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Comprehensive study on flame retardant polyesters from phosphorus additives

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ABSTRACT

In this work we have performed a comprehensive study on synthesis, processing, detailed material characterization and preliminary assessment of toxicity of relatively new flame retardant (FR) additives as a key for developing environmentally friendly fire safe polyesters. Two 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) based FR additives were synthesized using principles of green chemistry and incorporated via thermal processing in high temperature polyesters such as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT). The green synthesis strategies included (i) the use of N-chlorosuccinimide as a sustainable chlorinating agent for DOPO and (ii) a solvent and catalyst free microwave-assisted synthesis. Atomistic molecular dynamics (MD) simulations were employed in order to calculate the solubility parameters of these additives so as to estimate their compatibility in the polyesters. Detailed rheological measurements of the polyester/FR blends were carried out and the results indicated a clear difference in all three additives tested. Based on these analyses, 6H-dibenz[c,e][1,2]oxaphosphorin,6-[(1-oxido-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-yl)methoxy]-, 6-oxide (DOPO-PEPA) exhibited the highest compatibility with both polyesters and their blends and showed the highest thermal-oxidative stability guaranteeing stable and steady processing at high temperatures. All polyester/FR formulations exhibited higher flame retardancy compared to the virgin polyesters in the small scale fire tests. The FR additives were evaluated for their potential toxicity using a well-established *in vitro* platform. Our results indicate no acute cytotoxic potential for all FRs analyzed in two different cell types (the human lung epithelial cell line A549 and macrophages derived from the monocytic cell line THP-1) and under the chosen experimental conditions.

1. Introduction

There is increasing demand for the development of environmental friendly fire safe materials which fulfill both ecological and commercial requirements. In addition, these materials need to be fully characterized for their physical and chemical properties and their ease of processability for eventual industrial exploitation. Like in case of other additives, it is important that a flame retardant (FR) additive do not interfere with steady melt processing in typical polymer extruders. Therefore, it is required that the melt properties of the polymer/FR blends do not change significantly during the processing. Most common polymers are not suitable for fire safe applications and are rendered flame retardant by incorporating an FR additive in the polymer bulk or via coating on the surface. Incorporating FR additive in the bulk via thermal processing is relatively simple, economical and more durable to environmental influences. The key to reducing waste and improving sustainability of functional materials is to develop additives via green chemistry strategy. There are 12 important principles involved in green chemistry, for example, the chemical should be non-toxic, toxic raw materials and solvents should be avoided, high atom economy and the use of renewable feedstock [1].

Some halogenated flame retardants are prohibited [2] due the concerns regarding their toxicity [3]. In the last decades the

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impetus has shifted to the development of environmentally friendly flame retardants (FRs). Among the many classes of FR additives, new phosphorus containing FRs [4–7] are considered potential replacements for the toxic FRs [3]. More recently some phosphorus based FRs have also come under scrutiny of various regulatory and environmental agencies. Some phosphorus based FRs have been found to be toxic and are currently being phased out or their usage restricted [8–12].

A variety of new phosphorus compounds as potential replacement for toxic FRs have been synthesized by many researchers [4–7], however, in most cases the toxicity data of these compounds are unknown. Furthermore, they often employ synthesis strategies which do not follow the principles of green chemistry as outlined earlier, for instance, in some work phosphorus FRs have been synthesized with toxic carbon tetrachloride as reagent [13–16]. Among the phosphorus based FRs, development of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives have gained much attention in the research and industrial community due to its efficient and versatile FR action. They have recently been reported to be harmless for aquatic organisms and human cells [17,18]. DOPO and its derivative 6,6′-(ethane-1,2-diylbis(azanediyl))bis(6H-dibenzo[c,e][1,2]oxaphosphinine-6-oxide) (EDA-DOPO) do not induce acute cytotoxicity in human lung epithelial cell as well as human macrophages. Furthermore, both FRs are not neurotoxic and do not exhibit an influence on neural crest cell migration, or on the integrity of human skin equivalents. Furthermore, the two compounds have no effect on algae growth or daphnia viability at concentrations $\leq$400 μM [18] which is one of the tests required for REACH registration in Europe [19]. Another DOPO derivative 10-(2,5-dihydroxyphenyl)-9,10-dihydro-9-xa-10-phosphaphenanthrene-10-oxide (DOPO-HQ) has also been evaluated for its eco-toxicity and was found to have toxicity markedly lower than commercially prevalent phosphates [20].

In this work we have evaluated in detail two DOPO derivatives (Fig. 1) as potential FR additives to develop nontoxic flame retardant polyester based materials. The DOPO derivatives 6H-Dibenz [c,e][1,2]oxaphosphorin, 6-[(1-oxido-2,6,7-trioxa-1-phospha bicyclo[2.2.2]oct-4-yl)methoxy]-, 6-oxide (DOPO-PEPA), 3-(6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl)propanamide (AAM-DOPO) were synthesized taking into consideration the principles of green chemistry and processed with polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) to make FR films. In addition to the synthesized DOPO derivatives a commercial phosphorous based FR Aflammit PCO 960 was used in this study for comparison. This commercial additive is known to be suitable for polyester applications; however, there exist little information in the literature regarding its processability and FR efficacy. The initial choice of these additives for this work was based on their reported high thermal stability [15,21]. The compatibilities of the FRs with the polyesters were checked by means of atomistic molecular dynamics (MD) simulations of the solubility parameters of the components. Furthermore, rheological measurements were performed to assess the melt characteristics of different polyester/FR systems at the processing temperatures. The FR films were further evaluated for flammability using small scale fire tests. The toxicological profile of the additives was assessed using a well-established battery of *in-vitro* test. With these detailed multi-dimensional analyses, we aim to draw a comprehensive picture of the benefits of using these relatively new additives in combination with polyesters to develop environment friendly fire safe polyesters.

2. Experimental section

9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was purchased from Metadynea GmbH (Austria), all other chemicals for synthesis were purchased from Sigma Aldrich (Switzerland) and were used without further purification. Aflammit PCO 960 was purchased from Thor GmbH, Germany. 1-oxo-4-hydroxymethyl-2,6,7-trioxa-l-phosphabicyclo[2.2.2]octane (PEPA) was bought from Carbosynth Limited, United Kingdom. The base polymers polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) were provided by Serge Ferrari Tersuisse AG (Emmenbrücke, Switzerland) and Sukano AG (Schindellegi, Switzerland) respectively.

2.1. Synthesis of DOPO derivatives

2.1.1. Synthesis of DOPO-PEPA

DOPO (5.0 g, 23.1 mmol) was charged in a three-neck round bottomed flask connected to a condenser and N_2 inlet. Dry Toluene (50 mL) was added under nitrogen, followed by the addition of N-Chlorosuccinimide (NCS) (3.40 g, 25.4 mmol) in small portions via side arm under N_2 at ambient temperature. After complete addition, the reaction mixture was stirred at ambient temperature overnight. The white precipitates were removed by filtration under N_2 using Schlenk frit. The solvent was removed under vacuum. The residue was re-dissolved in dichloromethane (50 mL) and transferred under N_2 to a dropping funnel and was slowly added to a mixture of 1-oxo-4-hydroxymethyl-2,6,7-trioxa-l-phosphabicyclo [2.2.2]octane (PEPA) (4.17 g, 23.1 mmol) and triethylamine (2.80 g, 27.8 mmol) in dichloromethane (100 mL) at ambient temperature. The reaction was again stirred overnight at ambient temperature. The solvent was then completely removed and ethanol (50 mL) was added while stirring, forming a white product. The product was then collected by filtration and washed with ethanol and dried in vacuum at 80 °C until constant weight (4.45 g, 50% yield). The NMR data fit well with the earlier published reports (Fig. S1 of the Supporting Information) [15].

2.1.2. Synthesis of AAM-DOPO

DOPO (5.40 g, 25 mmol,), acrylamide (355 mg, 50 mmol) were placed in a heavy-walled glass vials sealed with aluminum crimp caps fitted with a silicon septum. The glass tube (with an inner diameter of 3 cm and a volume 60 mL) containing the reaction mixtures was sealed with a lid and heated in the microwave oven for 2 h at 120 °C (50 Bar, 1200 W) under N_2 atmosphere. The reactions were performed in Synthwave Microwave Single Reaction

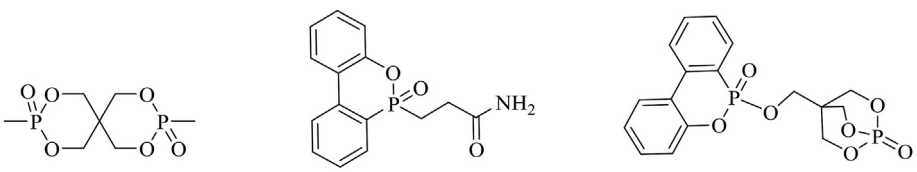

Fig. 1. General chemical structure of flame retardant additives.