Article

Coating Composites Based on Polyurea Elastomers with Increased Fire Resistance and Their Use as Roofing Systems

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Abstract: This paper presents the results of tests on elastomer coatings based on polyurea–polyurethane formulation with increased fire parameters. Coatings modified with flame retardants: bis(phenylphosphate) resorcinol (RDP), trischloropropyl phosphate (TCPP), and aluminum hydroxide (ATH) were tested. Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA/DTG) were used to investigate the structure and thermal stability. The effectiveness of resorcinol bis(phenylphosphate) (RDP), tris chloropropyl phosphate (TCPP), and aluminum hydroxide (ATH) on heat release rate (HRR), smoke release rate (RSR), and oxygen consumption was evaluated using cone calorimetry. The cone calorimetry results were correlated with the mechanical properties of the coatings. The cone calorimetry analysis showed suitable organophosphorus flame retardant (FR) performance, significantly decreasing HRR and oxygen consumption. Additionally, 15% TCPP caused a reduction of HRR by over 50%, obtaining 211.4 kW/m^2 and pHRR by over 55%, reaching 538.3 kW/m^2. However, organophosphorus flame retardants caused a significant deterioration of mechanical properties simultaneously. Introducing a mixture of two FRs (RDP/TCPP) resulted in obtaining a coating with improved fire resistance and maintained good mechanical strength. The polyurea–polyurethane coating, modified with a mixture of two RDP/TCPP retardants (10:5), was simulated for the burning of roof systems. The result of the simulation was assessed positively. Thus, finally, it was confirmed that the proposed polyurea–polyurethane coating achieved the assumed flame retardant level.

Keywords: polyurea; flame retardancy; thermal properties; cone calorimetry; tensile strength

1. Introduction

Polyurea is a material formed during the reaction of isocyanate and amine. It has become of great interest over the last decade. The global polyurea market was estimated at USD 1.22 billion in 2021 [1,2]. This interest is due to its excellent physicochemical properties, as well as development in the field of its application. Polyurea coatings are characterized by high resistance to mechanical stress, such as tensile stress and puncture [3,4]. The lack of joints and shallow content of open pores in the structure of polyurea-based coatings make these materials ideal in waterproofing and anticorrosion protection. Polyurea is also widely accepted as an environmentally friendly material. However, like most plastics, polyurea coatings are characterized by low fire resistance [5]. Thus, determining flammability properties and searching for an improvement in the fire resistance of polyurea has become a recent trend in research.

A perfect flame retardant (FR) coating should be easy to apply, have a low flame spread and release of smoke and toxic gases, have good adhesion to the underlying surface, be durable, and offer a low cost [6]. Obtaining polyurea-based coatings with improved flame

retardancy may allow them to meet the characteristics mentioned above and contribute to improving the safety of both new and existing buildings. Good durability, adhesion of polyurea to most materials (i.e., concrete, steel, bitumen surfaces), its fast reactivity, and relative moisture insensitivity can result in an excellent alternative to other fire protection systems such as fire protective boards, intumescent coatings, flexible blanket systems, or other spraying solutions [7].

New solutions in the fire protection field can be found in the literature. Recently, nanomaterials have received some attention in this area. Carbon nanotubes and nanosilica are often used as additives to increase fire resistance [8–11]. The recent research provided by Cheng-Fei Cao et al. has shown great fire resistance results of graphene oxide (GO) nanosheets combined with melamine diborate (M·2B) [12]. However, the high cost of nanomaterial production and the difficulty in introducing carbon materials into the polymer matrix are still the main barriers hindering these products' widespread usage.

Much research addresses the problem of polyurea elastomers' flammability [13–20]. There are many ways to reduce the flammability of polymeric materials, including polyurea [21]. At the same time, it is known that each modification, including the use of physical flame retardants, causes a change in other processing and utility properties of the material. Also, due to short reaction time, polyurea must be manufactured under specific conditions (pressure >150 bar and temperature ~70 °C) using specialized equipment. Hence, this creates limitations associated with the use of flame retardants, including maximum particle size and viscosity of processed components. The effective selection of flame retardants depends on the type of polymer and the conditions in which the material will be used. Materials to be used in construction for flexible waterproof coatings must meet a comprehensive, precisely defined set of criteria to obtain the required technical approvals. Only then can they be put into practice. Among them, the most common are inorganic additives, organophosphorus compounds, and intumescent paints. However, most studies show only the flammability effect of FRs without focusing on the mechanical properties of polyurea coatings.

This work aims to present the research results on new coatings based on polyurea using selected physical flame retardants and their mixtures, which do not impair their mechanical properties. These coatings are to meet all the requirements to obtain the technical approval necessary for building materials, enabling use in real conditions. Coatings modified with flame retardants: bis(phenylphosphate) resorcinol (RDP), trischloropropyl phosphate (TCPP), and aluminum hydroxide (ATH) were tested. These flame retardants were preliminarily selected due to their anti-flammability effect, as well as their low price. Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA/DTG) were used to investigate the structure and thermal stability. The effectiveness of RDP, TCPP, and ATH on heat release rate (HRR), smoke release rate (RSR), and oxygen consumption was assessed by cone calorimetry. The cone calorimetry results were correlated with the mechanical properties of the coatings.

The secondary objective of the research was to select the best mixture of flame retardants in terms of flammability and mechanical resistance of the modified polyurea coating. The novelty of this research lies in the fact that we also considered a mixture of selected flame retardants, taking into account a balance of the fire resistance and the mechanical parameters. The polyurea–polyurethane coating, modified with a mixture of two RDP/TCPP retardants (10:5), was simulated for burning roof systems. The result of the simulation was evaluated positively. Thus, it was finally confirmed that the proposed polyurea–polyurethane coating reached the assumed flame retardant level with no degraded mechanical properties.

2. Materials and Methods

2.1. Sample Preparation

The raw materials used in this work were the following: low-functional MDI-based prepolymer containing 15% NCO groups (Huntsman, Texas, CA, USA), N,N'-Bis(sec-

butylamine)diphenylmethane (Albemarle, Charlotte, NC, USA), diethyl toluene diamine (Lonza, Basel, Switzerland), propylene glycol (PCC Rokita, Brzeg Dolny, Poland), 1,3-propanediol (LyondellBasell, Rotterdam, the Netherlands), aluminum hydroxide (ATH), bis (resorcinol diphenyl phosphate) (RDP), and tris chloropropyl phosphate (TCPP).

The samples were prepared in a few steps. Firstly, part B was prepared. It was made of diamine, chain extender, polyether polyol, aliphatic diol, flame retardant, and the necessary catalyst. The prepared mixture was thoroughly mixed using a high-speed stirrer and poured into a cartridge together with the unmodified isocyanate (part A). The samples were sprayed onto polypropylene (PP) plates in a 1:1 volume ratio. In the calculations, the isocyanate index was established at 1.1. The polyurea–polyurethane elastomer samples were cured at room temperature for seven days. The amount of FR was set at 15% of the total weight of the compound. A reference sample without FR was also prepared according to the above procedure. To correctly analyze the combustion with the use of a cone calorimeter, approx. 4 mm thick coatings were made. The composition of the coatings and their names are given in Table 1.

Table 1. Prepared formulations of polyurea-based elastomers (Part B).

Sample	Ingredient Content [%bw]						
	M5020	**MPDiol**	**Ethacure 420**	**DETDA**	**RDP**	**TCPP**	**ATH**
Reference	69.6	4.6	10.1	12.1	0	0	0
15% ATH	52.3	4.6	11.8	12.1	0	0	30
15% TCPP	41.2	4.6	12.9	12.1	0	30	0
15% RDP	41.4	4.6	12.9	12.1	30	0	0
RDP/TCPP	43.3	4.6	12.7	12.1	20	10	0

2.2. Methods

2.2.1. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of polyurea–polyurethane copolymers were examined using a Bruker IFS 113 V spectrophotometer with the single quest reflection ATC accessory 187 IR affinity-1. Samples were tested in the 400–4000 cm^{-1} range at a resolution of 2 cm^{-1}. All characteristic wavenumbers were registered and compared with the reference sample.

2.2.2. Thermogravimetric Analysis (TGA/DTG)

According to the standard method PN-EN ISO 11,358 [18], mass loss was investigated with the Netzsch TG 209 Libra apparatus. Small specimens (approximately 10 mg) were prepared. The scanning was performed at temperatures ranging from 20 °C to 1000 °C at a heating rate of 5 °C/min in the air atmosphere. Each experiment was performed five times. The thermal degradation curve and a final residue were determined for each sample.

2.2.3. Cone Calorimetry

The cone calorimetry analysis was performed for selected coatings based on polyurea–polyurethane elastomers to characterize the burning course fully. The test was carried out in accordance with the applicable ISO 5660-1 [22]. The test samples had an area of 100 cm^2 and a thickness of 3pprox.. 4 mm. The heat flux was set at 50 kW·m^{-2}, and it was distant from the surface of the tested material by 25 mm. The combustion process of the tested materials took place in a horizontal position.

2.2.4. Tensile Tests

The tensile tests were performed for coatings with an average thickness of 2 mm, which results from the standard application of this plastic. The tests were carried out in accordance with ISO 527-2 [23], using the INSTRON 34TM-30 testing machine. Due to the high wear and tear of polyurea-based materials, 1BA test paddles were used. The tests were performed at the ambient temperature (approx. 20 °C).

3. Results and Discussion

This section describes the influence of flame retardants on the chemical, physical, and thermal properties of polyurea-based coatings compared to a standard recipe without FR content.

3.1. FT-IR Analysis

The resulting coatings were first characterized by FTIR spectroscopy (Figure 1). We concentrated the analysis on certain functional groups from fire retardants incorporated into the coating structure, such as the P–O group of TCPP and the P–O–Ar group of RDP.
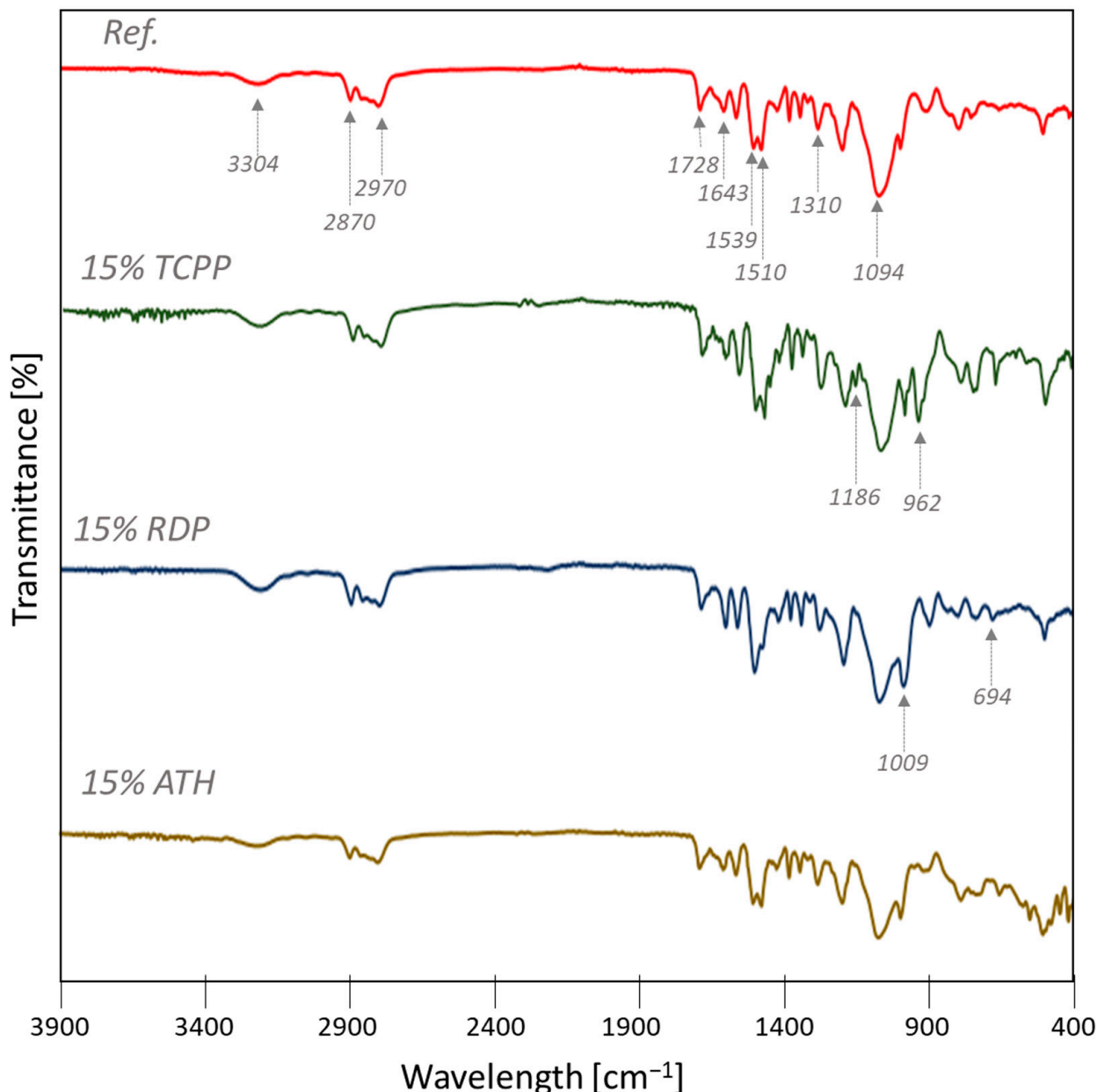
Figure 1. FTIR spectra of tested samples: reference and with additions of 15% RDP, 15% TCPP, and 15% ATH.

On the spectrum of the unmodified polyurea–polyurethane composite, specific bands are visible: a very strong absorption peak at 1094 cm^{-1}, attributed to the CN group of alkylamine stretch; strong peaks at 1510 and 1539 cm^{-1} associated with NO_2 bonds; peaks at

1643 and 1728 cm^{-1} indicating urea and urethane; and stretchable alkane and aldehyde CH groups at 2970 and 2870 cm^{-1}, respectively. Moreover, the absorption peak of the stretchable carboxyl group was found at 1310 cm^{-1}, and the amide bond at 3304 cm^{-1} [24–26]. In the range of 3200 ÷ 3600 cm^{-1}, only one N-H band is observed, which proves the complete reaction of the primary amines used to obtain the coating [25].

In the case of the coating containing 15% ADP, no additional bands from this compound were observed in the FTIR spectrum. This is due to the fact that this additive is an inorganic compound, inert to both alcohols and isocyanates. The spectrum containing a 15% addition of resorcinol bis(diphenylphosphate) (RDP) showed an increase in band intensity for the wavenumber 962 cm^{-1} and 1186 cm^{-1}. They correspond to the P–O single bond and the P–O–Ar group, respectively [25]. In the spectrum for the polyurea–polyurethane coating with the addition of 15% TCPP, the strongest band from this additive was recorded at the wavelength of 1009 cm^{-1}, associated with the P–O–C group. For the wavenumber equal to 694 cm^{-1}, a band corresponding to the Cl–C bond was also observed [25]. As can be inferred from the above spectra analysis, the formation of faint bands from flame retardants based on TCPP and RDP compounds is proven.
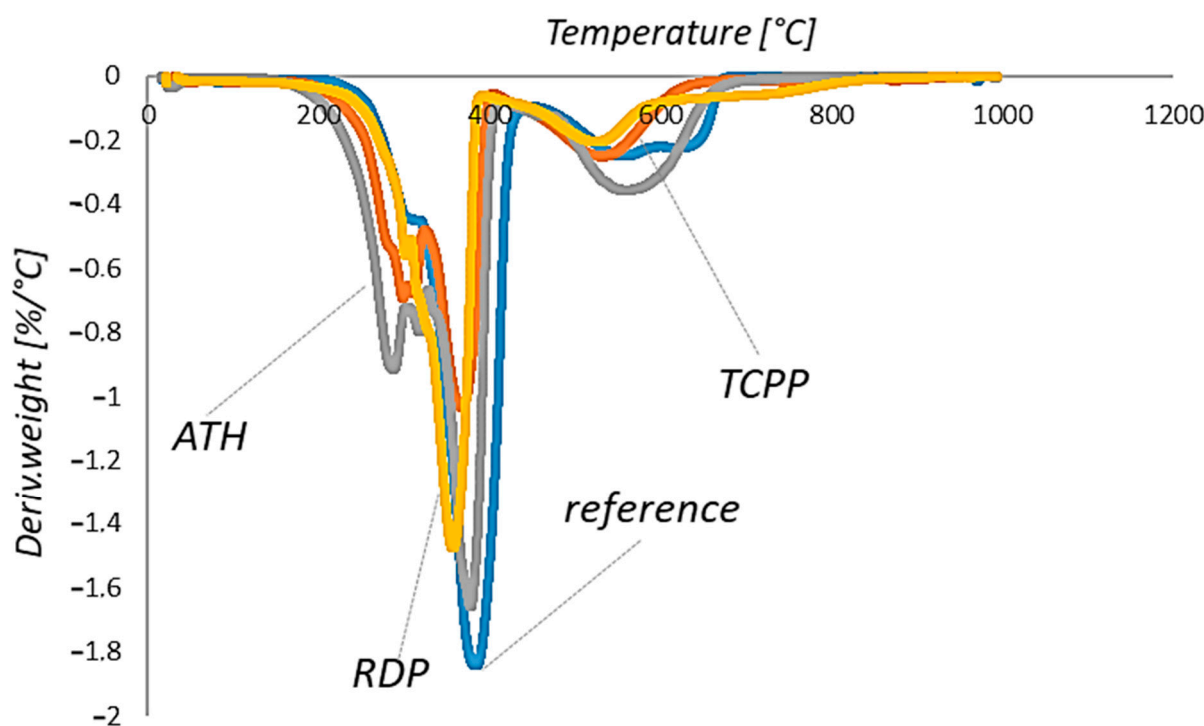
3.2. Thermogravimetric Analysis (TGA/DTG)

The thermal stability of flame retardants is important for processing, thermal stability, flame retardant properties, and end-use polymer product applications. The thermogravimetry analysis (TGA) method is applied to investigate the thermal degradation behaviors of the samples by measuring the volatilization of degradation products [27].

Thermogravimetric analysis of the obtained polyurea–polyurethane coatings showed changes in temperature resistance in relation to the reference sample. Figures 2 and 3 show the TGA/DTG profiles obtained for the tested coatings containing the addition of RDP, TCPP, and ATH flame retardants in the air atmosphere. All thermograms were compared with the results obtained for the reference coating. The parameters specific to coatings subjected to thermogravimetric analysis are listed in Table 2.
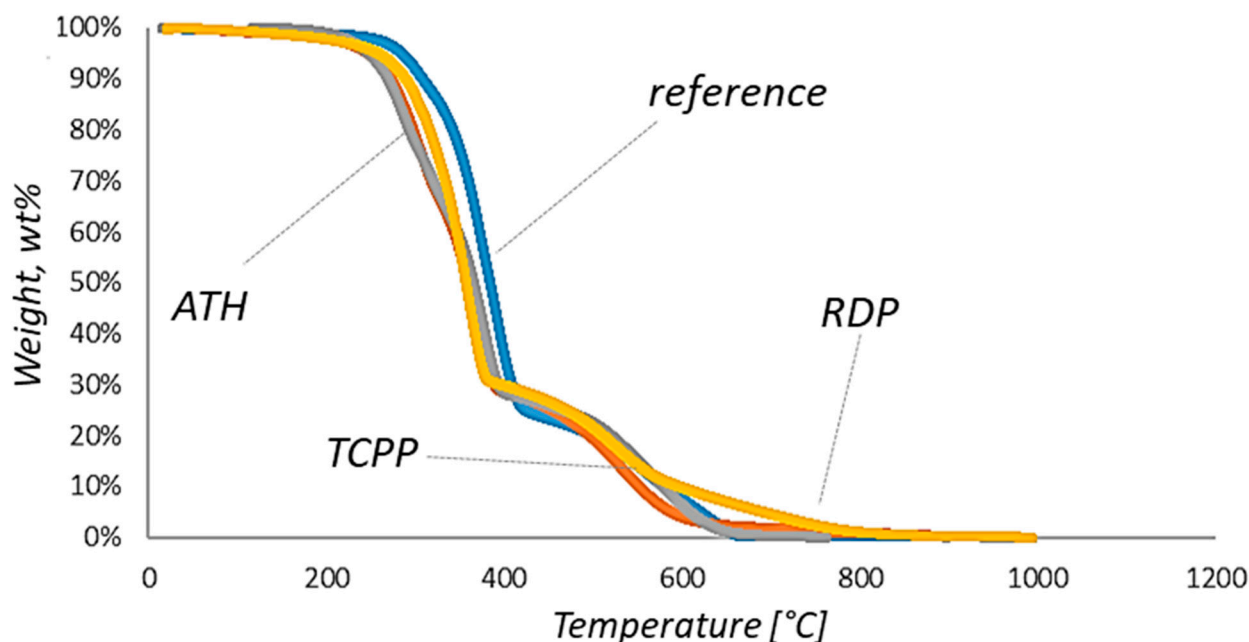
Figure 2. TGA curves of tested samples: reference and with additions of 15% RDP, 15% TCPP, and 15% ATH at a heating rate of 5 °C/min in the air atmosphere.

Figure 3. DTG curves of tested samples: reference and with additions of 15% RDP, 15% TCPP, and 15% ATH at a heating rate of 5 °C/min in the air atmosphere.

Table 2. Characteristic parameters for coatings subjected to thermogravimetric analysis.

Sample	Temperature after Degradation of 70% of the Sample [°C]	Residue at the End of the Test (T = 994 °C) [%]
reference	411.0	1.87
15% RDP	469.5	5.38
15% TCPP	400.1	2.32
15% ATH	439.2	10.21

The decomposition of coatings with the addition of an aluminum hydroxide flame retardant started at approx. 200 °C. The phenomenon of mass loss after reaching this temperature is related to the deodorization of aluminum hydroxide. The water released in this process is a cooling agent and reduces the concentration of volatile combustible products of polymer matrix pyrolysis. Flame-retardancy improvement of the polyurea coatings containing aluminum hydroxide appeared when the temperature over 400 °C was reached. The residue after combustion of the polyurea–polyurethane membrane with the addition of 15% ATH was 10.21%.

The analysis of the temperature resistance of the elastomeric coating containing the initial addition of resorcinol bis(diphenylphosphate) showed an increased rate of coating decomposition to a temperature of approx. 400 °C. This is related to the decomposition of the flame retardant, which occurs below the decomposition temperature of the polyurea-polyurethane elastomer. Over this temperature, the process slows down, providing the best efficiency between 400 and 550 °C. An increase in non-decomposed coating residue was also observed relative to the sample without the addition of RDP. For the reference sample, the non-degraded residue accounted for 1.87% of the initial weight of the coating, and for the sample containing 15% of the addition of resorcinol bis(diphenyl phosphate), this value was 5.38% of the initial weight.

In the case of a coating containing an additive based on tris(2-chloro-1-methylethyl phosphate), similarly to the RDP flame retardant, it decomposes at a lower temperature than the polymer matrix. The beginning of the decomposition reaction of this flame

retardant is already visible at a temperature of approx. 200 °C. The increased decomposition rate of the coating with the addition of TCPP is observed up to the temperature of 400 °C. The residue after combustion of the membrane containing 15% of tris(2-chloro-1-methylethyl) phosphate was 2.32% of the initial weight, so it was a value very close to the reference sample.

3.3. Cone Calorimetry

3.3.1. Effect on the Heat Release Rate

The most important parameter describing the burning behavior of plastics is the heat release rate (HRR). According to the principle of the combustion triangle, this parameter reflects the rate of thermal decomposition of the polymer matrix, which ultimately affects the amount of volatile combustible components in the gas phase. The most important task in the process of flame retarding is the effective reduction of released energy.

Figure 4 shows the HRR results obtained for polyurea–polyurethane coatings. The red line shows the average heat release rate for the reference sample over time. One can notice a sudden increase in the generated heat after exceeding 50 s. Much more volatile flammable compounds are produced at this point, resulting in a sharp temperature rise, known as a "flashover". During the combustion of the unmodified elastomeric polyurea-polyurethane coating, a very high peak of HRR (>1200 kW·m^{-2}) was noticed after approx. 85 s. After this time, the HRR value decreased sharply due to the burnout of most of the polymer coating. The addition of flame retardants significantly affected the development of the combustion process. The polyurea-based coatings containing organophosphorus FR showed a decrease of pHRR to values not exceeding 850 kW·m^{-2}. Additionally, the use of flame retardants caused the "flattening" of the heat release rate curve. In the case of aluminum hydroxide, this is due to its high heat capacity and cooling properties. In the case of organophosphorus compounds, the phenomenon of reducing HRR is associated with "scavenging" highly active hydrogen and hydroxyl radicals. Based on the results of this analysis, tris chloropropyl phosphate turned out to be the most effective flame retardant in terms of the rate of heat released.
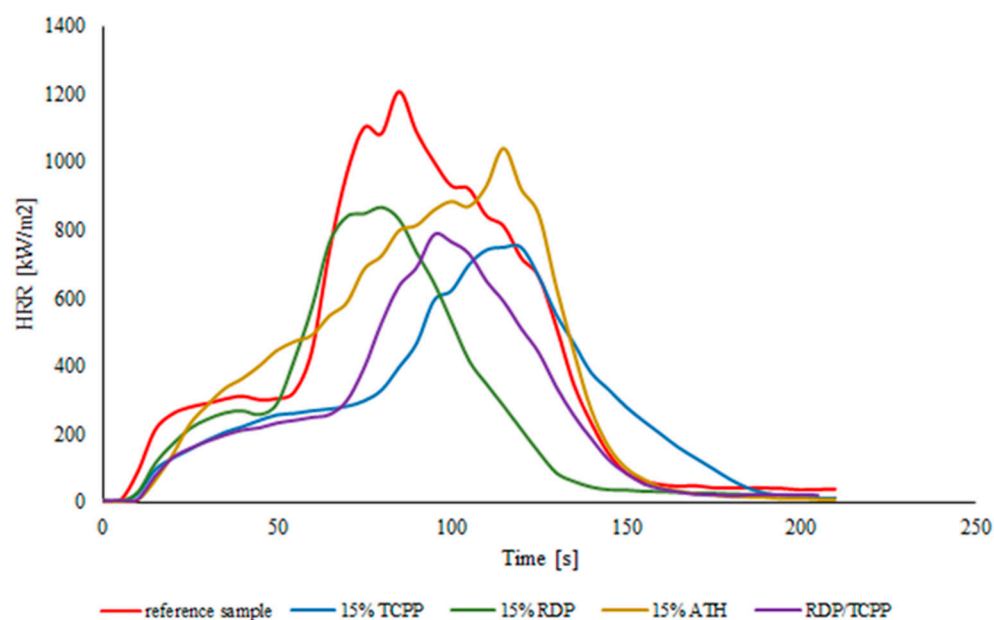
Figure 4. Heat release rate as a function of combustion time.

The values of average and maximum HRR values obtained for the analyzed coatings are presented in Table 3. The analysis of unmodified polyurea–polyurethane coating showed an average value of HRR = 423 ± 14 kW·m^{-2} and the maximum value of pHRR = 1175 ± 29 kW·m^{-2}. All flame retardant additives reduced both HRR and pHRR.

The most effective was TCPP, which reduced these values to 211 ± 78 kW·m^{-2} and 538 ± 185 kW·m^{-2}, respectively. Resorcinol bis (diphenyl phosphate) also caused a significant reduction of heat release rate, obtaining an average HRR of 255 ± 32 kW·m^{-2} and pHRR = 741 ± 137 kW·m^{-2}. Table 3 summarizes the cone data for polyurea-based coatings modified with various FRs.

Table 3. Cone data for polyurea-based coatings modified with different FRs.

Sample	HRR [kW/m^2]	pHRR [kW/m^2]	Consumption TSP]		
			of O$_2$ [g]	[m^2/m^2]	TTI [s]
Reference	423 ± 14	1175 ± 29	66 ± 7	18 ± 1	8 ± 1
15% RDP	255 ± 33	741 ± 137	38 ± 3	25 ± 3	10 ± 1
15% TCPP	211 ± 78	538 ± 185	36 ± 8	31 ± 3	10 ± 1
15% ATH	349 ± 36	855 ± 169	56 ± 2	13 ± 1	12 ± 2
RDP/TCPP	266 ± 58	654 ± 169	40 ± 8	32 ± 4	10 ± 2

3.3.2. Effect on Oxygen Consumption

Oxygen consumption is another parameter that determines the activity of flame-retardant compounds during the burning process of plastics. It describes the effectiveness of flame retardants in limiting oxygen access to the burning composition. Oxygen consumption may be registered by changes in oxygen concentration (Cp) over time.

The oxygen concentration registered for polyurea-based coatings is presented in Figure 5. A sharp increase in oxygen consumption can be noticed during the reference coating flammability tests after 50 s. The minimum O$_2$ concentration recorded for this sample was Cp ~ 16.6%, after approx. 85 s. The 15% load of ATH in the polyurea–polyurethane coating did not significantly affect the amount of consumed O$_2$. The maximum oxygen consumption was postponed by several seconds, occurring near 120 s. (Cp ~ 16.8%). The flame retardants based on organophosphorus compounds showed much more efficient behavior. TCPP and RDP flammability retardants caused an increase in the minimum oxygen concentration to 18.3% and 17.8%, respectively. The evolving oxygen consumption over time is presented in Figure 5.
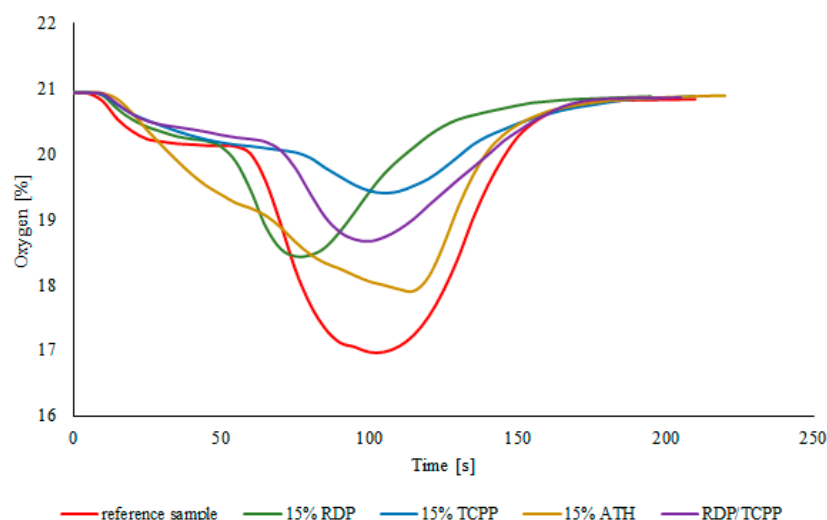
Figure 5. The changing concentration of oxygen as a function of combustion time.

3.3.3. Effect on Ignition Time

The use of conical calorimetry in the flammability analysis of plastics results in very accurate results that can be correlated with each other. During the tests, a heat flux of 50 kW·m^{-2} was established. The reference sample obtained a result of TTI = 8 ± 1 s. The presence of ATH, characterized by high heat capacity, extended the burning start time

by approximately 4 s, reaching TTI = 12 ± 2 s. The addition of organophosphorus flame retardants was not as effective as for ATH and caused a delay of the ignition time by approx. 2 s, obtaining results around 10 s. TTI results are also presented in Table 3.

3.3.4. Effect on Dynamics of Combustion Process

Polyurea-based coatings are primarily composed of organic materials, and therefore their combustion process can be divided into two distinct phases. The first phase, known as the condensed phase, is related to the pyrolysis process of the polymeric matrix. This process occurs without the presence of oxygen and involves the breaking down of long polymer chains into volatile and combustible products. The high heat energy of the flame can catalyze this decomposition process. The smaller molecules generated by the pyrolysis process enter the gas phase, where subsequent combustion processes occur. In this phase, highly reactive hydrogen radicals play a critical role, reacting with oxygen and carbon monoxide to drive the main exothermic reactions.

The dynamics of the combustion process of polyurea-based coatings are heavily influenced by their composition, particularly the amount and type of flame retardant additives used. The thermal decomposition of the reference sample is characterized by a relatively high rate of released heat, which also results in a high mass loss rate (MLR). Figures 6 and 7 reflect the impact of flame retardant additives on the coating's combustion process. The combustion dynamics of the sample with 15% aluminum hydroxide addition differs significantly from the reference sample. While a decrease in the rate of heat released during combustion can be observed in this sample (Figure 6), it does not correspondingly reduce the rate of mass loss (Figure 7). In fact, a significant increase in the rate of weight loss is evident, caused by the insufficient amount of flame retardant used. This phenomenon occurs due to the production of aluminum oxide during the dehydration of aluminum hydroxide at temperatures of 180–220 °C. Aluminum oxide can absorb a large amount of heat, close to 1170 kJ/kg. However, the amount of flame retardant used is too small to slow down the material decomposition process effectively. Instead, the low decomposition temperature of $Al(OH)_3$ accelerates the process.
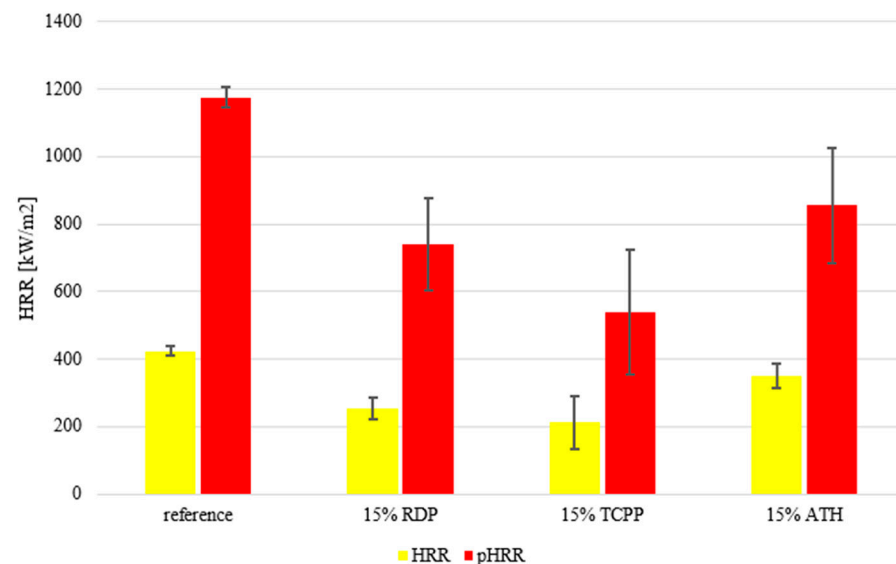
**Figure 6.** Heat release rate results.
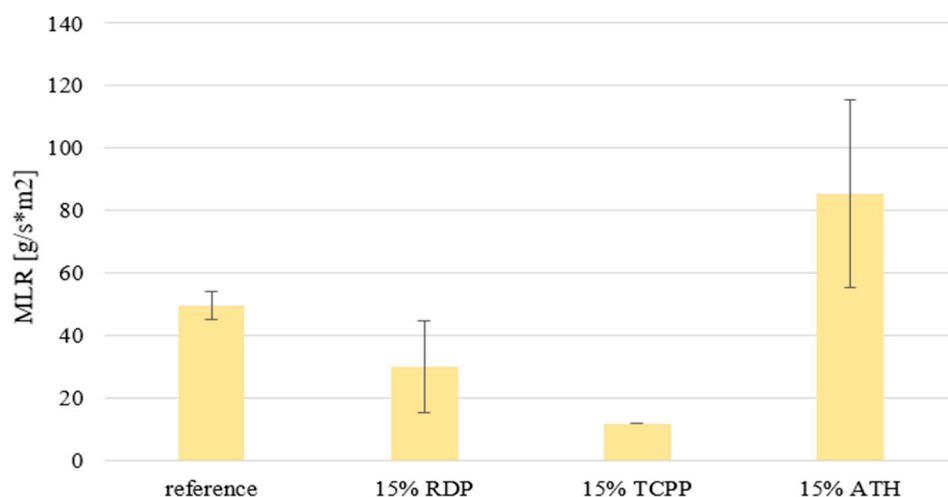
Figure 7. Mass loss rate results.

The flame retardants RDP and TCPP operate effectively in both the gaseous and condensed phases, and they have a greater impact on altering the course of the combustion process. As a result, both the rate of mass loss and the rate of heat release were significantly reduced in both cases.

3.3.5. Effect on the Smoke Release Rate (RSR) and Total Smoke Produced (TSP)

The cone calorimetry analysis allows us to determine the volume of gases released during combustion. This parameter is important in cases where we deal with the application of plastics in closed spaces with poor ventilation.
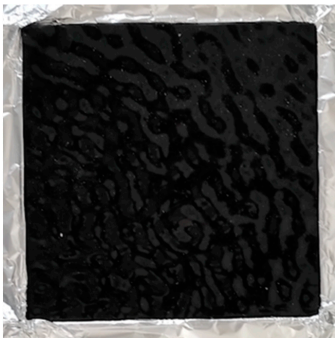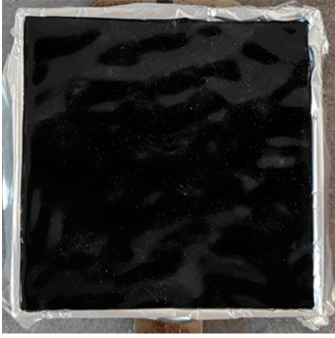
Figure 8 presents the smoke release rate (RSR) over time determined for all the prepared coatings. The RSR of the reference sample did not exceed the value of 20 $(m^2 \cdot s^{-1}) \cdot m^{-2}$. The addition of organophosphorus flame retardants significantly increased the volume of produced fumes, mainly due to the HCl and NH_3 released. ATH was the only flame retardant performing well in this area, causing a significant reduction of RSR. The total smoke produced (TSP) was also determined, as already presented in Table 3. The poorest performance was given by the coating containing the mixture of RDP/TCPP antipyrines, which was added in the ratio 10:5. TSP obtained for that sample reached a value of $32 \pm 3 \, m^2$. Compared with the reference sample (TSP = $18 \pm 1 \, m^2$), an almost 80% increase was observed, while 15% content of ATH caused the decrease of TSP, obtaining $13 \pm 1 \, m^2$.
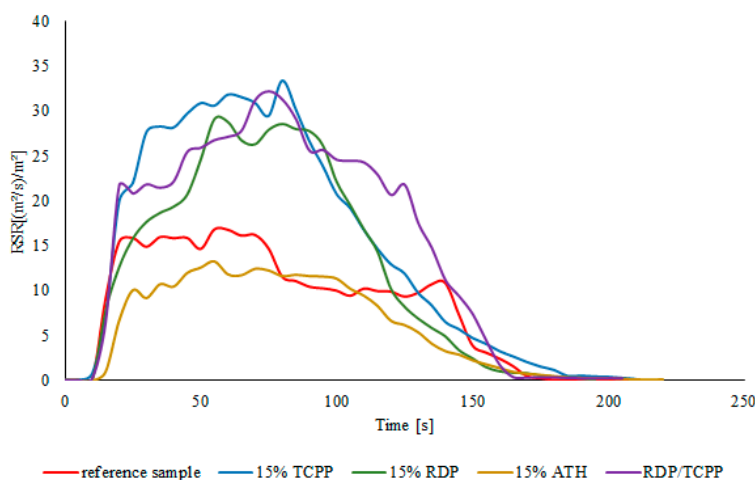
Figure 8. Smoke release rate as a function of combustion time.

Table 4 shows photos of elastomeric coatings subjected to cone calorimetry testing. The combustion of the reference sample resulted in almost complete degradation of the coating. In the photos presenting the result of burning membranes containing flame retardants based on resorcinol bis(diphenyl phosphate) and tris(2-chloro-1-methylethyl) phosphate, a carbon layer can be seen. In the photo of the coating with the addition of aluminum hydroxide after combustion, an inorganic residue can be seen coming from the flame retardant used (aluminum oxide).

Table 4. Polyurea-polyurethane coatings burnt in a cone calorimeter.

Sample	Before Burning	After Burning
reference		
15% RDP		
15% TCPP		
15% ATH		

3.4. Polyurea–Polyurethane Coating Modified with RDP/TCPP Mixture

Based on the results of tests on polyurea–polyurethane coatings with additives: 15% ATH, 15% TCPP, and 15% RDP, it was found that flame retardants based on tris(2-chloro-1-methylethyl) phosphate and resorcinol bis(diphenylphosphate) most effectively reduced flammability of polyurea–polyurethane coatings. Thus, a recipe for a polyurea–polyurethane coating modified with a mixture of these two retardants was developed. Due to the negative impact of the TCPP flame retardant on the mechanical properties of the coating, it was decided to introduce only 5% of this flame retardant into the elastomer coating. A flame retardant based on resorcinol bis(diphenyl phosphate) was used in the amount of 10%. Coatings with such a composition were subjected to further tests. The oxygen index was determined. Its value was 22.9 ± 0.1%. Compared to the reference value (21.6 ± 0.2%), there was an increase of 1.3 percentage points. Testing the mechanical strength of a coating containing a combination of two flame retardants, based on resorcinol bis(diphenyl phosphate) and tris(2-chloro-1-methylethyl) phosphate, allowed us to obtain a membrane with relatively high strength parameters. The maximum stress obtained during the test was 13.41 MPa ± 0.66 MPa, and thus a decrease in relation to the reference sample by 13% (15.5 MPa ± 1.32 MPa). The mean elongation at break measured during the test (342 ± 17%) was also positive, only 3% lower than the reference sample (352 ± 21%).

The burning process of the flame-retardant elastomeric polyurea–polyurethane coating recipe was characterized using cone calorimetry. During the test, parameters such as total heat released, heat release rate, total amount of smoke produced, ignition time, and oxygen consumption were determined. All parameters are presented in Table 5 and compared with reference values. The cone calorimetry test performed for the elastomer coating with the addition of RDP and TCPP flame retardants showed a reduction in the total heat released in relation to the reference value by over 40%. Parameters such as the average heat release rate (reduction by approx. 37%), the maximum heat release rate (reduction by approx. 44%), ignition time (extend by approx. 2 s), and total oxygen consumption (reduction by approx. approx. 40%) were determined. The parameter that deteriorated is the amount of smoke produced. It reached a value over 224% higher than the reference value.

Table 5. Results of the B-roof T1 test, carried out for a polyurea–polyurethane coating containing the addition of 10% RDP and 5% TCPP.

Test NO Coating Type		Sample 1		Sample 2		Sample 3		Sample 4	
The way the flames spread		▲	▼	▲	▼	▲	▼	▲	▼
External spread of fire [minutes and seconds]	100 [mm]	-	7′23″	-	6′22″	-	7′47″	-	6′56″
	200 [mm]	-	13′31″	-	-	-	12′53″	-	12′46″
	300 [mm]	-	-	-	-	-	-	-	-
	400 [mm]	-	-	-	-	-	-	-	-
	Measurement zone boundary	-	-	-	-	-	-	-	-
External damage length [mm]		60	318	18	220	20	480	90	345
Destruction	Internal Destruction Range [mm]	0	0	0	0	0	0	0	0
	Maximum failure length in each layer	60	318	18	220	20	480	90	345
	Flameless spreading in each layer	Not observed		Not observed		Not observed		Not observed	
	End time and end reason	22′38″ No visible burning		23′50″ No visible burning		24′39″ No visible burning		24′31″ No visible burning	
External failure surface [m^2]		0.12		0.12		0.12		0.12	

The combustion parameters of the modified coating with the addition of 10% RDP and 5% TCPP were already included in Table 3.

Photographs showing the coating with the addition of RDP and TCPP flame retardants are shown in Figure 9.

Figure 9. Photo of a polyurea–polyurethane coating with the addition of 10% RDP and 5% TCPP, before and after combustion.

3.5. Simulation of Combustion of the Entire Roof System

Each modification, including the use of physical flame retardants, changes the processing and functional properties of the material. Materials that are to be used, for example, in the construction industry for flexible waterproof coatings, must meet a specific set of properties in order to obtain the required technical approvals. Only then can they be put into practice. Table 5 shows the results of the roof system combustion test carried out in accordance with BN EN 13501-5. The roof system containing a polyurea–polyurethane coating with the addition of 10% RDP and 5% TCPP passed the B-roof (T1) test. The addition of organophosphorus flame retardants resulted in no flame spread up the burning roof system. External damage occurred mainly down the sample and averaged 341 mm in length. It should be noted that the migrating fire did not reach the border of the measurement zone in any direction, spreading the fire. No internal damage was observed for the performed flammability tests. For each test, the area of external damage reached the value of 0.12 m^2. All roof systems subjected to a combustion test were self-extinguishing after an average period of 23′55″.

The non-certified B-roof (T1) test of a roof system containing an unmodified polyurea–polyurethane coating was completed with a negative assessment of the burning process. The reference sample after 30′00″, due to continued burning, was extinguished manually. After this time, the length of the coating failure upwards and downwards was measured, reaching 150 mm and 200 mm, respectively. Table 6 presents photos of polyurea–polyurethane coatings with the addition of 10% RDP and 5% TCPP and the reference coating after the roof system combustion test. As can be seen, the parameters observed for the 10% RDP 5% TCPP mixture were much better than the ones for the unmodified reference material, both for the flame area and the structure of the roof coating after the burning process.

Table 6. Photos of polyurea–polyurethane coatings with the addition of 10% RDP and 5% TCPP and the reference coating after the roof system combustion test.

Sample	Before Burning	After Burning
reference		
10% RDP 5% TCPP (1)		
10% RDP 5% TCPP (2)		
10% RDP 5% TCPP (3)		

Table 6. *Cont.*

Sample	Before Burning	After Burning
10% RDP 5% TCPP (4)		

3.6. Tensile Tests

Dukarski et al. [21] described the influence of flame retardants (RDP, TCPP, and ATH) on the strength properties. Only aluminum hydroxide in a certain load (up to 10%) showed the strengthening effect of polyurea-based coatings in terms of maximum stress and stretching. Both RDP and TCPP caused a significant deterioration of these properties. Thus, similar tests were performed for the newly presented RDP/TCPP flame retardant mixture.

The characteristic parameters of the test are presented in Table 7. The results are compared with the polyurea-based coatings presented in the previous research. In this study, the tensile and elongation test showed relatively good durability properties of polyurea–polyurethane coating modified with a mixture of RDP and TCPP flame retardants. The tensile strength of RDP/TCPP showed a slight deterioration of 2 MPa (13 ± 1 MPa) compared with the reference sample. Elongation and Young's modulus also reached similar values to the unmodified coating. This phenomenon is explained by some sort of synergism between these two antipyrines. To our best knowledge, such an explanation has not been described yet in any research.

Table 7. Tensile test data of polyurea–polyurethane coatings modified by different flame retardants.

Sample	Tensile [MPa]	Elongation [%]	Young's Modulus [MPa]
reference	16 ± 1	352 ± 21	53 ± 7
15% RDP	11.2 ± 0.3	277 ± 3	79 ± 3
15% TCPP	7.3 ± 0.3	148 ± 7	97 ± 14
15% ATH	17 ± 2	305 ± 40	152 ± 10
RDP/TCPP	13 ± 1	342 ± 17	43 ± 2

4. Conclusions

This paper presents the results of tests on elastomer coatings based on polyurea–polyurethane formulation with increased fire parameters. Coatings modified with resorcinol bis(phenylphosphate) (RDP), trischloropropyl phosphate (TCPP), and aluminum hydroxide (ATH) flame retardants were tested. The content of these compounds was 15%. The effectiveness of RDP, TCPP, and ATH on heat release rate (HRR), smoke release rate (RSR), and oxygen consumption was assessed by cone calorimetry. The cone calorimetry results were correlated with the mechanical properties of the coatings. Cone calorimetry analysis showed good performance of organophosphate FRs, significantly reducing HRR and oxygen consumption. In addition, 15% TCPP reduced HRR by more than 50%, reaching 211.4 kW/m^2, and pHRR by more than 55%, reaching 538.3 kW/m^2. However, organophosphorus flame retardants also caused a significant deterioration of mechanical

properties. Introducing a mixture of two FRs (RDP/TCPP) resulted in a coating with increased fire resistance and good mechanical strength.

Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA/DTG) were used to investigate the structure and thermal stability of the modified coatings. FTIR analysis showed the presence of moieties mainly derived from organophosphorus compounds (RDP and TCPP). Due to the inorganic structure of aluminum hydroxide and its inert nature in relation to amine and polyol compounds, no visible changes in the spectrum were observed compared with the reference coating. Thermogravimetric analysis of the tested polyurea–polyurethane coatings showed the influence of flame retardant additives on the mass loss rate and their final weight. It was shown that the process of membrane decomposition begins earlier than in the reference sample, which was related to the decomposition of flame retardants at a lower temperature than the polymer matrix. In addition, the flame retardants based on RDP and ATH contributed to an increase in the weight of the coating residue at the end of the test, which did not decompose. The effectiveness of resorcinol bis(phenylphosphate) (RDP), trischloropropyl phosphate (TCPP), and aluminum hydroxide (ATH) on heat release rate (HRR), smoke release rate (RSR), and oxygen consumption was assessed by cone calorimetry.

The results of the oxygen index and cone calorimetry tests showed a significant improvement in the fire resistance of coatings with the addition of flame retardants TCPP and RDP. Tris(2-chloro-1-methylethyl) phosphate was the most effective in reducing the flammability of the coating. Its 15% content in the elastomer coating resulted in an increase of 2.5 percentage points concerning the reference value. A cone calorimetry study performed on this coating also showed a significant reduction in heat release rate, total heat release, or total oxygen consumption. However, using tris(2-chloro-methylethyl) phosphate (V) was associated with an increase in the amount of smoke produced by more than 76% compared to the reference sample. The flame retardant RDP also improved the oxygen index, although it was not as effective as in the case of TCPP. This was influenced by the presence of chlorine atoms in the TCPP additive, which additionally accelerated the process of inhibiting combustion in the gas phase. Flammability tests of elastomeric coatings containing aluminum hydroxide-based flame retardant showed a negative effect of this flame retardant on the oxygen index. The results obtained with the cone calorimeter were also unsatisfactory. Parameters such as the total energy released or the amount of oxygen consumed were only slightly improved compared to the reference sample. Nevertheless, ATH effectively reduced the amount of fumes produced, which may be important in studies reducing the toxicity of polyurea-based coatings. It also showed the most negligible impact on the mechanical properties of the polyurea-polyurethane coating.

This work aimed to obtain an elastomer coating based on a polyurea–polyurethane formulation with improved fire performance, thanks to the use of selected physical flame retardants with mechanical parameters that have not degraded. The conducted research focused on obtaining coatings intended for commercial application to roof systems. The membrane modified with a mixture of RDP and TCPP flame retardants showed an improvement in the most important parameters, including heat release rate, ignition time, amount of oxygen consumed, and oxygen index. The flammability test of the entire roof system turned out to be very important, thanks to which the ignition of the coating was simulated in real conditions. A positive assessment of the result of this test also confirmed the adequate flame retardancy of the coating with the use of organophosphorus flame retardants. It was equally important to maintain the mechanical properties of the membrane. The result obtained during the tests on the testing machine clearly indicated the lack of a significant effect of the modifying agents on the internal forces in the polyurethane coating. Thus, it was finally confirmed that the polyurea–polyurethane coating achieved the assumed flame-retardant level.

One should also note that polyurea is widely accepted as an environmentally friendly material. The proposed modifications do not affect this property. Also, we have not

observed new reactions and dangerous (toxic) compounds produced due to fire process and destruction.

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