Reusing finished leather waste to produce pigmented thermoplastic polyurethane composite

Diego Giehl¹, Éverton Hansen¹,²*, Luiz Carlos Robinson¹ and Patrice Monteiro de Aquim¹

Abstract
Footwear industries generate leather waste during the operation. Some of these wastes contain chromium, which may bring environmental concerns. This study aimed to reuse finished leather waste, the major part of these hazardous wastes, via producing a composite with thermoplastic polyurethane (TPU) for shoe soles. Finished leather waste containing black dyes and pigments was used to color the TPU. The finished leather waste was fragmented, milled, micronized and blended with TPU in a ratio of 10%, 15%, and 20% w/w to produce composite materials. The composite materials were evaluated by morphological and thermal characterizations, physical–mechanical analysis, and environmental tests (leaching and solubilization), which presented that the physical–mechanical and thermal properties were within the standard of shoe soles, and the composites can be classified as non-hazardous. The composites enabled a new way of coloring polymeric matrices and reusing leather waste.

Keywords Composite, Leather waste, Thermoplastic polyurethane, Coloring performance, Waste reuse

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1 Introduction

The leather process consists of a sequence of physical and chemical operations that have the purpose of pre-processing, tanning and providing properties according to the final product (touch, softness, color, elastic capacity, among others) [1, 2]. This material is widely used in fashion industry, clothes and shoes manufacture, and the development of high-tech functional articles (conductive, fireproof, antibacterial, and self-cleaning leather, among others) [3]. It is estimated that around 600,000 tons of solid waste (such as shaving, finished leather waste, and sludge) are produced worldwide by leather industries each year [4]. An average of 0.1 kg to 0.2 kg of finished leather waste are generated per pair of shoes manufactured in footwear industries [5]. These wastes are generated in the process of cutting leather pieces for the manufacture of shoes, in addition to removing both natural defects (veins, stretch marks, ticks, among others) and processing defects (tanning and finishing) [6]. Thus, the management of this waste is relevant for both generating companies and raw material suppliers [7]. Currently these wastes are sent to hazardous waste landfills. The recycling of these industrial wastes is considered as a long-term solution, to avoid the waste of resources [8].

Most finished leather wastes contain chromium (III), which is the main active ingredient of basic chromium sulfate [9]. The presence of chromium (III) classifies these wastes as hazardous, with the potential for chromium oxidation, producing highly toxic chromium (VI) [10–13]. Leather and footwear companies need to find sustainable alternatives to minimize the amount of leather waste generated and its disposal in industrial landfills [14]. Thus, this study aimed to reuse finished leather waste from the footwear industry to prepare thermoplastic polyurethane (TPU)-based soles. The presence of finished leather waste can provide coloration and improve mechanical properties of TPU.

Composites are materials that provide the combination of characteristics from different materials, resulting in optimized properties [15], as the mechanical reinforcement provided by the incorporation of one or more materials in a matrix [16]. TPU is a versatile polymer formed by segments of rigid and flexible molecules [17, 18]. The flexible part of the molecule corresponds to flexible polyl of ester groups or ether group, and the rigid segment refers to the urethane from diisocyanate and chain extender, providing elasticity and reinforcement in mechanical properties, respectively [19]. This material
is similar to rubber due to its mechanical elasticity and wear resistance [20].

Some authors have already developed composites combining thermoplastic materials with leather wastes to add physical–mechanical properties to polymers used in several areas, such as civil construction and furniture industry. The composite developed in this research aims to pigment a TPU-based polymeric matrix using the color of finished leather waste to the new material. The developed composite does not use additives, aiming to apply only TPU and finished leather waste, reducing the use of chemicals to obtain the new material (Additional file 1).

2 Material and methods
The methodology of this work is schematically presented in Fig. 1. The study consisted of the development and characterization of the composite and production of a shoe sole.

2.1 Materials
The materials used to produce the composite are black leather wastes from a footwear industry in southern Brazil and commercial polyester-based thermoplastic polyurethane. The TPU manufacturer (FCC industry) indicates that the material is suitable for the manufacture of shoe soles and technical parts. Typical hardness, specific gravity and abrasion values reported by the manufacturer are 75 (Shore A), 1.24 g/cm³ and 45 mm³, respectively.

2.2 Composite preparation
The composite TPU specimens were produced by applying three formulations containing 10% (COMP10), 15% (COMP15), and 20% (COMP20) w/w of finished leather waste, in addition to virgin TPU specimens. The finished leather waste was ground (TS 2X20/500 industrial crusher, Seibt), milled (knife mill MGHS 1.5/85, Seibt, with 8 mm sieve), and micronized (micronizer model 001, AX Plastics, 1300 rpm with 1.5 mm sieve). The average fiber length obtained was 1.5 mm. The finished leather waste was mixed and homogenized with TPU using a magnetic stirrer (model 5385, Bertel) in the defined proportions (10%, 15% and 20% w/w of finished leather waste) and extruded in a single screw extruder (model ES25 A56/11 4 hp, Seibt, rotation speed 50 rpm). This extruder had four heating stages, with an operating temperature profile of 105 °C (compound input), 120 °C, 130 °C and 140 °C. The material was granulated (model GR 01, AX Plastics, speed 1000 rpm) and injected (injector model Apta 80, Bonmaq) to produce the specimens and a shoe sole for subsequent blending resistance tests. The injection stage also had four heating stages, with 140 °C (input of the compound), 150 °C, 160 °C and 175 °C (transfer of the polymer to the mold). The process of obtaining composite test specimens is schematically presented in Fig. 2.

2.3 Characterization of composites, virgin TPU and finished leather waste
The characterization tests applied to the virgin TPU, finished leather waste, and the composites are described below.

- Scanning Electron Microscopy (SEM): Magnifications of 5000 times were used to visualize the structure of the new composites with a voltage of 10 kV (SEM model JSM-6510 LV, Instrument Jeol).
- Thermogravimetric Analysis (TGA): A temperature range of room temperature to 1000 °C was used, under a heating rate of 10 °C/min, in an inert nitrogen atmosphere, with a volumetric flow rate of 50 mL/min (equipment model TGA-51H, Shimadzu).
- Differential Scanning Calorimetry (DSC): The heating–cooling–heating cycle used was: 30 °C to 150 °C, 150 °C to −90 °C and −90 °C to 150 °C. The heating and cooling rate was 10 °C/min under inert nitrogen atmosphere conditions using a volumetric flow rate of 20 mL/min (equipment DSC 6000, Perkin Elmer).
- Fourier Transform Infrared (FTIR): The operating conditions of the equipment use a wavelength range from 4000 cm⁻¹ to 650 cm⁻¹ (equipment Frontier FTIR, Perkin Elmer).

![Fig. 1 The study methodology](image-url)
2.4 Physical–mechanical tests of composites and virgin TPU

The specimens of the developed composites and virgin TPU were evaluated for the following physical–mechanical parameters: abrasion (wear resistance due to volume loss using Maqtest abrasimeter, comparing to standard rubber specified in international standard [21]), Shore A hardness (indentation resistance, using Digimess durometer) [22], specific mass (using Shimadzu analytical balance) [23], heat fastness (using Quimis oven) [24], light fastness (using Quimis oven) [25], bending resistance (resistance to continuous bending at an angle of 90°, using Maqtest flexometer) [26], colorimetry (evaluated by transmittance analysis in the visible spectrum, which identifies at which wavelengths the sample has the highest/lowest transmittance), and color migration (using Quimis oven) [27].

2.5 Leaching and solubilization tests

Environmental tests were carried out to assess whether the composites are hazardous when disposed in the environment. The leaching and solubilization tests were performed for the finished leather waste and composites (COMP10, COMP15, and COMP20). The standards used were NBR 10005 [28] for leaching and NBR 10006 [29] for solubilization. This classification standard has also been used by previous study [30].

Samples were comminuted (passing through 9.5 mm mesh sieve). For the leaching test, 100 g of the comminuted material was added to two liters of the extraction solution (deionized water and glacial acetic acid to pH 2.88 ± 0.05). The mixture was placed in vials in a rotary shaker for 18 ± 2 h with a rotation of 30 ± 2 rpm and temperature of 25 °C. The leachate extract was filtered and analyzed for total chromium [31]. For the solubilization test, 250 g of the sample was added to a container. Distilled water was added to obtain a volume of one liter. A plastic film was placed over the container to prevent material contamination. After seven days, the solubilized extract was filtered and analyzed for total chromium.

3 Results and discussion

3.1 Characterization of composites, virgin TPU and finished leather waste

3.1.1 Morphological analysis

The SEM images of virgin TPU (a), finished leather waste (b), and the prepared composites COMP10 (c), COMP15 (d), and COMP20 (e) are shown in Fig. 3. The micrographs of COMP10 and COMP20 show good dispersion of the finished leather waste in the polymeric matrix, as there was no segregation between the continuous and dispersed phases. In COMP15 micrograph, it was not possible to observe the leather fiber in the polymeric matrix. The good dispersion of the finished leather waste demonstrates that the fiber length (1.5 mm) was small enough for its processing with TPU, resulting in the interaction and incorporation of fiber into polymeric matrix [32]. The interaction also depends on the type of polymer used. TPU and leather have similar main chains and functional groups, which makes them naturally have better compatibility compared with other composite systems [33].
3.1.2 Thermogravimetric analysis
Thermogravimetric analysis aims to quantify the deteriorated mass as a function of temperature. The results are organized in Table 1. TGA spectra are provided in Additional file 1.

The degradation of virgin TPU, COMP15 and COMP20 composites showed only one thermal event. The type of raw material and processing used to produce TPU can result in a homogenization of the rigid and flexible segments of the molecule. Thus, the thermogravimetric analysis can register only one thermal event, within the range corresponding to the rigid and flexible parts of the TPU [34]. Leather degradation occurred in three stages. The first stage (around 64 °C) is associated with the evaporation of water. The second stage is related to the collagen present in the leather waste, as well as the production of CO₂ resulting from this deterioration process (between 220 °C and 400 °C). The last stage (over 400 °C) is related to the decomposition of long polymer chains (with high molecular weight), as well as tanning agents present in the formulation of the leather tanning process [35].

3.1.3 Differential scanning calorimetry
The glass transition temperatures of virgin TPU samples and the developed composites are shown in Table 2. DSC spectra are provided in Additional file 1.

The glass transition temperature showed low variation with different additions of finished leather waste, indicating good thermal stability of the material. All the glass transition temperatures of samples were around –27 °C, similar to the temperatures identified in previous study [36].

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The TGA parameter of TPU, leather waste, and composites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>T&lt;sub&gt;onset&lt;/sub&gt; (°C)*</td>
</tr>
<tr>
<td>TPU</td>
<td>366.39</td>
</tr>
<tr>
<td>Leather waste</td>
<td>316.11</td>
</tr>
<tr>
<td>COMP10</td>
<td>294.80</td>
</tr>
<tr>
<td>COMP15</td>
<td>332.56</td>
</tr>
<tr>
<td>COMP20</td>
<td>363.13</td>
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</table>

* The weight loss attributed to the loss of absorbed water is not counted

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Differential scanning calorimetry for virgin TPU and composites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Glass transition temperature (°C)</td>
</tr>
<tr>
<td>Virgin TPU</td>
<td>–26.25</td>
</tr>
<tr>
<td>COMP10</td>
<td>–26.57</td>
</tr>
<tr>
<td>COMP15</td>
<td>–27.16</td>
</tr>
<tr>
<td>COMP20</td>
<td>–26.85</td>
</tr>
</tbody>
</table>
3.1.4 Analysis of the chemical structure by FTIR

The results of FTIR analysis are shown in Fig. 4. The 1650 cm$^{-1}$ and 1550 cm$^{-1}$ bands indicate, respectively, amide group I (CO elongation) and amide II group (CN elongation and NH flexion) [37]. These values are close to those found in this research, which were 1634 cm$^{-1}$ and 1547 cm$^{-1}$. These groups are characteristics of the structures present in collagen. The connections made for the formation of collagen triple helix were identified in the 1235 cm$^{-1}$ and 1452 cm$^{-1}$ bands. Similar bands (1239 cm$^{-1}$ to 1450 cm$^{-1}$) were identified in the analysis by Zhang Y. et al. [38].

The comparison between the FTIR spectra shows that the insertion of finished leather waste did not promote significant changes in the chemical structure of the TPU, presenting good compatibility between TPU and fibers in finished leather waste.

3.2 Physical–mechanical analysis

The results of the abrasion (a), Shore A hardness (b), density (c) and fastness to light and heat (d) tests of the virgin TPU and the developed composites are shown in Fig. 5.

The abrasion (Fig. 5a) obtained for virgin TPU was 30 mm$^3$, within the range specified by the material’s technical sheet (minimum of 0 mm$^3$ and maximum of 100 mm$^3$). With the addition of 10%, 15% and 20% of finished leather waste, abrasion increased to 47.33 mm$^3$ (COMP10), 88.66 mm$^3$ (COMP15), and 104.66 mm$^3$ (COMP20), resulting in lower resistance to wear. A material suitable for making soles in the footwear industry must present the volume loss less than 150 mm$^3$ [21], and the shoe sole must have an abrasion lower than 400 mm$^3$ [39]. All specimens met the applicable standards for the application in the production of shoe soles. Abrasion values were lower than those found for leather waste composites with PVB (between 290 and 350 mm$^3$) and PVC (above 400 mm$^3$) [33], demonstrating good potential for the composites developed in this study.

The hardness measured in the tests (Fig. 5b) resulted in 73 Shore A for the virgin TPU, within the range indicated in the material’s technical sheet (between 72 and 78 Shore A). The addition of finished leather waste to the polymeric matrix did not result in relevant changes in Shore A hardness. Brazilian [22] and international [41] standards for sole materials establish a range of 60 to 80 Shore A. Thus, composite materials (COMP10, COMP15 and COMP20) were approved for application in shoe soles.

The density (Fig. 5c) did not show relevant variation with the addition of finished leather waste in the polymeric matrix. The specific mass found in this work was similar to a previous study [19] for TPU with addition of thermoplastic amide (between 1.14 and 1.26 g/cm$^3$).

The results obtained for the analysis of fastness to light and heat (Fig. 5d) for virgin TPU and for all composites showed the fastnesses were established at least at Grade 4, which met the basic standards [24, 25].

3.2.1 Bending resistance

When the specimens were subjected to the bending resistance test, none of the samples showed progression from the initial hole of 2 mm. These results comply with the standard [26], which establishes that soles can reach up to 4 mm of progression (maximum) to be suitable for footwear. Therefore, all the prepared composites were approved for application in shoe soles.

After flexion tests on the specimens, tests were also performed on the injected shoe soles (Fig. 6). The sole injected with virgin TPU did not show progression from the initial hole of 2 mm, and the soles produced with COMP10, COMP15 and COMP20 showed the incremental progression of 0.33 mm, 0.96 mm and 2.66 mm, respectively. Despite the results showing an increase in the progression of the initial hole with the percentage increase of finished leather waste in the polymeric matrix, the progressions of all composites are lower than the maximum value of 4 mm [26]. Thus, TPU-based soles with finished leather waste have technical feasibility for the application in footwear soles.

3.2.2 Colorimetry

The transmittance spectra for the virgin TPU specimens, COMP10, COMP15 and COMP20 in the visible light
spectrum (400 to 700 nm) are presented in Fig. 7. The virgin TPU oscillated between 47 and 52%, and the finished leather waste presented transmittance between 46 and 50%. The composites showed similar transmittance results for different wavelengths of visible light between 44 and 46%, which are regardless of finished leather waste addition on the composites. The three composites presented a lower transmittance percentage compared to the virgin TPU. This similar configuration is related to the compatibility between the two materials, so the leather disperses homogeneously in the polymeric matrix [42].

3.2.3 Color migration
The specimens of the three composites (COMP10, COMP15, and COMP20) and the virgin TPU are shown in Fig. 8a, and the prepared shoe soles are shown in Fig. 8b. The composites with the three dosages of black
finished leather waste were colored compared with virgin TPU, achieving one of the objectives of this study, pigmenting the TPU without the addition of additional dyes and pigments.

The virgin TPU and the composites (COMP10, COMP15, and COMP20) presented grade 5 of color migration. Thus, all the specimens passed the test, as the standard for color migration in shoe soles [27].

### 3.3 Leaching and solubilization tests

The results of the environmental analyzes of leaching and solubilization of finished leather waste and composites are presented in Table 3.

The finished leather waste and the composites (COMP10, COMP15 and COMP20) showed a total chromium concentration of 0.265 mg/L, <0.050 mg/L, 0.206 mg/L and 0.138 mg/L, respectively (Table 3). These concentrations classified the materials as non-hazardous [28]. Although the leaching test did not exceed the chromium limit for finished leather waste, this material must be considered hazardous by the standard [10] due to its origin from a specific listed source. The purpose of applying the leaching test to TPU-based composites with different percentages of finished leather waste is to investigate the potential transfer of harmful substances from the composite to

<table>
<thead>
<tr>
<th>Sample</th>
<th>Leachate extract (mg/L)</th>
<th>Solubilized extract (mg/L)</th>
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<tbody>
<tr>
<td>Finished leather waste</td>
<td>0.265</td>
<td>0.198</td>
</tr>
<tr>
<td>COMP10</td>
<td>&lt;0.050</td>
<td>&lt;0.050</td>
</tr>
<tr>
<td>COMP15</td>
<td>0.206</td>
<td>&lt;0.050</td>
</tr>
<tr>
<td>COMP20</td>
<td>0.138</td>
<td>&lt;0.050</td>
</tr>
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</table>
the environment [43]. The results demonstrate that the materials were classified as non-hazardous.

In the solubilization tests, the finished leather waste exceeded (Table 3) the standard limit of 0.050 mg/L of total chromium [29]. As the finished leather waste exceeded the limit for solubilized extract and met the limit for leaching extract, it is classified as non-inert waste [10]. The solubilized extracts from composites COMP10, COMP15 and COMP20 showed total chromium concentrations below the quantification limit of the method (0.050 mg/L) (Table 3), and below the standard limit value of 0.05 mg/L [29]. These results classified the composites as non-hazardous and inert. Thus, the composites produced do not have the potential to transfer chromium to the liquid medium when contacting with water [43].

4 Conclusion
This study showed that reusing finished leather waste to produce pigmented thermoplastic polyurethane composite is a constructive strategy for the reuse of hazardous waste. The morphological observation, and thermal analysis showed good compatibility of the finished leather waste with polyurethane and thermal resistance of the composites. Physical–mechanical tests showed that all composites meet the standards for application in shoe soles.

The environmental analyzes classified the composites as non-hazardous and inert, indicating good immobilizing stability of chromium in the polymeric matrix without potential to transfer chromium from the composite to the environment. The incorporation of finished leather waste in TPU is a technically viable alternative to resources recycling of this industrial waste. The coloring technique requires only finished leather waste, without other additives, minimizing the consumption of chemicals for the production of the TPU-based composite.

Supplementary Information
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Additional file 1. TGA and DSC spectra.

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Author contributions
DG: Investigation, formal analysis, writing. EH: writing and validation. LCR: conceptualization, investigation and validation. PMdeA: conceptualization, validation and supervision.

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Data available on request from the authors.

Declarations

Competing interests
All authors declare that there are no competing interests.

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