Melamine poly(metal phosphates) as flame retardant in epoxy resin: Performance, modes of action, and synergy

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ABSTRACT: Melamine poly(metal phosphates) (MPMeP) are halogen-free flame retardants commercialized under the brand name Safire. Melamine poly(aluminum phosphate) (MPAlP), melamine poly(zinc phosphate) (MPZnP), and melamine poly(magnesium phosphate) (MPMgP) were compared in an epoxy resin (EP). The thermal decomposition, flammability, burning behavior, and glass transition temperature were investigated using thermogravimetric analysis, pyrolysis combustion flow calorimeter, UL 94 testing, cone calorimeter, and differential scanning calorimetry. While the materials exhibited similarities in their pyrolysis, EP + MPZnP and EP + MPMgP showed better fire behavior than EP + MPAlP due to superior protective properties of the fire residues. Maintaining the 20 wt % loading, MPZnP was combined with various other flame retardants. A synergistic effect was evident for melamine polyphosphate (MPP), boehmite, and a derivative of 6H-Dibenzo[c,e][1,2]oxaphosphinine-6-oxide. The best overall performance was observed for EP + (MPZnP + MPP) because of the best protection effectiveness of the fire residue. EP + (MPZnP + MPP) achieved V1/V0 in UL 94, and an 80% reduction in the peak heat release rate. This study evaluates the efficiency of MPMeP in EP, alone and in combination with other flame retardants. MPMeP is a suitable flame retardant for epoxy resin, depending on its kind and synergists. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43549.

INTRODUCTION

Epoxy resins and their fiber reinforced composites have become an important material in lightweight construction and for electrical and electronic equipment because of their excellent mechanical and electrical properties.[1,2] However, because they are hydrocarbon-based, epoxy resins require flame retardants for many of their typical applications. Halogenated flame retardants were widely used until recently, but have drawn criticism because of environmental concerns.[3–5] They are increasingly substituted with metal hydroxides, melamine derivatives and phosphorus-based compounds.[6–12] The main mode of action of halogenated flame retardants is flame inhibition in the gas phase; nevertheless, additional minor modes of action are often reported, such as carbonaceous charring induced in the condensed phase.[13,14] Metal hydroxides are characterized by several modes of action: fuel replacement in the condensed phase, endothermic decomposition cooling in the condensed phase, release of water diluting the fuel in the gas phase, cooling in the gas phase, and formation of a residual protective layer.[15,16] Adding melamine derivatives can produce increased char yield and a residual protection layer, and dilute the fuel in the gas phase.[17,18] Finally, phosphorous flame retardants are known to

harbor the ability to exhibit different modes of action: inducing carbonaceous charring in the condensed phase, the formation of efficient intumescent protection layers and glassy coatings, and flame inhibition.[19,20] Currently many phosphorous flame retardants are reported to show various modes of action depending on the polymer matrix and additional additives.[20–22]

One of the most effective and versatile halogen-free alternatives is melamine polyphosphate (MPP). It combines the benefits of phosphorus-based and melamine-based additives and often shows synergy with other flame retardants in epoxy resins and other polymeric materials.[23–28] An "enhanced version" of MPP, melamine poly(metal phosphate) (MPMeP), was recently developed and commercialized under the brand name Safire.[29,30] The performance of MPMeP as a flame retardant in polyamide was investigated by Bourbigot et al. with promising results.[31,32] This study intends to evaluate MPMeP as a flame retardant for epoxy resin, focusing on performance, modes of action, and synergy.

For this purpose, three different kinds of MPMeP, melamine poly(aluminum phosphate) (MPAlP), melamine poly(zinc phosphate) (MPZnP), and melamine poly(magnesium phosphate) (MPMgP), were incorporated into a common two-component epoxy resin system (EP), bisphenol A diglycidyl ether (DGEBA)

Table I. Chemical Structure and Appearance for MPAlP, MPZnP, MPMgP, MPP, AlPi-Et, DOPAc-Bu, AlO(OH), and SiO_2

Material	Chemical structure	Appearance
MPAlP	Polymeric salt	White powder, micron-sized
MPZnP	Polymeric salt	White powder, micron-sized
MPMgP	Polymeric salt	White powder, micron-sized
MPP	Polymeric salt	White powder, micron-sized
AlPi-Et	Low molecular weight Salt-like compound	White powder, micron-sized
DOPAc-Bu	Low molecular weight Organic compound	Yellow liquid
AlO(OH)	Mineral	White powder, micron-sized
SiO_2	Mineral	Light gray powder, sub-micron-sized (medium particle size 150 nm)

cured with isophorone diamine (IPDA). The resulting thermosets were investigated with regard to their thermal decomposition, flammability (reaction to small flame), burning behavior, and glass transition temperature, using thermogravimetric analysis (TGA), pyrolysis combustion flow calorimeter (PCFC),[33,34] UL 94 testing, cone calorimeter,[35–37] and differential scanning calorimetry (DSC). To search for and evaluate synergistic combinations, MPZnP was incorporated in combination with various other flame retardants at ratios of 1:1 and 1:2, and the resulting materials investigated in the same manner. MPP, diethyl aluminum phosphinate (AlPi-Et),[38] 6H-dibenz[c,e][1,2] oxaphosphorin-6-propanoic acid, butyl ester, 6-oxide (DOPAc-Bu),[39] boehmite (AlO(OH)), and an amorphous spherical silicon dioxide (SiO_2)[40,41] were chosen as possible synergists. For comparison, materials containing only one of the latter additives were also prepared, while the total load of all additives combined was 20 wt % for all materials. A synergistic effect is discussed for EP + (MPZnP + MPP), EP + (MPZnP + DOPAc-Bu), and EP + (MPZnP + AlO(OH)) as a potential explanation for the reduction in the peak heat release rate and total heat evolved in cone calorimeter tests as compared to EP.

EXPERIMENTAL

Materials

Unless stated otherwise, all raw materials were used as received. DGEBA (Araldite MY740) was purchased from Bodo Möller Chemie GmbH (Offenbach, Germany) and IPDA from Merck KGaA (Darmstadt, Germany). Table I gives an overview of the flame retardants used. MPAlP, MPZnP, and MPMgP were provided by Floridienne Chimie (Ath, Belgium). Obviously, the main difference between the three kinds of MPMeP is the kind of metal ion included. The metal ion influences the structure of MPMeP by acting as a coordination center. The structures are clearly different from MPP. Aluminum ions exhibit a threefold positive charge and prefer sixfold coordination, while magnesia and zinc ions are twofold positive and prefer fourfold coordination. Boehmite (Apyral AOH 30) was kindly donated by Nabaltec AG (Schwandorf, Germany), MPP (Melapur 200 70) by BASF SE (Ludwigshafen, Germany), AlPi-Et (Exolit OP 935) by Clariant Produkte (Deutschland) GmbH (Frankfurt am Main, Germany), amorphous silicon dioxide (Sidistar) by Elkem Silicon Materials (Oslo, Norway), and DOPAc-Bu (KCCS DOB11) by Krems Chemie Chemical Services AG (Krems, Austria).

Sample Preparation

DGEBA, IPDA, and the flame retardants were combined in a glass beaker and mixed thoroughly with a mechanical stirrer for at least 10 min. The total load of all flame retardants combined was 20 wt % in all cases (Table II). The mixture was poured into open aluminum molds with a layer height of 3 mm and put into an oven for 30 min at 80 °C, 30 min at 110 °C and 60 min at 160 °C. The materials were allowed to cool down to room temperature slowly to avoid cracking and then cut into plates of 100 mm × 100 mm (for cone calorimeter tests) or strips of 13 mm width (for UL 94 testing), respectively. Some amount of each material was also cryogenically grinded to obtain powder for TGA, DSC, and PCFC.

Measurements

DSC was performed on a DSC 204 F1 from NETZSCH (Selb, Germany). Two heating cycles ranging from 20 °C to 220 °C were applied to a sample mass of 12 ± 1 mg. For TGA, a TG 209 F1 Iris from NETZSCH (Selb, Germany) was used. A sample of 10 ± 0.1 mg was heated from 30 °C to 900 °C, applying a heating rate of 10 °C/min under nitrogen. Two measurements were performed and averaged for each material. A third sample was measured whenever the first two deviated from each other by more than 10%. UL 94 vertical and horizontal testing was performed in a burning chamber from Fire Testing Technology (FTT, East Grinstead, UK), in accordance with IEC 60695-11-10. Specimens 13 mm wide and 3 mm thick were used. For PCFC, a FAA Micro Calorimeter (FTT, East Grinstead, UK) was used, applying a heating rate of 1 °C/s from 150 °C to 750 °C to a sample weight of 5 ± 0.1 mg. Two measurements were performed and averaged for each material. A third sample was measured whenever the first two deviated from each other by more than 10%. Cone calorimeter (FTT, East Grinstead, UK) investigations were performed in accordance with ISO 5660. An irradiation of 50 kW/m² was applied with a distance between heating cone and specimen of 35 mm, taking into account the intumescence of some materials. It was pointed out in previous investigations that increasing the distance from 25 to 35 mm does not significantly alter the homogeneity of the applied heat

Table II. TGA Results

Material	$T_{5wt\%}$ (°C) ±2	PMLR (wt %/s) ±0.02	T_{PMLR} (°C) ±2	Residue (wt %) ±1.0	Cal. Residue (wt %)
MPAIP	377	0.05	389	46.0	–
MPZnP	345	0.05	393	41.9	–
MPMgP	368	0.05	385	46.8	–
MPP	383	0.08	390	27.9	–
AlPi-Et	431	0.60	477	13.2	–
DOPAc-Bu	272	0.32	363	–[a]	–
AlO(OH)	495	0.06	521	83.2	–
SiO$_2$	–	–	–	99.1	–
EP	346	0.30	373	9.5	–
EP + MPAIP	315	0.18	347	20.0	16.8
EP + MPZnP	324	0.20	357	19.4	16.0
EP + MPMgP	323	0.20	352	20.5	17.0
EP + (MPZnP + MPP 1:1)	324	0.21	350	18.7	14.6
EP + (MPZnP + AlPi-Et 1:1)	330	0.20	370	15.9	13.1
EP + (MPZnP + DOPAc-Bu 1:1)	309	0.20	362	13.9	11.8
EP + (MPZnP + AlO(OH) 1:1)	334	0.21	362	21.1	20.1
EP + (MPZnP + SiO$_2$ 1:1)	325	0.19	361	23.9	21.7
EP + (MPZnP + MPP 1:2)	322	0.20	351	18.8	14.1
EP + (MPZnP + AlPi-Et 1:2)	316	0.17	356	19.6	12.1
EP + (MPZnP + DOPAc-Bu 1:2)	304	0.20	363	11.7	10.4
EP + (MPZnP + AlO(OH) 1:2)	325	0.18	359	25.0	21.5
EP + (MPZnP + SiO$_2$ 1:2)	331	0.20	364	24.9	23.6
EP + MPP	324	0.22	349	17.6	13.2
EP + AlPi-Et	333	0.20	361	17.2	10.2
EP + DOPAc-Bu	286	0.22	347	13.7	7.6
EP + AlO(OH)	346	0.22	373	23.9	24.2
EP + SiO$_2$	342	0.20	370	28.1	27.4

Temperature of 5 wt % mass loss ($T_{5wt\%}$), peak mass loss rate (PMLR), temperature of peak mass loss rate (T_{PMLR}), residue at 900 °C and residue calculated for the superposition of the single contributions (Cal. Residue)
[a] DOPAc-Bu evaporated.

flux.[36,37] Samples were measured using a retainer frame including an additional simple thin wire cross to prevent buckling of the plates in the beginning of the test. Results were calculated for a sample surface area of 100 cm^2 despite the retainer frame, as the combustion of the specimens included the edges beneath the frame. Since some samples did not allow a distinctive point of flameout to be determined because of excessive intumescence, flameout was declared when the smoke production dropped below 0.01 m^2/s. This criterion was applied to all systems for comparability. Two measurements were performed and averaged for each material. A third specimen was measured whenever the first two deviated from each other by more than 20% in any characteristic parameter. The uncertainties in the different properties were quite different for each material. These differences were because of the large difference in heat release rates and to deformation during burning. Individual large and small uncertainties are indicated by the range between the measured values in some figures.

RESULTS AND DISCUSSION

Thermal Decomposition

The thermal decomposition of the epoxy resin materials was investigated by TGA. The results are shown in Table II. EP exhibited a fast one-step decomposition with a peak mass loss rate (PMLR) of 0.30 wt %/s at the temperature of the highest mass loss rate $T_{PMLR} = 373$ °C and a residue of less than 10 wt % (Figure 1).

For all EP + additive(s), the PMLR was significantly lowered (by 0.08–0.13 wt %/s) and the amount of residue strongly increased (by 8–19 wt %). The decomposition of EP + phosphorous flame retardant started at lower temperatures, indicating an interaction between EP and phosphorous flame retardants or their decomposition products.[42] The temperature for 5 wt % mass loss ($T_{5wt\%}$) was reduced by 0–60 °C, in most cases by around 20 °C. Likewise, T_{PMLR} was reduced slightly, by 0–26 °C. The interaction was also observed for the increase in residue.[42–44] The residues of all
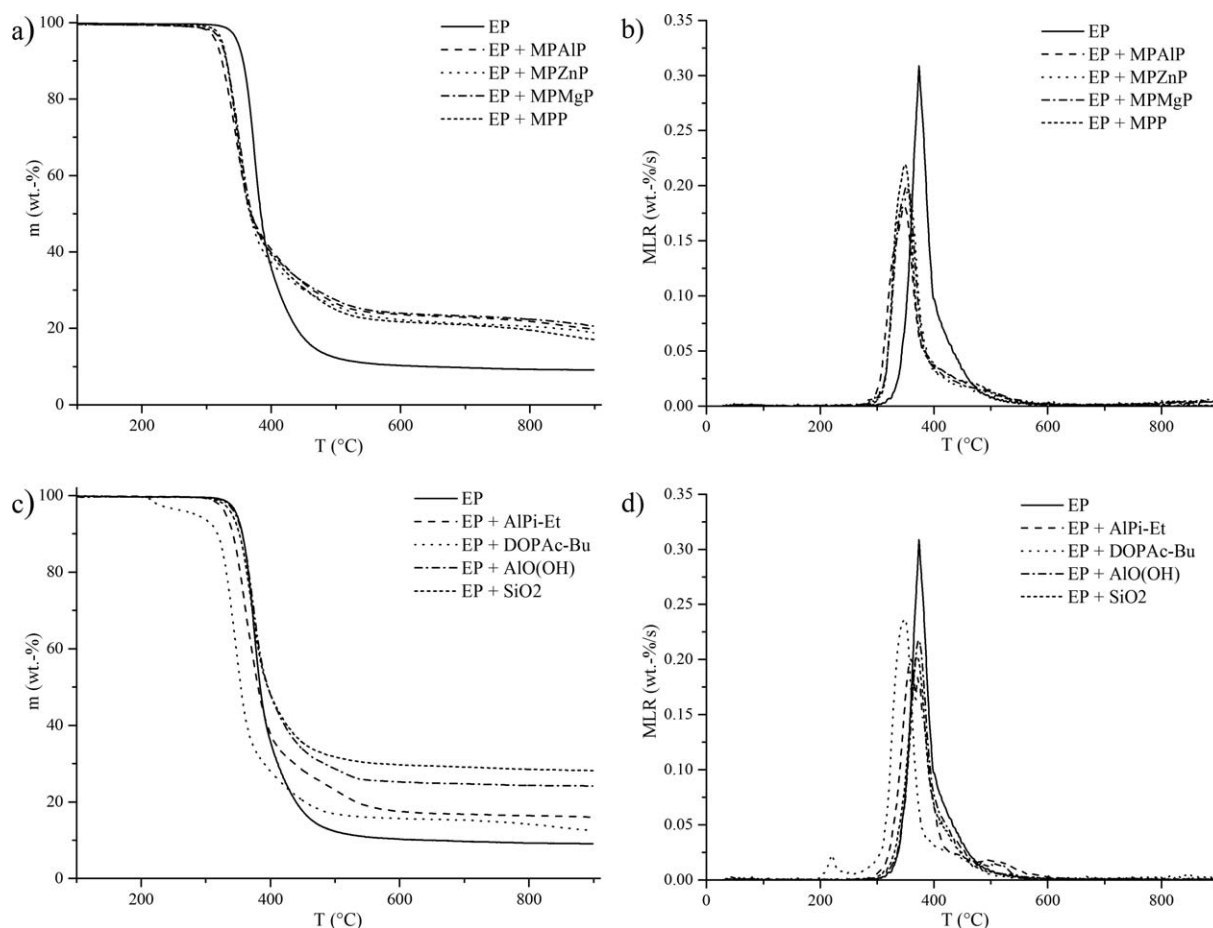
Figure 1. Thermal decomposition (a) mass and (b) mass loss rate for EP, EP + MPAlP, EP + MPZnP, EP + MPMgP, EP + MPP; thermal decomposition; (c) mass and (d) mass loss rate for EP + AlPi-Et, EP + DOPAc-Bu, EP + AlO(OH), and EP + SiO$_2$.

composites containing phosphorous flame retardants were significantly larger than the residues calculated for the superposition of the contributions of each component (Table II).

EP + MPAlP, EP + MPZnP, and EP + MPMgP all showed quite similar decomposition behavior, with a $T_{5 wt \%}$ of 315–324 °C and a PMLR of 0.18–0.20 wt %/s at 347–352 °C. This was quite similar to EP + MPP, as shown in Figure 1(a). EP + MPAlP, EP + MPZnP, EP + MPMgP, and EP + MPP exhibited a residue of roughly 20 wt %, twice the amount for EP. The lowest increase in residue, by only 2–4.5 wt % compared to EP, was observed for EP + (MPZnP + DOPAc-Bu 1:1), EP + (MPZnP + DOPAc-Bu 1:2), and EP + DOPAc-Bu. The $T_{5wt \%}$-values were lowered by 37 °C, 42 °C, and 60 °C, respectively, in accordance with higher DOPAc-Bu content. Apart from EP + DOPAc-Bu, the $T_{5wt \%}$ values of EP + (MPZnP + DOPAc-Bu) and EP + DOPAc-Bu were thus lower than for all other materials in this study. EP + DOPAc-Bu exhibited a small preliminary decomposition step at 220 °C [Figure 1(b)], losing about 3 wt %, attributed to the decomposition of DOPAc-Bu. This preliminary decomposition step did not occur for EP + (MPZnP + DOPAc-Bu), indicating an interaction between MPZnP and DOPAc-Bu during decomposition, hindering the release of mass. When aluminum diethyl phosphinate and melamine polyphosphate were combined in polyamides, instead of a reaction with the polymer

matrix a comparable reaction between the flame retardants was reported.[24,27] The T_{PMLR} was decreased by 26 °C for EP + DOPAc-Bu, but by only 10–11 °C for EP + (MPZnP + DO-PAc-Bu), and yet by 16 °C for EP + MPZnP. This observation further suggests a preferential interaction between MPZnP and DOPAc-Bu during the decomposition of EP + (MPZnP + DOPAc-Bu).

The highest residues occurred for EP + AlO(OH), EP + (MPZnP + AlO(OH)), EP + (MPZnP + SiO$_2$) (about 25 wt %), and particularly for EP + SiO$_2$ (28 wt %). These residues were three times the amount occurring for EP, as shown in Figure 1(c). This is explained by the mineral nature and thereby predominantly inert filler character of AlO(OH) and, even more so, of SiO$_2$. AlO(OH) releases a limited amount of water at increased temperatures, leaving behind a large amount of inert Al$_2$O$_3$. SiO$_2$ is not affected at all by the temperature range applied. SiO$_2$ did not influence the thermal decomposition of the matrix material. Therefore EP + SiO$_2$, containing 20 wt % of SiO$_2$, exhibited roughly 20 wt % more residue than EP. The $T_{5wt \%}$ and T_{PMLR} values for EP + AlO(OH) and EP + SiO$_2$ were not changed compared to EP.

In summary, all additives except DOPAc-Bu roughly doubled the amount of residue, or increased it even more in the case of

Table III. PCFC Results

Material	HRC [J/(gK)] ±10	THE (kJ/g) ±0.5	T_{max} (°C) ±2	Residue (wt %) ±1
EP	498	28.9	387	6.4
EP + MPAlP	291	22.1	358	21.2
EP + MPZnP	331	22.0	361	20.4
EP + MPMgP	333	21.3	361	22.3
EP + (MPZnP + MPP 1:1)	347	21.9	357	20.4
EP + (MPZnP + AlPi-Et 1:1)	403	24.9	389	15.4
EP + (MPZnP + DOPAc-Bu 1:1)	358	24.5	366	13.8
EP + (MPZnP + AlO(OH) 1:1)	389	22.8	368	21.2
EP + (MPZnP + SiO$_2$ 1:1)	381	22.7	370	23.2
EP + (MPZnP + MPP 1:2)	337	21.9	356	19.9
EP + (MPZnP + AlPi-Et 1:2)	390	24.8	383	16.2
EP + (MPZnP + DOPAc-Bu 1:2)	379	25.7	368	11.3
EP + (MPZnP + AlO(OH) 1:2)	419	23.1	370	21.8
EP + (MPZnP + SiO$_2$ 1:2)	399	22.5	371	24.2
EP + MPP	347	21.6	354	20.5
EP + AlPi-Et	351	25.2	375	17.3
EP + DOPAc-Bu	556	24.4	359	12.3
EP + AlO(OH)	403	23.0	389	22.5
EP + SiO$_2$	399	23.4	385	24.4

heat release capacity (HRC), total heat evolved (THE), temperature for highest oxygen consumption (T_{max}) and residue.

the mineral fillers AlO(OH) and SiO$_2$, which thus appeared promising for char/residue formation. The $T_{5 wt \%}$ and T_{PMLR} were reduced least by AlO(OH) and SiO$_2$, likewise because of their mineral filler nature.

Assessing the flammability potential via PCFC

Table III summarizes the results of the PCFC investigation. EP exhibited a high heat release capacity (HRC) of 498 J/(gK), a total heat evolved (THE) of 28.9 kJ/g, and a low residue of only 6.4 wt %. For EP + additive(s), the HRC was lowered by 80–200 J/(gK) in almost all cases, with the exception of EP + DOPAc-Bu, where the HRC was increased by 58 J/(gK) compared to EP. The fact that DOPac-Bu in EP + DOPAc-Bu did not perform well in PCFC investigations was not surprising, as the TGA results had already indicated that DOPac-Bu did not induce charring in the condensed phase. Mechanisms such as flame inhibition because of the release of volatiles containing phosphorus are not detected in PCFC because of the complete combustion in the combustor.[34] Phosphorus released in the gas phase actually contributes to heat production in PCFC. The THE for EP + additive(s) was lowered in all cases (by 3.2–7.6 kJ/g), while the amount of residue was strongly increased (by 5–18 wt %). The decrease in THE is correlated with the increase in residue, since the latter indicates that the material releases less fuel for combustion. Some materials showed a notable deviation in residue from the TGA (up to 3.7 wt %), as the heating rate applied in PCFC is six times greater. The decomposition of epoxy-based materials and other polymers, e.g. polyesters and polysiloxanes, was often shown to be dependent on the heating

rate[44–50] when the dominant decomposition pathway changed as a function of the heating rate.

EP + MPAlP, EP + MPZnP, EP + MPMgP, and EP + MPP showed notably improved performance: The HRC was reduced to roughly two thirds, while the THE was decreased by about 25%. This observation is explained by increased charring in the condensed phase, which flame retardants based on phosphates and polyphosphates are known to show in epoxy resins.[44,51–57] The strong condensed phase mechanism of MPAlP, MPZnP, MPMgP, and MPP in EP is also evident from the cone calorimeter investigations in this study.

EP + AlPi-Et and EP + DOPAc-Bu performed less well, since both AlPi-Et and DOPAc-Bu are flame retardants that work primarily via flame inhibition (incomplete fuel oxidation in the gas phase caused by radical scavenging). Since the PCFC enforces the complete combustion of all fuel released, a potential flame inhibition effect is negated. The THE was reduced by 13% for EP + AlPi-Et and 16% for EP + DOPAc-Bu, while the HRC was even higher in the case of EP + DOPAc-Bu than for EP. Under different circumstances, e.g., diffusion flames, the pyrolysis products of AlPi-Et and DOPAc-Bu provide flame inhibition, as was evident from the UL 94 and cone calorimetry tests in this study. In accordance with the PCFC results on HRC and THE, the amount of residue was lowered for EP + AlPi-Et and especially for EP + DOPAc-Bu.

AlO(OH) and SiO$_2$ worked mostly as fillers, improving the performance of EP by simply replacing polymer material. For EP + AlO(OH) and EP + SiO$_2$, containing 20 wt % of AlO(OH)

Table IV. UL 94 Results

Material	UL 94	Burning rate (mm/min)
EP	HB	25 ±2
EP + MPAlP	HB	< 1
EP + MPZnP	HB	< 1
EP + MPMgP	V1	–
EP + (MPZnP + MPP 1:1)	V1	–
EP + (MPZnP + AlPi-Et 1:1)	HB	< 1
EP + (MPZnP + DOPAc-Bu 1:1)	V1	–
EP + (MPZnP + AlO(OH) 1:1)	HB	< 1
EP + (MPZnP + SiO$_2$ 1:1)	HB	< 1
EP + (MPZnP + MPP 1:2)	V0	–
EP + (MPZnP + AlPi-Et 1:2)	V1	–
EP + (MPZnP + DOPAc-Bu 1:2)	HB	< 1
EP + (MPZnP + AlO(OH) 1:2)	HB	< 1
EP + (MPZnP + SiO$_2$ 1:2)	HB	23 ±3
EP + MPP	V0	–
EP + AlPi-Et	V0	–
EP + DOPAc-Bu	HB	< 1
EP + AlO(OH)	HB	< 1
EP + SiO$_2$	HB	23 ±1

Horizontal burning rates given with standard deviation.

or SiO$_2$, respectively, the HRC and THE were reduced by roughly 20% compared to EP. The corresponding residues were increased by roughly 20%, although a bit less for EP + AlO(OH) since AlO(OH) releases water during its conversion to Al$_2$O$_3$.

EP + (MPZnP + MPP), EP + [MPZnP + AlO(OH)], and EP + (MPZnP + SiO$_2$) showed superposition of the effects of the single additives on HRC and THE over the ratio of the additives to each other. For EP + (MPZnP + AlPi-Et) and EP + (MPZnP + DOPAc-Bu), some deviations were observed: EP + (MPZnP + DOPAc-Bu) showed a lower HRC, but a higher THE, while in the case of EP + (MPZnP + AlPi-Et) both HRC and THE were higher than expected for simple superposition of the effects of each flame retardant.

In summary, AlO(OH) and SiO$_2$ acted merely as fillers in EP, while AlPi-Et and especially DOPAc-Bu were even less effective in PCFC. The overall best performance in the PCFC investigation was exhibited by EP containing MPAlP, MPMgP, MPZnP, and/or MPP, because of the significant condensed phase mechanism of these flame retardants.

Reaction to Small Flame (UL 94)
Table IV shows the results of the UL 94 investigation of the materials. EP achieved an HB rating and exhibited burning dripping, igniting the cotton. EP + MPZnP and EP + MPMgP performed better than EP + MPAlP. Although both EP + MPAlP and EP + MPZnP failed the vertical test, the former exhibited quite lively combustion while the latter burned very slowly (but longer than 30 s). EP + MPMgP obtained the V1 rating.

EP + MPP and EP + AlPi-Et showed great performance; both materials self-extinguished quickly after flame application, resulting in a clear V0 rating. EP + (MPZnP + MPP) and EP + (MPZnP + AlPi-Et) were less effective than EP + MPP and EP + AlPi-Et in the UL 94 test (Table IV). EP + (MPZnP + DOPAc-Bu 1:1) achieved a vertical rating while EP + DOPAc-Bu did not, indicating a synergistic effect between MPZnP and DOPAc-Bu. AlO(OH) and SiO$_2$ were widely ineffective because of their limited influence on the decomposition behavior of EP, which was evident from TGA and PCFC. EP + AlO(OH), EP + [MPZnP + AlO(OH)], EP + SiO$_2$ and EP + (MPZnP + SiO$_2$) did not achieve any vertical rating. EP + SiO$_2$ and EP + (MPZnP + SiO$_2$) exhibited sparkling burning and ignited the cotton.

Forced Flaming Behavior
Table V summarizes the results of the cone calorimeter investigation of the materials, while Figures 2 and 3 show the corresponding heat release rate (HRR) curves over time. EP exhibited a total heat evolved (THE) of 76 MJ/m^2 and a high peak heat release rate (PHRR) of more than 1000 kW/m^2. The HRR curves show a shoulder shortly after ignition and a pronounced PHRR at the end of the main burning at ca. 120 s, before the HRR quickly decreased, but not to 0 as a subsequent burning stage followed. Near the end of flaming combustion the HRR curve reached a second minor maximum about a third as high as the PHRR (Figure 2). This basic HRR curve pattern, consisting of two stages, with the first yielding the PHRR and the second associated with a minor maximum HRR, was characteristic for all of the specimens investigated.

For EP + additive(s), the THE and PHRR were notably reduced. The second maximum in HRR was evident for all materials with a high PHRR, because of the shorter burning times and the pronounced shape of the HRR curve. For the materials with a low PHRR, a second maximum was hardly distinguishable because of the flat HRR curve. The ignition time was decreased by 10 s up to 17 s for all of the EP containing phosphorous flame retardants, corresponding well with their earlier start of decomposition observed in TGA. The ignition time of EP + AlO(OH) was at just 5 °C earlier than for EP, and that of EP + SiO$_2$ 13 °C earlier, both suggesting that not only earlier decomposition temperature influences the time to ignition, but also changes in physical properties such as changed viscosity or heat absorption.[58,59]

EP + MPAlP showed good performance, reducing the PHRR to about 50% compared to EP. EP + MPZnP and EP + MPMgP performed even better and quite similar to each other, with a reduction in PHHR to less than 30% of EP (Table V, Figure 2). The reduction in THE, EHC, and TML was similar for all of the melamine poly(metal phosphates) investigated. Adding MPAlP, MPZnP, or MPMgP to EP produced a limited flame retardancy effect in the gas phase (ca. 8% reduction in EHC). Since neither CO nor smoke, the typical products for incomplete combustion were increased, (Table V), it was concluded that the reduction in EHC was because of fuel dilution rather than flame inhibition. Significant fuel dilution is quite typical for melamine-based flame retardants that release NH$_3$.[17,18] In

Table V. Cone Calorimeter Results

Material	t_{ig} (s) ±4	THE (MJ/m²) ±4	PHRR (kW/m²) ±3–8%	TML (wt %) ± 2	EHC (MJ/kg)	TSR (m²/m²) ±300	COY (kg/kg) ±0.003	FIGRA [kW/(m²s)]	MARHE (kW/m²)
EP	54	75.8	1068	92.1	24.4	2720	0.0620	9.2	390
EP + MPAlP	40	60.0	540	80.9	22.6	2133	0.0534	8.6	304
EP + MPZnP	43	60.0	312	78.3	22.9	1991	0.0571	5.1	191
EP + MPMgP	44	57.3	298	77.7	22.0	2012	0.0625	3.8	186
EP + (MPZnP + MPP 1:1)	38	51.1	207	69.5	22.2	1419	0.0565	3.5	136
EP + (MPZnP + AlPi-Et 1:1)	43	51.2	405	86.1	17.7	3405	0.1275	5.0	232
EP + (MPZnP + DOPAc-Bu 1:1)	42	57.6	329	86.3	19.5	2723	0.0972	4.0	194
EP + (MPZnP + AlO(OH) 1:1)	43	57.2	438	72.7[a]	22.9	2003	0.0577	5.8	246
EP + (MPZnP + SiO₂ 1:1)	37	62.4	525	77.4[a]	23.8	2206	0.0559	8.8	312
EP + (MPZnP + MPP 1:2)	41	32.5	211	[b]	[b]	844	[b]	2.9	128
EP + (MPZnP + AlPi-Et 1:2)	41	53.8	435	87.8	18.1	3267	0.1316	4.5	238
EP + (MPZnP + DOPAc-Bu 1:2)	41	52.1	412	79.7	19.2	2693	0.1019	4.3	215
EP + (MPZnP + AlO(OH) 1:2)	43	57.9	575	74.4	23.0	1963	0.0548	6.4	285
EP + (MPZnP + SiO₂ 1:2)	37	65.6	681	78.4	24.1	2312	0.0597	9.9	370
EP + MPP	38	26.6	244	[b]	[b]	608	[b]	3.0	126
EP + AlPi-Et	41	55.8	492	85.3	18.8	3273	0.1485	5.1	260
EP + DOPAc-Bu	44	50.2	624	91.5	16.8	3929	0.1261	7.0	263
EP + AlO(OH)	49	65.5	870	79.4	24.1	2173	0.0598	10.0	358
EP + SiO₂	41	57.6	907	80.0	22.8	2065	0.0544	12.6	374

Time to ignition (t_{ig}), total heat evolved (THE), peak heat release rate (PHRR), total mass loss (TML), effective heat of combustion (EHC), total smoke release (TSR), carbon monoxide yield (COY) 2 minutes after ignition, fire growth rate (FIGRA) and maximum average rate of heat emission (MARHE).
[a] Uncertainty of ± 3%.
[b] Not available because of excessive intumescence (physical contact with heating cone.)
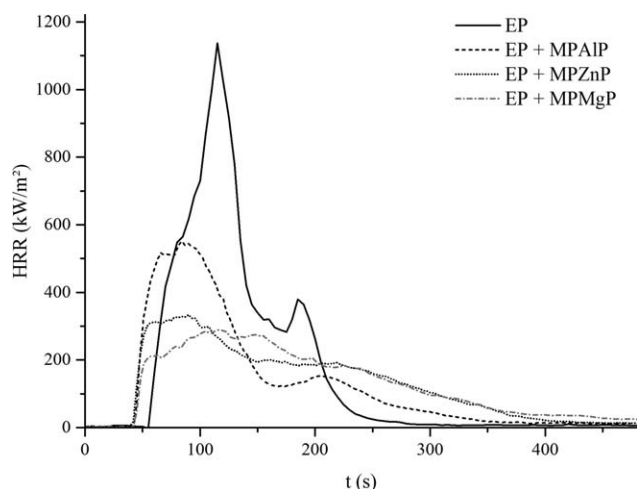
Figure 2. Heat release rate over time for EP, EP + MPAlP, EP + MPZnP, and EP + MPMgP.

the condensed phase they induce additional charring, so that the fuel release is reduced by ca. 14% compared to EP. The reduction in fuel release together with the reduction in the EHC of the fuel accounted for the reduction in THE. For all three materials EP + MPAlP, EP + MPZnP and EP + MPMgP, the THE was reduced by 21–24% because of carbonaceous charring in the condensed phase and fuel dilution in the gas phase. These modes of action, and the absence of flame inhibition, reduced the CO and smoke production at the same time. The percent reduction in PHRR was two to three times higher, indicating an additional distinctive protective effect of the fire residues with respect to the heat release rate.[60] The residual protection layer was the main mode of action with respect to PHRR, but quite different for EP + MPAlP, EP + MPZnP, and EP + MPMgP. Assuming that the same modes of action that diminish the THE diminish the PHRR analogously, the additional protective mode of action was estimated to reduce the PHRR of EP + MPAlP by 36%, of EP + MPZnP by 63%, and of EP + MPMgP by 63%. The difference in efficiency of the protection layer corresponded with the appearance of the fire residues. The fire residues of EP + MPZnP and of EP + MPMgP were very similar. They show a little bit more intumescence and a much more closed surface compared to the fire residue of EP + MPAlP. The fact that MPZnP and MPMgP exhibited very similar performance in EP, while MPAlP behaved differently, corresponds well with their different structures. Al, with its threefold positive charge, preferred sixfold coordination; whereas Zn and Mg, with their twofold positive charges preferred fourfold coordination. The MARHE values were reduced by 22% for EP + MPAlP and roughly halved for EP + MPZnP and EP + MPMgP compared to EP. Such a pronounced protective effect of the fire residue is typical for intumescent systems. Indeed, EP + MPAlP, EP + MPZnP, and EP + MPMgP all showed a moderate amount of intumescence, creating a residue a few centimeters in height (Figure 4, Table VI).

By comparison, EP + MPP showed significantly stronger intumescence, forming an excessive residue, part of which came into physical contact with the heating cone (Figure 4, Table VI).

Indeed, phosphates and especially polyphosphates are known to provide high char yield and strong intumescence in epoxy resins.[51–57] The strong intumescence of EP + MPP and EP + (MPZnP + MPP) resulted in a continuously low HRR and the lowest PHRR, MARHE, and FIGRA values of all materials in this study. Especially in the case of EP + (MPZnP + MPP), the PHRR was barely distinguishable because of the flat shape of the HRR curve [Figure 3(a)]. Likewise, the HRR of EP + MPP and EP + (MPZnP + MPP) faded much more slowly than for all other materials in this study. The mass loss and smoke production were also notably lower than for all other materials because of the strong char formation.

Various approaches have been made to quantify synergistic effects in flame retardancy.[61–66] In this work, the performance of the combinations of flame retardants in THE and PHRR was compared with the superposition of the effects expected for the single flame retardants. Since the total amount of flame retardant was always 20 wt %, our comparison considers the effects of any additional interactions or phenomena occurring when combining the two additives, as well as effects because of the nonlinear dependency of the flame retardancy on the concentration of the single additives.[61,62] The superposition was calculated based on the performance of the materials containing only one flame retardant and taking into account their fraction x when combined [eq. (1a)]. Or, in other words, a linear relationship was assumed between THE and PHRR and the ratio of the two flame retardants. The performance in cone calorimeter of the materials with the combined flame retardant approaches was compared with these calculated values (Tables VII and VIII). The percent deviation allows the proportional benefit of combining both flame retardants to be quantified. Furthermore, an index to quantify the synergistic efficiency (SE_A) was calculated according to eq. (2).[65,66] An $SE_A > 1$ indicates a synergistic effect, while an $SE_A < 1$ indicates an antagonistic effect.

$$\text{THE}^{calc}_{EP+(FR1+FR2)} = \frac{x_{FR1}}{x_{FR1}+x_{FR2}} * \text{THE}_{EP+FR1}$$
$$+ \frac{x_{FR2}}{x_{FR1}+x_{FR2}} * \text{THE}_{EP+FR2} \quad (1a)$$

$$\text{condition}: x_{FR1} + x_{FR2} = \text{const. for EP + FR1,}$$
$$\text{EP + FR2 and EP + (FR1 + FR2)} \quad (1b)$$

$$SE_A = \frac{\text{THE}_{EP} - \text{THE}_{EP+(FR1+FR2)}}{\frac{x_{FR1}}{x_{FR1}+x_{FR2}}*(\text{THE}_{EP} - \text{THE}_{EP+FR1}) + \frac{x_{FR2}}{x_{FR1}+x_{FR2}}*(\text{THE}_{EP} - \text{THE}_{EP+FR2})} \quad (2)$$

For EP + (MPZnP + MPP), the observed intumescence decreased and the THE increased compared to EP + MPP. In spite of this, the PHRR was lower than for EP + MPP and EP + MPZnP. At both mixing ratios (MPZnP:MPP = 1:1) and (MPZnP:MPP = 1:2), the PHRR was more than 20% lower than calculated for superposition assuming linear behavior with regard to the ratio (Table VIII), indicating a distinctive synergistic effect. The corresponding SE_A was relatively low (1.09/1.07), as was the change in the absolute PHRR value.

EP + AlPi-Et, EP + (MPZnP + AlPi-Et), EP + DOPAc-Bu, and EP + (MPZnP + DOPAc-Bu) exhibited an increased mass loss and likewise notably increased smoke production and CO yield.
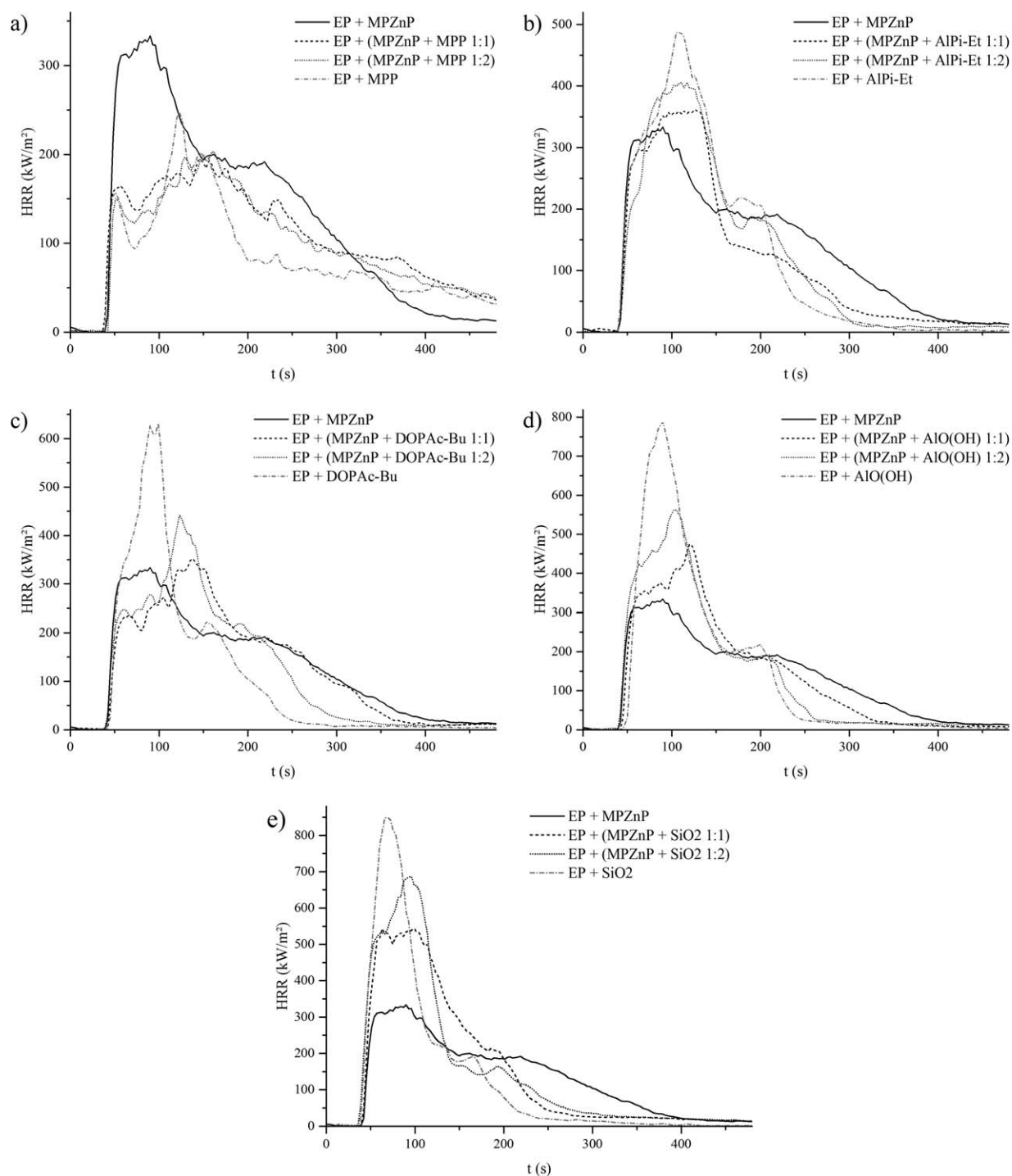
Figure 3. Heat release rate over time for EP + MPZnP and (a) EP + (MPZnP + MPP) and EP + MPP, (b) EP + (MPZnP + AlPi-Et) and EP + AlPi-Et, (c) EP + (MPZnP + DOPAc-Bu) and EP + DOPAc-Bu, (d) EP + (MPZnP + AlO(OH)) and EP + AlO(OH), and (e) EP + (MPZnP + SiO$_2$) and EP + SiO$_2$.

The corresponding effective EHC was lowered significantly, by 21–31% compared to EP, which is evidence for the strong flame inhibition effect of AlPi-Et and DOPAc-Bu in the gas phase. In the cases of EP + DOPAc-Bu and EP + (MPZnP + DOPAc-Bu 1:2), the strong flame inhibition effect was evident from a few short flashes before sustained ignition. For all other materials in this study, the EHC was lowered by only 1–10% and the CO

yield was not increased but slightly decreased (up to 15% compared to EP). The mass loss and smoke production were lower for EP + AlPi-Et than for EP + DOPAc-Bu, but higher for EP + (MPZnP + AlPi-Et) than for EP + (MPZnP + DOPAc-Bu). This difference in behavior indicates an interaction between MPZnP and DOPAc-Bu, which was also evident from the PHRR. The PHRR showed no deviation from superposition

Figure 4. Fire residues after cone calorimeter measurements of EP + MPZnP (left) and EP + MPP (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

assuming linear behavior for EP + (MPZnP + AlPi-Et), but was significantly lower than expected in the case of EP + (MPZnP + DOPAc-Bu), indicating a synergistic effect with an SE_A of 1.2 (Table VIII).

For EP + [MPZnP + AlO(OH)], a synergistic effect was evident with respect to both THE and PHRR. At both mixing ratios of MPZnP and AlO(OH), the SE_A was above 1.4 for THE and about 1.3 for PHRR, indicating a strong synergistic effect. However, since the absolute PHRR values were relatively high for EP + (MPZnP + AlO(OH)), the actual performance was insufficient. EP + AlO(OH) showed poor performance because of the limited influence of AlO(OH) on the decomposition of EP. The HRR curve of EP + AlO(OH) matched the shape of the HRR curve of EP relatively closely, with a reduction in THE of 14% and a reduction in PHRR of 19%. The mass loss was decreased by 14% for EP + AlO(OH) and by 15% for EP + MPZnP, but by 20% for

EP + (MPZnP + AlO(OH)), which further suggests an interaction between MPZnP and AlO(OH) during the combustion of EP + (MPZnP + AlO(OH)). SiO$_2$ turned out to be the least effective additive, showing even less influence than AlO(OH) on the decomposition and burning behavior of EP, as evident from the closely matching shape of the HRR curve of EP + SiO$_2$ to that of EP. EP + SiO$_2$, containing 20 wt % of SiO$_2$ as the only additive, exhibited a reduction in THE of 24% and reduction in PHRR of 14% compared to EP, suggesting the replacement of polymer as primary mode of action for SiO$_2$ as a flame retardant in EP. Consequently, both the THE and PHRR values for EP + SiO$_2$ and EP + (MPZnP + SiO$_2$) were among the highest of all materials in this study, while the MARHE and FIGRA indices were distinctively higher than for all other materials except for EP and EP + AlO(OH). While the PHRR values for EP + (MPZnP + SiO$_2$) were slightly lower than calculated for superposition assuming linear behavior of PHRR with regard to the ratio of additives (Table VIII), the corresponding THE values were even higher than calculated (Table VII). For EP + SiO$_2$, EP + (MPZnP + SiO$_2$), and EP + MPZnP, the total mass loss was barely altered (77.4–80.0%), further indicating that no significant interaction between MPZnP and SiO$_2$ took place during the combustion of EP + (MPZnP + SiO$_2$). As during the UL 94 test, sparkling burning was observed for EP + SiO$_2$ and EP + (MPZnP + SiO$_2$).

In summary, MPAlP, MPZnP, and MPMgP acted in both the gas phase and the condensed phase, but predominantly in the solid phase via the increase in residue and a distinctive protective layer effect. MPP showed similar modes of action, but was more effective as a single additive than MPAlP, MPZnP, and MPMgP because of superior intumescence. AlPi-Et and DOPAc-Bu both acted predominantly in the gas phase via a strong

Table VI. Appearance of the Fire Residues after Cone Calorimeter Investigation

| Material	Residue appearance
EP	Black, small amount (mostly at the edges)
EP + MPAlP	Black, inflated, rigid
EP + MPZnP	Black, inflated, rigid
EP + MPMgP	Dark gray, inflated, rigid
EP + (MPZnP + MPP 1:1)	Black, inflated, rigid
EP + (MPZnP + AlPi-Et 1:1)	Black, fissured, rigid
EP + (MPZnP + DOPAc-Bu 1:1)	Black, inflated, rigid
EP + (MPZnP + AlO(OH) 1:1)	Gray, inflated, brittle
EP + (MPZnP + SiO$_2$ 1:1)	Dark gray, inflated, brittle
EP + (MPZnP + MPP 1:2)	Black, highly inflated, rigid
EP + (MPZnP + AlPi-Et 1:2)	Black, fissured, rigid
EP + (MPZnP + DOPAc-Bu 1:2)	Black, fissured, rigid
EP + (MPZnP + AlO(OH) 1:2)	Gray, inflated, brittle
EP + (MPZnP + SiO$_2$ 1:2)	Gray, fissured, brittle
EP + MPP	Black, highly inflated, rigid
EP + AlPi-Et	Black, fissured, rigid
EP + DOPAc-Bu	Black, small amount (mostly at the edges)
EP + AlO(OH)	Light gray, flat lumps, brittle
EP + SiO$_2$	Light gray, flat lumps, brittle
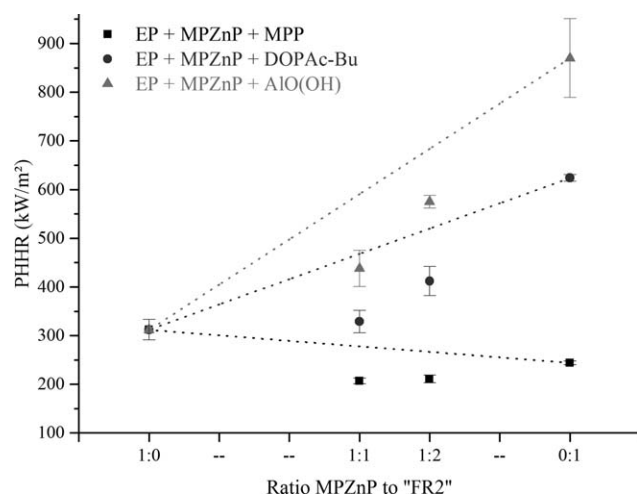
Figure 5. PHRR for EP + MPZnP, EP + (MPZnP + MPP), EP + (MPZnP + DOPAc-Bu), EP + (MPZnP + AlO(OH)), EP + MPP, EP + DOPAc-Bu, and EP + AlO(OH). Dotted lines: Calculated PHRR for superposition according to eq. (1).

flame inhibition effect. AlO(OH) and SiO_2 acted predominantly as fillers, improving the fire performance of EP through the replacement of polymer material. For the combinations of MPZnP with AlPi-Et, DOPAc-Bu, AlO(OH), SiO_2, and especially MPP, the increase in the residue and barrier effects became the dominant mode of action. A distinctive synergistic effect with MPZnP was evident for MPP, DOPAc-Bu, and AlO(OH). The PHRR values for EP + (MPZnP + MPP), EP + (MPZnP + DOPAc-Bu), and EP + (MPZnP + AlO(OH)) were significantly lower than expected for linear behavior, as illustrated in Figure 5.

Glass Transition Temperatures
The glass transition temperature is a key property for thermosets in applications as well as a good indicator of how the overall properties of the thermosets are changed through the addition of flame retardants.[67] Obtaining a V-0 classification without reducing the glass transition temperature is one of the

key challenges when developing flame retarded epoxy resin for electronics. The results are shown in Table IX. No significant deviation from the T_g of EP (less than 10 °C) was observed for almost all of the materials in this study, with the exception of EP + DOPAc-Bu and EP + (MPZnP + DOPAc-Bu). An increased content of DOPAc-Bu resulted in a lower T_g. The T_g was reduced by 32 °C for EP + (MPZnP + DOPAc-Bu 1:1), 42 °C for EP + (MPZnP + DOPAc-Bu 1:2), and 53 °C for EP + DOPAc-Bu compared to EP. This strong plasticizer effect of DOPAc-Bu in EP is because of its low molecular weight (344.35 g/mol) and high solubility in DGEBA/IPDA. Soluble additives of low molecular weight are known to be strong plasticizers.[68,69] In contrast, MPAlP, MPZnP, MPMgP, and MPP have very high molecular weights because of their polymeric structure; since they maintain their particle morphology, composites were formed. AlPi-Et, AlO(OH), and SiO_2 also showed little to no solubility in the uncured DGEBA/IPDA mixture because of their salt-like structure and particle morphology. MPAlP, MPZnP, MPMgP, MPP, AlPi-Et, AlO(OH), and SiO_2 were dispersed in the uncured DGEBA/IPDA mixture, resulting in composite materials after curing. DOPAc-Bu formed a homogenous mixture with DGEBA and IPDA, so that EP + DOPAc-Bu turned out to be the only transparent material except EP in this study. All of the composites show a T_g between 152 °C and 163 °C, which is not only a minor deviation from the T_g of EP (154 °C); most remarkably, the T_g remained unchanged or even slightly improved.

CONCLUSIONS

Three different kinds of melamine poly(metal phosphate), MPAlP, MPZnP, and MPMgP were incorporated into the epoxy resin DGEBA/IPDA (EP). EP + MPAlP showed about a 50% reduction in the PHRR, and EP + MPZnP and EP + MPMgP reduced the PHRR to less than 30% of the PHRR of EP in the cone calorimeter tests. MPAlP, MPZnP, and MPMgP acted predominantly in the condensed phase, accompanied by a minor fuel dilution. Smoke and CO production was reduced. The amount of fire residue increased and a protection layer effect occurred because of intumescence.

Table VII. Calculated and Measured THE, Deviation and Synergy Index for EP + (MPZnP + MPP), EP + (MPZnP + AlPi-Et), EP + (MPZnP + DOPAc-Bu), EP + (MPZnP + AlO(OH)), and EP + (MPZnP + SiO₂)

	THE (MJ/m^2)			
Material	Calc.	Found	Deviation	SE_A
EP + (MPZnP + MPP 1:1)	43.3	51.1	+18%	0.81
EP + (MPZnP + AlPi-Et 1:1)	57.9	51.2	−12%	1.37
EP + (MPZnP + DOPAc-Bu 1:1)	55.1	57.6	+5%	0.88
EP + (MPZnP + AlO(OH) 1:1)	62.8	57.2	−9%	1.43
EP + (MPZnP + SiO₂ 1:1)	58.8	62.4	+6%	0.79
EP + (MPZnP + MPP 1:2)	37.7	32.5	−14%	1.14
EP + (MPZnP + AlPi-Et 1:2)	57.2	53.8	−6%	1.18
EP + (MPZnP + DOPAc-Bu 1:2)	53.5	52.1	−3%	1.06
EP + (MPZnP + AlO(OH) 1:2)	63.7	57.9	−9%	1.48
EP + (MPZnP + SiO₂ 1:2)	58.4	65.6	+12%	0.59

Table VIII. Calculated and Measured PHRR, Deviation and Synergy Index for EP + (MPZnP + MPP), EP + (MPZnP + AlPi-Et), EP + (MPZnP + DOPAc-Bu), EP + (MPZnP + AlO(OH)), and EP + (MPZnP + SiO$_2$)

Material	PHRR (kW/m^2)			
	Calc.	Found	Deviation	SE_A
EP + (MPZnP + MPP 1:1)	278	207	−26%	1.09
EP + (MPZnP + AlPi-Et 1:1)	402	405	+1%	1.00
EP + (MPZnP + DOPAc-Bu 1:1)	468	329	−30%	1.23
EP + (MPZnP + AlO(OH) 1:1)	591	438	−26%	1.32
EP + (MPZnP + SiO$_2$ 1:1)	610	525	−14%	1.18
EP + (MPZnP + MPP 1:2)	267	211	−21%	1.07
EP + (MPZnP + AlPi-Et 1:2)	432	435	+1%	1.00
EP + (MPZnP + DOPAc-Bu 1:2)	520	412	−21%	1.20
EP + (MPZnP + AlO(OH) 1:2)	684	575	−16%	1.28
EP + (MPZnP + SiO$_2$ 1:2)	709	681	−4%	1.08

MPZnP was combined with MPP, AlPi-Et, DOPAc-Bu, AlO(OH), and SiO$_2$, at ratios of 1:1 and 1:2. EP + (MPZnP + AlPi-Et) and EP + (MPZnP + DOPAc-Bu) reduced PHRR to 30–40% of EP. V-1 ratings in UL 94 were achieved for some ratios. Both DOPAc-Bu and AlPi-Et provided strong flame inhibition. DOPAc-Bu exhibited a synergistic effect when combined with MPZnP in PHRR, whereas AlPi-Et did not. EP + (MPZnP + DOPAc-Bu) had a significantly lower glass transition temperature than EP because of the strong plasticizer effect of DOPAc-Bu in EP. SiO$_2$ and AlO(OH) acted predominantly as fillers, reducing the amount of polymer. EP + (MPZnP + SiO$_2$) turned out to be least effective, exhibiting higher THR and PHRR values than

almost all other materials in this study and sparkling burning that ignited the cotton in the UL 94 test. EP + (MPZnP + AlO(OH)) showed significant synergistic behavior in THE and PHRR. Nevertheless the absolute performance of EP + (MPZnP + AlO(OH)) was still weak. No classification was achieved in vertical UL 94. MPP exhibited similar modes of action as MPZnP, but provided significantly superior intumescence. EP + (MPZnP + MPP) showed great performance because of strong intumescence and a synergistic effect between MPZnP and MPP. The PHRR of EP + (MPZnP + MPP) was reduced by 80% compared to EP. The reduction was 20% lower than calculated for linear behavior over the ratio between MPZnP and MPP. EP + (MPZnP + MPP) thus provided V-0 ratings the lowest PHRR of all materials investigated.

This work evaluates the performance of melamine poly(metal phosphates) as a flame retardant in epoxy resin. It proposes melamine poly(metal phosphate) as suitable choice in multicomponent systems, particularly in synergistic combinations with other flame retardants. Within this study, the overall best performance was achieved for EP + (MPZnP + MPP).

Table IX. Glass Transition Temperatures

Material	T_g (°C) ±2
EP	154
EP + MPAlP	153
EP + MPZnP	158
EP + MPMgP	163
EP + (MPZnP + MPP 1:1)	160
EP + (MPZnP + AlPi-Et 1:1)	152
EP + (MPZnP + DOPAc-Bu 1:1)	122
EP + (MPZnP + AlO(OH) 1:1)	161
EP + (MPZnP + SiO$_2$ 1:1)	153
EP + (MPZnP + MPP 1:2)	158
EP + (MPZnP + AlPi-Et 1:2)	162
EP + (MPZnP + DOPAc-Bu 1:2)	112
EP + (MPZnP + AlO(OH) 1:2)	162
EP + (MPZnP + SiO$_2$ 1:2)	160
EP + MPP	158
EP + AlPi-Et	162
EP + DOPAc-Bu	101
EP + AlO(OH)	163
EP + SiO$_2$	159

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