GCNPM 2018

9th Conference

Green Chemistry and Nanotechnologies in Polymeric Materials

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Cracow, Hotel Qubus

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Faculty of Chemical Engineering and Technology

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Wednesday, 10.10.2018

17.00 - 20.00 Registration
19.00 - 21.00 Welcome Reception

Thursday, 11.10.2018

8.30 - 13.00 Registration
9.00 - 9.15 Conference Opening

I Session - Chairmen: Salvatore Iannace and and Dariusz Bogdał

9.15 **Keynote Lecture:** Ali Rizvi, Adel Ramezani Kakroodi, Chul B. Park: *Nanofibril technology for enhancing the mechanical properties and foaming ability*

9.50 Tamara Calvo-Correas, O. Echeverria, M. Angeles Corcuera, Arantxa Eceiza: *Impact of the combined use of magnetite nanoparticles and cellulose nanocrystals on shape-memory behaviour of polyurethane bionanocomposites*

10.15 Jana Kredatusová, Hynek Beneš, Sébastien Livi, Petra Ecorchard, Magdalena Konefał, Ewa Pavlova: *Poly(butylene adipate-co-terephthalate)/layered double hydroxide nanocomposites via in-situ polycondensation*

10.35 Jolanta Pulit-Prociak, Anita Staroń, Paweł Staroń, Jarosław Chwastowski, Sławomir Michałowski, Elżbieta Sikora, Marcin Banach: *Preparation of utility composites with the addition of silver nanoparticles*

10.55 - 11.25 Coffee break

II Session - Chairmen: Leonard Szczepkowski and Aleksander Prociak

The session dedicated to prof. Jan Pielichowski

11.25 **Keynote Lecture:** Tomasz Sterzyński*: Highly resistant thermoplastic composites with natural fibers; ecological aspects*

12.00 Dariusz Bogdał: *Intensification of oxidation and epoxidation reactions – microwave vs. conventional heating*

12.25 Paweł Chmielarz, Piotr Król: *Synthesis of well-defined polymers by atom transfer radical polymerization*

12.45 Anna Sienkiewicz, Piotr Czub, Karolina Pach: *Studies on the enzymatic degradation of epoxy-polyurethane materials based on modified vegetable oils*

13.05 Katarzyna Bialik-Wąs, Anna Ledwoń, Paweł Obrok, Rafał Bogucki: *Influence of different crosslinking methods on the properties of modified alginate hydrogels*

13.25 - 15.00 Lunch

III Session - Chairmen: Chul B. Park and Krzysztof Pielichowski

15.00 Andrea Lazzeri, Maria Kurańska, Aleksander Prociak, Andres Torres Nicolini, Ilaria Canesi, Patrizia Cinelli, Doriana Morganti: *Epoxidised used cooking oil as a reactive plasticizer for PLA*

15.25 Isabel P. Fernandes, Hélder M. Rafael, Albano M. Fernandes, Bernardo Nunes, Vera V. Pinto, Maria J. Ferreira, Maria Filomena Barreiro: *Development of new footwear materials within the Extralight Safe Shoe project*

15.50 Dawid Stawski, Stefan Połowiński, Izabella Krucińska, Zbigniew Draczyński, Lucyna Herczyńska: *Polylactide and its copolymers as a green alternative for synthetic polymers*

Development of new footwear materials within the Extralight Safe Shoe project

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Introduction

At present, footwear is considered as one of the most internationalized sectors of the Portuguese industry, having a major importance for the national economy, as it is proved by 2017 economic data: 83.3 billion shoes pairs were exported, representing an average value of 1.96 billion euros [1]. The remarkable progress of the footwear sector is strongly related with the investment in research and technological development made in the last years, along with an attentive surveillance of the market opportunities, which in its turns, allows the identification the latest consumer demands and of new business opportunities. One example of these novel tendencies is the actual society demand for lightweight and comfortable footwear, which prompted the development of ultralight (low-density) materials. Additionally, the evolution of consumers' environmental awareness, allied to the demand for bio-products, is considered a challenge for the footwear sector. Thus, both challenges motivated the development of new materials within the scope of the Extralight Safe Shoe project, namely ultralight microcellular polyurethanes and natural composite-based materials. In this context, the work performed was focused on: (i) the development of ultralight microcellular polyurethanes (PUs) with suitable properties for the production of midsoles for technical footwear, and (ii) the development of lighter and more flexible PU/cork composites for production of insoles.

Regarding the development of ultralight microcellular PU, the reduction of the PU density leads to the decrease of the raw-materials consumption promoting energy saving, together with weight reduction and footwear comfort increase. However, the materials to develop must guarantee the maintenance and/or improvement of the footwear's performance. One possible strategy for the microcellular PU density reduction involves the modification of the 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. These additives will be preferably located at the cell wall, leading to the density reduction of the final PU. Nevertheless, the effect of additives incorporation in the physico-mechanical properties of the PU must be evaluated. This requires a systematic study to determine the relationship between the used additive amount and the PU properties, namely in what concerns the impact absorption capacity.

In a general way, the obtained results evidenced the success of the adopted strategy at laboratorial level once the addition of the additive at a content of 3% (w/w, PU-basis leads to PUs with densities comprised between 0.35 and 0.30 g/cm^3, corresponding to a reduction of 30-40% comparatively with the base formulation (without additives), which is roughly 45 g/cm^3. Figure 1 shows the laboratorial set-up developed for the microcellular PUs synthesis, under controlled rise conditions. The evaluation of the impact absorption properties showed that the low density PUs are suitable for the production of midsoles, having in view ultralight safety shoes production. Moreover, the developed solution are being tested at industrial scale at the Portuguese footwear company AMFShoes.

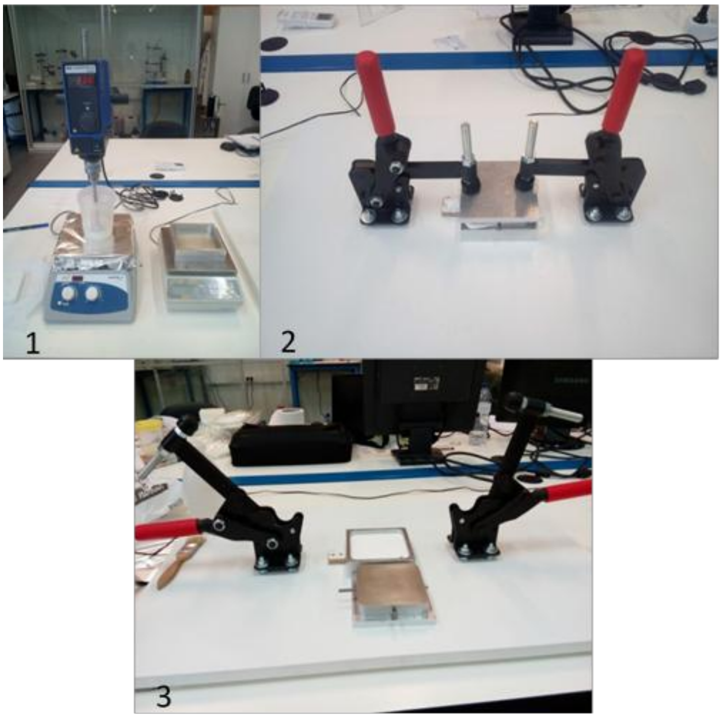

Fig. 1. *Experimental set-up used for the ultralight microcellular PU synthesis at laboratorial scale: (1) reactive mixture stirring and heating; (2) mold lid fixation system, and (3) system opening and PU demolding*.

Concerning the PU/cork composites for lighter and flexible insoles, the adopted strategy started with the identification of the main drawbacks of the traditionally used cork composites. One of these drawbacks is related with their low water absorption capacity, which is related with the hydrophobic character of the cork itself and the binder used for cork agglomeration. These features result in the low absorption of the sweat, promoting feet discomfort. Another drawback is related with the binder chemical nature, once it typically uses toluene diisocyanate (TDI), demanding their replacement by more friendly alternatives. Therefore, based on these issues, the adopted strategy comprises the substitution of the TDI-based binder by greener solutions such as water-based adhesives, the improvement of the water absorption properties through the incorporation of residual biomass, and the increasing in flexibility through the incorporation of recycled microcellular polyurethanes. This later solution will contribute for the integral valorization of the microcellular PU residues, which find application as raw-materials in the development of new materials. Moreover, the presence of the grinded PU residues as particles distributed along the cork composite matrix, is expected to act as elastic points increasing flexibility. Additionally, this strategy will be advantageous from an economical perspective, once it will reduce the cost associated with residues storage, transportation and deposition in landfills. The overall results pointed out the impact absorption properties increase, while the flex resistance was similar to the base formulations (without PU residues). These results evidenced a suitable behavior of the produced composites, having in view their utilization as footwear insoles. Figure 2 shows examples of the produced insoles

Considering the different approaches adopted for the development of PU/cork composites for lighter and flexible insoles production, the overall tested strategies, namely, the replacement of the TDI-based binder, incorporation of biomass residues, and of recycled microcellular PUs, resulted in the development of several formulations/products with improved properties, conforming the target applications. At this stage, these strategies are being tested and validated at industrial level by the 3DCork company.

Fig. 2. *Insoles samples produced by adding the grounded microcellular PU residues*.

Conclusions

This work presents the overall goals and results of the Extralight Safe Shoe project, considering the development of ultralight microcellular polyurethanes (PUs) with suitable properties for the production of midsoles for technical footwear, and (ii) the development of PU/cork composites for the production of lighter and flexible insoles. The best solutions, already validated at laboratorial level, are under industrial testing corroborating the interest and viability of the proposed strategies.

Acknowledgements

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References

1. APICCAPS, *Facts and Numbers 2018*.