



Skeletally Modified Polyamide Flame Retardant Coatings

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Abstract

The use of polyamide coatings for electrical applications is restricted mainly because of its inadequate flame retardant behaviour. In order to improve its flame retardant behaviour, polyamide is modified by incorporating phosphorus moiety in its backbone. The structure of the phosphorus and poly amide was confirmed by infrared spectroscopy (FT-IR), NMR, thermo gravimetric analysis (TGA), differential scanning calorimetry (DSC), UL-94 vertical burning tests and char residue tests. From the results obtained, we observe that the incorporation of phosphorus into the polyamide enhances its thermal stability and flame retardancy.

Keywords

Flame-Retardant Coatings, Polyamide-Phosphorus, Thermal Stability, UL-94

Subject Areas: Green Chemistry, High Polymer Chemistry, Organic Chemistry, Organic Polymer Materials

1. Introduction

Nylon (polyamide) was invented in 1928 by Wallace Carothers (DuPont) and it is considered to be the first engineering thermoplastic. It is one of many hetero-chain thermoplastics, which have atoms other than C in the chain. Nylon is created when a condensation reaction occurs between amino acids, dibasic acids and diamines.

Nylon is commonly used in the production of tire cords, rope, belts, filter cloths, sports equipment and bristles. It is particularly useful when machined into bearings, gears, rollers and thread guides. Though polyamide has good mechanical properties such as tensile strength, flexural strength and impact strength, its use in electrical industry has been restricted due to its inferior flame retardancy [1]-[4].

Polyamide can be made flame retardant either by the use of flame-retardant curatives or by incorporating reactive flame-retardant additives in the polymer backbone. Recently, researchers have mainly focused on the

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latter because the flame-retardants when chemically incorporated into the polymer structure result in advantages such as more stability and the less gas emission during either high temperature processing or burning. Simultaneously, the reactive approach can minimize negative impact upon physical and mechanical properties of the polymer. Phosphorus containing flame-retardants are preferably chosen, as they are more eco-friendly than the halogen containing ones [5]-[18].

Commercial polyamide 6,6 was prepared by poly-condensation reaction of hexamethylene diamine and adipic acid [1]. In this work, phosphorus is incorporated into the backbone of the polyamide by reacting phosphorus diamine with adipic acid in order to increase the flame retardant behaviour. It is characterized by means of IR, TGA, DSC and flame retardancy tests to evaluate its suitability for electrical applications.

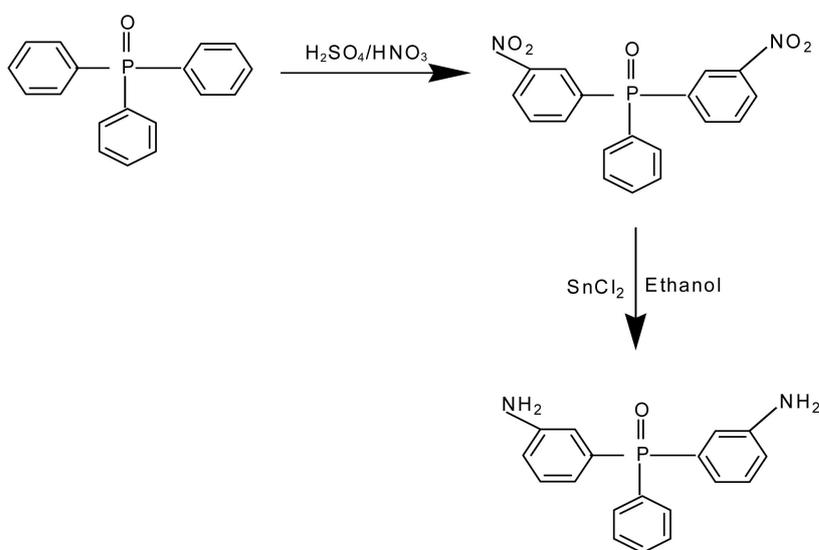
2. Experimental

2.1. Materials

Triphenyl phosphine oxide and Tin(II) chloride anhydrous were purchased from Alfa-Aesar (USA). Sulfuric acid, nitric acid, chloroform, ethanol, hydrochloric acid were purchased from SRL (India). Adipic acid was purchased from Alfa chem (USA).

2.2. Preparation of Phosphorus Diamine

Phosphorus diamine was synthesized according to the reported procedure [19]. The steps involved in the synthesis are shown in **Scheme 1**. Triphenyl phosphine oxide (27.8 g) was placed in a 500 ml round-bottomed flask equipped with stirrer and nitrogen atmosphere and 200 ml of 96% sulfuric acid was added. The reactant was dissolved and the reaction system was cooled to -5°C using freezing mixture. A solution of 14.5 g of fuming nitric acid in 100 ml of sulfuric acid was added drop wise over a period of 2 hrs. The reaction system was kept at room temperature for another 8 hrs. The reaction solution was hydrolyzed over 2 litres of ice. After the ice melted, the mixture was extracted with chloroform and washed with sodium bicarbonate aqueous solution until neutral pH. The solvent was removed and the solid residue was recrystallised from absolute ethanol. Bis (3-nitrophenyl) phenyl phosphine oxide was obtained. Then it was placed in a 1000 ml round bottom flask with 180 g of powdered anhydrous Tin(II) chloride. A solution of 200 ml fuming hydrochloric acid in 400 ml ethanol was introduced into the flask. The reaction mixture was stirred at room temperature for 5 hrs. The solution was concentrated and then neutralized with 25% NaOH aqueous solution. The obtained solution was extracted with chloroform and concentrated under reduced pressure. The solid obtained was recrystallised from dichloromethane to give the pure product.



Scheme 1. Synthesis of phosphorus diamine.

2.3. Synthesis of Polyamide 6,6

The phosphorus diamine obtained is made to react with the adipic acid by a polycondensation reaction to obtain polyamide with phosphorus moiety incorporated in the backbone [20]. The reaction is depicted in **Scheme 2**. Equal amounts of adipic acid and phosphorus diamine are taken and dissolved in a suitable solvent and stirring is continued until product is formed.

Then it is filtered using suitable solvent with the elimination of water molecules and subjected to drying and the product obtained in the powder form is weighed. Thus modified polyamide 6,6 is prepared subjected to various characterizations such as TGA, DSC and flame retardancy tests.

2.4. Characterization

The structure of polyamide was determined by IR, which was performed on Perkin-Elmer 781 infrared spectrometer using KBr pellets for solid samples. Glass transition temperature (T_g) of the samples was determined using DSC 2910 (TA Instruments USA) in the temperature range of room temperature to 200°C at a heating rate of 10°C min⁻¹. Thermal gravimetric analysis (TGA) was carried out using Thermal analyst 2000 (TA Instruments USA) at a heating rate of 10°C min⁻¹ in the temperature range from room temperature to 900°C. UL94 vertical burning tests were carried out for flame retardancy.

3. Results and Discussions

3.1. Spectral Analysis

Phosphorus diamine was synthesized and the structure was determined by IR spectrum. **Figure 1** shows the IR spectrum of phosphorus diamine. The peak at 1205.48 cm⁻¹ indicates the formation of P-Ph. The absorption peak for P=O and NH₂ were observed at 1452.05 cm⁻¹ and 3473.97 cm⁻¹ respectively [10].

Polyamide modified with phosphorus backbone was synthesized and structure was determined using IR spectrum depicted in **Figure 2**. The presence of P = O is observed in 1197.84 cm⁻¹, -NH stretching was found to be 3558.92 cm⁻¹ and the absorption peak of -COOH was found to be 1703.78 cm⁻¹. This confirms the presence of polyamide.

3.2. Thermal Gravimetric Analysis (TGA)

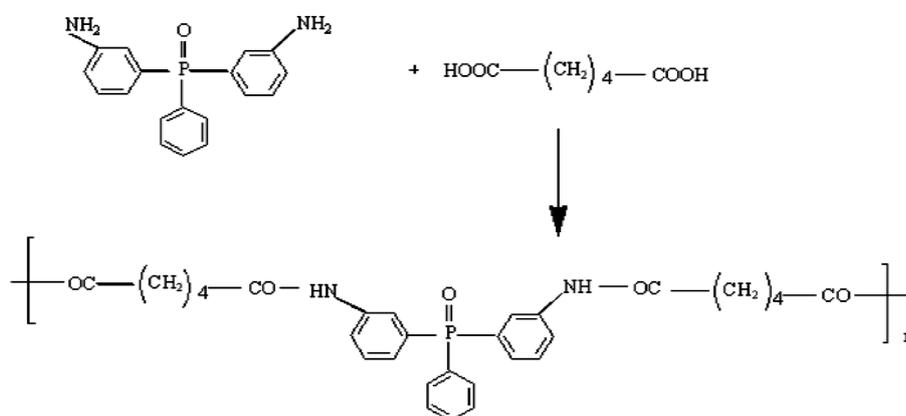
TGA studies of polyamide with phosphorus backbone was carried out to assess its thermal stability and char protecting nature. The thermogram of phosphorus modified polyamide as seen in **Figure 3**. Exhibits a double degradation pattern involving initial degradation at a temperature 94.2°C followed by a second degradation at 452°C respectively. The initial degradation at 94.2°C may be attributed to the decomposition of phosphate group, which forms a self healing layer that prevents further degradation of the material. Then second degradation takes place at 452°C indicating the thermal degradation temperature of the material. The comparison table of Glass Transition temperature (T_g) is given in **Table 1**. Furthermore, the char residue of phosphorus modified polyamide was found to be (60.85%) on the higher side, indicating the superior flame retardant behaviour of this material than nylon and other phosphorus based compounds reported by Van Krevlan. This excellent flame retardant nature of this material may be due to char protecting nature of the phosphorus moiety [21].

3.3. UL-94 Flame Retardancy Tests

Unmodified polyamide and phosphorus modified polyamide samples prepared as per UL-94 standard were tested by UL-94 vertical burning test [22] to evaluate their flame retardancy. The results are depicted in **Table 2**. The ratings are given for samples by subjecting them to vertical burning for 30 secs and noting down the time taken for each sample to sustain burning even after removing them from the flame. It is observed that phosphorus modified polyamide exhibits better flame retardant behaviour (V0 rating) than unmodified polyamide (V2 rating) indicating the superior char protecting nature of phosphorus.

3.4. Limited Oxygen Index vs Char Residue

Van Krevlan [23] proposed a correlation between char residue and limited oxygen index as seen in **Figure 4**. From this correlation, the limiting oxygen index value and flame retarding behaviour of materials can be



Scheme 2. Synthesis of modified polyamide.

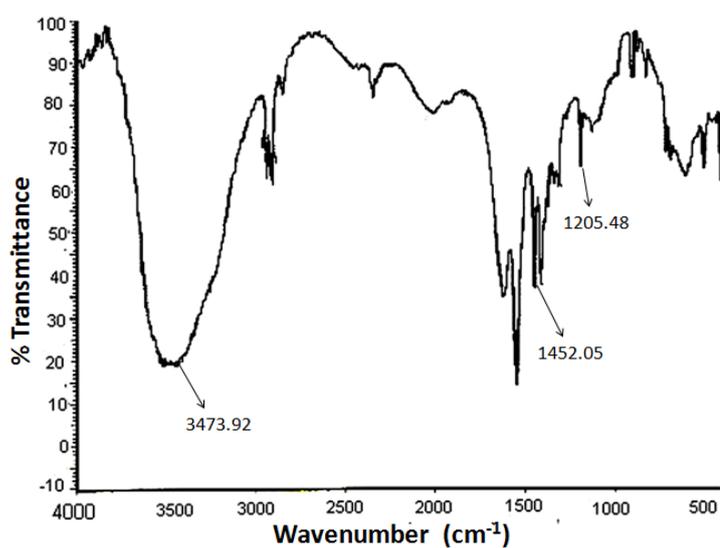


Figure 1. IR spectrum of phosphorus diamine.

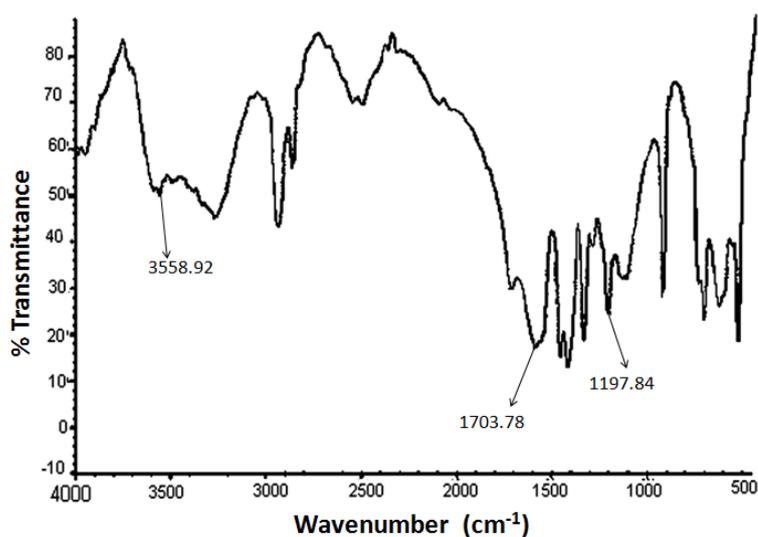


Figure 2. IR spectrum of modified polyamide.

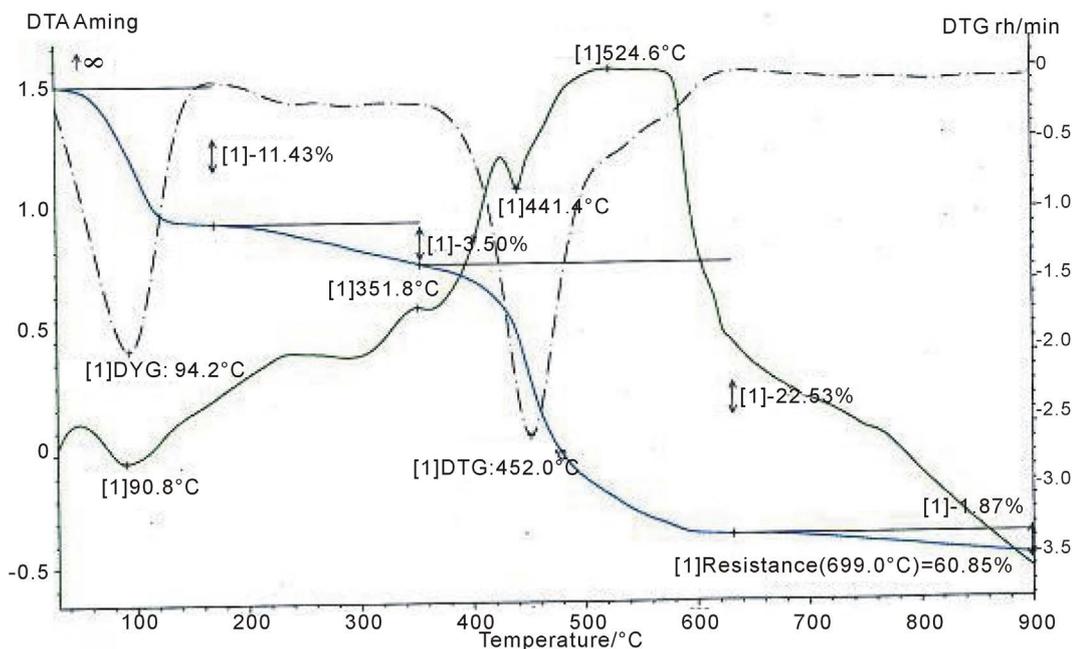


Figure 3. TGA analysis.

Table 1. Comparison of “Tg” values.

Material	Tg
Polyamide (commercial)	47°C - 50°C
Polyamide (with phosphorus backbone)	36.7°C

Table 2. UL-94 vertical burning tests ratings.

Material	Time	Rating	Remarks
Polyamide (commercial)	30 sec	V2	Flammable
Polyamide (with phosphorus backbone)	10 sec	V0	Flame retardant

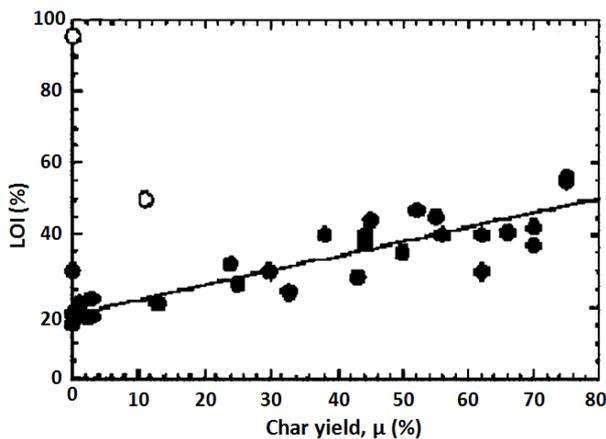
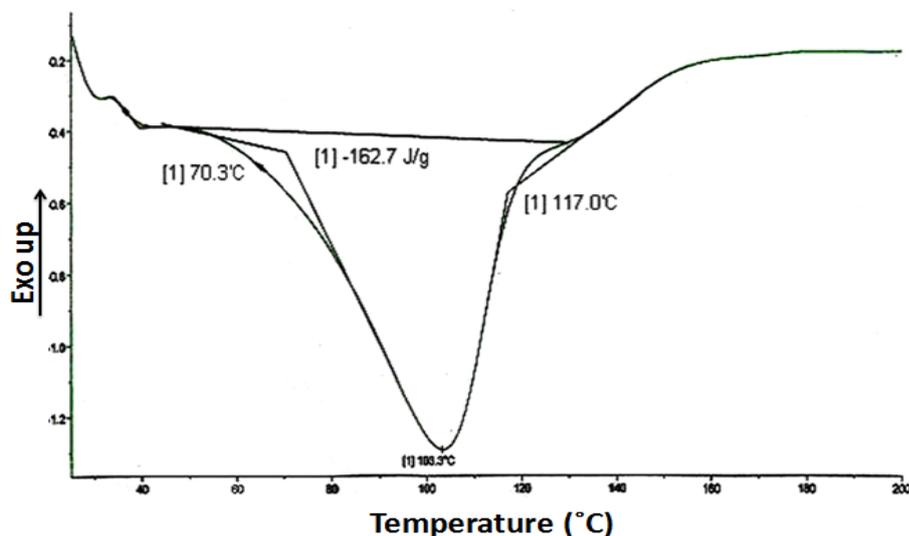


Figure 4. Correlation between char residue and limited oxygen index.

determined. From the TGA data the char residue of phosphorus modified polyamide is found and correspondingly the limiting oxygen index was reported to be 42. Higher the limited oxygen index value higher will be the flame retardancy.

Table 3. Determination of limited oxygen index.

Material	Limited oxygen index (LOI)
Polyamide (commercial)	18 - 20
Polyamide (with phosphorus backbone)	42

**Figure 5.** DSC analysis.

From the results (**Table 3**), it is concluded that the phosphorus-modified polyamide has superior flame retardancy than unmodified polyamide and materials that are currently used as flame-retardants.

3.5. DSC Analysis

DSC thermograms of unmodified nylon and phosphorus modified polyamide are depicted in **Figure 5**. From the thermograms, we observe that phosphorus modified polyamide exhibits lower Tg value than the unmodified polyamide (**Table 3**). This decrease in Tg value may be attributed to the presence of phosphorus which acts as an internal plasticizer [24].

4. Conclusion

Polyamide is made from flame retardant coating by reacting phosphorus diamine with adipic acid to get phosphorus modified polyamide. Spectral analysis was done using IR. Thermal stability, char nature, flame retardancy and Tg were evaluated by TGA, UL-94 vertical burning tests and DSC studies respectively. From the results, it can be seen that phosphorus modified polyamide has better thermal stability and flame retardancy. The data resulted from various studies support this observation. Hence, it is concluded that phosphorus-modified polyamide having improved thermal stability and flame retardancy may be used as flame retardant coating in electrical applications for better performance.

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