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Recycled PVC to eco-friendly materials for footwear industry: process and mechanical properties

Giovanna Marsura[1], **Juliana Otavia Bahú**[2], **Laura Plazas Tovar**[1*], **Romilda Fernandez-Felisbino**[1] and **Eliezer Ladeia Gomes**[1]

[1]*Departamento de Engenharia Química, Universidade Federal de São Paulo – UNIFESP, Diadema, SP, Brasil*
[2]*Centro de Estudos de Energia e Petróleo, Universidade Estadual de Campinas – Unicamp, Campinas, SP, Brasil*
***laura.tovar@unifesp.br**

Abstract

Recycling polyvinyl chloride (PVC) is a significant challenge for the footwear industry due to its short lifecycle and environmental impact. This study focused on recycling thermoplastic polyvinyl chloride (rPVC) from used sports shoes, sourced from a recycling company. The rPVC and thermoplastic polyurethane (TPU) were melt-blended and prepared using industrial injection molding with varying compositions. These polymer blends were then characterized morphologically, thermally, and mechanically. The recycled polymer blends demonstrated improved properties compared to the virgin polymers. Blending TPU with rPVC resulted in a material with notable hardness and enhanced abrasion resistance, with TPU/rPVC blends (67/33 and 50/50 wt.%) showing double the abrasion resistance of pure PVC. Additionally, the rPVC blend exhibited a rupture strength of 14.73 MPa, 1.6 times greater than virgin PVC. The TPU/rPVC blend (50/50 wt.%) also offered higher deformation resistance, indicating a more entangled and tensile structure. These advancements support the development of environmentally friendly footwear.

Keywords: *circular economy, polymer blend, polyvinyl chloride, thermoplastic polyurethane, upcycling*

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1. Introduction

The footwear industry promotes about 1.4% of global GHG emissions[1], and this encourages the footwear industry to improve its perception of environmental management by reusing different materials and footwear parts, improving profitability, and reducing operating costs[2]. Footwear comprises canvas, leather, and petrochemical-derived materials (plastic and rubber), and the design can be developed using faux leather made of synthetic components such as polyvinyl chloride (PVC) or thermoplastic polyurethane (TPU). Specifically, the sole comprises PVC (~8% wt. %) and TPU (~17% wt. %), and their blends[3].

Recycling the PVC materials used in shoe soles is crucial for promoting sustainable development and reducing pollution. Various methods, such as incineration, landfill, and mechanical, chemical, thermal, and biological recycling, have been employed for decades. However, these methods have resulted in increased emissions of hazardous exhaust gases, reduced landfill capacity by up to 10% by 2030 and high energy consumption[4]. Therefore, there is a need to explore alternative options for recycling materials based on TPU and PVC. Few studies have investigated the properties of TPU/PVC blends with recycled plasticized PVC (r-PVC)[5]. Interesting properties were obtained with 50% TPU/PVC blends, which showed better mechanical (impact strength) and chemical resistance[6]. The plasticizer action of TPU in the polymer blend was also noted since the deformability increased with TPU content, lowering its rigidity[7]. The abrasion resistance[8] and elongation at break[9] of these blends can also be improved by regulating the TPU content. However, these blends commonly use crosslinking agents, plasticizers, or modifiers[10], to improve the TPU miscibility in the PVC polymeric chains and enhance some mechanical properties.

The actual processing of the blends can also influence their final properties[11]. Injection molding, the typical processing method used to produce TPU-PVC shoe soles, involves parameters such as temperature, screw – shape, rotation speed and injection pressure, which affect the TPU/PVC performance[12]. The injection molding process allows for the preparation of blends to combine polymers and seek to integrate their best physical and chemical properties, producing a final material with more interesting characteristics, reducing costs, and obtaining eco-friendly end-products[2].

Adding TPU to PVC or recycled PVC to produce PVC-based blends is attractive from a commercial point of view, and benefits from achieving some of the SDGs agenda, such as Goal 15: Life on land providing a mitigation strategy for the carbon footprint. Their production encounters challenges due to the miscibility issues between PVC and TPU[7], and achieving desirable properties under conventional blending and reprocessing conditions remains difficult. Significant efforts have been devoted to understanding recycled PVC, but there is a notable gap in research on recycled PVC from the footwear industry, a readily available material. In this study, the properties of pure TPU/PVC and TPU/rPVC polymer blends processed by injection molding without other extra components (additives or fillers) are compared. The properties measured regarding shoe applications (density, abrasion, mechanical strength, thermal stability) substantiated the potential for the applicability of the reprocessed PVC blend (TPU/rPVC) for shoe soles, also contributing to the sustainability of the footwear sector.

2. Materials and Methods

2.1 Pure PVC, Pure TPU, and Recycled PVC materials

This research utilized pure polyvinyl chloride pellets (PVC) 60A (Braskem Co, Brazil, CAS number 9002-86-2, hardness 50–65 Shore A) and pure thermoplastic polyurethane pellets (TPU) Desmopan 3972AW (NeoRez® R-3972, Covestro Polymer Industry and Trade Ltda., Brazil, hardness 71–75 Shore A). Recycled PVC (rPVC) was sourced from Prisma Thermoplastic Compounds Ltda. (Campo Bom, Rio Grande do Sul, Brazil) and derived from the soles of various used sports shoes, primarily composed of PVC polymer. PVC and TPU were used as received, without additional treatment.

2.2 Recycled PVC Pretreatment

The pretreatment began with the rPVC (as received) being manually sorted into broad categories (such as "free-from-fragments" and "with-fragments") and the other sole components (other polymers), glass, paper, and metal components, such as eyelets, removed. The samples were then manually washed with soap and water, ultrasonicated to remove minor contaminants, dried in an air circulation oven at 80 °C for 3 hours, and subsequently automatically shredded and ground, the sieve size fraction used in this study is 2.8–4 mm. The pretreated rPVC was kept in the zipper bags for further processing and characterization.

2.3 Injection Molding

Before melt blending, the PVC, TPU, and rPVC samples were dried at 80 °C for four hours in an air circulation oven. The polymer blends were prepared by melt-mixed extrusion using a co-rotating twin-screw extruder coupled to an industrial injection molding machine (1500-740 LHN ACTUAL; HIMACO, Novo Hamburgo, Brazil) at a temperature of 80 °C with a screw speed of 200 rpm. The extrudate was cooled to solidification and then cut into pellets using a pelletizer. The polymer blends were dried at 80 °C for three hours in an air circulation oven and then kept in desiccators for 24 hours before injection molding. The electrical injection unit has a maximum injection velocity varying from 34 to57 g s^{-1} (hydraulic motor torque of 100.6 kgfm) facilitated by a four-zone (barrel/mold) screw varying from 50 to 65 mm diameter (L/D varying from1:18 to 1:13.8) and an injection volume varying from 406 to 687 cm^3. The nozzle, barrel and mold temperatures were maintained at 80, 160-170, and 120 °C, respectively (based on industrial operation). The TPU/PVC blend ratios were 100/0, 33/67, 50/50, 67/33, and 0/100 (wt.%) and the TPU/rPVC blend ratios were 50/50, 67/33, and 0/100 (wt.%).

2.4 Characterization

2.4.1 Density, thermogravimetric (TGA/DTG) and X-Ray Diffraction (XRD) analyses

Density was measured following ASTM D972 at around 25 °C, with results averaged from triplicates.

Polymer blends were examined using a Shimadzu DTG 60 thermogravimetric analyzer with platinum crucibles and approximately 10 mg samples, heated from room temperature to 600 °C at 10 °C/min in an oxidizing atmosphere (air flow rate=50 mL min^{-1}).

The diffractograms were obtained using a Bruker model D8 Advance diffractometer. The radiation was emitted by a Cu-Kα laser emitter (λ = 1.5418°), operating at 40 kV and 30 mA from 5 to 80° (2θ), with a Ni filter and angular speed of 2° min^{-1}.

2.4.2 Shore A Hardness

Shore A hardness was measured per ASTM D2240 using an analog tester with a 6 mm thick indenter, with data collected from three specimen points.

2.4.3 Abrasion resistance

The abrasion resistance was analyzed at room temperature according to the DIN ISO 4649 standard, using a MAQTEST abrasimeter using the following parameters: A cylindrical bar with corundum (aluminum oxide) grit 60 rotating at 40±1 cycles per minute, 4.2±0.4 mm lateral displacement, 150±0.2 mm cylinder diameter, 40±0.2 mm abrasion course, and 5.0±0.1 or 10.0±0.2 N vertical pressure (compression). The vertical inclination of the center of the axis of the specimen support was 3°, and the horizontal distance between the center of the cylinder and the center of the gripper was < 1 mm. Thus, the volume loss in mm^3 of the sample (Δ_V) is defined as the ratio between the mass loss (Δ_M in g) and the volume bulk density of the sample (ρ_B in g mm^{-3}). The results reported the mean value of triplicate experiments.

2.4.4 Tensile strength analysis

The tensile strength was determined in an EMIC – DL2000 universal testing equipment according to ASTM D638, using the 500 N load cell. The TPU samples were previously annealed at 90 °C for 20 h before the compression tests, resulting in a mean value of quintuplicate measurements.

3. Results and Discussions

3.1 Samples and X-Ray Diffraction (XRD)

Figure 1a, b shows the images of the polymeric blend specimens, TPU/PVC (100/0, 33/67, 50/50, 67/33, 0/100 wt.%), and TPU/rPVC (50/50, 67/33, 0/100 wt.%), respectively. No pores were found on their surfaces. Moreover, the injection molded plates presented an excellent visual appearance, free of bubbles and lumps and well-leveled. In Figure 1b, the specimens had a purplish color due to the PVC reused in recycling, and no transparency was observed. However, the coloration of the rPVC and its blends was homogeneous, with no thermal decomposition. Regarding texture, the recycled PVC and its blends were softer to the touch, and no porosity was noticed. The TPU/rPVC (33/67) blend had technical problems and could not be produced with the injection molding machine used in this work (image not shown).

The addition of PVC to the TPU did not alter the diffraction patterns (Figure 1c) of the TPU/PVC blends produced via mechanism described in Supplementary Material (S1 and Figure S1). These results indicated that the blends remained amorphous polymers, independent of the PVC added. In addition, some small diffraction peaks were observed at 42.6 and 49.4° for the pure TPU and its blends, which might be related to the additives used in the formulation of the TPU. According to the manufacturer, up to 2 wt.% of these additives (anti-hydrolysis agents, UV stabilizers, etc.) are added to improve the polymer-specific properties or processing characteristics[13]. Previous studies have also reported that TPU/PVC blends generally maintain an amorphous structure because of the nature of both polymers. For instance, Laukaitiené et al.[7] noted that TPU/PVC blends exhibit no significant crystallinity changes in XRD patterns, similar to the observations in this study.

3.2 Density

Density measurements are crucial for screening qualified samples before conducting further mechanical testing. As the TPU content increased, the density of the TPU/PVC polymer blends decreased. Specifically, the densities of the TPU/PVC polymer blends were measured as 1.209, 1.192, 1.196, 1.199, and 1.183 g/cm^3 for TPU contents

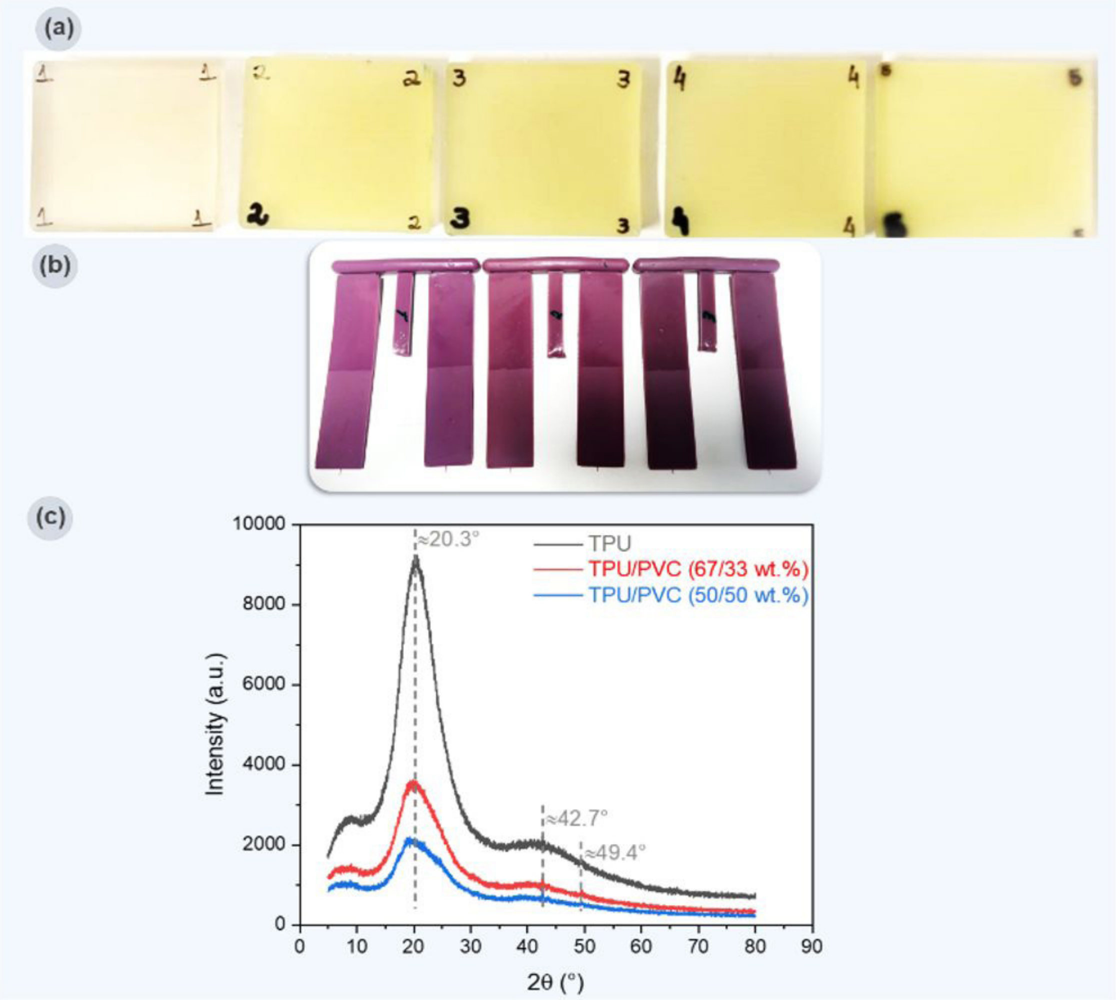

Figure 1. Visual appearance of the specimens (a) TPU/PVC polymer blends: (1) 0/100 wt.%, (2) 33/67 wt.%, (3) 50/50 wt.%, (4) 67/33 wt.%, (5) 100/0 wt.%; and (b) TPU/rPVC polymer blends: (1) 0/100 wt.%, (2) 50/50 wt.%, and 67/33 wt.%; (c) diffractograms of the polymer samples (pure TPU, TPU/PVC (50/50 wt.%) blend, and TPU/PVC (67/33 wt.%) blend.

of 0%, 33%, 50%, 67%, and 100 wt.%, respectively (see Supplementary Material, Figure S2). The densities calculated for the mixtures based on the densities of PVC (1.209 g/cm^3) and TPU (1.183 g/cm^3) accurately predicted these results, indicating that the number of voids in the blends was minimal. This consistency suggests that the melt blending conditions used were appropriate for this study.

The observed decrease in density with increasing TPU content aligns with the fact that TPU generally has a lower density than PVC[14]. However, it is important to address that TPU used in this study is a linear block copolymer, which differs from what might be implied by a "heterogeneous polymeric chain". In contrast to PVC, which has a more compact structure due to significant intermolecular forces, such as dipolar interactions between polymer chains, the density of TPU is lower not only because of its polymeric structure, but also because of its lower inherent density and less efficient packing. PVC's denser PVC structure results from strong intermolecular forces that enhance its compactness during the injection process.

The average apparent density of the TPU/rPVC polymer blend was 1.243 g/cm^3 (67/33 wt.%), 1.229 g/cm^3 (50/50 wt.%), and 1.267 g/cm^3 (0/100 wt.%). These findings corroborate recent research indicating a significant increase in the apparent density of TPU/rPVC polymer blends with higher PVC content[5,6]. This trend of decreasing density with increasing TPU content was also observed in the present study (Supplementary Material, Figure S2).

3.3 Thermal stability

TGA and DTG measurements were used to investigate the thermal stability of the TPU/PVC and TPU/rPVC blends. Table S1 (in Supplementary Material) reports the maximum decomposition temperatures obtained by TG/DTG curves. Figure 2a, b depicts the TGA profiles with four stages of thermal decomposition. The small degradation stage occurred in the temperature range from 100 to 145 °C, which can be attributed to the evaporation of water adsorbed on the polymer surface. The next degradation stage was in the temperature range from 145 to 367 °C, representing the main stage with a 79.0% mass loss (Figure 2a). According to Hamidi[15], dehydrochlorination and the formation of aromatic compounds from PVC can occur. However, the three peaks that appeared during this stage (at 189, 259, and 285 °C) suggest intermediate degradation stages related to interconnected chain scission mechanisms, due to the gradual reaction with oxygen. The third stage started at 365 °C with the appearance of three more peaks at 419, 430, and 451 °C, and ended at 480 °C, with a 13.0% mass loss (Figure 2a) related to the polyenes suffering scission in the oxidant atmosphere. Nagy et al.[14] discussed the oxidation mechanisms of polyenes during the thermal degradation of PVC, reporting that they occur in distinct steps. The last degradation stage was noted in the range from 480 to 530 °C with an 18.0% mass loss, related to the backbone of the polymer blend.

The TGA plots of the TPU/PVC polymer blends showed a behavior that appeared to be dictated by the PVC, mainly at 250 and 390 °C (Figure 2a). Above this temperature, the stages became similar, be it the pure polymer or the blend. Figure 2b shows a shift of the maximum decomposition temperature (T_d = 257 °C) as the TPU concentration decreased. The value of T_d shifted with increasing PVC or rPVC content due to extra interactions with the TPU, destabilizing the polymer blend. Thus, the addition of PVC or rPVC to TPU resulted in interactions that disrupted the thermal stability of the polymer blend. These interactions could be chemical, such as reactions between PVC/rPVC and TPU, or physical, such as changes in the heat distribution within the blend. Moreover, in the temperature range of 490 – 550 °C, the TPU/rPVC polymer blends underwent a significant weight loss, estimated at 12% (Figure 2b). The shift in the decomposition temperature range of the blend is attributed to the stabilization of the TPU by the migration of stabilization components from the rPVC.

3.4 Shore A Hardness

The hardness of pure TPU is related to the ratio of the rigid and flexible segments in its polymeric chains. According to Kim et al.[16], a 2.1 ratio (rigid/soft segments) corresponds to a TPU hardness of 70, in agreement with the TPU evaluated here (Figure 3a), which presented a Shore A hardness of 76 and a rigid/flexible segments ratio close to 2.8.

Regarding the TPU/PVC polymer blends, the Shore A hardness decreased slightly with the addition of PVC (TPU/PVC (33/67 wt.%) – Figure 3a), and up to the TPU/PVC blend composition of (67/33 wt. %), the Shore A hardness remained practically unaltered (Figure 3a). However, from this point up to the pure PVC, the Shore A hardness drastically reduced (Figure 3a), characterizing a non-linear behavior for this parameter. The recycled PVC Shore A hardness was higher than that of virgin PVC (75 > 62), in agreement with the data informed by the suppliers. Thus, the rPVC impacted the Shore A hardness of the TPU/rPVC polymer blends, which remained practically constant at any composition, ranging from 74–76 (Figure 3a). After reprocessing the PVC (rPVC), the Shore A hardness enhanced the thermal degradation of the process, which can decrease the polymer molar mass by reducing the polymeric chain size[17]. Also, to improve its flexibility, the plasticizer added to the PVC formulation could "detach" from the main PVC polymeric chain, reducing the flexibility of the PVC.

The rPVC polymer blends showed a Shore A hardness equivalent to that of pure TPU, which positively impacts the footwear industry, allowing for the possibility of using polymeric upcycling strategies[18]. This enables the replacement of virgin polymers (pure PVC) by recycled ones (rPVC) to produce polymeric soles with high-quality properties.

3.5 Abrasion resistance

In the abrasion test, the volume loss of the specimen after testing is inversely proportional to its abrasion resistance. Analyzing the results for TPU, virgin PVC, rPVC, and their blends, an increase in abrasion resistance can be seen as the amount of TPU in the blend increases (Figure 3b). The abrasion resistance of the TPU-PVC and TPU-rPVC blends revealed significant differences in their performance. The pure TPU exhibited the highest abrasion resistance at 30 mm^3, highlighting its durability. As the PVC content increased, the abrasion loss increased for the TPU/PVC

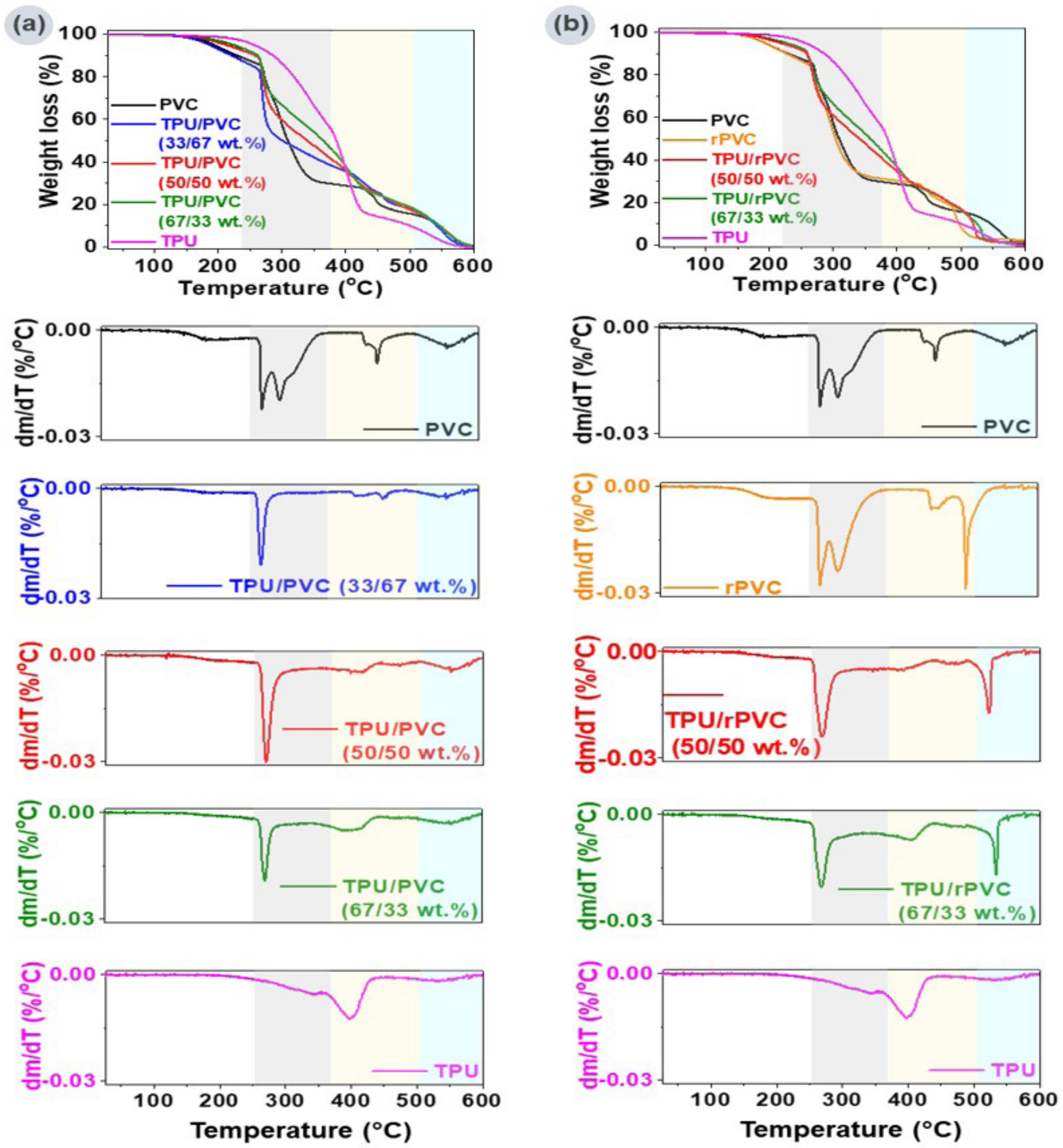

Figure 2. TGA plot and derivative curves of: (a) TPU/PVC polymer blends: 100/0, 33/67, 50/50, 67/33, 0/100 wt.%, and (b) TPU/rPVC polymer blends: 50/50, 67/33, and 0/100 wt.%.

(33/67 wt. %) showing 110 mm^3, compared to pure PVC at 120 mm^3. In contrast, the rPVC blends consistently performed better than PVC blends. For instance, TPU/rPVC (67/33 wt. %) shows 49 mm^3 abrasion loss, lower than the 60 mm^3 for TPU/PVC (67/33 wt.%) blend. This trend continued with equal concentrations of TPU and PVC/rPVC, with the rPVC blend (76 mm^3) outperforming the PVC blend (97 mm^3). These results suggest that, while TPU remains the most resistant to abrasion, incorporating rPVC instead of PVC can improve abrasion resistance in blends, making it a potentially better choice for applications where durability is crucial. The blends prepared with pure PVC had no linear trend, which might be related to an incompatibility between the PVC and TPU thermoplastics[9]. This is evident for blends with a higher proportion of virgin PVC. However, when the percentage of PVC is above 50 wt.%, the abrasion resistance starts to vary at a lower rate (Figure 3b). Another study demonstrated superior abrasion resistance for TPU/rPVC polymer blends (70/30 and 50/50 wt.%) as compared to pure and virgin PVC[8]. These blends reduced the need for solvent cleaning before use as an adhesive, reducing the amount of volatile organic compounds (VOCs) in the workplace. In addition, the costs of applying this blend were much lower than applying pure TPU. Ames[8] suggested that the blend TPU/rPVC (70/30 wt.%) showed the best processing conditions, as also observed in the present work for the TPU/rPVC blend (67/33 wt.%).

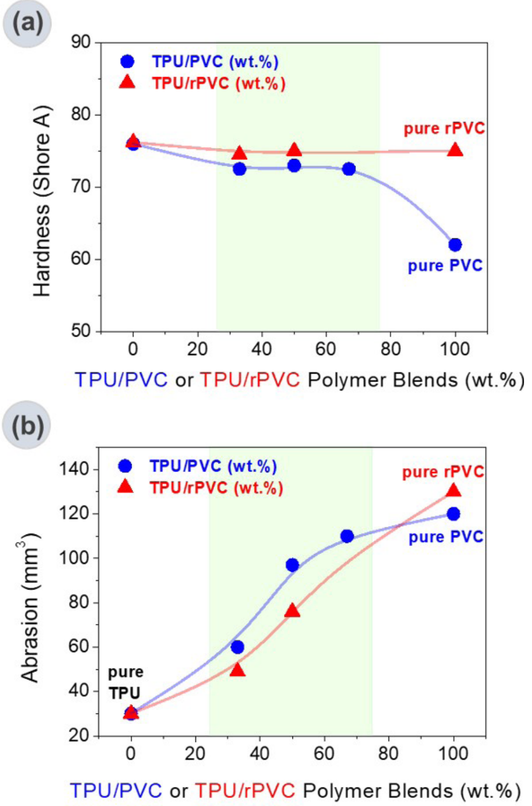

Figure 3. (a) Shore A hardness of the TPU/PVC and TPU/rPVC polymer blends. (b) Abrasion test results of the TPU/PVC and TPU/rPVC polymer blends.

Abrasion resistance is an essential property in the footwear industry, more specifically for shoe soles, since it is directly related to the main mechanical stress the sole suffers, extending its life cycle. According to the results, blends containing rPVC (30–50 wt%) could be a good option for a line of sustainable casual shoes, being linked to upcycling and sustainable development.

3.6 Tensile strength

The visual appearance of the specimens (Figure 4 a and b) after the tensile test was registered to assess the type of fracture and the stress caused by stretching. Table S2, from the Supplementary Material, summarizes the tensile test data for the polymers and blends evaluated. Also, Figures S3-S5 (Supplementary Material) present the force *versus* deformation curves for all the specimens and their replicates evaluated. For the virgin PVC and rPVC blends, elongation at rupture increased with an increase in the proportion of TPU in the blend, consistent with the flexible nature of TPU. Virgin TPU did not fracture during the test, evidence of its highly elastic behavior. The addition of virgin PVC shifts the force-deformation curves upwards (Figure 4c and d), with the material becoming more resistant to deformation due to the increase in Young's modulus, but not linearly as expected. In general, the blends have greater or equal tensile strength, deforming less at a specific applied force than pure PVC or TPU. This means that the interaction between the flexible/rigid segments of linear PVC or TPU chains provides materials with structures that are more resistant to deformation than individual polymers. The linear portion of the curves referring to virgin PVC (Figure 4c), with elastic deformation occurring up to 25 mm (applied force between 23–27 N). Except for pure TPU, the elastic limit occurred with 10 mm deformation (≈12 N) with a slight variation for TPU/PVC (67/33 wt.%) blend. This blend (Figure 4c) behaved similarly to TPU, but the presence of PVC made the material more resistant than all the other polymers and blends. The addition of 33 wt.% of PVC to the TPU provided desirable characteristics for better resistance of a shoe sole.

The addition of recycled PVC led to blends that were more deformation-resistant than pure TPU (Figure 4d), showing strength that was intermediate between TPU and recycled PVC, especially regarding the plastic deformation region. More significant tensile strengths were gradually obtained as the proportion of rPVC in the blend increased, with the linear chains of recycled PVC (smaller and more compact) gradually interreacting and intertwining with the flexible/rigid TPU segments, providing stronger materials as the proportion of recycled PVC increased. The elastic region behaved slightly differently from the plastic region. The elastic region (the linear portion of the curve) occurred up to ≈20 mm (applied force ≈30 N), except for pure TPU, and in this region the TPU/rPVC (50/50 wt.%) blend was slightly more resistant to deformation (black line) than pure PVC or the TPU/rPVC (67/33 wt.%) blend. In this case, the addition of 50 wt.% rPVC to the TPU might be interesting for some applications.

The addition of TPU to PVC alters its mechanical properties, increasing the elongation at break and decreasing the tensile strength. Similar effects have been observed in TPU/polypropylene blends, where a ductile-to-brittle transition occurs at specific blend ratios[19]. The miscibility of segmented polyurethanes (SPUs) and PVC blends depends on the hard-segment content of SPU and the presence of functional groups in PVC[20].

Figure 5a shows the elasticity modules of the blends. Comparing PVC and recycled PVC, the latter showed greater tensile strength and a larger elasticity modulus. For each type of PVC blend, the highest tensile strengths were TPU/PVC (67/33 wt.%) and TPU/rPVC (50/50 wt.%). Polyurethanes (TPU) generally show remarkable mechanical properties, with tensile strengths ranging from 20–60 MPa and elongation from 300 to 650%[21]. On the other hand, PVC has a tensile strength between 10–25 MPa and elongation between 150-400%[22]. The rupture strength curve (Figure 5b) for the TPU/PVC polymer blend (blue line) exhibited a rupture strength that has an inverse relationship with PVC content. This inverse correlation arises from the increased flow of TPU polymeric chains, necessitating a higher force for rupture. Notably, the TPU/rPVC blend with a TPU/rPVC composition of (67/33 wt.%) showed the highest rupture strength evaluated, surpassing that of pure TPU. The rupture strength of rPVC (14.73 MPa) was higher than that of virgin PVC (9.11 MPa), and the rPVC polymer blends with compositions similar to those of virgin PVC blends also showed higher tensile strengths. This result reinforces that

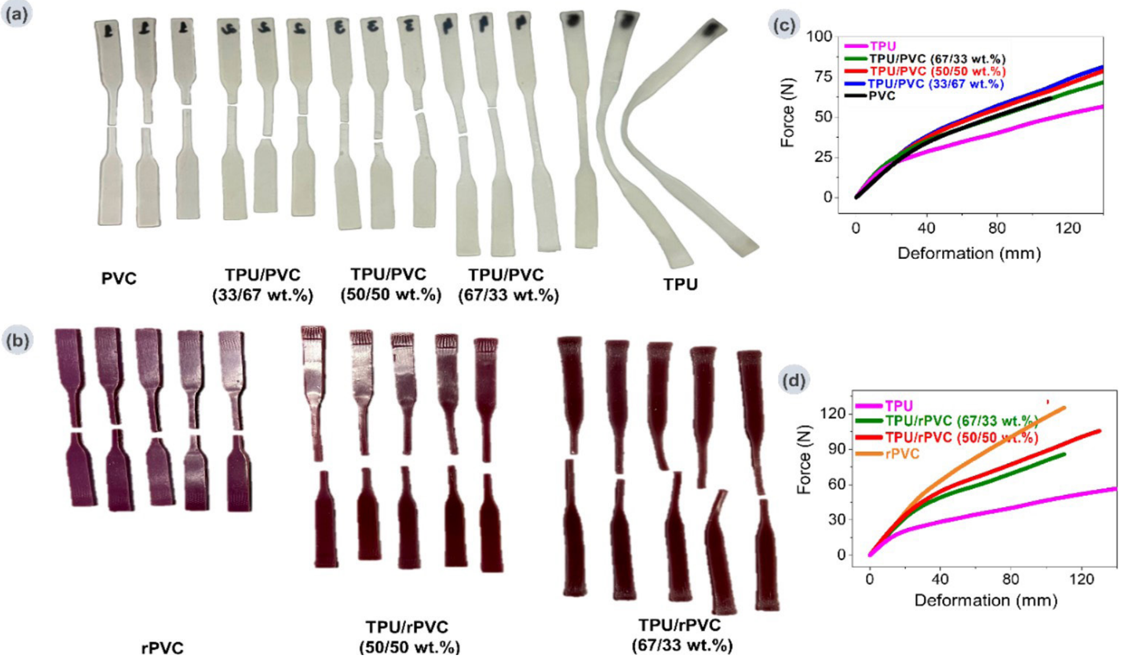

Figure 4. Specimens after applying the tensile test: (a) TPU/PVC polymer blends (0/100, 33/67, 50/50, 67/33, 100/0 wt.%); (b) TPU/rPVC polymer blends (0/100, 50/50, 67/33 wt.%). Force (N) versus deformation (mm) curves of: (c) TPU/PVC polymer blends (0/100, 33/67, 50/50, 67/33, 100/0 wt.%); (d) TPU/rPVC polymer blends (0/100, 50/50, 67/33 wt.%). Curves represent average behavior for each group.

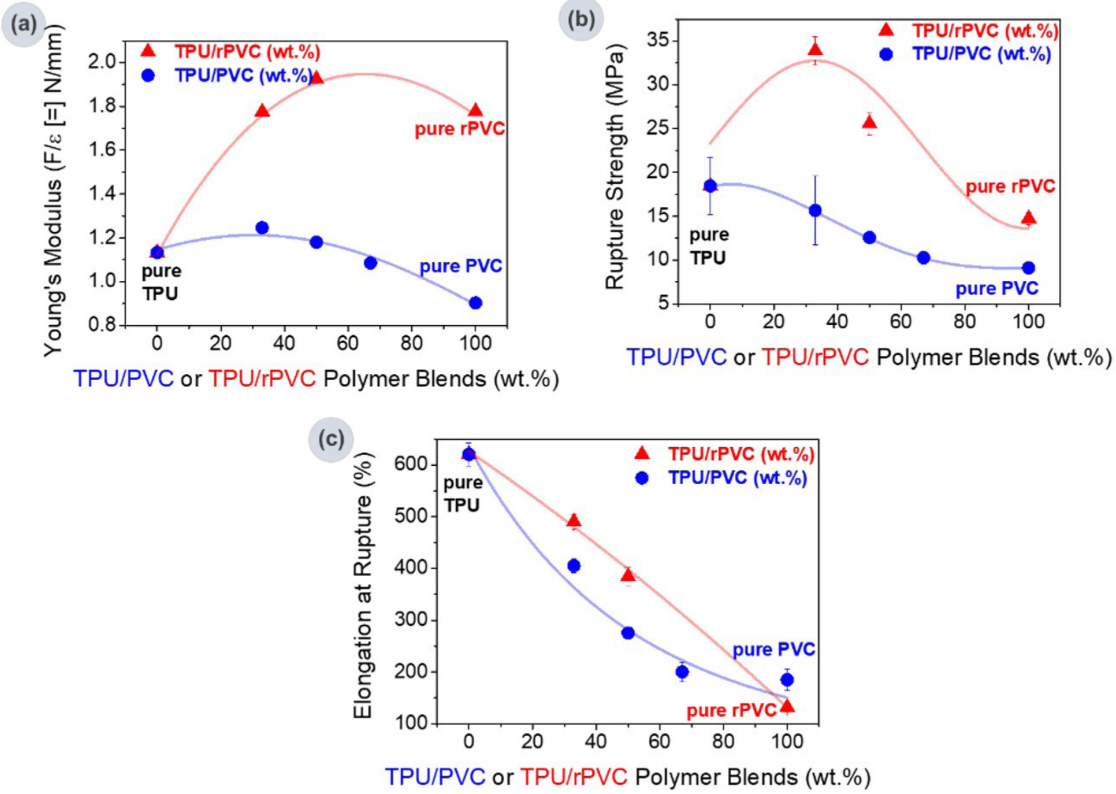

Figure 5. Results of mechanical testing of TPU, PVC, rPVC, and their blends: a) Young's modulus; b) rupture strength; c) elongation at rupture.

the denser and more entangled structure of rPVC provides greater resistance and, consequently, greater tensile strength.

The zero values obtained for the tensile stress measurements with strains of 10, 100, and 300% mean that rupture of the specimen occurred until reaching a specific strain. The values for elongation at rupture of the polymeric blends (Figure 5) increased with the TPU content of the blend, in agreement with previous results, which showed that the blends underwent greater elongation since the entanglement of PVC with TPU provided a greater flow of polymeric chains. The modulus of elasticity (Figure 5c) was higher in the blends with TPU and rPVC than in pure PVC. The results from both sources align well, confirming that blending TPU with PVC or rPVC enhances mechanical properties, such as tensile strength and elongation, with recycled PVC contributing positively to strength while reducing flexibility. The provided values and trends are consistent with the results reported in Laukaitienė et al.[7] and Ha et al.[9], as the TPU content increased to 20 wt. %, the yield strength decreased from 40.5 MPa to 20.3 MPa. This reduction in yield strength was accompanied by a significant decrease in tensile strength, which fell by approximately threefold, from 37.9 MPa to 13.8 MPa[7]. This reduction was expected because of the elastomeric nature of TPU[9].

Results for virgin PVC, TPU, and their blends (blue line) showed a gradual increase in elongation at rupture up to 33 wt.% TPU. These data support the observation that the elongation at rupture of the TPU/PVC blends remained relatively constant for TPU contents below 33 wt.%. In contrast, for TPU contents of >33 wt. %, elongation at rupture increases in an almost linear trend up to 100% TPU. For recycled PVC, TPU, and their blends (red line), the elongation at rupture presented a practically linear behavior with increased TPU content in the polymer blend, probably because the elongation of the blend formed was directly controlled by the interaction of the TPU with the structures formed, mainly by the TPU/rPVC proportions, making it easy to predict the elongation at break by a simple linear regression. Comparable observations were reported, with TPU/PVC blends exhibiting enhanced elongation at rupture in comparison to pure PVC[7]. The elongation at rupture increased proportionally with the TPU content. Specifically, TPU/PVC (40/60 wt. %) demonstrated approximately 150%[7].

Figure 6 presents the results obtained in the tensile tests for 10%, 100%, and 300% of the applied load. The tensile strength is evaluated from the load applied per unit area at the time of failure. The elongation represents the percentage increase in the length of the specimen under tension. The stresses at 10%, 100%, and 300% are related to the load necessary to produce the deformations related to these stresses. The results obtained with the load of 300% occurred because the specimen fractured before reaching

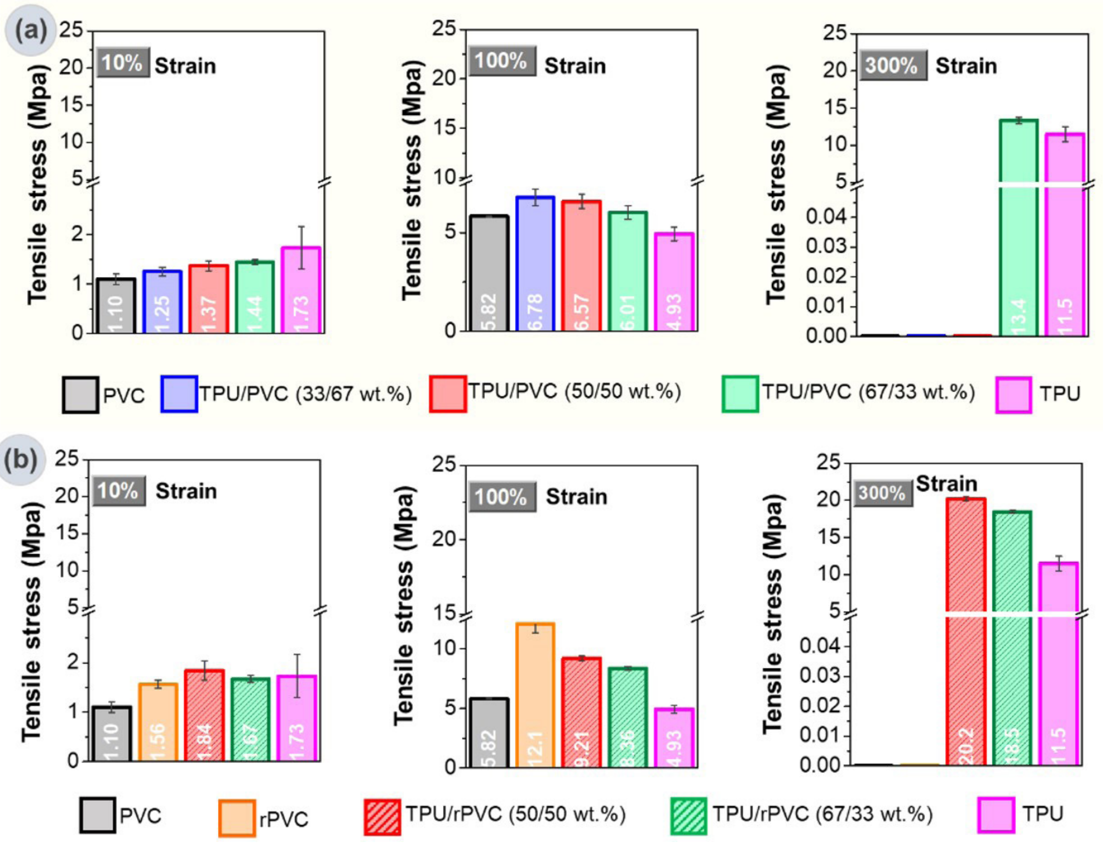

Figure 6. Stress results registered at 10%, 100%, and 300% deformation for the (a) TPU, PVC, and TPU/PVC blends, and (b) TPU, PVC, and rPVC blends.

the end of the test, but some specimens withstand great stress before they fracture. The strain values applied at 10%, 100%, and 300% followed technical standards that the market typically reports in the technical bulletin of the polymer sector. Figure 6a presents the stresses required for a 10% deformation of the polymers and their blends. All the stresses were below 1.9 MPa for this condition. Blends based on recycled PVC required greater tension than those required for virgin PVC blends. The TPU/rPVC (50/50 wt.%) blend was the most resistant in the tensile test under this condition. The virgin PVC blends showed increasing resistance with the TPU content. Figure 6b shows the stresses required for 100% deformation of the polymers and their blends. All stresses were between 4.9 and 12.2 MPa for this deformation, and the blends based on recycled PVC were more deformation-resistant. Under this tension, recycled PVC showed the greatest resistance to deformation of the polymers evaluated in this study.

TPU/PVC (67/33 wt.%), TPU/PVC (50/50 wt.%), and recycled PVC blends fractured before reaching 300% elongation (Figure 6). All stresses were below 21 MPa for this deformation except for the fractured polymers, and the blends based on recycled PVC proved to be more resistant to deformation, especially the TPU/rPVC (50/50 wt.%) blend, which withstood more than 20 MPa of tension without breaking. Polymer blends based on recycled PVC are generally more resistant and less elastic, so it is up to the footwear producer to adapt resistance, elasticity, and comfort to achieve an excellent cost-benefit ratio, maintaining the quality demanded by the consumer[23]. Similar observations were reported for TPU/PVC blends, demonstrating enhanced elongation at rupture compared to that of pure PVC. Recycled PVC in the blends generally resulted in increased tensile strength and better performance in terms of deformation resistance compared to virgin PVC. This study presents more favorable results than those already presented in the literature[24,25]. The origin of the recycled PVC used here (shoe soles from the footwear industry), was probably less heterogeneous in terms of manufacture, having undergone fewer structural alterations than the recycled PVC used by previous authors, which originated from landfills and civil construction, and was processed in cooperatives by mechanical recycling.

The origin and quality of recycled PVC are critical for producing TPU/PVC polymer blends that meet market demands for diverse applications. Our research introduces innovative blends utilizing recycled PVC, which demonstrate improved tensile strength and reduced elasticity. Further research and comprehensive testing are essential to validate the practicality of these materials for eco-friendly footwear. This includes evaluating the performance in real-world conditions, specifically assessing attributes such as comfort, durability, and overall functionality. Such studies are pivotal to confirming the suitability of these blends for sustainable manufacturing processes and ensuring their effectiveness in practical applications.

4. Conclusions

These findings demonstrate that blending TPU with PVC or recycled PVC (rPVC) yields materials with distinct and promising properties. X-Ray Diffraction analysis showed that these blends maintained an amorphous structure with only minor diffraction peaks related to the TPU additives. Density measurements confirmed that the blend compositions aligned closely with the theoretical predictions, indicating minimal voids and effective melt blending. Thermal stability tests revealed that while PVC content influenced the decomposition temperatures, rPVC exhibited higher thermal degradation than virgin PVC. Mechanical testing highlighted that TPU/rPVC blends, particularly those with higher rPVC content, offer superior tensile strength and elongation compared to both pure PVC and virgin TPU. These blends also generally exhibit lower abrasion losses than virgin PVC, making them suitable for applications such as footwear. These results suggest that TPU/rPVC blends are a viable option for eco-friendly and high-performance polymeric materials. Further investigations of their long-term durability and commercial applications are recommended.

5. Author's Contribution

- **Conceptualization** – Giovanna Marsura; Eliezer Ladeia Gomes.
- **Data curation** – Giovanna Marsura; Eliezer Ladeia Gomes.
- **Formal analysis** – Giovanna Marsura; Eliezer Ladeia Gomes; Juliana Otavia Bahú; Laura Plazas Tovar; Romilda Fernandez-Felisbino.
- **Funding acquisition** - Eliezer Ladeia Gomes.
- **Investigation** – Giovanna Marsura.
- **Methodology** – Giovanna Marsura; Eliezer Ladeia Gomes.
- **Project administration** – Giovanna Marsura; Eliezer Ladeia Gomes.
- **Resources** – Eliezer Ladeia Gomes; Romilda Fernandez-Felisbino.
- **Software** – NA.
- **Supervision** – Eliezer Ladeia Gomes; Romilda Fernandez-Felisbino.
- **Validation** – Giovanna Marsura; Juliana Otavia Bahú.
- **Visualization** – Giovanna Marsura; Eliezer Ladeia Gomes; Juliana Otavia Bahú; Laura Plazas Tovar.
- **Writing – original draft** –Juliana Otavia Bahú; Laura Plazas Tovar.
- **Writing – review & editing** –Juliana Otavia Bahú; Laura Plazas Tovar.

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Supplementary Material

Supplementary material accompanies this paper.

S1. Mechanism of TPU/rPVC Blends.

Figure S1. Scheme of the formation mechanism of TPU/rPVC polymer blends. MDI: 4,4'-Diphenylmethane diisocyanate; BDO: 1,4-Butanediol.

Figure S2. Density of blends prepared from pure TPU, pure PVC, and recycled PVC.

Figure S3. Tensile testing results for pure polymers: a) PVC, b) rPVC, and c) TPU.

Figure S4. Tensile test results for the blends: a) TPU/PVC (33/67 wt. %), b) TPU/PVC (50/50 wt.%), and c) TPU/PVC (67/33 wt.%).

Figure S5. Tensile testing results for recycled blends: a) TPU/rPVC (50/50 wt. %), and b) TPU/PVC (67/33 wt.%).

Table S1. Weight loss from thermogravimetric analysis for TPU/PVC polymer blends: 100/0, 33/67, 50/50, 67/33, 0/100 wt.%, and TPU/rPVC polymer blends: 50/50, 67/33, and 0/100 wt.%.

Table S2. Tensile test results for blends prepared from pure TPU, pure PVC, and recycled PVC

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