Synthesis, Characterization and Flame Retardancy of Amino Phosphate

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Abstract
Two phosphorus-containing flame retardant (FR) were synthesized and incorporated in the backbone of polyamide 6(PA6) by polymerization. The structure and spectroscopic data of these flame retardant were determined by Fourier Transform Infrared Spectroscopy (FTIR) and Elemental analysis. Flame-retardancy and thermal property of PA6 modified with CEP, and MMP were examined by LOI and TGA. The LOI value of PA6 shows ascending trend by adding FRs, and it rise from 24 to 31%. TGA data revealed that FR improves thermal stability of PA6. The on-set temperature was added at least 20 ℃.

1 Introduction

Nylon is one of largest engineering plastics used in electronically industry. There are many reports about flame retardant modification of Nylon. The flame retardant containing halogen, phosphorus, nitrogen and inorganic element are used for Nylon. Nitrogen contained phosphate is most used phosphorus-nitrogen flame retardant[1, 2]. Intumescent flame retardant attracts interest of researcher which contains acid source, carbon source and gas source in one composite. It is often nitrogen-contained phosphorus derivative[3, 4, 5]. Triazine phosphate is found to be good flame retardant which represents excellent flame retardancy and stands the test of wash[6, 7]. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) can be incorporated to nylon by react active P-H bond with unsaturated bond. However, it has a drawback related to its monofunctionality and can only be used in conjunction with other agents[8, 9, 10]. In this report, we are successful to synthesize two nitrogen-phosphorus containing FRs and investigate their influence on PA6.

. 2 Materials and testing methods

All chemicals were obtained from commercial sources and used without further purification. IR spectra were recorded with a Perkin-Elmer Paragon1000 (FT-IR, KBr). Element analysis was performed on a Heraeus CHN-Rapid element analyzer. TGA analysis was performed under nitrogen flow (20 cm^3/min) at heating rate 10℃/min from 25 to 600℃ with a Mettler Toledo model TGA/DSC 1. Limited oxygen index was test with Tarlin Scientific Corporation Stanton Redcroft FAT.

2.1 Sample preparation

2.1.1 Synthesis of dicyandiamide ethylene phosphate (CEP)

In a 500 ml glass four neck round bottom flask equipped with a mechanical stirrer, a thermometer, a circumference condenser, N_2 inlet and heating bath, Dicyandiamide (0.3mol) and $POCl_3$ (0.3mol) were mixed. The temperature was increased to appointed temperature. And then glycol (0.28mol) was added in. The react mixture was keep at this temperature for 2h while stirrer was open. The mixture was washed with water and filtered until pH value of filtrate come to 7. The product was dried to constant weight at 40℃ *in vacuo*. The final product, white solid powder, was obtained (yield: 85%).

2.1.2 Synthesis of melamine dimethyl phosphate (MMP)

In a 500 ml glass four neck round bottom flask equipped with a mechanical stirrer, a thermometer, a circumference condenser, N_2 inlet and heating bath, dimethyl phosphorochloridate (0.3mol)， 100ml carbon tetrachloride and melamine (0.3mol) were added. The temperature was increased to appointed temperature. The react mixture was keep at this temperature for 4h while stirrer was open. The mixture was washed with water and filtered until pH value of filtrate come to 7. The product was dried to constant weight at 60℃ *in vacuo*. The final product, white solid powder, was obtained (yield: 83%);

2.1.3 Preparation of flame retardant PA6 chip

The FRs was mixed with caprolactam at the loading varying from 0.6-4% by high shear mixing emulsification machine, respectively. The mixture was added into high pressure reactor and took the progress of ring open polymerization for 1h at 230℃ under the pressure less of 0.5MPa. Then the temperature was raised to 265℃, and pressure was released, the polymerization was maintained for 6h. The polymer was dried under constant pressure at 80℃ for 24h and 105℃ *in vacuo.* The FR PA6 chip was obtained. Non-modified PA6 was made at the same procedure.

3 results and discussion

3.1 Synthesis of CEP and MMP

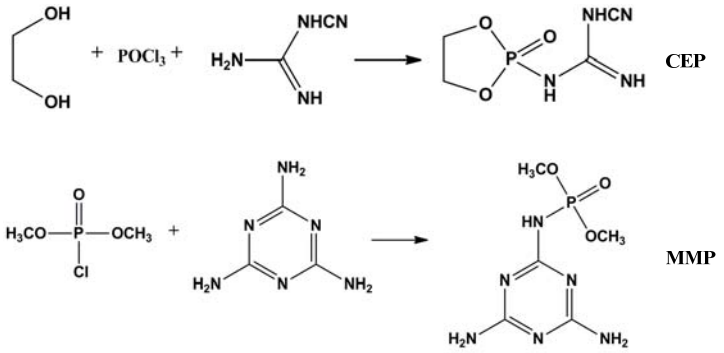
The synthesis route for CEP and MMP is presented in Scheme 1.

3.1.1 Synthesis of CEP

The main influence factor of this reaction is temperature. Higher temperature brings higher yields but darken the color of CEP, the influence of temperature was list in table 1. Yield at 70℃ is not as good as which at 80℃, but color of prior is much better than later one. For the purpose of keeping higher yield and remaining the color not too dark to deteriorate PA6 behavior, reaction temperature was chosen between 60 and 70℃.

Temperature(℃)	**30**	**40**	**50**	**60**	**70**	**80**	**90**
Yield（%）	-	52	63	84	88	90	90
Color	-	white	white	light yellow	yellow	brown	black

Table 1. The influence of temperature on the yields and color of CEP



Scheme 1. Synthesis route of CEP and MMP

3.1.2 Synthesis of MMP

Figure 2 shows changing of yield varying from reaction time at selected reaction temperature. It can be seen that best yield 83% was given at 60℃ for more than 3h. Lower temperature made reaction hard to take place. It might be result in lower temperature made reaction rate too slow to complete. At the same time, volatility of raw material decreased yield of product. As the temperature raised to higher than 70℃, there might be another problem that reaction was too active to control. Moreover, a mass of HCl could bring some raw material out from reaction system. It decreased yield of product likewise.

3.2 Characterization of CEP and MMP

The experimental mass fraction of CEP obtained by elemental analysis (calculated): P=16.1% (16.3%); N=29.6% (29.5%); O=25.5% (25.3); C=25.6% (25.3%); H=3.4% (3.7%). Instrumental analysis of CEP was carried out using Fourier transform infrared spectroscopy (FTIR). FTIR (KBr) (cm^{-1}): 1243 (vs, P=O), 975 (vs, P–O–C), 1400 (P-N), 3161, 3353 (N-H), 2361 (>C=N-). The experimental mass fraction of MMP obtained by elemental analysis (calculated): P=13.1% (13.2%); N=36.1% (35.9%); O=20.8% (20.5); C=25.4% (25.6%); H=4.6% (4.7%). Instrumental analysis of MMP was carried out using Fourier transform infrared spectroscopy (FTIR). FTIR (KBr) (cm^{-1}): 1270 (vs, P=O), 899 (vs, P–O–C), 1400 (P-N), 3130, 3380 (N-H).

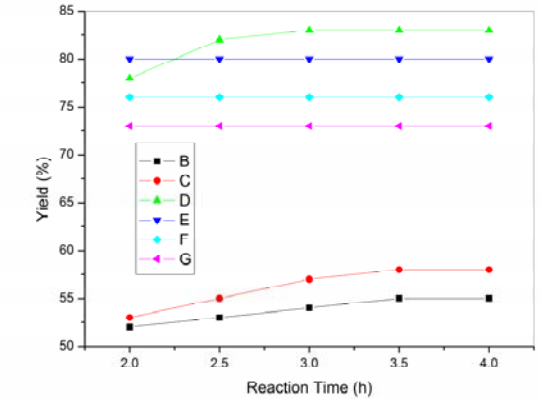


Figure 2. Yield changed with reaction time at varied temperature

(Note: reaction temperature, B:50-55℃； C: 55-60℃； D: 60-65℃； E: 65-70 ℃； F:75-80℃； G:80-85℃)

3.3 Flame retardant of PA6/FR composites.

Figure 3 show LOI value of PA6 modified with CEP and MMP. It can be seen that LOI of composite come to 27% when 3% of MMP was added in and CEP at 3.5% loading. The composite was so called nonflammable material, which can self-extinguish in air atmosphere. Comparing these two kinds of FRs, MMP raises LOI quickly at low add amount, but goes up slowly at higher loading than 3%. On the other hand, CEP present well at high FR loading. Which rise up to 27% at 3.5% loading and 29% at 4% loading. In terms of flame retardancy, MMP is better than CEP for PA6.

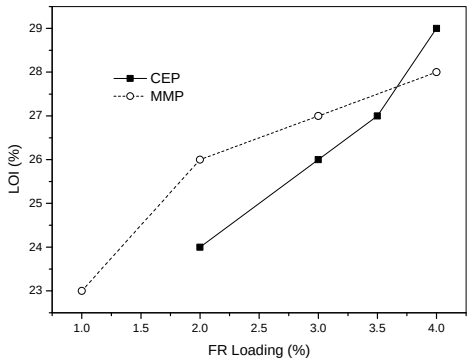


Figure 3. LOI value of PA6 modified by CEP and MMP

3.4 Thermal stability of PA6/FR composites.

Figure 4 show the TGA and differential weight loss DTG curve of FRPA6. The initial decomposition temperature (IDT) is characterized as the temperature at which the sample achieves a 5% weight loss. The temperature of 10% weight loss (T10) was also recorded. Table 2 reveals the TG data such as: Tonset, the initial temperatures thermal degradation; Tpeak, the temperature corresponding to the maximum degradation rate, Tendset, the final temperature at which the degradation process for each stage ends, and weight of the samples after the end of a decomposition process.

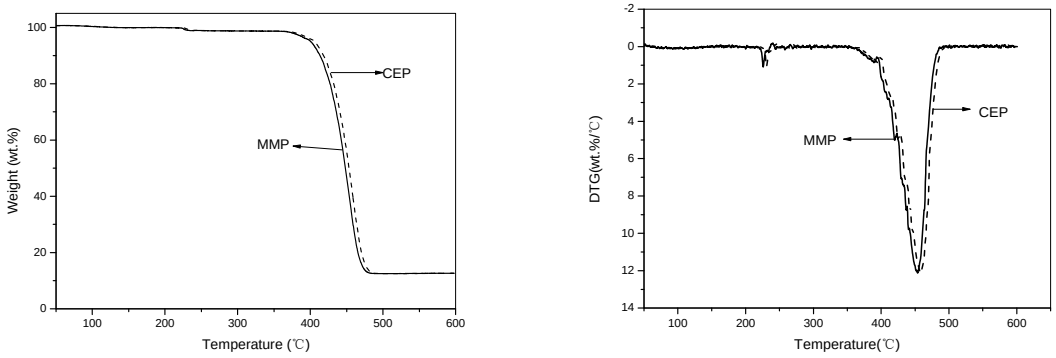


Figure 4. TGA and DTG curves of PA6/FR in Nitrogen

Sample	$T_{On\text{-}set}$	T_{10}	T_{Peak}	T_{Endset}	W_{Endset}
PA6[a]	340.83	350.24	352.13	356.67	3.55
MMP/PA6	400.51	413.42	426.97	484.16	12.65
CEP/PA6	400.92	413.69	427.31	483.33	13.06

Table 2. Thermal analysis data of PA6
(Note: a, the data come from another study in our laboratory, see reference [11])

From figure 4 and table 2, it can be found that the T_{Onset} of PA6 was postponed for about 60 centigrade. That is to say, PA6/FR composite can undergo much higher temperature than virgin PA6. At temperature lower than 400 centigrade, FRPA6 presents good flame retardancy. The temperature of decomposition region was enlarged to 85 rather than 16 centigrade of virgin PA6. At the end of decomposition process, residua of FRPA6 are higher than that PA6 left behind.

4. Conclusion

The synthesis of phosphorus-nitrogen containing flame retardant CEP and MMP were performed. The influence factors on the yields were considered. The structure of CEP and MMP were confirmed by FTIR and element analysis. These two FRs were incorporated in PA6 by in-situ polymerization. TGA and DTG analysis proved thermal information about the PA6/FR composite. The thermal stability of composite is better than virgin PA6. MMP presents good flame retardancy at low adding amount, but CEP show better property at higher loading than 3.5%.

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