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Mechanical, flammability and thermal degradation characteristics of rice straw fiber-recycled polystyrene foam hard wood composites incorporating fire retardants

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Abstract

Hard wood–polymer composite (HWC) was prepared, based on hot press technique, by mixing air-dried rice straw waste as a filler into a molten of chemically recycled extended polystyrene foam waste (PS) and its maleated form (PS-g-MA) as a matrix. Two fire retardants (FRs), namely zinc borate (ZB) and/or anhydrous magnesium hydroxide (MH), were dispersed into the composite to compensate for the poor thermal stability and flammability of the composite. Thermal properties of the reached HWC were evaluated by different techniques including thermogravimetric analysis, differential scanning calorimetric, in addition to, flammability analyses. Mechanical characterization was, also, rated based on tensile strength and elongation at break measurements. It was found that incorporation of the nominated fire retardants improved the thermal stability of the final products. Besides, flammability resistance was enhanced as ZB and/or MH was added to the hard wood–polymer composite formulation. The onset temperature of degradation and mass loss rates were significantly reduced in the presence of the FRs. The tensile strength of HWC was reinforced by marked additions of the FRs. The obtained data can fulfill the required optimal performance of the HWC to fire and mechanical characterizations which are necessary for many applications in the residential construction, transportation and furniture industries.

Keywords Polystyrene waste · Rice straw agro-waste · Hard wood composite · Flammability test · Thermal analyses

Introduction

Hard plastic composites (HPCs) are a new class of materials that merge the best features of wood and plastic to cover a wide range of applications [1]. Wood fiber-reinforced polymer composites are more environmental-friendly admitted materials that can be used in transportation, military applications, building and construction industries, packaging, consumer products, etc. [2]. The production of such composite materials, which meet the standards of green technology, has increased from 0.36 million tons in 2007 to 2.33 million tons in 2012. It is predicted that by 2020 their production will reach 3.45 million tons [3].

Strict safety and quality standards in many industries imposed a significant number of technical requirements on wood–plastic composites. One of the main factors limiting the use of HPCs in some industrial fields is flammability. The optimal performance of the HPCs to fire is necessary for many applications especially in the residential construction, transportation and furniture industries [1].

Hard plastic composites are increasingly being asked for assurance of product lifetime, particularly for components, which cannot be easily inspected or may fail catastrophically in service. Thermal stability is one of the demands that should be guaranteed to avoid such trouble.

Wood, polymer and wood–polymer composites are consisting of organic compounds which are mainly composed of carbon and hydrogen elements; for this reason, they are combustible [4]. It is impossible to make wood and HPCs incombustible, but it is possible to make them fire resistant. Fire retardants (thermal stabilizer) are

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additives added to improve thermal stability of wood–polymer composites. They must be inexpensive and easily processed with the HPCs ingredients. Furthermore, it must be eco-friendly during their life services or at the time of recycling of the products or at the dumping sites [5]. The effect of fire retardant on the properties of these composites depends on the structure of the materials used. Accordingly, characterization of the flammability of HPCs should be done by analyzing independently the properties of the matter constituting the composite.

The submitted work followed the flammability and thermal stability of a hard wood composite (HWC) made of the air-dried rice straw waste as filling lignocellulosic fibers and a molten of chemically recycled expanded polystyrene with its maleated form as polymer matrix.

It is known that cellulose and hemicelluloses enhance the flammability of wood, but lignin promotes the fire-retardant behavior of wood [1].

On the other hand, polystyrene is widely used as thermoplastic engineering polymer which is also poor fire performers in the absence of flame retardants.

There is little research studying the flammability of natural fiber and wood fiber–polymer composites in the literature [2], and the authors are indeed sure there is no research, or very rare, concerning the flammability and thermal stability of the HWC made of two waste materials, namely recycled polystyrene foam waste and rice straw agriculture waste.

The main objective of this work is the evaluation of mechanical, flammability and thermal characterizations of the nominated hard wood composite (HWC) when using zinc borate and/or magnesium hydroxide as non-halogenated flame-retardant additives aiming to enhance their thermal stability, reducing their flammability and influencing their mechanical performance.

Materials and methods

Raw materials

Rice straw (RS) was acquired as agricultural wastes from an Egyptian local field at the end of the harvest time. RS was dried in the open air of the farm. It was ground using a hammer mill that has a perforated metal plate with opening size of 2–3 mm. RS was used without any special treatment aiming to offer a simple process that has the advantages of adequate low cost for an easy applied application by local community dwellers. The air-dried process of the RS is not only energy saving, but also reserved its components. It served, in this study, as reinforcing lignocellulosic fiber filler. The average chemical composition of lignocellulosic moieties in the rice straw is represented in Table 1.

Table 1 Chemical composition of lignocellulosic moieties in rice straw fibers (%). *Source*: www.ecn.nl/phyllis

Hemicelluloses/%	Cellulose/%	Lignin/%
21.5–26.5	28.1–41	9.9–23.3

Recycled polystyrene foam (PS) was used as plastic matrix for lignocellulosic filler–PS composite formulation. The recycled PS was obtained from foam food ware and/or thermal insulating materials. The chemical recycling was recommended to reduce the big volume of PS foam waste where it was collected in acetone as solvent. That simply causes the tiny bubbles in the foam structure to come apart, and when acetone evaporates, a cluster of solid polystyrene (PS) would leave behind. Maleated polystyrene was prepared based on the recycled PS following the method previously published [6] and used as a coupling agent.

Magnesium hydroxide, zinc borate and other chemicals were used as received.

Compounding of HWC

For the plastic matrix formulation, the recycled PS and (PS-g-MA) were preheated in a Brabender Plasticorder at temperature 443 K and at a rotor speed of 50 rpm. The dried ground RS, ZB and/or MH were added gradually to the molten polymer (PS & PS-g-MA). The coupling agent (PS-g-MA) was added at the ratio of 7.5% of the mass of PS used to provide better performance for the HWC (i.e., (PS & PS-g-MA): RS at ratio 50/50 mass/mass [6]. Those constitutions were kept constant throughout the whole study, otherwise denoted. For complete dispersion of the fiber filler and the FRs in the dispersed matrix, the combination was mixed for 3–4 min to ensure a homogenous composite mixture. The reached amorphous wood composite liquor was removed from the Brabender and then pressed into different dimensions using laboratory hydraulic hot press at 443 K and at pressure of 40 kPa for 10 min. To avoid spring back of the sheet, it was placed on press molding at room temperature for more 10 min. The mass of the added mixture to the mold was controlled to obtain a nearly constant thickness under the nominated conditions. To elude the effect of pressing process on mechanical measurements, the obtained hard wood board was conditioned at ambient moisture and temperature for 24 h after demolding and then cut into specimens with specific dimensions needed for testing and characterization.

Testing and characterization

Mechanical measurements

The mechanical properties of the hard wood composites were assessed through tensile strength and elongation at break. The evaluations of the mechanical measurements were conducted according to ASTM D 638-2007 using the Advanced Universal Testing Machines GALDABINI, QUASAR 600, Italy, 2012. The measurements were performed at crosshead speed of 25 mm min^{-1} at room temperature. Each value obtained represented the arithmetic average of four samples.

Thermal analysis

Thermogravimertic analysis (TGA) and differential scanning calorimetric (DSC) measurements were carried out under nitrogen gas using a Universal version 4.7A apparatus of TA Instruments (SDT Q 600, version 20.9 Build 20), from room temperature up to 873 K at a heating rate of 283 K min^{-1}.

Flammability tests

Flammability performance of the free neat HWC and that containing the fire retardants was evaluated following the UL94 classification, according to ASTM D635 in horizontal position. The nominated HWC sample was held horizontally and a flame fueled by natural gas was applied to light one end of the sample. The time for the flame to reach from the first reference mark (25 mm from the end) to the second reference mark, which is at 100 mm from the same end, was measured. The samples, with dimensions 125 × 13 × 3 mm, were maintained at 296 K and 50% humidity for 48 h prior to analysis.

Results and discussion

Rice straws are inexpensive, renewable and environmentally admitted resources for synthesis of hard wood polymer composites and have tremendous potential to replace natural wood products as fillers.

Polystyrene (PS) foams are typical thermal insulation materials, which mainly comprise expanded polystyrene (EPS) and extruded polystyrene (XPS). Because of PS's low thermal conductivity, lightweight and good physical properties, it is widely used on building facade for energy conservation. Polystyrene foam wastes are enlarged due to their broad applications. The lignocellulosic rice straws (RS) fibers (as reinforcing filler) were added to chemically recycled polystyrene foam wastes and its maleated form (as dispersed polymer matrix), to formulate a hard wood product.

Mechanical performance, flammability, thermal stability in addition to fire-retardant behavior of the hard wood–polymer composites play a crucial role in determining the limit of their working temperature and the environmental conditions for uses. This work presents the main features of the fire retardancy of HWC by applying ZB and/or MH retardants.

Mechanical properties

In order to assess the effect of FRs on the mechanical performance of the prepared hard wood composites based on recycled polystyrene rice straw as formulation materials, their tensile strength and elongation at break properties had been evaluated (Tables 2, 3). However, the enhancements in those characters, strongly, depend on the interaction between the filler and polymer matrix, homogeneous distribution of filler in polymer matrix and good interfacial adhesion. It is worth noting that the tensile strength, in MPa, of the HWC products was raised and the elongations at break percent were reduced by increasing the added ZB and/or MH fire retardants. This could be explained on the basis that the escalated values of mechanical characteristics may be attributed to good filler to polymer matrix interaction, less voids and uniform dispersion of FRs in the polymer dispersed phase. During tensile test, the stress was assumed to transfer from the matrix to the fiber and the retardants directly. When FRs were added to the composite system that have better interfacial adhesion, the stress can be easily transferred leading to improvement in the mechanical properties up to 10 g of the MH to every 100 g of the HWC (Table 2). Also, the addition of FRs to the HWC composite system led to increase in the brittleness due to the rigidity of the inorganic salts (ZB and MH) particles. Behind that concentration, diminishments in the

Table 2 Effect of magnesium hydroxide content on the tensile strength (T.S.) and elongation at break of the hard wood composites[a]

$\mathrm{Mg(OH)}_2^{\mathrm{b}}$	T.S./MPa	Elongation/%	T.S. 1/MPa	Elongation 1/%
0	18.4	4.1	18.8	3.2
6.67	24.4	2.3	18.4	2.2
10.0	44.5	2.4	25.4	2.3
13.33	20.7	1.9	19.6	1.7
20.00	19.6	1.9	19.4	2.0

[a] 50:50 mass:mass, RS: PS/PS-g-MA

[b] MH: g 100 g^{-1} calculated based on the mass of the neat HWC

Table 3 Effect of magnesium hydroxide/zinc borate contents on the tensile strength (T.S.) and elongation at break of the hard wood composites[a]

$Mg(OH)_2$/ZB[b]	T.S./MPa	Elongation/%	T.S. 1/MPa	Elongation 1/%
0	18.4	4.1	18.8	3.2
3.33/3.33	19.5	1.8	19.1	1.4
6.67/6.67	28.7	2.3	17.5	1.8
10/3.33	21.5	2.3	16.0	2.0
10/10	18.8	1.7	15.2	2.0

[a] 50:50 mass:mass, RS: PS/PS-g-MA

[b] FRs mass: g 100 g^{-1} calculated based on the mass of the neat HWC

HWC tensile strength values and in the elongations at break were recorded. When the fire-retardant loading increased, the effective cross-sectional area of continuous phase is reduced, and/or the imperfect distribution of the filler through the polymer matrix, as well as very poor adhesion between the polymer resin and filler occurred and followed by decreases in tensile strength and in the elongations at break. The addition of too much of FRs can interrupt the composite homogeneity and could cause the agglomeration of ZB and/or MH. These made the stress not to disperse uniformly and resulted in reducing the mechanical properties of the final HWC [7]. Similar results were reported for rice straw/polypropylene composite materials [8].

Therefore, using the computed values of ZB and/or MH as FRs for the nominated HWC should enhance flame retardancy of the products but without sacrificing their mechanical properties. The same conclusion was reported by Abdullah and Ahmad [7].

After the mechanical measurements of the HWC were carried out, the scraps of each sample were collected, treated and repressed again into panel under the previous mentioned conditions (section "Materials and methods"). The obtained repressed sheet was subjected to anew tensile strength (T.S.1) and elongation at break (elongation 1) measurements, and the data obtained are given in Tables 2 and 3. The mechanical measurement behavior of the repressed HWC disclosed similar trend to that of the newly formulated HWC. This is an additional advantage for the candidate HWC under consideration as the product at the end of its usage time could be repressed and reutilized at nearly the same performance when mechanical characterization is concerned.

Flammability of the HWC

Table 4 shows the average burning rate in mm min^{-1}, measured in horizontal position based on ASTM-0635, of the HWC as a function of the increased mass of MH, as a fire retardant, added. Nearly fourfold reduction in the burning rate (mm min^{-1}) was remarked for the HWC, formulated from 50% molten recycled PS/PS-g-MA polymer matrix filled with 50% air-dried RS fibers, containing 20 g of magnesium hydroxide for each 100 g of HWC compared to the neat HWC. The lower contents of the MH might be not enough to form a char layer that can block heat and oxygen from the combustion zone of the composite. Comparable trend was described by Arao et al. [9].

The data based on flammability tests for the HWCs containing MH confirmed that the MH can act as good flame retardant to the nominated composite, markedly, at higher loading and consequently guarantee with wide applications of the HWC under consideration whenever the fire safety is required.

Thermal stability

Thermogravimetric analysis (TGA)

Thermogravimetery is a preferable technique to evaluate the performance of fire retardants and, consequently, the thermal stability of the HWC products under consideration. Figure 1 describes the mass losses, at temperatures course, of neat PS/PS-g-MA, neat HWC free of retardant and HWCs containing various types and masses of the retardants (Table 5). All of the TGA curves exhibited similar decomposition patterns except for the polymer matrix. Thermal decomposition of PS/PS-g-MA, under consideration, took place in two steps, while the all curves for HWC specimens showed three distinct degradation peaks.

Before the thermal degradation of the PS/PS-g-MA started, an increase of $\approx$ 2.4% in its mass was detected near 366 K. This increase in the mass is likely to be due to that the inlet nitrogen gas during analysis seemed to be partially moistened. On the other hand, the hygroscopic character of the succinyl anhydride grafted to PS that tends to form a succinic acid moiety [6], upon heating. Before 431 K, this amount of water claimed to be evaporated. The PS degradation, which constitutes the main bulk of the PS/PS-g-MA polymer matrix, is assumed to be initiated at weak link sites inherent to the polymer itself and that aroused during polymerization. Once all of the weak link sites have given away to initiation, the major mass loss of polymer occurred due to a random scission processes. A

Table 4 Average burning rate in mm min^{-1} of the neat hard wood composites (HWC) and HWCs containing increasing masses of magnesium hydroxide (MH)

Samples	Sample formulation/ %			MH[a] added/g	Average burning rate/mm min^{-1}
	PS	PS-g-MA	RS		
Neat HWC	46.25	3.75	50	0.00	22.7 ± 1.43
HWC-1	46.5	3.75	50	6.67	16.5 ± 1.35
HWC-2	46.25	3.75	50	10.0	13.2 ± 1.22
HWC-3	46.25	3.75	50	13.34	7.4 ± 1.40[b]
HWC-4	46.25	3.75	50	20.00	5.7 ± 0.10[b]

PS, the recycled polystyrene foam wastes; PS-g-MA, the maleated recycled PS; HWC, the hard wood composite; RS, the air-dried rice straw; MH, anhydrous magnesium hydroxide

[a] MH mass: g 100 g^{-1} calculated based on the neat HWC mass

[b] Was not exceeded the 2nd mark

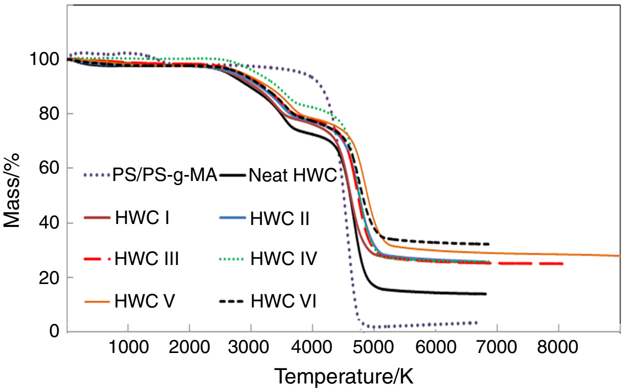

Fig. 1 TGA thermograms of recycled polystyrene foam with its maleated form and rice straw in a hard wood composite (50/50 wt/wt): effect of different types and added masses of the fire retardant

mass loss stage of about 7.5% was counted between 431 and 643 K and can be referred to the decomposition of polymer matrix in nitrogen atmosphere (Fig. 1). This loss may be attributed, mainly, to the complete degradation of PS-g-MAH. It is worth stating that the value of 7.5% is equal to the amount of the grafting part added to formulate the polymer matrix (Table 5).

It is reported that the reaction rate-limiting step of thermal decomposition of the commercial polystyrene is random chain-breaking reaction. A second mass loss stage was recorded between 555.9 and 671.2 K for decomposition of polystyrene in nitrogen. The maximum mass loss rate was noticed at 645.4 K with average activation energy, E_a, 92.2 kJ mol^{-1}.

Summarizing the mass loss for polymer matrix (i.e., Ps/PS-g-MAH) started near 398 K with the end set at $\approx$ 463 K and mainly referred to the unbounded water evaporation. The major mass loss step was computed at onset 658.44 K with a maximum mass loss rate (9.561% min K^{-1}) at 687.87 K (Fig. 2). It can be corroborated that the dramatic decline in the mass of PS/PS-g-MA formulation is due to its decomposition and production of low molecular weight hydrocarbons in addition to CO, CO_2 and H_2O.

For the neat HWC as well as the HWC composites containing the FRs, the TGA curves displayed more than one thermal degradation steps (Fig. 1). Mass loss of about

Table 5 Formulation of hard wood composite manufactured with fire retardants

Samples	Hard wood composites (HWC)/%			Added fire retardant[a]	
	PS	PS-g-MA	RS	MH	ZB
PS/PS-g-MA	92.5	7.5	–	–	–
Neat HWC	46.25	3.75	50	–	–
HWC-I	46.25	3.75	50	6.67	–
HWC-II	46.25	3.75	50	10	–
HWC-III	46.25	3.75	50	3.35	3.35
HWC-IV	46.25	3.75	50	6.67	6.67
HWC-V	46.25	3.75	50	10	3.35
HWC-VI	46.25	3.75	50	10	10

PS, the recycled polystyrene foam wastes; PS-g-MA, the maleated recycled PS; PS/PS-g-MA, the neat polymer matrix; HWC, the hard wood composite; RS, the air-dried rice straw; MH, magnesium hydroxide; ZB, zinc borate

[a] Mass of retardant added: g 100 g^{-1}, calculated based on the neat HWC mass

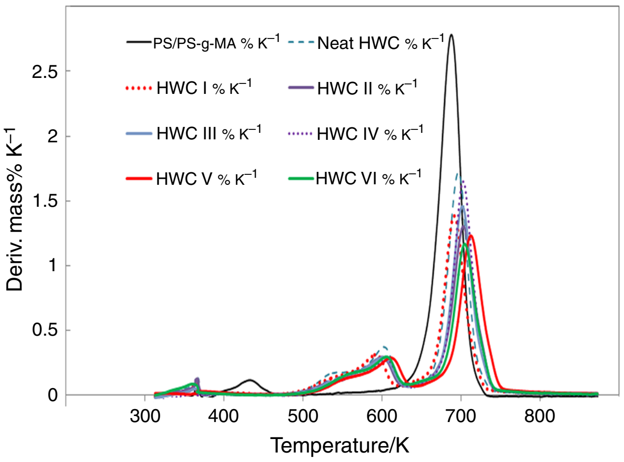

Fig. 2 DTG thermograms of recycled polystyrene foam with its maleated form and rice straw in a hard wood composite (50/50 mass/mass): effect of different types and added masses of the fire retardant

2.82% was observed at 375 K due to the gradual evaporation of absorbed moisture from the cellulosic materials. Further loss was noticed upon heating to 553 K with ratio of 8%. This latter loss can be attributed to the volatility of the smaller molecular weight hemicellulose. The second step, which is related to the degradation of lignocellulosic filler, assigned between 533 and near 673 K and can be attributed to the decomposition of wood ingredients such as cellulose, hemicelluloses and glycosidic cellulose linkage components. The third maximum degradation step existed between 623 and 773 K partially is due to the degradation of α-cellulose and lignin, which ultimately forms a char at around 743 K in addition to the decomposition of the polymer matrix as previously stated. Due to the interfering of the temperature intervals of hemicellulose, cellulose and lignin decompositions, they partially overlapped each other [10].

The data in Table 6 marked out elevations in the maximum decomposition temperatures of the all HWC formulations compared to the neat polymer matrix which can be counted as an indication for the improvement in thermal stability of the products. The same conclusion was reported by Durkin et al. [11]. The addition of natural RS filler seems to increase the thermal stability of composites due to the strong interfacial interaction imparted by the coupling agent [12, 13].

It could be stated that the maleic anhydride is likely to be the possible source for the improved thermal properties of HWC as also evidenced by the rise in the degradation temperature of the composites [14].

Owing to its low conductivity and its ability to char formation, the woody fiber filler, especially the lignin fraction, possesses some initial or natural fire resistance. As regards the effect of lignin content on the initial fire resistance, it has been reported that the strong bond of aromatic rings is thermally destructible under elevated temperature; in addition, the aromatic rings of lignin give good oxidation resistance, controlling fire growth and correspond to the char layer forming [13, 15].

The fire performance of a polymer wood composite depends not only on the structure of the forming materials but also on the type of the fire retardant used and its content in the product formulation.

Data in Table 6 and Fig. 1 show that the recorded values either for the onset (T_5) or for the maximum degradation ($T_{\max}$) temperatures of HWC containing FRs each fall within the same ranges, i.e., 547–563 and 697.5–701.7 K for T_5 and $T_{\max}$, respectively. Both temperatures were shifted to higher values than that computed for the HWC free of FRs (Table 6). Although very small enhancement was reached, this can confirm the role of the fire-retardant additives in improving the thermal stability of final products. Among many organic and inorganic compounds, anhydrous magnesium hydroxide (Mg $(OH)_2$) and zinc borate (ZB) are the most widely used flame-retardant additives for polymers and polymer composites formulation [16].

The first conventional flame retardant used in the present work was magnesium hydroxide which works via physical action, combining gas-phase and condensed-phase mechanisms. Upon heating, MH is converted into MgO and H_2O. The strongly endothermic reaction cools the condensed phase, MgO forms a protective layer on top of the sample and H_2O dilutes and cools the gas phase. The mineral MH reacted to MgO via the release of water vapor ≈ 31 mass% in one step nearly at 573 K.

Hydrates act as a chemical heat sink for the composite by absorbing some of the heat of combustion and lowering the temperature of the material near the flame during their endothermic decomposition, and as a result, the product is cooled. The water vapor released by the hydroxide diluted the gaseous reactants in the flame and restricting the access of oxygen through the composite surface. The endothermic decomposition of this hydroxide proceeds according to Eq. (1):

$$\mathrm{Mg(OH)_2} \rightarrow \mathrm{MgO} + \mathrm{H_2O} \quad \Delta H = 1.378\,\mathrm{kJ\,g^{-1}} \tag{1}$$

Zinc borate acts as flame retardant in both condensed and gas phases of the combustion process. However, its application as retardant has been limited due to its low dehydration temperature (starting near 463 K). The heat decomposition of ZB leads to the creation of a glassy protection layer which acts as a barrier for polymer chain oxidation. ZB shows the best synergetic effect with MH [1].

At elevated temperatures, this compound decomposes, releasing crystallization water molecules (about 15% by mass of water in the temperature range of 563–723 K)

Table 6 Thermogravimetric results of maleated recycled polystyrene, neat hard wood composite and hard wood composites containing various types and variable masses of the fire retardants

Samples	T_5/K	T_{50}/K	ΔT_{50}/K	T_{max}/K	Remain char[a]/%	ΔM/%
PS/PS-g-MA	658.4	683	263	687.6	0	− 13.84
Neat HWC	519	693	273	695.6	13.84	0
HWC-I	556	698	278	699.2	25.6	11.67
HWC-II	547	703	283	701.7	25.5	11.77
HWC-III	548	703	283	698	24.94	11.10
HWC-IV	548	685	275	697.5	25.77	11.93
HWC-V	563	698	278	700.4	27.27	13.43
HWC-VI	553	698	278	699.8	32.13	17.29

T_5 the onset temperature at which 5% mass loss occurs; T_{50}, the onset temperature at which 50% mass loss occurs; ΔT_{50} is T_{50} for HWC with retardant minus T_{50} for neat HWC [i.e., $\Delta T_{50} = T_{50}$ for sample with retardant $-$ T_{50} for neat HWC]

[a] Remain char/% at 773 K (based on the residue obtained); ΔM = the remain char of HWC with retardant/%, the remain char of neat HWC/%

which dilute the concentration of organic volatiles in the flame, reducing its temperature. After decomposition, the residual borate retained in the decomposed polymer would form a vitreous-like layer that slows the permeation of volatile compounds through the surface and restricts them from entering the gas phase.

The data represented in Table 6 and Fig. 1 showed that very small differences (not more than 276.7 K) are the maximum degradation temperatures for HWC recorded by varying the fire-retardant contents of MH (HWC-I & HWC-II) and/or even by combining the two retardants (HWC-III–HWC-VI). On the other hand, combining magnesium hydroxide with zinc borate in the masses of 10:10 (g 100 g^{-1}, calculated based on the mass of the neat HWC), in the HWC-VI formulation, showed a higher percentage of char compared to the all other composites formulations even that containing only magnesium hydroxide, namely HWC-II combination (Table 6). This indicated that the retarding effect caused by these two FRs could be of a synergetic effect and/or might be attributed to the separate flame retarding behavior of each of them [17].

The synergetic effect observed when magnesium hydroxide was used in combination with zinc borate could be due the high content of the two retardants in the HWC formulations; therefore, it can be established that to induce an active retardancy effect to the degradation process of the hosting HWC material, it is necessary to add a high mass content of fire retardants. However, as previously stated using high content of FRs should not be a reason for dismissing the acceptable mechanical characterization of the end product. Close conclusions were reported by Sanchez-Olivares et al. [18] and Sun et al. [19].

Onset degradation temperature, measured as the temperature at which 5% mass loss occurs, T_5, is shifted to higher temperatures for all HWCs relative to neat polymer matrix. This behavior was maintained throughout the thermal decomposition. T_{50}, the temperature at which 50% mass loss occurs, and T_{max}, temperature at maximum degradation rate, were also shifted to higher values for the all HWC products. It is worth noting that for pairs of the HWCs formulated in the presence of FRs, the ΔT_{50} were as high as 287 K; therefore, incorporating the fire retardant would accompanied with significant improvement in their thermal stability (Table 6).

Char mass differences for different formulations of hard wood composite are tabulated in Table 6. The assessed ΔM% was positive over the entire degradation temperature range for the all investigated composites tested. This showed that the neat recycled polystyrene foam waste–rice straw composites were more thermally stable than the neat polymer matrix. Also, the HWCs with fire retardants exhibited better fire performance over the HWC-free ones under the same thermodegradation processes involved. This is an additional evidence for the role of fire retardants in enhancing the thermal stability of the final products that manifested in the positive values for char accumulation at the end of the degradation process.

According to Van Krevelen, a liner correlation exists between the char residue and oxygen index (OI) of polymers [20]. This significant relationship can be computed according to the following formula.

$$\mathrm{OI} = \frac{(17.5 + 0.4\mathrm{CR})}{100}$$

where CR is the char residue as a percentage by mass.

To evaluate of thermal stabilities of the polymer matrix and its HWC composites, besides the potential of the flame retardants on their stabilities, the oxygen index values, as merit figures, are represented in Table 7. The OI values have been calculated based on the carbonaceous char (residual weight) at 773 K cited in TG thermograms.

Table 7 Char yields and oxygen index analysis of hard wood composites

Samples	Char yields/%	Oxygen index/%
PS/PS-g-MA	0	17.5
Neat HWC	13.84	23.036
HWC-I	25.60	27.74
HWC-II	25.50	27.70
HWC-III	24.94	27.48
HWC-IV	25.77	27.81
HWC-V	27.27	28.41
HWC-VI	32.13	30.35

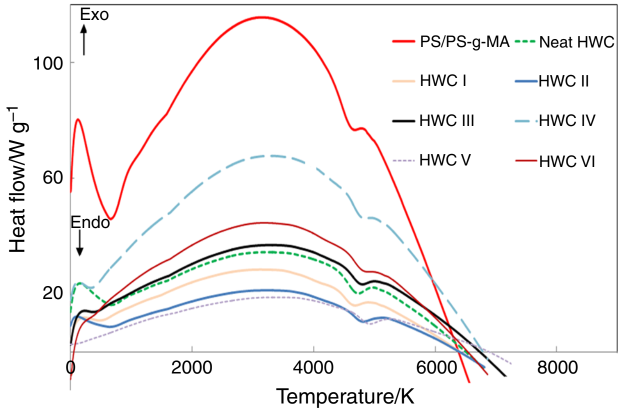

Fig. 3 DSC thermograms of recycled polystyrene foam with its maleated form and rice straw in a hard wood composite (50/50 wt/wt): effect of different types and added masses of fire retardant

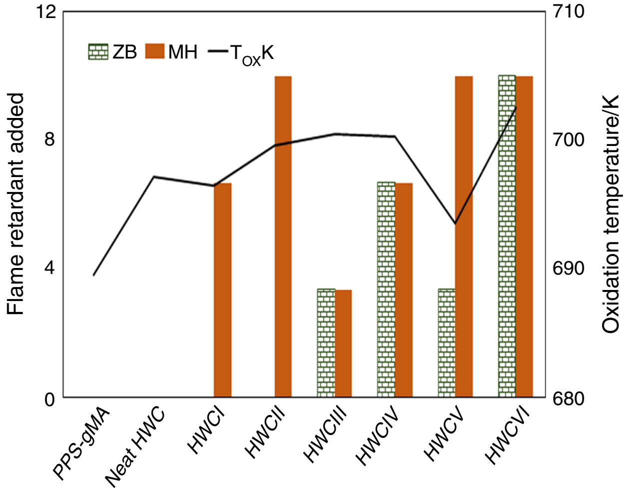

Fig. 4 Effect of ZB or/and MH content on the oxidation temperature of the hard wood composites

The burning process propagates through five consequent steps, namely heating, decomposition, ignition, combustion and propagation. Flame retardant can be achieved by the disruption of burning process at any of these stages that can lead to the termination of the process before actual ignition occurs. Table 7 shows that OI for all specimens of HWC was between 23 and 30. It was reported that materials exhibiting OI values above 26 should demonstrate self-extinguishing behavior. Therefore, the HWC end products containing ZB and/or MH showed acceptable flame-retardant properties [21].

Table 8 shows that the melting point, T_m, determined from DSC analysis for neat polymer matrix, neat HWC and HWC containing fire retardants was 437.2, 438.8 and 438.8 ± 273.25 K (mean value), respectively.

Figure 3 shows that the DSC profiles of HWC composites have the same features as the neat polymer, which proposed that there were no significant changes in their degradation mechanism and the decompositions might stem from the PS/PS-g-MA matrix [22].

Therefore, using ZB and/or MH as FRs for the nominated HWC enhanced flame retardancy of the products.

Figure 4 exhibits the relation between the oxidation temperature, T_{ox}, and the mass of flame retardant added to the HWC under investigation (Table 8). The flame-retardant effects are increased by increasing the oxidation temperature. It is clear from the figure that the prepared polymer matrix PS/PS-g-MAH and neat HWC had low oxidation temperature and consequently low flame-retardant characteristics. It is known that the first decomposition temperature of MH to release its hydrated water is 603 K [23]. The addition of MH to HWC-I at 6.63 g 100 g^{-1} of

Table 8 DSC data for neat polymer matrix, neat HWC and HWCs containing various types and variable masses of fire retardants

Samples	T_g/K	T_m/K	T_{0x}/K	ΔH/W g^{-1}	Energy of oxidation/kJ mol^{-1}
PS/PS-g-MA	363.28	437.2	689.5	10.54	92.2
Neat HWC	360.89	438.8	697.2	3.02	128.2
HWC-I	352.26	438.6	696.5	0.84	116.5
HWC-II	366.35	439.1	699.6	1.77	87.04
HWC-III	369.43	438.7	700.5	–	89
HWC-IV	353.98	438.8	700.3	2.4	113.3
HWC-V	371.19	438.6	693.5	–	75.85
HWC-VI	368.95	438.6	868.1	3.77	75.3

the HWC did not affect the oxidation temperature significantly, but upon escalating the mass to 10 g for each 100 g of HWC, the oxidation temperature increased to 701.7 K. On the other hand, the zinc borate is characterized by its high dehydration temperature [24]; therefore, the addition of both MH and ZB in equal mass to both HWC-III and HWC-IV acquired the composites flame retardancy at a wide range of temperatures and the resultant oxidation temperatures were nearly the same. The same result was reached for the HWC-VI formulation. The addition of MH in excess than ZB may lower the dehydration temperature of the latter and reduced the oxidation temperature as shown in case of HWC-V product. This reduction in oxidation temperature may be attributed to the producing of MgO. This oxide in turn reacts with the water evolved from ZB and may be impaired the flame-retardant effect of the latter.

Conclusions

In this study, the mechanical performance, thermal characteristics and flammability resistance of a newly developed hard wood composite, formulated from chemically recycled polystyrene foams and its maleated form with rice straw wastes in addition to zinc borate and/or magnesium hydroxide as fire retardants, were investigated employing the tensile strength measurements, TGA, DSC analyses besides to flammability test. This work introduced a new method to formulate a hard wood composite from two problematic wastes, namely the rice straw and the spent polystyrene foams. Besides, it provided a clear flammability, mechanical and thermal characterizations for the product under the impact of added fire retardants.

The tensile strength of HWC was reinforced by marked additions of the FRs. Also, the incorporation of fire retardants into the composites was generally found to enhance thermal stability of the products by acting as a superior insulator and mass transport barrier to the volatile products generated during decomposition, as well as by assisting in the formation of char residue after thermal degradation which acts as heat shielding on top of the samples. Sufficient fireproofing properties, however, may require high loadings of the fire retardants but without sacrificing their mechanical properties. The information gained from the present study is substantial when considering the use of these types of composites in industry applications.

The economical inputs of this study are depicted through utilizing two wastes as raw materials, instead of the virgin ones, to produce a cheap challenging hard wood tiles with acceptable specifications and can be used in different fields including car parts applicants, construction, furniture and other. The indirect revenue is that gained to the environment by avoiding the improper methods to get rid of the two wastes by either an opening air burning of rice straw or the illegal dumping of spent foam waste specially that take place in rivers, seas and oceans.

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