



Article Formation of an Ammonium Nitrate Fuel Oil Similar Type of Explosive under Fire Conditions: Materials Based on Selected Polymers (PUR)

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Abstract: Polyurethanes (PURs) are a group of polymers with the most versatile properties and the broadest spectrum of application. Their name comes from the urethane group. PURs were introduced to the market on a large-scale basis by Bayer in 1942, in the form of Perlon U and Igamid U fibers produced by gradual polyaddition of diisocyanates and polyols. The development of PURs-production technology and the multitude of applications resulted in their widespread use. This group is so extensive that polyurethanes alone accounted for about 6% of the global production of polymers (2019)—most of them in the form of foam. Therefore, polyurethane can be found in a huge number of products—some of them stored in the vicinity of ammonium nitrate (AN). In the previous two articles, we showed that polymers and AN—stored within the same building—in fire conditions may, under certain circumstances, spontaneously transform into a material of explosive properties. The aim of this article is to check whether PUR, when in contact with AN, creates additional hazards, similarly to the previously tested polymers.

Keywords: self-acting formation of explosives; ANFO; ammonium nitrate; polyurethane foam; sponge

1. Introduction

Polyurethanes (PURs) are a very important group of polymers with a wide range of applications in various industries. As foams, they are used mainly in the construction, furniture and automotive industries. Without appropriate additives, foamed polymers with the urethane group have a low activation energy, and are highly flammable and smoke-generating. Regardless of the particular type of polyurethane foams, requirements related to their use—apart from their mechanical and insulating properties—include the level of their susceptibility to fire. Free of flame retardants, polyurethane (PUR) foams are combustible materials that emit significant amounts of toxic gases and vapors in the combustion process (cyano group, carbon monoxide, derivatives of esters) [1]. Due to their prevalence in the immediate vicinity of humans, for safety reasons, PURs require the use of substances that retard their flammability, in order to meet the minimum requirements for individual groups of products in particular industries [2].

However, there are no test results as of yet that are widely available relating to whether products which contain foamed PUR and—at the same time—meet the non-flammability criteria, may show an explosive potential in combination with ammonium nitrate (AN). From our point of view, examining such a combination is important due to the significant probability of the formation of mixtures containing PUR or polyisocyanurate (PIR) as well as AN in farm buildings or warehouses where fertilizers are stored. This article is an evaluation of our two previous publications [3,4]—initially based on the real incident in



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). the French province of Loire in 2003 [5]—which discuss the explosive potential of mixtures containing polymers and AN. One can easily imagine a situation where crushed polyurethane foam—e.g., from sandwich panels, mounting foams or upholstered furniture and mattresses—stored in farm utility rooms, has access to collective packaging with AN-based fertilizers or their scattered remains, constituting a potentially explosive material. Such an event can significantly affect the development and the course of fires in farm buildings or in transport. Flammability standards and the consequences of their introduction for building and finishing materials or consumer electronics containing PUR are included in [6].

Examples of regulations that define American and European minimum requirements concerning flammability, as well as conclusions of the Stockholm and Basel conferences, for foamed polyurethane are included in [7–12]. The number of production methods of PURs and their varied application require some systematization. PURs, depending on the production method and application, may have variable chemical composition and hence a fairly wide range of thermal properties witnessed, e.g., during fires [13].

Polyurethanes are used in a number of application areas, such as mechanical and electrical engineering, electronics, construction, transport, medicine, furniture manufacturing, household materials, etc. The basic products made of PUR are technical articles, coatings, foams, adhesive materials, gaskets, synthetic leather and membranes. Foamed polymers with the urethane group make up a significant share of the overall number of foamed plastics due to their structural diversity (rigid, flexible or integral), and there are a multitude of ways to modify their composition, their proportions and their production methods as well as the catalysts used. The main differences between various products made of PUR may be related to their mechanical strength, ability to reduce noise, resistance to solvents and resistance to weather conditions. All of these differences depend on the components used and their mass ratio. The flammability of PUR products also depends on these factors, as well as physicochemical and mechanical parameters—which is particularly important when the products in question are used as building materials. Statistical data on fire victims indicate a significant percentage share of deaths caused by smoke and toxicity of gaseous fire products [14].

Solid PURs are thermoplastics with a lower melting point than analogous polyamides. However, they have inferior mechanical properties and are not as brittle as solid polyamides, at least at temperatures above 0 °C.

Because of these disadvantages, materials of this group pose a great risk in fire conditions. The pyrolysis and thermal decomposition of polyurethanes result in the emission of toxic aerosols and gases. In order to reduce this risk, both halogenated and non-halogenated compounds (flame retardants) are introduced into the PUR composition [15].

Higher carbonyl groups content—which increases the cohesive energy—makes PUR foams less combustible than polyethylene foams. The combustibility of PUR foams depends on their type, the degree of cross-linking of the polymer and the physical condition of the product (Figure 1 with abbreviations explanation in Table 1).

Neither of the sources [16,17] provide the heat-release rate (HRR) parameters and the degree of carbonization of PURs—most likely due to the broad interpretation of the "PUR" definition. For these substances, the only common feature is that they contain an urethane group, while the proportions and chemical composition—including, e.g., the type and content of flame retardants—vary in a significant way, depending on the application and structure of hard and soft foams, sponges, etc. For this reason, it is impossible for them to be allocated a common definitive value. Such a value can only be provided for a specific product or a more specific group of products.



Figure 1. Correlation between heat-release rate (HRR) and degree of carbonization for various polymers [16,17].

Polymer	ISO/ASTM Polymer Abbreviation	Temperature of Destruction [$^{\circ}$ C] 1
Acrylonitrile-butadiene-styrene	ABS	390
Ероху	EP	427
Polyamide	PA	411–448
Polyamideimide	PAI	485
Polybenzimidazole	PBI	584
Polybenzobisoxazole	PBO	742
Polybutyleneterephthlate	PBT	382
Polycarbonate	PC	476
Polyethylene	PE	399–411
Polyetheretherketone	PEEK	570
Polyetherimide	PEI	527
Polyethylenenaphthalate	PEN	455
Polyethersulfone	PESU	533
Polyethyleneteephthlate	PET	392
Polymethylmethacrylate	PMMA	354
Polypropylene	PP	354
Poly(2,6-dimethylphenyleneoxide)	PPO	441
Polyphenylsulfone	PPSU	557
Polystyrene	PS	319
Polysulfone	PSU	481
Polyvinylchloride	PVC	249–273
Polypara(benzoyl)phenylene	PX	476

Table 1. ISO/ASTM polymer abbreviation and temperature of destruction.

¹ Source: Encyclopedia of Polymer Science and Technology [16].

Thermal decomposition of PUR takes place as early as at >200 °C. With the temperature increase, especially in an inert-gas atmosphere, the proportion of hydrogen cyanide and carbon oxides in the decomposition products increases. There are also nitrogen oxides and nitriles among the decomposition products of PUR. Isocyanate vapors floating above the surface of the burned polymer condense, while liquid polyols undergo further decomposition [18]. Rigid polyurethane foams have a higher flash point than flexible foams.

Table 2 presents data of the characteristics of the combustible and explosive products of PUR foams.

Name of Combustion Product	Gaseous Product Mass mg/g Foam	Explosive Limits ¹
Carbon monoxide (CO)	70–250	12.5-75%
Hydrogen cyanide (HCN)	3.5–11	5.6-41%
Hydrogen sulfide (H_2S)	N/D	4.3–45%
Benzene (C_6H_6)	N/D	1.2-8%

Table 2. Combustible and explosive products of polyurethane (PUR) foams.

¹ Database of hazardous chemicals (Central Institute for Labor Protection—National Research Institute) [19].

In order to reduce the flammability of PUR foams, flame retardants are introduced into their composition. Examples of agents used in flexible foams are presented in an EPA report, "Flame Retardants Used in Flexible Polyurethane Foam: An Alternatives Assessment Update" [20].

Apart from the flame retardants presented, the effectiveness of flame retardant additives in the form of keratin and graphite was also tested, achieving very promising results, whereby, for selected foams, a fourfold reduction in the heat release rate (HRR) was observed [21]. A similar study was also carried out by a Spanish team [22]. On the other hand, the combination of modified graphene oxide and histidine (HGOA) better reduced the formation of smoke than the commonly used ammonium polyphosphate (APP) flame retardant [23].

Another area of research concerning the problems of PUR-foam behavior in a fire environment was addressed by Chinese scientists by examining the influence of pressure and angles of inclination—in relation to the surface—of elements made from this material on the dynamics of fire development [24,25].

PUR foams are very sensitive to elevated temperatures. Even temperatures of >100 °C lead to irreversible breaking of, i.e., allophanate bonds. At higher temperatures, further chemical groups contained in the polymer are decomposed (Table 3).

Bond	Decomposition Temperature Range [°C]
Allophanate	100–125
Biuret	115–125
Urea	160–200
Urethane	180–200
Substituted Urea	235–250
Carbodiimide	250–280
Isocyanurate	270-300

Table 3. Bond-decomposition temperatures of the main PUR functional groups ¹.

¹ Source: [26].

However, little is known about the mutual reactions when polyurethane foam or its char (pyrolysis product) come into direct contact with AN or another compound with oxidizing properties, and what consequences occur in fire conditions (e.g., in the case of a warehouse made of PUR insulated sandwich panels). The addition of flame retardants significantly reduces the combustible properties of PUR, but nothing is known about the combination of the material (char) with an oxidant—in this case, AN. Carbonization of the surface layers of burning PUR foams has long been observed.

2. Materials and Methods

For selected types of PUR, samples were taken for their common forms, most commonly found in utility items. The influence of the aging effect was also investigated in selected cases. The test mixtures were prepared for the material content of 8%, 20%, 50% and 75% in the same manner as described in the previous articles [3,4]. Differential scanning calorimetry (DSC) was used to analyze mixtures of AN with various PURs. It is one of the methods of thermal analysis of materials that can help to measure the heat flux received or supplied to the environment via a sample during its heating. This can assist in determining the temperatures of chemical reactions and physical changes of the material, as well as to determine the thermal effects of these changes. Processes were treated as explosive reactions when the total recorded heat effect of transformation (Δ H) was less than a minute (for a scanning speed of 10 °C/min). Tables 4–12 present thermal analysis of the samples used in the tests in the range of 50–400 °C. A thermal effect was observed for each of the plastics, indicating thermal decomposition.

Table 4. DSC analysis results of ammonium nitrate (AN) and new PUR foam mixture with different proportions.

Polymer Percentage [%]	Initiation Temperature of Reaction A [°C] (Explosive Reaction)	Enthalpy of Reaction A [J/g]	Initiation Temperature of Potentially Explosive Reaction [°C]
8	164.4 (298.5)	-878	298.5
20	163.3 (302.5)	-1195	286.4
50	161.0	-869	-
75	160.5	-667	-

Table 5. DSC analysis results of AN and 1 year old PUR foam mixture with different proportions.

Polymer Percentage [%]	Reaction Initiation Temperature [°C]	Reaction Enthalpy [J/g]
8	164.8	Complex process with both endo- and exothermic Reactions
20	162.3	-1344
50	162.4	-992
75	160.5	-462

Table 6. DSC analysis results of AN and 10 years old PUR foam mixture with different proportions.

Polymer Percentage [%]	Reaction Initiation Temperature [°C]	Reaction Enthalpy [J/g]
8	165.8	Complex process with both endo- and exothermic Reactions
20	164.5	-925
50	163.2	-1370
75	163.8	-544

Table 7. DSC analysis results of AN and T25 PUR foam mixture with different proportions.

Polymer Percentage [%]	Reaction Initiation Temperature [°C]	Reaction Enthalpy [J/g]
8	165.7	Complex process with both endo- and exothermic Reactions
20	163.5	-1920
50	161.4	-1104
75	160.5	-943

Polymer Percentage [%]	Reaction Initiation Temperature [°C]	Reaction Enthalpy [J/g]
8	165.8	Complex process with both endo- and exothermic Reactions
20	163.2	-1908
50	162.7	-1626
75	161.8	-755

Table 8. DSC analysis results of AN and 30 years old T25 PUR foam mixture with different proportions.

Table 9. DSC analysis results of AN and T117 PUR foam mixture with different proportions.

Polymer Percentage [%]	Reaction Initiation Temperature [°C] (of Explosion)	Reaction Enthalpy [J/g]
8	162.3 (206.1)	-1094
20	168.8	-1104
50	168.1 (214.5)	-1222
75	163.1	-658

Table 10. DSC analysis results of AN and T35 PUR foam mixture with different proportions.

Polymer Percentage [%]	Reaction Initiation Temperature [°C]	Reaction Enthalpy [J/g]
8	165.8	Complex process with both endo- and exothermic reactions
20	163.7	-1195
50	161.5	-1117
75	159.8	- 553

Table 11. DSC analysis results of AN and T117 PUR foam mixture with different proportions.

Polymer Percentage [%]	Reaction Initiation Temperature [°C]	Reaction Enthalpy [J/g]
8	238.9	-491
20	239.2	-299
50	237.7	-250
75	238.2	-270

Table 12. DSC analysis results of AN and T35 PUR foam and PUR foam char, mixture with different proportions compared to activated carbon.

Additive	Additive Percentage [%]	Reaction Initiation Temperature [°C]	Reaction Enthalpy [J/g]
Activated carbon	8	179.1	353
New PUR foam char	75	191.2	728
T25 foam char	8	238.9	491

PURs were mixed with AN in specified proportions (as described in [3,4]), while the test of the mixture of AN with PUR char in an atmosphere of pure nitrogen should be covered in additional research. The remaining test procedures were carried out in the same manner as previously described.

In order to reproduce the conditions on a larger scale, the samples were crushed by hand using an agate mortar, and the pre-frozen samples were cooled with liquid nitrogen (-196 °C). Thanks to this, changes in the structure of the material were avoided. The test specimens with a fraction of 0.29–0.1 mm were then placed in a chamber dryer at a temperature of 28 °C and a vacuum of 25 kPa for 24 h. The dried material was stored in a

desiccator under a nitrogen atmosphere (conditioning for at least 48 h). Such measures were necessary due to the hygroscopicity of some of the analyzed substances, particularly AN.

The mixture was prepared just before performing the analysis, thanks to which the risk of a chemical reaction between its components and the vessel walls was minimized. An analytical balance with an accuracy of ± 0.01 mg was used for preparation. Measured samples weighing 5.00 ± 0.15 mg were placed in a special aluminum vessel with a volume of 25 µL and a lid with a hole of 0.3 mm in diameter. The presence of the opening in the upper part of the vessel cover prevented a gradual increase in pressure in the analyzed sample due to the released gases, which is important as the decomposition parameters of AN change along with the pressure. The prepared sample was then placed in the DSC 3500 Sirius NETZSCH apparatus. Measurements were made with numerous repetitions to ensure that the results were fully reliable and repeatable.

Samples of polyurethane products were selected on the basis of the analysis of agricultural and utility premises where vegetables, fertilizers and chemicals used in agriculture are stored. Industrial storage rooms used for keeping ammonium nitrate were also analyzed. Two types of samples were selected for the analysis, namely hard insulation foams and soft mats made of sponge. The following samples were used in the analysis:

- Soft foam with a density of T25 (25 kg/m³). In order to minimize the leakage of other chemicals, a pure foam—without the addition of, e.g., dyes—was chosen. Two types of foam were used in a series of experiments. The first one was obtained directly from the manufacturer and had not been exposed to atmospheric agents, and the second sample was approximately 30 years old; due to the fact that it was installed in a confined space, it was not exposed to factors such as excessive moisture or wind. Due to its low density and good heat insulating properties, this type of foam is used for upholstery and furniture production, as well as for thermal and noise insulation in rooms.
- Soft foam with a density of T35 (35 kg/m³). The properties and practical application of the foam are similar to the T25 foam, but it is more resilient and mechanically durable. Foam obtained directly from the manufacturer was used for the experiment.
- Soft foam with a density of T117 (117 kg/m³). A new colorless foam was analyzed in the experiment.
- Rigid insulation foam with a hose applicator—yellow freon free foam, purchased in a DIY store. According to the information provided by the manufacturer, the foam is hardened by the impact of moisture. Three types of samples were used in the analysis. The first is fresh foam. It was placed on a previously cleaned and degreased metal plate, and then set aside for 24 h (drying time according to the manufacturer is 80 min). Then, it was cooled with liquid nitrogen, crushed and separated into fractions using mechanical sieves. The samples were then dried and sealed in airtight containers against daylight. Due to the fact that—in real conditions—the insulating foams may not be replaced for many years, samples of older insulating foams of similar composition were also tested. The samples were taken from internal utility rooms (storage chambers with controlled humidity and ventilation), and the foam applied one year and 10 years earlier was used for analysis. Before grinding, the top layer of foam and any contamination was removed. A further procedure for preparing the foams was analogous to the one presented earlier.
- The use of T35 foam and charred insulation foam. Due to the DSC diagrams obtained for ordinary foams and sponges, it was decided to test the behavior of the mixture of AN with char produced from the above-mentioned samples. The samples were placed in an oven heated to 350 °C for 10 min. Then, they were cooled and grinded in an inert gas atmosphere not to react with oxygen and water contained in the air. Then, the samples were prepared in the same way as described earlier.

It should be noted that the investigated phenomena relate to the microscale (~5 mg). A straightforward conversion of the experiments to a different scale is not possible. The number of additional physical factors on a regular scale (Mg) is too high. Heat transfer of the given facility should be taken into account as well as changes in heat capacity during the

melting process of the mixture components, changes in the degree of mixing, temperature gradient in the sample mass, etc. Research was conducted on a field scale, however, a number of logistical and experimental problems had to be resolved.

As a rule, each measurement was repeated five times. The observed deviations in the range of results depend on the determined measurement parameter. The deviations do not result from measurement errors but from the course of mechanisms of the process observed with the aid of DSC. The temperature determination depends on the nature of the phenomenon. In the case of rapidly occurring processes of an explosive nature (sharp peak), the differences between repetitions were below 0.2 °C. For the multi-stage changes in thermal degradation, the differences were as high as 2–3 °C. This is due to the accuracy of the sensor calibration and the efficiency of the peak deconvolution program as well as the precision of determining the "center of mass" for the maximum temperature.

Repeating the same measurement multiple times produced results scattered around a specified value. This value is a mean value. If all major sources of errors are eliminated, it is assumed that the remaining minor errors must result from the accumulation of a large number of independent factors, which in turn results in normal distribution. Deviations from normal distribution are taken as an indication that systematic errors have been omitted.

Determining thermal values is an even more complex problem. The fact that the instruments determine something very precisely does not necessarily indicate the parameter of the same value. The value of the heat effect is determined by point calibration. For the heat calibration points, several curves can be found, to which the measurement relates. The parameters determined by us define only the ranges of temperatures and heat in which, for the macro scale, we expect specific effects (e.g., an explosion). These are not isothermal changes, therefore no practical difference—in terms of fire safety—can be achieved by determining whether the process will start at a 1 $^{\circ}$ C variation.

3. Results

Figure 2 shows the DSC curve of pure AN (as a control) along with pure PUR foam to distinguish which peaks derive from which components.



Figure 2. DSC spectra of pure components of the tested mixtures, i.e., ammonium nitrate (endothermic character of melting and decomposition) and polyurethanes, in the form of foam and sponge (exothermic decomposition).

The analysis covered both rigid PUR insulation foam and soft foams used as insulating mats which are typically applied in multi-layer panels for the construction of industrial halls and as furniture foams. These materials were tested according to the same scheme as the previous ones, to see if they could show a similar effect on reactivity with AN, leading to a possible explosive decomposition after melting and mixing the materials.

Two types of material were tested: hardened sealing and insulation foam (rigid PUR) and soft foam, which is used as thermal or acoustic insulation, as well as in the furniture and automotive industries. The results of the analysis showed that—despite great similarities in the chemical composition—these two materials behave in a slightly different way under the influence of temperature. In the case of previously tested polymers, mixtures containing ~20% of polymer turned out to be the most dangerous in the event of fire—their preparation led to the release of a significant amount of heat or even an explosion. In the case of the analyzed polyurethanes, the behavior of the mixtures was more varied.

The first significant differences were observed for the insulation foam. The most important difference is that the decomposition of the mixture can be observed at very low temperatures, even before the AN in the mixture begins to melt. In the case of 20% mixture, the melting of AN as well as the onset of the decomposition reaction began at ~163.5 °C. Thereafter, up to the temperature of about 205 °C, a slow, fairly uniform release of heat was observed as a result of the decomposition reaction. Above this temperature, HRR of the decomposition reaction gradually decreased. The shape of the DSC curve indicates a complex mechanism for the decomposition of the mixture, but the decomposition ended at about 290 °C. This means that this mixture decomposes before pure AN decomposes in the same conditions. Despite the fact that the enthalpy of the decomposition reaction has a high value (-1195 J/g), due to its mild and slow course it can be concluded that it does not carry an immediate risk of explosion until the temperature reaches about 286.4 °C. Then, a potentially explosive process can be observed, which takes place after the decomposition of the most of the mixture mass. This may prove that the gaseous products (Figure 3).



Figure 3. DSC analysis of new polyurethane (PUR) foam and its mixtures with ammonium nitrate (AN). The arrows indicate fragments of curves (**A**) where the thermal decomposition of samples shows a character which is not explosive but is relatively rapid. It may be related to the self-ignition of AN and PUR decomposition products. The range corresponds to these phenomena.

The behavior of the 8% mixture was relatively similar. One can observe peaks indicating a similar course of the decomposition reaction. However, the temperatures at which similar processes probably take place change significantly. While the course of the AN melting reaction was almost identical, the decomposition of the mixture itself was much smoother, additionally illustrated by the lower reaction enthalpy value of -878 J/g (Table 4).

The course of the decomposition reaction changes significantly as the amount of polymer in the mixture increases. For a mixture containing a 50% mass of PUR, the reaction initiation temperature drops even further, to 161.0 °C. The decomposition reaction was much more rapid, ending at about 271.2 °C. This was followed by a slow decomposition of the remaining decomposition products of the mixture. The enthalpy of the described process was lower (-869 J/g); however, the heat was released much faster in the initial decomposition phase. In the course of the decomposition reaction, two distinct component reactions were distinguishable, but none of them proved to be explosive in the analyzed conditions. Further increasing the amount of polymer to 75% in the mixture did not significantly affect the behavior of the substance. The course of reaction is very similar to that described for the 50% mixture, although some differences can be observed in the reaction initiation temperature (160.5 °C), its completion (251.5 °C), and the amount of post-reaction residue. The main difference is the much lower reaction enthalpy (-667 J/g). There were no potentially explosive reactions (Figure 4).



Figure 4. DSC analysis of 1 year old PUR foam and its mixtures with AN.

In the case of the one-year-old foam which was taken from the area of its application, no potentially explosive reaction was observed for any of the analyzed mixtures. It is slightly different compared to the new foam. In particular, a mixture containing 8% of polymer was distinguished, whereby—during decomposition—an endothermic process could clearly be seen, which probably results from the thermal decomposition of AN. Apart from that, for this mixture, we can see that the remnants of the exothermic process occurred at the end of the decomposition reaction, however, unlike the sample with the new foam, due to the relatively low amount of heat released, it did not carry the risk of explosion (Table 5).

For the remaining samples, it is noticeable that in the course of the decomposition reaction, two stages of the decomposition reaction were observable. In addition, the amount of heat released during the reaction changes. In this case, the highest enthalpy can be observed for the decomposition process of the mixture containing 20% of the polymer, which was higher than in the case of the new foam (Figure 5).



Figure 5. DSC analysis of 10 years old PUR foam and its mixtures with AN.

The results obtained for the ten-year-old insulating foam show some similarity to the one-year-old foams. In this case, no potentially explosive reactions were observed, although at times the course may be quite rapid (>284 °C). The course of the decomposition reaction for mixtures containing 75% and 8% of polymer was very similar for mixtures based on one-year-old foam, while in the case of mixtures containing 50% PUR this behavior resembled the decomposition process of new foam. It is also worth noting that, in contrast to the previous mixtures, the highest reaction enthalpy, i.e., -1370 J/g, was recorded for the mixture containing 50% of polymer (Table 6).

Changes in the behavior of clean foam are also noteworthy. New PUR insulation foam is quite flexible and light yellow in color. Its structure, flexibility and appearance changed. However, we do not know all the factors that could have influenced its current state. Its decomposition with energy release took place much earlier; however, the heat-released flux has a much lower value (Figure 6).

The course of the decomposition reaction for the T25 foam was, in most cases, also not a violent one. Some of the observations for the rigid PUR are in line with those for the insulation foam. These include the decomposition of the mixture as early as during the melting of AN, as well as low (not exceeding 225 °C) temperature of completion of the decomposition process for 75% and 50% mixtures. There are quite significant differences between the given PUR contents in the mixture. They probably result from differences in the participation of the dominant decomposition mechanisms visible in the form of successive extremes of the thermal curve. Attention is drawn to the multi-stage and quite complex course of the reaction of mixtures containing 8% and 20% of the polymer, as opposed to the fairly simple course of the decomposition reaction for the 75% and 50% mixtures (Table 7).

In terms of fire safety, the 50% mixture decomposition reaction can be particularly dangerous. Its decomposition is accompanied by the release of a significant amount of heat in a short time. The effect resembles, at best, a very violent fire. It is worth noting that it is still a dangerous effect, and in the case of increased pressure or in the presence of other chemicals or contaminants, it may have a more rapid course (Figure 7).



Figure 6. DSC analysis of T25 PUR foam and its mixtures with AN. Arrow indicates potentially dangerous reaction but definitely not an explosive one.



Figure 7. DSC analysis of 30 years old T25 PUR foam and its mixtures with AN. The observed heat effect is more than 10 times greater than for pure components heated individually.

Another analyzed sample is the T25 foam produced in 1990, according to the applied markings. As in the case of insulation foam, some changes in the form of the material took place over time. The behavior under the influence of heat is an important change. For the 8% mixture, only processes without the release of large amounts of heat were observed. In the case of the mixture containing 20% of the polymer, an effect analogous to that of

the new insulation foam was observed—a violent but relatively minor exothermic process occurring at the end of the decomposition process. However, it is the decomposition of a mixture containing 75% and 50% PUR which can constitute a threat. In both cases, a very violent explosion-like process was observed, which—in the case of the 75% mixture—led to deformation of the measuring vessel during some of the repetitions (Table 8).

However, the observed effects should be associated with the chemical composition of PUR rather than with the aging process. On the basis of weathering of polymer-based sealants, no significant aging effects could be observed for this type of sample on this time scale [27]. The reason for such a behavior in foams is probably the change in the chemical composition of the production of PUR products over the years. In the past, the foaming processes used, e.g., freons, have now been banned for ecological reasons. Currently, pentane and CO_2/H_2O mixtures are used for foaming. For this reason, the likely cause of the described behavior is both a different chemical composition and changes in the production technology (Figure 8).



Figure 8. DSC analysis of T117 PUR foam and its mixtures with AN. The observed heat effect is more than 10 times greater than for pure components heated individually.

Another sample analyzed is dense T117 foam. In this case, quite an unusual course of the processes taking place in a function of temperature and dependent on the polymer content in the mixture was noted. We observed the explosive nature of decomposition for 8% and 50% samples. It is worth paying attention to the similar course of the mechanism in both cases. First, there a rapid decomposition reaction occurs, followed by an explosion of the mixture. However, for the 20% mixture and the 75% mixture, the decomposition was found to be relatively gentle. This is practically the first DSC course of this nature. The reactions for both mixtures differed in the heat effect and the explosion temperature. However, attention should also be paid to the relatively large amount of heat released in all cases (Table 9 and Figure 9).



Figure 9. DSC analysis of T35 PUR foam and its mixtures with AN. Arrow indicates potentially dangerous reaction but definitely not an explosive one.

The observations for the T35 foams are very similar to those for the T25 foam (Figure 5). This behavior was expected, mainly due to the high similarity between the foams—similar structure, chemical composition and density. From a safety point of view, a certain change in the behavior of the mixture containing 50% of the polymer is the most important. In the case of this foam, the behavior resembles an explosion to an even greater extent (Table 10).

The described reactions of the decomposition of PUR mixtures may suggest that, in most cases, they are not violent and potentially explosive. Both the pure polymer and pure AN decompose only at temperatures higher than 280 °C, while PUR/AN mixtures—at this temperature—are almost decomposed. PUR fires are known to be violent and emit large amounts of dense toxic fumes—which additionally indicates oxygen deficiency.

When analyzing the described mechanisms of PUR combustion, it has been observed in many cases that a reaction of an explosive nature is preceded by a slower decomposition of the mixture. This effect is observed, for example, with limited heat conduction through the sample material.

The reactivity of the char obtained during the thermal decomposition of PUR with AN was also checked as a potential factor causing an explosion during decomposition. The foam surface becomes charred quite easily (Figure 10).

The reaction between the char obtained by PUR pyrolysis and ammonium nitrate was analyzed. The choice of carrying out the experiments on the example of T35 foam was due to the lack of an explosive process and the visible two-stage process of decomposition described earlier (Table 11).

Effects showing an explosive character were observed for all tested mixture proportions in the range of 8–75%. For each of the mixtures, the explosion took place at a temperature of 238 ± 1 °C. They differ mainly in the observed thermal effect of the process. The strongest explosion occurred for the sample containing 8% of the polymer. It is worth noting that the explosions were in each case so strong that the deformation of the measuring vessels was observed (Figure 11).



Figure 10. DSC analysis of T35 PUR foam char and its mixtures with AN; range increased to ~238 °C. In this case, the thermal effect of decomposition of the mixture is several times greater than for the pure individual ingredients, and its nature corresponds to the explosion phenomenon.





A similar analysis was also carried out for the insulating foam, mainly because of its very characteristic course of a decomposition reaction. Figure 10 shows a comparison of the 75% mixture with the strongest mixture obtained for the T35 foam char and the

mixture with activated carbon in the proportions of 8%. In the case of char obtained from the insulating foam, a decomposition reaction of an inexplosive nature can be observed. The decomposition reactions for the AN mixture with char obtained from T35 foam and with the chemically pure activated carbon in the amount of 8% proceed in a very similar way, but they differ in the thermal effect. It is worth noting that there is a significant difference between the temperatures—the explosion in a mixture with pure carbon takes place approximately $60 \,^\circ$ C earlier (Table 12).

4. Discussion

The combustion process is accompanied—depending on the type of material, filling additives (fillers, flame retardants, etc.) and the temperature—by various intermediate stages, including the thermal decomposition of the polymer, depolymerization and transition to the gaseous state, dissociation, re-synthesis reactions, etc. In well-ventilated, high-energy developed fires, especially in the presence of combustible materials, large amounts of gaseous and aerosol products are released in the combustion zone and its immediate surroundings. These gases, in the presence of extinguishing agents (water, foam), undergo hydrolysis reactions, creating new chemical compounds [28].

It is not only polymers in the form of resins—which are the binder of plastics in addition to monomers—that may constitute the source of toxic gases. Toxic gases may also be products of fillers, carriers, plasticizers (softeners), stabilizers, dyes or pigments, catalysts, blowing agents, lubricants, antistatic agents and flame retardants—all of these used in production processes, depending on the needs and purpose of particular plastics. The most commonly used flame retardants are:

- Inorganic compounds of mineral origin, such as hydrated aluminum trioxide (Al₂O₂ x 3H₂O), magnesium oxide (MgO) and oxides of tin, antimony and molybdenum (SnO₂, Sb₂O₃, MoO₃);
- Phosphorus compounds (e.g., ammonium and magnesium phosphate as well as organic phosphorus compounds);
- Halogenated organic compounds (e.g., aliphatic, aromatic and cycloaliphatic chlorine and bromine compounds);
- Inorganic compounds.

Unfortunately, some of the older generations of flame retardants limit the flammability of polymers, but their vapors are the most toxic, and their intense release takes place in fire conditions.

Fluorides and chlorides of boron, aluminum or antimony (due to their availability, efficiency and low production costs), used on a large scale, have a serious disadvantage in fire conditions despite their numerous advantages. These are the catalytic properties of the cationic polymerization of both unsaturated and heterocyclic monomers, which lead to the release of hydrogen chloride [29].

Rigid polyurethane foam is an example of a material widely used in construction as an excellent thermal insulator; its expandable, hardening version is used as a mounting foam. It has excellent insulating properties, namely 10 cm of foam replaces 15–18 cm of polystyrene or mineral wool, while the foam is light (even lighter than polystyrene itself). At the same time, it is very susceptible to energy stimuli due to its chemical composition (nitrogen, carbon and hydrogen compounds). In addition to the fact that it is a highly smoke-generating material, one of the products of its combustion is hydrogen cyanide. Due to the numerous advantages of this material, its composition has been modified by increasing the amount of nitrogen, carbon and hydrogen compounds, which has resulted in the name being changed to polyisocyanurate (PIR). A change in composition significantly improved the resistance to the action of fire initiators, to such an extent that PIR tends to be considered a non-combustible material—which is not entirely true.

Only the fact that PIR burns on the surface is true, although manufacturers tend to forget that thermal decomposition occurs at temperatures similar to those at which wood carbonization occurs. The layer does not burn any further, still insulates very well and does

not significantly change its volume. Therefore, structures made of sandwich panels—in which PIR is an insulation and a stiffening component for two layers—are more durable during a fire than those with a polystyrene or PUR foam core, and the sandwich panel itself can easily obtain the classification of a research laboratory as a fire retardant product. This, however, is a subtle difference between "non-combustible" and "non-spreading" fire. In addition—as we have shown in the tests—surface combustion and carbonization of the outer layer of polyurethane foam may limit the spread of fire (which, as we are going to show in two examples, is also not always true) but in combination with AN it may constitute an explosive mixture. The examples mentioned are based on two high-rise fires, where the external façade of the building was made of aluminum sandwich panels filled with an allegedly non-combustible substance such as PIR.

In the Grenfell Tower building in London, a material which roughly corresponds to the PIR characteristics was used as a filler for the facade panels. On the entire facade of the building—even where the fire power did not entirely burn the panels, it is clear that the top layer became carbonized but the boundary layer remained yellow, i.e., according to the manufacturers' declarations, surface combustion actually took place. The fact that the people responsible for the renovation of the building realized that it is a combustible material is evidenced by a narrow strip of mineral wool—with a thickness and height of about 20 cm—delineating each inter-story level. If PIR was non-combustible, the troublesome installation of the wool strip would have no justification.

The official conclusions of the fire investigation confirmed the cause of the fire—a failure of a refrigerator in an apartment on the fourth floor. From there, the fire spread to the outside of the building and continued to spread over the combustible facade. This is similar to the case of the first Torch Tower fire in Dubai, where the exterior cladding is likely to be made of the same panels as in the case of the London high-rise. A cigarette butt blown by the wind or the residue of charcoal used to heat a shisha was considered to be the source of fire, which is further evidence of a significant overestimation of "non-flammability" of this finishing material [30]. This is merely an example of the behavior of PUR foam—a material generally considered safe during a fire in a building.

5. Conclusions

The most common phenomenon of an explosion in relation to the previously tested plastics in a mixture with AN was observed for a content of 20% of plastics in a mixture. The effect of the rate of energy release was several times greater than for pure components of the mixture. It turned out that in the case of PUR, the turn of events was different. The measurements results justify the statement that the observed results of the explosive effects of mixtures decomposition may be largely caused by the differences in PUR texture and its functional structure (foams, sponges, solid material). The issue of the reaction of ammonium nitrate (V) with char formed in large part during thermal decomposition/PUR fires was also considered. The addition of charcoal as an ANFO component was studied by [31]. However, the situation turned out to be more complex. Polyurethanes as a function of temperature often behave completely differently, despite similar functional properties. Hence, the explosion effect occurs—in the tested temperature range—in different ranges for different polymer contents in the mixture with AN. However, this does not change the fact that there is a potential of explosion in the event of a fire for objects in which these materials may be present.

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