Fire retardancy effect of aluminium phosphinate and melamine polyphosphate in glass fibre reinforced polyamide 6

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(Received 07 April, 2009; published: 03 April, 2010)

Abstract: The fire retardancy mechanism of aluminium diethyl phosphinate (AlPi) and AlPi in combination with melamine polyphosphate (MPP) was investigated in glass-fibre reinforced polyamide 6 (PA6/GF) by analysing the pyrolysis, flammability and fire behaviour. AlPi in PA6/GF-AlPi partly vaporises as AlPi and partly decomposes to volatile diethylphosphinic acid (subsequently called phosphinic acid) and aluminium phosphate residue. In fire a predominant gas-phase action was observed, but the material did not reach a V-0 classification for the moderate additive content used. For the combination of both AlPi and MPP in PA6/GF-AlPi-MPP a synergistic effect occurred, because of the reaction of MPP with AlPi. Aluminium phosphate is formed in the residue and melamine and phosphinic acid are released in the gas phase. The aluminium phosphate acts as a barrier for fuel and heat transport, whereas the melamine release results in fuel dilution and the phosphinic acid formation in flame inhibition. The higher amount of aluminium phosphate in PA6/GF-AlPi-MPP stabilised the residue in flammability tests in comparison to PA6/GF-AlPi, so that this material achieved a V-0 classification in the UL 94 test.

Introduction

Polyamide 6 (PA6) is an important engineering polymer for electrical and electronic applications and thus fire retardancy is needed [1, 2]. PA6 decomposes to volatile fuel and forms no residue. It is sensitive to loss of performance caused by additives. Compared to commodity plastics, PA6 is a moderately burning polymer; it possesses a V-2 classification in UL 94 tests. This is due to its low melt viscosity and therefore, in terms of its reaction to a small ignition source, improved melt flow and dripping behaviour. Because of hindered melt flow and probably wick effects, the glass-fibre (GF) reinforcement downgrades the flammability of PA6 to a HB classification. A halogen-free V-0 modification of PA6/GF is of great interest.

The action of flame retardants containing phosphorus has been well established and is based mainly on two different effects. The phosphorus acts in either the gas phase through flame inhibition, or the solid phase, through carbon char initiation and barrier formation [3-8]. The activity of phosphorus depends on its embedding in the flame retardant additive (i.e. oxidation state, chemical structure), the interaction with the polymer matrix (i.e. presence of heteroatoms) and the interaction with further additives (i.e. melamine, borates, metal salts).

For PA6, established solutions are observed for red phosphorus (~5-10 wt.-%) [9, 10] or various polyphosphates (~ 30 wt.-%) [11, 12, 13]. For these flame retardants

improvements were achieved in combination with different metal ions. The phosphorus acts mainly in the condensed phase, with metal ions enhancing the carbonaceous char formation of the polymer or stabilizing the resulting residue by formation of inorganic salts. Various kinds of organo-phosphorus additives in polyamides also provide fire retardance effects, such as phosphorus oxynitride [14], cyclic phosphonates or aryl phosphates [15].

Aluminium diethylphosphinate (AlPi) belongs to a new group of halogen-free fire retardants. Alone or in combination with melamine cyanurate it is very effective in glass-fibre reinforced poly(butylene terephthalate) (PBT) [16-18]. For these materials the fire retardancy effect is based on flame inhibition through the release of phosphorus species in the gas phase and the formation of both an aluminium phosphate and a carbonaceous char in residue. In glass-fibre reinforced polyamide 66 (PA66/GF) AlPi achieved acceptable fire retardancy action only in combination with melamine polyphosphate (MPP) [19]. This is caused by the formation of a very effective barrier of aluminium phosphate through interaction of the additives. In PA66/GF-AlPi-MPP the flame inhibition through release of phosphorus species is reported to play a role of minor importance [19].

In this work the fire retardancy mechanism of AlPi was investigated alone and in combination with MPP in PA6/GF. The decomposition in inert atmosphere (TG, TG-FTIR, TG-MS) and fire behaviour in different fire scenarios (Cone Calorimeter, UL 94, OI) were analysed. On the basis of the results a decomposition model is postulated. This decomposition model is crucial to understand the fire retardancy action of the AlPi.

Results and discussion

Mass Loss and Residue

PA6/GF decomposed in a single step between 600 and 700 K with a maximum of weight loss at 727 K (Table 1, Figure 1). A residue of 32 wt.-% remained, which represents the glass-fibre content in the sample. When MPP was added in PA6/GF-MPP, the maximum of main weight loss was shifted to lower temperatures at 655 K and a second mass loss step was created at 705 K. A residue of 35 wt.-% remained for this material. The decomposition behaviour of PA6/GF-MPP corresponds well to results described in the literature for PA6 with polyphosphate compounds [11-13].

The addition of AlPi shifted the maximum of decomposition rate for PA6/GF-AlPi to temperatures about 25 K lower than for PA6/GF; however the onset temperature was not affected. A residue of 34 wt.-% remained in residue. For PA6/GF-MPP-AlPi two decomposition steps were observed. Whereas the decomposition temperature of the main decomposition step (720 K) almost matched the decomposition temperature of PA6 in PA6/GF, the preceding, first decomposition step (603 K) did not correspond to any decomposition temperatures of the other materials. A residue of 37 wt.-% remained.

The additional preceding decomposition step and the increase in residue also have been reported for PA66 in the literature [19], when AlPi and MPP are added to PA66/GF-AlPi-MPP.

For further characterisation of decomposition processes, the decomposition kinetics was determined (Figure 2). The decomposition of PA6/GF was characterized by slightly increasing activation energy during the complete conversion (165 kJ mol^{-1} -

190 kJ mol⁻¹). PA6/GF-MPP showed a similar behaviour during the first 80% of conversion, but then the activation energy increased to a value clearly above 250 kJ mol⁻¹.

Fig. 1. Mass (a) and mass loss rate (b) of PA6/GF materials, heating rate 10 K min⁻¹ (PA6/GF = solid line, PA6/GF-MPP = open circles, PA6/GF-AIPi = open triangles, PA6/GF-AIPi-MPP = massive squares).

Tab. 1. Mass loss (ML) and maximum mass loss rate temperatures ($T_{\max}$) of all materials.

PA6/GF +	-	MPP	AIPi	AIPi-MPP	Error
Preceding Mass Loss Step					
$T_{\max}$ / K				603	± 2
ML / wt.-%				13.0	± 1
Main Mass Loss Step					
$T_{2\text{wt.}\% \text{ main step}}$ / K	650	604	648	652	± 2
$T_{\max}$ / K	727	655	701	719	± 2
ML / wt.-%	68.3	55.9	66.9	49.4	± 1
Subsequent Mass Loss Step					
$T_{\max}$ / K		700			± 5
ML / wt.-%		9.0			± 2
Residue at 1175 K					
Mass / wt.-%	32.1	33.6	35.1	36.7	± 1.5

The two activation energies of PA6/GF-MPP correspond to the two decomposition steps in TG experiments. The decomposition between 600 and 680 K corresponds with the activation energy of ~ 180 kJ mol⁻¹; the decomposition step between 680 and 750 K with an activation energy > 250 kJ mol⁻¹. In literature on PA6 a similar activation energy pattern versus conversion from 160-180 kJ mol⁻¹ has been reported [11], whereas the presence of melamine polyphosphate decreased the activation energy by about 30-50 kJ mol⁻¹. Activation energies around 200 kJ mol⁻¹ are typical for “simple” polymer decomposition.

Fig. 2. Determination of decomposition activation energy for PA6/GF materials (PA6/GF = solid line, PA6/GF-MPP = open circles, PA6/GF-AIPi = open triangles, PA6/GF-AIPi-MPP = massive squares).

The process of decomposition can be described as single bond scission and subsequent proton or electron transfer. Values above 250 kJ mol^{-1} indicate more “complex” decomposition pathways, which happen especially at later stages of decomposition. These decomposition processes can be described as scission of several bonds and complex proton or electron transfer reaction. Typically the formation of methane and carbonaceous char (cross linking) results (disproportionation reaction) or condensation reactions take place.

When AIPi was added in PA6/GF-AIPi, the activation energy was increased by a total of about $20\text{--}30 \text{ J mol}^{-1}$ compared to PA6/GF. This increased activation energy was also observed for PA6/GF-MPP-AIPi during the main mass loss step above 20% conversion. According to the change in activation energy the process of “simple” polymer decomposition must be influenced. Constant activation energy of 155 kJ mol^{-1} occurred below 20% of conversion and is attributed to the small preceding decomposition step at around 600 K. This process is probably not linked to polymer decomposition. The increase in the activation energy of polymer decomposition through addition of AIPi was also observed for PBT materials containing AIPi [17].

Evolved gas analysis

Caprolactam, ammonia, water and carbon dioxide were identified as decomposition products of PA6/GF through evolved gas analysis using TG-FTIR and TG-MS. These decomposition products are in accordance with the literature [11, 24, 25]. The characteristic band positions and mass fragments are summarized in Table 2; Figure 3 shows characteristic infrared spectra. For the addition of MPP in PA6/GF-MPP no significant change in PA6 decomposition products occurred compared to PA6/GF but the additional release of melamine derivatives. It is known that MPP in polyamides releases melamine [11, 26]. The decomposition behaviour of MPP differs depending on the chemical environment. MPP alone decomposes mainly by ammonia release and melon formation [27], for MPP in PA66/GF a similar decomposition pathway

occurred as in PA6/GF [19] and for MPP in HIPS only the decomposition to isocyanic acid and CO₂ was observed [28].

Tab. 2. Characteristic band positions (IR) and mass fragments (MS) of evolved gases from all PA6/GF samples, the underlined band positions are used to determine product release rates.

	FTIR / cm ⁻¹	MS / g e ⁻¹
Caprolactam	2935, 2870, <u>1711</u>	26, 39, 42, 54, 67
CO ₂	<u>2360</u> , 2330, 660	44
NH ₃	<u>966</u> , 926	16, 17
H ₂ O	<u>3854</u> , (4000 -3400)	17, 18
Phosphinic acid	3652, 1272, 1240, <u>855</u> , 766	
Phosphinate	<u>1146</u> , 1085, 774	
Ethene	<u>947</u>

Fig. 3. Characteristic evolved gas spectra of PA6/GF-AIPi (a) and PA6/GF-AIPi-MPP (b) at various decomposition times.

For PA6/GF-AIPi the vaporisation of AIPi and phosphinic acid were detected during the main decomposition step (Figure 3a). During the first decomposition step PA6/GF-MPP-AIPi releases phosphinic acid and melamine derivatives (Figure 3b); no vaporisation of AIPi was observed, not even at greater decomposition times or

higher decomposition temperatures. For both materials containing AlPi the release of ethene was observed at temperatures between 740 and 800 K.

No significant differences existed between the four materials in the product release rates for caprolactam, ammonia, water and carbon dioxide.

Residue Analysis

For residues of all PA6/GF materials a continuous loss of characteristic amide (3290 , 1636 , 1535 , 1263 cm^{-1}) and hydrocarbon (2933 , 2861 , 1460 cm^{-1}) signals occurred with increasing temperature [11, 13, 24]. Weak signals around 3490 , 1720 and 1435 cm^{-1} were observed during the decomposition, which indicates infrared absorption by ammonium or carboxyl ions. At the end of the decomposition process only broad signals of glass fibres around 1400 and 920 cm^{-1} remained.

Fig. 4. Characteristic residue IR spectra of PA6/GF-AlPi (a) and PA6/GF-AlPi-MPP (b) at various decomposition steps and temperatures in comparison to PA6/GF and AlPi spectra.

When MPP was added to PA6/GF-MPP, additional signals were created during the decomposition, which are caused by the formation of phosphoric esters (1080 , 980 , 900 cm^{-1}) and polyphosphoric acid (1220 , 1080 , 970 , 900 cm^{-1}). Besides the glass-fibre signals in residue, signals of inorganic phosphates (1240 , 1000 , 900 , 750 cm^{-1}) were also detected [11, 13, 24].

The spectra of residue analysis are shown in Figure 4a for PA6/GF-AlPi and in Figure 4b for PA6/GF-AlPi-MPP. PA6/GF-AlPi lost the amide and hydrocarbon

signals; the signals of the phosphinate salt remained during the complete decomposition of polymer and vanished when the polyamide signals were already gone. In residue only the signals of glass fibres remained. In contrast PA6/GF-AlPi-MPP showed clearly reduced phosphinate signals after the preceding decomposition step of 15 wt.-%. The polyamide signals were not changed at this stage of decomposition. No signals of phosphoric esters or polyphosphoric acid like for PA6/GF-MPP occurred during the further decomposition of the material, but signals of inorganic phosphates were found around 1080 cm^{-1} . The vibration energy of 1100 cm^{-1} is characteristic for orthophosphates [16, 19]. Similar results in residue analysis were found for PA66/GF materials containing AlPi [19].

Decomposition Model

PA6 decomposed mainly by amide bond scission and formation of caprolactam. Hence no residue remained. However the polymer also decomposes in part through the release of ammonia, carbon dioxide, water and hydrocarbons. In consequence a small amount of highly cross-linked carbon-nitrogen or carbon-oxygen species remained in residue. This minor decomposition pathway will be not considered in the decomposition models for the materials containing AlPi.

Fig. 5a. Decomposition model of PA6/GF-AlPi: demonstrated gaseous (grey boxes with frame) and solid (grey boxes) decomposition products.

When MPP is added to PA6 the phosphate forms phosphoric esters with the hydrocarbons of polymer matrix. This effect is initiated by the interaction of the hard alkaline Lewis character of the phosphate and the hard acidic Lewis character of the α -carbon at the amide bond. This reaction decreases the decomposition temperature, but not the activation energy for the main decomposition process. The decomposition of phosphoric esters is characterised by high activation energy (cross-linking). Such decomposition models for polyamide and polyamide-MPP have been proposed in the literature [25].

Fig. 5b. Decomposition model of PA6/GF-AIPi-MPP: demonstrated gaseous (grey boxes with frame) and solid (grey boxes) decomposition products.

Adding AIPi to PA6/GF decreases the decomposition temperature slightly and increases the activation energy of the decomposition process. A cross-linking process as for PA6/GF-MPP can be excluded. The decomposition products of PA6 are not significantly changed compared to PA6/GF. In PA6/GF-AIPi part of the flame retardant vaporises and part interacts with the polymer through the formation of phosphinic acid. The release of ethene was observed and in addition an increased

residue amount compared to PA6/GF. The release of ethene at high temperatures is characteristic for the decomposition of AlPi at higher temperatures (disproportionation reaction) or an interaction with the polymer [16, 17]. So part of aluminium and phosphorus must remain in residue.

An interaction between PA6 and phosphinate in PA6/GF-AlPi similar to the interaction of PA6 and polyphosphate in PA6/GF-MPP does not occur, because no evidence for the formation of phosphorus esters is detected.

The proposed decomposition mechanism is shown in Figure 5a. Both decomposition pathways of AlPi occurred, the polarisation of carbonyl bonds and subsequent vaporisation of AlPi as well as the hydrogen transfer reaction from polymer and phosphinic acid release. When all of the AlPi decomposes by release of phosphinic acid and aluminium phosphate formation, the residue increases by about 3.8 wt.-%. In the experiment an increase of about 3 wt.-% (Table 3) was observed, hence the decomposition of AlPi is the major decomposition pathway as opposed to vaporisation.

When both flame retardants in PA6/GF-MPP-AlPi are combined, an additional preceding decomposition process with a lower activation energy was observed, which is caused by the reaction of the additives [19] (Figure 5b). Melamine and diethylphosphinic acid are formed and released in the gas phase. The theoretical mass loss (11.2 wt.-%) of this reaction corresponds with the experimental result (13.0 wt.-%). No vaporisation of AlPi takes place in PA6/GF-MPP-AlPi. The third diethyl phosphinate unit at the aluminium ion decomposes by interaction with the polymer and release phosphinic acid in the gas phase. The content of AlPi is slightly higher (+10%) compared to the phosphate units in MPP (hyper stoichiometric), so AlPi also decomposes in part through interaction with the polymer and the release of phosphinic acid. In contrast to PA6/GF-AlPi for PA6/GF-AlPi-MPP, this reaction is of minor importance. Aluminium phosphate remains in residue. The theoretical residue (34.2 wt.-%) is similar to the residue of the experiment (36.7 wt.-%).

Flammability

The flammability (reaction to a small flame) is summarized for all PA6/GF materials in Table 3. PA6/GF and PA6/GF-MPP achieved a HB classification in UL 94 test and both materials showed similar OI values of 23%. The results correspond to data in the literature. For PA6/GF a HB classification and an OI of < 22% is well known [2]. Less than 20 wt.-% MPP in polyamides gives no significant improvement of flammability (UL 94), however above 30 wt.-% V-0 classifications were achieved and OI > 30% [1, 2, 11]. The presence of glass fibres decreases the fire retardancy effect [29]. In contrast to melamine cyanurate, the MPP in PA6 does not influence the melt viscosity; it acts through char and barrier formation [11].

For both materials containing AlPi the OI is crucially increased; by about 12% for PA6/GF-AlPi and about 10% for PA6/GF-AlPi-MPP, approaching values > 32%. PA6/GF-AlPi-MPP achieves a V-0 classification, but PA6/GF-AlPi fails the vertical UL 94 tests. Indeed, the material with the highest OI (34.8%) fails, whereas the combination of AlPi-MPP (32.9%) obtains a V-0 classification. Thus OI and UL 94 performance do not correlate with each other. However, the test result of PA6/GF-AlPi is quite close to a vertical classification, because no burning rate in horizontal test was observable. In the literature on PA66/GF materials containing AlPi similar

results in flammability have been observed [19] indicating that several flame retardancy mechanisms are active and compete with each other. Analogous to PA66/GF-AIPi-MPP, different char properties such as the improved mechanical stability are proposed as a reason for PA6/GF-AIPi-MPP performing better than PA6/GF-AIPi.

Tab. 3. Flammability for all PA6/GF materials.

PA6/GF +	-	MPP	AIPi	AIPi-MPP	Error
UL 94	HB	HB	HB	V-0	
Burning rate/ mm min^{-1}	16	23	0	-	± 3
OI / %	22.8	22.6	34.8	32.9	± 1

Heat Release and Mass Loss

All materials burned with good reproducibility and left a residue. The residue consisted of the glass-fibre pad and - depending on the material - more or less carbon char in between. All residues showed slight intumescence behaviour, the residues of PA6/GF-MPP and PA6/GF-AIPi were slightly delaminated.

Fig. 6. HRR and THR for all materials using an irradiation of 50 kW m^{-2} .

Figure 6 shows examples of the HRR and THR; in Table 4 the characteristics of all experiments are summarized. The HRR of PA6/GF showed the characteristic behaviour of a material containing GF: the strong peak HRR after ignition were observed and the drop in the HRR curve when the visible pyrolysis zone passed into

the remaining glass-fibre pad, accompanied by a subsequent HRR plateau-like behaviour. A residue of 32 wt.-% remained, which is reasonably attributed to the glass-fibre content. The heat of combustion of the volatiles for PA6/GF of 27.5 kJ g⁻¹ agrees with results reported in the literature [30].

When MPP was added to PA6/GF-MPP, the peak HRR decreased by about 55 kW m⁻² compared to PA6/GF, whereas no change in the subsequent plateau HRR was observed. The THR and residue formation of PA6/GF-MPP was not affected. The THR/TML was reduced by about 0.2 kJ g⁻¹m⁻², which is higher than the fuel dilution impact expected for MPP decomposition releasing incombustible volatiles.

When AlPi was added in PA6/GF-AlPi, the peak HRR decreased by about 150 kW m⁻² compared to PA6/GF and the subsequent plateau HRR was reduced. The THR was decreased by about 10 MJ m⁻² and residue was increased by about 2 wt.-%. The THR/TML was reduced by about 0.3 kJ g⁻¹m⁻². Flame inhibition occurred due to the release of phosphorus species in the gas phase.

Tab. 4. Cone calorimeter results (error based on the maximum derivation of averaged value).

PA6/GF +	-	MPP	AlPi	AlPi-MPP	Error
Peak HRR / kW m ⁻²	478	423	326	230	10
THR / MJ m ⁻²	118	114	105	98	3
Residue / wt.-%	33.1	32.7	34.8	38.8	1.0
THR TML ⁻¹ / MJ m ⁻² g ⁻¹	2.75	2.55	2.42	2.33	0.05

The combination of MPP and AlPi in PA6/GF-MPP-AlPi reduced the peak HRR by about 250 kW m⁻², the THR by about 20 MJ m⁻² and THR/TML by about 0.4 J m⁻² g⁻¹ compared to PA6/GF. The residue increased by about 6 wt.-%. Thus the results clearly show that the combination of both additives results in greater flame retardancy than expected from a simple superposition of both additive effects. Using MPP and AlPi in PA6/GF-MPP-AlPi shows a synergy with respect to HRR and THR. The observed aluminium phosphate formation in pyrolysis experiments is proposed to improve the fire behaviour through an optimised barrier effect, whereas the melamine decomposition still results in fuel dilution and phosphinic acid release in flame inhibition. The additional benefit observed in the amount and chemical structure of organic-inorganic residue for PA6/GF-AlPi-MPP correlates with the V-0 UL 94 test performance.

Conclusions

The pyrolysis and fire behaviour of PA6/GF containing AlPi, MPP and AlPi + MPP were studied in order to investigate the fire retardancy mechanisms in these glass-fibre reinforced materials. Models for the main decomposition pathways are proposed based on a comprehensive characterization of thermal behaviour and the volatile and non-volatile decomposition products (TG-FTIR, FTIR-ATR). The flammability of the materials was investigated using OI and UL 94, and the fire behaviour for forced-flaming conditions using a cone calorimeter at an irradiation of 50 kW m⁻². The flame retardancy mechanisms were discussed for the gas and condensed phases.

The phosphorus in PA6/GF-MPP, through formation of phosphate esters, initiates the decomposition of the polymer matrix and remains in residue. Due to the low additive content the material showed only a small fire retardancy action.

The AlPi in PA6/GF-AlPi partly vaporises as AlPi and partly decomposes to volatile phosphinic acid and aluminium phosphate residue. In fire a major gas-phase action was observed. In flammability test an OI value of ~35% was achieved, but only HB classification in UL 94 tests.

AlPi and MPP in PA6/GF react with each other and release melamine and phosphinic acid in the gas phase. In the residue aluminium phosphate is formed. In fire a very good aluminium phosphate barrier was observed and a gas phase action, comprising the fuel dilution effect of melamine and flame inhibition effect of phosphinic acid. The reaction product of the additives in residue stabilised the carbonaceous residue better than the aluminium phosphate formed by AlPi alone. As a consequence the materials achieve a V-0 classification and an OI of 33%.

Experimental part

Materials

Four different materials based on PA6 including 30 wt.-% glass fibres (PA6/GF) were investigated: PA6/GF, PA6/GF-AlPi, PA6/GF-MPP and PA6/GF-AlPi-MPP. The chemical structures of the additives are shown in Figure 7.

Fig. 7. Chemical structure of additives used.

A total flame retardant loading of 18 wt.-% was used in PA6/GF-AlPi-MPP, with AlPi as major component and MPP as synergist. The amount of AlPi and MPP was the same as used in PA6/GF-AlPi and PA6/GF-MPP, respectively. The samples were provided by Clariant Produkte (Deutschland) GmbH (Germany) as granulate, sticks for the UL 94 and OI tests, as well as plates for cone calorimeter investigations.

Pyrolysis Behaviour

Thermogravimetry (TG) experiments were performed using TGA/SDTA 851 (Mettler Toledo, Germany), applying a nitrogen flow of 30 ml/min. The samples for TG-FTIR measurements (about 15 mg) were heated in alumina pans from room temperature up to 1200 K at heating rates of 10 K min⁻¹; for evaluating the kinetics (about 10 mg), at heating rates of 1, 2, 5 and 10 K min⁻¹. The apparatus-specific deviations (buoyant force) were estimated by blank measurements and all results were corrected by these measurements. The kinetics was determined by software of Netzsch, using the Ozawa Flynn method. The TG was coupled with a Fourier transform infrared spectrometer (FTIR) Nexus 470 (Nicolet Instruments, Germany) using a transfer line (heated to 525 K) with an inner diameter of 1 mm and a length of 1500 mm. The FTIR gas analysis cell was heated to 515 K. The infrared spectrometer equipped with

a DTGS KBr detector operated with an optical resolution of 4 cm^{-1} , using 16 scans for a spectrum. The product identification was performed using characteristic spectra by means of characteristic peak positions indicating chemical compounds and reference spectra taken from databases. Product release rates were evaluated using the height of product specific peaks versus time.

The IR investigations of solid residues were done using attenuated total reflection (ATR, Smart Orbit Accessory) in a Nicolet 6700 FT-IR spectrometer (Thermo Scientific) with a DTGS KBr detector. The residues were collected by TG experiments, 32 scans were taken for a spectrum and an optical resolution of 4 cm^{-1} was used.

The TG-MS system consisted of a TG/DTA 220 (Seiko, Germany) coupled with a QMG 421C quadruple mass spectrometer (Balzer, Liechtenstein) [20, 21]. The TG experiments were performed in nitrogen air flow of 200 ml min^{-1} . The samples (about 5 mg) were heated in alumina pans from ambient temperature up to 1200 K at a heating rate of 10 K min^{-1} . The online coupling was done using a quartz capillary (heated at 423 K, diameter of 100 μm). In practice, the capillary restricts the detectable masses to $< 120\text{ m/e}$.

Fire Behaviour

The flammability (reaction to a small flame) of the materials was tested according to IEC 60695-11-10 respectively to UL 94 and the oxygen index (OI) according to ISO 4589. Specimens with a size of $12.5 \times 3 \times 125\text{ mm}^3$ were used for both tests. Hence, the geometry of the sticks was not the common specimen size for OI measurements; however, this dimension ensures accurate OI results [22].

Fire behaviour was characterized by a cone calorimeter (Fire Testing Technology, UK) according to ISO 5660. The method enables investigation of the heat release rate (HRR), mass loss rate (MLR) and carbon monoxide production rate. The integration of HRR determines the total heat release (THR) and the integration of MLR leads to the total mass loss (TML). An external heat flux of 50 kW/m^2 was applied. All measurements were done in duplicate. The volatile products were ignited by spark ignition. All samples (specimen size: $100\text{ mm} \times 100\text{ mm} \times 5\text{ mm}$) were measured in a horizontal position using an open aluminium tray. The experiment was stopped when flames were extinguished and no further significant mass loss was observed. The minimum in CO production against the end of fire was defined as flame-out, to separate the afterglow from the combustion process [23].

Acknowledgements

The authors thank E. Dümichen (BAM), the German Research Foundation (DFG) (BR 3376/1-1) and Clariant Produkte (Deutschland) GmbH, especially W. Krause, H. Bauer and S. Hörold, for their support.

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