Synthesis, thermal stability, and flame retardancy of PA66, treated with dichlorophenylphosphine derivatives

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ABSTRACT
Synthesis, thermal stability, and flame retardancy of PA66, treated with derivatives of dichlorophenylphosphine, are reported. With an aim to improve the thermal stability and flame retardancy of PA66, along with improving its consistency, several new derivatives of dichlorophenylphosphine, namely bis-(4-carboxyanilino) phenyl phosphamide (BNPO), N-benzoic acid-(ethyl-N-benzoic acid formamide) phosphamide (NENP), poly-N-aniline-phenyl phosphamide (DPPD), and bis-N-benzoguanamine-phenyl phosphamide (MCPO), were synthesized, which resulted in end amino or carboxyl. FTIR, 1H NMR, MS, and elemental analysis confirmed the chemical structures of the synthesized flame retardants. Interestingly, thermal stabilities and flame retardancies of PA66 improved, however, the intrinsic viscosities ($\eta$) and viscosity average molecular weights ($M_\eta$) decreased with grafting of the flame retardants. Moreover, the consistency was overcome conformingly using SEM without interfacial effect.

KEYWORDS
synthesis; thermal stability; flame retardancy; phosphorus; nitrogen

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INTRODUCTION
Polyamide 66 (PA66) is prepared by the copolymerization of amines and carboxylic acids and has either amine, carboxyl, or both of them as end groups. It is an engineering plastic, which is versatile and is endowed with excellent mechanical properties and good processability. Hence, it is widely used in engineering applications, due to its polar and polymorphic nature. However, the applications of PA66 are highly limited, due to flammability of virgin PA66. Methods to improve flame retardancy of PA66 include, preparation of PA66 composites by adding melamine cyanurate, red phosphorous, or clay as flame retardants, as reported by Gijsman, Jou, and Rath [3].

In recent years, intumescent flame retardants (IFR) have been widely used in flammable polymers. Compared to conventional flame retardants, several satisfactory advantages of IFR are as follows: they have high efficiency, they are halogen free, and environmentally friendly. Many studies reported IFR to be a mixture of three components, namely an acid source, a carbon source, or blowing agent. The acid source, essentially comprises polyphosphoric acid, which promotes the formation of an impermeable char layer, in the process of heating. The carbon source gets dehydrated by the acid, which then gets released from the acid source and forms a semisolid and insulating carbonaceous layer on the polymeric surface. The blowing agent expands to form a multicellular char by releasing nonflammable gases.

However, the conventional IFR still has some disadvantages. For instance, to achieve a high level of flame retardancy, a certain amount of additive loading was necessary. Poor consistency and non-uniform dispersity were unavoidably with flame-retardant additives. The mechanical properties of the flame-retardant material were compromised, especially the impact strength decreased significantly. Moreover, the common flame retardants, which cannot withstand temperature above 200 °C, could not be incorporated into engineering plastics. In recent decades, several novel IFRs, which contained a combination of an acid source, carbon source, or blowing agents together to form a complex compound were prepared to improve the thermal stability of flame retardants, source, carbon source, or blowing agents.

As mentioned above, the consistency and dispersity of flame-retardant PA66 was improved by incorporating flame-retardant additives, which included several new derivatives of dichlorophenylphosphine, namely bis-(4-carboxyanilino) phenyl phosphamide (BNPO), N-benzoic acid-(ethyl-N-benzoic acid formamide) phosphamide...
(NENP), poly-N-aniline-phenyl phosphamide (DPPD), and bis-N-benzoguanamine-phenyl phosphamide (MCPO). These additives polymerized with PA66 prepolymer, which resulted in end amino or carboxyl groups. Effective flame-retardant elements, such as phosphorus and nitrogen, were incorporated into the PA66 main chain, thereby improving the consistency and dispersity of flame-retardant additives.

**Synthesis of BNPO**

BNPO was synthesized by acylation reaction of aminobenzoic acid (27.00 g, 0.20 mol) with phenylphosphonic dichloride (19.50 g, 0.10 mol) at 80 °C and at a stirring speed of 200 rpm for 4 h. The yield reached 91% after filtration and drying under 100 °C for 12 h.

**Synthesis of NENP**

NENP was obtained by a two-step chemical reaction. First, dichlorophenylphosphine (19.50 g, 0.10 mol) in a dry addition funnel (100 mL), was added dropwise to a three round bottom flask with acrylic acid (9.36 g, 0.13 mol), over 2 h at 90 °C. The temperature was then raised to 120 °C gradually over a period of 4 h. This was followed by addition of aminobenzoic acid (27.00 g, 0.20 mol) to the colorless solution obtained above. The mixture was stirred at a speed of 200 rpm and maintained at 80 °C for 4 h. Finally, the white powder was obtained after filtration and drying under 100 °C for 12 h, and the yield reached 84%.

**Synthesis of DPPD**

DPPD was prepared as follows: phenylphosphonic dichloride (5.850 g, 0.030 mol) was added drop wise to a mixture of 1,4-benzenediamine (3.348 g, 0.031 mol) and triethylamine (6.060 g, 0.060 mol) at 5 °C, and the mixture was carefully maintained at 80 °C for another 5 h. Then, the final product was acquired through filtering and drying under 100 °C for 12 h, and the yield reached 87%.

**Synthesis of MCPO**

MCPO was obtained by the reaction of phenylphosphonic dichloride (9.75 g, 0.05 mol) and benzoguanamine (18.70 g, 0.10 mol) at 80 °C at a stirring speed of 200 rpm for 8 h. Following this, the mixture was processed by filtering and drying under 100 °C for 12 h, and the yield reached 89%.

**Polymerization of FR PA66**

Flame-retardant PA66 (FR PA66) was obtained by polymerization, in which 5 wt.% of the PA66 prepolymer was replaced with an equivalent amount of BNPO, NENP, DPPD, and MCPO under reaction conditions of 1.7 MPa, 210 °C and 0.1 MPa, 280 °C, respectively. The samples of FR PA66 containing BNPO, NENP, DPPD, and MCPO were designated as FR-1, FR-2, FR-3, and FR-4, respectively.

**Results and discussion**

**Characteristic of BNPO**

The route for BNPO synthesis is shown in Scheme 1, the FTIR data are shown in Figure 1. The appearance of new transmittance peak at 3306 cm⁻¹ (P–N–H) and the disappearance peak at 565 cm⁻¹ (P–Cl) of DCPO indicated the completion of the acylation reaction.[14] The 1H NMR results (Table 1 and Figure 5) showed appearance of signals at δ = 10.2 (carboxyl), 7.5–8 (benzene ring), 3.4 (NH) ppm in case of BNPO. From the results of mass spectra (MS)
in Figure 6, it can be clearly seen that the molecular weight of BNPO was 396. And the elemental analysis showed that the measured values were in close agreement with the theoretical values, listed in Table 2. Thus, the structure of BNPO was confirmed by FTIR, 1H NMR, MS, and elemental analysis.

**Characteristic of NENP**

The route for NENP synthesis is shown in Scheme 2. The Fourier transform infrared spectroscopy data are shown in Figure 2. FTIR spectra of NENP showed new characteristic peaks at 3306 cm⁻¹ (P–N–H), 1265 cm⁻¹ (CN), 1180 cm⁻¹ (PO), which confirmed its structure in consideration of the disappearance peak at 565 cm⁻¹ (P–Cl) of DCPP.[15] In case of NENP, the 1H NMR signals appeared at 10.2 (carboxyl), 7.6–8 (benzene ring), 3.4 (NH), 2.6 (CH) ppm which were noted in Table 1 and Figure 5. And Figure 6 showed that the molecular weight of NENP tested by MS was 452. Thus, from the FTIR, 1H NMR, MS, and elemental analysis listed in Table 2, the structure of NENP was confirmed.

**Characteristic of DPPD**

The route for DPPD synthesis is shown in Scheme 3, and Figure 3 shows the FTIR spectrum. The FTIR of DPPD
MCPO, the $^1$H NMR signals (Figure 5) appeared at 11.2 (NH$_2$), 6.5–8 (benzene ring), 3.5 (NH) ppm. The molecular weight of MCPO was 496 which was calculated from the result of MS in Figure 6. Thus, the structure of MCPO was confirmed by FTIR, $^1$H NMR, MS, and elemental analysis listed in Table 2 which showed the measured values were in close agreement with the theoretical values.

Thermal stability of FR PA66

The synthesis route of PA66 prepolymer is shown in Scheme 5, and the polymerization process of FR PA66 is shown in Scheme 6. The intrinsic viscosities ($\eta$), viscosity average molecular weights ($M_\eta$), and melt flow indexes (MFI) of FR PA66 are listed in Table 3.

The TGA curves of PA66 are shown in Figure 7. Under nitrogen atmosphere and at ambient pressure, the initial decomposition temperatures ($T_{\text{init}}$) of FR-2 (347 °C) and FR-3 (338 °C) were found to be lower than those of pure PA66 (385 °C). But as the contents of NENP and DPPD prepolymers reached 5 wt.%, respectively, the peak temperatures of weight loss ($T_{\text{max}}$) increased by 19 and 34 °C, respectively, as compared to pure PA66 (437 °C) (Figure 8). Therefore, the rate of mass loss reduced remarkably. The thermal behavior of FR-PA66 in nitrogen atmosphere indicated that the incorporation of NENP and DPPD improved the thermal stability of PA66, although the initial decomposition temperatures decreased.

On the other hand, the $T_{\text{init}}$ of FR-1 (421 °C) and FR-4 (410 °C) were higher than pure PA66 (Figure 7) when the contents of BNPO and MCPO prepolymers reached 5 wt.%, and the $T_{\text{max}}$ increased by 35 and 37 °C, respectively, compared to 437 °C for pure PA66 (Figure 8). Thus, the thermal behavior of the FR-PA66 improved significantly in nitrogen atmosphere after addition of BNPO and MCPO. Interestingly, there were two heat release peaks of FR-3.
The DSC curves of FR-PA66 obtained under nitrogen atmosphere are shown in Figures 9 and 10. Table 4 lists the DSC data of FR-PA66. The incorporation of flame retardants decreased the melting point (\(T_m\)) and glass transition temperature (\(T_g\)), probably due to the barrier effect of rigid benzene rings in the NENP chains. With an increase in the number of benzene rings, the barrier effect obviously restricted the movement of the PA66 chains, thereby compared those of FR-1, FR-2, and FR-4. This may be due to the different structures of DPPD which contained short molecular chain. The breakage of DPPD chain firstly took place and released PO-free radicals when FR-3 was heated, then the reaction between PO-free radicals and PA66 chain segment was triggered, leading to the secondary heat release peak.

Based on the TGA and DTG results, the improved thermal stability could be probably attributed to the flame retardants containing benzene rings, which possess excellent heat resistance compared to CH\(_2\) chains. A conjugated system with a strong electron withdrawing ability is formed in the process of thermal decomposition of benzene rings around the P=O group. This requires more heat absorption for rendering the stable system disordered.[16] At the same time, the PO free radicals released from aryl phosphine oxide were capable of increasing the degree of crosslinking in PA66, in the process of thermal decomposition. Therefore, the heat resistance of PA66 chain segments improved.[17] The details of TGA analysis are listed in Table 4.

**Scheme 5.** The synthetic route of PA66 prepolymer.

**Scheme 6.** The polymerization of flame retarded PA66.

The DSC curves of FR-PA66 obtained under nitrogen atmosphere are shown in Figures 9 and 10. Table 4 lists the DSC data of FR-PA66. The incorporation of flame retardants decreased the melting point (\(T_m\)) and glass transition temperature (\(T_g\)), probably due to the barrier effect of rigid benzene rings in the NENP chains. With an increase in the number of benzene rings, the barrier effect obviously restricted the movement of the PA66 chains, thereby
UL-94 ratings were found to be higher with relatively higher contents of flame retardants. Moderate contents of BNPO, NENP, DPPD, and MCPO prepolymer (5 wt.%) improved the highest LOI values. This explains the N–P synergistic effects between P and N atoms in the main chains of FR-PA66. In general, N–P synergistic action could be explained by the interaction between P and N flame retardants, producing macromolecular substances with higher thermal stabilities, to further consolidate the condensed phase.[19] V-0 ratings were achieved when BNPO, NENP, DPPD, and MCPO prepolymer contents reached 5 wt.%. The above observed phenomenon can be explained by the fact that flame retardancy promotes the formation of nitrogen-containing nonflammable gases. This blocks the transfer of combustion improver and flammability gas, and effectively shortens the after-flame time. Additionally, the phosphorus element in flame retardant can make up for the lack of the condensed phase composition. Therefore, decreasing the rate of the crystallization of PA66 matrix. [18] Hence, $T_m$ and $T_g$ especially of DPPD flame-retardant PA66 decreased.

**Flame retardancy of FR PA66**

The results of limiting oxygen index (LOI) and horizontal vertical combustion tests (UL94) using 3.2-mm-thick FR-PA66 polymers are listed in Table 5. LOI values and

**Table 3.** The physical constant of PA66.

| Samples    | Intrinsic viscosity [$\eta$] (dl/g) | Viscosity average (molecular weight/$M_\eta$) | Melt flow index (g/10 min) |
|------------|-----------------------------------|---------------------------------------------|----------------------------|
| Pure PA66  | 106.1                             | 13,960                                      | 40                         |
| FR-1       | 103.5                             | 13,487                                      | 44                         |
| FR-2       | 105.1                             | 13,778                                      | 41                         |
| FR-3       | 102.3                             | 13,271                                      | 45                         |
| FR-4       | 104.4                             | 13,650                                      | 43                         |

**Figure 7.** The DSC curves of FR PA66 (cooling).

**Figure 8.** The combustion pictures of FR PA66.

**Figure 9.** The fracture surfaces of FR PA66.

**Figure 10.** The DSC curves of FR PA66 (cooling).
To study the consistency of FR-PA66, modified by BNPO, NENP, DPPD, and MCPO, the fracture surfaces were studied by scanning electron microscopy (SEM). The SEM images shown in Figure 12 clearly indicated that the FR-PA66 had an increase in the flame-retardant content increases the melt viscosity and decreases the dropping rate. It effectively blocks the transfer of internal heat of the melt, drips to the surface, and reduces the flammability of the melt drips.[20] The pictures of combustion FR-PA66 are shown in Figure 11.

### Table 4. The details of TGA and DSC results.

| Samples | \( T_{\text{init}} \) (°C) | \( T_{\text{max}} \) (°C) | \( T_{\text{m}} \) (°C) | \( T_{\text{g}} \) (°C) |
|---------|-----------------|-----------------|-----------------|-----------------|
| Pure PA66 | 385 | 437 | 266 | 231 |
| FR-1   | 421 | 472 | 263 | 229 |
| FR-2   | 347 | 456 | 250 | 219 |
| FR-3   | 338 | 471 | 235 | 190 |
| FR-4   | 410 | 474 | 262 | 224 |

### Table 5. The Flame retardancy properties of PA66 resin.

| Samples | LOI | UL94 | Melt drips | Self-extinguish/s |
|---------|-----|------|-------------|-------------------|
| Pure PA66 | 24  | V-2  | Yes         | 3                 |
| FR-1    | 26  | V-0  | Yes         | 6                 |
| FR-2    | 28  | V-0  | No          | 7                 |
| FR-3    | 29  | V-0  | No drips    | 5                 |
| FR-4    | 27  | V-0  | No drips    | 7                 |

**Figure 11.** The combustion pictures of FR PA66.
PA66 was improved after incorporation of BNPO, NENP, DPPD, and MCPO. The flame retardancy of PA66 reached V-0 and crossed 27% (LOI), which meant that the FR-PA66 was not inflammable. The SEM results also showed how the poor consistency and dispersity of FR PA66, containing flame-retardant additives, was overcome by polymerization reaction between PA66 prepolymer and flame retardants.

**Conclusions**

In conclusion, the synthesis, thermal stability, and flame-retardant properties of PA66, treated with derivatives of dichlorophenylphosphine, namely bis-(4-carboxyanilino) phenyl phosphamide (BNPO), N-benzoic acid-(ethyl-N-benzoic acid formamide) phosphamide (NENP), poly-N-aniline-phenyl phosphamide (DPPD), and bis-N-benzoguanamine-phenyl phosphamide (MCPO), have been discussed. The chemical structures of BNPO, NENP, DPPD, and MCPO were confirmed by FTIR, NMR, MS, and element analysis, and the characteristic P–N–H bonds in the compounds were verified. The results of TGA and DSC demonstrated that the thermal stability of PA66 was improved after incorporation of BNPO, NENP, DPPD, and MCPO. The flame retardancy of PA66 reached V-0 and crossed 27% (LOI), which meant that the FR-PA66 was not inflammable. The SEM results also showed how the poor consistency and dispersity of FR PA66, containing flame-retardant additives, was overcome by polymerization reaction between PA66 prepolymer and flame retardants.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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