

Effects of Magnesium Hydroxide and Its Synergistic Systems on the Flame Retardance of Polyformaldehyde

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ABSTRACT: An inorganic flame retardant, magnesium hydroxide (MH) with series synergists including melamine (ME), linear novolac resin (LNR), and triphenyl phosphate (TPP) was incorporated with polyformaldehyde (POM) resin in this article. The obvious advantage of the system is that the used flame retardant and the synergists possess multiflame retarding mechanisms and multifunctions. The prepared flame retardant POM could achieve UL94 V-0 rating (1.6 mm) with optimum flame retardant/synergists formulations, showing satisfactory flame retardance. Vari-

ous characterization methods including pyrolysis-gas chromatogram-mass spectrometer (Py-GC-MS) analysis, scanning electron microscope (SEM) observation, and thermogravimetric analysis (TGA), were used to investigate the interaction among the components and reveal the corresponding synergistic mechanisms. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 968–974, 2012

Key words: polyformaldehyde; flame retardance; magnesium hydroxide; synergistic effect

INTRODUCTION

As a widely applied engineering plastic, POM possesses good mechanical properties, low friction coefficient and good wearability, excellent fatigue resistance, and relatively low price among the existing engineering plastics.¹ However, POM is highly flammable due to its unique “unzipping” thermal decomposition,² which leads to a rapid decomposition of the macromolecular chain to produce a great amount of formaldehyde (easily oxidized to formic acid in the air) with a high heating value. Additionally, the produced formic acid, as a catalyst, further accelerates the decomposition of the resin again to produce more acid, thus constituting a vicious circle. Based on this degradation mechanism, POM shows high flammability and its limiting oxygen index (LOI) is only 15, almost the lowest among all polymers,³ which seriously restricts its applications in the fields with fire-resistance requirement such as automobile, construction, electrical and electronic industries, etc. Therefore, developing flame retardant POM is significant in both academe and industry.

Addition of flame retardants is a conventional way to endow polymers with flame retardance. However, it was not very successful in developing commercial flame retardant POM in the past years. An important reason lies in the actual difficulty to look for a suitable and efficient flame retardant for this polymer. As the big sphere crystalline structure of POM results in the poor compatibility between the resin with most flame retardants, as well as some flame retardants with acidity easily accelerates the decomposition of POM, the optional flame retardants for POM are very limited. On the other hand, it is known that from the previous investigations, a single flame retardant generally needs a high loading level for the expected flame retardancy at the price of serious deterioration in other material performances, e.g., processability and mechanical properties. Therefore, it is difficult to obtain satisfactory comprehensive performances.

Halogen flame retardants are widely used for various polymers, whereas these flame retardants generally accelerate the decomposition of POM due to the catalytic action of the halide groups.² Accordingly, the related researches mainly focus on halogen-free flame retardant POM. DuPont, Asahi Chem, and Asahi Kasei used some phosphorus flame retardants including amidine phosphate, ammonium polyphosphate and red phosphorus, etc., to improve the flame retardance of POM,^{3–6} nevertheless, there was no very successful commercial product up to now. Polyplastics⁷ disclosed a combination of a phosphorus-containing compound, a basic nitrogen-containing compound, and an aromatic one (react with

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formaldehyde) to prepare flame retardant POM, but it seems the process was complicated and the mechanical properties of the material still needed improvement. Generally, it is still a big challenge worldwide to obtain the flame retardant POM satisfying commercial requirements.

From the previous investigations, it can be seen that some phosphorus-containing flame retardants (nitrogen-phosphorus compounds or red phosphorus) were involved in common. However, the relatively poor thermal-stability for most phosphorus-containing flame retardants (decomposed into phosphorus acids) easily promotes the degradation of POM. Therefore, it is difficult to load a great amount of phosphorus-containing compounds as the main flame retardant.

Compared with phosphorus-containing compounds, inorganic flame retardants, such as magnesium hydroxide (MH) possess many advantages including environment-friendliness, good smoke and melt drip suppression, and a low cost, thus increasingly applied in polymer materials in recent years.⁸⁻¹² However, few investigations were reported concerning inorganic flame retardant POM system due to its high loading level. Feng et al.¹³ used aluminum hydroxide as the flame retardant of POM, but the obtained material could not pass vertical burning test even with 60 wt % flame retardant. Accordingly, how to improve the efficiency and overcome the difficult dispersion of inorganic flame retardants is a key problem to develop the flame retardant POM on commercial scale.

To solve the above problems, our group has all through focused on the design and use of some synergists that can effectively improve the flame retarding efficiency of inorganic flame retardant systems.¹⁴ In this article, an efficient synergistic system using MH as a main flame retardant, with linear novolac resin (LNR) as a macromolecular charring agent, melamine (ME) as a formaldehyde-absorbing agent, and triphenyl phosphate (TPP) as a charring promoter and lubricant was adopted to prepare flame retardant POM. It was found that the components had contribution to the flame retardance in either the gaseous phase or condensed one, and their physical and chemical interactions promoted the quick formation of a continuous and compact char layer. The test results indicated that the prepared flame retardant POM could achieve the best flame retardancy (UL94 1.6 mm V-0 rating) even at a low MH loading, showing a promising commercial prospective.

EXPERIMENTAL

Materials

POM resin (M90 pellets, copolymer) was supplied by Yuntianhua, China. MH (the average particle

size: 1250 mesh) was purchased from Yingkou Universal Powder Engineering, China. ME was obtained from Sichuan Chemical, China. LNR (the weight-average molecular weight is 650, and the melt point is 100°C) was provided by Henan Bangde Chemical Engineering, China. TPP was purchased from Chengdu Kelong Chemical Reagent Factory. Antioxidant (Ciba IRGANOX 245) was a hindered phenol product of Ciba, Switzerland.

Preparation of the flame retardant POM composites

POM pellets, MH powder, and synergists (LNR was full dried in an oven) were weighted, premixed, and then melt-blended by a corotating twin screw extruder (TSSJ-25/33 (ϕ : 25 mm and L/D: 33), manufactured by KQCEC of Chenguang Research Institute of Chemical Industry, China) at 170 ~ 185°C with a screw rotation speed of 150 ~ 180 rpm. Then the extruded pellets were injection molded into standard bars for further tests by a injector (K-TEC 40 Teromatik Milacron Corporation, Germany), with a hold time of 10 s, a plasticizing temperature of 170 ~ 195°C.

Characterization

The vertical burning tests of the samples were carried out by using a CZF-3 horizontal and vertical burning tester according to UL94-2006 standard. The sheet dimensions were 127.0 × 12.7 × 3.2 mm³ and 127.0 × 12.7 × 1.6 mm³, respectively.

The gaseous decomposition products of the original POM and flame retardant POM were measured by HP5890SA pyrolysis-gas chromatogram-mass spectrometer (Py-GC-MS) (the air, pyrolysis temperature: 500°C), and the relative intensity of the produced formaldehyde and formic acid were determined (The standard intensity of another decomposition product, dioxolane, was set as 100).

The thermogravimetric analysis (TGA) of LNR (no dry), TPP, and their mixture were conducted on a TA Q500 TGA thermal analyzer, with the air flow of 100 mL/min. The test temperature range was from 30 to 700°C with a heating rate of 10°C/min.

The char residues of the burnt bars after vertical burning test were gilt under vacuum, and then were observed by a HITACHI S3400 scanning electron microscope (SEM) instrument with 10 kV accelerating voltage.

RESULTS AND DISCUSSION

Flame retardancy

Table I listed the UL94 results of the flame retardant POM with different synergist formulations. It can be seen that from Table I, the system with only MH

TABLE I
UL Vertical Burning Results of the Flame Retardant POM with a Single Synergist

Material formulations (wt %)	UL94 Vertical flammability		
	3.2 mm	1.6 mm	Dripping
POM (100)	NR ^a (Burn out)	–	Yes
POM/MH (45/55)	NR (Burn out)	NR	No
POM/MH/ME (45/50/5)	NR ($t_1^b = 27$ s)	NR	No
POM/MH/LNR (45/50/5)	NR ($t_1 = 18$ s)	NR	No
POM/MH/TPP (45/50/5)	NR (Burn out)	NR	No

^a NR, no rating.

^b t_1 , the average after-flame time of the first flame application.

involved could effectively suppress the melt drips, but the vertical flame retardancy was not obviously improved even with a high loading level of MH. The tested bars were quickly burnt out and it could not pass any rating, which demonstrated that only MH is inefficient for the flame retardance of POM. In the rest formulations in Table I, the shortened t_1 time for the systems with a single synergist, indicated that these systems had improved flame retardance to different degree compared the system with only MH involved. The results confirmed the existent synergistic effects between MH and these compounds.

However, it seemed that the above systems with a single synergist still could not obtain the expected flame retardance satisfying the commercial requirements (V0 rating). Therefore, the combinations of the above synergists were considered for further improvement of the flame retardance. Table II showed the UL94 test results of the MH systems with the composite synergists, and the systems possessed obviously improved flame retardance than those with a single synergist. Particularly, the ternary synergists system including ME, LNR, and TPP showed the best rating (UL94-1.6mm V0) among all the ones, which was also the best flame retardancy among the flame retardant POM reported in the related references. This exciting result implied that the possibility preparing commercially flame retard-

ant POM with high performances. However, on the other hand, it is also equally important to reveal the corresponding synergistic mechanisms. Accordingly, the following section will focus on the investigation and discussion concerning the synergistic actions.

The synergistic mechanisms

As a relatively complicated multisynnergists system, improvement of the actual flame retardance would attribute to the respective and collective actions of the flame retardant, synergists, and flame retardant with synergists or one synergist with another. These actions involve series complicated physical and chemical processes, so it is difficult to be accurately described. However, based on our experimental results and some recognized theories, the qualitative description for the mechanisms can be established as Scheme 1.

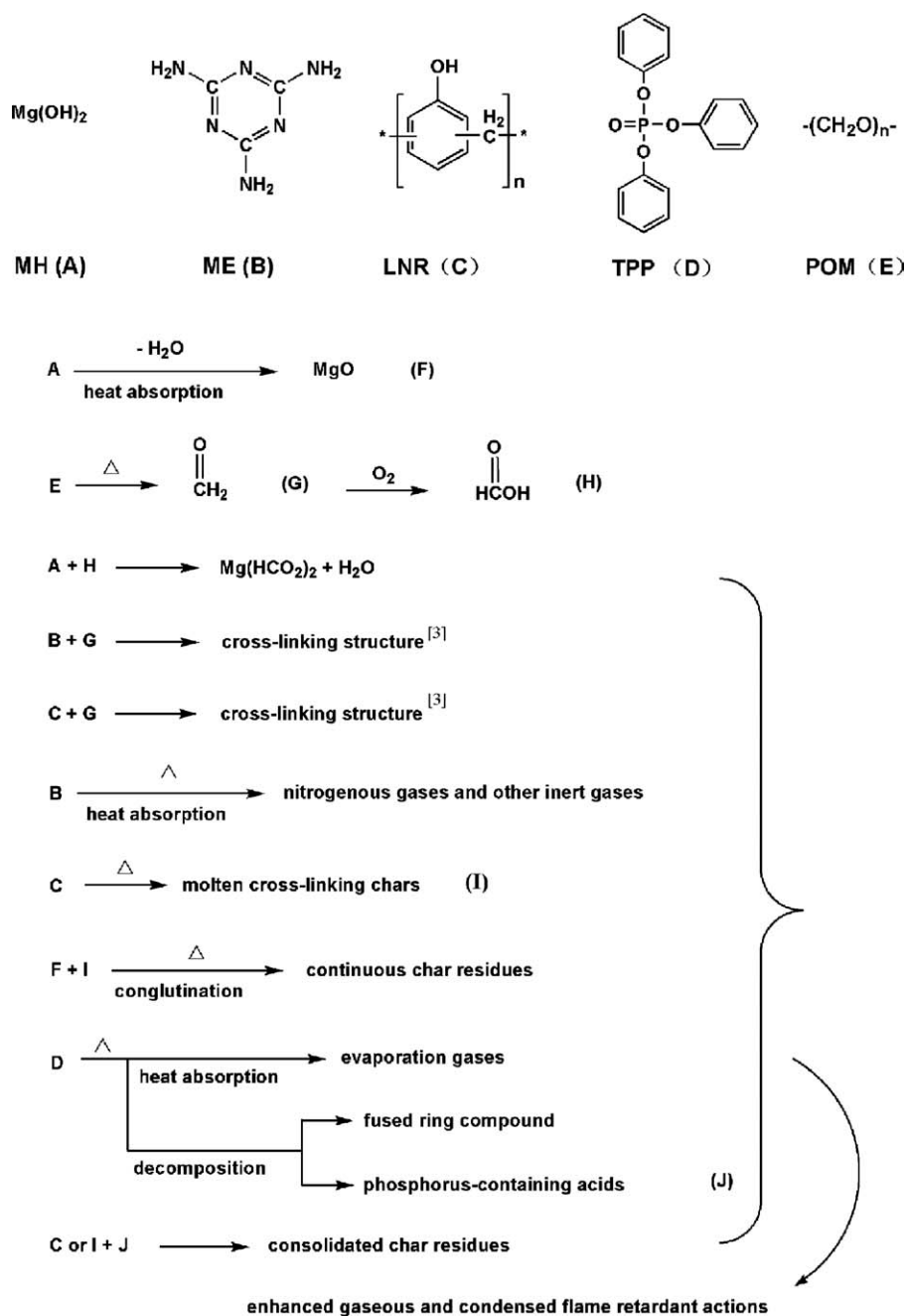
In the above synergists system, the mechanism of the main flame retardant, MH, is clear. This inorganic flame retardant depends on the decomposition decalcination and crystal water release, as well as the produced MgO particles as the barrier. However, without formation of a protective char layer due to lack of a charring agent, the system with only MH shows very low flame retardancy. An outstanding advantage of MH is obvious suppression effects on the melt drips during the flame because the inorganic particles (including MH and produced MgO) can increase the melt viscosity and hold back the polymer melt flow. Additionally, as an alkali hydroxide, MH can neutralize the produced formyl acid, therefore contributing to the thermal-stability enhancement of POM. In fact, no degradation phenomena (e.g., foaming or pungent smell of formaldehyde) appeared during the processing. Accordingly, this is another important advantage by using MH as the flame retardant of POM.

Both ME and LNR in the synergists system are efficient formaldehyde-absorbing agents, even with a low content, can effectively absorb formaldehyde. The mechanisms were described as the reactions between the formaldehyde and $-\text{NH}_2$ of triazine or

TABLE II
UL Vertical Burning Results of the Flame Retardant POM with Composite Synergists Systems

Material formulations (wt %)	UL94 Vertical burning test	
	3.2 mm (t_1/t_2 (s) ^a)	1.6 mm (t_1/t_2 (s))
POM/MH/ME/LNR (45/35/15/5)	V-0 (1/1)	V-1 (5/13)
POM/MH/ME/TPP (45/37/15/3)	V-2 (7/26)	NR
POM/MH/ LNR/TPP (45/47/5/3)	V-0 (2/5)	V-1(3/12)
POM/MH/ME/LNR/TPP (45/33/15/5/2)	V-0 (1/1)	V-0(1/2)

^a t_1/t_2 = average after-flame time of five test bars after the first/second flame application.



Scheme 1 Synergistic flame retardant mechanism of MH/ME/LNR/TPP flame retardant POM.

phenolic hydroxyl of LNR, which were confirmed in our previous research.¹⁴ The formaldehyde and formic acid absorbing effects for different components can be evaluated by Py-GC-MS analysis. The relative peak intensity of the produced formaldehyde and formic acid in gas chromatogram spectra for the systems were listed in Table III. Compared with the original POM, the relative intensity for the systems-containing MH and synergists were remarkably weakened, implying the decreasing release amount of the formaldehyde and formic acid. Among them, the POM/ME system had the weakest intensity, which indicated that ME was the most efficient

TABLE III
The Relative Intensity of the Pyrolysis Products from the Original POM and Flame Retardant POM

Material formulations	Relative intensity of formaldehyde and formic acid
POM	6956
POM/MH (90/10)	2478
POM/novolac (90/10)	1461
POM/ME (90/10)	655

The peak of dioxolane was set as the standard intensity: 100.

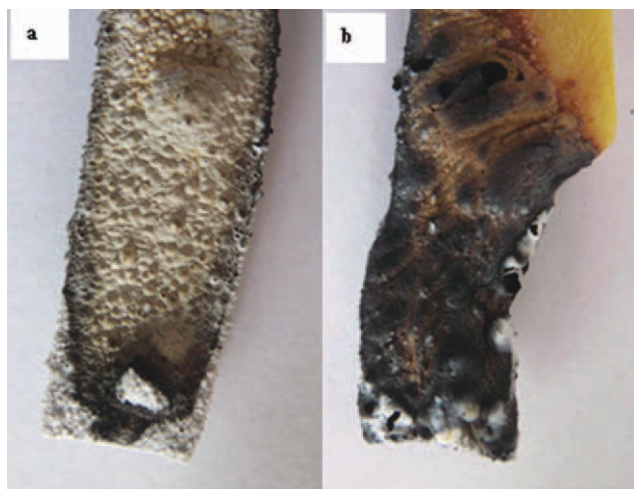


Figure 1 Digital photographs of test bars (1.6 mm) for flame retardant POM formulations after the first flame application at vertical burning test: (a) POM/MH = 45/55 and (b) POM/MH/LNR = 45/40/15. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

formaldehyde-absorbing agent and played the main role of decreasing the formaldehyde (formic acid) content during the degradation and combustion.

Another function of ME was contributing the flame retardancy in gaseous phase by releasing nitrogen-containing inert gases, which can dilute the concentration of the oxygen and flammable gases, thus slowing down the flame rate. Similarly, LNR also played other important roles in the system, an adhesion agent and charring agent. With a strong polarity, low melt point (about 100°C) and high flowability, LNR can quickly melt and effectively wet the particle surface of MH also with hydroxyl groups, in early compounding stage. With gradual thermosetting (about 170–190°C) at the processing temperature, the crosslinking resin can tightly combine the interface of MH particles and POM resin matrix, helpful to increase the interfacial adhesion. At the flame temperature of POM, with MH decomposed into MgO, this charring resin is correspondingly converted to crosslinking char that still combines and encapsulates the MgO particles, advantageous to remain them in the condensed phase rather than getting out as those systems without char formation. Additionally, the remained MgO, as the supporting skeleton of the char, can also consolidate the char layer to a degree. This consolidation effects has been confirmed in the flame retardant filled polyamide system with LNR as a charring agent.¹⁵

Therefore, the collective action of MH and LNR made the consolidated char successfully constituted, obviously, this is very important for POM without

charring capability to enhance the flame retardance in the condensed phase. The digital photo in Figure 1 showed the char of MH flame retardant POM with and without LNR, respectively. Obviously, there was a great amount of produced char with the addition of the charring resin, however, almost no char generated except the ash for the latter.

Although the MH/ME/LNR system showed obviously increased char amount, it was noticed that the flame retardancy was remarkably improved only with another synergist, TPP involved. The difference in flame retardance of the two systems with and without TPP probably results from different the char formation rate, char structure, as well as the thermal stability of the char layer. As is well known, as a phosphorus-containing flame retardant, TPP easily evaporates into gaseous phase at 230–280°C, and at a higher temperature, decomposes into fused ring compounds and phosphorus-containing acid.^{16–20} A small amount of the acid will catalyze the charring process of the LNR to quickly form the condensed char layer in the early combustion stage, thus making the fire self-extinguish before burning into the inner martial.

To confirm the interaction between TPP and LNR, TG analysis was conducted. The experimental TG and direct superposition with the TG (DTG) curve [Fig. 2(b)] of the mixture with a certain ratio was from factual record by the thermal analyzer, and the calculated TG and DTG curves [Fig. 2(b)] for TPP/LNR mixture were obtained by DTG curves of TPP and LNR [Fig. 2(a)] according to the same weight percent with the experimental mixture. Assumed no reaction for the mixture, the experimental TG curve should superimpose on the calculated one. Obviously, the fact that the experimental and calculated curves mismatched, further confirmed the interaction between the two components.

It was noticed that the first weight loss (200–300°C) occurred at a higher temperature and in this stage, the experimental curve showed a lower weight loss rate than the calculated one. It confirmed that the evaporation of TPP, in the mixture, was restrained by the formed shielding char. As a result, some TPP molecules could remain in the mixture until decomposed into phosphorous-containing acid.

If without any reaction, there was no residue remained for the LNR/TPP mixture at 650°C, in air condition according to the calculated TG curve. Actually, the amount of the solid residues at the same temperature was about 10 wt % in the experimental TG curve. That was to say, the reactions between the two compounds had a significant influence on the formation of the char residues. With temperature rise, the produced phosphorous-containing acid from TPP involved in the dehydration of LNR, and promoted the crosslinking and charring

reactions. In addition, the peak value (500–600°C) in the experimental DTG curve was much lower than that in the calculated one, which further confirmed that the reactions between LNR and TPP were beneficial to increase the char formation rate and the thermo-oxidative stability of the produced char layer.

Figure 3 showed the morphology of the final char layer of MH/ME/LNR and MH/ME/LNR/TPP flame retardant POM by SEM. Their morphology was very different even with only 2% TPP involved for the latter. Obviously, the former was coarse and porous, but the latter was visibly more smooth and compact, which possessed better barrier effects to block off the flammable gas diffusion and fire spread, therefore showing much better flame retardancy.

CONCLUSIONS

MH flame retardant POM with ME/LNR/TPP composite synergists achieved UL-94 (1.6 mm) V-0 rating.

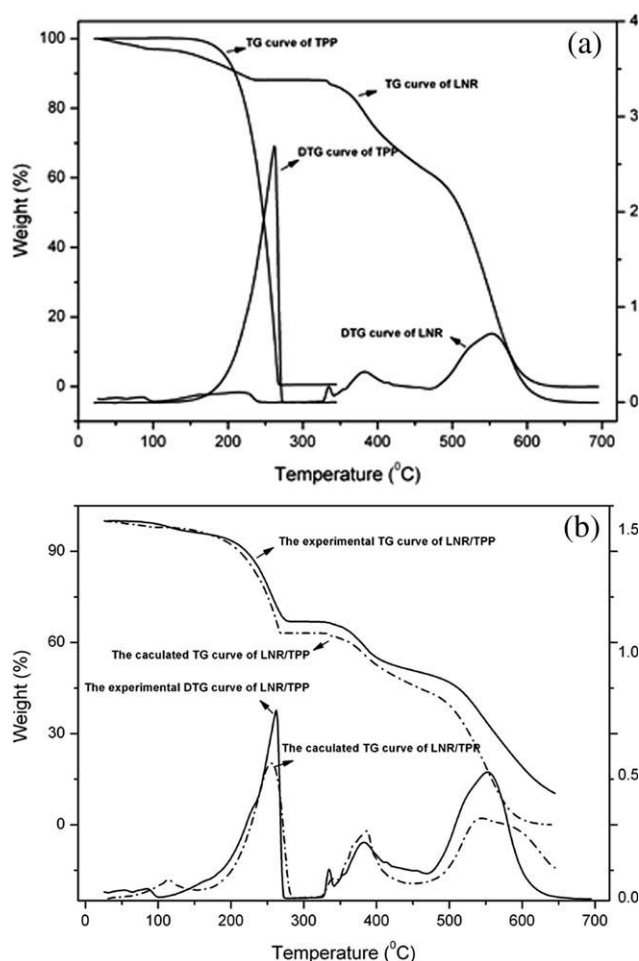


Figure 2 TG and DTG curves of (a) LNR and TPP, and (b) the experimental and calculated LNR/TPP mixture (LNR/TPP = 5/2).

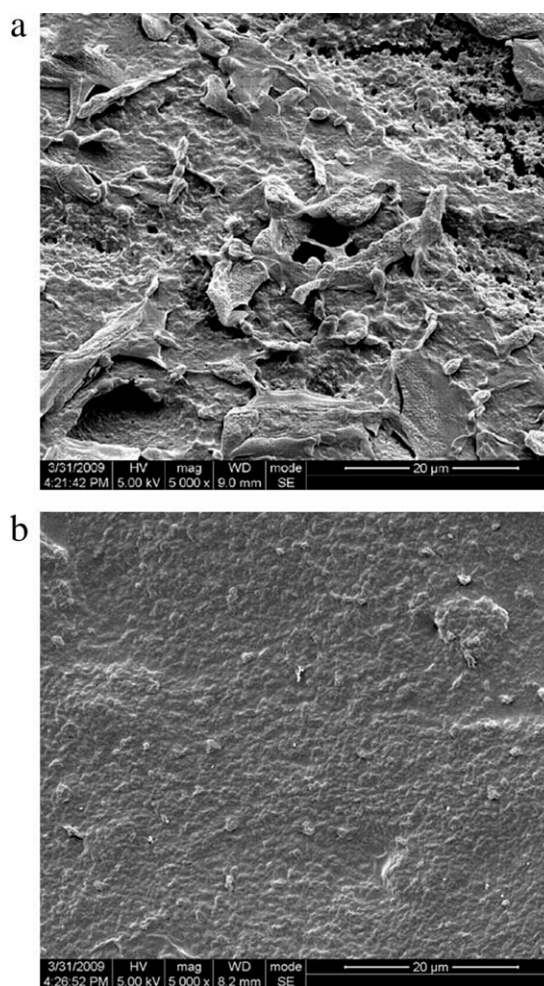


Figure 3 SEM microphotographs of residual char layers for flame retardant POM systems after vertical burning test: (a) POM/MH/ME/LNR = 40/40/15/5 and (b) POM/MH/ME/LNR/TPP = 40/38/15/5/2.

ing. The respective and collective actions of these components made the system possess multiflame-retarding mechanisms including the absorption of the degraded products of POM, decalescence, the melt suppression, the dilution of flammable fuel and oxygen in the gaseous phase, and the construction of the consolidated char layer in the condensed phase. This flame retarding technology provided a new direction in developing the flame retarded POM with very good fire resistance.

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