6 WORKSHOP

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WORKSHOP PROCEEDINGS

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P43. THE USE OF BIO-BASED ADDITIVES (LIGNIN, STARCH AND CELLULOSE) IN THERMOPLASTIC POLYURETHANE FORMULATIONS TO ENHANCE THE BIODEGRADABILITY OF FOOTWEAR COMPONENTS

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Introduction

Thermoplastic polyurethanes (TPUs) are one of the most widely used polymeric materials. They can be used in an extensive range of applications, including automotive, footwear, interior design, adhesives, coatings, textile and biomedical. In what concerns the footwear sector, it is estimated that TPU based components represent about 60% of the whole European production of footwear components [1]. On the other hand, the use of a wide variety of additives in TPU formulations (e.g. pigments, coatings and fillers) limits the possibility of recycling. In such scenario, biodegradable polymers could offer an excellent solution to the environment hazard posed by the conventional materials [2]. Therefore, given the widespread use of TPUs and associated waste management problems, it makes sense to invest on the development of more biodegradable and environmental compatible solutions. For this purpose, the incorporation of bio-based and biodegradable additives is being studied in the last years [2-4]. The incorporation of a biodegradable compound, even at a low content in a TPU formulation, can promote biodegradation. It will constitute a preferential site for microorganisms' attack thus favouring biodegradation initiation and progression.

In this work, a base TPU used in the footwear industry was modified by compounding with three bio-based additives (lignin, starch and cellulose). Biodegradability of the resulting materials was evaluated in agar plate tests against the fungi *Aspergillus niger* ATCC16404, the gram negative bacteria *Pseudomonas aeruginosa* ATCC9027 and an association of both (consortium). In a second phase soil tests have been also performed.

Experimental

Strategy. Compounding with bio-based additives was chosen as a straightforward approach to increment biodegradability of a selected polyester-based TPU used in the footwear industry. The chosen bio-based additives were: (1) Sarkanda lignin (2) potato starch, and (3) microcrystalline cellulose Avicell PH101.

Samples. Samples have been prepared by the casting method. Samples of the base TPU (used as control) and the TPU mixed with the chosen additives at a content of 4% (w/w) have been produced. Briefly, the TPU pellets were dissolved in dimethylformamide (DMF) resulting in a homogeneous solution with 47.0% (w/w) of non-volatile content. For lignin incorporation, a solution of sarkanda lignin at a concentration of 0.195 g/ml was prepared in DMF. The microcrystalline cellulose was suspended in DMF being the final concentration 0.0935 g/ml. For the potato starch, a mixture with glycerol was prepared at ratio of 3:2 (w/w). The TPU was mixed with different amounts of each additive solution/mixture, in order to obtain a final concentration of 4% (w/w), following by vigorous stirring during 10 minutes to promote homogenization. Then, the mixture was degasified under reduced pressure prior to the cast in a round Teflon mould with a diameter of 10.2 cm. Finally, the TPU films were dried first at 105 ºC during 12 h followed by additional drying at 60 ºC during 24 h under reduced pressure.

Biodegradation assays. Biodegradation assays were performed in agar plates using TPU samples with a dimension of 6x6 mm. The agar was inoculated using the fungi *Aspergillus niger* ATCC16404, the gram negative bacteria *Pseudomonas aeruginosa* ATCC9027 or an association of both (consortium). These microorganisms were selected based on previous screening study comprising a wide range of microorganisms, including both bacteria and fungi. The assays were performed on agar plates containing Sabouraud dextrose agar or Nutrient agar, for *A. niger* and *P. aeruginosa*, respectively. For the assays with the consortium, Sabouraud dextrose agar plates were inoculated both with *P. aeruginosa* and with square samples (1x1 cm) of *A. niger* mycelium. The plates were incubated for 30 days at 30 ºC for *A. niger,* and 37 ºC for *P. aeruginosa* and the consortium. All biodegradation assays have been performed in duplicate. For the biodegradation assays in soil, square samples (1x1 cm) were introduced in a soil medium (organic matter >45% (w/w), moisture=65% (w/w)) during 6 months, being the samples biodegradation evaluated in a monthly basis. Two temperatures (37 and 58 ºC) were assayed. For both tests (agar plate and soil), biodegradation was evaluated as weight loss, after sample recovery, washing with ethanol and drying at ambient conditions. All the samples weights were considered stable when the difference between two consecutives values was inferior to 2.0 mg.

Results and discussion

Concerning sample degradation in the agar plate tests, the weight loss was slightly higher in the assays performed with *P. aeruginosa*, when compared with the ones carried out with *A. niger*. However, the weight loss improved significantly when using the consortium *P. aeruginosa + A. niger* (Fig.1 (a)). These results evidence the existence of a synergistic activity between fungal and bacterial degradation. In what concerns the tested additives, lignin (TPU+4L) gave the best results for both tests with the isolated microorganisms, while with the consortium the best results were achieved with cellulose (TPU+4C). Regarding the biodegradation assays performed in soil at 37 ºC, the higher weight loss after 6 months was 36.6% for the sample TPU+4L, while for the base TPU only 10.5% was achieved. For the soil test at 58ºC (Fig. 1 (b)) the maximum weight loss for the base TPU was 37.0% (6 months period), whereas the samples modified with additives presented weight losses above 50% after the 4th month, with partial disintegration being observed for the sample TPU+4L. For the 5th and 6th month sampling, samples' recovering was not possible due to its high level of disintegration.

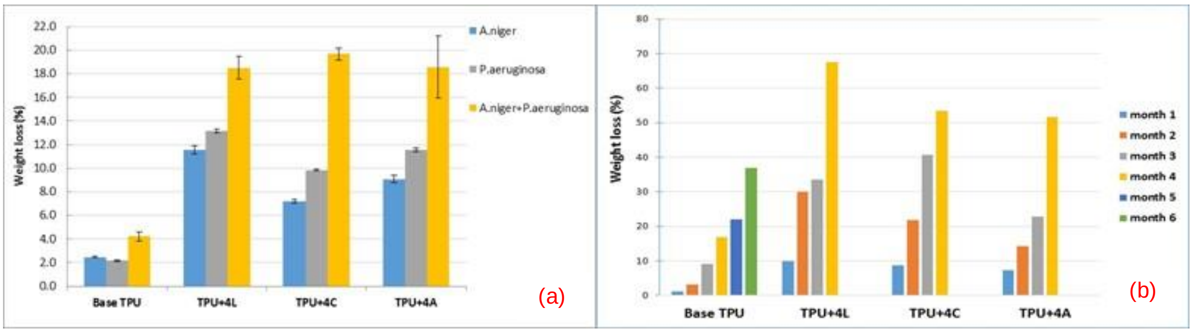

Fig. 1. Weight loss of TPU samples achieved in: (a) the agar plate tests with *A. niger*, *P. aeruginosa*, and the consortium (1 month), and (b) the soil tests at 58ºC (monthly sampling till 6 months).

Conclusions

The results obtained with both methodologies evidenced the positive effect of the tested bio-based additives (lignin, cellulose and starch) on TPU biodegradability, being the most favourable results registered for the samples modified with 4% of Sarkanda lignin.

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References

[1] T. Staikos, R. Heath, B. Haworth, S. Rahimifard, Proceedings of the 13th CIRP International Conference on Lyfe Cycle Engineering (2006) 497-502.
[2] M. Flieger, M. Kantorová, A. Prell, T. Rezanka, J. Votruba, Folia Microbiologica, 48 (2003) 27.
[3] L. Ignat, M. Ignat, C. Ciobanu, F. Doroftei, V.I. Popa, Industrial Crops and Products, 34 (2011) 1017.
[4] C. Ciobanu, M. Ungureanu, L. Ignat, D. Ungureanu, V.I. Popa, Industrial Crops and Products, 20 (2004) 231.