

Effect of Phosphorus Flame Retardants on the Flammability of Sugar-based Bioepoxy
Resin

Szolnoki B., Toldy A., Marosi Gy.

Accepted for publication in Phosphorus Sulfur and Silicon and the Related Elements

Published in 2019

DOI: [10.1080/10426507.2018.1539855](https://doi.org/10.1080/10426507.2018.1539855)

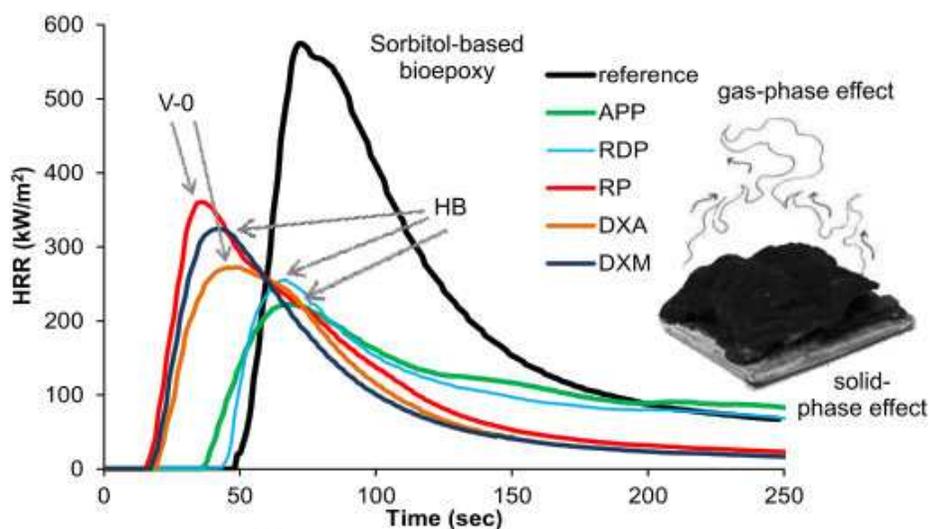
Effect of Phosphorus Flame Retardants on the Flammability of Sugar-based Bioepoxy Resin

Beáta Szolnoki¹, Andrea Toldy², György Marosi¹

¹ Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, Budapest, Hungary

² Department of Polymer Engineering, Budapest University of Technology and Economics, Budapest, Hungary
bszolnoki@mail.bme.hu

GRAPHICAL ABSTRACT



Abstract The flame retardancy of sorbitol-based epoxy resin is targeted. From the bioepoxy 3% phosphorus-containing matrix samples were prepared. Surprisingly, only HB classification of UL-94 test was reached with the application of ammonium polyphosphate (APP) and resorcinol bis(diphenylphosphate) (RDP). V-0 was reached in the case of red phosphorus (RP) and ammonium salt of DOPO (DXA), while the melamine salt resulted in HB rating, due to the lower P-content of the sample. In the meantime, the highest LOI value was reached in the case of APP. The V-0 red phosphorus composition, however, has an LOI of as low as 25 V/V%. In the case of the thermogravimetric analysis, the application of red phosphorus resulted in significantly increased thermal stability, but faster degradation than in the case of the reference. The RDP showed somewhat decreased stability, due to the less stable phosphorus ester bonds. The amount of the charred residues is increasing with the flame retardant content, but to different extents depending on the type of flame retardant. The highest values were reached with APP. Regarding the cone calorimeter results; the lowest heat release rate belongs to the APP-containing sample, while the V-0 compositions (RP and DXA) show poorer performance in this respect.

Keywords Flame retardancy; Phosphorus flame retardants; Bioepoxy resin

Received xx yyyy 2018; accepted xx yyyy 2018, International Conference on Phosphorus Chemistry 2018

Beáta Szolnoki acknowledges the financial support received through the PREMIUM post-doctorate research program of the Hungarian Academy of Sciences. Andrea Toldy acknowledges the financial support received through the János Bolyai Scholarship of the Hungarian Academy of Sciences. This research was supported by the Hungarian Research Fund (OTKA K120592 and OTKA K112644), and the Higher Education Excellence Program of the Ministry of Human Capacities in the framework of the Water science & Disaster Prevention research area of the Budapest University of Technology and Economics (BME FIKP-VÍZ).

INTRODUCTION

The need for the development of polymers originating from renewable sources and being recyclable, or more favorably biodegradable at the end of their life-cycle, is increasing with the decreasing amount of the mineral oil stock and with the spreading of the environmental awareness. Epoxy resins are widely used in different industries due to their favorable properties (e.g. chemical mechanical and electrical resistance, stiffness), especially in those cases, where their relatively high price is balanced by their technological advantages (e.g. electronic industry, transportation). However, the main disadvantage of the bioepoxy matrices, as well as the mineral oil-based ones, is the flammability of the organic matrix.

The use of halogen-containing flame retardants needs to be decreased due to environmental reasons¹. Their most promising substitutes are the phosphorus-containing flame retardants as the P element exists in various oxidation states, resulting in extremely wide and versatile possibilities²⁻⁵. Phosphorus-containing flame retardants can act both in the solid^{6,7} - and the gas phase^{4,8}. The phosphorus-containing gases, produced during combustion, are less toxic than the decomposition products of the halogen-containing flame retardants⁹, and the developing phosphoric acid can react with the degraded polymer, forming a stable charred surface layer. Phosphorus-containing fire retardants are particularly effective in cured epoxy resins, and especially in the most sugar-based bioepoxy resins, as they have a charring effect due to the high concentration of OH-groups.

In this work we aimed at answering both renewability and fire-safety demands: the flame retardancy of a commercially already available, renewable sorbitol-based bioepoxy resin cured with a cycloaliphatic amine hardener was investigated. Environmentally favorable phosphorus flame retardants were applied in different concentrations, so that the epoxy resin samples contained the same amount of phosphorus (1, 2 and 3 mass%, respectively). Several flame retardants were compared including ammonium polyphosphate (APP), resorcinol bis(diphenyl phosphate) (RDP), red phosphorus (RP) and DOPO-derivatives (DXA and DXM). The criteria for the flame retardant selection were: commercial availability, having different physical form (solid/liquid) and showing different mode of action (gas/solid phase action, or their combination). The thermal stability and flame retardant efficacy of the different compositions

was tested by means of thermogravimetric analysis (TGA), UL-94, limiting oxygen index (LOI) and mass loss type cone calorimeter tests, respectively.

RESULTS AND DISCUSSION

LOI and UL-94 tests

The chemical structure of the epoxy resin components and the applied flame retardants can be seen on Figure 1. The LOI values and UL-94 ratings of the reference and flame retarded samples are summarized in Table 1.

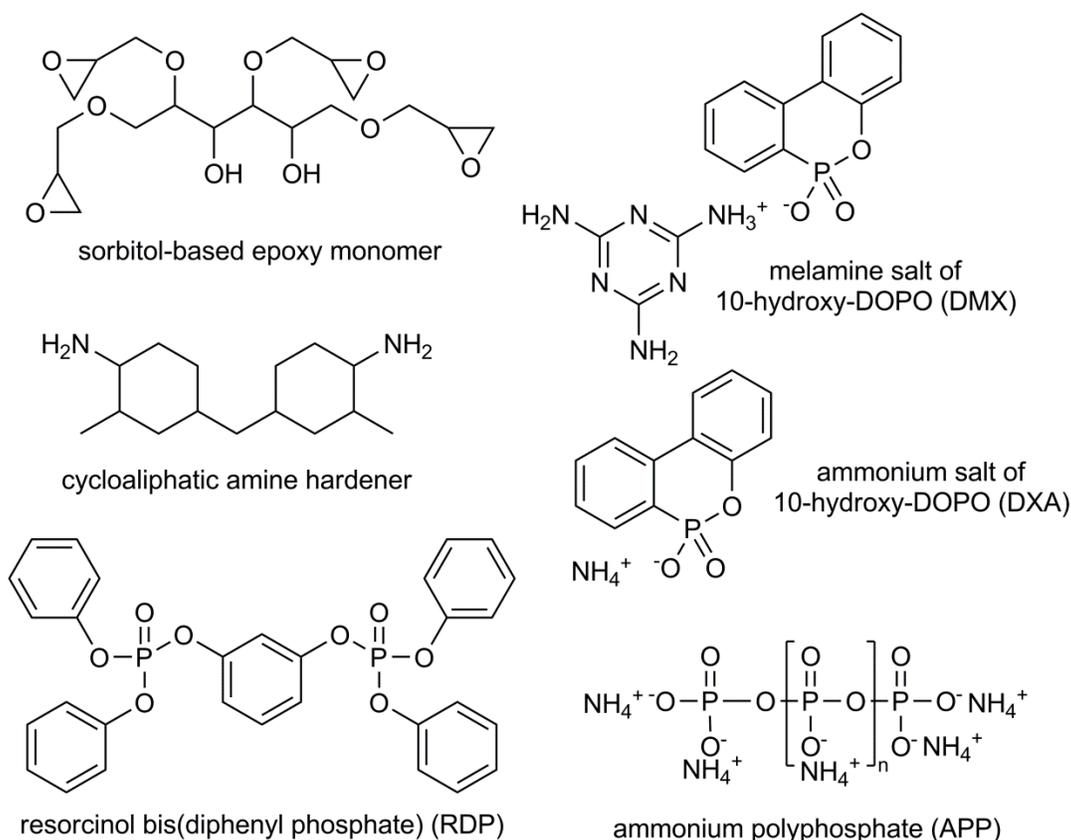


Figure 1 Chemical structure of the epoxy resin components and the applied flame retardants

The LOI value of the samples significantly increases with the addition of flame retardant to the matrix, however, according to the results, the effect of the different types of flame retardants is diverse. In the case of the ammonium polyphosphate (APP), resorcinol bis(diphenyl phosphate)

Received xx yyyy 2018; accepted xx yyyy 2018, International Conference on Phosphorus Chemistry 2018

Beáta Szolnoki acknowledges the financial support received through the PREMIUM post-doctorate research program of the Hungarian Academy of Sciences. Andrea Toldy acknowledges the financial support received through the János Bolyai Scholarship of the Hungarian Academy of Sciences. This research was supported by the Hungarian Research Fund (OTKA K120592 and OTKA K112644), and the Higher Education Excellence Program of the Ministry of Human Capacities in the framework of the Water science & Disaster Prevention research area of the Budapest University of Technology and Economics (BME FIKP-VÍZ).

(RDP) and melamin and ammonium salts of 10-hydroxy-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), the LOI value gradually increases with the increasing P-content, meanwhile, in the case of red phosphorus, there is no significant difference between the samples. This phenomenon suggests that the red phosphorus, which acts only in the solid phase and cannot enter to the combustion zone, is not able to influence the radical processes of the flaming. In the case of the flame retardants with more pronounced gas-phase effect, the measured LOI values are higher, 28-29 V/V%. On the other hand, the highest oxygen index value was reached with the use of the intumescent ammonium polyphosphate, as the formed charred layer effectively hinders the gas transport from the polymer to the combustion zone.

Table 1 LOI and UL-94 results of the reference and flame retarded samples

| Sample | LOI (V/V%) | UL-94 |
|-----------|---------------|----------------------------------------|
| reference | 20 | HB (20 mm/min) |
| APP_1%P | 27 | HB (vertical 1 st ignition) |
| APP_2%P | 30 | HB (vertical 1 st ignition) |
| APP_3%P | 31 | HB (vertical 2 nd ignition) |
| RDP_1%P | 25 | HB (vertical 1 st ignition) |
| RDP_2%P | 27 | HB (vertical 1 st ignition) |
| RDP_3%P | 28 | HB (vertical 2 nd ignition) |
| RP_1%P | 26 | HB (vertical 1 st ignition) |
| RP_2%P | 25 | V-1 |
| RP_3%P | 25 | V-0 |
| DXA_1%P | 25 | HB (vertical 1 st ignition) |
| DXA_2%P | 27 | HB (vertical 2 nd ignition) |
| DXA_3%P | 29 | V-0 |
| DXM_1%P | 27 | HB (vertical 1 st ignition) |
| DXM_2%P | 29 | HB (vertical 2 nd ignition) |

Received xx yyyy 2018; accepted xx yyyy 2018, International Conference on Phosphorus Chemistry 2018

Beáta Szolnoki acknowledges the financial support received through the PREMIUM post-doctorate research program of the Hungarian Academy of Sciences. Andrea Toldy acknowledges the financial support received through the János Bolyai Scholarship of the Hungarian Academy of Sciences. This research was supported by the Hungarian Research Fund (OTKA K120592 and OTKA K112644), and the Higher Education Excellence Program of the Ministry of Human Capacities in the framework of the Water science & Disaster Prevention research area of the Budapest University of Technology and Economics (BME FIKP-VÍZ).

The UL-94 results show no clear tendencies. With the addition of red phosphorus and ammonium salt of DOPO (DXA) V-0 rating was reached, while in the case of DXM the samples burned until the holding clamp. This is attributed to the low P-content of the additive and consequently high amount needed to reach the same phosphorus content of the matrix (see the Experimental): the extremely high viscosity of the DXM_3%P matrix impeded the sample preparation. As a general rule, 3% P-content is sufficient to reach appropriate flame retardancy⁵, thus it was surprising, that neither APP, nor RDP was found to be effective enough to reach V-0 rating. Mixed flame retardant formulations containing both APP and RDP were also prepared with 3% P-content¹⁰. It was found, that due the balanced solid- and gas phase mechanism of the combined flame retardant composition a synergistic effect reveals between the solid, intumescent-type flame retardant (APP) and the liquid RDP (which acts mainly in the gas phase as radical scavenger), resulting in a LOI value of 34 V/V% and V-0 rating¹⁰.

Thermogravimetric analysis

The thermal stability of the reference and 3% P-containing samples was determined by thermogravimetric analysis. The measured mass reduction as a function of temperature is shown on Figure 2. The thermally less stable formulation is the RDP-containing one, due to the less stable phosphorus ester bonds present in the molecule; its degradation starts at a temperature 15°C lower than the reference, while that of the red phosphorus-containing sample starts at around a temperature 20°C higher than the other samples, in this case with a sudden mass decrease, similarly to the reference resin. In the case of the other formulations the degradation process is more prolonged, especially in the case of ammonium polyphosphate. Due to the effect of the flame retardants (except RDP), the temperatures belonging to 50% mass decrease increased, which can be attributed to the degradation delaying effect of the flame retardants.

Received xx yyyy 2018; accepted xx yyyy 2018, International Conference on Phosphorus Chemistry 2018

Beáta Szolnoki acknowledges the financial support received through the PREMIUM post-doctorate research program of the Hungarian Academy of Sciences. Andrea Toldy acknowledges the financial support received through the János Bolyai Scholarship of the Hungarian Academy of Sciences. This research was supported by the Hungarian Research Fund (OTKA K120592 and OTKA K112644), and the Higher Education Excellence Program of the Ministry of Human Capacities in the framework of the Water science & Disaster Prevention research area of the Budapest University of Technology and Economics (BME FIKP-VÍZ).

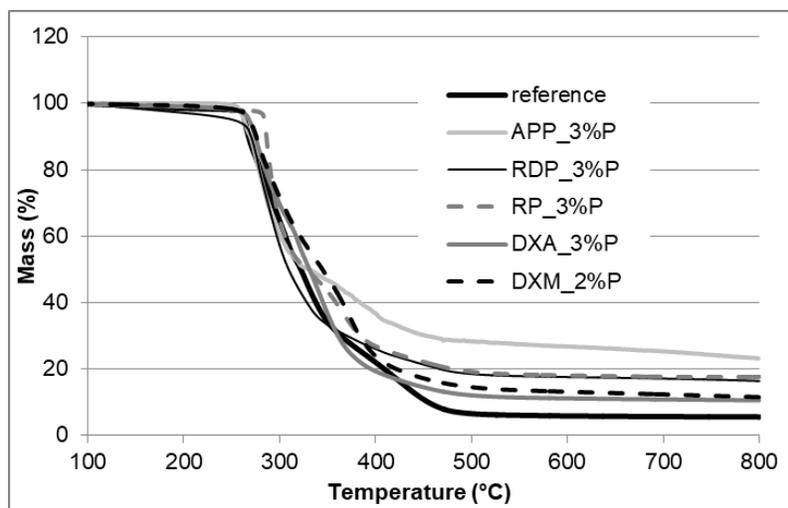


Figure 2 TGA curves of the reference and 3% P-containing samples

The amount of the charred residues at 800°C is increased in case of all types of flame retardants. The addition of the DOPO-derivatives resulted in doubled amount of residue, i.e. around 10% instead of 5% for the reference. The red phosphorus (RP) and the resorcinol bis(diphenylphosphate) (RDP)-containing samples reached almost the same result, however, due to different reasons. The pure solid-phase effect of the RP obviously produces high amount of char, meanwhile although RDP has significant gas-phase effect^{10,11,12}, its aromatic structure promotes the char formation resulting in high amount of residue. The highest residue belongs to the intumescent APP (23%).

Mass Loss Calorimetry

The mass loss calorimetry measurements are used for the determination of complex properties of the combustion, i.e. heat release rate (HRR), time to ignition, etc. The recorded HRR curves are displayed on Figure 3. Based on the results, it can be stated that the peak of heat release rate decreases by 30-50% due to the incorporation of flame retardants to the matrix. Despite the V-0 rating in UL-94 measurements, the most modest effect was observed in the case of red phosphorus. The DOPO-derivatives showed somewhat better flame retardant efficacy, but the best result was reached in the case of the APP containing sample.

Received xx yyyy 2018; accepted xx yyyy 2018, International Conference on Phosphorus Chemistry 2018

Beáta Szolnoki acknowledges the financial support received through the PREMIUM post-doctorate research program of the Hungarian Academy of Sciences. Andrea Toldy acknowledges the financial support received through the János Bolyai Scholarship of the Hungarian Academy of Sciences. This research was supported by the Hungarian Research Fund (OTKA K120592 and OTKA K112644), and the Higher Education Excellence Program of the Ministry of Human Capacities in the framework of the Water science & Disaster Prevention research area of the Budapest University of Technology and Economics (BME FIKP-VÍZ).

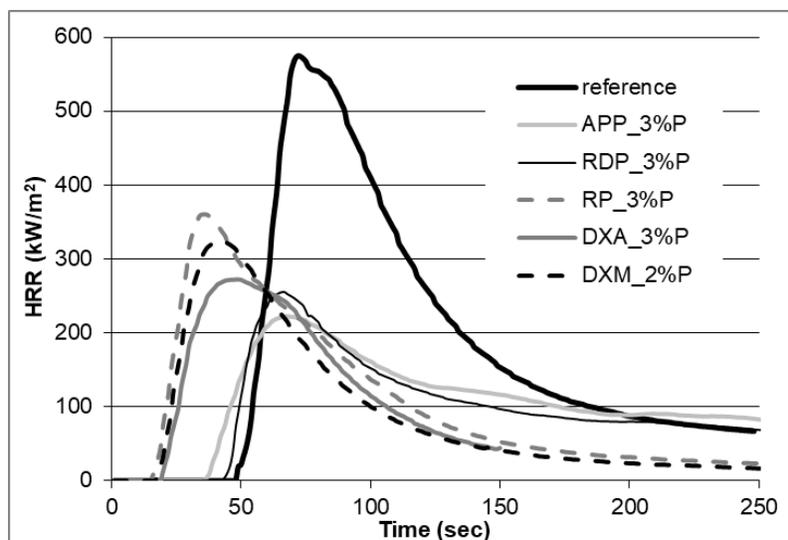


Figure 3 Heat release curves of the reference and 3% P-containing samples

To understand these results, the mode of action of the different flame retardants needs to be taken into account: Although the red phosphorus, acting only in the solid-phase, forms a carbonaceous layer, this layer is not charred as in the case of the ammonium polyphosphate, thus it can be oxidized much easier during the combustion. The ammonium salt of the DOPO acts only in the gas phase according to the manufacturer, thus the flame spreading is slackening by the radical scavenger mechanism. Meanwhile, in the case of DXM, the melamine modifies the char structure, besides the gas-phase effect of the DOPO. The RDP acts mainly in the gas phase, but due to its aromatic structure, it has some solid-phase effect as well.

CONCLUSIONS

From the sorbitol-based bioepoxy 3% phosphorus-containing matrix samples were prepared and tested. To reach the same P-loading, different amounts of flame retardants were added, according to their P-content. Surprisingly, only HB classification of UL-94 test was reached with the application of APP and RDP. V-0 was reached in the case of red phosphorus and ammonium salt of DOPO, while the use of the melamine salt of DOPO resulted in HB classification, due to the lower P-content of the sample. On the other hand, the highest LOI value was reached in the case of APP. The V-0 red phosphorus containing composition, however, has an LOI of as low as 25 V/V%. Regarding the cone calorimeter results, the V-0 compositions (RP

Received xx yyyy 2018; accepted xx yyyy 2018, International Conference on Phosphorus Chemistry 2018

Beáta Szolnoki acknowledges the financial support received through the PREMIUM post-doctorate research program of the Hungarian Academy of Sciences. Andrea Toldy acknowledges the financial support received through the János Bolyai Scholarship of the Hungarian Academy of Sciences. This research was supported by the Hungarian Research Fund (OTKA K120592 and OTKA K112644), and the Higher Education Excellence Program of the Ministry of Human Capacities in the framework of the Water science & Disaster Prevention research area of the Budapest University of Technology and Economics (BME FIKP-VÍZ).

and DXA) show a moderate flame retardant effect, while the lowest peak of heat release rate (equivalent to 60% reduction compared to the reference) belongs to the APP-containing sample.

EXPERIMENTAL

As a bioepoxy matrix sorbitol polyglycidyl ether (trade name Erisys GE-60), received from Emerald Performance Materials, was cured with a cycloaliphatic amine-type hardener (3,3'-dimethyl-4,4'-diaminodicyclohexylmethane (MH3122)), supplied by IpoX Chemicals Ltd. The chosen cycloaliphatic hardener provides a relatively rigid backbone of the cured polymer, resulting in high glass transition temperature of the reference resin (124 °C)¹⁰. As flame retardant additives ammonium polyphosphate (**APP**) (NORD-MIN JLS APP, supplier: Nordmann Rassmann), resorcinol bis(diphenyl phosphate) (**RDP**) (Fyrolflex RDP, supplier: ICL Industrial Products), red phosphorus (**RP**) (RP6500, supplier: Clariant) and two types of DOPO-derivatives (**DXA-12**: ammonium 6H-dibenzo[c,e][1,2]oxaphosphinin-6-olate 6-oxide and **DXM-11**: melamine salt of 10-hydroxy-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, received from Metadynea Austria) were used. The characteristics of the flame retardants are detailed in Table 2.

Table 2 Properties of the flame retardants

| Name | Physical appearance | P-content (%) | Amount needed for 1% P in the matrix (% of the matrix) |
|------|---------------------|---------------|--------------------------------------------------------|
| APP | white powder | 31-32 | 3.2 |
| RDP | yellowish liquid | 10,7 | 9.3 |
| RP | reddish-brown paste | 43-47 | 2.2 |
| DXA | white powder | 12-12.5 | 8.2 |
| DXM* | white powder | 8.4-8.7 | 11.7 |

*Maximum P-content in the matrix was 2% due to the high viscosity of the flame retarded resin

Epoxy resin samples of gradually increasing phosphorus content (1, 2 and 3%) were prepared. The curing procedure consisted of isothermal heat steps: 2 h at 80°C, 2 h at 120°C.

Received xx yyyy 2018; accepted xx yyyy 2018, International Conference on Phosphorus Chemistry 2018

Beáta Szolnoki acknowledges the financial support received through the PREMIUM post-doctorate research program of the Hungarian Academy of Sciences. Andrea Toldy acknowledges the financial support received through the János Bolyai Scholarship of the Hungarian Academy of Sciences. This research was supported by the Hungarian Research Fund (OTKA K120592 and OTKA K112644), and the Higher Education Excellence Program of the Ministry of Human Capacities in the framework of the Water science & Disaster Prevention research area of the Budapest University of Technology and Economics (BME FIKP-VÍZ).

The thermal stability was determined using a TA Q5000 device of TA Instruments in the range of 25-800°C, heating rate: 10 °C/min, N₂ gas flow rate: 30 ml/min. Platinum-HT sample pan was used, the sample size was about 15 mg in each case.

The fire behaviour of the reference and flame retarded systems was characterized by **limiting oxygen index** measurements (LOI, according to ISO 4589). The sample size was 120 mm × 15 mm × 4 mm. Standard **UL-94** flammability tests (according to ISO 9772 and ISO 9773, respectively) were also carried out with a sample size of 120 mm × 15 mm × 4 mm. **Mass loss type cone calorimeter** tests were carried out by an instrument made by FTT Inc. using the ISO 13927 standard method. Specimens (100 mm × 100 mm × 2 mm) were exposed to a constant heat flux of 25 kW/m² and ignited.

REFERENCES

1. <https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32002L0096:EN:HTML> (accessed sept 05, 2018)
2. Lu, S.Y.; Hamerton, I. *Prog Polym Sci*, **2002**, 27, 1661-1712.
3. Shieh, J.-Y.; Wang, C-S. *Polymer*, **2001**, 42, 7617-7625.
4. Braun, U.; Balabanovich, A. I.; Schartel, B.; Knoll, U.; Artner, J.; Ciesielski, M.; Döring, M.; Perez, R.; Sandler, J. K. W.; Altstädt, V.; et al. *Polymer*, **2006**, 47, 8495-8508.
5. Hergenrother, P. M.; Thompson, C. M.; Smith Jr., J. G.; Connell, J. W.; Hinkley, J. A.; Lyon, R. E.; Moulton, R. *Polymer*, **2005**, 46, 5012-5024.
6. Gérard, C.; Fontaine, G.; Bellayer, S.; Bourbigot, S. *Polym Degrad Stabil*, **2012**, 97, 1366-1386.
7. Kandola, B.K.; Horrocks, A.R. *Fire retardant materials*, Horrocks, A.R.; Price, D. eds. Woodhead Publishing Limited: Cambridge, 2001, pp.182-213.
8. Zhang, W.; He, X.; Song, T.; Jiao, Q.; Yang, R. *Polym Degrad Stabil*, **2014**, 109, 209-217.
9. Chung, Y.; Kim, Y.; Kim, S. *J Ind Eng Chem*, **2009**, 15, 888-893.
10. Szolnoki, B.; Bocz, K.; Marosi, G.; Toldy, A. *Polymers*, **2016**, 8, 322.
11. Toldy, A.; Niedermann, P.; Rapi, Z.; Szolnoki, B. *Polym Degrad Stabil*, **2017**, 142, 62-68.
12. Pomázi, Á.; Szolnoki, B.; Toldy, A. *Polymers*, **2018**, 10, 1081

Received xx yyyy 2018; accepted xx yyyy 2018, International Conference on Phosphorus Chemistry 2018

Beáta Szolnoki acknowledges the financial support received through the PREMIUM post-doctorate research program of the Hungarian Academy of Sciences. Andrea Toldy acknowledges the financial support received through the János Bolyai Scholarship of the Hungarian Academy of Sciences. This research was supported by the Hungarian Research Fund (OTKA K120592 and OTKA K112644), and the Higher Education Excellence Program of the Ministry of Human Capacities in the framework of the Water science & Disaster Prevention research area of the Budapest University of Technology and Economics (BME FIKP-VÍZ).