13th INTERNATIONAL
CHEMICAL AND BIOLOGICAL
ENGINEERING CONFERENCE

ChemPor 2018

BOOK OF EXTENDED ABSTRACTS

October 02 - 04, 2018. Aveiro, Portugal

Provisional version

ORDEM
DOS
ENGENHEIROS

universidade de aveiro
theoria poiesis praxis

This volume contains the provisional version of the extended abstracts presented at the 13th International Chemical and Biological Engineering Conference (CHEMPOR 2018), held in Aveiro - Portugal, from the 2nd to the 4th of October, 2018.

University of Aveiro & Ordem dos Engenheiros

13th International Chemical and Biological Engineering Conference (CHEMPOR 2018)

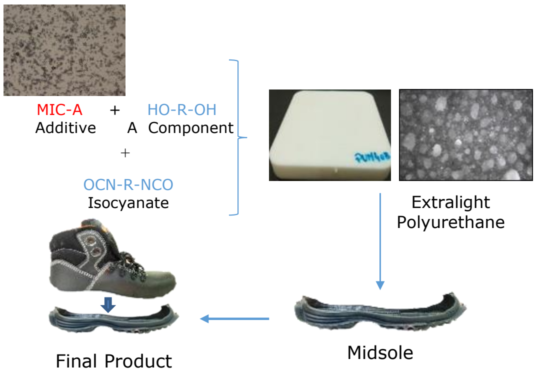
Book of Extended Abstracts

Edited by:
João Araújo Pereira Coutinho
Carlos Manuel Silva
Inês Portugal
Ana Barros-Timmons
Anabela Aguiar Valente
Dmitry Victorovitch Evtyugin
Mara Guadalupe Freire
Pedro Jorge Carvalho

universidade de aveiro
theoria poiesis praxis

Ultralight microcellular polyurethanes for the production of technical footwear components

H. Rafael[1], I.P. Fernandes[1], H.T. Gomes[1], V. Pinto[2], A.M. Fernandes[3], M.J. Ferreira[2], M.F. Barreiro[1]
[1]Mountain Research Centre (CIMO) and Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Polytechnic Institute of Bragança, Campus de Santa Apolonia - 5300-253 Bragança, Portugal
[2]Centro Tecnológico do Calçado de Portugal (CTCP), Rua de Fundões - Devesa Velha, 3700-121 S. João da Madeira, Portugal,
[3]AMF Lda, Rua São Cipriano nº 658 Tabuadelo, 4835-461 Guimarães, Portugal.
* barreiro@ipb.pt



Today's society demands lightweight and comfortable footwear products, which represents a market opportunity for the footwear industry, motivating the development of new low-density (ultralight) materials. This research is dedicated to the development of ultralight microcellular polyurethanes (PUs) with suitable properties for the production of midsoles for technical footwear. In this context, the studies performed in this work aimed at reduce the density of microcellular PUs by the incorporation of additives based on expandable thermoplastic microspheres. Samples of a base formulation were modified by the incorporation of 1, 2 and 3% of the additive. The produced materials result in PUs with densities that varied from 0.45 to 0.30 g/cm^3. The performed characterization pointed out for PUs with adequate technical properties, with particular emphasis for impact absorption, which evidenced the suitability of the developed materials for the production of midsoles for ultralight safety shoes.

Introduction

Today's society demands lightweight and comfortable footwear products, which represents a market opportunity for the footwear industry, motivating the development of low-density (ultralight) materials. In this context, the application of low density microcellular polyurethane (PU) materials is an area of interest due to low weight, cost and reduction of raw materials consumption. The materials to develop must guarantee the maintenance and/or improvement of the final footwear performance. One of the possible strategies to be used for microcellular PU density reduction involves the modification of its cellular structure, i.e., by increasing the number of cells and improve the homogeneity of their distribution within the PU physical structure. This can be accomplished through the incorporation of hollow and/or expandable microparticles into the PU formulation. However, the additive incorporation should maintain and/or improve the physico-mechanical properties of the obtained PU, which requires a systematic study in what concerns the evaluation of the used amounts and relationship with properties.

Materials and Methods

The PUs were synthetized from a polyester-based polyol and methylene diphenyl diisocyanate (MDI). It corresponds to a base chemical system used for midsoles production at industrial level. The formulation was established based on an A/B (A: polyol, chain extensor and catalyst mixture; B: isocyanate) weigh ratio of 100/76. The selected additive was a commercial grade product, based on expandable thermoplastic microspheres with an average size of 10-16 µm, named MIC-A. Two types of formulations were assayed: the base formulation (PUB, base PU without MIC-A) and the modified formulations comprising the addition of 1, 2 and 3% (w/w, PU-basis) of MIC-A. The samples were identified as follows: PUXB or PUXAY, where X is the sample number, B correspond the base formulation, A identifies the samples containing MIC-A and Y the MIC-A content used. The PU samples were produced in closed mold in order to control the density. Base PUs with target density of 45-50 (typical value), and modified PUs with target densities of 35 and 30 g/cm^3, were produced by reducing the mass of the PU mixture transferred to the mold in 30 and 40% (relative to the base PU). The adopted synthesis procedure consisted on the mixture of the polyol, chain extensor, catalyst and MIC-A (when used) during 10 minutes at 500 rpm, under heating at 45°C. Next, the amount of the required MDI was added and the stirring was increased for 1500 rpm until the gel time was achieved (typically 5 s). After, a controlled amount of the reactive mixture was rapidly transferred to the mold, and the lid was set and fixed. Then, the PU was left to cure inside the mold during 240 s. After this time period, the PU was demolded and stored at ambient temperature in the absence of the light, for further studies. The PUs cellular structure was characterized by optical microscopy (OM), using a Nikkon Eclipse Ni-U optical microscope, equipped with a digital camera and the software NIS Elements Br. The cells size was measured based on the objectives calibration. Fourier Transform Infrared Spectroscopy (FTIR) was used to evaluate the effect of the additives incorporation on PU chemical structure. PUs spectra were obtained in ATR mode using a FTIR (ABB Model MB3000) equipped with a diamond crystal. The spectra were acquired in the range between 550 and 4000 cm^{-1} using a resolution of 16 cm^{-1}, and by co-adding 32 scans per minute. The PUs density was evaluated according to the ISO 2420:2002 standard, and the impact absorption properties evaluated according to the Footwear Technological Center (CTCP) internal method using a flat base punch. The return energy and the maximum deceleration are the most relevant parameters in the assessment of the material's impact absorption properties. The reference values are: maximum deceleration $\leq$280 m.s^{-2} and energy return between 30% and 50%, being these values established for complete footwear.

Results

The assessment of the cellular structure by OM allowed to observe differences between the base PU and the modified ones (MIC-A incorporation). Figure 1 shows the images of OM obtained for all the PU samples. By comparing the obtained images, a reduction of cell size was noted as the MIC-A content increases; namely the size varied from 16-286 µm for the PUB sample to 5-157 µm for the PU5A3. Regarding cells homogeneity, the appearing of a rise amount of cells will small size was evidenced, as the MIC-A content increased. Also, the presence of the MIC-A on the cell wall was identified, allowing the reduction of the cell wall density and, consequently, the final PU density. The density results are described on Table 1. Analyzing these data, it can be noticed that the PU density varied from 0.50 for sample PUB1 to 0.30 g/cm^3 for PU5A3. These values are in good agreement with the experimental strategy implemented for the PU samples production, once the PU mass transferred to the mold was reduced in 30% and 40%, respectively for the target densities of 0.35 and 0.30 g.cm^{-3}.

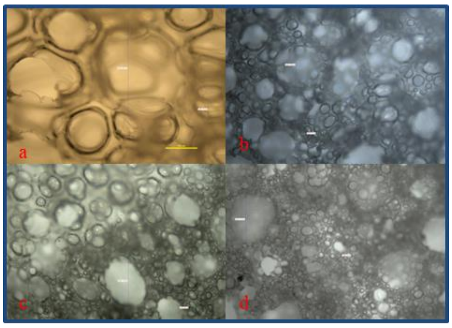


Figure 1. OM images of microcellular PUs (magnification 100 X): (a) base formulation (PUB) and formulations modified with different MIC-A contents: (b) (PUA1) 1%; (c) (PUA2) 2%; and (d) (PUA3) 3%.

Regarding PUs FTIR analysis, namely the spectra shown in Figure 2, the vibration assigned at 3330 cm^{-1} correspond to the NH stretching from the urethane, while the one at 1720 cm^{-1} is identified as the carbonyl groups from the urethane and ester (polyol) stretching, being maintained in all samples. Moreover, when comparing the PUB spectrum with those of the modified samples, no additional vibrations are identified, pointing for the absence of chemical reactions between the additive and the PU matrix. Thus, it can be concluded that the MIC-A incorporation has no influence on the chemical structure of the resultant PU.
Relatively to the impact absorption properties, these are related with the comfort characteristics. The dynamic analysis of the material ability to absorb the impact on the heel, when subjected to a standard impact weight, is correlated with the degree of impact absorption of the material. The maximum deceleration and the percentage of energy are the most important properties once they represent, respectively the damping and resilience. Regarding to the maximum deceleration, lower values represent a better capacity to absorb the impact. On the other hand, higher values of energy return show an improved resilience. Regarding the results of the impact absorptions of the PUs, presented on Table 1, a general analysis shows that all the produced PUs present values of maximum deceleration and energy return that fulfill specifications values: maximum deceleration $\leq$280 m.s^{-2} and energy return between 30% and 50%, despite these values being established for complete footwear (composed by midsole and sole), which is expected to have higher performance. It can be also noted that: (1) The maximum deceleration values varied between 183-266 m/s^2 while the return energy varied between 36-46%; (2) The base formulation sample, PUB2 (density 0.45 g/cm³) has the lowest value of maximum deceleration (183 m/s^2) and the highest value of energy return (46%); (3) The samples PU1A2 (density 0.36 g/cm^3) and PU2A3 (density 0.34 g/cm^3) show a maximum deceleration values of 201 m/s^2 and 186 m/s^2, respectively, and an energy return value of about 37%. Moreover, the density reduction results, in a general way, in PUs (PU3A1, PU4A2 and PU5A3) with higher maximum deceleration values, increasing from 210.29 to 232.93 m/s^2 with the rise of MIC-A content from 1 to 3%. However, the energy return of this samples does not present a similar behavior, since it varies from 36.34% to 40.73% when the MIC-A content rises from 1 to 2% (PU3A1, PU4A2), while for a MC-A content of 3% the energy return decreased to about 35.94% (PU5A3). Based on these results, it can be concluded that the low density PUs, present adequate impact absorption properties, being suitable for the production of midsoles for ultralight safety shoes.

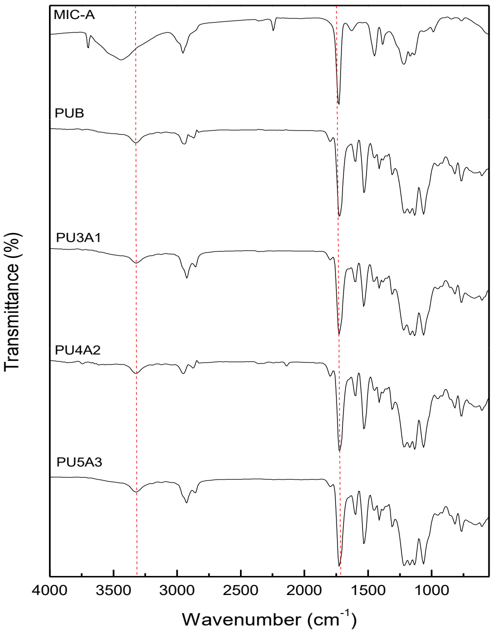


Figure 2. FTIR spectra for PU base formulation and PUs modified with 1, 2 and 3% of MIC-A.

Conclusion

This work presented a simple strategy that allows the production of low density microcellular PUs. The tested additive proved to be suitable to reduce PUs density without impair material's physico-mechanical properties. The impact absorption properties evidenced the suitability of the developed PUs for the production of midsoles for ultralight safety shoes.

Table 1. Impact absorption values of the produced PUs.

Sample	**Density (g.cm^{-3})**	**Maximum Deceleration (m.s^{-2})**	**Return Energy (%)**
PU1B	0.50	266.64	42.88
PU2B	0.45	183.03	46.04
PU1A2	0.36	201.09	36.76
PU2A3	0.34	186.18	37.22
PU3A1	0.31	210.29	36.34
PU4A2	0.31	225.22	40.73
PU5A3	0.30	232.93	35.94

Acknowledgements

POCI-01-0145-FEDER-006984 (LA LSRE-LCM) and UID/AGR/00690/2013 (CIMO), financed by FEDER, through POCI-COMPETE2020 and FCT. Project n.º 017570 - Extra LightSafeShoe – Development of polymeric solutions for technical footwear, co-financed by COMPETE2020 through PT2020 and FEDER.