Synergistic Effect of Melamine Polyphosphate with Macromolecular Charring Agent Novolac in Wollastonite Filled PA66

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ABSTRACT: In this article, macromolecular charring agent linear novolac (NA) was served as a synergist with nitrogen-phosphorous flame retardant melamine polyphosphate (MPP) for the flame-resistance of wollastonite (WT) filled polyamide 66 (PA66). The investigations showed that MPP/NA system possessed obvious synergistic effects by increasing the charring rate and amount, therefore, showing much higher flame retardancy than the filled PA66 flame retarded with MPP alone. The corresponding char layer structure of MPP/WT/PA66 and MPP/NA/WT/PA66 was investigated and their difference was analyzed. In addition, as a multifunctional additive, NA could act as a compatibilizer and lubricant in the system, and endowed the material with improved mechanical performance and processability. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 45–49, 2010

Key words: filled polyamide 66; flame retardant; macromolecular charring agent

INTRODUCTION

PA66 is a widely applied engineering plastic because of its excellent mechanical properties, chemical stability, good resistance to friction and oil, high thermal distortion temperature, and good electric properties.[1,2] On many occasions, PA66 with inorganic filler shows higher application value when compared with neat PA66 by remarkably improved rigidity, dimensional stability, thermal distortion temperature, as well as much lower cost.[3–6] As is well known, PA66 is a flammable polymer with limiting oxygen index of 25%.[1] Due to the low melt viscosity and some oligomers produced from the decomposition of PA66, unfilled PA66 shows a great amount of melt drips during its combustion, leading to fast spread of the fire. On the other hand, the melt-dripping process is advantageous to the removal of the combustion heat and latent fuel, oligomers; therefore, PA66 has self-extinguishing ability with melt dripping and can pass UL94 V2 rating. However, for inorganic fillers filled PA66, its flame retardancy is even worse than neat PA66 because the addition of fillers increases the melt viscosity and suppresses melt drips, thus weakening the effects of heat and fuel remove, as a result, the combustion duration of the material is correspondingly extended. Generally speaking, filled PA66 cannot pass any UL94 rating, which restricts its applications in some important fields such as electric and electronic (E&E) industries. Accordingly, flame retardant filled PA66 with high performance is badly needed.

Adding flame retardants is the most efficient method endowing polymers with flame retardancy. Halogen-containing compounds are traditional flame retardants applied in filled or reinforced PA66, but the release of heavy smoke and corrosive gas during combustion makes this kind of flame retardants challenged in recent years, and some corresponding products have been forbidden in some countries. On this background, halogen-free flame retardants attract much attention at present. Among existing halogen-free flame retardants suitable for PA66, melamine polyphosphate (MPP) is a typical nitrogen-phosphorous flame retardant[7] with the advantages of low toxicity and low smoke (the structure of MPP is showed in Scheme 1). The flame retarding mechanism of MPP is similar to that of intumescent flame retardants. Above 350°C, MPP is decomposed into melamine and phosphoric acid; the two decomposition products play the roles of gas source and acid source, respectively. The further decomposition
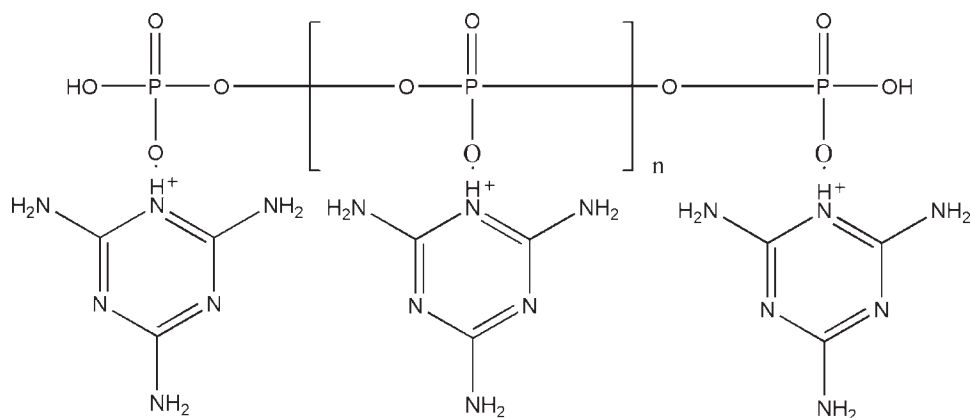
Scheme 1 The molecular structure of MPP flame retardant.

product of melamine, N-containing inert gas can dilute the concentration of the oxygen and fuel gas supporting the combustion, and the acid source can catalyze the dehydration of polymers, thus forming char barrier isolating the bulk material and the flame surface.[8–12] However, it was found that it is difficult to obtain satisfactory flame retardancy for PA66 by only using MPP as flame retardant; therefore, developing an efficient synergist with MPP is needed. Some metal salts or ions were proved to be synergistic with MPP in flame retardant polyamide materials. Ulrike et al.[9] used a synergist system combining aluminum phosphinate and MPP, and the flame retardancy test results showed that the introduction of aluminum phosphinate could effectively enhance the barrier effects of the produced char layer. To modify the stability as well as the compatibility of metal salt in PA resin, Li et al.[13] designed and synthesized zinc-ion-modified melamine polyphosphate (Zn-MPP) that was applied in glass fiber reinforced PA66 system. It showed that Zn-MPP flame retardant reinforced PA66 had improved flame retardancy resulting from the formation of more stable char layer, also maybe from capture of the free radicals in the gaseous phase.[14] In other investigation, it was found that introducing special acid source can also improve the charring ability. In our previous study,[15] thermal-plastic polyurethane (TPU)-encapsulated solid acid was adopted as a synergist with MPP in flame retardant filled polyamide improved the carbonation efficiency of polyamide, and greatly consolidated the flame retarding mechanism in condensed phase.

For MPP flame retardant system, constructing the char layer of high quality is a key factor to obtain good flame retardancy. Due to the lack of charring component in MPP molecule, the charring source comes from the flame retarded polymer itself, e.g., PA66 resin, thus leading to relatively lower charring efficiency. As a result, the quality of the produced char layer is low and hard to endow the polymer

material with good barrier effects. Based on the aforementioned reason, adding additional charring agent should be an effective method to further improve the flame retardancy of MPP flame retardant system. However, there are some difficulties in practical application for this method. Except the poor compatibility between PA66 resin and general charring agents, e.g., pentaerythritol, which can deteriorate the mechanical properties of PA66, the relative lower thermal stability of general charring agents in the processing temperature of PA66 (260–280°C) also makes them difficult to be combined with MPP. Considering the above shortcomings of traditional small molecular charring agents, in our investigation, a macromolecular charring agent, novolac resin (NA) was introduced into MPP flame retardant filled PA66 system. With good thermaldynamical compatibility[16] with polyamide, high thermal stability, excellent charring performance, and aid-dispersion effects on inorganic fillers in PA66 resin, MPP/NA flame retardant PA66 has satisfactory flame retardancy, mechanical properties and processabilty showing a promising commercial prospective in the future.

EXPERIMENTAL

Materials

PA66, pellet (MFI = 10.8 g/min), Shenma Engineering Plastics; MPP (Scheme 1), self-made[15]; NA (Mw = 650, mp ≈ 100°C), purchased from Henan Bangde Chemical Engineering Company, China, and its structure is shown as Scheme 2; Wollastonite (average particle size = 3 μm), purchased from South Wollastonite Industrial.

Preparation of flame retardant PA66 samples

A certain amount of MPP, NA, WT, PA66, and other additives were premixed in a high-speed mixer and
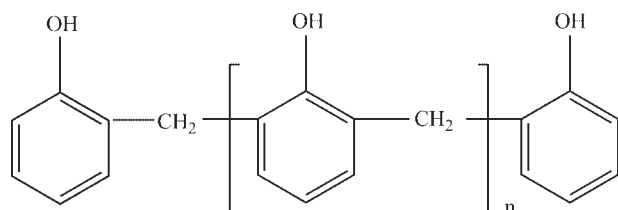
Scheme 2 The linear novolac structure.

then extruded by a twin-screw extruder (φ: 30mm, L/D: 32, model: SLJ-30 Longchang Chemical Machinery Plant,China). The temperature of the extrusion was set as 250–275°C, and the screw rotation speed was 150 r/min. The test bars were prepared by injection molding (injector: K-TEC 40 Ferromatik Milacron, Germany), the cycle time: 45 s, the injection temperature: 260–280°C, and the pressure : 20–60 bar. The samples' compositions were indicated in Table. I.

CHARACTERIZATION

The vertical burning test was conducted by a CZF-3 horizontal and vertical burning tester, with $127 \times 12.7 \times 3.2$ mm^3 and $127 \times 12.7 \times 1.6$ mm^3 bars according to the UL-94 test. The tensile strength and the elongation at break of the materials were examined using a RG L-10 material tester according to ISO 527, and the Izod notched impact strength of the materials were measured using a ZBC-4B impact strength tester according to ISO 580. The residual chars of the burned materials were gilt under vacuum before observed by a JEOL JSM-5900LV SEM instrument, with 20 kV accelerate voltage. The thermo gravimetric analysis of the flame retardant polymer was carried out on a WRT-2R thermal analyzer by shanghai precision and scientific instrument, with a heating rate of 10°C/min, from 25 to 800°C and an atmosphere flow of 100 mL/min. The melt index was tested at 265°C according to ISO 1133 using a CS-127C-AWR-660 melt indexer by Custom Scientific Instruments.

TABLE I
The UL94 Test Results of Flame Retardant PA66

MPP/NA/ WT/PA66 (wt %)	Melt drips	UL-94 rating	
		3.2 mm	1.6 mm
25.0/0/25/50	Yes	Fail	Fail
20.0/5.0/25/50	Yes	V-1	V-1
18.8/6.2/25/50	Yes	V-0	V-1
16.6/8.4/25/50	Yes	V-0	V-1
15.0/10.0/25/50	No	V-0	V-0
12.5/12.5/25/50	No	V-0	V-0
10.0/15.0/25/50	No	V1	Fail

RESULTS AND DISCUSSION

The flame retardancy and synergistic mechanism

Table I compared the effect of MPP/NA ratio on the flame retardancy of WT filled PA66. It could be observed that during the UL94 test, the system added with 25 wt % MPP alone had very long flame time and serious melt dripping and could not pass any UL94 rating showing low flame retarding efficiency. With increase of the NA content, the flame retardancy was greatly improved. It could be seen that the corresponding flame retardant material rapidly formed char layer on the flame surface, thus effectively suppressed melt dripping and realized self-extinguishment in a short time, confirming the remarkable synergistic effects of MPP/NA system. Furthermore, it was found that the synergistic effects greatly depended on MPP/NA ratio. At the ratio of 3 : 2 and 1 : 1, UL94 1.6 mm V-0 rating could be achieved, but for the system at 3 : 2 ratio, its flame time was shorter. Therefore, this weight ratio of 3 : 2 was determined as the optimum proportion of MPP/NA.

Compared with MPP/WT/PA66, the remarkable flame retardancy improvement of MPP/NA/WT/PA66 was attributed to the introduced NA that had higher charring efficiency than PA66. NA is a typical charring polymer, and its charring mechanism can be described as follows: on one hand the hydroxyl groups of NA can dehydrate with the acid group of MPP and form chars; on the other hand, with multi-aromatic structure, NA itself has a high charring rate. However, PA66 needs the intermediate transformation process of isocyanate to form chars, and the charring rate and amount is obviously lower than NA; therefore, the introduction of NA can help faster formation of the char layer with high quality.

Figure 1 compared the appearance of the char layer of MPP/WT/PA66 and MPP/NA/WT/PA66, respectively. Obviously, there was some obvious difference between them. The char layer of MPP/WT/PA66 was coarse and discontinuous, by contrast, that of MPP/NA/WT/PA66 was much more
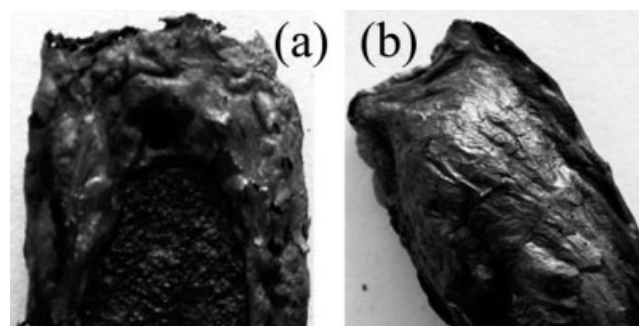
Figure 1 The photographs of the char layer of flame retarded composites after UL94 test: (a) MPP/WT/PA66 and (b) MPP/NA/WT/PA66.
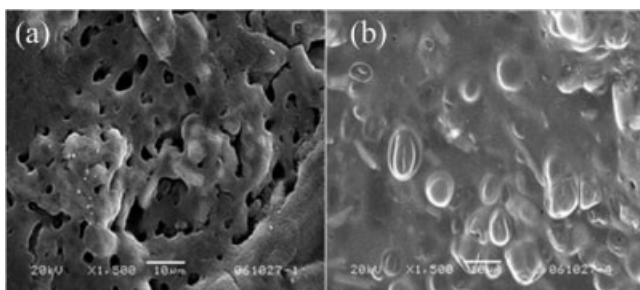
Figure 2 The SEM photographs of (a) MPP/WT/PA66 and (b) MPP/NA/WT/PA66.

smooth, continuous and intumescent, and the thickness of the latter was obviously larger than that of the former. To further reveal the difference in charring behavior of the both systems, SEM was conducted to investigate the micromorphology of their char layers (Fig. 2). Clearly, there were many holes and cracks observed in MPP/WT/PA66 system, and such porous and open char layer structure could not effectively shield and isolate the bulk material and the flame; therefore, the combustion heat, the oxygen and the decomposed products of PA66 diffused along these holes and cracks, and it was hard to obtain good flame retardancy. For MPP/NA/WT/PA66 system, there were no obvious holes and cracks observed, and the char layer showed typical closed morphology. Obviously, this closed char structure could exert ideal barrier effects, thus advantageous to the improvement of the flame retardancy. More interesting, some bubble-like structure was observed on the char layer surface of the latter.

The above remarkable difference in char layer structure was due to the follows. For MPP/WT/PA66 system, WT particles were distributed in PA66 resin. During the combustion, PA66 resin had dominant degradation compared with its carbonization. With the decomposition of PA66 resin around the WT particles, the filler particles lost the support of the resin matrix and easily fell off the char layer surface, thus forming the observed holes. However, the situation was very different for MPP/NA/WT/PA66 system. As the linear novolac resin was a polar resin with phenol hydroxide groups in its molecular chains, NA has good compatibility with both PA66 (through intermolecular hydrogen bonds) and WT particles (also with —OH groups on the surface). Additionally, the linear NA has very low melt point (only 100°C) and low melt viscosity. Its melt could effectively wet the surface of WT particles and carried the filler particles evenly dispersed in PA66 resin matrix. Accordingly, NA resin preferred to adhere on the surface of WT particles. Served as a macromolecular charring agent, NA resin could rapidly form firm char layer on the filler particles surface; therefore, the WT particles could be well encap-
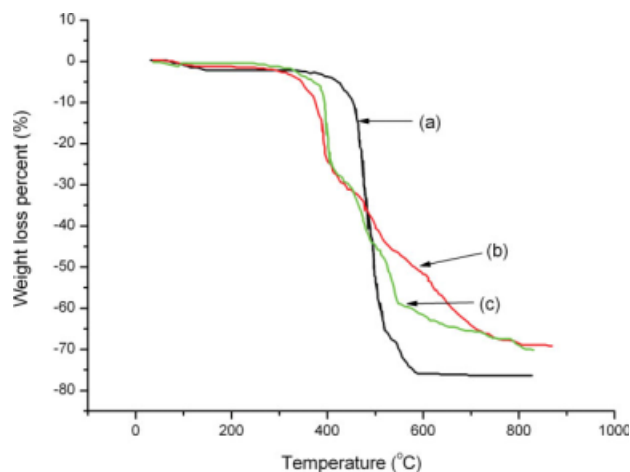

Figure 3 TGA cures of different samples: (a) WT/PA66, (b) MPP/NA/WT/PA66, and (c) MPP/WT/PA66. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

sulated and supported by the newly produced solid char layer rather than falling off like only MPP involved system, avoiding the formation of the holes and cracks. Furthermore, with the filler incorporated, the char layer could be effectively reinforced and became more compact and dense, accordingly, possessing higher strength and better barrier effects. Additionally, the char formation rate of the NA on the surface of WT particles is obviously faster than that of PA66 resin around the filler, the char layer from NA could more rapidly expand as compared to that from PA66 resin itself, thus leading to the generation of the bubble-like structure on the char layer surface. TGA and DTG analysis (Figs. 3 and 4) also demonstrated the remarkable improvement in condensed phase for MPP/NA/WT/PA66 system. From Figure 3, it could be seen that MPP/NA/WT/
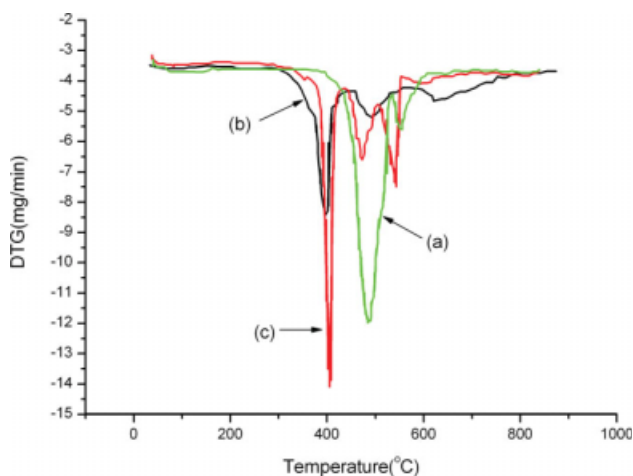

Figure 4 DTG cures of different samples: (a) WT/PA66, (b) MPP/NA/WT/PA66, and (c) MPP/WT/PA66. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
The Mechanical Properties of Flame Retarded PA66

FR materials	Tensile strength (MPa)	Elongation at break (%)	Izod notched impact strength (kJ/m^2)
MPP(25%)/WT(25%)/PA66(50%)	51.7	0.78	1.5
MPP(15%)/NA(10%)/WT(25%)/PA66(50%)	60.6	1.3	1.6

PA66 (b) and MPP/WT/PA66 (c) systems had lower initial weight loss temperature but higher weight percent of residue compared with WT/PA66 system (a). This is because without acid source in the latter, PA66 resin itself could not effectively form char, so the resin almost degraded into small molecules during heating. For the systems with MPP involved, the decomposed product of MPP, phosphoric acid, could catalyze the resin to degrade into more amount of char remained in the residue. Comparing (b) and (c), it could be seen that the introduction of NA made the weight loss rate obviously decrease due to the formation of more compact and dense char layer, which could more effectively hold back the transfer of the heat and the degradation products. Similarly, from the DTG curves in Figure 4, it could be seen that the maximum thermal decomposition rate of the MPP/NA/WT/PA66 was 8.44 mg/min, far smaller than 14.12 mg/min of MPP/WT/PA66 system. Obviously, NA-containing system provided less fuel gas during the degradation, thus advantageous to the improvement of the flame retardancy.

The mechanical properties and the processability of flame retardant PA66

In addition to flame retardancy, mechanical properties and processability are important for flame retarded polymers. Particularly for flame retardant polymer loaded by inorganic fillers, the addition of either flame retardant or inorganic filler can seriously deteriorate these properties. Accordingly, how to obtain the flame retarded filled polymers with good comprehensive performance is of the interest for the researchers. As mentioned above, with high polarity, low melt point and low melt viscosity, linear NA resin is compatible with PA66, effectively wets the surface of inorganic filler and improves the dispersion of the filler particles in PA66 resin, i.e., NA plays the multiroles of compatibilizer, aid-dispersion agent and lubricant. From the Table II and Table III, it can be seen that MPP/NA/WT/PA66

has remarkably improved mechanical properties and melt flowability as compared to MPP/WT/PA66 system. Obviously, the multifunction of NA is significant to obtain the flame retardant filled PA66 with good comprehensive performance.

CONCLUSIONS

Adopting linear NA and MPP synergist system for flame retardant WT filled PA66, the flame retardant filled PA66 with high performances was prepared. The macromolecular charring agent NA could make up the shortcoming of the low charring efficiency of PA66 resin itself, and accelerated the formation of closed, compact and firm char layer that encapsulated the wollastonite particles, showing effective barrier to the heat, oxygen and fuel gas. Therefore, MPP/NA/WT/PA66 system possesses much better flame retardancy than MPP/WT/PA66, and the former can achieve UL94 1.6mm V0 at 25% MPP/NA loading level. Due to the compatibilizing and lubricating effects of linear NA, MPP/NA/WT/PA66 system also shows much better mechanical properties and melt flowability, thus endowing the materials with satisfactory comprehensive performances.

References

1. Jou, W. S.; Chen, K. N.; Chao, D. Y.; Lin, C. Y.; Yeh, J. T. Polym Degrad Stab 2001, 74, 239.
2. Liu, Y.; Wang, Q. Polym Degrad Stab 2006, 91, 3103.
3. Gachter, R.; Muller, H. Plastics Additives Handbook; Hanser Gardner Publications Inc.: Cincinnati, 1993; p 489.
4. Tanaka, H. Polym Eng Sci 1999, 39, 817.
5. Unal, H. Sci Eng Compos Mater 2002, 10, 407.
6. Jia, J. H.; Yuan, H. L.; Xia, W. G. Plastics 2005, 34, 10.
7. Camino, G.; Costa, L. Rev Inorg Chem 1986, 8, 69.
8. Vandersall, H. L. J Fire Flammab 1971, 2, 97.
9. Ulrike, B.; Bernhard, S.; Mario, A. F.; Christian, J. Polym Degrad Stab 2007, 92, 1528.
10. Dabrowski, F.; LeBras, M.; Delobel, R.; LeMaguer, D.; Bardollet, P.; Aymarni, J. In Influence of Glass Fibres, Flame retardant 2002; Grayson, S.J., Ed.; Interscience Communication: London, UK, 2002; p 127.
11. Menachem, L. Polym Adv Technol 2001, 12, 215.
12. Jahromi, S.; Gabielse, W.; Braam, A. Polymer 2003, 44, 25.
13. Li, L. P.; Li, B.; Fei, T. J reinforced plast compos 2008, 27, 277.
14. Mao, W. Y.; Li, Q. L.; Zhou, Y. M. Insulating Mater 2007, 40, 32.
15. Wang, Z. Y.; Feng, Z. Q.; Liu, Y.; Wang, Q. J Appl Polym Sci 2007, 105, 3317.
16. Huang, P. T.; Kwei, T. K.; Pearce, E. M.; Levchik, S. V. J Polym Sci Part A: Polym Chem 2001, 39, 841.

TABLE III
MI Values of Flame Retarded Composites

FR materials	MI (g/10min)
MPP(25%)/WT(25%)/PA66(50%)	6.5
MPP(15%)/NA(10%)/WT(25%)/PA66(50%)	8.7