Experimental Investigation of the Pyrolysis of Synthetic Materials Exposed to External and Internal Fires

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Abstract. Consideration was given to the issue of flammability during the thermal decomposition of synthetic materials used for the constructions to isolate the process equipment and building structures. The experimental research data obtained for the thermal decomposition of synthetic materials with the measurements of temperature as a function of the time of thermal radiation were given including a change in the mass and structure of the specimens of synthetic materials exposed to the thermal radiation during the fire. The obtained experimental data enabled the substantiation of the process of the thermal decomposition of synthetic materials depending on time and temperature and also a change in the mass of the specimens of synthetic materials before and after the tests.

1 Introduction

Synthetic materials include the substances that are produced from other elementary substances using the method of organic synthesis. Synthetic materials are high molecular organic compounds, i.e. the polymers [1-3]. Dry coal distillation or coking products, oil sublimation products and wood processing products are used as a raw material for synthetic materials [4, 5]. Synthetic materials differ by a high content of carbon and most of them contain no oxygen [6]. Therefore, these require for their burning an ample amount of air $(10-12 \text{ m}^3/\text{kg})$ [7, 8].

During their heating, synthetic materials start melting with the formation of the liquid layer on their surfaces. This liquid layer cannot be held on the vertical and inclined surfaces captured by fire and runs off the structure. As a matter of fact, the liquid layer on such surfaces has a thickness within 1 to 2 mm. The running off liquid forms on the floor of the premises or on the ground surface a layer of several centimeters that spreads and captures other not yet burning objects [9, 10]. Table 1 gives the elementary composition of some synthetic materials.

Polymer (synthetic) material	С	Н	0	Ν
Isoprene rubber	88.25	11.75	-	I
Caprolactam	63.70	9.75	14.2	12.35
Natural rubber	88.25	11.75	I	I
Polypropylene	85.4	14.6	1	1
Polyacrylate	55.90	6.9	37.2	I
Polyethylene	85.80	14.2	I	I
Phenol-formaldehyde resin	78.80	5.05	16.15	I

Table 1. Elementary composition of synthetic materials [8].

At the present time, the products made of synthetic materials find a wide application in a person's life, mainly during the construction and operation of the premises in residential buildings. However, being in great demand these products are dangerous for the health and life of a person [10, 11] in the

case of the outbreak of internal [12] and external fires [12-15]. In addition, the burning of synthetic materials results in the release of dangerous combustion products that have a degrading effect on the environmental ecology [16-20].

In contrast to solid organic materials (wood) [21], synthetic materials can melt and evaporate and these get charred and release the products in a gaseous aggregate state during the thermal decomposition or pyrolysis [22, 23]. It should be noted that synthetic materials can potentially release twice as much thermal energy during the combustion. Under the action of thermal energy, these materials are much easier decomposed into the fuel in a gaseous aggregate state capable of burning [24]. The products of the thermal decomposition of the synthetic fuel are also subject to much easier inflammation in comparison to the products derived from the natural fuel [8, 25]. Taking into consideration the above, we can state that the timely detection of the source of fire can considerably reduce the arrival time of the fire-rescue units to the place of fire to rescue the people in the fire danger and minimize the consequences of the fire [26, 27]. Hence, the studies of the factors of the fire danger and thermal decomposition or pyrolysis processes of synthetic materials in the case of the fire spread are of vital importance and should be resolved.

Much attention is paid to the studies of the structure of synthetic materials, including a change of it and to their combination with different compounds and appropriate investigations are carried out in this field [28-31]. As for the thermal decomposition of synthetic materials and the danger of their inflammation, we can mark out the research done by the authors in [32] that gives the "Pyrolysis" model that can predict the thermal decomposition both of the charred and non-charred synthetic materials. It is envisaged in the case of charring that the swelling of the material is controlled by the amount of coal formed during decomposition reactions taking into consideration the coal porosity. It should be noted in this case that the given model was calibrated only for the three types of easily inflammable materials such as polystyrene, polycarbonate BPA and the reinforced fiber of the polymer composite and in its turn it limits the sphere of application of this model and the use of synthetic materials for construction purposes.

In paper [33], the authors suggest the numerical model of the multiphase Pyrolysis that includes the tracking of the surface of movable boundary including the formation of the charred material and the detailed simulation of the chemical kinetics of the burning. Using the conical calorimeter, such materials were studied as wood (pine) and polyethylene of a low density. This model enables the investigation of the charring process of the materials and the measurement of the concentration of toxic gases (CO, CO₂) during the material decomposition and it is primarily related to the wood and the investigation of the thermal decomposition of synthetic materials and first of all the melting of it requires additional studies.

The authors of [34] study the pyrolysis phenomenon and investigate experimentally and numerically the combustion of polystyrene and its composites that include modified ammonia polyphosphate and grapheme. During the investigations, we determined the thermodynamics of synthetic materials including the reaction heat, specific heat capacity and the heat conduction that was additionally obtained by the measurement of rate at a mass loss during the tests performed using the conical calorimeter. The investigations carried out are aimed mainly at the determination of physical and chemical properties of synthetic materials and not at the effect of fire factors.

Paper [35] delves into the investigations carried out to specify a decrease in the combustion rate of polymer by treating it with the flame retardant agent. The simulation showed that the chemical kinetics of the "fire cycle" results in more than additive effect of different fire retardants if these act in a manner to reduce both the pyrolysis rate of polymer and the oxidation of light substances in comparison with the combined fire retardants by acting in one phase. However, the studies of the thermal decomposition of synthetic material during the heat radiation depending on the distance to the fire source have not been conducted.

This paper suggests carrying out experimental investigations to study the effect of the thermal radiation on synthetic materials that are used for construction purposes, for example, polyethylene foam and foamed and extruded polystyrenes. During the investigation we will study the process of thermal decomposition and a change in the structure of the specimens of synthetic materials before and after the tests.

The purpose of this research was to carry out the experimental investigation to determine the dependence of temperature on the thermal radiation time, including a change in the mass and structure of the specimens of synthetic materials that are used for construction purposes and are exposed to the thermal radiation of the fire.

2 Materials and Research Methods

As test specimens of synthetic materials, we used during the experiment the polyethylene foam [36] (PEF, polyethylene foam and PET, metalized polyethylene) with the dimensions of $120 \times 120 \times 10$ mm, the foamed polystyrene [37] with the dimensions of $120 \times 120 \times 15$ mm and the extruded polystyrene [38] with the dimensions of $120 \times 120 \times 20$ mm that are used for construction purposes to isolate the process equipment and building structures. To study the effect of the thermal radiation on the specimens of synthetic materials during the fire spread we used the electric heater with the voltage of 220 V at a frequency of 50 Hz and the power of 1.5 kW manufactured in Ukraine and it was arranged opposite to the specimens and parallel to the radiator amid the three heating elements at a distance of 150 mm, as shown in Fig. 1.



Fig. 1. General view of investigation conditions: 1 – the heater, 2 – the extruded polystyrene, 3 – the polyethylene foam, 4 – the foamed polystyrene

The screen in the form of the metal sheet was arranged between the heater and the brick. The temperature of material specimens was measured in an inactivated state and then the heater was brought to mode and the screen was removed. Afterwards, the screen was lowered every 30 seconds and the temperature was measured. The surface temperature of the specimens of synthetic materials was recorded using Thermal Imaging Camera manufactured by the FLIR Systems Estonia OÜ Company [17]. Fig.2 shows the investigation arrangements.



Fig. 2. Measuring the material surface temperature

During the thermal radiation of the specimens of synthetic materials we observed a change in the structure of the synthetic material. A change zone is marked by the red marker in Fig.3.



Fig. 3. A view of the specimens of synthetic materials during their thermal decomposition under the thermal radiation

Experimental investigations were carried out in the two stages. During the first stage the specimens were heated using the electric heater and the temperature was measured at an interval of 30 s during 9 minutes.

During the second stage, the investigation was carried out to determine the changes in the mass of the specimens of synthetic materials before and after the tests. The measurements were taken using the electronic jewelry Digital Table Top Scale manufactured in China with a maximum weighing weight of 500 g and the error within 0.1g, and the division value of 0.01 g. Fig.4 shows the investigation arrangements.



Fig. 4. Measurement data obtained for the mass of the specimens of synthetic materials before and after the tests

3 Discussions of Results

Table 2 gives the research data obtained for the mass of the specimens of synthetic materials before and after the tests.

Description of synthetic	Specimen mass	Specimen mass	A change in
materials	before the tests,	after the tests, [g]	the specimen
	[g]		mass, [%]
Polyethylene foam	4.49	4.20	- 6.46
Foamed polystyrene	4.26	3.72	- 12.68
Extruded polystyrene	7.89	8.20	+ 3.93

Table 2. Measurement data obtained for the mass of the specimens of synthetic materials

The research data obtained for the effect of temperature on the specimens of synthetic materials and a change in their mass are given in Fig.5.



Fig. 5. The relationship of temperature on the surface of the specimens of synthetic materials as a function of time during the thermal radiation

This research paper delves into the thermal decomposition or pyrolysis of synthetic materials (polyethylene foam, the foamed and extruded polystyrenes) used for construction purposes. During the investigation we managed to read the time and temperature of the start of the pyrolysis of synthetic materials (Fig.5) and record a change in the mass of material specimens before and after the tests (Tab.2). It was also established that a rapid increase in the temperature on the surface of synthetic materials occurs already after 2.5 minutes (the surface temperature of the polyethylene foam is equal to 92 °C, of the foamed polystyrene is 92 °C and of the extruded polystyrene is 102 °C). At the 4th or 5th minute we observe a change in the material structure (Fig.5), the domain of a change is marked with the red line in Fig.3. It should be noted that the start of a change in the material structure results in its thermal decomposition with the release of toxic and combustible gases. The premises where the experiments were carried out had a specific unpleasant odor and the material surface temperature was equal to 129°C for the polyethylene foam, 123 °C for the foamed polystyrene and 134 °C for the extruded polystyrene. At the 9th minute the material surface temperature attained its maximum and constant value (155 °C for the for the polyethylene foam, 151 °C for the foamed polystyrene and 164 °C for the extruded polystyrene)

Table 2 gives the mass measurement data for the specimens of synthetic materials before and after the tests. It should be noted that a change in the mass of the specimens of synthetic materials was decreased for the polyethylene foam by 6.46 % and for the foamed polystyrene by 12.68% while for the extruded polystyrene the mass was increased by 3.93 %. It means that a decrease in the mass of synthetic materials is relating to the decomposition and subsequent evaporation and an increase in the mass results from the oxidation of air with oxygen with the subsequent swelling of the material.

To prevent the thermal decomposition of synthetic materials used for construction and domestic purposes by the consumers it is reasonable to apply the fire–proof compositions on their surfaces (gypsum plaster, etc) [39, 40], the paints, and impregnate the materials with fire retardants, for example as for other materials [41-43] and in the case of their inflammation it is recommended to use the mist water fire-fighting equipment [44, 45] with appropriate performances [46-50].

The carried out investigations enable the substantiation of the pyrolysis process of synthetic materials taking into consideration the time, temperature and a change in mass for the further development of mathematical models. Simultaneously, during our future investigations we plan to improve the protection of the materials using fire-proof compositions and carry out the investigations in a broader temperature range.

Summary

Experimental investigations were carried out to define the time, the temperature and a change in the mass of synthetic materials before and after the tests due to their use for construction purposes exposing these to the effect of the thermal radiation of the fire. The obtained research data show that a change in the structure of the materials is observed after 4 or 5 minutes of the thermal radiation of the specimens accompanied by the start of the process of their thermal decomposition and the specimen temperature is equal to 129 °C for the polyethylene foam, 123 °C for the foamed polystyrene and 134 °C for the extruded polystyrene. As for the measurement data obtained for a change in the mass of the specimens of synthetic materials was decreased for the polyethylene foam by 6.46 % and for the foamed polystyrene by 12.68 % while for the extruded polystyrene it was increased by 3.93 %. It is indicative of that a decrease in the mass of synthetic materials is relating to the thermal decomposition with the subsequent evaporation and an increase in the mass results from the oxidation of air with oxygen with the subsequent swelling of the material.

On the whole, the obtained research data enable the establishment of the danger of the process of the thermal decomposition of synthetic materials.

Hence, the investigations carried out to establish a danger of the inflammation of synthetic materials used for construction purposes to isolate the process equipment and building structures enable the solution of many problems relating to the prevention and elimination of the development of internal and external fires.

References

[1] N. Sytnik et al., Determination of the influence of natural antioxidant concentrations on the shelf life of sunflower oil, Eastern-European Journal of Enterprise Technologies, 4/11 (106) (2020) 55–82.

[2] V. Andronov et al., Efficiency of utilization of vibration-absorbing polimer coating for reducing local vibration, Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu, 6 (2014) 85–91.

[3] V. Slyusar et al., Improvement of the model of object recognition in aero photographs using deep convolutional neural networks, Eastern-European Journal of Enterprise Technologies, 5/2 (113) (2021) 6–21.

[4] S. Vambol et al., Research of the influence of decomposition of wastes of polymers with nano inclusions on the atmosphere, Eastern-European Journal of Enterprise Technologies, 6/10 (90) (2017) 57–64.

[5] O. Vambol, A. Kondratiev, S. Purhina, M. Shevtsova, Determining the parameters for a 3Dprinting process using the fused deposition modeling in order to manufacture an article with the required structural parameters, Eastern-European Journal of Enterprise Technologies, 2/1 (110) (2021) 70–80. [6] A.V. Kondratiev, V.E. Gaidachuk, Mathematical analysis of technological parameters for producing superfine prepregs by flattening carbon fibers, Mechanics of Composite Materials. 57, 1 (2021) 91–100.

[7] L. Chernyak, N. Merezhko, T. Karavayev, Ecological safety of polymeric materials on the base of polystyrene, Commodities and markets, 9/1 (2010) 189–193.

[8] Demidov, P. G., Shandyba, V. A., Shcheglov, P. P. Combustion and properties of combustible substances, (1981) 272.

[9] Kerber S. et al. Impact of ventilation on fire behavior in legacy and contemporary residential construction. – Underwriters Laboratories, Incorporated, 2010.

[10] Ventyljatory i ventyljacija u pozhezhnij ohoroni / Shymon Kokot-Ѓura; Pereklad z pol. Volodymyra Dubasjuka (shvaleno dlja vykorystannja u systemi sluzhbovoi' pidgotovky rishennjam aparatnoi' narady GU DSNS Ukrai'ny u L'vivs'kij oblasti vid 11.08.2020) № 17. – L'viv: «SUPRON1», 2020 – 72 s.

[11] B. Pospelov et al., Mathematical model of determining a risk to the human health along with the detection of hazardous states of urban atmosphere pollution based on measuring the current concentrations of pollutants, Eastern-European Journal of Enterprise, 4/10 (106) (2020) 37–44.

[12] S. Ragimov et al., Physical modelling of changes in the energy impact on a worker taking into account high-temperature radiation, Journal of Achievements of Materials and Manufacturing Engineering, 1(91) (2018) 27–33.

[13] B. Pospelov et al., Defining the features of amplitude and phase spectra of dangerous factors of gas medium during the ignition of materials in the premises, Eastern-European Journal of Enterprise Technologies, 2/10 (116) (2022) 57–65.

[14] B. Pospelov et al., Development of the method of operational forecasting of fire in the premises of objects under real conditions, Eastern-European Journal of Enterprise, 2/10 (110) (2021) 43–50.

[15] B. Pospelov et al., Short-term fire forecast based on air state gain recurrency and zero-order Brown model, Eastern-European Journal of Enterprise Technologies, 3/10 (111) (2021) 27–33.

[16] V. Sadkovyi et al., Development of a method for assessing the reliability of fire detection in premises, Eastern-European Journal of Enterprise Technologies, 3/10 (117) (2022) 56–62.

[17] S. Vambol et al., Analysis of the ways to provide ecological safety for the products of nanotechnologies throughout their life cycle, Eastern-European Journal of Enterprise Technologies, 1/10 (85) (2017) 27–36.

[18] O. Rybalova et al., Development of methods for estimating the environmental risk of degradation of the surface water state, Eastern-European Journal of Enterprise Technologies, 2/10 (92) (2018) 4–17.

[19] V. Sadkovyi et al., Construction of a method for detecting arbitrary hazard pollutants in the atmospheric air based on the structural function of the current pollutant concentrations, Eastern-European Journal of Enterprise Technologies, 6/10 (108) (2020) 14–22.

[20] B. Pospelov et al., Use of uncertainty function for identification of hazardous states of atmospheric pollution vector, Eastern-European Journal of Enterprise Technologies, 2/10 (104) (2020) 6–12.

[21] D. Dubinin et al., Numerical simulation of the creation of a fire fighting barrier using an explosion of a combustible charge, Eastern-European Journal of Enterprise Technologies, 6/10 (90) (2017) 11-16.

[22] Y. Danchenko et al., Research into surface properties of disperse fillers based on plant raw materials, Eastern-European Journal of Enterprise Technologies, 5/12 (89) (2017) 20–26.

[23] NFPA 921. Guide for Fire and Explosion Investigations. Massachusetts, 2017 [USA].

[24] D. Dubinin et al., Experimental Investigations of the Thermal Decomposition of Wood at the Time of the Fire in the Premises of Domestic Buildings, Materials Science Forum, 1066 (2022) 191–198.

[25] B. Pospelov et al., Development of the method for rapid detection of hazardous atmospheric pollution of cities with the help of recurrence measures, Eastern-European Journal of Enterprise, 1/10 (97) (2019) 29–35.

[26] V. Vambol et al., Substantiation of expedience of application of high-temperature utilization of used tires for liquefied methane production, Journal of Achievements in Materials and Manufacturing Engineering, 87(2) (2018) 77–84.

[27] D. Dubinin et al., Research and justification of the time for conducting operational actions by fire and rescue units to rescue people in a fire | Istraživanje i opravdanje vremena izvođenja operativnih akcija vatrogasno-spasilačkih postrojbi za spašavanje ljudi u požaru, Sigurnost, 64 (1) (2022) 35–46.

[28] D. Dubinin et al., Investigation of the effect of carbon monoxide on people in case of fire in a building | Ispitivanje djelovanja ugljičnog monoksida na ljude u slučaju požara u zgradi, Sigurnost, 62 (4) (2020) 347–357.

[29] Y. Danchenko et al., Research of the intramolecular interactions and structure in epoxyamine composites with dispersed oxides, Eastern-European Journal of Enterprise Technologies, 6/12 (90) (2017) 4–12.

[30] Y. Danchenko et al., Study of the free surface energy of epoxy composites using an automated measurement system, Eastern-European Journal of Enterprise Technologies, 1/12 (91) (2018) 9–17.

[31] O.Z. Dveirin, O.V. Andreev, A.V. Kondrat'ev, V.Ye. Haidachuk, Stressed state in the vicinity of a hole in mechanical joint of composite parts, International Applied Mechanics. 57, 2 (2021) 234–247.

[32] K. Afanasenko et al., Epoxidized Dinaphthol Application as the Basis for Binder with Advanced Carbonation Level to Reducing its Flammability, Materials Science Forum, 1006 (2020) 41–46.

[33] A. Y. Snegirev et al., A new model to predict pyrolysis, ignition and burning of flammable materials in fire tests, Fire Safety Journal, 59 (2013) 132–150.

[34] T. B. Y. Chen et al., A multiphase approach for pyrolysis modelling of polymeric materials, Experimental and Computational Multiphase Flow, 5 (2023) 199–211.

[35] J. Gong et al., Pyrolysis mechanism and combustion behaviors of high impact polystyrene improved by modified ammonium polyphosphate and graphene, Journal of Thermal Analysis and Calorimetry, 147 (2022) 12815–12828.

[36] B. Camino, G. Camino, The chemical kinetics of the polymer combustion allows for inherent fire retardant synergism, Polymer Degradation and Stability, 160 (2019) 142–147.

[37] DSTU EN 14313:2019 Vyroby teploizoljacijni dlja budivel'nogo obladnannja ta promyslovyh ustanovok. Promyslovi vyroby z pinopolietylenu (PEF). Tehnichni umovy (EN 14313:2009 + A1:2013, IDT). Kyiv, 2019 [in Ukrainian].

[38] DSTU B EN 13163:2012 Materialy budivel'ni teploizoljacijni. Vyroby zi spinenogo polistyrolu (EPS). Tehnichni umovy (EN 13163:2008, IDT). Kyiv, 2012 [in Ukrainian].

[39] DSTU EN 13164:2019 Materialy budivel'ni teploizoljacijni. Vyroby z ekstrudovanogo pinopolistyrolu (XPS). Tehnichni umovy (EN 13164:2012 + A1:2015, IDT) Kyiv, 2019 [in Ukrainian].

[40] K. V. Korytchenko et al., Enhancing the Fire Resistance of Concrete Structures by Applying Fire-Retardant Temperature-Resistant Metal Coatings, Materials Science Forum, 1038 (2021) 500-505.

[41] K. V. Korytchenko et al., Advanced detonation gun application for aluminum oxide coating, Multidisciplinary journal «Functional Materials», 27 (1) (2020) 224-229.

[42] A. Kovalov et al., Treatment of Determination Method for Strength Characteristics of Reinforcing Steel by Using Thread Cutting Method after Temperature Influence, Materials Science Forum, 1006 (2020) 179–184.

[43] V. Sadkovyi et al., Fire resistance of reinforced concrete and steel structures, Kharkiv: PC TECHNOLOGY CENTER, (2021) 180.

[44] Y. Otrosh et al., Assessment of the technical state and the possibility of its control for the further safe operation of building structures of mining facilities, E3S Web of Conferences, 123(3):01012 (2019).

[45] D. Dubinin et al., Improving the installation for fire extinguishing with finely-dispersed water, Eastern-European Journal of Enterprise Technologies, 2/10 (92) (2018) 38–43.

[46] K. Korytchenko et al., Experimental investigation of the fire-extinguishing system with a gasdetonation charge for fluid acceleration, Eastern-European Journal of Enterprise Technologies, 3/5 (93) (2018) 47–54.

[47] A. Kasimov et al., Numerical study of the process of compressing a turbulized two-temperature air charge in the diesel engine, Eastern-European Journal of Enterprise Technologies, 6/5 (96) (2018) 49–53.

[48] K. Korytchenko et al., Numerical simulation of initial pressure effect on energy input in spark discharge in nitrogen, Problems of Atomic Science and Technology, 122 (4) (2019) 116–119.

[49] K. Korytchenko et al., Experimental research into the influence of twospark ignition on the deflagration to detonation transition process in a detonation tube, Eastern-European Journal of Enterprise Technologies, 4/5 (100) (2019) 26–31.

[50] K. Korytchenko et al., Experimental investigation of arc column expansion generated by highenergy spark ignition system, Problems of Atomic Science and Technology, 118 (9) (2018) 225–228.

[51] K. Korytchenko et al., Challenges of energy measurements of low-energy spark discharges, 2020 IEEE KhPI Week on Advanced Technology (KhPIWeek), (2020) 421–424.