Polyurethane improvement by glasses fibres, acoustic, mechanical and thermal application

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Abstract: Polyurethanes and glass fibres offer nowadays very interesting possibilities of their utilization related to the modification of the basic material. Possible combinations of these materials stem from their specific properties, e.g. acoustical properties, high resistance against mechanical stress, the ability to modify damping of transfer and decrease burning rate. Polyurethanes and glass fibres have been used in different forms in aviation, automotive industry and engineering. Materials for such application should be able to deal with moisture, random mechanical shocks, elevated or low temperature, dirt or fungi. Glass component at the polymer surface extends application possibilities. Particular application however demands certain ratio of fibrous or pulverous glass, i.e. density gradient of glass component in the polymer. Each application also calls for specific ratio of both compounds and/or their conditions. Eventually, economical aspect should be considered, as glass reinforced polymers should be available for reasonable price.

Key-Words: Polyurethanes – PUR, fabric glasses - FG, coefficient sound absorption - SAC, fire protection, flammability, damping

1 Introduction
Polyurethanes have been used in virtually all fields of production industry – cabinetmaking, automotive, aviation and in last few years also in the space program, in the research of damping components in space shuttles cabins. Broad range of polyurethanes has many possible applications, though one should not ignore economical aspect of each specific solution. Research is mainly focused to the field of aviation, to obtain materials for noise and vibration damping, with improved incombustibility to meet safety requirements. Resulting combination of polyurethane and glass fibre must first of all provide high acoustic absorption in the frequency range typical for human ears, tensile and compression resistance, abrasion resistance and impact resistance. Material should also have relatively low thermal conductivity, incombustibility or at least self-extinguishing properties. Last fire-safety standards determine whether the particular combination of polymer and glass fibre will be used in automotive, aviation or engineering industry. For example the combination of polymer and glass for aviation purposes must meet requirements of fire service tests FAR and JAR (standards for testing in aviation JAR/FAR 23 and JAR/FAR 25). In case that the material cannot be used in aviation, it can still be utilised for noise damping in engineering devices, where it is exposed to harsh environment (moisture, dirt, fungi) and sufficient lifetime is the main criterion, as the material should maintain high coefficient of acoustic absorption. Materials for automotive industry should notably provide good acoustic properties – high coefficient of acoustic absorption and damping [1, 2].

2 Theoretical background
Linear polyurethanes which are used in acoustic insulations for noise and mechanical damping represent a group of polymers with very broad range of properties and thus applications. Almost 50 \% of PUR production is used for manufacturing of soft foams, which have excellent acoustic, mechanical and thermal properties. Polyurethanes are produced by a reaction of more-functional
isocyanates with poly-alcohols. Urethane bond, characteristic for polyurethanes, has large effect on thermal stability, Fig. 1.

![Urethane bond](image)

**Fig. 1 Urethane bond**

Open and closed modification of pores has considerable effect on the shape of a curve obtained by measurement with Kundt’s impedance tube. Polymeric structure with open pores (Fig. 2) is very important for transformation of acoustic energy to thermal as a result of air circulation on the surface of building blocks, i.e. walls of open pores [3].

![Open and close cells of polyurethane](image)

**Fig. 2 Open and close cells of polyurethane**

Curves in Fig. 3 show difference between acoustic absorption of open and closed pores. Acoustic absorption is defined as a ratio of absorbed and incident acoustic energy generated inside the Kundt’s tube, in the frequency range 20 Hz – 6400 Hz. Values of the coefficient near 1 indicate maximal absorption, and values near 0 represent maximal reflexivity [4].

Very often is absorption expressed in the means of NRC – noise reduction coefficient, thought this value does not provide enough information about the whole frequency range, rather about its segments (octaves) in the frequency range to 4000 Hz. Nevertheless, this value has been used in commercial polyurethanes and can possibly by used as another technical parameter for choice of suitable PUR.

The basic formula of the sound absorption coefficient is:

$$\alpha = \frac{\text{Acoustic Energy Absorbed}}{\text{Acoustic Energy Incident}} \quad [-] \quad (1)$$

For the sound absorption coefficient (SAC) is very important frequency dependence and structure of the mass – open or close cell, big or small porosity and size of pores inside structure of polyurethanes. Basic different between open- and close-cell can be seen in Fig. 2. In this case are two types of cells that can be seen in structure of polyurethane foams.

![Sound absorption coefficient (open / closed pores)](image)

**Fig. 3 Sound absorption coefficient (open / closed pores)**

Porosity characterizes ratio of matter and gas in the volume of polymeric block. It has significant effect on behaviour of acoustic absorption. When considering polymer – glass combination, there is a main challenge in finding a compromise between pores size and size of the glass fibres. The effect of porosity on acoustical properties is demonstrated in Fig. 4.

![Porosity and sound absorption coefficient](image)

**Fig. 4 Acoustic absorption – high and low porosity in volume of PUR**

Uniform pores size is needed to achieve optimal acoustic absorption. In such structure, uniform glass fibres density can be reached. In commercial polyurethanes, though, the distribution function is rather broad. Thus small pores will prevent glass fibre from passing through it. One could obtain structures with almost uniform pores size, which would be ideal form polymer – glass application. Such structures are however very costly. Pores size in polyurethane is ranging between $10^{-3}$ and $10^{-4}$ m, with desired porosity 80 to 95 %.
Fig. 5 Real cell sizes of commercially Polyurethane – S3535

Determination of material thickness form optimal absorption follows simple rule – the thicker the material, the better the acoustic absorption. Human hearing is in most cases exposed to sound in the frequency range from 20 to 8000 Hz. As a rule of a thumb, following equation can be used to suggest material thickness for a specific frequency:

\[ h = \frac{1}{10} \cdot \frac{c}{f_m} \text{[m]} \]  \hspace{1cm} (2)

Where: \(c\) – speed of sound (\(\text{ms}^{-1}\)); \(f_m\) – lowest frequency where is sound absorption needed.

Materials for acoustic applications should be non-flammable, with reduced flammability or self-extinguishing. Normally, polyurethanes are flammable. There are different ways how to deal with this problem. Flame retarders can be incorporated into the material during the production process or a surface film with low flammability can be used. The main drawback of the latter method is decrease in acoustic absorption. Technically rather complicated, but very efficient is the implantation of fibrous material into the polyurethane pores. Density of fibres in the volume of PUR can be either constant or it can vary with the increasing distance from the surface of the material. Choice of fibrous material itself is also very important – pure glass has excellent fire resistance, but conditioning of its surface with resins can negatively alter this property.

3 Materials and methods

Materials used for this research are specified in Table 1.

<table>
<thead>
<tr>
<th>PUR</th>
<th>(\rho (\text{kg.m}^{-3})*)</th>
<th>(k (\text{kPa})**)</th>
<th>(\sigma (\text{kPa})***)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S3535</td>
<td>35</td>
<td>3,5</td>
<td>130</td>
</tr>
<tr>
<td>N1820</td>
<td>18</td>
<td>2,4</td>
<td>80</td>
</tr>
<tr>
<td>CMHR</td>
<td>35</td>
<td>3,2</td>
<td>120</td>
</tr>
<tr>
<td>H4055</td>
<td>40</td>
<td>5,5</td>
<td>160</td>
</tr>
</tbody>
</table>

Table 1 Characteristics of examined polyurethanes (\(\rho\) – density, \(k\) – stiffness of polyurethane, \(\sigma\) – tensile strength)

*ČSN 645411, DIN 53420
**ČSN 645411, DIN 53577
***ČSN 645431, DIN 53571

S3535 and CMHR3532 are materials with elevated non-flammability and self-extinguishing properties, mostly used for upholstery, insulation and other applications in vehicles. N1820 and H4055 are traditional porous structures, widely used for general upholstering. The above mentioned materials are displayed in Figure 7 to 10.

Fig. 7 CMHR3532

Fig. 8 H4055
Technical glass used for application in PUR is grinded prior to use. Length of the fibres is reduced from initial $10^{-1}$ – $10^{-2}$ m to $10^{-4}$ m and thickness of about $10^{-5}$ m. Lubricated glass fibres exhibit good resistance against moisture, running water, fungi and chemicals. For this reasons are glass fibres ideal candidate for incorporation into the PUR structure [5, 6].

Acoustic absorption was measured with Kundt’s impedance tube (type 4602, Brüel and Kjær), in the frequency range from 20 Hz to 6400 Hz. Polyurethane samples were prepared in form of circles, with diameter 100 mm and thickness 30 mm.

Combustion resistance was measured according to standards, with a Bunsen burner, on the sample surface, with the flame burning through the whole sample thickness. Observed parameter is time needed for the flame to burn through the whole sample thickness. Total heat value was measured with the IKA C 200 calorimeter, in the oxygen atmosphere.

**4 Results and discussion**

Glass fibres can greatly improve properties of polyurethanes. One of the leading factors affecting incorporation of glass fibres into the PUR structure is size of pores and porosity of polymeric material. Size of the pores has essential influence on the distribution of fibres in the mass of the polymer (Fig. 14). Glass fibre density in the material is function of pores size, as following formulation suggests:

$$n = \frac{m}{\rho}$$

where $n$ is the number of fibres, $m$ is the mass of fibres, and $\rho$ is the density of fibres.

**Fig. 13 Density of glass fibres in volume of PUR for sample thickness 10 mm. A – density of fibres in the distance of 50 % of the sample thickness (measured from the surface), B – density of fibres in the distance of 30 % of the sample thickness – 3mm, C – density of fibres in the distance of 0 – 10 % of the sample thickness – 1mm [7].**

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Glass fibre density gradient in PUR has fundamental effect on the resulting acoustic properties, namely acoustic absorption coefficient. The value of acoustic absorption coefficient can be increased by tens of percent on a 10 mm thick PUR sample when glass fibres are applied. Even higher increase of absorption in the frequency range from 20 to 6400 Hz can be obtained when an air gap with the same thickness as the polymer sample itself is created behind the sample.

4.1 Sound absorption coefficient
Four different materials were examined. Results are given in the Table 1. Acoustic properties are presented in Figures 16 and 17.

4.2 Flammability
Materials for application in aircraft engine mechanisms have to withstand harsh environment, especially with respect to elevated temperatures. Application of glass fibres into the PUR surface and structure can significantly suppress fire propagation not only on the material surface, but also through the material. Following figure demonstrates position of flame towards tested sample.

Figure 19 shows behaviour of samples exposed to direct flame. For a sample modified by glass

![Fig. 15 High density and low density](image1)

![Fig. 16 SAC - PUR S3535 (+FG and NO AIR)](image2)

![Fig. 17 SAC – PUR S3535 (+FG and with AIR)](image3)

![Fig. 18 types of position flame (face, edge and direct ignition)](image4)

![Fig. 19 – Flame burning through the sample, A – pure polyurethane, B – polyurethane with glass fibres](image5)
fibre, the destruction caused by the flame is about 50 % lower. Glass fibres also increase time which the material is able to resist combustion ([t]=seconds), see Figure 20.

![Time of burning PUR and PUR+FG](image)

Fig. 20 Time of burning PUR and PUR+FG

Total heat value of samples modified by glass fibres is about 30 % lower, compared to pure polyurethane. These results also show the role of glass fibres in increasing the fire resistance of polymer samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S3535 FG 30%</th>
<th>S3535 FG 10%</th>
<th>S3535 FG 0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>v1</td>
<td>20,417</td>
<td>25,901</td>
<td>27,533</td>
</tr>
<tr>
<td>v2</td>
<td>20,568</td>
<td>24,806</td>
<td>27,647</td>
</tr>
<tr>
<td>v3</td>
<td>21,028</td>
<td>24,834</td>
<td>27,444</td>
</tr>
<tr>
<td>v4</td>
<td>22,568</td>
<td>25,108</td>
<td>27,930</td>
</tr>
<tr>
<td>Average MJ/kg</td>
<td>21,145</td>
<td>25,162</td>
<td>27,638</td>
</tr>
<tr>
<td>St.deviation</td>
<td>0,711</td>
<td>0,369</td>
<td>0,150</td>
</tr>
</tbody>
</table>

Table 2 Heat of combustion - S3535 (MJ/kg)

4 Conclusion
Addition of glass fibres into the polyurethane structure has great influence on acoustic properties of final product. An increase of 30 to 40 % in the value of sound absorption coefficient was observed. Thus a significant shift of peaks toward lower frequencies is achieved in octave regions. This is very convenient in applications with high noise concentration, generated in low frequencies (machine and engine mechanisms). Incorporation of glass fibres into PUR structure can improve flame resistance about 40 % with respect to pure material. The results show that with 30 % weight increase (application of glass fibre) better acoustic properties and better flame resistance is achieved. This is reached without sample thickness increase, which is of high importance for insulation application in aviation.

Acknowledgement
This article was created with support of Operational Program Research and Development for Innovations co-funded by the European Regional Development Fund (ERDF) and national budget of Czech Republic, within the framework of project Centre of Polymer Systems (reg. number: CZ.1.05/2.1.00/03.0111). Research work of Veronika Struhařová was co-supported by the internal grant of TBU in Zlin no. IGA/13/FT/11/D funded from the resources of specific university research.

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