EFFECT OF CARBON NANOTUBES ADDITION ON THE PROPERTIES OF FLEXIBLE POLYURETHANE FOAMS

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1 Introduction
Flexible polyurethane foams (FPFs) are polymer materials with a large number of applications in daily life. They are used mainly in upholstered chairs, mattresses, automotive and packing, due to their low density and wide range of physical and mechanical properties, which can be controlled during production process [1-3]. The production of polyurethane foams is based on the reaction between isocyanates and compounds containing active hydroxyl groups such as polyols [4,5]. During the formation of flexible polyurethane foam, water reacts with the isocyanate group and produces carbon dioxide gas. The carbon dioxide gas will provide volume for bubble expansion and occupy over 95% of the final volume of the product [6]. FPFs are highly flammable materials. The factors which further increases flammability of FPFs are their porous and open-cell structure, where the oxygen can easily pass through the foam structure [7]. It provides a serious fire hazard and it is extremely dangerous in case of fire because of toxic fumes evolved during combustion and high rate of heat release. During the combustion of flexible polyurethane foam, a substantial quantity of toxic fumes is evolved. These toxic combustion products are mainly CO, CO₂, HCN and NO₂. CO and HCN compounds are particularly dangerous. Carbon monoxide (CO) is dangerous for people at any concentration. In lower concentrations, it causes loss of movement coordination, and in higher concentrations, it may lead to sudden death. Hydrogen cyanide (HCN) is one of the most toxic gases. Only 0.011% vol. causes death after 30 to 60 minutes, and 0.025% vol. causes sudden death. The amount of smoke evolved during combustion depends on many factors, including the ambient temperature, the type of ignition, the type of combustion and the availability of oxygen [8]. For this reason foams used especially in furniture industry are required to fulfill many safety standards in order to provide health security for people [9]. Therefore, there is a large need for studies in this area. FPFs can be modified by the addition of flame retardants or by the changes in the polymer structure, which can improve thermal stability of FPFs. In recent years, a popular flame retardants used in FPF were bromine and chlorine compounds. They provide an effective way to reduce the flammability of FPF, but they are also halogen compounds that evolve dioxins, furans and other toxic substances during a fire. For this reason, these fillers have been banned in some countries (e.g., Germany). Restriction laws have also been imposed on the use of halogen compounds. For example, in February 2003 Restriction of Hazardous Substances Directive (RoHS) was adopted by the European Union. This directive restricts use of six hazardous substances including brominated flame retardants. Moreover, from 1989 exist Montreal Protocol on Substances that Deplete the Ozone Layer. The treaty is structured around several groups of halogenated substances containing chlorine or bromine compounds. These restrictions have led to the search for new fillers, that can reduce the flammability of polymers while remaining environmentally friendly and relatively safe for human health [9].

In this work carbon nanotubes were used in order to assess possibility of improving thermal stability and maintain desired physical and mechanical properties. Carbon nanotubes (CNTs) are allotropic form of carbon with a cylindrical nanostructure. They are very long and thin, with length to diameter ratio much higher than any other material. Increasingly used in many applications like aircraft or electronic products. The main advantages of CNTs are low density, good mechanical, thermal and electrical properties [10-12]. Their high aspect ratio allows to...
form a network at very low loading in the polymer matrix. This leads to improve mechanical, flame retardant and rheological properties [13]. Moreover, the price of CNTs decreased over last years. For this reasons, it was decided to use CNTs to assess properties of FPFs modified by this filler. Recently, some research has been carried out regarding the use of CNTs as a method of modification of some properties of FPFs [14,15]. CNTs are also the most widely studied nanofibrous materials as a flame retardants to polymer materials. Some studies were conducted in the area of flame retardancy of PMMA, EVA, PS, PP, PA6 or LDPE filled by CNTs [12]. The main problem related to the usage of CNTs is their poor dispersion [16,17], which is very important factor in the production process. Many research groups have focused on the possibility of improving dispersion of CNTs by theirs functionalization with many organic, inorganic and organometallic structures [18]. Furthermore, a special devices like three-roll mill or ultrasounds are used to obtain a good dispersion of carbon nanotubes in polymer matrix. These mechanical methods were tested in this study.

2 Experimental
2.1 Materials
Four types of FPFs were tested in this study. The first foam was pure flexible polyurethane foam (FPF), and the others were made with the addition of a carbon nanotubes. The polyol used to produce the FPFs was Arcol Polyol 1108 from Bayer Materials Science. Toluene diisocyanate (TDI) from Zachem S.A. was used as an isocyanate. Water was used as a blowing agent. At the beginning of the production of the FPFs, some part of the polyol was mixed with a specified quantity of the filler. Three methods of dispersion of CNTs in polyol were used: mechanical stirrer (S), ultrasounds (U) and three-roll mill (M) in order to assess which method allows to obtain the best properties of FPFs. Then, this mixture was mixed with the remainder of the polyol. In the present work FPFs with the addition of 0.25 wt % of CNTs (Nanocyl) was examined. Foams tested in this study were produced in Ciech Pianki S.A.

2.2 Methods
The characterization of the foams has been carried out using Fourier transformed infrared spectroscopy (FTIR), apparent density (AD), flexibility (F), hardness (H) and irreversible strain (IS) measurements, in order to assess the influence of CNTs on the physical and mechanical properties of tested materials. Moreover, thermogravimetric analysis (TGA), Dynamic mechanical analysis (DMA) and linear flammability (LF) tests were done to assess thermal stability and fire resistance of FPFs.

2.2.1. Physical and mechanical measurements
The apparent density tests were carried out according to PN-77/C-05012.03. The samples were measured and weighed. The value of the apparent density was calculated as a mass/volume ratio. The hardness tests were carried out according to PN-EN ISO 3386 1:2000 using a Zwick machine. Cuboid foams with sizes of 100 × 100 × 50 mm were placed in handles and compressed. The hardness value was the force required to compress the foam to 40 % of its height. Flexibility tests were conducted according to PN C 04255:1997. Three samples of 80 × 80 × 50 mm of each foam were measured. Irreversible strain tests were conducted according to PN-77/C-05012.10.

2.2.2. Fourier transform infrared spectroscopy (FT-IR)
FT-IR was performed using a Nicolet 6700 equipment. The tested samples were scanned 64 times with a resolution of 4 cm⁻¹ over the wavenumbers range from 4000-400 cm⁻¹. The spectral analyses were performed using an Omnic spectral analyser.

2.2.3. Thermogravimetric analysis (TGA)
TGA was used to analyze the thermal stability of the prepared foams. The TGA were performed using a TA Instruments TGA Q500. Samples of ~8 mg were heated to 600 °C at a heating rate of 10 °C/min in a nitrogen atmosphere.

2.2.4. Dynamic mechanical analysis (DMA)
DMA were carried out in a DMA Q800 from TA Instruments. Rectangular samples with dimensions of 10 × 10 × 5 mm were tested using a multi-frequency mode with a compression clamp. The samples were heated at a heating rate of 3 °C/min from -100 to 60 °C. The frequency of the measurements was 5 Hz.
2.2.5. Flammability measurements
Linear flammability tests were carried out according to PN ISO 3795:1996. Samples were exposed to the action of a low energy flame. During this test, the time to flame extinguishment or time to burning of the whole foam was defined.

3 Results and discussion
3.1 Physical and mechanical properties
Results obtained from physical and mechanical measurements are presented in table 1. It could be observed that addition of CNTs to FPFs leads to decrease the values of apparent density, hardness and flexibility. The lowest value of apparent density was obtained to CNTs dispersed with the usage of ultrasounds. The lowest values of hardness and flexibility were observed to foam with CNTs dispersed with the usage of three-roll mill. The value of irreversible strain was changed only in foam modified by the addition of CNTs dispersed by mechanical stirrer. Summarizing, addition of CNTs to the flexible polyurethane foam, makes only slight changes in the physical and mechanical properties, regardless of the dispersing method. It indicates, that presence of CNTs in foams does not have a huge influence on the structure of flexible polyurethane foam. This could be also observed in the values of the rise time of tested foams, which are presented in Fig. 1. Addition of CNTs to the FPFs, led to the shortening their rise time (especially to the foam with CNTs dispersed by the mechanical stirrer and ultrasounds). However, these results remain within the acceptable norms. This means that taking into account physical and mechanical properties of FPFs, CNTs could be successfully used.

3.2 Fourier transformed infrared spectroscopy
Fourier transformed infrared spectroscopy is a research technique that allows the chemical structure of a tested material to be analyzed. The influence of added fillers on changes in the chemical structure of the foams was researched. The FT-IR spectra of the investigated materials are presented in Fig. 2. The typical bonds observed in polyurethanes are presented below. The peak at 3295 cm\(^{-1}\) is assigned to the N–H stretching vibrations. The peaks at 2971 and 2867 cm\(^{-1}\) are from the asymmetric and symmetric stretching vibrations of CH\(_3\), respectively. The peak at ~1710 cm\(^{-1}\) is assigned to the stretching vibrations of hydrogen-bonded C=O groups. The peak at ~1532 cm\(^{-1}\) is from amide II (urethane N–H bending + C–N stretching). The peak at 1089 cm\(^{-1}\) is assigned to the C–O–C stretching vibrations [19-21]. Comparing spectra of modified foams with unmodified FPF, it could be seen that each typical peaks for polyurethanes are present in tested foams and only slight changes in absorbance value are present. Moreover, there are not observed additional peaks and there is no huge differences between peaks achieved to foams with different dispersion method. It means that the addition of carbon nanotubes into the flexible polyurethane foam does not have a great influence on the chemical structure of the tested foams.

3.3 Thermogravimetric analysis
Results obtained from thermogravimetric analysis are presented in table 2. From TG curves, presented in Fig. 3 and Fig. 4 there were set \(T_{5\%}, T_{50\%}\) and residue values. From DTG curves of tested materials, presented in Fig. 5 there were set \(T_{\text{max}_1}\) and \(T_{\text{max}_2}\) values. It could be observed in Fig. 5 that decomposition of FPFs occurs in two well defined stages, which is in a good convergence with polyurethane decomposition [21,22]. \(T_{\text{max}_1}\) is defined as the temperature of the maximum rate of decomposition of rigid segments in polyurethane. The addition of CNTs, regardless of the dispersion method, reduced this value in comparison with the value of FPF without fillers. This temperature is also connected with the amount of the hard segments in the macromolecule of flexible polyurethane foam. \(T_{\text{max}_2}\) corresponds to the temperature of the maximum rate of decomposition of soft segments of the polyurethane. The addition of CNTs dispersed by three-roll milling led to an increase in the value of \(T_{\text{max}_2}\), while addition of CNTs dispersed by the usage of mechanical stirrer or ultrasounds, led to an decrease in this value. The temperature corresponding to 5 % mass loss (\(T_{5\%}\)) is considered to be the initial temperature of the sample's decomposition process [23]. The value of 5 % mass loss were slightly decreased in the foams with the addition of CNTs dispersed by mechanical stirrer and ultrasounds, in comparison to the value for FPF without fillers. Higher value of this temperature was observed only in foam with the addition of CNTs dispersed by the usage of three-roll mills. The temperature of 50 % mass loss corresponds to the temperature range of the decomposition of soft
segments, and determines thermal stability of tested materials. The value of this temperature increased in each modified foams. The largest increase was observed in the foam with CNTs dispersed by the usage of three-roll mills. These results means, that addition of CNTs dispersed by three-roll milling allows to obtain foam with improved thermal stability.

3.4 Dynamic mechanical analysis
DMA is research technique that makes it possible to reveal some parameters of polymer materials, such as the glass transition temperature, the energy dissipation and the stiffness. Dynamic mechanical analysis refers to the determination of storage modulus, loss modulus and damping property subjected to the sinusoidal force. Hence this analysis provides the information on the molecular level behaviour of the polymer [24]. This analysis measures the mechanical properties of materials as a function of temperature or frequency. In this study, the storage modulus and the glass transition temperature (Tg) were estimated. These results are presented in table 3. SM values were obtained from SM curves (presented in Fig. 6). The storage modulus values describes the stiffness of the material and its ability to store energy [25]. It could be observed that the addition of CNTs makes this value lower than this value obtained to unmodified FPF. The lowest value of SM was achieved to the foam modified by the addition of CNTs dispersed by the usage of three-roll mill. This result indicates that this foam had the lowest energy absorption of the tested foams. SM value closest to FPF was achieved by foam modified with the addition of CNTs dispersed by the usage of ultrasounds. Tg values were obtained from tan δ curves, which is the most common technique of determining the glass transition temperature [25,26]. It was observed that the Tg values decreased as the result of CNTs addition. The lowest value of Tg was achieved to flexible foam modified by the addition of CNTs dispersed with the usage of ultrasounds. Foams modified by the addition of CNTs dispersed by the usage of mechanical stirrer and three-roll mill achieved the same Tg values.

3.5 Fire resistance
The linear flammability test results show that the addition of CNTs to the flexible polyurethane foams leads to improve their fire resistance, especially in foams prepared with the usage of mechanical stirrer and ultrasounds. No changes in this value were observed to foam with the addition of CNTs dispersed by the usage of three-roll mill. The lowest value of linear flammability was achieved to foam with carbon nanotubes dispersed by the usage of ultrasounds.

4 Conclusions
Results of these preliminary studies in the area of flexible polyurethane foams modified by the addition of carbon nanotubes shows, that this type of modification change physical, mechanical and thermal properties of flexible polyurethane foams. Results of measurements made in this study shows that usage of three-roll mill and ultrasounds, allows to obtain foams with desired properties. These methods could be the good dispersion methods for carbon nanotubes used as a method of modification of flexible polyurethane foams. Moreover, it was also found that, it is possible to improve thermal stability and fire resistance of flexible polyurethane foams by the addition of carbon nanotubes, but these results must be confirmed by other, more detailed measurements. For this reason, further research are needed in this area.

Acknowledgements
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Table 1. Physical and mechanical properties of FPFs.

<table>
<thead>
<tr>
<th>Material</th>
<th>AD [kg/m³]</th>
<th>H [kPa]</th>
<th>F [%]</th>
<th>IS [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FPF</td>
<td>23.7</td>
<td>3.03</td>
<td>45.0</td>
<td>2.4</td>
</tr>
<tr>
<td>FPF+CNTs_S</td>
<td>23.6</td>
<td>2.69</td>
<td>44.6</td>
<td>3.3</td>
</tr>
<tr>
<td>FPF+CNTs_U</td>
<td>23.1</td>
<td>2.48</td>
<td>43.6</td>
<td>2.4</td>
</tr>
<tr>
<td>FPF+CNTs_M</td>
<td>23.3</td>
<td>2.10</td>
<td>43.2</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Table 2. Selected parameters of FPFs obtained from TGA.

<table>
<thead>
<tr>
<th>Material</th>
<th>T₅% [°C]</th>
<th>T₅₀% [°C]</th>
<th>Residue [%]</th>
<th>Tmax₁ [°C]</th>
<th>Tmax₂ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FPF</td>
<td>238,8</td>
<td>349,7</td>
<td>1,15</td>
<td>276,9</td>
<td>372,2</td>
</tr>
<tr>
<td>FPF+CNTs_S</td>
<td>237,5</td>
<td>353,7</td>
<td>0,91</td>
<td>273,0</td>
<td>371,3</td>
</tr>
<tr>
<td>FPF+CNTs_U</td>
<td>237,5</td>
<td>354,8</td>
<td>0,96</td>
<td>274,2</td>
<td>371,6</td>
</tr>
<tr>
<td>FPF+CNTs_M</td>
<td>239,0</td>
<td>358,8</td>
<td>0,99</td>
<td>273,5</td>
<td>375,7</td>
</tr>
</tbody>
</table>

Table 3. Selected parameters of tested foams obtained from DMA.

<table>
<thead>
<tr>
<th>Material</th>
<th>Tg[kg/m³]</th>
<th>SM [kPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FPF</td>
<td>-31</td>
<td>2.8</td>
</tr>
<tr>
<td>FPF+CNTs_S</td>
<td>-34</td>
<td>2.2</td>
</tr>
<tr>
<td>FPF+CNTs_U</td>
<td>-35</td>
<td>2.5</td>
</tr>
<tr>
<td>FPF+CNTs_M</td>
<td>-34</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Fig. 1. Rise time values of tested foams.
Fig. 2. FT-IR spectra of tested foams.

Fig. 3. TG curves of FPFs obtained from TGA.

Fig. 4. TG curves of FPFs obtained from TGA.

Fig. 5. DTG curves of FPFs obtained from TGA.

Fig. 6. Storage modulus curves of FPFs obtained from DMA.
Fig. 7. Loss modulus curves of FPFs obtained from DMA.

Fig. 8. Linear flammability of tested foams.

References


bismaleimide/carbon fiber/buckypaper composites”. 


