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INVESTIGATION OF THE EFFECT OF AUTOCLAVE AGING ON POLYURETHANE FOAMS WITH LOW VOC CONTENT

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Abstract

Six flexible polyurethane foam recipes using low VOC additives were formulated and the prepared samples were analysed for their mechanical and acoustic properties pre and post autoclave aging. The results were compared with a reference foam comprising traditional additives. Promising results were obtained, particularly in acoustic performance, with two formulations (W2, W3) exhibiting superior sound absorption compared to the reference sample. However, after the autoclave aging the value of the sound absorption coefficient drops suddenly in a given frequency range, which may also indicate the degradation of the cell structure. The compressive strength of the samples were lower in case of four out of six samples, which can be due to their lower density. Adjustments in foaming reaction could potentially mitigate this issue. After the autoclave aging the compressive strength significantly reduced in all cases including the reference sample, which indicates that when the foams are utilized in wet environments for extended periods of time they cannot be further used for bearing applications.

Keywords: *polyurethane, autoclave aging, VOC, flexible foam*

1. Introduction

Polyurethane (PU) is a versatility material with a wide range of applications, and it presents significant advancements in recent years (Eling et al., 2020; Suleman et al., 2014). One of the major developments is the integration of low volatile organic compound (VOC) additives, addressing environmental concerns as well as enhancing material performance (Inagaki et al., 2020; Rothe, Cordelair, and Wehman, 2001).

The use of low emission polyurethane foam formulations emphasizes the importance of environmental expectations and consumer safety (Engels et al., 2013). These additives aim to reduce the release of harmful volatile compounds, aligning with recent regulatory standards and consumer preferences for eco-conscious products (Huhtasaari et al., 2020). However, the possible interactions with these additives and the degradation routes when exposed to extreme conditions remains an important subject of investigation.

Low-emission additives created on the principle that, unlike traditional alternatives, they can react with the raw materials, particularly with the NCO-group of isocyanates, thereby becoming part of the polymer chain being formed. This is an effective way to reduce potential emissions, but it can cause concerns about the stability of the foams, especially when exposed to accelerated conditions.

Autoclave aging serves as a crucial method for simulating environmental conditions such as high temperature, pressure and humidity, assessing the long-term durability of polyurethane foams (Tcharkhtchi et al., 2014). By subjecting samples to elevated temperatures and pressures, similar to real-life usage circumstances, researchers can gain insights into material behaviour over extended periods of time (Koshute, Blaszkiewicz, and Neal, 2020). This process becomes particularly relevant for polyurethane foams containing low emission additives, as understanding their stability under diverse conditions is necessary for ensuring product reliability and performance sustainability (Casati et al., 2020).

One concern during autoclave aging relates to the potential degradation of mechanical properties, especially load-bearing capacity (Tian et al., 2016; Boubakri et al., 2010). Polyurethane foams are often utilized in applications requiring structural support, where their ability to withstand compressive forces is critical (Samali et al., 2019; Khan et al., 2020). Understanding how aging influences the mechanical characteristics of foams with low emission additives is essential for evaluating their long-term usability in applications such as car seat foams (Rasshofer and Weigand, 2001). Factors such as changes in cell structure and chemical composition may contribute to alterations in compressive strength and resilience over time (Sonnenschein et al., 2008; Tian et al., 2016).

Aging and degradation related to elevated conditions such as high humidity can also impact other important characteristics of cellular materials, such as the acoustic performance (Yang et al., 2022). These materials find widespread use in noise insulation and sound absorption applications, where their ability to dampen sound waves is essential (Tao et al., 2021; Rastegar et al., 2022; Arenas and Crocker, 2010). Degradation effects may alter the foam’s ability to reduce noise, potentially compromising acoustic performance (Arenas and Sakagami, 2020). Changes in foam density, porosity, and viscoelastic properties could influence sound transmission and absorption characteristics, requiring careful examination to ensure continued efficacy in acoustic applications (Sharma et al., 2023).

This paper is aims to explore the autoclave aging of flexible moulded polyurethane foams with the prime objective of investigating the potential degradation effects, particularly in case of load-bearing capacity and acoustic properties. It should be underlined that the long-term performance and durability of such innovative foam formulations can be studied by means of comprehensive analysis of the degradation effects. This is critical information for insights required to advise on product designs, optimize manufacturing processes, and meet the shifting industry standards for sustainable high-performance materials.

2. Materials and Methods

2.1 Materials and flexible foam production

For comparability, the raw materials of flexible polyurethane foam samples were in each case an MDI (methylene diphenyl diisocyanate) isomeric mixture (Ongronat TR 4040, Wanhua-BorsodChem, average NCO: 32.5 m/m%) and polyether-type base polyol (Wanol F3160, Wanhua). The base polyol was formulated before adding the isocyanate. The following additives were premixed in each polyol mixtures: water as a foaming agent, cell opening polyol (Alcupol F3231, Repsol) and crosslinking catalyst (Tegoamin DEOA 85, Evonik). In the case of the reference sample, various traditional catalysts (DABCO 33- LV, Evonik; Jeffcat ZF 22, Huntsman) and a conventional surfactant (Tegostab B4113, Evonik) were used. In addition, for the low emission formulations polyol mixtures were prepared (W1–W6) with 6 different formulas, containing low VOC catalysts (DABCO NE 300, Evonik; DABCO NE 1550, Evonik; DABCO NE 1090, Evonik; Niax EF-600, Momentive; Jeffcat ZF 10, Huntsman) and surfactants (Tegostab B8734 LF2, Evonik; Tegostab B8715 LF2, Evonik).

The samples were produced using the FOAMAT 285 foam qualification system. The system determines the most important parameters of the foaming reaction, such as start time, foaming time, shrinkage, product density, etc. The samples were prepared in 1-liter paper cups and the recipes were calculated for a total weight of 60 g in each case, which ensures an ideal foam rise for these combinations. During the cup tests, an NCO index of 1.0 (100) was used in all cases.

2.2 Mechanical testing

During the mechanical tests the compression test method of Test C of ASTM D3574 (complex test standard for flexible polyurethanes) was applied with minor changes. For the tests, cylinders with a diameter of 30 mm and a height of 35-40 mm were cut from the original samples shown in *Figure 1*. The test samples obtained in this way 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 data obtained at the end is called Compression Force Deflection (CFD). The measurements were performed before and after autoclave aging, thus examining the effect of long-term use in wet conditions of the material. The degree of change is determined by the pressure depth-force curve difference ($\Delta F_{50\%}$). If the degree of change is too great (greater than 15%), then the material can no longer be used for compressive stress. It is also necessary to document the change in the sample height (Δh), in which case a deviation of more than 5% is considered a significant change.

Figure 1. *Flexible polyurethane foam samples for the mechanical and acoustic tests*

2.3 Acoustic testing

In order to examine the acoustic properties of the produced flexible polyurethane foams, the sound absorption coefficients (α) were determined in the higher frequency range using an impedance tube. For the measurements, AED 1000 – AcoustiTube impedance tube was used, which is a laboratory measurement system for determining the sound absorption coefficient and impedance of test samples according to the transfer function method described in the EN ISO 10534-2 standard, and according to ASTM E1050. The frequency range of the measurement is limited by the geometry of the impedance tube and the distances between the microphones. During the tests, tubes with an internal diameter of 30 mm was used for the measurements, in which case the useful frequency range is 200–4700 Hz. 3 microphones were operated, so the measurements of the lower and upper frequency range could be performed in a single measurement. Similarly to the mechanical tests, for the acoustic measurements, cylinders with a diameter of 30 mm and a height of 35-40 mm were cut out of the samples *(Figure 1)* and the acoustic measurements were performed before and after autoclave aging. A more detailed description of the method is contained in previous research paper (Mester et al., 2021).

2.4 Autoclave aging

In order to determine the changes in the tested material properties (compressive force deflection, sound absorption coefficient) during long-term use in wet conditions, standard aging tests were performed using a steam autoclave. The ASTM D3574 standard contains three different aging test methods, of which I used Test J in this case, which is an autoclave aging test. In doing so, the samples were kept in a steam sterilizing autoclave (Biobase) for 2 hours at 120 ±5 °C at a pressure limit of 140 kPa (Procedure J2, modified duration). After aging, the samples were conditioned under the requirements specified in the standard (23 ±2 °C, 50 ±5% relative humidity) for at least two hours before repeating the various tests (mechanical and acoustic tests).

3. Results

3.1 Compression tests

The compression force deflection (CFD) test was performed according to ASTM D3574 Test C before and after autoclave aging (ASTM D3574 Test J) for the reference sample (Ref) and samples with low volatile organic compound content (W1-W6). The final force values ($F_{50\%,0}$; $F_{50\%,1}$) were measured at 50% of the original sample height after one minute. The change in strength and sample height after aging was calculated *(Table 1)*.

Table 1. *Compression test results according to ASTM D3574 Test C before and after autoclave aging.* $F_{0;\,50\%}$ *is the force measured at 50% sample height before aging,* $F_{1;\,50\,\%}$ *is the force measured at 50% sample height after the autoclave aging* $\Delta F50\%$ *is the force decrease in percentage after the aging process,* h_0 *is the original sample height,* h_1 *is the sample height after autoclave aging,* Δh *is the height decrease in percentage after aging.*

Sample ID	$F_{0;\,50\%}$ [N]	$F_{1;\,50\%}$ [N]	$\Delta F_{50\%}$ [%]	h_0 [mm]	h_1 [mm]	Δh [%]
Ref	7.30	5.80	*20.57*	39.28	38.71	*1.45*
W1	7.70	5.80	*24.65*	39.62	38.69	*2.33*
W2	7.02	5.30	*24.51*	38.16	38.09	*0.18*
W3	6.22	4.54	*26.97*	34.32	34.05	*0.79*
W4	12.37	9.91	*19.85*	40.52	40.19	*0.82*
W5	5.60	4.34	*22.44*	39.16	39.20	*–0.10*
W6	5.01	3.43	*31.47*	40.20	40.08	*0.31*

Observing the results, it is clear that the change in strength after aging is greater than the reference sample (Ref), with the exception of sample W4. The standard defines a change in force of over 15% as significant, which is greater in all cases (also in the case of the reference sample), it is likely that structural degradation occurred in the samples, which considerably reduced their load capacity.

In all cases, the change in the sample height is relatively small, the standard describes a change of less than 5% acceptable, so from this point of view, the samples are satisfactory after autoclave aging.

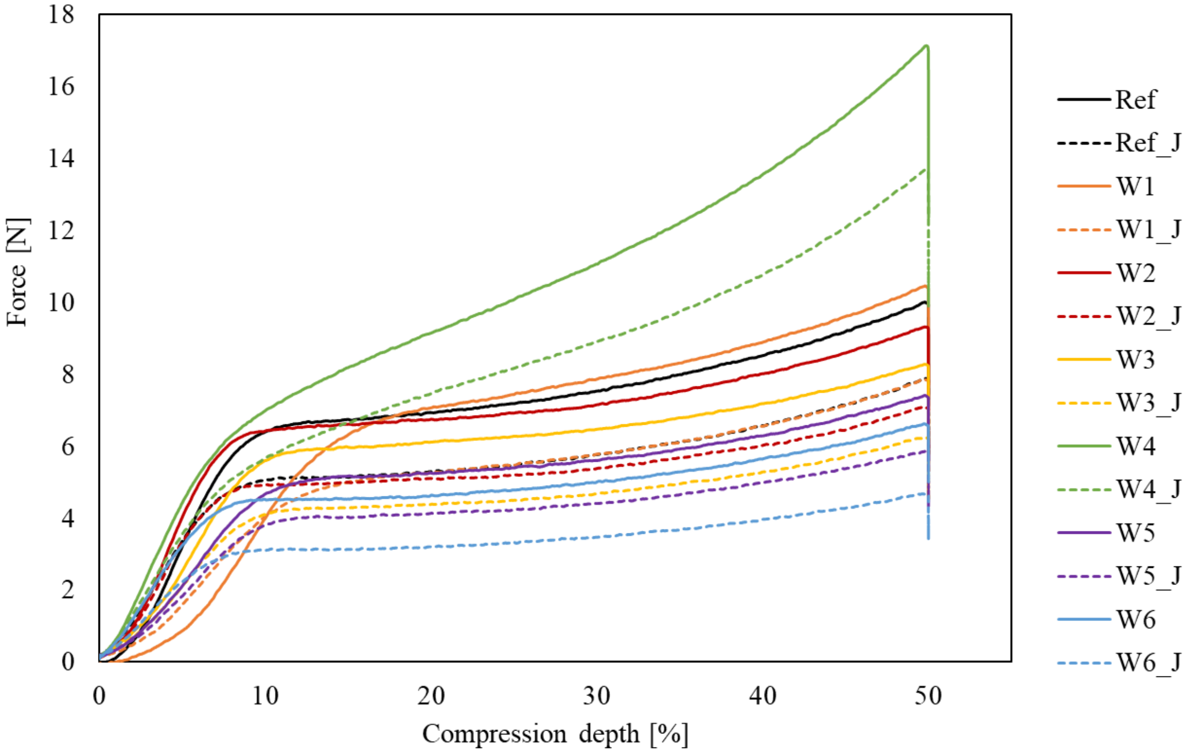

Figure 2. *Compressive strength curves at 50% compression before and after autoclave aging (mark:J)*

As can be seen in *Figure 2*, the reference sample (Ref) has a higher compressive strength than the low VOC samples, except for two samples (W1, W4), but it is important to note that the density of the developed samples is slightly lower than that of the reference sample. This can probably be improved with further formula fine-tuning.

3.2 Sound absorption

Both the reference sample (Ref) and the developed low VOC content samples (W1–W6) behaved as expected from the porous sound absorbing material used in industry before the autoclave aging.

As can be seen in *Figure 3*, the sound absorption coefficient (α) increases steadily and then reaches a maximum (0.8–0.9) 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. During the current measurement series, 100% sound absorption (α = 1) was achieved by samples W3 and W5 at the end of the tested frequency range, however, overall, the measured values can still be said to be adequate sound absorption. There is a significant difference in the behaviour of the samples before and after autoclave aging, in most cases the value of the sound absorption coefficient drops suddenly in a given frequency range (2200–3200 Hz), which may also indicate the degradation of the cell structure.

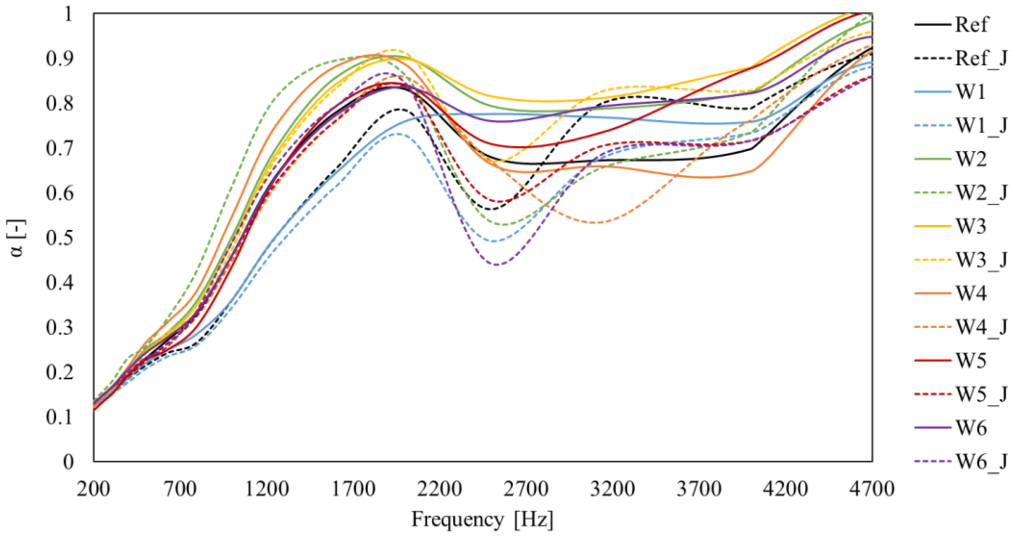

Figure 3. *Average curves of sound absorption coefficient (α) before and after autoclave aging (mark: J)*

If we compare the change in the sound absorption coefficient (α) for the different samples, it can be seen that, with the exception of the W1 and W4 samples, better sound absorption is experienced in all cases than in the case of the reference sample (Ref) before the aging process. The W1 sample had the worst sound absorption, with a maximum α value of around 0.75, which it reached later than the other samples, around 2000 Hz. The largest fluctuation can be observed in the case of the W4 sample, which, although it gave the highest α value (~0.9) at the local maximum, then dropped to a value of 0.6, which is the lowest in the given frequency range (~2500–4000 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.

4. Summary

Six polyurethane foam recipes containing additives with low VOC content of different compositions have been developed. The mechanical (compressive stress) and acoustic (sound absorption) properties before and after autoclave aging were examined and compared with a reference foam containing traditional additives. The obtained results proved to be promising, especially in the case of acoustic measurements, in which four out of six of the developed low VOC samples had better sound absorption than the reference sample. However, as a result of autoclave aging, the sound absorption in a given frequency range is significantly reduced for most samples (especially samples W1, W2, W6), which may indicate that some degradation has occurred in the structure of the open-cell foams. In the case of mechanical tests, due to the lower density, most samples had a lower compressive strength than the reference sample, but this can presumably be improved by adjusting the formulation. When examining the change in force after autoclave aging, it can be observed that the decrease was over 15% in all cases, which is considered significant, so it is also assumed that the cell structure suffered degradation. Based on these results it is planned in the future to adjust the sample parameters, such as density and strength by making some formulation refinements. This requires fine-tuning the amount of additives, such as blowing agent and catalysts that influence the various foaming parameters.

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