Freie Universität Berlin

Fire residues design: the chemistry behind synergistic effects in multicomponent polymeric systems

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Abbreviations

(L)OI	(Limiting) Oxygen index
µCT	Micro-computed tomography
AlPi	Aluminium diethylphosphinate
APP	Ammonium polyphosphate
ATR-IR	Attenuated total reflectance infrared spectroscopy
CP	Cross-polarization
DGEBA	Bisphenol A diglycidyl ether
EHC	Effective heat of combustion
EP	Cross-linked epoxy resin
FID	Free induction decay
FR	Flame retardant
HRR	Heat release rate
IPDA	Isophorone diamine
MARHE	Maximum average rate of heat emission
MAS	Magic angle spinning
MH	Magnesium hydroxide
MPP	Melamine polyphosphate
MPZnP	Melamine poly(zinc phosphate)
NMR	Nuclear magnetic resonance
PHRR	Peak heat release rate
PPO	Poly(phenylene oxide)
REDOR	Rotational echo double resonance
S600	Melamine poly(magnesium phosphate), Safire® 600
SEBS	Styrene-etylene-butylene-styrene co-polymer
SEM	Scanning electron microscopy
Si	Dimethyl- and methylvinyl siloxane

TG-FTIR	Thermogravimetry coupled with Fourier transform infrared spectroscopy
THE	Total heat evolved
t_{ig}	Time to ignition
TML	Total mass loss
TPE-S	Thermoplastic elastomer based on styrene
TRAPDOR	Transfer of population in double resonance
XRD	X-Ray diffraction
ZB	Zinc borate

1.   Introduction

1.1.   State of the art

Polymeric materials are used in daily life since decades and the market is still growing. If we think about our households, most of the items are made from synthetic polymers. The reason for it is their high processability and relatively low cost. Nonetheless at the same time they increase the potential fire risk since many of them are highly flammable. Hence the suitable resistance to high temperatures and fire is nowadays required for many applications. As a result, the production of flame-retarded polymers developed greatly in last years to reduce the probability of undergoing fires. However, improving the flame retardancy of the polymers is not a trivial task. Not only the type of the flame retardant additive is important, but also the required load to achieve desired result is crucial. Any change to a polymeric system (by replacing the part of the polymer with the additive) will influence its properties and the final performance. Hence, the amount of additive should be high enough to ensure required fire retardant properties, but at the same time should not exceed the maximum load for maintaining desired mechanical or electrical properties, for instance. Another essential issue is environmental aspect. For long time halogenated flame retardants were a leader due to their high effectiveness at low concentration, but since the concerns regarding potential toxicity grow, market demands now more and more halogen-free additives. One of the most promising approaches is development of efficient halogen-free multicomponent systems, where the right combination of several flame retardants/synergists/fillers yields in satisfying performance-additive concentration ratio.
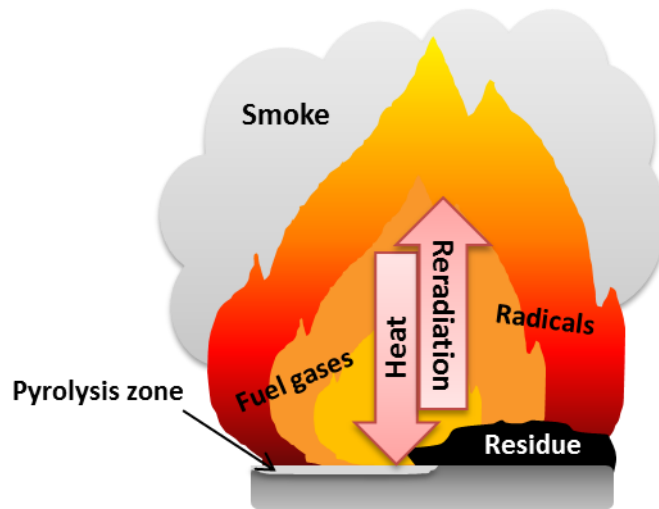
Figure 1. The phenomena occurring during burning of the material.

Before designing formulations with good flame retardant performance, the burning process of the material has to be understood first. When the polymer is ignited, decomposition products are formed which can react with oxygen from the air and produce flame and heat. Part of the heat is transferred back to the surface and sustains the flow of flammable volatile degradation products (Fig. 1). On the other hand, some of the polymers are able to form char at the cost of released volatiles, leading to reduction in combustible gases. Additionally, formed residue may act as a protection layer which preserves the underlying material and works as a barrier for gas transport to the flame. Thus, flame retardants may act in various ways via different mechanisms in solid, liquid or gas phase and eliminate or reduce production of combustible gases as well as enhance the char formation. Flame retardants reduce the risk of ignition and further they reduce the risk of fire propagation. In general, two main types of action regarding the nature of the process are distinguished:

- Physical action, e.g. cooling the substrate in endothermic process, diluting the fuel gases (e.g. release of inert volatile products) or formation of protective layer (inorganic and/or organic).

- Chemical action, e.g. eliminating the OH and H radicals (flame inhibition).

It is essential to find the right equilibrium between the final performance of the sample and the total loading of the flame retardants. To achieve this, the behavior of flame retardants during the decomposition, as well as the interactions with the polymer matrix has to be known.

This work is focused on analysis of halogen-free multicomponent flame retardant systems, their performance, chemical interactions and decomposition products, to increase the knowledge about mechanisms, which will improve the ability to design optimized formulations in the future.

1.2. Task and approach

The aim of this work is the scientific understanding of the flame retarding effects on pyrolysis and combustion. Moreover, the relationships between mechanisms, structure and performance was investigated in selected systems. For that purpose several methods were chosen to study the chemical interactions between components of more complex materials. As model systems, two types of polymers were chosen as a matrix: thermoplastic elastomer and thermoset. Both types of material present poor performance in terms of fire, but at the same time are widely used in many applications, including electronic, engineering, transportation or constructions, where the good fire resistance is needed. Therefore strong emphasis is put on developing well flame retarded polymers.

Many of the applications are based on excellent mechanical or electrical properties. In order to keep alterations in those properties as low as possible, the load of flame retardants has to be kept small. One of the approaches is the use of multicomponent systems. Synergistic effects

and chemical interactions between components allow improving the flame retardant properties while maintaining a low additive loading. Different combinations were chosen to have good and comprehensive results and overview of various interactions between additives and polymer matrix. All of the flame retardants chosen for this work were halogen free, and at least one of the flame retardant in each investigated system was containing phosphorus in the structure.

1.3. Materials

1.3.1. Polymer matrix

Thermoplastic elastomers (TPE) are defined as block co-polymers or polymer blends which share some of their properties with vulcanized rubbers at room temperatures (e.g. flexibility), but get softer and melt when heated. The melting process is reversible and allows remolding or reprocessing of the material. The thermoplastic elastomer system used in this work is based on styrene (TPE-S). TPE-S samples were provided by industrial partner SKZ Wurzburg. The polymer was based on styrene-ethylene-butylene-styrene block copolymer (SEBS, Fig. 2) and was initially mixed with polypropylene and mineral oil (and in case of flame retarded systems also with other additives) in the twin-screw extruder to obtain granulate. In the next step the samples in desired shapes were obtained by injection molding process. All the components of the polymer matrix are highly flammable, burn fast, produce high amounts of smoke and do not form residue. It is challenging to find the optimal additives without increased loading.
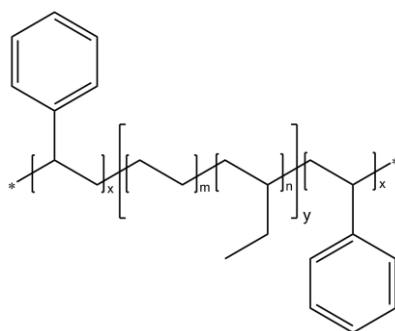
Figure 2. Structure of SEBS.

Thermosets are rather rigid at room temperatures. Moreover, they cannot be melted due to cross-links in their structure and they are insoluble in most solvents. In this study, epoxy resin based on bisphenol A diglicyd ether (DGEBA) was used. The samples were prepared by mixing DGEBA, isophorone diamine (IPDA, hardener) and additives (for flame-retarded systems) in a glass beaker using a laboratory mixer. Mixtures prepared in this manner were put in aluminium trays (110 × 110 mm) and placed in the oven to obtain the crossed-linked material. The structures of epoxy resin, hardener and cross-linked polymer are shown in Fig. 3. After curing and cooling down to room temperature, plates were cut into desired size. Similarly as in case of TPE-S, the epoxy resin is burning easily without residue formation, motivating the strong need for flame retardants.
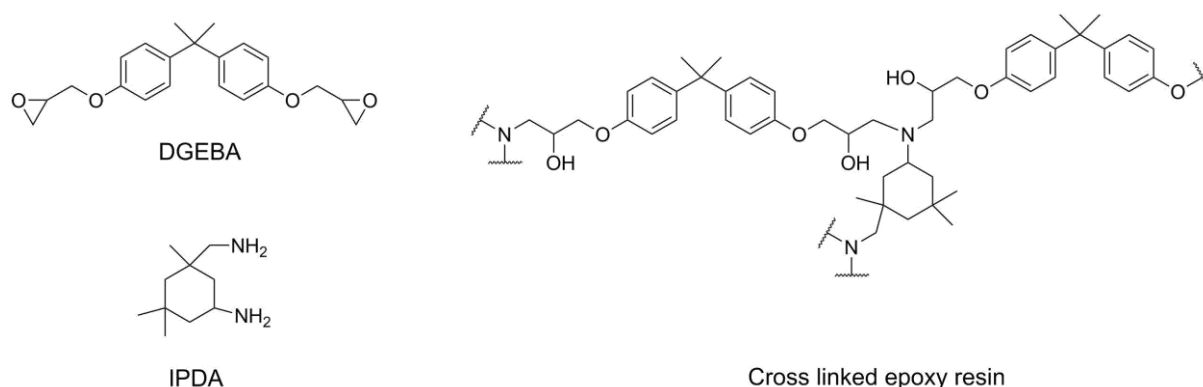
Figure 3. Structures of DGEBA, IPDA and cross-linked epoxy.

1.3.2. Flame retardants

As additives aluminium diethylphosphinate (AlPi), ammonium polyphosphate (APP), magnesium hydroxide (MH), zinc borate (ZB), dimethyl- and methylvinyl siloxane (Si), poly(phenylene oxide) (PPO), melamine poly(magnesium phosphate) (S600), boehmite (AlO(OH)) and melamine polyphosphate (MPP) were chosen. All of the additives are commercially available and widely used in flame retarded polymers.

Phosphorus based flame retardants are leading in the market among other halogen-free additives. They can both act in gas phase as radical scavengers and flame inhibitors or stay in the solid phase and promote residue formation. Most of the times both of the mechanisms are present.

Aluminium diethylphosphinate (AlPi) is a well-known flame retardant which is mainly active in the gas phase, releasing phosphorus species during the decomposition. Those species are reacting with highly reactive H- and OH-radicals in the fire and thus cause flame inhibition.

$$PO^\bullet + H^\bullet \rightarrow HPO$$
$$PO^\bullet + OH^\bullet \rightarrow HPO_2$$
$$HPO^\bullet + H^\bullet \rightarrow H_2 + PO^\bullet$$
$$HPO_2^\bullet + H^\bullet \rightarrow H_2O + PO$$
$$HPO_2^\bullet + H^\bullet \rightarrow H_2 + PO_2$$
$$HPO_2^\bullet + OH^\bullet \rightarrow H_2O + PO_2$$
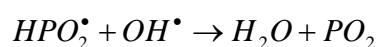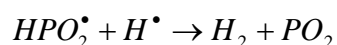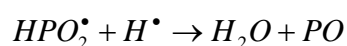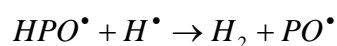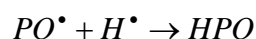
AlPi was reported as suitable flame retardant especially for oxygenated polymers like thermoplastic polyesters. However, for the polyolefines the results were less promising. Usually AlPi is used in combination with synergists [1-3]. It is explained by the fact that although the efficiency is improved with increasing the concentration, it levels off before

reaching good flame retardant effect [4]. Thus, in case of polyolefines, synergists and multicomponent system must be used.

The second prominent phosphorus-based additive is APP. Contrary to AlPi, the mode of action is focused on condense phase reaction via intumescence. The intumescent systems cause swelling of the material and formation of multicellular layer acting as an insulation barrier. To enable intumescence, three components have to be present: an inorganic acid source, a blowing agent and a char former. The released acid esterifies the carbon rich component, while the mixture of materials melts. Subsequently, formed ester decomposes which leads to inorganic-carbon residue formation. At the same time released gases form the bubbles and a foam-like structure is formed. At the end the solidification occurs. Additionally, during the decomposition of APP, ammonia is released which also causes fuel dilution. Moreover, the formation of ultraphosphate occurs, which works as additional stabilization of the protective layer. Melamine poly(magnesium phosphate) and melamine phosphates are causing the intumescence in the similar way as APP. Melamine polyphosphate combines advantages of phosphorus and nitrogen rich flame retardants. Recently, new modification of MPP – melamine poly(metal phosphates) were developed to improve the performance [5-12]. As reported in literature, MPP decomposes to APP and the formation of ultraphosphate occurs as well. In conclusion, thermal degradation of MPP/APP leads to formation of highly cross-linked –P-O-P- structure while releasing ammonia and water to the gas phase [13].
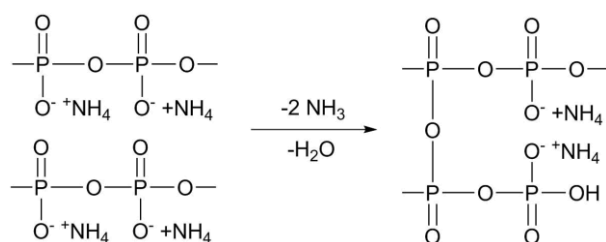
Magnesium hydroxide and zinc borate (hydrate) are inorganic fillers which act in gas phase as well as in condensed phase. Magnesium hydroxide is thermally stable up to 300 °C which makes it a suitable additive for thermoplastic materials where often high processing temperatures are needed. During the decomposition it releases water in an endothermic process which cools down the system and also dilutes the fuel gases [14, 15]. Additionally, smoke suppressing effects are observed [16-18]. For zinc borates not only water release is observed, but it is believed that they promote cross-linking of the material and increased charring. Moreover, they can form an inorganic protective layer when combined with other fillers [19, 20].

$$Mg(OH)_2 \xrightarrow{T} MgO + H_2O$$
$$2ZnO \cdot 3B_2O_3 \cdot 3H_2O \xrightarrow{T} 2ZnO \cdot 3B_2O_3 + H_2O$$
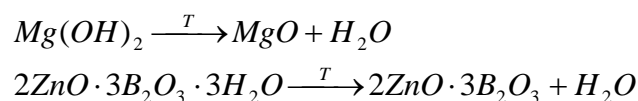
Boehmite, similarly as MH or ZB is an inorganic filler, which transforms to aluminium oxide with the release of water.

$$2AlO(OH) \xrightarrow{T} Al_2O_3 + H_2O$$
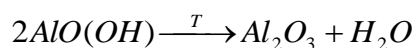
Additionally, the oxides formed during the decomposition can further react with other additives like phosphorus compounds forming an inorganic residue. For example zinc phosphate and borophosphate are formed in a multiple-step reaction as proposed in literature [21].

$$10(HPO_3)_n + 2ZnO \cdot 3B_2O_3 \rightarrow 6BPO_4 + P_4O_{10} + 2ZnO + 15H_2O$$
$$3ZnO + \frac{1}{2}P_4O_{10} \rightarrow Zn_3(PO_4)_2$$
$$2Zn_3(PO_4)_2 + 2BPO_4 \rightarrow B_2O_3 + 3Zn_2P_2O_7$$
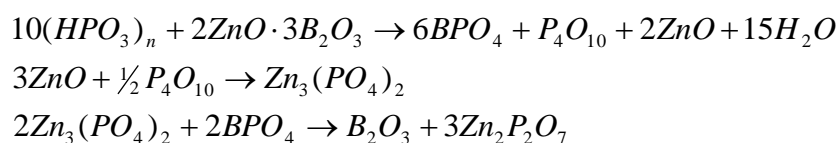
Poly(phenylene oxide) is a well-known charring agent which undergoes the Fries-type rearrangement reaction (Fig. 4) [22, 23]. The ether bond in the backbone is replaced by a C−C bond and leads to formation of highly cross linked residue, which acts as the protective layer.
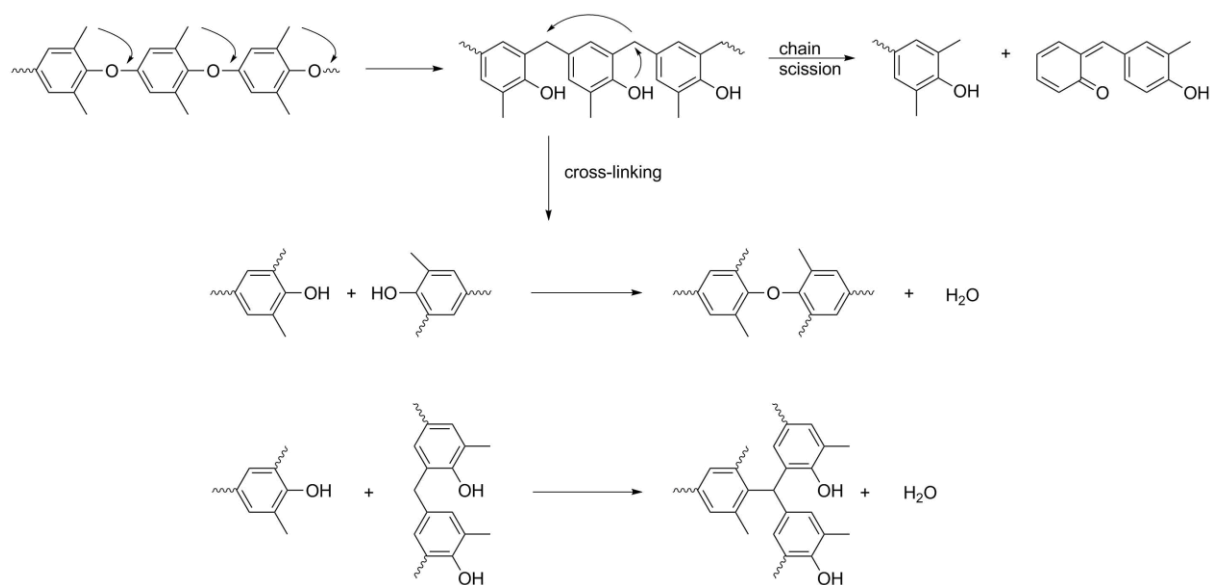
Figure 4. Thermal decomposition of PPO [24].

All above mentioned additives are commercially available and used in flame retardant formulations. Nevertheless the detailed analysis of the interactions between two or more additives in multicomponent polymeric systems is still missing in the literature.

1.4. Multi-methodical approach

To get a better comprehension of the processes occurring during the thermal decomposition of chosen materials, multiple analytical methods and fire tests were performed. The complex analysis of the results gave strong insight in the decomposition mechanisms which were correlated with the final performance. To monitor the decomposition of the materials with simultaneous analysis of the gas phase products, thermogravimetric analysis coupled with

Fourier transform infrared spectroscopy (TG-FTIR) was used. Infrared spectroscopy was used also for observation the decomposition process in the condensed phase by Linkam hot stage cell and attenuated total reflectance (ATR-IR) spectroscopy. The reaction to small flame was tested by UL 94 and limiting oxygen index (LOI) to determine flammability of the materials. The cone calorimeter test was used to compare the materials in terms of fire behavior under forced flaming condition. Furthermore, the residues remained after cone calorimeter test were analyzed by solid state nuclear magnetic resonance spectroscopy (NMR).

1.4.1. Pyrolysis

When the fire occurs and the flames are covering the material, most of the oxygen is consumed in the flame and the decomposition of the material is driven mainly by pyrolysis. Thus the knowledge and understanding the pyrolysis process is crucial for further performance improvement consideration. For that purpose TG-FTIR and Linkam hot stage cell were chosen to monitor the changes in the material during pyrolysis. In TG-FTIR the mass loss under constant heating rate is monitored and simultaneously the IR spectra of the gas phase are collected. Thanks to that the distinct mass loss steps are correlated with the belonging gas phase composition. However not all of the products are volatiles; therefore hot stage cell was used as supportive information source about the changes in the condensed phase. Similarly as in TG, the heating rate is kept constant and the IR spectra of the condensed phase are collected over time.

1.4.2. Comprehensive fire behavior

One of the most important information in terms of performance is the reaction to fire. The cone calorimeter is a bench scale testing apparatus used to investigate the performance of the material under forced flaming condition. It provides important information about fire risks like heat release rate (HRR) or time to ignition (t_{ig}) and about fire hazards, e.g. smoke release or CO production. Additionally, mass loss during the test is monitored via built in load cell. The scheme of the cone calorimeter apparatus is presented in Fig. 5. The cone calorimeter test is used for comparing and ranking the materials in terms of fire behavior. Before starting the test, the heat flux has to be chosen and calibrated. In all presented results the heat flux of $50\,kW/m^2$ was used, which represents well-developed fire scenario. Furthermore, the distance between the bottom of the cone heater and the specimen surface plays an important role. Only well-adjusted distance can assure uniform irradiation over the sample surface. The homogenous irradiance on the inner area of the specimen is achieved when distance between 0 and 40 mm is used [25]. In presented work the distance of 35 mm was chosen. The cone calorimeter test allows ranking materials in terms of ignition time, heat release rate or smoke production, but it has to be noted that those parameters depend strongly on the used setup. Thus always the same apparatus and setup should be used to ensure obtaining reliable results. Additionally, when a row of materials is compared, not only the specimen size but also the thickness has to be the same. The specimen in size of 100×100 mm and defined thickness is placed under the cone heater and exposed to the heat while a spark igniter is placed above the surface. High temperature causes material decomposition on the top and release of volatile products. As soon as the minimum concentration required for ignition is reached, the sample starts to burn. During the test the data about the oxygen consumption (which is then calculated to HRR), smoke production and mass loss are collected, which are then plotted as a function of time. Already the shape of the HRR curve gives important information about the

fire behavior of the material [26]. Further information like total heat released (THR), peak heat release rate (PHRR), t_{ig}, or effective heat of combustion (EHC) are used for direct comparison of different materials. The main task of flame retardants is to reduce HRR, which is achieved by different modes of action (cooling down the system by release of incombustible gases or formation of insulation barrier).
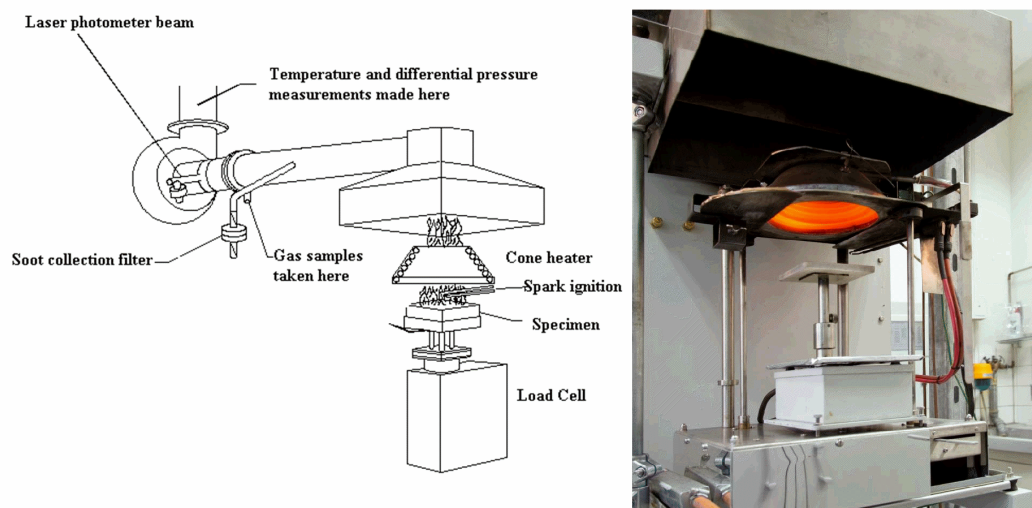
Figure 5. Scheme of the cone calorimeter (left) (drawing by NIST) and zoom on the switched on cone heater (right).

1.4.3. Fire residues analysis

To fully understand the chemistry controlling the decomposition and burning process in the flame retarded polymers, the information about the composition of the residue is needed. Several methods were chosen to obtain comprehensive data about the chemical composition of the residues, such as elemental analysis or ATR-IR. However the most valuable input was achieved by the use of solid state nuclear magnetic resonance (NMR). Solid state NMR is a powerful analytical tool, giving information about the chemical structures and the

crystallinity. Many advantages of this technique make it a perfect tool for detailed fire residue analysis.

The NMR technique was developed at the turn of ´40s and ´50s independently by Edward Mills Purcell and Felix Bloch. They shared the Nobel Prize in Physics in 1952 for their work. NMR spectroscopy is one of the nondestructive testing methods and is based on the phenomena of absorption and re-emission of electromagnetic irradiation by nuclei in the atoms. It is a unique technique which provides detailed information about the structure, dynamics or chemical environment of molecules.

In short the acquisition of the NMR spectrum involves following steps:

- Irradiation of the sample with a short and powerful pulse of radiation from radio frequency (RF) range.

- Digital acquisitions of signal as a function of time.

- If signal-to-noise ratio requires signal averaging, the experiment is repeated and the data are added up. There has to be the delay between each experiment pulse to allow establish spin re-equilibrium at a rate governed by relaxation time T_1.

- Fourier transformation from time-domain signal to frequency-domain spectrum.

This work focuses on the solid-state NMR. The basic principle of the measurement is the same as in liquid NMR, however, due to limited mobility of the molecules in the solid material the measurement has to be conducted under special conditions. In the solid state all interactions of nuclear spins show anisotropic behavior, resulting often in complex spectra with broad and featureless line shapes. It was found out that by rotating the sample under certain angle with the respect to the external magnetic field B_0 the lines are getting narrower

and easier to interpret. This angle was named "magic angle" (equal to 54°74′), and the technique itself is named magic angle spinning (MAS) [27].

To overcome long T_1 and enhance the signal of the low natural abundant nuclei, often cross-polarization (CP) technique is used. This technique allows to transfer polarization from nuclei with short T_1 (e.g. ^1H) to the nuclei of interest (e.g. ^{13}C), enhancing the signal and shorten the relaxation time. At first the 90° pulse is applied on protons, which causes the deflection of the magnetization vector in the x-y-plane. Subsequently both channels (in this case ^1H and ^{13}C) are irradiated at the same time with a long power pulse. The RF power ratio of these pulses has to be tuned so the transition energy for both nuclei is the same. The basis for this method was introduced by Hartmann and Hahn and it is often referred as Hartmann-Hahn cross polarization [28, 29]. Afterwards, the signal is detected while high power ^1H decoupling occurs. In the decoupling process on the ^1H channel is applied a long radio frequency band with high power. This leads to temporary averaging of the heteronuclear dipole-dipole interaction. In reality, different ^1H and ^{13}C species have different resonance frequencies. To achieve the uniform excitation and the full polarization transfer, the power of the applied RF pulse on the ^1H-channel is continuously reduced from 100% to 50% (Fig. 6).
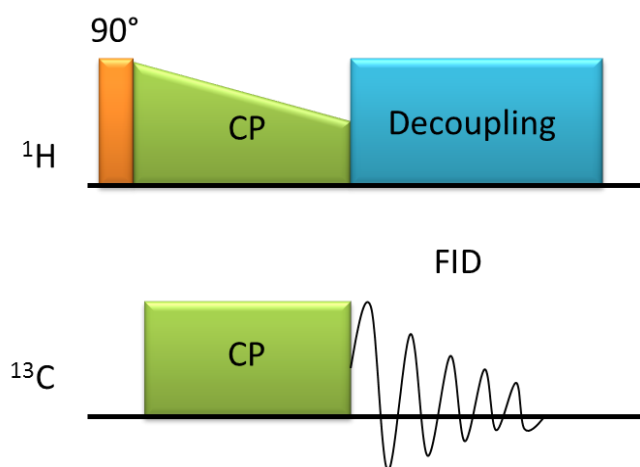

Figure 6. Schematic presentation of cross-polarization principle (FID – free induction decay).

In this work, two additional advanced NMR techniques were used, namely transfer of population in double resonance (TRAPDOR) and rotational echo double resonance (REDOR). They allowed interpreting more complex spectra and gave detailed information about the chemical structures. The double resonance experiment requires a MAS probe equipped with at least two RF channels for observed (I) and non-observed nucleus (S). Usually three-channel probe (additional channel for ^{1}H) is used in order to use CP technique additionally.

REDOR NMR was developed for measuring interatomic distances using the heteronuclear dipolar coupling in solid samples. Since the dipolar coupling depends strongly on the distance between two nuclei, REDOR technique can give important information about the structure in solid material. Usually REDOR is used for characterization of pair of -½ nuclei. In the REDOR a rotor-synchronized echo sequence is applied on the observed nucleus (e.g. [27]Al). In a second experiment, RF pulses (180° pulses) are irradiated on the other nuclei to recouple the heteronuclear dipole interaction which is otherwise suppressed by the sample rotation (MAS). Dipolar dephasing RF pulses are applied on the non-observed nucleus (e.g. [31]P). The experiments are usually performed as a set of measurements with and without applying irradiation on the channel of non-observed nuclei (Fig. 7). When those pulses are off the REDOR rotor-synchronized sequence gives a full-echo spectrum (S_0). In the next step the 180° pulses are irradiated on non-observed nuclei and the recoupling of the heteronuclear interaction occurs, which leads to the decay in signal due to the fact that part of the magnetization applied on observed nuclei cannot refocus. The reduction of the signal is strongly dependent on the dipolar coupling between two nuclei and hence the distance [30, 31]. In effect we obtain REDOR spectrum (S). The difference between S_0 and S (ΔS) and its intensity represents how much of the dipolar coupling between two nuclei was restored.
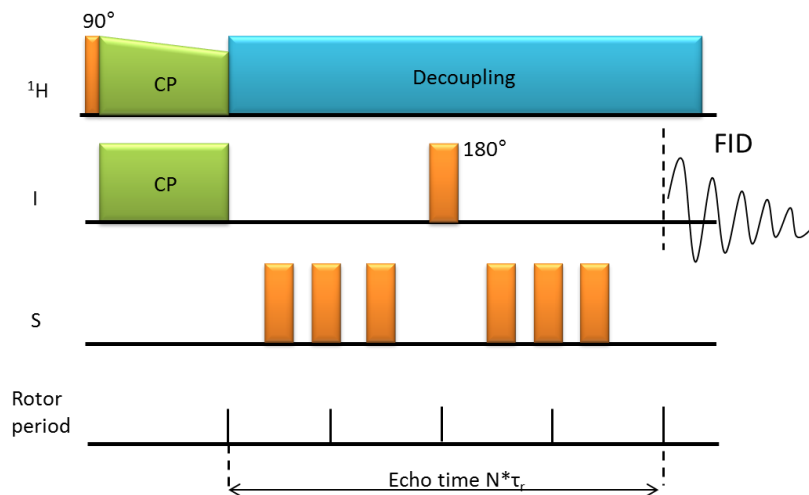
Figure 7. Schematic pulse sequence of REDOR NMR pulse sequence (with CP), where N – number of the rotor cycles, τ_r – rotor period (time of one rotation). There are two 180° pulses on S-channel per rotor period, one at ½ of the rotor period and second at the completion of each rotor period. A single 180° pulse on I-channel replaces S-pulse in the middle of evolution period.
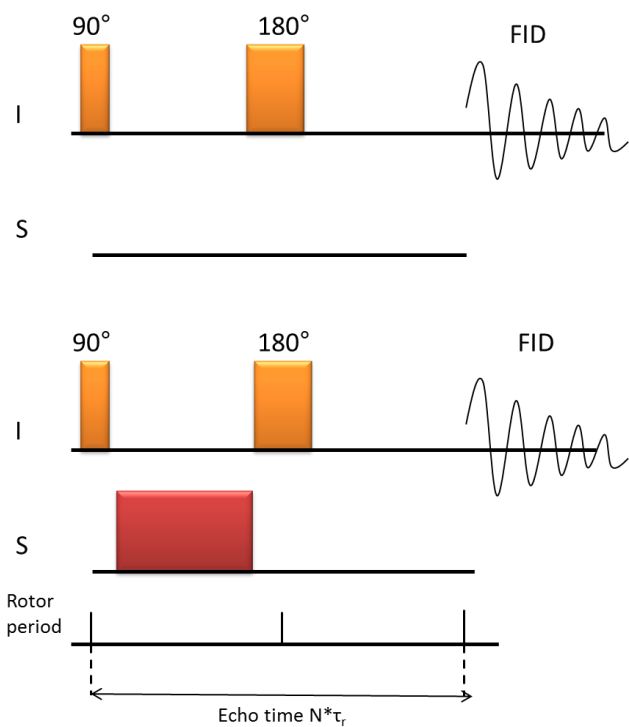
Figure 8. Schematic pulse sequence of TRAPDOR NMR experiment. In first experiment there is no S-pulse. In second part continuous irradiation is applied.

The TRAPDOR NMR technique was developed shortly after REDOR NMR and it is used if the second nucleus has a spin larger than ½ (quadrupole). It is based on the same principle. However, in TRAPDOR pulse sequence instead of several short pulses, continuous irradiation of the non-observed nuclei is applied, resulting in population transfers between energy levels. As a result, part of the signal for observed nuclei cannot refocus and the intensity is reduced (Fig. 8) [32, 33].

The above mentioned NMR techniques resulted in detailed information about the chemical structure. Different nuclei were chosen to observe, depending on the composition of the sample and the information needed. Since in every polymeric material at least one component was phosphorus-based, all samples were analyzed via ^{31}P and ^{13}C MAS NMR, and for particular materials further ^{27}Al, ^{11}B and ^{29}Si MAS NMR experiments were performed. The double resonance techniques provided significant information about the structures present in the fire residue.

2.   Scientific goal

Flame retardant polymers are widely used in everyday life and strong emphasis is put on designing new formulations which will be more efficient at lower concentration of additives. Halogenated flame retardants are working well, especially in the gas phase causing flame inhibition, but the toxicity concerns have caused increased demand of halogen-free flame retardants.

The aim of the presented work was to understand the chemical interactions in selected multicomponent systems. When the material is exposed to high temperatures several processes occur. The components of the system are not only decomposing, but also interacting with each other or with decomposition products. Only complex composition analysis of the gas and condensed phase can give full understanding of the chemistry in the system. When it is compared with the performance of a particular system, it is possible to design more optimized flame-retarded systems.

To increase the knowledge about the interplay between sample composition, decomposition products and the performance when exposed to fire, two common polymer matrices and several commercially available flame retardants were chosen for this study. The results describing different multicomponent systems were published in three first-authorship publications and two co-authorship publications.

In the first publication (chapter 3.1) the influence of the potential synergists: zinc borate (ZB) and magnesium hydroxide (MH) on the fire properties was investigated in the system based on TPE-S/AlPi. The structural changes in the condensed phase were investigated via IR and NMR spectroscopy. Moreover, the pyrolysis volatile products and the decomposition process were analyzed by TG-FTIR. The complex analysis allowed identifying the interactions

occurring between AlPi and inorganic filler. This study gave important information about the chemistry in the flame retarded polyolefine systems. It was shown that both MH and ZB interact in the condense phase with AlPi giving different types of phosphates. Those phosphates are contributing in the residue formation and result in additional stability. Moreover, it was shown that depending on the type of inorganic additive, the mode of action of AlPi may change from working in gas phase (which is rather typical) to condense phase.

A comprehensive study of two phosphorus additives, AlPi and APP, most prominent halogen-free flame retardants, in model system TPE-S/Si/PPO was presented in the second publication (chapter 3.2). The multimethodical approach was chosen to monitor the changes in the structure and adequate fire performance. Special focus was put on the detailed analysis of the fire residues via ATR-IR, Raman spectroscopy and solid-state NMR. It was reported that formation of silicophosphate, which most probably works as additional stabilizer of the char, strongly depends on the phosphorus source. A systematic comparison of those two most popular phosphorus-based additives have led to better understanding of the modes of action and the chemical interactions between all the components.

Additionally, large sample series of multicomponent flame retarded TPE-S systems was investigated in terms of fire behavior and published in a co-authorship article (chapter 3.3). Several commercially available additives were chosen to have overview of different mechanisms and modes of actions and their influence on the fire performance. The comprehensive investigation of a wide range of materials allowed indicating the most promising combinations.

The last two publications are focused on different polymeric system – epoxy resin. Three additives, AlPi, MPP and boehmite were proposed as synergists for novel flame retardant melamine poly(magnesium phosphate) (chapter 3.4) and melamine poly(zinc phosphate)

(chapter 3.5). The material series was chosen in a way that it was possible to calculate the synergistic indexes. Clear synergistic effects were observed, especially between MPP and poly(metal phosphate). The chemical interactions between the additives were identified mostly by solid state NMR and gave significant clarification of the chemistry standing behind the synergy. Moreover, the analysis of the fire residues via µCT revealed how the inner structure changes depending on the synergist used.

3.   Publications

3.1.   Interactions in multicomponent flame-retardant polymers: Solid-state NMR identifying the chemistry behind it

This article was accepted and published.

Author contribution:

- Concept of the work and design of the working plan.

- Choosing the materials and approach for this study.

- Thermogravimetric analysis and IR analysis.

- Contribution to cone calorimeter experiments.

- Main contribution to NMR experiments.

- Collection, analysis and interpretation of the data.

- Scientific discussion, conclusions, writing the manuscript.

Abstract

Distinct approaches are used to reduce the fire risks of polymers, a key issue for many industrial applications. Among the variety of approaches, the use of synergy in halogen-free multicomponent systems is one of the most auspicious. To optimize the composition of such flame-retardant systems it is essential to understand the mechanisms and the corresponding chemistry in the condensed phase. In this work different methods are used, including cone calorimeter, thermogravimetry (TG), and TG-FTIR, with the main focus on the solid-state NMR analysis of the solid residues. The structural changes in the condensed phase of two thermoplastic elastomer systems based on copolymer styrene-ethylene-butylene-styrene (TPE-S) were investigated: TPE-S/aluminium diethylphosphinate (AlPi)/magnesium hydroxide (MH) and TPE-S/AlPi/zinc borate (ZB)/poly(phenylene oxide) (PPO). Strong flame inhibition is synergistically combined with protective layer formation. ^{13}C-, ^{27}Al-, ^{11}B- and ^{31}P MAS NMR (magic angle spinning nuclear magnetic resonance) experiments using direct excitation with a single pulse and ^{1}H-^{31}P crosspolarization (CP) were carried out as well as double resonance techniques. Magnesium phosphates were formed during the pyrolysis of TPE-S/AlPi/MH, while for the system TPE-S/AlPi/ZB/PPO zinc phosphates and borophosphates were observed. Thus, the chemistry behind the chemical interaction was characterized unambiguously for the investigated systems.

3.2.   Aluminium diethylphosphinate versus ammonium polyphosphate: A comprehensive comparison of the chemical interactions during pyrolysis in flame-retarded polyolefine/poly(phenylene oxide)

This article was accepted and published.

Author contribution:

- Concept of the work and design of the working plan.

- Choosing the materials and approach for this study.

- Thermogravimetric analysis and IR analysis.

- Contribution to cone calorimeter experiments.

- Main contribution to NMR experiments.

- Collection, analysis and interpretation of the data.

- Scientific discussion, conclusions, writing the manuscript.

Abstract

A systematic comparison of chemical interactions and fire behaviour is presented for the thermoplastic elastomer (block copolymer styrene-ethylene-butylene-styrene) (TPE-S)/diethyl- and methylvinylsiloxane (Si)/poly(phenylene oxide) (PPO), flame-retarded with aluminium diethylphosphinate (AlPi) and with ammonium polyphosphate (APP), respectively. TPE-S/APP/Si/PPO performed better in the cone calorimeter test (reduction in peak heat release rate from 2042 to 475 kW m^{-2}), but TPE-S/AlPi/Si/PPO in the flammability tests (oxygen index (OI) and UL 94). This difference was caused by the different modes of action of APP (more in the condensed phase) and AlPi (mainly in the gas phase). Thermogravimetry coupled with Fourier transform infrared spectroscopy (TG-FTIR) was used to analyse the mass loss and the evolved gas products, while a Linkam hot-stage cell to investigate the decomposition in the condensed phase. Moreover, a detailed analysis of the fire residues was done using solid-state NMR. ^{13}C MAS NMR showed that both flame-retarded compositions form graphite-like amorphous carbonaceous char, originating from PPO. ^{31}P MAS NMR and ^{29}Si MAS NMR delivered important information about interaction between phosphorus and the siloxane. For TPE-S/AlPi/Si/PPO aluminium phosphate and silicon dioxide occurred, while also silicophosphate was produced in TPE-S/APP/Si/PPO. The direct comparison of two of the most prominent halogen-free flame retardants containing phosphorus delivered meaningful insights into the modes of action and molecular mechanisms controlling flame retardancy.

3.3. Halogen-free fire retardant styrene-ethylene-butylene-styrene-based thermoplastic elastomers using synergistic aluminum diethylphosphinate-based combinations

Kirsten Langfeld, Antje Wilke, Aleksandra Sut, Sebastian Greiser, Bernhard Ulmer, Vlad Andrievici, Patrick Limbach, Martin Bastian, Bernhard Schartel, *J. Fire. Sci.* **2015**, 33(2), 157-177

This article was accepted and published.

Author contribution:

- NMR measurements, interpretation of the spectra and description.

Abstract

Multicomponent flame retardant systems containing aluminum diethylphosphinate in thermoplastic styrene–ethylene–butylene–styrene elastomers are investigated (oxygen index, UL 94, cone calorimeter, and mechanical testing). Solid-state nuclear magnetic resonance, scanning electron microscopy, and elemental analysis illuminate the interactions in the condensed phase. Thermoplastic styrene–ethylene–butylene–styrene elastomers are a challenge for flame retardancy (peak heat release rate at 50 kW m^{-2} >2000 kW m^{-2}, oxygen index = 17.2 vol%, no UL-94 horizontal burn rating) since it burns without residue and with a very high effective heat of combustion. Adding aluminum diethylphosphinate results in efficient flame inhibition and improves the reaction to small flame, but it is less effective in the cone calorimeter. Its efficacy levels off for amounts >~25 wt%. As the most promising synergistic system, aluminum diethylphosphinate/melamine polyphosphate was identified, combining the main gas action of aluminum diethylphosphinate with condensed phase mechanisms. The protection layer was further improved with several adjuvants. Keeping the overall flame retardant content at 30 wt%, aluminum diethylphosphinate/melamine polyphosphate/titanium dioxide and aluminum diethylphosphinate/melamine polyphosphate/boehmite were the best approaches. An oxygen index of up to 27 vol% was achieved and a horizontal burn rating in UL 94 with immediate self-extinction; peak heat release rate decreased by up to 85% compared to thermoplastic styrene–ethylene–butylene–styrene elastomers, to <300 kW m^{-2}.

3.4. Synergy in flame-retarded epoxy resin: Identification of chemical interactions by solid-state NMR

This article was accepted and published.

Author contribution:

- Concept of the work and design of the working plan.

- Choosing the materials and approach for this study.

- Thermogravimetric analysis and IR analysis.

- Contribution to cone calorimeter experiments.

- Main contribution to NMR experiments.

- Collection, analysis and interpretation of the data.

- Scientific discussion and conclusions.

- Preparing and writing the manuscript.

Abstract

The potential synergists aluminium diethylphosphinate (AlPi), boehmite (AlO(OH)) and melamine polyphosphate (MPP) were compared in flame-retardant epoxy resin (EP)/melamine poly(magnesium phosphate) (S600). The pyrolysis, the fire behaviour as well as the chemical interactions in the gas and condensed phases were investigated by various methods. Flammability was investigated by cone calorimeter and oxygen index (OI). The thermal and thermo-oxidative decomposition were studied by thermogravimetric analysis coupled with FTIR spectrometer. The special focus was on the investigation of structural changes in the condensed phase via solid-state NMR of ^{27}Al and ^{31}P nuclei. By the comparison of epoxy resin with only one additive or with S600 in combination with AlPi, AlO(OH) or MPP, it was possible to calculate the synergy index. The best performance in terms of fire behaviour was observed for EP/S600/MPP with a PHRR (peak heat release rate) of 208 kW m^{-2} due to slight synergy. In the case of THE (total heat evolved), clear synergy occurred for EP/S600/AlPi and EP/S600/AlO(OH). By solid-state NMR, different phosphates and aluminates were identified, indicating the chemical interactions between S600 and AlPi, AlO(OH) or MPP. The systematic multi-methodical approach yielded insight into the synergistic effects in the flame-retarded epoxy resin.

3.5. Melamine poly(zinc phosphate) as flame retardant in epoxy resin: Decomposition pathways, molecular mechanisms and morphology of fire residues

Patrick Müller, Michael Morys, Aleksandra Sut, Christian Jäger, Bernhard Illerhaus, Bernhard Schartel, *Polym. Degrad. Stabil.* **2016**, 130, 307-319

This article was accepted and published.

Author contribution:

- Contributing to interpretation of NMR spectra.

- Scientific discussion.

Abstract

Synergistic multicomponent systems containing melamine poly(metal phosphate)s have been recently proposed as flame retardants. This work focuses on the decomposition pathways, molecular mechanisms and morphology of the fire residues of epoxy resin (EP) flame retarded with melamine poly(zinc phosphate) (MPZnP) to explain the modes of action and synergistic effects with selected synergists (melamine polyphosphate (MPP) and AlO(OH), respectively). The total load of flame retardants was always 20 wt%. The decomposition pathways were investigated in detail via thermogravimetric analysis coupled with Fourier transform infrared spectroscopy. The fire residues were investigated via elemental analysis und solid-state nuclear magnetic resonance spectroscopy. The morphology of intumescent fire residues was investigated via micro-computed tomography and scanning electron microscopy. EP + (MPZnP + MPP) formed a highly voluminous residue that showed structural features of both EP + MPZnP and EP + MPP, resulting in a highly effective protection layer. EP + (MPZnP + AlO(OH)) preserved the entire quantity of phosphorus content during combustion due to the formation of $Zn_2P_2O_7$ and $AlPO_4$.

4. Summary

Multicomponent flame retarded formulations are nowadays widely used, especially for polymers with poor burning resistance. The reason for it is the increased demand of halogen-free formulations while maintaining low loadings of flame retardants. Nevertheless, there is still sometimes lack in understanding of the chemistry occurring during the pyrolysis and decomposition process of such systems. The scientific understanding of the interactions between particular additives in multicomponent polymers is crucial for optimization of flame retarded polymers.

In this work, complex and comprehensive investigations of multicomponent flame-retarded polymers are presented. The chosen approach was based on a multi-methodical study of the pyrolysis, decomposition process and burning behavior. Various methods were used to identify the decomposition products formed in the gas and condensed phase, such as thermogravimetry, infrared spectroscopy, solid-state NMR and cone calorimeter. As a polymer matrix two widely used polymers, thermoplastic elastomer based on styrene (TPE-S) and epoxy resin (EP) were chosen as most suitable for investigation. Both polymers are commonly used in various applications, where good performance in terms of fire is needed. Unfortunately, when used alone, they burn very fast. Hence, flame-retarded formulations have to be used. As a solution, multicomponent compositions are proposed to achieve the best result at relatively low additive concentration. Different flame retardants, fillers and synergists were chosen and proposed as suitable for this purpose. Moreover, detailed analysis of the fire residues as well as pyrolysis products delivered significant insight into the chemical interactions standing behind good final performance. The investigated materials were divided in groups to have the best overview over the results.

In case of TPE-S the potential synergists for AlPi were investigated (chapter 3.1 and 3.3). It was shown that the synergistic effects improve the fire performance without the need of increased additives amount. When AlPi was used alone as a flame retardant, it was not possible to achieve good results. The reason for it is the mode of action of AlPi – it works in the gas phase as a flame inhibitor, but it is not able to protect the polymer matrix and does not increase the residue formation. The whole material is consumed in the fire. Nevertheless, when potential synergists, such as magnesium hydroxide or zinc borate are used together with AlPi, significant improvement of the performance is observed. Furthermore, detailed analysis of the residues by solid state NMR showed that different kind of inorganic phosphates (e.g. magnesium phosphate, zinc phosphate) were formed during burning. Thus the chemistry behind the synergistic effects was identified.

Moreover, the efficiency difference between AlPi and APP when used in TPE-S/Si/PPO system (chapter 3.2) was reported. Two most promising phosphorus based additives with different modes of action were selected to study the pyrolysis and fire behavior. Detailed analysis of the pyrolysis products in the gas phase by IR and identification of the structures in the fire residue via solid state NMR gave a far-reaching understanding of the mechanisms controlling the flame retardancy. It was found out that APP is a more suitable additive for polyolefines than AlPi.

For the EP systems potential synergists for novel flame-retardants based on melamine poly(metal phosphate) were selected and investigated in terms of fire behavior (chapter 3.4 and 3.5). The combinations with one additive or two additives were tested to evaluate synergistic effects. It was found out that the best results (i.e. the lowest peak of heat release) were reached when poly(metal phosphate) was combined with MPP. It was suggested that the synergy was not only in the means of chemistry but also in residue structure. For example the

residue of epoxy resin with MPP and melamine poly(zinc phosphate) was analyzed by μCT and the features of residues when only one additive was used were found. Thanks to that the resulting residue was more stable and provided better thermal insulation than for other combinations.

Detailed and comprehensive analysis of chosen model system gave meaningful insights in the chemistry and mechanisms controlling the fire behavior and decomposition process of multicomponent polymeric systems. The scientific-based approach presented in this work is a step forward in designing optimized flame retarded polymers.

5. Zusammenfasung

Mehrkomponenten-flammschutzsysteme sind heutzutage in vielen Anwendungen weit verbreitet, insbesondere für Materialien mit schlechter Verbrennungsbeständigkeit. Deshalb ist der erhöhte Bedarf an halogenfreien Formulierungen unter Beibehaltung geringer Flammschutzmittelkonzentration nötig. Dennoch fehlt es bisweilen an mangelndem Verständnis der Chemie, die während der Pyrolyse- und Zersetzungsprozesse solcher Systeme auftritt. Das wissenschaftliche Verständnis der Wechselwirkungen zwischen bestimmten Additiven in Mehrkomponentenpolymeren ist entscheidend für die Optimierung von flammgeschützten Polymeren.

In dieser Arbeit wird eine komplexe und umfassende Untersuchung von flammgeschützten Mehrkomponenten-Polymeren vorgestellt. Der gewählte Ansatz basiert auf einer multimethodischen Untersuchung der Pyrolyse, des Zersetzungsprozesses und des Verbrennungsverhaltens. Verschiedene Verfahren wurden verwendet, um die im Gas und in der kondensierten Phase gebildeten Zersetzungsprodukte zu identifizieren, wie Thermogravimetrie, Infrarotspektroskopie, Festkörper-NMR und Cone-Kalorimeter. Als Polymermatrix wurden zwei am meisten verwendete Polymere, thermoplastisches Elastomer auf Basis von Styrol (TPE-S) und Epoxidharz (EP) als am geeignetsten für die Untersuchung ausgewählt. Beide Polymere werden üblicherweise in verschiedenen Anwendungen eingesetzt, wo gute Brandschutzeigenschaften erforderlich sind. Allerdings, wenn alleine verwendet, verbrennen sie sehr schnell und ohne Rückstandsbildung. Daher müssen flammgeschützte Formulierungen verwendet werden. Als Lösung werden Mehrkomponentensysteme vorgeschlagen, um das beste Ergebnis bei relativ niedriger Additivkonzentration zu erzielen. Verschiedene Flammschutzmittel, Füllstoffe und Synergisten wurden gewählt und als geeignet für diesen Zweck vorgeschlagen. Darüber

hinaus lieferte eine detaillierte Analyse der Brandrückstände sowie Pyrolyseprodukte einen deutlichen Einblick in die chemischen Wechselwirkungen, die für gute Ergebnisse verantwortlich sind. Die untersuchten Materialien wurden in Gruppen aufgeteilt, um den besten Überblick über die Ergebnisse zu erhalten.

Im Falle von TPE-S wurden die möglichen Synergisten für AlPi untersucht (Kapitel 3.1 und 3.3). Es wurde gezeigt, dass die synergistischen Effekte die Brandleistung ohne die Notwendigkeit einer erhöhten Additivmenge verbessern. Wenn AlPi allein als Flammschutzmittel verwendet wurde, war es nicht möglich, gute Ergebnisse zu erzielen. Der Grund dafür ist die Wirkungsweise von AlPi - es wirkt in der Gasphase als Flammeninhibitor, ist aber nicht in der Lage, die Polymermatrix zu schützen und erhöht nicht die Rückstandsbildung, so dass das gesamte Material verbrannt wird. Wenn jedoch potentielle Synergisten wie Magnesiumhydroxid oder Zinkborat zusammen mit AlPi verwendet werden, wird eine signifikante Verbesserung der Leistung beobachtet. Ferner zeigte eine detaillierte Analyse der Rückstände durch Festkörper-NMR, dass unterschiedliche Arten anorganischer Phosphate (z. B. Magnesiumphosphat, Zinkphosphat) während des Brennens gebildet wurden. So wurde die Chemie hinter den synergistischen Effekten identifiziert.

Darüber hinaus ist die Effizienzdifferenz zwischen AlPi und APP bei Verwendung in TPE-S/Si/PPO-System (Kapitel 3.2) präsentiert. Zwei vielversprechende Additive auf Phosphorbasis mit unterschiedlichen Wirkungsweisen wurden ausgewählt, um die Pyrolyse und das Brandverhalten zu untersuchen. Eine detaillierte Analyse der Pyrolyseprodukte in der Gasphase durch IR und die Identifizierung der Strukturen im Brandrückstand mittels Festkörper-NMR lieferten ein weites Verständnis der Mechanismen, die die Flammschutzeffekte steuern. Es wurde herausgefunden, dass APP ein geeigneteres Additiv für Polyolefine als AlPi ist.

Für die EP-Systeme wurden Synergisten für neuartige Flammschutzmittel auf der Basis von Melaminpoly(metallphosphat) ausgewählt und hinsichtlich des Brandverhaltens untersucht (Kapitel 3.4 und 3.5). Die Kombinationen mit einem Additiv oder zwei Additiven wurden getestet, um synergistische Effekte zu bewerten. Es wurde herausgefunden, dass die besten Ergebnisse (d. H. die niedrigste maximale Wärmeabgaberate) erreicht wurden, wenn Poly(metallphosphat) mit MPP kombiniert wurde. Es wurde vorgeschlagen, dass die Synergie nicht nur in der Chemie, sondern auch in der Rückstandsstruktur liegt. Beispielsweise wurde der Rückstand des Epoxidharzes mit MPP und Melaminpoly(Zinkphosphat) durch µCT analysiert, und die Eigenschaften von Rückständen, wenn nur ein Additiv verwendet wurde, wurden aufgeklärt. Dadurch war der resultierende Rückstand stabiler und sorgt für eine bessere Wärmedämmung als für andere Kombinationen.

Die detaillierte und umfassende Analyse der gewählten Modellsysteme lieferte bedeutende Einsichten in die Chemie und Mechanismen, die das Brandverhalten und den Zersetzungsprozess von mehrkomponentigen Polymersystemen steuern. Der in dieser Arbeit vorgestellte Ansatz ist ein Schritt vorwärts bei der wissenschaftlich-fundierte Entwicklung von optimierteren flammgeschützten Polymeren.

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