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Synthesis of non halogenated flame retardant for polypropylene

Sanjay D Jadhav**Abstract**

Recent patent and literature found a growing interest in synthesis of non-halogenated flame retardants due to the environmental consideration. The present work is synthesizing non-halogenated ecofriendly flame retardant for polypropylene. The polypropylene are highly flammable at room temperature. The syntheses of flame retardant enhance the LOI value of polypropylene & seize the antidripping property of polymer. The FR compound have found broad applications because of there good thermal stability, high efficiency & low volatility.

Keywords: flame retardant, polypropylene, non-halogenated flame retardant, thermal stability

1. Introduction

Flame retardant has very important role to play in today's science and technological field and considering various aspect and application areas for the same. The key & main good aspect of polypropylene is its ability to be used in a wide range of fibrous forms & non-oven forms because of its characteristic property. The low melting point of polypropylene (160-170°C) is an advantage in many non-ovens processing step. Polypropylene is extremely difficult to retard^[1-3]. Pure polypropylene is highly flammable at room temperature & leaves almost no char^[4]. Limited application of polypropylene is due to its flammability & low limiting oxygen index value 17.45^[5].

The world consumption of polyolefins and, more specifically polypropylene (PP), represented more than 50 million tons in 2009 and is estimated to have had an average annual growth rate of 4% for the period from 2010 to 2020^[6]. In contrast to other polymers like polystyrene or polyvinyl chloride, PP is widely used in producing engineering plastics.

Traditionally halogen containing compounds blended with synergistic agent like antimony trioxide are used flame retardant of polypropylene. Safety aspect & environmental concern theses flame retardant is limited because of evolution of toxic gases & corrosive smoke during combustion^[7]. Researcher Chiu & Wang^[8] have studied dynamic flame retardancy of polypropylene filled with ammonium polyphosphate.

One way recognized to develop effective intumescent systems is the use of metal hydroxides such as magnesium and aluminum. Nevertheless, a high amount of additive is required, about 60 wt% and 25 wt% to 30 wt% for single or mixture of FR, respectively^[9]. Chen *et al.*^[10] have studied the effect of magnesium hydroxide on mechanical properties & thermal behavior of polypropylene. Adivarekar *et al.*^[11] synthesizes the non-halogenated phosphorous based flame retardant compound for the application of polypropylene. They found the enhancement of limiting oxygen index value of polypropylene also arrest the antidripping property. Metco *et al.*^[12] prepared FR thermoplastic polymer containing recycled rubber, polyethylene, ethylene vinyl acetate copolymer & intumescent additive system.

Aluminum polyphosphate $Al(OH)_3$ and APP/ethylene diamine phosphate are suitable flame retardant^[13]. Rejia *et al.*^[14] studied the effect of APP/nano clay system on the flammability of the epoxy material. Different modifications were carried out to increase the surface area of APP including chemical reaction or mixing to increase its efficiency when used as flame retardant material^[15-16]. The thermal behavior of PP improves by introduction of phosphorous & nitrogen intumescent flame retardant. The halogen free Intumescent FR system have the advantage of low toxicity, low corrosion & absence of melt dripping^[17-19].

Considering the toxicological concern regarding FRs, the present work is aimed at synthesizing an ecofriendly Phosphorous-Nitrogen based non-halogenated flame retardant for polypropylene. The synthesized FR compound is compounded with polypropylene matrix & its flammability performance in terms of LOI & UL-94 has been studied.

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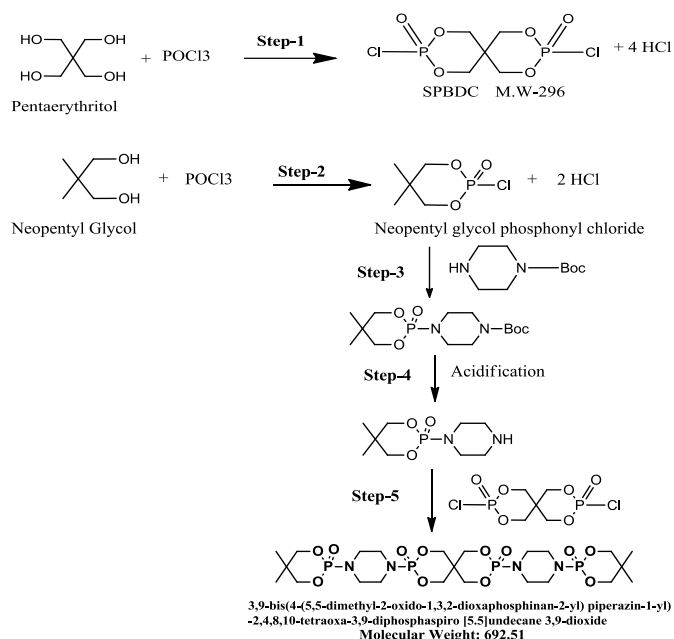
2. Material & Methods

2.1 Material

For the synthesis of flame retardant molecule, Pentaerythritol & Neopentyl glycol purchased from SD Fine Mumbai. Phosphorous Oxychloride purchased from Excel Industries Ltd. Boc piperazine purchased from Cata-Pharma Ltd, Nasik. Triethyl amine purchased from Molychem, Sodium hydroxide flakes 96% & HCl 35% purchased from SD fine & All Solvents are used from a technical grade.

Polypropylene is one of the most commonly used thermoplastic material owing to its easy processing & good mechanical strength. Polypropylene chips REPOL H200FG with melt flow index 20 were obtained from Reliance industries Mumbai.

2.2 Reaction Scheme



2.3 Synthesis of FR compound

Step-1: Synthesis of SPBDC

Take 1.0 mole pentaerythritol followed by 5.5 mole phosphorous Oxychloride in reaction flask. The resulting mixture was applied to nitrogen atmosphere and stirred at RT for 1 hour. Then the mixture was heated to 60 °C and then allowed to react at same temperature for 2 hour again the mixture was heated to 80 °C and stirred for 2 hour. Thereafter mixture was heated to 100 °C-105 °C for 20 hour. The generated HCl gas was absorbed or neutralized using dilute NaOH solution.

The resulting mixture was cooled to RT and filtered the solid and washed with Dichloromethane. Purification is done by Acetone & MDC Dry the product.

Result

Appearance: White crystalline powder

Melting point: 235-240 °C

Assay by phosphorous content: 99.7%

Cl%: 23.55, P%-20.81

Step-2: Neopentyl glycol Chloro phosphate

Added 1 mole of Neopentyl glycol and Dichloromethane in reaction flask. The resulting mixture was cooled to 10 °C add slowly 1 mole Phosphorous Oxychloride to the mixture for 4 hour. The mixture was heated to 35 °C and then allowed to react

at same temperature for 4 hours. The generated HCl gas was absorbed by using NaOH solution. After 4 hr solvent was removed by vacuum distillation white crystalline product was formed. The same crystalline product take in Cyclohexane Stir & Filter. Dry the product in oven at 75 °C. Yield: 99%

Result

Appearance: White crystalline powder

Melting point: 100-105 °C

Assay by chloride titration: 98.25%

Chloride %: 23.5 (Theoretical-23.9%)

Step-3: tert-butyl 4-(5, 5-dimethyl-2-oxido-1, 3, 2-dioxaphosphinan-2-yl) piperazine-1-carboxylate

Add 1 mole Neopentyl glycol chlorophosphate (Step-2 product) followed by chloroform. Cool the mass below 20 °C. Mix the 1.05 mole Boc-Piperazine in chloroform & added the boc-piperazine solution to reaction mass for 1Hr, then stir the mass at same temperature for 01 hour. Then add 2 mole Triethyl amine base slowly in reaction mass then stir the reaction mass as ambient temperature for 01 Hr. Heat the reaction mass up to 55 to 60 °C and reflux the mass for 12 Hr., at which reaction was monitored by TLC.

Cool the mass at RT and washed with water (3 X 250 ml) and saturated solution of NaCl (2 X 150 ml). The organic layer dried over anhydrous sodium Sulphate, Filtered & the solvent is removed from vacuum distillation. The resulting white solid is purified in MDC-Hexane & dry the product in vacuum oven at temp-65-70 °C. Yield: 75%

Result

Appearance: White powder

Melting point: 165-170 °C

Assay by HPLC: 99.10%

N% -8.30, P% -9.21

Step-4: Synthesis of 5, 5-dimethyl-2-(piperazin-1-yl)-1, 3, 2-dioxaphosphinane 2-oxide

Add step-III product (1.3M) followed by methanol under stirring & cool the mass upto 0 °C. Add 8 mole HCl (1:1) in the above solution keeping reaction mass temp.0 - 5 °C within two Hrs & stir the mass at 0 °C for next 5 Hr. Reaction mixture is warm at room temp for 3 Hrs & then at 40-45 °C for 12 Hr. Remove solvents by vacuum distillation and conc. Aqueous mass will remain at the bottom of the flask Cool the concentrated aqueous mass upto 0 °C and make alkaline i.e. PH-14 using aqueous NaOH solution (approx. 10%). Extract the solution using MDC for complete extraction use MDC three times. Combine all extracts and dry the organic mass using sodium sulphate Organic phase receive from three extraction combine & for removal of traces of moisture dry over sodium sulphate. The Solvent is filtered & remove the solvents under vacuum to formed white product the resulting white solid is purified in MDC -Hexane. Product is dried at 50-60 °C under vacuum Yield: 98.5%

Result

Appearance: White crystalline powder

N%: 11.85 & P%: 13.13

Step-5: Synthesis of Final FR compound

Add 1 mole Step-1 product followed by Acetonitrile as a solvent under stirring at room temperature and continue aging for next half an hour. Add 2.04 mole step-4 product. Cool the reaction mass below 10 °C & then gradually add 2 mole of

Triethyl amine keeping reaction mass temp. 10-15 °C. Heat the reaction mass upto 65 °C and keep aging at same temperature for next 6.0 hr. and then cool the reaction mass to room temp.

Filter and purify the same with chloroform and acetone sequentially. Using vacuum oven dry the product at 60-65 °C. Yield: 78%

Result

Appearance: White crystalline powder

Melting point: 355 °C

N%: 8.06 & P%: 17.85

Spectral Analysis:

IR analysis: (Solid state, KBr pellet) $\nu_{\text{cm}^{-1}}$ 2970 (CH₃ Aliphatic), 2893 (CH₂), 1342 (C-N), 1249 (P=O), 1220 (P-N)

¹H NMR analysis: (500 MHz, CdCl₃, RT) δ in ppm, 0.893 (s, 6H, -CH₃), 1.205 (s, 6H, -CH₃), 3.289 (t, 16H, N-CH₂), 3.946 (q, 4H, O-CH₂), 4.163 (q, 2H, O-CH₂a), 4.325 (q, 4H, O-CH₂), 4.452 (q, 2H, O-CH₂b), 4.633 (q, 2H, O-CH₂c), 4.732 (q, 2H, O-CH₂d)

¹³C NMR: (500 MHz, CdCl₃, RT) δ in ppm, 18.665 (-CH₃), 20.22 (-CH₃), 31.37 (CH₃)₂-C-(CH₂)₂, 35.43(CH₂)₂-C-(CH₂)₂, 44.01 (N-CH₂), 69.08 (CH₂)₂-C-(CH₂)₂, 77.9 (CH₃)₂-C-(CH₂)₂

2.4 Preparation of Flame retardant polypropylene

Compounding of polypropylene chips with Phosphorous & Nitrogen flame retardant

The PP chips were dried in a vacuum dryer for 2 hr at 60 °C to remove traces of water. Before melt spinning the PP pallets were compounded with synthesized FR compounds in twin screw co rotating extruder where RPM screw was 60. The compounding of FR into PP was done using 20, 25 & 30% conc of FR compounds. The temperature of five zones in extruder were 175, 185, 195, 210 & 220 °C

Melt spinning of FR PP Filaments

The melt spinning of the PP pallets blended with FR was carried out on laboratory melt spinning machine. The temperature of this spinning extruder zones maintained were 190, 200 & 220 °C. The extruder zone was provided with a nitrogen gas to prevent oxidation of PP.

The pallets melt to form a molten mass, which moves further to metering pump & then to Die head zone. The filament extruded from the spinnerets were cooled down by blowing cool air in 1.5 meter long quench duct. The filament were guided to the godet roller subsequently and were taken over to the draw rollers. The drawing was carried out by two stage drawing method at draw ratio of 3. The filament were finally fed to the take up winder machine over the condenser arm wheel, which applies tension to the yarn & controls the speed of The spindle, ensuring that consistent package could be formed.

2.5 Characteristics and testing of FRPP

Determination of Limiting oxygen Index (LOI)

The polypropylene pallets were compounded with Flame retardant compound & the melt spun into filament which were further subjected to compression moulding to form a sheet of FR polymer composite. The moulded sheet was used to find out limiting oxygen index (LOI) using the method ASTM D-2863. The sheet was clamped to the holder in a chamber &

ignited with fire source till it catches fire & burns entire length of specimen.

Determination of UL-94 (vertical test)

The test for flammability of plastic material used in parts for electronic devices and appliances is commonly known as UL-94. In the vertical flame test, a flame is applied to the base of the specimen held in the vertical position and the extinguishing times are determined upon removal of the test flame method to evaluate the flame retardancy is UL-94 vertical burning test (ASTM D 3801). In this test method, the samples were tested in vertical setting to determine the rate of the burning. According to the UL-94 the test specimen are used in size 150 X 13 X 3 mm³. In this test total 10 specimens (2 sets) are tested

3. Results & Discussion

The results LOI & UL-94 vertical tests are as follows

Sr. No	Concentration of FR %	LOI %	UL-94 test results
01	0	17.9	Fail
02	20	21.5	V-2
03	25	23.2	V-2
04	30	25.7	V-0

V-0: Burning stops within 10 seconds after two applications of ten seconds each of a flame to a test bar. NO flaming drips are allowed.

V-1: Burning stops within 60 seconds after two applications of ten seconds each of a flame to a test bar. NO flaming drips are allowed.

V-2: Burning stops within 60 seconds after two applications of ten seconds each of a flame to a test bar. Flaming drips ARE allowed.

Results shows that the flame retardancy of the polypropylene increases with increase in conc. of FR compounded into polymer. The LOI of the control PP is 17.9 and with the introduction of 20% FR compounds into PP, LOI value are reaches to 21.5 which is considerably increase in a flame retardancy. Similarly when conc of FR compounds is increased to 25% & 30% the LOI values obtained for increases to 23.2 & 25.7 respectively.

Also in the UL-94 burning test The test shows that UL-94 test fail in control PP whereas with the introduction of 20% FR compound into PP, passed the V-2 test also 25% FR compound shows just fail in V-01 test & 30 % FR compound loading in PP passed in the stringent burning V-0 test. The increasing flame retardancy of polypropylene with increasing conc of FR compound may be attributed to the higher amount of P content present in the polymer which act as in condensed phase. During burning, phosphorous decomposes relatively at lower temp due to weak phosphonate bond & forms a surface layer of char. The charred layer formed on the surface is its difficult to burn & can insulate the underlying polymer against further thermal degradation, it acts as physical barrier restricting the oxygen access. From the data a Linear relationship between flame retardancy of PP & concentration of FR compound loaded can be observed.

4. Conclusion

Non-halogenated ecofriendly flame retardant compound synthesized by using phosphorous precursor of neopentyl glycol & pentaerythritol has imparted flame retardancy to polypropylene. A linear relationship between flame retardancy of polypropylene and concentration of flame

retardant compound loaded has been observed. The LOI % of FRPP is found to be increased by increasing concentration of FR compounds. Also in the UL-94 vertical burning V-0 test pass at 30% concentration of FR compound

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