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Flame-Retardant Properties of Acrylonitrile–Butadiene–Styrene/Wood Flour Composites Filled with Expandable Graphite and Ammonium Polyphosphate

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ABSTRACT: Expandable graphite (EG) and ammonium polyphosphate (APP) were used to improve the flame retardancy of acrylonitrile–butadiene–styrene based wood–plastic composites (WPCs). A synergistic effect between EG and APP on the flame retardancy of the WPCs was proposed. The results show that the highest limited oxygen index (LOI) of 34.2% and a V-0 rating were achieved when the ratio of EG to APP 12.5:7.5; this comprised 20 wt % of the total amount. However, LOI values of the samples with EG and APP alone were only 30.5 and 24.5%, respectively. Thermogravimetric analysis indicated that the flame retardants improved the amount of residue. The EG and EG/APP additives greatly decreased the peak heat release rate and suppressed smoke according to cone calorimetry testing. The scanning electron microscopy analysis indicated that the surface of the wormlike char was covered with a granular substance, which may have been the viscous phosphoric acid or poly(phosphoric acid) decomposed from APP. The flame-retardant additives worsened the mechanical properties of the WPCs. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40281.

KEYWORDS: composites; flame retardance; properties and characterization

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INTRODUCTION

Wood–plastic composites (WPCs) are materials made with a dispersion of wood flour (WF) as a filler or reinforcing agent in a melting plastic matrix. WPCs unite the durability of plastics and the cheapness of wood fibers. In addition, WPCs are environmentally friendly, biodegradable, and renewable.[1–4] However, the plastic portion of WPCs is inherent ignitable. The development of fire retardants to decrease their inflammability is required to increase commercial utilization.[5] However, limited research on the flame retardancy of WPCs has been carried out.[6–9] Acrylonitrile–butadiene–styrene (ABS) has good performance and is widely used in electrical products, automobile manufacturing, and so on. It is predictable that ABS-based WPCs may have good performances. Until now, relatively few studies focused on WPCs based on an ABS matrix have been carried out, especially on their flame retardancy. Yeh et al.[10] studied the mechanical properties of WPCs formulated with virgin and recycled ABS as matrices, respectively.

The combination of expandable graphite (EG) and phosphorus-containing flame retardants used as an intumescent flame-retardant (IFR) system has been already investigated in many studies.[5,11–15] EG is an intrinsic graphite intercalation compound intercalated with some oxidants, such as sulfuric acid. This kind of compound, known as an IFR additive, which provides good flame retardance to unsaturated polyester/epoxy interpenetrating polymer networks, is inexpensive and is constantly used as a blowing agent and carbonization compound.[5,15–19] EG acts over a condensed-phase mechanism.

Ge et al.[15] found that there was a synergistic effect between EG and ammonium polyphosphate (APP) on the flame retardancy of ABS. Meng et al.[16] studied the effects of EG and APP on the flame retardancy and mechanical properties of rigid polyurethane foam. When the loading of the flame retardant was 15 wt % (APP/EG = 1:1), the limited oxygen index (LOI) reached 30.5 vol %. Thirumal et al.[20] found that the higher particle size of EG was, the better the mechanical properties and fire-retardant properties of PUF were. To date, research on the flame retardancy of WPCs has rarely been reported.

In this study, we took advantage of different ratios of EG and APP as IFR systems. The effects of flame retardants on the flammability, thermal decomposition, and mechanical properties of WPCs were studied by LOI, UL-94 testing, thermogravimetric analysis (TGA), cone calorimetry (CONE), and a mechanical instrument. The surface of the char residues after LOI testing was observed by scanning electron microscopy (SEM).

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Table I. Compositions of All of the Samples

Sample	ABS (g)	WF (g)	EG (g)	APP (g)
WPC	60.0	40.0	0.0	0.0
WPC/EG	48.0	32.0	20.0	0.0
WPC/EG/APP1	48.0	32.0	15.0	5.0
WPC/EG/APP2	48.0	32.0	12.5	7.5
WPC/EG/APP3	48.0	32.0	10.0	10.0
WPC/EG/APP4	48.0	32.0	7.5	12.5
WPC/EG/APP5	48.0	32.0	5.0	15.0
WPC/APP	48.0	32.0	0.0	20.0

EXPERIMENTAL

Materials

ABS resin (PA-757) was purchased from Chi Mei Corp. (Taiwan). A 100-mesh poplar WF was used. EG was supplied by Shijiazhuang Kepeng Fire-Retardant Materials Plant (China). APP was purchased from Shandong Taixing Fine Chemicals Co., Ltd. (China).

Sample Preparation

The formula of the WPCs, which consisted of 60 wt % ABS and 40 wt % WF, was based on our preliminary experiment. In addition, the flame retardants accounted for 20 wt % of the total. All of the raw materials were dried at 80°C for 8 h in an oven. The composition details are shown in Table I. All of the samples were prepared by means of melting the components on a RM-200A type torque rheometer (Hap Harbin Electric Technology Co., Ltd.) and mixing for 8 min at 180°C with a rotational speed at 50 rpm; they were then hot-pressed into sheets on a curing machine under at 180°C for 3 min and cut into test samples.

Characterization

LOI was characterized by a JF-3 instrument (Jiangning, China) according to ISO 4589-1984. The UL-94 test was performed according to ASTM D 3801 procedures with a CZF-2 type instrument (Jiangning, China). TGA was carried out on a Pyirs-1 type thermogravimetric analyzer under an air flow at a heating rate of 10°C/min from room temperature (25°C) to 750°C. The weight of the samples was kept within 4–5 mg. The combustion behavior of the samples was performed on a Stanton Redcroft type (England) cone calorimeter according to ISO 5660-1 under a heat flux of 50 kW/m^2. A QuanTa200 scanning electron microscope (Netherlands) was used to observe the surface morphology of the char residue after LOI testing. Before graphing, the surface of the residues was treated by gold coating. The tensile strength and flexural strength were tested with a TA-20 computer controlled universal testing machine (Shenzhen Reger Instrument, China). Tensile strength tests were performed according to ASTM D 638 with a crosshead speed of 5 mm/min. Flexural strength tests were performed according to ASTM D 790 with a crosshead speed of 2 mm/min and a support span length of 64 mm.

Table II. Flame Retardancy of the Samples

Sample	LOI (%)	UL-94
WPC	19.8	No rating
WPC/EG	30.5	V-0
WPC/EG/APP1	33.0	V-0
WPC/EG/APP2	34.2	V-0
WPC/EG/APP3	32.5	V-0
WPC/EG/APP4	30.0	V-0
WPC/EG/APP5	28.9	V-1
WPC/APP	24.5	No rating

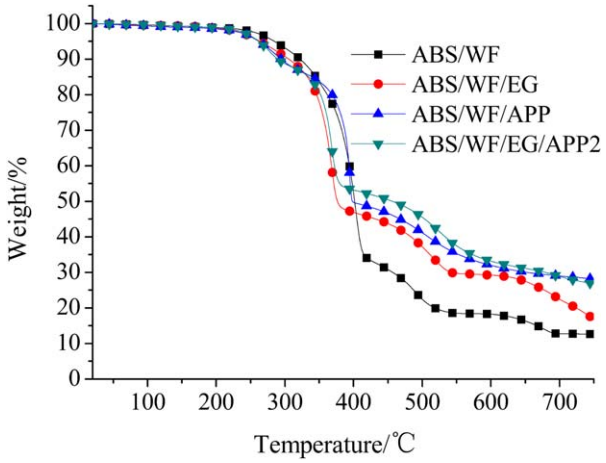

Figure 1. TGA curves of the samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Flame Retardancy

Table II shows the flame retardancy of the samples. The LOI of the WPCs was only 19.8% with no rating in the UL-94 test. The LOI values of the WPC containing 20 wt % EG (WPC/EG) and that containing 20 wt % APP (WPC/APP) were 30.5 and 24.5%, respectively. With the total amount of EG and APP maintained at 20 wt %, the best ratio of EG to APP was 12.5:7.5, and the LOI value reached 34.2%. This result confirmed that the mixture of EG and APP was more efficient than with EG or APP alone in a certain proportional range, and

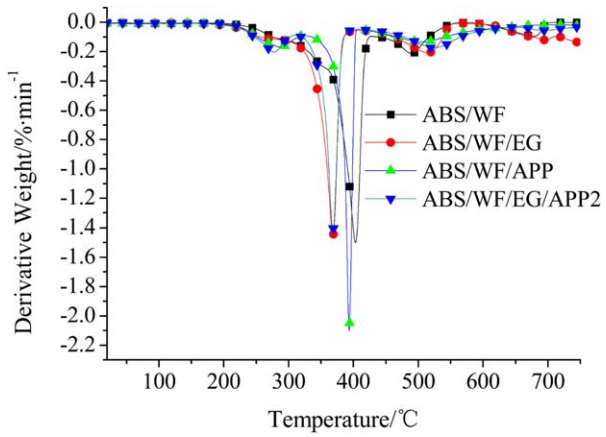

Figure 2. Differential thermogravimetry curves of the samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. TGA Data for Different Samples

Sample	$T_{5wt\%}$ (°C)	T_{peak1} (°C)	T_{peak2} (°C)	Residue at 750°C (wt %)
WPC	284.5	403.5	489.6	12.9
WPC/EG	263.5	368.2	513.8	16.8
WPC/APP	261.9	393.4	506.7	28.1
WPC/EG/APP2	262.0	368.4	523.4	26.8

there was a synergic effect between EG and APP[15]. As the UL-94 test results shown in Table II, both the pure WPC and WPC/APP failed to classify the level. Nevertheless, all of the samples containing EG and APP passed the V-0 rating, except WPC/EG/APP5.

The reason for the higher LOI value of WPC/EG was the decomposition of EG, which formed a large amount of thermally stable, wormlike carbonaceous residue and nonflammable gases, such as CO_2 and SO_2, when it was heated. These residues could endure high temperatures and protect the substrate from heat sources by greatly slowing down the heat and mass transfer.[21,22] For that of WPC/APP, this was mainly due to the NH_3, H_2O, and poly(phosphoric acid) produced by APP at high temperatures, which dilute the oxygen and flammable molecular fragments in the gas phase.[15,16] In addition, the decomposed products of APP could crosslink the wood to form more stable char residue in the condensed phase. Nevertheless, the mixture of EG and APP combined the advantages of the previous two. In the gas phase, the decomposition of APP and EG released nonflammable gases (CO_2, SO_2, NH_3, etc.), which could dilute the combustible gases. In the condensed phase, the char barrier was reinforced by the poly(phosphoric acid) generated from APP. Thus, a denser char layer was formed to retard the transfer of gas and heat. However, this was not always the case. When the APP content was excessive, the amount of carbon source formed by EG was insufficient. On the contrary, the char layer was too loose to act as a barrier.[15,23] Therefore, there existed an optimal ratio of EG and APP. The best quality of the char layer was formed at this ratio (EG/APP = 12.5:7.5), which showed the highest LOI value and the best flame-retardant efficiency.

TGA

The thermal degeneration behaviors of some samples were studied by TGA under an air flow. The TGA and differential thermogravimetry curves of different samples are shown in Figures 1 and 2. The main data of TGA are listed in Table III.

Table IV. CONE Data Obtained for the Samples

Sample	PHRR (kW/m^2)	AHRR (kW/m^2)	Total smoke release (m^2/m^2)	Residue (%)	Burning time (s)
WPC	351.2	219.1	2915.8	22.0	360
WPC/EG	175.9	84.1	1098.3	46.9	750
WPC/APP	221.8	138.2	2720.2	31.3	460
WPC/EG/APP2	188.5	87.3	1399.7	42.7	750

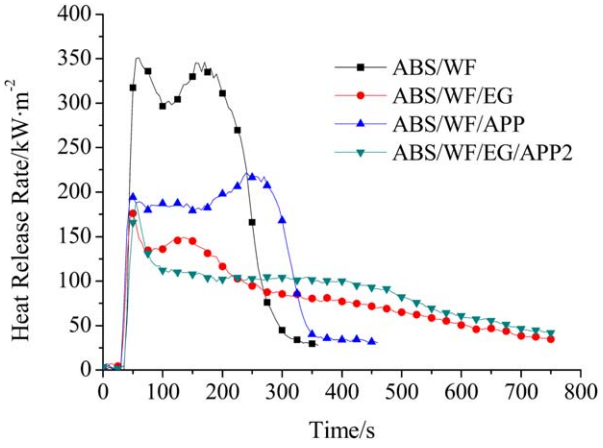

Figure 3. HRR curves of the samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

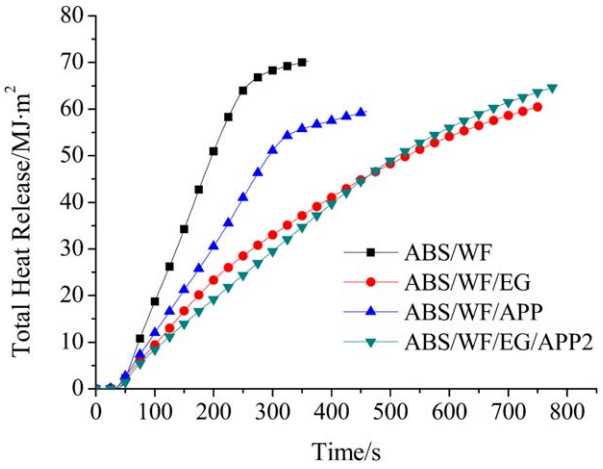

Figure 4. THR curves of the samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5. Photograph of the samples after CONE testing: (A) WPC/EG/APP2 and (B) WPC/EG. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

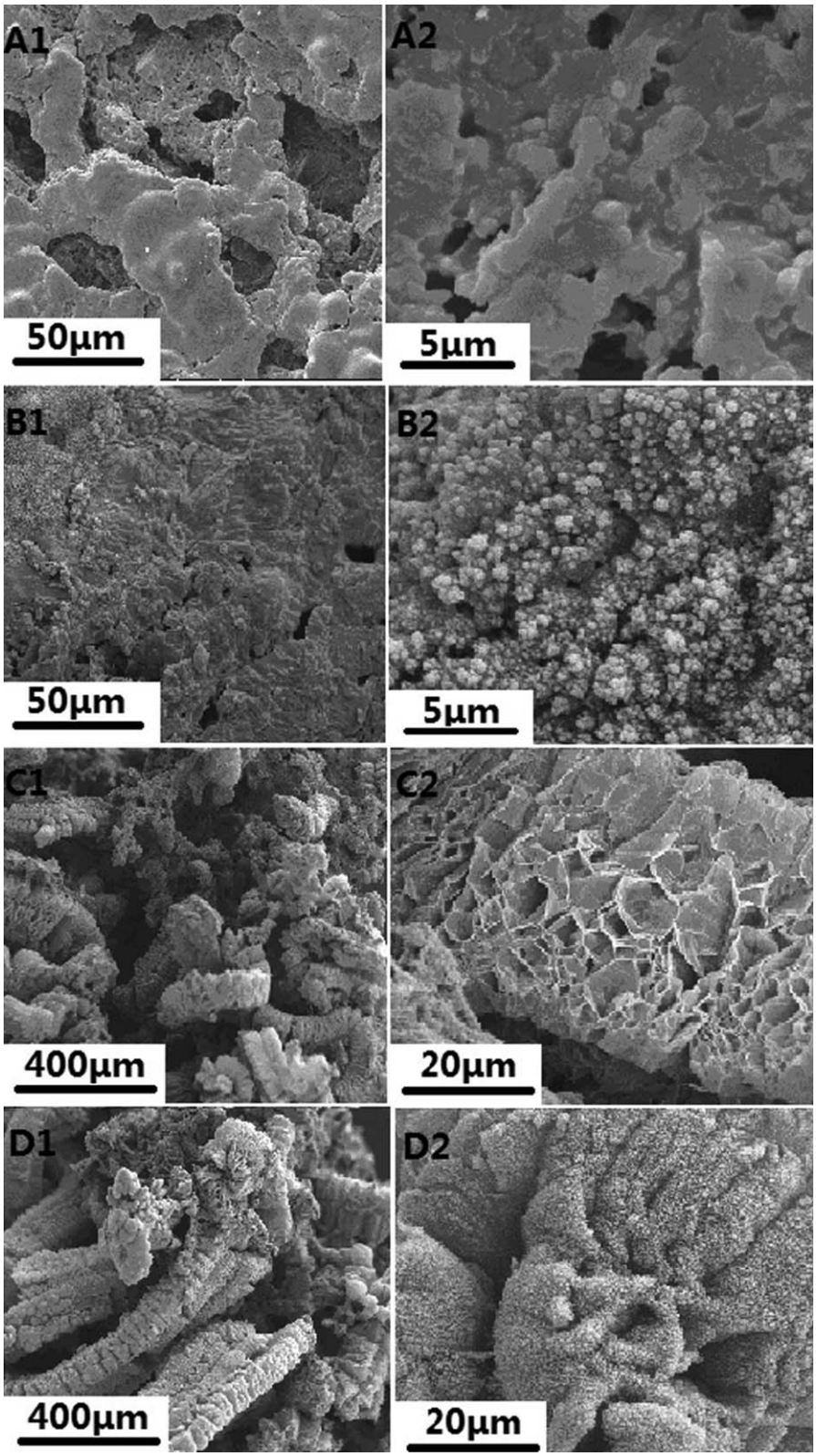

Figure 6. SEM micrographs at different magnification samples: (A1,A2) WPC, (B1,B2) WPC/APP, (C1,C2) WPC/EG, and (D1,D2) WPC/EG/APP2.

The TGA curves showed that all of the samples mainly underwent a two-step thermal degeneration. The 5% weight loss temperature ($T_{5wt\%}$) of the WPCs was 284.5°C, but that of WPC/EG, WPC/APP, and WPC/EG/APP2 decreased to 263.5, 261.9, and 262.0°C, respectively. The first peak temperature (T_{peak1}) of the WPCs was higher than those of systems with

different flame retardants. However, in the second step of thermal degeneration, the situation was reversed. The second peak temperature (T_{peak2}) values of the three flame-retarded systems were higher than that of the WPCs because of the fire-retardant mechanism of EG, APP, or the combination of the two, as mentioned previously. The stable char formed by EG covered on the substrate in the WPC/EG system may have been blown away by the air flow for its loosened structure.[15] In WPC/EG/APP2, the poly(phosphoric acid) decomposed by APP acted as an adhesive for the residue; this resulted in a more compact char layer, which was conducive to isolating the substrate from heat. The residue at 750°C of the WPCs was only 12.9%, and that of WPC/EG was slightly improved. The residues of WPC/APP and WPC/EG/APP2 were greatly improved at 750°C.

CONE

The CONE test is widely known as the best fire test and yields results similar to real fires. The results of the test can be used to assess the fire performance of a material in a real fire environment.[24] The heat release rate (HRR), total heat release (THR), peak heat release rate (PHRR), total smoke rate (TSR), and residues were obtained from the test. Table IV shows some of the important data obtained from the test.

All of the samples showed a typical HRR curve with two peaks, except for WPC/EG/APP2 (Figure 3).[25,26] And the THR of WPCs filled with flame retardant was lower than that of WPCs (Figure 4). The decrease in HRR after the first peak was due to the formation of char, which acted as a barrier.[26] The PHRR of the WPCs reached 351.2 kW/m^2, and its average heat release rate (AHRR) was as high as 219.1 kW/m^2 (Figure 3 and Table IV). The burning time of the WPCs was only 360 s. Because of the catalyzed-forming char, which served as a barrier between the heat source and substrate, the burning time (450 s) of WPC/APP was prolonged as well as its PHRR and AHRR decreased to 221.8 and 138.2 kW/m^2, respectively. For WPC/EG and WPC/EG/APP2, the burning time was further delayed, and both PHRR and AHRR decreased further. As the results show, both PHRR and AHRR of WPC/EG were a bit lower than those of WPC/EG/APP2 (Table IV). This was because the char layer of WPC/EG [Figure 5(A)] was much thicker than that of WPC/EG/APP2 [Figure 5(B)]. The thicker char layer of WPC/EG may offset the disadvantage caused by its incompact structure during combustion. The char residues of the fire-retarded WPC were largely improved (Table IV). Obviously, the IFR could greatly improve the flame-retardant properties of the WPCs.

The TSR of ABS/WF was as high as 2920 m^2/m^2 and was twice as much as that of ABS/WF/EG and almost triple that of ABS/WF/EG/APP2 (Table IV). The results indicate that the wormlike char with a large specific surface formed by EG could effectively absorb and suppress the production of ABS-based WPCs. However, for ABS/WF/APP, the TSR was 2727m^2/m^2; this indicated that APP was not an effective smoke suppressant.

SEM

To better understand the action of the flame retardant, further study of the morphological structures of char residues after the LOI test were observed by SEM. The SEM micrographs of the samples are shown in Figure 6.

The surface of WPC/APP [Figure 6(B1,B2)] had less holes and cracks than that of WPC [Figure 6(A1,A2)]. A glasslike coating, which may be caused by viscous phosphoric acid or poly(phosphoric acid) decomposed from APP and as shown in Figure 6(B1), was observed on the surface. Figure 6(C1,D1) shows wormlike char, and the char of WPC/EG/APP2 was more compact [Figure 6(D1)].[10] Moreover, we found that the surface morphologies of WPC/APP and WPC/EG/APP2 were very different from each other in higher magnification [Figure 6(C2,D2)]. The surface of WPC/APP was smooth; this demonstrated the loosened structure of this char produced by EG alone. That of WPC/EG/APP2, on the contrary, showed a surface of wormlike char covered in a granular substance, which may have been the viscous phosphoric acid or poly(phosphoric acid) from the decomposition of APP. This resulted in a more compact char layer and more effective fire retardancy in the ABS-based WPC.

Table V. Mechanical Properties of the ABS-Based WPCs

Sample	Tensile strength (MPa)	Flexural strength (MPa)
WPC	32.41	50.02
WPC/EG	20.10	43.08
WPC/EG/APP1	24.36	36.42
WPC/EG/APP2	22.35	37.82
WPC/EG/APP3	23.04	37.07
WPC/EG/APP4	20.46	29.77
WPC/EG/APP5	20.18	33.31
WPC/APP	18.11	28.99

Mechanical Properties

Because WPCs are materials widely used in many areas, the mechanical properties need to be tested. The influence of flame-retardant additives on the mechanical properties of WPCs was investigated. The results are shown in Table V. Because of the poor compatibility of EG and APP with ABS-based WPCs, the mechanical properties of the WPCs were dramatically destroyed. For example, compared with WPCs, the tensile and flexural strengths of WPC/EG decreased by 38.0 and 13.9%, respectively. We observed that the samples containing EG had both a higher tensile strength and a higher flexural strength than those containing WPC/APP.

CONCLUSIONS

In conclusion, the flame retardant improved the flame retardancy of the ABS-based WPCs. A synergistic effect between EG and APP was proposed in flame retarding ABS-based WPCs, and the best ratio was EG/APP = 12.5:7.5. The flame retardant decreased the thermal stability of WPC, but the char residue and fire retardancy of the WPCs were greatly improved. The SEM micrograph of WPC/EG/APP2 confirmed that the char structure was more compact compared with that of WPC/EG; this offered an explanation as to why WPC/EG/APP2 had a higher LOI than WPC/EG. The flame-retardant additives worsened the mechanical properties of the ABS-based WPC, such as the tensile strength and flexural strength.

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