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Thermal degradation and flammability properties of multilayer structured wood fiber and polypropylene composites with fire retardants

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Single and multi-layer structured wood fiber and polypropylene composites (WPPCs) filled with magnesium hydroxide (MH), expandable graphite (EG), or ammonium polyphosphate (APP) were prepared. Thermal and flammability properties of composites were determined by thermogravimetric analysis and cone calorimetry. Results of both thermogravimetry and cone calorimetry indicated that single layer WPPC filled with MH, EG or APP had reduced the HRR and THR, and increased the mass of residue compared with the control sample. The results on fire performance of multilayer structured WPPC indicated that the improvement or depravation on fire retardance properties of the WPPC depends on the different mechanism of fire retardants. EG showed the best fire retardance properties in multilayer structured WPPC system compared to MH and APP. Furthermore, the use of the EG in the cap layer greatly reduced the heat and smoke release of the overall multilayer structured composites compare to single layer fire retardant WPPC. The residues of combusted WPPC after cone calorimetry test were characterized by scanning electron microscopy (SEM), the results further revealed that the presence of EG in the cap layer could protect the underlying substrate from degradation and char formation.

Introduction

Wood plastic composites (WPCs) have a considerable fire risk in comparison to solid wood since the polyolefin (such as polyethylene and polypropylene) in WPCs is inherently ignitable.^{1,2} Therefore, it is important and necessary to develop fire retardant treated WPCs to expand their commercial utilization. The most expeditious method used to acquire fire retardancy is incorporation of fire retardants during the manufacturing process.^{3,4}

With the growing environmental issues, the application of halogenated fire retardants is gradually becoming restricted.^{5,6} Three of the most common fire retardants for polyolefin are magnesium hydroxide (MH), expandable graphite (EG), and ammonium polyphosphate (APP).^{7–11} All three chemicals have been used in WPCs. MH effectively reduced the flammability (almost 50%) of natural fiber filled polypropylene composites, but had a negative effect on mechanical properties.^{12,13} EG had the highest potential for flame retardancy on WPCs, which showed the best performance against fire from cone calorimetry and radiant panel testing compared with two different ammonium polyphosphates and nitrogen-containing fire retardants.^{14,15} Wood fiber and polypropylene composites with APP showed the best fire performance at vertical burning, and led to an auto-extinguishing. Moreover, the APP

treatment can effectively reduce the heat release rate compared to the untreated specimens.^{16,17}

It is generally recognized that the amount of fire retardant for satisfying the fire-retarding requirement of the WPCs depends on both its chemical structure and distribution. However, for a given fire retardant type, the distribution is a key factor in order to achieve the maximum performance of the whole composite system.¹⁸ So far, the uniform distribution of fire retardant is commonly used for WPCs.¹⁹ To meet the requirements of fire retardant standards for practical use especially in residential construction, and decking and furniture industry, fire retardant loading has to be more than 20 percent for WPCs. The consequence is that the mechanical properties of the composites dramatically decreased and the costs increased.

Compared to the uniform distribution, a multilayered distribution of a fire retardant in WPCs was less reported. Through combining molten multiple layers with various properties into one profile, multilayer structured composites with better properties such as water resistance, air entrapment, oxygen barrier, and increased toughness can be obtained.²⁰ The cap layer plays an important role in modifying the overall composite properties. For instance, it has been shown that different cap layers, and material compositions had notable effects on ultraviolet resistant, mechanical and thermal properties of multilayer structured WPCs.^{21–27} Therefore, the cap layer could help provide composites with relatively better fire resistant properties, and lower the overall fire retardant contents at the same time. However, the use of MH, EG, and APP in multilayer structured WPCs (e.g., in the cap layer to modify overall composite properties) has not been reported. The objectives of this study were: (a) to determine thermal degradation and fire resistant properties of the single layer wood fiber and polypropylene composites (WPPCs) with MH, EG and APP; and (b) to study the effect of MH, EG and APP in the cap layer on fire

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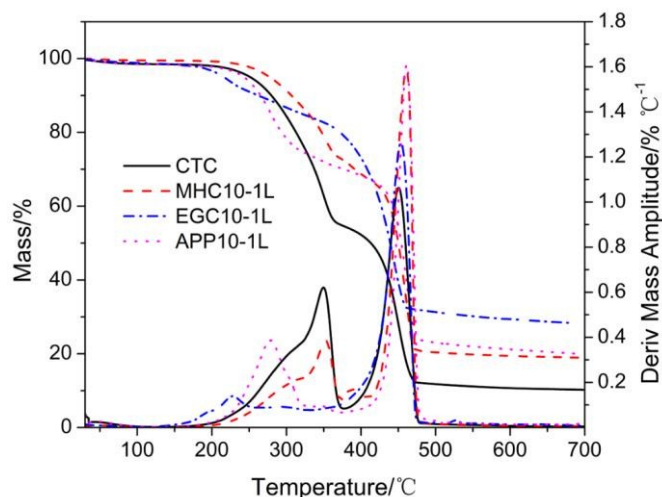


Fig. 1 TG and DTG curves of single layer WPPC samples at a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$.

resistant properties of double and three-layer WPPC. The influence of cap layer formulation on overall composite performance was performed in order to provide a fundamental guidance for designing high-performance multilayer structured WPPC with reduced amount of fire retardants.

Results and discussion

Thermal degradation analysis

Single layer WPPC with and without fire retardants. Fig 1 shows that the mass loss of the single layer WPPC samples was separated into two main stages resulted mainly from the thermal decomposition of WF and PP.²⁸ At the first thermal decomposition stage, a distinct thermal decomposition peak appeared at $350\text{ }^{\circ}\text{C}$, $352\text{ }^{\circ}\text{C}$, $231\text{ }^{\circ}\text{C}$, $279\text{ }^{\circ}\text{C}$ for CTC, MHC10-1L, EGC10-1L, and APPC10-1L, respectively. It indicated that EG and APP promoted the thermal degradation of WF in WPPC system earlier and char formation. Especially, EG slowed the thermal decomposition of WF in the EGC10-1L system because the decomposition rate of EGC10-1L was much lower compared with CTC. MH did not effect on the wood flour decomposition, and the weak peak at $398\text{ }^{\circ}\text{C}$ for MHC10-1L was normally considered as the result of thermal decomposition of MH.²⁹ At the second decomposition stage, the temperature peak for the maximum loss rate representing PP resin decomposition changed from $450\text{ }^{\circ}\text{C}$ to $461\text{ }^{\circ}\text{C}$, $454\text{ }^{\circ}\text{C}$ and $462\text{ }^{\circ}\text{C}$ for MHC10-1L, EGC and APPC, respectively. The mass of residue was 10.21%, 18.87%, 28.22% and 19.82% for CTC, MHC10-1L, EGC10-1L and APPC10-1L, respectively. It demonstrated that the improved thermal stability of the PP base resin by addition of MH, EG or APP. In MHC10-1L system, the magnesium oxide decomposed from MH attached on the surface of composites, which improved thermal stability of the PP base resin.²⁹ For APPC10-1L system, polyphosphoric acid generated from

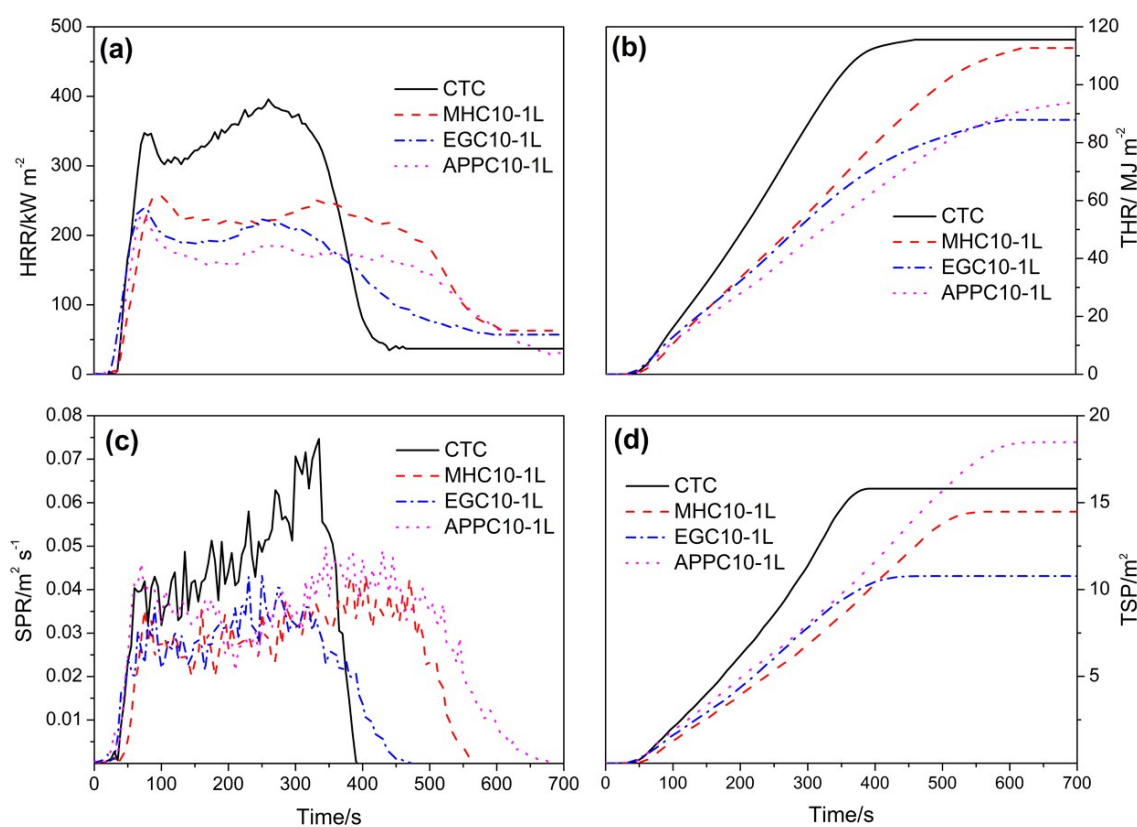


Fig. 2 Fire performance of single layer WPPC samples: (a) HRR, (b) THR, (c) SPR, and (d) TSP.

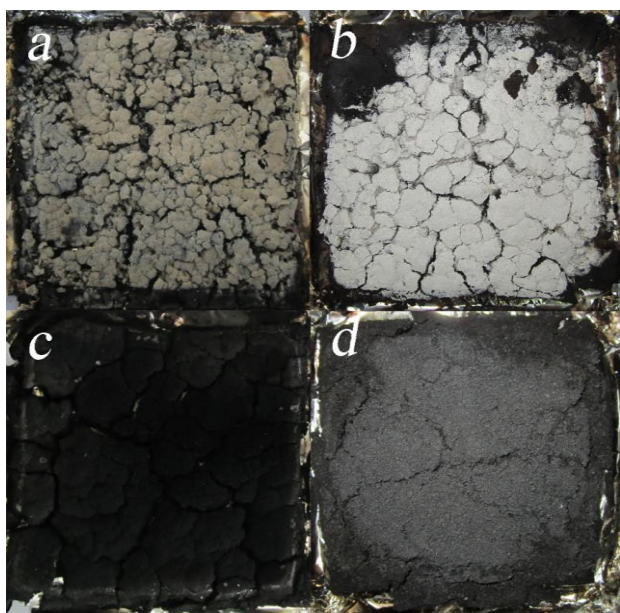


Fig. 3 The digital photographs of residual char after cone calorimeter test: (a) CTC, (b) MHC-1L, (c) APPC10-1L, (d) EGC10-1L.

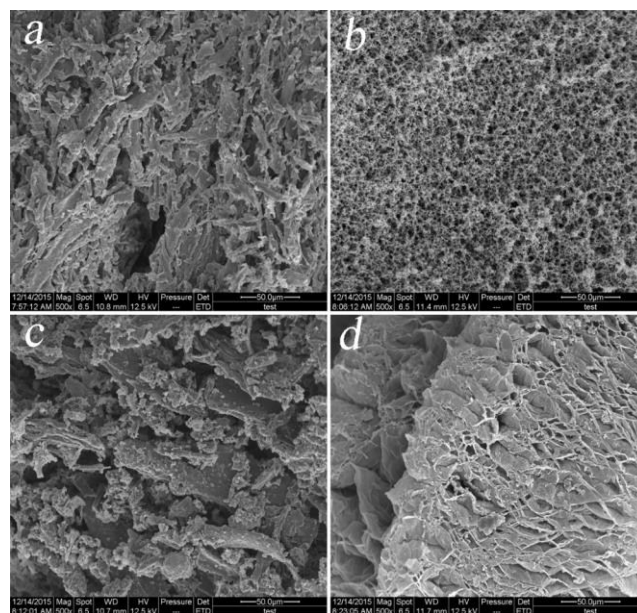


Fig. 4 The SEM micrographs of residual char after cone calorimeter test: (a) CTC, (b) MHC-1L, (c) APPC10-1L, (d) EGC10-1L.

the APP can further combine with the char from the degradation of wood fiber, and it may increase the decomposition temperature and mass of residue.¹⁴ However, in EGC system, a huge amount of swollen and dense char were formed in the first stage effectively to protect the PP base resin from degradation, which resulted in the most residue compared with other samples.

Fire retarding and smoke suppression performance

Single layer WPPC with and without fire retardants. As shown in Fig 2a, the HRR of CTC sample shows the typical shape from a wood sample, with one peak in the beginning and one peak at the end.³⁰ For the fire-retarded WPPC, the first HRR peak (P1-HRR) and especially the second peak of HRR (P2-HRR) were reduced, and the combustion time was prolonged. The presence of fire retardants resulted in early charring and suppressing heat release rate in the first stage and then possibly followed by char-surface rupture in the second stage. The addition of APP made the first stage lower while the second stage had a smooth and the lowest peak. Because the interaction between WF and APP can create a firm layer of char during combustion,³¹ APP can then reduce the P2-HRR of WPPC the most. However, the THR of EGC10-1L was the lower compared with other samples (Fig 2b), which was ascribed to the shortened of combustion time by auto-extinguishing.

Generally, the combustion process of materials can be divided into three stages:³² (1) non-flaming mode appearing before ignition, (2) flaming mode, and (3) after glowing mode. The smoke emission occurs in both non-flaming and flaming stages, while there is no smoke evolved in after-glowing stage. Fig. 2c clearly shows the first two combustion stages of WPPC on the basis of the time scale. The SPR of APPC10-1L was increased in the non-flaming stage, while MHC10-1L and EGC10-1L were considerably decreased in both the non-flaming and the flaming steps. The TSP of the samples followed the order EGC10-1L < MHC10-1L < CTC < APPC10-1L (Fig. 2d).

The mass of residue after cone calorimeter test was 13.80%, 19.02%, 29.19% and 22.46% for CTC, MHC10-1L, EGC10-1L and APPC10-1L, respectively. The results revealed that EG could greatly promote the formation of intumescent char layers, which could efficiently prevent the gas transfer between the flame zone and the burning substrate and thus prohibited the smoke produce of WPPC. However, as a result of the gaseous ammonia released by the degradation of APP,³³ leading to the increase of TSP for APPC10-1L.

In order to better understand the differences in fire retardant properties for different WPPC systems, the digital photographs and SEM micrographs of residual char after cone calorimeter test are shown in Fig. 3 and Fig. 4. As shown in Fig. 4a, there almost is rare char residue for WPPC without fire retardant. The residue greatly increased for WPPC with fire retardants (Fig. 3b-3d). In contrast to CTC, the white protective layer on the surface for MHC10-1L (Fig. 3b), thicker and more compact char layer was formed for APPC10-1L (Fig. 3c), and swollen and dense char was formed for EGC10-1L (Fig. 3d). Meanwhile, the carbon framework of char for CTC after combustion was observed by SEM (Fig. 4a). The char residue of MHC10-1L is coraloid network structure with plenty of holes (Fig. 4b). That is because a plenty of decomposed gases for MH permeates through the char layer, thus fragments the char layer. The char residue of APPC10-1L is continuous and blocky with less holes in the surface (Fig. 4c), because the cross-linked polyphosphoric acid formed on heating can provide a stable and compact char layer and more effective fire retardancy in the WPPC.³⁵ Fig. 4d shows the wormlike char due to the expansion of EG, which more effectively prohibited the smoke produce of WPPC. These results further proved the results of heat and smoke release of APPC10-1L and EGC10-1L.

Single and multi-layer structured WPPC with MH. The multilayer structured WPPC containing MH in the cap layer was compared with the single layer WPPC with MH. Fig 5a shows that the HRR curve of MHC10-2L was similar with the HRR curve of MHC

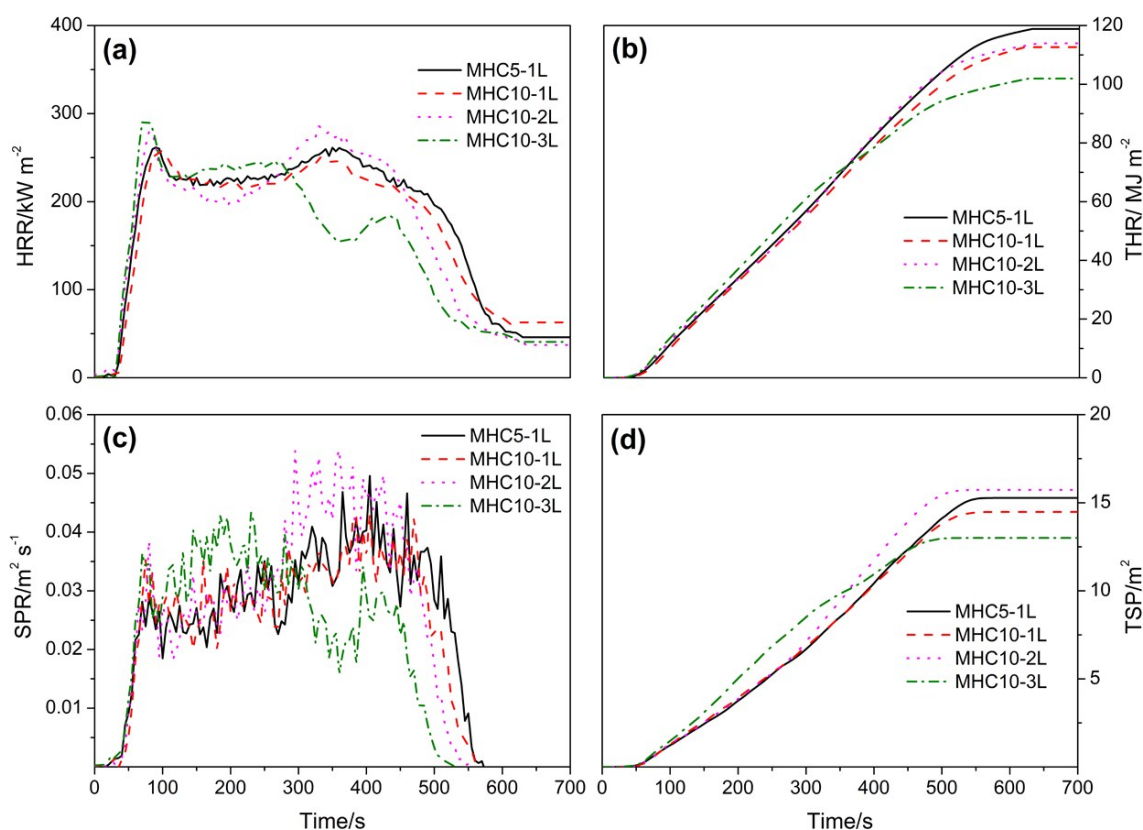


Fig. 5 Fire performance of single and multilayer structured WPPC samples with MH: (a) HRR, (b) THR, (c) SPR, and (d) TSP.

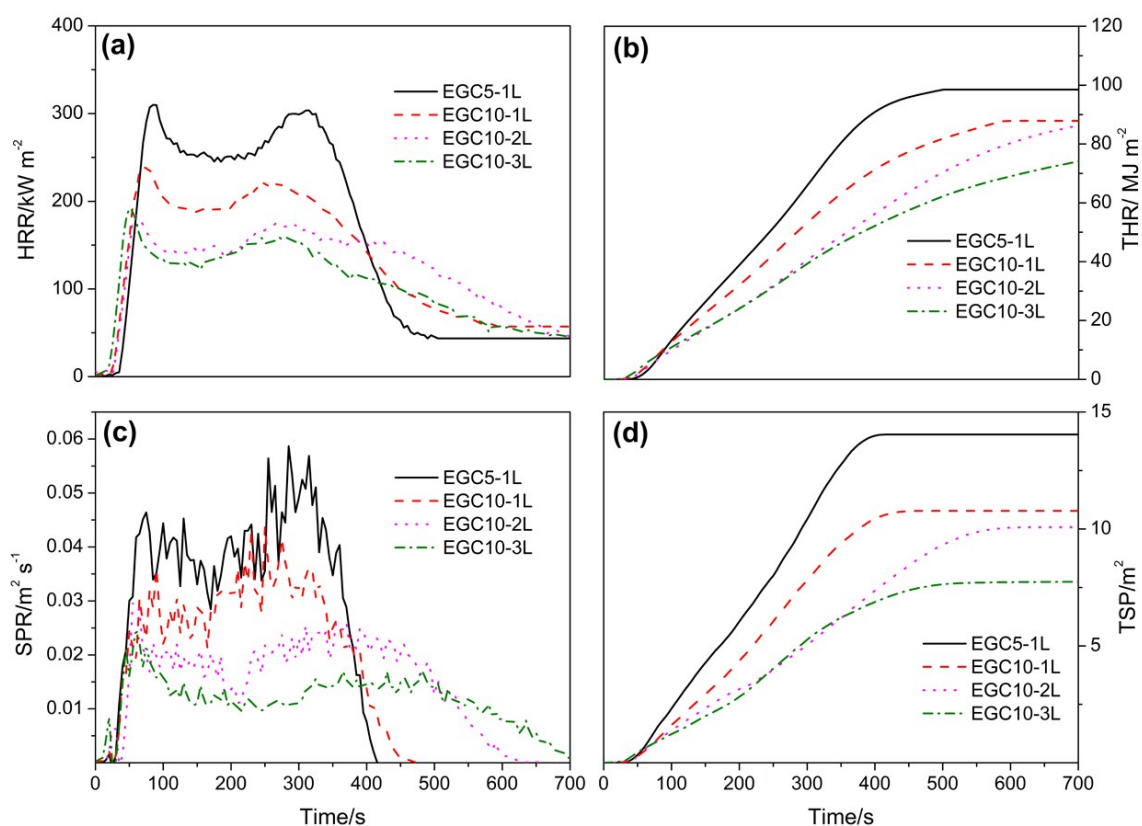


Fig. 6 Fire performance of single and multilayer structured WPPC samples with EG: (a) HRR, (b) THR, (c) SPR, and (d) TSP.

10–1L, and both the THR curves of MHC10–2L and MHC10–1L were lower than MHC5–1L. The best improvement in P2–HRR and THR appeared in the sample of MHC10–3L (Fig 5a and 5b). It was reported that MH was decomposed as the result of the endothermic reaction, in which heat energy was consumed.³⁴ Because of MHC10–3L had two fire-retarded cap layers on the top and bottom, the decomposition of MH in both top and bottom layers consumed the heat energy to suppress the heat release with the combustion processing, until the conflagration of core layer caused the next peak HRR.

Fig 5c displays that the SPR of MHC10–2L was higher than other samples during the testing time of 300 to 400s, while the SPR of MHC10–3L was decreased during this period. In regard to the smoke-suppression mechanism of MH, it was summarized that the oxides of metals obtained as a by-product of decomposing created a non-flammable protective layer on the surface of the composites.³⁴ For MHC10–2L, the smoke was easily released when the combustion proceed to the core layer because of the non-flammable protective layer got weaker with the dissipated of MH in the cap layer. However, for MHC10–3L, because the heat transfers from surface to inside, the thicker magnesium oxide protective layer on the surface could delay the decomposition of inside materials. Therefore, the decomposition of MH in the bottom layer later than the top layer. Moreover, most smoke produced from the bottom materials was blocked and absorbed due to permeated through the magnesium oxide protective layer in the bottom, char layer in the core, and another magnesium oxide protective layer on the top, which shows the reduction on SPR and TSP curves (Fig. 5c and 5d).

Single and multi-layer structured WPPC with EG. Fig. 6a indicates that the addition of EG in cap layer reduced the P1–HRR and P2–HRR considerably. Compared to that of EGC10–1L, the P1–HRR and P2–HRR values of EGC10–3L were reduced by 20.6% and 28.7%, and the P1–HRR and P2–HRR values of EGC10–2L were reduced by 23.6% and 21.5%. More importantly, not only the peak HRR but also the THR was decreased for EGC10–3L and EGC10–2L (Fig. 6b). This result demonstrated that the presence of EG in the cap layer was feasible for improving the fire retardancy of overall multilayer structured WPPC. Because 20 percent of EG in the cap layer could promoted more swollen and dense formed on the surface of multilayer structured WPPC, which effectively protect the underlying substrate from degradation. Moreover, more swollen and dense char in the cap layer adsorbed and suppressed the smoke produce from the core layer. As shown in Fig. 6c and 6d, the SPR and TSP of the multilayer structured WPPC with EG were both lower than single layer WPPC with EG, and EGC10–3L showed the best performance on suppression of smoke. It indicated that the thickness of cap layer played the minor role in improving the fire retardant performance compared to the multi coating on the core layer. The whole coating method on the core layer is a hopeful way to improve the flammability properties of composites.

Fig. 7 shows the morphology of the combusted residues of WPPC with EG after cone calorimeter test. For EGC10–1L, the residues from cone calorimeter test constituted with a swollen and loosen char (Fig. 7a–1), which seems brittle and easy to collapse (Fig. 7a–2). For EGC10–2L and EGC10–3L, the residues exhibits a higher swollen char layer on the surface and continuous and firm char layer in the bottom (Fig. 7b–1 and 7c–1). To further investigate the microscopic

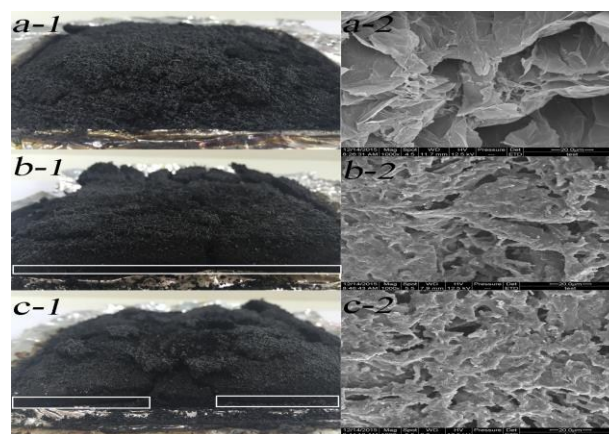


Fig. 7 The morphology of the combusted residues of WPPC with EG after cone calorimeter test: (a-1 and 2) EGC10–1L, (b-1 and 2) EGC10–2L, (d-1 and 2) EGC10–3L.

structure of char layer, the residues char of core layer of EGC10–2L and EGC10–3L was observed by SEM (Fig. 7b–2 and 7c–2). Compared with the residue of EGC10–2L, more little carbonaceous particles combined together to form a successive, thick and compact physical structure char for EGC10–3L. This structure further proved that the swollen and dense char in the cap layer limits the heat transfer into core layer materials, protecting WF and PP in core layer from degradation and char formation.

Single and multi-layer structured WPPC with APP. Fig 8a and 8b show that both HRR and THR of APPC10–2L and APPC10–3L were higher than these from APPC10–1L. The P1–HRR and P2–HRR of multilayer structured WPPC with APP were considerably increased compared to theses from APPC10–1L. Unlike to multilayer structured WPPC with EG, the addition of APP in the cap layer played a negative role in fire retardance property in the overall multilayer structured WPPC. This probably due to the different fire retardant mechanism of APP in comparison with EG. Generally, the fire mechanism of APP is the phosphates decomposed from APP are able to cross-link wood fiber, which conducive to dehydration of cellulose and char formation, and thereby increases the amount of residue formed.³¹ In the case of single layer APPC10–1L, the uniform distribution of APP in the whole materials increased the cross-link chance between phosphates and wood fiber. However, for multilayer structured WPPC with APP, only a limited quantity wood fiber in the cap layer could be able to cross-link with phosphates, therefore, the fire retardant performance in the overall multilayer structured WPPC was deteriorated compared to the single layer APPC10–1L.

The sample of APPC10–2L exhibited the greatest smoke release compared to other samples (Fig. 8c and 8d). The SPR of APPC10–3L was a slight lower than that of APPC10–1L during the process of combustion, but due to the burning duration was extended, the TSP of APPC10–3L was higher compared to that of APPC10–1L. In APP fire retardant composites system, the smoke release was a positive correlation with the content and distribution of APP in the composites. For multilayer structured WPPC with APP, the negative efficacy in reducing smoke release may attributed to the high APP content in cap layer degraded and released much inflammable gases leading to the incomplete combustion of composites.^{35,36} Therefore, much more smoke was formed. The results indicated that the better way to improve the fire retardance property was uniform distribution of APP

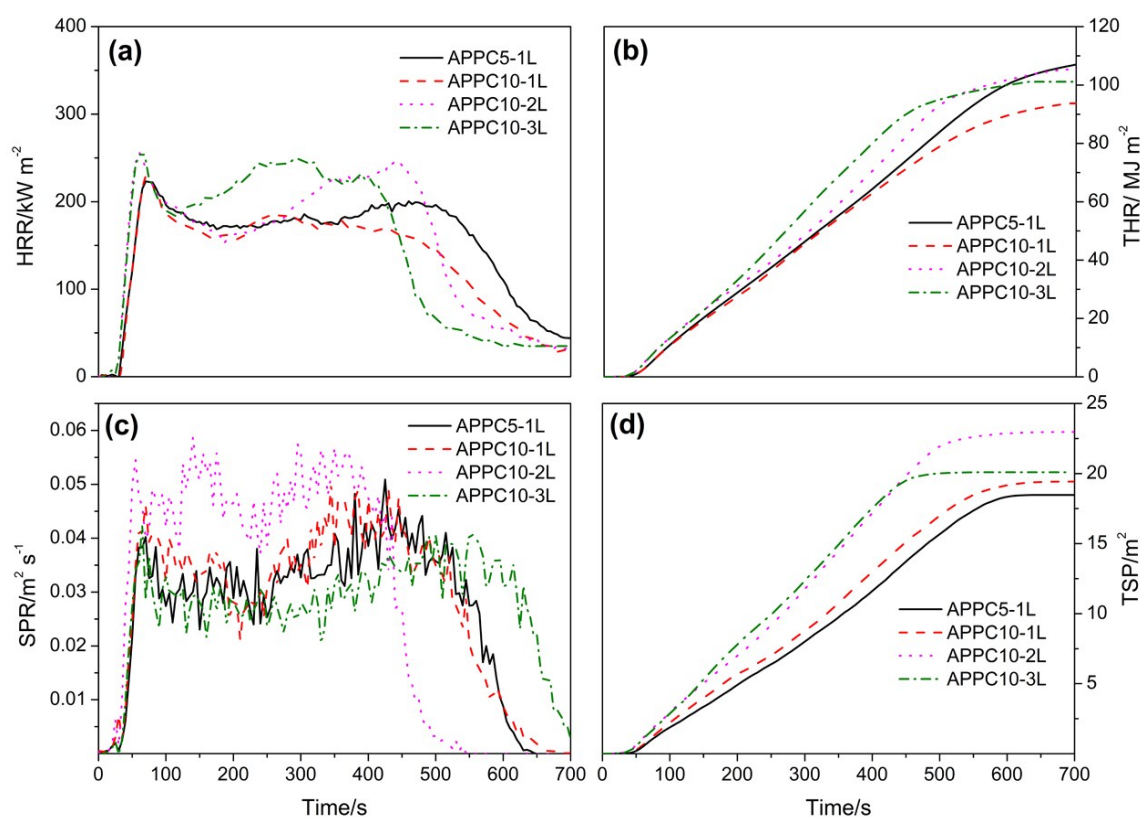


Fig. 8 Fire performance of single and multilayer structured WPPC samples with APP: (a) HRR, (b) THR, (c) SPR, and (d) TSP.

in the overall composites compared to the multilayered distribution.

Experimental

Materials

Commercial fire retardants of MH (MAGNIFIN H-5), EG (220-80N), and APP powders (200503) were provided by Albemarle Co. (Baton rouge, LA, USA), Graftech International Holding Inc. (Lakewood, OH, USA), and JLS Flame Retardants Chemical Co.Ltd. (Hangzhou, Zhejiang, China), respectively. Moreover, the structure of EG is lamellar, and crystal II structure for the APP. Pine wood fiber (WF) with 20 mesh particle size was supplied by American Wood Fiber Inc. (Schofield, WI, USA). Neat polypropylene copolymer (PP

(H00C-00) with a melt flow index of $0.7\text{g } 10\text{min}^{-1}$ at $230\text{ }^{\circ}\text{C}/2.16\text{ kg}$ was purchased from Ineos Olefins & Polymer Co. (League City, TX, USA). Maleic anhydride grafted polypropylene pellet (MAPP) (EastmanTMG-3003) was provided by Eastman Chemical Products Co. (Kingsport, TN, USA), and used as compatibilizer for immiscible WF and PP blends. Lubricant powder (TPW 306) was supplied by Struktol Co. (Stow, OH, USA), and was used to improve the processing performance of the products.

Preparation of multilayer structured WPPC

Table 1 and Table 2 list the sample formulations for the single layer WPPC and the cap-layer only of multilayer structured WPPC, respectively. The formulation for the core layer was WF: PP: MAPP:

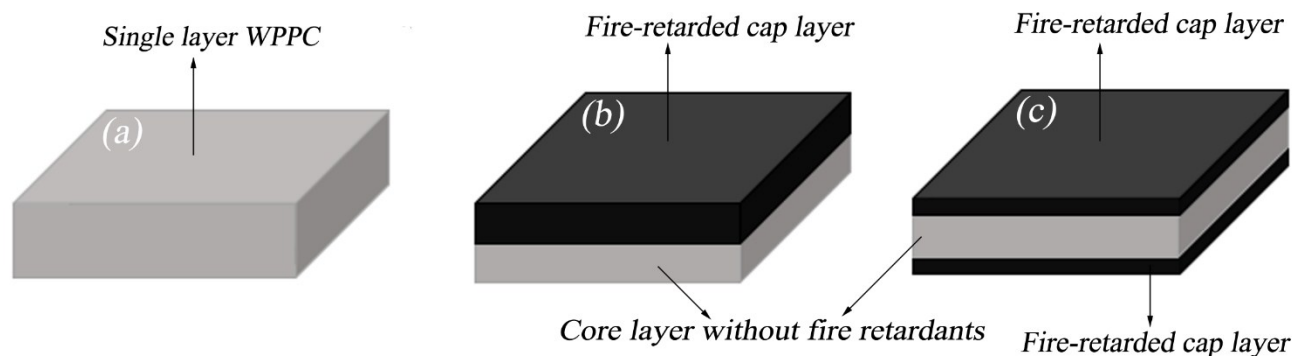


Fig. 9 Single layer WPPC (a); double layers WPPC (b); three layers WPPC (c).

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Table 1 Sample formulations of Single layer WPPC

| Sample | WF (%) | PP (%) | MH (%) | EG (%) | APP (%) | MAPP (%) | Lubricant (%) |
|-----------|--------|--------|--------|--------|---------|----------|---------------|
| CTC | 60 | 33 | 0 | 0 | 0 | 2 | 5 |
| MHC5-1L | 55 | 33 | 5 | 0 | 0 | 2 | 5 |
| MHC10-1L | 50 | 33 | 10 | 0 | 0 | 2 | 5 |
| EGC5-1L | 55 | 33 | 0 | 5 | 0 | 2 | 5 |
| EGC10-1L | 50 | 33 | 0 | 10 | 0 | 2 | 5 |
| APPC5-1L | 55 | 33 | 0 | 0 | 5 | 2 | 5 |
| APPC10-1L | 50 | 33 | 0 | 0 | 10 | 2 | 5 |

WF—wood fiber, PP—neat polypropylene, MH—magnesium hydroxide, EG—expandable graphite, APP—ammonium polyphosphate, MAPP—maleic anhydride grafted polypropylene.

Table 2 Sample formulations of cap layer only of multilayer structured WPPC

| Sample | Cap layer | | | | | | | Thickness (mm) |
|-----------|-----------|--------|----------|---------------|--------|--------|---------|----------------|
| | WF (%) | PP (%) | MAPP (%) | Lubricant (%) | MH (%) | EG (%) | APP (%) | |
| MHC10-2L | 40 | 33 | 2 | 5 | 20 | 0 | 0 | 2 |
| MHC10-3L | 40 | 33 | 2 | 5 | 20 | 0 | 0 | 1 |
| EGC10-2L | 40 | 33 | 2 | 5 | 0 | 20 | 0 | 2 |
| EGC10-3L | 40 | 33 | 2 | 5 | 0 | 20 | 0 | 1 |
| APPC10-2L | 40 | 33 | 2 | 5 | 0 | 0 | 20 | 2 |
| APPC10-3L | 40 | 33 | 2 | 5 | 0 | 0 | 20 | 1 |

Lubricant: = 60: 33: 2: 5 wt%. Three different fire retardants and loading levels (i.e., 0, 5, and 10 wt% of the total weight of the overall composites) were used to fabricate single and multi-layer structured WPPC, including single layer WPPC as control (CTC), single layer WPPC with 5% or 10% MH (MHC5-1L or MHC10-1L), single layer WPPC with 5% or 10% EG (EGC5-1L or EGC10-1L), single layer WPPC with 5% or 10% APP (APPC5-1L or APPC10-1L), double or three-layer WPPC with 20% MH in cap layer (MHC10-2L or MHC10-3L), double or three-layer WPPC with 20% EG in cap layer

(EGC10-2L or EGC10-3L), double or three-layer WPPC with 20% APP in cap layer (APPC10-2L or APPC10-3L).

WF was dried in a convection oven at 105 °C for 24 hours before being used. A Leistritz Micro-27 co-rotating parallel twin-screw extruder (Leistritz Corporation, Allendale, NJ) with a screw speed of 55 rpm was used to manufacture the composites. The Leistritz machine was equipped with two mass-in-loss feeders, and was controlled by an independent computer with commercial software. The extrusion temperature profile ranged from 160 to 180 °C. All the

composites were then fabricated into a mold of $100 \times 100 \times 4 \text{ mm}^3$ using a conventional one-opening hot press. The temperature, pressure, and pressing time were $170 \text{ }^\circ\text{C}$, 10 MPa , and 300 seconds , respectively. The multilayer structured WPPC was formulated with one core layer without fire retardant in combination with MH, EG or APP in the cap layer. Figure 9 displays the schematic of single and multilayer structured WPPCs. The mass fraction of fire retardants in the cap layer was 20 percent, and the thickness of cap layer was $2.0 \pm 0.05 \text{ mm}$ for the double layers WPPC. The three layers WPPC was a sandwich structure, and the thickness of both cap layers was $1.0 \pm 0.05 \text{ mm}$. Therefore, the actual mass fraction of fire retardants in the overall multilayer structured WPPC was 10 percent, which was the same amount as single layer fire retardant treated WPPC.

Thermal analysis

Thermal behaviors of the single layer WPPC were performed on a TA Instrument TGA Q50 thermogravimetric analyzer (TA Instruments Inc., New Castle, DE, USA) from room temperature to $700 \text{ }^\circ\text{C}$ at a heating rates of $5 \text{ }^\circ\text{C min}^{-1}$. Approximately 5 mg of each sample was used to examine under nitrogen atmosphere, and the characteristic temperature and residual weight were determined for each composite.

Fire testing

Cone calorimeter tests were carried out according to the standard of ISO 5660-1-2002 using a cone calorimeter (FTT0007 Standard, East Grinstead, UK) under a heat flux of 50 kW m^{-2} .³⁷ Each specimen for tests was $100 \times 100 \times 4 \text{ mm}^3$ in size. The parameters of heat release rate (HRR), total heat release (THR), smoke production rate (SPR) and total smoke production (TSP) for various composite formulates were established. Three replicate specimens were tested for each group.

Scanning electron microscopy

The morphology of the char residues after cone calorimeter test was observed by a QUANTA 200 scanning electric microscopy (FEI Co. Hillsboro, Oregon, USA). The char residues were covered with gold before examination.

Conclusions

Single and multi-layer structured WPPC with MH, EG, and APP were successfully prepared, and their thermal stability and flammability properties were characterized. The results showed that the three layers structured WPPC in the presence of MH or EG in the surface layer exhibited lower heat and smoke release compared with the single layer WPPC. However, incorporation of APP caused greater heat release and smoke production in the multilayer structured WPPC than in the single layer WPPC. The three layers structured WPPC incorporated with EG on its surface layer showed the best fire retardance and smoke suppression properties. Thus, multilayer manufacturing technology as a structural modification is a promising way to improve the flammability properties of WPCs. The use of such a structure gives an opportunity to reduce the fire retardants contents

of the overall composites, thus increasing the environment friendliness and lowering the cost of WPCs.

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