

The effect of different impact modifiers in halogen-free flame retarded polycarbonate blends – I. Pyrolysis

Birgit Perret, Bernhard Schartel*

BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany

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ABSTRACT

In this first of two papers, the thermal decomposition of bisphenol A bis(diphenyl phosphate)-flame retarded polycarbonate (PC) blends with different impact modifiers was studied. The impact modifiers were an acrylonitrile–butadiene–styrene (ABS), a poly(n-butyl acrylate) (PBA) rubber with a poly(methyl methacrylate) (PMMA) shell and two silicone–acrylate rubbers consisting of PBA with different amounts of polydimethylsiloxane (PDMS) and different shells (PMMA and styrene–acrylonitrile, SAN). The focus of this work was to study the impact of the acrylate and silicon–acrylate rubbers with respect to pyrolysis and flame retardancy in comparison to common ABS. Thermogravimetry (TG) was performed to investigate the pyrolysis behaviour and reaction kinetics. TG in combination with FTIR identified the pyrolysis gases. Solid residues were investigated by FTIR-ATR. PC/ABS shows two-step decomposition, with PC decomposing independently from ABS at higher temperatures. Pure acrylate rubber destabilises PC due to interactions between the rubber and PC, which leads to earlier decomposition of PC. Using silicone–acrylate rubbers led to similar results as PC/ABS with respect to pyrolysis, reaction kinetics and analysis of the solid residue; hence the exchange of ABS for the silicone–acrylate rubbers is possible.

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1. Introduction

Polycarbonate/acrylonitrile–butadiene–styrene blends (PC/ABS) are the polymer blends most commonly used worldwide because of good mechanical and thermal properties, such as high toughness, rigidity and good heat resistance. They are easy to process with acceptable costs. A main application area for PC/ABS blends is electrical engineering [1] where a high level of flame retardancy is demanded. PC/ABS blends are effectively flame retarded with halogen-free, phosphorus-containing flame retardants such as bisphenol A bis(diphenyl phosphate) (BDP) [2–4], which turned out to be a good alternative to flame retardants containing halogen.

The thermal decomposition and burning behaviour of PC/ABS blends flame retarded with BDP have been discussed in the literature before [4–6]. It was proven that BDP acts in the gas phase as well as in the condensed phase in PC/ABS. In the gas phase it acts via flame inhibition with PO radicals working as scavengers for hydroxyl and hydrogen radicals. Thus oxidation processes in the flame are restrained and the heat release rate is decreased [7]. In the condensed phase BDP promotes the formation of residue via crosslinking reactions, most probably with rearranged PC and

incorporation into the cross-linked network. A barrier against heat and pyrolysis gas transport is formed which decreases the heat release.

The flame retardant action of phosphorous compounds is dependent on the thermal decomposition of the polymer to which they are added [8–11]. In particular interactions between phosphorous compounds and decomposition products of the polymer or other additives play a major role [11–13]. In several works it was proven that the action of phosphorous compounds can change from gas-phase to condensed-phase mechanisms and vice versa when the system is modified, for instance by replacing some compounds with others [8,13–17]. Also, the gas-phase mechanism of BDP in PC/ABS is reported to be switched off by adding zinc borate [18]. Thus the question is whether and how different impact modifiers influence the pyrolysis and the fire retardancy of BDP-flame retarded PC blends.

Poly(n-butyl acrylate) (PBA) shows good properties as an impact modifier and is already used in poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA) [19,20]. Because of its elastic properties, polydimethylsiloxane (PDMS) is also proposed as a possible impact modifier for PC. A secondary interesting aspect of PDMS is its high thermal stability [21], and its flame retardancy potential in some polymers [22]. For this reason PDMS might enhance the performance of the blend not only with respect to mechanical properties. The replacement of the already approved

* Corresponding author.

E-mail address: bernhard.schartel@bam.de (B. Schartel).

Table 1

Composition of the investigated materials.

	PC/BDP/R1/wt%	PC/BDP/R2/wt%	PC/BDP/R3/wt%	PC/BDP/ABS/wt%	PC/wt%	ABS/wt%	PDMS/wt%
PC	71	71	71	71	100	–	–
BDP	12.5	12.5	12.5	12.5	–	–	–
PTFE/SAN	0.9	0.9	0.9	0.9	–	–	–
R1	15	–	–	–	–	–	–
R2	–	15	–	–	–	–	–
R3	–	–	15	–	–	–	–
ABS	–	–	–	15	–	100	–
PDMS	–	–	–	–	–	–	100

Table 2

Composition of the acrylate rubbers.

	PBA/wt%	PDMS/wt%	SAN/wt%	PMMA/wt%
R1	75	–	–	25
R2	44	38	18	–
R3	74	9	–	17

impact modifier ABS by PBA and PBA/PDMS in BDP-flame retarded PC blends is a promising new approach to be studied with particular respect to the thermal decomposition and fire behaviour.

In this study a PC/PBA blend and two PC/PBA/PDMS blends were examined in comparison to a PC/ABS. All blends were flame retarded with BDP. The pyrolysis was studied in terms of effects on thermal decomposition and decomposition mechanisms.

2. Experimental

Four different blends of PC with different impact modifiers were investigated. All blends were flame retarded with 12.5 wt% BDP. All blends included 0.9 wt% of a master batch of polytetrafluoroethylene (PTFE) and styrene–acrylonitrile (SAN) in the ratio of 1:1. All blends were mixtures of unbranched PC and impact modifier in the ratio of 4.7:1. The following impact modifiers were used: First a PBA rubber (R1) surrounded by a shell of PMMA, second (R2) and third (R3) were silicone–acrylate rubbers based on PBA and PDMS. R2 had a shell of SAN. R3 was enclosed by a shell of PMMA. The amounts of PBA, PDMS and the shell materials differed in each blend. The fourth blend contained ABS in the ratio of A:B:S = 21:13:66. The exact composition of each material is given in Tables 1 and 2. Additionally PC, ABS, R1, R2, R3 and PDMS were measured for the purpose of comparison. All materials except PDMS were provided by Bayer MaterialScience AG, Dormagen, Germany. PDMS was a secondary standard from Aldrich.

The thermal decomposition was investigated by thermogravimetry (TG) (TGA/SDTA 851, Mettler Toledo, Germany). For evolved gas analysis the TG was coupled with Fourier transform infrared spectrometry (TG-FTIR, Nexus 470, Nicolet, Germany). All measurements were carried out under nitrogen at a heating rate of 10 K min^{−1}. Kinetic investigations were performed by varying heating rates of 1, 2, 5 and 10 K min^{−1}. The activation energy was determined by the method of Ozawa–Flynn–Wall [23]. The sample weight was 10 mg for each measurement. All values for residues were taken at the end of the main decomposition step.

To investigate the decomposition process within the condensed phase, TG measurements were carried out under nitrogen at a heating rate of 10 K min^{−1} and stopped after a particular weight loss. After cooling, the remaining residues were analysed by ATR-FTIR (Nexus 470, Nicolet with the “Smart Orbit Single Reflection Diamond ATR” tool).

3. Results and discussion

3.1. Mass loss

In Fig. 1 the thermal decomposition of PC, ABS, R1, R2, R3 and PDMS is shown. The temperatures at the maximum of the decomposition step and the mass loss for each step are given in Table 3. PC and ABS decomposed in one single step with a temperature at the maximum weight loss (T_{\max}) of 798 K for PC and 689 K for ABS, respectively. PDMS decomposed in a broad one-step decomposition with a T_{\max} of 845 K. The acrylate and silicone–acrylate rubbers decomposed in two steps. The two steps for the pure acrylate rubber R1 were not clearly separated. The mass loss rate of the first step was lower, with a $T_{\max1}$ of 572 K in comparison to the second step with a $T_{\max2}$ of 673 K. For the silicone–acrylate rubbers R2 and R3 both steps were well separated

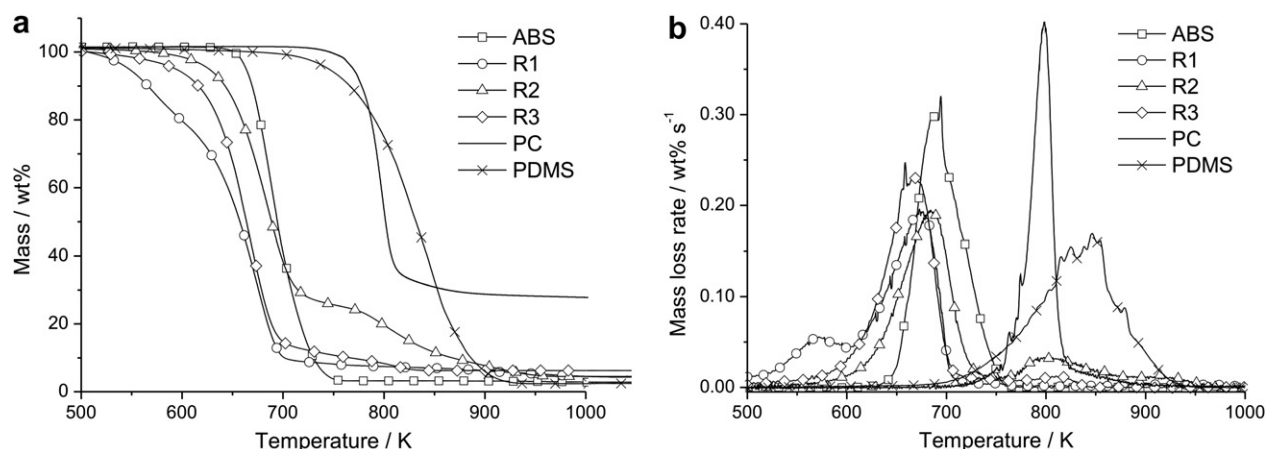


Fig. 1. Mass (a) and mass loss rate (b) of ABS, R1, R2, R3, PC and PDMS measured under nitrogen at a heating rate of 10 K min^{−1}.

Table 3

Thermal decomposition of PC, ABS, the acrylate and silicon-acrylate rubbers and PDMS under nitrogen and a heating rate of 10 K min⁻¹.

	PC	ABS	R1	R2	R3	PDMS
Mass Loss Step 1						
$T_{\max 1}/K \pm 2$	–	689	572	679	665	–
$ML_1/\text{wt}\% \pm 1.0$	–	96.8	21.4	72.6	89.9	–
Mass Loss Step 2						
$T_{\max 2}/K \pm 2$	798	–	673	809	811	845
$ML_2/\text{wt}\% \pm 1.0$	68.5	–	69.5	21.9	3.8	97.6
Residue/ $\text{wt}\% \pm 1.0$	31.5	3.2	9.1	5.3	6.3	2.4

Table 4

Thermal decomposition of the blends under nitrogen and a heating rate of 10 K min⁻¹.

	PC/BDP/ABS	PC/BDP/R1	PC/BDP/R2	PC/BDP/R3
Mass Loss Step 1				
$T_{\max 1}/K \pm 2$	700	689	693	678
$ML_1/\text{wt}\% \pm 1.0$	23.8	–	22.3	23.0
Mass Loss Step 2				
$T_{\max 2}/K \pm 2$	802	788	799	801
$ML_2/\text{wt}\% \pm 1.0$	50.1	–	50.9	51.6
Residue/ $\text{wt}\% \pm 1.0$	26.1	25.1	25.8	25.4

and the thermal decomposition began at higher temperatures than for R1. The $T_{\max 1}$ for R2 was 679 K, the $T_{\max 1}$ for R3 665 K. The second decomposition step for R2 and R3 was smaller than the first one, and $T_{\max 2}$ was nearly the same for both materials within the margin of error between 809 and 811 K. The T_{\max} and the height of this second step fit very well with the decomposition of PDMS; hence this second step indicates the thermal decomposition of the PDMS inside the silicone-acrylate rubber.

In R1 the ratio of the height of the mass loss rate between the first and second decomposition steps is 1:4. Since the ratio of the amounts of PMMA and PBA in the rubber is also 1:4, the first step in R1 is attributed to the thermal decomposition of PMMA and the second to the thermal decomposition of PBA. In contrast to R1 the presence of PMMA in R3 resulted in no additional decomposition step around 570 K. The presence of PDMS seems to shift or stabilise the thermal decomposition of PMMA: The PMMA decomposed together with the PBA at higher temperatures.

The characteristics for the thermal decomposition of the four blends are given in Table 4. PC/BDP/ABS, PC/BDP/R2 and PC/BDP/R3 decomposed in two main steps (Fig. 2), where the temperature range of $T_{\max 1}$ for the first step were between 678 and 700 K with

a mass loss between 22 and 24 wt%. The temperature of $T_{\max 2}$ for the second step of these three blends ranged between 799 and 802 K with a mass loss between 50 and 52 wt%. The first step in all blends is related to the decomposition of the rubber and the second step reflects the decomposition of the PC. The $T_{\max 1}$ for all three blends (PC/BDP/ABS, PC/BDP/R2 and PC/BDP/R3) was shifted to somewhat higher temperatures in comparison to ABS, R2 and R3. This shift is probably caused by embedding in the PC matrix hindering the product release. The thermal decomposition of the PC was similar for using ABS, R2 or R3 rubbers in PC. The amount of residue for the three blends were between 25 and 26 wt%; hence the silicone-acrylate rubbers do not influence the formation of residue in terms of the yield.

The thermal decomposition of PC/BDP/R1 differed significantly from PC/BDP/ABS, PC/BDP/R2 and PC/BDP/R3. No clear separation of decomposition steps was observed and at least three decomposition processes overlap each other. A first maximum in mass loss rate curve was observed at 689 K; the second main maximum $T_{\max 2}$ at the end of the decomposition occurred at 788 K. Between the two main maxima another minor maximum occurred at 728 K. The thermal decomposition of PC starts at lower temperatures than in PC/BDP/ABS, PC/BDP/R2 and PC/BDP/R3, as indicated by the reduced temperature of the $T_{\max 2}$. The addition of the pure acrylate rubber obviously decreases the thermal stability of the PC. No decomposition occurred at around 570 K, which would correspond to the decomposition of PMMA. The decomposition of PC/BDP/R1 finished slightly earlier, but the amount of residue for PC/BDP/R1 did not differ from that of PC/BDP/ABS, PC/BDP/R2 and PC/BDP/R3.

3.2. Reaction kinetics

The activation energy versus conversion (Fig. 3) data confirm the results received by mass loss and mass loss rate. The activation energy curves of PC/BDP/ABS, PC/BDP/R2 and PC/BDP/R3 exhibit similar shapes. Two different decomposition processes were observed, indicated by two different values of activation energy in the regions below (first process) and above (second process) 30% conversion. While the activation energy of the first process differed within the blends due to the different rubbers used, the activation energy of the second process was almost the same and reached a plateau at around 50% conversion. This indicates a decomposition mechanism typical for the distinct rubbers and subsequently the same decomposition of PC in PC/BDP/ABS, PC/BDP/R2 and PC/BDP/R3. All three blends showed a minimum of activation energy at a conversion of around 30%, which indicates an interaction

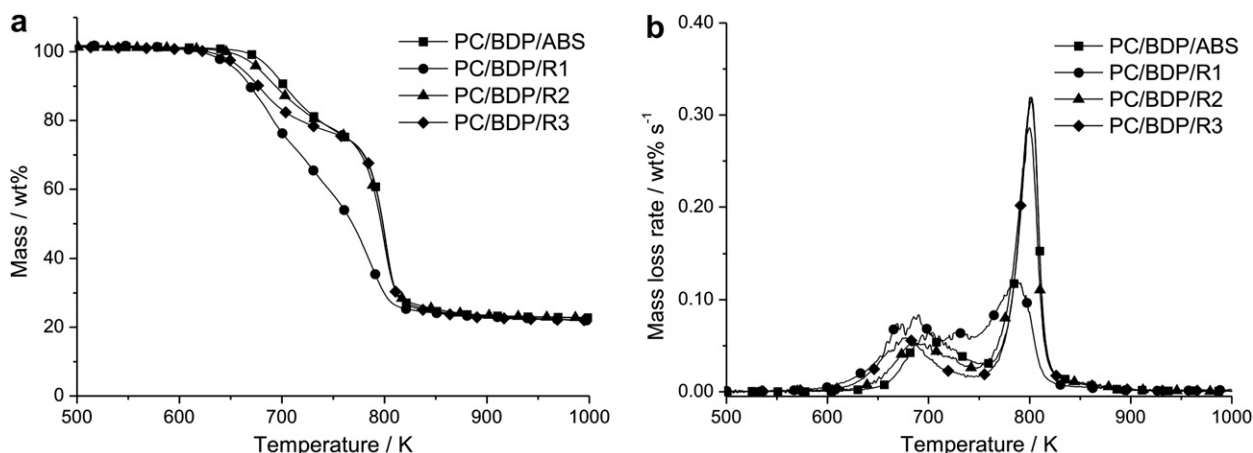


Fig. 2. Mass (a) and mass loss rate (b) of the blends measured under nitrogen at a heating rate of 10 K min⁻¹.

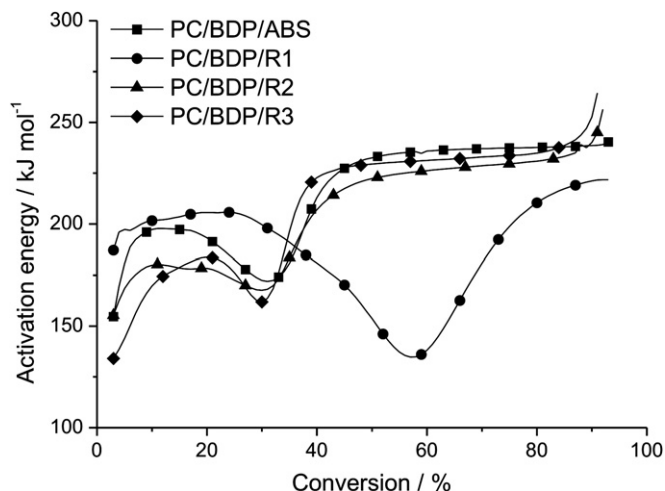


Fig. 3. Reaction kinetics.

between decomposition products of the rubber component, BDP and PC, when PC starts to decompose.

The activation energy pattern of PC/BDP/R1 differed significantly from the other blends. After a first plateau and a subsequent minimum the activation energy increased again up to the end of the reaction and did not reach a plateau. The minimum observed appeared at a conversion of around 60% and is much deeper and broader than for PC/BDP/ABS, PC/BDP/R2 and PC/BDP/R3. This broad and significant minimum indicates an interaction between the rubber and PC which enhances the decomposition of the blend. The strong overlap of decomposition processes in PC/BDP/R1 also shows that the decomposition of PC is changed in comparison to PC/BDP/ABS, PC/BDP/R2 and PC/BDP/R3.

3.3. Volatile pyrolysis products

The analysis of the pyrolysis gases of the pure ABS and the first decomposition step of PC/BDP/ABS via FTIR mainly showed absorption bands from stretching vibrations of aliphatic components ($R-CH_2-R$, $R-CH_3$) between 2990 and 2830 cm^{-1} and styrene derivatives at 3074 and 3029 cm^{-1} from stretching vibrations of the aromatic ring ($C_{Ar}-H$), at 1630 cm^{-1} from stretching vibrations

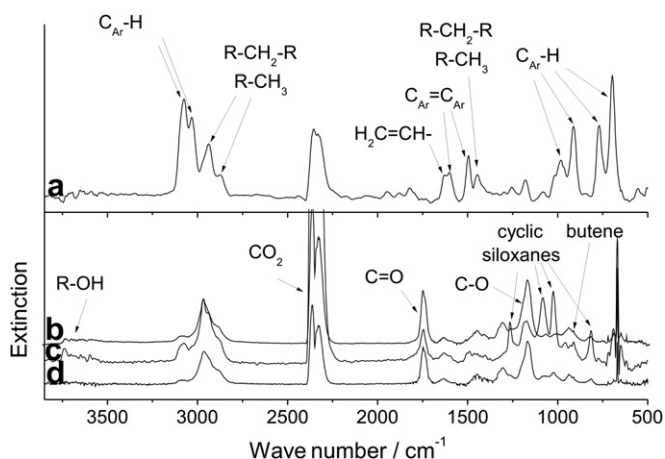


Fig. 4. FTIR spectra of the first decomposition step of (a) PC/BDP/ABS, (b) PC/BDP/R1, (c) PC/BDP/R2 and (d) PC/BDP/R3 with the characteristic bands used for product identification.

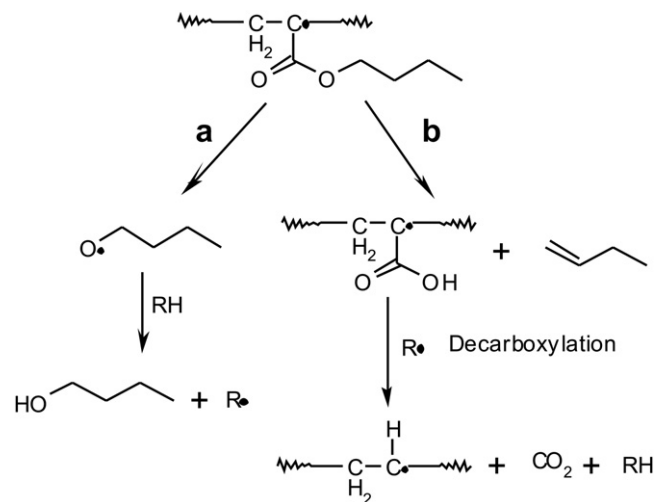


Fig. 5. Different decomposition pathways of the thermal decomposition of poly *n*-butyl acrylate, where (a) is the elimination of an alkoxide and release of butanol and (b) is the elimination of butene and formation of an acid functionality with subsequent decarboxylation.

from unsaturated side groups ($H_2C=CH-$), at 1600 and 1494 cm^{-1} from stretching vibrations of the aromatic ring ($C_{Ar}=C_{Ar}$) and deformation vibrations of $C_{Ar}-H$ of the aromatic ring at 982, 910, 771 and 965 cm^{-1} (Fig. 4a for PC/BDP/ABS). Acrylonitrile or its decomposition products were not detected either in ABS or in PC/BDP/ABS. The results are as expected from the literature [24–26], where it is reported that ABS mainly decomposes into aliphatic products resulting from butadiene and styrene monomers and its derivatives, such as dimers, trimers, methyl styrene and toluene, all originating from the styrene compound.

The spectrum of the first decomposition step of R1 corresponds well with the spectrum of neat methyl methacrylate exhibiting a characteristic absorption band at 1747 cm^{-1} coming from the carbonyl group ($C=O$) and other absorption bands at 1447 (from deformation vibrations of aliphatic groups, $R-CH_2-R/R-CH_3$), and at 1305 and 1167 cm^{-1} from stretching vibrations of the $C-O$ bond in the ester group. No additional absorption band from other products occurred. This confirms the assumption from mass loss and mass loss rate that only PMMA is decomposed in this step. In the literature it is also reported that the main decomposition product of PMMA is the monomer which is formed via β -scission, i.e. depolymerisation, of the main polymer chain [27,28].

The pyrolysis gases of the second decomposition step of R1, the first steps of R2 and R3 and the first steps of PC/BDP/R1, PC/BDP/R2 and PC/BDP/R3 showed absorption bands for alcohols ($R-OH$) at

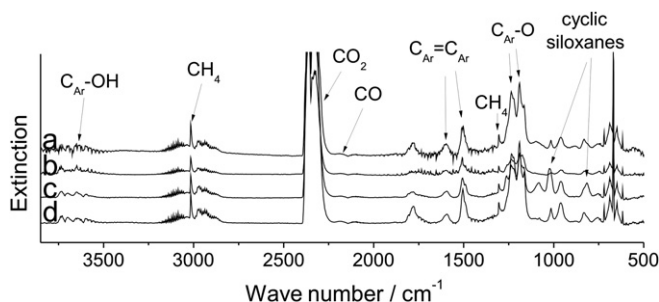


Fig. 6. FTIR spectra of the second decomposition step of (a) PC/BDP/ABS, (b) PC/BDP/R1, (c) PC/BDP/R2 and (d) PC/BDP/R3 with the characteristic bands used for product identification.

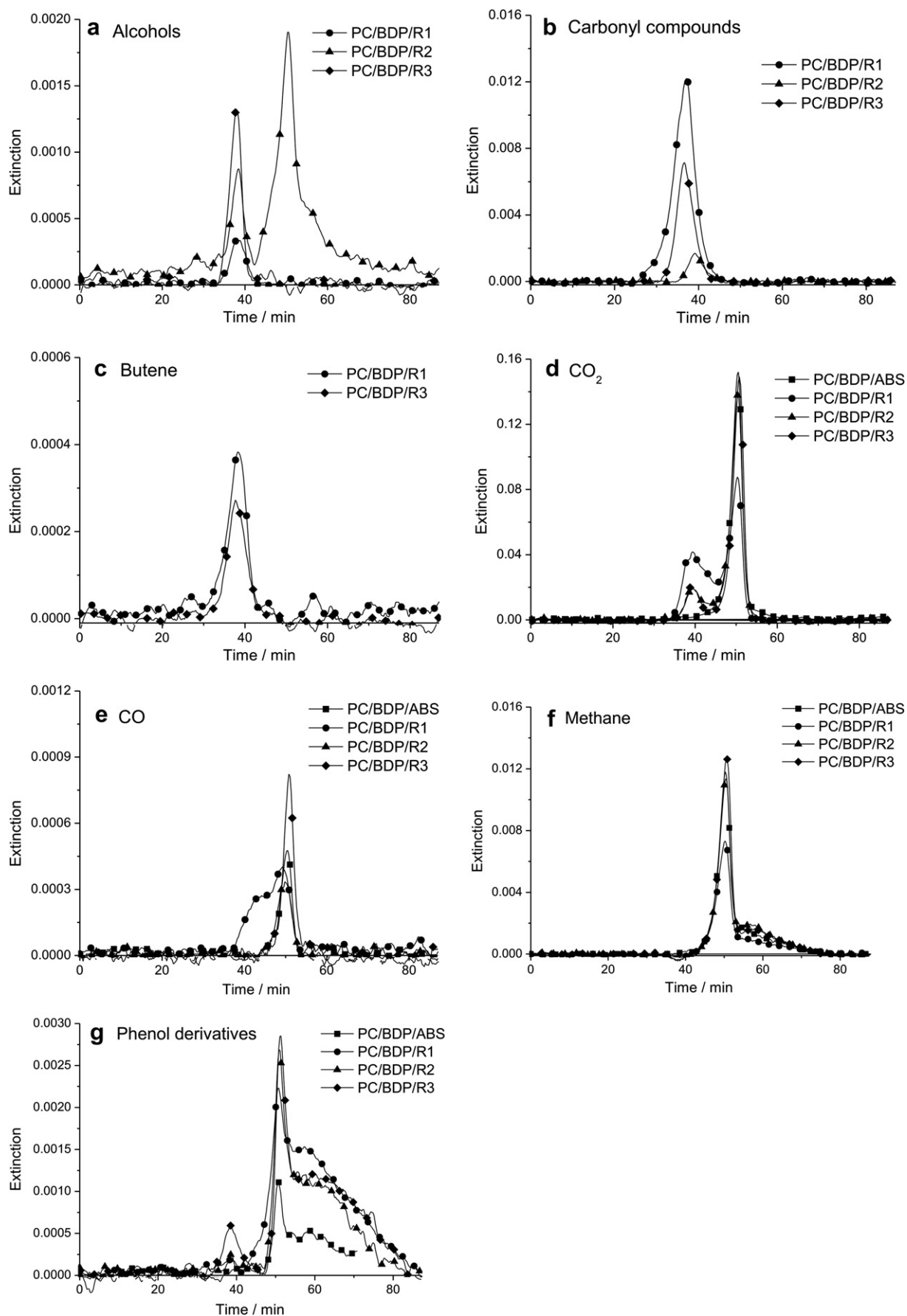


Fig. 7. Product release rates of (a) alcohols, (b) carbonyl compounds, (c) butene, (d) CO₂, (e) CO, (f) methane and (g) phenol derivatives for PC/BDP/R1, PC/BDP/R2, PC/BDP/R3 and PC/BDP/ABS.

3758–3550 cm^{-1} , carbonyl compounds ($\text{C}=\text{O}$) at 1745 cm^{-1} , carbon dioxide at 2361 cm^{-1} , deformation vibrations of aliphatic groups ($\text{R}-\text{CH}_2-\text{R}/\text{R}-\text{CH}_3$) at 1447 cm^{-1} , C–O stretching vibrations of the ester group at 1305 and 1167 cm^{-1} and a particular absorption band from butene at 912 cm^{-1} as the main decomposition products. The spectra of the first decomposition step of PC/BDP/R1, PC/BDP/R2 and PC/BDP/R3 are given in Fig. 4. PBA decomposes mainly by two decomposition pathways, either via elimination of an alkoxide group with the release of butanol (Fig. 5 a) or via elimination of butene and formation of an acid function which is subsequently decarboxylated (Fig. 5 b). A third decomposition pathway of PBA is the depolymerisation into the monomer concluded from absorption bands of carbonyl compounds identified in the second step of R1 and the first steps of R2, R3, PC/BDP/R1, PC/BDP/R2 and PC/BDP/R3. In the spectrum of the first decomposition steps of R3, PC/BDP/R1 and PC/BDP/R3 no distinction between the carbonyl compounds resulting from PBA or PMMA or even other carbonyl compounds was possible because of similar absorption bands in the complex infrared spectra. However, the identified products fit well with the decomposition products of PBA described in the literature [29]. Apart from the absorption bands indicating the decomposition products of PBA, additional absorption bands of styrene origin from the SAN shell were identified in the IR spectra, associated with the first decomposition step of R2 and PC/BDP/R2.

The major decomposition products monitored for the second main decomposition step in PC/BDP/ABS, PC/BDP/R1, PC/BDP/R2 and PC/BDP/R3 are CO_2 , methane (3015 and 1305 cm^{-1}), CO (2178 cm^{-1}) and phenol derivatives (3652 cm^{-1} from $\text{C}_{\text{Ar}}-\text{OH}$ stretching vibrations, 1601 and 1509 cm^{-1} from $\text{C}_{\text{Ar}}=\text{C}_{\text{Ar}}$ stretching vibrations from the aromatic ring, 1235 and 1190 cm^{-1} from $\text{C}_{\text{Ar}}-\text{O}$ stretching vibrations) (Fig. 6) which fit very well with the decomposition of PC described in the literature [30–32].

The product release rates of selected pyrolysis gases from the second decomposition step of PC/BDP/ABS and the first and the second decomposition steps of PC/BDP/R1, PC/BDP/R2 and PC/BDP/R3 are presented in Fig. 7.

The product release rates of the first decomposition step differed, especially between PC/BDP/R1 and PC/BDP/R3, even though the amount of acrylates (PBA and PMMA) in the blend differed by only around 2 wt%. The release of alcohols for PC/BDP/R1 was much lower than from PC/BDP/R2 and PC/BDP/R3. The release of carbonyl compounds and butene in PC/BDP/R1 was much higher. The release of CO_2 in the first decomposition step of PC/BDP/R1 was also higher and remained at a high level between the first and the second decomposition steps in comparison to PC/BDP/R2 and PC/BDP/R3. Another significant difference between the blends with an acrylate compound was the release of carbon monoxide

between the first and the last decomposition steps of PC/BDP/R1. The maximum of CO at 43 min in PC/BDP/R1 corresponds well to the minor maximum at 728 K measured in thermogravimetry. PC/BDP/R2 and PC/BDP/R3 did not release any CO in the first decomposition step. Butene was not analysed for PC/BDP/R2 due to disturbing absorption bands of styrene origin from the SAN shell.

Supporting the data and interpretation of the thermal analysis (mass loss, mass loss rate and kinetics), the product release rates showed that the silicon–acrylate rubbers in PC/BDP/R2 and PC/BDP/R3 decompose in the same way while the acrylate rubber in PC/BDP/R1 decomposes by means of a changed decomposition mechanism.

Characteristic absorption bands for hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane were identified during the thermal decomposition of R2 and R3 as well as during thermal decomposition of PC/BDP/R2 and PC/BDP/R3 (Figs. 4 and 6). Both siloxanes were observed in both of the decomposition steps of the neat rubbers and also in both decomposition steps of the two blends. In the literature it is described that PDMS mainly decomposes into hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane via an intramolecular transition state [33,34]. In both rubbers as well as in both blends the amount of hexamethylcyclotrisiloxane is higher than that of octamethylcyclotetrasiloxane. This was also detected in neat PDMS. The reason is the higher stability of 6-membered rings in contrast to 8-membered rings. Remarkable is that in R2 the main amount of the siloxanes occurs in the second decomposition step, while in R3 most of the siloxanes are released in step one. The same results were monitored for the two blends (Fig. 8). It is proposed that this is due to statistical reasons. PDMS and PBA bond with each other via copolymerisation. The number of monomer units of each PDMS block within the chain underlies a statistical distribution. The acrylate compound is decomposed during the first step of thermal decomposition. This leads to a release of short volatile PDMS chains at the lower temperatures typical for the decomposition of PBA. Longer PDMS blocks remain in the condensed phase and decompose at the higher decomposition temperatures typical for PDMS. Since the amount of PDMS in R2 is more than four times higher than in R3, the probability of longer PDMS blocks in R2 is higher. More siloxanes are released in the second decomposition step.

3.4. Solid residue

Fig. 9 shows the spectra obtained for the condensed phase before decomposition and at particular weight losses. The spectra of the initial blends show the following typical absorption bands resulting from the PC: at 3059 cm^{-1} aryl-H stretching bands of

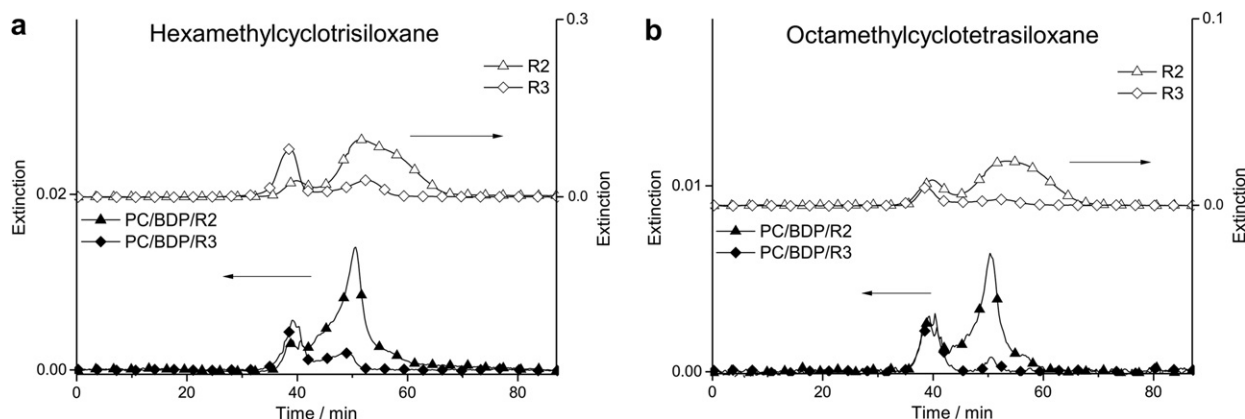


Fig. 8. Product release rates of (a) hexamethylcyclotrisiloxane and (b) octamethylcyclotetrasiloxane for R2, R3, PC/BDP/R2 and PC/BDP/R3.

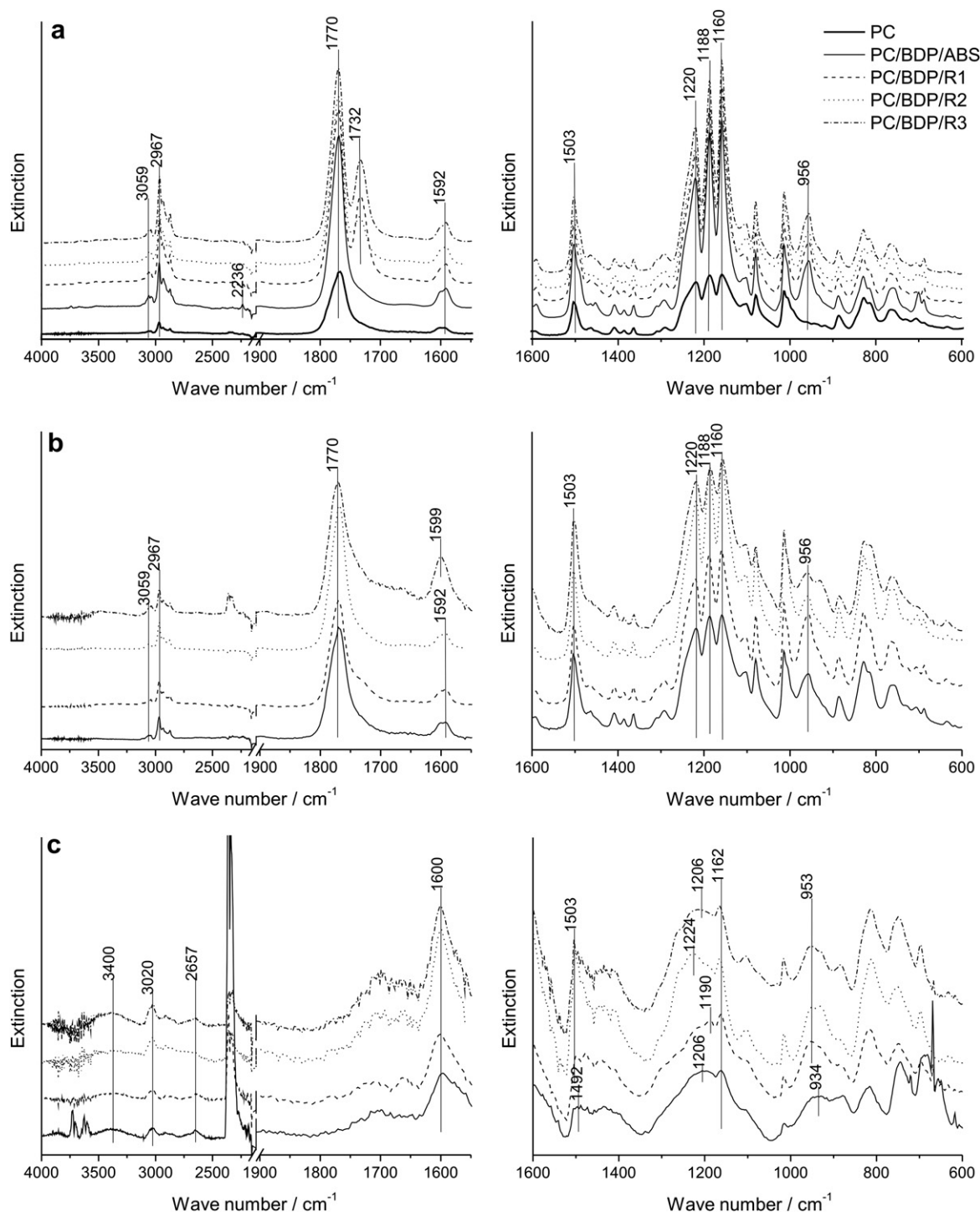


Fig. 9. FTIR-ATR spectra of (a) initial materials, (b) after 25 wt% of mass loss and (c) after 75 wt% of mass loss from PC (thick solid line), PC/BDP/ABS (thin solid line), PC/BDP-R1 (dashed line), PC/BDP-R2 (dotted line) and PC/BDP-R3 (dashed–dotted line). Some spectra are stretched for better visualisation.

aromatic rings, at 2967 cm^{-1} aliphatic C–H stretching bands of CH_3 - and $-\text{CH}_2$ - groups, at 1770 cm^{-1} C=O stretching band of the carbonate group, at 1592 and 1503 cm^{-1} C=C- stretching bands of aromatic rings, at 1220 and 1160 cm^{-1} asymmetrical O-(CO)-O stretching bands of the carbonate group, at 1188 cm^{-1} deformation band of the quaternary carbon atom of the isopropyl group. These absorption bands correspond well with the literature [35]. At 956 cm^{-1} a P–O-aryl stretching vibration from BDP [36] was identified but no other additional absorption bands from BDP were

found due to the similar spectroscopic groups and the lower concentration of BDP in comparison to PC. In the blend of PC/BDP/ABS a supplementary absorption band was found at 2236 cm^{-1} , arising from the $-\text{C}\equiv\text{N}-$ stretching vibrations of acrylonitrile from the ABS. In the blends of PC with the acrylate and the silicon-acrylate rubbers, one band at 1732 cm^{-1} was found resulting from the C=O vibration of the carbonyl group of the acrylate rubber content. The latter two absorption bands are the only differences within the spectra of the four blends in the initial state.

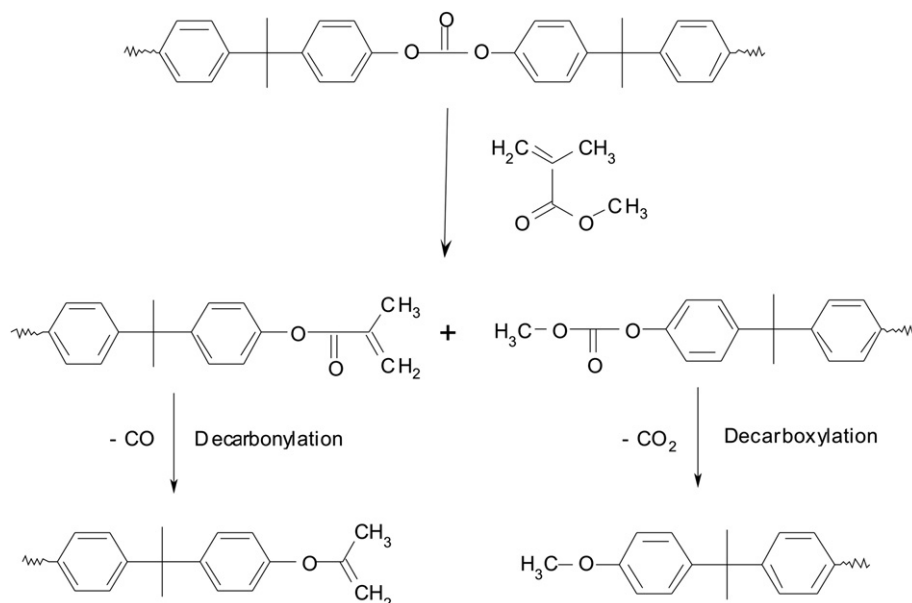


Fig. 10. Suggested interaction of monomer of PMMA with PC during thermal decomposition of PC/BDP/R1 in the gas phase.

After 25 wt% mass loss the spectra did not show any significant change apart from the absorption bands from the impact modifiers. These bands were gone in good correspondence to mass loss, mass loss rate, kinetics and evolved gas analysis. After a mass loss of 25 wt% the impact modifier was decomposed and vaporised while the PC was still existent in the solid phase. The absorption band at 956 cm^{-1} did not show any change either. Thus the BDP structure also was still present in the condensed phase.

After 75 wt% of mass loss the spectra of the four blends differed significantly from the spectra of the initial blends. Typical spectra of graphite-like materials were obtained, which indicate a partial decomposition of PC into carbonaceous char. The disappearance of the $\text{C}=\text{O}$ stretching band at 1770 cm^{-1} as well as the shift and the reduction of the bands at 1220 and 1160 cm^{-1} confirm the decomposition of the carbonate group. Also the isopropyl group was thermally decomposed because of the disappearance of the absorption band at 1188 cm^{-1} . New aromatic structures dominated the solid residue, as indicated by the enlargement of the aryl-H bands at around 3020 cm^{-1} and the broadening and shift of all other aromatic absorption bands [35,37,38]. The band at 956 cm^{-1} was broadened and shifted to lower wave numbers which indicates a crosslinking of the phosphorus with polyaromatic structures. The shift for PC/BDP/ABS was stronger than for PC/BDP/R1, PC/BDP/R2 and PC/BDP/R3. This indicates other or more crosslinking reactions of phosphorus in the condensed phase. Two new absorption bands appeared in all four spectra: a broad band at 3400 cm^{-1} from stretching vibrations of $-\text{OH}$ groups arising from phenolic compounds formed during thermal decomposition, and a weak band at 2657 cm^{-1} which is attributed to $\text{PO}-\text{H}$ stretching vibrations. This band indicates $\text{O}-\text{H}$ groups in polyphosphates.

3.5. Proposed interactions

The thermal decomposition of PC/BDP/R1 shows an overlap of at least three steps and the decomposition of PC starts earlier than in PC/BDP/ABS, PC/BDP/R2 and PC/BDP/R3. Also the additional preceding step measured in the pure acrylate rubber R1 coming from the thermal decomposition of PMMA is missing. The results from thermal analysis and the enhanced CO_2 and CO production in

the first decomposition step of PC/BDP/R1 indicate an interaction between the acrylate rubber R1 and PC. Fig. 10 illustrates the suggested reaction between the acrylate rubber and PC. At the beginning of the thermal decomposition of PC/BDP/R1 PMMA decomposes via depolymerisation into the monomers (MMA), but due to the embedding in PC it can not leave the system immediately; hence it undergoes a reaction with molecules of the surrounding PC, which leads to an earlier decomposition of PC in PC/BDP/R1. An exchange of the ester group of the MMA and the carbonate group of PC takes place. New molecules arise from this, carrying methyl carbonate and methylacrylate end groups. The decarboxylation of the methyl carbonate groups and the decarbonylation of the methylacrylate groups yield molecules with methyl ether or isopropenyl ether end groups. The changed decomposition mechanism for PC also leads to a changed decomposition mechanism of PBA in comparison to PC/BDP/R2 and PC/BDP/R3. In PC/BDP/R1 PBA strongly generates the acid function under elimination of butene (reaction pathway b in Fig. 5); hence more butene is detected, the butylenecarboxylic acid which is formed undergoes further decarboxylation, which again enhances the CO_2 production or leaves the system unchanged. This is confirmed by the product release rate of the carbonyl compounds, which is higher than expected. After the amount of PMMA is consumed during thermal decomposition, PC returns to its normal reaction pathway as in PC/BDP/ABS, PC/BDP/R2 and PC/BDP/R3. As a result the release of pyrolysis products from the decomposition of PC (CO_2 , CO , methane and phenol derivatives) is lower in PC/BDP/R1 due to the lower amount of PC involved.

4. Conclusions

The influence on thermal decomposition of different impact modifiers in polycarbonate flame retarded with BDP was investigated and compared with a common PC/ABS blend flame retarded with BDP. These alternative impact modifiers were an acrylate rubber (PBA) with a PMMA shell (R1) and two silicon-acrylate rubbers (R2 and R3) with different amounts of PDMS and different shell materials (SAN and PMMA).

Mass loss and mass loss rate showed no significant difference between PC/BDP/ABS and PC/BDP/R2 and PC/BDP/R3. Also, the reaction kinetics were very similar to PC/BDP/ABS. The released products of the thermal decomposition of PC and the solid residues taken at different stages of decomposition also showed no significant difference between these three blends; it is concluded that the silicone–acrylate rubbers decompose independently from the PC decomposition and do not influence the thermal decomposition of PC directly. From this state of investigation it seems to be possible to exchange ABS with R2 and R3 in terms of thermal stability due to the very similar behaviour of PC/BDP/R2 and PC/BDP/R3 in comparison to PC/BDP/ABS.

In contrast to this, the pyrolysis of PC/BDP/R1 was clearly different. The thermal decomposition clearly indicated that more than two reaction processes were involved and PC started to decompose earlier. An interaction of the decomposition products of the rubber and PC was clearly proven by evolved gas analysis and a reaction mechanism between decomposition products of the rubber and PC was suggested. All in all this interaction led to a blend having lower thermal stability than the others, such that an exchange of ABS by a pure PBA rubber with PMMA shell is not advantageous regarding the investigated properties from this stage of investigations.

Neither replacing ABS by R1, which actually indicates some potential to worsen the flammability, nor by R2, nor by R3 in PC blends exhibit clear advantages with respect to thermal stability or residue amount corresponding to the char yield in a fire. Mainly only a change in pyrolysis products was observed due to the different materials used in particular during the first decomposition step or for the beginning of polymer consumption, respectively. The replacement of hydrocarbons by pyrolysis products with less effective heat of combustion, in particular in the case of R2, is proposed to deliver at least some potential for a flame retardancy effect. Further compared to ABS a reduction in smoke release is reasonable. Indeed the investigation of the fire behaviour in the second of this series of two papers points out the increase of PDMS content as a route for optimising the flame retardancy. However, the investigated different impact modifiers are obviously primarily impact modifiers. They are not optimised to act as multifunctional additives improving the mechanical properties and the fire behaviour. Using such multifunctional additives is a promising route for future developments.

The flammability and the burning behaviour under forced flaming conditions of the discussed materials are reported in the second part of this series.

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