

Retardant treated and untreated upholstery PUR foams comparison based on the thermal analysis and cone calorimetry results

Emília Orémusová¹, Andrea Majlingová^{2*}, Qiang Xu³, Cong Jin⁴

¹ Department of Fire Protection, Technical University in Zvolen, Faculty of Wood Sciences and Technology, T. G. Masaryka 24, 960 01 Zvolen, Slovak Republic; email: emilia.oremusova@tuzvo.sk

² Department of Fire Protection, Technical University in Zvolen, Faculty of Wood Sciences and Technology, T. G. Masaryka 24, 960 01 Zvolen, Slovak Republic; email: andrea.majlingova@tuzvo.sk

³ School of Mechanical Engineering, Nanjing University of Science and Technology, 200 Xiao Ling Wei, 210014 Nanjing, Jiangsu, P. R. China; email: xuqiang@njust.edu.cn

⁴ Nanjing University of Science and Technology, 200 Xiao Ling Wei, 210014 Nanjing, Jiangsu, P. R. China; email: jincong@njust.edu.cn

* Corresponding author: andrea.majlingova@tuzvo.sk

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Abstract

The materials used in the composition of the upholstered furniture are composed of flammable organic materials which may contribute in the case of a fire to its development. In the paper, there are introduced the results of thermal and cone calorimetry analyses and fire hazard assessment for upholstery polyurethane (PUR) foams, which make up a substantial part of the upholstered furniture composition. Among the PUR foams tested belonged soft foam types as KF 5560, DEFLAMO KF 4545 – with reduced flammability, high-elastic V 4010, high-elastic VF 6020 with reduced flammability and standard N 5063. For the evaluation of PUR foams, we chose the thermal analysis methods - thermogravimetry and differential scanning calorimetry, according to STN EN ISO 11358 and STN EN ISO 11357-1, and cone calorimetry method (ISO 5660). The results showed the effect of retardation on the assessment parameters. The samples with retardation treatment achieved better thermal stability than samples without retardation treatment. The lowest standard thermal stability the standard N 5063 PUR5 foam sample achieved. In the differential scanning calorimetry analyses, all the samples showed significant exothermic effect. As the most hazardous in terms of amount of heat released was determined the N 5063 PUR5 foam, which released the largest amount of heat ($4,199.9 \text{ J g}^{-1}$) at temperature of $322.4 \text{ }^\circ\text{C}$. In the second decomposition stage, in temperature range of $449 - 595 \text{ }^\circ\text{C}$, it released heat of $3,099.2 \text{ J g}^{-1}$. The cone calorimetry results showed that from heat release rate (HRR) peak point of view the least fire hazardous was KF 4545 PUR2 foam (363.90 kW m^{-2}), followed by KF 5560 PUR1 foam (390.01 kW m^{-2}), VF 6020 PUR4 foam (417.29 kW m^{-2}), N 5063 PUR5 foam (417.49 kW m^{-2}), and the most fire hazardous was V 4010 PUR3 foam (683.07 kW m^{-2}). Those results were also confirmed by time to ignition, time to HRR peak and total heat release values.

Keywords: PUR foam; thermal analysis; thermogravimetry; differential scanning calorimetry; cone calorimetry

1 Introduction

Combustible insulation materials, such as the commonly used wood and wood-based materials, foams of polyurethane (PU/PUR), polystyrene (PS) and polyisocyanurate (PIR); and constitutes represent potential fire hazards for life and health of residents. Their flammability and fire risk have drawn increasing attention from both scientific and industrial communities. For the residence fire, bedding and upholstered furniture are the first item ignited in roughly 19% of fatal fires [1]. In a white

paper launched at the EU parliament in 2014, entitled “Europe is playing with fire”, Fire Safe Europe called on the European Commission to act to improve fire safety in buildings [2].

When talking about the of fire protection in buildings, the optimal level depends on a large extent on the amount and type of flammable materials and substances that occur in them. As mentioned above, flammable materials, which are relatively common in building sites, include polymeric materials (e.g. wood, wood-based materials, plastics (including polyurethane foams), and linen and upholstery fabrics). Some polymers, especially porous polymers with a large specific surface area, such as polyurethane foam [3-5], fabrics [6-9], and wood [10], burn easily, releasing a large amount of heat, flame and smoke in association with generation of many droplets during the burning process, and thereby threatening people’s lives and property. A progressive approach to reduce the flammability of polymers is to apply the flame retardants.

Recent trends in flame retardancy of polyurethane foams (PUR) and, in general of polymers, have been deeply influenced by regulation requirements and by the concept of "sustainable development" which implies that the fire retardants should present a low impact on human health and environment during the whole life cycle of the polymer; it concerns then also the toxicity and the density of smoke developed during burning of the materials. Therefore, the reduction of the amounts of brominated compounds used in flame retardancy formulations is one of the main aims of the research in this field, although this reduction is not very easy because of their very high effectiveness [11].

Recently, Modesti et al. [11] reviewed and discussed novel halogen-free flame-retardant systems for polyurethane foams. They studied the charring compounds which may lead to the development of different char morphologies: compact, intumescent and "glassy-like" char layers. The advantages and disadvantages of each system on fire behaviour and thermal stability of polyurethane foams was analysed. Attention was put on possible synergistic effects arising from suitable mixing of them. In the flame retardants analyses, there were involved the phosphorus-based compounds (phosphates, elementary phosphorous and novel hypophosphites), intumescent systems (for example expandable graphite) as well as glass precursors like borates, alumino-silicates and glass modifiers. The recent interest in nanocomposites, potential application and benefits of layered silicates on fire behaviour and thermal stability of PUR foams was also reported.

To test the fire and thermal properties of PUR foams several standardized and progressive analytical methods are deployed. Yang and Nelson [12] used cone calorimetry to test the newly developed flame retardants of PUR foams. Hu and Wang [13] applied cone calorimetry (CC), thermogravimetric analyses (TGA) and scanning electron microscopy (SEM) to study the effect of the additives on the physical mechanical property, fire behaviour and thermal stability of PUR, PIR (polyisocyanurate) foams. Chen and Jiao [14] studied smoke suppression properties and synergistic flame-retardant effect on thermoplastic polyurethane (TPU) composites using the smoke density test (SDT), cone calorimeter (CC), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The influence of carbon fillers on the thermal properties of polyurethane foams studied Ciecierska et al. [15]. For the study, they used thermogravimetry analysis (TGA) combined with infrared (IR) measurements. Gao et al. [16] investigated the improved mechanical property, thermal performance, flame retardancy and fibre behaviour of lignin based rigid polyurethane foam nanocomposites using Fourier transform infrared (FTIR) spectroscopy, size exclusion chromatography (SEC), thermogravimetric analysis, differential scanning calorimetry (DSC), limiting oxygen index (LOI) testing and cone calorimetry. Liu et al. [17] studied the thermal stability and pyrolytic gases of a series of flame retarded PIR – PUR foams using the thermogravimetry (TG) and thermogravimetry combined with Fourier transform infrared spectroscopy (TG-FTIR) methods. Besides, they used also Py-GC-MS analyses to study the toxicity of PIR-PUR foams combustion products. Cone calorimetry was applied to determine the heat release rate (HRR). To study the form of combustion products, the scanning electron microscopy (SEM) was used. Thermogravimetric analysis (TGA) combined with FTIR (TG-FTIR), LOI testing, smoke density rating (SDR), cone calorimetry and X-ray photoelectron spectroscopy was used to study smoke and toxicity suppression properties of ferrites on flame-retardant polyurethane-polyisocyanurate foams [18]. Liu et al. [19] also studied the catalysis of boron phosphate on the thermal stability and char forming in flame retarded PUR-PIR foams using the cone calorimetry, thermogravimetric analysis, microscale combustion calorimetry and TG-FTIR-MS methods. Xu et al. [20] conducted two scale tests, microscale

and bench scale to analyse the flammability of a flexible polyurethane foam. Microscale tests included simultaneous thermal analysis coupled to Fourier transform infrared spectroscopy (TG-FTIR) and microscale combustion calorimetry (MCC). Using these methods, they obtained data on evolved gas components, heat release rate per unit mass, total heat release, derived heat release capacity and minimum ignition temperature. Bench scale tests were performed on cone calorimeter to obtain data on peak heat release rate per unit area, effective heat of combustion, minimum incident heat flux for ignition and total heat release per unit area of different incident heat fluxes.

In this paper, there are introduced the methods, procedures and results used to determine the thermal properties of selected types of flame retardant treated and untreated upholstery foams. To determine the thermal properties of the PUR foams the TG/DTG, DSC and CC calorimetry analyses were performed.

2 Material and Methods

The objective of the experiment was to study the differences in fire and thermal properties of selected retardant treated and untreated upholstery PUR foams and to assess the fire based on the thermal analysis and cone calorimetry results.

2.1 PUR foam samples

Among the PUR foams tested belonged soft foam types KF 5560 (PUR1), DEFLAMO KF 4545 (PUR 2) - with reduced flammability, high-elastic V 4010 (PUR3), high-elastic VF 6020 (PUR4) with reduced flammability and standard N 5063 (PUR5).

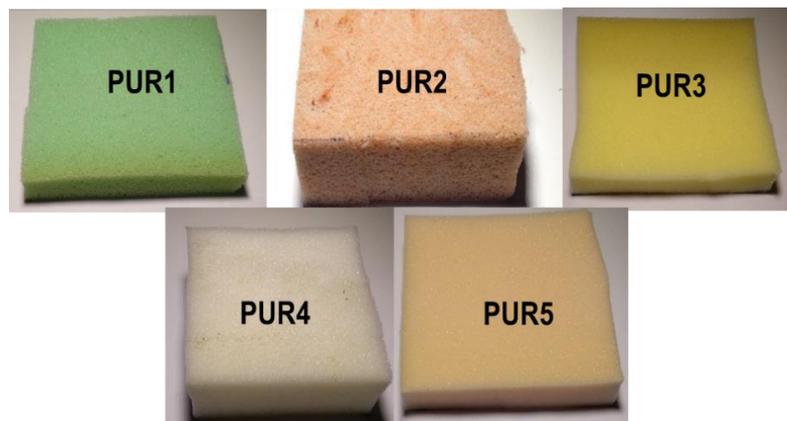


Fig 1. Samples of PUR foams used for testing

In Figure 1, there are introduced the samples used in the analyses. Table1 presents the basic parameters of tested PUR foams.

Tab. 1 Basic parameters of tested PUR foams

Sample	Foam type	Resistance to compression (kPa)	Density (kg m ⁻³)	Note
PUR1 – KF 5560	Comfort	6.0	55	Flame-retardant treated
PUR2 – DEFLAMO KF 4545	Comfort	4.5	45	Flame-retardant treated
PUR3 – V 4010	Viscoelastic	1.0	40	Untreated
PUR4 – VF 6020	Viscoelastic	2.0	60	Flame retardant treated
PUR5 – N 5063	Normal	6.3	50	Untreated

2.2 Methodology

To study the fire and thermal properties of PUR foams, we used the thermal analysis methods – thermogravimetry (TG) and differential scanning calorimetry (DSC), according to STN EN ISO 11358 [21] and STN EN ISO 11357-1 [22], and cone calorimetry method according to ISO 5660 [23].

All the tests were provided in the Accredited Laboratory of the Fire Research Institute of the Ministry of Interior of the Slovak Republic.

In the thermogravimetric analysis (TG / DTG), all samples were tested on a Mettler TA 3000 thermal analyser with the processor TC 10A, and TG 50 thermogravimetric scales, at an air flow rate of 200 ml min⁻¹, heating rate of 10 °C min⁻¹ and under standard test room conditions. The STEP program was used for the measurement of mass loss step changes. The type of temperature sensor Pt100 was used in the heater body of thermogravimetric scales. As a test sample holder, the Mettler MET-24123 corundum (Al₂O₃) crucible was used. Each sample was conditioned for at least 24 hours prior to testing under standard test room conditions. The temperature recording interval was of 35 up to 700 °C. For temperature calibration, materials with given Curie temperatures were used: Isatherm (144.5 °C), Nickel (357.0 °C) and Trafoperm (748.0 °C). During the analysis, the percent mass loss and carbon residue of a test sample was recorded while the samples were being heated at above specified rates in an appropriate environment.

Using the differential scanning calorimetry (DSC), the difference between the heat flux (energy) supplied to the test sample and the reference sample as a function of temperature was measured, while the test and reference samples being exposed to the selected temperature program. All the samples were tested on a Mettler TA 3000 thermal analyser, with the processor TC 10A completed with measurement cell DSC 20, at air flow rate of 50 ml min⁻¹ and at heating rate of 10 °C min⁻¹.

With the DSC method, the changes in the reaction enthalpy of individual samples of PU foams were measured. Within the given temperature range, the reaction heat was determined, and the maximum heat generation rate was characterized by the maximum exothermic peak temperature on the thermo-analytic curve at a temperature range of 35 – 600 °C. There were also obtained the quantitative results such as: maximum peak temperature (T_{MAX}), i.e. maximum deviation temperature of the curve from the baseline; temperature interval, i.e. the interval, in which the individual exothermic / endothermic effects and the amount of heat released from the sample were recorded.

In the thermogravimetric analysis, there was studied the thermal stability of the sample and in the differential scanning calorimetry the change of enthalpy. The evaluation criteria for the thermal analysis were mass loss, carbon residue, initial and final temperatures, enthalpy change, and the amount of heat released. The weight of the samples in the thermal analyses was of 10 ± 2 mg.

To determine the ignition time, peak heat release rate, peak heat release rate time, the effective combustion heat and the total heat released, the cone calorimetry (dual calorimeter) method was used. To test the PUR foam which are thermally thin a special holder was made from stainless steel 9.1 cm × 9.1 cm × 0.3 cm which was placed into the main holder supplied with cone calorimeter. The holder was isolated from its bottom by 5 mm thick layer of kaowool. The samples were wrapped into aluminium foil and isolated from the bottom of the holder by 5 mm layer of kaowool. The centre of the samples was situated 6 cm from the lowest part of the cone heater. The temperature on the regulator of the cone radiator was set at 680 °C which corresponds to the heat flux density of 25 kW m⁻². The thickness of PUR foam samples was of 20 mm (PUR1, PUR4 and PUR5) and of 45 mm (PUR2 and PUR3). The samples were spark ignited. The heat release rate was calibrated by burning of the methane standard. The reproducibility of burning experiments as it concerns the ignition time, heat release rate, mass loss and total smoke production under conditions of piloted ignition was good provided that the holders with sample were initially conditioned to the room temperature.

3 Results and Discussion

In the following three five subchapters the results of thermal, LOI and cone calorimetry analyses are introduced.

3.1. TG/DTG analysis results

The TG curve of the PUR1 sample showed a four-stage thermal degradation process. The first stage of thermal degradation took place in the temperature range of 100 – 275 °C with the mass loss of 17.15 %. In the second stage of the thermal degradation, the highest mass loss, i.e. the mass loss peak (T_{MAX}), was found at temperature of 323 °C. The thermal degradation process in this stage occurred in the temperature range of 275 – 430 °C and the mass loss was of 64.78 %. The third stage occurred in the temperature range of 430 – 620 °C with the mass loss of 14.90 %. In the fourth stage the mass loss was of 2.03 % and took place in the temperature range of 620 – 671 °C. The carbon residue of PUR1 sample was of 1.14 %.

The PUR2 sample was subjected to thermal degradation process in three stages. The first stage was found in the temperature range 110 – 262 °C and the mass loss was of 14.4 %. The second stage of thermal degradation took place in the temperature range of 262 – 367 °C, with the highest mass loss (63.79 %) found at temperature of 304.3 °C. The third stage of degradation process was found in the temperature range of 367 – 620 °C and the mass loss was of 20.60 %. The remaining carbon residue of the PUR2 sample was of 0.30 %.

The course of the TG curve of the PUR3 sample represents a four-stage thermal degradation process. Thermal degradation of the PUR3 sample began in the temperature of 133 °C and terminated at temperature of 694 °C. The first stage was found in the temperature range of 133 – 265 °C. The mass loss was of 8.34 % in this stage. The second stage with highest mass loss (68.71 %) was found in the temperature range of 265 – 350 °C. The temperature at which the maximum mass loss occurred was 323 °C. The third stage of thermal degradation process took place in the temperature range of 350 – 420 °C and was represented by the mass loss of 15.09 %. In the fourth stage, in the temperature range of 420 – 694 °C, the mass loss of the sample was of 6.67 %. The remaining carbon residue of PUR3 sample was of 0.46 %.

The TG curve of the PUR4 sample was like PUR3 sample due to the four-stage thermal degradation process. The first stage of thermal degradation took place in the temperature range of 119 – 231 °C and represented the mass loss of 9.65 %. The second stage was found in the temperature range of 231 – 280 °C and the mass loss of the sample was of 12.23 %. In the third stage of thermal degradation process, in the temperature range of 280 – 400 °C, the maximum mass loss of 69.62 % was found at temperature of 333.7 °C. The fourth stage occurred in the temperature range of 400 – 570 °C and it was characterised by the lowest mass loss (7.52 %). The remaining carbon residue of PUR4 sample was of 0.35 %.

The course of TG curve of the PUR5 sample was like PUR1, PUR3, and PUR4 samples due to the four-stage thermal degradation process. The first stage was found in the temperature range of 100 – 291 °C with the mass loss of 38.21 %, which represents the highest mass loss in comparison to the other stages. The maximum mass loss occurred at temperature of 272.3 °C. The second stage occurred in the temperature range of 291 – 326 °C and the mass loss was of 18.39 %. The third stage of thermal degradation took place in the temperature range of 326 – 429 °C with the mass loss of 28.99 %. The fourth stage was found in the temperatures range 429 – 694 °C and the mass loss was of 13.78 %. The remaining carbon residue was of 0.25%.

Applying the thermogravimetric method, we have obtained important data on the course of thermal degradation of each sample tested. The resulting values for the PUR foams are introduced in Table 2.

Tab. 2 Summarized thermogravimetry analyses results

Sample	$T_I / ^\circ\text{C}$	$T_{MAX} / ^\circ\text{C}$	$T_F / ^\circ\text{C}$	$T_F - T_I / ^\circ\text{C}$	RR C600 / %
PUR1	100	323.0	671	571	1.14
PUR2	110	304.3	620	510	0.30
PUR3	133	323.0	694	561	0.46
PUR4	119	333.7	570	451	0.35
PUR5	100	272.3	694	594	0.25
Average	112 ± 14	311.3 ± 24	650 ± 54	537 ± 57	0.50 ± 0.37

* Note: T_I – initial temperature; T_{MAX} – temperature at which mass loss peak was achieved; T_F – final temperature; RR – resistant residue.

According to the results achieved, we can state that the initial thermal degradation process started at temperature of 113 °C. At this temperature, the TG curves begin to point out a slight mass loss. The maximum mass loss occurred in the second stage of thermal degradation process, except the samples PUR4 and PUR5, where, in the case of PUR 4 sample, it was found in the third stage and in the case of PUR5 sample already in the first stage of thermal degradation process. The temperatures at which the maximum mass loss was achieved were close or within the temperature range of 304.3 – 333.7 °C, except the PUR5 sample, where the maximum mass loss was achieved at temperature of 272.3 °C.

3.2 DSC analysis results

From the PUR foam fire hazard point of view, it is important to determine the temperature interval, when the thermal degradation reactions have an exothermic effect. For this purpose, the differential scanning calorimetry was used.

In the DSC analysis of the PUR1 sample we found two stages of thermal degradation process. The sample showed the exothermic effects. The first stage of thermal degradation took place in the temperature range of 254 – 451 °C, where the amount of heat released was of 3,315.4 J g⁻¹. The second stage began at 451 °C and was not completed. From the DSC curve, it was evident that the amount of heat released increased and the sample was not completely decomposed.

The DSC analysis of the PUR3 sample confirmed the two-stage thermal degradation process, although the second stage differed significantly from the first stage in the amount of heat released. Thermal degradation process was not completed in this case. The first stage of thermal decomposition process took place in the temperature range of 243 – 450 °C, where the heat release was of 3,877.8 J g⁻¹. At temperature of 322.3 °C, there was a sharp rise in the heat release value, which peaked at temperature of 342.7 °C. In the second stage, in the temperature range of 450 – 595 °C, the heat release was of 1,818.2 J g⁻¹. The total amount of heat released by the PUR3 sample was of 5,696 J g⁻¹.

According to DSC results, we can state that the thermal degradation process of the PUR4 sample had two stages. From a temperature of c.a. 340 °C up to the temperature of 595 °C, the heat release values were very similar. The first signs of thermal degradation, according to the DSC curve, occurred at temperature of 214 °C, and at temperature of c.a. 340 °C, there was recorded a higher release of heat from the sample. The total heat released from the sample was of 7,393 J g⁻¹. Also, in this case, the thermal degradation process was not completed.

DSC analyses results of the PUR2 and PUR5 samples were comparable. They varied with temperature intervals and the amount of heat released. Both samples as well as the other PUR samples (PUR1, PUR3 and PUR4) did not undergo complete thermal degradation process. In the case of PUR2 sample, the highest amount of heat released was at temperature of 591.5 °C. During the incomplete thermal degradation process, the PUR2 sample released 6,537.6 J g⁻¹ of heat. The PUR5 sample released the highest amount of heat (4,199.9 J g⁻¹) at temperature of 322.4 °C. In the second thermal degradation stage, in the temperature range of 449 – 595 °C, the PUR5 sample released 3 099.2 J g⁻¹ of heat.

In the DSC analysis of the PUR foams samples, we obtained quantitative results on the course of their thermal degradation process. Those results, i.e. comparison of initial and final temperatures, enthalpy change values, and the amount of heat released values are introduced in Table 3.

Tab. 3 Summarized DSC analyses results

Sample	$T_i / ^\circ\text{C}$	$T_f / ^\circ\text{C}$	$T_{MAX} / ^\circ\text{C}$	Heat released /J g ⁻¹	Enthalpy change peak 1 / J g ⁻¹	Enthalpy change peak 2 / J g ⁻¹
PUR1	254	595	349.3	6,514.7	3,315	3,199
PUR2	259	595	591.5	6,537.6	3,179	3,359
PUR3	243	595	342.7	5,696.0	3,878	1,818
PUR4	214	595	380.3	7,393.0	4,070	3,323
PUR5	244	595	322.4	7,299.1	4,200	3,099
Average	243 ± 17	595	397 ± 110	6,688.1 ± 691	3,728 ± 457	2,860 ± 700

From the results is clear that the initial temperatures of the samples were comparable. The PUR1 and PUR2 samples showed the existence of a retardation treatment because the samples had a higher initial temperature. The reason of only one value of final temperatures for all samples was the fact that thermal degradation process was not completed since the maximum temperature of the measuring apparatus was reached during the testing.

The DEFLAMO retardant treated PUR2 sample released the highest amount of heat at temperature of nearly 600 °C. The lowest amount of heat PUR3 sample released.

3.3 Cone calorimetry results

From the cone calorimetry we obtained the information on ignition time, peak heat release rate, peak heat release rate time, the effective combustion heat (EHC) and the total heat released (THR).

The HRR curves are illustrated in Figure 2 and the summarized results of cone calorimetry analyses are introduced in Table 4.

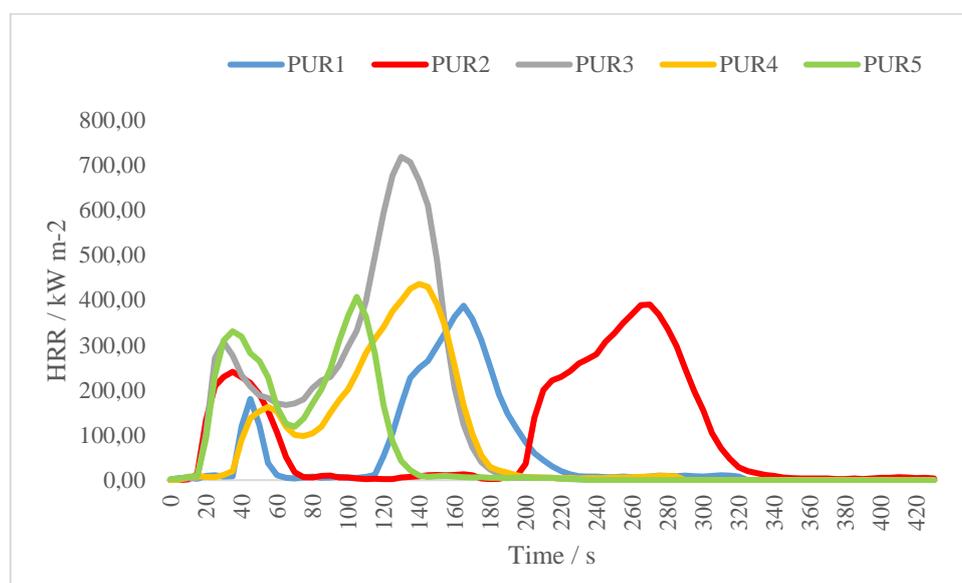


Fig 2. HRR curves of PUR foams

As shown in Figure 1, all the PUR foam samples were ignited at lower incident heat fluxes. All of them showed two-stage course of thermal degradation process, which was also described by Pitts (2014) [24], Ezinwa et al. [25], Lefebvre et al. [26] and Xu et al. [20].

Tab. 4 Summarized cone calorimetry results

Sample	Weight / g	Time / s	EHC / MJ kg ⁻¹	Peak HRR / kW m ⁻²	Peak HRR time / s	THR / MJ m ⁻²
PUR1	8.00	20-37 100-207	28.50	390.01	165	24.10
PUR2	15.50	5-57 166-305	24.50	363.90	270	39.79
PUR3	14.70	4-163	28.60	683.07	130	51.13
PUR4	11.00	19-176	25.50	417.29	140	32.80
PUR5	7.90	5-123	31.90	417.49	105	27.02
Average	11.42 ± 3.59	–	27.80 ± 2.92	454.35 ± 129.80	162 ± 64.10	35.00 ± 3.59

According to data introduced in Table 4, we can state that the longest time to ignition showed the samples PUR1 and PUR4. Both were treated by flame retardant. We expected similar behaviour by sample PUR2, which was also treated with flame retardant but it had comparable time to ignition values like the non-treated PUR foam samples. The maximum value of HRR was recorded by the PUR 5

sample, representing the normal type of PUR foam without any flame-retardant treatment. The lowest value of HRR was recorded by PUR2 sample, which also reached its HRR peak latest (after 270 s). From the THR point of view, we can state that the maximum amount of heat released the PUR3 (V 4010) sample.

4 Conclusions

Thermal analysis and cone calorimetry still belong among the progressive analytical methods to study the fire and thermal properties of materials. In this study we investigated the fire and thermal parameters of five PUR foams commonly used in furniture of residences as well as in industry. Based on the results of TG / DTG, DSC and cone calorimetry we stated the fire hazard rating of all the tested PUR foams.

The results pointed out the effect of retardation on the assessment parameters. The samples with retardation treatment achieved better thermal stability than samples without retardation treatment. The thermal (TG / DTG, DSC) analyses results pointed out the flame retardant non-treated standard N 5063 PUR foam to be the most fire hazardous due to its lowest thermal stability. The cone calorimetry results confirmed its fire hazard, although the most fire hazardous from ignition time and HRR peak values was found the flame retardant non-treated V 4010 PUR foam sample. N 5063 PUR foam followed the V 4010 in the order of fire hazard.

Results of this study are immediately applicable in the fire safety practice, as an input parameter for modelling of compartment fires as for design of new PUR foam products with higher resistance to fire.

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References

- [1] Pitts, WM. Applied heat flux distribution and time response effects on cone calorimeter characterization of a commercial flexible polyurethane foam. *Fire Technol.*, 2014; 50:635-72.
- [2] Fire Safe Europe-White paper, 2014. Available online: www.firesafeurope.eu
- [3] Luo, F., Wu, K., Li, Y. et al. Reactive flame retardant with core shell structure and its flame retardancy in rigid polyurethane foam. *J. Appl. Polym. Sci.* 2015; 132:42800-42808
- [4] Xu, Z., Liu, L., Wang, SQ. et al. Synergistic effect of expandable graphite and aluminum hypophosphite on flame-retardant properties of rigid polyurethane foam. *J. Appl. Polym. Sci.* 2015; 132:42842-42851
- [5] Xu, W., Wang, G., Zheng, X. Research on highly flame-retardant rigid PU foams by combination of nanostructured additives and phosphorus flame retardants. *Polym. Degrad. Stab.* 2015; 111:142-150
- [6] Alongi, J., Carletto, RA., Di Blasio, A. et al. Intrinsic intumescent-like flame retardant properties of DNA-treated cotton fabrics. *In Carbohydr. Polym.* 2013; 96:296-304
- [7] Reddy, PRS., Agathian, G., Kumar, A. Ionizing radiation graft polymerized and modified flame-retardant cotton fabric. *Radiat. Phys. Chem.* 2005; 72:511-516
- [8] Chen, DQ., Wang, YZ., Hu, XP., et al. Flame-retardant and anti-dripping effects of a novel char-forming flame retardant for the treatment of poly(ethylene terephthalate) fabrics. *Polym. Degrad. Stab.* 2005; 88:349-356
- [9] Didane, N., Giraud, S., Devaux, E. 2012. Fire performances comparison of back coating and melt spinning approaches for PET covering textiles. *Polym. Degrad. Stab.*, 2012; 97:1083-1089

- [10] Phanphanich, M., Mani, S. Impact of torrefaction on the grindability and fuel characteristics of forest biomass. *Bioresource Technology*, 2011; 1029(2):1246-1253
- [11] Modesti, M., Lorenzetti, A. 2010. Recent trends in flame retardancy of polyurethane foams. In *Flame Retardants: Functions, Properties and Safety*. 2000, p. 185-218
- [12] Yang, F. Nelson, G. L. Halogen-Free Flame-Retardant Flexible Polyurethane Foams via a Combined Effect of Flame Retardants. In *Fire and Polymers VI: New Advances in Flame Retardant Chemistry and Science*. ACS Symposium Series, 2012, 1118: 139-149
- [13] Hu, XM., Wang, DM. Enhanced fire behavior of rigid polyurethane foam by intumescent flame retardants. *Journal of Applied Polymer Science*, 2013; 129(1):238-246
- [14] Chen, XL., Y. Jiang, YF., Jiao, CM. Smoke suppression properties of ferrite yellow on flame retardant thermoplastic polyurethane based on ammonium polyphosphate. *Journal of Hazardous Materials*, 2014; 266: 114-121
- [15] Ciecierska, E., Jurczyk-Kowalska, M., Bazarnik, P. et al. The influence of carbon fillers on the thermal properties of polyurethane foam. *J Therm Anal Calorim*, 2016; 123(1):283-291
- [16] Gao, L., Zheng, G., Zhou, Y. et al. Improved mechanical property, thermal performance, flame retardancy and fire behavior of lignin-based rigid polyurethane foam nanocomposite. *J Therm Anal Calorim.*, 2015; 120(2): 1311-1325
- [17] Liu, YL., He, JY., Yang, RJ. et al. The Thermal Properties and Flame Retardancy of 9,10-Dihydro-9-oxa-10-phosphaphenanthrene 10-Oxide (DOPO)-Mg/Polyisocyanurate-Polyurethane Foam Composites. *Bulletin of the Chemical Society of Japan*, 2016; 89(7):779-785
- [18] Liu, X., Xu, DM., Wang, YL. et al. Smoke and toxicity suppression properties of ferrites on flame-retardant polyurethane-polyisocyanurate foams filled with phosphonate. *Journal of Thermal Analysis and Calorimetry*, 2016; 125(1):245-254
- [19] Liu, X., Wang, JY., Yang, XM. et al. Application of TG/FTIR TG/MS and cone calorimetry to understand flame retardancy and catalytic charring mechanism of boron phosphate in flame-retardant PUR-PIR foams. *Journal of Thermal Analysis and Calorimetry*, 2017; 130(3):1817-1827
- [20] Xu, Q., Jin, C., Majlingova, A. et al. Evaluate the flammability of a PU foam with double-scale analysis. *J Therm Anal Calorim.*, 2019; 135(6): 3329-3337
- [21] STN EN ISO 11358-1: 2015. *Plastics - Thermogravimetry (TG) of polymers - Part 1: General principles (ISO 11358-1:2014)*
- [22] STN EN ISO 11357-1: 2017. *Plastics - Differential scanning calorimetry (DSC) - Part 1: General principles (ISO 11357-1:2016)*
- [23] ISO 5660-1:2015 *Reaction-to-fire tests – Heat release, smoke production and mass loss rate – Part 1: Heat release rate (cone calorimeter method) and smoke production rate (dynamic measurement)*
- [24] Pitts, WM. Applied heat flux distribution and time response effects on cone calorimeter characterization of a commercial flexible polyurethane foam. *Fire Technol.*, 2014; 50:633-634
- [25] Ezinwa, JU., Robson, LD., Obach, MR. et al. Evaluating models for predicting full-scale fire behavior of polyurethane foam using cone calorimeter data. *Fire Teechnol.*, 2014; 50:693-719
- [26] Lefebvre, J., Bastin, B., Le Bras, M. et al. Flame spread of flexible polyurethane foam: comprehensive study. *Polym. Test.*, 2004; 23:281-290