

Melamine Polyphosphate/Silicon-modified Phenolic Resin Flame Retardant Glass Fiber Reinforced Polyamide-6

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ABSTRACT: The halogen-free flame retardance of glass fiber reinforced polyamide-6 (PA6) is an everlastingly challenge due to well-known wick effect. In this research, a novel system composed of a nitrogen–phosphorous flame retardant, melamine polyphosphate combined with a macromolecular charring agent, silicon-modified phenolic resin (SPR), was employed to flame-retard glass fiber reinforced PA6. It exhibited obvious synergistic effect between the two components at a proper ratio range. The flame retardance of the composites can be remarkably improved due to the increased amount and improved thermal stability of the produced char. The flame resistance tests indicated that the synergism system with an optimized ratio achieved V0 (1.6 mm) rating of UL94, 25.2% of Limited Oxygen Index, and only 338.2 W/g of the heat release peak rate. The corresponding synergistic mechanisms were investigated by the characterizations including the thermal gravimetric analysis, carbonation test, and the char morphology observation. It confirmed that the introduced SPR could accelerate the carbonation of PA6 resin, which was in favor of the construction of denser and more continuous charring structure. In addition, the flame retardant materials also indicated the acceptable mechanical properties, showing the advantages in the overall performance. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2171–2176, 2013

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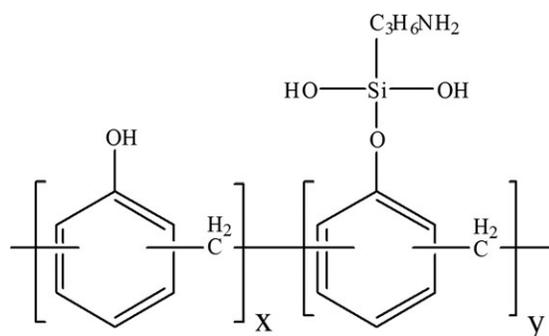
INTRODUCTION

Polyamide-6 (PA6) is an important engineering plastic extensively applied due to its excellent performance. To further improve the heat distortion temperature, dimensional stability, strength, and modulus in the practical applications, glass fibers (GF) are usually incorporated to this polymer to prepare glass fiber reinforced PA6 (GFRPA6) composites.¹ However, the introduced GF remarkably increases the flammability of the composites due to the wick effect, leading to much more difficult flame resistance of GFRPA6 compared with neat PA6, which greatly restricts the applications of the composites in some important fields such as automobile manufacture, construction, electrical, and electronic (E&E) industries.

In order to endow GFRPA6 composites with flame retardance, various flame retardants are added into the materials. Traditional halogen flame retardants with satisfactory flame resistance have been commercially used in the past years, but the release of some toxicants during their decomposition caused series of ecological problems.^{2,3} Accordingly, halogen-free flame retardants are paid more and more attention in the replacement of the halogen ones. Among the commercial halogen-free products,

melamine-based flame retardants possess particular advantages such as innocuity, low smoke, and white color.^{4,5} Melamine polyphosphate (MPP), as a typical melamine-based flame retardant with high nitrogen and phosphorus contents, is very suitable for glass fiber reinforced polyamide.⁶ However, similar to most halogen-free flame retardants, the efficiency of MPP is lower than that of traditional halogen ones. Therefore, a high loading is generally needed for the expected flame retardance [over 30% MPP loading for UL-94 V0 rating (1.6 mm)], which seriously deteriorates the processability and mechanical properties of the composites.

To overcome the above disadvantages of MPP, the researchers have looked for some synergists including iron-montmorillonite, zinc borate, aluminum phosphinate, pentaerythritol, and so on, to improve the efficiency and decrease the loading level of MPP.^{7–9} The practical use indicated that these synergists were not perfect because of unsatisfactory flame retardance, decreased compatibility as well as high costs. In our previous investigations, MPP/solid acid showing obvious synergistic effect was successfully applied in GFPA6,¹⁰ but the additional encapsulation treatment was needed to improve the poor compatibility



Scheme 1. Molecular formula of SPR ($X/Y = 1/2$).

between the solid acid with the resin matrix. Additionally, we also found that the common linear phenolic resin as a macromolecular charring agent, exhibited the synergistic effect combined with MPP in PA6/mineral filler by improving the charring process in the condensed phase.¹¹ However, in GFRPA6 composite with remarkable wick effect, such as synergism system only displayed slight improvement of the flame retardance in due to lower charring efficiency (The char formation cannot make up the quick decomposition of the char with a high flame rate). The above positive results still gave us a revelation: the flame retardance would be probably enhanced if employing a modified phenolic resin with better charring capacity instead of the common one. Herein, a silicon-modified phenolic resin (SPR) synthesized in our group is combined with MPP to flame-retard GFRPA6. This macromolecular charring agent could effectively supply the carbon source and improved the flame resistance in the condensed phase. It also had good compatibility between SPR with PA6 and the flame retardant composite exhibited acceptable mechanical properties, showing the advantages in the overall performance.

EXPERIMENTAL

Materials

PA6 pellets: purchased by Yueyang Petro-Chemical, Yueyang, China; MPP: provided by Sichuan Yulong, Co., Chengdu, China; GF: TP560, provided by Jushi Group, Chengdu, China; Liner SPR powder with molecular weight 720, synthesized in our group,¹² its molecular formula is shown as Scheme 1.

Preparation of Flame Retardant GFRPA6

A weighted amount of PA6 pellets (45 wt %), GF (30 wt %), MPP/SPR flame retardants (25 wt %, their ratio varied with the formulations) were pre-mixed and then the mixture was extruded by a twin-extruder (SLJ-30, screw diameter ϕ is 30 mm, aspect ratio L/D is 32; Longchang Chemical Machinery Company, China). The extruded pellets were injected into standard test bars by an injector (K-TEC 40; Terromatik Milacron, German). The set temperature range in the twin-extruder and the injector were 220–260°C.

Characterization

Underwriters Laboratories-94 (UL-94) vertical burning test was carried out according to ASTM D3801-1996 using a CZF-3 vertical burning tester (the dimension of the test bar: 127 × 12.7 × 1.6 mm³). The flame retardance of the materials was classi-

fied as different rating including V0, V1, V2, and NR (no rating).

The Limited Oxygen Index (LOI) values of the materials were measured by an ATLAS LOI instrument with 120 × 6.5 × 3 mm³ bars according to ASTM D2863-1970.

Micro-scale combustion calorimeter (MCC), FAA type, manufactured by Fire Testing Technology, Britain, was used to determine the peak of heat release rate (pHRR) and the total heat release (THR) of the materials with a heating rate of 1°C/s from 75 to 750°C. One sample was measured three times with the average value as the final result.

TG analysis of the samples [PA6, SPR, PA6/SPR (3.75/45 weight ratio), PA6/MPP/GF, and PA6/SPR/MPP/GF] were performed by a TA Q-500 TGA thermal analyzer with a heating rate of 10°C/min, a temperature range from 30 to 700°C, and an air flow of 100 mL/min.

Carbonation tests of the flame retardant materials were performed by heating the samples at 500–800°C for 0.5 h in a Muffle furnace. The residues weight percent (RWP) were calculated by the following formula.

$$\text{RWP} = 100\% \times (\text{Original weight} - \text{Residual weight}) / \text{Original weight}$$

Tensile strength and flexible strength were tested by an Instron universal testing machine according to ASTM D-638 and ASTM D-790, respectively. Izod notched impact strength was tested by an XJ-40A impact tester according to ASTM D-256.

RESULTS AND DISCUSSION

Flame Retardance Evaluation

Figure 1 and Table I showed the variation of the LOI and vertical flame data of the flame retardant GFRPA6 with different MPP/SPR ratio. The system with only MPP involved (0% percent SPR) indicated unsatisfactory flame retardance in the GFRPA6. Its LOI was only 20.3 [only increasing 1.8 compared

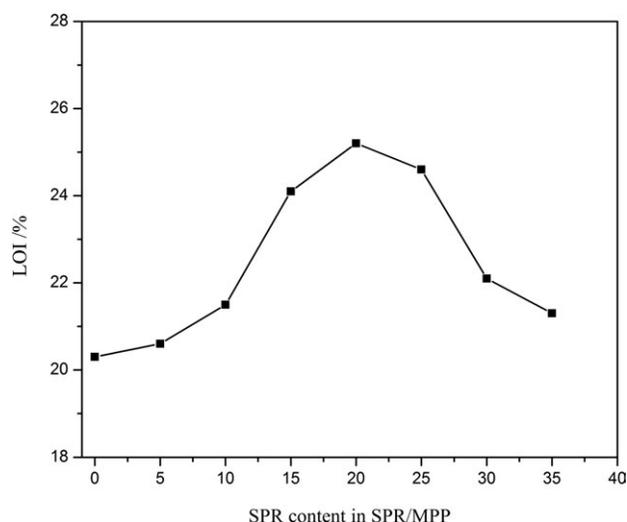


Figure 1. The LOI of the flame retardant GFRPA6 with different SPR/MPP ratio (The total content of SPR/MPP in the composite: 25%).

Table I. The Vertical Flame Test of the Flame Retardant GFRPA6 with Different SPR/MPP Ratio (The Total Content of SPR/MPP in the Composites: 25%)

SPR content in SPR/MPP (%)	Extinction time (s) after the first 10 s ignition	Extinction time (s) after the second 10 s ignition	Total extinction time (s)	Rating
0	No extinction	-	-	NR
5	No extinction	-	-	NR
10	8.2	No extinction	-	NR
15	2.7	3.5	6.2	VO
20	2.1	3.0	5.1	VO
25	3.2	4.1	7.3	VO
30	7.6	16.7	24.3	V1
35	11.2	No extinction	-	NR

with GFRPA6 without any flame retardant (18.5)] and the vertical flame could not self-extinguish (the same NR with GFRPA6). With low SPR contents (below 10% in MPP/SPR), the LOI values enhanced a little but the vertical flame test results basically kept unchanged (no extinction). With relatively higher SPR contents (15–25% in MPP/SPR), the LOI had remarkable incensement (over 24) and the vertical flame could self-extinguish in a short total time (5.1–24.3 s), indicating the synergistic effect between MPP and SPR in the ratio range. With SPR content further increased (over 30% in MPP/SPR), the flame resistance showed a downward trend. The flame retardance variation was explained as that a low content SPR cannot effectively increase the carbon source, but a high content SPR in MPP/SPR correspondingly decreased the amount of the main flame retardant MPP in the material. Both the ratio ranges were disadvantageous to obtain satisfactory flame retardance. The above results demonstrated that MPP/SPR ratio had important influence on the synergism, and only a medium ratio (SPR content in the synergism system: 15–25%) can achieve an optimum balance between the flame retardant and the charring agent. Considering that SPR with a number of rigid benzene rings in its macromolecule, easily increases brittleness of the composites, a relatively lower SPR content (15% in MPP/SPR) in the synergism range, was adopted to prepare the flame retardant GFRPA6 (3.75 wt % SPR in the composites).

Aside from the LOI and vertical flame tests, MCC analysis was also performed to evaluate the flame retardance of the above systems. As a laboratory-scale calorimeter, MCC can conveniently determine the flammability parameters of materials including pHRR and THR based on oxygen consumption during combustion. Figure 2 and Table II showed the corresponding MCC data of GFRPA6, MPP/GFRPA6, and MPP/SPR/GFRPA6.

Table II. The pHRR and THR of GFRPA6, MPP/GFRPA6, and MPP/SPR/GFRPA6 (SPR Content in SPR/MPP: 15%)

Sample	pHRR (W/g)	THR (kJ/g)
GFRPA6	564.8	22.5
MPP/GFRPA6	405.4	19.4
MPP/SPR/GFRPA6	338.2	16.8

GFRPA6. MPP/SPR/GFRPA6 indicated much smaller pHRR and THR values than MPP/GFRPA6 (only 83.4 and 86.6% of the latter), implying the former had a lower flame rate and more incomplete combustion degree. In accordance with the previous LOI and vertical flame test results, MCC analysis further confirmed the existence of the synergism between MPP and SPR based on the caloric variation.

The Synergism Mechanisms

As is well known, the flame resistance mechanism for most nitrogen–phosphorous flame retardants belongs to an intumescent mode. A typical intumescent system generally involves three components including a blowing agent, acid catalyst, and charring agent. Such a system can experience an intensive expansion to form foamed char, and construct a heat and oxygen barrier resulting in quick self-extinguishment of burning materials. MPP begins to decompose at about 340°C and releases some nitrogen-containing inert gases and phosphorus-containing acids, which constitute two basic components (the blowing agent and acid catalyst) of an intumescent system. However, the only carbon source in MPP/GFRPA6 composite is PA6 resin. The degradation of PA6 generally includes two modes¹³: one is complete depolymerization to produce volatile

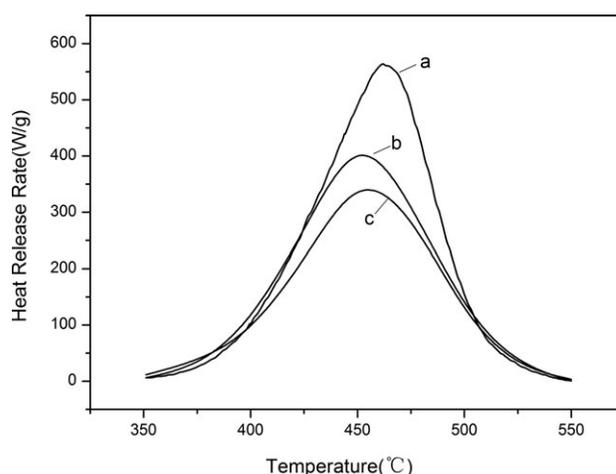


Figure 2. The HRR curves of (a) GFRPA6, (b) MPP/GFRPA6, and (c) MPP/SPR/GFRPA6 (SPR content in SPR/MPP: 15%).

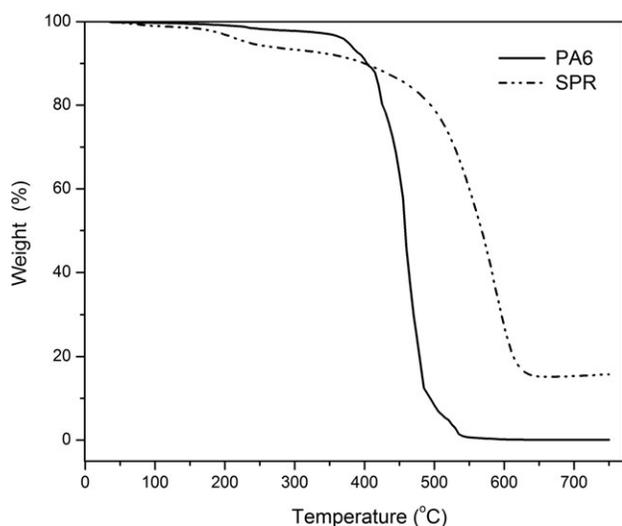


Figure 3. The TG curves of PA6 and SPR.

products with low molecular weight, such as caprolactam, cyclopentanone, and so on, and obviously, this mode has no contribution to the charring process; the other is incomplete depolymerization to produce oligomers, which can further form series of complicated crosslinking compounds through isomerization, thus constituting the basis of the char. Certainly, the charring process greatly depends on the environmental factors such as the temperature, oxygen concentration, and catalysis effect of the produced acids. Generally speaking, with a high temperature and oxygen concentration, the resin tends to fully burn and the degradation is dominated by the complete depolymerization mode. A high temperature can accelerate the decomposition of those isomerization products, and accordingly it cannot remain the stable char structure. With only PA6 served as the carbon source, the charring is obviously insufficient to achieve good flame retardance in the condensed phase.

As a typical thermal-setting polymer with excellent thermal stability, phenolic resin is widely used as a charring agent in many flame retardant polymer formulations.^{14–17} Liner phenolic macromolecules first crosslink when heated. At a higher temperature (even over 600°C), the produced crosslinking structure only undergoes a slow degradation converting into the char with highly thermal stable fused-ring structure through the condensation of the neighbor benzene rings. Compared with the common phenolic resin, SPR possessed markedly enhanced thermal stability and charring capacity by introducing the thermal-resistance element Si onto the phenolic macromolecule. Our research revealed that the charring ratio of the SPR was almost 27 times higher than that of the common phenolic resin.¹² On one hand, the improved charring performance results from that the obvious electronegativity difference between Si and O leads to a high ionization tendency of Si—O bond, which generates the dipole induction on the neighbor hydrocarbon and benzene ring to improve the thermal-resistance of these groups.¹⁸ On the other hand, a number of Si—O bonds with higher bond energy (451 kJ/mol) replace the Ph—O bonds (bond energy: 345 kJ/mol), thus greatly increasing the

decomposition activation energy. Furthermore, the SPR can be oxidized into the compounds with highly crosslinking Si—O—Si bonds involved in the condensed phase. The crosslinking structure can effectively increase the strength and also improve the barrier effect of the char layer.

Accordingly, the macromolecular charring agent SPR is a necessary complementarity of the carbon source for MPP/GFRPA6 system. The charring capability of PA6 and SPR were compared by TGA as shown in Figure 3. PA6 displayed a much higher decomposition rate and obviously lower residue ratio at high temperature range (only 0.18 wt % remained at 600°C), showing almost complete depolymerization without charring. But for SPR, it can remain 15.3% residual char even at 700°C. Consequently, the carbon source composed of SPR/PA6 mixture should possess better charring performance than only PA6. In addition, our research also revealed that the charring process of the mixture carbon source were not isolated but facilitated each other. Figure 4(a) is the experimental TG curve of SPR/PA6 with 3.75/45 weight ratio (the same SPR/PA6 ratio with SPR/MPP/GFRPA6 composite), and Figure 4(b) is the calculated TG curve by overlapping the TG curves of SPR and PA6 according to the above weight ratio. If without any interaction for their respective charring process, the experimental TG curve should basically superpose the calculated one. In fact, it can be seen that the former was always above the latter, confirming the occurrence of their charring interaction. This can be explained as follows: as the produced stable char from SPR can form a shield to effectively wrap PA6 resin and insulate the heat and oxygen, it was in favor of the incomplete combustion of PA6 (increasing the possibility producing isomerization products), therefore promoting the carbonation of PA6. Similarly, the charring process of PA6 also contributed to the stabilization of the char structure from SPR.

For the comparison of the charring performance of the composites, TG analysis of MPP/GFRPA6 and SPR/MPP/GFRPA6 was also conducted in Figure 5. The fact that the latter had 51%

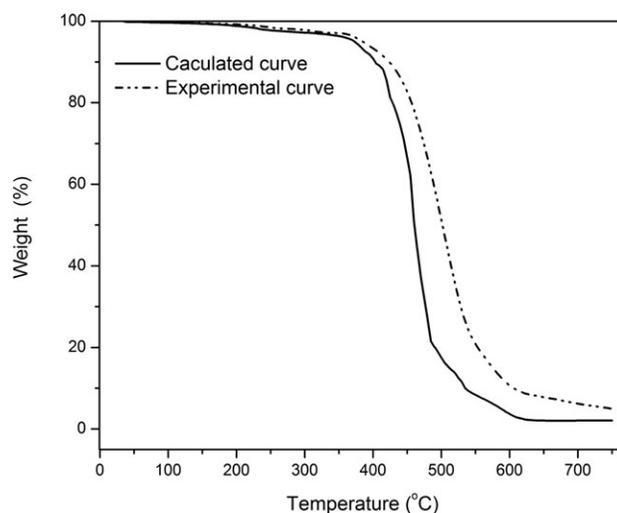


Figure 4. Experimental and calculated TG curves of PA6/SPR (weight ratio SPR/PA6 = 3.75/45).

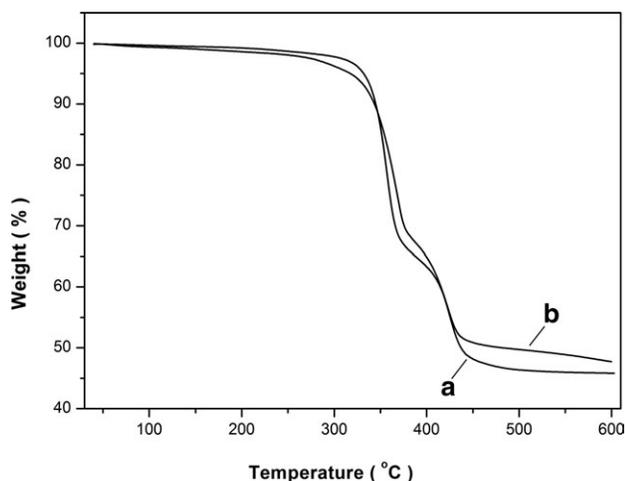


Figure 5. The TG curves of (a) MPP/GFRPA6 and (b) MPP/SPR/GFRPA6.

residual char, obviously higher than 45% of the former, confirmed the remarkable contribution of SPR to promote the charring of the composite.

Figure 6 is the carbonation test results of MPP/GFRPA6 and MPP/SPR/GFRPA6 at different carbonation temperature. It can be seen that the latter had higher residue (composed of GF and char) weight percent at all the carbonation temperature ranges, showing this system had higher charring amount. Additionally, the residue weight percent of both systems indicated decrease tendency with increasing temperature (As GF was not decomposed, the decrease was only caused by the variations of the char amount), implying more char structure became instable and decomposed at a higher temperature range. However, the decrease extent for the two systems was very different. The residue weight percent of MPP/GFRPA6 was reduced from 46.1% (500°C) to 32.4% (800°C), almost 13.7% lost due to the decomposition of the char, but that of MPP/SPR/GFRPA6 was reduced from 49.7% (500°C) to 41.9% (800°C), only 7.8% loss.

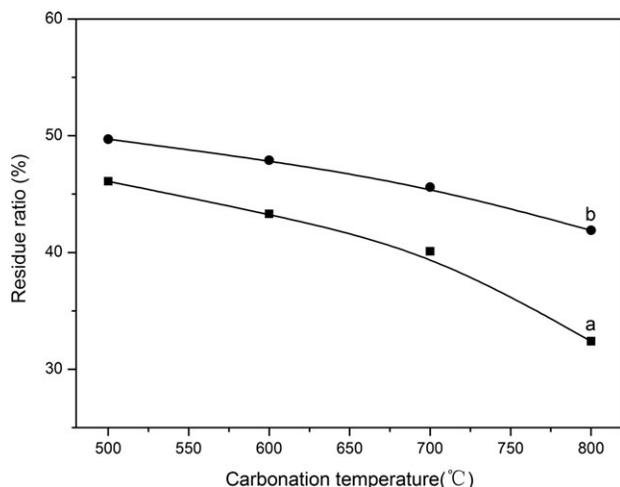


Figure 6. The residue ratio at different carbonation temperature (a) MPP/GFRPA6 and (b) MPP/SPR/GFRPA6.



Figure 7. The char morphology of the burned bars (UL94 test, the flame time: 20 s) of (a) MPP/GFRPA6 and (b) MPP/SPR/GFRPA6.

Obviously, MPP/SPR/GFRPA6 possessed not only more charring amount at the same temperature but also better thermal stability of the char at a higher temperature.

Finally, the char morphologies of the above materials after UL94 flame test were shown in Figure 7. It can be observed that the volume of the produced char of MPP/SPR/GFRPA6 was evidently larger than that of MPP/GFRPA6. Furthermore, the former also exhibited denser and more continuous structure in favor of constructing the barrier to the heat, oxygen, and volatile fuel.

The Mechanical Properties

Mechanical properties are key performance for flame retardant polymers. As the amide groups in PA6 chains and the phenolic hydroxyl groups remained in SPR macromolecule can interact to form hydrogen bonds, the compatibility between PA6 and SPR is improved, therefore advantageous to improving the mechanical performance. From the mechanical properties of MPP/SPR/GFRPA6 and MPP/GFRPA6 listed in Table III, it can be seen that the difference between them was not very obvious. The former showed better tensile and flexible strength reflecting the stiffness of the materials, but the latter exhibited better impact strength reflecting the toughness. The rigidity of SPR with a number of benzene rings explained the reason resulting in the difference.

CONCLUSION

It was confirmed the remarkable synergistic effect for SPR/MPP flame retardant GFRPA6. A Total of 15–20% SPR in SPR/MPP greatly enhanced the LOI, shortened the vertical flame time, and decreased the pHRR and THR compared with only MPP system. As a thermal-set macromolecular charring agent, SPR showed much higher charring capacity than PA6. It not only increased the charring amount but also effectively improved the thermal-resistance of the char by producing the crosslinking and fused-ring structure, thus denser and more continuous char structure could be constructed. In addition, the good compatibility between PA6 and SPR also contributed to the accepted mechanical properties. The combined satisfactory overall

Table III. The Mechanical Properties of MPP/GFRPA6 and MPP/SPR/GFRPA6

Sample	Tensile strength (MPa)	Flexible strength (MPa)	Notched impact strength (kJ/m ²)
MPP/GFPA6	110.5	118.2	8.6
MPP/SPR/GFPA6	117.4	127.3	8.0

performance provided the novel synergism system with a promising application in halogen-free flame retardant GFRPA6.

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