The Investigation of Melamine Polyphosphate Flame Retardant Polyamide-6/Inorganic Siliciferous Filler with Different Geometrical Form

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ABSTRACT: Melamine polyphosphate (MpolyP) was used to flame retard polyamide-6 filled with siliciferous fillers including fibrous wollastonite, laminar talc, and spherical glass bead. The mechanical performance, flame retardancy of these flame retarded materials, and the influence of these fillers on charring behavior were investigated. The results show that wollastonite/MpolyP/PA6 system has the best mechanical properties as compared with talc/MpolyP/PA6 and glass bead/MpolyP/PA6 system due to good reinforcing effects of the fibrous filler in resin matrix. Otherwise, the char morphology observation shows that spherical glass beads separates from the char matrix during the expansion of the char layer, which hardly improves the char quality. However, fibrous wollastonite and laminar talc can well combine with the char layer, thus enhancing the flame retardancy as a part of the charred layer. It is proved that the laminar talc favors the formation of more condensed char because of its barrier effects, and the fibrous wollastonite with quite high aspect ratio can effectively reinforce both the resin and the charred layer, which leads to the remarkable improvement of the flame retardancy. Consequently, polyamide-6/MpolyP/wollastonite system shows the best flame retardancy among the above systems. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2046–2051, 2009

Key words: silicate fillers; geometrical form; melamine polyphosphate; flame retardancy; polyamide-6

INTRODUCTION

Polyamide-6 (PA6) is an important engineering plastic.[1,2] In order to modify its moisture absorptivity, heat distortion temperature, dimensional stability and modulus, as well as to reduce its cost in practical applications, inorganic fillers are usually incorporated.[3–14] However, the flame retardancy of the filled PA6 is poor, thus restricting its application in automobile, electrical and electronic (E&E) industries.

To improve the fire-resistance of PA6/inorganic filler systems, some flame retardants are applied. Halogen flame retardants possess good flame retardancy and have been commercially used in the filled polyamide composites in the past years. However, the release of some toxicant during their decomposition is a big ecological problem. In recent years, halogen-free flame retardants are hence badly needed for replacing halogen ones, among which, melamine-based flame retardants have attracted more attentions due to their advantages such as innocuity, low smoke, and white color. Melamine-based flame retardants include nitrogen and nitrogen–phosphorus composite type, and the latter is more suitable for the flame retardant PA6 composites. For instance, nitrogen–phosphorus composite flame retardant, Melamine polyphosphate (MpolyP), is widely reported in the formulation of glass fiber reinforced PA6. However, few investigations on melamine-based flame retardant PA6/inorganic filler system have been reported.

Most nitrogen–phosphorus flame retardants belong to intumescent type which possesses either condensed phase (from phosphorus-containing component) mechanism or gaseous mechanism (from nitrogen-containing component), and the intumescent flame retardancy greatly depends on the formation of the protective charred layers.[15] Some laminar fillers such as clay, montmorrillonite, and talc can increase the barrier properties of the char of intumescent flame retardant system, thus effectively improving the flame retardancy.[16–21] Almeras et al.[18] investigated the effects of talc on the flame retardancy of APP/PA6. It showed that talc can increase fire protective performance due to the formation of a ceramic-like protective shield on the surface of the burning materials. Hao et al.[21] investigated flame
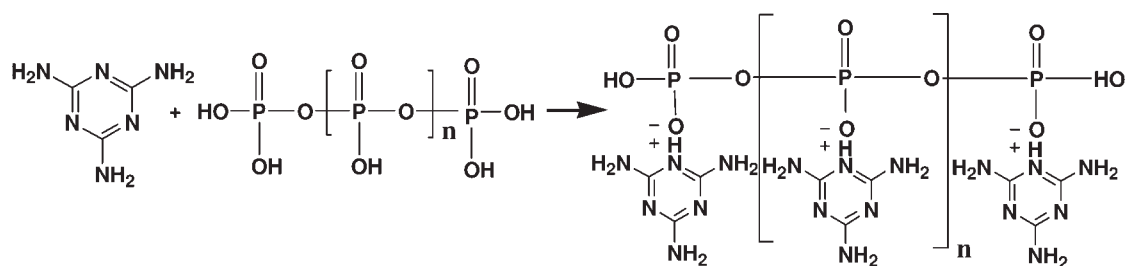
Scheme 1 The reaction equation of preparation of MpolyP.

retardancy and antidripping effects of modified montmorrillonite/PA nanocomposites. It was found that the silicate layers affected the char by increasing the barrier properties. For fibrous fillers, there are a lot of investigations on their reinforcement on resin matrix, however, their synergistic effects on flame retardancy has not been reported so far.

In this article, MpolyP synthesized by our group was used to flame retard PA6/inorganic fillers system. The effects of the siliciferous filler with typical geometrical form (including fibrous wollastonite, laminar talc, and spherical glass bead) on the materials performance and charring behavior were systematically investigated.

EXPERIMENTAL

Materials

Melamine and polyphosphoric acid were provided by Chengdu Kelong Chemical Reactant Plant, China; wollastonite, a fibrous product with particle size 10 μm was provided by Xinyu Nanfang Wollastonite Company, China; talc, a lamellar product with particle size 10 μm was provided by Chengdu Youhe Chemical Corporation, China; glass bead, a spherical product with particle size 10 μm was provide by Mian Yang, USM Ltd; PA6, YH800, pellets, were provided by Baling Petrochemical Corporation, China; Silane coupling agent, KH550, NH_2–CH_2–NH_2–CH_2-CH_2–$Si(OC_2H_5)_3$, were purchased from Chengdu Sitong Chemical Reactant Plant, China.

Preparation of MpolyP flame retardant

A certain amount of *N,N*-dimethyl formamide was placed in a glass flask. Melamine was added to the solvent with stirring at 100°C, and then polyphosphoric acid was added into the solution. The reaction mixture was stirred for 3 h at 160°C and then cooled down to room temperature. The obtained product was filtrated and dried, and pulverized to fine powder. The reaction equation is listed in Scheme 1.

Formulations and preparation of the flame retarded composites

Silane coupling agent (1 wt %) and the filler were mixed in a high-speed mixer for 5 min to obtain the surface-treated fillers.

The treated fillers, MpolyP and PA6 with a certain proportion were premixed in a high-speed mixer for 8 min and then extruded in a twin-screw extruder at temperature 240–250°C(Φ: 30 mm, *L/D*: 32, SLJ-30 Longchang Chemical Engineering Equipment Co., China) and cut into pellets. The obtained pellets were dried in a vacuum oven at 100°C for 4 h and then injection molded into standard specimens at 250–260°C (K-TEC 40 Terromatik Milacron Corporation, Germany). The formulations of the flame retardant composites are listed in Table I.

Characterization

The vertical burning test was conducted on a CZF-3 horizontal and vertical burning tester according to

TABLE I
Formulations of the Flame Retarded Composites

| FR composites | Components | | | | |
	PA6 (wt %)	MpolyP (wt %)	Glass bead (wt %)	Talc (wt %)	Wollastonite (wt %)
PA6/MpolyP	70	35	0	0	0
PA6/MpolyP/glass bead	50	25	25	0	0
PA6/MpolyP/talc	50	25	0	25	0
PA6/MpolyP/wollastonite	50	25	0	0	25

the America National UL-94 test ASTM D3801. The size of the bar was $127 \times 12.7 \times 1.6$ mm^3.

The Limiting Oxygen Index (LOI) values were measured according to ASTM D2863 on an ATLAS Limiting Oxygen Index instrument. The size of the bar was $120 \times 6.5 \times 3$ mm^3.

The surface of the residual charred layer of the burned bars in LOI test was observed by a digital camera. It was also coated with a conductive gold layer and observed by a JEOL JSM-5900LV SEM.

The tensile strength and the flexural 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 strength of the residual charred layers of the flame retarded filled PA6 was examined using an Instron universal test machine RG L-10. The charred layer was placed on a circular flat and suffered a pressure, and the load was then recorded when the charred layer is broken.

RESULTS AND DISCUSSION

Analysis of the synthesized flame retardant

MpolyP is generally synthesized by polycondensation of melamine phosphate at high temperature. The shortcoming of this route lies in its complicated process. In this investigation, polyphosphoric acid-melamine route was adopted to synthesize MpolyP (Scheme 1). Figure 1 is the FTIR spectrum of the obtained flame retardant product. The characteristic peaks of the melamine polyphosphate were observed at 3133.8 cm^{-1}and 2843.7 cm^{-1} assigned to the vibration absorption of —NH^{3+}, 2696.7 cm^{-1} assigned to the vibration absorption of O—H groups, 1385.4 cm^{-1} assigned to the vibration of C—N groups of the triazine rings, 1282.12 cm^{-1} and 1178.8 cm^{-1} assigned to the vibration of P=O bonds, 970.2 cm^{-1} assigned to the vibration absorptions of P—O in P—O—H groups, and 888.7 cm^{-1} assigned to the
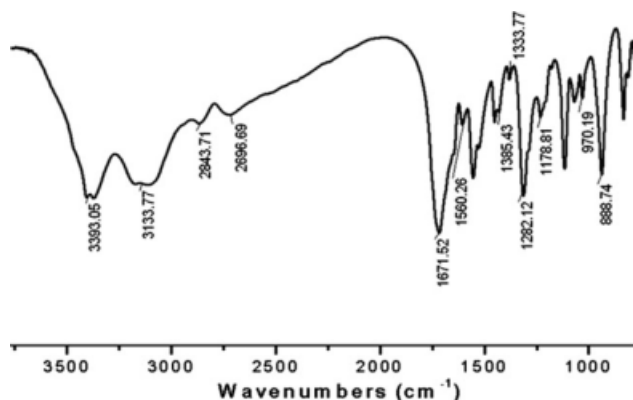

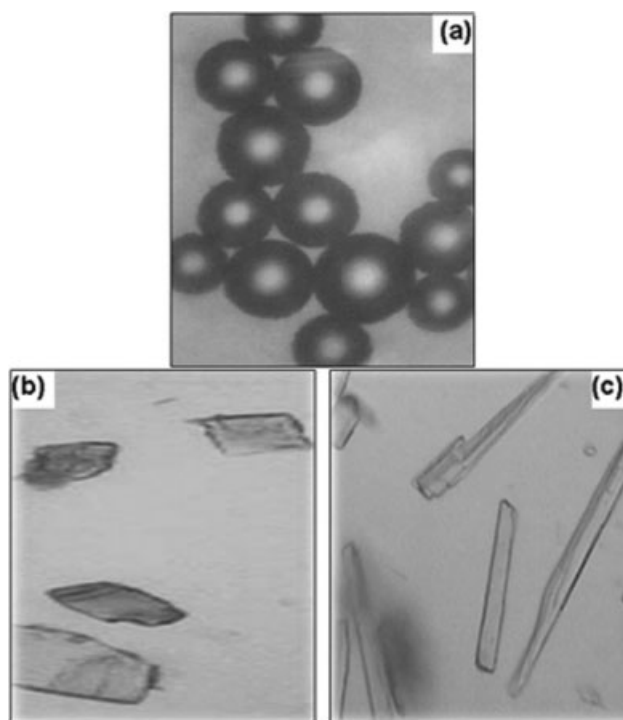**Figure 1** FTIR spectrum of the prepared MpolyP flame retardant.

Figure 2 Photographs of (a) glass bead, (b) talc, and (c) wollastonite ($\times$400).

vibration of P—O—P bonds. The agreement with the FTIR analysis in the Ref. 22 confirms that the product was MpolyP.

Flame retardancy

In our investigations, three inorganic siliciferous fillers with similar particle size but different geometrical form were used to fill PA6. As shown in Figure 2, wollastonite was fibrous filler with quite high aspect ratio, talc was laminar sheet, and glass bead was spherical form.

Tables II and III list the results of the UL94 and LOI measurements of PA6/MpolyP, PA6/MpolyP/wollastonite, PA6/MpolyP/talc, and PA6/MpolyP/glass bead. It can be seen that, accompanied with serious melt drops, PA6/MpolyP had the lowest LOI (29.0%) and UL94 rating (V2). With the addition of

TABLE II
UL94 Combustion Data of Flame Retarded Composites

FR composites	Average combustion duration time of bar (s)	Melt drip	Rating (1.6 mm)
PA6/MpolyP	4.1	Dripping	V-2
PA6/MpolyP/glass bead	3.8	No dripping	V-0
PA6/MpolyP/talc	2.6	No dripping	V-0
PA6/MpolyP/ wollastonite	1.0	No dripping	V-0

TABLE III
LOI Values of Flame Retarded Composites

FR composites	LOI (%)
PA6/MpolyP	29.0
PA6/MpolyP/glass bead	33.0
PA6/MpolyP/talc	34.5
PA6/MpolyP/wollastonite	35.5

the inorganic fillers, the flame retardancy was remarkably improved. The three filled systems achieved V0 rating at 25% MpolyP loads, and there was no melt dripping. Comparing the flame retardancy of these samples with different fillers by combustion time and LOI values, it is clear that the flame retardant PA6 system filled with fibrous wollastonite possessed the shortest combustion time (only 1.0 s) and the highest LOI (35.5%), showing the best flame retardancy. For the flame retardant PA6 filled with laminar talc, its flame retardancy was medium (combustion time: 2.6 s, LOI: 34.5%). In comparison, PA6/MpolyP/glass bead showed the

lowest flame retardancy (combustion time: 3.8 s, LOI: 33.0%).

Analysis of the charred layer

As a nitrogen–phosphors composite flame retardant, MpolyP involves an acid catalyst (phosphors acid) and a blowing agent (melamine). Its flame retarding mechanism is based on the formation of the protective intumescent charred layer on the surface of the burning materials, thus isolating the interior material from the fire, and also holding back the transfer of the combustion heat and the produced volatile gas. Accordingly, the formation of the charred layer is greatly related to the final fire-resistance of the flame retardant polymer materials. Because the added fillers are incombustible during the combustion of polymer matrix, they remain in the condensed phase and become the components of the charred layer. Therefore, the fillers have great influence on the formation and the final properties of the charred layer.

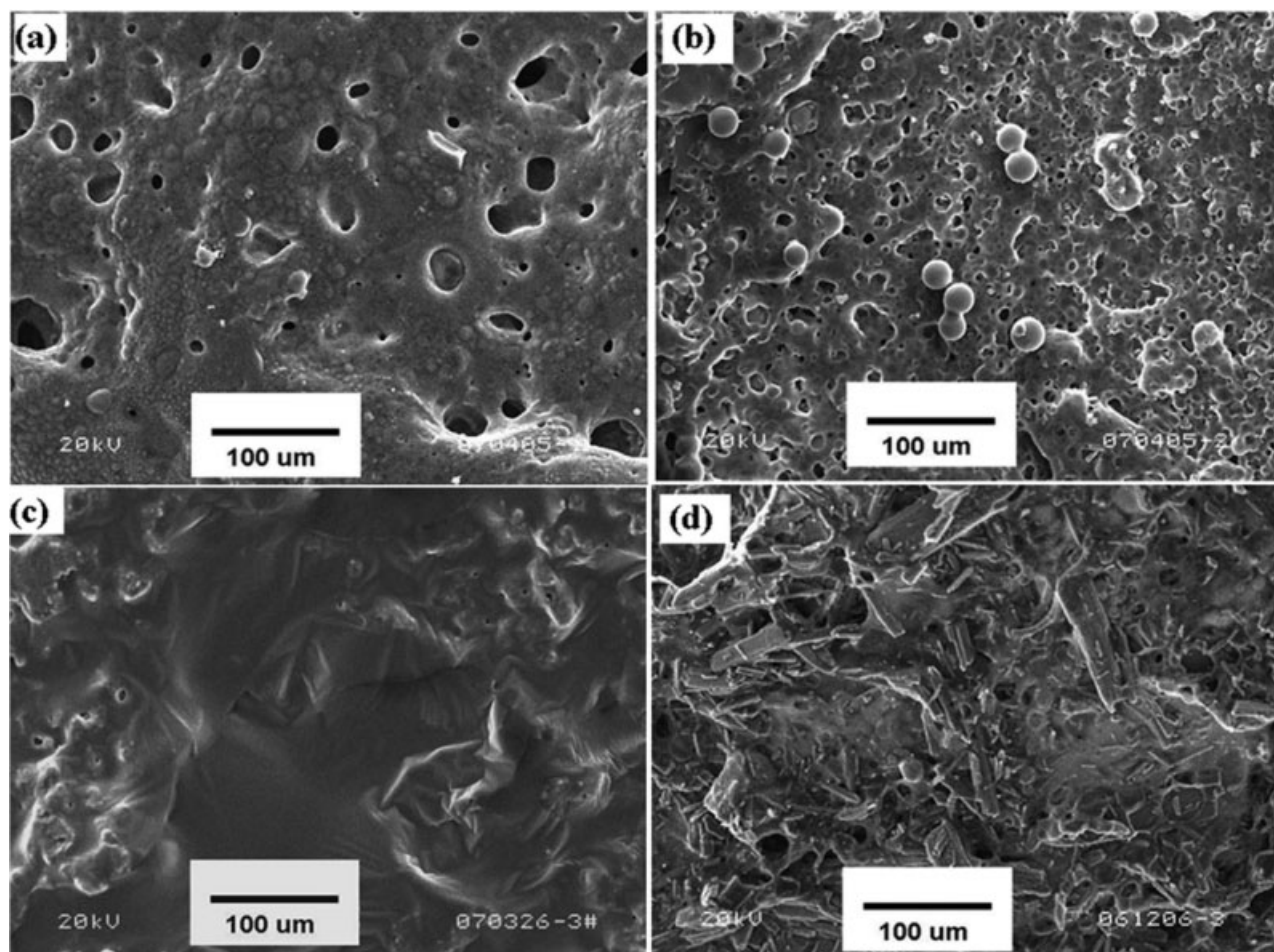SEM observation revealed the microscopic morphology of the formed char [Fig. 3]. It can be seen

Figure 3 SEM photographs of the residual charred layer after LOI testing of flame retarded composite (a) PA6/MpolyP, (b) PA6/MpolyP/glass bead, (c) PA6/MpolyP/talc, and (d) PA6/MpolyP/wollastonite.

TABLE IV
The Mechanical Properties of Flame Retarded Composites

FR composites	Tensile strength (MPa)	Flexural strength (MPa)
PA6/MpolyP	56.7	64.3
PA6/MpolyP/glass bead	40.4	59.2
PA6/MpolyP/talc	55.0	35.7
PA6/MpolyP/wollastonite	74.4	97.4

TABLE V
The Strength of the Residual Charred Layer after UL94 Testing of Flame Retarded Composites

FR composites	Load (N)
PA6/MpolyP	1.24
PA6/MpolyP/glass bead	1.69
PA6/MpolyP/talc	2.16
PA6/MpolyP/wollastonite	4.55

that many pores were distributed on the surface of charred layer of PA6/MpolyP. Undoubtedly, it is difficult for the porous charred layer to effectively isolate the heat and volatile gas, which was in agreement with the lowest flame retardancy of this system. For the charred layer of PA6/MpolyP/glass bead, it was found that many glass bead particles were separated from the char matrix, showing their rather poor interfacial combination. In addition, there were also many small pores observed in the char. It is obvious that the addition of the glass bead cannot effectively improve the charred layer structure. In comparison, PA6/MpolyP/wollastonite and PA6/MpolyP/talc systems showed much condensed and compact charred layer. It can be seen that both wollastonite and talc particles were encapsulated by the char, suggesting much better combination between the filler and the char as compared with the glass bead system. The difference in the combination degree of filler and charred layer should be attributed to the different geometrical forms of these fillers. Because of the typical spherical form and very smooth surface, glass bead had a low sliding friction coefficient. During the formation of the charred layer, original resin-filler interface is changed into char-filler interface. As the latter interfacial combination became looser than the former, the spherical glass

bead particles easily slid out of the charred layer during the expansion process. The separation between the filler and the char resulted in the decline of the char quality. Contrastively, fibrous wollastonite and laminar talc can be well incorporated with the formed char, thus became a part of the charred layer, improving the quality of the char.

However, the morphology of the charred layer of the wollastonite and talc systems still showed considerable difference. It can be seen that the char surface of the wollastonite system was obviously coarser, and the interlaced fibrous fillers were embedded in the char. Although the char surface of the talc system was much smoother, the addition of the laminar talc particles made the charred layer more condensed than wollastonite system. Theoretically, the charred layer structure with laminar fillers involved should be more advantageous to obtain the better flame retardancy due to the good barrier effects. However, the fact that PA6/MpolyP/wollastonite system had the best flame retardancy indicated a different conclusion, which should be further discussed.

According to general experiences, higher condensed degree of the charred layer undoubtedly favors the flame retardancy. However, the influence of the charred layer strength on the flame retardancy is generally neglected. In fact, the charred layer with high strength can effectively resist the breakage, e.g.,
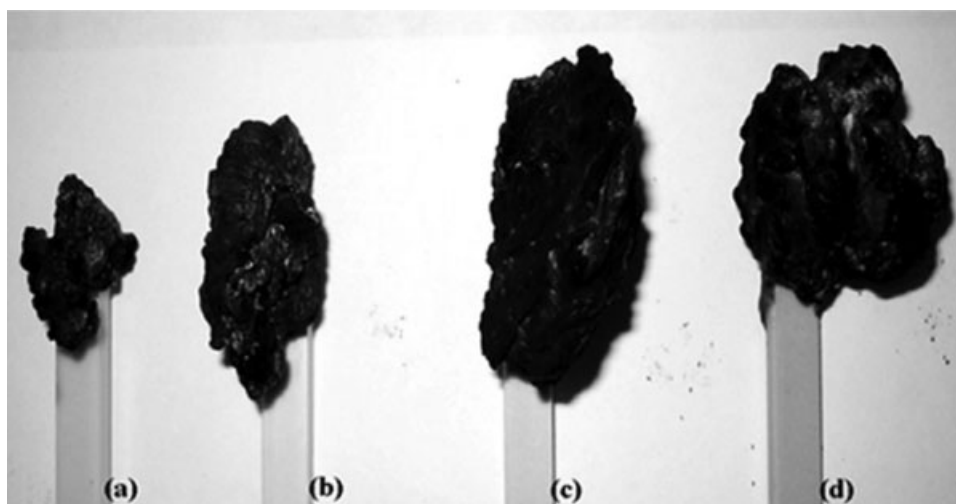

Figure 4 Photographs of the specimen after LOI test of (a) PA6/MpolyP, (b) PA6/MpolyP/glass bead, (c) PA6/MpolyP/wollastonite, and (d) PA6/MpolyP/talc.

collapse during the combustion process, which will endow the materials with remarkably improved flame retardancy. Accordingly, a possible explanation concerning the above results is the reinforcement of fibrous filler on the charred layer.

It is well-known that the fillers with high aspect ratio can effectively reinforce resin matrix. From the mechanical performance listed in Table IV, it can be seen that the tensile strength and flexural strength of PA6/MpolyP/wollastonite reached 77.4 MPa and 97.4 MPa respectively, much higher than those of PA6/MpolyP (56.7 MPa, 64.3 MPa), PA6/MpolyP/talc (55.0 MPa and 35.7 MPa), and PA6/MpolyP/glass bead (40.4 MPa and 50.2 MPa) systems, showing obviously reinforced effects of this fibrous filler. During the combustion, although the original resin matrix was converted into the char, the fillers remained in the charred layer as dispersion phase. In fact, the formed charred layer can be regarded as a new matrix, and the fibrous filler can still reinforce this matrix, leading to the enhanced strength of the char.

In order to confirm the above explanation, the strength test of the charred layer of above systems was conducted by compressing the charred layer till its breakage using universal test machine. From the data listed in Table V, it is obvious that the charred layer of PA6/MpolyP/wollastonite system had the highest strength (4.55 N), much higher than that of PA6/MpolyP (1.29 N), PA6/MpolyP/glass bead (1.69 N), and PA6/MpolyP/talc systems (2.16 N), confirming the reinforcement of the fibrous fillers on the charred layer.

Figure 4 is the digital photograph of the charred layer of the samples with the same burning length (5 cm). It can be seen that all filled systems had higher charring amount than PA6/MpolyP. Among the three filled systems, PA6/MpolyP/glass bead had obviously lower charring amount than PA6/MpolyP/wollastonite and PA6/MpolyP/talc. Obviously, the results are in agreement with the strength of the above char layers. It can be explained as the better the reinforcement of the filler is, the less damage of the intumescent char of the corresponding flame retardant materials suffer, accordingly, higher amount of the char residue is remained.

CONCLUSIONS

The geometrical forms of the fillers have important effects on the flame retardancy of the materials, the spherical glass beads were easily separated from the formed char layer, thus resulting in the lowest flame retardancy. Fibrous wollastonite and laminar talc showed much better combination with the charred layer, and became a part of the formed char. PA6/MpolyP/talc formed quite smooth intumescent charred layers, and the fibrous wollastonite can effectively reinforce both the resin matrix and the charred layer. Meanwhile, it is found that that the filler system with better reinforcement suffers less damage of the intumescent char, therefore, such a system possess higher amount of residual char. As a result, PA6/MpolyP/wollastonite had the highest flame retardancy and mechanical properties among the three siliciferous filler filled systems.

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