



Solid-state NMR on thermal and fire residues of bisphenol A polycarbonate/silicone acrylate rubber/bisphenol A bis(diphenyl-phosphate)/(PC/SiR/BDP) and PC/SiR/BDP/zinc borate (PC/SiR/BDP/ZnB) – Part I: PC charring and the impact of BDP and ZnB

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ABSTRACT

Structural changes in the condensed phase of bisphenol A polycarbonate (containing 0.45 wt% poly(tetrafluoroethylene))/silicone acrylate rubber/bisphenol A bis(diphenyl-phosphate) (PC/SiR/BDP) and PC/SiR/BDP/zinc borate (PC/SiR/BDP/ZnB) during thermal treatment in nitrogen atmosphere and in fire residues were investigated by solid-state NMR. ^1H , ^{11}B , ^{13}C and ^{31}P NMR experiments using direct excitation with a single pulse and ^1H – ^{31}P cross-polarization (CP) were carried out including $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^{31}\text{P}\}$ double-resonance techniques (REDOR: Rotational Echo Double Resonance) on a series of heat-treated samples (580 K–850 K). Because many amorphous phases occur in the solid residues, and solid-state NMR spectroscopy addresses the most important sites carbon, phosphorus and boron, this paper is the key analytical approach for understanding the pyrolysis and flame retarding phenomenon in the condensed phase of PC/SiR/BDP and PC/SiR/BDP/ZnB.

For the system PC/SiR/BDP it is shown that (i) at temperatures around 750–770 K (main decomposition step) carbonaceous charring of PC occurs and arylphosphate structures are still present, reacted in part with the decomposing PC; (ii) for higher temperatures from 770 K the phosphorus remaining in the solid phase increasingly converts to amorphous phosphonates and inorganic orthophosphates with a minor amount of crystalline orthophosphates; and (iii) ^1H – $^{31}\text{P}\{^1\text{H}\}$ CP REDOR and ^1H – $^{13}\text{C}\{^{31}\text{P}\}$ CP REDOR NMR experiments suggest that the phosphates and phosphonates are bound via oxygen to aromatic carbons, indicating the interaction with the carbonaceous char.

When ZnB is added to the system PC/SiR/BDP, (i) ZnB leads to a slightly enhanced PC decomposition for temperatures below 750 K; (ii) α - $\text{Zn}_3(\text{PO}_4)_2$ and borophosphate (BPO_4) are formed in small amounts at high temperatures suggesting a reaction between BDP and ZnB during thermal decomposition; and (iii) most of the borate remains in the solid residues, forming an amorphous pure borate network, with the BO_3/BO_4 ratio increasing with higher temperatures.

The NMR data of thermal and fire residues are highly correlated, underlining the importance of this work for understanding the pyrolysis and flame retardancy mechanisms in the condensed phase during the burning of the PC/SiR blends.

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1. Introduction

For various reasons over the last decades there has been increasing market demand for halogen-free flame retarded polymeric materials. Various flame retardants containing phosphorus are the most successful alternatives to replace flame retardants

containing halogen, especially in engineering polymers for electronics, electrical engineering and transportation [1–5]. One outstanding example is bisphenol A polycarbonate (PC) blends flame retarded with arylphosphates [6–8]. Commercial systems using this substance nearly always contain additional ingredients such as anti-dripping agents (mostly poly(tetrafluoroethylene) (PTFE)), inert fillers (talc, fibres, ...), stabilizers (protection against hydrolysis, light, ...), etc. to meet the specific property profiles, but these also influence fire behaviour [8–10]. The impact modifier used in PC blends is based mostly on acrylonitrile-butadiene-

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styrene (ABS). Compared to PC, ABS is characterized by a lower time to ignition, higher effective heat of combustion, less (or no) charring and higher smoke production [11, 12]. Consequently, silicone acrylate rubber (SiR) was proposed as an alternative for ABS. The interactions between the different components [13] as well as the ability of arylphosphates to exhibit several different flame retardancy mechanisms [8] constitute a demanding and complex challenge for fundamental material science and harbour the potential for future commercial optimization and development.

Despite the commercial success of arylphosphate flame retarded PC blends, their flame retardancy mechanisms and resulting structure property relationship are still a subject of current research. The key to understanding the flame retardancy mechanisms and efficiency is to understand the pyrolysis of the materials [8,14,15]. The actual pyrolysis determines the carbonaceous charring (reduction of fuel release), residue morphology and properties (barrier and shielding properties), the formation of inorganic glassy residue (residue coating optimizing the residue properties), and the release of phosphorus-containing decomposition products (flame inhibition in the gas phase).

Thus the focus of this study is on the elucidation of the structural changes taking place in the solid residues of PC/SiR blends, flame retarded with bisphenol A bis(diphenyl-phosphate) (BDP) in combination with a tiny amount of PTFE, during thermal decomposition as well as in fire tests. In a second series of samples the influence of zinc borate (ZnB), which contains water and is known as a synergist to different flame retardants [16], is investigated. As the solid residues of PC/SiR/BDP with and without ZnB consist mostly of amorphous phases, solid-state NMR was used to study the solid phases in the residues.

In this part, a detailed ^{11}B , ^{13}C and ^{31}P NMR investigation of the solid residues is presented with particular emphasis on (i) the identification of the various decomposition products of PC, BDP and ZnB and (ii) the quantification of borate phases in the solid residues as a function of the thermal history. To achieve these goals, ^1H , ^{11}B , ^{13}C and ^{31}P NMR measurements using direct excitation and ^1H – ^{31}P cross-polarization (CP) were carried out, including $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^{31}\text{P}\}$ double-resonance techniques such as REDOR (Rotational Echo Double Resonance [17]) and 2D HETCOR (heteronuclear correlation) on sets of heat-treated samples (580 K–850 K) annealed in nitrogen atmosphere. The influence of silicon on flame retarded PC will be presented and discussed separately in detail in part 2 of this series [18].

2. Experimental

2.1. Sample preparation

Mixtures of PC, 15 wt% SiR, 12.5 wt% BDP and 0.9 wt% PTFE/styrene-acrylonitrile SAN masterbatch, with and without 5 wt% ZnB ($\text{Zn}_2\text{B}_6\text{O}_{11} \cdot 3.5\text{H}_2\text{O}$) (PDF 35–433, [19]) were investigated after thermal decomposition. Since in all of the investigated materials the PTFE/SAN masterbatch is used as an anti-dripping agent, hereafter the abbreviation PC in this paper refers to PC plus 0.45 wt % PTFE. The SiR is based on polydimethylsiloxane (PDMS) and poly (*n*-butyl acrylate) with a poly(methyl methacrylate) shell. The PDMS content of SiR is 82 wt%. All samples provided by Bayer MaterialScience AG as plates were powdered in a cryomill for both tube furnace treatment and the NMR measurements.

Thermal treatment was carried out in a horizontal quartz tube furnace (inner diameter: 38 mm, length: 40 cm) under a nitrogen flow of 100 ml min^{-1} . The materials were placed in a quartz boat and heated up to the set-point temperature (between 630 K and 850 K) at a rate of 10 K min^{-1} . After 30 min at constant temperature

the samples were cooled under nitrogen gas flow. Then all samples were homogenized.

A cone calorimeter (FTT, UK) was used to prepare quenched fire residues, applying a heat flux of 50 kW m^{-2} . Samples ($50 \times 50 \times 0.3 \text{ mm}$ plates) were wrapped in aluminium foil and burned horizontally. 50 s after ignition the fire residues were quenched in liquid nitrogen to interrupt burning and avoid the subsequent thermo-oxidation of the hot residue. The loose top char layer represents the char at the end of burning, whereas material taken from the layer underneath constitutes the pyrolysis zone.

2.2. Methods

The masses of thermal residues were determined using a TGA/SDTA 851 (Mettler Toledo, Gießen, Germany) up to 1150 K. The starting sample masses were about 15 mg. The nitrogen flowed at a rate of 30 ml min^{-1} and a heating rate of 10 K min^{-1} was used.

Solid-state NMR experiments were performed on a Bruker DMX 400 (9.4 T) and on a Bruker Avance 600 spectrometer (14.1 T), both equipped with wide-bore magnets. All experiments were carried out at room temperature using magic angle sample spinning (MAS) for solid-state NMR experiments. Proton decoupling was carried out with a 15° two-pulse phase modulation (TPPM) sequence [20].

^{13}C MAS NMR spectra (single-pulse excitation) were recorded using single-pulse excitation at a Larmor frequency of 100.6 MHz (9.4 T). The MAS frequency was 13 kHz using a 4-mm triple-resonance MAS NMR probe. The ^{13}C 90° pulse length was 4.25 μs . To ensure the detection of fully relaxed spectra, a repetition time of $5 \cdot T_1$ (T_1 being the longitudinal relaxation time) is necessary. The longest ^{13}C T_1 time was found for the 150 ppm signal with about 20 s, therefore a repetition time of 100 s was used for all samples. 256 scans were accumulated. The ^{13}C chemical shifts (δ) are reported relative to TMS, with glycine as a secondary standard, setting the COOH resonance to $\delta = 176.4 \text{ ppm}$.

^{31}P MAS NMR spectra (single-pulse excitation) were recorded under the same conditions at 161.9 MHz. The ^{31}P 90° pulse length was 3.7 μs , a repetition time of 600 s (the longest T_1 time (α -Zn (PO_4)₃) is about 120 s) was used for all samples, and 64 scans were accumulated. The ^{31}P chemical shifts (δ) were calibrated versus 85% phosphoric acid ($\delta = 0 \text{ ppm}$) using hydroxyapatite as a secondary standard, setting the resonance at 2.3 ppm.

^1H – $^{31}\text{P}\{^1\text{H}\}$ CP REDOR experiments ($^{31}\text{P}\{^1\text{H}\}$ Rotational Echo Double Resonance after ^1H – ^{31}P cross polarization) were carried out at 14.1 T using a 4-mm triple-resonance MAS NMR probe and a sample spinning frequency of 12.5 kHz. The ^{31}P 90° (180°) pulse length was 3.8 μs (8.1 μs). The 180° ^1H pulse lengths for REDOR were 7.2 μs . The ^1H – ^{31}P CP step prior to the REDOR sequence was carried out using a ^1H 90° pulse length of 3.6 μs , a contact time of 2 ms and a repetition time of 3 s. The ^{31}P spin-lock field was held constant, while the ^1H spin-lock field was ramped down to 50% of its initial value [21]. Up to 18,432 scans were accumulated for a single evolution time. ^1H high-power decoupling (TPPM) was applied.

^1H – $^{13}\text{C}\{^{31}\text{P}\}$ CP REDOR experiments were also carried out with the set-up described above. A sample spinning of 12.5 kHz was used. The ^{13}C 90° and 180° pulse lengths were 4 μs and 8 μs , respectively. The ^{31}P 180° pulse lengths for REDOR were 7.5 μs . The ^1H – ^{13}C CP step prior to the REDOR sequence was carried out using a ^1H 90° pulse length of 3 μs , a contact time of 1 ms and a repetition time of 2 s. Ramped-CP as well as ^1H TPPM decoupling was applied. For the evolution time of 20 ms, 20,480 scans were accumulated.

^{11}B MAS RSE NMR (RSE: rotor-synchronized echo detection for suppressing probe background) experiments were performed at 14.1 T (Larmor frequency of 192.5 MHz) using a 4-mm triple-resonance MAS NMR probe and a MAS frequency of 12.5 kHz. The

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