RECYCLING CYCLE OF MATERIALS APPLIED ON THERMOPLASTIC POLYURETHANE

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ABSTRACT

The selection of tools for the *management* of *footwear waste has currently become a* concern *to footwear designers, background studies demonstrated this professionals have little understanding on the end of life of applied materials. This study applied an Ecodesign tool named Recycling Cycle of Materials (RCM) on thermoplastic polyurethane (TPU) in three reprocessing cycles (RCM1, RCM 2, and RCM 3) of grinding, drying and injection molding. The samples were submitted to characterization techniques as* TGA, FTIR, density, *Shore A hardness, resistance to traction and compression, properties that could influence the TPU performance in product design applications. The TGA, FTIR and density results exhibited thermal and physical stability without mischaracterization after three reprocessing cycles. Reduced useful life of products was observed due to the gap of the maximum tensile stress from 21.08 MPa reference to 9.04 MPa in RCM 3. It was concluded that recycled TPU in RCM 1 had a performance compatible to its original application, in RCM 2 it was different from the original, and in RCM 3 there was high mechanical degradation.*

KEYWORDS: *Ecodesign, Recycling Cycle of Materials, Thermoplastic Polyurethane, TPU, Footwear*

I. INTRODUCTION

Nowadays, the environmental efficiency achieved in the disposal of residues from the production of footwear tends to be overcome by the market demand, short life cycle and lack of recycling, resulting in landfills or abandonment in the natural environment [1,2]. International concerns with the use of natural resources produced measures such as the Kyoto protocol, ISO 14000 and Brazilian law 12.305 of August 2010 that instituted the National Policy on Solid Waste [3,4]. These agreements attribute liability to producers for the waste generated in productive processes and industrial facilities [3,4]. According to Yüksel [5], industrial metabolism must keep raw materials circulating within the system and by means of reuse and recycling within a closed cycle. In 2016, the Brazilian footwear production was approximately 899 million of pairs, equivalent to 4.4% of the world footwear production [6].

Between 1993 and 2008, the Nike´s Reuse-A-SHOE program has recycled more than 21 million pairs of athletic shoes. It uses a “slice-and-grind” technique, where each shoe is cut into three slices – rubber outsole, foam midsole and fabric upper for subsequent milling and reuse of materials in track surfaces, interlocking gym flooring tiles, playground surfacing and consumer products [2,7]. Similarly, the Innovative Manufacturing and Construction Research Centre (IMCRC) of the University of Loughborough, UK has developed a system for separating and recovering useful materials from old footwear. It is able to granulate and segregate leather, plastic foams and rubber

[2,8]. Guarienti [9] reported that although research and material technology stand out in the implementation of sustainability, footwear designers have little understanding on the topic. Francisco et al. [10] concluded that the lack of data on the characterization of waste has a negative effect on the development of processes for the production of footwear residues and risks undermining its management. Rahimifard and Staikos [1] have shown that the complex material mixture of modern shoes and the wide variety of construction techniques used necessitates the use of an automated recycling process that will impact on end-of-life products. According the presented theme, this study applied the Recycling Cycle of Materials (RCM) tool on thermoplastic polyurethane (TPU) making use of technical-scientific parameters to contribute to a better understanding of designers in the process of material selection. The parameters were obtained using the characterization of thermal, physical and mechanical properties of TPU.

Presented the theme, the paper is structured in the background theory of Recycling Cycle of Materials tool and the thermoplastic polyurethane; method describes material, equipment and parameters applied; next the collected results and discussion; finally the future work and acknowledgments

1.1 Recycling Cycle of Materials (RCM)

According to Pahl et al. [11], the end-of-the life cycle and the recycling of products must be planned from the initial conceptual development instructions up to the final details of new products. In this scenario, the recycling of plastic solid waste (PSW) is hampered by the low-cost of virgin raw materials and those materials, which were significantly compromised after suffering successive processing cycles [12,13]. The deformation of properties, such as toughness and stability, stems from the contamination between different materials, molecular degradation and the presence of low molar mass compounds [12,13].

According to the waste management model referred to Staikos and Rahimifard [1], a reduced diversity of raw materials simplifies mechanical or chemical processes of waste recovery from post-consumer footwear, promoting the reuse of recycled material for lower performance applications. Manzini and Vezzoli [14] classified post-consumer waste as the material that has passed through the hands of a final consumer and has been discarded for disposal or recovery. Ashton et al. [15] pointed out that the selected applications for recycled materials is little widespread, especially in the case of mixed polymers, in which the mechanical properties can vary from the original application. Jacques [7] suggested that the selection of materials should be aligned to the goals of end-of-life products, covering both resistance and durability requirements as well as footwear performance. The selection of materials requires a large multifactorial analysis throughout the life cycle, and therefore, shoe designers have to go through a difficult decision-making process [16].

In this context, the concept of Ecodesign has emerged as a systematic approach to environmental management by including environmental aspects of product design [17]. *RCM* is a design project *tool* proposed by Cândido et al. [18]. This tool provides scientific and technical support for the selection of materials (Figure 1) to determine their mechanical properties and plan strategies to extend their useful life after recycling.

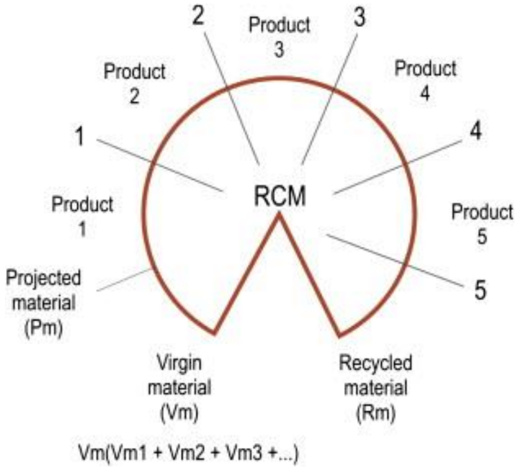

Figure 1. Organizational chart of RCM application; Cândido et al. (2011).

The RCM contains a set of data that characterizes the mechanical properties of materials by considering the amount of recycling cycles used [18]. These data can be compared to the original properties of the projected material (Pm) to evaluate the application of reprocessing of end-of-life products either into the same product system (closed loop) or into different ones (open loop) [1,18]. For Ashby [19] the selection of materials for designers and engineers is based on technical information obtained by scientific tests. The RCM aligns the research regarding material selection due to the use of processing techniques and characterization of materials, statistical analysis and determination of properties [19,20]. In this line of research, it was conducted a study on recycling that included the characterization of sunglasses seized by the Brazilian federal revenue agency [21]. Vidales [21] identified technical subsidies for recycling the sunglasses in four reprocessing cycles using characterization techniques, such as FTIR spectroscopy, thermogravimetric analysis (TGA), physical and mechanical tests. Recent research applied RCM tool as model to analyze multi-material tooth brush, by mechanical recycling and result polymer blends characterization [15].

1.2 Thermoplastic Polyurethane (TPU)

Plastics and rubbers are the predominant materials used by the Brazilian footwear industry. The national production was precisely 908.9 million pairs in 2017 [6]. Plastics and rubbers have been used as alternatives to leather, especially in casual and sport model soles, equivalent to 50.3% of the Brazilian footwear industry production [6,22]. The selection of materials for shoe soles depends on the physical and mechanical properties that provide footwear performance to offer users comfort and well-being [22]. Palhano [23] pointed out the influence of physical-mechanical properties, such as hardness, density and stiffness of ethylene-vinyl acetate (EVA), polyurethane (PU), thermoplastic polyurethane (TPU), styrene-butadiene rubber (SBR) and wood, on the biomechanical performance of shoe soles. Among these materials, the PU has an annual output that reached more than 18 million tons, applied mainly (34%) in shoes [24,25]. It can be classified mainly in foams (rigid or flexible) and in the denominated CASEs (coatings, adhesives, sealants and elastomers) [26]. For the CASEs uses, they can be found in sports shoes, athletic tracks and electronic products, among others [26].

The TPU emerged commercially in the 1950s, over the next decade it was introduced to the footwear industry, with flexible formulation in applications that require lightness, mechanical and chemical strength, abrasion, comfort, flexibility and shock absorption [27-29]. The adhesion of TPUs to the upper part of the shoe contributes to their use in soles of safety boots, golf and football shoes, roller protective gears and heels [29]. TPUs bridge the gap between rubber and plastics, as they offer mechanical performance characteristics of rubber but can be processed as thermoplastic [28,30]. The thermoplastic polymers become moldable at a certain elevated temperature and solidify upon cooling. This behavior is often known as heat-fugitive cross-links due to the loss of molecular bonds resulting from the combination of molecular blocks with different glass transition temperature (Tg) and melting temperature (Tm) [27]. TPU is a block copolymer synthesized from polyols, isocyanates and glycols, resulting in blocks of urethane and ether or ester, which can be flexible (amorphous region) and rigid (crystalline region) wich are responsible for the elastic and stiff behavior of the chain [27,31,32].

Bonab and Manas-Zloczoew [32] reported the presence of hard segments that act as physical crosslinks by exhibiting elastic behavior similar to that of vulcanized conventional elastomers.

Simón et al. [26] highlighted the growing industrial and academic interest in recycling processes. According to Qi and Boyce [28], the reprocessing by conventional thermoplastic techniques contributes to TPU recyclability. According to the ASTM D5033 [33], recycling of materials may be classified into primary, secondary, tertiary, and quaternary: primary recycling encompasses the recycling of industrial waste materials in the original application; secondary recycling encompasses the recycling of waste to different product from the original application; tertiary recycling involves the production of basic chemical monomers from plastic waste; quaternary involves incineration with energy recovery. Solid plastic waste recovery through mechanical processes is part of the secondary recycling [13]. In these processes, the polymer is ground into flakes, granules or powder, without changing the polymer chemical structure [26]. The quality and composition of the grind material allows the composition of intermediate blends, which will determine their application in low or high-performance products [34]. Símon et al. [26] concluded that the simplicity and low cost of these processes constitute a successful competitive advantage on TPU recycling.

II. MATERIALS AND METHODS

In the present study we used a Desmopan® 1080A by Covestro, which is a plasticizer-free thermoplastic polyurethane (ester-based) block copolymer grade, with a hardness between 80 to 84 Shore A, which is suitable for injection molding [35]. The used materials were stored in plastic containers in the absence of direct light at a temperature of 23 °C and relative humidity of 50% [36]. Virgin TPU was injected in specimens for the characterization of first injection cycle or Pm. Next, the three recycling sequences (RCM1, RCM2, and RCM 3) were performed by grinding the specimens (Figure 2a), drying the granules (Figure 2b) and injecting new specimens (Figure 2c). At the end of each recycling cycle, 30 specimens were sampled for characterization using FTIR, thermogravimetric analysis, hardness Shore A scale, tensile strength, compression and density tests.

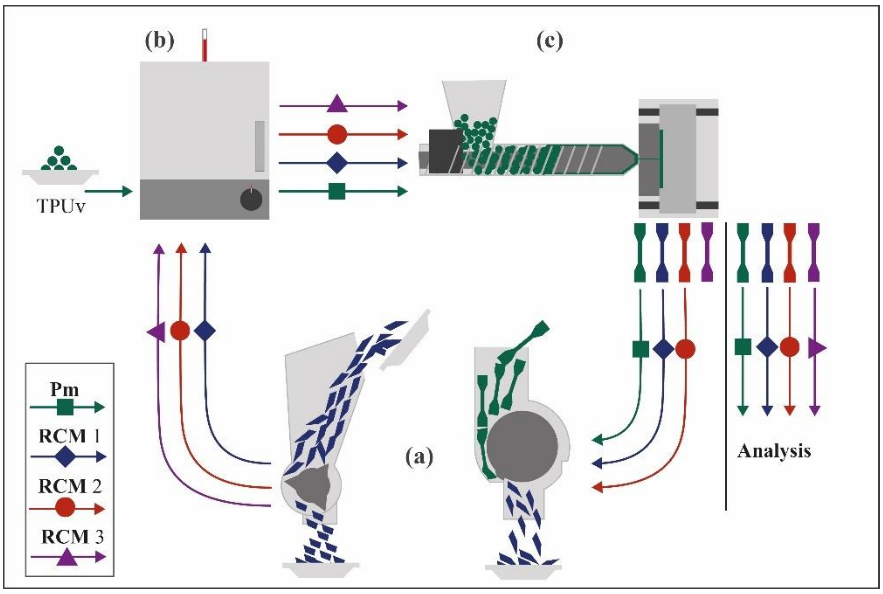

Figure 2. Flowchart of RCM application on TPU, adapted from Cândido et al. (2011) and Vidales (2013) p. 39.

The virgin fractions were dried at 80°C temperature for 3 – 4,5 hours using a DeLeo® dry heat sterilization equipment [37]. The injection molding machine used was a Mini-injector, AXPlásticos®. General specifications include a 16 mm thread, length to diameter ratio of 24:1, manufactured in SAE 8550 nitriding steel, with a 1.5 HP motor, 1:10 reduction [38]. Injection molding allows simultaneous injection of sample geometries according to ASTM D638-14 and ASTM D256-10e1 standards [39,40]. Due to the reduced size of the feed input of the injection, two subsequent milling processes were employed: (1) SM® 300 knife mill, 10 mm sieve and 1500 rpm; and (2) MGAS 27180 rotary knife mill (SEIBT®). Table 1 shows increased drying time and reduced processing temperatures due to adjustments caused by the presence of moisture and injection defects**.**

Table 1. Variables for drying and injection molding in Pm, RCM 1, RCM 2 and RCM 3 cycles.

	Drying (h)	M. Injection Zone 1 (ºC)	M. Injection Zone 2 (ºC)	M. Injection Zone 3 (ºC)	M. Injection Zone 4 (ºC)	Mold opening (s)	Fill time (s)	Fill velocity (%)
Pm	3.0	190	200	210	35	27	5.0	50
RCM 1	4.5	190	195	200	35	20	7.8	40
RCM 2	4.5	190	195	200	35	15	7.8	40
RCM 3	4.5	190	195	195	35	15	9.0	50

Chemical characterization of vibrational infrared absorption spectrum was obtained using a PERKINELMER Spectrum™ 100 FT-IR spectrometer (resolution 4 cm $^{-1}$, band range 4000 to 650 cm^{-1}, 16 scans), using accessory ATR. Density was determined in accordance with *ASTM* D792-13 [41]. The room temperature for the test was ± 23ºC and 50% relative humidity procedure A. Measurements were made using an analytical scale (*QUIMIS*, Model: *Q–500L210C*), with 0.001 *g* accuracy and calibration mass that ranged from 1 *g* to 210 *g.*

A *Bareiss* analogue Shore A scale was used according to the ASTM standards. The ASTM D2240-14 determines that a test specimen should have a minimum thickness of 6 mm [42]. According to item 6.2.1 of the standard, the bar specimens were cut into two halves of approximately 3.12 mm in thickness and arranged overlapping by mirroring the lower surfaces. A Shimadzu TA-50 was used for the thermogravimetric analysis. Temperature ranged between 23ºC to 800°C at a heating rate of 10°C min^{-1} under nitrogen (N_2) purge [41-47]. The samples were obtained by cutting the bar specimens weighting approximately 10 to 20 mg, in compliance with the ASTM E1131-08 standards [48]. The mechanical properties were obtained using a Shimadzu® EZ- LX equipment for tensile and compression tests. For the tests, the speed parameters were 200 mm/min for traction [37] and 5 mm/min and 50% of sample deformation for compression [23,48]. Following the TPU manufacturer recommendations, for the compression test, the specimens were annealed at 90° C for 20 hours.

III. RESULTS AND DISCUSSION

The results of the FT-IR analysis (Figure 3a) for all the recycling cycles showed a decrease in peak intensity and absorbance bands at 3332 cm^{-1} (N-H), 2957 cm^{-1} (C-H), 1528 cm^{-1} (R-C-NH) which are characteristic of TPU [44,49,50]. The increase intensity of peaks 1596 cm^{-1} (C=C) and 814 cm^{-1} (C-H) indicate increase presence of aromatic rings in polymer chain [50,51]. In relation to CH groups, there was a variation in symmetric and asymmetric stretching in RCM 1 and 2, respectively. Peaks of lesser intensity occurred at 1728 and around 1694 due to the presence of free aromatic and hydrogen-bonded carbonyl groups (C=O), which characterizes the TPU flexible and rigid segments [32]. Figure 3b shows the range bounded by the rectangle in Figure 4a. In peaks between 1100 - 1300 cm^{-1}, which characterize the ester group (C-O), peaks of lesser intensity were observed at 1309 cm^{-1} and 1138 cm^{-1} as well as a strong decrease in peak intensity at 1219 cm-1 [52]. There was also a weak increase in peak intensity at 1252 cm^{-1} (C-O), 1075 cm^{-1} and a strong increase in peak intensity at 1018 (C-O) respectively [51]. A decrease in peak intensity, a characteristic of TPU, may indicate chain scission by thermal and mechanical degradation [54].

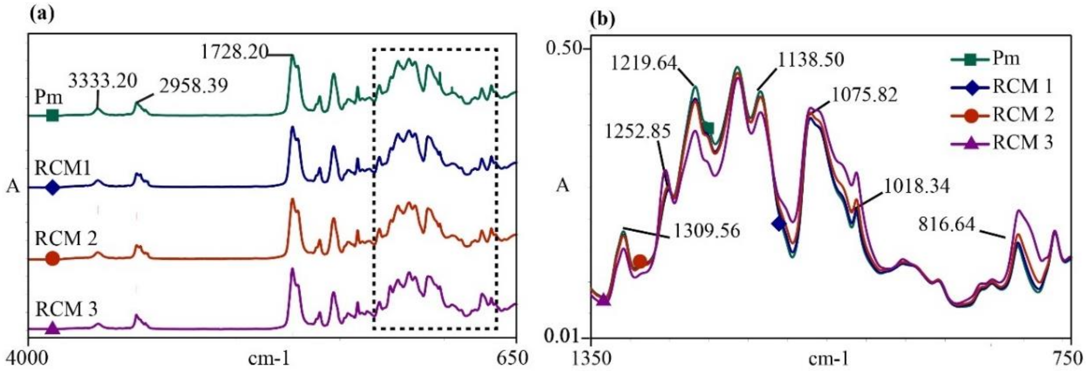

Figure 3. a) Result of FTIR of the Dm, RCM 1, RCM 2 and RCM 3; b) Details of changes in the range 750 to 1350 cm^{-1}.

In the thermal degradation curves (Figure 4a) obtained through thermogravimetric analysis (*TGA*), two degradation steps with similar behavior were observed in all samples. First step occurring approximately at 300 ºC, with a 70% loss of the total mass of the sample, attributed to the degradation of the urethane group and to secondary reactions present in the rigid segment [44,53]. The rates of degradation curves stabilized between 400 and 500° C, and the second step occurred between 500 and 700° C, mass loss between 20 and 30% attributable to the degradation of the flexible segment in polyols, urea stable or isocyanates [44,53]. Figures 4a and 4b show an anticipation of the degradation temperature with an increase in degradation rates and narrowing of the thermal zone of the RCM 1 and 3 degradation curves in relation to the Pm.

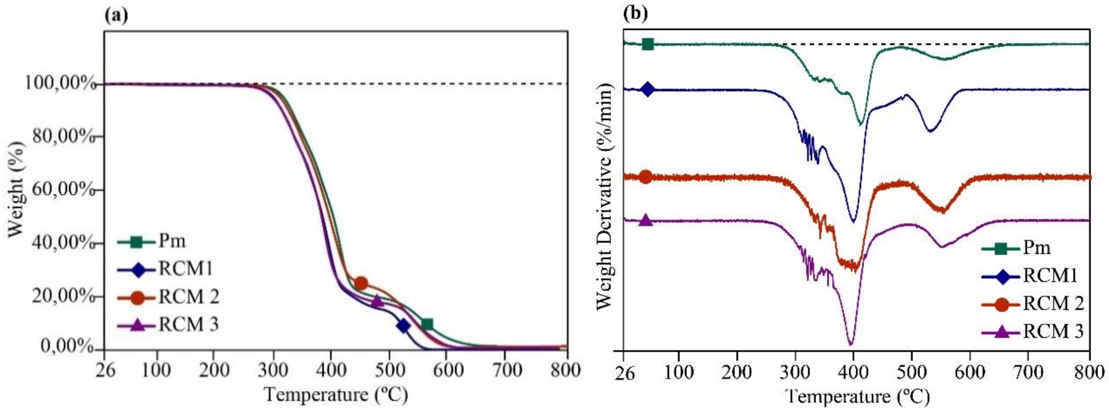

Figure 4. a) Average TGA curves of the Pm, RCM1, RCM2 and RCM 3; b) Curves (DTG) derived from the average TGA curves.

The results of the density tests (Table 2) did not indicate any significant variation of this property over the recycling cycles. The similarity of the results obtained for the recycling cycle samples with material designed using the FT-IR, TGA and density analyses showed physical and thermal stability following milling, drying and injection without changing the TPU. The 78 Shore A hardness value achieved for Pm (Table 2) was compatible to the 75 Shore A hardness value obtained for TPU, according to Palhano [23]. During the reprocessing stages, the hardness value increased by approximately one standard deviation in RCM 1 and RCM 2, and stabilized in RCM 3. These results corroborate those reported in the literature on technical feasibility of TPU recycling [26-28,30,54]. Although the physical and thermal stability of materials could be observed, the degradation and aging processes after every reprocessing cycling of polymers, such as TPU, may reduce the strength of plastic material [12,13,54]. Xie et al. [54] indicate the high shear stress in processing and strength applied during the application on TPU may lead to rupture of polymer chains in stress cracking (SC) susceptible to free radicals associated with oxidegradation [54]. Table 2 shows the results of physical and mechanical properties of Pm, RCM 1, RCM 2 and RCM 3.

Table 2. Properties in the application of RCM on TPU

Properties	Unity	**Pm**	**RCM 1**	**RCM 2**	**RCM 3**	SD
Density	Kg/m³	1226.02	1246.46	1222.12	1215.61	13.32
Hardness	Shore A	78	80.3	82.8	82.4	2.21
Young modulus	GPa	0.029	0.021	0.019	0.019	0.005
Tensile stress (100 %)	MPa	4.43	3.85	4.51	4.59	0.34
Tensile stress (300 %)	MPa	8.67	6.90	7.40	7.10	0.79
Tensile stress at break	MPa	21.08*	14.74*	13.86	9.04	3.41
Elongation at break	%	714.35*	714.33*	709.36	465.75	123.49
Compress stress (50%)	MPa	5.39	4.13	5.06	5.12	0.55

*No break (500 mm equipment limit amplitude).

In the limit amplitude of the equipment for Pm and RCM 1, no breaks of specimens were observed during the traction test. However, there was a decrease of 30.08% of the total stress. RCM 2 specimens showed breaks close to the displacement limit or after seconds under high shear stress, within 5 minutes interval [39] and an average total stress value close to that of RCM 1. For the RCM 3, the maximum stress reduced to 42.88% from the PM initial value. There was also loss of material elasticity, causing the specimens to break in an average elongation of 34.8%, lower compared to that of Pm. By observing the Young modulus values, the stress at 100% and 300% and maximum at each stage, we noted the hardening phenomena under deformation and strain-induced crystallization of the flexible segments added to reorientation of the rigid segments, increasing the resistance to fatigue and disruption of TPU, when it is exposed to severe impact or elongation [54,55]. Wang et al. [55] explained that in these phenomena there was no neck formation during the elongation process. Our study observed that, despite the high deformation that occurred in all specimens, the value for the maximum stress at break was significantly higher compared to that of Young modulus [55]. There were no significant changes in the values (Table 2) of density and maximum compression stress, over the recycling cycles.

IV. CONCLUSION

The results obtained by the traction and hardness test, different from those achieved through the FTIR and TGA techniques, require evidence of mechanical property degradation. Therefore, it will be possible to create strategies and extend the useful life of materials by correlating the data with the requirements of the projected materials [18]. However, considering the waste management model, which aims to recycle post-consumer footwear materials in open or closed-loop recycling, further discussion is needed on the analysis of properties that impact the performance requirements for footwear [1,7]. The RCM 1 properties should be considered for reuse in the original application. The degradation of the RCM 2 mechanical properties, particularly the specimen breaks, showed the reuse of this material in applications different from the original product. The results identified in the properties of the RCM 3 revealed the degradation of the mechanical properties and the need to recover the original performance by combining it with virgin raw materials.

Authors have been described the lack of technical support to shoe designers on the life cycle of materials used in the footwear industry [7,9,10]. It is expected that the dissemination of studies on the application of RCM in academic research or in the industry may broaden the knowledge regarding the mechanical properties of recycled materials. The provision of data to shoe designers can provide for new strategies and applications to extend the life cycle of materials, and therefore, minimize the use of raw materials and the amount of post-consumer waste.

V. FUTURE WORK

The study was focused on the characterization of mechanical properties, towards the continuation of the research can be analyzing properties such as stiffness; surface roughness, color; and subjective perception of recycled material by users in product design applications.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge support from the Architecture Faculty, UFRGS, the Laboratory of Design and Material Selection (LdSM), the Laboratory of Corrosion, Protection and Recycling

(LACOR), Laboratory of Advanced Polymers (LPA) and the Laboratory of Ceramic Materials (LACER) for providing the equipment's to carry out this work. We also would like to thank the Prisma Montelur company for donating the thermoplastic polyurethane necessary for this research, and the research funding agency *CAPES* for the scholarship.

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