



Phosphorus flame retardant polybenzoxazine foams based on renewable diphenolic acid



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ABSTRACT

Flame retardant polybenzoxazine foams were prepared in a two step process, by heating mixtures of the benzoxazine derived from renewable diphenolic acid (DPA-Bz) with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) or 9,10-dihydro-9-oxa-10-(1-hydroxy-1-methylethyl) phosphaphenanthrene-10-oxide (DOPO-2Me) as additives. In the first step partial curing was achieved at different times and temperatures. In the second step, these materials underwent self foaming when heated at 220 °C. By means of a factorial design 2³ the effect of curing conditions and type of additive on the foam density were evaluated. DOPO-2Me additive was found to partially react with the DPA-Bz leading to a decrease in the glass transition temperature of the materials. The cellular structure of the foams was characterized by scanning electron microscope in terms of cell size, cell size distribution, closed-cell content and anisotropy ratio. The presence of DOPO-2Me into the solid precursors and foams greatly influenced the thermal degradation and the flame retardancy properties as evaluated by TGA, LOI and UL-94 respectively.

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1. Introduction

One very desirable property for sustainable polymers is flame retardancy. The use of flame retardants to reduce combustibility of the polymers, and smoke or toxic fume production, therefore becomes a pivotal part of the development and applications of new materials. The application of reactive flame retardants involves either the design of new, intrinsically flame retardant polymers or modification of existing polymers. Halogenated flame retardants have been the most common systems used up to date. However many of them, specially brominated flame retardants, are nowadays restricted in many countries due to their migration to the environment, toxicity and the formation of hydrogen halides and dioxins during combustion [1]. These drawbacks have increased the amount of research into the development of innovative and environmentally friendly halogen-free flame retardant polymers [2]. The development of high performance halogen-free “green” polymeric materials for electronics, electrical, aerospace, and transportation continue demanding high performance flame retardants.

Phosphorus-containing polymers are well recognized for their flame retardant properties, and they are increasingly becoming more popular than their halogen counterparts, as they generally give off non-toxic combustion products.

A new approach to environmentally friendly flame retardants not only involves the design of halogen-free systems but also the use of renewable resources. The growing demand for petroleum-based products and the resulting negative impact on the environment, plus the scarcity of non-renewable resources, are some of the many factors that have recently focused interest on the field of polymers derived from non-petrochemical feedstock [3].

Phenolic foams are inexpensive commercial thermosetting materials used when fire resistance is desired [4,5]. Recently, a new type of rigid phenolic foams [6] derived from a polybenzoxazine obtained from renewable diphenolic acid (DPA) was reported [7]. DPA is emerging as a potential “green” candidate to displace bisphenol A because of its similar chemical structure, its lower price and because it has an extra functionality (carboxylic acid) which may be utilized for polymer synthesis.

With the aim of improving in the flame retardance of these foams, this work deals with the incorporation of a phosphorus-containing compound. Among organophosphorus flame retardants, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives have been shown to induce excellent

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flame retardant properties. Since 1972, this cyclic organophosphorus compound, and its derivatives have been used to make many synthetic flame retardant resins [8]. Few examples of the use of these organophosphorus compounds as flame retardant additives in foams have been reported. In flexible polyurethane foams, the addition of methyl ester of DOPO [9,10] and amino substituted DOPO [11] showed very high flame retardant efficiency and good thermal stability. Another recent approach was based in the use of maleated DOPO in rigid bio-foams. The resulting materials exhibited high mechanical properties, flame resistance and an improvement in biodegradability [12].

This study was focused on obtaining halogen-free flame retardant renewable polybenzoxazine foams by mixing the previously synthesized DPA-based benzoxazine (DPA-Bz) with DOPO or with 9,10-dihydro-9-oxa-10-(1-hydroxy-1-methylethyl)phosphaphenanthrene-10-oxide (DOPO-2Me). After a partial polymerization at different temperatures and times, the resulting resins led to a series of rigid foams by decarboxylation at higher temperatures (Scheme 1).

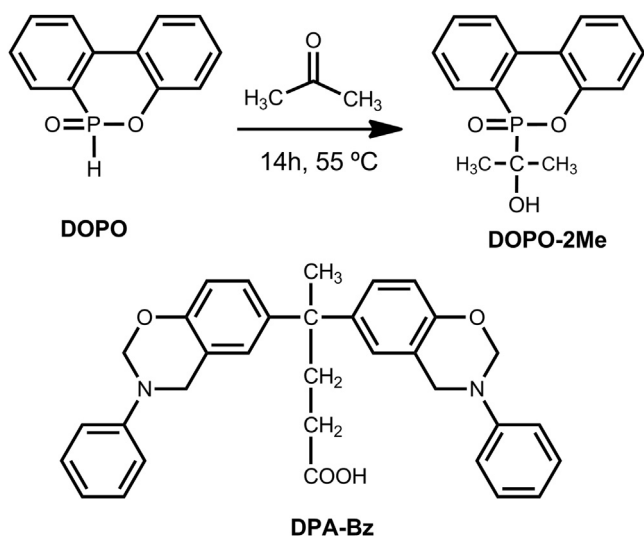
To explore how the experimental conditions affect the preparation of rigid foams, a factorial design 2^3 was used to analyze the influence of the process variables (temperature, time and type of additive) on the foam density value.

Thermal stability of the foams was studied by TGA and flame retardancy was evaluated using UL-94 burn and LOI tests.

2. Experimental

2.1. Materials

The following chemicals were obtained from the sources indicated and used as received: ammonium sulfate (Scharlau), potassium bromide (Panreac), paraformaldehyde (Probus) and 4,4'-bis(4-hydroxyphenyl)pentanoic acid (DPA) (Aldrich). 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) (Aismalibar S.A) was previously dehydrated at reduced pressure for 3 h/130 °C, 1 h/145 °C and 1 h/160 °C. 1,3,5-Triphenylhexahydro-1,3,5-triazine, [7] 4,4'-bis-[6-(3-phenyl-3,4-dihydro-2H-1,3-benzoxazine)]pentanoic acid (DPA-Bz) [7] and 6,8-dimethyl-3-phenyl-2H,4H-benzo[e]1,3-oxazine (2,4-Me-Bz) [13] were synthesized according to reported procedures.



Scheme 1. Chemical structures of DOPO, DOPO-2Me and DPA-Bz.

2.2. Synthesis of 9,10-dihydro-9-oxa-10-(1-hydroxy-1-methylethyl)phosphaphenanthrene-10-oxide (DOPO-2Me) (Scheme 1)

For the synthesis of DOPO-2Me a reported procedure [14] was modified as follows: to a 100 mL round-bottomed flask equipped with a condenser and a magnetic stirrer, 5 g (0.023 mol) of DOPO and 14 mL (0.190 mol) of acetone were added. The mixture was heated at 55 °C for 14 h and then was kept in the refrigerator overnight. The precipitate which formed was collected by filtration, washed with cold acetonitrile (20 mL) and subsequently was crystallized from chloroform (4 mL/g) and dried overnight at 60 °C. The desired product was obtained as white crystals in a yield of 60%.

$^1\text{H NMR}$ (DMSO- d_6 , δ ppm): 8.24–8.15 (1H, Ar-H), 8.14–8.13 (1H, Ar-H), 7.97–7.92 (1H, Ar-H), 7.81–7.87 (1H, Ar-H), 7.62–7.56 (1H, Ar-H), 7.43–7.39 (1H, Ar-H), 7.26–7.22 (2H, Ar-H), 5.5–5.49 (1H, –OH, J_{PH} : 6.8 Hz), 1.41–1.37 (3H, CH_3 , J_{PH} : 14.8 Hz), 1.27–1.23 (3H, CH_3 , J_{PH} : 14.8 Hz).

$^{31}\text{P NMR}$ (DMSO- d_6 , δ ppm, H_3PO_4): 36.6.

FTIR (cm^{-1}): 3276 (–OH); 1594, 1477, 1430, 1117, 1006 (P-C_{Ar}); 1203 (P=O); 1225, 916 (P-O-C_{Ar}); 783 (P-C); 1134 (C–O), 746 ($\text{C}_{\text{Ar}}\text{-H}$).

2.3. Crosslinking reaction

Appropriate amounts of DPA-Bz and DOPO or DOPO-2Me were dissolved in dichloromethane. Solvent was removed from the solution by evaporation at 45 °C for 60 h and then at 140 °C for 10 min at reduced pressure. The amount of DOPO-2Me and DOPO used was 15.6 wt.% and 15.3 wt.% of the total weight of the mixture which corresponds in both cases to a 1 wt.% P. Resin bars were obtained by transferring the mixture to a Teflon mold (cavity dimension: 1 cm \times 1.5 cm \times 0.3 cm) and compressing under a pressure of 9.1 MPa using a manual hydraulic press (15-ton sample press SPECAC equipped with water cooled heated platens). Ten samples were prepared by varying the type of phosphorus compound, polymerization time and temperature. The curing conditions are shown in Table 1. A neat polybenzoxazine sample was also prepared in the same way for the sake of comparison. Unfoamed materials are denoted with a P in the text and in forthcoming tables and figures.

2.4. Foaming process

A sample of previously synthesized polymer was placed in a conventional oven and heated from 30 °C to 220 °C at a heating rate of 2.8 °C/min for 2 h. After foaming, the sample was allowed to cool slowly to room temperature. The surface was peeled off before analysis. A neat polybenzoxazine foam was also prepared in the

Table 1
Experimental plan of a 2^3 design and results for foam density property.

Run	Analyzed factor			Response
	Temperature (°C)	Time (h)	Additive ^a	Density (kg/m^3)
F1	140	4	A	131.3
F2	150	4	A	186.2
F3	140	8	A	198.2
F4	150	8	A	210.1
F5	145	6	A	161.2
F6	140	4	B	151.2
F7	150	4	B	171.3
F8	140	8	B	196.5
F9	150	8	B	228.2
F10	145	6	B	142.3

^a A: DOPO; B: DOPO-2Me.

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