

# Flame Retarding Glass Fibers Reinforced Polyamide 6 by Melamine Polyphosphate/Polyurethane-Encapsulated Solid Acid

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**ABSTRACT:** Melamine polyphosphate and thermal-plastic polyurethane (TPU)-encapsulated solid acid were applied for flame retardant glass fibers reinforced polyamide 6 (GFPA6). The introduction of TPU would change the interfacial property between glass fibers (GFs) and polyamide 6 (PA6), weakening the "candlewick effects" of GFs in PA6. Serving as a synergist, solid acid containing sulfur (CAS) played the role of a strong acid source, which could promote the system to form much more condensed and closed char layers. Macromolecular charring agent, TPU, was able to accelerate the charring process. In addition, TPU encapsulat-

ing on the unstable solid acid could isolate CAS from PA6 resin, preventing the chemical interaction between them, which would cause the degradation of material. This established technology provided an effective approach to prepare halogen-free flame retardant GFPA6 with UL94-1.6 mm V0 rating and good mechanical performance, showing a promise in the future commercial application. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3317–3322, 2007

**Key words:** flame retardance; polyamide 6; glass fibers; melamine polyphosphate; synergistic agent

## INTRODUCTION

Polyamide 6 (PA6) is a kind of engineering plastic used widely. It possesses excellent properties such as high strength and toughness, good electric performance, oil-resistance, wear-ability, and easy processing. However, PA6 belongs to flammable material for its LOI is only 23, generating a great deal of heat, smoke, and melt drops while burning. Therefore, flame retardant PA6 is in great demand.<sup>1</sup> GFPA6 shows much higher mechanical properties and heat transition temperature, as a result, more extensive applications as compared with neat PA6. But, flame retardance of GFPA6 is much more difficult than that of PA6, for the introduction of glass fibers (GFs) will remarkably accelerate the combustion of PA6, which is called the "candlewick effect" of GFs. Therefore, flame retardance of GFPA6 becomes a global challenge which has attracted so many attempts.<sup>2–8</sup> Halogen-containing flame retardants still show the best flame retardancy for GFPA6 at present<sup>2–4,8</sup>, but their disadvantages lie in easy emigration, poor stability under ultraviolet radiation, and release of poisonous gases in combustion.<sup>1</sup> So, halo-

gen-containing products have been restricted much more in recent years. Among halogen-free flame retardants, inorganic compounds including magnesium hydrate ( $Mg(OH)_2$ ) are environment-friendly flame retardants,<sup>5,7,9</sup> but their high loading makes the mechanical performance of the obtained materials decline heavily. Nitrogen-containing or phosphorus-containing flame retardants possess good fire retardancy on PA6, but short effect for GFPA6. Comparably, some melamine(ME)-based compounds, especially those phosphorus-containing products, have proved better for GFPA6.<sup>1,2,9–14</sup> Take melamine polyphosphate (MPP)<sup>15–17</sup> for example, it combines the flame retardant mechanism of both gaseous phase (from nitrogen-containing component) and condensed phase (from phosphorus-containing component), showing N-P synergistic effects. MPP is decomposed into melamine phosphate (MP) and melamine pyrophosphate (MPy) above 350°C in the presence of PA6,<sup>15</sup> then the produced MP is further decomposed into phosphoric acid and melamine, serving as acid source and gas source, respectively. PA6 itself is the carbon source which will react with acid source to generate condensed remains and then form melted substance under high temperature. With the blowing of the gases from melamine, the melted substance is intumesced to form porous foam char layers, which can isolate heat, oxygen, and smoke from the combustion of PA6 effectively.<sup>9</sup> MPP can improve the fire retardancy of GFPA6, but

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adopting it alone, at a low loading level, cannot endow GFPA6 with satisfying flame retardancy.

Some solid acids, e.g., silico-tungstic acid, show synergistic effects with MPP in flame retardant GFPA6,<sup>18</sup> but too expensive. In this study, we took a low cost solid acid containing sulfur (CAS) as a substitute, which showed even better synergistic effects compared with conventional acids. A disadvantage of CAS is the poor compatibility with PA6 matrix. In addition, PA6 is easy to react with acid substance, and the inorganic acid from the decomposition of CAS will cause the degradation of PA6, thus leading to the deterioration of the mechanical performance of the obtained materials seriously.

In this investigation, MPP was prepared through heat polymerization of MP at 300°C, serving as the main flame retardant for GFPA6. TPU resin-encapsulated solid acid composite (TES) was used as synergistic agent in this system. Encapsulating layer TPU, a kind of macromolecular charring agent, also a good compatilizer between CAS synergist and PA6 matrix, was used for avoiding the direct contact between acid substance and PA6, which would bring the degradation of PA6. The flame retardancy and mechanical performance of the obtained materials, as well as the flame retardant mechanism of the flame retarded system were investigated.

## EXPERIMENTAL

### Materials

The following materials were used within this research work:

Melamine (ME): Industrial grade, Sichuan Chemical Plant, China.

Phosphoric acid: AR, Chengdu Kelong, Chemical Reactant Company, China.

Polyamide 6 (PA6) pellet: relative viscosity 3.2, Balin Petroleum and Chemical Subsidiary Company, China Petroleum and Chemical Corp., China.

Glass fiber (GF): TP560, Zhejiang Tongxiang, Glass Fiber Plant, China.

TPU: ESA-480, Shenzhen Pepson, Industrial Corp., China.

CAS: AR, Chengdu Kelong, Chemical Reactant Company, China.

### Apparatus

The following apparatus were used within this research work:

Twin-screw extruder: SLJ-30, screw diameter is 30 mm, aspect ratio L/D is 32, Longchang

Chemical Machinery Plant, China.

Injector: K-TEC 40, TERROMATIK MILACRON Corp., Germany.

High speed pulverizer: FW-400A, Beijing Zhongxing Weiye, Instrument Company, China.

### Preparation of MPP

A calculated amount of ME was dispersed in boiling water, and then phosphoric acid aqueous solution was added into the reaction system with stirring. After 10 min, the heater was moved away while the stirring continued staying for a while. Then the product was cooled, filtrated, dried and pulverized into MP powder. Finally, the MP powder was heat-treated at 300°C in an oven for 6 h, and then the obtained MPP was pulverized into fine powder.

### Preparation of synergistic agent

TPU and the solid acid were roll mixed by a double-roller at 160°C for 15 min to prepare TES, and then the product was pulverized into powder.

### Preparation of flame retardant GFPA6

A weighted amount of PA6 pellets, GFs, MPP powder, synergistic agent TES, and antioxidant were pre-mixed, and then extruded by a twin-extruder. The extruded pellets were injected into standard testing bars for the test of combustibility and mechanical properties.

### Characterization

The encapsulated structure of synergistic agent TES, dispersed in CCl<sub>4</sub> solvent, was observed by a Hitachi H-600 transmission electron microscope.

The vertical burning test was conducted by a CZF-III horizontal and vertical burning tester. (127 × 12.7 × 1.6 mm<sup>3</sup> bars according to UL94 test ASTM D3801-1996 standard).

The LOI parameters of specimens were measured by an ATLAS limiting oxygen index instrument. (120 × 6.5 × 3 mm<sup>3</sup> bars according to ASTM D2863-1970 standard).

The tensile strength and bend strength of the materials were examined using a REGEER material tester according to GB/T 1447-2005 standard and GB/T 1449-2005 standard, respectively. The izod notched impact strength was measured using a ZBC-4B impact strength tester according to GB/T 1043-93 standard.

The molding samples were broken off after 20 min-freezing in liquid nitrogen, and then the ruptured surfaces of testing bars as well as the residual chars of the burned materials were gilt under vac-

**TABLE I**  
**Flame Retardancy and Mechanical Properties of GFPA6 Materials with Different MPP and Synergist Contents**

Specimens	PA6/GF/MPP/TES	UL94-1.6 mm	Mechanical properties			
			Tensile strength (MPa)	Rupture elongation (%)	Impact strength (kJ/m <sup>2</sup> )	Bend strength (MPa)
1.	40/30/30/0	F <sup>a</sup>	122.0	6.1	5.7	180.6
2.	35/30/35/0	F	117.2	5.0	4.2	175.0
3.	39/30/30/1	F	116.8	5.4	4.9	176.6
4.	37/30/30/3	V-0(26s) <sup>b</sup>	104.2	5.0	4.3	162.7
5.	35/30/30/5	V-0(14s)	85.8	4.9	3.8	155.5
6.	33.75/30/30/6.25	V-0(15s)	74.8	4.1	3.5	137.5

<sup>a</sup> Failure.

<sup>b</sup> tf, i.e. the total duration (five specimen) of flaming combustion.

uum before observed by a JEOL JSM-5900LV SEM instrument, with 20 kV accelerate voltage.

The TG analyses of samples were carried out on a TA Q500 TGA thermal analyzer with a heating rate of 10°C/min, from 30 to 700°C, and an atmosphere flow of 100 mL/min.

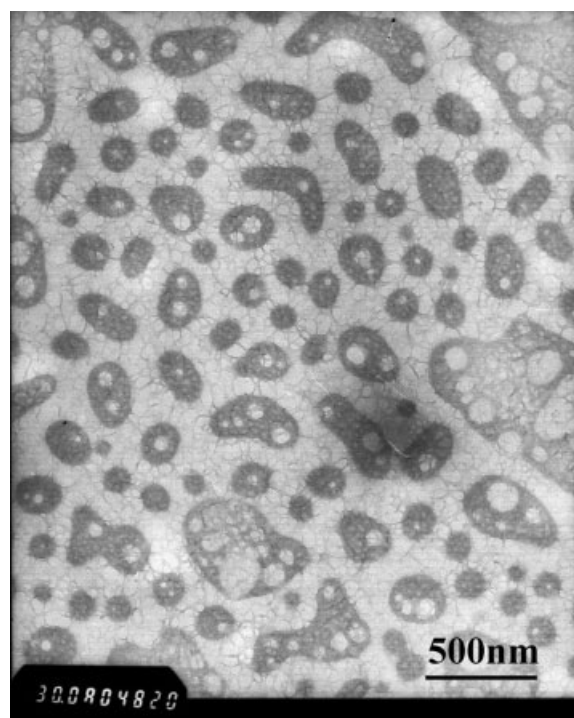
## RESULTS AND DISCUSSION

### Performance of the flame retardant GFPA6 materials

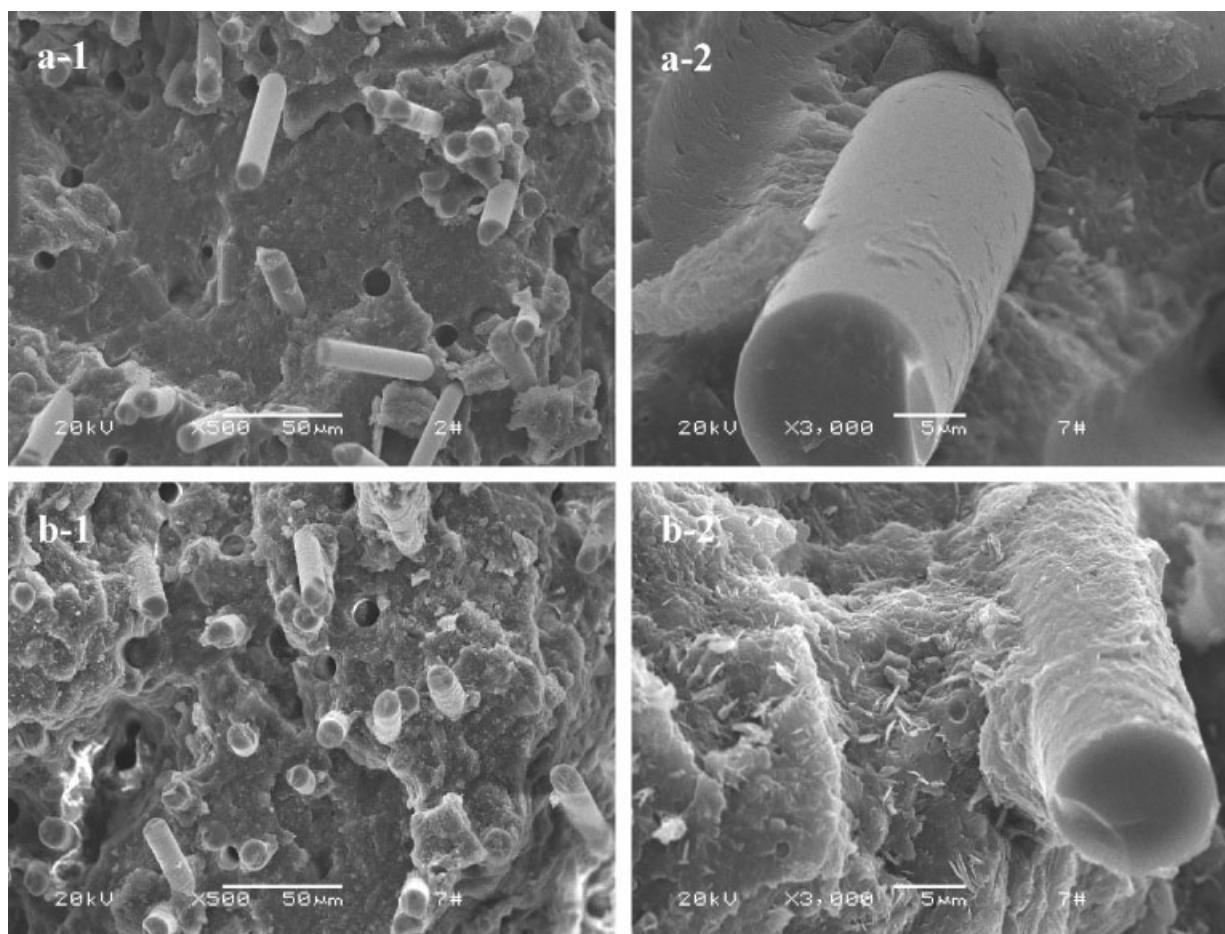
Table I lists the flame retardancy and mechanical properties of GFPA6 with different contents of MPP and synergist. It can be concluded that, the specimens flame retarded by MPP alone, i.e., No.1 (MPP loading level: 30 wt %) and No. 2 (MPP loading level: 35 wt %), cannot achieve UL94-1.6 mm V0 rating, which, in fact, cannot pass V0 rating for 3.2 mm bars (the data are not listed). With the addition of synergist TES, the flame retardancy of materials is improved obviously, and specimen Nos. 4–6 with 3 wt %, 5 wt %, and 6.25 wt % of synergist, respectively, (MPP loading level is kept in 30 wt %) can pass V0 rating for 1.6 mm bars easily. Furthermore, the total after-flame time shows a decline tendency with the increase of TES content, signifying the remarkable synergistic effects of TES. The LOI parameters of specimen Nos. 1 and 6, flame retarded by MPP alone and by MPP together with synergist TES, were tested to be 29 and 33%, respectively. It also can be deduced from LOI test that, the synergistic effect of TES on MPP flame retarded GFPA6 is visible, and the introduction of TES can improve the flame retardancy of the obtained materials greatly, which is consistent with the result of vertical burning test.

However, the negative effects of TES on the mechanical performance of the flame retardant GFPA6 are great, and the increases in TES content makes the tensile strength, impact strength, and bend strength of materials decrease heavily. Obviously,

there are two-sided influences of the synergist on the material's performances: improvement of the flame retardancy, while deterioration of the mechanical properties. Therefore, adding as small amount of TES as possible on the condition that the V0 rating is achieved should be advisable in preparing the flame retardant GFPA6 with high performance. It can be found that, with only 3 wt % of TES can make the GFPA6 materials pass UL94-1.6 mm V0 rating, and the tensile strength, rupture elongation, impact strength, and bend strength are 104.2 MPa, 5.0%, 4.3kJ/m<sup>2</sup>, and 162.7 MPa respectively, showing a good comprehensive performance.



**Figure 1** TEM photograph of synergistic agent TES powders.



**Figure 2** SEM photographs of the surface of glass fibers for different samples: (a) PA6/GF/MPP = 40/30/30 (wt %), (b) PA6/GF/MPP/TES = 33.75/30/30/6.25 (wt %).

### Encapsulation structure of synergistic agent TES

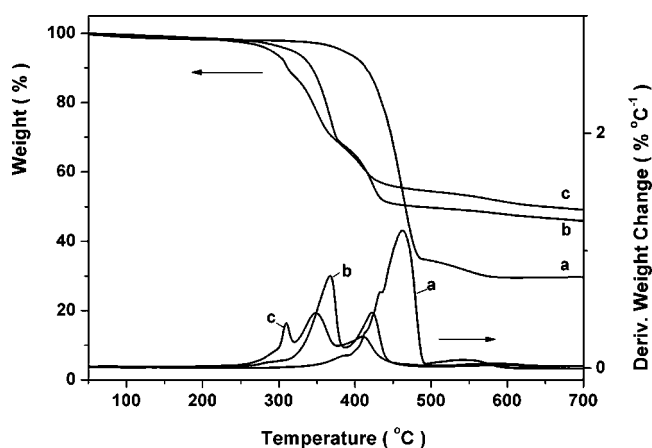
Figure 1 shows the morphology and structure of TES powder. It can be seen clearly that the solid acid particles were encapsulated by TPU layers. Some of the encapsulated products contain only several particles while others contain more. This encapsulated structure is beneficial to the isolation and compatibilization effects, which can reduce the negative influences from the direct contact between solid acid particles and PA6 matrix, thus improving the mechanical performance of materials.

### Flame retardant mechanism of MPP/TES flame retardant GFPA6

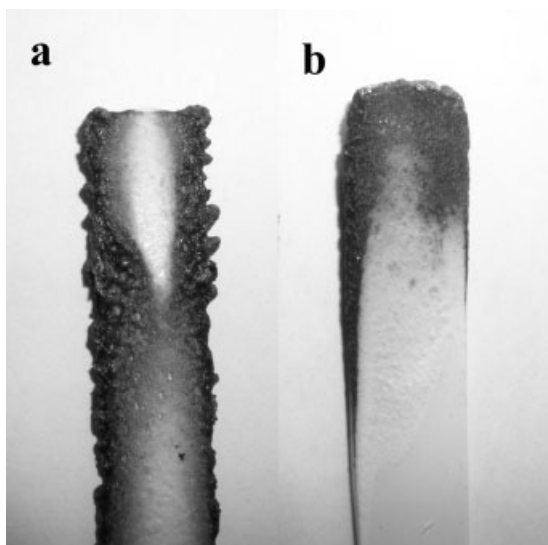
Surface morphology of glass fibers in PA6/GF/MPP and PA6/GF/MPP/TES systems

Figure 2 shows the SEM photographs of the ruptured surfaces of the bars for PA6/GF/MPP and PA6/GF/MPP/TES systems. It can be seen that, between the two systems, there are obvious differences in the surface morphology of GFs. In PA6/GF/MPP system [Fig. 2 (a-1 and a-2)], the interfaces

between GFs and PA6 matrix are clear, and the surfaces of GFs are relatively smooth, almost without attachment. However, the surfaces of GFs in PA6/GF/MPP/TES system [Fig. 2 (b-1 and b-2)] are attached by many flocculent substances. The formation



**Figure 3** TG and DTG curves of different samples: (a) PA6/GF = 70/30 (wt %), (b) PA6/GF/MPP = 40/30/30 (wt %), (c) PA6/GF/MPP/TES = 33.75/30/30/6.25 (wt %).

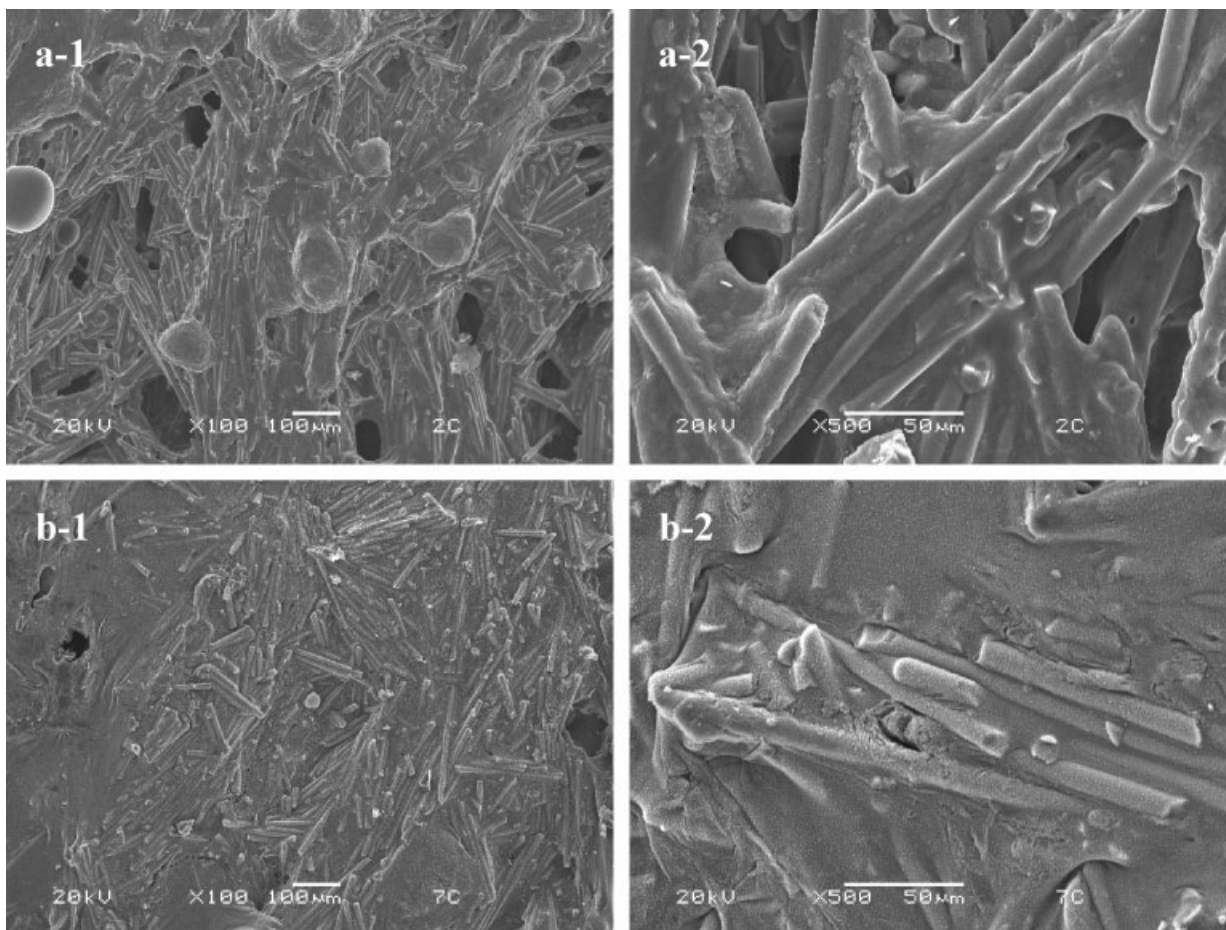


**Figure 4** Photographs of 1.6 mm thick bars for different samples after vertical burning test: (a) PA6/GF/MPP = 40/30/30 (wt %), (b) PA6/GF/MPP/TES = 33.75/30/30/6.25 (wt %).

of such morphology in the latter system should be related to the interaction between GFs and TPU. The much more obscure interface of GF-resin in the PA6/GF/MPP/TES system means that TPU has better compatibility with GFs as compared with PA6, thus conglutinating on the surfaces of GFs preferably.

“Candlewick effects” of GFs in PA6 may involve complicated processes and there were few references reported concerning its detailed mechanism. However, it is undoubted that the “candlewick effects” of GFs in PA6 is related to the interfacial properties of GF-resin. As is known, the molecular structure of TPU is different from that of PA6, i.e., PA6 and TPU are composed of  $-\text{NH}-\text{CO}-$  units and  $-\text{NH}-\text{O}-\text{CO}-$  units, respectively. The latter probably interact with the groups on the surfaces of GFs more easily.

From earlier analysis on the surface morphology of GFs dispersed in resin, it is clear that, the change of surface morphology of GFs caused by the introduced TES probably weakens the “candlewick



**Figure 5** SEM photographs of carbon layers for different samples: (a) PA6/GF/MPP = 40/30/30 (wt %), (b) PA6/GF/MPP/TES = 33.75/30/30/6.25 (wt %).

effects" of GFs in PA6, thus improving the flame retardancy of PA6/GF/MPP/TES system.

#### Thermal analysis

Figure 3 shows the TG and DTG curves of PA6/GF, PA6/GF/MPP, and PA6/GF/MPP/TES systems. It can be seen that, adding MPP alone would reduce the decomposition temperature ( $T_d$ ) of GFPA6, however, the weight percent of remnants at 700°C increased greatly, from 30 to 46%. In addition,  $T_d$  further declined in the system containing TES, and the amount of remnants showed the highest value (49%) among the above systems. Accordingly, the addition of TES can improve the proportion of the condensed phase component effectively. The maximum rate of heat weight loss of PA6 is reduced by MPP and TES, as shown in DTG curves, indicating the deceleration of heat release and slowdown of combustion process. As a result, the flame retardancy of materials is improved for a great extent.

#### Char layers of different samples after combustion

Figure 4 shows the photographs of bars (1.6 mm thickness) of PA6/GF/MPP and PA6/GF/MPP/TES systems after combustion. It is observed that the flammability of the latter is much less than that of the former. From the surface of burned bars, it can be seen that the formed char layers are relatively puffy for the former, which possess many foamed protuberances. However, the char layers are much more condensed and closed for the latter, indicating that this system can form char layers more effectively while burning, thus having better flame retardancy.

SEM photographs as illustrated in Figure 5 show microscopic structures of char layers of the above systems. For PA6/GF/MPP system [Fig. 5 (a-1 and a-2)], there are many holes in the surface of the char layers, indicating that the layers are not continuous and compact, leading to poor fire-resistance. While the char layers of PA6/GF/MPP/TES system [Fig. 5 (b-1 and b-2)] are obviously more compact, and few holes are observed in the surface. It can be drawn that the burned remnants of the latter are more than that of the former, so the latter system is able to form char layers with preferable isolating function effectively, which can interdict the burning of materials.

It shows accordant results with TG analysis from the earlier macroscopic and microscopic observations of char layers, which further confirm that the introduction of TES can reinforce the condensed phase. The improved condensed phase can prohibit the combustible gases and decomposed products of polymer from diffusing outwards more effectively, as well as prevent the heat and oxygen from trans-

ferring inside, propitious to hold back the burning of materials, thus greatly improving the flame retardancy of GFPA6.

The synergistic effects of TES include two sides: one is the charring effects of macromolecular charring agent TPU, the other is the catalytic effects of CAS. The decomposed product of CAS is  $H_2SO_4$ , of which the acidity is much higher than that of conventional acid source,  $H_3PO_4$ , from the decomposition of MPP. Therefore, the composite acid source ( $H_3PO_4$  and  $H_2SO_4$ ) in PA6/GF/MPP/TES system exhibits better catalytic effects in accelerating the formation of char layers as compared with single acid source ( $H_3PO_4$ ) in PA6/GF/MPP system.

## CONCLUSIONS

MPP was used as main flame retardant and TPU-encapsulated solid acid CAS composite was served as synergistic agent for the flame retardance of GFPA6. It has been proved that with 30 wt % of MPP and 3 wt % of synergistic agent, the reinforced PA6 (GF: 30 wt %) can pass UL94-1.6 mm V0 rating and the tensile strength, rupture elongation, impact strength, and bend strength are 104.2 MPa, 5.0%, 4.3kJ/m<sup>2</sup>, and 162.7 MPa, respectively, showing good comprehensive performance. It also indicated that the synergistic agent existed could increase the solid residues at high temperature, reduce the velocity of weight loss while heating, produce more continuous and compact char layers, thus weakening the "candlewick effect" of GFs in reinforced PA6 system and improving the flame retardancy of the obtained materials effectively.

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