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This article is dedicated with great respect and affection to Professor Hatsuo Ishida, on the occasion of his 70th birthday.

Examining the influence of organophosphorous flame retardants on the thermal behaviour of aromatic polybenzoxazines

Martin Taylor^a, Gabriel Cavalli^{a,†} and Ian Hamerton^{*b}

^a Department of Chemistry, Faculty of Engineering and Physical Sciences, University of Surrey, Guildford, Surrey, GU2 7XH, U.K.

^b Bristol Composites Institute (ACCIS), Department of Aerospace Engineering, School of Civil, Aerospace, and Mechanical Engineering, Queen's Building, University of Bristol, University Walk, Bristol, BS8 1TR, U.K.

* To whom correspondence should be addressed.

† Present address: School of Engineering and Materials Science, Queen Mary University of London, 327 Mile End Road, London, E1 4NS, U.K.

Abstract: 2,2-bis(3,4-Dihydro-3-phenyl-2H-1,3-benzoxazine)propane (BA-a) is blended with three different commercial organophosphorous compounds, bis(4-hydroxyphenyl)phenylphosphine oxide (BHPPO), diphenyl phosphoramidate (DPPA), and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), at a range of loadings (1 – 10 wt %). Incorporation of all dopants resulted in a reduction in the temperature of the initiation of the curing mechanism (by some 30-60 K), but only the DOPO truly moved the curing into a lower temperature regime by decreasing the end temperature by 25 K (DPPA lowered this by 5 K). DPPA and DOPO were also shown to have a significant effect on the enthalpy of polymerisation with each decreasing the value by 50 J/g. Differential scanning calorimetry (DSC) rescan indicated all three additives have a positive impact on the glass transition temperature of poly(BA-a) with increases of 9 K (BHPPO) and 14 K (DPPA DOPO). Thermogravimetric analysis (TGA) indicates that all additives had little effect on the magnitude of char formed (BHPPO and DPPA both increased the char yield by 3%, whereas DOPO reduced the final char yield by 3%). However, importantly the mechanism of thermal degradation for poly(BA-a) differs for all three additives and was shown to change with increasing concentration. DOPO had the greatest effect on promoting the formation of char at elevated temperatures.

Keywords: Polybenzoxazines, flame retardants, organophosphorous compounds, polymerisation, thermal stability.

INTRODUCTION

Polymers and their composites are being applied increasingly in the aerospace industry in recent years [1], more recently composites have been used in commercial airliners, most notably in the case of the Airbus A350 and Boeing 787 which comprise up to 50 % composite by volume [2,3]. Composites are now being applied in the primary structure of aircraft so their integrity is very important, developing methods to improve toughness of neat resins and trying to understand how the toughening agent works is the first step in developing robust composites. Polybenzoxazines (PBZs) show promising thermal and mechanical performance for these applications, but improvements in toughness are required before this can be a reality. The potential for the use of oligomers based on engineering thermoplastics have been examined for some years as modifiers in aerospace composite matrices [4,5], due to their inherent toughness and the ability to blend them more easily than high molecular weight species without incurring the penalty of high melt viscosity.

Another considerable drawback of BZs is that they are typically slow to react, requiring curing temperatures in the range of 200 °C [6,7]. High curing temperatures are a major limitation for the adoption of PBZs in advanced industrial applications, when compared to other competitor resins; for instance, epoxies may be cured at comparatively modest temperatures (60 °C and 120 °C), yet still achieve relatively high values of dry T_g (150 °C). Compounds containing an active hydrogen atom, such as carboxylic acids and phenols have been widely established as effective catalysts for the ring-opening polymerisation of BZs [8], which as already mentioned proceeds *via* a cationic mechanism. Other compounds that have been investigated as initiators involve Lewis acids [9], bi-functional catalysts [10], phosphonic and sulfonic acids [11] as well as basic compounds such as amines and imidazoles [11]. However, from the viewpoint of practical applications, the use of strong catalysts may severely compromise the shelf life of one-pot formulations [12].

Traditionally halogens have been used to improve flame resistance, acting in the gas phase through the formation of radicals that quench high-energy radicals. However, increasingly concern over the detrimental environmental impact and toxicity of the combustion products have led to legislation to ban their use [13] and organophosphorous flame retardants are becoming increasingly popular [14] to the extent that they have become an industry standard. Organophosphorous fire retardants act primarily like char in the condensed phase but *via* a different mechanism. They are intumescent in

nature and swell upon exposure to heat or flame to form a porous foamed mass which is usually carbonaceous and acts as a barrier to heat, air and pyrolysis product. It usually works in synergy with char in protecting the polymer and arises as a consequence of the thermal generation of phosphorus acids.

The reactive addition of phosphorus containing compounds based on mono-phenyl phosphoric acid (MPPA) has been reported with phenol formaldehyde resins [15]. The char yield in air increased from 52% without phosphorus to 66% with MPPA indicating the role of phosphorus in imparting thermo-oxidative resistance to the polymer. The enhancement was found to be greater when the phosphorus was introduced at the monomer stage and this is the approach taken in this work. PBZs are typically not inherently self-extinguishing and the use of flame retardant additives to promote char forming reactions is one of many methods that might be employed. To date, some limited studies have been carried out on PBZs following the incorporation of organophosphorous compounds such as the 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) group, which informs its use in the present study. There are literature precedents for the phosphine oxide group into other more established thermosets. For example, bis-phenoxy (3-hydroxy) phenyl phosphine oxide (BHPPO) has been copolymerised with an epoxy resin to form a flame retardant epoxy resin (BHPPO-EP). The addition of the phosphine oxide group increased the char yield from 20.2% to 51.8% under nitrogen at 800 °C, but did reduce the mechanical properties of the polymer [16]. The aim of the present work is to perform a systematic analysis of the effects of three organophosphorous compounds that have the potential to accelerate the polymerisation reaction and enhance the thermal stability, without detriment to the physical properties of the unmodified PBZ.

EXPERIMENTAL SECTION

Materials. 2,2-bis(3,4-Dihydro-3-phenyl-2H-1,3-benzoxazine)propane (BA-a) was supplied by Huntsman Advanced Materials (Basel, Switzerland) as Araldite MT35600. Three organophosphorous compounds were employed: 9,10-dihydro-9-oxa-10-oxide (DOPO), bis(4-hydroxyphenyl)phenylphosphine oxide (BHPPO), and diphenylphosphoramidate (DPPA) (Carbosynth Ltd.) (Figure 1). Following characterization using ¹H NMR, Raman spectroscopy and elemental analysis to determine identity, all reagents were used as received without further purification.

Figure 1. Structures of the organophosphorous flame retardants used in this work.

Blending of small-scale polymer samples. The monomer BA-a (1 g) was melted (m.p. = 58–70 °C) using a thermostatted oil bath, poured into a pre-weighed sample bottle and mixed for two minutes with a narrow spatula to disperse the desired quantity of the organophosphorous compound (1, 2, 4, 6, 8, and 10 wt %, *i.e.* 0.01 – 0.1 g) within the monomer. Once solid, the samples were broken up to form a powder.

Instrumentation and test methods. Differential scanning calorimetry (DSC) was undertaken using a TA Instruments Q1000 running TA Q Series Advantage software on samples (4.0 ± 0.5 mg) in hermetically sealed aluminium pans. Experiments were conducted under flowing nitrogen (50 cm³/min.) at a heating rate of 10 K/min. from room temperature to 300 °C, cooled to room temperature at 20 K/min, then rescanned to 250 °C at 10 K/min (to determine the glass transition temperature, T_g). In order to gauge the reactivity of the monomer in the bulk, dynamic DSC analysis was performed on all of the systems.

Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 (operating TA Q Series Advantage) on the previously cured DSC samples (3.0 ± 0.5 mg), which had a well-defined thermal history. Samples were placed in a platinum crucible and were heated from room temperature to 800 °C at 10 K/min in nitrogen (60 cm³/min).

RESULTS AND DISCUSSION

Exploring the effects of the additives on polymerisation behaviour. The DSC data for the scanning experiments are shown in Figure 2 and Table 1 as a function of the additive and concentration. In each case, the unmodified BA-a is included for comparison. The profile of the thermogram for the BA-a is typical for the commercial (rather than highly purified) monomer, with a narrow range spanning around 50 K, nearly symmetrical with a slight tail to higher temperatures.

Figure 2. DSC data 10 K/min under nitrogen showing effect of different additives: DOPO (top), BPPO (middle) and DPPA (bottom).

In the present work, it is notable that the addition of BHPPO has little effect on the shape or magnitude of the polymerisation exotherm in concentrations up to 4 wt %; beyond this concentration both the peak shape broadens and the onset of the polymerisation is significantly reduced to lower temperature. DPPA has a more marked effect, with even 2 wt % causing a change in the onset of polymerisation (by *ca.* 10 K), with the profile of the exotherm become more skewed at higher additive loadings (> 6 wt %). The case of DOPO provides the most marked change in the profile of the exotherm, with even 1 wt % causing a large reduction (30 K) in the onset in the polymerisation and peak maximum, a broadened peak profile. As the concentration is increased still further, the exothermic peak becomes still broader until at higher loadings (> 6 wt %), the peak becomes distinctly bimodal. This observation is by no means surprising as BPPO comprises two phenol groups bonded to the central P atom, which have been previously reported are good catalysts for the polymerisation of BZs [12]. Generally, it was observed that a reduction in the value of onset polymerisation was accompanied by an increase in the enthalpy of polymerisation (ΔH_p), which broadly indicates a higher degree of conversion. The potential for tautomerisation to occur (Figure 3), to yield a stronger nucleophile with a labile hydrogen and lone pair explains the increased reactivity in this case.

Figure 3. Tautomerisation of DOPO

Table 1 shows the results of the DSC analysis of BA-a doped with each additive as a function of concentration. The melting temperature of the monomer changed little within the different series of each blend. The glass transition temperature of the cured blends (reflecting the change in network formation) generally rises with increasing additive concentration and this is shown graphically in Figure 4.

Table 1. DSC Data for BA-a organophosphorous blends (10 K/min, under nitrogen, 50 cm³/min.)

Dopant (wt %)	T _m (°C)	T _{op} (°C)	T _{max} (°C)	T _{ep} (°C)	ΔH _p (J/g)	T _g (°C) ^a
0	39-43	182-199	235-244	295-300	341-344	153-157
DOPO						
1	40	155	217	295	347	158
2	42	160	215	284	341	172
4	40	147	211	290	347	166
6	41	135	198	270	320	173
8	41	142	186	280	298	169
10	40	142	183	270	291	172
BHPPO						
1	42	175	240	298	358	140
2	41	171	239	298	347	160
4	42	165	233	297	357	161
6	41	158	236	298	362	165
8	41	155	233	298	356	166

10	42	150	218	298	355	166
DPPA						
1	42	181	237	300	356	156
2	42	172	232	300	345	163
4	42	157	228	295	337	161
6	41	150	223	290	326	175
8	41	156	225	290	335	168
10	42	145	220	290	297	170

Key:

T_m = melting temperature, T_{op} = onset of polymerisation exotherm, T_{max} = Peak maximum of exotherm, T_{ep} = endpoint of polymerisation exotherm, T_g = glass transition temperature, ΔH_p = polymerisation enthalpy.

^a Recorded following cycle 1: 27-300 °C at 10 K/min, cycle 2: cool 10 K/min to 27 °C and cycle 3: 27-300 °C at 10 K/min.

Figure 4. Influence on cure reaction and final properties as a function of the different additives: DOPO (top), BPPO (middle) and DPPA (bottom).

Determining thermal stability of selected organophosphorous blends. Thermogravimetric analysis (TGA) was conducted to evaluate the mass loss as a function of temperature for the poly(BA-a) and in cured blends containing various concentrations of the additives (Table 2). A preliminary experiment was conducted on the unmodified poly(BA-a) (Figure 5) and agreed with published work [17,18] which has confirmed that the initial mass loss occurs at around 250-280 °C, with the loss of amine species accounting for the majority of the loss. The bulk of the mass loss occurs between 300-450 °C, associated with the degradation of phenolic moieties [19,20]. Finally, the formation of char tends to occur at temperatures above 500 °C and the typical yield for poly(BA-a) resin has been identified [21] to be around 30 % at 800 °C, which is in close agreement with the

present work. The incorporation of the additives was found to have significant effects on the

Figure 5. TGA data for poly(BA-a) blends at 10 K/min under nitrogen.

thermal stability of poly(BA-a), but in quite a different manner reflecting the decomposition chemistry of the additive. The concept that phosphorus has a synergistic relationship with other known flame retardants was investigated by Choi *et al.* [22]. The presence of nitrogen within polymers is known to act as a flame retardant by forming inert gases that dilute the reaction in the flame and cause the flame to extinguish. The weight loss rate of phosphorous-containing resins is typically lower than that of the phosphorus-free resin for the thermoxidative degradation. Char yields under nitrogen (as studied here) show no significant differences among the phosphorus-containing resins and the phosphorus-free resin, while under air char yields increased with increased phosphorus content. The presence of phosphorus increases the limiting oxygen index (LOI) values even when the phosphorus content is low, and no significant differences with the phosphorus content are observed [23].

DOPO has little influence on the temperature regime in which the initial degradation ($T_{5\%}$) takes place (Figure 6), but appears to be more important as the degradation proceeds (*e.g.* the presence of 6 wt% DOPO reduces $T_{10\%}$ by up to 20 K). On the other hand, the char yield is very similar, seemingly undergoing a slight reduction as DOPO content increases. Given that this is a measure

of the mass of the char, it is insensitive to the type of char formed, which might be the case if DOPO promotes a less dense ash, which breaks down as the heat is increased rather than forming a solid mass. In direct contrast, DPPA serves to increase the temperature at which the initial degradation occurs (*e.g.* the presence of 6 wt% DPPA increases $T_{5\%}$ by up to 20 K), but becomes less influential as the degradation proceeds; there is a modest increase in char yield with additive content. DOPO is one of the earliest researched phosphorus-based dopants used as a flame retardant dating back to 1972. Variants of DOPO have been developed within the last decades affording various DOPO-derivatives with P–C, P–N and P–O bond functionality. The majority of P–C bonded DOPO derivatives find application as flame retardants in epoxy resins as reactive (covalently bound) and additive dopants. It has been shown to improve char yield and the limiting oxygen index (LOI) [24,25]. This rigid and bulky group contains P–O–C bonds of unusually high thermal stability, which can be attributed to the protection afforded to the O=P–O moiety by the aromatic phenylene groups and hydrogen bonding [14].

Table 2. TGA data for BA-a blends containing different flame retardants (FR) acquired at 10 K/min (nitrogen)

FR	FR (wt%)	Temperature (°C) at which weight loss (%) recorded				Y_c (%)
		5 %	10 %	20 %	50 %	
-	-	280-282	321-329	348-351	435-444	30-31
DOPO	1	276	315	342	425	30
	2	295	319	358	437	31
	4	273	306	349	430	28
	6	282	304	345	426	28
	8	277	306	339	419	27
	10	276	301	328	417	27
BHPPO	1	250	295	346	425	31
	2	271	303	347	421	31
	4	278	309	349	419	32
	6	285	308	348	425	33
	8	289	306	346	424	33
	10	287	309	348	431	34
DPPA	1	285	331	357	439	30
	2	288	324	354	436	31
	4	296	335	356	434	31

	6	303	331	351	434	33
	8	311	328	351	426	32
	10	311	319	347	426	33

Key: Y_c = Residual mass recorded at 800 °C, poly(BA-a) was analysed three times and a range of temperatures is given.

The presence of phenylphosphine oxide group has shown an improvement in the thermal stability of PBZs except for the combination with methylamine. In that case the introduction of methylamine into three different types of phenylphosphine oxide structures, only bis(4-hydroxyphenyl)phenylphosphine oxide (BHPPO) showed a 14% improvement in char yield. However, the combination with the bis(4-hydroxyphenoxy-4'-phenyl)phenylphosphine oxide (BPPPO) backbone and an acetylene functional group on the aniline showed a profound effect on the thermal stability of polybenzoxazine, demonstrated by a char yield as high as 76%. Generally, the use of phenylphosphine oxide based dopants was shown to bring forward the onset of degradation to lower temperatures, but lower the rate of heat release of the polymer, meaning it took longer to char. Phenylphosphine oxides were also found to increase the glass transition temperature (T_g) of the polymer, which was attributed to the strong polar interactions within the chains due to the dopant being added as a reactive system [22].

In the present work, BHPPO displays somewhat intermediate behaviour: with a significant drop in the onset of degradation of poly(BA-a) (*e.g.* the presence of 1 wt% BHPPO reduces $T_{5\%}$ by up to 30 K, but 6 wt% BHPPO increases $T_{10\%}$ by some 3 K). The char yield experiences a modest increase in char yield (of *ca.* 4 wt % with the maximum incorporation of BHPPO).

Figure 6. TGA data for poly(BA-a) blends at 10 K/min under nitrogen.

Investigating the influence of additive concentration on degradation mechanism. Two samples of poly(BA-a) (prepared containing 4 and 10 wt % BHPPO) were examined under identical conditions and the TGA data are presented in Figure 7. At the lowest concentration of BHPO, the degradation mechanism (revealed by the DTG trace) is very similar to the unmodified poly(BA-a) with three main mass losses. Yet, even when the concentration of DPPA is increased significantly (to 10 wt %), there is only a subtle change in the apparent mechanism of the polymer degradation. The three distinct regions of the degradation pathway remain well defined with a growth in the higher temperature, char forming reaction.

Figure 7. TGA data for poly(BA-a) containing 4 wt % (top) and 10 wt % BHPPO (bottom) at 10 K/min under nitrogen.

A further three samples of poly(BA-a) (prepared containing 1, 6 and 10 wt % DPPA) were examined under identical conditions and the TGA data are presented in Figure 8. At the lowest concentration of DPPA, the degradation mechanism (revealed by the DTG trace) is very similar to the unmodified poly(BA-a) with three main mass losses. At the higher concentrations of DPPA, there is a subtle change in the apparent mechanism of the polymer degradation. The three distinct regions of the degradation pathway become less well defined with a growth in the higher temperature, char forming reaction.

Figure 8. TGA data for poly(BA-a) containing 1 wt % (top), 6 wt% (middle) and 10 wt % DPPA (bottom) at 10 K/min under nitrogen.

Finally, three samples of poly(BA-a) (prepared containing 1, 2, and 8 wt % DOPO) were examined and the TGA data are presented in Figure 9. In this case as the concentration of DOPO in the blend

is increased, there is distinct change in the apparent mechanism of the polymer degradation. At a level of 1 wt% DOPO, the pattern of degradation resembles more closely the data for unmodified poly(BA-a), with the highest rate of mass loss relating to the breakdown of the aromatic ring structures. As the amount of DOPO in the blend is increased the profile changes significantly with the intensity (and hence rate of the mass loss) of the highest temperature process, relating to char formation, is also enhanced (at the expense of the ring breakdown, which is reduced).

Figure 9. TGA data for poly(BA-a) containing 1 wt % (top), 2 wt % (middle) and 8 wt % DOPO (bottom) at 10 K/min under nitrogen.

CONCLUSIONS

Incorporation of all additives resulted in a reduction in the temperature of the initiation of the curing

mechanism, but only the DPPA and DOPO samples decreased the temperature for the conclusion of the reaction (i.e. moved the cure process to a lower temperature regime). The energy released by curing was consistent throughout for BHPPO but DPPA and DOPO lowered the enthalpy as the mass increased. The T_g increased for all three samples as the amount of additive contained in the sample increased. DOPO had the greatest influence on cure mechanism (by change in onset, end and polymerisation enthalpy). This was beneficial in terms of onset and end temperatures but not in enthalpy. A lower enthalpy suggests fewer cross-links and a curing that has not reached its full potential and can leave the material weaker. The rise in T_g for all three suggests a higher degree of intramolecular interactions between the chains.

TGA was conducted on the samples cured by DSC. TGA was used to determine the degradation mechanism and observe how it changes due to the dopants. A char yield was left at the end of the program with a higher char yield indicating less material has been degraded. The pattern of degradation for BA-a based materials was shown to be a small initial decrease in mass caused by the breaking of single bonds followed by a sharp decrease caused by the breaking of benzene rings and char formation before plateauing once char had formed. DPPA was shown to have the least effect on the degradation mechanism with char formation occurring at a slightly lower temperature than poly(BA-a). Char yield did increase by 3 % though suggesting the phosphorus aided the formation of char through its intumescent properties. DPPA changed the mechanism by greatly promoting the formation of char. By the midpoint of the series char formation was the main process of degradation. It also increased the temperature at which the onset of degradation occurred. Char yield also increased by 3 % over the series showing phosphorus did have an effect on the char. DOPO had the most dramatic effect on the degradation mechanism and the char yield of poly(BA-a). The addition of just 1 % DOPO promoted char formation to the main process of degradation. Char yield however decreased as the percentage of DOPO in the sample increased. The thermograms produced by the DOPO doped samples showed degradation in the later part of the trace. This showed the phosphorus has a large impact in the formation of char but the char formed was not stable. The next phase of this work will involve conducting flame testing to examine combustion and heat release using cone calorimetry on the best performing of these materials in reinforced composite samples.

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