Express Polymer Letters Vol.18, No.10 (2024) 964–975
Available online at www.expresspolymlett.com
https://doi.org/10.3144/expresspolymlett.2024.74

Research article

Comparative analysis of thermal degradation effects on traditional and low-emission flexible polyurethane foams

Enikő Hornyák-Mester[1,2], *Miklós Varga*[1], *Lilla Márta Sőrés-Tölli*[1], *Dóra Mentes*[1], *Alpár F. Hatvani-Nagy*[1], *Peter Werner Groh*[2], *Béla Viskolcz*[1,3], *Gábor Muránszky*[3], *Béla Fiser*[1,3,4]*

[1]Higher Education and Industrial Cooperation Centre, University of Miskolc, 3515 Miskolc-Egyetemváros, Hungary
[2]Magyar Olaj- és Gázipari Nyrt. 1117 Budapest, Dombóvári út 28.
[3]Institute of Chemistry, University of Miskolc, 3515 Miskolc-Egyetemváros, Hungary
[4]Department of Physical Chemistry, Faculty of Chemistry, University of Lodz, 90-236 Lodz, Poland

Received 9 May 2024; accepted in revised form 26 June 2024

Abstract. The degradation of different flexible polyurethane foams for molded application after thermal aging were compared. A reference sample using traditional higher emission additives and four samples of different composition using low-emission additives were compared. For the modified samples volatile organic compound (VOC) and semi-volatile organic compound (FOG/SVOC) contents fell well below the benchmarking limits, which indicates that the selected low-emission additives are incorporated into the polymer chain. To examine different material properties and for evaluating changes due to increased temperature exposure for a prolonged period of time mechanical and acoustic tests were carried out before and after dry heat aging. It was found that two low emission samples exhibited superior sound absorption compared to the reference sample along with less significant change after aging in the acoustic properties. The compressive strength was lower than the reference as a result of lower product densities. However, the change in compressive strength after aging was less than 15% (with one exception), which is acceptable according to the standard requirements. Thermogravimetric analysis was also performed and revealed that no significant difference can be observed between the examined samples due to heat degradation, indicating that the modifications made to reduce VOC content did not adversely affect the foam's resistance to thermal degradation.

Keywords: *additive, circular economy, degradation promoter, mechanical properties, polyurethane foam, thermal aging, thermogravimetric analysis*

1. Introduction

Polyurethane foams (PUF), known for their versatile properties, have become fundamental materials across numerous industries [1]. However, the environmental impact associated with the emission of volatile organic compounds (VOCs) has urged a revaluation of traditional foam formulations [2, 3]. As the demand for eco-friendly materials continues to increase, the development of low-emission polyurethane foams has appeared as a crucial area of industrial research [4–6].

Achieving a complete reduction in VOC emissions requires the integration of low VOC additives such as catalysts and surfactants into polyurethane foam formulations [7, 8]. Harmonious interactions between these additives can enhance the efficiency of the foaming reaction, resulting in reduced emissions during the curing process [9]. The development of integrated systems addressing both catalysts and surfactants is a critical step toward comprehensive volatile reduction in polyurethane foams [7].

---

*Corresponding author, e-mail: bela.fiser@uni-miskolc.hu

The environmental obligation to reduce VOC emissions has driven investigations into catalysts that can assist the polyurethane foam formation process while minimizing the release of harmful compounds [8, 10–13]. Low VOC catalysts, such as tertiary amine alternatives, have shown potential in promoting the so-called gelling reaction (the reaction between isocyanates and polyols) and in some cases the foaming reaction (the reaction between isocyanate and water) with reduced emissions, contributing to a greener and more sustainable polyurethane foam production [11, 14, 15]. Two promising techniques that have surfaced in recent research are immobilization via functionalization and molecule augmentation [16].

Surfactants play a fundamental role in polyurethane foam formulation, influencing cell structure, foam stability, and mechanical properties [7]. However, traditional surfactants often contribute to volatile emissions [17, 18]. Recent innovations in surfactant development involve the design of low VOC alternatives that maintain efficient foam stabilization [4, 19].

The adoption of non-emissive additives brings several advantages to the production of low-emission polyurethane foams. By molecular modifications, the risk of VOC emissions is significantly reduced, aligning with the broader goal of sustainable and environmentally responsible foam manufacturing. However, challenges exist, particularly in ensuring that these modified catalysts maintain their catalytic efficiency and do not compromise the overall foam performance.

Understanding how thermal degradation affects these materials helps in predicting their lifespan and maintaining their performance standards. Many applications of polyurethane foams, such as components in automotive interiors, require adherence to safety standards that include emission control. Studying thermal degradation is crucial to ensuring that these materials comply with safety regulations throughout their service life [1]. Insights gained from thermal degradation studies allow for the optimization of foam formulations. By understanding the mechanisms and effects of thermal degradation, the chemical composition and manufacturing processes can be modified to enhance the thermal stability of foams [20]. With advancements in materials science, new additives and fabrication techniques have emerged. Investigating thermal degradation helps in evaluating the efficacy of these innovations and their ability to improve the thermal resilience of polyurethane foams [21]. Tcharkhtchi *et al.* [22] investigated the mechanical (tensile) properties of polyurethanes after thermal aging at various temperatures (85 and 120 °C) significantly affects its mechanical properties especially elastic modulus and stress at break, reflecting the complex interplay of cross-linking in degradation processes. Pellizzi *et al.* [23] investigated the effect of natural aging of polyurethanes with different methods, including compression force deflection test. The study identified the ester/hydroxyl band ratio as a reliable indicator of polyurethane foam degradation, correlating chemical changes observed via ATR-FTIR with mechanical property loss, such as decreased elasticity. Yang *et al.* [24] assessed the effect of thermal aging on acoustic properties of polyurethane foams. The article found that thermal aging significantly reduces the acoustic performance of partially reticulated polyurethane foam, primarily due to decreased static airflow resistivity and heat-induced membrane damage.

The thermal processes of various polymer products are also often investigated by thermogravimetric analysis. Jiao *et al.* [25] investigated the thermal degradation characteristics of volatile products of rigid polyurethane foams using TG-FTIR-MS. Rigid polyurethane foam undergoes a three-stage thermal degradation in air and a two-stage process in nitrogen, with degradation significantly accelerated in air due to oxygen, starting from 200 °C with urethane bonds breaking into isocyanates and polyols, and producing primary amines, secondary amines, vinyl ethers, and carbon dioxide at higher temperatures. Chen *et al.* [26] characterized the volatile compounds of flame-retardant polyurethane foams using TG-FTIR. The article found that tricresyl phosphate (TCP) effectively enhances the flame retardancy of polyurethane foam composites by promoting char formation and reducing toxic gases containing NCO groups, while increasing the emission of nonflammable carbon dioxide during thermal degradation.

However, there are relatively few studies available in the literature regarding the connection between VOC content and degradation due to aging although manufacturers inform that quality degradation may occur in some aging varieties with the use of low-emission additives. Thermal stability plays a critical role in the performance and longevity of polyurethane foams in many applications. Polyurethane foams are widely used in various industries, including construction, automotive, and furniture, where they are often exposed to varying temperatures. Understanding thermal degradation is essential for developing foams that maintain their structural integrity and functional properties under thermal stress. This study aims to address these concerns by evaluating the thermal stability of low-VOC polyurethane foams with varying formulations, focusing on how thermal aging impacts their mechanical and acoustic properties. By doing so, it seeks to enhance the overall performance and environmental safety of polyurethane foams, ensuring they meet the rigorous demands of their intended applications while minimizing VOC emissions.

2. Materials and methods

2.1. Materials and sample preparation

Flexible molded polyurethane foam samples were produced using an MDI (methylene diphenyl diisocyanate) isomer mixture (Ongronat TR 4040, Wanhua-BorsodChem, Kazincbarcika, Hungary; average NCO: 32.6 m/m%) and a polyether-type polyol (Wanol F3160, Wanhua, Yan Tai Shi, China). The base polyol was pre-formulated before the addition of the isocyanate, using water as blowing agent, cell opening polyol (Alcupol F3231, Repsol, Madrid, Spain), different traditional catalysts (DABCO 33-LV by Evonik, Essen, Germany; Jeffcat ZF 22 by Huntsman, Texas, USA; Tegoamin DEOA 85 by Evonik, Essen, Germany) and a traditional surfactant (Tegostab B4113, Evonik, Essen, Germany). In order to achieve a low volatile organic matter content, recipe modifications were made in several steps on the basis of the previously determined factors causing emissions [27]. Thus, a total of four low-emission polyol mixtures with different formulations (LE1–LE4; Table 1) were prepared, which were then tested in each case by reacting with the same type of Ongronat TR 4040 isocyanate similarly to the reference sample.

To obtain low-emission PU samples, two gel catalysts (DABCO NE 1090 and DABCO NE 1550 by Evonik, Essen, Germany), two blow reaction catalysts (Jeffcat ZF 10 by Huntsman, Texas, USA; and DABCO NE 300 by Evonik, Essen, Germany) and two surfactants (Tegostab B8734 LF2 and Tegostab B8715 LF2 by Evonik, Essen, Germany) were selected from the low-VOC portfolio of PU additive manufacturers, and were formulated to yield flexible moulded PU foam (for details, see Table 1). The dosage of the additives was determined according to recommendations from manufacturers, and was fitted to the reference formulation, in terms of reactivity and foam density. The OH numbers of these polyol formulations were calculated.

The samples were produced using the FOAMAT 285 Foam Qualification System (Format Messtechnik GmbH, Karlsruhe, Germany). The schematic simplified diagram of the manufacturing method is shown in Figure 1. The system determines the most important parameters of the foaming reaction, such as start

Table 1. The formulas of the reference polyol sample (Ref) and the prepared low-emission polyol samples (LE1–LE4) are given in php (per 100 parts of polyol) and their calculated OH numbers.

Materials	Function	Ref [php]	LE1 [php]	LE2 [php]	LE3 [php]	LE4 [php]
Wanol F3160	base polyol	100.00	100.00	100.00	100.00	100.00
Water	foaming agent	4.00	4.00	4.00	4.00	4.00
Tegoamin DEOA 85	crosslinking catalyst	0.50	0.50	0.50	0.50	0.50
Tegostab B4113	surfactant	0.50				
Tegostab B8734 LF2	surfactant (low emission)		0.80	0.80		
Tegostab B8715 LF2					0.80	0.80
DABCO 33-LV	amine gel catalyst (TEDA)	0.15				
DABCO NE 1090	amine gel catalyst (low emission)		0.50		0.50	
DABCO NE 1550				0.50		0.50
Jeffcat ZF 22	amine blow catalyst (BDMAEE)	0.10				
Jeffcat ZF 10	amine blow catalyst (low emission)		0.10	0.10		
DABCO NE 300					0.10	0.10
Alcupol F3231	cell opening polyol (polyether triol, 5000 g/mol)	1.00	1.00	1.00	1.00	1.00
Total OH-number		**271.09**	**268.66**	**269.56**	**268.64**	**269.54**

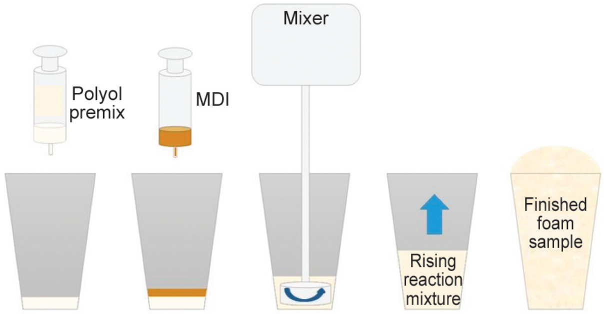

Figure 1. Simplified sample preparation method of flexible polyurethane foam samples using the FOAMAT 285 foam qualification system.

time, rise time, density, shrinkage *etc*., and it is also possible to determine and compare the kinetics of the foam rise profiles. The samples have been prepared in 1 l paper cups and calculated to yield total foam weight of 60 g in each case, which provides an ideal foam rise in the case of the reference recipe given above. The mixing time was 8 seconds, and the test time was 240 s in each case. During the sample preparations, an NCO-index of 1.0 (100) was used for each sample.

The foaming process in this case is equivalent to an open mold process. The choice of foaming conditions significantly influences the foam's microstructure, which in turn impacts its overall properties and performance. Open mold foaming tends to result in a less controlled expansion of the foam, leading to a more heterogeneous cell structure compared to foams produced under constrained conditions. This variability in cell structure can affect material properties and thermal stability.

2.2. Determination of VOC and SVOC content

The volatile organic compound (VOC) and semi-volatile organic compound (SVOC) content was determined according to the VDA 278 standard with some minor changes. VDA 278 is an internationally accepted, standardized test procedure for non-metallic materials, primarily used in the automotive industry to evaluate VOC and FOG content. The measurements were made at least one week but no more than 10 days after production with a gas chromatography measuring system (GCMS-QP2020, Shimadzu Corp., Kyoto, Japan) equipped with a mass selective detector with a cryofocusing unit. During the VOC content analysis, the sample is heated to 90 °C and kept there for 30 min. The VOC value is calculated in toluene equivalents and determines substances in the boiling point/elution range of *n*-pentacosane (C25). To determine the 'fogging' (FOG or SVOC *i.e.* semi-volatile organic compound) value, the sample is kept in the desorption tube after the VOC analysis and heated to 120 °C and kept there for 60 min. The fogging value is the sum of the semi-volatile substances calculated in hexadecane equivalent that elute from the retention time of *n*-tetradecane (C14) to the retention time of n-dotriacontane (C32). Further details about the measurement method can be found in the standard description and in our previous articles [27].

2.3. Acoustic measurements

To investigate the acoustic damping properties of the prepared flexible polyurethane foams in the higher frequency range, the normal incident sound absorption coefficients (α) were determined using the impedance tube technique. For the measurements, the AED 1000 - AcoustiTube® (Akustikforschung Dresden GmbH, Dresden, Germany) impedance tube was used, according to the transmission function method described in EN ISO 10534-2 and ASTM E1050. In this study, tubes with an internal diameter of 30 mm have been used for the measurements, in which case the useful frequency range is 150–6600 Hz, respectively. Three microphones were used, thus, the measurements for the lower and upper frequency range could be performed in a single measurement. The acoustic measurement was carried out before and after aging to determine the effect of long-term sound insulation use of the samples. The method is further discussed in a previous study [28].

2.4. Mechanical testing

Compression force deflection (CFD) was measured using a universal material testing machine (Zwick-Roell Z010, Zwick GmbH, Ulm, Germany) according to Test C of ASTM D3574 (complex test standard for flexible polyurethanes) with changes in the suggested sample geometry and sample number. For the tests, cylinders with a diameter of 30 mm and a height of 35-40 mm were cut. Two samples were measured in each case, and the average values are demonstrated. The test samples are compressed to 50% of their original height, applying a compressive load on their entire surface, and then held there for 1 minute, while measuring the change in force. The measurements were performed both before and after dry aging, thus examining the effect of long-term use of the material. The extent of the change is determined by the evaluation of the compression depth-force curves (decrease in force). If the degree of change is too large (higher than 15%), the material can no longer be used for compressive stress (Equation (1)):

$$\Delta F_{50\%} = \frac{\Delta F_{50\%,0} - \Delta F_{50\%,1}}{\Delta F_{50\%,0}} \tag{1}$$

where $\Delta F_{50\%}$ – force reduction after dry heat aging at 50% compression, $F_{50\%,0}$ – force measured at 50% compression, $F_{50\%,1}$ – force measured at 50% compression after dry heat ageing (Equation (2)):

$$\Delta h = \frac{h_0 - h_1}{h_0} \cdot 100 \tag{2}$$

where Δh – decrease in height of the sample after dry heat aging, h_0 – height of the original sample, h_1 – height of the sample after dry heat aging.

2.5. Dry heat aging

A standard aging test was performed to assess the impact of prolonged use of the foams. ASTM D3574 Aging Test K, a dry heat aging technique, was followed. The samples were aged for 23 h at 140 °C in a laboratory drying oven (POL-EKO Aquaterra SLW240, Wodzislaw Slaski, Poland). Following the aging process a minimum of two hours of conditioning under the specified parameters (23±2 °C and 50±5% relative humidity), the mechanical and acoustic measurements were retaken, and the resulting changes were evaluated.

2.6. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on the reference sample and the samples with low emission additives, which were conducted at the Bay Zoltán Research Institute using a thermal analyzer (SETSYS 16/18, Setaram, Texas, USA). Thermogravimetric analysis (TGA) is a thermal test method, during which the change in mass of the tested sample is measured as a function of temperature. The components of the tested sample evaporate or decompose at different temperatures. These cause several mass-loss steps in the mass-change-temperature curve that allow us to quantify the components. The TG curve very sensitively indicates any mass changes that occur as a result of heating. The DTG curve is the differential curve of this, it emphasizes the partial processes of mass changes and their exact location even more and makes them visible. TGA is very useful when characterizing polymers containing additives at different concentrations to determine the amount of mass loss based on the different relative volatilities of the individual components. The thermal stability of the sample can be determined based on the kinetic analysis of the decomposition profile. The test was carried out in the temperature range of room temperature to 700 °C. The heating rate was 10 °C/min. The measurements were carried out in an inert atmosphere (argon gas).

3. Results and discussion

3.1. Foaming parameters and density

The results obtained from the FOAMAT 285 foam qualification system for flexible polyurethane foams, including both the reference sample (Ref) and the low-emission formulations (LE1–LE4), reveal interesting insights into the foaming characteristics of each formulation (Table 2).

The start time, which indicates the onset of the foaming process after the mixing of foam components, varies slightly across the samples. The reference sample (Ref) initiates foaming after 12.0 s, while that of low emission formulations split into two groups, indicating significantly slower start when DABCO NE1090 catalyst is present.

In terms of rise time, which measures the duration for the foam to reach its maximum expansion height, there are notable differences between the reference sample and the low VOC formulations. The reference sample (Ref) demonstrates a rise time of 136.0 s, while the low-emission formulations (LE1–LE4) display varying rise times ranging from 95.7 to 120.8 s. Interestingly, some low-emission formulations, such as LE2 and LE3, show shorter rise times compared to the reference sample, indicating faster expansion rates, most likely due to the presence of DABCO NE 1550.

Furthermore, the shrinkage ratio, representing the percentage decrease in foam volume after expansion and curing, offers insights into the dimensional

Table 2. Foam formation parameters of flexible polyurethane foam (reference sample (Ref) and the prepared low-emission samples (LE1–LE4)) determined with FOAMAT 285.

		Ref	LE1	LE2	LE3	LE4
Start time	[s]	12.0	17.8	12.6	17.4	13.5
Rise time	[s]	136.0	120.8	95.7	118.7	95.7
Shrinkage ratio	[%]	5.2	3.3	3.3	2.7	2.6

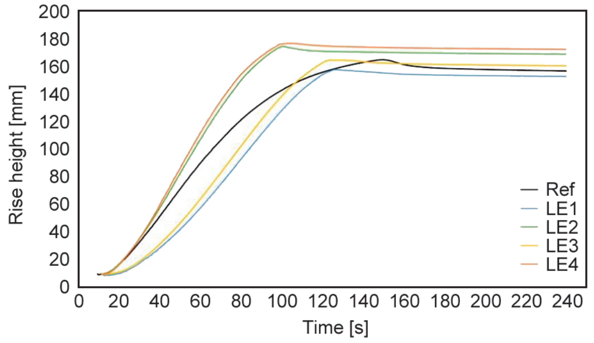

Figure 2. Foam rise profiles of flexible polyurethane foam (reference sample (Ref) and the prepared low-emission samples (LE1–LE4)) obtained with FOAMAT 285.

stability of the foams. The reference sample (Ref) exhibits a shrinkage ratio of 5.2%, indicating a reduction in volume during the foaming process. In contrast, most low VOC formulations (LE1–LE4) demonstrate lower shrinkage ratios, ranging from 2.6 to 4.7%. More moderate shrinkage was obtained where DABCO NE 300 catalyst and Tegostab B8715 LF2 silicone was applied. This suggests reduced volume loss and improved dimensional stability in these formulations. The overall foam rise profiles of the samples are presented in Figure 2.

The evaluation of these results highlights the differences in foaming characteristics between the reference sample and the low VOC formulations, and thus, the need of fine tuning of formulations when the additives are varied.

The overall product density of the flexible PU foam samples was also assessed for three prepared samples pro recipe at different times (Table 3).

The reference sample displayed consistent density values, providing a benchmark for comparison. In this experiment series, LE1 formulation demonstrated the closest average density to the reference sample. The density of foams made with low emission formulations (LE1–LE4) fell into two groups, indicating significantly lower density for LE2 and LE4, in which DABCO NE 1550 gel catalyst is applied. This finding coincides with the faster rise of said foams (see Figure 1), indicating that at these predetermined additive levels, DABCO NE 1550 performed the best in achieving the given density with the least amount of blowing agent demand. At the same time, LE4 formulation also performed well in foam shrinkage. From these results it has to be noted that in the future, further adjustments in formulation are recommended to achieve similar densities to the reference foam with the adjustment of the amount of blowing agent (water) and blow catalyst, but for the sake of equivalence. However, in this study the same amount of water content as well as blow catalyst was used in order to examine formulations with a similar composition as much as possible.

Table 3. Product densities of flexible polyurethane foam (reference sample (Ref) and the developed low-emission samples (LE1–LE4)) obtained with FOAMAT 285.

Sample ID		Ref	LE1	LE2	LE3	LE4
Test 1	[g/l]	50.3	47.8	43.0	46.5	43.6
Test 2	[g/l]	49.7	48.5	44.6	47.0	45.2
Test 3	[g/l]	48.9	51.1	44.9	48.1	43.7
Average density	**[g/l]**	**49.6**	**49.1**	**44.2**	**47.2**	**44.2**
Standard deviation	[g/l]	*0.70*	*1.74*	*1.02*	*0.82*	*0.90*

3.2. Volatile organic compounds

The developed samples (LE1–LE4) were tested for volatile organic matter (VOC) and semi-volatile organic matter (SVOC or FOG, referring to the term ‘fogging’) content according to the previously applied VDA 278 based protocol. The measurements were carried out one week after the date of production, and then compared to the reference sample (Ref) with previous measurement results obtained. During the tests, in accordance with the requirements of the standard, the VOC value was measured twice, of which the higher value must be taken into account, and the FOG value must be measured once.

Before the measurement series, calibration was performed to determine the response factors of the reference materials (toluene: $R_{\text{f, toluene}} = 0.1878$ and hexadecane: $R_{\text{f, hexadecane}} = 0.1054$). In addition, before each series of measurements, blank tests were carried out in each case, and the results of which was subtracted from the measurement results during the evaluation. In the case of foam-type samples, the standard recommends a sample weight of 15±2 mg, which was followed in all cases. The comparison of the total VOC and FOG emission values thus obtained for the defined reference sample (Ref) and the developed low-emission samples (LE1–LE4) is contained in Table 4.

As can be seen, in the case of VOC content, there is a significant decrease in all cases compared to the reference sample. In the case of VOC, based on the literature, a value below 100 µg/g corresponds to industrial expectations, which, based on the measurements, three of the low emission samples meet with

Table 4. Comparison of volatile organic compound (VOC) and semi-volatile organic compound (SVOC/FOG) content based on total emissions for the reference sample (Ref) and prepared low-emission samples (LE1–LE4).

Sample ID	Total emissions	
	VOC [µg/g]	FOG [µg/g]
Ref	433.5	369.0
LE1	93.4	245.3
LE2	90.3	229.6
LE3	123.6	114.9
LE4	44.8	121.7

the exception of LE3. In all cases of the FOG measurements, significantly lower total values were obtained than for the reference sample. Based on the literature, the industrial requirement for the total FOG value is below 250 µg/g, which all the developed foam samples (LE1–LE4) met. However, several factors contribute to measurement uncertainty, including instrumental limitations, sample handling procedures, measurement background and operator proficiency, for this reason, an error factor should be anticipated in the obtained values. The best overall performance was achieved with formulation LE4. It is also important to note that the replaced additives were selected based on the components identified in the VOC content of the reference sample, thus a greater reduction in the VOC content was expected, which corresponds to the results obtained.

The evaluation of identified compounds in the VOC results reveals decreasing concentrations across samples compared to the reference (Table 5).

The presence of triethylenediamine in the identified compounds completely disappeared in samples LE1–LE4 compared to the reference sample, indicating successful elimination of this compound in the low emission formulations. All low-emission samples show no detectable levels of bis(2-(dimethylamino) ethyl) ether, suggesting effective elimination of this compound. The different siloxane type compounds exhibit varying concentrations across the samples, with all low-emission samples showing significantly lower levels compared to the reference sample. Nitrobenzene shows no detectable levels in all samples except for a small concentration in sample LE4. Benzyl alcohol exhibits varying concentrations across samples, with two low-emission samples, LE1 and LE3 showing higher levels compared to the reference sample. However, the last two mentioned components do not come from additives, so their detected level does not depend on the modifications made.

3.3. Sound absorption coefficient measurements

Both before and after dry aging, the reference sample and low-emission counterparts behaved as usually the porous sound-absorbing materials can be expected. The sound absorption coefficient (α) increases steadily and then reach a maximum where it fluctuates, but its value remains around 0.8 in most cases, which means that their sound absorption is extremely good in the given frequency range (Figure 3). None of the samples achieved 100% sound absorption (α = 1) during the current measurement series, however, the obtained values can still be said to be adequate sound absorption. The samples before and after aging behaved similarly, in most cases there is only a small change due to aging, which is extremely positive. In the case of most samples, there is a local maximum around 1700 Hz, after which the value of the absorption coefficient decreases to an average of 0.7, and at higher frequencies increases back to ~0.9. If we compare the change in the sound absorption coefficient (α) for the reference material and the low-emission samples, it can be seen that in the case

Table 5. Compounds identified with NIST library and present in large quantities in the VOC content of the reference sample (Ref) and their quantity in the prepared low-emission samples (LE1–LE4).

Identified compound	Ref [µg/g]	LE1 [µg/g]	LE2 [µg/g]	LE3 [µg/g]	LE4 [µg/g]
Triethylenediamine	39.64	0.00	0.00	0.00	0.00
Bis(2-(dimethylamino)ethyl) ether	30.52	0.00	0.00	0.00	0.00
Cyclotrisiloxane, hexamethyl-	53.12	3.31	12.01	0.50	0.14
Cyclotetrasiloxane, octamethyl-	26.64	0.99	3.62	0.26	0.00
Cyclopentasiloxane, decamethyl-	9.50	0.57	2.36	0.97	0.31
Heptasiloxane, hexadecamethyl-	5.01	1.04	1.00	3.08	0.43
Benzene, nitro-	3.99	0.00	0.00	0.00	0.37
Benzyl alcohol	1.21	1.84	0.00	2.57	0.00

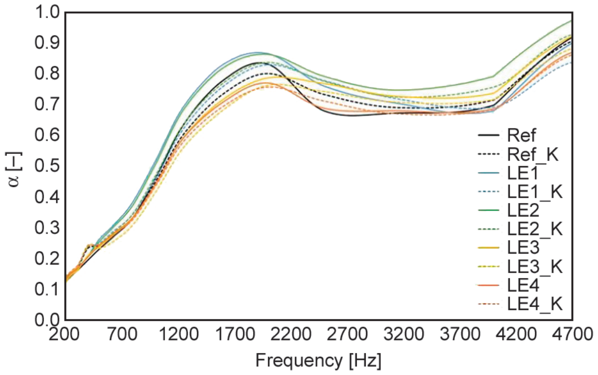

Figure 3. Average curves of sound absorption coefficient (α). The samples (reference sample: Ref and the prepared low-emission samples: LE1–LE4) were tested before and after aging. The average curves of samples after dry aging (ASTM D3574 Test K) are denoted by _K.

of the LE1 and LE2 samples, the sound absorption was better over the entire test range (*i.e.* higher value of α) than in the case of the reference sample. The LE4 sample had the worst sound absorption, with a maximum α value of around 0.75, which was reached slightly later than the other samples, around 1800 Hz. The largest fluctuation can be observed in the case of the reference sample, which, at the highest α value was around 0.85 at the local maximum, then fell to a value of 0.65, which is the lowest in the given frequency range (~2500–3200 Hz). It may be worth noting that the developed samples probably had a larger average cell size due to the lower density, which may also cause a difference in sound absorption capabilities which would also explain the improvement seen in the reference sample after aging, since probably a small cell degradation occurred, which in this case could be beneficial in terms of sound absorption in a given frequency range.

3.4. Results of compression tests

Compression force deflection (CFD) test according to ASTM D3574 Test C were performed in case of the reference sample (Ref) and the low-emission samples (LE1–LE4) before and after dry heat aging (ASTM D3574 Test K). The final force values ($F_{50\%,0}$; $F_{50\%,1}$) were measured at a compression of 50% of the original sample height after one minute. The change in compression strength and sample height after aging were calculated (Table 6).

Table 6. Compression test results according to ASTM D3574 Test C before and after dry heat aging (ASTM D3574 Test K) on the reference sample (Ref) and on the developed low-emission samples (LE1–LE4). $F_{50\%,0}$ is the force measured at 50% compression; $F_{50\%,1}$ is the strength measured at 50% compression after ageing; h_0 is the height of the original sample; h_1 is the height of the sample after aging; $\Delta F_{50\%}$ is the amount of force reduction; and Δh is the decrease in height of the sample.

Sample ID	$F_{50\%,0}$ [N]	$F_{50\%,1}$ [N]	$\Delta F_{50\%}$ [%]	h_0 [mm]	h_1 [mm]	Δh [%]
Ref	6.15	5.54	9.90	37.04	36.69	0.95
LE1	4.58	4.16	9.15	35.66	35.53	0.38
LE2	3.52	2.91	17.18	37.05	37.58	–1.44
LE3	3.94	3.38	14.11	38.78	39.67	–2.28
LE4	3.12	2.73	12.53	38.97	39.28	–0.81

Observing the results, it is clear that the strength change after aging ($\Delta F_{50\%}$) of low-emission samples is significantly greater than the that of reference. A difference of over 15% is significant and cannot be explained with the observed differences in the density. Most probably, inappropriate foam curing can be attributed to such loss in foam strength. It has to be noted that most low emission catalysts are reactively bound to the polyurethane structure during polymerization, and thus, their molecules become more and more inaccessible to reactive species at the late stage of the polymerization. This period is extremely important in terms of creating bonds between polymer microphases and it is responsible for creating polymer strength. Such a negative effect can be practically overcome by the use of salt-like (non-volatile) back-end curing catalysts. In our future studies, along with such reformulations, it would also be worth verifying with microstructural tests since the stability of the foam structure is an important industrial requirement.

It is important to mention that, in all cases with one exception there was a difference of less than 15% between the strength values before and after aging, which, according to the standard, is the limit value that is considered a significant deviation and quality deterioration. Based on this, three out of four low-emission samples (LE, LE3, LE4) have adequate strength even after aging. The change in the sample height (Δh) is insignificant (less than ±2.5%), therefore, in this respect, the samples meet the standard requirements.

Figure 4 shows the force change curves before and after dry heat aging until the compression up to 50% sample height is reached, as well as during holding

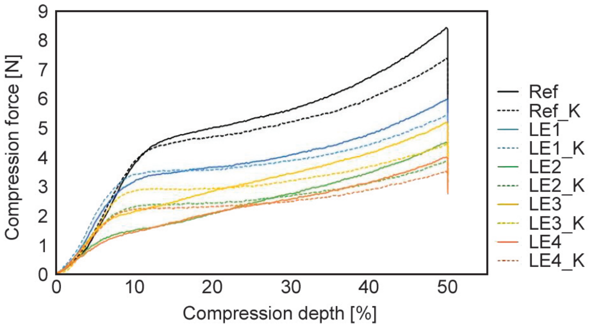

Figure 4. ASTM D3574 Test C (Compression Force Deflection) force measurement at 50% sample height before and after dry aging (ASTM D3574 Test K) (title: _K) on the reference sample (Ref) and on the prepared low-emission samples (LE1–LE4).

at the given height for one minute, when a decrease in force is visible on the curves due to the relaxation of the elastic foam samples.

3.5. Thermogravimetric analysis

The mass loss curves of the thermogravimetric analysis and the DTG curves (the first derivative of the TG curve) of the low emission samples (LE1–LE4) and the reference sample (Ref) are included in Figure 5.

As can be seen, in the case of most samples, only a small deviation can be observed compared to the thermogravimetric behavior of the reference sample. The decomposition processes during heating can be divided into three main stages. In the first stage (~70–220 °C) the samples are dried with a very small weight loss (0.4–1.1%). This indicates that this stage is dominated by water evaporation and a few small molecule products, and most of the chemical bonds have not yet begun to break down. Volatile organic compounds are also removed in this stage. Interestingly, the curves of the reference sample and the low emission samples roughly overlap at this stage, which indicates that there is no significant difference between the samples in terms of mass change. In the second stage (~250–550 °C) a large weight loss is observed, during which the samples lose 75–79% of their weight. Here, the difference between the reference and low VOC samples is already more visible in some cases, especially in the case of LE3 and LE4 samples, where the second stage starts at a higher temperature. At the beginning of the second stage (~250 °C), the depolymerization begins and the dissociation of the urethane bond takes place, thereby releasing the isocyanate groups. In the range between ~300–500 °C, in an inert atmosphere, oxidation products are formed from the polyether chain, which causes a high degree of mass loss. The maximum mass loss temperatures (T_{max}) can be read at the inflection point of the mass loss curve (or at the

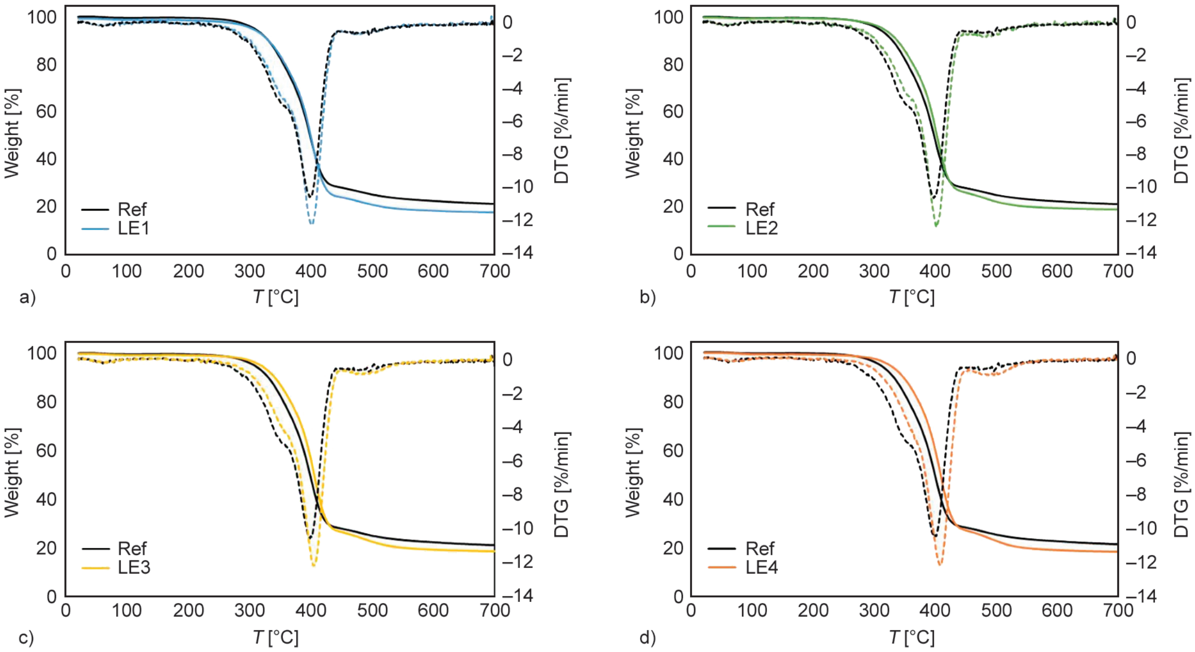

Figure 5. The thermogravimetric analysis on the low-emission samples (LE1–LE4) compared with the result of the reference sample (Ref). a) Mass loss (TG) and mass loss rate (DTG) curves of LE1 and Ref samples, b) mass loss (TG) and mass loss rate (DTG) curves of LE2 and Ref samples, c) mass loss (TG) and mass loss rate (DTG) curves of LE3 and Ref samples, d) mass loss (TG) and mass loss rate (DTG) curves of LE4 and Ref samples.

minimum point of the DTG curve). In the case of the reference sample, this value is found at 398 °C, even for the low VOC samples they were between 401–409 °C. In the third stage (~550–700 °C), only a small weight loss occurs, where, based on the literature, polyureas decompose along with the formation of olefins and aromatic compounds. At the end of the temperature range (700 °C), roughly ~20% of the original sample mass remains, the reason being that the decomposition of long carbon chain compounds only takes place at higher temperatures under inert conditions. It is interesting to observe that the low emission samples had slightly less leftover weight than the reference sample, especially in the case of LE1 and LE4 samples. From this, it can be concluded that their thermal decomposition in the third stage is slightly greater than in the case of the reference sample.

Overall, the similarity in the TGA curves indicates that the thermal degradation mechanisms and the temperatures at which significant weight loss occurs are consistent across all samples. This suggests that the chemical composition and structure of the foams are relatively similar, particularly in terms of the polymer backbone and any major composition. Despite the presence of different additives in each formulation, the overall impact of these additives on the thermal degradation behavior might be minimal. This could mean that the additives used do not significantly alter the decomposition temperature or the rate of thermal degradation of the polyurethane matrix. Thus, all formulations likely achieve a comparable level of thermal stability, which is a positive outcome if thermal stability is a desired property. It suggests that the modifications made to reduce VOC content did not adversely affect the foam's resistance to thermal degradation.

4. Conclusions

Four polyurethane flexible foam formulas of different compositions containing low-emission additives have been designed and tested by foaming and reactivity/phasical examination of the foams. As a result of the tested formula changes volatile organic compound (VOC) and semi-volatile organic compound (FOG) contents showed significant decrease compared to the reference sample which was formulated with traditional additives. The kinetic and foam stability (shrinkage) test revealed that low-emission samples were comparable to the reference sample. However, the product densities are slightly lower than in the case of the reference foam, indicating that the new formulations allow the application of less blowing agent (water). In order to observe the effect of thermal degradation on the different material properties, compression tests and sound absorption tests were performed before and after dry aging. The obtained results proved to be promising, low-emission samples showed comparable sound absorption to the reference sample, with two out of four samples showed higher sound absorption coefficient (α) on the entire examined frequency range than the reference sample with less significant change in α due to aging. In the case of the compression force deflection tests, after the aging process, in most cases, a difference of less than 15% was observed in the compressive force, which is considered acceptable based on the standard, so the samples (with one exception) meet the requirements. Based on these finding, under the influence of dry heat flexible polyurethane foam samples formulated with low-emission additives do not suffer significantly larger degradation based on their tested properties than the reference foam sample made with traditional additives.

According to the results of the thermogravimetric analysis, examining the entire spectrum of the processes that occur under the influence of heat, no significant changes occur due to the use of low-emission additives, which suggests that the modifications made to reduce VOC content did not adversely affect the foam's resistance to thermal degradation.

These are industrially particularly important findings, as they prove that foams with a low-emission composition that meet environmental protection requirements continue to have material properties that meet the expectations when used at high temperatures.

Acknowledgements

This research was supported by the National Research, Development and Innovation Fund (Hungary) within the TKP2021-NVA-14 project. Project no. C1532779 has been implemented with the support provided by the Ministry of Culture and Innovation of Hungary from the National Research, Development and Innovation Fund, financed under the KDP-2021.

References

[1] Gama N. V., Ferreira A., Barros-Timmons A.: Polyurethane foams: Past, present, and future. Materials, **11**, 1841 (2018).
https://doi.org/10.3390/ma11101841

[2] Naldzhiev D., Mumovic D., Strlic M.: Polyurethane insulation and household products – A systematic review of their impact on indoor environmental quality. Building and Environment, **169**, 106559 (2020).
https://doi.org/10.1016/j.buildenv.2019.106559

[3] Yan M., Zhai Y., Shi P., Hu Y., Yang H., Zhao H.: Emission of volatile organic compounds from new furniture products and its impact on human health. Human and Ecological Risk Assessment: An International Journal, **25**, 1886–1906 (2018).
https://doi.org/10.1080/10807039.2018.1476126

[4] Eling B., Tomović Ž., Schädler V.: Current and future trends in polyurethanes: An industrial perspective. Macromolecular Chemistry and Physics, **221**, 2000114 (2020).
https://doi.org/10.1002/macp.202000114

[5] Brodzik K., Faber J., Łomankiewicz D., Gołda-Kopek A.: In-vehicle VOCs composition of unconditioned, newly produced cars. Journal of Environmental Sciences, **26**, 1052–1061 (2014).
https://doi.org/10.1016/S1001-0742(13)60459-3

[6] Inagaki C., Adachi A., Inoue K.: Development of low smell and low VOC polyurethane foam. Transactions of Society of Automotive Engineers of Japan, **51**, 203–208 (2020).
https://doi.org/10.11351/jsaeronbun.51.203

[7] Huhtasaari M. S., Plaumann R., Grimminger J., Kniss J. G., Womack F. D.: Catalysts and silicone surfactants for reduced VOC emissions of polyester slabstock foam. in 'API Polyurethanes Expo 2001, Columbus, USA' 431–441 (2020).
https://doi.org/10.1201/9780429332609-60

[8] Sakai M., Ishikawa A., Morii M., Kiuchi K.: Non-VOC catalysts for HR molded foams used in automotive seating applications. in 'API Polyurethanes Expo 2001. Columbus, USA' 33–39 (2020).
https://doi.org/10.1201/9780429332609-6

[9] Dworakowska S., Bogdał D., Zaccheria F., Ravasio N.: The role of catalysis in the synthesis of polyurethane foams based on renewable raw materials. Catalysis Today, **223**, 148–156 (2014).
https://doi.org/10.1016/j.cattod.2013.11.054

[10] Suzuki T., Tokumoto K., Takahashi Y., Kiso H., van Maris R., Tucker J.: Zero emission polyurethane catalyst – Reactive strong gelling amine. TOSOH Research and Technology Review, **57**, 13–21 (2013).

[11] Li R., Liu L., Liu Y., Wang B., Jang Y. J., Zhang J.: Research progress of amine catalysts for polyurethane. Topics in Chemical and Material Engineering, **1**, 54–57 (2018).
https://doi.org/10.26480/icnmim.01.2018.54.57

[12] Rothe J., Cordelair H., Wehman C.: New catalysts for low VOC in flexible slabstock foam. Journal of Cellular Plastics, **37**, 207–220 (2001).
https://doi.org/10.1106/X6BV-73PB-6FQC-KCRN

[13] Sridaeng D., Jitaree W., Thiampanya P., Chantarasiri N.: Preparation of rigid polyurethane foams using low-emission catalysts derived from metal acetates and ethanolamine. e-Polymers, **16**, 265–275 (2016).
https://doi.org/10.1515/epoly-2016-0021

[14] Kometani H., Tamani H., Masuda T., Gay K. M., van Maris R.: The investigation of amine emissions from polyurethane foam. in 'Polyurethanes Conference 2000: Defining the Future Through Technology. Westin Copley Place, Boston, USA' 11–21 (2000).

[15] Waleed H. Q., Csécsi M., Konyhás V., Boros Zs. R., Viskolcz B., Fejes Z., Fiser B.: Aliphatic tertiary amine catalysed urethane formation – A combined experimental and theoretical study. Physical Chemistry Chemical Physics, **24**, 20538–20545 (2022).
https://doi.org/10.1039/D2CP00728B

[16] Wegener G., Brandt M., Duda L., Hofmann J., Klesczewski B., Koch D., Kumpf R. J., Orzesek H., Pirkl H. G., Six C., Steinlein C., Weisbeck M.: Trends in industrial catalysis in the polyurethane industry. Applied Catalysis A: General, **221**, 303–335 (2001).
https://doi.org/10.1016/S0926-860X(01)00910-3

[17] Hillier K., Schupp T., Carney I.: An investigation into VOC emissions from polyurethane flexible foam mattresses. Cellular Polymers, **22**, 237–259 (2003).
https://doi.org/10.1177/026248930302200402

[18] Hillier K., King D. A., Henneuse C.: Study of odours coming out of polyurethane flexible foam mattresses. Cellular Polymers, **28**, 113–144 (2009).
https://doi.org/10.1177/026248930902800201

[19] Sikorski M., Wehman C., Cordelair H.: New additive solutions for low VOC in HR molded foams. Journal of Cellular Plastics, **36**, 294–309 (2000).
https://doi.org/10.1177/0021955X0003600404

[20] Chattopadhyay D. K., Webster D. C.: Thermal stability and flame retardancy of polyurethanes. Progress in Polymer Science, **34,** 1068–1133 (2009).
https://doi.org/10.1016/j.progpolymsci.2009.06.002

[21] Shakirova G. D., Romanova N. V., Shafigullin L. N.: The influence of heat treatment on the quality of vehicle component parts made of rigid polyurethane foam. Materials Science Forum, **989**, 10–15 (2020).
https://doi.org/10.4028/www.scientific.net/MSF.989.10

[22] Tcharkhtchi A., Farzaneh S., Abdallah-Elhirtsi S., Esmaeillou B., Nony F., Baron A.: Thermal aging effect on mechanical properties of polyurethane. International Journal of Polymer Analysis and Characterization, **19**, 571–584 (2014).
https://doi.org/10.1080/1023666X.2014.932644

[23] Pellizzi E., Lattuati-Derieux A., Lavédrine B., Cheradame H.: Degradation of polyurethane ester foam artifacts: Chemical properties, mechanical properties and comparison between accelerated and natural degradation. Polymer Degradation and Stability, **107**, 255–261 (2014).
https://doi.org/10.1016/j.polymdegradstab.2013.12.018

[24] Yang S. S., Lee J. W., Kim J. H., Kang Y. J.: Effect of thermal aging on the transport and acoustic properties of partially reticulated polyurethane foams. The Journal of the Acoustical Society of America, **152**, 2369–2381 (2022).
https://doi.org/10.1121/10.0014913

[25] Jiao L., Xiao H., Wang Q., Sun J.: Thermal degradation characteristics of rigid polyurethane foam and the volatile products analysis with TG-FTIR-MS. Polymer Degradation and Stability, **98**, 2687–2696 (2013).
https://doi.org/10.1016/j.polymdegradstab.2013.09.032

[26] Chen X., Huo L., Jiao C., Li S.: TG–FTIR characterization of volatile compounds from flame retardant polyurethane foams materials. Journal of Analytical and Applied Pyrolysis, **100**, 186–191 (2013).
https://doi.org/10.1016/j.jaap.2012.12.017

[27] Hornyák-Mester E., Mentes D., Farkas L., Hatvani-Nagy A. F., Varga M., Viskolcz B., Muránszky G., Fiser B.: Volatile emissions of flexible polyurethane foams as a function of time. Polymer Degradation and Stability, **216**, 110507 (2023).
https://doi.org/10.1016/j.polymdegradstab.2023.110507

[28] Mester E., Pecsmány D., Jálics K., Filep Á., Varga M., Gráczer K., Viskolcz B., Fiser B.: Exploring the potential to repurpose flexible moulded polyurethane foams as acoustic insulators. Polymers, **14**, 163 (2021).
https://doi.org/10.3390/polym14010163