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Feathers as a Flame-Retardant in Elastic Polyurethane Foam

Abstract

An account is given herein of research results for composites of elastic polyurethane (EPUR) combined with milled poultry feathers. We present the properties of keratin fibres obtained from feathers and the change in those properties which the feathers induce in the EPUR foam. The structure of the composites was determined by spectrophotometric (FTIR), thermal (DSC) and thermogravimetric (TGA) analyses as well as by scanning electron microscopy (SEM). Assessed were also the burning- and acoustic properties, and thermal conductivity. The addition of ground feathers to EPUR increases its limiting oxygen index and reduces the effect of "falling drop". Another benefit is a distinct increase in the temperature of the maximum degradation rate of the foam hard phase.

Key words: polyurethane, elastic foam, feathers, keratin, flame retardant.

made resin producers look into new alternative environmentally-friendly additives (e.g. graphite, phosphorous compounds) fit to curb polymer flammability [6, 7].

Keratin in the form of ground poultry feathers is an interesting candidate to play the role of an anti-pyrene [8]. Feathers are a burdensome waste in poultry slaughterhouses, which presents itself as a cheap raw material for the manufacture of composites [9].

In 2010, the consumption of poultry meat in Poland and world-wide amounted to 5 mln and 60 mln tons, respectively. Feathers make up 5% of the poultry mass [9], hence about 75 thousand and 3 mln tons of feathers are annually available in Poland and world-wide, respectively.

In pursuit of innovative solutions to utilise renewable materials, at the Institute of Biopolymers and Chemical Fibres, Łódź, Poland a method [10 - 13] to reduce the flammability of polyurethane foam with the addition of poultry feathers has been prepared and applied for a patent.

A tenacity close to that of polyamide fibres is featured by poultry feathers, fibres of which are much finer in diameter than wood fibres, for example [8]. Such properties make feather- originating keratin fibres a suitable polymer filler [10, 11]. Compared to traditional cellulosic fillers, feathers have a low density ($0.89 \text{ g} \times \text{cm}^{-3}$), as well as being good thermal and acoustic insulation material that is abundant and cheaply available. The positive properties of feathers are grounded in the porous air-filled structure [14, 15]. A further advantage is the length to diameter proportion of the keratin fibres prepared [8]. The unique (multi-branched) structure of

the fibre makes it an ideal material for the preparation of composites by methods which provide a random distribution of the fibre, for example in injection moulding [15]. Keratin fibres from poultry feathers find an increasing outlet as fillers in composites with thermoplastic or thermoset matrix [14]. The concept of using poultry feathers to play the role of a flame retardant may be actually labelled a novelty [12].

Environmental protection has been the main motive that turned attention toward poultry feathers. The core objective of the research was to the use of keratin fibres as a replacement for additives commonly applied to elastic EPUR resins for the production of furniture and acoustic insulation.

Experimental

The impact of the addition of processed poultry feathers upon EPUR resins used in the manufacture of furniture and car seats was estimated, with the main point being flame-retardant properties of the feathers.

Two kinds of EPUR were used. The foam products were prepared on a laboratory scale in open moulds. Semi- industrial trials with closed moulds were made at Polychem Systems Co Poznań, Poland .

Materials used

- Polyol, trade name ALFAPUR POLYOL FM 3900 (Alfa Systems Ltd, Brzeg Dolny, Poland)
- Izsocyanate, trade name ALFAPUR ISO FM 3900 (Alfa Systems Ltd., Brzeg Dolny, Poland)
- Poultry feathers from a slaughterhouse

Introduction

Polyurethane elastic foam (EPUR) materials are commonly used in furniture construction [1] and in civil engineering as acoustic insulation [2]. Gaining popularity are polymeric composites filled with natural renewable materials [3]. The beneficial, useful and ecological properties of such products along with well- known processing techniques foster their widening use.

Demands that are placed on EPUR foams concern not only mechanical-and physical-chemical properties but, in fact, mainly inflammability [4]. Underpinned by a well- developed cell structure, EPUR foams burn readily. The burning releases hazardous fumes and gases [5]. Various additives like anti-pyrenes, including those containing halogens, are used to limit the flammability. Many of the halogen-containing anti-pyrenes have been banned by EU regulations for their environmental-unfriendliness. It has

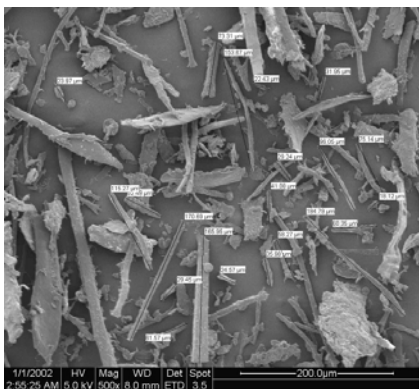


Figure 1. SEM image of keratin fibres.

Breaking up of the feathers

Purified, wet feathers were disintegrated several times:

- by cutting on a guillotine- about 1.5 h
- by grinding on a disk mill, Sprout-Waldorom; slot 0.3 mm, time ca. 4.5 h
- by grinding on a disk mill, Sprout-Waldorom; slot 0.1 mm, time ca. 8 h.

The material was then centrifuged and dried in a lacquer dryer with 30 sieves for 3 h at 80 °C, then ground in a disintegrator (KMW, 1953 KARLSTAD SWEDEN) for 10 min, and next in a ball mill for 8 h. Prepared material (see Figure 1, page 120) that way, resembling powder in appearance, is hereinafter termed keratin fibres.

The bicomponent blend PUREX EPI 20 Polychem Systems Ltd, Poznań, Poland was used without flame retardant additives to prepare an elastic foam on a semi-industrial scale.

Keratin fibres were used as a filler and flame retardant.

Preparation of PUR foam modified with keratin fibres

Trials on lab scale

Keratin fibres were added to a plastic container holding 100 g of polyol. The components were mixed for 5 minutes with an agitator at 2000 r.p.m. Isocyanate was then added to the mixture in the amount of 62 g, and the mixture was again agitated at the same r.p.m. for 2 minutes. The thick mixture was prepared put into a vinidur mould lined with alu-foil heated up to 60 °C, at which the foaming was performed. The foam was left for 16 hours at ambient temperature and then cured for 60 minutes at 120 °C.

10 – 15% of the flame retardant is usually added to the EPUR. We made

trials with similar amounts of keratin fibres (KF): 10% keratin fibres (EPUR_A+10% KF) and 16.5% keratin fibres (EPUR_A+16.5% KF). The choice of the amount of KF added was made by comparing that of classical flame retardants.

Trials on semi-industrial scale

Keratin fibres were added to polyol pre-blends in the amount of 10% and 16% of the total mass of substrates used to prepare the foam (sum of polyol, diisocyanate and fibres). The pre-blend prepared was agitated at 50 r.p.m. with the isocyanate component at a weight proportion adequate to the given foam (the proportion of substrates for the preparation of EPUR on a semi-industrial scale is the know-how of Polychem Systems Co, Poznań, Poland and is therefore not disclosed in the present work). The mixture was then put into a closed mould (size: 30 × 30 × 5 cm). Prior to analysing, the sample was seasoned for 14 days at ambient conditions.

The elastic EPUR foams prepared were made with a content of keratin fibres of 10 % (EPUR+10% KF) and 16 % (EPUR+16 % KF).

Analytical methods

Fourier transform infrared spectroscopy (FTIR) was performed using a Nicolet FT-IR 6700 apparatus (USA) to determine the chemical structure of the filler, flexible foam, and composites. Spectra were recorded in the range from 400 to 4000 cm⁻¹, at a resolution of 4 cm⁻¹ and count of 64. Data analysis was performed using Omnic software. A baseline correction with CO₂ and H₂O was made to eliminate the impact of the compound's residues from the analysis.

Thermal analysis of the filler, flexible foam, and composites was made by thermogravimetry (TGA) and differential scanning calorimetry (DSC).

Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q500 (USA). The analysis was conducted with a heating rate of 10 °C/min, from room temperature to 800 °C for keratin fibres and to 700 °C for flexible foam and composites. Samples weighing approximately 10 mg were used in an air atmosphere.

Dynamic mechanical analysis (DMA) was made using a TA Instrument DMA Q800 (USA). Samples with dimensions of 10 × 10 × 10 mm and a compression clamp were used. DMA was made at a constant frequency of 1 Hz, an amplitude of 30 μm, and heating rate of 3 °C/min in the temperature range of -100 °C to 20 °C.

Scanning electron microscopy (SEM) was made using a QUANTA 200 F-MY FEI CO. (USA) microscope with an accelerating voltage of 2 kV. A series of SEM images, acquired at different magnifications, were used to study the structures of the keratin fibre as a filler, the flexible foam, and composites. Prior to SEM analysis, the samples were coated with gold by a vacuum sprayer - Q150R S to increase their conductivity. The thickness of the fibres cut was measured with the use of software adapted to operate in a Quanta environment called ANALYSIS Docu, prepared by Soft Imaging System Co.

The apparent density was measured in accordance with PN-77/C-05012.03 (corresponding to PN-EN ISO 845:2000). The value of the apparent density was calculated as a mass/volume ratio.

Estimation of inflammability by the method of limiting the oxygen index (LOI)

Inflammability was assessed by LOI at ambient temperature according to Standard PN-EN ISO 4589-2:2006. LOI is defined as the lowest volume concentration of oxygen in a mixture of oxygen and nitrogen, indispensable to maintain the burning after kindling with a small ignition source.

$$LOI = \frac{[O_2]}{[O_2] + [N_2]} \cdot 100\% \quad (1)$$

where [O₂] & [N₂] – oxygen and nitrogen concentration in the environment of the burning sample.

Assessment of the ignition hazard in a horizontal burning test

This test was accomplished according to Standard PN-EN 60695-11-10, with a 50 W test flame and horizontal position of the sample, as well as the use of a testing device provided by Fire Testing Technology Co. The EPUR foams tested were 140 × 50 mm in size and 5 ± 0.1 mm in thickness. The kindling flame was 15 - 20 mm high. The B kindling method

(progressive) was adopted. The range of burning (80mm) was considered a criterion of the burning.

Estimation of the heat transfer coefficient (HTC) of EPUR foam exposed to heat radiation

Insulation properties of the elastic EPUR foams and composites were tested in accordance with Standard PN-EN ISO 6942:2005. Prior to testing, the samples were conditioned at 20 ± 2 °C and $65 \pm 2\%$ RH for 27 hours. During the testing, the temperature was kept in the range of 24 - 26 °C and RH 40 - 45%.

Assessment of the acoustic properties of PUR foams

The sound absorption coefficient was determined according to Standard PN-EN ISO 10534-1. Measurements were made in an impedance pipe - Type 4206. A pipe 100 mm in diameter for low frequency (50 - 1600 Hz), and 29 mm diameter for high frequency (500 - 6400 Hz) were used, as well as a pipeless probe. For each EPUR 5 mm thick foam sample, three measurements were made in the 50 - 1600 Hz range and three in the 500 - 6400 Hz range of the sound frequency.

Results of the investigation and discussion

Characteristics of keratin fibres

Figure 2 presents the FTIR spectrum of the keratin fibres applied.

Keratin proteins give rise to several characteristic absorption bands, known as amide A (3265 cm^{-1}), amide B (3070 cm^{-1}), amide I ($1626 - 1732\text{ cm}^{-1}$), amide II ($1450 - 1536\text{ cm}^{-1}$), and amide III (1250 cm^{-1}), as well as bands of the stretching vibration of asymmetric C-H bonds (2917 cm^{-1}) and symmetric bonds (2852 cm^{-1}). The C-S stretching vibration corresponds to a 702 cm^{-1} peak in the IR spectrum [16].

The fibres were also characterised by the thermal analytical methods: DSC and TGA. Figure 3 presents the results of the DSC analysis of keratin fibres.

In the DSC thermogram of the keratin fibres examined, three endothermic peaks can be seen: the first one in a temperature range of about 55 °C - 98 °C, the second in the range of about 125 - 213 °C, and the third at about 213 - 236 °C. The first two peaks relate to the evaporation of water, and the third to the melting of pro-

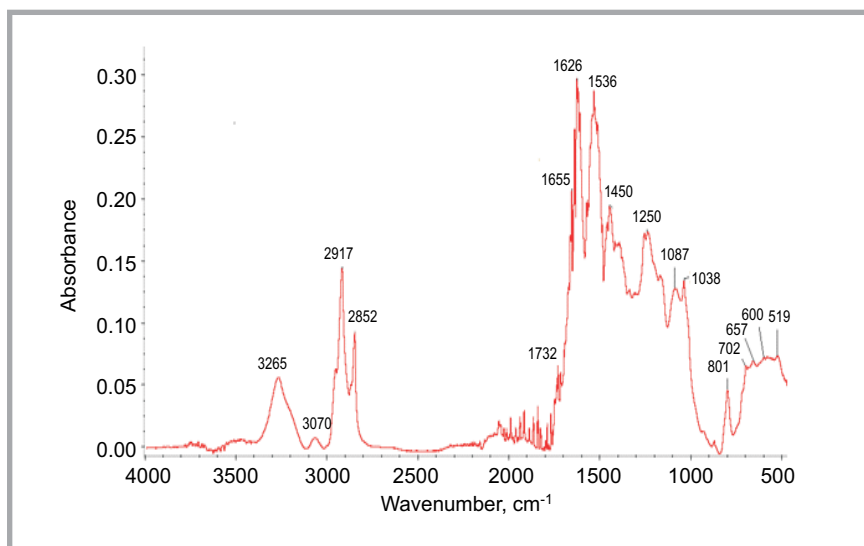


Figure 2. FTIR spectrum of keratin fibres.

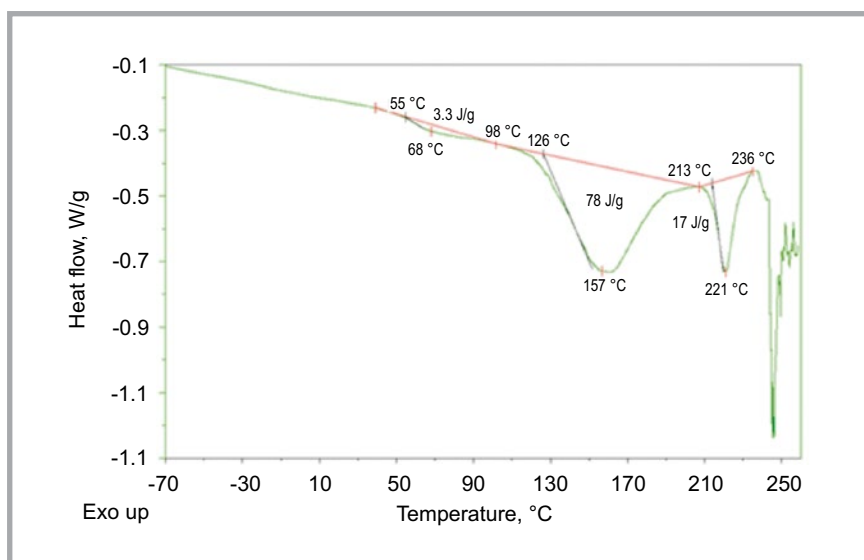


Figure 3. DSC thermogram of keratin fibres.

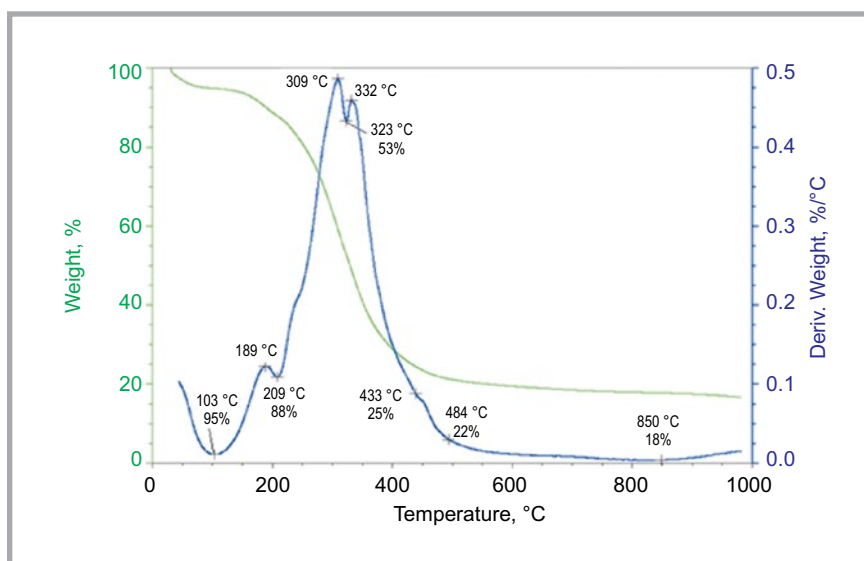


Figure 4. TG and DTG thermograms of keratin fibres.

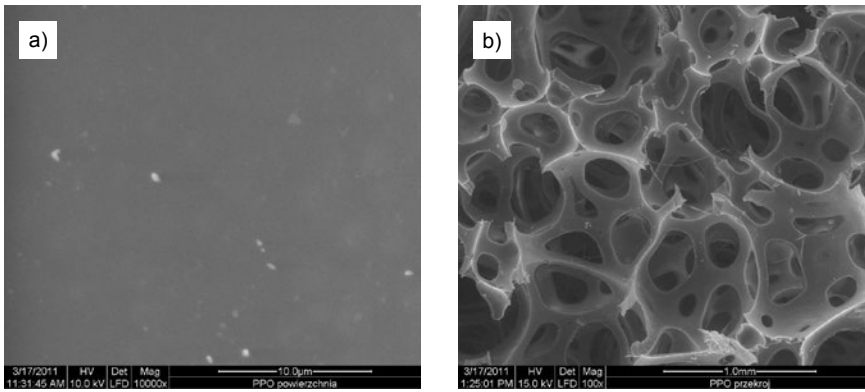


Figure 5. SEM images of EPUR_A foam, unmodified: surface (a), cross-section (b).

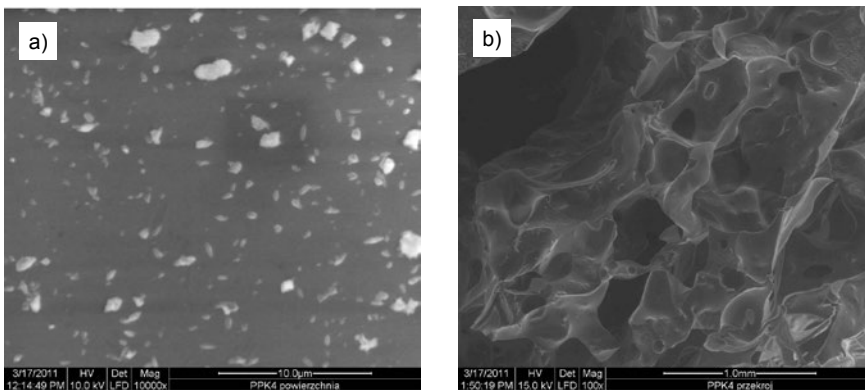


Figure 6. SEM images of EPUR_A + 10 K foam, modified with keratin fibres in the amount of 10%: surface (a), cross-section (b).

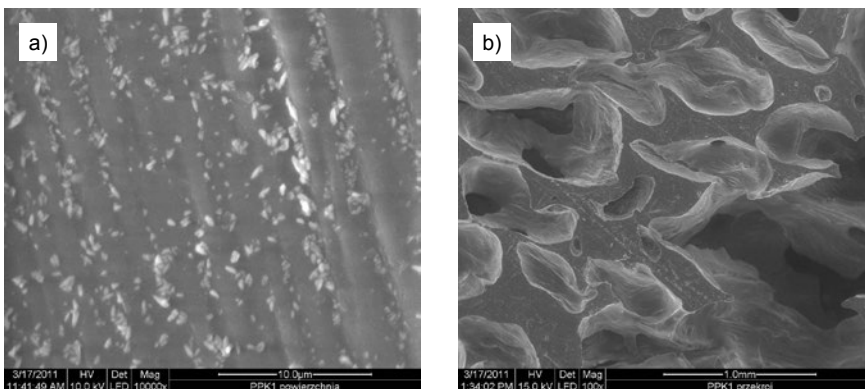


Figure 7. SEM images of EPUR_A + 16.5 K foam, modified with keratin fibres in the amount of 16.5%: surface (a), cross-section (b).

tein compositions bridged by di-sulfides [17]. Senoz et al. [18] observed in the range of 225 - 250 °C the presence of an endothermic peak related to melting. The range of the peak depended upon the thermal history of the sample. As for the keratin fibre sample examined, the peak appears in the range of 213 - 236 °C, with a melting temperature of 220 °C and enthalpy of transition - 17 J/g. In the work of Senoza et al. [18], at a heating-up rate of 10 °C/min (as in this work) the enthalpy of the transition amounted to 19.8 J/g, close to our result. Keratin degrades at a temperature above 236 °C. The degrada-

tion process was analysed using the mass change (TG) and curve of differential mass change (DTG), which are presented in **Figure 4** (see page 121).

When heated, polymeric materials first deliver volatile gases and water. In keratin, the process starts at about 50 °C and comes to an end at about 103 °C, resulting in a mass loss of 5.0 wt.%. This is then followed by distinct phases of degradation. The first peak at about 103 - 209 °C, with the maximum degradation rate at 189 °C (T_{max1}), and mass loss of about 7% (m_1), may, according to

Senoza et al., also relate to the loss of water. They found that, on the basis of TGA analysis and gas spectroscopy, that below 209 °C, water associated in different ways with keratin is still delivered, which stems from the differentiated structure of keratin, which contains polar hydrophilic groups and segments inclined to form hydrogen bonds [19]. The next peaks: one in the range of 209 - 323 °C, with the maximum at 309 °C (T_{max2}), and the third one at 323 - 433 °C, with the maximum at 332 °C (T_{max3}) and mass loss of 35 wt.% (m_2), and approx. 28 wt.% (m_3), respectively, may be related to the disappearance of disulfide bridges in keratin. There follows a fourth peak in the range of 433 - 483 °C, with the maximum at 449 °C (T_{max4}) and mass loss of 3% (m_4), which is also probably related to the degradation of disulfide bridges. After heating at 850 °C, ash remains in the amount of about 18 wt.%. The degradation rate of the decomposition products increases beyond 850 °C.

It is known from literature [17] that N- and S- containing compounds, originating from acids in the proteins, and disulfide bridges make up the main portion of pyrolysis feather products. Inorganic gases (NH₃, CO₂, SCS, SCO, H₂S, and SO₂) and thiols are formed in the first phase of degradation, followed by nitriles and aromatics in the second step.

The singular steps of keratin degradation comprise the following phenomena: evaporation of loosely bound water (up to about 105 °C), desorption of fast bound water (100 - 160 °C), destruction of structural nets other than those formed by di-sulfide bridges (130 - 240 °C), destruction of bonds in the proteins (140 - 260 °C), destruction of di-sulfide bridges (130 - 280 °C), the melting of the crystalline phase (230 - 250 °C), the forming of aromatic bonds (250 - 400 °C), the forming of cyclic amines (300 - 380 °C), and the degradation of aromatic bonds and cyclic amines (380 - 600 °C) [18].

The preparation of keratin fibres adopted in this work did not cause changes in their characteristic when compared to keratin derived from other sources (wool, hair, horns, hoofs), as analysed by other researchers) [17, 18]. Analysis of quantitative changes proceeding during the degradation of the fibres used was made for the first time, enabling the interpreta-

tion of the test results of the EPUR composites prepared.

Figure 1 shows an SEM image of ground keratin fibres used as EPUR fillers. Dimensions of the fibres were measured: length - in the range of 18 - 185 μm , and thickness - 5 - 18 μm (see page 120).

Test results of foams prepared on a laboratory scale

SEM images were taken of selected lab scale EPUR foams, both unmodified and modified with keratin fibres. Pictures showing the foam surface and cross-section are presented (see **Figures 5, 6 & 7**).

Unmodified foams (**Figure 5**) contain oval pores of size in the 30 - 80 μm range. These are interconnected by pores with a size of 10 - 50 μm . An addition of 10% of keratin fibres (**Figure 6**) induces a change in the pore shape and dimensions. The pores take irregular shapes of polyhedrons, with dimensions varying in the range of 30 - 100 μm , and are interconnected with only a few pores of a size below 30 μm . The composites with a 16.5% content of keratin fibres (**Figure 7**) have elongated pores 30 - 120 μm long and 30 - 60 μm wide interconnected by very few pores of 10 - 30 μm size. The addition of a larger amount of keratin involves an increase in pore size and decrease in the amount of open pores. The result is a change in foam properties.

It was an objective of the investigation to assess whether keratin fibres could work as flammability-limiting agents in elastic EPUR foams. For foams prepared on a lab-scale, the limiting oxygen index was estimated and the horizontal burning test performed to this end (**Table 1**).

As can be seen in **Table 1**, the addition of keratin fibres results in an increase in LOI and a limitation of the burning speed in the horizontal test, in which the undesired dropping effect did not appear as well. The improved inflammability could have been caused instead by the presence of keratin fibres and by the higher foam density and limitation of the amount of open pores, which can be seen in the structure images.

Examination of structure and properties of elastic foams prepared on a semi-industrial scale

To confirm the impact of keratin fibres upon the properties of the elastic polyurethane foams, trials were made to prepare such foams on a semi industrial scale using closed moulds.

Table 1. Flammability of elastic PUR foams with keratin fibres, prepared on a lab-scale; The data presents the average score of five measurements with standard deviation of 0.5% and 0.5 mm/min respectively.

Symbol of foam	Limiting oxygen index (LOI), %	Horizontal burning test mm/min
EPUR _A	20.0	25
EPUR _A +10% K	25.0	22
EPUR _A +16.5% K	26.7	20

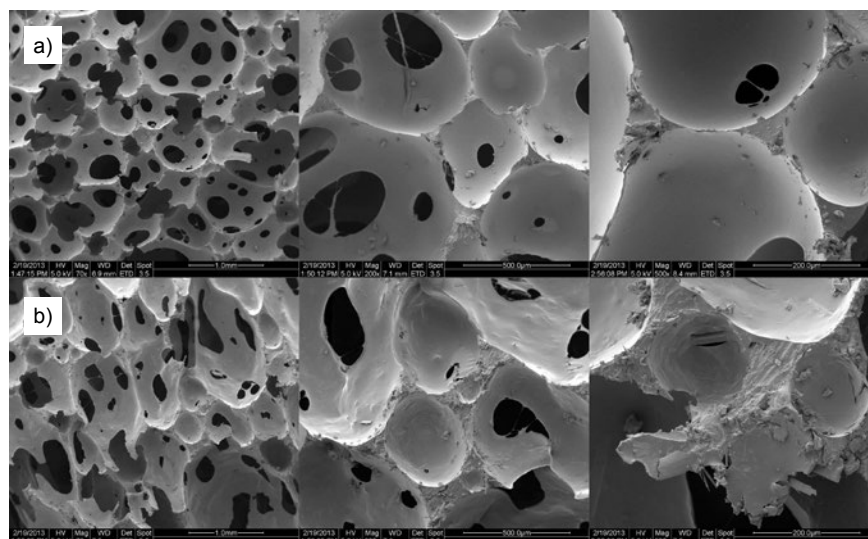


Figure 8. SEM images of the surface and cross section of PUR foams unmodified (a) and modified with 10% of keratin fibres (b). Magnification: 70 \times ; 200 \times ; 500 \times .

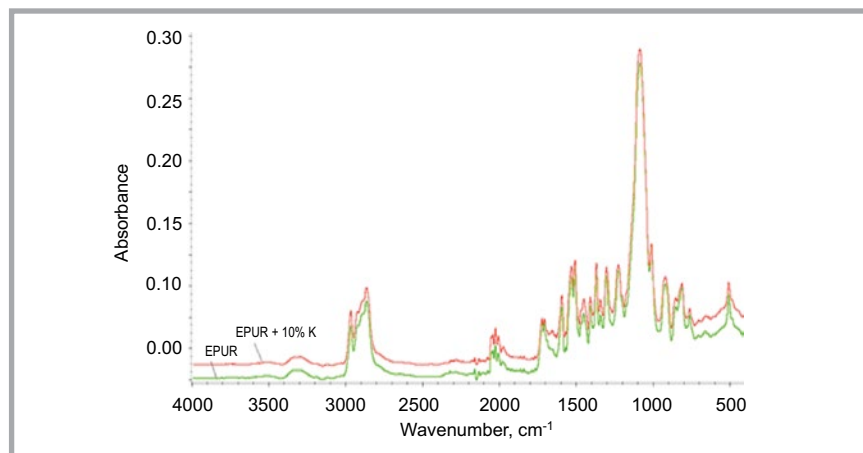


Figure 9. FTIR spectra of EPUR foams made on a semi-industrial scale.

Images were taken of the surface and cross section of EPUR both unmodified and modified with 10 wt% of keratin fibres, prepared on a semi-industrial scale. Some of the images can be seen in **Figure 8**.

Unmodified foams made on a semi-industrial scale contain oval pores with a size in the 400 - 950 μm range. These are interconnected by pores of 50 - 350 μm size. The addition of 10% of keratin fibres to the foam (EPUR+10% K) induces a change in the pore shape and dimensions. The pores take irregular oval

shapes with varying dimensions: length - 700 - 1800 μm , width - 400 - 1200 μm , and are interconnected with only a few oval pores in a size range of 200 - 1000 μm . The foams made in closed moulds on a semi-industrial scale have larger pores. As on a lab-scale, the addition of keratin fibres to EPUR results in a change in pore size and an increase in the amount of closed pores.

Infrared spectroscopy (ATR technique) was harnessed to illustrate the changes in the EPUR chemical structure (**Figure 9**).

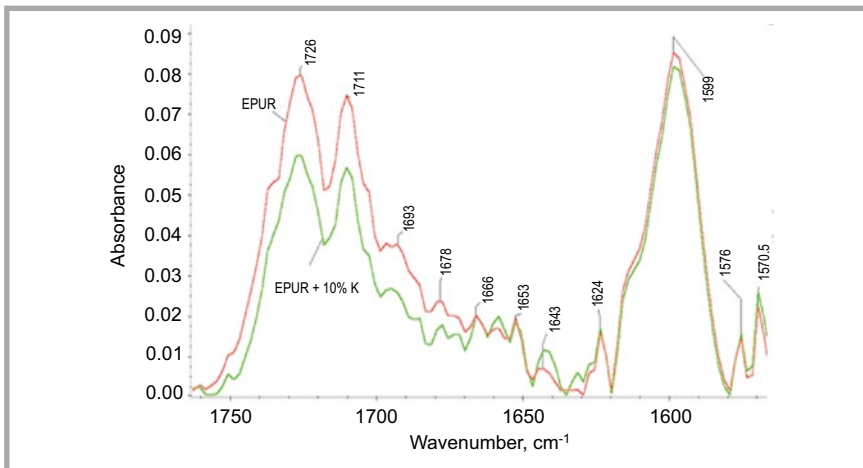


Figure 10. FTIR spectrum of polyurethane within the range 1760 and 1580 cm^{-1} .

Polyurethane macromolecules are built up of two different segments: flexible and rigid. As a result of phase separation, flexible and rigid phases are formed in the material. In the course of phase separation, hydrogen bonds are formed in the rigid phase; index R is an indication of the amount of hydrogen bonds. These bonds are responsible for the degree of phase separation (DPS). The properties of polyurethanes are, among others, a result of DPS change [20]. The addition of a filler to the polyurethane matrix usually causes a change in the DPS [21, 22]. The amount of hydrogen bonds and DPS in the PUR may be assessed on the basis of the change in absorbency fields, which is related to defined groups present in their macromolecules.

To estimate the signal strengths, peak modelling of the infrared active carbonyl

bands (Figure 9) was carried out using Gaussian curve-fitting method software OMNIC 7.3. The carbonyl absorption bands were deconvoluted into component bands. Peak areas of these bands were measured, the contribution of urea (U_1) groups calculated using Equation 2, the content of urethane (U_2) groups calculated using Equation 3, and the carbonyl hydrogen-bonding index $R_{C=O}$ was calculated using Equation 4. Moreover the degree of phase separation (DPS) was obtained through Equation 5.

$$U_1 = \frac{\sum A_{1i}}{\sum A_i} \quad (2)$$

$$U_2 = \frac{\sum A_{2i}}{\sum A_i} \quad (3)$$

$$R_{C=O} = \frac{A_{B1} + A_{B2}}{A_{F1} + A_{F2}} \quad (4)$$

Table 2. Characteristic of hard phase of EPUR and EPUR with 10% of keratin

Samples	EPUR	EPUR+10% K
Carbonyl groups in hard phase		
Contribution, %		
ordered bidentate ureas in organized phase (1629 - 1639 cm^{-1})	3	10
ordered bidentate ureas in unorganized phase (1644 - 1666 cm^{-1})	14	22
ordered monodentate ureas (1672 - 1679 cm^{-1})	8	8
disordered monodentate ureas (1685 - 1690 cm^{-1})	10	1
free ureas (1693 - 1700 cm^{-1})	8	16
ordered urethanes (1704 - 1711 cm^{-1})	31	36
disordered urethanes (1715-1722 cm^{-1})	13	9
free urethanes (1743 - 1751 cm^{-1})	13	0
Contribution of all groups		
urea	43	56
urethane	57	44
Phase separation		
R	3.80	5.35
DPS	0.79	0.84

$$DPS = \frac{R_{C=O}}{R_{C=O} + 1} \quad (5)$$

where: U_1 & U_2 are contributions of urea (1) and urethane (2) groups; A_{1i} & A_{2i} are the absorbance of carbonyl groups of urea (1) and urethane (2) groups, respectively, and A_i is the absorbance of carbonyl groups; A_{b1} , A_{b2} — the respective surface areas of bands from vibrations related to the hydrogen bond of the amine or carbonyl groups of urea (1) and urethane (2) bonding. A_{f1} , A_{f2} — the respective surface areas of bands from vibrations unrelated with the hydrogen bond of the amine or the carbonyl groups of urea (1) and urethane (2) bonding (Figure 10).

Results of the characteristic of chemical structure of the hard phase of EPUR s are presented in Table 2.

Keratin added to the polyurethane matrix promotes a larger amount of urethane bonds, which may be the result of the reaction between isocyanate groups and

Table 3. Results of the analysis of curves drawn in the DMA examination.

EPUR samples	Tg tan δ , °C	E' R-plateau, MPa
EPUR	- 41	0.021
EPUR+10% K	- 45	0.037

OH groups of the free and bounded water in the keratin fibres.

The amount of both free urea and urea compounds connected by hydrogen bonds with other rigid segments increases. There is an increase in the hydrogen bond index and DPS, reflecting the changes proceeding in the structure of the EPUR hard phase induced by the addition of keratin. Such changes may affect the EPUR mechanical properties and thermal characteristic [20]. A thermal dynamic mechanical analysis (DMA) was made to determine the mechanical properties of the foams investigated. Results are shown in Figure 11.

Curves of the dependence of the storage modulus and loss modulus on the temperature for EPUR with and without keratin fibres take a similar course; however, at low temperature the storage modulus and loss modulus are distinctly higher for EPUR with keratin fibres. The temperature of the glass transition of the soft phase of the foams prepared was derived from the curve of the dependence of tan

δ on the temperature as the maximum on the curve ($T_{g \tan \delta}$) (Table 3).

The storage modulus was also set in the plateau area of the high elastic state occurring in the foams analysed at low temperature ($E'_{R\text{-plateau}}$). The storage modulus is much higher in the foam with keratin compared with the unmodified one. In foams with keratin, the glass transition temperature is much lower, indicating that keratin eases phase separation in the polyurethane matrix. It is a confirmation for the DPS value calculated.

The thermal resistance of EPUR was assessed by means of thermogravimetric analysis, the results of which are shown in Figure 12.

From the course of the mass change curves (TG) it may be concluded that a distinct difference appears in a temperature range of about 280–350 °C, pointing to a higher thermal resistance of EPUR foam with keratin fibres. Two large peaks related to the degradation of both foams can be seen in the DTG curves. Details of the TGA analysis of both foams are compiled in Tables 4 and 5

It was assumed that the temperature of % mass loss ($T_{2\%}$) relates to the delivery of a volatile substance. The lower the temperature, the more such a substance is contained in the material. The temperature is lower in the composite than in plain EPUR, confirming that the addition of keratin fibres results in a higher content of the volatile substance. On the base of the investigation by Senoza et al. [18], it may be concluded that water represents the majority of the volatile substance. It is assumed that the start of degradation in polyurethanes occurs in relation to the 5% mass loss. In pure EPUR the $T_{5\%}$ temperature is 9 °C higher, pointing to a lower thermal resistance of the composites in that temperature range. In the first degradation phase of polyurethanes in a temperature range of 85 to 200 °C, the destruction process of allophanian probably begins, with biuret, urea and urethane compounds occurring in the hard phase [27]. Further degradation at higher temperature is shown in Table 5. After the degradation at 600 °C, a similar mass thereof remains

A peak related to the change in the degradation rate can be observed in both materials: it begins at 247 °C and ends at 313 °C for EPUR, and 317 °C for EPUR with keratin fibres. The slight shift in the

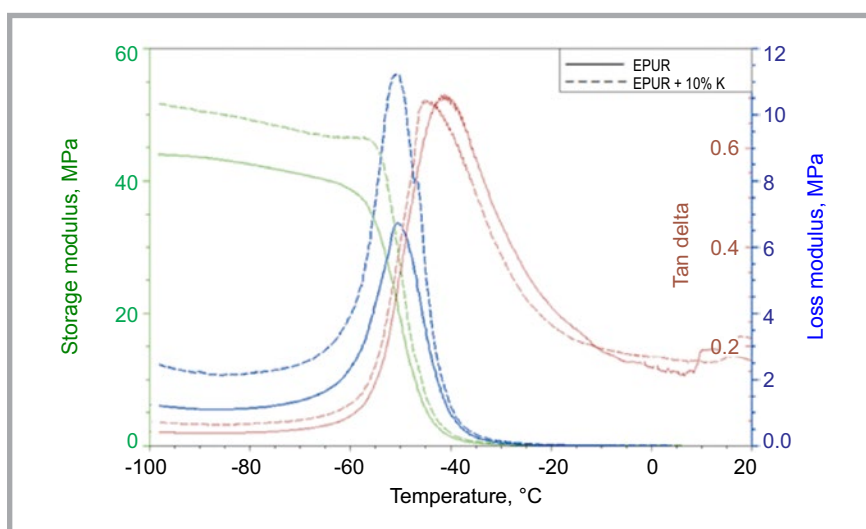


Figure 11. Influence of keratin fibres on the storage modulus and $\tan \delta$, as determined by DMA.

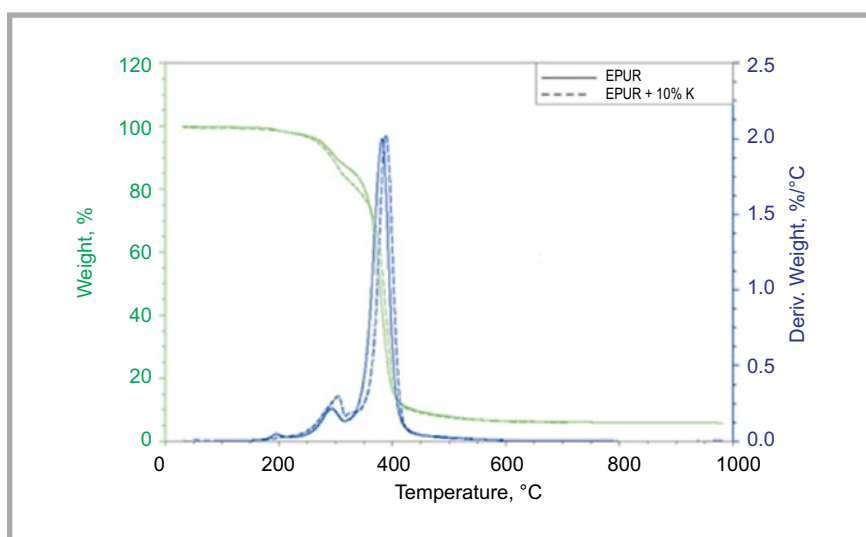


Figure 12. Change in sample mass and derivative of mass change for EPUR and EPUR with 10% of keratin fibres.

Table 4. Results of analysis of the mass change curves for EPUR and EPUR with 10% of keratin; δ - standard deviation in testing results obtained in 3 measurements for each of the sample.

Samples	T2%, °C	δ (T), °C	T5%, °C	δ (T), °C	U ₆₀₀ , %	δ (U), %
EPUR	219.2	1.1	274.6	0.2	6.0	0.1
EPUR+10% K	216.0	1.5	265.6	1.1	5.9	0.1

Table 5. Results of analysis of curves of the mass change derivative in EPUR and EPUR with 10% of keratin fibres.

Samples	Tmax ₁ ± δ (T) (peak range), °C	m ₁ ± δ (m), %	Tmax ₂ ± δ (T) (peak range), °C	m ₂ ± δ (m), %
EPUR	290.4 ± 1.0 (247 - 313)	10.0 ± 0.5	382.5 ± 0.4 (313 - 410)	73.7 ± 0.8
EPUR+10% K	303.1 ± 0.6 (247 - 317)	13.2 ± 0.2	388.4 ± 0.9 (353 - 418)	71.1 ± 0.5

peak's finish indicates that the degradation of keratin overlaps the polyurethane matrix degradation effect.

The peak relates to the degradation of compounds in the hard phase. During

the peak, EPUR loses about 10% of its weight, while a 13% loss occurs in EPUR with keratin fibres, which confirms the presumption that the degradation of keratin proceeds along with that of the hard phase. The temperature of

Table 6. Value of limiting oxygen index (LOI) of EPUR foams; the data presents the average score of five measurements with standard deviation of 0.5%.

Sample	LOI %
EPUR	19.8
EPUR+10% K	22.3

Table 7. Classification of material burning resistance.

Value of LOI, %	Flammability class
below 21	Easy combustible
21 – 28	Combustible
28 – 60	Slow burning (self distinguishing)
above 60	Incombustible

maximum degradation speed rises by about 13 °C during that phase, giving evidence for a higher thermal resistance of keratin fibre-containing EPUR. Supposedly the change is a result of the formation in the keratin fibre-containing EPUR of a larger amount of urea compounds with a decomposition temperature much higher than that of the urethane compounds.

Detailed analysis of the DTG curve implies that T5% adopted as an assessment criterion for the starting point of polyurethane and composite degradation is inadequate. The degradation of the hard phase in EPUR with and without keratin fibres begins at about 247 °C, which is much lower than the T5% temperature.

The second peak begins in EPUR straight after the completion of the hard phase degradation and ends at 410 °C. This peak relates to the soft phase in polyurethanes. In EPUR with keratin fibre, the start of the second peak, related to the acceleration of degradation, is shifted by about 40 °C. Mass loss during the degradation between the first and second peaks amounts to about 6.5%, probably

in the keratin fibres. The temperature of the maximum degradation speed of the soft phase in EPUR with keratin fibres is about 6 °C higher than for T_{max2} EPUR.

Results of the thermogravimetric analysis indicate that keratin increases the thermal resistance of the elastic foam. The oxygen index was estimated to confirm the thermal resistance of both foams (Table 6).

LOI is often used as an auxiliary criterion to assess the fire danger posed by a product (Table 7). It is recognized as a measure of the material's disposition to burning. The lower the LOI value, the more the material is inclined to burning. LOI is a very handy index to compare the inflammability of resins, textiles and textile composites, as well as to assess modification methods leading toward improving the burning resistance.

In some countries, LOI is used to establish burn-resistance classification systems (usually informal with a limited range). Shown below is one such system used in the resin industry in the USA (sometimes in Poland too).

Modification with keratin produced an increase in LOI in the EPUR from 19.8% to 22.3%, that is by nearly 13% (Table 6). The material jumped from the easily combustible to the combustible category. During the tests it could be observed that plain EPUR behaves like a typical thermoplastic material: the burning was accompanied by plasticising and a drift of polymer droplets on the material surface. Conversely keratin fibre-modified EPUR revealed burning behavior similar to that of thermoset plastics i.e. there was no plasticising nor droplet drift. The combustion left behind a brittle, porous, carbonised residue.

As reported by Brebu and Spiridon [17], in the first phase of keratin degradation, about 7% of water is delivered, which could have been the reason for the retarded ignition of the foam. This is then followed by the delivery of N- and S-containing compounds, which may restrain the combustibility of keratin fibre - containing composites. This supposition calls for explanation in further works devoted to composites of EPUR with keratin.

In the course of the investigation it was explained that the much higher LOI of the EPUR foams with keratin made on a lab scale is a result of a density change in the foams.

The next step of the investigation was concerned with the examination of the sound absorption of the EPUR foams with a keratin fibre content.

Graphs presenting the change in sound absorption with varied frequency are shown in Figure 13. Both graphs have a similar run, resembling the characteristic of foams commonly used in civil engineering [23].

The EPUR foams tested had a density similar to that of commercially offered secondary foamed ones. They are designed for use in furniture, mainly upholstery (mattresses, cushions, fillings, pillows etc). The addition of keratin fibres causes a drop in density of about 4.5%. In polyurethane foams with a 20 mm thickness used as acoustic insulation, the average value of the sound absorption coefficient (Table 8) amounts to $\alpha_{fm} = 0.4$ [23]. In the elastic foams tested the coefficient is much lower, with the content of keratin fibres adding to the decrease. It must, however, be stressed that 5mm thick foams were tested, hence four times thinner than the commercial ones.

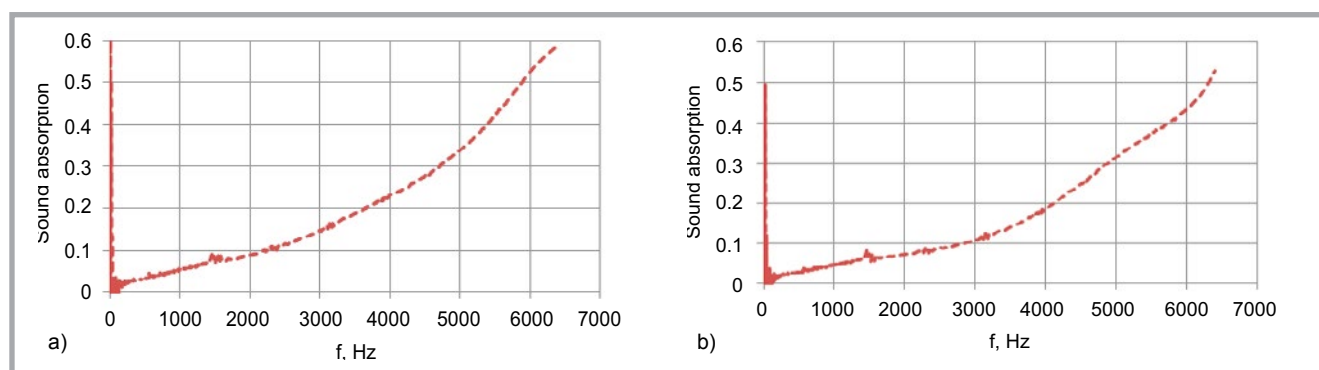


Figure 13. Sound absorption coefficient as a function of the frequency for EPUR (a) and EPUR+10% KF (b).

It is well known [24, 25] that aside of density, porosity or pore wall thickness, the capacity to absorb sound (coefficient) depends also on the material thickness. Thinner foams absorb faintly, particularly in the lower frequency range. It may be, therefore, assumed that thicker composite foams would absorb sound to the same extent as commercial EPUR foams. In many applications, EPUR foams also play the role of thermal insulators. Their heat-transfer coefficient was therefore estimated. In **Figure 14** a graph is shown illustrating the kinetics of heat transfer through elastic EPUR foams.

The *heat transfer coefficient (WPC)* is in Standard PN-EN ISO 6942, WPC, defined by the equation

$$WPC = \frac{GSC_p}{GSC_o} \quad (1)$$

where:

GSC_p – density of the heat flux permeating the sample,

GSC_o – density of the heat flux striking the sample [adopted – 2.1 kW/m²].

The value of the density of the heat flux GSC_p for each of the samples tested was calculated on the basis of the curve [T = f(t)], from the equation:

$$GSC = \frac{M \cdot c \cdot R}{A \cdot \alpha}, \text{ kW/m}^2 \quad (2)$$

where:

M – mass of the copper plate of the calorimeter, 0.036 kg,

c – specific heat of the copper, 0.385 kJ/kg °C,

R – rate of temperature increase of the calorimeter in the part of the curve analysed, °C/s, - the R numeral value equals the slope of a straight line of the approximate linear function in the interval of the function analysed $T = f(t)$,

A – area of the copper plate surface, (0.0025 m²),

α – absorption coefficient of the black-painted copper plate of the calorimeter, $\alpha = 0.9$.

The heat transfer coefficient is the same in both materials, equaling about 0.13 (**Table 9**), which is a very low value compared with fire-protection materials, but positive from the point of view of insulation materials applied in building construction.

Table 8. Sound absorption coefficient of the materials tested.

Sample tested	Density, kg/m ³	Sound absorption coefficient α_f								
		Frequency, Hz								α_{fm}
		125	250	500	1000	2000	4000	6000		
EPUR	0.108	0.015	0.02	0.03	0.05	0.09	0.23	0.51	0.14	
EPUR+10% K	0.103	0.01	0.015	0.028	0.04	0.08	0.20	0.43	0.11	

Table 9. Heat transfer coefficient, WPC, of the EPUR foams tested.

Sample tested	R, °C/s	Density of heat flux GSC_p , kW/m ²	WPC
EPUR	0.048	0.278	0.132
EPUR + 10% K	0.047	0.273	0.130

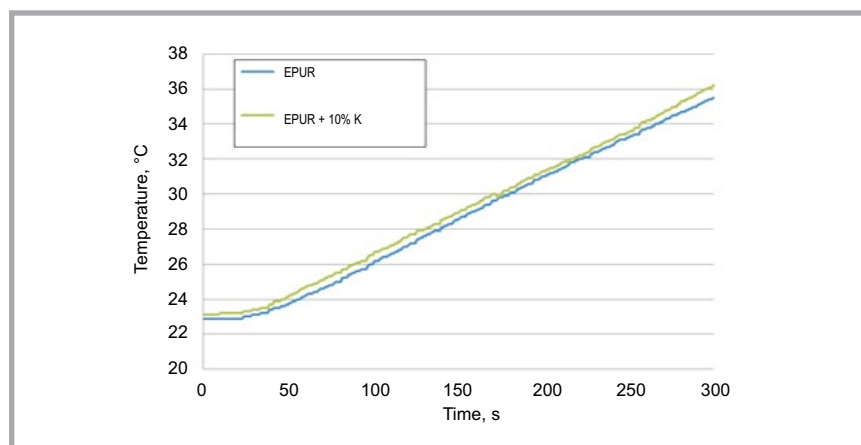


Figure 14. Change in temperature of a calorimeter shielded with elastic PUR foam, lodged in a heat radiation field.

Summary and conclusions

It was found that the keratin fibre filler derived from feathers examined resembles in structure keratin fillers prepared from other resources investigated by others [17, 18]. The addition of keratin fibres has an impact upon the foaming process, in consequence of which the structure of the composites obtained undergoes changes. Combustibility tests gave evidence that EPUR foams modified with the addition of crumbled keratin fibres (several to several tens of micrometers in length) made the material safer in respect of inflammability. The lower combustibility of the modified EPUR foams is manifested by a prolonged time before permanent ignition, an increase in the limiting oxygen index and by a lower maximum burning temperature attained in a shorter time than in the reference foam. These changes may be explained using the delivery of free and bound water, followed by that of N- and S-containing compounds. From the point of view of the combustion run, it is essential that there is a lack of droplets of the degraded products drifting during the burn-

ing, which could feed the fire and cause a secondary self-ignition.

The addition of keratin causes a decrease in EPUR density. Structural changes induced in the foams by keratin fibre result in an inferior ability to absorb sound by about 20%. However, the composites obtained are still material with very good acoustic isolation properties. The keratin-containing composites reveal thermal isolation properties similar to those of plain EPUR.

Investigation of the modification of EPUR within the present work has documented the possibility of modifying the composition of blends for the manufacture of polyurethane foams. Modification with keratin fibres fosters better inflammability resistance.

It must be highlighted that within this work no optimisation was made of the keratin fibre-content in the EPUR resin. Work in that direction will be continued in further research projects. It is hoped that even better results will be attained with an optimised content of the fibre.

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