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Intrinsically flame retardant epoxy resin – Fire performance and background – Part II

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ABSTRACT

The flame retardant mechanism of a newly synthesized phosphorus-containing reactive amine, which can be used both as crosslinking agent in epoxy resins and as flame retardant, was investigated. The mode of action and degradation pathway were investigated by in situ analysis of the gases evolved during the degradation by thermogravimetric measurements coupled online with infrared (TG-EGA–FTIR) and mass spectroscopy (TG/DTA-EGA–MS) and by solid residue analysis by infrared (ATR) spectroscopic methods and X-ray photoelectron spectroscopy (XPS). It was observed that the main difference in the degradation of the reference and the flame retardant system is that the degradation of the latter begins at lower temperature mainly with the emission of degradation products of the phosphorus amine, which act as flame retardants in the gas phase slowing down the further degradation steps. At the high temperature degradation stage the solid phase effect of the phosphorus prevails: the formation of phosphorocarbonaceous intumescent char results in a mass residue of 23.4%. The ratio of phosphorus acting in gas phase and solid phase, respectively, was determined on the basis of thermogravimetric and XPS measurements.

1. Introduction

Epoxy resins have been commercially available for 60 years and have found use mainly in industrial applications where their exceptional characteristics such as good adhesion to many substrates; moisture, solvent and chemical resistance; low shrinkage on cure; outstanding mechanical and electronic resistance properties justify their higher costs compared to other thermosets. They are widely used as adhesives, surface coatings, laminates and matrix materials in electronic, transport and aerospace industries, however their thermal and fire resistance needs to be improved in many applications. Fire retardancy, as an outstanding requirement of safety, is one of the key challenges for society in our century. The increasing focus on the health and environmental compatibility of flame retardants has drawn the attention to the organophosphorous reactive flame retardants [1–3]. The new European Directive 2002/95/EC [4], 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 in the market from 1 July 2006, also facilitates the development and increased use of phosphorus flame retardants. In the 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 of them. 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 the current literature an increasing number of papers deal with the mode of action of reactive organophosphorous flame retardants in an epoxy resin matrix [3,5,6], however there are no references dealing with the degradation of aliphatic epoxy resin systems. Earlier studies focus on aromatic epoxy and aromatic phosphorus compounds such as DOPO and derivatives. Concerning the mode of action of organophosphorous flame retardants both condensed phase and gas phase actions have been reported, but only few systematic studies are available taking into account the chemical structure of the phosphorus compound, the chemical environment, and the interaction with the polymer matrix during

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degradation. Hergenrother et al. [6] found that with increasing oxidation state of phosphorus the condensed state action is increasing. Similarly, Braun et al. [3] observed that decreasing the oxidation state of phosphorus resulted in an increase of the flame retardancy, which was supposed to be explained by the increasing gas phase action. Nevertheless, no reference was found dealing with the determination of the ratio of phosphorus acting in solid phase and gas phase, respectively.

In this work the mode of action and degradation pathway of an aliphatic epoxy resin system was investigated by analysis of the gases evolved during the degradation by thermogravimetric measurements coupled with infrared and mass spectroscopy and by solid residue analysis by infrared spectroscopic methods and X-ray photoelectron spectroscopy. The ratio of phosphorus acting in the gas phase and solid phase, respectively, was determined on the basis of thermogravimetric and XPS measurements. The better understanding of the degradation mechanism is crucial for further improving the fire retardant performance of epoxy networks.

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/cm^3, hydrolysable chlorine content: 1.5 mass%) used 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/cm^3; 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.

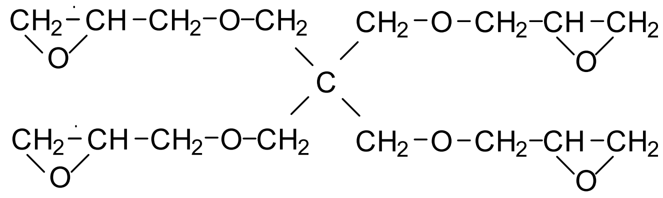
A newly synthesized phosphorus-containing reactive amine, TEDAP (amine number: 510–530 mg KOH/g; viscosity at 20 °C: 400 mPa s; curing time: 7 days at 25 °C, 4 h at 80 °C) (Scheme 3) was used as flame retardant [7].

2.2. Methods

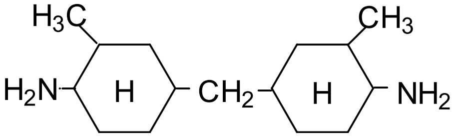
Preparation of epoxy resin samples: the epoxy and curing agent amine components were mixed at room temperature in a glass beaker in order to obtain a homogenous mixture. A silicone mould 120 mm long, 15 mm wide and 3 mm thick was used for preparing the cured samples.

The fire resistance was characterized by Limiting Oxygen Index measurement (LOI, according to ASTMD 2863), UL-94 test (according to ASTM 1356-90 and ANSI//ASTM D-635/77), Mass Loss Calorimeter (according to ISO 13927, Fire Testing Technology, heat flux of 50 kW/m^2), and Glow Wire Flammability Index test (GWFI, PTL DR. GRABENHORST, D-8652 Stadtsteinach, T03.34 type apparatus, according to IEC 60695-2-12).

The thermal treatment of the cured epoxy resin samples was done in the furnace of a TA Instruments AR2000 type rheometer. The temperature program consisted of a linear part with a heating rate of 10 °C/min from room temperature to the appropriate temperature (in the temperature range of 200–400 °C) and a subsequent 10 min isotherm part at the final temperature.



Scheme 1. Main component of Eporezit AH-16.



Scheme 2. Main component of Eporezit T-58.

The attenuated total reflection infrared (ATR-IR) spectroscopic measurement of the epoxy resin samples after thermal treatment was done on a Labram type ATR-IR apparatus (Jobin Yvon, France). The IR spectra were processed using LabSpec 4.02 software.

The gases evolved during thermal degradation of the epoxy resin were analysed using coupled techniques:

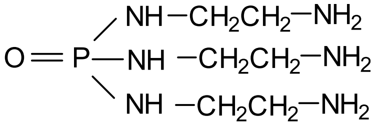
TG/DTA–MS: A TA Instruments SDT 2960 apparatus was coupled with Balzers Instruments Thermostar GSD 300 T3 type mass spectrometer (detector: Quadrupole CH-TRON, operating methods: SCAN, MID). The coupling element was a quartz transfer tube heated to 200 °C. First, mass spectra of the evolved gaseous mixtures were continuously scanned and collected between $m/z = 1–200$ (SCAN-mode), then 64 mass/charge numbers were selected and their ion currents were monitored in Multiple Ion Detection (MID) mode with the measuring time of 0.5 s for each channel. Samples with initial mass of 7–11 mg were heated in an open Pt crucible. The temperature program consisted of a linear part with a heating rate of 10 °C/min from 20 °C to 600 °C in air.
TG–FTIR: TGA 2050 type thermogravimetric analyzer was coupled to a Bio-Rad Excalibur Series FTS 3000 type FTIR spectrophotometer with external gas cell heated to 180 °C. The temperature program consisted of a linear part with a heating rate of 10 °C/min from 20 °C to 600 °C in air. Samples with initial mass of 42–110 mg were heated in open Pt crucible.

For performing an elemental analysis of the pyrolysis residues X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Kratos XSAM 800 type spectrometer (15 kV, 15 mA) using 1253,6 eV energy characteristic X-ray of Mg K$\alpha_{1,2}$ radiation. It was focused on a spot having a diameter of ~2 mm. The general spectra were taken with an energy step of 0.5 eV steps up to 1250 eV, while the detailed spectra were taken in 0.1 eV steps.

3. Results

The flame retardancy of the AH-16–T-58 reference epoxy resin and the flame retarded AH-16–TEDAP system was compared in detail in the previous article of the authors [7]. In this paper, after a short summary of flame retardancy results, we compare the degradation mechanisms of the two systems and investigate the mode of action of the organophosphorous flame retardant.

The synthesized phosphorus-containing amine, TEDAP is suitable for substitution in place of 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 HB UL-94 rating of the reference epoxy



Scheme 3. Structure of the synthesized phosphorus-containing reactive amine, TEDAP.

resin. The peak of heat release was reduced from 960 kW/m^2 to 110 kW/m^2 compared to the non-flame retarded epoxy resin, furthermore the time to ignition increased from 49 s to 98 s, which increases the time to escape in case of a fire.

The aim of this study was to find a reason behind the excellent flame retardant properties of the synthesized phosphorus-containing amine in an aliphatic resin matrix and to make a contribution to understanding the mode of action of organophosphorous flame retardants in epoxy resins in general and extending the knowledge to aliphatic epoxy resin systems.

3.1. TG/DTA–MS and TG–FTIR in situ analysis of the evolved gases (EGA) during thermal degradation

The gases evolved during thermal degradation of epoxy resin were analysed using coupled techniques. The chemical structure of the epoxy resin is different from those that have been studied earlier, therefore not just reference data but also new information was expected from the analysis of pristine epoxy.

The degradation of the two epoxy resin systems studied was divided into temperature regions which are demonstrated in Figs. 1 and 2 showing the TG and dTG curves of the TG/DTA–MS measurements.

According to these results the degradation of the TEDAP-containing epoxy resin begins at about 100 °C lower temperature than the reference system, however the maximum value of derivative mass loss (dTG) is 5× lower than in case of the reference system. After the main degradation (250–350 °C) step there is a plateau-like part in mass loss (350–480 °C), especially in case of the flame retarded system. This stage is followed by an intensive, high temperature degradation (480–600 °C), the mass residue is 23.4%, while in the case of the reference system amount of residue is almost negligible.

According to the TG/DTA–MS spectra of the gases evolved from the AH-16–T-58 reference epoxy resin sample (Fig. 3) the following can be concluded:

- emission of H_2O (m/z: 18) due to the dehydration of the secondary alcohol in epoxy resin is detected from 270 °C and has a maximum intensity at 295 °C,
- formation of CO_2 (m/z: 44) can be detected from 230 °C and has two maxima at 295 °C and 535 °C,
- the formation of hydrocarbon derivatives (m/z: 55) can be detected from 260 °C and has two maxima at 295 °C and 320 °C,
- emission of ketone derivatives (m/z: 58) starts at 220 °C and reaches its maximum intensity at 290 °C (according to ATR-IR results – see Section 3.2 – the intensity of the C═O signal (~1722 cm^{-1}), probably due to ketene formation in the solid phase, diminishes at 300 °C),
- the formation of HCl (m/z: 36) can be detected from 230 °C and has two maxima at 295 °C and 325 °C (the formation of HCl is due to the ~1.5 mass% hydrolysable chloride content of the AH-16 epoxy component as a residue of its synthesis from epichlorohydrin).

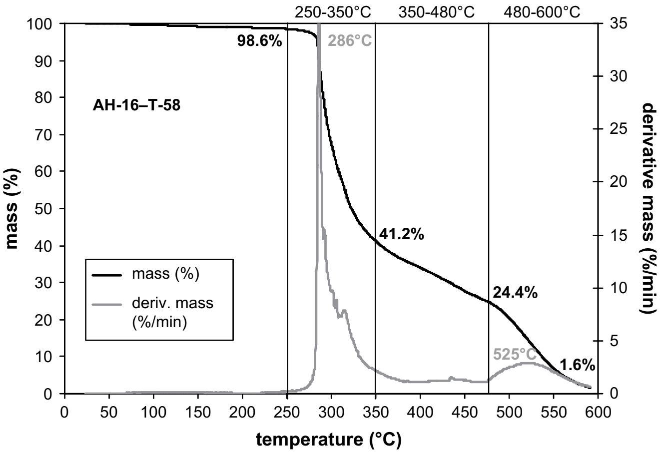


Fig. 1. TG and dTG results of AH-16–T-58 reference epoxy resin system in air.

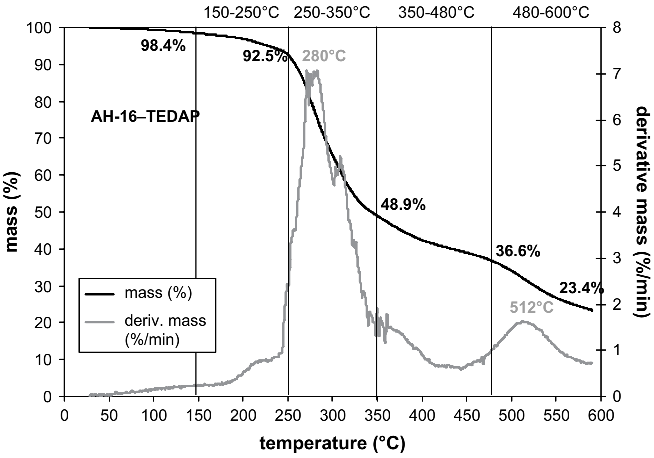


Fig. 2. TG and dTG results of AH-16–TEDAP flame retarded epoxy resin system in air.

Compared to the degradation products of epoxy resins published in the literature [8] in this case, of course, no phenolic derivatives were found and not even their aliphatic analogues (e.g. ethanol) were detected, instead, formation of ketone derivatives was proved. This difference in the degradation pathway is due to the differences in the epoxy resin matrix: in case of aromatic systems the formation of phenolic derivatives results in an increased energy gain by the formation of a more stable aromatic structure than in case of the aliphatic system, where no alcohol formation occurs.

The degradation of aliphatic phosphorus segments in epoxy resins has not yet been studied, thus we compared the TEDAP cured epoxy resin to the AH-16–T-58 reference.

According to the TG/DTA–MS spectra of the gases evolved from AH-16–TEDAP flame retarded epoxy resin sample (Fig. 4) the following can be concluded:

- emission of H_2O (m/z: 18) due to the dehydration of the secondary alcohol in epoxy resin is detected from 220 °C and has a maximum intensity at 280 °C,

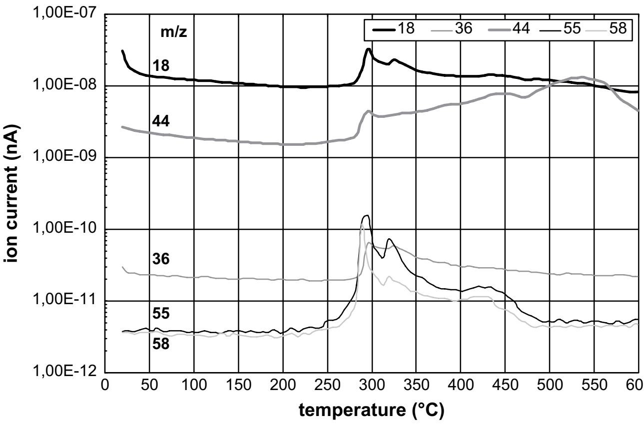


Fig. 3. TG/DTA–MS spectra of the gases evolved from the AH-16–T-58 reference epoxy resin sample.

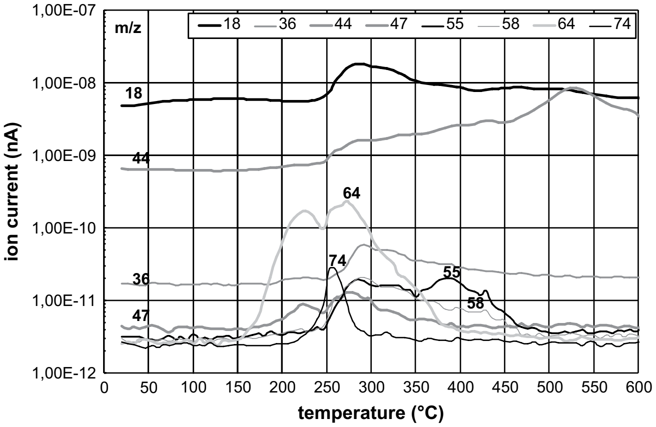


Fig. 4. TG/DTA–MS spectra of the gases evolved from AH-16–TEDAP flame retarded epoxy resin sample.

- formation of CO_2 (m/z: 44) can be detected from 220 °C and has two maxima at 280 °C and 530 °C,
- the formation of hydrocarbon derivatives (m/z: 55) can be detected from 150 °C and has two main maxima at 285 °C at 390 °C,
- at 300 °C, the emission of ketone derivatives (m/z: 58) in the gas phase reaches its maximum intensity (according to ATR-IR – see Section 3.2 – results, the intensity of C═O signals (~1729 cm^{-1}), probably due to ketene formation in the solid phase, diminishes at this temperature),
- the formation of diethyl ether (m/z: 74) was detected in the temperature region of 210–300 °C and has a maximum at 260 °C,
- phosphorus is not only active in the solid phase, but also in the gas phase: the P═O fragment (m/z: 47) of TEDAP appears already at 160 °C in the gas phase and has two maxima at 225 and 280 °C,
- the formation of HCl (m/z: 36) can be detected from 185 °C and has a maximum at 290 °C (as mentioned before, the formation of HCl is due to the 1.5 mass% hydrolysable chloride content of the AH-16 epoxy component). Both in case of the reference and the flame retarded system, the shape of the curves describing the elimination of H_2O and HCl is very similar, which means that the elimination of these small molecules from the secondary alcohol containing site of the epoxy matrix occurs at the same temperature. As the degradation of the flame retarded system occurs at lower temperatures than in case of the reference system, the formation of HCl is also shifted towards lower temperatures.
- formation of ethyl chloride (m/z: 64) can be detected from 150 °C and reaches its maximum intensity at 225 °C and 270 °C.

The gases evolved during thermal degradation of epoxy resin were also analysed by the FTIR technique, which permits rapid and simultaneous measurement of high resolution IR spectra of complex gaseous mixtures. The aim of TG–FTIR measurements was to determine the exact amount of CO and detect or exclude the presence of some low molecular weight and aromatic compounds, whose unambiguous detection was not possible by other means.

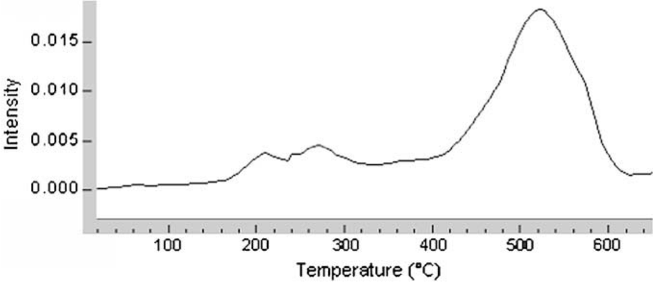


Fig. 5. Gram–Schmidt thermogram of the AH-16–T-58 epoxy resin system determined by TG–FTIR analysis.

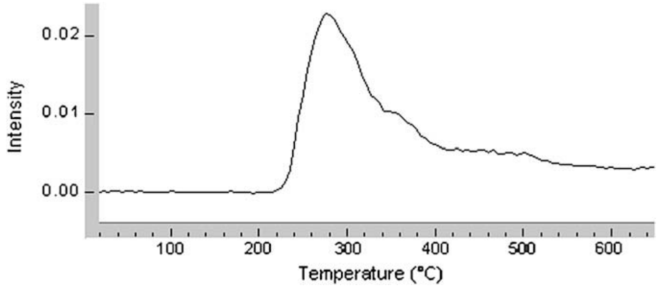


Fig. 6. Gram–Schmidt thermogram of the AH-16–TEDAP epoxy resin system determined by TG–FTIR analysis.

Gram–Schmidt thermograms indicate the overall quantitative distribution of the evolved gases during the thermal degradation (Figs. 5 and 6). Both in the case of the AH-16–T-58 reference epoxy resin system and in the AH-16–TEDAP epoxy resin system evolved gases could be detected from ~200 °C, however in the reference system the maximum of volatile products emission occurred at 520 °C, while in the flame retarded epoxy resin system the maximum was at 270 °C, which means that the phosphorus-containing flame retardant promoted the evolution of gas phase degradation products in the early stage of the degradation.

Furthermore the TG–FTIR technique allowed the determination of the quantitative distribution of CO, which was not possible by the TG/DTA–MS technique due to the overlapping of key ion fragments of CO with other compounds and also the formation of aromatic compounds, HCN and NH_3 could be excluded, based on the lack of the appropriate characteristic signals.

3.2. ATR-IR analysis of the solid residue during thermal degradation

Characterization of the char formed in various stages of combustion is an important step towards complete understanding of the fire retardancy mechanism. The methodology elaborated for analysing charring consists of a heat treatment at different temperatures and a subsequent ATR-IR analysis of the surface of the degraded polymer.

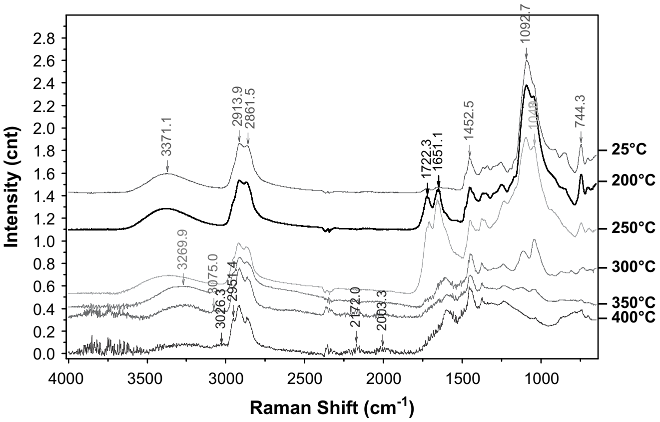


Fig. 7. ATR-IR spectra of the AH-16–T-58 reference epoxy resin system after heat treatment from 25 °C to 400 °C.

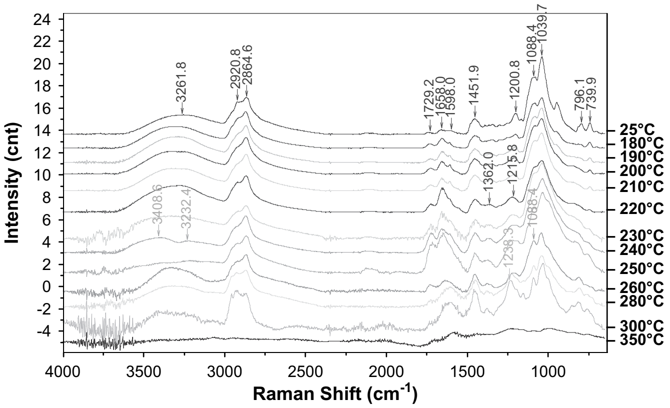


Fig. 8. ATR-IR spectra of the AH-16–TEDAP epoxy resin system after heat treatment from 25 °C to 350 °C.

According to the ATR-IR spectra of the reference epoxy resin AH-16–T-58 (Fig. 7) the following can be concluded:

- the thermal decomposition of the epoxy resin sample begins with the dehydration of the secondary alcohol and formation of C═C double bonds at 200 °C in the solid phase (~ 1651 cm^{-1}) (the changes in the solid phase could be detected earlier than the corresponding gas phase change: according to TG/DTA–MS results the evolution of H_2O could be detected only from 270 °C, whereas the maximum intensity of the C═C double bound signal in the solid phase is at 250 °C),
- the intensity of C═O signals (~ 1722 cm^{-1}) starts to increase at 200 °C, most probably due to ketene formation in the solid phase, at 300 °C this signal diminishes,
- from 250 °C the intensity of out of plane –CH bond (~ 744 cm^{-1}) is gradually decreasing, probably due to the splitting off of the –CH_3 group in the T-58 amine hardener,
- the intensity of C–O–C ether signal (~ 1093 cm^{-1}) is decreasing as the degradation occurs, while the signal of the alcoholic C–O bond (~ 1043 cm^{-1}) is collaterally increasing; above 300 °C the intensity of both starts to decrease and diminishes at 400 °C,
- at 300 °C the signal of the H-bonded –OH groups (~ 3371 cm^{-1}) disappears and the signal of the secondary –NH groups at ~ 3270 cm^{-1} replaces it,
- above 350 °C the double bond formation (~ 2172 cm^{-1} C═N, N═N; ~ 3075 cm^{-1} C═C), aromatization processes (~ 3026 cm^{-1} vinyl-benzene) and chain splitting of the aliphatic chains (~ 2955 cm^{-1}) –CH_3 occur in the solid residue.

According to the ATR-IR spectra of the AH-16–TEDAP flame retarded epoxy resin sample (Fig. 8) the following can be concluded:

- the thermal decomposition of the epoxy resin sample begins with the dehydration of the secondary alcohol and formation of C═C double bonds, which can be detected at 180 °C in the solid phase (~ 1658 cm^{-1}) (the changes in the solid phase could be detected earlier than the corresponding gas phase change: in the gas phase according to TG/DTA–MS results the emission of H_2O is detected from 220 °C, where the signal of C═C double bonds has a maximum intensity),
- the C═O signal (~ 1729 cm^{-1}) can be detected also at 180 °C, its intensity starts to increase significantly at 230 °C, most probably due to ketene formation in the solid phase, at the 300 °C this signal diminishes,
- the intensity of the C–O–C signal (~ 1088 cm^{-1}) is gradually decreasing until 240 °C, then the intensity starts to increase again, which can be ascribed to the splitting of the C–O–C bond and the consequent ether formation,
- there is an interesting phenomenon at 240 °C: instead of the broad signal of NH_2 (~ 3260 cm^{-1}) two peaks appear at ~ 3232 cm^{-1} and ~ 3408 cm^{-1}, the first one is the original amine peak, while the latter can be ascribed to the formation of the –OH groups when the C–O–C bond splits,
- the signal of P═O is shifted from ~ 1200 cm^{-1} (N_3P═O in TEDAP) to ~ 1215 cm^{-1}, which can be ascribed to the splitting of P–N bonds in TEDAP and reaction with the formed alcohols

Table 1
Summary and correlation between the evolved gas and solid residue analyses

Evolved gases, detected fragments	AH-16–T-58 gas phase		AH-16–TEDAP gas phase		Change in solid phase	AH-16–T-58 solid phase		AH-16–TEDAP solid phase	
	Start (°C)	Peaks (°C)	Start (°C)	Peaks (°C)		Temperature (°C)	Change	Temperature (°C)	Change
H_2O	270	295	220	280	C═C	200–	↑	180–	↑
					OH H-bonded	–300	↓	240	↑
CO_2	230	295, 535	220	280, 530					
CO	270	285	230	245, 510					
Hydrocarbon derivatives	260	295, 320	150	285,390	–CH_3	350–	↑	300–	↑
					–CH	250–	↓		
P═O from TEDAP	–	–	160	225, 280	N–P═O	–		220–	↓
					C–P═O	–		220–	↑
					P–N–C			220–	↓
Ketone derivatives	220	290	190	300	C═O	200–300		180–300	↑↓
					C–O–C	250–400	↓	–240	↓
								240–	↑
					C–O	250–300	↑↓		
					NH sec H-bonded	300–	↑		
					C═N, N═N	350	↑	300	↑
					C_6H_5–CH═CH_2	350	↑	–	
HCl from AH-16	230	295, 325	185	290					

Explanations: ↑ increase, ↓ decrease.

Table 2
Summary of main changes during the degradation steps of epoxy resin systems

Mass loss	AH-16–T-58			AH-16–TEDAP		
	Temperature region (°C)	Integrated mass variation (%)	Gases evolved	Temperature region (°C)	Integrated mass variation (%)	Gases evolved
Initial	−250	−1.4	Negligible effects	150–250	−7.5	P-containing gases
Main	250–350	−58.8	- H_2O - CO_2 - CO - Ketone deriv. - Hydrocarbon deriv.	250–350	−51.1	- H_2O - CO_2 - CO - Ketone deriv. - Hydrocarbon deriv. - P-containing gases
Subsequent	350–480	−75.6	Slow-up of volatile evolution	350–480	−63.4	Slow-up of volatile evolution
High temperature	480–600	−98.4	- CO_2 - CO	480–600	−76.4	- CO_2 - CO

to form P–O bonds instead of P–N bonds; this is also indicated by the decreasing intensity of the P–N–C bond ($\sim$740 cm^{-1}) signal,
- according to the more and more sharp shape of the C–O–C ($\sim$1088 cm^{-1}) and P–N–C ($\sim$1040 cm^{-1}) signals, it can be concluded that after 220 °C the absorption bands differentiate, which means that the degree of ordering increases and more regular structure is formed during the degradation process until 300 °C,
- above 300 °C double bond formation ($\sim$2170 cm^{-1} C$=$N, N$=$N) and chain splitting of the aliphatic chains ($\sim$2950 cm^{-1} –CH_3) occur in the solid residue.

3.3. *Discussion*

On the basis of the current volatile product, solid residue and mass loss result studies, models are postulated and summarized for the degradation of the AH-16-T-58 and AH-16–TEDAP epoxy resin systems. First correlation was established between the results of the evolved gas and solid phase analyses, then the main changes during the degradation of epoxy resin systems were summarized according to degradation temperature regions.

The correlation between the changes in gas phase and solid phase is summarized in Table 1.

In some cases there is a shift in temperature and the changes are detected earlier in solid phase than is the appropriate gas evolved (e.g. C$=$C formation in solid phase – H_2O evolved in the gas phase), but in general the solid phase results confirm and help to give an explanation of gas phase results.

The degradations of the reference and flame retarded epoxy resins are compared in Table 2.

According to these results the main difference in the degradation of the reference and the flame retardant system is that the degradation of the TEDAP-containing epoxy resin begins about 100 °C lower mainly with the emission of the degradation products from TEDAP: the TG/DTA–MS results indicate the presence of PO radicals in the gas phase. In TEDAP the P atom in the P$=$O fragment is chemically bound to three N atoms and not to C or O atoms as in most organophosphorous flame retardants. Therefore the evolution of PO-containing species is facilitated because the binding energy of C–N bonds is lower than that of the C–C and C–O bonds [3]. The mentioned P-containing species act as flame retardant in the gas phase slowing down the further degradation steps: the maximum value of derivative mass loss (dTG) is 5× lower than in case of the reference system. After the main degradation step the mass loss curve roughly takes the form of a plateau (Figs. 3 and 4). In the case of the flame retarded system this plateau is much higher and has a lower gradient, because the mass loss is significantly lower and the rate of mass loss is slower than in case of the reference system due to the solid phase action of phosphorus. This stage is followed by an intensive, high temperature degradation, where the solid phase effect of the phosphorus is prevailing: the amount of emitted phosphorus-containing gases is negligible, and the formation of phosphorocarbonaceous intumescent char results in a mass residue of 23.4% in the TG, while in the case of the reference system the amount of residue is negligible.

According to these statements it can be concluded that the outstanding flame retardancy results are due to the effect of phosphorus in both gas and condensed phase. Initially the gas phase action of phosphorus is crucial for slowing down the resin degradation before ignition and thus increasing the time to ignition to double of the original value. During high temperature degradation the solid phase action of phosphorus results in reduction in the rate and extent of char oxidation. As a result, the peak of heat release rate decreased to 1/10 of the original value and mass residue is significantly increased.

In order to determine the ratio of phosphorus acting in gas phase and solid phase, respectively, supplementary XPS measurements of the char residue of mass loss calorimeter measurements were done to determine the elemental composition of the remaining char (Tables 3 and 4). The mass residue of the TG

Table 3
XPS results of solid residue of AH-16–T-58 sample after cone heater treatment compared to the original mass concentration of the same material disregarding H

Peak	Position BE (eV)	FWHM (eV)	Raw area (CPS)	RSF	Atomic mass	Atomic conc. (%)	Mass conc. (%)	Original mass conc.[a] disregarding H[b] (%)	Relative change in mass conc. (%)
O 1s	530.3	3.9	2930.2	0.7	16.0	13.22	16.68	28.91	−42.31
N 1s	396.4	3.2	1104.0	0.5	14.0	7.26	8.02	3.37	138.27
C 1s	282.0	2.1	7615.6	0.3	12.0	79.52	75.31	67.72	11.21

[a] Calculated according to the sample composition determined on the basis of epoxy equivalent and amine number.
[b] H was disregarded in order to obtain comparable data with XPS results.

Table 4
XPS results of solid residue after cone heater treatment of AH-16–TEDAP sample compared to the original mass concentration disregarding H

Peak	Position BE (eV)	FWHM (eV)	Raw area (CPS)	RSF	Atomic mass	Atomic conc. (%)	Mass conc. (%)	Original mass conc.[a] disregarding H[b] (%)	Relative change in mass conc. (%)
O 1s	532.3	3.0	6589.2	0.7	16.0	22.80	27.05	30.95	−12.59
N 1s	399.7	2.7	900.9	0.5	14.0	4.54	4.72	10.26	−54.01
C 1s	284.6	2.0	8760.5	0.3	12.0	70.16	62.49	55.00	13.61
P 2p	134.2	2.0	519.9	0.5	31.0	2.50	5.74	3.79	51.56

[a] Calculated according to the sample composition determined on the basis of epoxy equivalent and amine number.
[b] H was disregarded in order to obtain comparable data with XPS results.

measurements was not sufficient for XPS analysis, therefore, a homogenized sample was taken from the broken char residue from the mass loss calorimeter measurements.

First of all, it has to be mentioned that the differences between the two epoxy resin systems are clearer in the case of mass loss calorimeter measurements (sample mass: 48 g), where the conditions are closer to real fire conditions, than in the case of TG measurements in air (sample mass: 10 mg). The mass residue of the TEDAP-containing system increased from 23.4% to ∼50% due to upscaling, while the mass residue value of the reference remained approximately the same under both circumstances.

The differences in the original elemental compositions are well-marked (Tables 3 and 4): the flame retarded system contains 10.26% N, acting as spumific agent and 3.79% P responsible for acid formation during the degradation, both are essential components in intumescent flame retardancy. On the other hand, the reference epoxy resin only contains 3.37% N.

According to the XPS results it can be concluded that in the AH-16–T-58 sample a significant enrichment in N and depletion in O was observed, however as the mass residue of the reference is negligible, it has no noteworthy effect. In case of AH-16–TEDAP sample, depletion in both N and O was observed. Due to charring, in both cases enrichment in C was detected, while in the flame retarded system the P-content also increases by approximately 50%. Considering that in this case the mass loss calorimeter measurement residue is ∼50% of the original mass, it can be concluded that approximately 75% of the originally present P stays in the solid phase, while 25% of it acts in the gas phase, which is in accordance with the IR analysis of the solid residue and TG/DTA–MS and TG–IR analysis of the evolved gases during thermal degradation.

4. Conclusions

This study aimed at making a contribution towards the better understanding of the behaviour of reactive phosphorus-containing flame retardants in aliphatic epoxy resins by determining their role in different degradation steps and the exact ratio of phosphorus acting in the gas phase to that in the solid phase.

It was determined that the main difference in the degradation of the reference and the flame retardant systems is that the degradation of the epoxy resin containing the synthesized phosphorus-containing reactive amine (TEDAP) begins at a temperature which is about 100 °C lower than that of unmodified one, mainly with the emission of degradation products of TEDAP (PO radicals), which was shown by the TG–MS coupled technique. The evolved phosphorus-containing gases act as flame retardant in the gas phase slowing down the further degradation steps: the maximum value of derivative mass loss is 5× lower than in case of the reference system.

It was stated that at high temperature degradation stage the solid phase effect of the phosphorus prevails: the amount of emitted phosphorus-containing gases is negligible, while the formation of phosphorocarbonaceous intumescent char results in a mass residue of 23.4% in TG, whereas in case of the reference system the amount of residue is basically negligible. The enrichment of the intumescent char in carbon and phosphorus was proved by XPS measurements.

Based on the mass loss and XPS results of the solid residue, it was determined that ∼25 mass% of the originally introduced phosphorus acts in gas phase, while the other 75 mass% stays in the solid phase. It was concluded that this double effect of phosphorus is the reason for the outstanding flame retardancy of the AH-16–TEDAP system: at the beginning the gas phase action of phosphorus is responsible for the increase in the time to ignition, while at high temperature the solid phase action results in a reduction of the peak of heat release rate and an increased mass residue.

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