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Experimental research on the thermal properties of innovative insulation boards made of polyurethane-polyisocyanurate (PUR/PIR)

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In this work, the results of investigations of polyurethane materials were presented. Innovative materials based on polyurethane-polyisocyanurate (PUR/PIR) foam were obtained. Different types of additives (flame retardants, aerogels – additives that decrease thermal conductivity) are used in the composition of PUR/PIR foam. Foams are a type of composite composed of two phases: continuous (polyurethane polymers) and dispersed (composed of gases). All samples have been tested for thermal parameters: thermal conductivity, specific heat, and thermal diffusivity. Then they have been compared with each other and with a reference sample (RS) without additives. Based on the research, it was shown that innovative insulation materials were characterized by thermal conductivity λ in the range of 0.0254–0.0294 W/(m · K). The thermal properties of foams depending on the type and chemical composition of the material. Depending on the used substrates, their molar ratio, type, synthesis conditions, modifying agents and catalysts, a different polyurethane material is obtained.

Keywords: polyisocyanurate (PIR), polyurethane (PUR), thermal properties, insulating buildings materials, aerogels.

INTRODUCTION

Nowadays, in all branches of industry, solutions related to the reduction of greenhouse gases are implemented. As part of the work of the European Commission, a new strategy growth for countries of the European Union, which aims to reduce climate change, has been developed (The European Green Deal 2019)[1]. The European Green Deal has become the basis of European Union Legislation in this regard. This deal aims to achieve both no net emissions of greenhouse gases by 2050 and economic growth that is not dependent on the use of natural resources.

The heating of buildings, along with transport, is one of the main sources of pollution (including CO_2) – especially in big cities in Poland. Heating is responsible for approximately 40% of the total energy consumption in the world[2]. For example, in the UK, 19% of the total CO_2 emissions can be associated with the heating of buildings[3]. Due to this, new solutions for insulating buildings are expected in the construction industry. Three types of insulation materials are mostly used: expanded polystyrene, mineral wool, and rigid polyurethane foam[4]. In industrial practice, polyurethane-polyisocyanurate (PUR/PIR) foams are used as insulation for buildings. Moreover, due to their use in many applications, they have different properties, which depend on their purpose. Polyurethane foams have better mechanical properties than polyisocyanurate foams, but they are extremely flammable. In turn, polyisocyanurate foams have higher thermal stability and lower flammability than polyurethane foams[5]. In practice, PUR/PIR foams are products that combine the above-mentioned properties. Most of the PUR/PIR foams that are used for building insulation must be characterized by appropriate values of thermal conductivity λ, specific heat Cp, and thermal diffusivity a. PUR/PIR foams are not disposable products. They are filling, and insulating materials inside the wall used to construct many kinds of building – including modular buildings. Any waste products generated during the process of production PUR/PIR foams or walls can be processed in the process of glycolysis into substrates for the production of further PUR/PIR foams – way of recycling[6].

Aerogels are a state-of-the-art thermal insulation material, and currently have the highest commercialization potential[7]. Aerogels can be utilized as additives that increase their thermal-insulation properties of many insulating materials. In some applications, aerogels can be used as a bulk material[8], whereas in buildings they are usually applied as aerogel glazing[9] or blankets[10]. They can also be employed in the building structure – inside bricks[11], or incorporated in cement/plaster composites[12]. Moreover, they are ultra-light materials that are made by replacing liquid (trapped in the gel) with gas. Due to their high porosity (usually above 90%), and a very developed specific surface area (500–1200 $m^2 \cdot g^{-1}$), they are very good thermal insulators. Other essential properties of aerogels include their low density (~0.03–0.3 [g/cm^3]), superinsulation performance (0.012–0.025 [W/(m · K)]), ultra-low dielectric constant (k = 1.0–2.0), and low index of refraction (~1.05)[13]. Silica aerogels are synthesized in the "sol-gel" process, in which alkoxide silicones or silica salts are usually used as precursors[14]. This is an economic and effective way of synthesizing aerogel materials and usually enables high-quality materials with uniform and small-size particles to be obtained. There are a few steps involved in the sol–gel process, including the preparation of precursors, gelation (hydrolysis and condensation), aging, surface modification (solvent exchange), and drying. There are three drying methods for silica aerogel: supercritical drying (SD), ambient pressure drying (APD), and freeze drying[15].

Limited flammability is needed and necessary for the practical application of PUR/PIR foam. Halogen additives are still used for this purpose, for example,

tris(2-chloro-1-methylethyl)phosphate (TCPP)[16]. A significant disadvantage of halogen additives is the emission of very toxic and corrosive fumes from the fire area to the environment during combustion. The legislation of the European Union gradually limits the use of halogen-containing flame retardants and prefers more ecologically halogen-free additives. Halogen-free flame retardants are still being developed in regards to growing their effectiveness[17, 18]. For some time intumescent flame retardant systems are becoming more popular[19] and are considered as an environmentally friendly solution.

When different types of additives (flame retardants, aerogels – additives that decrease thermal conductivity, etc.) are used in the composition of PUR/PIR foam, particular attention should be paid to the preparation of the composition of the polyurethane system. Every modification of PUR/PIR foams changes their properties. Some additives do not strongly interact with the polymer matrix, and can therefore cause a deterioration of the mechanical and thermal properties of the PUR/PIR foams[20].

To sum up, novel polyurethane systems for application in buildings require modification to obtain increased thermal-insulation properties. Better thermal-insulation properties will contribute to the better insulation of buildings and the reduction of the emission of greenhouse gases to the environment. An advantageous feature (added value) of the additives that increase the thermal--insulation properties (for example aerogels) of PUR/PIR foams is that they can also reduce the possible adverse effect of other additives (e.g. flame retardants – necessary in the composition of modern PUR/PIR foam) on the values of thermal conductivity λ.

In this publication, novel PUR/PIR were obtained in the presence of halogen-free flame retardants (IFR), and in the presence of an additive that increases their thermal-insulation properties – modified aerogel (MA). PUR/PIR foams were tested with regard to the values of thermal conductivity λ, specific heat Cp, and thermal diffusivity a. All modifications of PUR/PIR foams can be influenced by their thermal properties.

Flame retardant additives are absolutely necessary to obtain novel PUR/PIR foams. This is due to having to comply with fire safety requirements. However, flame retardant additives indirectly influence on thermal-insulation properties of PUR/PIR materials. For this reason extremely important is the study of the thermal-insulation properties of a complete foaming system (PUR/PIR with flame retardants, and with an additive that increases their thermal-insulation properties). Therefore all results thermal-insulation properties of PUR/PIR foams concern foams with IFR and MA together. The influence of these additives on PUR/PIR foams is discussed by analysing the values of thermal conductivity λ, specific heat Cp, and thermal diffusivity a. Results were compared with model foam. Model foam is PUR/PIR foam obtained without any additives, in the laboratory, as a sample for study, but according to commercial polyurethane insulation products recipe. It is a reference sample against which other modified PUR/PIR foams are compared. Analysis of flame retardant properties of PUR/PIR foams is a different wide problem beyond the scope of this work.

The innovation of this work is using a novel additive that increases the thermal-insulation properties (MA) of PUR/PIR foams, together with flame retardant systems. Achieved decreasing of thermal conductivity λ is significant for producers of PUR/PIR foams and is competitive in the market of insulating materials. Currently, there is no such solution on the market. The researches concerning analysing the values of thermal conductivity λ, specific heat Cp, and thermal diffusivity a, of PUR/PIR compositions together with (intumescent flame retardant) IFR and MA are also original.

In the article, the test results of other materials are compared with the reference sample (RS). RS is the sample of PUR/PIR foam without additives, which was made in the laboratory, according to the commercial recipe. Only PUR/PIR foam made by the same method – in the same scale – can be compared to each other. Based on these dependencies, the analogous behaviour of PUR/PIR foams on an industrial scale can be predicted. Investigations of thermal parameters of novel PUR/PIR foams, made in the industry, are plane in the future.

MATERIALS

The method of obtaining aerogels

Silica aerogels modified with an organic compound were obtained during the research described in this paper. The developed material had a hybrid organic-non--organic structure, which facilitated its even dispersion in the PUR/PIR foam.

Hybrid aerogels were prepared using the sol-gel method, which involves the hydrolysis of tetraethoxysilane and the condensation of a hydrolysis product in an aqueous mixture that contains alcohol and an ammonium compound. The modifying compound in the form of a mixture with a catalytic system was introduced at the beginning of the synthesis in the amount of 5% in relation to the amount of pure silica. Afterwards, the gels were subjected to the aging process, modification with the use of a hydrophobizing agent, and a two-stage drying process (pre-drying at the first stage in the flow of air, then changing the temperature and basic drying). Importantly, the obtained hybrid aerogels did not require drying in supercritical conditions.

The structure and surface composition of the hybrid aerogels was measured using scanning electron microscopy and energy-dispersive X-ray spectroscopy (JSM – 6490LV JEOL Company). The SEM image of the hybrid aerogel shows the structure of loose, light, pollen-like particles that are bound together into larger agglomerates. The obtained results of the energy-dispersive X-ray spectroscopy (EDS) analysis confirm the effectiveness of modifying silica aerogel. In the EDS spectra, the peaks characteristic of the elements that are present on the surface of a tested sample were recorded. Carbon was observed on the surface of the modified product, which indicates the presence of an organic compound (Figure 1).

The prepared aerogels were also analyzed with regard to their specific surface area (using a TriStar II 3020 V1.03 camera from Micromeritcs Company, Norcross, GA, USA). The obtained values of the Brunauer–Emmett–Teller (BET) specific surface area for the tested

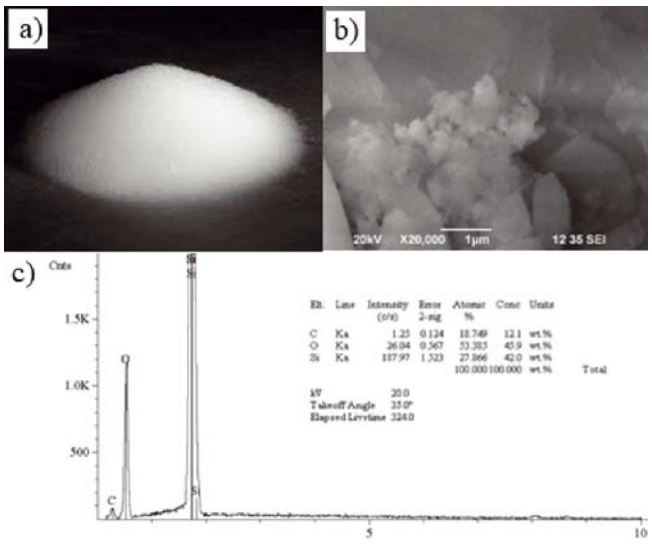

Figure 1. Photo (a), SEM (b) and EDS analysis (c) of the hybrid aerogel

hybrid aerogels were within the range of 800–900 [m^2/g], with a recorded pore size of above 10 nm. Depending on the used modification method, the hybrid aerogels had a value of the Lambda coefficient within the range of 0.022–0.029 [W/(m · K)]. In our studies, modified aerogels with the lowest lambda parameters were used. A beneficial effect on the thermal parameters of PUR/PIR foams was expected, especially in the presence of necessary IFR in the PUR/PIR compositions.

The method of obtaining modified rigid polyurethane foams

The novel PUR/PIR foam described in this article was developed with halogen-free flame retardants and an additive (modified aerogels (MA)) that increases its thermal insulation properties. New kinds of intumescent flame retardant (IFR), containing phosphorus and nitrogen, were used for this purpose. Four types of IFR were used in the PUR/PIR compositions, and they differed in terms of their proportion of nitrogen to phosphorous. The aerogels were modified by organic compounds by the method described above in detail. The modification aimed to improve the compatibility between the aerogels and the polymer matrix.

The novel PUR/PIR foam, which was modified using IFR and MA, was obtained in the presence of a special catalytic system. As a result of the polycyclo trimerization of aromatic polyisocyanates, polyisocyanurate rings were formed, which in turn gave the foam its specific properties. Moreover, the insulation foams were also produced in a typical way by mixing two liquids (isocyanate and polyol) with a blowing agent and surfactants.

The composition of the produced foams is summarized in Table 1. The reference sample (RF) did not contain IFR and MA. The samples modified with various types of IFR and MA were marked with symbols MS1-MS8. To preparation of modified PUR/PIR foam four types of halogen-free flame retardant (IFR-1 to IFR-4 – they differed in terms of their proportion of nitrogen to phosphorous) and two types of modified aerogels (MA-1 and MA-2) were used. Due to the patent procedure in Poland related to the composition and method of producing modified foams, it is not possible to provide a more precise quantitative composition. However, this information is not essential to draw the conclusions presented in this publication.

Table 1. Composition of the novel PUR/PIR foams used in the research

Tested sample	IFR	MA
RS	0	0
MS1	IFR1	MA1
MS2	IFR1	MA2
MS3	IFR2	MA1
MS4	IFR2	MA2
MS5	IFR3	MA1
MS6	IFR3	MA2
MS7	IFR4	MA1
MS8	IFR4	MA2

The results of the investigations of the modified PUR/PIR foams were compared with foams without additives made in the same way and conditions – RS. Therefore, all the results are of a comparative (model) nature. Many parameters of PUR/PIR foams are influenced by the method of their preparation e.g. laboratory or industrial, and therefore they cannot be compared. However, the effectiveness of individual additives that can be seen on a laboratory scale can be correlated with the effectiveness of the same additives on an industrial scale.

Material RS is a reference sample of PUR/PIR foam, made in the laboratory according to the commercial recipe. The test results of other materials are compared with RS sample. We do not compare the properties of PUR/PIR foams made on a laboratory scale with PUR/PIR foams made on an industrial scale. The influence of production methods on thermal properties is very significant – which we mentioned in the introduction.

EXPERIMENTAL SET-UP

The thermal parameters (thermal conductivity λ, volume specific heat Cv, and thermal diffusivity a) of all the obtained innovative samples and commercial samples were tested using the Isomet 2114 device after 7 days of conditioning under a constant temperature of 20 °C ±2 °C and humidity of 50% ±5%. The accuracy of the measuring device in this study was 5%.

The proposed measurement method is based on measurements carried out in non-stationary conditions. Measurement methods based on undefined thermal conductivity usually lead to the determination of thermal diffusivity by testing the temperature change during the heating or cooling of the sample. By means of the proposed measuring stand, it is possible to perform a measurement that does not require a specific heat flow. The device analyzes temperature changes resulting from the response of the tested material to the flow of thermal impulses. These changes are measured by changeable probes that are attached to a meter connected to a computer recording the results (Figure 2). The dimensions of the tested samples were 10 cm x 10 cm x 20 cm. During the measurements, the amount of heat generated by the device is known. This heat propagates radially in the sample. The increase in the sample's temperature varies linearly with regard to the logarithm of time. This dependence allows for the direct determination of the thermal conductivity of the tested material[21, 22].

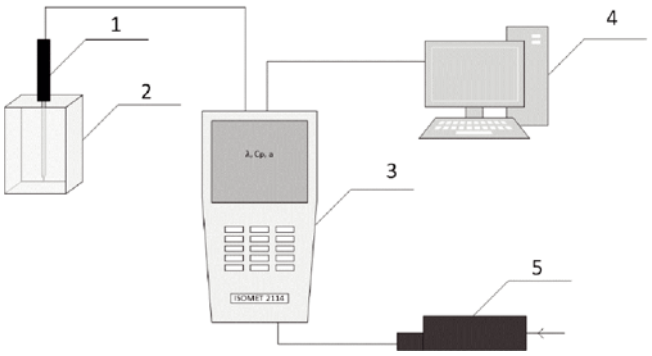

Figure 2. Scheme of the experimental stand for measuring thermal properties of building materials: 1 – needle probe, 2 – test sample, 3 – Isomet 2114 device, 4 – computer, 5 – power supply

The proposed device has a wide measuring range and can be used, among others, for insulation materials, concrete, gypsum, geopolymers, plastics, glass and minerals. The measuring range depends on the probe and covers the λ values from 0.015 to 6.0 [W/(m · K)], and the Cv values from 0.04 to 3.0 [MJ/(m^3 · K)]. The meter has two optional probe types: needle probes for soft materials, and surface probes for hard materials. The working ranges of the measuring needle probe used in the research were 0.015 to 0.05 [W/(m · K)] and 0.04 to 1.0 [MJ/(m^3 · K)]. The measurement data are saved in the internal memory of the device or the computer memory. In the presented experiment, the measurements were carried out with a needle probe (Figure 3).

Figure 3. Investigations of the thermal properties of the insulating foam

EXPERIMENTAL RESULTS AND DISCUSSION

Density results

All the samples were weighed after 7 days of incubation in hygrothermal conditions. By knowing the dimensions and mass of the samples, their volumetric density ρ_{b1} was determined using a simple relationship (1):

$$\rho_{b1} = \frac{m}{V} \quad (1)$$

Based on the measured thermal parameters, it was also possible to calculate density ρ_{b2} from dependence (2):

$$\rho_{b2} = \frac{\lambda}{a \cdot c_p} \quad (2)$$

The obtained values of the densities ρ_{b1} and ρ_{b2} of all the samples did not differ by more than 1%, despite the use of different calculation methods (Table 2). When using the first formula, the density was calculated based on the known masses and volumes of the samples, and in the second case, it was determined based on their measured thermal properties. The good compliance of the calculations is also shown in Figure 4. The generalized dependence $\rho_{b1} = f(\rho_{b2})$ was proposed. The density of the reference material was ρ_{b1} = 34.32 [kg/m^3] and ρ_{b2} = 34.21 [kg/m^3]. The density results of the modified samples are presented in Table 2.

Table 2. The calculated bulk density of the tested samples

Tested sample	Bulk density ρ_{b1} [kg/m^3] *Calculated from Formula (1)	Bulk density ρ_{b2} [kg/m^3] *Calculated from Formula (2)
RS	34.32	34.21
MS1	36.99	36.65
MS2	35.64	35.69
MS3	37.51	37.47
MS4	39.52	39.68
MS5	35.77	35.78
MS6	37.14	37.14
MS7	36.80	36.71
MS8	38.17	38.15

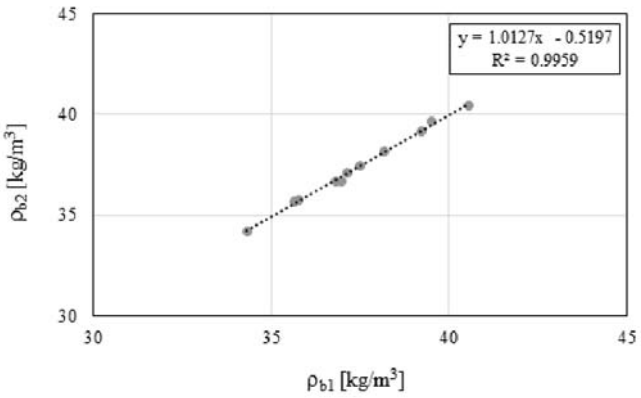

Figure 4. Graph of the dependence between ρ_{b1} and ρ_{b2} of the tested foams

The result of testing the thermal properties

During the tests, the thermal conductivity (λ), volumetric specific heat (Cv), and thermal diffusivity (a) of all the samples were measured. Six measurement series were performed for each sample. The obtained results and statistical data are presented in Table 1a (Appendix). The specific heat Cp, expressed in J/(kg · K), was calculated by dividing the measured volumetric heat capacity Cv by the material's volume density ρ_{b1}.

If the standard deviation of the random variable X is unknown, the distribution of the arithmetic mean of sample $\overline{X}$ is very well approximated by the Student's t--distribution. The Student's random variable is defined as follows (3):

$$t = \frac{\overline{X} - \mu}{s} \tag{3}$$

where: s – the standard deviation of the sample, μ – the expected value.

A probability density function of this random variable is expressed using Formula (4):

$$f(t,n) = \frac{\Gamma\left(\frac{n+1}{2}\right)}{\Gamma\left(\frac{n}{2}\right)\sqrt{n\pi}}\left(1 + \frac{t^2}{n}\right)^{-\frac{n+1}{2}} \tag{4}$$

where Γ(x) is the Euler gamma function.

The detailed form of the probability density function depends on the number of degrees of freedom (n – 1). The graph of this function is symmetrical in relation to t = 0, and the smaller the number of degrees of freedom (n – 1), the more "flattened" it gets. The fewer observations (measurements) that are conducted to calculate the mean value $\overline{X}$, the more this value will deviate from the real (expected) value of the random variable X. Of course, with an increase in the number of degrees of freedom, the Student's t-distribution tends to the normal distribution N(0, 1).

If the tested random variable has the N(μ, σ) distribution, and the standard deviation is unknown, we build the confidence interval using the Student's t-distribution with the probability density expressed by Formula (4). We then obtain dependence (5):

$$P\left(-t_{n-1;\alpha/2} \le \frac{\overline{X} - \mu}{s}\sqrt{n} \le t_{n-1;\alpha/2}\right) = 1 - \alpha \tag{5}$$

After simple transformations, we finally receive dependence (6):

$$P\left(\overline{X} - t_{n-1;\alpha/2}\frac{s}{\sqrt{n}} \le \mu \le \overline{X} + t_{n-1;\alpha/2}\frac{s}{\sqrt{n}}\right) = 1 - \alpha \tag{6}$$

where α is the assumed significance level, and 1 – α is the confidence level.

By having the results of n measurements, the parameters such as mean value $\overline{X}$, and also standard deviation s that was calculated from the sample, were determined. The intervals of the actual measured values – thermal conductivity λ, specific heat Cp, and thermal diffusivity a – were estimated with a certain probability. For all the performed measurements, the measurement uncertainty was assessed based on the Student's t-distribution. Based on statistical calculations, and with the assumed confidence level of 95%, the confidence intervals of the measured thermal properties were determined[23]. With a probability close to one, the sought values of the thermal parameters (λ [W/(m · K)], Cp [J/(kg · K)], a [mm^2/s]) of the foams samples are within the intervals shown in Table 3.

Foams MS2, MS5, MS6, MS7 and MS8 had lower values of thermal conductivity λ than the RS sample (model foam sample). Among them, the MS8 foam had the best insulating properties. The thermal conductivity of this material was at the level of 0.0254 [W/(m · K)], and was 4.2% lower than the RS sample (Figure 5a).

Table 3. The calculated confidence intervals of the measured thermal properties of the foams

Tested sample	Designated confidence intervals
RS	P (0.0244 ≤ λ ≤ 0.0283) = 0.95
	P (1667.1 ≤ Cp ≤ 1743.9) = 0.95
	P (0.4105 ≤ a ≤ 0.4932) = 0.95
MS1	P (0.0252 ≤ λ ≤ 0.0282) = 0.95
	P (1601.5 ≤ Cp ≤ 1628.2) = 0.95
	P (0.4368 ≤ a ≤ 0.4648) = 0.95
MS2	P (0.0257 ≤ λ ≤ 0.0259) = 0.95
	P (1626.3 ≤ Cp ≤ 1667.8) = 0.95
	P (0.4317 ≤ a ≤ 0.4451) = 0.95
MS3	P (0.0285 ≤ λ ≤ 0.0302) = 0.95
	P (1684.7 ≤ Cp ≤ 1709.9) = 0.95
	P (0.4534 ≤ a ≤ 0.4707) = 0.95
MS4	P (0.0269 ≤ λ ≤ 0.0284) = 0.95
	P (1621.0 ≤ Cp ≤ 1635.6) = 0.95
	P (0.4081 ≤ a ≤ 0.4272) = 0.95
MS5	P (0.0250 ≤ λ ≤ 0.0259) = 0.95
	P (1609.7 ≤ Cp ≤ 1650.9) = 0.95
	P (0.4306 ≤ a ≤ 0.4425) = 0.95
MS6	P (0.0259 ≤ λ ≤ 0.0272) = 0.95
	P (1682.3 ≤ Cp ≤ 1704.9) = 0.95
	P (0. 4099 ≤ a ≤ 0. 4338) = 0.95
MS7	P (0.0257 ≤ λ ≤ 0.0259) = 0.95
	P (1629.2 ≤ Cp ≤ 1654.3) = 0.95
	P (0.4250 ≤ a ≤ 0.4301) = 0.95
MS8	P (0.0249 ≤ λ ≤ 0.0259) = 0.95
	P (1610.3 ≤ Cp ≤ 1625.3) = 0.95
	P (0.4037 ≤ a ≤ 0.4193) = 0.95

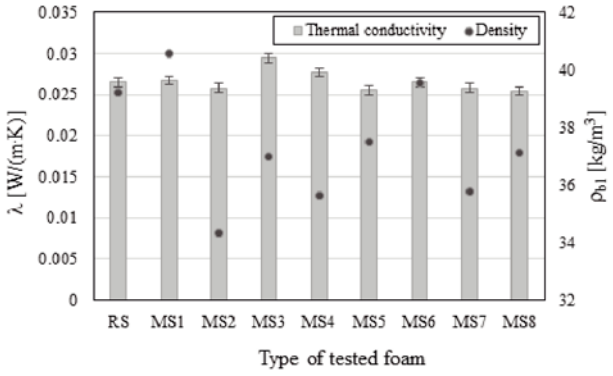

Figure 5a. The obtained average values of the thermal conductivity of the modified foam samples and reference sample

Thermal diffusivity a is a specific material property that characterizes heat conduction in transient conditions. This value allows for the determination of how quickly a material reacts to temperature changes. To be able to predict the behavior of a material during cooling, and to simulate spatial temperature changes, it is necessary to know the value of thermal diffusivity. This is required in the case of calculations using the Fourier differential equation for transient heat conduction. The thermal diffusivity coefficient indicates the speed with which temperature changes from one plane to another, i.e. a material's susceptibility to temperature equalization while being heated or cooled in certain places. During the measurements, almost all the modified samples had lower values of thermal diffusivity when compared to the reference sample RS. The lowest value, 0.4115 [mm^2/s], was registered for the MS8 sample, and it was lower than the reference sample by 8.9%. The only case in which

the value increased by 2.2% when compared to the RS sample was for the MS3 sample (Figure 5b).

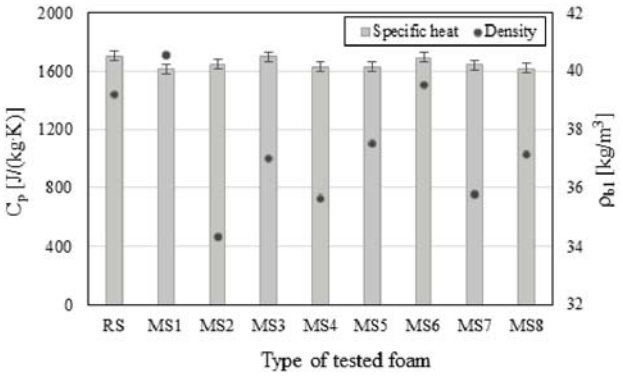

Figure 5b. The obtained average values of the thermal diffusivity of the modified foam samples and reference sample

During the experiment, it was noticed that all the modified samples (MS1-MS8) showed lower specific heat values when compared to the reference sample. The MS1 and MS8 samples had the lowest values of 1614.9 [J/(kg · K)] and 1617.8 [J/(kg · K)], respectively. They were lower by 5.3% and 5.1% when compared to the RS reference sample. Properly made materials can be used for thermal insulation and fire resistance due to their low thermal conductivity λ and high specific heat Cp (Figure 5c).

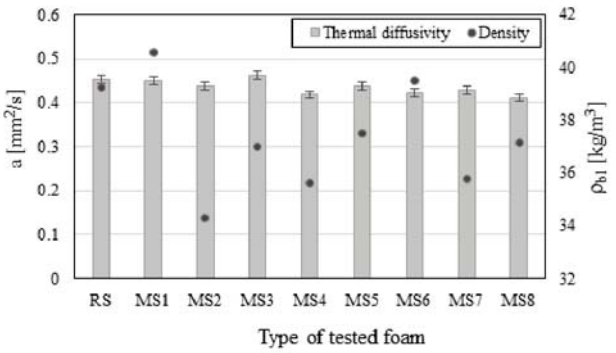

Figure 5c. The obtained average values of the specific heat of the modified foam samples and reference sample

The experimental values obtained during the tests, with marked 5% errors, are presented in graphs 6a–6c. It was noticed that with an increasing density ρ_{b1}, the value of thermal conductivity λ increases (Figure 6a), whereas the values of thermal diffusivity a (Figure 6b) and specific heat Cp (Figure 6c) decrease. The bars presented in all graphs in the work are marked with values +/– 5% from the calculated values of thermal conductivity, specific heat and thermal diffusivity.

The thermal properties of foams depending on the type and chemical composition of the material. Depending on the used starting materials, their molar ratio, type, synthesis conditions, modifying agents and catalysts, a different polyurethane material is obtained. Foams are a type of composite composed of two phases: continuous (which are PUR/PIR polymers) and dispersed (composed of gases). The polymer is responsible for the mechanical properties and the gas for the insulation properties of the foams produced.

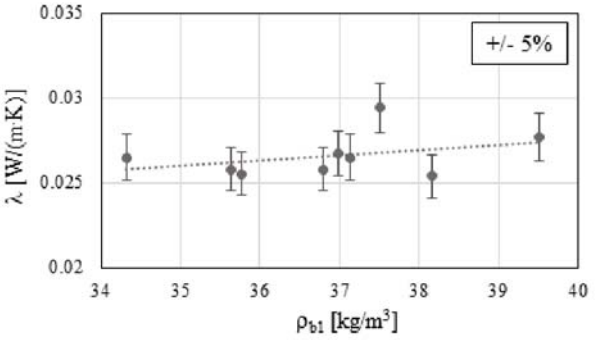

Figure 6a. Graph of the dependence between the thermal conductivity of the reference foam (RS) modified foams (MS1-MS8) and density

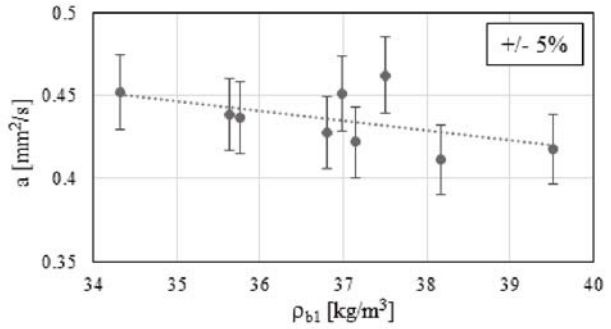

Figure 6b. Graph of the dependence between the thermal diffusivity of the reference foam (RS) modified foams (MS1-MS8) and density

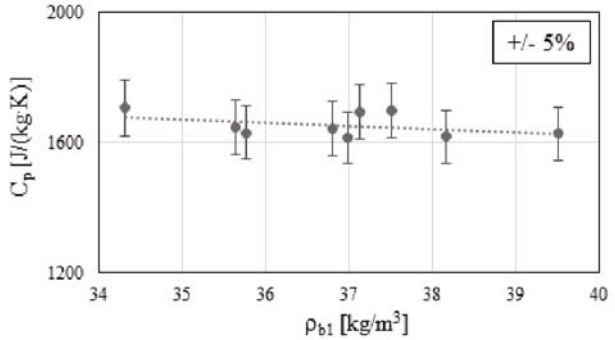

Figure 6c. Graph of the dependence between the specific heat of the reference foam (RS) modified foams (MS1-MS8) and density

PUR/PIR foams are a material with a cellular structure. The cell wall thickness of typical low-density foams is approximately 0.5–1 μm. Often the pores of expanded foams are filled with gases with better thermal insulation properties than air. In foams, heat transport takes place due to conduction of gases enclosed in the foam cells, conduction of the polyurethane matrix, radiation and convection. In modern foams, heat transport through the polyurethane matrix and radiation are of great importance. In these materials, the greatest amount of heat is transferred through conduction, a significant part of which is allocated to gases (60–80% of the thermal conductivity value), and less to the skeleton. In low-density foams, gas is approximately 92–98% by volume. The heat transfer in the polymer matrix is therefore low due to its low content (a few percent of the entire foam volume). The lowest values of the thermal conductivity coefficient in rigid PUR / PIR foams are obtained for a density of 30–40 kg/m^3 with assumed pore sizes in the order of nanometers.

CONCLUSIONS

The paper presents tests of selected thermal properties of innovative PUR/PIR foams, which were modified with halogen-free IFR flame retardants and modified aerogel MA to improve their thermal conductivity.

The foams marked with symbols MS8 and MS5 had the lowest value of thermal conductivity λ. It amounted to [W/(m · K)] and 0.0254 [W/(m · K)], respectively. It was noted that the obtained foams had a density within the range of 34.3–39.5 [kg/m^3].

Four PUR/PIR foams (MS2, MS5, MS7, MS8) had lower values of the λ parameter than the reference RS foam. Material RS is a reference sample of PUR/PIR foam, made in the laboratory according to the commercial recipe. The test results of other materials are compared with RS sample. Therefore, materials with better-insulating properties, than those obtained according to the industrial recipe, were obtained.

The density of the obtained foams was calculated in two ways: first – based on the known masses and volumes of the samples, and second – based on their measured thermal properties. The obtained results, when using both calculation methods, differed by no more than 0.9%.

Many foam parameters are influenced by the method of their preparation. For this reason, the results of modifying foams obtained using various methods, e.g. laboratory and industrial, cannot be directly analyzed. However, if individual modifiers are effective when tested on a laboratory scale, a similar effectiveness should be expected on an industrial scale. Such a comparison may be an interesting comparative (model) issue.

Analyzing the research results, it can be concluded that using IFR and MA together, PUR/PIR compositions with improved thermal properties (with decreased values of thermal conductivity λ) were obtained.

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APPENDIX A

Table 1A. The obtained values of the thermal parameters of the commercial insulation foams, RS reference sample and modified samples, and also the calculated statistical parameters.

LITERATURE CITED

1. The European Green Deal, Brussels, 11.12.2019 COM (2019) 640 final, https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52019DC0640.

2. Gupta, A., Badr, Y., Negahban, A. & Qiu, R.G. (2021). Energy-efficient heating control for smart buildings with deep reinforcement learning. *J. Buil. Engin.* 34, 101739. DOI: 10.1016/j.jobe.2020.101739.

3. Naldzhiev, D., Mumovic, D. & Strlic, M. (2020). Polyurethane insulation and household products – A systematic review of their impact on indoor environmental quality. *Buil. Environ.* 169, 106559. DOI: 10.1016/j.buildenv.2019.106559.

4. Khaleel, M., Soykan, U. & Çetin, S. (2021). Influences of turkey feather fiber loading on significant characteristics of rigid polyurethane foam: Thermal degradation, heat insulation, acoustic performance, air permeability and cellular structure. *Construc. Buil. Mater.* 308, 125014. DOI: 10.1016/j.conbuildmat.2021.125014.

5. Wirpsza, Z. (1991). *Poliuretany: Chemia, Technologia, Zastosowanie*, Wydawnictwa Naukowo Techniczne, Poland.

6. Heiran, R., Ghaderian, A., Reghunadhan, A., Sedaghati, F. & Thomas, S. (2021). Glycolysis: An efficient route for recycling of end of life polyurethane foams. *J. Polymer Res.*, 28(1), 1–19.

7. Gao, T., Jelle, B.P., Gustavsen, A. & Jacobsen, S. (2014). Aerogel-incorporated concrete: An experimental study. *Constr. Buil. Mater.* 52, 130–136. DOI: 10.1016/j.conbuildmat.2013.10.100.

8. Schmidt, M. & Schwertfeger, F. (1998). Applications for silica-based aerogel products on an industrial scale. *Materials Research Society Online Proceedings Library* 521, 179–184.

9. Leung, C.K.K., Lu, L., Liu, Y., Cheng, H.S.S. & Tse, J.H. (2020). Optical and thermal performance analysis of aerogel glazing technology in a commercial building of Hong Kong. *Energy Buil. Environ.* 1 (2), 215–223. DOI: 10.1016/j.enbenv.2020.02.001.

10. Nocentini, K., Achard, P., Biwole, P. & Stipetic, M. (2018). Hygro-thermal properties of silica aerogel blankets dried using microwave heating for building thermal insulation. *Energy Buil.* 158, 14–22. DOI: 10.1016/j.enbuild.2017.10.024.

11. Wernery, J., Ben-Ishai, A., Binder, B. & Brunner, S. (2017). Aerobrick – An aerogel-filled insulating brick. *Energy Procedia* 134, 490–498. DOI: 10.1016/j.egypro.2017.09.607.

12. Berardi, U. (2017). The benefits of using aerogel-enhanced systems in building retrofits. *Energy Procedia* 134, 626–635.

13. Karamikamkar, S., Naguib, H.E. & Park, C.B. (2020). Advances in precursor system for silica-based aerogel production toward improved mechanical properties, customized morphology, and multifunctionality: A review. *Adv. Colloid Interf. Sci.* 276, 102101. DOI: 10.1016/j.cis.2020.102101.

14. Gurav, J.L., Jung, I.K., Park, H.H., Kang, E.S. & Nadargi, D.Y. (2010). Silica Aerogel: Synthesis and Applications. *J. Nanomater.*, 409310. DOI:10.1155/2010/409310.

15. Pan, Y., He, S., Gong, L., Cheng, X., Li, C., Li, Z., Liu, Z. & Zhang, H. (2017). Low thermal-conductivity and high thermal stable silica aerogel based on MTMS/Water-glass co-precursor prepared by freeze drying. *Mater. and Design* 113, 246–253.

16. Xu, D., Yu, K. & Qian, K. (2018). Thermal degradation study of rigid polyurethane foams containing tris (1-chloro-2-propyl) phosphate and modified aramid fiber. *Polymer Testing*, 67, 159–168.

17. Jankowski, P. & Kędzierski, M. (2011). Synthesis of polystyrene of reduced flammability by suspension polymerization in the presence of halogen-free additives. *Polimery*, 56(1), 20–26.

18. Jankowski, P. & Kijowska, D. (2016). The influence of parameters of manufacturing hybrid flame retardant additives containing graphite on their effectiveness. *Polimery*, 61(5), 327–333.

19. Jankowski, P. & Kędzierski, M. (2013). Polystyrene with reduced flammability containing halogen-free flame retardants. *Polimery*, 58(5), 342–349.

20. Wang, S.X., Zhao, H.B., Rao, W.H., Huang,, S.C., Wang, T., Lioa, W. & Wang, Y.Z. (2018). Inherently flame-retardant rigid polyurethane foams with excellent thermal insulation and mechanical properties. *Polymer* 153, 616–625, DOI: 10.1016/j.polymer.2018.08.068.

21. Prałat, K., Jaskulski, R., Ciemnicka, J., Makomaski, G. (2021). Analysis of the thermal properties and structure of gypsum modified with cellulose based polymer and aerogels. *Arch. Civil Engin.*, 66(4). DOI: 10.24425/ace.2020.135214.

22. Prałat, K., Grabowski, M., Kubissa, W., Jaskulski, R. & Ciemnicka, J. (2019). Application of experimental setup for the thermal conductivity measurement of building materials using the "hot wire" method. *Sci. Review Engin. Environ. Sci.*, 2019(1), 153–160. DOI: 10.22630/PNIKS.2019.28.1.14.

23. Buczkowska, K.E., Prałat, K., Ciemnicka, J., & Koper, A. (2021). Comparison of the Thermal Properties of Geopolymer and Modified Gypsum. *Polymers* 13(8), 1220. DOI: 10.3390/polym13081220.