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Abstract

A new industrial revolution, with sustainability and circularity at its heart, and led by brands of fashion and automotive sectors, finds its motivations in the ecological transition where production can no longer be disconnected from ethical, social and environmental assessments. Leather production is a complex process which produces liquid, gaseous and solid wastes. In particular, solid wastes represent the 31% of the total and are made up of wastes from splitting, shaving, finishing and trimming residues, with significant environmental impacts associated. In this project sustainability and circularity paradigms have been approached by developing new printable polymer bio-composite from leather wastes for Additive Manufacturing (AM). Leather shavings have been used as fillers for PLA and TPU polymeric matrices to produce bio-composite as suitable material for Fused Filament Fabrication (FFF). In particular, shavings from wet-state leather, grinded in three different particle sizes, have been used. Wastes have been preliminary characterized from a chemical and eco-toxicological point of view. The grinded material has been morphologically analyzed to determine the particle size distribution and exploring correlations with the final material properties. Thermal and mechanical performances of the bio-composites have been assessed considering three different fillers contents and three different grinding sizes. The bio-composites have been subsequently tested in FFF devices as novel 3D printable materials.

Keywords: Leather, Leather waste, Shavings, Additive manufacturing, FFF, Filament fused fabrication, Sustainability, Circularity, Reuse, 3D printing, PLA, TPU, particle size distribution, PSD

1. **Introduction**

Leather production is a process where wastes of food industry (animal hides and skins) is reused as by-product to create a durable, stable, and high added value material. The process involves specific chemical and physical treatments that modify the macromolecular collagenous structure. Leather is used in many industrial, including products for fashion, personal protective equipment (e.g. safety shoes or gloves), as upholstery material for furniture, car interiors or for cleaning purposes.

Under the pressure of fashion brands [3] and automotive groups, tanning industry is revolutionizing its production paradigm by implementing new business models based on the concepts of circular economy and sustainable development via more energy efficient processes, the reduction of environmental footprints and the reuse of wastes of industrial production [1] as by-products for new materials and applications. This also responds to the commitments set out in the United Nations 2030 Agenda for Sustainable Development [2] that on the one hand requires the optimization of the management of natural resources involved into the processes and on the other hand it requires the minimization of the disposal of wastes that must be reintroduced as much as possible into the industrial system. The enormous production of solid waste by tanneries is determining a transition for companies which, in some cases, are reconfiguring themselves no longer exclusively as producers of a single raw material (leather), but also as suppliers of by-products from the wastes generated. With reference to the entire tanning process from raw material to finished leather, considering the Italian production, the 31% of the total residuals is made up of solid processing waste deriving from splitting, shaving, trimming or buffing operations; in terms of relative quantities, each square meter of finished leather generates 1.65 kg of waste of which approximately 0.5 kg solid. Globally, the entire tanning industry produces 1.7 billion square meters of leather, corresponding to a value of 34 billion euros [1] and approximately 600 tons of solid waste, 150 tons of which consisting in shavings and tanned trims. For the pre-tanning stages, wastes recovery and reuse are already widely developed especially as raw materials of other industrial sectors. Examples of applications of these kinds of wastes, that takes advantage of not contaminated collagenous materials, are pharmaceutical and cosmetic products, fertilizers in agriculture feed [5], fuel producing [6-9] or adhesives [10]. Otherwise, tanned split leathers are used as pigmented split or suede leathers [23].

With reference to chemically processed leathers, solid residues such as shavings represent about the 33% of total wastes and the 75% of solid wastes. They have already found a market as a polymer filler/reinforcement for the production of other materials such as leather fiber board [11-12] (upholstery material as defined in EN 15987:2015 [13]) or for the production of chemicals for tanning process [14-22]; other by-products, such as trimming, which may therefore contain chemicals from the retanning, dyeing, fat liquoring and finishing stages (less than the 7%), on the other hand, have found their reuse in small leather goods or footwear industry after assembly in patchworks.

About the reuse of leather wastes as filler in composite materials, many studies have been carried out using both thermoplastic and thermosetting polymers as matrix [4]. This project has been focused on the application of PLA and TPU for novel bio-composites suitable for Additive Manufacturing applications. The choose of these materials is due to commercial and sustainability motivations. From the sustainability point of view, the interest towards composites is due to the increased demand of eco/bio-composites made from natural biodegradable material (e.g. PLA) and from renewable resources (eg. bio-TPU) to replace conventional matrix deriving from petrol-based polymers [24]. Polylactic acid (PLA) is a bioplastic produced from the fermentation of biomass of natural product as corn, sugarcane or potatoes and, due to its biocompatibility and biodegradability, it is used in many applications in substitution of petrol-based plastics for automotive components, food packaging, degradable plastic. [25]. With a view on circularity, some studies have been carried out on PLA filled using different natural reinforcements and nanoparticles as clay, talc [26-29], carbon-based nanoparticles [30] and natural fibers [31-32]. Specific studies using collagen from leather wastes have been carried out on the mechanical and thermal characterization of PLA filled with animal fibers from wet-blue buffing (leather waste) in different concentrations that show the multiuse purpose applications of such material [33]. About TPU, this polymer is widely used in many applications for its processability and elastomeric behavior; however, its production is highly dependent on fossil-based polyols and isocyanates. In this study, polyurethanes derived from polyols from vegetable oils (as soybean, castor, sunflower, palm oils) have been considered. The substitution of petroleum-based polyols provides a significant reduction in the carbon footprint and a positive impact on the life cycle assessment [34]. From a

commercial point of view, PLA and TPU are one of the most used polymers as thermoplastic filaments for FFF techniques. The eventual printability of traditional TPU composites could be the starting point for the verification of the use of bio-TPU for more sustainable processes.

In this project sustainability and circularity paradigms have been approached by the key enabling technology (KET) of Additive Manufacturing (AM) through the production of polymer compounds using leather shavings. In particular, Fused Filament Fabrication (FFF) techniques have been considered. Additive manufacturing is a layer-by-layer production process able to create components with complex geometries at low cost and minimizing wastes [35]. FFF is an AM technology based on the extrusion of a melted thermoplastic polymer filament, that has become popular and widely used due to the availability of low costs and open-source devices. In FFF the filament is melted in a heated nozzle and deposited on a working plate layer by layer in the XY plane according to specific path identified in the design projecting of the component [36]. From the material point of view, a suitable FFF process depends on the correct material heating and depositing on the working plate, that means the proper setting of extrusion temperature and speed, layer thickness, deposit angles and geometry of the layers [37].

This study has been focused on the use of grinded shavings of leather as reinforcement for PLA and TPU matrices. Before testing the filaments in FFF devices, leather wastes and bio-composites have been chemically, morphologically and physically characterized. In particular, tensile tests, DSC, TGA, DMA and rheological tests have been carried out for a comparison with the performances of the original polymers. Three different concentrations of filler have been considered to verify the effect of the filler content on the material performance; furthermore, to verify the effects of particle size distribution, shavings have been grinded using 3 different sieve sizes. After the material characterization, composites materials have been produced in filaments and tested in FFF for printability verification studies.

2. **Material and Methods**

1. *Leather wastes*

The leather waste used was a wet blue bovine leather shaving for automotive applications. Shavings have been reduced grinded by a Pulverisette 19 (Fritsch, Germany) using three different sieve dimensions: 0.5 mm, 1.5 mm and 4.0 mm.

The different grinded particulates have been morphologically characterized using an image-based method for the determination of particle size distribution using an Optika microscope model SZP-10 equipped with a Full HD HDMI camera Optikam HDMI PRO; the image with a resolution of 1920 x 1080 pixels have been subjected at a digital image processing (DIP) using open-source image editing software Gimp version 2.10.32, as described before [38].

Chemical and physical characterization of shavings have been carried out. Ecotoxicological analysis of the wastes have been carried out to verify the compliance of the material to the reference legislation and standard requirements for leather. In particular, the have been carried out the test below:

- Tetra, trichloro, dichloro, monochloro and pentachlorophenol content in accordance with ISO 17070,
- Total metal content in accordance with ISO 17072-2 using ICP Thermo Fisher ICAP RQ,
- Formaldehyde content in accordance with ISO 17226-1 using HPLC Shimadzu LC 20 AD,
- Hexavalent chromium in accordance with ISO 17075-2 using Ion Chromatograph Dionex ICS-3000

Furthermore, for a complete characterization, the following chemical and physical tests have been carried out:

- Humidity and volatile matter at 50°C, 90°C, 102°C and 150°C in accordance with ISO 4684,
- DSC and TGA analysis of leather wastes using a TA STD Q600 instrument.

1. *Bio-composites*

For the scope of the present paper, TPU (produced by Filoalfa) and PLA (produced by Filoalfa) commercial polymers have been used. Polymer pellets and leather waste shavings of different particle size were compounded in a Xplore MC 15 HT Micro Compounder for two minutes at 100 rpm and a temperature of 180°C. Polymer composites of 3 different concentrations were prepared: 10%, 20% and 30% in weight. For manufacturing of 1.75 mm filaments for 3D printing, composites were pelletized again and re-extruded with the same compounder, but with a continuous feeding at 15 rpm and the help of a stretching line to control the final filament diameter.

The polymer composites were characterized with the following tests:

- Tensile properties (tensile strength and elongation at yield) in accordance with ASTM D638 using a dynamometer Instron 5967 model equipped with a 100 daN load cell with a crosshead speed of 10 mm/min. Young's modulus has been determined in the range from 0.05 % to 0.25%, where the crosshead speed was kept at 1.0 mm/min; test pieces have been prepared out using Hot Press 3100 (Collins, Germany) at a temperature of 180°C and pressure 100 ± 10 bar for 2 minutes after which the samples were allowed to cool down under same pressure, using circulation of cold water.
- Dynamic Mechanical Analysis using a TA Instrument DMA 850 Discovery equipped with tensile clamps in strain control with an amplitude of 50 micron at a frequency of 1 Hz. The variations of glass transition temperature (Tg), storage modulus E' and loss modulus E'' have been assessed.
- DSC-TGA analysis using TA Instrument STD Q600 instrument. DSC tests have been carried out in nitrogen with a temperature ramp of 5°C/min up to 200°C. TGA analysis have been carried out in nitrogen at a heating rate of 10°C/min up to 800°C.
- Rheological measurements were carried out using an ARES (Rheometric Scientific) rotational rheometer in nitrogen and after drying samples in an oven at 80°C for 24 hours, in order to avoid degradation phenomena by the presence of humidity. Tests have been carried out in an oscillatory regime (range 0.1-100 rad/s) at 190°C and using parallel plates with a diameter of 25 mm.

1. *Fused filament fabrication*

To verify the printability of bio-composites, qualitative tests using 3D printing Bamboo mod. X1C have been carried out by setting the following initial parameters: 50 mm/sec, diameter of the nozzle 0.40 mm, layer height 0.20 mm (1 layer per run for PLA and 2 for TPU) and bed temperature of 65°C. Different extrusion temperatures have been tested to identify the suitable printing one, carrying out single linear depositions (run) of 100 mm. Tests have been preliminary carried out on PLA and TPU neat (without fillers); from the morphological analysis of the run, the minimal optimal printing temperature has been identified. In particular, the correct flowability of the compound, the continuity, size uniformity of runs has been analysed. Starting from the minimum printing temperatures identified, the same tests were executed on the 20% composites as representative materials.Prior the printability tests, all the filaments have been thermally pre-treated at 60°C for at least 4 hours to eliminate the excess of humidity and, hence, to minimise material degradation. For each temperature and printing speed, from the morphological analysis of the runs, the printability has been defined as "pass" or "fail". Subsequently, to verify the welding between layers and the stability of the entire printing process during the production of components, test cube of 15 mm base and

10 mm height have been produced without top cover layer. The deposition strategy provided 2 base layers with alternate orientation of 45° and 4 perimeters consisting in 2 layers. Fusion 360 software has been used for designing the stl file of the test cube.

3. Results and Discussion

1. *Characterization of leather wastes*

In Table 1, the results of the chemical characterization of leather wastes are reported. Overall, limited to the tests listed above, the leather wastes were found compliant to eco-toxicological requirements. The results show the compliance of shavings to the regulations requirements and its possible use as a by-product for polymers. From a processing point of view, the results suggest a thermal pretreatment of wastes is necessary before compounding with polymers to reduce the humidity and volatile substances, so to limit defects and porosities. Thermal pre-treatment of at least 2 hours at temperatures above 85°C have been carried out.

Table 1a – Chemical characterization of leather wastes

Test Item	Conditions	Method	Unit	Value
Humidity and volatile matter	50°C	ISO 4684	%	5.8
	90°C		%	10.1
	102°C		%	10.9
	150°C		%	12.1
Chrome		ISO 17072-2	mg/kg	17338
Aluminum				71.2
Iron				119.7
Titanium				9.6
Zirconium				10.1
Lead				< LOD
Cobalt				< LOD
Nickel				< LOD
Cadmium				< LOD

Table 1b – Chemical characterization of leather wastes

Substance	Regulatory Reference	Method	Limit	Pass / Fail
Azodyes	Reg. (EC) 1907/2006 REACh Res. 43	ISO 17234	30 mg/kg	Pass

Substance	Regulatory Reference	Method	Limit	Pass / Fail
Hexavalent chromium	Reg. (EC) 1907/2006 REACh Res. 47	ISO 17075-2	3 mg/kg	Pass
Clorophenols	National Regulations	ISO 17070	1 – 5 mg/kg	Pass
Dimethyl fumarate (DMF)	Reg. (EC) 1907/2006 REACh Res. 61	ISO 16186	0.1 mg/kg	Pass
Alkanes, C_{10}-C_{13}, chlorine (SCCP)	Regulation (EU) No 2019/1021		1500 mg/kg	Pass
Perfluorooctane sulfonate acid PFOA	Regulation (EU) No 2019/1021		0.025 mg/kg	Pass
Perfluorooctane sulfonate acid PFOS			10 mg/kg	Pass
PFOA derivatives			20 mg/kg	Pass
Organostannic compounds	Reg. (EC) 1907/2006 REACh Res. 20	I.M. ISO 17072-2	0.1% tin by weight	Pass
Nonylphenol $C_6H_4(OH)C_9H_{19}$	Reg. (EC) 1907/2006 REACh Res. 46	ISO 18218-2	0.1% in chemicals	Pass
Nonylphenol ethoxylates $(C_2H_{4O})nC_{15}H_{24}O$			0.1% in chemicals	Pass
Nickel	Reg. (EC) 1907/2006 REACh Res. 27		0.5 ug/cm2/week	Pass
Phtalates (DEHP, DBP, BBP, DIBP)	Reg. (EC) 1907/2006 REACh Res. 51		0.10%	Pass
Phtalates (DINP, DIDP, DNOP)	Reg. (EC) 1907/2006 REACh Res. 52		0.10%	Pass
Formaldehyde	Japan law 112	J.L. 112 Method	< 16 mg/kg for infants	Pass
	Reg. (EC) 1907/2006 REACh Res. 72	ISO 17226	< 75 mg/kg with contact	Pass
			< 150 mg/kg non-contact	Pass

To assess the morphological characteristics of particulates, a DIP method has been used for the determination of Particle Size Distribution (PSD) of grinded leather wastes with sieves of 4.0 mm, 1.5 mm and 0.5 mm [38]. The results of the study on the size distribution have shown that the use of smaller sieves determines a reduction of the particle surface area and its distribution. While using 4.0 sieve the most frequent surface area value is about 10000 square microns, for 1.5 and 0.5 sieve it is about 7000 but with a less dispersed distribution of particle size. Obviously, the printability of filaments is directly related to the distribution of sizes, so grinding that determines smaller particles shall be preferred. For this reason, grinded leather using 0.5 mm sieve have been uses for filament production.

DSC and TGA analysis of leather wastes has been carried out to verify that no degradations or reactions in the range of extrusion temperature and filament deposition temperatures could occur. Tests have been carried out up to 800°C with a temperature rate of 10°C/min. The results have shown that degradation occurs at temperatures above 300°C, that is above the extrusion temperatures for filament production and printing.

2. *Mechanical tests on bio-composites*

TPU and PLA bio-composites have been prepared in 3 different compositions (w/w): 10%, 20%, 30% of grinded leather waste using 0.5 mm sieve. To verify the influence of particles dimension, tests have been carried out on 1.5 mm and 4.0 mm too at the reference concentration of 20%. Elastic modulus (MPa) in the linear region between 0.05% and 0.25%, tensile resistance as the stress at yield (zero slope) in MPa, percentage elongation at yield (zero slope) and percentage elongation at break have been assed.

SAMPLE	YOUNG'S MODULUS (MPA)		TENSILE STRESS AT YIELD (MPA)		ELONGATION AT YIELD (%)		ELONGATION AT BREAK (%)	
	VALUE	ST. DEV	VALUE	ST. DEV	VALUE	ST. DEV	VALUE	ST. DEV
PLA	1798.9	440.9	77.4	3.2	6.5	1.1	7.9	3.7
10%PLA_0.5mm	2406.4	86.1	76.0	3.3	4.7	0.5	4.9	0.6
20%PLA_0.5mm	2394.8	122.4	70.1	4.7	4.0	0.1	4.0	0.1
30%PLA_0.5mm	2402.6	179.3	71.4	5.4	4.6	0.6	4.7	0.7
20%PLA_1.5mm	2198.7	135.1	58.7	6.6	3.8	0.5	3.8	0.5
20%PLA_4.0mm	2160.3	190.8	55.4	14.7	4.5	1.1	4.6	1.1

Table 2: Tensile properties of PLA bio-composites

SAMPLE	YOUNG'S MODULUS (MPA)		TENSILE STRESS AT YIELD (MPA)		ELONGATION AT YIELD (%)		ELONGATION AT BREAK (%)	
	VALUE	ST. DEV	VALUE	ST. DEV	VALUE	ST. DEV	VALUE	ST. DEV
TPU	51.6	0.2	36.9	1.9	524.5	27.8	527.1	28.1
10%TPU_0.5mm	66.1	5.5	28.7	3.4	345.3	52.9	406.9	21.3

SAMPLE	YOUNG'S MODULUS (MPA)		TENSILE STRESS AT YIELD (MPA)		ELONGATION AT YIELD (%)		ELONGATION AT BREAK (%)	
	VALUE	ST. DEV	VALUE	ST. DEV	VALUE	ST. DEV	VALUE	ST. DEV
20%TPU_0.5mm	123.6	12.6	24.7	0.5	127.9	18.1	133.0	18.5
30%TPU_0.5mm	186.7	11.6	24.1	1.6	79.1	9.6	81.2	8.7
20%TPU_1.5mm	131.0	7.9	23.1	1.0	111.1	11.7	119.8	13.6
20%TPU_4.0mm	104.9	7.8	20.0	2.0	121.8	44.9	144.1	51.8

Table 3: Tensile properties of TPU bio-composites

As evident, for both PLA and TPU bio-composites, the higher the concentration of reinforcement, the stiffer the material becomes (increasing modulus). With reference to the final properties of the compounds, for PLA the increase of the concentration of the filler determines variations within the 10% of tensile resistance and a decrease of elongation at yield of about 30%. Also, for TPU the tensile resistance reduces with the increment of filler concentration up to 35% and a remarkable reduction of the elongation at yield.

In general, the increase in stiffness and brittleness, related with a decrease in tensile strength and elongation at yield, could determine negative effects on the printability or in the feeding system of 3D printing device.

In table 2 and 3, the particle size effects at the reference concentration of 20% have been considered too. For PLA/leather waste bio-composites, the reduction in the dimensions of particulates corresponds to an increase of modulus and of tensile strength, while there are no evident differences for elongation at yield. Furthermore, for TPU bio-composites the reduction of size of particles determines the increase of tensile strength, while, for the other properties, no relevant tendencies have been noticed.

3. *Thermal and Thermomechanical characterization of compounds by DSC, TGA and DMA*

In FFF 3D printing techniques the starting printing material is in solid state, so it is fundamental a proper a thermal characterization to verify the softening and melting temperatures for a suitable setup of printing parameters. Otherwise, it is important to verify that the complete fusion of eventual crystalline phase of polymer occurs for a more efficient process.

SAMPLE	Tg	E' (25°C)	E' (90°C)	E'' (25°C)	E'' (90°C)
	(°C)	(MPA)	(MPA)	(MPA)	(MPA)
PLA	74.6	3732	25	293	14
10%PLA_0.5mm	73.7	1867	25	180	10
20%PLA_0.5mm	70.6	1511	11	133	4
30%PLA_0.5mm	70.5	1035	18	117	5
20%PLA_1.5mm	70.9	1344	12	129	4
20%PLA_4.0mm	70.2	994	12	60	4

Table 4: DMA results for PLA bio-composites

SAMPLE	Tg_1 (°C)	Tg_2 (°C)	E' (25°C) (MPA)	E' (100°C) (MPA)	E'' (25°C) (MPA)	E'' (100°C) (MPA)
TPU	-39.1	12.3	16.36	7.62	1.51	0.46
10%TPU_0.5mm	-38.0	17.2	52.95	25.05	5.66	1.70
20%TPU_0.5mm	-38.7	13.3	161.80	62.73	19.81	5.80
30%TPU_0.5mm	-35.9	20.6	161.30	59.45	19.69	6.18

Table 5: DMA results for TPU bio-composites

In table 4 and 5, the results of DMA tests are reported for the different compound concentrations; for PLA the particle size influences have been studied too. Glass transition temperatures have been evaluated from the minimum point of the first derivative in the temperature of the storage modulus. Value of the storage modulus and loss modulus at 25°C and 90°C/100°C have been reported too. As expected TPU show two glass transitions, one corresponding to the soft segments and the other to the hard segments. It is noted, however, that all Tg values are overestimated, probably due to the high heating rate for DMA tests. However, for both polymers a slight variation in the glass transition temperature (Tg_1 for TPU) was detected as the reinforcement concentration increases. It can be observed that the glass transition temperatures of PLA did not change with addition of leather particles of different sizes.

The DMA analysis shows a different effect of reinforcement for PLA and TPU. The storage and the loss modulus of PLA decreases by increasing the filler concentration, while for TPU both moduli increase with the concentration of the filler. Obviously, changing of the viscoelastic behavior of materials could determine a change in printability of composite with reference to neat polymers.

From DSC analysis, it appears that both PLA and TPU have low degree of crystallization. A very small melting peak is visible for PLA at approximately 150°C, which is not affected by the presence of leather particles. Overall, the typical transition temperatures expected from PLA and TPU have been confirmed by DMA and DSC, which are compatible with conventional extrusion settings. In the end, TGA analysis have shown that also the degradation temperatures of all the compounds are not related with the filler content and are well above the temperatures involved in extrusion and printing processes.

4. *Rheological characteristics of compounds*

The rheological behavior of compounds is fundamental because it provides direct information not only on the workability of the materials but also on the structure-morphology correlations; otherwise, given the correlation between the printability and the viscosity of the material, it is important to verify that there are no significant variations in viscosity that could affect the printing quality of the composite materials compared to the unfilled polymers. For both polymers, as expected, an increment of viscosity has been verified. The complex viscosity, in fact, progressively increase up to approximately 40% for the 30% composites compared with the unfilled polymers. The effects of these slight viscosity increases, close to the printing temperatures, will be considered qualitatively when the optimal printing temperature will be assessed.

5. *Printability of bio-composites*



(a)



(b)

Figure 1: Printing temperature for pure PLA (a) and PLA/WB20% bio-composite (b)

To classify a filament as “printable”, some specifications shall be complied with. The filament shall melt and have a viscosity low enough to determine a stabile flow of material through the nozzle, maintaining the shape under the solicitation due to the printing process and gravity. To ensure a good adhesion between adjacent layers, the material must be able to inter-diffuse across the interface. As described above, compounds printability using FFF devices have been assessed qualitatively by the morphological evaluation of 100 mm line (run). Figure 1 shows runs carried out for pure PLA (a) at different temperatures for the specified 3D printing settings. As evident for the printability of PLA a minimum temperature of the nozzle of 200°C shall be set. After determining the pure polymer printing temperature, the PLA/20%WB and TPU/20%WB filaments have been tested. The results of the qualitative analysis are reported in table 6.

SAMPLE	SPEED (mm/sec)	TEMP. (°C)	PRINTABILITY
PLA	50	185	FAIL
	50	190	FAIL
	50	195	FAIL
	50	**200**	**PASS**
	50	**205**	PASS
	50	**210**	PASS
	50	**215**	PASS
PLA/20%WB	50	195	FAIL
	50	200	FAIL
	50	205	FAIL
	50	210	FAIL
	50	**215**	**PASS**
	20	**210**	**PASS**
	20	215	PASS
TPU	50	240	**PASS**
	30	240	PASS
TPU/20%WB	50	240	FAIL
	30	240	**PASS**

Table 6: Printability of bio-composites

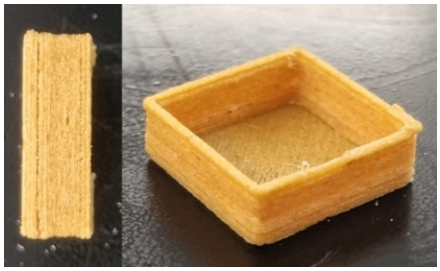


Figure 2: PLA/WB20% test cube

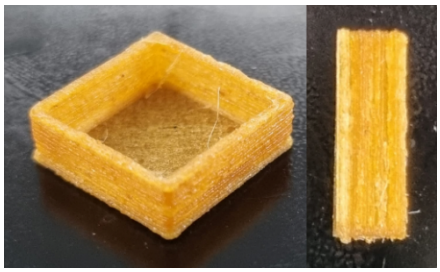


Figure 3: TPU/WB20% test cube

In table 6, the results of printability tests are summarized, indicating with “pass” the runs that provide enough printability in terms of continuity and homogeneity of the printed line. For PLA/20%WB composite, 200°C and 50 mm/sec conditions have been set, that are the same initial settings found as suitable for pure PLA printings. In those conditions PLA bio-composite did not show a sufficient printability, showing a continuous shape but a not uniform density along the run. This is probably related to a not enough flowability of the fuse into the nozzle due to the increment of viscosity of PLA after compounding. For this reason, the temperature has been increased till 215°C at 50 mm/sec where the printability has been considered as “pass”. In order to limit the degradation of PLA at high temperatures, speed and temperature of the nozzle have been reduced, finding a good printability at 210°C and at 20 mm/sec.

Otherwise, for TPU and TPU/20%WB composites temperature of 240°C and speed of 30 mm/sec have been identified as optimal conditions for printing. In general, with reference to pure polymer, for PLA compounds the printed line surface presented a rougher surface probably for an increment of the porosity

due to a not complete evaporation of the humidity during the extrusion process for filament fabrication or before the printing process.

To verify the welding between layers and the stability of the FFF process, test cubes of 15 mm base and 10 mm height have been produced. For TPU composite (figure 3) no differences have been observed in comparison to pure TPU. Otherwise, for PLA composite (figure 2), some imperfections were observed in correspondence with the changes in direction of the nozzle that could be caused by the material embrittlement.

4. **Conclusion**

In this work, PLA ed TPU composites reinforced using wet-blue grinded leather wastes have been studied as novel materials for fused filament fabrication Additive Manufacturing technologies. Different concentrations of leather waste in bio-composites have been studied to assess the mechanical, thermal and rheological changes compared with to pure polymers. Both PLA and TPU composites have shown an embrittlement of mechanical behavior corresponding to the increase of elastic modulus and a reduction of tensile strength; for PLA the loss of yielding phenomenon has been noted: the breaking stress is reduced and is close to the yielding stress.

Among the concentrations under investigation the 20% composites have been considered as reference for FFF printability tests. For each pure polymer the optimal printing temperature have been determined at a specified speed of the nozzle; the same parameters were used as a starting set of parameters for the composite materials. For PLA the minimum printable temperature has been identified in 200°C at 50 mm/sec; at the same temperature, the PLA bio-composite did not pass the printability test probably for the increase of viscosity. The material resulted printable increasing the temperature at 215°C or at 210°C reducing the nozzle speed at 20°C. For TPU and TPU bio-composite, the minimum printable temperature has been identified at 240°C at 30 mm/sec.

In conclusion, with a view to circularity, wet-blue leather shavings can be used as reinforcement of PLA and TPU to produce filament for Fused filament fabrication Additive Manufacturing techniques.

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