

Intrinsically flame retardant epoxy resin — Fire performance and background — Part I

A. Toldy*, P. Anna, I. Csontos, A. Szabó, Gy. Marosi

Department of Organic Chemical Technology, Budapest University of Technology and Economics, PO Box 91, 1521 Budapest, Hungary

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Abstract

The flame retardant effect of newly synthesized phosphorus-containing reactive amine, which can be used both as crosslinking agent in epoxy resins and as a flame retardant, was investigated. The effect of montmorillonite and sepiolite additives on the fire induced degradation was compared to pristine epoxy resin. The effect of combining the organophosphorous amine with clay minerals was also studied. It could be concluded that the synthesized phosphorus-containing amine, TEDAP can substitute the traditional epoxy resin curing agents providing additionally excellent flame retardancy: the epoxy resins flame retarded this way reach 960 °C GWFI value, 33 LOI value and V-0 UL-94 rating — compared to the 550 °C GWFI value, 21 LOI value and “no rate” UL-94 classification of the reference epoxy resin. The peak of heat release was reduced to 1/10 compared to non-flame retarded resin, furthermore a shift in time was observed, which increases the time to escape in case of fire. The flame retardant performance can be further improved by incorporating clay additives: the LOI and the HRR results showed that the optimum of flame retardant effect of clay additives is around 1 mass% filler level in AH-16–TEDAP system. Applying a complex method for mechanical and structural characterization of the intumescent char it was determined that the flame retarded system forms significantly more and stronger char of better uniformity with smaller average bubble size. Incorporation of clay additives (owing to their bubble nucleating activity) results in further decrease in average bubble diameter.

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Keywords: Epoxy resin; Clay; Organophosphorous reactive amine flame retardant; Flame retardance; Degradation mechanism

1. Introduction

Epoxy resins are extensively used as adhesives, surface coatings, laminates and matrix materials in electronic, transport and aerospace industries due to their exceptional characteristics like good adhesion to many substrates; moisture, solvent and chemical resistance; low shrinkage on cure; outstanding mechanical and electronic resistant properties. However, having an organic matrix, their thermal and fire resistance needs to be enhanced in many application areas. Fire retardancy, as an outstanding element of safety, is one of the key challenges. There are two main approaches to achieve flame retardancy: the additive and the reactive approaches.

Although the additive way provides a simple and cost-effective solution, it has some drawbacks as well: in most cases to achieve adequate effect high percentage of the additive is needed, which significantly influences the properties of the polymer matrix. Furthermore as the additive is not chemically incorporated into the polymer structure, it can lead to the possibility of loss from the polymer during either high temperature processing by migration to the surface or in the early stages of combustion. Additionally, the transition of additives to the gaseous phase can cause the smoke from the burning material to become loaded with toxic compounds.

The above mentioned disadvantages of this approach may be eliminated with nano-level dispersion of the additive: due to high specific surface of the additive and nano-scale interactions with the polymer matrix, even at very low filler concentration nanocomposites often reveal remarkable improvement of mechanical properties, thermal properties and flame retardancy compared to

* Corresponding author. Tel.: +36 1 463 1348; fax: +36 1 463 1150.

E-mail address: atoldy@mail.bme.hu (A. Toldy).

virgin polymer and conventional microcomposites [1–3]. Especially great attention has been paid to clay nanoadditives due to their low cost and large quantity. Furthermore, the migration to the polymer surface, mentioned as one of the disadvantages of additive flame retardants, can become an advantage in this case, as clay nanoparticles migrating to the surface of the polymer matrix form an excellent mass and heat barrier improving flame retardant properties. Nevertheless, clay nanoparticles alone do not provide sufficient fire retardant effect, and it is necessary to combine them with other, approved flame retardants.

Lately the reactive type of flame retardancy was given much attendance because of the disadvantages of additive flame retardants described above. In addition, the increasing focus on the health and environmental compatibility of flame retardants has drawn attention to the organophosphorous reactive flame retardants [4–6]. The new European Directive 2002/95/EC [7], requiring the substitution of some widely used brominated flame retardants (polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE)) in new electrical and electronic equipment put on the market from 1 July 2006, also facilitates the growth of phosphorous flame retardants.

Understanding the concept of the reactive flame retardancy serves as a model for planning the flame retardancy of other polymers. In case of epoxy resins the phosphorus-containing chemical unit, providing the flame retardant effect, can be incorporated into the epoxy component, the crosslinking agent or into both. From the many possible alternatives the combination of an aliphatic epoxy component – more difficult to flame retard than the aromatic ones – and a simple phosphorus-containing crosslinking agent was chosen.

In this work the effect of montmorillonite and sepiolite additives on the fire induced degradation was compared to pristine epoxy resin matrix. The flame retardant effect of newly synthesized phosphorus-containing reactive amine, which can be used both as crosslinking agent in epoxy resins and as flame retardant, was investigated. The effect of combining the organophosphorous amine with clay minerals was also studied.

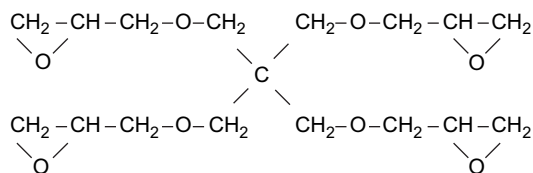
2. Experimental

2.1. Materials

The polymer matrix was ER type Eporezit AH-16 (non-modified, resin like reactive dilutant, epoxy equivalent: 160–175; viscosity at 25 °C: 800–1800 mPa s; density at 25 °C: 1.24 g/cm³) applied with Eporezit T-58 curing agent (amine number: 460–480 mg KOH/g; viscosity at 20 °C: 100–200 mPa s; density at 20 °C: 0.944 g/cm³; curing time: 2 days at 25 °C) supplied by P + M Polimer Kémia Kft., Hungary. Schemes 1 and 2 show the main components of Eporezit AH-16 and Eporezit T-58.

A newly synthesized phosphorus-containing reactive amine, TEDAP (amine number: 510–530 mg KOH/g; viscosity at 20 °C: 400 mPa s; curing time: 7 days at 25 °C, 4 hr at 80 °C) was used as flame retardant.

Unmodified Na montmorillonite (MMT) (product of Microtec, Eurotrade) and Bentone SD-1 (bentonite based



Scheme 1. Main component of Eporezit AH-16.

organoclay product of Rheox Inc.) type montmorillonite (MMT); Pangel S9 (untreated) and Pangel B40 (organomodified) sepiolites (SEP) (products of Tolsa Ltd) were applied as clay additives. This way ER samples, respectively, containing 1, 2 and 5% MMT and SEP were prepared.

2.2. Methods

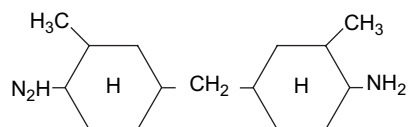
The epoxy and amine components were mixed at room temperature or in case of TEDAP at its melting point, by hand in a glass beaker in order to obtain a homogenous mixture. The clay particles were added to the epoxy component and stirred for 1 h with a magnetic stirrer at 80 °C in order to obtain a good dispersion. A silicone mould 120 mm long, 15 mm wide and 3 mm thick was used for preparing the cured samples.

Amine number of the curing agents was determined by titration according to ASTM D2074-92(1998).

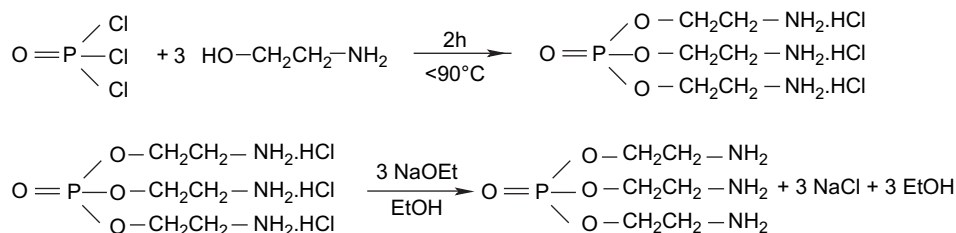
The fire resistance was characterized by Mass Loss Calorimeter (according to ISO 13927, Fire Testing Technology, heat flux of 50 kW/m²), glow wire flammability index test (GWFI, according to IEC 60695-2-12), UL-94 test (according to ASTM 1356-90 and ANSI//ASTM D-635/77, respectively) and limiting oxygen index measurement (LOI, according to ASTM D 2863).

A rheological method for char characterization elaborated by Duquesne et al. [8] was developed further for more detailed mechanical and structural characterization of the char. Measurements were carried out in a TA Instruments AR2000 type rheometer, at room temperature, applying 1 Hz frequency and 0.1% relative elongation and 1000 μm gap. One gram of the epoxy resin samples was cured in the lower plate of the rheometer at room temperature. The plates of the rheometer were opened to the maximum distance, then the sample of given amount in the lower plate was heated up to 450 °C. Due to the heat effect char formation occurred. Then the upper plate was moved to the lower with constant speed (30 μm/s) and the normal force transduced by the charred layer was constantly detected and registered. The lower and upper plates had the same diameter, in order to obtain an average result characterizing the whole sample surface.

Scanning electron microscopy (SEM) images were taken with JEOL 5500 LV instrument.



Scheme 2. Main component of Eporezit T-58.



Scheme 3. Synthesis of TEAP.

The MS FAB measurements were performed on ZAB-2SEQ spectrometer. The MALDI-TOF measurements were taken on Bruker BiFlex III MALDI-TOF apparatus and evaluated with XMASS 5.0 software. The ^{31}P NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4 MHz. Chemical shifts are downfield relative to 85% H_3PO_4 . The infrared spectroscopic measurements were made on Bruker Tensor 37 type FTIR apparatus, using NaCl-window, resolution: 4 cm^{-1} , detector: DTGS.

3. Results and discussion

3.1. Synthesis of the organophosphorous compounds

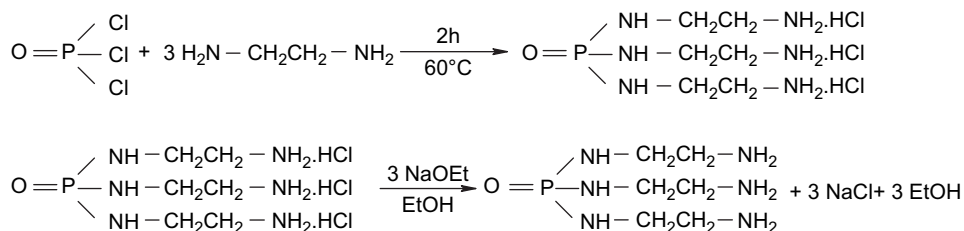
3.1.1. Synthesis of $\text{P}(\text{O})(\text{OCH}_2\text{CH}_2\text{NH}_2)_3$ (TEAP) from POCl_3

The synthesis of $\text{P}(\text{O})(\text{OCH}_2\text{CH}_2\text{NH}_2)_3$ from starting material POCl_3 was carried out according to the literature [9] (Scheme 3).

To 6.03 ml (0.1 mol) of $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$ 3.11 ml (0.033 mol) of POCl_3 was added dropwise with continuous stirring in 2 h at a rate that the temperature of the reaction mixture does not exceed 90°C . After 2 h 20 ml of toluene was added and the mixture was stirred for 1 h. Toluene was removed by decantation and a solution of 6.8 g (0.1 mol) NaOEt and 40 ml of 96% EtOH was added and the mixture was stirred for 3 h at 60°C . The formed NaCl was filtrated to give the product in 90% yield. The product was characterized by ^{31}P NMR chemical shifts and mass spectroscopical data obtained from MS FAB. ^{31}P NMR (CDCl_3) δ 2.79; MS, m/z (rel. int.) 228 (M^+ , 7).

3.1.2. Synthesis of $\text{P}(\text{O})(\text{NHCH}_2\text{CH}_2\text{NH}_2)_3$ (TEDAP) from POCl_3

The synthesis of $\text{P}(\text{O})(\text{NHCH}_2\text{CH}_2\text{NH}_2)_3$ from starting material POCl_3 was carried out analogously to the reaction described above (Scheme 4).



Scheme 4. Synthesis of TEDAP.

To the solution of 10 ml toluene and 2.67 ml (0.03 mol + 0.01 mol excess) of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ solution of 20 ml toluene and 0.93 ml (0.01 mol) of POCl_3 was added dropwise with continuous stirring in 30 min at a rate that the temperature of the reaction mixture cooled to 0°C does not exceed 5°C . After stirring for 2 h at 60°C the toluene was removed by decantation and a solution of 2.04 g (0.03 mol) NaOEt and 60 ml of 96% EtOH was added and the mixture was stirred for 3 h at 60°C . The formed NaCl was filtered to give the product in 80% yield. The product was characterized by ^{31}P NMR chemical shifts, mass spectroscopical data obtained from MS MALDI-TOF and FTIR spectra. ^{31}P NMR (DMSO) δ 6.64; MS, m/z (rel. int.) 225 (M^+ , 64); FTIR (cm^{-1}) 740 (P–N–C), 950 (P–N–C), 1216 (P=O), 3354 (N–H).

3.2. Application of clay additives and organophosphorous compounds in epoxy resin matrix

3.2.1. Incorporation of montmorillonite and sepiolite additives into epoxy resin matrix

The effect of clay additives on flame retardancy was investigated by LOI, UL-94, HRR and mass loss measurements.

According to the LOI results (Table 1) it can be concluded that the clay additives improved the LOI of the reference AH-16–T-58 epoxy resin and by increasing their quantity the LOI slightly increased. Both in case of MMT and SEP the untreated clays had more significant effect on the flame retardancy. The best result was achieved using 5% untreated SEP.

The effect of clay additives was also investigated by HRR and mass loss measurements. The HRR of AH-16–T-58 matrix containing 1, 2 and 5% of untreated MMT and SEP, respectively, can be seen in Figs. 1 and 2.

The clay additives reduced the peak of HRR and in case of 1% additive a shift in time to ignition was observed, especially in case of untreated MMT additive. It is also an interesting notification that by increasing the amount of clay additives the form

Table 1
LOI and UL-94 results of AH-16–T-58 samples containing clay additives

Clay mineral additive	AH-16–T-58 matrix	
	LOI%	UL-94
–	21	–
1% Untreated MMT	24	HB
2% Untreated MMT	24	HB
5% Untreated MMT	25	HB
1% Organophilized MMT	21	HB
2% Organophilized MMT	22	HB
5% Organophilized MMT	22	HB
1% Untreated SEP	25	HB
2% Untreated SEP	26	HB
5% Untreated SEP	27	HB
1% Organophilized SEP	24	HB
2% Organophilized SEP	24	HB
5% Organophilized SEP	25	HB

of the HRR curve changes: the second peak of HRR is gradually diminishing. This phenomenon may be explained by considering the following processes during burning: The main heat release peak caused by the burning of the evolved gas phase degradation products is followed by a plateau on the HRR curve due to the protective layer formed from solid decomposition products. When the pressure of the evolved gases becomes higher than the value that the barrier layer can bear, the combustible gases burst out and the whole process starts again. The gradually diminishing second peak of HRR is suggesting a reinforcing effect of clay on the char that maintains this way its barrier effect and thus avoids the reactivation of the heat releasing process. Thus it was essential to find a method for complex characterization of the char developed during the burning process and to estimate the effect of clay additives and flame retardants on the mechanical and structural characteristics of the char.

3.2.2. Incorporation of organophosphorous crosslinking agent into epoxy resin matrix

According to preliminary LOI and UL-94 measurements, from the two synthesized organophosphorous compounds TEDAP seemed to be more suitable as flame retardant: it increased the LOI of the AH-16–T-58 epoxy resin from 21 to 33, and the UL-94 value from no rate to V-0, while TEAP increased the LOI only to 28 and resulted in HB UL-94 classification. Furthermore the synthesis of TEDAP was more convenient than the synthesis of TEAP.

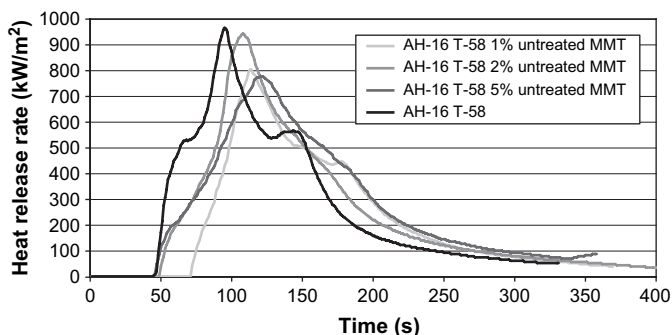


Fig. 1. Effect of untreated MMT on HRR in AH-16–T-58 epoxy resin matrix.

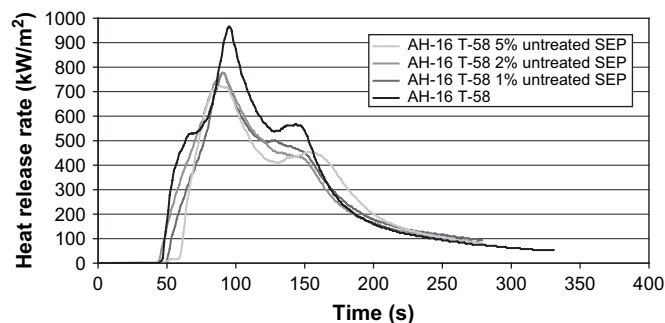


Fig. 2. Effect of untreated SEP on HRR in AH-16–T-58 epoxy resin matrix.

In order to investigate the flame retardant effect of TEDAP, T-58 curing agent was replaced by TEDAP in 20, 40, 60, 80 and finally in 100 mass%. The appropriate amount of TEDAP to replace T-58 was calculated according to its amine number in order to reach the same level of curing.

The fire retardancy of these samples was evaluated by LOI, UL-94, HRR and mass loss measurements. The LOI and UL-94 results are given in Table 2.

Increasing the proportion of TEDAP and so the P concentration in the system, a clear increase of the flame retardancy can be seen. To achieve the V-0 UL-94 classification 60 mass% of the original crosslinking agent T-58 was replaced by TEDAP. Best results – LOI of 33 and V-0 UL-94 classification – were reached when the original amine was completely replaced by TEDAP, which provides 3.5 mass% of P in the epoxy resin.

The flame retardancy was also investigated by mass loss and HRR measurements. The heat release rate (HRR) of AH-16–T-58–TEDAP series in the function of TEDAP proportion can be seen in Fig. 3.

According to the HRR results it can be determined that by increasing the proportion of TEDAP and so the phosphorus content, the peak value of HRR is decreased which shows a good correlation with LOI and UL-94 results. The biggest decrease in peak HRR was observed when the original amine was completely replaced by TEDAP: the peak HRR was reduced to approximately its tenth value. Also a significant shift in time was observed, which increases the time to escape in case of fire.

3.2.3. Combination of montmorillonite and sepiolite additives with reactive amine flame retardant

The fire retardancy of these samples was evaluated by LOI and mass loss and HRR measurements. The LOI and UL-94 results are given in Table 3.

Table 2
LOI and UL-94 values in the function of TEDAP proportion in case of AH-16–T-58 samples

Sample	P-content (mass%)	LOI (%)	UL-94
AH-16–T-58 reference	–	21	No rate
AH-16–T-58–20% TEDAP	0.7	26	HB
AH-16–T-58–40% TEDAP	1.4	29	HB
AH-16–T-58–60% TEDAP	2.1	29	V-0
AH-16–T-58–80% TEDAP	2.8	29	V-0
AH-16–100% TEDAP	3.5	33	V-0

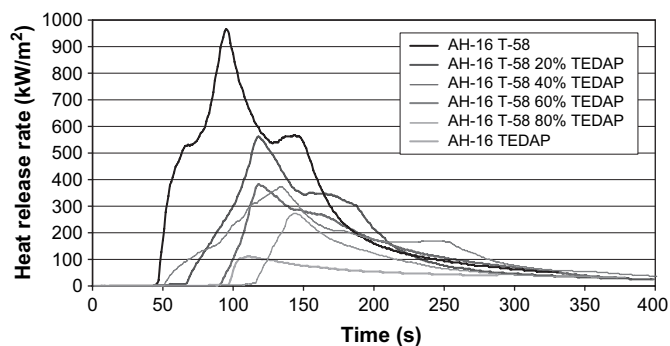


Fig. 3. Heat release rate in the function of TEDAP proportion in case of AH-16–T-58 samples.

According to these results it can be concluded that in addition to the effect of TEDAP there was a further increase in LOI applying 1% clay additive. However, incorporating more additive did not improve the LOI results, moreover, in case of SEP it deteriorated the LOI values.

The effect of clay additives was also investigated by HRR and mass loss measurements. The HRR of AH-16–T-58 reference and AH-16–TEDAP matrix containing 1, 2 and 5% of untreated MMT and SEP, respectively, can be seen in Figs. 4 and 5.

By replacing the T-58 with the phosphorus-containing TEDAP the peak HRR value decreased approximately to its 1/10 value, furthermore, a shift in time to ignition of about 50 s was observed. By adding clay additives to the AH-16–TEDAP matrix better results were obtained only in case of applying 1% additive: the value of peak HRR decreased or stayed at same level and a further significant shift in time to ignition was detected. If 2 or 5% clay was added the peak of HRR increased compared to the AH-16–TEDAP matrix, although the above mentioned shift in ignition time was observed as well.

Both the LOI and the HRR results showed that the optimum of flame retardant effect of clay additives is around 1 mass% filler level. In order to investigate this behaviour the

Table 3
LOI and UL-94 results of AH-16–TEDAP samples containing clay additives

Clay mineral additive	AH-16–TEDAP matrix	
	LOI%	UL-94
–	33	V-0
1% Untreated MMT	35	V-0
2% Untreated MMT	33	V-0
5% Untreated MMT	33	V-0
1% Organophillized MMT	36	V-0
2% Organophillized MMT	35	V-0
5% Organophillized MMT	35	V-0
1% Untreated SEP	34	V-0
2% Untreated SEP	30	V-0
5% Untreated SEP	30	V-0
1% Organophillized SEP	34	V-0
2% Organophillized SEP	31	V-0
5% Organophillized SEP	32	V-0

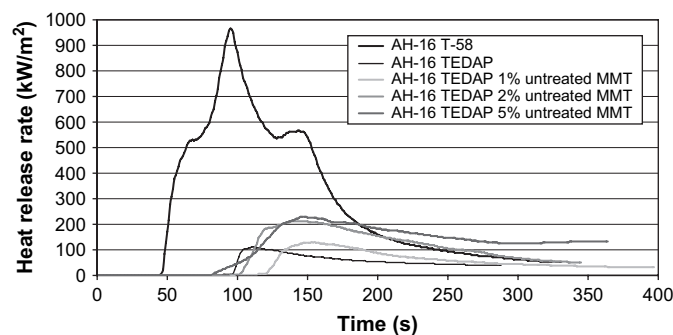


Fig. 4. Effect of untreated MMT on HRR in AH-16–TEDAP epoxy resin matrix.

mechanical and structural characterization of the char was done by a method described above (Fig. 6).

Fig. 7 shows the normal force transduced by the char as a function of the distance between the plates of the rheometer. Moving the upper plate downward the normal force takes up a nearly constant value, which can be considered proportional to the strength of the individual bubbles. After breaking the charred structure the normal force increases significantly because of the compression of the charred layer. As the mass of the samples was the same, the first point of the measurement characterizes the char volume, while the gap, before sudden increase of the normal force, is proportional to the remained mass of the sample. In contrast to the previously reported method [10], where the decreasing gap was expressed in percentages taking into account the initial height of the char, in this case the value of the gap was displayed as an absolute value in order to be able to compare the real char volumes. The average normal force before sudden increase of the normal force can be considered as a characteristic parameter of the char strength, while the scattering of the normal force correlates with the diameter of the formed bubbles in the char: small, uniform fluctuation refers to small bubble diameter and uniform, flexible char; while sudden decrease in normal force proves the presence of bubbles with big diameter, which causes the char to have an uneven, rigid structure.

Comparing the AH-16–T-58 reference and AH-16–TEDAP flame retarded systems (Table 4), it can be determined that the

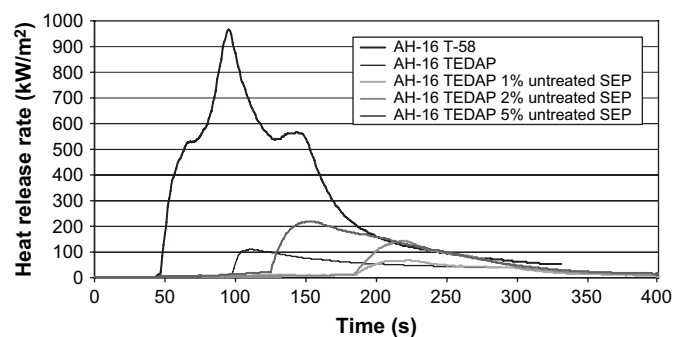


Fig. 5. Effect of untreated SEP on HRR in AH-16–TEDAP epoxy resin matrix.

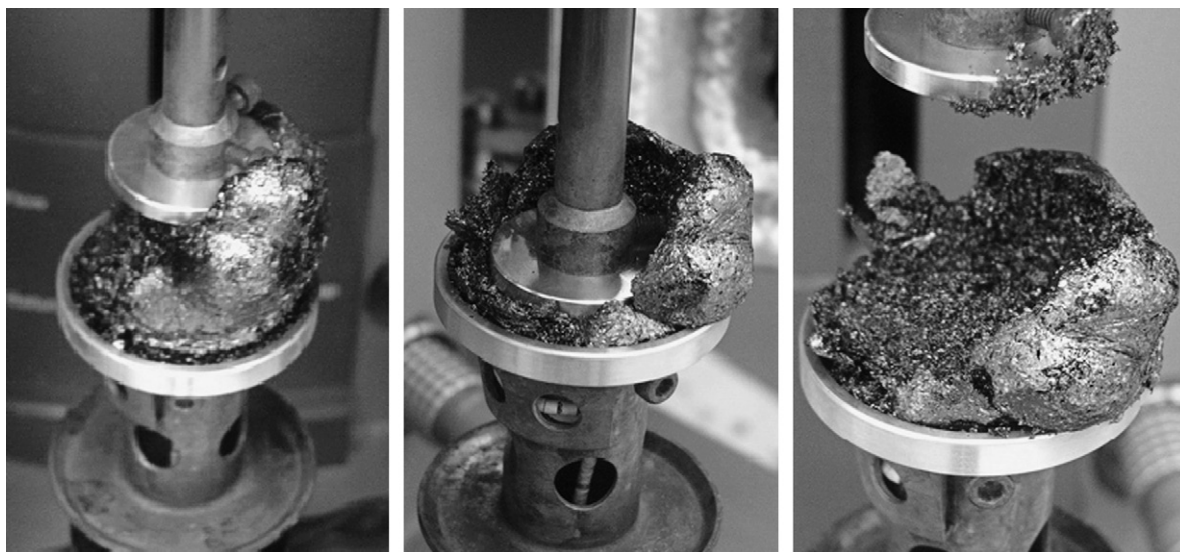


Fig. 6. Mechanical destruction of the intumescent char of AH-16–TEDAP system.

flame retarded system forms significantly more char than the reference. Furthermore, the char of the reference sample is a more rigid char, with bigger average bubble diameter, while the flame retarded system provides a stronger, more uniform char with smaller average bubble size. Including untreated SEP in the reference system the average bubble diameter decreases resulting in a more uniform char. In case of the flame retarded systems the incorporation of the untreated SEP decreases the average bubble size, but this is a relatively smaller effect compared to the already significant effect of intumescent flame retardant. No significant difference was observed in the function of clay amount, so further investigation is needed to interpret the different effect of the increasing amount of clay on the LOI and HRR results in the reference and the flame retarded systems. Most probably the bubble nucleating effect of the clay additive is dominant, which requires only a small filler content to reach the appropriate effect. Furthermore, as TEDAP is more polar than the original T-58 hardener, it can be assumed that by increasing the additive amount the decrease in crosslinking enthalpy (due to adsorption of the crosslinking agent) becomes more significant than in case of T-58 (reported elsewhere

[11]), which leads to lower crosslinking density and deteriorating flame retardancy.

In order to make the bubble size reducing effect of clay additives even more clear several SEM images were taken (Figs. 8 and 9) and analysed by Olympus DPSOFT imaging software. The estimated average bubble size was $410 \pm 30 \mu\text{m}$, while the incorporated 1% untreated MMT reduced it to $255 \pm 30 \mu\text{m}$.

GWFI measurements were done in order to estimate the industrial applicability of this new flame retarded epoxy resin system in electrical and electronic equipments. By increasing the amount of TEDAP and so the proportion of phosphorus a linear increase in GWFI can be seen (Table 5). Applying 100% TEDAP the best GWFI value according to the standard can be achieved: The GWFI value of 960°C means that the epoxy resin cured with TEDAP can be used in electrical and electronic equipments for unattended use continuously loaded, or equipment to be used near the central supply point of a building; both in parts in contact with, or retaining in position current-carrying parts and in enclosures and covers not retaining current-carrying parts in position.

4. Conclusions

The synthesized phosphorus-containing amine, TEDAP can substitute the traditional epoxy resin curing agents, additionally providing excellent flame retardancy: the epoxy resins flame retarded this way reach 960°C GWFI value, 33 LOI value and V-0 UL-94 rating – compared to the 550°C GWFI value, 21 LOI value and “no rate” UL-94 classification of the reference epoxy resin. The peak of heat release was reduced to its 1/10 compared to non-flame retarded epoxy resin, furthermore a shift in time was observed, which increases the time to escape in case of fire event. The flame retardant performance can be further improved by incorporating clay additives: the LOI and the HRR results showed that the optimum

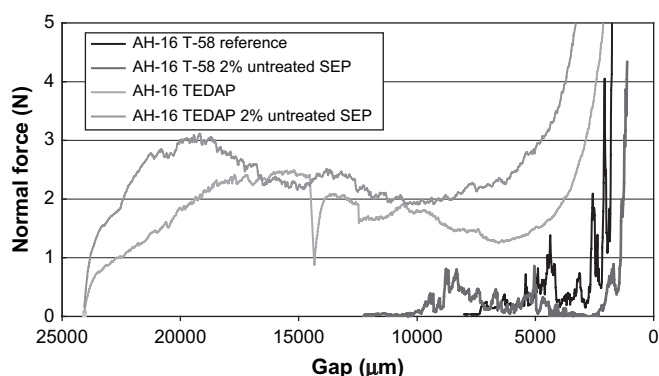


Fig. 7. Effect of untreated SEP on the char characteristics.

Table 4
Effect of untreated SEP on the char characteristics

	Maximum gap (μm)	Gap before total compression ^a (μm)	Average normal force before total compression ^a (N)	Maximum normal force before total compression ^a (N)	Maximum deviation (N)
AH-16–T-58 reference	8021	1632	0.427	2.09	9.08
AH-16–T-58–2% Pangel S9	12 820	1121	0.172	0.85	0.78
AH-16–TEDAP	24 075	2119	1.71	2.48	1.52
AH-16–TEDAP–2% Pangel S9	24 075	3295	2.31	3.11	0.2

^a Point in the normal force vs gap diagram where the normal force suddenly begins to increase due to total compression of char.

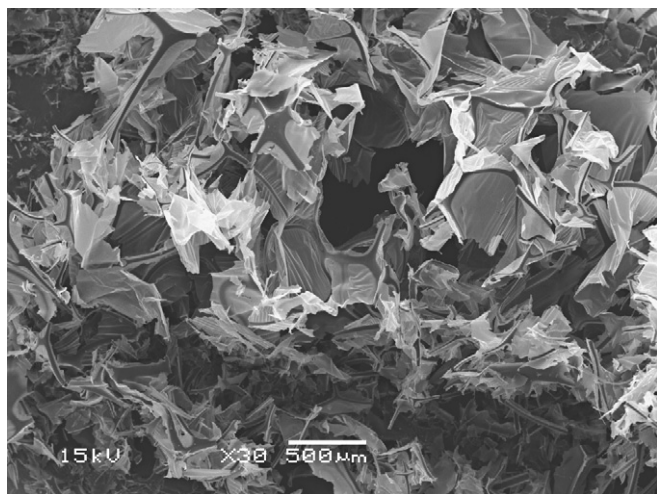


Fig. 8. SEM image of AH-16–TEDAP char.

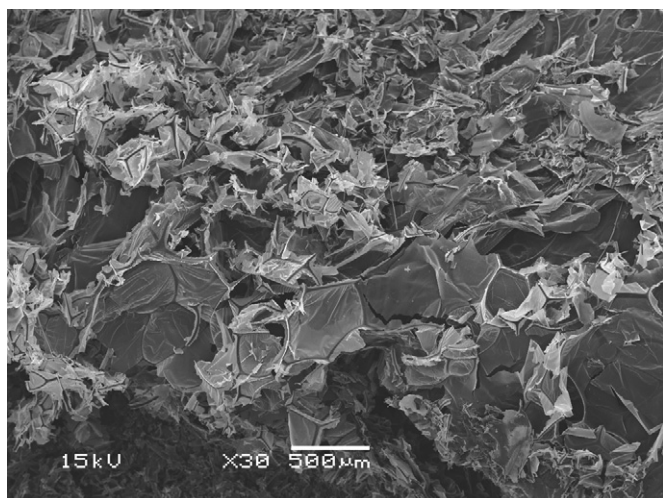


Fig. 9. SEM image of AH-16–TEDAP 1% untreated MMT char.

Table 5
GWFI values in the function of TEDAP proportion in case of AH-16–T-58 samples

Sample	P-content (mass%)	GWFI value ($^{\circ}\text{C}$)
AH-16–T-58 reference	–	550
AH-16–T-58–20% TEDAP	0.7	550
AH-16–T-58–40% TEDAP	1.4	650
AH-16–T-58–60% TEDAP	2.1	750
AH-16–T-58–80% TEDAP	2.8	850
AH-16–100% TEDAP	3.5	960

of flame retardant effect of clay additives is around 1 mass% filler level in AH-16–TEDAP system.

A new method was elaborated for mechanical and structural characterization of the char: it can be determined that the flame retarded system forms significantly more and stronger char of better uniformity with smaller average bubble size. Incorporation of clay additives (owing to their bubble nucleating activity) results in further decrease in average bubble diameter.

According to these results the epoxy resin flame retarded by this phosphorus-containing amine is appropriate for all electronic appliances, the achieved GWFI value (960°C) means that it can be used in equipment for unattended use continuously loaded under stringent conditions. Varying the ratio of the non-phosphorous curing agent and the phosphorus-containing one the widest range of demand for various level of flame retardancy can be fulfilled.

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