

# The structure and properties of viscoelastic polyurethane foams with Fyrol™ and keratin fibers

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**Abstract:** The subject of the research presented in this article is viscoelastic polyurethane foams (VPF) made using a halogen free flame retardant additive – Fyrol™ – and keratin fibers. The foams were made with varying isocyanate index. For their modification, Fyrol PNX LE and Fyrol PNX were used as well as keratin fibers obtained from poultry feathers. Foams were characterized by means of techniques such as infrared spectroscopy, thermogravimetric analysis and differential scanning calorimetry. The changes in the patterns of the foams were analyzed using a scanning electron microscope. Moreover, flammability of selected foams was defined using a cone calorimeter and oxygen index. Compression set of the foams was assessed. As a result, it was concluded that the use of a Fyrol mixture with keratinous fibers preferably reduces permanent deformation of foams and a fire hazard caused by their usage.

**Keywords:** viscoelastic polyurethane foams, Fyrol, keratin fibers, structure, permanent deformation, flammability.

## Struktura i właściwości pianek lepkosprężystych z Fyrol™ i włóknami keratynowymi

**Streszczenie:** Przedmiotem badań omówionych w artykule są poliuretanowe pianki wiskoelastyczne (VPF) otrzymane z dodatkiem bezhalogenowego środka uniepalniającego – Fyrol™ – i włókien keratynowych. Pianki wykonano w warunkach różnej wartości indeksu izocyjanianowego. Do ich modyfikacji wykorzystano Fyrol PNX LE (F-LE) i Fyrol PNX (F) oraz włókna keratynowe, pozyskane z piór drobiowych. Pianki charakteryzowano metodami spektroskopii w podczerwieni, analizy termogravimetrycznej, różnicowej kalorymetrii skaningowej oraz mikroskopii skaningowej. Oceniano także palność wybranych pianek na podstawie indeksu tlenowego (OI) oraz przebieg spalania za pomocą kalorymetru stożkowego. Na podstawie odkształcenia trwałego pianek po ścisnieniu i OI stwierdzono, że modyfikacja pianek poliuretanowych mieszaniną Fyrolu z włóknami keratynowymi wpływa korzystnie na zmniejszenie odkształcenia trwałego pianek oraz ich palność, a w konsekwencji na ograniczenie zagrożenia pożarowego spowodowanego ich użytkowaniem.

**Słowa kluczowe:** wiskoelastyczne pianki poliuretanowe, Fyrol, włókna keratynowe, struktura, odkształcenia trwałe, palność.

Viscoelastic polyurethane foams (VPF), also known as shape memory foams, are open-celled foams from the group of flexible polyurethane foams (FPF) [1]. Viscoelastic foam is characterized by slow recovery after compression. The main application is the high quality mattress and pillow segment, where viscoelastic foams

distribute the body weight over a larger area. For several years these foams have been of particular interest in the industry, and have been manufactured for approx. 45 years [2, 3]. The production of these foams constitutes approx. 30 % of the market share of foam block slabstock PUR [4].

The physical and mechanical properties of FPF depend on the structure of their pores [5, 6] but also on their microstructure [7–11]. The network structure in typical FPF foam is comprised of both chemical and physical crosslinks as well as the copolymer dispersions. The chemical crosslinks arise from the use of a hydroxyl polyol of functionality greater than two, whereas the physical crosslinks arise from the phase-separated hard-segment domains (urea and urethane segments).

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In the foaming process of the flexible foams the structure of hard domains formed of urea linkages is completely arranged [7]. Although both types of crosslinks enhance the foam's physical properties, the physical crosslinks are labile at high temperatures and high humidity, thus dramatically altering the foam's properties [12].

VPF foams are one of the FPF varieties produced at an isocyanate index of less than 100 with an excess of hydroxyl groups. The use of substrates with such a ratio leads to macromolecules made up of shorter rigid and flexible segments than in the case of the foams made at isocyanate index close to 100. In addition, typical VPF foams are manufactured from several types of polyols. In the mixture of applied polyols the so-called visco- or crosslinker polyols [13] have the largest share. Such a foam formulation leads to macromolecules whose structure significantly impedes the process of phase separation [8]. As a result of the synthesis of these foams, their soft and hard phases are mixed [9, 10]. On the basis of FT-IR analysis Dounis and Wilkes [11] found that at the isocyanate index of 100 in flexible foams the highest concentration of well organized hard segments can be obtained. They also confirmed that the amount of well-ordered bidentate urea decreased at indices below 100. These observations lead to a conclusion that the increased covalent crosslinking decreases hard segment domain perfection prior to completion of phase separation. These results were confirmed in the analysis using wide-angle X-ray scattering (WAXS). In the VPF foams the increasing index caused the short-range order of the hard segments to decrease. The process of phase separation in these foams can also be assessed on the basis of the glass transition temperature of the soft phase ( $T_{g1}$ ). This temperature decreased with decreasing crosslinking due to mixing phase [14].

Viscoelastic foams are intended for the manufacture of mattresses, which should add to the comfort of sleep, but also be characterized by increased thermal resistance. One of the possibilities to increase the thermal resistance of these foams is the use of additives reducing their flammability [15]. So far, in the production of the FPF have also been used more halogen supplements, but there are attempts to use alternative non-halogenated flame retardants. These are, for instance, ammonium polyphosphate (APP), expandable graphite, melamine, triphenyl phosphate, tricresyl phosphate (TCP), Emerald Innovation™ NH-1 or Fyrol™ HF-5 [15]. The use of additives reducing flammability (flame retardants) may lead to changes in the process of foams synthesis.

There were also reports about the possibility of the use of keratin fibers and flour as additives reducing flammability of polymers [16, 17]. Wrześniewska-Tosik *et al.* [17] used 10–17 wt % of the keratin fibers for commercial modification of FPF foam. They found that the addition of ground feathers to FPF increases its limiting oxygen index and reduces the effect of “falling drop”.

The aim of the study was to analyze the properties of viscoelastic polyurethane foams modified with kera-

tin fibers and organophosphorus compounds which increase resistance to fire.

## EXPERIMENTAL PART

### Materials

For the synthesis of polyurethane foams component A (polyols and additives, FAMPUR) was used as well as component B - ONGRONAT® TR 4040 [4,4'-methylenediphenyl diisocyanate (MDI), BorsodChem]. The component A composition is “know how” of FAMPUR company.

As modifiers there were used:

- keratin fibers (K), poultry feathers from a slaughterhouse. The method of preparing keratin fibers was described in [17];

- Fyrol™ PNX LE (F-LE, ICL Industrial Products), containing 19 wt % of phosphorus. The foams with this Fyrol distinguish extreme low VOC (volatile organic compounds) emissions;

- Fyrol™ PNX (F, ICL Industrial Products), with 19 wt % of phosphorus.

The primary ingredient of Fyrols is oligomer of phosphoric polyester type, moreover, it includes phosphoric acid and phosphorus oxide (V).

### Foams obtaining

Foams were obtained in a single step, the components of the mixture were vigorously stirred and immediately dispensed into the mold. The 1–8 foams synthesis were carried out at an ambient temperature of 21 °C, while the 9–12 at 18 °C. The markings, the foams' composition and information about the course of the synthesis are given in Table 1.

### Methods of testing

- The apparent density ( $D$ ) was calculated by measuring the weight and volume of the sample. The weight of the samples was determined with an accuracy of  $\pm 0.001$  g and dimensions of the samples were measured with an accuracy of  $\pm 0.01$  mm.

- The chemical constitution of the VPFs was confirmed based on the infrared absorption spectra recorded using a Nicolet 6700 spectrophotometer (Thermo Electron Corporation) equipped with the ATR (attenuated total reflection) unit. Each sample was scanned 64 times in the wave number range of 4000–400  $\text{cm}^{-1}$ . The results were analyzed using the OMNIC Spectra 2.0 software (Thermo Nicolet).

- The thermal analyses of synthesized foams were determined using differential scanning calorimetry, DSC Q1000 (TA Instruments) in the helium atmosphere and using hermetic aluminum pans.

- Observations of the foam structure were performed using a scanning electron microscope Hitachi TM3000.

**Table 1. Samples' marking, their composition and synthesis parameters**

Seq.	Sample denotation	Isocyanate index	Type and amount of additives wt % (in conversion to 100 g of component A)	Rising time, s	Gel time, s
1	INCO-75	75	0	100	150
2	3 K	75	3 K	100	190
3	3 K-12 F-LE	75	3 K + 12 F-LE	270	450
4	INCO-80	80	0	95	145
5	12 F-LE	80	12 F-LE	280	305
6	3 K-12 F-LE A	80	3 K + 12 F-LE	250	370
7	12 F	80	12 F	200	225
8	3 K-12 F	80	3 K + 12 F-LE	160	290
9	INCO-85	85	0	135	210
10	2 K	85	2 K	135	210
11	2 K-8 F-LE	85	2 K + 8 F-LE	160	240
12	2 K-12 F-LE	85	2 K + 12 F-LE	180	480

Parallelograms with side of approx. 1 cm were cut out of the foam core coated with a thin layer of gold using a Polaron coater. The spraying process was run at a current of 6 mA for 100 s. Observation of the samples was performed using the acceleration voltage of 15 keV.

– Compression set was determined on samples 50 x 50 x 50 mm, cut so as to compress them in the direction of the growth of foams. Three series of foams were examined, annealed for 22 hours at 70 °C, and compressed by 50 %, 75 % and 90 % of the original size. Lightweight samples were measured after 0.5 h at room temperature.

– Thermal degradation of the foams was analyzed using TGA thermogravimeter (TA Instruments model Q500). The samples with a mass of  $10 \pm 1$  mg were tested, placed in platinum plates, heated at 10 °C/min from room temperature to 1000 °C under an atmosphere of nitrogen. For the analysis of the results, the program Universal Analysis 2000 version 4.7a of TA Instruments was used.

– The foams were also characterized using a cone calorimeter (Fire Testing Technology Ltd.) in accordance with ISO 5660:2002. The samples with the dimensions of 100 x 100 x 8 mm were tested by heat flux at 35 kW/m<sup>2</sup>.

– Determination of ignitability *via* oxygen index (OI) was performed according to PN-EN ISO 4589-2:2006. OI was analyzed using FTA II (Polymer Labs Associates A/S).

## RESULTS AND DISCUSSION

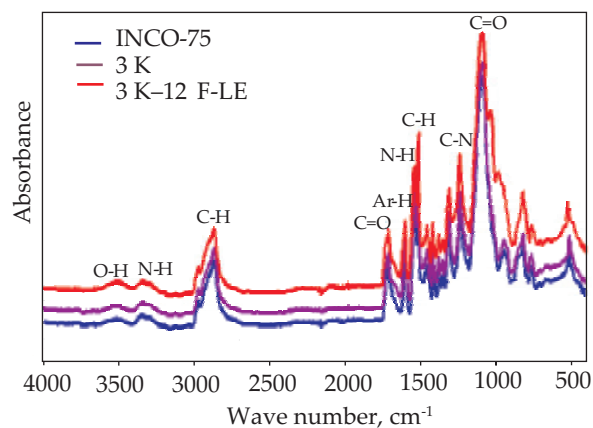
As part of the work VFP were made of varying isocyanate index of keratin fibers (K) and Fyrol (F-LE or F), which increase their resistance to fire. The synthetic course of the foams was analyzed. Start time of the foams was very short and it was less than 10 s, so for the tested foams only the rising time and gel time were registered.

Introduction to approx. 3 wt % of filler in the form of K does not result in any significant changes in growth time and the gelling time of foams while that of F and F-LE causes considerable elongation of the synthesis of foams.

However, this effect is significantly higher for the foam with F-LE. For mixtures of Fyrol and keratin fibers, the growth time and the gelling time are greater than those of foams with Fyrols.

Both types of Fyrol inhibit the growth process and the process of foam gelling. Fyrol introduction may increase the pH of the reaction medium, resulting in a reduced rate of reaction of isocyanate groups with hydroxyl groups and amine [18].

To analyze changes in the chemical structure of foams with modifiers, ATR FT-IR analysis was conducted. The result of foam analysis with INCO-75 and its modification are shown in Fig. 1.



**Fig. 1. FT-IR spectra of foams with isocyanate index 75, unmodified, with keratin, and modified with keratin fibers and Fyrol PN-X-LE**

The spectra (Fig. 1) are representative of samples which are the subject of the article. In the range of wave number 3300–3500 cm<sup>-1</sup> appear bands also from reaction substrates. Wave number 3345 cm<sup>-1</sup> originates from stretching vibration, symmetrical and asymmetrical, assigned to N-H bond. The band in the vicinity of wave number 3500 cm<sup>-1</sup> is derived from the group -OH from water or unbound polyols. Clearly outlining a range of

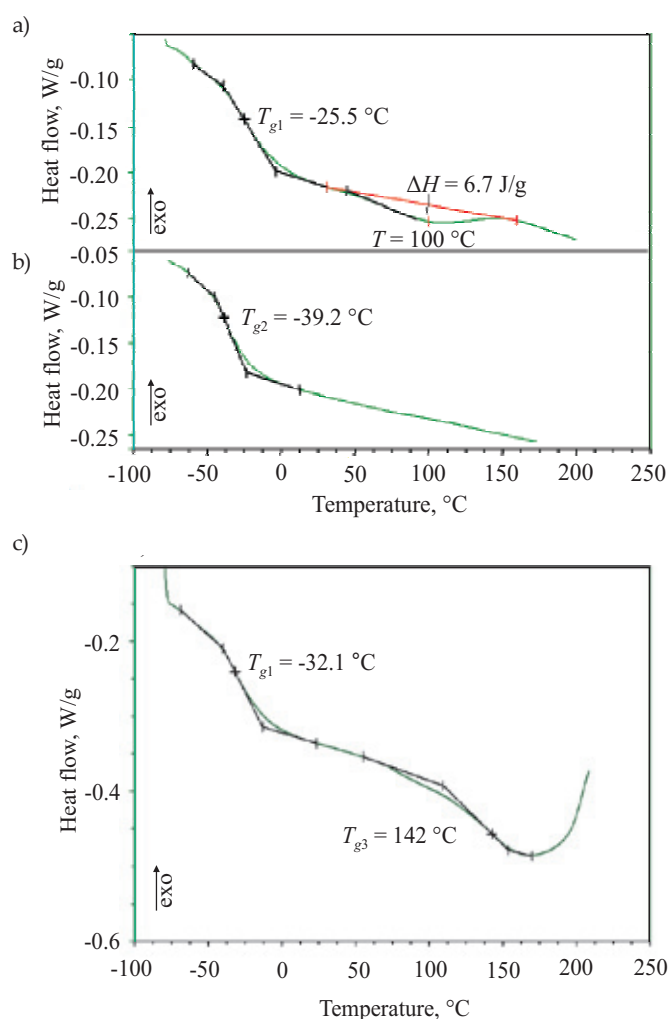
**Table 2.** The results of DSC curves' analysis of the produced samples and apparent density

Sample	$T_{g1}'$ , °C	$T_{g2}'$ , °C	$T_i$ , °C	$\Delta H$ , J/g	$T_{g3}'$ , °C	$D$ , kg/m <sup>3</sup>
INCO-75	-25.5	-39.2	100	4.8	–	43.7 ± 0.2
3 K	-23.8	-38.3	111	8.1	–	44.2 ± 0.4
3 K-12 F-LE A	-32.1	-47.6	–	–	142	49.8 ± 0.5
INCO-80	-16.9	-30.4	100	12.5	–	43.4 ± 0.2
12 F-LE	-24.9	-45.0	121	8.2	–	45.3 ± 1.0
3 K-12 F-LE	-31.2	-48.1	–	–	121	46.5 ± 1.7
12 F	-26.2	-38.0	111	7.7	–	44.7 ± 1.1
3 K-12 F	-28.3	-42.5	–	–	128	46.8 ± 2.0
INCO-85	-11.9	-30.9	98	14.0	65	43.1 ± 0.3
2 K	-14.1	-23.8	–	–	56	44.6 ± 0.5
2 K-8 F-LE	-18.2	-30.5	–	–	65	47.7 ± 0.9
2 K-12 F-LE	-24.7	-33.9	–	–	94	47.5 ± 0.4

wave number 2867 cm<sup>-1</sup> and 2970 cm<sup>-1</sup> originates from stretching vibrations within groups -CH<sub>2</sub> in the soft segments formed from polyols [19]. There was no band in the vicinity of wave number 2270 cm<sup>-1</sup> attributable to the binding of -NCO derived from unreacted isocyanate [19]. In all of the analyzed samples there were also observed bands derived from bonds vibrations of C=O (1708 cm<sup>-1</sup>), C=C from aromatic ring (1597 cm<sup>-1</sup>) bending and deformation vibrations derived from N-H bonds within HNC=O (1538 and 1511 cm<sup>-1</sup>), H<sub>3</sub>C-C (1458 cm<sup>-1</sup>), -O-CH<sub>2</sub> (1413 cm<sup>-1</sup>) and  $\nu_{\text{asym}}$  CO/sym within the group -NCO-O (1234 and 917 cm<sup>-1</sup>) in -C-O-C- group [19]. In the range around 760 cm<sup>-1</sup> the band represents a C-H bond from the aromatic ring. Introduction of Fyrol into sample 3 K-12 F-LE A causes a distinct change in intensity and bands shift. This increases the intensity of the bands at 3511 cm<sup>-1</sup>, 1230 cm<sup>-1</sup>, 1029 cm<sup>-1</sup>, 985 cm<sup>-1</sup>, 945 cm<sup>-1</sup> and 820 cm<sup>-1</sup>. A similar change in the intensity of bands was observed after the introduction of Fyrol into other samples: 12 F-LE, 3 K-12 F-LE, 12 F and 3 K-12 F. Increasing the intensity of the band at 3511 cm<sup>-1</sup> indicates that in these foams after synthesis remains greater number of -OH groups. Increased becomes the intensity of the amide III band at 1234 cm<sup>-1</sup>. This absorbance band is assigned to the deformation vibration of the N-H bond and the deformation vibration of the N-C-O bonds, while the band at 1029 cm<sup>-1</sup> is associated with the deformation vibration of the -CN groups. These results indicate that the fillers inhibit the reaction of the -OH groups with -NCO ones and confirm the observations formulated on the basis of the analysis of the stages of the synthesis.

Exemplary DSC thermograms of the analyzed material are shown in Fig. 2, and the results of their analysis in Table 2. Basing on the DSC thermograms was defined glass transition temperature of the soft phase in the first heating cycle ( $T_{g1}$ ) and in the second heating cycle ( $T_{g2}$ ).

In some curves obtained during the first heating cycle, insofar as the changes in the hard phase there is an en-



**Fig. 2.** DSC curves: a) INCO-75 foam 1<sup>st</sup> heating cycle, b) INCO-75 foam 2<sup>nd</sup> heating cycle, c) 3 K-12 F-LE foam

dothemic peak with a minimum at temperature  $T$ , the enthalpy changes  $\Delta H$ . On the other curves in this temperature range the glass transition temperature of the hard phase ( $T_{g3}$ ) is visible.

Temperature  $T_{g1}$  of foams increases with amount of hard segments after using greater amount of -NCO [11]. However, after the introduction of Fyrol and both types of modifiers the  $T_{g1}$  is reduced, regardless of INCO matrix, indicating that in the soft phase of these foams there are fewer dispersed hard segments.  $T_{g2}$ , determined in the second heating cycle, is substantially lower than indicated in the first heating cycle. This indicates that after the second heating cycle in the soft phase there are fewer dispersed hard segments than after synthesis. These results show the ordering of the foams' hard phase occurred during the initial heating. A part of the substrates for the production of foams are characterized by a functionality of over 2; it brings along the occurrence in the foams' macromolecules of rigid segments both of linear or branched forms. This type of hard segments' structure means that after the synthesis process much of their part is dispersed in the soft phase, and the process of annealing of the foams results in a further separation process of the hard phase.

Temperature of the endothermic peak in the DSC thermograms of foams INCO-75 and INCO-80 does not

change, and the enthalpy of the transition is increased. The increase in enthalpy changes may be the result of increasing the amount of hydrogen bonds linking the rigid segments, when their number increases in foams [14, 20, 21].

For the foam modified with Fyrol the temperature of the endothermic change shifts toward higher temperatures and the enthalpy of the transition decreases. On the basis of this observation it can be assumed that after the use of Fyrol the structure of rigid segments is changed. This is confirmed by the results shown in the works of Martin *et al.* [21, 22]. Those works found that increasing length of the rigid segment causes an increase in the temperature of this transformation.

Conversion order-disorder in the hard phase of polyurethanes is linked to dissociation of the hydrogen bonds in this phase [23]. In the analyzed foams with a change in length of the rigid segment, as evidenced by the higher temperature of the transition, decreases the number of hydrogen bonds connecting them. This is probably a cause of the reduction of enthalpy conversion order-disorder in the foams [21, 22].

On DSC curves of foams with isocyanate index of 75 and 80 with the addition of a mixture of keratin fibers and Fyrol we can observe the occurrence of the second conversion associated with glass transition of the

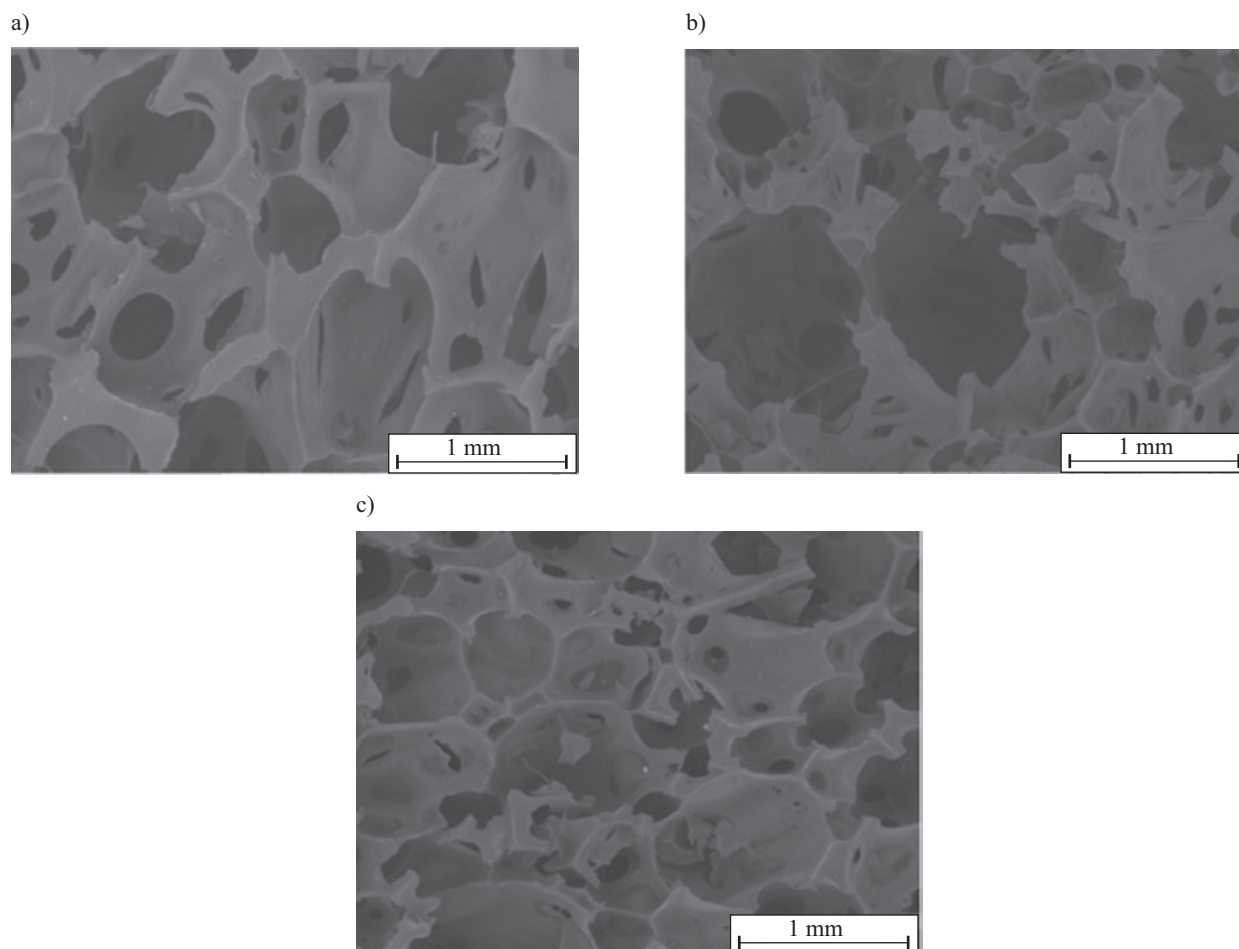


Fig. 3. Examples of SEM image of foams a) INCO-75, b) 3 K, c) 3 K-12 F-LE

hard phase in the range of 121–142 °C. For the foams INCO-85 with and without the addition of modifiers  $T_{s3}$  is significantly lower at 56–94 °C. Based on the results of the DSC analysis it can be concluded that when the foam formation reaction takes longer then in the foams more branched rigid segments are formed instead of linear ones. The basis for such an assumption is the results of the Jin *et al.* [24, 25]. The glass transition temperature of the hard phase of foam is higher the fewer rigid segments there are in macromolecules of the foams. It may happen that in the foams there are formed longer and/or more branched hard segments, or mixtures thereof. The bases for such an assumption are the results of the work of Martin *et al.* [21, 22]. After the second glass transition at approx. 180 °C the process of degradation of foam macromolecules starts.

Apparent density of foams and modified foams ranges from 40 to 48 kg/m<sup>3</sup> (Table 2). The introduction of modifiers results in a slight increase in apparent density. The introduction of modifiers causes changes in the structure of the foam, as exemplarily was shown in Fig. 3.

SEM images of the foams suggest that the use of modifiers causes significant changes in the structure of the macropores, their sizes are reduced and a larger number of interruptions in the pore walls appears.

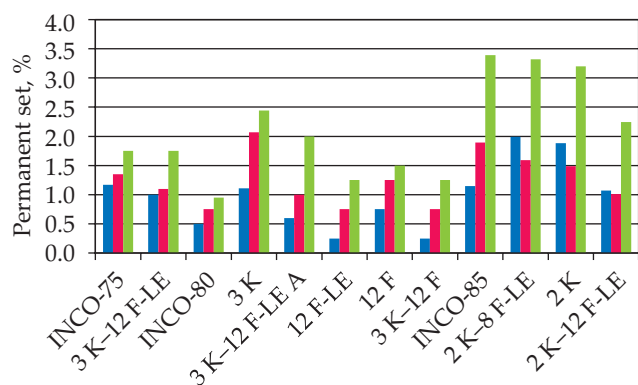


Fig. 4. The results of measurements of permanent deformation after the compression of foams; compressed by 50 % (blue), 75 % (red), 90 % (green)

In the case of foams containing both types of modifiers permanent deformations are much lower than for unmodified foams and lower than for foams or keratin fibers or Fyrol (Fig. 4). Smaller distortions in foams with the addition of both types of modifiers are the result of changes in the structure of the hard phase. Another factor which can influence the reduction of permanent deformations in foams with the addition of the two types of modifiers may be a smaller amount of pores in the foams, as evidenced by their higher apparent density (Table 2).

Example curves obtained during the TGA analysis are shown in Fig. 5. The results of analysis of the obtained curves of changes in mass in function of temperature (TG) and weight change derivative (DTG) are summarized in

Table 3. From the curve of TG there were determined the loss of 2 wt % temperature ( $T_{2\%}$ ), loss of 5 wt % temperature ( $T_{5\%}$ ), and the residue after degradation at 700 °C ( $U_{700}$ ). From the DTG curve there were determined temperatures of maximum rate of degradation of the three phases observed in these curves ( $T1$ ,  $T2$ ,  $T3$ ) and the maximum rate of degradation of these steps ( $V1$ ,  $V2$ ,  $V3$ ). It may be concluded basing on the analysis of Fig. 5 that the first and second stages of degradation connected with degradation of the hard phase of foams begin at much lower temperatures for the foam containing a mixture of modifiers, as compared to the unmodified foam. The use of modifiers can alter the degradation rate of individual steps in the process of thermal decomposition.

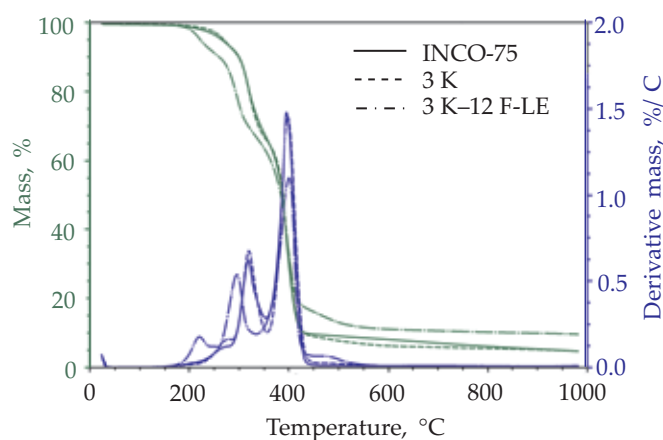


Fig. 5. List of TGA foams with isocyanate index 75

$T_{2\%}$  and  $T_{5\%}$  significantly decrease after the introduction of each of the modifiers, and mixtures thereof.  $T_{5\%}$  considered as the origin of the degradation of the foams with Fyrols and modifiers mixture is reduced by about 40 °C, and the use of keratin fibers results in a reduction of the temperature by several degrees compared to the unmodified foams. Similar changes are observed in  $T1$ . Such a large reduction in the decomposition temperature may be the result of changes in the structure of hard segments in these foams. Polymers of linear macromolecules have higher heat resistance than polymers of branched chain [26, 27]. It can therefore be assumed that VPF of a lower temperature of the first stage of degradation (3 K–12 F-LE, 12 F-LE, 3 K–12 F-LE A, 12 F, 3 K–12 F, 2 K–8 F-LE, 2 K–12 F-LE) have macromolecules containing more branched hard segments.  $V1$  of foams with keratin fibers increases, regardless of the isocyanate index of the matrix. In contrast, in the foams with Fyrol and modifiers mixture  $V1$  is in ranges between 0.16 and 0.18 %/°C for all the foams regardless of the type of matrix. These changes indicate that in the first stage of degradation of these foams takes place a degradation of branched hard segments.

For the second stage of degradation the introduction of keratin does not change the  $T2$ , the introduction of Fyrol and modifiers mixture reduces  $T2$  by 15–20 °C, but only in foams with isocyanate index of 75 and 80.  $T3$  differs slightly.  $V1$ , after the introduction of keratin fibers,

**Table 3.** Results of TGA analysis of produced foams

Sample	$T_{2\%}$ °C	$T_{5\%}$ °C	$T_1$ °C	$V_1$ %/°C	$T_2$ °C	$V_2$ %/°C	$T_3$ °C	$V_3$ %/°C	$U_{700}$ %	$OI$ %
INCO-75	222	265	270	0.12	318	0.62	397	1.47	7.1	18.0
3 K	218	269	274	0.16	320	0.67	400	1.45	5.9	19.1
3 K-12 F-LE	201	222	220	0.18	296	0.54	400	1.10	10.6	23.3
INCO-80	236	267	274	0.17	310	0.70	393	1.45	6.4	18.4
12 F-LE	203	223	221	0.18	295	0.55	399	1.07	10.2	22.8
3 K-12 F-LE A	200	222	220	0.18	298	0.51	399	1.45	11.0	23.0
12 F	193	218	218	0.17	300	0.57	402	1.10	9.6	23.0
3 K-12 F	191	218	218	0.16	304	0.50	400	1.89	11.0	23.1
INCO-85	249	269	279	0.23	316	0.76	390	1.44	5.9	–
2 K	243	264	274	0.27	316	0.56	393	1.52	6.2	–
2 K-8 F-LE	205	235	222	0.17	306	0.54	397	1.22	10.9	–
2 K-12 F-LE	197	221	220	0.16	299	0.52	392	1.22	11.4	–

is increased regardless of the isocyanate index of the matrix. But for foams with Fyrol and a mixture of modifiers  $V_2$  is approx. 0.51–0.56 %/°C. These trends indicate that in this step a degradation of segments with similar chemical structure takes place. A significant decrease in the rate of degradation suggests that in the material the amount of hard segments having a higher heat resistance is increased. These are most probably rigid segments of linear structure.

The use of Fyrol and modifiers mixtures reduces the decomposition rate of the soft phase (step 3 of the degradation process). Probably the process of formation of branched rigid segments in the macromolecules of the foams favors, such an arrangement of soft segments, which limits the ability of these segments to degrade.

Analysis of resistance to flame action in a cone calorimeter allowed to establish that the use of keratin fibers reduces the maximum heat rate release ( $HRR_{max}$ ) only by approx. 10 % (Fig. 6a) and the use of Fyrol and mixtures of Fyrol and keratin fibers reduces it significantly, by approx. 84 % (Fig. 6b).

Time to ignition is adversely reduced both after application of keratin fibers and Fyrol and mixtures thereof.

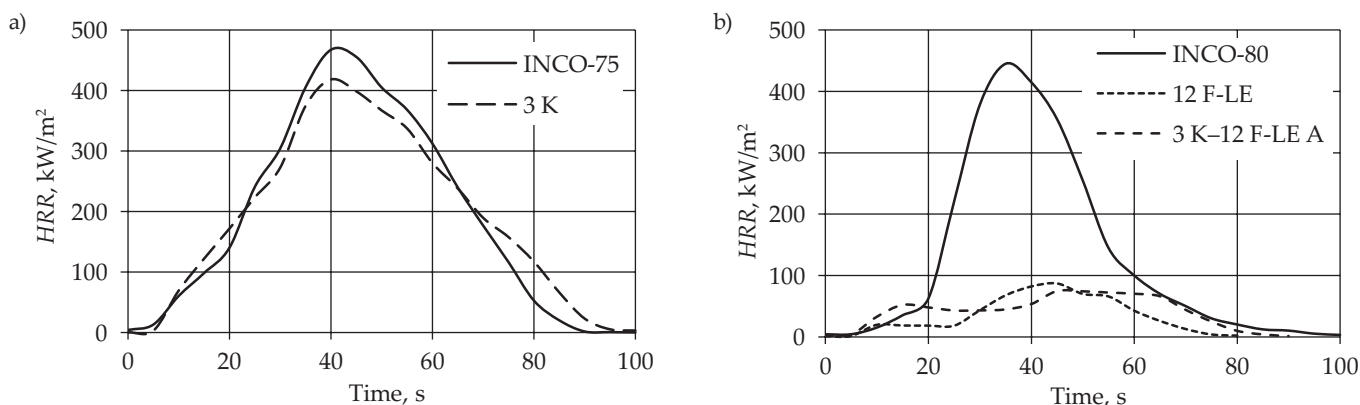
For example, in the foam of isocyanate index of 80 the time to ignition is 12 s, after the application of Fyrol – 3 s and using a mixture of keratin fibers and Fyrol it is 4 s. In VPFs with modifiers, significant amount of hard segments is distributed during the soft phase. Distributed hard segments degrade easier, which can cause reduction of time to ignition.

According to equation (1), basing on the results of the analysis in a cone calorimeter, the risk of fire caused by using some of the materials tested was calculated [26]:

$$ZP = \frac{HRR_{max}}{TTI} \quad (1)$$

where:  $ZP$  – fire hazard,  $HRR_{max}$  – maximum heat rate release,  $TTI$  – time to ignition.

For the foam of isocyanate index 80  $ZP = 38$ , for the 12 F-LE foam  $ZP = 29$  and for the 3 K-12 F-LE foam  $ZP = 18$ , so that the use of keratin fibers significantly reduces the risk of fire. The changes of oxygen index ( $OI$ ) resulting from the use of both types of modifiers (Table 3) were also rated. Application of Fyrol and mixtures thereof with keratin raises  $OI$  of foams to the level of hard burning materials.



**Fig. 6.** Results of analysis of foams using a cone calorimeter: a) INCO-75 with and without the addition of keratin fibers 3 K, b) INCO-80 supplemented with Fyrol 12 F-LE, and a mixture of additives 3 K-12 LE A

## CONCLUSIONS

Raw materials for the production of viscoelastic foams favor the formation of macromolecules of different structure of the soft and rigid phase. Unmodified foams having a various isocyanate index form macromolecules of linear and branched segments forming their soft phase and linear and branched their rigid segments, which build their hard phase. In this group of analyzed foams a considerable amount of hard segments is dispersed in the soft phase. Such a structure of the foams is indicated by the presence of glass transition temperature of the soft phase in the range of 11.9–32.1 °C. The range of this temperature in the tested foams is typical of viscoelastic foams.

Some of the tested rigid segments form the hard phase, wherein the rigid segments are connected by hydrogen bonds. The more rigid segments in macromolecules of foams (with the greater of isocyanate index) the more hydrogen bonds are contained in their hard phase. This is indicated by a greater endothermic enthalpy of conversion with a minimum at approx. 100 °C. Similar in structure are foams with isocyanate index of 75 and 80, containing keratin fibers or Fyrol. Minimum temperature of endothermic conversion in hard phase of this group of foams is higher than that of unmodified foams, which may result from an increase in length of their rigid segments.

The construction of foams' macromolecules modified with a mixture of Fyrol and keratin fibers is different from those discussed earlier. In these foams a considerably smaller amount of hard segments is dispersed in the soft phase, which is the result of created more branched hard segments. Such a structure of macromolecules is the reason for changing thermal characteristics of these foams. They are characterized by the glass transition temperature of the soft phase lower by several degrees than that of unmodified foam. Furthermore the elements of structure formed from hard segments constitute the hard phase with a glass transition temperature varying with the number of rigid segments in foams. The fewer rigid segments in the foams' matrix the higher glass transition temperature of the hard phase of foams with a mixture of modifiers.

The results of the thermogravimetric analysis of foams confirm the description of the structure of tested materials proposed on the basis of DSC analysis.

From the standpoint of foam application permanent set of foam after compression is extremely important. Among those materials, the best properties of each group of foams are characterized by foams containing both types of modifiers. Increasing the amount of branched hard segments in the hard phase of foam favors the reducing of permanent deformation of foams after compression.

Another factor determining the suitability of the foams for many applications is their flame resistance. Foams with Fyrol and a mixture of modifiers are characterized by much higher resistance to flame than the unmodified foams. The use of keratin fibers, in Fyrol mix brings about

a lesser risk of fire as compared to the foams modified with Fyrol alone.

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