



ELSEVIER

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytestPOLYMER
TESTING

Material Behaviour

Synergy between melamine cyanurate, melamine polyphosphate and aluminum diethylphosphinate in flame retarded thermoplastic polyurethane

Aleksandra Sut^a, Elke Metzsch-Zilligen^b, Michael Großhauser^b, Rudolf Pfaendner^b, Bernhard Schartel^{a,*}^a Bundesanstalt für Materialforschung und -prüfung (BAM), Unter den Eichen 87, 12205, Berlin, Germany^b Fraunhofer-Institut für Betriebsfestigkeit und Systemzuverlässigkeit LBF, Schlossgartenstr. 6, 64289, Darmstadt, Germany

ARTICLE INFO

Keywords:

Thermoplastic polyurethane
Synergy
Melamine cyanurate
Melamine polyphosphate
Aluminum diethylphosphinate
Rapid mass calorimeter

ABSTRACT

The multicomponent flame retardant system of melamine polyphosphate (MPP), melamine cyanurate (MC) and aluminum diethylphosphinate (AlPi) is proposed and investigated for thermoplastic polyurethane (TPU). The synergy between those additives and the resulting superior fire performance are discussed. Systematically varied sets of flame retarded TPU with various MPP/MC/AlPi ratios were investigated in terms of fire behavior, pyrolysis products and mechanical properties. The total amount of the additives was always 30 wt.-%. Further, the influence of various AlPi concentrations was investigated. The optimal MPP:MC ratio was determined while keeping the amount of AlPi constant. The combination of 8 wt.-% MPP, 12 wt.-% MC and 10 wt.-% is proposed as the most promising halogen free flame retardant formulation for TPU, because it yielded a reduction in PHRR from 2660 kW/m² (TPU) to 452 kW/m² and enabled V-0 classification in the UL 94 test. Combinations of MPP and MC as well a high concentration of AlPi are beneficial for the mechanical properties e.g. tensile strength and elongation at break of the formulations and could be a strong competitor to commercial flame retarded TPUs.

1. Introduction

Thermoplastic polyurethanes (TPUs) are an important class of polymers widely used in numerous applications, one of the major areas being the cable industry. The regulations for materials used in cables are strict, especially for applications as building products, and require high flame retardancy. Therefore, the thermal stability, decomposition process and performance upon thermal stress are of high interest when designing new compounds. TPU does not usually fulfill those requirements due to extensive burning and flaming dripping. The fire behavior is determined by the chemical structure of TPU [1–3]. The polymer chain consists of alternating hard and soft segments, which provides a copolymer-like structure and attendant properties. Once the material is ignited, decomposition of the hard segments occurs and TPU softens, melts and finally creates pool fires. Burning liquid spreads easily, leading to fire propagation. Different flame retardant approaches have been proposed in the literature [4–9] and the extensive reviews were given by Toldy [10] and Levchik [11]. Nevertheless, reduction of the fire risk and flammability of polymers that burn as strongly as TPU is not an easy task. Excessive loading with additives may lead to deterioration in mechanical properties, whereas low concentrations will not

be efficient enough. For a long time, halogen-based flame retardants were used with great success, since they provide satisfying results even at lower loadings. However, due to toxicity and environmental concerns, the market is requiring more halogen-free solutions. As an ideal compromise, multicomponent systems are proposed [12–14], where the combination of two or more additives leads to increased flame retardancy through synergistic interactions. This approach was proposed in our previous work [15] and used in the following study, where the combination of three commercially available flame retardants – melamine polyphosphate (MPP), melamine cyanurate (MC) and aluminum diethylphosphinate (AlPi) – was used as a synergistic flame retardant mixture for TPU.

Each of the flame retardants mentioned above represents different main mode of action. MPP combines the benefits of phosphorus and melamine-based flame retardants, and is widely used in various polymers to promote both charring and the formation of highly crosslinked phosphorus-carbon structures [16,17]. MC is often used as a synergist for phosphorous flame retardants, and its main mode of action is generally fuel dilution by ammonia release [18,19]. Further, it is widely used in polyamide 6, in which MC enhances dripping [20], but also in TPU [21,22]. Additionally, when combined with other additives, it may

* Corresponding author.

E-mail address: bernhard.schartel@bam.de (B. Schartel).<https://doi.org/10.1016/j.polymeresting.2019.01.001>

Received 23 October 2018; Received in revised form 20 December 2018; Accepted 3 January 2019

Available online 09 January 2019

0142-9418/© 2019 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license

<http://creativecommons.org/licenses/by-nc-nd/4.0/>.

induce a supportive condensed phase mechanism. AlPi is known for its strong flame inhibition properties [23,24] and works especially well in oxygenated polymers like polyamides and polyesters [25–28]. As its contribution to the condensed phase and residue formation is rather low, AlPi is rarely used as a stand-alone flame retardant. Recently it was proposed as a part of the multicomponent polyolefin system [29] and it is also known for synergistic interactions with nitrogen-based flame retardants like MC [30]. The combination of all three flame retardants was proposed as a suitable system for TPU, where fire performance is improved through synergistic interactions and superior contributions to the gas and condensed phase modes of action, without excessive amounts of additives. To achieve optimal fire performance, a systematic set of materials with different MPP, MC and AlPi concentrations was analyzed in terms of fire behavior, pyrolysis products and mechanical properties.

2. Materials

The polyether-type TPU (Elastollan® 1185A10, BASF SE) was chosen as polymer matrix. The additives used in this study were melamine polyphosphate (MPP; Melapur 200, BASF SE), melamine cyanurate (MC; Melapur MC 50, BASF SE) and aluminum diethylphosphinate (AlPi; Exolit OP 1230, Clariant SE). They were compounded with the TPU in a twin-screw extruder (W&P ZSK 18, Coperion GmbH). Two-millimeter thick films were obtained by coupling the extruder via gear pump with a cast film line (chin roll, Dr. Collin GmbH). The extrusion temperature was 190 °C; the throughput 6 kg/h with a screw revolution of 500 min⁻¹. The total amount of additives was set to 30 wt.-% and the ratios between MPP, MC and AlPi are presented in Table 1.

3. Methods

The fire behavior of the investigated materials was evaluated via rapid mass calorimeter (RMC) and cone calorimeter. The RMC was used as a high-throughput screening method, as recently proposed in the literature [31,32]. RMC consists of a modified mass loss calorimeter (Fire Testing Technology, FTT, UK), with its balance replaced by a linear motion unit (Oriental Motor, JP) to provide semi-automatic sample exchange. The heat release rate (HRR) is measured via thermocouples placed in the chimney of the calorimeter, in accordance with ISO 13927. For this test, parts of the films were cut into specimens of 20 mm × 20 mm, wrapped in aluminum foil and exposed to the external heat flux of 50 kW/m². The distance between the sample surface and the cone heater was set to 25 mm. The cone calorimeter was used as a reference method in which forced flaming conditions are simulated according to ISO 5660. Compared to RMC the size of the cone plates was 100 mm × 100 mm and the heat flux was set to 50 kW/m². The distance between the cone heater and the specimen surface was 35 mm, to provide homogenous irradiance of the inner area and to ensure enough distance in the case of moderate intumescence [33]. In order to determine the flammability of the materials, test specimens with a

Table 1
Weight percent ratio of MPP, MC and AlPi used as flame retarding system for TPU.

MPP:MC ratio			AlPi increase		
MPP wt.-%	MC wt.-%	AlPi wt.-%	MPP wt.-%	MC wt.-%	AlPi wt.-%
0	25	5	12	18	0
5	20	5	10	15	5
10	15	5	8	12	10
15	10	5	6	9	15
20	5	5	–	–	–
25	0	5	–	–	–

width of 13 mm were cut out of the film sheets and were tested in a burning chamber (FTT, UK) according to IEC 60695-11-10. All specimens were conditioned at 23 °C and 50% relative humidity for a minimum of 48 h prior to test.

The pyrolysis and its decomposition products were studied by thermogravimetry coupled with FTIR spectrometry (TG-FTIR). The mass loss during decomposition under nitrogen atmosphere was monitored using TG 209 F1 Iris (Netzsch Instrument, Germany). The TG chamber and the spectrometer (Tensor 27, Bruker Optics, Germany) were connected by a transfer line heated up to 260 °C to enable continuous recording of the gas phase IR spectra. The specimen mass was 5 mg.

The samples for mechanical testing were stamped out of the produced films in pull direction. Quasi static tensile tests according to ISO 527-1 were performed at a velocity of $v = 100$ mm/min using a universal tensile testing machine (zwickLine 2.5, Zwick GmbH & Co.KG) at standard atmosphere according to ISO 291 at 23 °C and 50% relative humidity. The tensile strains were directly measured in the lateral and transverse directions using an optical extensometer.

4. Results and discussion

4.1. Influence of the MPP:MC ratio

4.1.1. Fire behavior: rapid mass calorimeter and cone calorimeter

A systematic series of materials with different concentrations of melamine cyanurate (MC) and melamine phosphate (MPP) was investigated using RMC and cone calorimeter. The aluminum diethylphosphinate (AlPi) content was kept constant at 5 wt.-%. In the RMC test the TPU sample burned completely very fast. Addition of MC and AlPi led to a significant reduction in the peak heat release rate (PHRR, Fig. 1 a and c) in TPU with 0/25/5 MPP/MC/AlPi as compared to the non-flame retarded sample, but it still produced the highest peak among all flame retarded samples. In addition, the shape of the curve is different from other flame retarded materials; before the peak maximum was reached, a distinct shoulder occurred. Replacing just 5 wt.-% of MC with MPP produced a significant change in the PHRR (sample 5/20/5). However, the decrease in the PHRR in the rapid mass calorimeter is not linear with the increase in MPP content. It was clearly observed, that combining all three additives led to a stronger reduction in PHRR than when no MC or MPP was present in the system, 0/25/5 and 25/0/5 respectively. This observation indicates the synergy between MC and MPP in TPU/MPP/MC/AlPi systems. The strongest synergistic effect was observed for the combination 10/15/5, as its PHRR value was the lowest and differed most from the calculated superposition (Fig. 1 c, dashed line).

Similar conclusions were drawn from cone calorimeter investigations, where the differences in the HRR curves (Fig. 1 b) were more pronounced. TPU burned fast with a high PHRR of 2660 kW/m², and the HRR curve had a characteristic shape. At first a small plateau-like region is observed, followed by a sharp peak in HRR. Right after the PHRR was reached, flameout occurred. This type of shape, where the high PHRR is reached at the end of burning, is characteristic for non-charring materials [34]. As was reported in previous work [15], the two stages differ significantly in burning behavior, which is attributed to the chemical structure of TPU. The first stage is controlled mainly by hard segment decomposition, where the sample softens and the burning is not so intense. Subsequently a liquid pool fire is created and the sample burns intensively with strong boiling; this phase is controlled mainly by soft segment decomposition.

All flame retarded samples ignited earlier than TPU, suggesting interaction with the polymer matrix. Addition of 25 wt.-% of MC and 5 wt.-% AlPi led to a 70% decrease in PHRR as compared to TPU. The shape of the HRR curve was similar to the HRR curve of TPU, with the plateau region followed by a peak observed in HRR. When MPP was present in the system, even at low loadings, the change in the HRR

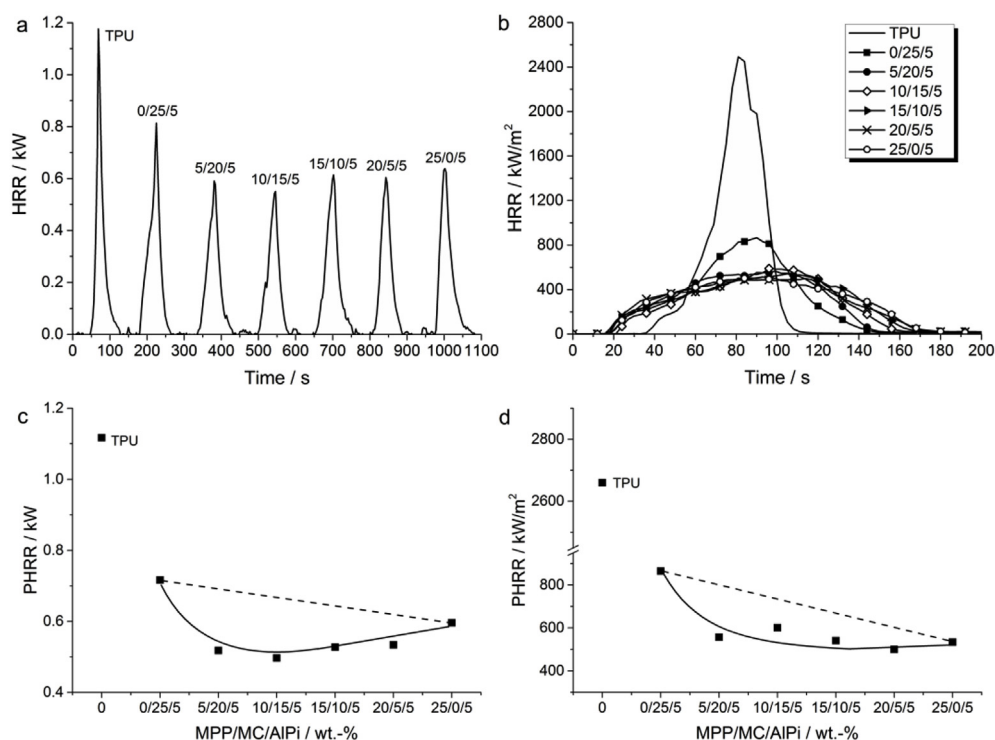


Fig. 1. HRR curves for different MPP:MC ratios at constant AlPi concentration from rapid mass calorimeter (a) and cone calorimeter (b) together with corresponding PHRR dependency on the MPP:MC ratio (c and d, respectively).

curve shape was evident. There was no distinguishable peak and a steady burning plateau was observed. Moreover, the samples burned longer than those without MPP. The differences in PHRR between various MPP concentrations were more subtle than in the rapid mass calorimeter (Fig. 1 d), but the synergistic behavior was noticeable. The cone calorimeter and rapid mass calorimeter results were very consistent and in good agreement.

Each of the flame retardants used – MPP, MC and AlPi – represents a different main mode of action, so to attain the most benefits, the right concentration ratios are needed. The gas phase activity is monitored by the effective heat of combustion (THE/TML), measured in the cone calorimeter (Fig. 2 a). A significant decrease was observed for all flame retarded materials compared to TPU. In 0/25/5 the reduction was about 30% as a result of the combined effects of fuel dilution (MC) and flame inhibition (AlPi). Replacing 5 wt.-% of MC with MPP did not affect the effective heat of combustion, but with increased MPP content a slight decrease in gas phase activity was indicated. Moreover, similarly as for the PHRR, the change was not linear; so that at 10/15/5 the optimal MPP/MC/AlPi ratio was reached, indicating a synergism (Fig. 2 a). The combination of a protective layer and fuel storage (MPP), fuel

dilution due to MC, and flame inhibition caused by AlPi resulted in the lowest THE/TML. When the MPP concentration exceeded the MC content, a slight increase in THE/TML was observed due to the limited contribution of MPP to gas phase activity. However, the synergistic effect in the effective heat of combustion is in the same range as the uncertainty, whereas the synergy in the residue is more pronounced. The residue yield rose along with melamine polyphosphate content (Fig. 2 b), but again, the increase was not linear. A significant change in the amount of residue was observed when 5 wt.-% MC was replaced by MPP, whereas differences between 15, 20 and 25 wt.-% were more subtle. All cone calorimeter data are summarized in the Table 2. Considering all of the main parameters monitored in the cone calorimeter, the optimal concentration ratio was 10/15/5.

In the UL 94 test (reaction to small flame) TPU achieved a V-2 classification. The specimen extinguished within less than 10 s after removing the flame, but during this time many small burning drops were formed and ignited the cotton placed under the sample. The flame retarded combinations presented a slightly different behavior. In most of the tests no dripping was observed during the first flame exposure, but the specimen started to melt. During the second flame application,

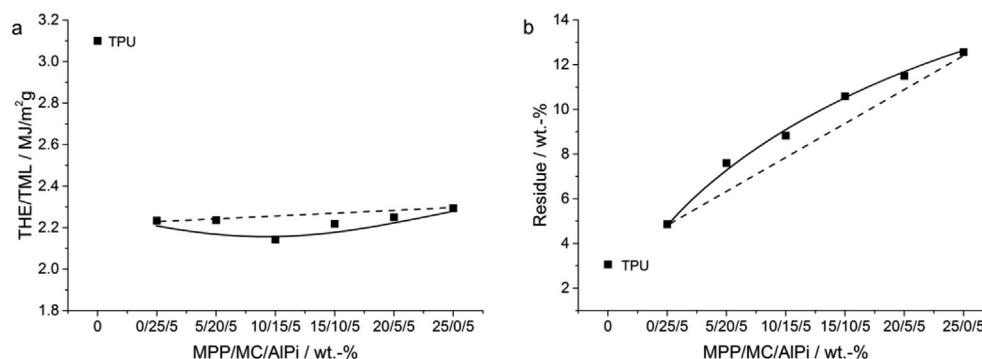


Fig. 2. The dependency of different MPP:MC concentrations on the/TML (a) and residue yield (b) in cone calorimeter.

Table 2

Cone calorimeter data of TPU and flame retarded TPU. PHRR – peak heat release rate; THE – total heat evolved; THE/TML – effective heat of combustion.

Material (MPP/MC/AIPi)	PHRR kW/m ²	THE MJ/m ²	THE/TML MJ/m ² g	Residue wt.-%	UL 94
TPU	2660 ± 168	66 ± 1	3.1 ± 0.1	3.1 ± 0.3	V-2
0/25/5	865 ± 61	52 ± 2	2.2 ± 0.1	4.9 ± 1.9	V-0
5/20/5	558 ± 9	54 ± 1	2.2 ± 0.1	7.6 ± 0.1	V-0/V-2
10/15/5	601 ± 13	50 ± 2	2.1 ± 0.1	8.8 ± 0.3	V-0
15/10/5	541 ± 5	54 ± 2	2.2 ± 0.1	10.6 ± 0.1	V-0/V-2
20/5/5	500 ± 15	53 ± 1	2.2 ± 0.1	11.5 ± 0.1	V-0
25/0/5	534 ± 20	54 ± 2	2.3 ± 0.1	12.6 ± 0.2	V-0

dripping and/or melt flow was observed, but the cotton was not ignited, resulting in a V-0 classification. The exceptions were the 5/20/5 and 15/10/5 mixtures, where one of five specimens from the set ignited the cotton at the second exposure to flame; therefore those materials were on the border between V-0 and V-2.

4.1.2. Pyrolysis: mass loss and volatiles

Mass loss during the pyrolysis process was monitored via thermogravimetry (TG) (Fig. 3 a). All flame retarded materials started to decompose slightly earlier than TPU (Table 3, T_{5%}) and the difference became larger when more MPP was in the sample, indicating stronger interaction with the polymer matrix.

The residue yield increased with MPP content and clear synergy occurred (Fig. 3 b), as all the residue yields lay way above the line associated with the superposition, especially the 10/15/5 and 15/10/5 mixtures. Above 10 wt.-% MPP content the residue amount remained at a similar level, which is consistent with the conclusions drawn from the cone calorimeter tests.

A closer look at the mass loss rate curves (Fig. 3 c) shows that all flame retarded formulations had three distinguishable decomposition steps, but in some cases there was a clear shift in the temperatures and a merging of the first two steps. TPU decomposed in two major steps, dominated by hard segment and soft segment decomposition, respectively. At the end of the test the material was consumed nearly completely with only 1 wt.-% of residue left (Table 3). In 0/25/5 three distinct peaks were identified. At first mostly polymer matrix decomposed, in particular, hard segments of the TPU chain. The temperature of the maximum mass loss rate was 15 °C lower than for TPU and the mass loss was slightly higher (Table 3, Δm₁). The second step was attributed mainly to MC decomposition and the release of ammonia and melamine in the gas phase. At this point around 22 wt.-% mass was lost, which corresponds well with the MC content (25 wt.-%). Afterwards further pyrolysis of TPU proceeded and soft segments decomposed. Subsequent replacement of MC by MPP caused the disappearance of the middle step related to MC decomposition. Additionally, the last decomposition step, which was dominated by soft segment decomposition, was shifted towards temperatures lower than for TPU (Table 3, Δm₂). As the MPP content increased, the first step was separated, so that a shoulder was distinguished at around 343 °C with mass loss of 17 wt.-% and 22 wt.-% for 20/5/5 and 25/0/5, respectively. This step was related to the partial release of melamine from MPP. The detailed temperatures and mass loss for each step are summarized in Table 3.

The combination of TG with Fourier transform infrared spectroscopy (FTIR) allowed identifying the gas products evolved during the pyrolysis process. The volatiles were carried in the nitrogen flow to the spectrometer via transfer line. The temperature of 260 °C was chosen to minimize the risk of the products condensation in the transfer line.

The IR spectra for each material taken at second decomposition step are presented in Fig. 4 a. This step was chosen as the most representative for the analysis, where the volatiles coming from both polymer and additives were observed. The complete set of the FTIR spectra covering all decomposition steps are presented in the

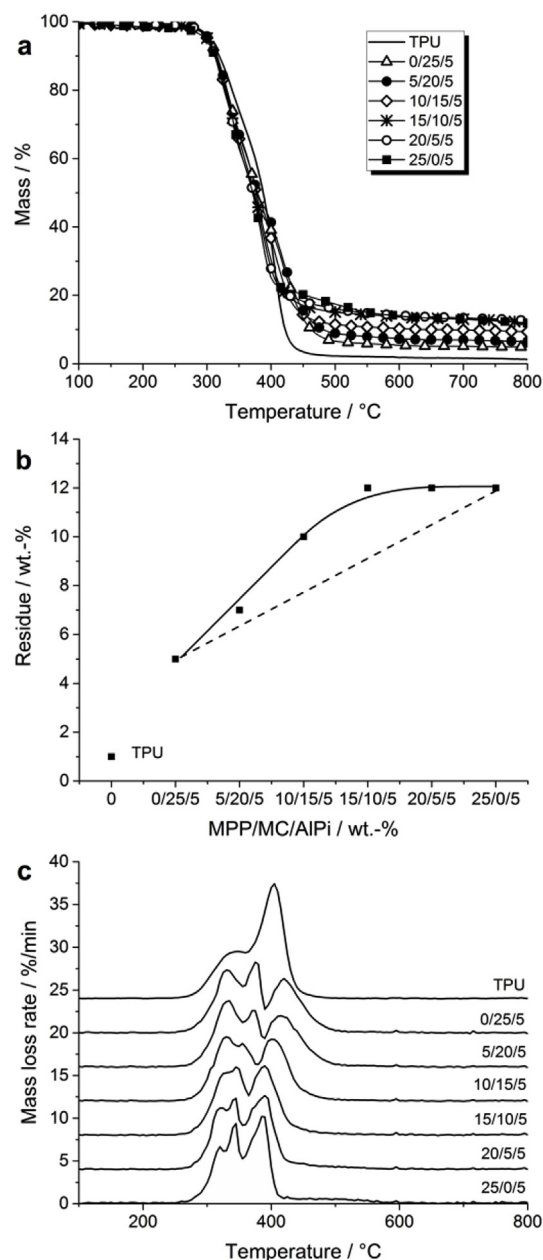


Fig. 3. Mass curves for different MPP:MC ratios at constant AIPi load (a), residue amount (b) and mass loss rate curves (c).

supplementary data (S.1). Since only 5 wt.-% of AIPi was contained in each material, no typical bands of its decomposition products (e.g. phosphinic acid) were observed in the gas phase, due to either low intensity or overlapping by other signals. When no MPP was in the material (0/25/5) mainly TPU decomposition products were detected, like methylene diphenyl diisocyanate (MDI, 2286–2247 cm⁻¹), along with volatiles coming from MC, namely ammonia (968, 929 cm⁻¹) and cyanic acid (~3530 cm⁻¹) [15]. Ammonia as an inert gas is responsible for fuel dilution, as observed in the cone calorimeter. As the MC concentration decreased in favor of MPP, ammonia and HOCN were less pronounced. Moreover, MDI signals were less intense, and new bands attributed to tetrahydrofuran (THF, 2982–2872, 1082, 909 cm⁻¹) appeared and CO₂ (2360–2313, 667 cm⁻¹) started to dominate the spectrum, especially in the 25/0/5 sample. Those bands were attributed to the soft segments of TPU [3,35]. This suggests changed TPU decomposition and explains the shift in temperatures observed in the mass loss rate curves. When the MPP concentration reached 20 wt.-% and above,

Table 3

Thermal decomposition characteristics of investigated materials. $T_{5\%}$ – temperature at which 5 wt.-% of the material was lost; $T_{1,2,3}$ – temperature of the maximum mass loss rate at 1st, 2nd and 3rd step; $\Delta m_{1,2,3}$ – mass loss at each decomposition step. Residue was taken at 800 °C.

Material (MPP/MC/AlPi)	$T_{5\%}$ °C +/-1-2	T_1 °C +/-1-2	Δm_1 wt.-% +/-1	T_2 °C +/-1	Δm_2 wt.-% +/-1	T_3 °C +/-1-4	Δm_3 wt.-% +/-1	Residue wt.-%
TPU	305	346	31	–	–	404	68	1.3 ± 0.5
0/25/5	302	331	36	376	22	420	37	4.9 ± 0.1
5/20/5	305	333	35	371	18	413	39	6.9 ± 0.5
10/15/5	301	339	50	shoulder		398	39	10.2 ± 0.7
15/10/5	301	shoulder		345	45	391	43	12.0 ± 0.1
20/5/5	301	323	23	343	17	392	47	12.4 ± 0.2
25/0/5	300	317	18	342	22	386	48	12.5 ± 0.5

additional bands of melamine (multiple bands between 1699 and 1223 cm^{-1}) were identified, indicating that part of MPP interacted in the condensed phase while the rest was released as volatiles in the gas phase. It explains well the observations made in the cone calorimeter and thermogravimetry, where the residue increase was not linear with the MPP concentration. On the other hand, released melamine provides worse fuel dilution than ammonia from MC, which in turn explains the higher effective heat of combustion for materials whose MPP content was slightly higher than MC.

To observe the changes in the condensed phase, the residues after the cone calorimeter test were ground into homogenous powder and analyzed by ATR-FTIR (Fig. 4 b). As it is known from the literature, MPP leads to the formation of highly crosslinked char rich in phosphorus. Indeed, in the formulation with 25 wt.-% MPP the corresponding bands are observed. The signal at 1600 cm^{-1} was attributed to the aromatic structure of carbonaceous materials, and gained in intensity when oxygen was present in the functional groups. The double band at 1134 and 964 cm^{-1} corresponded to P–O and P=O bonds, which are part of the crosslinked phosphorus residue. As the amount of the MPP in the material decreased, these bands lost intensity; however, in the 10/15/5 sample a new band appeared at 1259 cm^{-1} and was attributed to the P=N bonds formed during interaction of the melamine cyanurate with MPP and/or AlPi. The intensity of this signal increased along with increased MC content. When there was no MPP in the sample (0/25/5), the phosphorous bonds merged into one weak peak at 1076 cm^{-1} , which was attributed to the P–O/P–OH bond [36].

4.1.3. Mechanical testing

Table 4 shows the measured elongation at break and tensile strength for samples where the MPP:MC ratio was varied. The two compounds 5/20/5 and 10/15/5 show a similar elongation at break of around 380%; the maximum tensile strength is found for the compound 5/20/5 with a value of 23.2 MPa. The synergy between MPP and MC opens up with the look at the compounds 0/25/5 and 25/0/5. Both show the minimum values for the elongation at break and tensile strength

Table 4

Elongation at break in % and tensile strength in MPa measured via quasi-static mechanical tests with a velocity of $v = 100 \text{ mm/min}$.

Material (MPP/MC/AlPi)	Elongation at break %	Tensile strength MPa
0/25/5	293.7 ± 63.2	16.7 ± 3.4
5/20/5	373.4 ± 34.6	23.2 ± 1.7
10/15/5	380.5 ± 4.4	20.9 ± 0.4
15/10/5	346.1 ± 32.2	19.1 ± 0.9
20/5/5	347.8 ± 5.2	17.7 ± 0.9
25/0/5	214.5 ± 34.0	11.0 ± 1.2

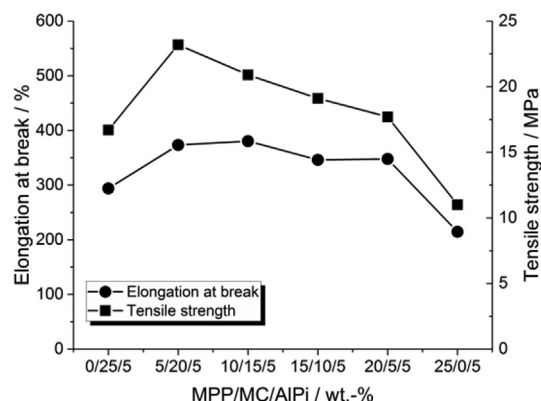


Fig. 5. Elongation at break in % (circles) and tensile strength in MPa (squares) for the continuous variation of the MPP:MC ratio at constant AlPi loading.

(Fig. 5). The elongation at break and the tensile strength values decrease with the reduction of MC content and the lowest point was reached for the compound 25/0/5 with 214.5% and 11.0 MPa. On the other side replacement of 5% MC through 5% MPP results in a substantial improvement of the mechanical values. All of the investigated

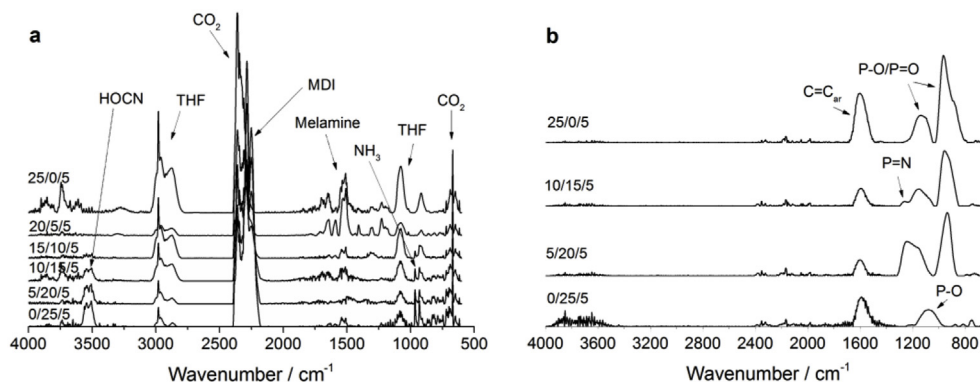


Fig. 4. Gas phase FTIR spectra of investigated materials taken at temperatures according to T_2 (Table 3) (a) and ATR-FTIR spectra of the residues (b).

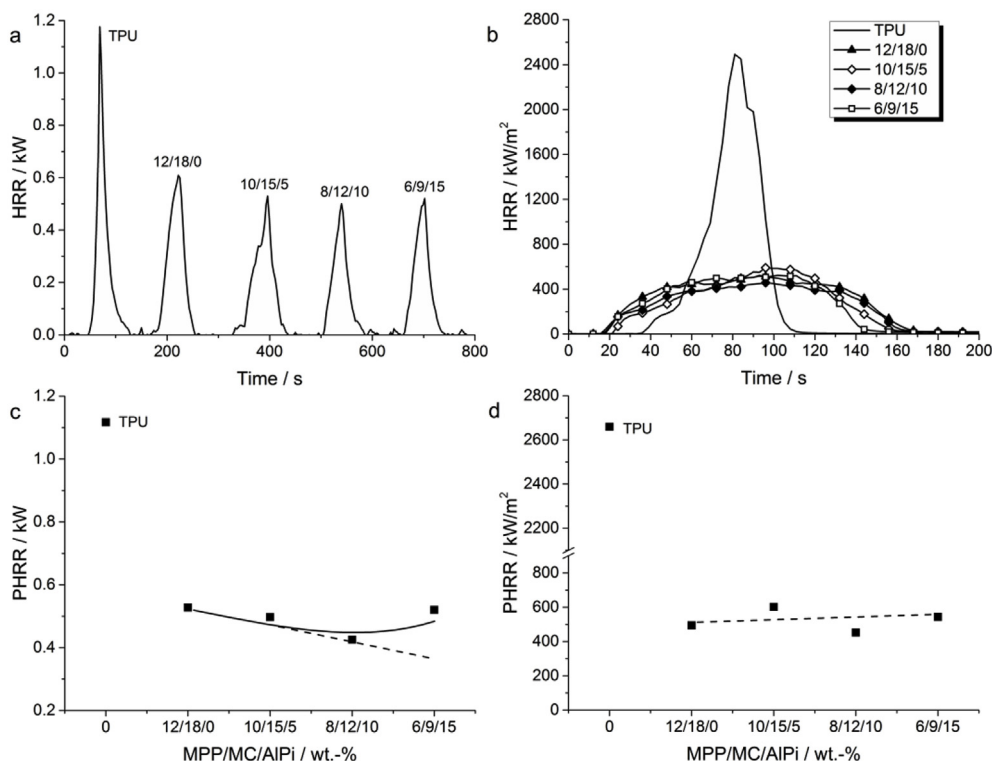


Fig. 6. HRR curves for various AlPi concentrations from rapid mass calorimeter (a) and cone calorimeter (b) together with corresponding PHRR dependency on the MPP:MC ratio (c and d, respectively).

materials can compete with the commercial flame retarded TPU type (Elastollan[®] 1185A10FHF) with respect to their mechanical properties (Elongation at break $282.3 \pm 3.4\%$ and tensile strength 21.4 ± 1.0 MPa) [15].

4.2. Influence of AlPi concentration

Based on the conclusions made on the relationship between MPP and MC, the ratio 2:3 was chosen as the optimal one. A slight surplus of melamine cyanurate provided good fuel dilution and led to reduction in the effective heat of combustion, whereas melamine polyphosphate content was still high enough to provide sufficient residue and protective layer formation. In the following section, the influence of the AlPi concentration on fire performance was investigated.

4.2.1. Fire behavior: rapid mass calorimeter and cone calorimeter

All materials were tested first in the rapid mass calorimeter to assess their performance (Fig. 6 a). A clear reduction in PHRR by almost half was observed in the 12/18/0 system compared to TPU. Replacing part of the MPP/MC mixture with AlPi led to a further decrease in PHRR. The reduction was comparable for all materials with AlPi, except for 8/12/10 where the difference in PHRR was much stronger. Additionally, a slight increase in PHRR was observed for the 6/9/15 mixture (Fig. 6 c). Two effects are behind this phenomenon. The decrease in the effectiveness of phosphorus-based flame retardants is well known [23,37], i.e. increasing P content improves performance until it approaches a limit, after which no further enhancement or even slight decay in efficiency occurs (Fig. 7a). Furthermore, reducing the amount of MPP causes the residue yield to decrease; therefore less efficient protective layer is formed. In the cone calorimeter (Fig. 7 b and d), a strong reduction in PHRR by about 85% was observed for flame retarded samples; they also burned significantly longer than TPU. The lowest PHRR was achieved for the 8/12/10 formulation, as in the rapid mass calorimeter, and leveling off occurred for 15 wt.-% AlPi as well, albeit not as pronounced as in the small-scale test.

As to the effective heat of combustion (Fig. 7 a), strong reduction is observed for 12/18/0 due to intense fuel dilution caused by the release of ammonia from MC. Addition of AlPi provides supplementary flame inhibition. With the increase of AlPi content, a distinct linear decrease was observed up to 10 wt.-%, whereas the difference between 10% and 15% was much lower, as the effectiveness of AlPi in the gas phase abates. On the other hand, the residue (Fig. 7 b) increased significantly for the 12/18/0 formulation compared to TPU, but the subsequent replacement of MPP/MC with AlPi caused a nearly linear decrease in yield, and rapid decay was observed for the 6/9/15 formulation. Hence it was concluded that addition of more than 10 wt.-% of AlPi not only does not improve effectiveness, but also causes deterioration of some other properties. All cone calorimeter parameters are presented in Table 5.

In the UL 94 test (reaction to small flame) all flame retarded materials behaved similarly. Upon the first inflammation the specimen started to melt, but often no drips were formed. As soon as the burner was removed, the specimen extinguished within seconds. After the second application of the flame, dripping was observed and the cotton ignited; therefore a V-2 classification was reached. The exception was the 10/15/5 sample, where fewer drops were observed and the cotton was not ignited, resulting in V-0 classification. One of the reasons behind this might be the synergy due to adjusted modes of action. When no AlPi is added to the mixture, no flame inhibition occurs, whereas an excess of AlPi (too little MPP/MC) reduces the condensed phase mode of action so that more flammable drops are formed.

4.2.2. Pyrolysis: mass loss and volatiles

The pyrolysis process proceeded in two main steps for all flame retarded materials (Fig. 8). The first step contains the hard segment decomposition of TPU as well as the MC decomposition as a shoulder. Similarly, as in the cone calorimeter, the addition of flame retardants led to a reduction in the temperature at which 5 wt.-% of the material was lost due to interactions within the additive-polymer matrix, but the difference was smaller (Table 6, $T_{5\%}$). The same tendency was observed

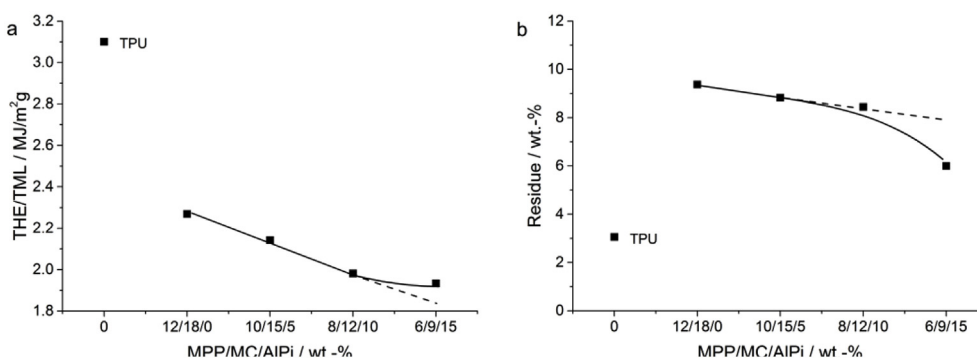


Fig. 7. The dependency of different AlPi concentrations on the/TML (a) and residue yield (b) in cone calorimeter.

Table 5

Cone calorimeter data of TPU and flame retarded TPU with increasing AlPi content. PHRR – peak heat release rate; THE – total heat evolved; THE/TML – effective heat of combustion.

Material (MPP/MC/AlPi)	PHRR kW/m ²	THE MJ/m ²	THE/TML MJ/m ² g	Residue wt.-%	UL 94
TPU	2660 ± 168	66 ± 1	3.1 ± 0.1	3.1 ± 0.3	V-2
12/18/0	494 ± 30	54 ± 1	2.3 ± 0.1	9.4 ± 0.6	V-2
10/15/5	601 ± 13	50 ± 2	2.1 ± 0.1	8.8 ± 0.3	V-0
8/12/10	452 ± 6	48 ± 1	2.0 ± 0.1	8.4 ± 0.1	V-2
6/9/15	543 ± 19	48 ± 1	1.9 ± 0.1	6 ± 0.3	V-2

for the first step, which was dominated by the decomposition of TPU's hard segments (T_1). In contrast, the second stage shifted towards higher temperatures with increasing AlPi content (T_2). In this phase, not only soft segments of TPU underwent pyrolysis, but also AlPi, so that the temperature difference between 12/18/0 and 6/9/15 was about 29 °C. It is worth mentioning that no separate step attributed to MC decomposition was observed besides a shoulder in the 10/15/5 sample (Fig. 8 b). As described in our previous work, adding more than 10 wt.-% MC leads to the appearance of a separate step [15]. Since no such observations were made in the presented study, it is assumed that the interactions in the condensed phase caused a different decomposition model whose steps are merging/overlapping. The residue amount was comparable for all flame retarded materials, due to the fact that AlPi has a limited contribution to residue formation in the TG.

To complete the investigation of the interactions between the additives, the gas phase was analyzed by an FTIR spectrometer coupled with TG via the transfer line. The spectra taken at the second decomposition step for each flame retarded material are presented in Fig. 9 a. The complete FTIR spectra covering all decomposition steps are presented in the supplementary data (S.2). As observed before, MPP does not contribute to the gas phase except for traces of melamine seen in the

Table 6

Thermal decomposition characteristics of flame retarded TPU with increasing AlPi content. $T_{5\%}$ – temperature at which 5 wt.-% of the material was lost; $T_{1,2,3}$ – temperature of the maximum mass loss rate at 1st, 2nd and 3rd step; $\Delta m_{1,2,3}$ – mass loss at each decomposition step. Residue was taken at 800 °C.

Material (MPP/MC/AlPi)	$T_{5\%}$ °C +/-1-2	T_1 °C	Δm_1 wt.-% +/-1	T_2 °C +/-1-4	Δm_2 wt.-% +/-1	Residue wt.-%
TPU	305	346	31	404	68	1.3 ± 0.5
12/18/0	307	340 ± 1	46	391	46	8.0 ± 0.1
10/15/5	301	339 ± 8	50	398	39	10.2 ± 0.8
8/12/10	302	330 ± 1	44	414	47	8.6 ± 0.3
6/9/15	300	330 ± 1	41	420	51	7.6 ± 0.4

12/18/0 sample. Other signals were attributed to TPU decomposition products, like CO₂, MDI and THF, and the last of these overlapped the NH₃ bands coming from MC. As the MPP/MC content decreased, the TPU products became less prominent until the THF signal disappeared nearly completely; only the ether bond at 1109 cm⁻¹ remained. On the other hand, no traces of AlPi or its volatile products were observed in the gas phase. Only in the 6/9/15 sample was a weak signal at 851 cm⁻¹ detected and attributed to the P–C bond. It was concluded that AlPi reacts significantly in the condensed phase with the polymer matrix and/or MPP/MC. This explains well why the decrease in effective heat of combustion observed in the cone calorimeter was somewhat lower than expected.

The ATR-FTIR spectra of the residues after the cone calorimeter test are shown in Fig. 9 b. For better comparison, the spectra of 12/18/0 and 10/15/5 are enhanced two times. In the formulation without AlPi (12/18/0) the residue consisted of highly crosslinked carbonaceous char rich in phosphorus, which was formed mainly by MPP (C=C_{ar} 1585 cm⁻¹, P–O–P 970 cm⁻¹, P–O–C 875 cm⁻¹). Replacing part of MPP/MC with AlPi led to a decrease in the intensity of those signals, but a new band of P=N appeared (1259 cm⁻¹), which became more

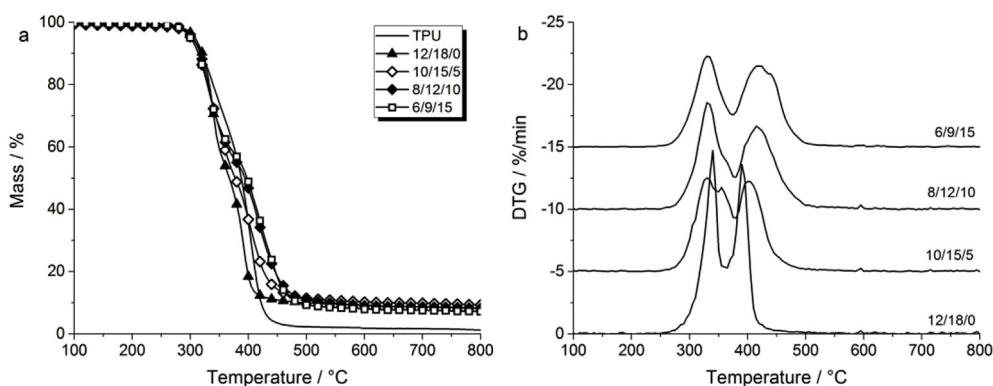


Fig. 8. Mass loss and differential thermograms of materials with variable AlPi concentrations.

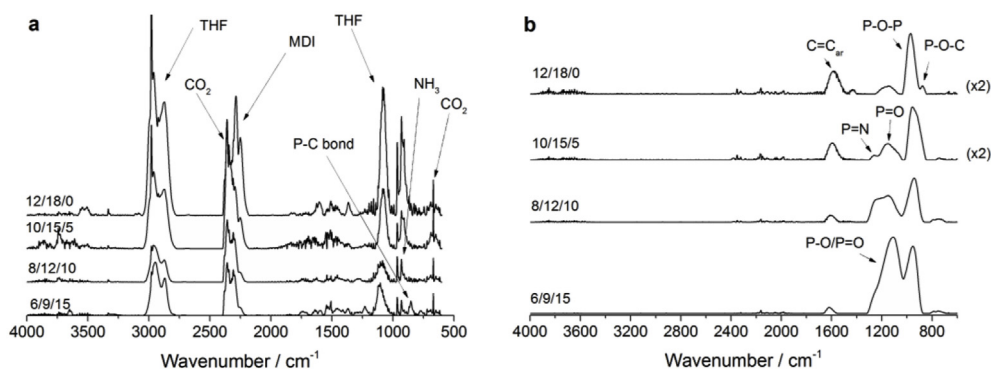


Fig. 9. Gas phase FTIR spectra taken at the second decomposition step (a) and ATR-FTIR spectra of the residues after cone calorimeter test (b).

prominent in the 8/12/10 formulation. When AlPi was the major additive (6/9/15) the spectrum was dominated by P–O/P=O bonds at 1112 cm^{-1} and 950 cm^{-1} , which were attributed to AlPi and/or its decomposition products [36]. This complements the observations from the gas phase and confirms that what takes place here is not only the typical AlPi gas phase activity, but also pronounced activity in the condensed phase influencing the chemical structure due to various interactions with MPP and MC.

4.2.3. Mechanical testing

Table 7 shows the measured elongation at break and tensile strength for all samples with an increasing percentage of AlPi at constant MPP:MC ratio of 2:3 (overall flame retardant loading: 30%). With increasing AlPi content the elongation at break rises from 312.6% up to 421.5% while the tensile strength increases from 20.0 up to 25.7 MPa. These values are at the same level as the values from the variation in MPP:MC ratio, however it seems, that a high concentration of AlPi is beneficial for the mechanical properties (Fig. 10).

5. Conclusions

A systematic series of flame retarded TPU samples was investigated in terms of fire behavior and the pyrolysis process to understand the interplay between MPP, MC and AlPi in the polymer and its influence on final performance. In each material used in this work, the total amount of additives was 30 wt.-%. The study of the ratio between MPP and MC at a constant AlPi load revealed that the most benefits are obtained when the 2:3 ratio was used, i.e. in the 10/15/5 sample (MPP/MC/AlPi). In the cone calorimeter, synergistic effects were observed in PHRR and EHC as well as in residue formation, and the latter was observed in thermogravimetry as well. Moreover, nearly all flame retarded materials achieved V-0 classification in the UL 94 test. Subsequently, materials with 0, 5, 10 and 15 wt.-% AlPi at 2:3 MPP:MC ratio were investigated. The 8/12/10 formulation showed the best performance, with a reduction of PHRR from 2660 kW/m^2 (TPU) to 452 kW/m^2 and V-0 classification in UL 94 test. Above 10 wt.-% AlPi a slight leveling off was observed. The results suggest that the synergy in TPU/MPP/MC/AlPi systems occurred due to both an adjusted balance between different modes of action and optimized interactions during

Table 7

Elongation at break in % and tensile strength in MPa measured via quasi-static mechanical tests with a velocity of $v = 100\text{ mm/min}$.

Material (MPP/MC/AlPi)	Elongation at break %	Tensile strength MPa
12/18/0	312.6 ± 51.2	20.0 ± 2.7
10/15/5	380.5 ± 4.4	20.9 ± 0.4
8/12/10	401.0 ± 7.9	22.7 ± 0.5
6/9/15	421.5 ± 4.8	25.7 ± 0.6

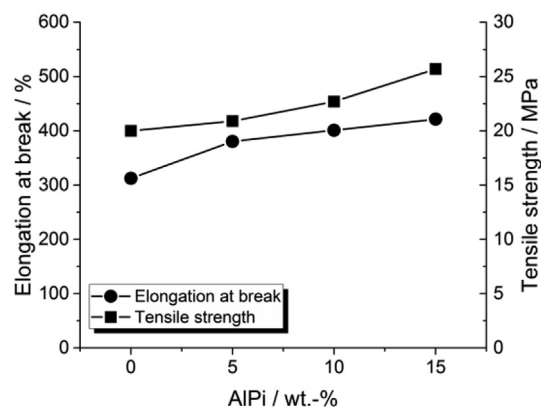


Fig. 10. Elongation at break in % (circles) and tensile strength in MPa (squares) for increasing of the AlPi content at constant MPP:MC ratio.

the pyrolysis process.

Similar as for the flame retardant performance, the mechanical properties of the formulations are influenced through the loading of the components. Combinations of MPP and MC as well as high concentration of AlPi are beneficial for the mechanical properties e.g. tensile strength and elongation at break of the formulations. Replacement of 5% MC through 5% MPP results in an increase of elongation at break from 293.7 to 373.4% and an increase in tensile strength from 16.7 to 23.2 kJ/m^2 . In addition an increase of the AlPi concentration at constant MC/MPP ratio results in further improvement of the mechanics. In any case the achieved values are superior to commercial products.

The understanding of mutual relations, interactions and synergy between different additives in a multicomponent flame retarded system is crucial for successful design of well performing polymeric materials used in various applications. This study demonstrated that both the type of the flame retardant and the ratio between the components are important and play a significant role.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to legal or ethical reasons.

Funding

The IGF-Project [19078 N/2] of the Research Association was supported by the Arbeitsgemeinschaft industrieller Forschungsvereinigungen (AiF) within the framework of the program “Förderung der Industriellen Gemeinschaftsforschung (IGF)” of the German Federal Ministry for Economic Affairs and Energy, based on a resolution by the Deutscher Bundestag.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymertesting.2019.01.001>.

References

- [1] D.K. Chattopadhyay, D.C. Webster, Thermal stability and flame retardancy of polyurethanes, *Prog. Polym. Sci.* 34 (2009) 1068–1133.
- [2] N. Grassie, G.A. Perdomo Mendoza, Thermal degradation of polyether-urethanes: 5. Polyether-urethanes prepared from methylene bis(4-phenylisocyanate) and high molecular weight poly(ethylene glycols) and the effect of ammonium polyphosphate, *Polym. Degrad. Stabil.* 11 (4) (1985) 359–379.
- [3] M. Herrera, G. Matuschek, A. Kettrup, Thermal degradation of thermoplastic polyurethane elastomers (TPU) based on MDI, *Polym. Degrad. Stabil.* 78 (2002) 323–331.
- [4] T. Engelmann, A. Luks, O. Töpfer, R. Sauerwein (Eds.), *New Aluminium Hydrates as Flame Retardant Fillers for TPU*, 61st International Wire & Cable Symposium, 2012 (Providence, RI, USA).
- [5] X. Chen, C. Ma, C. Jiao, Synergistic effects between iron-graphene and ammonium polyphosphate in flame-retardant thermoplastic polyurethane, *J. Therm. Anal. Calorim.* 126 (2016) 633–642, <https://doi.org/10.1007/s10973-016-5494-7>.
- [6] M. Lin, B. Li, Q. Li, S. Li, S. Zhang, Synergistic effect of metal oxides on the flame retardancy and thermal degradation of novel intumescent flame-retardant thermoplastic polyurethanes, *J. Appl. Polym. Sci.* 121 (2010) 1951–1960, <https://doi.org/10.1002/app.33759>.
- [7] R.E. Myers, E.D.J. Dickens, E. Licursi, R.E. Evans, Ammonium pentaborate: an intumescent flame retardant for thermoplastic polyurethanes, *J. Fire Sci.* 3 (1985) 432–449.
- [8] A.D. Naik, G. Fontaine, S. Bellayer, S. Bourbigot, Salen based Schiff bases to flame retard thermoplastic polyurethane mimicing operational strategies of thermosetting resin, *RSC Adv.* 5 (2015) 48224–48235, <https://doi.org/10.1039/C5RA06242J>.
- [9] S. Bourbigot, T. Turf, S. Bellayer, S. Duquesne, Polyhedral oligomeric silsesquioxane as flame retardant for thermoplastic polyurethane, *Polym. Degrad. Stabil.* 8 (2009) 1230–1237, <https://doi.org/10.1016/j.polymdegradstab.2009.04.016>.
- [10] A. Toldy, G. Harakály, B. Szolnoki, G. Marosi, Flame retardancy of thermoplastic polyurethanes, *Polym. Degrad. Stabil.* 97 (12) (2012) 2524–2530.
- [11] S.V. Levchik, E.D. Weil, Thermal decomposition, combustion and fire-retardancy of polyurethanes – a review of the recent literature, *Polym. Int.* 53 (2004) 1585–1610, <https://doi.org/10.1002/pi.1314>.
- [12] M.M. Velencoso, A. Battig, J.C. Markwart, B. Scharrel, F.R. Wurm, Molecular fire-fighting – how modern phosphorus chemistry can help solve the flame retardancy task, *Angew. Chem. Int. Ed.* 57 (33) (2018) 10450–10467, <https://doi.org/10.1002/anie.201711735>.
- [13] B. Scharrel, B. Perret, B. Dittrich, M. Ciesielski, J. Krämer, P. Müller, V. Altstädt, L. Zang, M. Döring, Flame retardancy of polymers: the role of specific reactions in the condensed phase, *Macromol. Mater. Eng.* 301 (2016) 9–35, <https://doi.org/10.1002/mame.201500250>.
- [14] A. Wilke, K. Langfeld, B. Ulmer, V. Andrievici, A. Hörold, A. Limbach, M. Bastian, B. Scharrel, Halogen-free multicomponent flame retardant thermoplastic styrene-ethylene-butylene-styrene elastomers based on ammonium polyphosphate-expandable graphite synergy, *Ind. Eng. Chem. Res.* 56 (29) (2017) 8251–8263, <https://doi.org/10.1021/acs.iecr.7b01177>.
- [15] A. Sut, E. Metzsch-Zilligen, M. Großhauser, R. Pfaendner, B. Scharrel, Rapid mass calorimeter as a high-throughput screening method for the development of flame-retarded TPU, *Polym. Degrad. Stab.* 156 (2018) 43–58, <https://doi.org/10.1016/j.polymdegradstab.2018.08.004>.
- [16] S. Jahromi, W. Gabrielse, A. Braam, Effect of melamine polyphosphate on thermal degradation of polyamides: a combined X-ray diffraction and solid-state NMR study, *Polymer* 44 (2003) 25–37.
- [17] P. Müller, M. Morys, A. Sut, C. Jäger, B. Illerhaus, B. Scharrel, Melamine poly(zinc phosphate) as flame retardant in epoxy resin: decomposition pathways, molecular mechanisms and morphology of fire residues, *Polym. Degrad. Stabil.* 130 (2016) 307–319, <https://doi.org/10.1016/j.polymdegradstab.2016.06.023>.
- [18] U. Braun, B. Scharrel, Flame retardancy mechanisms of aluminium phosphinate in combination with melamine cyanurate in glass-fibre-reinforced poly(1,4-butylene terephthalate), *Macromol. Mater. Eng.* 293 (2008) 206–217.
- [19] U. Braun, H. Bahr, H. Sturm, B. Scharrel, Flame retardancy mechanisms of metal phosphinates and metal phosphinates in combination with melamine cyanurate in glass-fiber reinforced poly(1,4-butylene terephthalate): the influence of metal cation, *Polym. Adv. Technol.* 19 (2008) 680–692.
- [20] S.V. Levchik, A.I. Balabanovich, G.F. Levchik, L. Costa, Effect of melamine and its salts on combustion and thermal decomposition of polyamide 6, *Fire Mater.* 21 (1997) 75–83.
- [21] D. Tabuani, F. Bellucci, A. Terenzi, G. Camino, Flame retarded Thermoplastic Polyurethane (TPU) for cable jacketing application, *Polym. Degrad. Stabil.* 97 (2012) 2594–2601.
- [22] Y. Eckstein, L.E. Hewitt, B.B. Fudala, Flame Retardant Thermoplastic Polyurethane Containing Melamine Cyanurate, (2003) WO 2003/066723.
- [23] S. Brehme, T. Köppl, B. Scharrel, V. Altstädt, Competition in aluminium phosphinate-based halogen-free flame retardancy of poly(butylene terephthalate) and its glass-fibre composites, *E-Polymers* 14 (3) (2014) 193–208.
- [24] S. Brehme, B. Scharrel, J. Goebels, O. Fischer, D. Pospiech, Y. Bykov, M. Döring, Phosphorus polyester versus aluminium phosphinate in poly(butylene terephthalate) (PBT): flame retardancy performance and mechanisms, *Polym. Degrad. Stabil.* 96 (2011) 875–884.
- [25] E.D. Weil, S.V. Levchik, *Flame Retardants for Plastics and Textiles*, second ed., Hanser, Munich, 2016.
- [26] U. Braun, B. Scharrel, M.A. Fichera, C. Jäger, Flame retardancy mechanisms of aluminium phosphinate in combination with melamine polyphosphate and zinc borate in glass-fibre reinforced polyamide 6,6, *Polym. Degrad. Stabil.* 92 (2007) 1528–1545.
- [27] M. Klatt, B. Leutner, M. Nam, H. Fisch, WO 99/57187; 1999.
- [28] S. Constanzi, M. Leonardi, WO 2005/121232; 2005.
- [29] K. Langfeld, A. Wilke, A. Sut, S. Greiser, B. Ulmer, V. Andrievici, P. Limbach, M. Bastian, B. Scharrel, Halogen-free fire retardant styrene-ethylene-butylene-styrene-based thermoplastic elastomers using synergistic aluminium diethylphosphinate-based combinations, *J. Fire Sci.* 33 (2015) 157–177.
- [30] E. Jenewein, H.-J. Kleiner, W. Wanzke, W. Budzinsky, WO 97/39053; 1997.
- [31] S. Rabe, B. Scharrel, The rapid mass calorimeter: understanding reduced-scale fire test results, *Polym. Test.* 57 (2017) 165–174, <https://doi.org/10.1016/j.polymertesting.2016.11.027>.
- [32] S. Rabe, B. Scharrel, The rapid mass calorimeter: a route to high throughput fire testing, *Fire Mater.* 41 (2017) 834–847, <https://doi.org/10.1002/fam.2420>.
- [33] B. Scharrel, M. Bartholmai, U. Knoll, Some comments on the use of cone calorimeter data, *Polym. Degrad. Stabil.* 88 (2005) 540–547.
- [34] B. Scharrel, T.R. Hull, Development of fire-retarded materials – interpretation of cone calorimeter data, *Fire Mater.* 31 (2007) 327–354.
- [35] B. Stuart, *Infrared Spectroscopy: Fundamentals and Applications*, Analytical Techniques in the Sciences, John Wiley & Sons, Ltd., Chichester, 2004.
- [36] L.C. Thomas, *Interpretation of the Infrared Spectra of Organophosphorus Compounds*, Heyden & Son Ltd., London, 1974.
- [37] S. Rabe, Y. Chuenban, B. Scharrel, Exploring the modes of action of phosphorus-based flame retardants in polymeric systems, *Materials* 10 (2017) 455.