

Analysis of flammability and smoke emission of rigid polyurethane foams modified with nanoparticles and halogen-free fire retardants

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Abstract Using one-step method, rigid polyurethane foams were made, modified with developed fire retardant systems containing halogen-free flame retardants and nanofillers in the form of multi-walled carbon nanotubes or nanoscale titanium dioxide. The materials were subjected to a test using a cone calorimeter and smoke-generating chamber, and selected samples were further analyzed via thermogravimetry and oxygen index. Moreover, the products of thermal degradation of selected samples were identified using gas chromatography with mass spectrometer. Conducted flammability tests confirmed the presence of a synergistic effect between the used nanofillers and halogen-free flame retardants. It has been observed that the carbonized layer, the formation of which favored the presence of nanoadditives, inhibits the combustion process. Furthermore, nanofillers influenced favorably reduction in the amount and the number of occurring products of thermal degradation.

Keywords Rigid polyurethane foams · Halogen-free flame retardants · Oxygen index · Cone calorimetry · Smoke chamber · Thermal analysis

Introduction

Rigid polyurethane foams (RPUF) are used in many areas, including construction industry as one of the best commercially available insulation materials. RPUF have very good mechanical properties, resistance to aging and water and also atmospheric factors [1–4]. Unfortunately, rigid polyurethane foams have also some disadvantages, among which special attention should be paid to flammability and toxicity of the gas products emitted during thermal degradation and combustion [5].

Combustion of polymeric materials is an exothermic reaction of the catalytic oxidation of organic compounds carried by energy supplied in the form of heat and forming free radicals. This phenomenon is accompanied by heat, light and combustion products (gases, smoke). The ability to ignite the polymer depends primarily on the availability of oxygen, temperature and its physicochemical properties. In contrast, the combustion process is conditioned, among others, by composition, chemical structure and density of the material, porosity, size, shape and structure of the product [6].

The thermal decomposition of non-fire retarded polyurethane foams in air is generally quite well understood. Generally, the initial decomposition of the foam (>300 °C) results in the volatilization of isocyanates, amines and “yellow smoke”, leaving behind polyols in the condensed phase. These polyols are fragments and volatilize as the temperature increases (>600 °C), leaving behind a char. This char can decompose further, leaving behind a residue, to produce simple organic fragments and some polycyclic aromatic hydrocarbons (PAHs). In the gas phase, isocyanates, amines and “yellow smoke” are begun to decompose at >600 °C into low molecular weight nitrogen-containing fragments (such as benzonitrile, aniline and

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hydrogen cyanide (HCN)). At >800 °C these compounds further fragment into simple molecules (such as HCN, CO, CH₄ and CH₂O) and PAHs [7, 8].

Rigid polyurethane foams are carbonized during combustion. This process leads to the reduction in the amount of heat released during the combustion of polymers and affects the amount and type of the emission. Formation of carbon by restricting access of the flame to the deeper layers of the material prevents the formation of low molecular weight organic compounds, which support the fuel process. Unfortunately, the amount of formed carbon layers in the combustion of rigid polyurethane foams is relatively low [6].

Research and development units and chemical corporations around the world are currently carrying out numerous works related to the improvement in thermal stability and fire resistance of rigid polyurethane foams. RFUP flame retardancy can be achieved by the addition of flame retardants [1–6, 9], the task of which is usually to delay ignition, slow the process of combustion and pyrolysis, reduce emissions of smoke, and reduce the phenomenon of dripping. The group of fire retardants includes, among others, compounds containing halogens such as bromine and chlorine, compounds of phosphorus and nitrogen, and hydroxides of aluminum and magnesium [10]. Most flame retardants with built-in halogen atoms currently attract a lot of controversy, mainly because of their safety and corrosion properties of gases released [11].

The most frequently used halogen-free flame retardants, apart from aluminum hydroxide and magnesium, containing compounds are phosphorus/nitrogen. Flame retardants based on Mg(OH)₂ and Al(OH)₃ prevent heating up of the material to the ignition temperature, and the water vapor, along with degradation products, is released into the combustion zone reducing the concentration of combustible products and oxygen. As a consequence, the flame temperature is lowered and the resultant oxides form a protective layer, on the surface of the material, limiting the movement of the volatile degradation products to the flame and oxygen to the burning material. The group of flame retardants containing phosphorus and nitrogen includes, among others, phosphaphenanthrene phosphonamidates [12], ammonium polyphosphate [13, 14], polydopamine [15], triphenylphosphate [16], dimethyl methylphosphonate [17], dimethylpropanphosphonate [18], hexaphenoxy cyclotriphosphazene [19] and aluminum phosphinate [4, 20, 21].

A relatively new group of measures that increase the thermal stability and reduce the flammability of polymers, are nanoparticles. The advantage of nanocomposites is the possibility to obtain satisfactory results using only a few percent of the filler, while in the case of traditional flame retardants these quantities reach up to 60%. Otherwise,

nanomaterials exhibit improved rheological properties, higher mechanical strength and lower emission of fumes [22–24]. The most commonly used nanofillers are layered silicates [25], nano-SiO₂ [26], titanium oxide and carbon nanotubes (CNT) [4, 27, 28]. During combustion, composite nanoparticles can migrate to the surface of the polymer and assist in the formation of carbon layer [29, 30]. The combination of nanomaterials with conventional flame retardants, leading to the formation of synergistic effect between those substances, is currently the subject of numerous studies [23, 25, 31–33].

Wang et al. [34] reported that the introduction of graphene nanoparticles to polybutylene succinate (PBS) containing melamine poliphosphate favorably affects the formation of carbon and increases the thermal stability of the polymer. On the basis of the cone calorimeter test it was found that the values of maximum rate of heat release (pHRR) and total heat generated (THR) of polybutylene succinate containing 18% melamine phosphate and 2% of graphene were, respectively, 63 and 23% lower compared to the results obtained for pure PBS. The paper also presents the results for the materials modified with polyhedral oligomeric silsesquioxane (POSS), but the synergistic effect in combination with melamine poliphosphate was significantly lower in comparison with graphene. In addition, increased quantities of fumes are released, which is not observed in the case of materials of melamine phosphate and graphene.

These results are contrary to those described by Didane et al. [35]. The authors reported the results for flammability testing of polyethylene terephthalate (PET) using a 9 mass% of flame retardant agent based on the zinc phosphinate, and three types of POSS, which have referred to the unmodified PET and PET with 10 mass% a/m retardant. It has been observed that the introduction of 1 mass% POSS contributed to the reduction in the maximum HRR from 500 kW m⁻² for PET and 365 kW m⁻² for PET with flame retardant to 214 kW m⁻² in the case of one of the types of nanofillers. In addition, for the same kind of POSS emissions of carbon dioxide at a level similar to the values obtained for unmodified PET was observed.

The aim of this study was to produce nanocomposites of rigid polyurethane foams modified with halogen-free fire retardants with reduced flammability and smoke emissions. Prepared materials were analyzed using the cone calorimeter and the single-chamber test; under obtained results, the initial selection of the proposed flame retardant systems was done. In the next stages of work, for the selected compositions, thermogravimetric analysis and oxygen index were performed. Also, specified were the nature and quantity of the substances present in the exhaust fumes and emitted during the thermal decomposition. The analysis made it possible to assess the effectiveness of the

proposed system on the behavior of materials containing them in the conditions of pyrolysis and combustion.

Materials and methods

Materials

To prepare the materials, open-cell polyurethane foam EKOPRODUR 0612 PCC Prodex (PURO), intended for thermal insulation coatings for water pipes and heating systems in residential and industrial buildings, was used. A combination of three halogen-free liquid fire retardants included: triethylphosphate (TEP) from Minova Ekochem SA, dimethylpropanphosphonate (DMPP), the trade name Levagard[®]DMPP from LANXESS GmbH and the cyclic phosphorus compound named Addroce CT 93 FR (FR CT) from Walter Thieme Handel GmbH, were used. Also three flame retardants in the form of powder, i.e.: aluminum hydroxide under the trade name Reflamal S 30 (ATH) from Walter Thieme Handel GmbH, ammonium polyphosphate (APP) named Exolit AP 750 from Clariant GmbH and zinc borate (ZB) from Nordmann, Rassmann GmbH were applied. As nanofillers were used: multi-walled carbon nanotubes (MWNTs) with a diameter of 20 to 30 nm and a length of 10 to 30 μm from Cheap Tubes Inc. and nano-sized titanium dioxide (TT) with a grain size of 20 nm from Sigma-Aldrich Co. LLC.

Processing

The materials were prepared by a single-stage method of components A and B, and the isocyanate index equaled 1.1.

Production started with the preparation of mixtures of nanoparticles and three flame retardants marked as TEP, FR CT 93 and DMPP. Flame retardant composition was subjected to a mechanical mixing process using three speeds corresponding to 7000, 10,000 and 17,000 rpm with mixing time about 3 min. In order to prevent overheating of the compound cooling with ice-water bath was applied. The mixture was then subjected to a process of homogenization using the ultrasonic disperser Q Sonic 700. The amplitude of the operation was 50 with the homogenization time of about 5 min for each mixture. The obtained mixtures and selected flame retardant powder (ATH, APP or ZB) were introduced into component A, comprising a catalyst, a surfactant and a blowing agent and mixed again via mechanical stirring. The duration of the process was 3–5 min, and the maximum speed of the stirrer did not exceed 17,000 r min^{-1} . In a final step, the resulting mixture was added to ingredient B, and after mixing, it was poured into an open mold. The total proportion of flame retardant substances and nanofillers was 30 mass% relative

to the component A in individual materials. Additionally, a polyurethane foam comprising only three liquid-halogen flame retardants (PURO 7) and a foam with no additives (PURO 8) were made. The compositions of the materials produced are summarized in Table 1.

Characterization methods

Fire tests

Burning behavior of investigated materials was determined based on research conducted using the cone calorimeter device from Testing Technology Ltd. in accordance with the procedure described in ISO 5660-1. The specimens with dimensions $100 \times 100 \times 10$ mm were irradiated horizontally at a heat flux of 35 kW m^{-2} . In addition, the optical system with silicon photodiode and a helium–neon laser allowed continuous measurement of the optical density of smoke. Spark ignition was used to ignite the pyrolysis products, and the result of the burning test was the arithmetic average of at least three measurements.

The flammability properties of materials were examined also by oxygen index (OI) test, according to the summary procedure (procedure C) described in EN ISO 4589-2, allowing determination of the minimum OI values. The samples used for measurement were rectangular-shaped beams of the measuring $150 \times 10 \times 4$ mm. The bar is placed in a column for measuring the minimum oxygen concentration in the oxygen–nitrogen mixture at which the sample burned. The test was carried out for at least three samples from each batch.

Smoke generation

Optical density of smoke was determined by Smoke Density Chamber from Fire Testing Technology Ltd. in accordance with the document ISO 5659-2. During the test, each of the samples with dimensions of $75 \times 75 \times 10$ mm was exposed to an external heat flux of 25 kW m^{-2} . The optical system allowed the continuous measurement of the optical density of smoke (D_s), and based on the curve of D_s , parameter VOF 4, which informs how much smoke is generated in the first 4 min of fire, was determined. The values were the arithmetic average of three surveys.

Identification of thermal degradation and combustion products

One of the objectives of this work was the determination of toxic products that can be evolved in the combustion and thermal degradation of polyurethane materials. Experiments were carried out in the steady-state tube furnace (Purser furnace, ISO/TS 19700), which has been used

Table 1 Compositions of produced nanocomposites with the rigid polyurethane foam

Type of additives/% mas.	Recipe number							
	PURO 1	PURO 2	PURO 3	PURO 4	PURO 5	PURO 6	PURO 7	PURO 8
TEP	7	7	7	6	6	6	15	
FR CT 93	4.5	4.5	4.5	3.5	3.5	3.5	9	
DMPP	3	3	3	2.5	2.5	2.5	6	
ATH	15			15				
APP		15			15			
ZB			15			15		
MWNTs	0.5	0.5	0.5					
TT				3	3	3		
The total content of additives/% mas.	30	30	30	30	30	30	30	0

specifically to generate toxic products from real fires under different temperature conditions. The furnace allowed the identification of the products emitted not only directly during the thermal degradation of test materials, but also as a result of secondary reactions between the products. The samples (5 g) of selected materials in special test specimen boats were delivered into the furnace tube. Then, the samples were heated from room temperature to 600 °C at a heating rate of 10 °C min⁻¹ in air, with the gas flow rate of 20 L min⁻¹. When the furnace temperature reached 300, 450 and 600 °C, it was maintained for the 5 min and the samples of thermal degradation products were collected from mixing chamber of furnace using solid-phase microextraction (SPME) technique and the carboxen/polydimethylsiloxane (CAR/PDMS) fiber coating. After collection (5 min), the SPME fiber desorbed immediately in the gas chromatograph injector for analysis. The released species have been identified using gas chromatograph (GC 7890 A, Agilent Technologies, USA) with mass spectrometer (MSD 5975, Agilent Technologies, USA). Chromatographic separation was achieved on a HP-5MS fused-silica capillary column (30 m × 0.25 mm × 0.25 μm film thickness) using helium as the carrier gas at 1 mL min⁻¹. The oven temperature was maintained at 40 °C for 10 min, increased by 5 °C min⁻¹ to 240 °C and held for 8 min. The GC injector port was 250 °C. The MSD was operated by electronic impact (70 eV) in scan mode (25–450 m/z).

Thermal stability

A thermogravimetric analysis (TG) of the prepared materials was conducted using a TGA Q500 from TA Instruments. From each of the series, at least one sample of 9.0 ± 1 mg was cut and tested in an atmosphere of nitrogen or air, with flowing gas at a rate 30 mL min⁻¹ in the

chamber and 70 mL min⁻¹ in the oven. Based on the curves and using the Universal Analysis software version 4.1 D, the initial degradation temperature, the temperature of maximum rates of mass loss and percentage of char residue at 950 °C were specified. The samples were heated from room temperature to 950 °C at a rate of 10 °C min⁻¹.

Results and discussion

Summary results of the flammability and smoke emission tests, conducted with cone calorimeter and smoke-generating chamber, are given in Table 2. Designations of the individual samples are consistent with the indications given in Table 1.

A relatively short ignition time of open-cell polyurethane foams was due to the cell structure of this type of materials [36]. The introduction of flame retardants caused a shortening of the time, followed by the ignition of the tested materials from 5 to as much as 1 s, in the case of the sample labeled PURO 2. The presence of flame retardant systems contributed to the intensification of the process of degradation of the polymer, which has been described in the literature [34]. The assessment of listed values Time to Ignition (Table 2) shows that the analyzed parameter was badly affected by the combination of halogen-free flame retardants with nanofillers in the form of multi-walled carbon nanotubes.

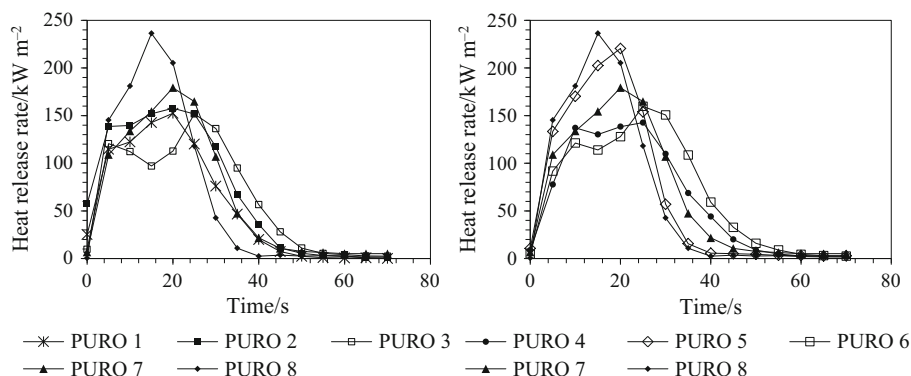
On the graph presented in Fig. 1, heat release curves of PUR foams nanocomposites with divided into the series and reference materials were juxtaposed. Heat release rate is one of the key parameters used to evaluate the burning behavior of materials. It has been proven that doubling HRR can lead to more than threefold reduction in survival time of victims, which was not observed in the case of an increased time to ignition or toxic potential of plastics [37].

Table 2 Flammability and smoke emission of produced composites

Sample designation	TTI/s	pHRR/kW m ⁻²	MARHE/kW m ⁻²	SEA/m ² kg ⁻¹	TSR/m ² m ⁻²	D _{s,max}	VOF 4
PURO 1	2 (0.6 ^a)	161.72 (10.7)	124.0 (3.6)	697.02 (9.4)	228.8 (26.6)	88.15 (1.0)	189.17 (8.8)
PURO 2	1 (0.6)	160.65 (3.3)	138.8 (4.9)	881.92 (125.3)	318.9 (16.7)	82.79 (8.7)	176.57 (8.8)
PURO 3	2 (0.6)	142.20 (21.3)	114.2 (14.9)	767.13 (47.2)	273.8 (22.1)	94.15 (9.5)	197.74 (20.8)
PURO 4	4 (0.7)	148.98 (6.6)	118.0 (6.8)	782.93 (85.5)	218.8 (16.6)	87.64 (15.8)	150.74 (38.1)
PURO 5	4 (1.4)	214.07 (11.4)	150.0 (15.0)	874.35 (26.8)	290.8 (13.1)	103.14 (3.6)	206.56 (10.1)
PURO 6	4 (0.7)	158.07 (12.4)	123.6 (8.3)	644.02 (30.7)	230.8 (26.5)	90.29 (4.4)	183.93 (12.9)
PURO 7	4 (0.0)	168.35 (10.1)	125.8 (7.8)	843.00 (35.0)	325.0 (27.1)	92.11 (3.8)	219.24 (4.6)
PURO 8	5 (1.4)	194.27 (40.5)	139.5 (27.2)	709.60 (88.1)	256.8 (29.1)	104.30 (7.8)	189.71 (4.7)

^a The values in parentheses are the standard deviations

Fig. 1 Effects of nanoparticles and halogen-free fire retardants on the heat release behavior of PUR foams



For most of the mixtures, except for the sample PURO 5, there was a reduction in the maximum rate of heat release. Comparing the results obtained for a reference sample PURO 7 with the values determined for nanocomposites, it was found that the replacement of a small amount of flame retardants with nanoadditives resulted in further lowering the amount of heat release. These observations may indicate the occurrence of synergistic effect between nano-fillers and flame retardant. The lowest pHRR values, lower compared to non-modified polyurethane foams by 37 and 30%, were obtained for samples PURO 3 and PURO 4. The reason for the reduction in the values was the formation of permanent char on the composites' surface, limiting heat and mass exchange between the materials and the flame [38]. Ye et al. [39] observed that the MWNTs introduced to polymer contained different amount of magnesium hydroxide as fire retardant caused the formation of nano-filler network structures and compact charred layers, but also increase in the thermal stability due to nanotubes strength and integrity in the charred layers. The synergistic effect between nanofillers and halogen-free fire retardants has also been confirmed in the previous literature [34, 40, 41]. The similar results were observed for the maximal average heat release emission, basing on which it

is possible to predict the development of fire in full-scale conditions.

Another extremely important fire feature is the fumes emission accompanying the pyrolysis and combustion of polymeric materials. Numerous studies have shown that limited visibility resulting from the formation of fumes, constituting a gas phase along with the suspended products of incomplete combustion, is the reason for the death of the prevailing number of victims [37, 42]. The parameters used to evaluate the emission of fumes according to the research conducted using the cone calorimeter are specific extinction area (SEA) and total smoke release (TSR). Parameter SEA, corresponding to the surface light-absorbing particles of smoke produced by the combustion of 1 kg of material [43], was reduced compared to the unmodified PUR foam only for the material designated as 6 and slightly for PURO 1. As for the total amount of the emitted fumes, the lowest values were obtained for mixtures PURO 1, 4 and 6. The flame retardant based on aluminum hydroxide, which was introduced to the PURO 1 and PURO 4, is a widely used means of limiting the emission of smoke. In turn, the flame retardant comprising zinc borate activated its ability to suppress the fumes only in combination with nanoparticles of titanium dioxide.

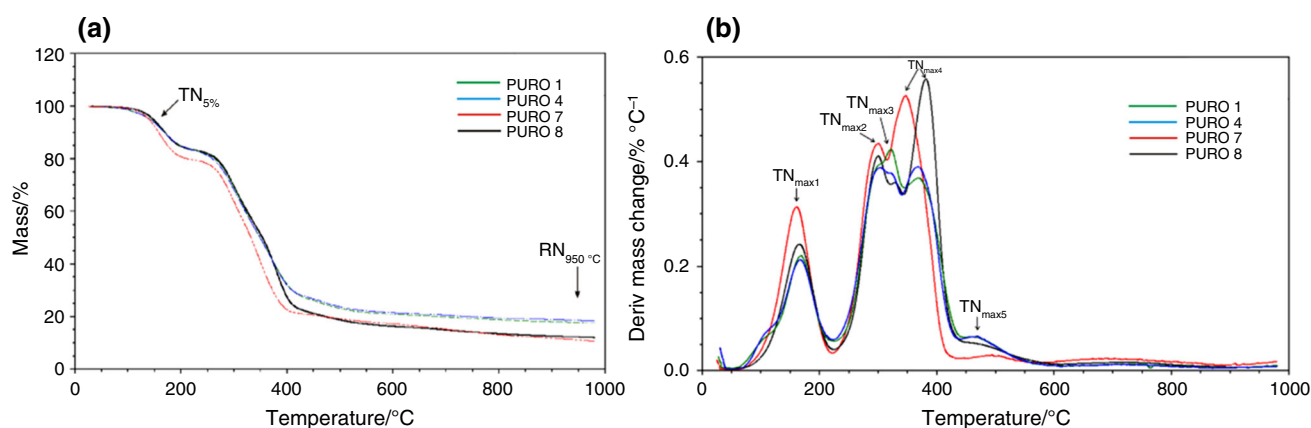


Fig. 2 TG (a) and DTG (b) curves of selected composites and reference materials for analyses conducted in an inert atmosphere

Table 3 Temperature values determined based on the TG and DTG curves of the selected composite mixtures investigated in nitrogen atmosphere

Sample	Inert atmosphere						
	TN ₅ /°C	TN _{max1} /°C	TN _{max2} /°C	TN _{max3} /°C	TN _{max4} /°C	TN _{max5} /°C	RN _{950°C} /%
PURO 1	143	168	301	321	369	480	17.6
PURO 4	141	167	302	322	367	468	18.4
PURO 7	139	161	301	–	348	500	10.8
PURO 8	147	164	300	330	381	480	12.0

Table 4 OI and temperature values determined based on the TG and DTG curves of selected composite mixtures investigated in air

Sample	Air atmosphere						OI/%
	TA _{5%} /°C	TA _{max1} /°C	TA _{max2} /°C	TA _{max3} /°C	TA _{max4} /°C	PA _{950°C} /%	
PURO 1	145	167	201	294	521	7.2	≥26 (0.2)
PURO 4	138	162	208	291	528	7.6	≥26 (0.2)
PURO 7	142	164	203	293	518	0.5	≥26 (0.2)
PURO 8	146	164	205	291	520	1.0	≥25 (0.2)

Smoke-generating chamber is a tool used to assess the emission of fumes in the cumulative (static) conditions. The introduction of developed systems of nanofillers and halogen-free flame retardants reduced the maximum optical density of smoke ($D_{s,max}$). The lowest values of $D_{s,max}$ were obtained for samples PURO 2 and 4 (Table 2). Similar results were observed for parameter VOF 4. The results do not coincide with those obtained on the basis of the test performed using the cone calorimeter, which is a dynamic (flow) method of research used to assess the emission of fumes of the materials [42].

Basing on the performed analysis of flammability and fumes produced, one sample containing the given nanofiller was selected for further study, including the determination of thermal stability, oxygen index and toxicity of

fumes emitted. Among the polyurethane foams modified with multi-walled carbon nanotubes, the composite labeled PURO 1 was chosen, while PURO 4 was selected among the series containing titanium dioxide. The results obtained for the above-mentioned materials were compared to those defined for reference materials PURO 7 and 8.

Thermal stability of the prepared materials was investigated using mass loss curves (TG) by determination of the temperatures corresponding to 5% of mass loss ($T_{5\%}$). The onset degradation point of foam with no modifications was 147 °C, while application of the developed flame retardant systems resulted in a slight decrease in degradation onset for experiments in both air and inert atmosphere. Similar results have been previously reported in the literature [9, 34, 43]. The phosphorus-containing flame retardants

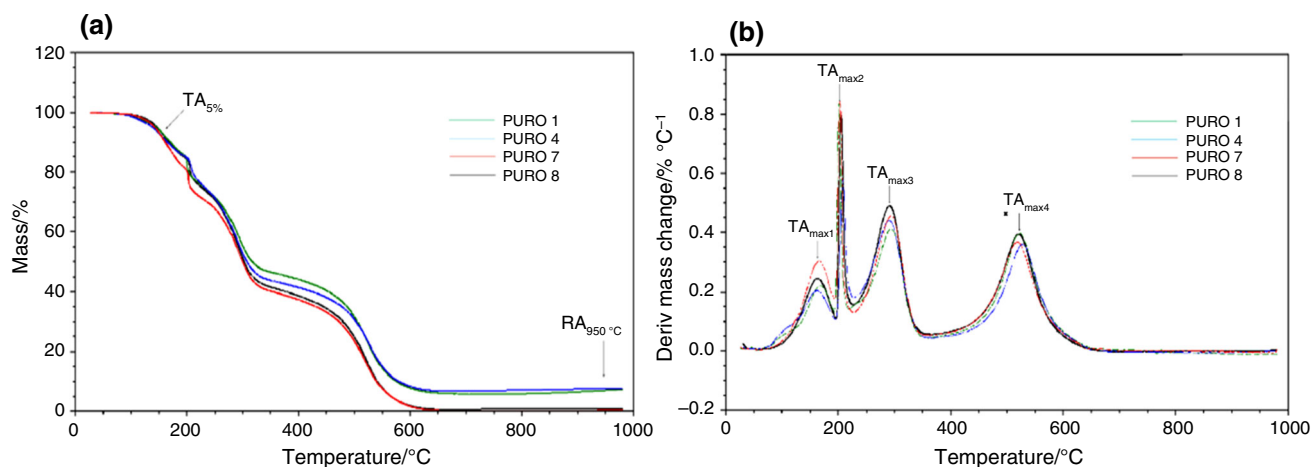


Fig. 3 TG (a) and DTG (b) curves of selected composites and reference materials for analyses conducted in air

applied in the study undergo decomposition at increased temperature and react with the polymer, which contributes to the formation of a char layer on the materials surface. The presence of nanofillers additionally favored the formation of char layer, which was confirmed by TG curves (Fig. 2) and increased amounts of residue at 950 °C in the case of composite materials (Tables 3, 4). The formation of char layer limits the mass loss and increases the thermal stability of the polymer [34]. The samples modified with the multi-walled carbon nanotubes were characterized with slightly increased thermal stability among other composites. The TG and DTG curves obtained in the course of the study were compared in order to precisely analyze the processes of thermal degradation in air and inert atmosphere (Fig. 2b, 3b; Tables 3, 4). As evidenced by the obtained results, the thermal degradation of examined foams involves degradation steps with maximum at temperatures in the range 161–168 °C (TN_{max1} , TA_{max1}) in both air and inert atmosphere. This signal is probably related to the degradation of the urethane rigid segments [44]. Furthermore, the analyses in air indicate the degradation step with maximum at 201–208 °C (TA_{max2}) characterized by fast degradation rate. The former signal might correspond to the degradation of the products formed by decomposition of the rigid segments occurring in the initial degradation step. Presence of this signal is clearly related to the effect of oxygen on the decomposition process. The temperature range related to the first degradation step for the processes conducted in nitrogen atmosphere is similar to the range related to two first degradation steps for analyses performed in air.

Further degradation processes observed in air (TA_{max3}) take place in temperature range of 228–360 °C, while the same processes were observed in nitrogen atmosphere at ca. 220–320 °C (TN_{max2}). Moreover, the degradation in nitrogen atmosphere involved third step (TN_{max3}) at

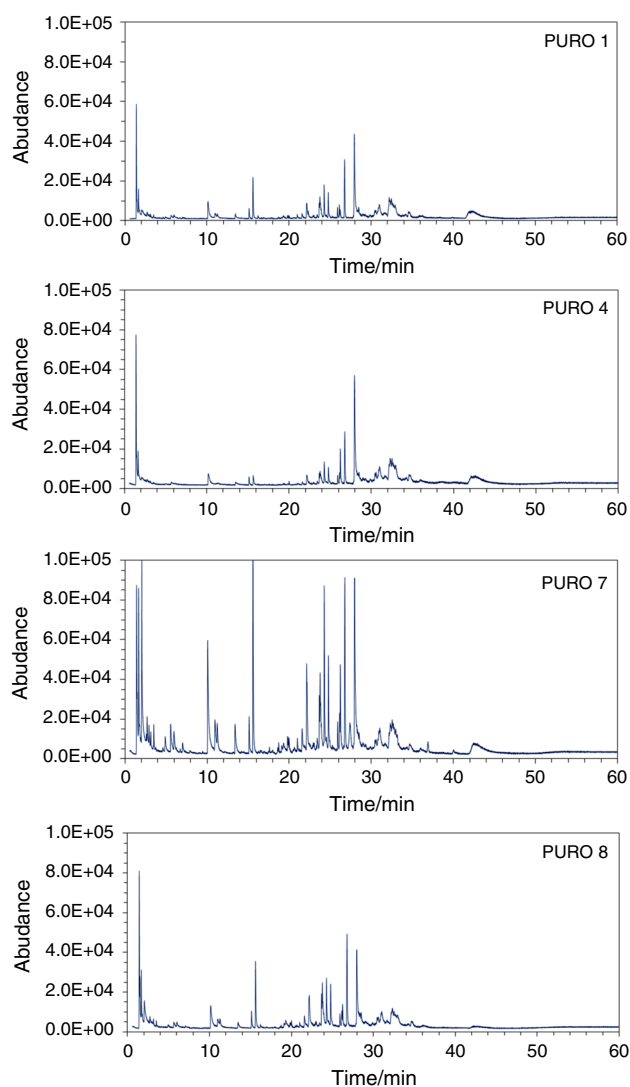
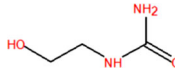

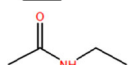
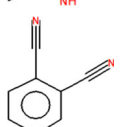
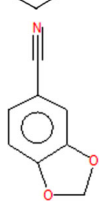
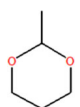
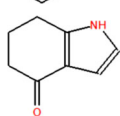
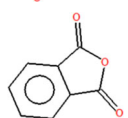
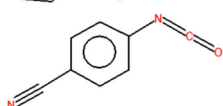


Fig. 4 Total ion chromatograms from analysis of volatile products obtained during thermal degradation of selected rigid polyurethane materials at 300 °C

Table 5 List of products formed during the thermal degradation of selected rigid polyurethane foams at 300 °C

Nr	Retention time/min	Name of compound (CAS Registry No.)	Molecular structure	Peak area/% at 300 °C for:			
				PURO 1	PURO 4	PURO 7	PURO 8
1	1.40	Carbon oxides		15.26	21.15	5.62	12.85
2	1.66	Isopropenyl acetate (CAS: 108-22-5)		5.31	5.89	5.80	3.87
3	2.07	Acetic acid (CAS: 64-19-7)		–	–	11.68	–
4	2.94	Ethyl ethanimidate (CAS: 208-07-3)		–	–	2.07	2.62
5	5.58	Propanoic acid, 2-oxo-, methyl ester (CAS: 600-22-6)		–	–	1.87	–
6	10.14	2-Propanone, 1-hydroxy-, acetate (CAS: 592-20-1)		4.39	1.64	9.00	5.44
7	11.25	1,2-Propanediol diformate (CAS: 53818-14-7)		–	–	1.86	–
8	15.14	Isocyanatobenzene (CAS: 103-71-9)		2.20	1.94	1.84	2.14
9	15.61	Methoxyformamidine (CAS: 2440-60-0)		8.30	1.84	9.07	8.93
10	21.59	Cycloserine (CAS: 68-41-7)		–	–	1.14	1.66
11	22.15	1-Acetyl-3-methylurea (CAS: 623-59-6)		4.35	–	5.45	1.91
12	22.61	2-(Aminoxy)butanoic acid		2.01	–	–	4.90
13	23.68	Isopropyl acetate (CAS: 108-21-4)		2.56	–	–	–
14	23.76	2-Propanol, 2-nitroso-, acetate (ester) (CAS: 6931-04-0)		1.31	1.30	2.00	3.85
15	23.80	Isopropyl glycidyl ether (CAS: 4016-14-2)		5.76	–	0.90	1.50
16	24.27	2,4-Dimethyl-1,3-dioxolane-2-methanol (CAS: 53951-43-2)		5.25	4.63	5.63	4.73

Table 5 continued

Nr	Retention time/min	Name of compound (CAS Registry No.)	Molecular structure	Peak area/% at 300 °C for:			
				PURO 1	PURO 4	PURO 7	PURO 8
17	24.79	(2-Hydroxyethyl)urea (CAS: 2078-71-9)		1.84	3.84	3.19	5.28
18	25.91	1,3-Dioxolane (CAS: 646-06-0)		1.97	1.55	1.11	1.42
19	26.13	N-Ethylacetamide (CAS: 625-50-3)		15.26	1.74	1.18	1.70
20	26.56	1,2-Benzenedicarbonitrile (CAS: 91-15-6)		–	–	–	12.85
21	26.26	Piperonylnitrile (CAS: 4421-09-4)		–	6.97	3.65	2.80
22	26.78	2-Methyl-1,3-dioxane (CAS: 626-68-6)		12.35	12.41	7.64	4.88
23	27.96	1,5,6,7-Tetrahydro-4-indolone (CAS: 13754-86-4)		27.14	35.10	13.72	3.87
24	27.97	Phthalic anhydride (CAS: 85-44-9)		–	–	3.23	–
25	28.08	4-Isocyanatobenzonitrile (CAS: 40465-45-0)		–	–	–	2.62

temperatures in the range of 320–345 °C. Those stages are most likely related to the degradation of urea rigid segments and products of their decomposition [45, 46].

The fourth step ($T_{N_{max4}}$) was observed in nitrogen atmosphere at temperature range of 345–450 °C and fifth step ($T_{N_{max5}}$) at range of 450–620 °C. For the experiments performed in air, the fourth degradation step ($T_{A_{max4}}$) was observed at 360–670 °C. The mass loss in that stage is associated with other segments of the remaining structure, including ether groups. Moreover, in those stages the by-products of pyrolysis or oxidization are also decomposed.

Highly porous lightweight polyurethane foams tend to have fast flame spread with the oxygen index in the range between 16 and 18 $V V^{-1}$ [9]. The value of OI for the analyzed commercial polyurethane foam was relatively

high and not less than 25% $V V^{-1}$. The use of the proposed flame retardant systems resulted in only a slight increase in the parameter for the other samples. No visible changes in the results between the reference sample PURO 7 and composites lead to the conclusion that the use of nanofillers did not affect the test results. The obtained values allow to classify the composites as flame-resistant materials ($21 \leq OI \leq 28$).

All tested rigid polyurethane foams the largest amount of gases and fumes were emitted when the thermal degradation and combustion occurred at 300 °C. Gas chromatography data of the volatile samples released from selected materials during thermal degradation at 300 °C are shown in Fig. 4. The largest quantities of hazardous substances were created during the thermal degradation of the

sample PURO 7, which contain the addition of three non-halogen flame retardants (Table 1). While during degradation of PURO 2, the smallest quantity of products was created. Moreover, the amount of products released during the decomposition of the PURO 2 was also slightly lower than the quantity of the substance produced during the thermal decomposition of the foam does not contain any additives (PURO 8). In Table 5 are presented compounds identified in samples of gases and fumes, which were emitted during the thermal degradation of selected rigid polyurethane foams. The largest number of substances was detected and identified when the thermal decomposition of samples PURO 7 and 8 occurred. In the largest quantities, the products such as isopropenyl acetate, 2-propanone-1-hydroxy-acetate, methoxyformimidine, 2,4-dimethyl-1,3-dioxolane-2-methanol, (2-hydroxyethyl)-urea, 2-methyl-1,3-dioxalane and 1,5,6,7-tetrahydro-4-indolone were formed. Moreover, during decomposition of the foam PURO 8, the substances 1,2-benzenedicarbonitrile, piperonylonitrile and 4-isocyanatobenzonitrile were produced, not detected in other tested materials. Less of the compounds were identified in the gases and fumes emitted during the decomposition of PURO 1 and PURO 4. However, the type of major products remained unchanged in comparison with the reference samples.

After comparing the results obtained during the combustion of the nanocomposite and reference material, it has been found that the addition of nanofillers reduces the amount of evolved products and also effects on their type.

Conclusions

Within the framework of this work, the recipes of flame retardants for rigid polyurethane foams, containing nanofillers (MWNTs, TT) and halogen-free flame retardants, were prepared. The produced materials were subjected to a series of tests allow to characterize their flammability and smoke emission. Moreover, for selected composites thermal stability, oxygen index and the identification of products released during the thermal degradation and combustion of these materials were also determined.

Increasing the thermal stability and reducing the flammability of composites were achieved by the formation of the carbonized coating on the surface of composites, which limited the access of fire into the deeper layers of the material and inhibited the formation of radicals. The formation of char, confirmed by thermogravimetric analysis, was favored by the presence of nanoadditives. The amount of emitted smoke was reduced by the applying appropriate flame retardants, especially the flame retardant based in aluminum hydroxide. The results of a study conducted by means of the cone calorimeter confirmed the presence of a

synergistic effect between the used nanofillers and halogen-free flame retardants. Using the steady-state tube furnace and gas chromatograph with mass spectrometer allowed the identification of the major organic substances presented in the gases and fumes emitted during the combustion of selected polyurethane foams. It was found that the addition of nanofillers reduces the amount and the number of emitted products.

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