Biobased Additives as Biodegradability Enhancers with Application in TPU-Based Footwear Components

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ABSTRACT: Among the wide variety of materials employed in the manufacture of shoes, thermoplastic polyurethanes (TPUs) are one of the most widely used. Given its widespread use, and associated waste management problems, the development of more biodegradable and evironmentally compatible solutions is needed. In this work, a polyester-based TPU used in the footwear industry for outsoles production was modified by compounding with lignin, starch and cellulose at content of 4% (w/w). The biodegradability was evaluated by using agar plate tests with the fungi *Aspergillus niger* ATCC16404, the Gram-negative bacteria *Pseudomonas aeruginosa* ATCC9027 and an association of both (consortium), and soil tests at 37 °C and 58 °C. The obtained results evidenced a positive effect of the tested biobased additives, the most favourable results being registered with lignin. These results were corroborated by the structural modifications observed by FTIR analysis. Additionally, mechanical tests prove the suitability of using the lignin modified TPUs for footwear outsoles production.

KEYWORDS: Thermoplastic polyurethanes, biodegradation, compounding, biobased additives

1 INTRODUCTION

At present, footwear is considered as one of the most internationalised sectors of the Portuguese industry of significant importance to the national economy. This sector seeks to affirm itself in market niches with high technical and scientific requirements, value-added properties and high quality standards, resulting in a demanding research and technological development investment. Moreover, there has been an increasing interest in reducing the environmental impact of this sector by seeking more sustainable and biobased solutions. Among the extensive range of materials employed in shoe production, polymers are mostly used since they can cover a versatile array of properties in terms of strength, lightness, durability and resistance to degradation; with thermoplastic polyurethanes (TPUs) assuming a dominant position [1].

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In the footwear industry, it is estimated that TPU-based footwear components represent about 60% of the entire European production of footwear components. Due to the presence of diverse additives (e.g., pigments, coatings, and fillers), TPUs are not easily recycled, being biodegradable solutions an excellent way to minimise the environmental hazard posed by their disposal [2]. In this context, renewable biobased carbon feedstocks are attracting considerable interest; they present the intrinsic value of a reduced carbon footprint and an improved lifecycle analysis, in agreement with a sustainable development. Hence, it is expected that the forthcoming materials for daily uses, such as footwear components, will be increasingly generated from biomass [3].

In a general way, polyurethanes can present a certain degree of biodegradability, which varies as a function of composition, processing and environmental conditions. However, their biodegradation rates are considerably low and may be improved by the incorporation of biodegradable structural units in the polymer backbone [4]. In this manner,

biodegradable TPUs can be envisaged by using biobased polyols [3, 5–10], isocyanates [11–13] and chain extenders [6, 14]. However, they can present limited mechanical properties for shoe sole applications, making it necessary to develop strategies towards their improvement, e.g., reinforcement with inorganic nanoparticles [14]. Biodegradability can also be enhanced by incorporating biodegradable fillers, such as lignin [5, 15, 16], lignocellulosic residues [17] or starch [18], among others, which can act as preferential sites for microorganisms to attack, thus favouring biodegradation initiation and progression. Previous works have reported that polyurethanes, especially the polyester-based ones, can be biodegraded by a wide range of microorganisms [19]. Ester bonds are known to be labile to enzymatic activity and hydrolysis, in opposition to their ether counterparts, which are more resistant [14, 20–22]. Regardless of the polyurethane type, the microbial degradation process must consider the degradation of the urethane bonds and that of the polyol segments [23]. Concerning microorganisms, fungi act mainly through colonization and production of various extracellular enzymes that breakdown the ester, urethane and urea groups into smaller components [24]. For some strains of bacteria, e.g., *Pseudomonas sp.*, the produced enzymes enable bacteria adhesion to the TPU surface with consequent hydrolysis to metabolites [25].

In this work, a straightforward approach was applied to enhance the biodegradability of a polyester-based TPU used in the footwear industry for the production of soles. The adopted strategy consisted in modifying the base TPU through compounding with different biobased additives (lignin, starch and cellulose), following a set of previous studies of our group dealing with commercially available solutions with limited results [26]. The biodegradability of the resulting materials was evaluated by means of agar plate tests and biodegradation assays in soil. These methodologies were selected as they are described in the literature as being the most frequently applied for this purpose [20, 24, 27–31]. Structural modifications of the TPUs subjected to the biodegradation tests were inspected by FTIR spectroscopy. Based on the obtained results, the best formulation was selected for outsoles production at a pilot scale. The mechanical properties of the modified TPUs' outsoles, including hardness (Shore A), density, abrasion resistance, tear strength, tensile strength and elongation at break, flex resistance and fatigue resistance, were assessed in order to evaluate the maintenance of the functional characteristics related to footwear performance and wearability.

2 EXPERIMENTAL

2.1 Materials

A polyester-based TPU was supplied by Procalçado, S.A., a Portuguese footwear company. The Sarkanda lignin was obtained from Granit S.A. (Switzerland) and microcrystalline cellulose Avicel PH101 was acquired from Sigma-Aldrich (USA); dimethylformamide and the potato starch were purchased from Panreac Química (Spain), while glycerol was obtained from Scharlab (Spain). The agar, the Sabouraud dextrose agar, the fungi *Aspergillus niger* ATCC16404 and the bacteria *Pseudomonas aeruginosa* ATCC9027 were purchase from Liofilchem Bacteriology Products (Italy), while the Cetrimide agar was purchase from HiMedia Laboratories (India).

2.2 TPU Samples Preparation

Samples of the base TPU (used as control) and the TPU mixed with the chosen additives at a content of 4% (w/w) were prepared by the casting method. Briefly, the TPU pellets were dissolved in dimethylformamide (DMF), resulting in a homogeneous solution with 47.0% (w/w) of nonvolatile content. For lignin incorporation, a solution of Sarkanda lignin at a concentration of 0.2 g/ml was prepared in DMF. The microcrystalline cellulose was suspended in DMF with a final concentration of 0.1 g/ml. For the potato starch, a mixture with glycerol was prepared at a 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), followed by vigorous stirring for 10 minutes to promote homogenization. Then, the mixture was degasified under reduced pressure prior to casting in a round Teflon mould with a diameter of 10.2 cm. Finally, the TPU films were dried, first at 105 °C for 12 h, followed by additional drying at 60 °C for 24 h under reduced pressure.

2.3 Biodegradation Assays

Biodegradation assays were performed in agar plates using TPU samples of 6 × 6 mm and thickness of 2.0 mm. The agar was inoculated using the fungi *A. niger* ATCC16404, the Gram-negative bacteria *P. aeruginosa* ATCC9027 or an association of both (consortium). 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 *P. aeruginosa*, the inoculum was adjusted to approximately 0.5 McFarland turbidity standard and spread over the agar plates. The TPU sample was aseptically

transferred to the agar surface and inoculated with 100 µL of the *P. aeruginosa* inoculum. The degradation assays with *A. niger* were performed as previously described [20]. Briefly, a concentrated spore suspension was prepared by scraping the *A. niger* mycelium with a sterilized loop. The suspension was filtered to remove agar and mycelium residues and centrifuged (15 min, 4000 rpm). The obtained pellet was resuspended in 5 mL sterile distilled water, used for spore count in a Neubauer chamber and diluted to a final concentration of approximately 1×10^6 spores/mL. The agar plates were spread with the spore suspension, which was also used for sample inoculation (100 µL). For the assays with the consortium, Sabouraud dextrose agar plates were inoculated both with the described *P. aeruginosa* inoculum solution and with square samples (1 × 1 cm) of *A. niger* mycelium. The plates were incubated for 30 days at 30 °C for *A. niger*, and at 37 °C for *P. aeruginosa* and for the consortium. All the biodegradation assays done in agar plates have been performed in duplicate. For the biodegradation assays in soil the procedure established was designed according to the general guidelines of the ISO 20200:2004 standard [32]. Briefly, square samples (1 × 1 cm, thickness 2.0 mm) of all TPUs were introduced in a soil medium (organic matter > 45% (w/w), moisture = 55% (w/w)) during 6 months, being the samples biodegradation evaluated on a monthly basis. Two temperatures (37 °C and 58 °C) were assayed.

2.4 Weight Loss Determination

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 sample weights were considered stable when the difference between two consecutive values was inferior to 2.0 mg. The weight loss was calculated according to the formula:

$$\text{Weight Loss}(\%) = \left(\frac{wi - wf}{wi}\right) \times 100 \qquad (1)$$

where: *wi* is the initial weight of the sample and *wf* is the weight of the sample after the biodegradation test.

2.5 FTIR Analysis

The FTIR spectra were collected on a PerkinElmer FTIR spectrometer (model Spectrum BX, USA) in transmittance mode, operating in attenuated total reflectance (ATR) with a Golden Gate single reflection diamond crystal (Specac, USA). Spectra were recorded between 650 and 4000 cm^{-1} at a resolution of 4 cm^{-1} and co-adding sixteen scans. The base TPU and the modified TPU samples, before and after being submitted to the biodegradation tests, were analysed without any previous preparation. No baseline correction or spectra normalization have been performed.

2.6 Outsole Prototype Production and Mechanical Properties Evaluation

The outsole prototypes, based on the best performing formulation according to the biodegradation assays (TPU+4L), were produced at pilot scale by using an injection moulding machine (Main Group Technologies Srl, Italy). Briefly, the TPU and lignin were mixed at the desired proportion and homogenised at a temperature ranging from 170 °C to 190 °C (from feeding to metering zone). The mould was filled at an injection pressure above 100 bar. The produced outsoles were characterized with regard to Shore A hardness, density, abrasion resistance, tear strength and elongation, flex and fatigue resistance.

The Shore A hardness measurement was done using an Affri durometer (Italy) according to ISO 868:2003 standard. Density was determined according to ISO 2781:2008 standard. Abrasion resistance was evaluated as referred to in the EN 20871:2001 standard using outsole test pieces on Pegasil abrasion equipment by ZIPOR (Portugal). The tear strength was measured according to ISO 20872:2001, the tensile strength and elongation were determined following ISO 22654:2001 using a Pegasil Jupiter model dynamometer by ZIPOR (Portugal). The flex resistance was evaluated by applying the ISO 17707:2005 standard using a "Bennewart" flexing machine with cold chamber from Pegasil (ZIPOR, Portugal). The fatigue resistance (Ross Flex) was determined according to BS 5131-2.1:1991 using a "ROSS" flexing machine from Pegasil by ZIPOR (Portugal).

3 RESULTS AND DISCUSSION

3.1 Biodegradation Assays

In this work, compounding with biobased additives (lignin, starch and cellulose) was attempted as a strategy to improve TPU biodegradation. According to Ignat and coworkers, the incorporation of 4% of lignin in a polyester-based polyurethane increased the biodegradability, while TPU blending with starch plasticized with glycerol has also been reported to improve the TPU biodegradability [15, 18]. Microcrystalline cellulose is a biodegradable biopolymer used as standard material in biodegradation evaluation according to the

ISO 14855-1 standard [33]. Moreover, studies of TPU reinforcement with microcrystalline cellulose have also been reported [34, 35].

First, the biodegradability of three modified TPUs was evaluated by using the agar plate test with the Gram-negative bacteria *P. aeruginosa* and the filamentous fungi *A. niger*, as both microorganisms are referred to as being able to degrade polyester-based polyurethanes [19, 25, 36, 37]. The selection of these microorganisms was also based on a previous screening study comprising a wide range of microorganisms, including both bacteria and fungi (data not shown). Additionally, the consortium *P. aeruginosa* + *A. niger* was also tested since a superior biodegradation performance is generally reported with microorganisms' consortium compared to single microbial strains. However, studies on the biodegradation activity of specific *fungi* + *bacteria* consortium concerning polymers in general, and TPU in particular, are still scarce [37], with most works performed so far focusing on the biodegradation of persistent organic pollutants.

Subsequently, the modified TPU samples were also tested for biodegradation in soil at 37 °C and 58 °C during 6 months, to assess the mesophilic (37 °C) and thermophilic (58 °C) microorganisms' ability to degrade these samples. Also, the assay at 58 °C allows simulating the real composting conditions.

3.1.1 Biodegradation in Agar Plate

In a first approach, agar plate tests were performed to evaluate if the TPU samples could inhibit the bacteria and/or fungi growth. Visually, it was possible to observe the growth of mycelium or the formation of a biofilm on the samples' surface, for fungi and bacteria respectively. To confirm bacteria viability, the biofilm was recovered and inoculated in a selective agar for *P. aeruginosa* isolation (cetrimide agar). After incubation the viability was confirmed by bacteria growth and the appearance of a typical blue-green pigmentation around the colonies. Regarding the consortium *P. aeruginosa* + *A. niger*, the visual observation of plates during the incubation period showed a faster growth of bacteria than that of fungi. Regarding the samples' weight loss, as expected and regardless of the tested microorganism, modest weight loss percentages were achieved for the base TPU sample (Figure 1). Also, the sample degradation was slightly higher in the assays performed with the fungi when compared to the bacteria, with best results being achieved for the consortium *P. aeruginosa* + *A. niger* (Figure 1); even so, the higher weight loss registered was around 4.0%. Hence, this modest biodegradation rate highlighted the need for modification of the polyester-based TPU to increment its biodegradability. Concerning the degradation of the TPU samples containing lignin (TPU+4L), starch (TPU+4S) and cellulose (TPU+4C), the weight loss was slightly higher in the assays performed with *P. aeruginosa*, when compared with the ones carried out with *A. niger* (Figure 1). The weight losses registered with *P. aeruginosa* were 13%, 10% and 11% for the samples TPU+4L, TPU+4C and TPU+4S, respectively. For *A. niger* the weight losses were slightly lower, namely 11% for TPU+4L, 7% for TPU+4C and 9% for TPU+4S, which can also be related to the inoculum type since *A. niger* was inoculated in sporal form, thus the first week of incubation was needed for its growth and complete spreading of the mycelium, while *P. aeruginosa* growth occurred in the first 24 hours of incubation and thereafter. When using the consortium *P. aeruginosa* + *A. niger* the weight loss improved significantly for all the samples (Figure 1), with the higher values achieved being around 20% for the TPU+4C. In this case, *A. niger* inoculation was performed using the fungi mycelium, which allowed a much faster growth, with the plates being completely covered by the mycelium after the second day of incubation. The inoculation in sporal form was not feasible since its growth was much slower and it would be inhibited by the bacteria colonies completely developed. As can also be observed in Figure 1, the obtained weight loss results evidenced the existence of a synergistic activity between fungal and bacterial degradation, which can be a result of the combined potential of the consortium to produce enzymes with catabolic activity [37]. This behaviour can be a possible outcome of the different mechanisms used by both microorganisms for attacking the TPU sample, since the *A. niger* access the sample through mycelium growth and production of extracellular enzymes that breakdown the molecular chains of the TPU favouring the access of the *P. aeruginosa* enzymes to accomplish further degradation. Concerning the tested additives,

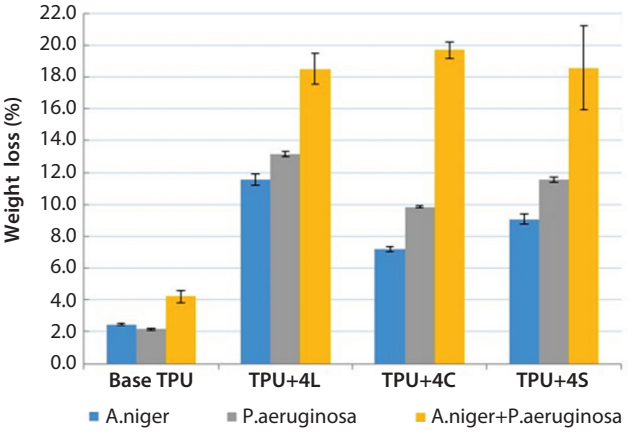

Figure 1 Weight loss of TPU samples achieved in the agar plate tests with *A. niger*, *P. aeruginosa*, and the consortium (30 days).

lignin (TPU+4L) gave the best results in the tests with both the isolated microorganisms, while for the consortium the best results were achieved with cellulose (TPU+4C).

3.1.2 *Biodegradation in Soil*

The biodegradation assays in soil were carried out during 6 months at 37 °C and 58 °C. Figure 2a shows the experimental setup used for the TPU samples incubation. The tested samples were evaluated monthly, namely by visual inspection for signals of biodegradation, and the sample weight loss determined. The visual inspection of the base TPU samples tested at 37 °C allowed observing a progressive mycelium growth until the end of the test (Figure 2b). A light change of the sample colour from yellowish white to lustreless yellow was also noticed, suggesting the occurrence of a low degradation. For the modified samples (images not shown) the microorganisms' growth on the surface was visible for all samples since the 1st month, being more prominent at the 6th month. The presence of small holes and cracks on the samples' surfaces was also noticed, being more significant for the sample TPU+4L. The base TPU sample tested at 58 °C also showed a light mycelium growth in the 1st month, with samples being completely covered by mycelium after 6 months testing, as shown in Figure 2c. Also, the sample presented several cracks on the surface and it became more brittle, indicating a substantial degradation. A colour change from a yellowish white to brown was also observed. For the modified samples, visual analysis was only performed until the 4th month of the assay since afterwards a high level of disintegration was reached. All modified samples tested at 58 °C were completely covered by mycelium just at the end of the 1st month, with recovered samples presenting several cracks and holes on the surface that increased during the test. The 4th month samples were much more brittle than the original ones, being broken by hand. For the TPU+4C and TPU+4S the colour changed from transparent white to brown.

Regarding the biodegradation assays performed in soil at 37 °C, the higher weight loss after 6 months was 36.6% for the sample TPU+4L (Figure 3), while for TPU+4C and TPU+4S the weight loss ranged from approximately 27 to 30%. For the base TPU a significantly lower weight loss (10.5%) was achieved. These results evidence the positive outcome of the base TPU modification with the tested biobased additives in what concerns the biodegradation increment, as previously indicated by the test plate results. According to the literature, the majority of fungi and bacteria existing on soil are mesophilic organisms, with most of them presenting a great suitability to degrade polysaccharides and cellulose. Also, thermophilic basidiomycetes, known as being holders of a unique ability to efficiently degrade lignin, can be present, although to a lower extent at 37 °C [38]. Hence, the biodegradation of the modified TPU samples' outcomes from the microbial activity of this wide range of microorganisms.

For the soil test at 58 °C (Figure 4) 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, recovery of the modified TPU samples was not possible due to their high level of disintegration. The base TPU used in this work is a polyester-based type and its weight loss, despite being significantly lower compared to the modified samples, was considerably higher than some previously reported results. Krasowska *et al*. studied the biodegradation of three types of polyurethane (two ester-based and one ether-based) in compost during 24 months, and reported a maximum weight loss of about 14% at the end of a 6-month period at ambient temperature [31]. In the present study, the highest degradation showed by the TPU+4L sample was attributed to the predominant presence of basidiomycetes at 58 °C, which are

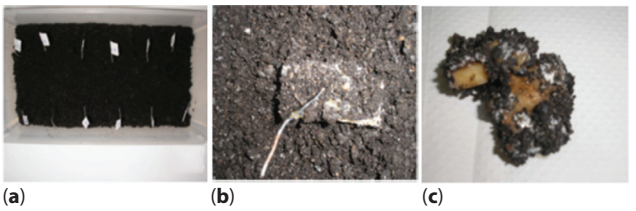

Figure 2 Biodegradation in soil: experimental setup for samples' incubation (**a**), detail of the base TPU biodegraded in soil at 37 °C (**b**) and at 58 °C (**c**), after 6 months.

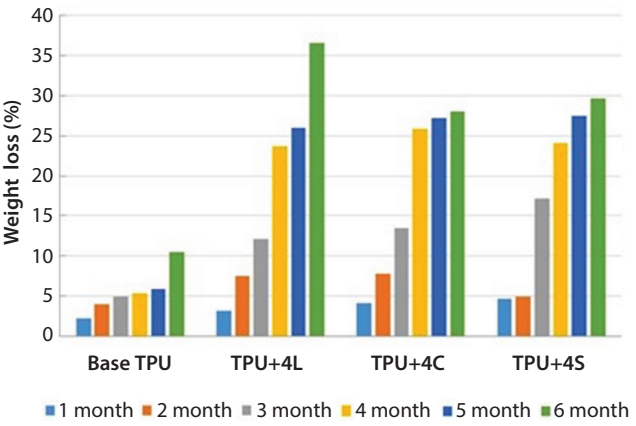

Figure 3 Weight loss of TPU samples achieved in the soil biodegradation assay at 37 °C (monthly sampling till 6 months).

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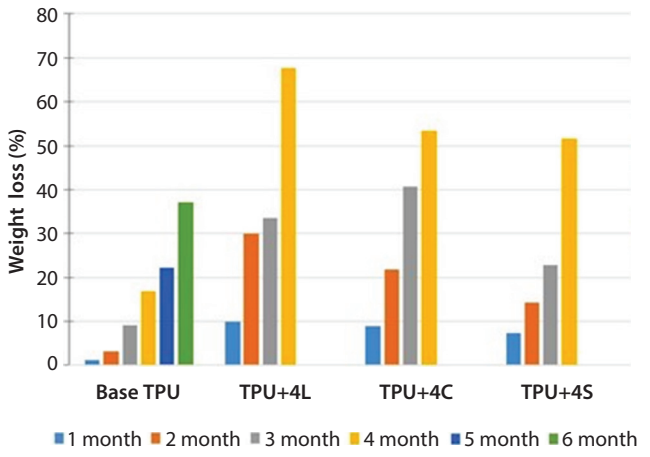

Figure 4 Weight loss of TPU samples achieved in the soil biodegradation assay at 58 °C (monthly sampling till 6 months).

described as being efficient in lignin degradation in addition to having the ability to effectively degrade cellulose and starch [39].The results presented in Figures 3 and 4 demonstrate the successful outcome of the TPU modification with the chosen biobased additives, in particular with lignin. Moreover, the level of disintegration reached suggests the possibility of integrating modified TPU materials in the conventional composting process.

3.2 FTIR Analysis

The structural modifications of the TPU samples subjected to biodegradation in soil were inspected by FTIR. The microbial attack by the soil microorganisms is expected to break both urethane (-O-CO-NH-) and ester bonds (-CO-O). The generated degradation products of polyester-based polyurethanes are often described in the literature as being alcohols and amine derivatives with acid intermediates [25]. For the studied samples, the structural differences revealed by FTIR are shown in Figure 5. The spectra of the biodegraded samples at 37 °C correspond to the samples recovered after 6 months of burial, while samples tested at 58 °C correspond to the samples' spectra recovered after 4 and 6 months of burial, for the modified and base TPU, respectively. As expected, no major changes occurred in the initial spectra for the samples TPU+4C and TPU+4S due to the low amount of incorporated additive (4%). However, for the TPU+4L sample spectra, a small increase in the bands at 2920 and 2850 cm^{-1} (CH_2 asymmetric and symmetric stretching) was noticed, since the peaks became sharper due to the lignin presence. The region comprised between 3700 and 3100 cm^{-1}, is dominated, in the original samples, by the hydrogen-bonded N-H stretching vibration associated with the urethane group (centred at 3330 cm^{-1}). As the degradation occurred, two shoulders appeared, one around 3500 cm^{-1} (attributed to the OH stretching vibration), and the other around 3290 cm^{-1} (attributed to the free N-H stretching vibration). These features were noticed for all the modified TPU samples after 6 months of degradation at 37 °C, being more perceptible when samples were submitted to biodegradation in soil during 4 months at 58 °C. For the base TPU, this effect was only noticed at 58 °C after 6 months. In the carbonyl region the main feature noticed was a decrease in the band assigned at 1720 cm^{-1} (free and hydrogen-bonded carbonyls from ester and urethane groups) for all the modified TPU samples tested at 37 °C, this decrease being more prominent for the TPU+4L. For the modified TPU samples tested at 58 °C, the decrease of the carbonyl bands is sharper and accompanied by a displacement to lower frequencies (around 1700 cm^{-1}). Analysing the base TPU spectra, it is worth mentioning a small decrease of the carbonyl bands only after 6 months of degradation at 58 °C. The peak assigned to the CO-O symmetrical stretching vibration is found around 1163 cm^{-1} and its decrease due to the microbial attack is remarkably noticed for the TPU+4L tested at 37 °C, being undercover by the surrounding vibrations for 58 °C. The diminishing of this vibration was also detected for the TPU+4S and TPU+4C and the base TPU samples degraded at 58 °C, being more evident for the TPU+4S. These structural modifications and the broadening of the 3500 cm^{-1} region that suggest the formation of alcohols' derivatives, point out the ester group degradation. Regarding the peak at 713 cm^{-1} (CH_2 out-of-plane bending) assigned in the original samples, a complete disappearance was noticed for all modified TPUs at both temperatures, indicating the size reduction of the TPU molecular chains. For the base TPU degraded at 58 °C, the decrease of this vibration is also noticed.

Summarising, when urethane linkage degradation occurs, a modification at the N-H stretching region, denoting the appearance of amine and alcohol derivatives, together with a decrease of the carbonyl band, is expected. This pattern occurs markedly for the modified TPU samples degraded at 58 °C. If degradation of the ester linkage occurs, besides the change of the CO-C stretching vibration, a modification at 3700 and 3100 cm^{-1} region, emphasizing the appearance of alcohol derivatives (3500 cm^{-1}), is observed. This pattern was registered with particular emphasis on the TPU+4L sample. Therefore, the structural modifications detected by the FTIR analysis are in good agreement with the weight loss registered in the biodegradation tests with respect to the TPU+4L sample's superior biodegradation.

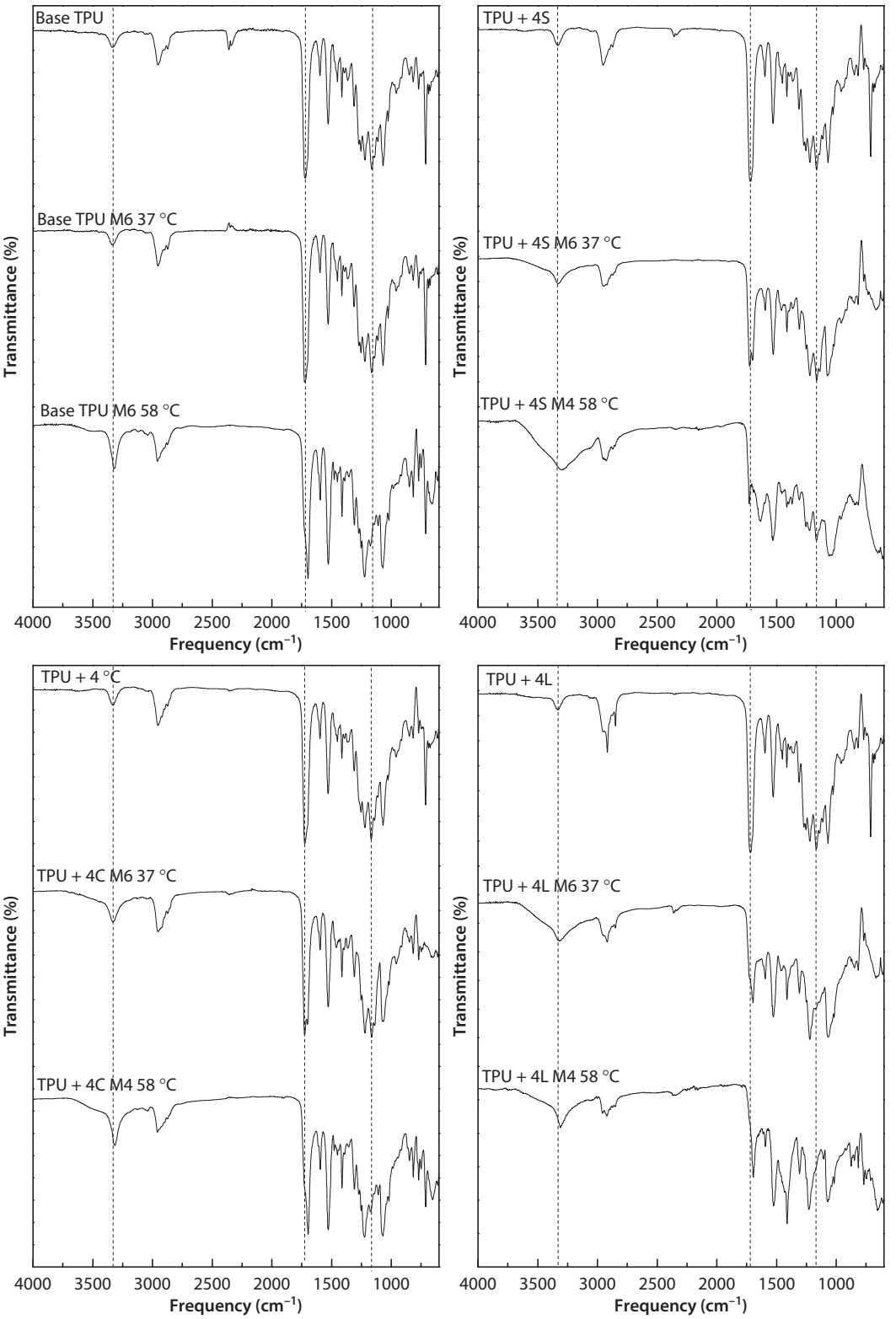

Figure 5 FTIR-ATR spectra obtained for the studied TPU samples: before and after biodegradation in soil during 6 months at 37 °C and 58 °C for the base TPU, and 6 months at 37 °C and 4 months at 58 °C for TPU+4S, TPU+4C and TPU+4L.

Table 1 Results of the outsoles mechanical properties tests and specifications according to the standards applied.

Tested material	Property	Standard	Specification	Obtained result
TPU+4L	Hardness (Shore A)	ISO 868:2003	60–80	70–71
	Density (Mg/m^3)	ISO 2781:2008	–	1.16
	Abrasion resistance (mm^3)	EN 20871:2001	Max[1]. 250	228 (+/–23)
	Tear strength (N/mm)	ISO 20872:2001	Min[2]. 8.0	24.2 (+/–2.1)
	Tensile strength (MPa)	ISO 22654:2001	Min. 8.0	11.1 (+/–1.4)
	Elongation at break (%)	ISO 22654:2001	Min. 300	629 (+/–63)
	Flex resistance (mm)	ISO 17707:2005	Max. 4.0	0.0
	Fatigue resistance (mm/kc)	BS 5131-2.1:1991	Max. 0.10	0.0

[1] Maximum value
[2] Minimum value

3.3 Mechanical Tests of the Produced Outsoles

Considering the biodegradation results obtained for the modified TPUs, the best performing formulation, corresponding to the TPU+4L, was selected for outsoles production at pilot scale. In order to evaluate the maintenance of the functional characteristics related to footwear performance and wearability, the mechanical properties of the produced outsoles were evaluated. The results obtained for the hardness (Shore A), density, abrasion resistance, tear strength, tensile strength and elongation at break, flex resistance and fatigue resistance are summarized in Table 1. As can be observed, the hardness (Shore A) was 70-71, being within the specified range. The registered abrasion resistance shows a mean sample volume loss of 228 mm^3, being inferior to the maximum reference value of 250 mm^3, while the value of the tear strength was 24.1 N/mm, which is substantially higher than the specification (minimum 8.0 N/mm). For the tensile strength and the elongation at break, higher values were obtained (11.1 MPa and 629%) when compared with the reference ones (minimum of 8.0 MPa and 300%). For the flex resistance, no cut growth or initiation of crack appearance was detected at the end of the test. Regarding fatigue resistance, even after a small cut being done, no propagation was detected after 150,000 cycles of flexing, showing that the tested material (TPU+4L) has an excellent resistance. Analysing the overall results, it can be concluded that the produced outsoles present mechanical properties that completely fulfil the standard specifications for footwear application.

4 CONCLUSIONS

The results obtained with both assayed methodologies evidenced a positive effect of the tested biobased additives (lignin, cellulose and starch) in the improvement of the TPU biodegradability, the most favourable results being registered for the samples modified with 4% of Sarkanda lignin (67% weight loss after 4 months at 58 °C in soil). These results were corroborated by the structural modifications detected by the FTIR-ATR analysis. Moreover, the results of the mechanical properties evaluation proved the suitability of the TPU modified with 4% of lignin for footwear outsoles production. The produced outsoles, beyond presenting improved biodegradability, can also contribute to minimise the environmental impact of this type of materials.

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