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To cite this version:

Chi Hu, Serge Bourbigot, Thierry Delaunay, Marion Collinet, Sophie Marcille, et al.. Synthesis of isosorbide based flame retardants: Application for polybutylene succinate. Polymer Degradation and Stability, 2019, Polymer Degradation and Stability, pp.9-17. 10.1016/j.polymdegradstab.2019.03.016 . hal-02153132

HAL Id: hal-02153132
https://hal.univ-lille.fr/hal-02153132v1

Submitted on 12 Jun 2019

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PII: S0141-3910(19)30104-1

DOI: https://doi.org/10.1016/j.polymdegradstab.2019.03.016

Reference: PDST 8821

To appear in: *Polymer Degradation and Stability*

Received Date: 22 November 2018

Revised Date: 19 March 2019

Accepted Date: 22 March 2019

Please cite this article as: Hu C, Bourbigot S, Delaunay T, Collinet M, Marcille S, Fontaine Gaë, Synthesis of isosorbide based flame retardants: Application for polybutylene succinate, *Polymer Degradation and Stability* (2019), doi: https://doi.org/10.1016/j.polymdegradstab.2019.03.016.

Synthesis of isosorbide based flame retardants: application for polybutylene succinate

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Key words: polybutylene succinate, isosorbide, synthesis, flame retardancy

Abstract: This article deals with the improvement of flame retardancy of polybutylene succinate (PBS) using isosorbide modified by sulfur, silicon or phosphorus as fire retardants (FRs). The syntheses of these FRs are detailed, and all molecules were analyzed by liquid state nuclear magnetic resonance (NMR). Prior to be incorporated into PBS, the thermal stability of all flame-retardants was analyzed by thermogravimetric analysis (TGA). The results showed that all FRs exhibit thermal stabilities (>170°C) suitable for the processing of PBS (140°C). The fire properties of the PBS formulations were investigated and it was shown that i) sulfur modified FRs showed no improvement of PBS flame retardancy, ii) silicon modified FRs showed slight improvement acting as char forming agent when blending with intumescent FR, iii) performances of phosphorus modified FRs depend on the oxidation degree of phosphorus when evaluated by cone calorimetry, and at UL-94 tests these phosphorus modified FRs achieved V-0 rating with dripping without ignition of the cotton.

I Introduction

Researches and applications of polymers and additives derived from the bio-mass had great development during the last decades.[1,2,3,4,5] These materials can be good alternatives to petroleum-based materials due to their special properties: better bio-degradability, renewability, low toxicity, and low environmental impacts etc. Nowadays, chemical intermediates such as 1,4-butandiol, succinic acid, adipic acid can be produced by fermentation of starch in an industrial scale. These compounds can be used as building blocks for bio-based polymers or as starting molecules for further modification.

Polybutylene succinate (PBS) is a polymer produced by polycondensation of 1,4-butandiol and succinic acid.[6] Its good processability permits various processing methods such as injection molding,[7,8] film extrusion,[9] flat and split yarn,[10] filament[11] etc. It has also a wide range of applications in agriculture, packaging and medical articles due to its good mechanical properties (i.e. close to polypropylene and polyethylene). Furthermore, its mechanical properties were furtherly improved by blending with low cost natural fibers,[12,13,14,15] that can extend its applications in some engineering fields (e.g. electric & electronic, construction and transportation). However, its high flammability limits the applications in these fields, and it is necessary to improve its flame retardancy to meet the legislation and the industrial demands.

Flame retardants derived from bio-mass have recently shown increasing interests. Isosorbide, also named as 1,4:3,6-dianhydro-D-sorbitol, which is a diol derived from starch, can be easily chemically modified due to its hydroxyl groups.[16,17] Modification of isosorbide as flame retardants was mainly carried out by phosphorylation.[18,19,20,21,22] These isosorbide based FRs were used to flame retard polylactide,[22] polystyrene[19,20] and epoxy resin[21], but until now, their effect in PBS was not investigated. Moreover, the improvement of flame retardancy of polymers was only based on phosphorus modifications, therefore it is of interest to study the effect of some other chemical modifications of isosorbide (e.g. sulfur and silicon) on fire retardancy properties.

For these reasons, this paper presents firstly three different chemical modifications of isosorbide i.e. by sulfur, silicon or phosphorus functional groups. The thermal stability of these isosorbide FRs was studied by thermal degradation analysis (TGA) and their fire properties were evaluated using UL-94 and mass loss cone calorimetry (MLC) when incorporated into PBS, are presented.

II Experimental

II.1 Materials

PBS bionolle^{TM} 1001MD was supplied by Showa Denko. For syntheses, solvents and most of the reagents (except 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)) are supplied by Sigma-Aldrich and ThermoFisher Scientific. DOPO (**Figure 1**) is supplied by Tokyo Chemical Industry (TCI).

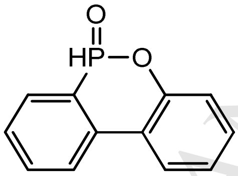


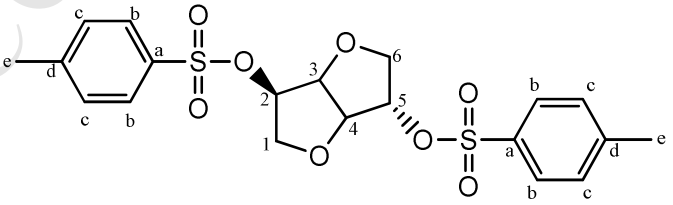
Figure 1: chemical structure of DOPO

PBS and the synthesized FRs are mixed in a DSM Xplore Micro15 twin-screw micro-extruder at 140°C for 10 min with a rotating speed of screw of 50 rpm. Square shape samples (50 × 50 × 3 mm) for MLC test and bar specimens (127 × 12.7 × 3.2 mm) for UL-94 test are prepared by compression molding at 140°C, 20 kN for 2 min, 40 kN for 6 min.

II.2 Synthesis of isosorbide based FR

^{1}H, ^{13}C and ^{31}P (for phosphorus compounds) NMR measurements were performed on a Bruker Advance 400 (400 MHz). Tetramethylsilane (TMS) was used as a reference for the measurement of ^{1}H NMR. The measurements were performed in deuterated chloroform ($CDCl_3$) or dimethylsulfoxide-d_6 (DMSO) and the chemical shift was noted in ppm (δ).

Di-tosyl-isosorbide (Dti) (Figure 2 Error! Reference source not found.**):**



Di-tosyl-isosorbide (Dti)

Figure 2: chemical structure of Di-tosyl-isosorbide (Dti)

To a round bottom flask at 0°C, 3.51 g (24 mmol) of isosorbide was added in 10 mL of pyridine under N_2 flow. Then, a solution of 9.10 g (48 mmol) of 4-toluenesulfonyl chloride in 25 mL of pyridine was added dropwise, over a period of 15 min then the mixture was stirred for 3 hours. Afterward, the reactor was placed in a refrigerator overnight. The mixture was poured in 200 mL of icy water and stirred for 1 h. The obtained white solid was filtered and washed successively with water, 0.2 M of HCl and water again. The white solid was recrystallized in ethanol affording Di-tosyl-isosorbide as a white powder with a yield of 93 %.

^{1}H NMR (CDCl$_3$, stand. TMS): δ (ppm) 2.45 (6H, s, H-e), 3.67-3.71 (1H, m, H-6), 3.82-3.95 (3H, m, H-1 and 2H-6), 4.48 (1H, t, H-4), 4.59 (1H, t, H-3), 4.83-4.86 (2H, m, H-2 and H-5), 7.43 (4H, d, J_{HcHb}=8 Hz, H-c), 7.78 (4H, d, J_{HbHc}=8 Hz, H-b). **^{13}C NMR dec^{-13}C (CDCl$_3$, stand. TMS):** δ (ppm) 21.7 (s, C-e), 69.7 (s, C-6), 73.3 (s, C-1), 78.2 (s, C-5), 80.3 (s, C-3), 83.2 (s, C-2), 85.6 (s, C-4), 127.9 (s, C-b), 130.1 (s, C-c), 132.9 (s, C-d), 145.5 (s, C-a).

Polydimethylsiloxane isosorbide (PDMSi) (Figure 3 Error! Reference source not found.**):**

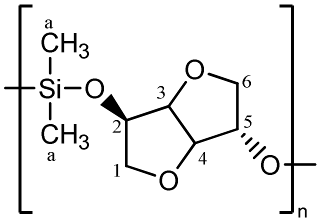


Figure 3: Chemical structure of Polydimethylsiloxane isosorbide (PDMSi)

To a round bottom flask equipped with a condenser, 16.56 g (113.4 mmol) of isosorbide was added in 100 mL of toluene and 50 mL of triethylamine under N_2. The temperature was allowed to rise up to 89°C. Then, 13.80 mL (113.4 mmol) of dichlorodimethylsilane was added, dropwise to the mixture. The mixture was maintained at 89°C and stirred for 1 h. The white formed solid during the reaction was removed by filtration and the filtrate was evaporated in order to remove toluene. The residue was dissolved in 100 mL of dichloromethane. Extraction of the organic layer was achieved five times with 200 mL of water. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. A semi-transparent yellowish solid was obtained with a yield of 95 %.

^{1}H NMR (CDCl$_3$, stand. TMS): δ (ppm) 0.06 to 0.22, (6H, m, H-a), 3.49 and 3.79-3.97 (4H, m, 2H-1 and 2H-6), 4.27 to 4.62 (4H, m, H-2, H-3, H-4 and H-5). **^{13}C NMR dec^{-1}H (CDCl$_3$, stand. TMS):** δ (ppm) -2.4, -0.6, 1.1 (m, C-a), 71.2 (m, C-6), 72.2 (m, C-5), 73.1 (m, C-1), 73.7 (m, C-3), 81.4 (m, C-2), 88.2 (m, C-4).

Polymethylphenylsiloxane isosorbide (PMPSi) (Figure 4 Error! Reference source not found.**):**

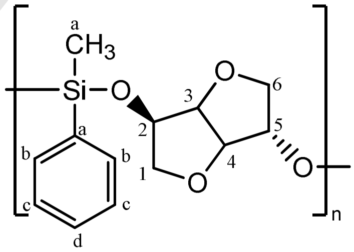


Figure 4: Chemical structure of Polymethylphenylsiloxane isosorbide (PMPSi)

The synthesis of PMPSi was done according to the same protocol as PDMSi using 18.4 mL (113.4 mmol) of dichloromethylphenylsilane, a semi-transparent yellowish solid was obtained with a yield of 92 %.

^{1}H NMR (CDCl3, stand. TMS): δ (ppm) 0.39-0.46 (3H, m, H-a), 3.48-3.96 (4H, m, 2H-1 and 2H-6), 4.32-4.59 (4H, m, H-2, H-3, H-4 and H-5), 7.35-7.41 (3H, m, 2H-d and H-e), 7.54-7.65 (2H, m, 2H-c). **^{13}C NMR dec^{-1}H (CDCl$_3$, stand. TMS):** δ (ppm) -3.5 (m, C-a), 71.2 (m, C-6), 73.5 (m, C-5), 75.7 (m, C-1), 77.5 (m, C-3), 81.5 (m, C-2), 88.2 (m, C-4), 128.2 (m, C-d), 130.6 (m, C-c), 133.3 (m, C-e), 134.1 (m, C-b).

Polyphenylphosphate isosorbide (PPPAI) (Figure 5 Error! Reference source not found.**):**

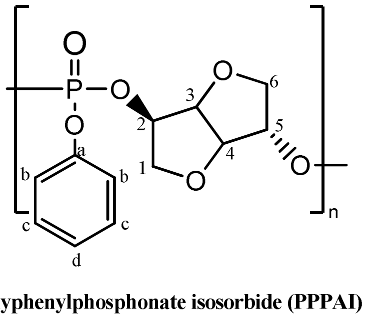


Figure 5: Chemical structure of Polyphenylphosphate isosorbide (PPPAI)

To a round bottom flask equipped with a condenser, 8.30 g (56 mmol) of isosorbide and 338 mg (2.5 mmol) of 4-Dimethylaminopyridine (DMAP) were added under N_2. The temperature was then brought to 90°C until the DMAP was totally dissolved. Afterward, 7.9 mL (56 mmol) of dichlorophenylphosphate were added dropwise over a period of 20 min. Upon the completion of the addition, the temperature was allowed to slowly rise to 120°C and the mixture was stirred for 4 h then the reaction was open to vacuum for another 1 h. A solution of NaOH (0.1 M) in water was set to react with HCl released during the reaction. The product was then dissolved in 100 mL of dichloromethane, followed by five times extraction with water. The organic layer was dried over $MgSO_4$, after the filtration, the solvent of the mixture was removed under reduced pressure. The product was obtained as a brown solid with a yield of 72 %.

^{1}H NMR ($CDCl_3$, stand. TMS): δ (ppm) 3.52 to 4.95 (8H, m, H of isosorbide), 7.14-7.25 (3H, m, 2H-c, H-d), 7.29-7.40 (2H, m, 2H-b). **^{13}C NMR dec^{-1}H ($CDCl_3$, stand. TMS):** δ (ppm) 70.7 (m, C-1), 73.9 (m, C-6), 77.6 (m, C-2), 80.9 (m, C-5), 81.9 (m, C-3), 86.2 (m, C-4), 120.1 (m, C-c), 125.7 (m, C-b), 129.9 (m, C-d), 148.2 (m, C-a). **^{31}P NMR (dec^{-1}H, CDCl3):** δ (ppm) -8.1 (m), -7.7 (m)

Polyphenylphosphonate isosorbide (PPPI) (Figure 6 Error! Reference source not found.**):**

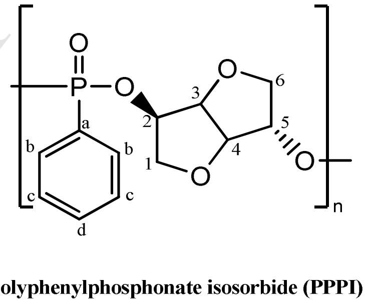
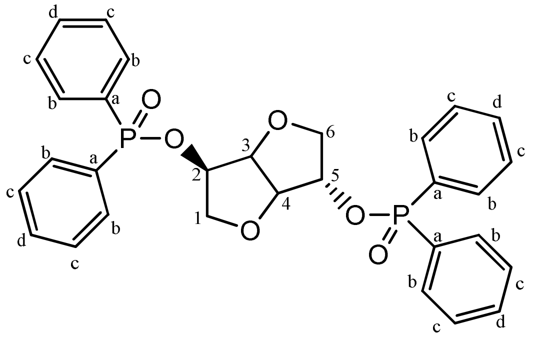


Figure 6: Chemical structure of polyphenylphosphonate isosorbide (PPPI)

The synthesis of PPPI was done according to the same protocol as PPPAI: with 7.9 mL (56 mmol) of phenylphosphoric dichloride, a dark brown solid was obtained with a yield of 85 %.

^{1}H NMR ($CDCl_3$, stand. TMS): δ (ppm) 3.64 to 4.88 (8H, m, H of isosorbide), 7.48-7.79 (5H, m, aromatic protons). **^{13}C NMR dec^{-1}H ($CDCl_3$, stand. TMS):** δ (ppm) 70.4 (m, C-1), 74.3 (m, C-6), 75.5 (m, C-2), 79.8 (m, C-5), 80.9 (m, C-3), 86.4 (m, C-4), 125.7 (m, C-a), 128.7 (m, C-c), 131.8 (m, C-b), 133.1 (m, C-d). **^{31}P NMR (dec^{-1}H, $CDCl_3$):** δ (ppm) 18.9 (s), 19.7 (s)

Diphenylphosphinate isosorbide (DPPII) (Figure 7 Error! Reference source not found.**):**



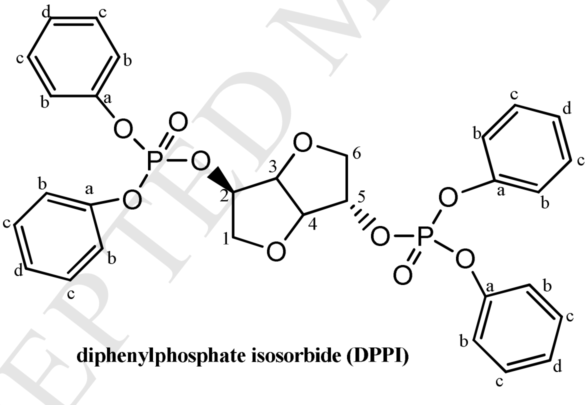
diphenylphosphinate isosorbide (DPPII)

Figure 7: Chemical structure of Diphenylphosphinate isosorbide (DPPII)

The synthesis of DPPII was done according to the same protocol as PPPAI: with 23.8 mL (112 mmol) of diphenylphosphoric chloride, a brown solid was obtained with a yield of 74 %.

^{1}H NMR (CDCl$_3$, stand. TMS): δ (ppm) 3.72-4.89 (8H, m, isosorbide protons), 7.34-7.91 (20H, m, aromatic protons). **^{13}C NMR dec^{-1}H (CDCl$_3$, stand. TMS):** δ (ppm) 70.6 (d, J_{C1P}=3.7Hz, C-1), 74.3 (d, J_{C2P}=5.90 Hz, C-2), 74.8 (d, J_{C6P}=4.38 Hz, C-6), 78.9 (d, J_{C5P}=5.88Hz, C-5), 81.2 (d, J_{C3P}=4.27 Hz, C-3), 86.4 (d, J_{C4P}=3.92 Hz, C-4), 128.6, 131.4, 131.9 (m, C-b, C-c and C-d), 129.7 (m,C-a). **^{31}P NMR (dec^{-1}H, CDCl$_3$):** δ (ppm) 32.6 (m), 33.4 (m).

Diphenylphosphate isosorbide (DPPI) (Figure 8 Error! Reference source not found.**):**



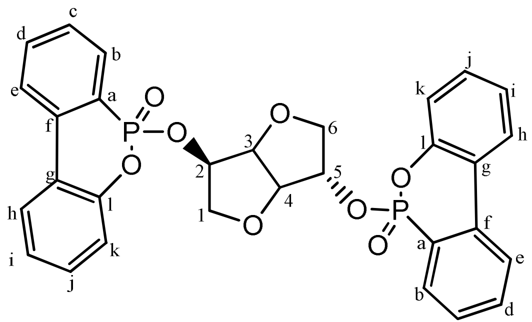
diphenylphosphate isosorbide (DPPI)

Figure 8: Chemical structure of Diphenylphosphate isosorbide (DPPI)

The synthesis of PPPI was done according to the same protocol as PPPAI: with 23.2 mL (112 mmol) of diphenylphosphate chloride, a brown solid was obtained with a yield of 65 %.

DPPI: **^{1}H NMR (CDCl$_3$, stand. TMS):** δ (ppm) 3.72-3.89 (4H, m, 2H-1 and 2H-6), 4.56, 5.04 (2H, m, H-3 and H-4), 5.08 (2H, m, H-2 and H-5), 7.21 to 7.39 (m, aromatic protons). **^{13}C NMR dec^{-1}H (CDCl$_3$, stand. TMS):** δ (ppm) 70.1 (d, J_{C1P}=3.96 Hz, C-1), 73.7 (d, J_{C2P}=5.98 Hz, C-2), 74.3 (d, J_{C6P}=4.39 Hz, C-6), 78.4 (d, J_{C5P}=5.86 Hz, C-5), 80.7 (d, J_{C3P}=3.95 Hz, C-3), 85.9 (d, J_{C4P}=3.87 Hz, C-4), 120.1-129.7 (m, C-b, C-c, C-d), 150.3 (m, C-a). **^{31}P NMR (dec^{-1}H, CDCl$_3$):** δ (ppm) -11.2 (s) -12.1 (m), -13.1 (d).

Di-DOPO-isosorbide (DDi) (Figure 9 Error! Reference source not found.**):**



Di-DOPO-isosorbide (DDi)

Figure 9: Chemical structure of Di-DOPO-isosorbide (DDi)

Isosorbide (11.72 g, 80.3 mmol) was added to a solution of 34.57 g (160.6 mmol) 9,10-dihydro-9-oxa-10-phosphahenanthrene-10-oxide (DOPO) in 100 mL of dichloromethane. Then 23.0 mL of triethylamine was added and the mixture was cooled down from 25°C to 0°C using an ice bath. Afterward, 16.0 mL tetrachloromethane was added dropwise, in the mixture over a period of 1 h. This reaction was then carried out overnight at room temperature. The mixture was filtrated, and the filtrate was extracted five times with 200 mL of water. Organic layer was dried with $MgSO_4$, filtrated and concentrated under reduced pressure. Finally, the mixture was recrystallized in ethanol. White crystal was obtained with a yield of 43 %.

DDi: **^{1}H NMR (DMSO, stand. TMS):** δ (ppm) 3.48 (2H, m, H-6), 3.73 (2H, m, H-1), 4.36 (1H, m, CH-4), 4.52 (1H, m, H-3), 4.80 (1H, m, H-5), 5.01 (1H, m, H-2), 7.23-7.41 (4H, m, 2H-i and 2H-k), 7.41-7.56 (2H, m, 2H-j), 7.56-7.69 (2H, m, 2H-c) 7.80-7.95 (4H, m, 2H-b and 2H-d), 8.15-8.29 (4H, m, 2H-e and 2H-h). **^{13}C NMR dec^{-1}H (DMSO, stand. TMS):** δ (ppm) 71.1 (m,C-1), 73.7 (m, C-6), 76.2 (m, C-2), 79.8 (m, C-5), 80.9 (m, C-3), 86.3 (m, C-4), 120.4 (m, C-i/C-k), 120.9 (m, C-f), 122.4 (m, C-g), 125.2 (m, C-i/C-k), 125.7 (m, C-e/C-h), 126.4 (m, C-e/C-h), 129.3 (m, C-c), 130.5 (m, C-b/C-d), 131.5 (m, C-j), 134.7 (m, C-b/C-d), 136.7 (m, C-a), 149.5 (m, C-l). **^{31}P NMR (dec^{-1}H, DMSO):** δ (ppm) 9.6 (m), 10.7 (m).

II.3 Methods

Thermogravimetric analysis (TGA) measurements were carried out on a Setaram TG92-16. Samples were contained in silica crucibles robed with gold sheet. They were grinded into powder using a cryo-grinder (500 µm filter) before the analysis. Fluid flow rate was set at 100 mL/min, nitrogen or air were chosen to examine the decomposition of the materials in pyrolysis or thermo-oxidative conditions. A heating rate of 10°C/min was used. The onset temperature is taken at 2 % mass loss (noted as $T_{2\%}$).

Fire Testing Technology (FTT) mass loss calorimeter device (ISO 13927, ASTM E906) is used as one of the fire tests. The external heat flux used in the experiment was 35kW/m^2 and the distance between the sample holder to the heat source was 25 mm. The samples were wrapped in aluminum foil and were placed on a ceramic backing board. Their upper side was exposed to the heater. The measured parameters (i.e. ignition time (TTI), heat release rate (HRR) and total heat release (THR)) present an error margin within ± 10 %. Three measurements were performed to check the repeatability. The other fire test used in the study was UL-94 test (ASTM D3801). A set of 5 bars was tested for each material, and their classifications were noted as no classified (NC), V-2, V-1 and V-0.

III Results and discussions

A schematic representation of the synthesis of isosorbide based FRs including the reaction conditions and the abbreviations used are presented in **Figure 10**. The modification of isosorbide was based on two methods: i) for the reaction where a sulfur, silicon or phosphorus chloride react with isosorbide, a nucleophile substitution of the halogen group (in the phosphorus, silicon or sulfur based molecule) by the isosorbide was carried out in a basic solution (trimethylamine (NEt_3), pyridine or 4-Dimethylaminopyridine (DMAP)). ii) For the reaction where 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) containing a P-H bond was used, an Atherton-Todd (AT) reaction was achieved. In this AT reaction, a chlorine donor, carbon tetrachloride was used to create an intermediate phosphoryl halide with DOPO which can be consequentially substituted by isosorbide to form the ester.

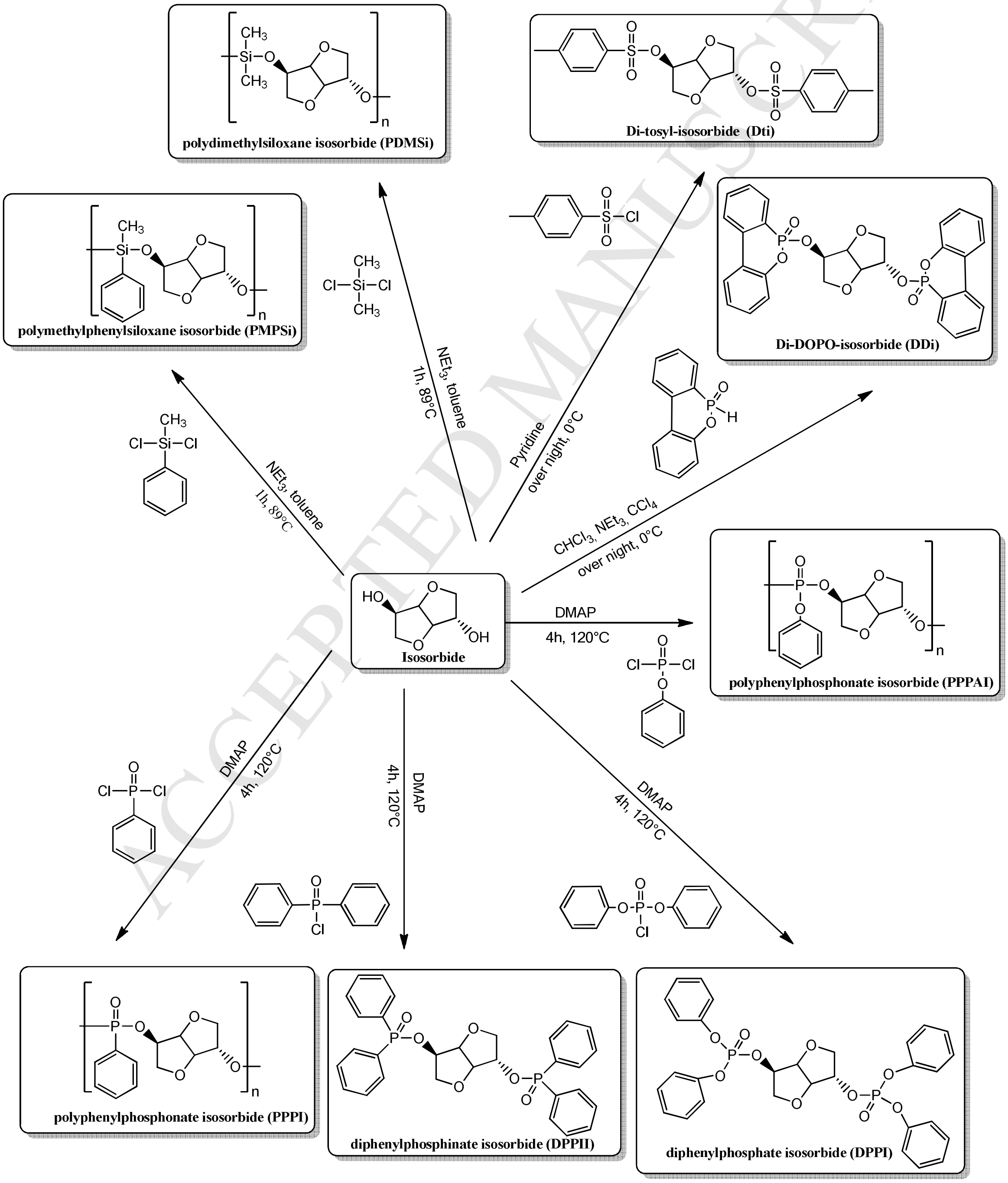


Figure 10: modification of isosorbide by sulfur, silicon and phosphorus functional groups

III.1 Sulfur modified isosorbide

The approach for making sulfur modification of isosorbide is because sulfur based FRs are often considered as effective FRs. Indeed, the sulfur based FRs act in the gaseous phase by quenching the free radicals or in the condensed phase promoting the charring of the material.[23,24,25,26,27] However, as far as we know, none have been described to flame retard PBS. Isosorbide can be easily modified by sulfur containing group (tosyl function) via a reaction of 4-toluenesulfonyl chloride with isosorbide at 0°C in pyridine (**Figure 10**).[28]

Thermal stability of the Dti under air shows that the degradation starts at 250°C (**Figure 11**) which is appropriate for the processing of PBS. TG curve of Dti shows two main degradation steps, which occurs from 250°C to 300°C and from 450°C to 600°C respectively. It can be observed that during the first step of decomposition, the mass loss is 70% taking place in a sharp window of 50°C which can be assigned to the departure of the tosyl group. During the second step of degradation, the mass loss is 27% between 450°C and 600°C leaving a 3% residue at 800°C.

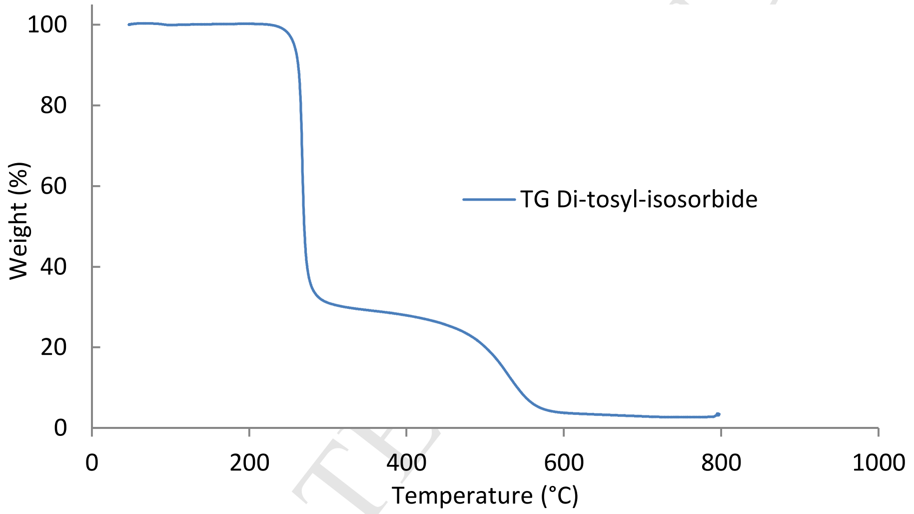


Figure 11: Thermal stability of Di-tosyl-isosorbide (Dti) (10°C/min under air)

Fire properties of PBS/Dti (80/20) formulation were evaluated by MLC (**Figure 12** and **Table 1)**. It shows that Dti does not provide any improvement to the fire properties of PBS. Indeed, pHRR is increased by 41 %, TTI is decreased by 50 s and THR is decreased by 2 %. None of the major factors of the MLC test is improved with this FR. The synthesized Dti is a sulfonate and the sulfonate-based FRs are often reported to flame retard acrylonitrile butadiene styrene (ABS),[29] polycarbonate (PC),[30,31,32] co-polymer of PC and polyester[33] and aromatic polyester[34]. It has not been reported that sulfonates were used to flame retard aliphatic polyesters. Unsuccessful performance of this sulfonate compound in PBS may be caused by the fact that the sulfonate provide a smaller charring effect in the condensed phase than sulfate[35] and sulfamate,[36] and/or the sulfonate provide a weaker effect in the gaseous phase than disulfide[37] and sulfenamide[38]. Furthermore, Dti may promote the degradation of the polymer matrix, which can be also the explanation of the ineffectiveness of this FR in MLC test. As Dti does not show any improvement of the flame retardancy for PBS in MLC test, the UL-94 test was not performed. Thus, the modification of isosorbide was then focused on silicon or phosphorus based compounds.

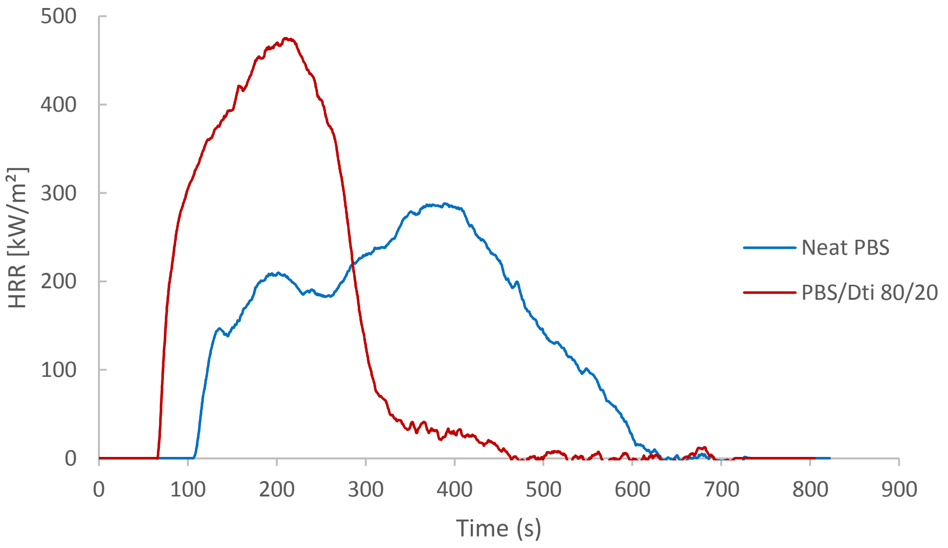


Figure 12: MLC test of PBS and PBS/Dti (50 x 50 x 3 mm^3, 35 kW/m², 25 mm)

Table 1: Results of MLC tests for PBS and PBS/Dti

Ratio **[*wt.*%]**	**pHRR** **[kW/m²]**	**THR** **[MJ/m²]**	**t$_{ignition}$** **[s]**	**t$_{flameout}$** **[s]**	**residue**
Neat PBS	282	91	122	605	2%
PBS/Dti 80/20	475 (+41%)	90 (-2%)	69	310	1%

III.2 Silicon modified isosorbide

The silicon based FRs are often considered to improve the yield and the quality of the forming char. They have been proven to be efficient to flame retard polycarbonate.[39] Moreover, it was reported that fumed silica could improve the flame retardancy of PBS especially when blended with APP and melamine. [40] Thus, in our case, polydimethylsiloxane isosorbide (PDMSi) and polymethylphenylsiloxane isosorbide (PMPSi) was synthesized respectively by reaction of dichloride dimethylsilane and dichloridemethylphenylsilane with isosorbide at 89°C in toluene in presence of triethylamine (**Figure 10**).

The thermal stability of PDMSi and PMPSi were evaluated under air (**Figure 13**). The degradation temperature of PDMSi starts at 172°C. It is noteworthy that the thermal stability changes a lot when methyl group is substituted by a phenyl group. The degradation temperature of PMPSi is increased to 273°C (+ 101°C). Thus, these two molecules are suitable for the processing in PBS. Especially, PMPSi has a relatively high degradation temperature, therefore besides PBS, it could be compounded with other polymers exhibiting higher processing temperature. Furthermore, PMPSi has a residue yield of 17 % that is higher than that of PDMSi (9 %).

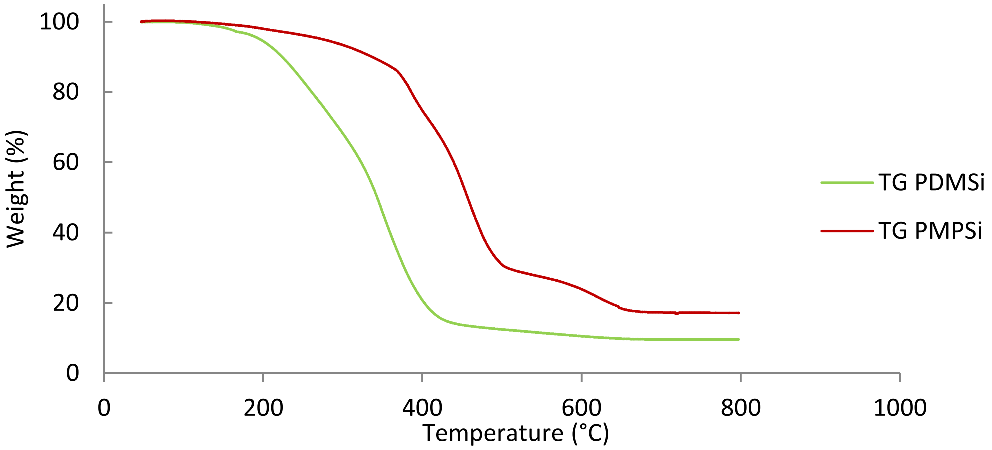


Figure 13: Thermal stability of polydimethylsiloxane isosorbide (PDMSi) and polymethlphenylsiloxane isosorbide (PMPSi) (10°C/min under air)

When 10 wt% of PDMSi and PMPSi are incorporated in PBS, no improvement of the flame retardancy of PBS was found at MLC test (**Figure 14**, **Figure 15** and **Table 2**): pHRR is increased by 26 % and 28 % respectively, and the other parameters are similar as those of neat PBS. Literature indicates that silicon based compounds can be blended with phosphorus and nitrogen based FRs to enhance the fire retardancy of PBS.[41] Thus, ammonium polyphosphate (APP) was added to our silicon based FR system (**Figure 14, Figure 15** and **Table 2**). It shows that for 10 wt% of PDMSi or PMPSi combined with 20 wt% of APP, the pHRR is decreased by 34 % and 32 % respectively and the THR is decreased by 27 % and 26 % respectively. However, compared to PBS/APP 70/30, which exhibits 19 % of decrease of pHRR and 25 % of decrease of THR, the addition of PDMSi and PMPSi showed only a slight improvement. Photos of the residual chars of PBS/PDMSi/APP 70/10/20 and PBS/PMPSi/APP 70/10/20 after the MLC test are presented on **Figure 16**. For the two residues, part of the char is white suggesting the formation of silica at the surface of the residues. However, the quantity of the char is too low to make an efficient protective layer at the surface of the material. Results of UL-94 test (**Table 2**) shows also that the incorporation of PDMSi and PMPSi have no significant improvement on the fire retardancy of PBS: without APP, PBS/PDMSi and PBS/PMPSi have no classification in UL-94 test. No protective char is formed during the test and the drops formed ignite the cotton. Even with 20 wt% of APP added into the formulations, for PBS/PDMSi/APP and PBS/PMPSi/APP only V-1 can be achieved.

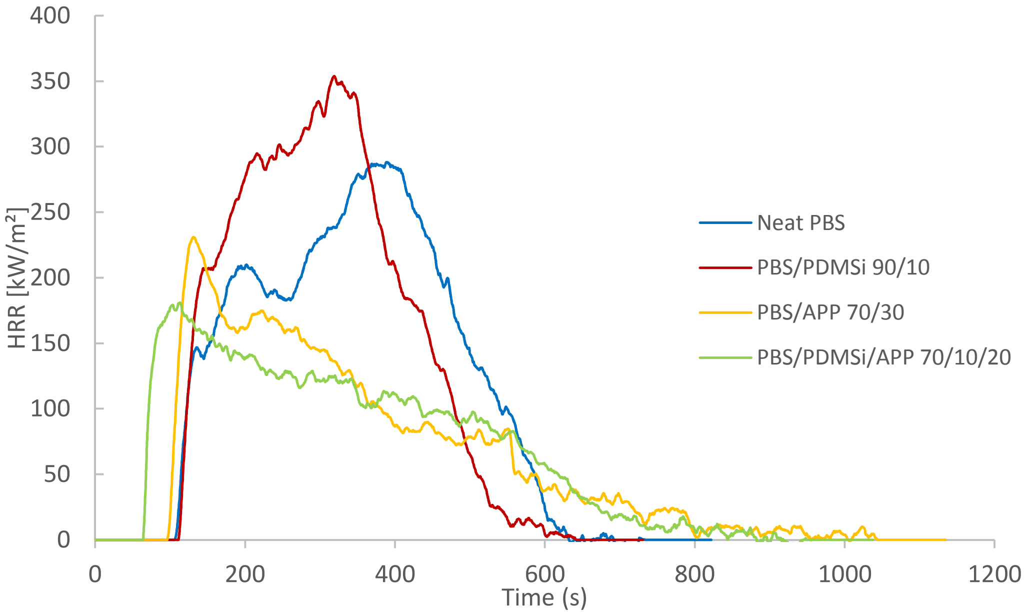


Figure 14: MLC tests of PBS with PDMSi and APP (50 x 50 x 3 mm^3, 35 kW/m², 25 mm)

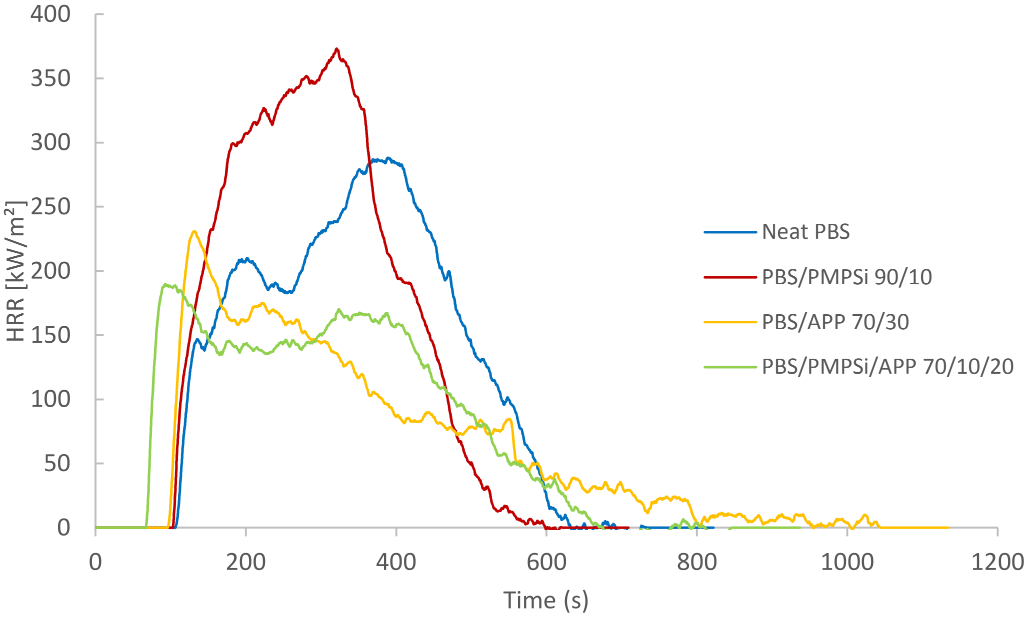


Figure 15: MLC tests of PBS with PMPSi and APP (50 x 50 x 3 mm^3, 35 kW/m², 25 mm)

Table 2: Results of MLC tests of PBS with PDMSi, PMPSi and APP

Ratio [*wt.%*]	**pHRR [kW/m²]**	**THR [MJ/m²]**	**$t_{ignition}$ [s]**	**$t_{flameout}$ [s]**	**residue**	**UL-94 (3.2 mm)**	**drippings**
Neat PBS	283	91	110	605	2%	NC	yes
PBS/PDMSi 90/10	354 (+26%)	93 (+5%)	114	538	2%	NC	yes
PBS/PMPSi 90/10	371 (+28%)	95 (+5%)	116	520	1%	NC	yes

PBS/APP 70/30	231 (-19%)	67 (-25%)	99	712	31%	V-0	No
PBS/PDMSi/APP 70/10/20	181 (-34%)	67 (-27%)	67	844	23%	V-1	No
PBS/PMPSi/APP 70/10/20	192 (-32%)	66 (-26%)	69	678	24%	V-1	No

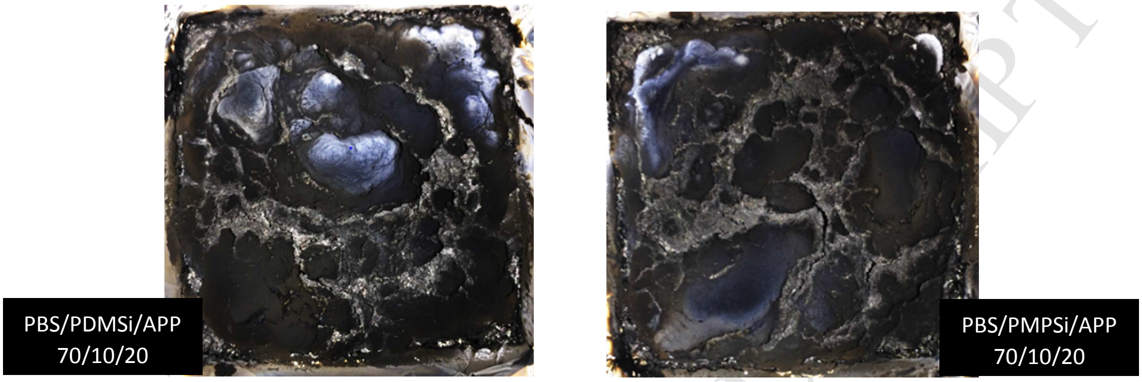


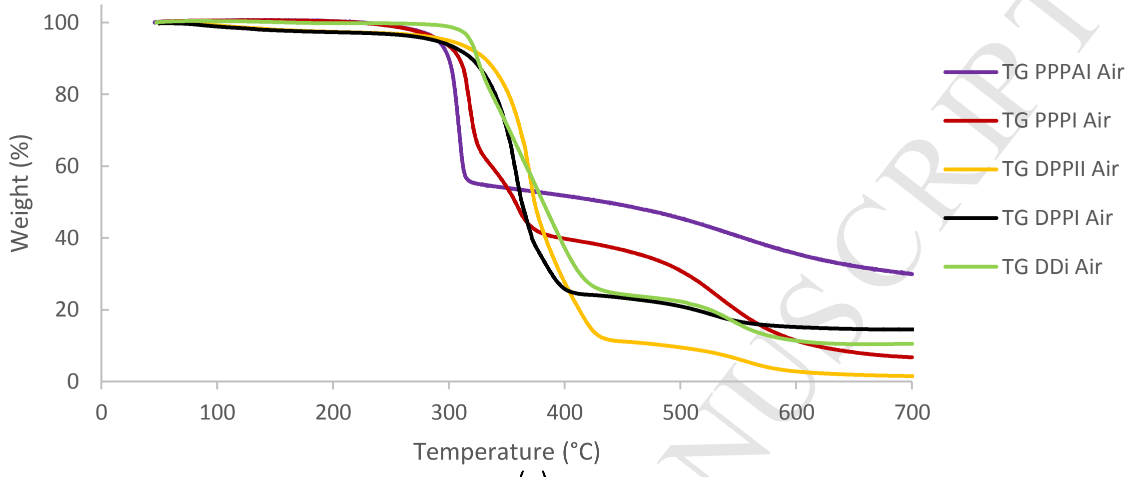
Figure 16: MLC residual char of PBS/PDMSi/APP 70/10/20 (left) and PBS/PMPSi/APP 70/10/20 (right)

III.3 Phosphorus modified isosorbide

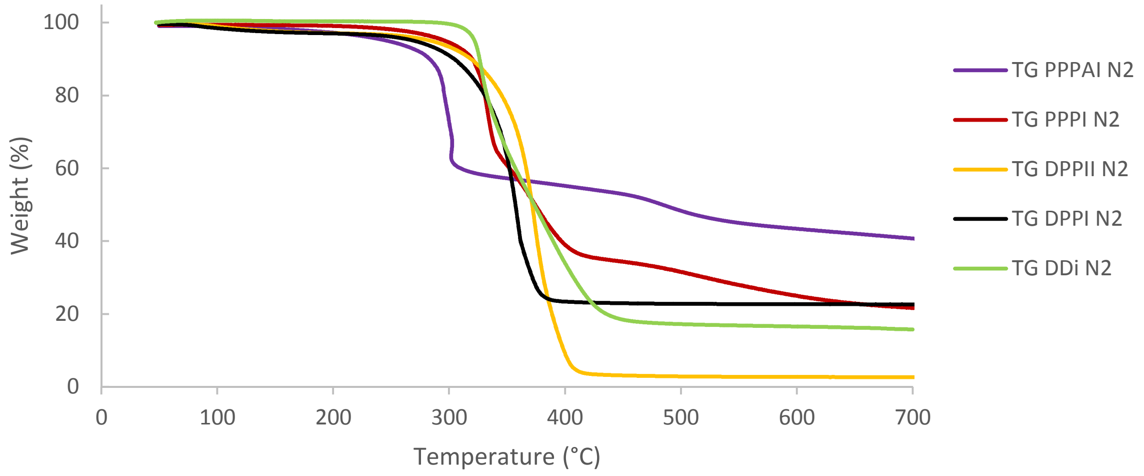
According to the literature, phosphorus based compounds are the most used FRs to improve the flame retardancy of PBS.[42,43,44,45] Different phosphorus based modification of isosorbide were carried out in this study including low molecular weight products and polymers. Modifications with different oxidation state of the phosphorus were also performed. Polyphenylphosphate isosorbide (PPPAI), polyphenylphosphonate isosorbide (PPPI),[22] diphenylphosphinate isosorbide (DPPII)[19,21] and diphenylphosphate isosorbide (DPPI) [19,21] were synthesized respectively by reaction of dichlorophenylphosphate, phenylphosphoric dichloride, diphenylphosphoric chloride and diphenylphosphate chloride with isosorbide at 120°C in presence of 4-Dimethylaminopyridine (DMAP) (**Figure 10**). Di-DOPO-isosorbide (DDi)[21] was synthesized by reaction of DOPO with isosorbide in dichloromethane at 0°C in presence of triethylamine and tetrachloromethane (**Figure 10**).

Thermal stability of these synthesized phosphorus based isosorbide was evaluated by TGA (**Figure 17**) (**Table 3**). It shows that all these molecules can be added to PBS at its processing temperature. PPPAI has two degradation steps under air, the first step is from 280°C to 320°C which has 45 % mass loss; the second degradation step is above 400°C which has 26 % mass loss. PPPI has three degradation steps under air, the first degradation step is from 290°C to 330°C which has 36 % mass loss; the second step is from 330°C to 400°C which has 23 % mass loss; the third step is above 400°C which has 32 % mass loss. DPPI has only one degradation step under nitrogen from 300°C to 420°C, whereas it has two degradation steps under air: the first step is from 295°C to 430°C and the second step is above 450°C. DPPII has also only one degradation step under N_2 from 297°C to 430°C, whereas under air an additional degradation step is observed above 450°C. The same phenomenon was observed for DDi, it has only one degradation step under N_2 from 320°C to 460°C, and an additional degradation step is observed above 460°C. The oxidation degree of phosphorus influences also the quantity of residue, the highest char yield is obtained with the phosphates (PPPAI and DPPI). The residue of PPPAI reaches 40 % and 29 % in N_2 and in air respectively which is more than that obtained in PPPI (21 % in N_2 and 7 % in air) which is a phosphonate. Same phenomenon is found for DPPI, which has

21 % and 15 % residue in N_2 and in air respectively, whereas almost no residue is found for DPPII (3 % in N_2 and 1% in air) which is a phosphinate. It can be concluded that higher oxidation state of phosphorus promotes the formation of the residual char. It is noteworthy that the oxygen has a great influence on the degradation steps and the residue yield. With air, it occurs additional decomposition steps in some cases (DPPII and DDi), and the residue yield is always higher under N_2. It makes sense because oxidation creates a transient char that is furtherly degraded by oxidation at higher temperature.[46]



(a)



(b)

Figure 17: Thermal stability of PPPAI, PPPI, DPPI, DPPII and DDi under a) Air and b) N_2 (10°C/min)

Table 3: Thermal stability and residues of phosphorus modified isosorbide

	PPPAI	PPPI	DPPII	DPPI	DDi
$T_{2\%}$ (°C) Air	279	295	297	295	305
Residue (%) Air	29	7	1	15	10
$T_{2\%}$ (°C) N_2	289	294	297	299	321
Residue (%) N_2	40	22	3	21	15

The results according to MLC are presented in **Figure 18** and **Table 4**. Mauldin et al.[22] have shown that by incorporation of 15% of PPPI in PLA, V-0 rating could be achieved in UL-94 test. Therefore our formulations contained 15% of the isosorbide based FRs. Firstly, all these phosphorus based FRs do not permit to decrease the pHRR when incorporated in PBS. Secondly, it is observed that the performances depend on the oxidation state. With low degree of oxidation, phosphinate (DPPII) or phosphonate (DDi) shows the improvement of the ignition time and a flame extinguishing phenomenon is observed before the ignition suggesting the action of phosphorus species in the gas phase. With higher degree of oxidation, phosphates show higher char yield, however this char had no protective effect in the test.

In UL-94 test, the systems PBS/phosphorus modified FRs present good performances, indeed, no visible burning was observed (bar and drops) during the experiment, and the formation of drops cannot ignite the cotton. These formulations can thus achieve V-0 rating (**Table 4**). The results obtained in the UL-94 test are quite different than those obtained in the MLC test. It can be explained by several facts: i) thermal radiation is the heat source for MLC test, and for UL-94 test, heat convection is the major heat source. Indeed, the different types of heat source may cause different behavior. ii) Unlike the MLC test which has a forced ignition system, the formation of these drops in UL-94 test take away matters and heat from the bar which can explain the 'no visible burning' observed during the test. iii) Moreover, our previous study[47] indicates that with the action of phosphorus flame retardants in the gaseous phase, the temperature of the drops can be decreased, hence the cotton cannot be ignited by the drops.

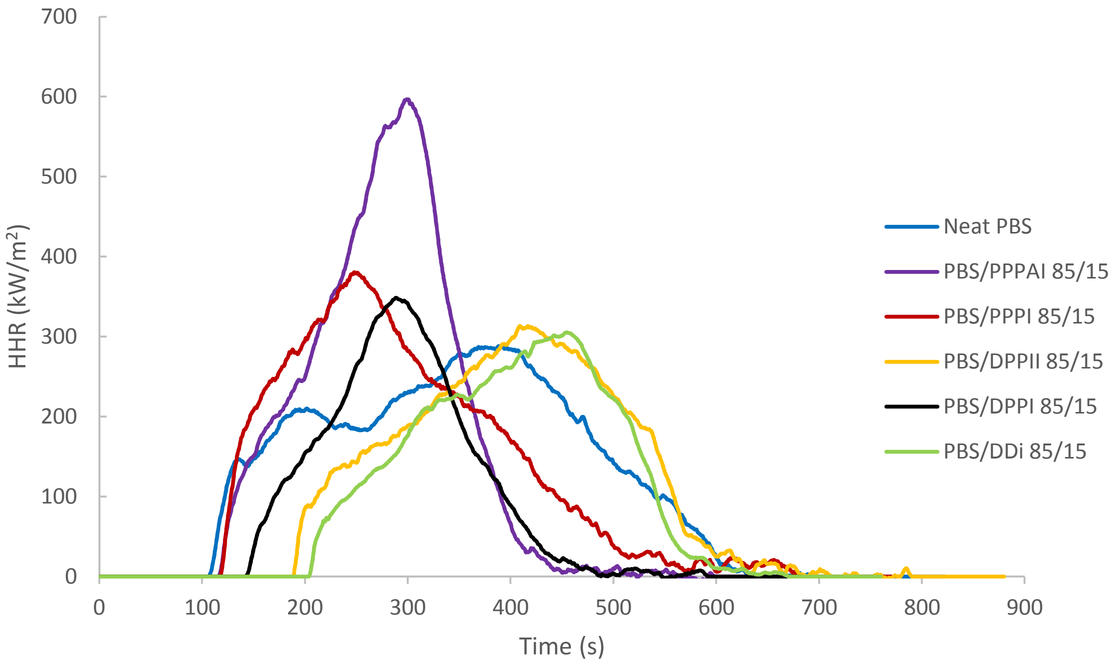


Figure 18: MLC test of PBS with PPPAI, PPPI, DPPII, DPPI and DDI (50 x 50 x 3 mm^3, 35 kW/m², 25 mm)

Table 4: Results of MLC test of PBS with PPPI, PPPAI, DPPII, DPPI and DDi

Ratio [*wt.%*]	pHRR [kW/m²]	THR [MJ/m²]	$t_{ignition}$ [s]	$t_{flameout}$ [s]	residue	UL-94 (3.2 mm)	dripping
Neat PBS	283	91	110	605	2%	NC	yes
PBS/PPPI 85/15	380 (+35%)	86 (-6%)	121	518	4%	V-0	yes
PBS/PPPAI 85/15	596 (+107%)	114 (+24%)	119	436	7%	V-0	yes

PBS/DPPII 85/15	325 (+15%)	83 (-9%)	194 (+84s)	628	1%	V-0	yes
PBS/DPPI 85/15	345 (+22%)	84 (-9%)	148 (+38s)	455	4%	V-0	yes
PBS/DDi 85/15	312 (+11%)	79 (-13%)	205 (+95s)	559	1%	V-0	yes

IV Conclusion

This paper describes the synthesis of a series of new isosorbide-based FRs. These compounds were obtained by chemical modification of isosorbide by sulfur, silicon or phosphorus with different oxidation state. Particularly, these structure-property relationship studies are helpful to design new efficient flame retardant additives for PBS. The thermal stabilities of these FRs have shown that they are all stable enough to be incorporated into PBS at its processing temperature. The fire properties of the PBS/modified isosorbide formulations evaluated by MLC and UL-94 indicate that Sulfur modification of isosorbide shows no improvement in MLC tests (pHRR higher than that of the neat polymer). The use of silicon-based isosorbide alone does not bring significant improvement of fire retardancy of PBS. Nevertheless, when combined with APP, these silicon based FRs can improve the performance of PBS according to cone calorimetry. In the case of the phosphorus compounds, different performances according to the oxidation state of the phosphorus were observed. It was indirectly shown that the lower oxidation degree of phosphorus (phosphonate and phosphinate) leads to an action in the gaseous phase and higher oxidation degree (phosphate) leads to an action in the condensed phase. Therefore, in this paper it has been shown that the phosphorus modification of isosorbide is a promising way to flame retard PBS when UL-94 test is required. Meanwhile, by using isosorbide-based FRs, it improves the content of bio-based material in the formulation.

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- Sulfur, silicon or phosphorus modified isosorbide compounds were successfully synthesized
- The isosorbide based flame-retardants exhibit thermal stability higher than 170°C.
- Formulations based on PBS and phosphorus modified isosorbide achieved V-0 rating at UL-94 test