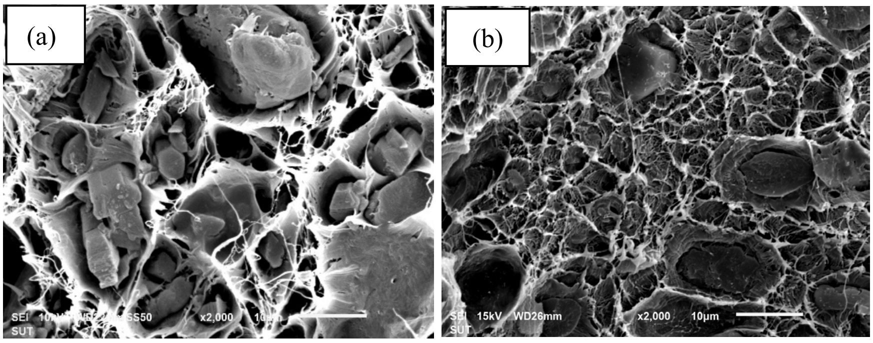


Figure 3 SEM micrographs of tensile fractured surface of rHDPE composites (a) APP/AT/rHDPE and (b) APP/AT/rHDPE/MAPE (2000×).

Conclusions

Incorporating untreated sawdust resulted in an increase in tensile strength and tensile modulus of rHDPE but a decrease in elongation at break and impact strength. Mechanical properties of alkali treated sawdust/rHDPE were higher than that of untreated sawdust/rHDPE composites. With the addition of flame retardants, i.e. APP, ATH and ZB, tensile strength, elongation at break and impact strength of the composites were decreased while tensile modulus and flame retardancy were improved. APP showed the highest efficiency in reducing the burning rate of AT/rHDPE composite. Furthermore, MAPE enhanced the mechanical and flame retarding properties of the composite.

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