Impact of Nanofillers On The Mechanical Properties And Fire Resistance of Wood High Density Polyethylene Composites

Ben Ammar, D.[1], Koubaa A.[1], Migneault, S.[1], Bouafif H.[2] and Hadidane M.[1]

[1] Chaire de recherche du Canada en valorisation, caractérisation et transformation du bois, Université du Québec en Abitibi-Témiscamingue

[2] Centre Technologique des résidus industriels CTRI

Abstract

In the present work, the effects of different nanofillers on mechanical properties and flame retardant mechanism of wood-high density polyethylene composites WHDPEC were studied with three nanofillers namely, an organically modified nanoclay, a nanometric fumed silica and a nanometric fumed alumina. Samples had been prepared by twin-screw extrusion with percentages 1%, 3% and 5% of nanofillers and 20%, 30% and 40% of fibers. Mechanical testing indicated that the reinforcement in the nanocomposites was more effective than that in the nonfilled composites. The nanoclay filled composites proved more effective than alumina and silica filled composites in reinforcement. It was revealed from the cone calorimeter tests that the peak of heat release rate (PHRR) and the specific mass loss rate MLR decreased significantly for the nanoclay.

Introduction

WPCs are nowadays more interesting than solid wood (Ashori, 2008) because they are renewable source, low-cost, and lightweight materials (Sombatsompop & Chaochanchaikul, 2004). They are widely used in building and transportation. The main components of WPC are both flammable organic materials. Usual WPC products are currently produced based on Polypropylene PP and polyethylene PE, therefore, flame-retardant solutions are sought for WPC based on these polymers. The thermoplastics used in WPC are usually limited to those with melting points below 200°C, due to the thermal degradation of lignocellulosic components (Schirp & Su, 2016). HDPE is used as thermoplastic matrix in WPC during this study. Therefore, the main objective is to flame retard WPC without sacrificing their mechanical properties. Nanocomposites have attracted researchers and industrials attention as flame retardants. The addition of nanoclay can improve not only the fire performance but also the mechanical properties of wood-polymer composites (Chungui Zhao et al., 2004; Deka & Maji, 2011; Faruk & Matuana, 2008; Guo et al., 2007). As an alternative to halogenated flame-retardants, which are not an environment friendly flame-retardants, our approach has been to optimize burning wood-polymer composites by the addition of inorganic additives. This study aims to determine inorganic nanofillers flame retardant effectiveness and mechanisms of flame retardancy in filled wood-plastic composites WPC. The cone calorimeter bench-scale test is one of the most useful tests that tries to simulate real fire scenarios (Babrauskas, 1995). The different fire tests usually used don't have same material responses to fire. Unlike the UL-94 test that measures the response to a removed fire source and self-extinction time, cone calorimeter test measures the response to constant fire source with time. But, the presence of test conditions makes that some good correlations can be seen between cone calorimeter and UL-94 tests (Morgan & Bundy, 2007). The combustion cycle had been well studied.

Combustion process of any type of fuel source, either wood or polymer constitutes a cycle of three steps that occur in this order: heating of the fuel source, decomposition of the fuel source into combustible and no combustible materials and finally ignition of the combustible fuel and air mixture to produce a flame. The decomposition of the fuel source is initially done by an external ignition source that starts the cycle. Once the combustion process is started and the fuel/air mixture remains constant the heat generated by the exothermic ignition of the fuel is enough to keep the combustion cycle going.

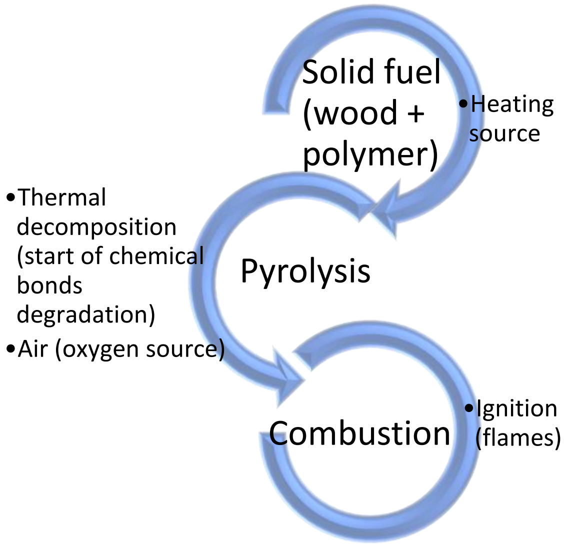

Figure 1: Combustion process layout

The chemistry of combustion process is well-studied, but the exact mechanism of producing some of products is still not completely understood. It's insane to think that we can stop materials from burning, that's why the main issue of studies is fire retardancy. In order to retard plastics burning, the combustion cycle has to be stopped. A burning plastic has two phases: a vapor phase and a condensed phase (Rusanov, 1994). The idea is to try stopping the fire in the condensed phase or/and the vapor phase.

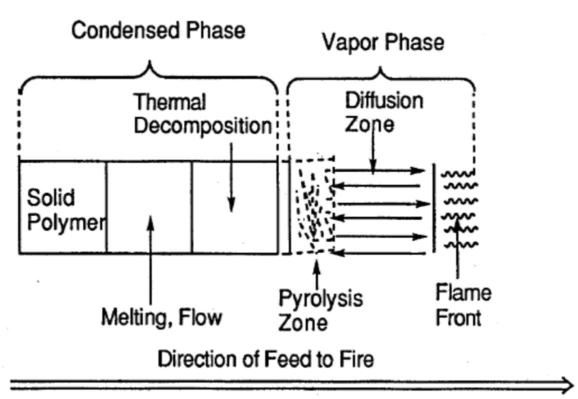

Figure 2: representation of combustion phases (Stevens, 1999)

Fire-retardants had been classified into six categories: additives that increase the char formation at a lower temperature than that where untreated material begins to degrade (ammonium orthophosphate dihydrogen , Sodium chloride, etc.), additives that act as flame-free traps in the flame (halogenated compounds), intumescent chemicals that form a barrier on the surface of the material (sodium silicates), chemicals that increase thermal conductivity of the material, chemicals that dilute combustible gases from the material with non-combustible gases (borax) and additives that reduce the heat content of volatile gases (ammonium phosphate, sodium tetraborate) (Rowell, 2012). In most of cases, a given flame retardant works by several of these mechanisms.

The mechanical properties of composites in the presence of wood fibers and nanoclays are highly dependent on the proportion of compatibilizing agent. It can be better incorporate a minimum of 7% coupling agent (Zhong et al., 2007).

Although most studies have used montmorillonite (nanoclay), some researchers have worked with spherical nanoparticles such as octylsilane-modified silica because of their ability to improve the thermal and mechanical properties of nanocomposites (Deka & Maji, 2011). Fumed silica particles accumulated near the composite surface act as a thermal insulation layer and reduce the polymer concentration near the surface, creating a less flammable material. (Zanetti et al., 2002) Nanoclays act as barrier effect by developing surrounding char, which prevent composite combustion. Fumed alumina, as a metallic oxide, act like as nanoclays by the “barrier effect” but also, inhibit radical reactions in gaseous phase.

Experimental

1) Materials

The experiments were carried out on a mixture of aspen fibers which were dried in the open air. A high-density polyethylene HDPE supplied by the Canadian company Union Carbide Chemicals and Plastics® was used as polymeric matrix with a density of 0.96 g/cm^3 and a melt index of 4.9 g/10 min. To ensure bridging between the hydrophobic macromolecules of the polymer and the hydrophilic wood fibers, a percentage of 3% of coupling agent namely maleic anhydride modified polyethylene (MAPE) was used. Three nanometric minerals were used with reported specific surface area of 100 and 150 cm^2/g for fumed alumina AEROXIDE® Alu C 805 and fumed silica AEROSIL® R 805 respectively. The organically modified nanoclay GARAMITE has an average particle size of 10 µm.

2) Samples preparation

Firstly, wood flour, HDPE and flame retardants were dried at 70°C for 2h to remove any moisture content and ensure good dispersion of the nanofiller in the mixture. Secondly, the blends were premixed and then extruded by a twin-screw extruder THERMO SCIENTIFIC HAAKE POLYLAB OS, Germany. The temperature range of the twin-screw extruder was 160-170°C and screw speed was 100 rpm. Standard tensile (ASTM D638), flexural (ASTM D790), notched Izod (ASTM D256) and cone calorimetric (100*100*3 mm^3) specimens were injection-molded using an injection-molding machine. After injection molding, the specimens were placed in a desiccator for 24h prior to the test.

3) Analysis of samples

3.1) *Mechanical tests*

Mechanical properties like tensile strength and bending strength and impact IZOD were measured.
3.2) *Cone calorimeter test*

The flammability properties, including peak heat release rate PHRR, mass loss rate MLR, time to ignition TTI, and others, were measured by cone calorimetry test at 50 kW/m^2 in accord with ASTM E-1354/ISO-5660. All test samples were horizontal.

Results and Discussion

1) Mechanical properties

Table 1 lists the mechanical properties of nanofilled and nonfilled composites. An increase in strength and modulus can be shown (table 1) for nanofilled composites. With increasing nanoclay loading, the strength and modulus of wood/HDPE/nanoclay composites increase, while the notched impact strength and the elongation at break decreases (figure 3). It may be interesting to see that all reported mechanical properties decrease with increasing nanoalumina percentage (table 1).

Table 1: Mechanical properties of nanofilled and nonfilled WPC

	Tensile modulus MOE (GPa)	Tensile strength MOR (MPa)	Flexural strength (MPa)	Elongation at break ε_{break} (%)	IZOD impact strength (J/m)
20WPC	1,1	28,3	38,7	7,7	22,5
20WPC1AL	0,94	27,5	24,8	7,45	14,9
20WPC3AL	0,86	22,8	24,2	7,14	17,3
20WPC5AL	0,76	22	23,5	6,63	17,5
40WPC	1,82	38,7	52,8	4,13	18,2
40WPC5GA	2,19	40,9	57,8	3,16	9,4
40WPC5AL	1,29	31,6	41,2	3,78	10,3
40WPC5SI	1,32	22	42,6	3,65	13,8

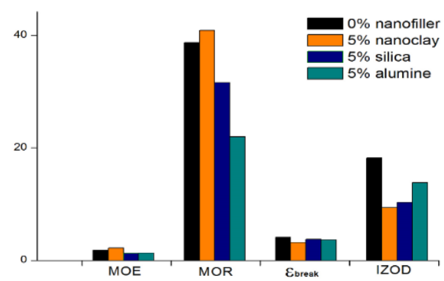

Figure 3: Mechanical test results for 40WHDPEC nanofilled with 5%.

2) Flammability properties

The cone calorimeter test results of Heat Release Rate HRR (KW/m^2), Total Heat Release THR (MJ/m^2), CO and CO_2 production (g/s) are illustrated in figure 4.

The heat release rates of the 20% WPC samples filled with 3% of additives (Figure 4a) shows that the addition of nanoclay reduced HRR of the composites more than the addition of silica and alumina. Same results are noted for the total heat release rate THR of samples, which is obtained by integrating the HRR curve over the test time (Figure 4b). It’s the area under the curves that is compared. THR reduced more with nanoclay and alumina.
CO and CO_2 production curves (Figures 4c and 4d) observation suggests that nanosilica is the most gas producing nanofiller and that nanoclay is on the contrary, the less gas producing one.

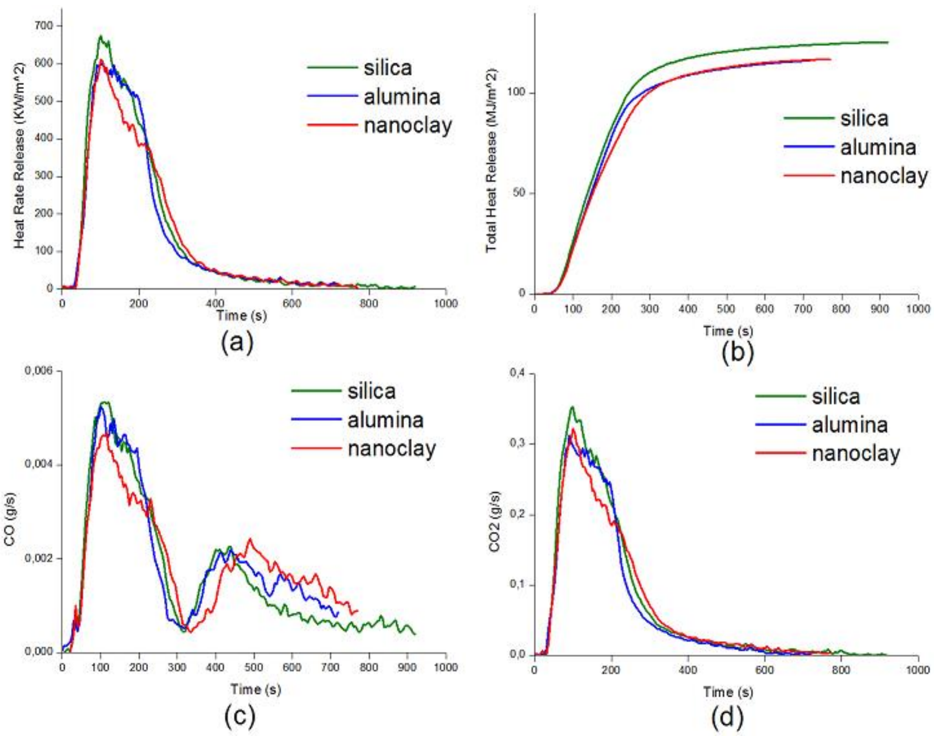

Figure 4: Cone calorimeter results of 20WPC samples filled with 3% additives: (a) Heat Release Rate HRR (KW/m2), (b) Total Heat Release THR (MJ/m2), (c) CO production (g/s) and (d) CO2 production (g/s).

The table 2 summarize the most reported and commonly used cone calorimetry parameters.
The ignition time TTI (s) is the time required for a material subjected to a given heat flux to ignite. The faster the material ignites, the faster the spread of the flame. TTI nanoclay presents a significant increase (figure 5).

The Total Heat Release THR and the maximum heat output or peak heat release rate (PHRR) are considered to be the most important parameters from the point of view of materials flammability. In general, a material with a low PHRR will cause less damage to the surrounding environment than that with a high PHRR.

Table 2: Summary cone calorimeter data and commonly used parameters, 0.5mm thickness, 50kW/m2 heat flux

Material	TTI (s)	PHRR (kW/m^2)	Time to PHRR(s)	FPI	THR (MJ/m^2)	FIGR	MLR (g/m^2s)	TSR (m^2/m^2)	TSP (m^2)	TOC (g)
20WPC1SI	27,50	722,50	97,50	27,16	113,05	7,48	9,02	898,90	7,95	71,20
20WPC3SI	30,50	694,80	97,50	22,87	124,40	7,14	10,97	1088,20	9,60	78,05
20WPC3GA	33,50	582,35	105,00	17,37	113,20	5,57	9,31	1069,75	9,45	70,80
20WPC3AL	28,50	644,46	105,00	22,64	106,55	6,13	12,07	871,55	7,70	66,65
30WPC1SI	32,00	631,42	102,50	19,77	111,35	6,16	10,91	929,35	8,20	69,95
30WPC5SI	29,50	560,32	102,50	19,00	106,65	5,49	9,92	975,45	8,60	66,85
40WPC5GA	32,00	401,71	85,00	12,58	109,45	4,75	5,79	1129,90	10,00	68,75
40WPC5SI	34,50	501,93	90,00	14,57	105,85	5,58	8,29	1059,45	9,35	66,45

The figure 5 shows that nanoclay present the lowest PHRR followed by nanoalumina. The PHRR of 20WHDPEC with 3% nanofiller are around 694 kW/m² (Silica), 644 kW/m² (alumina) and 582 kW/m² (nanoclay). It can be said that nanoclay reduced the PHRR 17% more than nanosilica. The remarkable decrease of the PHRR contributes to the improved flammability properties of WPC.

From the PHRR and TTI, (Petrella 1994) has established an arbitrary classification of risk factors for Flashover Propensity Index (FPI). The higher the FPI, the greater the risk of flashover. According to figure 5, nanoclay has the lowest FPI with an index of 17,3 compared to nanosilica that presents an index of 22,8. To simplify interpretation of cone calorimetry data, indices have been introduced for fires with developing hazards, such as FIGRA (fire growth rate which is equal to the PHRR (t) / t quotient). This index is deduced from the PHRR. The table 2 presents FIGRA data and shows that FIGRA varies depending on the type and the percentage of nanofiller.

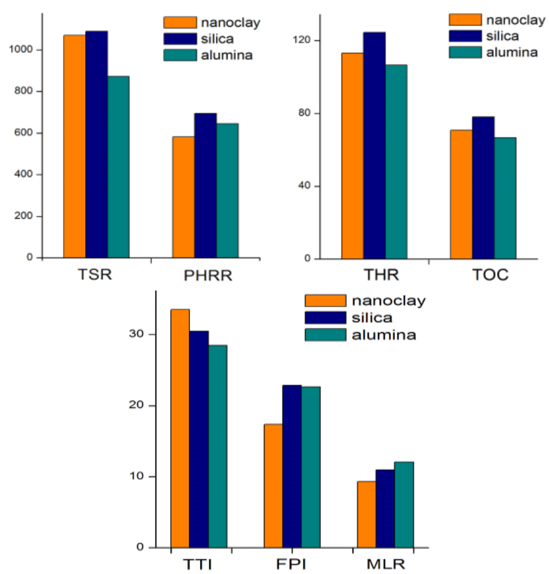

Figure 5: Cone calorimeter most important parameters

Nanosilica Clearly shows the highest amounts of total smoke released TSR, total smoke produced TSP and total oxygen consumed TOC (figure 5).

Conclusion

In this paper, we have shown mechanical, thermal and flammability effectiveness on various nanofilled wood-plastic composites WPC. The wood-high density polyethylene composites WHDPEC were prepared by twin-screw extruder technique. The nanofilled composites show mechanical properties amelioration than the nonfilled WPC. The nanoclay filled composites proved more effective than alumina and silica filled composites in reinforcement. Through qualitative cone calorimeter test analysis of HRR, THR, CO and CO_2 rate curves, trends of fire behaviour can be seen. Nanoclay presents the lowest values and so is considered as the more effective retardant fire nanofiller.

Upon quantitative analysis, it has been revealed notable decreases of the PHRR, contributing to the decreased fire risk properties. It has also been showed significant TTI and FPI increase for nanoclay.

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