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Fire retardancy mechanisms of arylphosphates in polycarbonate (PC) and PC/acrylonitrile-butadiene-styrene

The key role of decomposition temperature

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Abstract The pyrolysis of polycarbonate (PC) and PC/acrylonitrile-butadiene-styrene (PC/ABS) with and without arylphosphates (triphenylphosphate TPP, resorcinol-bis(diphenyl phosphate) RDP and bisphenol A bis(diphenyl phosphate) BDP) is investigated by thermal analysis as key to understanding the flame retardancy mechanisms and corresponding structure–property relationships. The correspondence between the decomposition temperature range of arylphosphates and PC is pointed out as prerequisite for the occurrence of the reaction between arylphosphate and structures that are typical for the beginning of PC decomposition. Resulting cross-linking enhances charring in the condensed phase and competes with the alternative release of phosphate in the gas phase and thus flame inhibition. Flame inhibition was identified as the main flame retardancy mechanism. The additional condensed phase mechanisms optimise the performance.

Keywords Arylphosphates · BDP · Flame retardance · PC · PC/ABS

Introduction

Flame-retardant bisphenol A polycarbonate (PC) and bisphenol A polycarbonate/acrylonitrile-butadiene-styrene blends (PC/ABS) are important engineering materials, especially for electrical engineering [1, 2]. Several flame retardants for PC/ABS are common. In addition to many halogen-containing compounds, there is an increasing preference for halogen-free flame retardants, such as phosphorus-containing additives [3, 4]. Triphenylphosphate (TPP), resorcinol-bis(diphenyl phosphate) (RDP) and bisphenol A bis(diphenyl phosphate) (BDP) are among these effective non-halogenated flame-retardants [5–7]. Such arylphosphates are used most commonly for PC/ABS blends [8]. TPP causes flame inhibition in the gaseous phase; RDP mainly flame inhibition, but also some charring in the condensed phase; and BDP acts in the gaseous phase as well as in the condensed phase during the process of the material burning [9, 10]. In the gaseous phase the aryl phosphates act via flame inhibition, delivering PO radicals which replace the hydrogen and hydroxide radicals and thus reduce combustion efficiency. In the condensed phase they convey the cross-linking of the partially decomposed polymer material and enhance dehydrogenation. Arylphosphates acting in the condensed phase result in charring that yields both a decreased fuel production and an increased barrier against transport processes, such as heat and pyrolysis gases.

The flame-retarding action of phosphates is dependent on the decomposition and vaporization of the compound used, but also on interactions with the pyrolysing polymer and with other additives influencing the decomposition [9, 11–14]. Moreover, small changes in the system can result in large changes in the mechanisms. Not only can distinct flame retardancy mechanisms of phosphorous compounds be enhanced, it is even possible to switch between gas phase and condensed phase ones [15–18]. Thus a detailed understanding of the flame retardancy mechanisms is a challenge for the future tailored development of flame retarded polymeric materials. One important aspect in optimising and adjusting flame retardancy is exploiting chemical reactions at the right place, time and temperature. The common use of flame retardants containing Br is

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indicative of this point. Br-containing flame retardants are used even though the flame inhibition activity of HI is higher than that of HBr, since the low bond dissociation energy of I–C bonds results in release at temperatures far below those of polymer decomposition [19]. It is the aim of this contribution to address the role of the decomposition temperature both of arylphosphates and of PC in the flame retardancy effect and efficiency of arylphosphates in PC and PC/ABS.

Therefore, the decomposition of PC, TPP, RDP, BDP, PC/BDP, PC/ABS, PC/ABS/TPP, PC/ABS/RDP and PC/ABS/BDP was examined. All PC blends contain an additional small amount of PTFE. The flammability and burning behaviour were monitored. The systematic approach reveals an illuminating insight into the role of the decomposition temperature both of PC and of arylphosphates for the flame retardancy effect and efficiency in PC and PC/ABS. The conclusion of this work may have an essential impact on the future development of flame retardants for PC/ABS.

Experimental

All investigated PC/ABS blends and PC/BDP consisted of unbranched polycarbonate based on bisphenol A. TPP had a molecular mass of $M_{\mathrm{TPP}} = 326.3$ g mol^{-1}. The BDP (molecular mass of $M_{\mathrm{BDP}}(n = 1) = 692.6$ g mol^{-1}) and RDP ($M_{\mathrm{RDP}}(n = 1) = 574.4$ g mol^{-1}) used show an averaged number of repeating units of $n = 1.1$ and 1.2–1.3, respectively. PTFE was added to PC/ABS blends and PC/BDP as a master batch consisting of coagulated 1:1 mixture of SAN and PTFE. PTFE changes the viscosity of the polymer melt and in particular it prevents dripping in the UL 94 test [9]. PC/ABS, PC/ABS/BDP, PC/ABS/TPP and PC/ABS/RDP were blended with ABS in the ratio of PC:ABS = 4.7:1. All investigated blends with and without the distinct arylphosphates showed the same blend morphology. The ABS particles had a size of several hundreds of manometers up to a few micrometers and were embedded within the homogenous PC matrix phase. The ABS ratio was A:B:S = 21:13:66. The ABS was not observed as a homogeneous phase but was characterized by core shell structures, since butadiene rubber particles were grafted with SAN. All materials were compounded and provided as granulates and test specimen by Bayer MaterialScience AG (Dormagen, Germany). All specimen were manufactured by injection moulding. Actually two sets of materials were received, consisting of PC/BDP and PC/ABS/BDP (set 1) and PC/ABS, PC/ABS/BDP, PC/ABS/RDP and PC/ABS/TPP (set 2), based on different batches of PC. The different PC batches exert no significant influence on the results obtained by thermal analysis, but unfortunately do have a significant influence on burning behaviour in cone calorimeter tests, due to different deformation behaviours. This difference in burning behaviour was taken into account by separating the discussions of the two different sets. The exact contents for each material are given in Table 1 ($\leq$1 mass% corresponds to processing adjuvants not specified). Additionally the neat materials such as PC, TPP, RDP, BDP and ABS were analysed in thermal analysis.

For the investigation of thermal decomposition a TG (TGA/SDTA 851, Mettler Toledo, Germany) was used. All measurements of thermal decomposition were performed under nitrogen with a heating rate of 10 K min^{-1}. The sample mass for each measurement was 10 mg. The standard deviation for thermogravimetry was about 1 mass%. For the investigation of the forced flaming behaviour a cone calorimeter (FTT, UK) was used following ISO 5660-1/2 [20–22]. An external heat flux of 50 kW m^{-2} was used. The dimensions of the samples were 100 × 100 × 3 mm and they were arranged horizontally in a frame. For assessing the heat release propensity [23], in particular when total oxidation of the pyrolysis gases occurs, a pyrolysis combustion flow calorimeter (PCFC) (FTT, UK) was used. The samples (5 mg) were thermally decomposed in the pyrolyser under a nitrogen atmosphere with a heating rate of 1 K s^{-1} up to 1,023 K. The pyrolysis gases were transferred into the combustor where they were oxidised completely under a nitrogen/oxygen atmosphere in the ratio of 80:20 vol%. The temperature in the combustor was 1,173 K. The flammability of the materials was investigated by limiting oxygen index (LOI) following ISO 4589

Table 1 Investigated materials (remaining mass% is other additives)

	PC/BDP/mass%	PC/ABS/mass%	PC/ABS/BDP/mass%	PC/ABS/RDP/mass%	PC/ABS/TPP/mass%
PC	86	82	71	71	71
ABS		17	15	15	15
BDP	12.5		12.5		
RDP				12.5	
TPP					12.5
PTFE	0.45	0.45	0.45	0.45	0.45

with a sample size of 80 × 10 × 4 mm, and by UL 94 vertical (V2, V1, V0) and horizontal (HB) classifications following IEC 60695-11-10 with a sample size of 120 × 12.5 × 1.5 mm.

Results and discussion

Thermal decomposition

In Fig. 1 the mass and mass loss rate curves of PC, BDP and PC/BDP are shown and compared with the PC/BDP curves calculated assuming a superposition of the decomposition processes of the PC and BDP contained. In Table 2 the main thermal analysis results are given for PC, BDP and PC/BDP. PC and BDP decompose in one decomposition step, whereby the temperature for maximum mass loss (T_{max}) for BDP was located at 738 K; T_{max} for PC lies at 798 K. PC gave a residue of 31.5 mass%, while BDP decomposed almost without charring. The two decomposition processes overlapped only marginally. PC/BDP decomposed between 661 and 858 K in a main decomposition step and a small preceding shoulder. T_{max} of the shoulder was 740 K and T_{max} of the main step was 801 K. Thus the observed mass and mass loss rate curves of PC/BDP are very similar to the ones calculated based on the simple superposition of characteristics of both components. The temperatures for maximum mass loss correspond well to $T_{\mathrm{max1(calculated)}}$ at 738 K and the $T_{\mathrm{max2(calculated)}}$ at 798 K of the calculated decomposition curve. The decomposition temperatures relate to the ones of the neat materials. Hence the second decomposition step of PC/BDP resulted from the PC decomposition; the shoulder from the BDP decomposition. Based on the thermal analysis it is concluded that no significant reaction between BDP and PC occurs or that it is of rather negligible importance with respect to decomposition temperatures and residue.

The addition of ABS to PC without BDP changes the decomposition behaviour of the components significantly (Fig. 2; Table 3). While neat ABS and neat PC decomposed in a single decomposition step, with the two curves barely overlapping, the blend of PC/ABS decomposed in two strongly overlapping steps. The first decomposition step is related to the decomposition of ABS, the second step is related to the decomposition of PC. The temperatures for maximum mass loss shift notably in comparison with the pure components. The T_{max} for the first step shifted 26 K to higher temperatures compared to the neat compound; the second step shifted about 22 K to lower temperatures. A significant interaction between ABS and PC occurred influencing both the release of ABS and PC decomposition. A further reason for the shift in the first ABS mass loss step may be the embedding of the ABS phase in the PC matrix, which can be proposed to hinder the easy release of ABS decomposition products. The change in decomposition of the PC indicates a strong interaction between PC and ABS or decomposition products of ABS, which leads to a thermal destabilisation of PC. This is also fortified by comparing the decomposition of PC/ABS with the curves calculated assuming only a superposition of the decomposition processes of the PC and ABS contained (Fig. 2). Further, the thermal

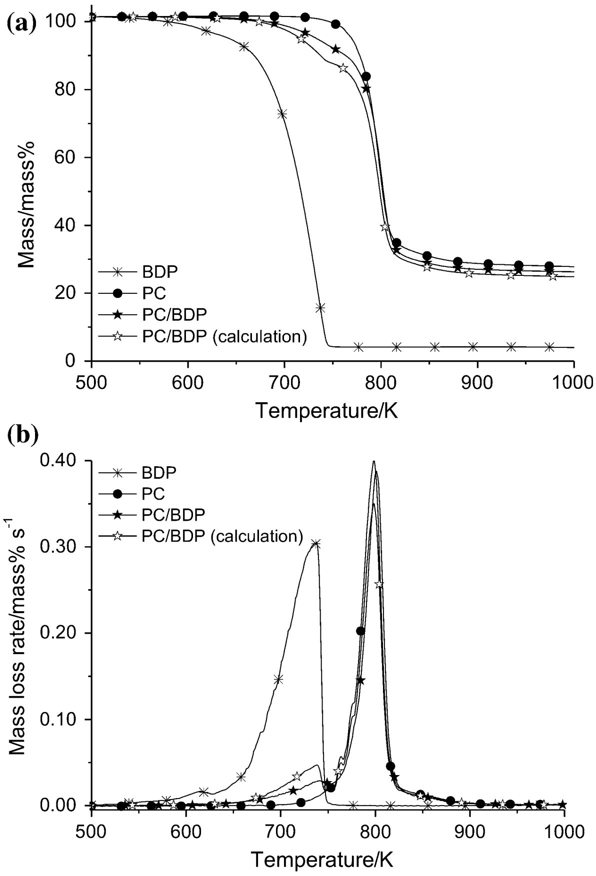

Fig. 1 Mass (**a**) and mass loss rate (**b**) for BDP, PC and PC/BDP under nitrogen (heating rate 10 K min^{-1}) compared with PC/BDP curves calculated assuming a superposition of the decomposition processes

Table 2 Thermal analysis of BDP, PC and PC/BDP

	PC	BDP	PC/BDP	Error
T_{max1}/K		738	740	±2
$\mathrm{ML_1}$/mass%		95.8	7.7	±1
T_{max2}/K	798		801	±2
$\mathrm{ML_2}$/mass%	65.5		64	±1
Residue/mass%	31.5	4.2	28.3	±1

ML mass loss

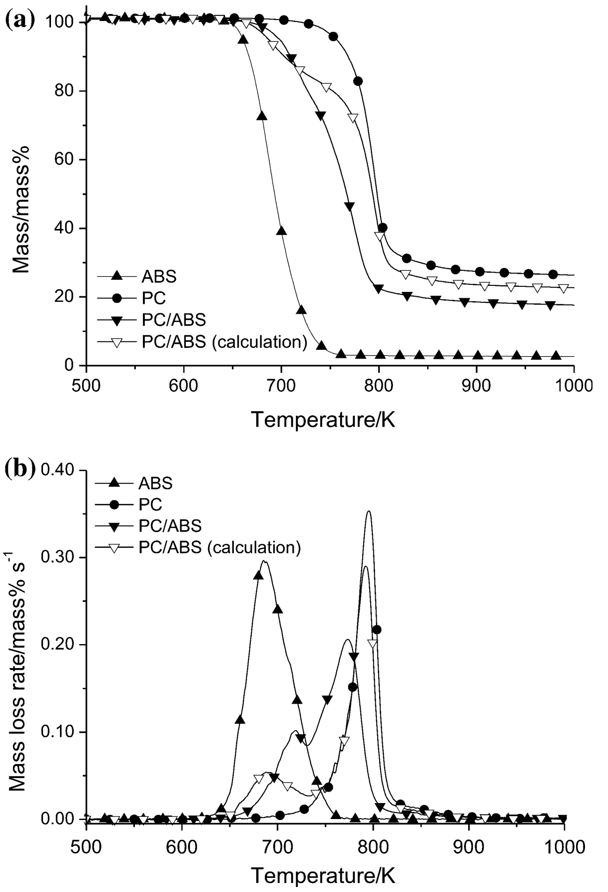

Fig. 2 Mass (**a**) and mass loss rate (**b**) for ABS, PC and PC/ABS under nitrogen (heating rate 10 K min^{-1}) compared with PC/ABS curves calculated assuming a superposition of the decomposition processes

decomposition of PC/ABS results in a clear reduction in char in comparison to the calculated PC/ABS curve.

The addition of BDP to PC/ABS resulted in two well-separated decomposition steps (Fig. 3; Table 3) corresponding to ABS and PC decomposition, respectively, where T_{max2} of the PC decomposition fit well with the decomposition temperature of neat PC. Thus adding BDP to PC/ABS shifts the PC decomposition of PC/ABS back towards higher temperatures. T_{max1} of ABS was also shifted back to temperatures lower than for PC/ABS, but still showed a decomposition temperature 10 K higher than neat ABS. Thus the observed mass and mass loss rate curves of PC/ABS/BDP are strongly different compared to the decomposition of PC/ABS and BDP, but become somehow similar to the ones calculated based on the simple superposition of characteristics of PC, ABS and BDP (Fig. 3). However, the shifting-back of the ABS decomposition was only around half of the effect observed for PC/ABS, but the shifting-back of the PC decomposition was even larger than the effect observed for PC/ABS at the same time. Further, the char yield of PC in PC/ABS/BDP was significantly increased compared to the ones calculated based on the simple superposition of characteristics of PC/ABS + BDP as well as of PC + ABS + BDP. A simple switching off of the interaction between PC and ABS was ruled out as explanation. A significant reaction between BDP and the decomposing PC of PC/ABS is concluded, which changes the decomposition temperatures competing with the effects observed for PC/ABS without BDP and increases the char yield. This reaction of BDP with decomposing PC was observed for PC/ABS/BDP, when the temperature region for BDP release overlaps with the PC decomposition of PC/ABS (Fig. 3), but not for PC/BDP, when the BDP release happens before the decomposition of PC (Fig. 1). These conclusions are confirmed by comparing the influence on the decomposition using different arylphosphates discussed in the following.

Table 3 Thermal analysis of PC, ABS, PC/ABS and PC/ABS/BDP

	PC	ABS	PC/ABS	PC/ABS/BDP	Error
T_{max1}/K		689	715	699	±2
ML_1/mass%		96.8	20.9	24.7	±1
T_{max2}/K	798		776	800	±2
ML_2/mass%	65.5		56.4	46.6	±1
Residue/mass%	31.5	3.2	22.7	28.7	±1

In Fig. 4 and Table 4 the thermal decomposition of TPP, RDP and BDP is compared, along with PC/ABS. The molecular masses of the three arylphosphates differ in the order of TPP < RDP < BDP. The T_{max} of the mass loss rate is in the same order of TPP < RDP < BDP. The difference in the T_{max} between TPP and BDP is around 160 K, the difference between RDP and BDP is around 55 K. There is almost no overlap between the mass loss rate curves of TPP and the PC decomposition of PC/ABS, whereas the part of the decomposition of RDP and BDP extended into the temperature range typical for the decomposition of PC in PC/ABS. The overlap of the decomposition processes is larger for BDP than for RDP.

The influence on the decomposition of PC/ABS by adding TPP, RDP and BDP is shown in Fig. 5 and Table 4. Because of its lower decomposition temperature, TPP is released before the decomposition of PC/ABS in a corresponding preceding small decomposition step. PC/ABS/TPP decomposes in three steps. Apart from the preceding release of TPP, the mass loss rate curve looked almost similar to the mass loss rate curve of PC/ABS. The residues of PC/ABS and PC/ABS/TPP were almost the same; no significant interaction occurred between TPP and the PC decomposition in PC/ABS. PC/ABS/BDP and PC/ABS/RDP decomposed in only two decomposition steps. PC/ABS/RDP decomposed somewhat similarly to PC/ABS/

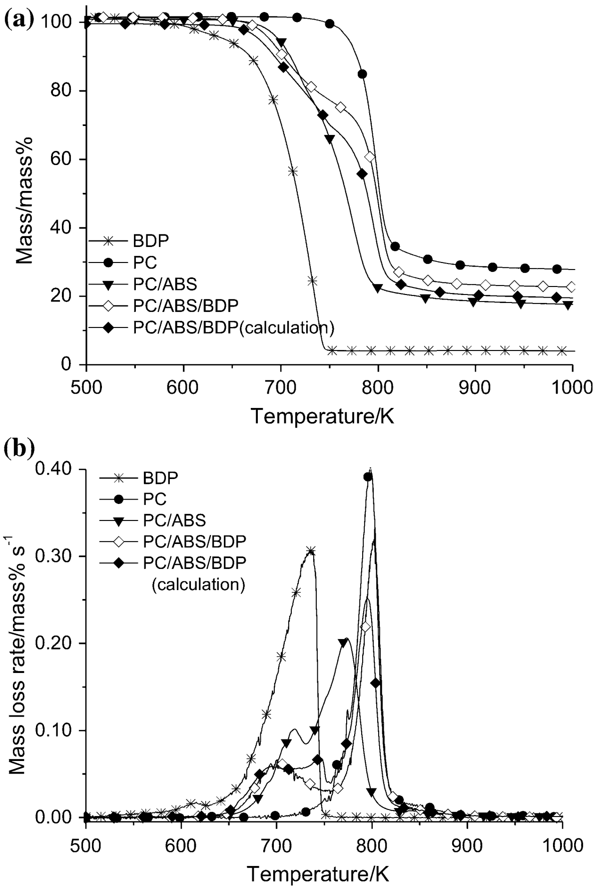

Fig. 3 Mass (**a**) and mass loss rate (**b**) for BDP, PC, PC/ABS and PC/ABS/BDP under nitrogen (heating rate 10 K min^{-1}) compared with PC/ABS/BDP curves calculated assuming a superposition of the decomposition processes

BDP. The $T_{\max}$ of both the ABS and the PC decomposition shifted in comparison to PC/ABS without arylphosphate, as was already discussed for PC/ABS/BDP. The amount of residue for PC/ABS/RDP was lower than that for PC/ABS/BDP, but higher than that for PC/ABS/TPP. The decomposition of PC/ABS/RDP started around 20 K lower than that of PC/ABS/BDP, which can be explained by the earlier decomposition of RDP. The thermal decomposition of PC/ABS/TPP, PC/ABS/RDP and PC/ABS/BDP and thus the reaction with the PC decomposition of the three arylphosphates within a PC/ABS blend increased in the same order as the decomposition temperature for the neat arylphosphates.

The thermal analysis shows the enhancement of decomposition of PC (lower decomposition temperature and lower char yield) by ABS and the propensity of arylphosphates for a reaction with PC that increases the decomposition temperature and also increases the residue. The occurrence of the impact of arylphosphate on PC decomposition correlates empirically with the degree of overlap between the decomposition temperature ranges. A rather negligible impact was observed between BDP and PC when the overlapping of the decomposition temperature ranges of BDP and PC was negligible, whereas the significant overlap between BDP and PC decomposition in PC/ABS (Fig. 3) resulted in a significant reaction between BDP and early decomposition products of PC in PC/ABS/BDP. The overlapping between the arylphosphate release and the PC decomposition in PC/ABS increases in the order TPP < RDP < BDP (Fig. 4), as does the influence between the arylphosphate and PC. This empirical structure–property relationship is well illustrated and quantified to some degree by comparing the residue yields with residue yields calculated based on a superposition of the components (Table 5). The additional residue for PC/BDP lies within the margin of error; hence there is hardly any char-enhancing effect for BDP and PC. The residues for PC/ABS and PC/ABS/BDP differ significantly from those calculated. The residue of PC/ABS is about 3.6 mass% lower than expected; the residue of PC/ABS/BDP is 8.6 mass% higher than estimated. The impacts of the arylphosphates on enhancing char are ordered as follows: TPP (2 mass%) < RDP (4.6 mass%) < BDP (8.6 mass%).

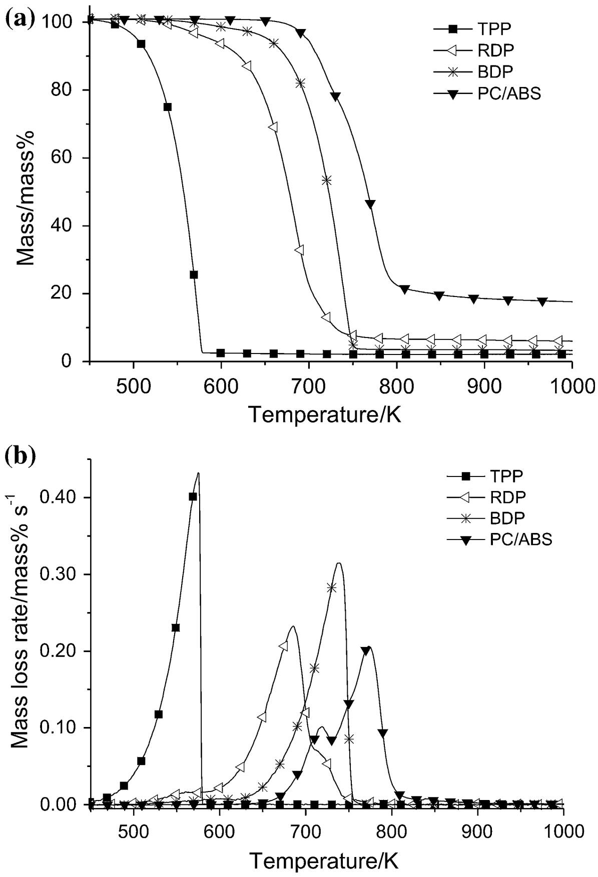

Fig. 4 Mass (**a**) and mass loss rate (**b**) for TPP, RDP, BDP and PC/ABS under nitrogen (heating rate 10 K min^{-1})

The overlapping decomposition temperature ranges of arylphosphate and PC was observed as an empirical

Table 4 Thermal analysis of TPP, RDP, BDP, PC/ABS, PC/ABS/TPP, PC/ABS/RDP and PC/ABS/BDP

	T_{max}/K ±2	ML/mass% ±1	T_{max1}/K ±2	ML_1/mass% ±1	T_{max2}/K ±2	ML_2/mass% ±1	Residue/mass% ±1
TPP	577	97.3					2.7
RDP	684	90.3					6.9
BDP	736	95.8					4.2
PC/ABS			715	20.9	776	56.4	22.7
PC/ABS/TPP	558	9.8	703	19.2	779	49.2	21.8
PC/ABS/RDP			694	26.5	799	48.5	25.0
PC/ABS/BDP			699	24.7	800	46.6	28.7

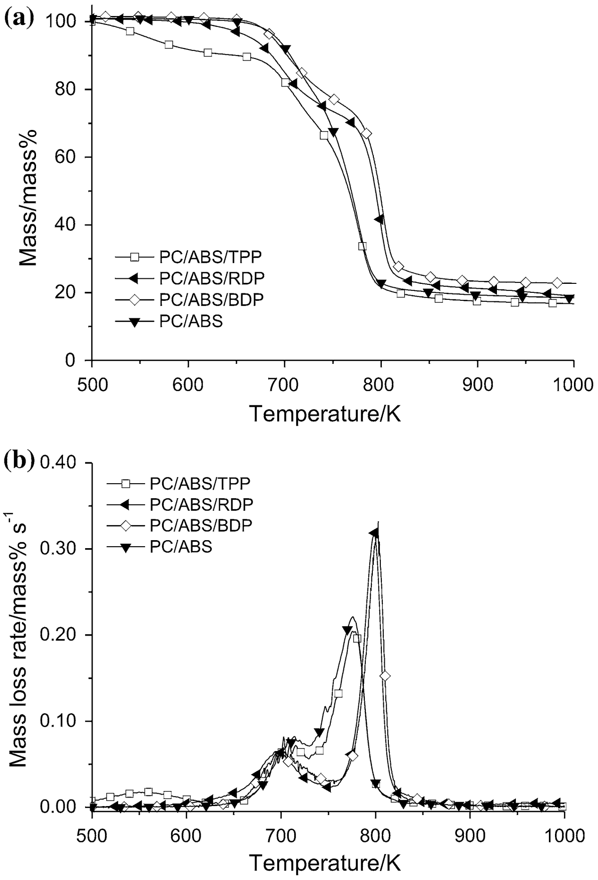

Fig. 5 Mass (**a**) and mass loss rate (**b**) for PC/ABS/TPP, PC/ABS/RDP, PC/ABS/BDP and PC/ABS under nitrogen (heating rate 10 K min^{-1})

Table 5 Residues compared with the calculated residues based on superposition of the residues of the components for PC/BDP, PC/ABS, PC/ABS/BDP, PC/ABS/RDP and PC/ABS/TPP

	Residue/mass%		
	Calculated from components		Experimental
PC/BDP	PC (86 mass%)	BDP (12.5 mass%)	
	27.1 +	0.5	
	= 27.6		28.3
PC/ABS	PC (82 mass%)	ABS (15 mass%)	
	25.8 +	0.5	
	= 26.3		22.7
PC/ABS/BDP	PC/ABS (86 mass%)	BDP (12.5 mass%)	
	19.5 +	0.5	
	= 20.0		28.7
PC/ABS/RDP	PC/ABS (86 mass%)	RDP (12.5 mass%)	
	19.5 +	0.9	
	= 20.4		25.0
PC/ABS/TPP	PC/ABS (86 mass%)	TPP (12.5 mass%)	
	19.5 +	0.3	
	= 19.8		21.8

prerequisite for the reaction between arylphosphates and PC. Thus a reaction with decomposition products of PC, namely the reaction of arylphosphate with Fries rearranged PC structures (Fig. 6.), was proposed as a key reaction. At higher temperatures PC undergoes rearrangement reactions [24–26] such as the Fries rearrangement. Fries rearrangements are known to induce the cross-linking of PC within the solid residue and therefore the enhancement of the charring. Arylphosphates undergo transesterification reactions with the PC. They catalyse the Fries rearrangement of the PC so that more hydroxyl groups are generated. Further arylphosphates take part in the cross-linking reactions and are integrated into the char network. The reaction between arylphosphate and the rearranged PC structure competes with the release of arylphosphate. The greater the amount of arylphosphates released before the decomposition of PC starts, the less impact is observed. This also means that the thermal destabilisation of the PC in PC/ABS is what actually makes the reaction between BDP and PC possible.

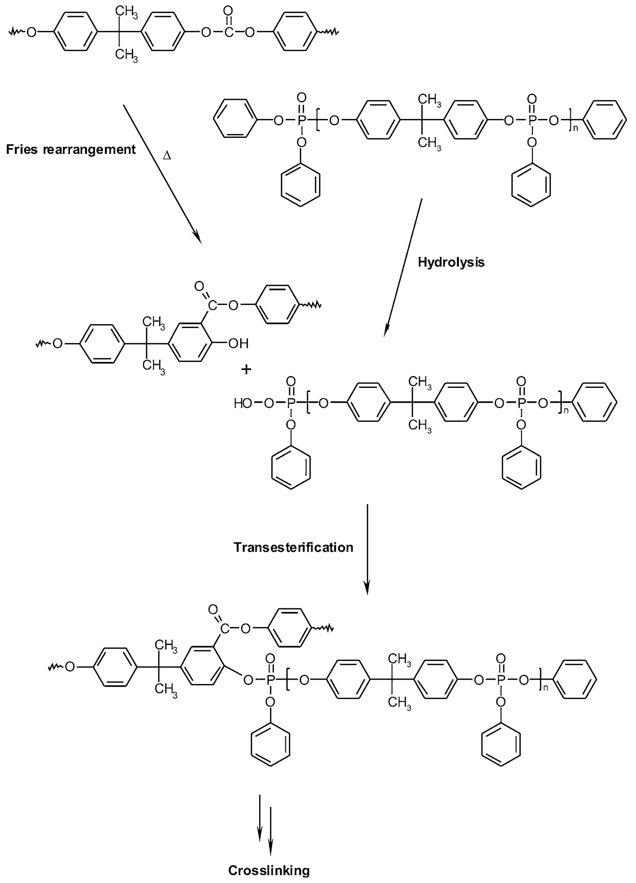

Fig. 6 Fries rearrangement of PC and the transesterification reaction with hydrolysed BDP

Burning behaviour

From the thermal analysis it was concluded that all investigated arylphosphates release phosphorus (in the form of phosphates) in the gas phase, most probably causing a flame inhibition in fire tests. Further, an additional flame retardancy effect is expected through enhanced residue formation due to the interaction of arylphosphates and rearranged units of PC. This flame retardancy mechanism in the condensed phase was concluded to depend significantly on the correspondence between the decomposition temperatures of the arylphosphate and the PC. When both mechanisms occur, flame inhibition, due to the release of phosphate, and charring, due to phosphate reacting in the condensed phase, apparently compete with each other.

In Table 6 the results of cone calorimeter and PCFC investigations are summarized for the two sets of samples (since the two sets are based on different batches of PC the results are only comparable within each set). The results confirm the conclusions from thermal analysis and, moreover, determine whether a gas phase mechanism or a condensed phase mechanism is active, or both. The fire risk total heat evolved (THE), the fire residue and the combustion efficiency (χ) are shown as characteristic results from the cone calorimeter (irradiation 50 kW m^{-2}). The combustion efficiency is calculated using the ratio THE/ML (ML = mass loss) measured in the cone calorimeter, divided by the heat of combustion for the total oxidation of the volatiles (h_c^0), which is given by the PCFC (Eq. 1) [15]:

$$\chi = \frac{\mathrm{THE/ML}}{h_c^0} \tag{1}$$

The combustion efficiency is a direct measure of the flame inhibition effectiveness; the residue for the residue formation. The fire risk (THE) depends on both effects [27]. The combustion efficiency, the total heat release divided by the sample mass (HR) and the residue measured in the PCFC are summarized in Table 6. Since a total oxidation of the pyrolysis gases takes place in the PCFC, HR is a measure for the fire hazard propensity that disregards flame inhibition, but accounts for the effective heat of combustion of the volatiles (h_c^0) and charring. The latter influence is monitored separately by investigating the residue.

In general the residues observed in the cone calorimeter were systematically larger than the residues in thermal analysis. The residues monitored by the PCFC were smaller than the residues in thermal analysis. The less complete decomposition in the cone calorimeter is quite common and is due to heat protection occurring in the macroscopic sample. The smaller residue in the PCFC may be caused by the higher heating rates, which favour the scission of the polymer chain and the release of small volatile pyrolysis products [11]. Thus more complex decomposition pathways including rearrangements and subsequent cross-linking are reduced. ABS does not contribute to charring because it decomposes with almost no residue; hence the main charring agent in the investigated blends is the PC component. Comparing the fire residues of PC/BDP with PC/ABS/BDP monitored in the cone calorimeter, it becomes clear that for PC/ABS/BDP (71 mass% PC) the char yield of the PC component is around 10% higher than in PC/BDP (86 mass% PC). Assuming that the PC char yield is reduced by adding ABS, as observed in the thermal analysis, the char-enhancing effect of BDP in PC/ABS/BDP is clearly higher than in PC/BDP. The structure–property relationship was also confirmed by comparing the fire residues of the cone calorimeter and the PCFC for PC/ABS, PC/ABS/TPP, PC/ABS/RDP and PC/ABS/BDP. The char yield increases in the order of TPP < RDP < BDP.

The different degrees of consumption of arylphosphate in cross-linking reactions in the condensed phase correspond to the change in phosphorus released in the gas phase. PC/BDP is assumed to show a lower combustion efficiency (χ) than PC/ABS/BDP, even though the

Table 6 Cone calorimeter and PCFC results for all materials

Sample	Cone calorimeter			PCFC	
	THE/MJ m^{-2} ± 5	Residue/mass% ± 3	χ ±0.02	HR/kJ g^{-1} ± 0.3	Residue/mass% ± 0.4
Set A					
PC/BDP	49.9	31.1	0.76	17.3	24.4
PC/ABS/BDP	54.7	27.9	0.78	19.5	19.4
Set B					
PC/ABS	59.9	29.0	0.96	22.2	18.4
PC/ABS/BDP	45.3	35.1	0.82	21.4	20.5
PC/ABS/RDP	45.7	31.5	0.80	20.9	20.3
PC/ABS/TPP	44.8	32.9	0.78	22.2	16.7

THE total heat evolved, χ combustion efficiency, *HR* total heat release divided by the sample mass

difference is, strictly speaking, within the margin of error. The χ of TPP, RDP and BDP is ordered: TPP < RDP < BDP. Thus an increase in condensed phase activity of arylphosphate goes along with a decrease in flame inhibition in the gas phase.

The combustion efficiency of PC/ABS (0.96) is very close to 1, indicating the nearly complete combustion of the volatile pyrolysis products in the well-ventilated fire of the cone calorimeter. In all investigated materials adding arylphosphate results in very similar combustion efficiencies between 0.76 and 0.82. Thus a very similar flame inhibition occurs in the materials. The χ values for the three arylphosphates confirm the previous results that all act in the gaseous phase [15]. Further, since the THE is reduced by 23–26% the flame inhibition is the main flame retardancy effect, accounting for around ¾ of the flame retardancy observed. However, the condensed phase action of the arylphosphates in PC/ABS blends is clearly indicated.

In Table 7 the materials' reaction to a small flame (flammability) is summarized using the LOI and the UL 94 tests. Neat PC has an LOI of 27.0% and a UL 94 classification of V-2 (for a sample thickness between 0.75 and 2.4 mm). The addition of BDP to PC as flame retardant strongly enhances the LOI value to 39.1% and meliorates the performance in the UL 94 to V-0. In contrast, the addition of ABS to PC gives a poor performance because it lowers the LOI to 23.6%, failing the vertical test, but passing the horizontal test in the UL 94. PC/ABS flame retarded with BDP leads to a high LOI value of 29.2% for materials from set A and 28.2% for materials from set B. The difference between the two sets of materials is within the margin of error and both PC/ABS/BDP investigated achieve V-0 classification in UL 94. PC/ABS/BDP, PC/ABS/RDP and PC/ABS/TPP show similar good performances in both flammability tests. A slightly better result seems to occur for TPP and RDP than for BDP with respect to LOI, even though the difference is within the margin of error. It is assumed that the high LOI value for PC/BDP and the slightly better performance of TPP and RDP correspond to the higher gas phase flame retardancy action, because it is said that the LOI is quite sensitive to flame inhibition [16]. What is more, all materials show a suitable improvement in flammability due to the combination of a main gas phase and an additional condensed phase mechanism as already has been reported to be a successful approach [28].

Table 7 Flammability of PC/BDP and PC/ABS/BDP from set A and flammability of PC/ABS, PC/ABS/BDP, PC/ABS/RDP and PC/ABS/TPP from set B

	LOI (%) ± 1	UL 94 (1.5 mm)
Set A		
PC/BDP	39.1	V-0
PC/ABS/BDP	29.2	V-0
Set B		
PC/ABS	23.6	HB
PC/ABS/BDP	28.2	V-0
PC/ABS/RDP	29.8	V-0
PC/ABS/TPP	29.8	V-0

Conclusions

The thermal decomposition and the fire behaviour of polycarbonate with and without ABS and with and without arylphosphate (BDP, RDP and TPP) as flame retardants were investigated. Both flame retardancy mechanisms occurred, charring in the condensed phase and flame inhibition in the gas phase. A very similar flame inhibition occurs in all of the investigated materials and was characterized as the main flame retardancy effect. The additional condensed phase action of the arylphosphates is crucially dependent on the material environment, in particular on the interaction with the decomposing PC. Indeed, small changes in the system result in significant changes in the mechanisms. BDP works differently in PC, in which a more exclusive release of phosphorus-containing products results in flame inhibition, than in PC/ABS, in which the release of phosphorus-containing products results in flame inhibition and enhancing of PC-charring. A significant interaction between BDP and the PC structure, most probably after Fries rearrangement, occurs only in the condensed phase of PC/ABS, but not in pure PC. In terms of mass loss rate monitored by thermal analysis, the reason for this difference in the case of PC/ABS is a shift in the decomposition temperature of PC towards the decomposition temperature of BDP. The resulting overlap of both decomposition areas enables significant interactions between arylphosphate and the rearranged PC structure typical for the beginning of PC decomposition. BDP reacts via transesterification between phosphate groups of BDP and phenolic groups of PC. The resulting cross-linking leads to an enhancement of charring. As long as the thermal decomposition of BDP does not overlap with PC decomposition, only the release, and thus a gas phase mechanism, is preferred, as is shown for PC/BDP. The same structure–property relationship between thermal decomposition and flame retardancy mechanisms is observed when TPP, RDP and BDP are compared. The increasing decomposition temperature (TPP < RDP < BDP) increases the activity in the condensed phase due to the improved availability of the reaction partners, which are rearranged PC structures. Since the consumption of phosphate in the condensed phase competes with the release in the gas phase, flame inhibition decreases as the condensed phase mechanism increases.

It is concluded and emphasized in this work that a detailed description of the pyrolysis of each system by thermal analysis is the key to understanding the flame retardancy mechanisms and the corresponding structure–property relationships. In particular, the correspondence between the decomposition temperature range of arylphosphates and the PC decomposition is pointed out as prerequisite for enhanced charring in the condensed phase. It has not escaped our notice that the understanding of this prerequisite immediately suggests a possible way to adjust the flame retardancy mechanism of arylphosphates in PC materials.

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