

Preparation of Polyamide Resin-Encapsulated Melamine Cyanurate/Melamine Phosphate Composite Flame Retardants and the Fire-Resistance to Glass Fiber-Reinforced Polyamide 6

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ABSTRACT: In this study, melamine cyanurate (MCA)/melamine phosphate (MP) composite flame retardants were synthesized in the solution of phosphoric acid/polyamide 6 (PA6). Phosphoric acid acted as the solvent of PA6, catalyst of melamine-cyanurate self-assembly reaction and reactant of melamine-phosphoric acid reaction. With the consumption of the acid, the pH value of the system increased, and the solved PA6 precipitated on the surface of the flame retardant particles to form polymeric encapsulation. This technology realized the synthesis and surface modification of the flame retardants in one process. The catalyst and solvent, phosphoric acid, was finally converted into the prod-

uct MP, and need no an additional removing process. The encapsulated MCA/MP (EMCMP) composite flame retardants were successfully applied in the fire-resistance to glass fiber (GF)-reinforced PA6. Because the encapsulated layer of EMCMP was also PA6, good interfacial compatibility and effective dispersion of EMCMP in PA6 resin can be obtained, and the corresponding flame retardant materials showed excellent flame retardancy and mechanical performance. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1773–1779, 2006

Key words: melamine cyanurate; melamine phosphate; flame retardant; surface modification; polyamide 6

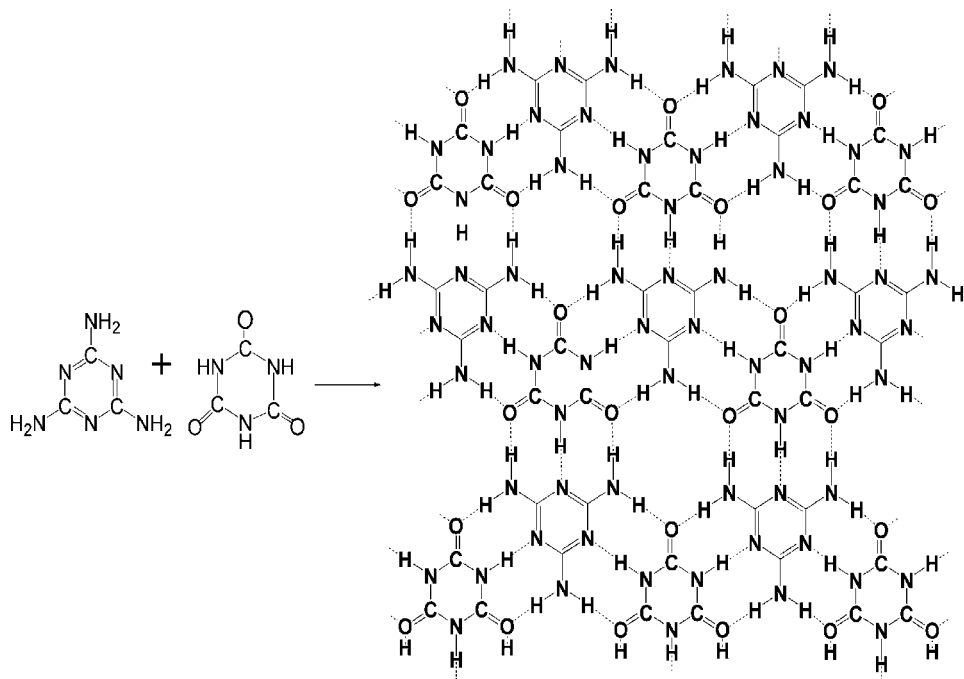
INTRODUCTION

PA6 is an important engineering resin widely applied. With a low softening point and insufficient mechanical performance for neat PA6, glass fiber-reinforced PA6 is generally used. However, neat PA6 or reinforced PA6 is flammable with a low limiting oxygen index (LOI) value and cannot achieve UL94 1.6 mm V0 rating, thus restricting the applications in some important fields, particularly in electrical and electronic industries. Accordingly, flame retardant PA6 is badly needed. In recent years, halogen-free flame retardant polymers have been developed to replace traditional halogen systems as the results of the recognized ecological and physical toxicity of the latter. Great efforts have been devoted to this field; however, halogen-free fire-resistance of GF-reinforced PA6 is still a global challenge currently because of the “candle wicking” effects of glass fiber. How to solve this problem is of great academic and industrial interests.

Melamine cyanurate (MCA) is a nitrogen-containing flame retardant focused on increasingly for its advantages including halogen-free, high nitrogen content, low smoking, and innocuity.¹ It is usually synthesized by melamine-cyanurate self-assembly in aqueous system (Scheme 1) with inorganic acid or alkali metals compounds (phosphoric acid, sodium hydroxide, etc.) as a catalyst that should be removed through filtration and wash after reaction to avoid disadvantageous effects on the properties of MCA.^{2–4} The fire-resistance mechanism of MCA on PA6 was known as that this flame retardant generates an endothermic decomposition to produce melamine and cyanurate above 350°C. The latter promotes the pyrolysis of PA6, and the produced oligomers melt rapidly dripping, thus removing a great deal of combustion heat.^{5,6} It proved that MCA is efficient for the flame retardancy of unreinforced PA6 at 8–10% loading level achieving UL94 1.6 mm V0 rating. However, it shows low efficiency on GF-reinforced PA6 and can only reach V2 rating. In our previous investigations,⁷ it was found that introducing MP into MCA can enhance the flame retardancy when compared with the use of MCA only. MP is a phosphorus-containing flame retardant that synthesized by melamine-phosphoric acid reaction (Scheme 2). MCA/MP composite flame retardants can well play nitrogen-phosphorus (N-P) synergistic effects, and

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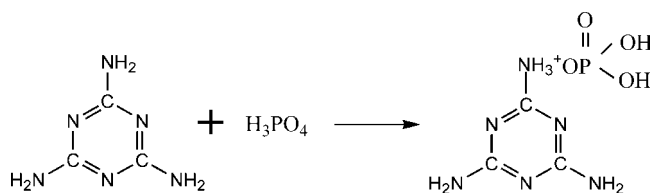
Scheme 1 Melamine-cyanurate self-assembly.

markedly increase a condensed phase process. However, it still has problems if only using the blend of MCA/MP (BMCMP) in GF-reinforced PA6 system because a rather high loading level flame retardants are needed for the expected flame retardancy; as a result, the mechanical performance of the engineering resin is greatly deteriorated. Actually, this is a common problem of many flame-retarded polymers.

To keep satisfactory flame retardancy and mechanical properties at a high loading level of flame retardant, good compatibility, and dispersion of flame retardants in polymer matrix are key factors. Unfortunately, few polymer/flame retardant systems can meet these conditions. Accordingly, the surface modification of flame retardants is important and significant. A Japanese patent⁸ reported the technology of adopting polyvinylalcohol (PVA) to encapsulate MCA. The modified product showed a remarkably improved dispersion in polymer matrix. However, because of a low decomposition temperature of PVA itself, the modified MCA cannot be applied in PA6. An US patent⁹ reported a sol-gel method (adopting sol of silicon, aluminum, antimony, etc.) to realize the surface modification of MCA, but its process seems quite complicated; moreover, there has not been any commercially application report regarding it so far.

In this study, a novel technology with the synthesis and surface modification of flame retardants involved in one process was established. In our process, MCA/MP composites were prepared in phosphoric acid/PA6 resin solution through melamine-

cyanurate and phosphoric acid-melamine reactions. Phosphoric acid is the catalyst of melamine-cyanurate reaction and solvent of PA6 resin, and it also reacts with melamine to be converted into MP. With the consumption of phosphoric acid, the system pH value increases, and the solved PA6 resin is gradually precipitated on the flame retardant particles to form encapsulation layer, thus realizing the surface modification. This technology has the following advantages: (1) the synthesis and surface modification of the composite flame retardants are simultaneously realized in a simple process; (2) phosphoric acid plays important roles as the solvent, catalyst, and reactant, and is finally converted into the product without an additional removing process; (3) the encapsulated layer of the prepared flame retardants is the same with the flame-retarded polymer; accordingly, EMCMP has a good compatibility and dispersion in the polymer matrix. The test results in this study also proved that the corresponding flame retardant GF-reinforced PA6 convincingly obtained very good flame retardancy and mechanical properties.



Scheme 2 Melamine-phosphoric acid reaction.

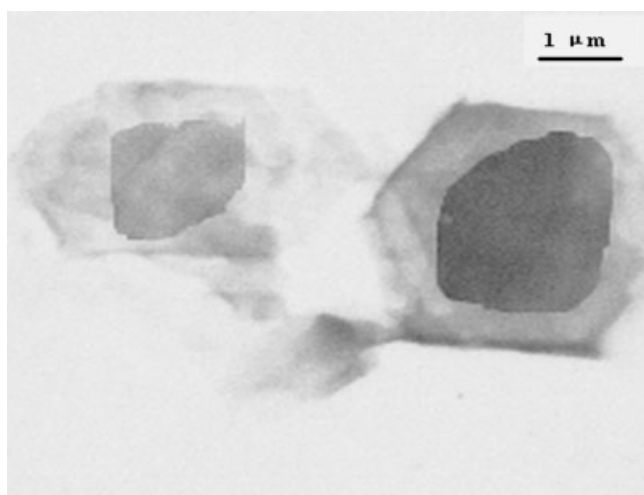


Figure 1 TEM photograph of EMCMP particles.

EXPERIMENTAL

Materials

Melamine powder product, Sichuan Chemical Company Limited Cooperation, China; Cyanurate powder product, Sichuan Chemical Company Limited Cooperation, China; Phosphate acid, Changzheng Chemical Reactant Company, China; PA6 pellet (MFI, 7.2 g/10 min), Yueyang Petrol-Chemical Cooperation, China; MCA powder, Sichuan Fine Chemistry Institute, China were used.

Preparation of PA6 encapsulated MCA/MP composite flame retardants

A weighed amount of PA6 resin was solved in phosphoric acid solution with stirring and heating, and the

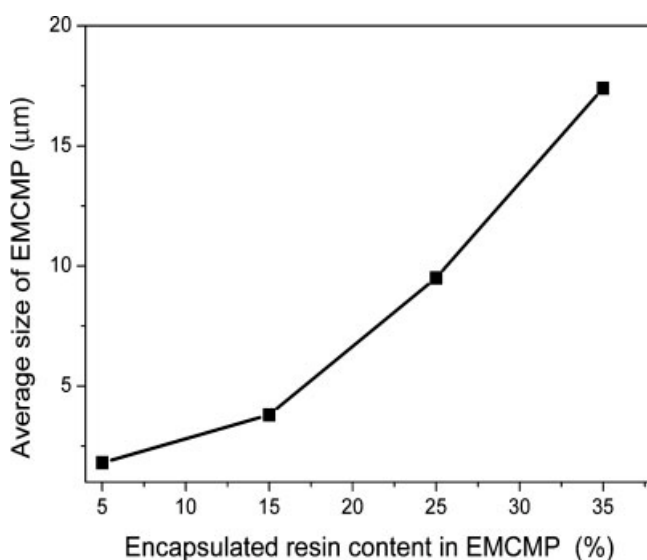


Figure 2 The relationship between the encapsulated resin content and the particle size of EMCMP.

calculated cyanurate and melamine were added into this system in turn. Melamine-cyanurate and melamine-phosphoric acid reactions were conducted in 90°C for 2 h with intensive stirring, and ended when the system pH value reached 6. Finally, EMCMP were obtained after filtration and drying processes.

Preparation of the flame-retarded PA6

A calculated amount of EMCMP or BMCMP, PA6 pellet, and GF (20%) were premixed, and then the mixture was extruded into pellet by twin-screw extruder at a temperature 230–240°C (ϕ : 30mm, L/D : 32, model: SLJ-30 Longchang Chemical Engineering Equipment Company, China). Finally, the bars for testing were prepared by injection molding at a temperature 240–255°C (injector: K-TEC 40 Terromatik Milacron Corp., Germany).

Characterization

The morphology of the EMCMP was observed by a JEM100cx TEM instrument. The LOI values were measured by an ATLAS limiting oxygen index instrument with $120 \times 6.5 \times 3\text{-mm}^3$ bars according to ASTM D2863-70. The vertical burn test was conducted by a CZF-3 horizontal and vertical burning tester, with $127 \times 12.7 \times 3.2\text{-mm}^3$ and $127 \times 12.7 \times 1.6\text{-mm}^3$ bars according to UL-94 test ASTM D3801. The tensile strength of the materials were examined using an Instron 4302 material tester according to ASTM D-638, and the notched Izod impact strength of the materials was measured using an XJ-40A Impact strength tester. The fractured surface of the injection-molded specimen was coated with a conductive gold layer, and the morphology of the flame retardant in poly-

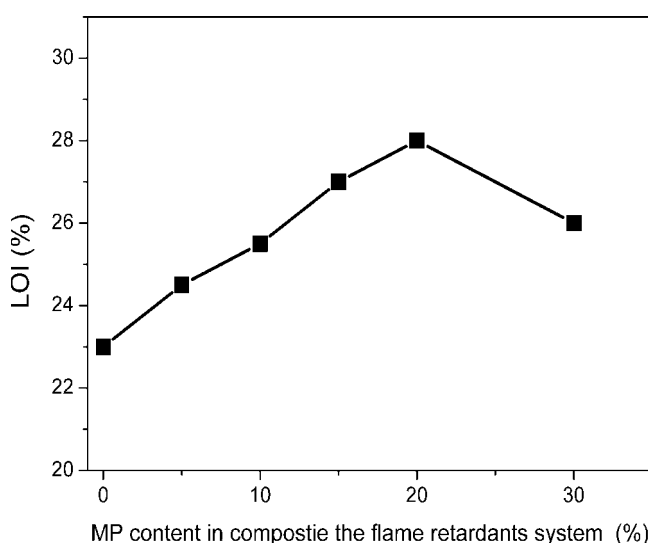


Figure 3 The LOI of GF-reinforced PA6 loaded by EMCMP in different MCA/MP weight ratio (EMCMP loading level: 25%, encapsulated resin in EMCMP: 20%).

TABLE I
UL94 1.6 mm Rating of GF-Reinforced PA6 Loaded by EMCMP in Different MCA/MP Weight Ratio

MP content in MCA/MP (%)	<i>t</i> (s) ^a	UL94 1.6 mm thickness
5	—	F
10	54.8	V2
15	29.6	V0
20	20.4	V0
30	57.1	V2

Encapsulated resin content in EMCMP: 25%, EMCMP loading level: 20%.

^a Total duration time (five specimens) of combustion.

mer matrix was observed by a HITACHI X-650 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Morphology and particle size analysis of the obtained EMCMP

As well known, PA6 is acid-soluble resin and precipitates in high pH system. For our reactions, it is just a process with decreasing acidity. Melamine-cyanurate self-assembly is a thermodynamically spontaneous process with a predominant rate when compared with melamine-phosphoric acid reaction. At the beginning, phosphoric acid mainly acted as the catalyst of melamine-cyanurate reaction, and its consumption rate was slow and the system had a basically unchanged pH value. With cyanurate consumed up, the neutralization reaction between melamine and phosphoric acid became the main process. In this stage, phosphoric acid was consumed as a reactant, and the

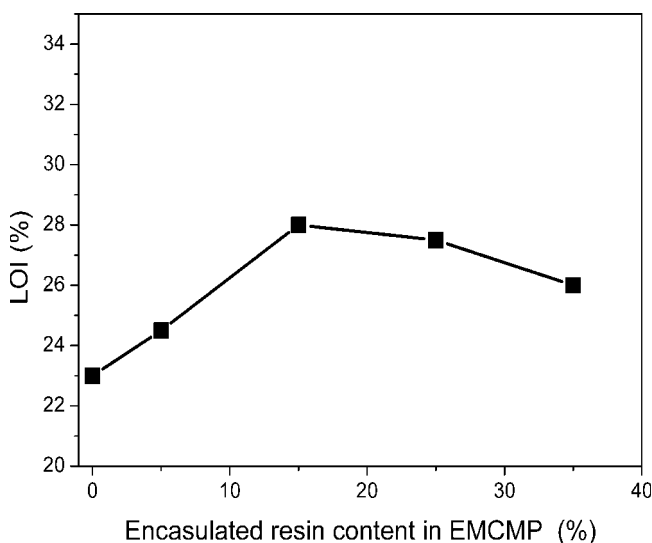


Figure 4 The LOI of GF-reinforced PA6 loaded by EMCMP with different encapsulated resin content (EMCMP loading level: 25%, MCA/MP weight ratio: 4/1).

TABLE II
UL94 1.6 mm Rating of GF-Reinforced PA6 Loaded by EMCMP in Different Encapsulated Resin Contents

Encapsulated resin content in EMCMP (%)	<i>t</i> (s) ^a	UL94 1.6 mm thickness
5	61.4	V2
15	28.6	V0
25	20.4	V0
40	51.8	V2

EMCMP loading level, 20%; MCA/MP weight ratio, 4/1.

^a Total duration time (five specimens) of combustion.

system pH value increased, leading to the precipitation of solved PA6 to form polymeric-encapsulated layer on the flame retardants surface. Figure 1 is the TEM photograph of EMCMP particles. It can be clearly identified the resin encapsulation layer and flame retardant inside. Additionally, it was found that the obtained particle size of EMCMP increased with the enhancement of the solved PA6 resin content in the system as shown in Figure 2. This can be explained as that a higher content PA6 resin thickened the encapsulation layer. On the other hand, EMCMP with higher content resin preferably generated interparticle conglutination and agglomeration, also causing the particle size enlarged.

Relationship between MCA/MP ratio and the flame retardancy

The relationship between the flame retardancy and MCA/MP ratio was investigated through the LOI and UL94 tests as shown in Figure 3 and Table I. It can be seen that at an invariable EMCMP loading level (PA6 resin was set with 20%), the flame retard-

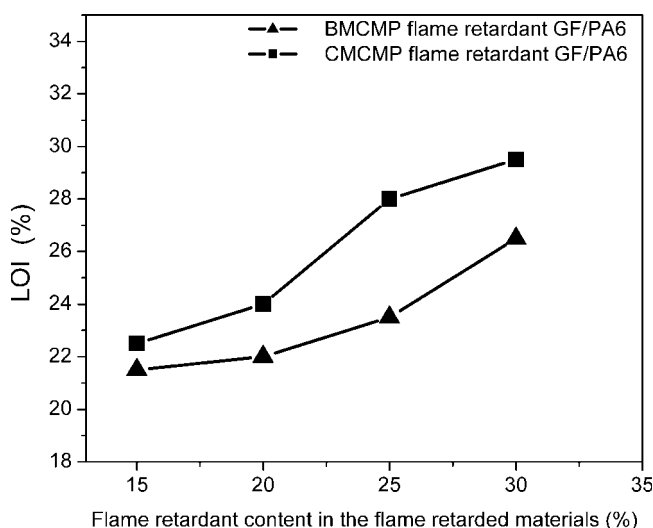


Figure 5 The LOI of EMCMP and BMCMP flame retardant GF-reinforced PA6 at different loading level (flame retardant loading level: 25%).

TABLE III
UL94 1.6 mm Rating of EMCMP and BMCMP Flame Retardant GF-Reinforced PA6 at Different Loading Level

Flame retardant content (%)	UL94 1.6 mm thickness	
	BMCMP flame retardant GF/PA6	EMCMP flame retardant GF/PA6
15	F	F
20	F	V2
25	F	V0
30	V2	V0

Encapsulated resin content in EMCMP, 25%; MCA/MP weight ratio in EMCMP and BMCMP, 4/1.

ant GF-reinforced PA6 showed the highest LOI when MCA/MP weight ratio was 4/1. UL94 1.6 mm rating was in agreement with the LOI test results, and the flame retardant polymer possessed the highest rating (with melt drips) as well as the shortest self-extinguishing time in the same MCA/MP weight ratio, which revealed that the flame retardancy of EMCMP was greatly dependent on the proportion of the two flame retardants. As well known, MCA is nitrogen-containing flame retardant without acid source in its molecule; accordingly, its condensed phase mechanism is relatively weak. As phosphorus-containing flame retardant, MP generates phosphoric acid during decomposition, which can overcome the lack of acid source of MCA and remarkably consolidate the condensed phase, thus showing nitrogen-phosphorus (N-P) synergistic effects. Currently, N-P synergism has been well recognized; however, its processes and mechanisms are not well understood. The accepted viewpoints involve the interaction between N-containing and P-containing compounds producing macromolecular substance such as $(PNO)_x$ or $(PN)_x$ with high thermal stability to consolidate the condensed phase flame retardancy.¹⁰ Generally, the N/P composite flame retardants show better fire-resistance than individual component does; accordingly, they are preferably adopted in many flame retardant systems, but the actual synergistic effects are related to polymer varieties and N/P proportion. Obviously, EMCMP possesses greatly improved flame retardancy due to N-P synergistic effects, and this is an outstanding advantage of this flame retardant.

Relationship between encapsulation resin content and the flame retardancy

Encapsulated resin can effectively help the dispersion of flame retardants in polymer matrix during melt-compounding, and the determination of its optimum content in EMCMP is important. Accordingly, with an invariable EMCMP loading level (25%) and MCA/MP weight ratio (4/1), the effects of encapsulation resin content on the flame retardancy were investigated. In Figure 4, with the increase of the encapsulated resin, it can be seen that the LOI of the flame retardant GF-reinforced PA6 experienced first increase then decline tendency. For the MCA/MP flame retardants system without encapsulation resin, its LOI was only 25. When 15% PA6 resin involved in EMCMP, the LOI of the corresponding flame retardant materials reached the highest value 29, showing much higher value than the former. However, with further increase of the encapsulation resin content, the LOI began to decrease. This was because too high proportion of the encapsulated resin correspondingly decreased the weight percentage of MCA and MP in the composite system, causing the insufficiency of the flame retardants. Accordingly, only a medium encapsulated resin amount can obtain desired flame retardancy. UL94 test in Table II also showed consistent results. It can be seen that only 15 and 25% resin-encapsulated systems can achieve UL94 1.6 mm V0 rating (with melt drips), but the former had better flame retardancy with a shorter self-extinguishing time. This analysis indicated that a medium encapsulated PA6 resin was advantageous to obtain good fire-resistance.

Relationship between the flame retardant loading level and the flame retardancy

After determining the optimum encapsulated resin/MP/MCA ratio (4/1/1), the flame retardancy of the GF-reinforced PA6 at different EMCMP loading level was studied when compared with BMCMP (MCA/MP ratio: 4/1) flame retardant system. Figure 5 and Table III reviewed the LOI and UL94 1.6 mm rating of these two systems. It can be seen that the LOI of EMCMP system showed obviously higher values

TABLE IV
Mechanical Properties of EMCMP and BMCMP GF Flame Retardant GF-Reinforced PA6

Flame retardant materials	Tensile strength (MPa)	Izod notched impact strength (J/m)	Flexural strength (MPa)
PA6/GF (80/20)	118	121	130
EMCMP/PA6/GF (25/55/20)	101	81	116
BMCMP/PA6/GF (25/55/20)	81	46	83

Encapsulated resin content in EMCMP, 25%; MCA/MP weight ratio in EMCMP and BMCMP, 4/1.

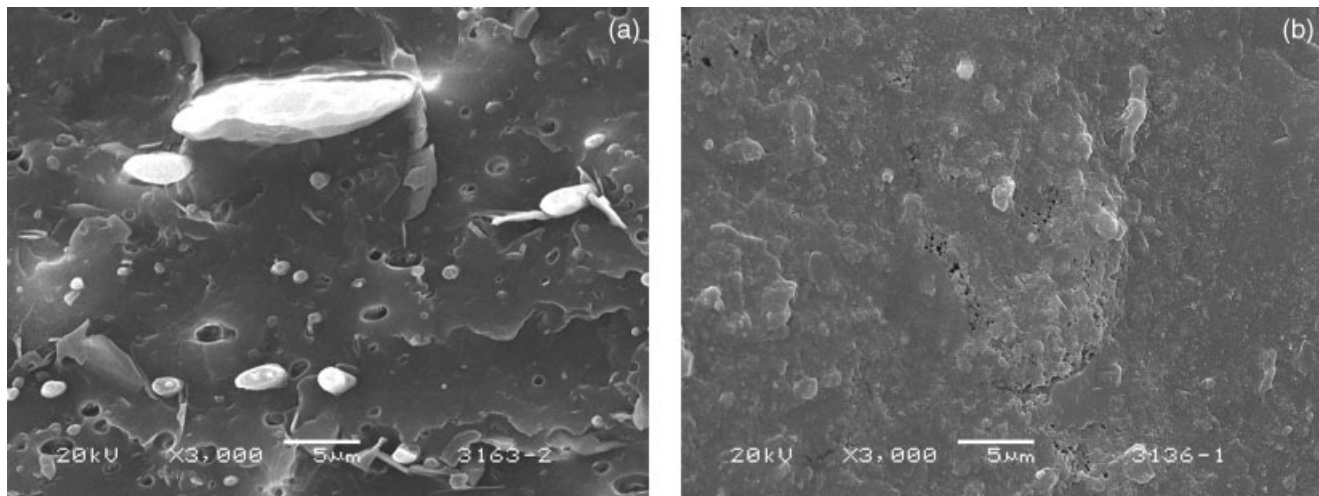


Figure 6 Morphology of (a) BMCMP and (b) EMCMP in PA6 matrix.

than BMCMP system at the same loading level. The former can reach 1.6 mm V0 rating (with melt-drip) at 25% EMCMP loading level, but the latter can only achieve V2 rating even at 35% loading level. Obviously, in the same MCA/MP ratio, BMCMP cannot effectively flame retard GF-reinforced PA6 but EMCMP showed satisfactory effects.

Mechanical properties of the flame retardant GF-reinforced PA6

Mechanical properties are key performance for flame-retarded polymers. However, the addition of flame retardants always results in their deterioration. However, the surface modification just like EMCMP can solve those problems to a certain extent. Table IV listed various mechanical properties of EMCMP and BMCMP flame retardant GF-reinforced PA6 at 25% loading level. It can be seen the tensile strength, impact strength, and flexural strength of the former reached 101 MPa, 81 J/m, and 116 MPa, respectively, only 14%, 33%, and 11% decrease when compared with those of non-fire-resistance system. However, BMCMP system experienced 31%, 63%, and 36% decrease. Obviously, EMCMP system can keep substantial material mechanical performance and make the flame-retarded materials have a higher commercial value.

Morphology analysis of the flame retardant dispersed in PA6 matrix

With the same flame retardant components, the compatibility and dispersion in polymer matrix are key factors influencing materials flame retardancy and mechanical properties. To better explain the great difference in the performance of EMCMP and BMCMP flame retardant systems, the investigation on the morphology of the flame retardant particles in the polymer matrix is necessary. Figure 6 compared the mor-

phology of EMCMP and BMCMP in PA6 matrix, and it showed BMCMP had much bigger particle size, and the phase interface between the flame retardants and the resin matrix was very clear; moreover, some holes resulted from the extrication of the flame retardant particles can be observed, indicating the compatibility and dispersion were poor. But for EMCMP system, the interface between the flame retardant and the resin showed obscure, and it was hard to distinguish their phase morphology, showing miscible tendency between EMCMP and PA6 matrix. Obviously, the compatibility and dispersion of EMCMP in resin was greatly improved through the surface modification. This is because the encapsulated layer of the flame retardants had the same material with the flame-retarded polymer, and during melt compounding process, the out layer of the flame retardant can be plasticized, deform, and well conglutinate with PA6 matrix, and form the phase morphology advantageous to obtain high flame retardancy and mechanical properties.

CONCLUSIONS

A novel technology was adopted to synthesize MCA/MP composite flame retardants in phosphoric acid/PA6 resin solution, and simultaneously realized *in situ* surface modification of the flame retardant through the encapsulation of the precipitated PA6. The obtained flame retardant was applied in flame retardant GF-reinforced PA6, and the results showed that EMCMP had optimum flame retardancy in a proper encapsulated resin/MCA/MP proportion. With the same materials between the encapsulated layer of the flame retardant and the flame-retarded polymer, the compatibility and dispersion of EMCMP in PA6 were markedly improved. The corresponding flame retardant

GF-reinforced PA6 showed very good fire-resistance and mechanical properties. This new technology is promising to solve the problems of halogen-free flame retardant GF-reinforced PA6, and has commercial application prospect.

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