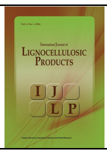

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A novel method for manufacturing of wood flour/PP composites with better fire retardancy and mechanical properties

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Abstract

This study was conducted to investigate the effects of applying methods and amount of ammonium polyphosphate (0, 2 and 4 wt%) on fire retardancy and mechanical properties of wood flour/polypropylene composites. The results showed that addition of fire retardant improved the mechanical properties such as tensile and flexural strengths and fire retardancy of composites. But by increasing of fire retardant impact strength decreased. The scanning electron microscopy observation on the fracture surface of the composites indicated that fire retardant had a uniform dispersion in the wood flour/PP composites. The observations showed that saturation of wood flour with fire retardant had a positive effect on mechanical properties and fire retardancy.

Keywords: Fire retardancy; Mechanical properties; Saturation.

1. Introduction

Wood plastic composite (WPC) combines the favorable performance and cost feature of both wood and plastics (Stark et al., 2010; Hull et al., 2011). The usage of natural fibers in a polymer matrix can improve the mechanical properties of polymer composites, in additional wood plastic composites act as an environmentally friendly way to decrease the use of petroleum based plastics (Pan et al., 2012).

Polypropylene, due to the low density, high chemical and water resistance and good processing is widely used in the manufacturing of wood-plastic composites (Zhang et al., 2012). But high flammability has greatly limited its wider applications so we should treat it with fire retardant (Liu et al., 2009). Compatibility between natural fibers and polymer matrix is low, so compatibilizers such as maleic anhydride–grafted polypropylene should be used to improve the bonding between polymer matrix and fibers (Garcia et al., 2009).

The addition of cellulose materials to polymer enhances the strength and stiffness properties of resultant material (Nikolaeva et al., 2011). But as organic materials, the polymers and the wood fibers are very sensitive to flame. Due to the development of applications of these products for furniture and residential construction industry, it is essential to treat them against fire (Ayrilmis et al., 2011).The usage of fire retardant additives is one strategy to improve fire resistance. Thermal decomposition and combustion of organic agents, produce toxic substances, and thus to produce safe composites, fire retardant additives must be chosen from the phosphorous and inorganic materials (Seetapan et al., 2011).

Flammability of fibers can be reduced with flame retardant by either surface coating or direct incorporation into the mixture of wood and plastic. Due to rising environmental problems, many laws have been created to restrict or prohibit the applications of halogen- containing flame retardants (Song et al., 2010).

Ammonium polyphosphate (APP) is one of the most commonly used flame retardant in natural fiber reinforced polymer composites. APP is the mixture of the phosphorous-nitrogen synergism, which is known to swell. In a heated environment, APP will foam, creating a barrier that will prevent heat and Oxygen from the flammable surface. It can improve charring; APP also reduces smoke production, inhibits smoking and helps resist flame migration (Stark et al., 2010).

Pan et al. (2012) indicated that addition of APP could decrease the heat release rate and total smoke release of wood flour-high density polyethylene (HDPE) composites, while, the composite showed a decrease in tensile elongation at break and impact strength. Anna et al. (2003) studied surface treated cellulose fibers in flame retarded PP composites, and one of their results showed that the addition of APP to the cellulose fiber containing composite would improve fire retardancy. Cinausero et al. (2011) investigated synergism on fire properties between nanosized hydrophobic oxides and ammonium polyphosphate flame retardant additive. Their results showed that peak of heat release rate and smoke opacity had been decreased.

The aim of this study was to evaluate the flammability of natural fiber reinforced polymer composites affected by the addition of APP-based fire retardant using two different methods of adding, by Slide Fire Test Apparatus (SFTA).

2. Materials and methods

2.1. Materials

The polypropylene (PP) used in this study was a homo polymer pellet, grade Z30S, ρ: 0.90 g/cm^3, melt flow index (MFI) 25 g/10 min, was supplied by Arak petrochemical company in Iran. Wood fiber was prepared from Sanaye Choobe Khazar Company in Iran (MDF Caspian khazar). The fibers contained a mixture of six species of *beech, alder, maple, hornbeam, poplar* and *paulownia* cut from the neighboring forests. Wood fibers were converted into wood flour which was screened. Wood flour collected over the screen with mesh of 60 was used for this study. Wood flour was dried at 105 ^{o}C to constant weight before processing. 2 wt% stearic acid was used for lubricant. Maleic anhydride- grafted polypropylene (PP-g-MA) was supplied by Kimiya Baspar Asia Company in Iran and 3-Wt.% of it was used as a Compatibilizer. Fire retardant (APP) was supplied from Serva Feinbiochemica Heidelberg, (New York). Ammonium polyphosphate was added to the wood flour as table 1.

The weight ratio of fire retardant was based on the weight of wood flour, and the weight ratio of MAPP and lubricant were based on the whole weight of wood flour–PP composites.

2.2. *Treating of wood flour*

Half of wood flour was treated by flame retardant suspension. At first the wood flour was poured on mesh fabric, and then it was placed in saturated cylinder for 2 hours with 4 atmospheres at constant pressure. After finishing saturation process, wood flour was out of the cylinder. Due to the penetration, distribution and stabilization of flame retardant, wood flour was air dried for 2 weeks in laboratory. Then saturated wood flour was dried to achieve a moisture content of 0-1%, at 105 ^{o}C in an oven.

Table 1. Composition of wood flour-PP composites (%- by weight).

Sample code	Conditions	PP	Treated & untreated Wood flour	Compatibilizer (%) (whole weight of WPc)	Fire retardant (%) (wood flour)	Lubricant (%) (whole weight of WPc)
Control	P46W49	46	49	3	0	2
1	P45W48F2	45	48	3	2	2
2	P44W47F4	44	47	3	4	2
3	P46TW247	46	47	3	2	2
4	P46TW445	46	45	3	4	2

Note: P= PP, W= untreated wood flour, TW= treated wood flour, and F= fire retardant.

2.3. Processing of wood flour-PP composites

For parts of work, PP, untreated wood flour, fire retardant, stearic acid and MAPP were blended in an internal mixer. And for other part of work, PP, treated wood flour, stearic acid and MAPP were blended in an internal mixer. The barrel temperature was 175 °C and the screw speed was 60 rpm. After mixing, the bulky composites were granulated by chipper. Flexural and tensile specimens were molded by an injection machine. The temperatures of the barrels increased from 145, 150, to 160 °C. Injection pressure was 1800 psi and the screw speed was 80 rpm. Fire testing samples were prepared by laboratory press (OTT).

2.4. Test procedure

2.4.1. Flammability testing

Due to the unavailability of standard testes by cone calorimeter, we used the apparatus that was built in Shahid Rajaee teacher training university. This apparatus is called the Slide Fire Test Apparatus (SFTA), similar to the ISO 11925 small flame ignitability test.

Fire retardant tests were carried out following ISO11925-3 standard by using Slide Fire Test Apparatus (SFTA). In this apparatus, the specimen was vertically mounted on a holder and exposed to a Bunsen- type burner held at 45 ° to the surface of the specimen for 120 s. The burner was fixed on a slide moving back and forth, equipped with an adjustable stop to keep flame at a certain distance from the specimen. While the slide is back, the burner is turned on; the slide is then pulled forward abruptly to expose the flame to the specimen. After 120 s, the slide is pulled back to prevent over-exposure of the specimen to the flame (Rangavar et al., 2012). Once the flame was extinguished or the specimen was no longer burning, the length and width of the burnt area were measured. The weight is also determined before and after the test to measure the weight loss. The specimen size for this test was 150 mm × 130 mm × 9 mm.

2.4.2. Mechanical properties

Flexural test was performed according to ASTM D790. Before testing, the test specimens were conditioned at ambient for 2 weeks to reach moisture equilibrium with the environment. This is because WPCs take much longer to equilibrate than plastics. A three-point loading system was utilized with a crosshead speed of 2 mm/min. Flexural modulus of elasticity (MOE) and modulus of rapture (MOR) were calculated according to ASTM D790.

Tensile properties of wood flour-PP composites were examined according to ASTM D638. Crosshead speed was 2 mm/min. Tensile and bending tests were conducted using a Universal Testing Machine (Schenk-Treble). Specimens were tested following ASTM D256 for notched Izod impact strength. Impact test was performed with a pendulum apparatus (Santam model SIT20D) using conventional V notched specimens. The hammer weight and the impact energy were 0.818 kg and 5J, respectively. Three replicate specimens were tested for each formulation.

2.5. Statistical analysis

Statistical analysis was conducted using SPSS software program, version 20. Factorial experiments were performed on the data to conclude significant differences at the 95% level of confidence.

2.6. Scanning electron microscopy (SEM)

To better understand the diffusion of fire retardant in wood flour/PP composites, the fracture surfaces of the tensile tested samples were observed using Scanning Electron Microscope (Hitachi HHS-ZR). The surfaces were coated with gold before examination.

3. Results and discussion

3.1. Fire retardancy properties

The longest ignition time was found in specimens impregnated with 4% ammonium polyphosphate (45.03 s); and the shortest one was found in control specimens without fire retardant (26.22 s) (Figure 1).

Glowing time did not show much difference between the four treatments. The longest glowing time in wood flour-PP composites was found in APP-impregnated specimens, similar to the result of ignition time (Figure 2).

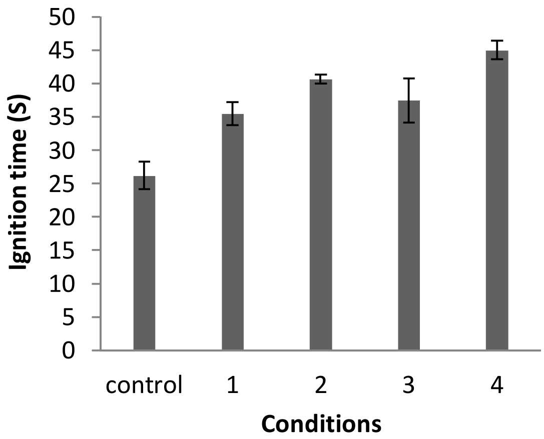

Figure 1. Ignition time of the five treatments.

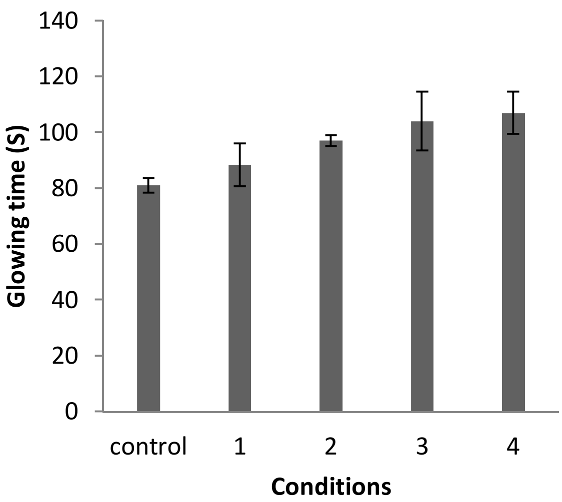

Figure 2. Glowing time of the five treatments.

Ignitibility was measured by observing the time for sustained ignition of the specimen and the time the spot starts to glow were reported as the ignition time and glowing time respectively.

Ammonium polyphosphate is an effective swelling fire retardant for a lot of cases of polymer-based composites. It has a main group of chain phosphate with high molecular weight. Its efficiency is because of increasing of the char formation through a condensed phase reaction. App can decay wood or natural fiber to form char. Addition of APP to the wood composite precipitate the first step of decomposition. In this stage, APP interacts with wood composite to produce volatile compounds and phosphorus rich layer, that could protect the polymer matrix against heat, after that the protective layer would decompose to produce the polymer matrix at the second stage. The resulted carbonaceous char is less-flammable than before (Zhang et al., 2012). Because of these reasons, it can be seen that the addition of fire retardant (APP) to wood flour- PP composites can significantly increase the ignition time and glowing time (Figures 1 and 2). Rangavar et al., (2012) were reported the same results about increasing of ignition and glowing times.

The lowest carbonized area was found in specimens impregnated with 4% APP and the highest carbonized area was in the control specimens (Figure 3) and the highest weight loss was observed in control specimens (0.89%) and the lowest weight loss was found in impregnated specimens with 4% APP (0.48%) (Figure 4).

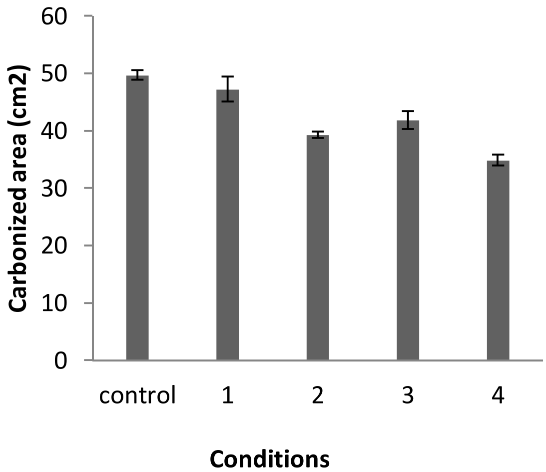

Figure 3. Carbonized area of the five treatments.

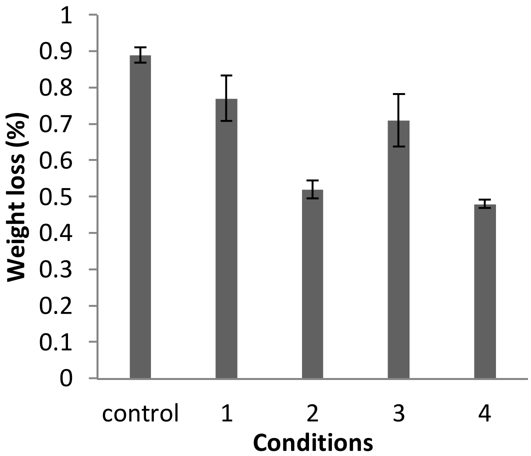

Figure 4. Weight loss rate of the five treatments.

After the addition of fire retardant no bubbles are formed during burning and the flame spread out much more slowly than in non-additivated specimens (Garcia et al., 2009). In addition, only the external surface of the specimens was burnt, while the inner part was not changed. So the mass loss rate and carbonized area of samples were decreased (Figures 3 and 4). This was consistent with a previous study reported by Rangavar et al. (2012). Pan et al. (2012) also found that addition of APP to wood flour-PP composites reduced the mass loss rate of specimens.

3.2. Mechanical analysis

Addition of fire retardant to wood flour–PP composites increased MOR and MOE. The highest MOR and MOE were observed in specimens with 4% fire retardant (Figures 5 and 6).

The mechanical properties of the wood flour-PP composites are shown in Figures 5 and 8. It can be seen that MOR, MOE and tensile strength were increased as fire retardant content increased. The addition of wood flour increased the modulus of the composites; this is because the wood flour is stiffer than neat polymer (Garcia et al., 2009). As a rigid material, the fire retardant had a higher stiffness than PP and wood flour, so the addition of fire retardant caused a higher flexural modulus of the wood flour/PP composites. Pan et al., (2012) also found that addition of APP to wood flour/PP composites improved the flexural strength of specimens.

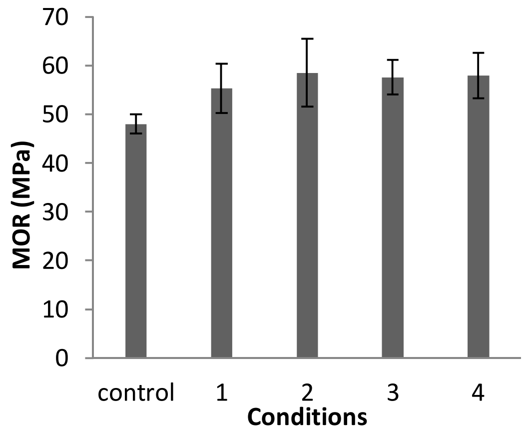

Figure 5. Modulus of rapture of the five treatments.

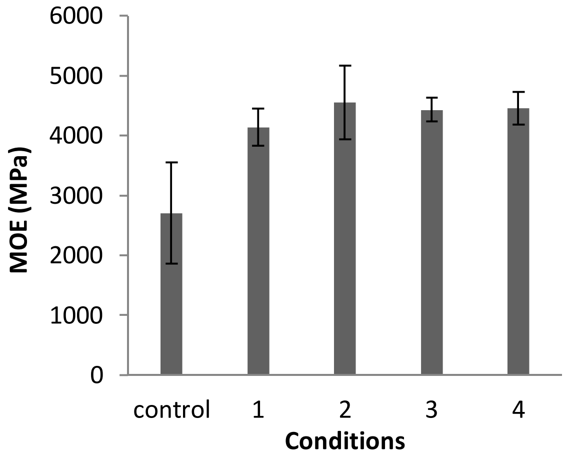

Figure 6. Modulus of elasticity of the five treatments.

The SPSS analysis showed that tensile strength was significantly increased by addition of fire retardant. The highest tensile strength was found in specimens impregnated with 4% APP (Figure 7).

Higher PP amount in the wood flour-50 formulation indicated a decrease in the porosity of the wood-plastic composites, when PP melts around 210 °C. However, the inorganic particles of the fire retardant used in treatments do not melt in the wood plastic composites during processing because of their higher melting temperatures. For these reason, they stay as powder in the WPC and increase the porosity content of the WPCs (Ayrilmis et al., 2011). Flexibility of samples was increased and stress concentration was reduced by increasing of the porosity, so tensile strength improved in compare with the control specimens.

The impact strength of the composites is reported in Figure 8. To improve the flammability properties of the wood plastic composites, fire retardant was added to the system. However, it can be seen that the impact energy of the composites decreased slightly from 5.57 to 5.47 J/m as fire retardant content increased. It can also be seen that in impregnated specimens, the impact energy increased.

The increase in amount of fire retardant caused a decrease in impact strength (Figure 8). It can be attributed to a weak interface between the fire retardant and matrix and resultant micro cracks within the specimens (Zhang et al., 2012). Another reason is because of energy scattering by the fire retardant with more rigid (Pan et al., 2012). The impact properties reduction in APP treated wood-plastic composites has also reported by other researchers such as: Stark et al. (2010), Pan et al. (2012), Zhang et al. (2012).

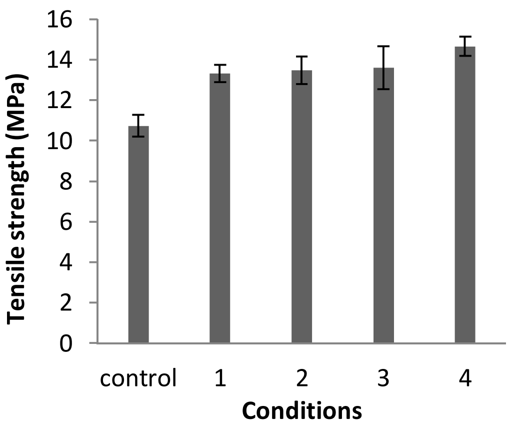

Figure 7. Tensile strength of the five treatments.

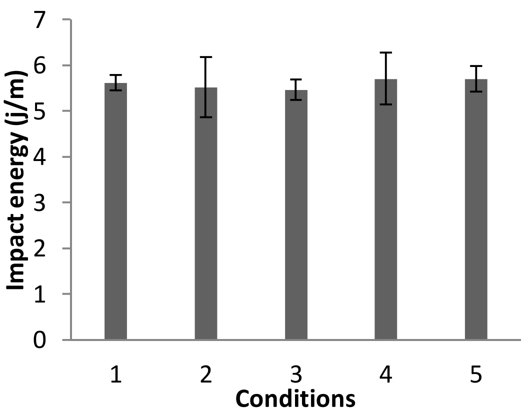

Figure 8. Impact energy of the five treatments.

3.3. Scanning electron microscopy

SEM micrographs of the fracture surface of the PP/wood flour composites affected by fire retardant are shown in Figure 9. It can be seen that fire retardant was uniformly distributed into the matrix phase. Furthermore, it was difficult to observe microcaps in the structure of the wood flour/PP composites without fire retardant and composites that were created with saturated wood flour with fire retardant as shown in Figure 9c and 9d.

On the other hand, the SEM micrographs show formation some of the voids and micro-gaps in the structure of the fire retardant composites. It seems these voids are formed during the combustion reaction due to high expansion of the fire retardant agent. Figure 9 also shows that some of the wood flour was pulled out from the polymer matrix phase with no resin adhering to the fibers, suggesting that existence of the fire retardant agent had a negative effect on the formation of interface.

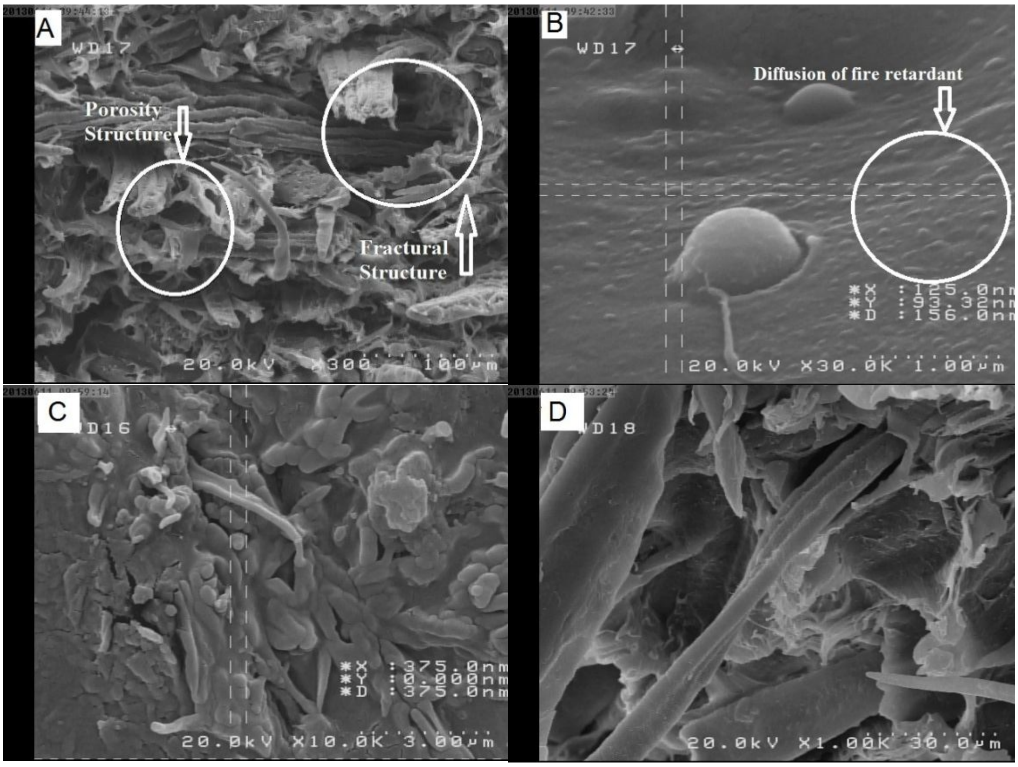

Figure 9. SEM observation of the composites (A and B) P50W50F4, (C) P50TW450, (D) P50W50.

4. Conclusions

Fire retardant treated wood-plastic composites based on PP and wood flour were made. The flammability behavior and mechanical properties of these composites were investigated in this study. APP–based fire retardant had a positive effect on fire performance of wood flour-PP composites, and it could improve both the ignition and glowing time and also, decrease the carbonized area and mass loss rate. By increasing fire retardant from 0 to 4 w%, flexural strengths of composites were increased and impact strength decreased due to higher stiffness of the fire retardant. The SEM observation on the fracture surface of composites indicated that the fire retardant had a better dispersion in composites, and it could expand enormously in the course of a combustion reaction. Should be noted that the saturation of wood flour with fire retardant had a positive effect on the mechanical properties and flammability.

Acknowledgment

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