POLITECNICO
MILANO 1863

School of Industrial and Information Engineering
Master of Science in Mechanical Engineering

EAM OF RECYCLED TEXTILE NYLON: STUDY OF RECYCLING PROCESS AND PRINTABILITY

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Academic Year 2021-2022

RINGRAZIAMENTI

Desidero ringraziare coloro che mi hanno aiutato nella stesura di questa tesi con preziosi suggerimenti, critiche costruttive ed osservazioni: a loro va la mia più profonda gratitudine e il massimo rispetto.

Ringrazio anzitutto il mio relatore, Prof. Matteo Strano, che ha dimostrato la massima disponibilità nei miei confronti e una profonda fiducia.

Significative gratitudine e stima vanno anche al mio correlatore, Ing. Matteo Fabrizio, sempre pronto a fornire strumenti e consigli utili in ogni momento trascorso in laboratorio.

Inoltre, vorrei ringraziare il Prof. Luca Angelo Di Landro, il Prof. Marcello Colledani e i ragazzi del CIRC-eV per la disponibilità nel concedermi l'utilizzo di strumentazione fondamentale per il progetto e per il loro indispensabile contribuito nell'acquisizione di risultati.

Un sentito grazie anche all' Ing. Valerio Mussi e all' Ing. Francesco Cacciatore per avermi affiancato con la loro grande esperienza durante le prove sperimentali.

Ringrazio pielleitalia per aver fornito le t-shirts, materia prima del progetto, e Direct 3D per la collaborazione nei test con il pellet extruder.

Un ringraziamento particolare va alla mia famiglia, che mi ha sempre supportato durante il percorso di studi e che ha creduto nelle mie capacità.

Un pensiero va alle persone che mi sono state vicine durante questi anni. In particolare, Mari, distante ma sempre presente, Antonio, per la dedizione, la pazienza e la forza che mi ha trasmesso, Veronica e Andrea, parte del passato, del presente e sicuramente del futuro, Chiara e Gloria, che si sono dimostrate ottime amiche. A tutti coloro che ho incontrato e con cui ho condiviso le mie esperienze, dico grazie.

Infine, dedico questa tesi a me stessa, al mio ottimismo e alla mia tenacia, senza i quali nulla sarebbe possibile.

ABSTRACT

This thesis work has the objective to develop a brief, inexpensive and low environmental impact process chain to obtain an extrusion additive manufacturing printed product starting from an end-of-life textile nylon product. In the first part, for the recovery of textile nylon from nylon t-shirts, a purely mechanical procedure is implemented, with the target to obtain feedstock plastic material in the form of pellets. Preliminary material testing is described for each step of the process and for each employed machine. Characterization of the recycled nylon is also carried out, with the definition of density and colour variability of the pellets, and the results of the DSC analysis are shown. In the second part, the application of the recovered material to extrusion additive manufacturing is illustrated. The experimentation is conducted in order to understand whether the recycled material has good prospects of being 3D printed. The EFeSTO machine is employed for the purpose. The study of printability is carried out by varying some relevant parameters, like extruder and nozzle temperatures, layer fan speed and bed temperature, according to the quality of the prints output. Not only the recycled material is analysed, but also virgin nylon is printed in order to compare the results. Lastly, a blend made up of 30% in mass of recycled nylon is employed for the potential improvement of the printing quality.

Keywords: Extrusion additive manufacturing, recycling, textile nylon, EFeSTO, printability, process chain

ESTRATTO

L’obiettivo di questo lavoro di tesi è quello di sviluppare una catena di processo corta, poco costosa ed a basso impatto ambientale per passare da un prodotto tessile in nylon a fine vita ad un prodotto stampato 3D per estrusione. Nella prima parte, per il recupero di nylon tessile da magliette in nylon, è stata implementata una procedura di tipo puramente meccanico, con il fine di ottenere del feedstock in materiale plastico nella forma di pellet. Per ogni step e per ogni macchinario impiegato, sono stati effettuati test preliminari sul materiale. Inoltre, il nylon riciclato è stato caratterizzato, con la definizione della densità e della variabilità dei colori dei pellet, e sono stati presentati i risultati della calorimetria differenziale a scansione (DSC). Nella seconda parte, è stata illustrata l’applicazione del materiale recuperato nella produzione additiva tramite estrusione. La sperimentazione è stata condotta per capire se il materiale riciclato avesse potenzialità per essere stampato in 3D. La stampante EFeSTO è stata impiegata a tale scopo. Lo studio della stampabilità è stato effettuato variando alcuni parametri importanti, come temperature in camera di estrusione e dell’ugello, velocità della ventola e temperatura della superficie su cui si stampa, in base alla qualità delle stampe in uscita. Non solo il materiale riciclato è stato analizzato, ma anche il nylon vergine è stato stampato per paragonare i risultati. Infine, una miscela composta dal 30% in massa di nylon riciclato è stata utilizzata per il potenziale miglioramento della qualità di stampa.

Parole chiave: stampa 3D, riciclo, nylon tessile, EFeSTO, stampabilità, catena di processo

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1. INTRODUCTION

Circular economy is a model of production and consumption, which involves the extension of material life and complete recovery of materials, with the aim to maintain the value of the product as long as possible and to minimise the waste. Circular economy has been gaining popularity since it helps minimize emissions, opens up new market prospects and, principally, increases the sustainability of production and improve resource efficiency.

Textile industry is one of the greatest sources of pollution worldwide. The process of textile recycling would allow the achievement of two relevant benefits: to avoid the treatments for production of raw materials and to create an alternative route for the disposal of waste streams. The beneficial potential of textile recycling is strictly linked to synthetic fibers. Among these, Nylon is a versatile and performant plastic fiber. It is used in packaging, clothing and carpets, as well as for industry-specific purposes like fishing nets.

The majority of plastic waste is made of thermo-softening polymers, which can be re-melted and reformed into new items, in a practice known as mechanical recycling. Chemical recycling, instead, converts polymeric waste by changing its chemical structure to produce substances that are used as products or as raw materials for the manufacturing of products. However, this option is more expensive, and it can be responsible for the emission of toxic pollutants.

Recycled thermoplastics or leftover thermoplastic material from any process can be used as raw materials in Additive Manufacturing processes. 3D printing can therefore act as a circular economy strategy where plastic waste can be directly converted into a useful feedstock material. As a matter of fact, 3D printing is a circular process itself. In fact, the manufactured objects as well as the produced wastes can be transformed back into raw material and used to re-feed the printer. Moreover, in order to reduce the reduction in quality that occurs during manufacturing, it is also common use to mix recycled polymer with virgin material.

The objective of this work is to develop a brief, inexpensive and low environmental impact process chain to obtain an extrusion additive manufacturing printed product starting from an end-of-life textile nylon product.

To achieve the objective, mechanical recycling will be purely implemented. In general, it is the most effective approach, in terms of time, economic cost, carbon footprint and environmental impact. Moreover, all types of thermoplastics can be mechanically recycled, in principle, with little or no loss of quality. This aspect makes the process also versatile.

The experimental study is divided in two parts. In the first one, the development of a recycling process to recover textile nylon from nylon t-shirts will be described: through a sequence of mechanical processes, pellets of plastic material will be obtained from the textile fibers, and processes like grinding and extrusion will be involved. Characterization of the recycled nylon will also be carried out, with the evaluation of density and colour variability of the pellets, and the results of DSC analysis will be shown.

In the second part, the recovered material will be used for extrusion additive manufacturing. In this part, it will be evaluated whether the recycled material has good prospects of being 3D printed. The EFeSTO machine will be employed for the purpose. With this machine, the material will still be subjected to mechanical processing, in line with the whole recycling chain.

The study of printability will be carried out by varying some relevant parameters according to the quality of the prints output. Eventually, the assessment of suitable working parameters will be pursued. Not only the recycled material will be evaluated, but also virgin nylon will be printed in the same way in order to compare the results. Lastly, a blend made up of recycled and virgin nylon will be employed for the potential improvement of the printing quality.

2. STATE OF THE ART

2.1 CIRCULAR ECONOMY

Traditionally, economy is based on a linear process (*figure 1*): raw materials are transformed into products, and eventually they are thrown away as waste. However, increasing importance is being given to a different strategy, that is circular economy. It is a production model that focuses on the minimization of waste of natural resources and that consists of sharing, reuse, restoration and recycling of materials, with the aim to prolong their life as long as possible. In fact, after the first production cycle and usage by the consumer, once the product has fulfilled its purpose, the materials it is made of can be, when possible, reintroduced in the production cycle and are continuously reused in order to generate further value (*figure 1*).

While the approach "take, make and dispose" depends on the availability of high quantity of low-cost resources and energy, in circular economy the product is the resource itself and it never becomes waste.

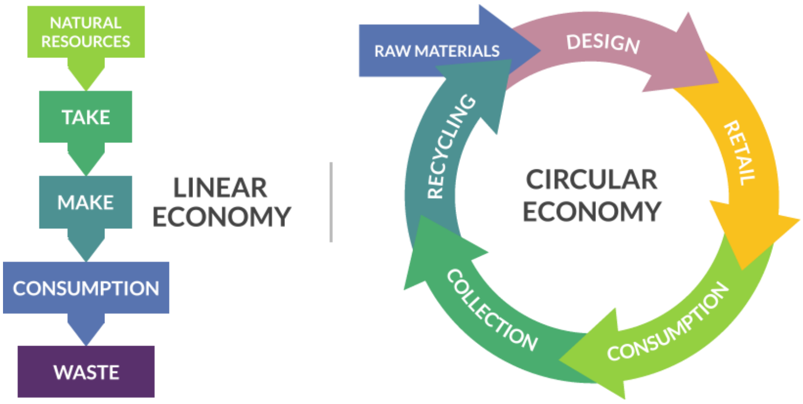


Figure 1. Linear economy vs circular economy

The terms "open-" and "closed-" loop recycling are frequently used to describe two different types of recycling in the circular economy. Typically, open-loop recycling presumes that materials will be cascaded to lower value uses due to degradation in quality, whereas closed-loop recycling presumes to keep materials flowing within the same product value chain [1].

Globally, great focus is being given to find solutions to the issue of plastic waste. It results that a total of 8.3 billion tonnes of plastic products were manufactured from 1950 to 2015, while 6.3 billion tonnes of plastic waste were generated. However, only 9% of the waste has been recycled, and 12% has been burnt with or without energy recovery. The rest has been poured into the natural environment [2]. The reuse and recycling rate of plastics in Europe is still very low, especially compared to other materials such as paper, glass and metals. Europe produces about 25.8 million tonnes of plastic waste annually and <30% of this waste is collected for recycling [3]. According to some research, in the United States, a significant amount of plastic waste was landfilled in 2019: about 86% of total plastic waste managed that year. Approximately 9% of total plastic waste was combusted, and 5% was recycled [4]. In Asian countries and regions, not only the plastic waste generated domestically but also the imported waste faces great challenges in the solid waste treatment and recycling system. In 2016, Asia generated over 121 Mt of plastic waste and imported over 11.4 Mt. even with current regulations, the effective management and recycling of plastic waste still has a long way to go [5].

Of utter importance is the work done by the Ellen MacArthur Foundation [6], a charity that promotes the transition to a circular economy. They develop and spread the idea of a circular economy, and work with business, academia, policymakers, and institutions to mobilise systems solutions at scale, globally.

2.2 AM FOR CIRCULAR ECONOMY

Sustainable production is required to reduce waste, raw materials, electricity, paper, packaging fuel, and other resources. Compared to the conventional manufacturing process, there are many positive environmental advantages of additive manufacturing technologies [7]. For instance, there is less waste of raw material and the use of new and smart materials: it can minimise plastic waste by using only the material required for final component manufacturing and minor support structures. Not only does 3D printing reduces waste, but it also allows for reuse. Therefore, it can be said that AM embraces the principles of circular economy.

Sauerwein et al. [8] explored the possibilities and effectiveness of 3D printing in the recycling of materials for the maintenance of the circular economy. As a matter of fact, additive manufacturing offers a wide range of opportunities to achieve a high level of sustainability in production, such as product attachment through personalization, resource efficiency through complex geometries, reparability and improved efficiency and local empowerment through distributed manufacturing. Being able to customize the product means attempting to improve the bond between user and product so to extend product lifetime. The fact that AM allows the creation of complex geometries can lead to a reduction of material usage and part consolidation, resulting in simplified assembly lines and reduced energy consumption. Moreover, the digitalization makes it possible to store spare parts digitally and produce them on-demand, reducing the need for inventories and transportation, since digital files can be sent to be produced locally. Finally, AM is recognised as a production technique that could favour repair: in fact, broken parts can be imitated and reproduced. Some AM technologies can even print directly onto existing surfaces.

Nonetheless, several challenges need to be overcome in order to achieve a complete circular economy in AM. To this end, it is essential to identify some materials that should be durable and that have a high reuse value. According to Colorado et al. [9], the recycled materials used in 3D printing can be classified into four large groups based on raw materials: plastics, metals, ceramics and composites. Among these, from the environmental sustainability of the processes point of view, metals are the most suitable for an optimal circular economy, due to their high recyclability. However, plastics are among the materials of higher usage in AM. They are also the focus of intense research as a result of their negative impact on the environment. It is generally hoped that materials with improved recyclability, reuse, or circularity will be more feasible for future use in AM, as national policies increasingly shift manufacturing to green materials and processes.

2.2.1 Recycling of thermoplastic materials for AM

Through AM, polymer and recycled polymer-based products can be manufactured. Recycled polymer-based AM is expected to be crucial for circular economy, as such will enable future sustainable design and manufacturing methods. Despite the clear potential for AM to be embedded in a circular economy, recycling is a complex process that involves several processing steps, as it is schematized in *figure 2* [10]. The first step in the recycling of plastic waste is the collection of plastic waste. It can be collected directly from industries, major retailers, and local authorities. After collection, the sorting of plastics is a critical process: the waste is separated according to its grade and type, while metals or any other impurity can be also removed. Manual and automated techniques (such as dry, air, electrostatic, or mechanical sorting) have been used to sort waste plastics. Afterwards, waste is cut into pieces and cleaned to avoid the presence of foreign materials. Then, it is mixed with additives like stabilisers, plasticisers, and lubricants as per requirement and extruded to form filaments for the FDM process. Similarly, fibers from worn out composites are also separated and used as reinforcement in filaments.

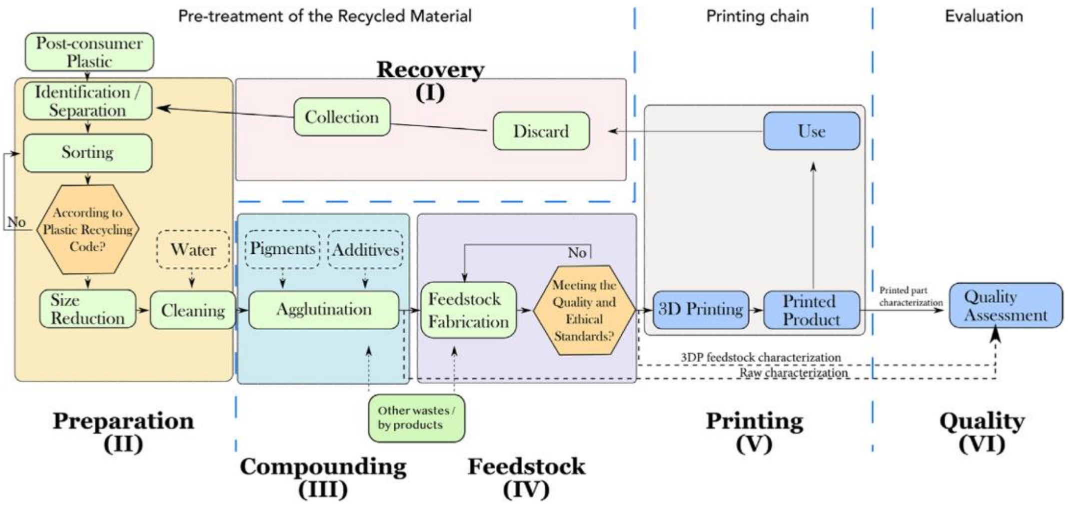


Figure 2. Recycling process (from [10])

Focusing on the main technologies used, Fused Deposition Modelling (FDM) is a popular material extrusion-based AM process used for manufacturing polymer and polymer-based composites, mainly due to characteristics such as rapid processing, simplicity and cost-efficiency [11]. As a matter of fact, recyclable thermoplastics can be used as raw materials in the extrusion process to produce AM feedstock, subject to property optimisation and satisfying the printing characteristics requirements. When printing, AM feedstock material is initially converted to a molten state by heating above the glass transition or melting temperature. The melt is then fed through the nozzle, which moves according to the shape of the model, and the melt is deposited layer by layer until the full part is printed.

The possibility of using recycled polymers in FDM creates routes for the efficient management of polymeric waste. However, in order to meet the application requirements, it is imperative to understand the performance of the recycled polymer products manufactured through AM.

Efforts have been made by the researchers in developing recycled polymer made products with a comparison with the corresponding virgin materials. Anderson [12] compared the properties of parts 3D printed with virgin polylactic acid (PLA) to those printed with recycled PLA. Mechanical testing encouragingly showed that with the recycled filament, mechanical properties such as tensile strength, shear strength and hardness were very similar to the ones of the virgin material, while tensile modulus of elasticity was statistically unchanged. In another work, Woern et al. [13] compared virgin PLA pellets to four recycled polymers: PLA regrind of 3D printed parts (the most common 3-D printed plastic), recycled ABS pellets (the second most common 3-D printed plastic), recycled PET pellets (the most common waste plastic), and recycled PP chips (the second most common waste plastic).

Kumar et al. [14] observed improvements in the mechanical properties of HDPE/LDPE-recycled polymers when reinforced with Fe powder, expanding the range of possibilities for the preparation of feedstock filaments for FDM. With the same intent, Zander et al. [15] processed blends of waste PET, PP and polystyrene (PS) as viable feedstock material.

Kumar et Czekanski [16] exploited waste SLS powder, mainly composed of polyamides, to develop tough and strong filaments for FDM, with the premise that powder is a suitable material form to melt and make filaments, since materials of various specific weights and sizes can be minutely mixed, achieving uniform distribution in a filament. The adopted methodology is shown in *figure 3*.

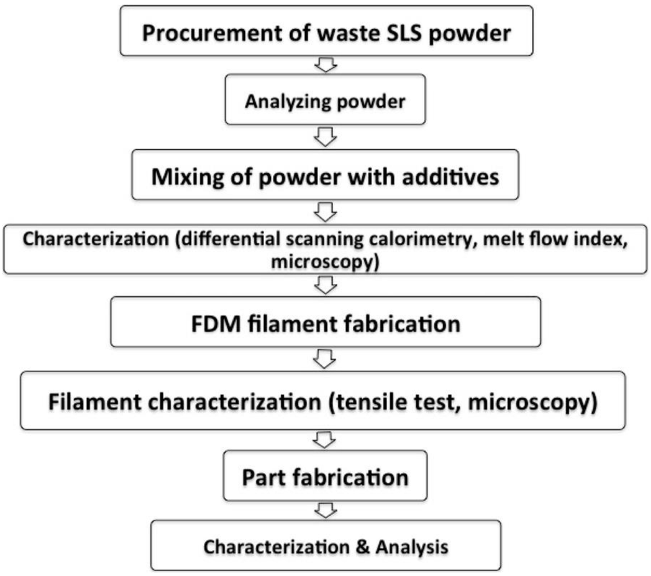


Figure 3. Methodology to make products from SLS powders [16].

The properties of the resulting filaments are in *table 1*.

Table 1. Mechanical properties of various filaments tested (from [16]*)*

Filament Composition	Young's Modulus [MPa]	Tensile strength [MPa]	Elongation at break [%]
100%PA	700	25	Did not break (>700)
87.5%PA+12.5%WC	800	30	700
75%PA+25%WC	920	40	400
62.5%PA+37.5%WC	1170	45	300
50%PA+50%WC	1300	60	260

Singh et al. [17] succeeded in multi-material printing of various thermoplastics, recycled ABS, PLA and HIPS polymers, for functional prototypes with different combinations of top, middle, and bottom layers.

Table 2. Review of plastic material recycling for AM (Adapted from [10])

Author	Year	Recycled Material	Source	Ref
Anderson	2017	PLA		[12]
Woern et al.	2018	ABS, PLA, PET, PP	Size distribution	[13]
Kumar et al.	2019	HDPE, LDPE		[14]
Zander et al.	2019	PET, PS, PP	Soda bottles, yogurt containers	[15]
Kumar et Czekanski	2018	Polyamide 12		[16]
Singh et al.	2019	ABS		[17]

The thesis project by Esercizio [18] analysed the case study of Reflow, a recycled filament producer for FDM. Within the work, tensile and mechanical tests on recycled and virgin filaments of PLA and PETG were performed, showing that the first-recycled filaments produced by Reflow do not lead to a loss in mechanical performance, but, on the contrary, presented better test results overall compared to the virgin ones.

In another thesis project, Halo [19] worked on the mechanical characterization of 3D printed ABS, as virgin, recycled and exposed to UV light radiation. Also, carbon fiber reinforced ABS was employed. It was shown that the material maintains on average its original characteristics, even if reprinted, therefore in favour of a complete reuse of this polymer in a circular perspective.

2.3 NYLON

Nylon is the first commercially successful thermoplastic polymer synthesized. The main fields of application are the textile and the industrial ones. The uses of nylon fibers in the textile industry are various: tights, swimwear, sportswear, but also furniture such as curtains, rugs, carpets and upholstery fabrics, fishing nets, umbrellas are manufactured. It is also employed in the medical field for sutures and special gauzes. For industries, the relevance of nylon lies in its possibility to be transformed into a highly robust and versatile plastic exploitable for hundreds of applications.

The most advantageous properties of nylon are:

- High tensile strength and modulus of elasticity
- Excellent resistance to abrasion
- Extremely good impact properties
- Low coefficient of friction
- Relevant resilience
- Light weight
- Convenient price-quality ratio

On the other hand, nylons are hygroscopic, and will absorb or desorb moisture as a function of the ambient humidity; the absorption of water will change some of the material's properties. Moreover, despite this polymer doesn’t burn, it easily melts.

A variety of commercial nylons are available including PA6, PA11, PA12, PA6,6, PA6,10, and PA6,12. The most widely used nylons are PA6,6 and PA6. Polyamides are used most often in the form of fibers, although engineering applications are also of importance. PA6,6 is prepared from the polymerization of adipic acid and hexamethylenediamine, while PA6 is prepared from caprolactam, which has the structure presented in *figure 4*.

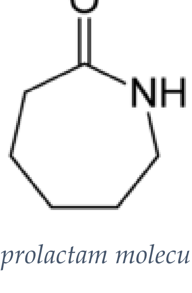


Figure 4. Caprolactam molecular structure

2.3.1 Recycling of nylon for AM

With a melting point of 220°C, PA 6 is used in a wide variety of applications due to its good performance/cost ratio. Although it has traditionally been used in industrial manufacturing methods, it has become more and more popular in the 3D printing sector because of its interesting mechanical properties and its ability to create high-performance parts. However, nylon is a much more difficult material to 3D print when compared to standard plastics such as PLA or ABS. Its operating temperature range is 250-270°C, so a suitable working environment must be ensured so that it does not shrink.

As far as materials such as polyamide 6/6,6/12 used for 3D printing via FDM are concerned, the available literature about their mechanical, electrical and thermal properties is limited, with only a few reports available on the mechanical properties, probably due to the difficulties of the material’s processing in FDM 3D printing, such as distortion and warping of these materials, and the fact that on crystallization, they may have volume reduction associated with the formation of ordered, closely packed regions during crystallization. In addition, the mechanisms that could occur while recycling process based on melt processing methods is done have not been yet fully elaborated.

Lozano-Gonzàlez et al. [20] subjected PA6 to successive injection moulding cycles in order to evaluate the degradation of the material, in terms of behaviour of the physical-mechanical properties, and the possibility to recycle it multiple times. It was shown after 10 cycles that PA6 can be processed up to seven times without further effect on its physical–mechanical properties and morphology; the only registered change was the colour (*figure 5*).

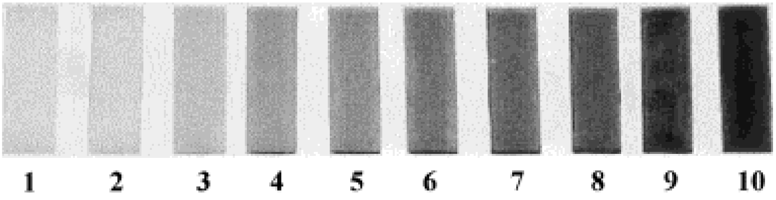


Figure 5. Colour change in nylon after 10 cycles of injection moulding (from [20])

In the area of additive manufacturing, increasing attention is being paid to the use of different types of nylon to form 3D printing filaments. It is worth noting that recycled nylon granulates, to be directed to extrusion processes, can be effectively obtained through a variety of recycling processes.

Farina et al. [21] studied the rheological, thermal, and mechanical properties of recycled PA6 based filaments for FDM, demonstrating the high technical potential of the screw-extrusion process as a manufacturing technique for nylon recycling, since the analysed filaments presented excellent mechanical strength, and stable thermal properties after recycling, which makes them feasible to use for various 3D printing applications. The results show that the caprolactam regeneration route enables the newly formed material to retain high physical and mechanical properties. The analysed filaments are commercially available from Aquafil and the evaluated properties are shown in *table 3* (adapted from [21]).

Table 3. Properties of nylon 6 based filaments for FDM (adapted from [21]*)*

	AQ27000	**AQ34000**	**AQ27000-B**	**AQ34000-B**	**AQ24000-T**
Reinforcement	-	-	5% in ABS SM295	5% in ABS SM295	30% in TiO2
MFI (Melt Flow Index) [g/10 min]	24.69	21.71	19.24	20.26	39.09
Yield strength [MPa]	76.20	85.99	86.91	81.21	55.79
Young modulus [GPa]	1.64	1.61	2.34	1.50	0.76
Wear resistance [μm]	95		92		
3D printing feasibility					
Heated printing plane	yes		yes		
First layer extrusion speed	65%		50%		
Surrounding temperature	23°C		23°C		
Print speed	50 mm/s		40 mm/s		
Nozzle diameter	0.4 mm		0.4 mm		
Extrusion temperature	235°C		230°C		

Boparai et al. [22] carried out the thermal characterization of waste PA6 based nano-composite material, demonstrating that the incorporation of filler materials (Al and Al2O3) in PA6 matrix improves the thermal resistance parameters of NC material and qualifying it as an alternative material for the fabrication of FDM filament. Some relevant parameters (MFI, crystallization peak temperature and melting peak temperature) are reported in *table 4*.

Table 4. Comparison between waste nylon 6 and nanocomposites thermal properties ([22]*)*

Material	MFI [gm/10 min]	Tc[°C]	Tm[°C]
Waste Nylon-6	10.61	176.10	219.03
NC	2.30	178.36	218.18

Recycled nylon can be subjected to thermal, oxidative, and mechanical degradation during process, which may decrease the mechanical properties of recycled nylon. In order to overcome this problem, modification by combining recycled nylon with virgin nylon is considered. Maspoch et al. [23] investigated thermal, mechanical and rheological properties of a sample of recycled and filled PA6, as function of the number of reprocessing operations (3 times) and of the fraction of recycled material (15, 30 and 50 %) added to the virgin material. It resulted that the properties of the recycled material remained below the virgin, and the best combination of both appeared to be the mixture with 30% of recycled fraction, which showed a loss of properties similar to 3 reprocessing operations.

The thesis work by Khan and Ansari [24] focuses on the effect of change in printing parameters on the mechanical properties of the additively manufactured Nylon-6 parts. Three types of samples were printed, for tensile, bending and compression test, eight samples of each category were printed and tested for the analysis. Parameters like printing nozzle temperature, raster angle, infill ratio were discussed.

2.4 RECYCLING OF TEXTILES

There is much discussion within the fashion and wider textiles industry regarding the overall sustainability and environmental impact of textile products and garments. The impact of textiles on the environment is well documented: that the global production of textiles accounts for 10% of the world's carbon emissions demonstrates a clear need for solutions to reduce or help prevent this problem from worsening [25]. However, a great deal of textile material is not dealt with in a circular way. It was estimated that a full truck of textiles is sent to incineration or landfill every second, worldwide. Recycled materials used in textiles production account for only about 1%. The situation in the EU is slightly better, with infrastructure for the collection, reuse and recycling of textiles in place or being developed in several Member States. However, even in the EU collection rates are estimated to be as low as 25%, with large differences between Member States [26]. Moreover, textile production is constantly growing, since nowadays clothing is not only an essential good, but also a fashion item and as such it has gained a shorter life span. The main objective of textile recycling is to turn end-of-life products into new fibrous material with similar to virgin material properties. Recycling of textiles takes place to a limited extent and when it takes place, it is often a matter of downcycling where the recycled material is of lower quality and functionality than the original material. Current technologies can recover fibers from textiles made up of a single type of filament, whereas it is more complex to process multi-material ones. The first and most immediate solution would be to design fabrics with the purpose of recycling.

Harmsen et al. [27] classified textile fibers based on their main chemical bonds, as fibers with the same kinds of bonds usually have similar chemical and physical characteristics. They distinguished the six principal polymer groups for textile fibers (cellulose, polyamide, polyester, polyurethane, polyolefin and polyacrylic) and designed a new classification of textile recycling technologies, based on the level of disassembly (fiber, polymer, monomer) combined with mechanical, physical and chemical recycling. In particular:

- Mechanical methods break down the fabric and retain the fibers by cutting, tearing, shredding or carding. The fiber length is reduced as an unwanted side effect and some dust is generated.

- Physical methods use physical processes to make the fibers or polymers suitable for reprocessing, either by melting or dissolving them. The structure of the fibers is changed, but the polymer molecules that make up the fibers remain intact.
- Chemical methods exploit chemical processes to break down fibers and polymers. The polymers that make up the fibers are either modified or broken down, sometimes to their original monomeric building blocks. This can be done by chemical or biological methods (e.g., with enzymes).

Chemical recycling can turn lower grade inputs and materials that are difficult to recover into higher grade outputs suitable for a variety of applications. It enables textiles to be part of a sustainable open loop recycling system, in which materials cascade up and down the quality ladder in response to market demand [1]. Many companies and other organizations are taking innovative approaches to solve the problem of textile waste: extending the life of textile products, making textile products more recyclable, and creating markets for recycled textiles.

RESYNTEX is a H2020 project, launched in June 2015, with the ambitious aim of using industrial symbiosis to produce secondary raw materials from unwearable textile waste, for which there are currently few or no end-of-life options with a marketable value [28]. The RESYNTEX process works to convert this residual textile waste into feedstocks for the chemical industry. Bell et al. [29] proposed an estimation of the quantities of residual textile waste across the EU-28 which could be suitable for the RESYNTEX process, provided information on the markets for the expected chemicals outputs from the process and, also, investigated industry developments in sorting and recycling technologies for textiles.

Table 5. Industry developments in sorting and recycling technologies for textiles (Adapted from [29]*)*

Company	Partnership	Object	Ref
Worn Again	H&M, Kerin Group	Polyester-cotton blend separation	[30]
Ioniqa Technologies		Removal of colour from PET plastic	[31]
Lenzing	Inditex Group	Collection of cellulosic waste	[32]
Re:newcell		Recycle of cellulosic fibers	[33]
Evrnu™	Levi Strauss & Co.	Regeneration of fiber from cotton waste	[34]

A team of free-lance Technicians (Giuseppe Fabozzi, Aldo Malara and Edoardo Ponzecchi), in cooperation with the National Research Center “Next Technology Tecnotessile” and Sergio Dell’Orco, President of “Dell’Orco & Villani srl” Textile Machinery Manufacturing Company, have developed and patented a new clean process for the recycling of textile scraps and the recovery of the individual components [35]. This new technological process is named “PTF-COLDPLAST”, and it allows to separate the thermoplastic fibers from the natural ones: from any fabric of mixed components, it is possible to separate polyester, nylon and elastomers from the natural or artificial fibers. The advantage of this technology consists of the fact that the thermoplastic materials are recovered and transformed directly into 100% pure powders or granules, which can in turn be reused in industrial processes; the remaining natural and artificial fibers instead, still in the form of the original fabric, can be opened and reused in the processes of traditional textile spinning and the production of nonwovens.

Figure 6 schematizes the life cycle of textile products and the possible paths they can take at the end of their life. These include reuse and recovery, in addition to disposal. If a product can be reused the way it is, it is directed to the consumer again. Otherwise, the material it is made of can be recovered. In particular, upcycling and downcycling are distinguished. The first one refers to the fact that the material is employed as raw material to manufacture the same product and that it returns to the same level of the production cycle. In the specific case of fabrics, textile fibers are subjected to a new spinning process, to create fabrics again. The second one, instead, consists of the use of the recovered material for a different kind of production. Usually, this happens when the quality of the material is reduced after a life cycle, and it can't be restored. As it can be seen from the scheme, upcycling creates a closed loop, while downcycling an open loop.

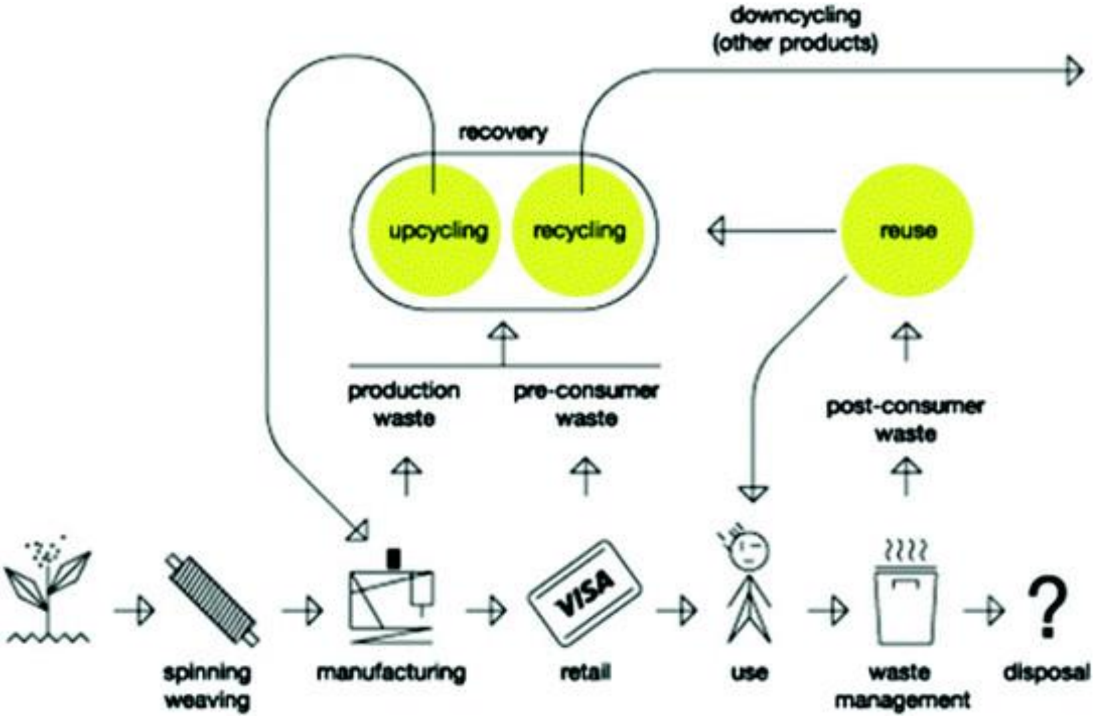


Figure 6. Life cycle of textiles

2.4.1 From textile to textile

One aspect of the circular economy for textile-based products is reuse and resale. This helps prolonging clothing life. However, when talking about recycling, one usually refers to the recovery of the material with the aim to use it either in the same field or in a different one. Textile-to-textile recycling is the process of breaking down a garment or piece of cloth into its constituent fibers, and then creating a new textile or garment from those fibers. Anyways, as clothing brands experiment with textile-to-textile recycling models, there is quest for new fabrics built around closed loop processes that could help accelerate this progress. Examples of recent innovation in this field include Econyl, X2 Plus, Returnity and SaXcell (*table 6*) [36].

Table 6. Examples of textile-to-textile innovations

	Fiber	**Application**	**Production methods**
Econyl	Nylon	Sportswear and outdoor clothing	Chemical processes
X2 Plus	Polyester	Task seating and soft seating	
Returnity (Backhausen)	Polyester	Workwear and outdoor clothing	Shredding and melt spinning
SaXcell	Cellulose	Textile industry	Chemical processes

Developed through a partnership between the Hong Kong Research Institute of Textiles and Apparel (HKRITA) and the H&M Foundation, the Green Machine [37] uses a closed-loop system of water, heat, pressure and green chemicals to fully separate and recycle cotton and polyester blends into new fibers, in a cost-effective and time-efficient manner. The outputs are long polyester fibers of good quality, which can be used to make new garments, and cellulose powder, which can be used within the fashion industry and beyond.

REDRESS is a collaborative project between M&S and the IfM and funded by the Innovate UK competition 'Supply Chain Innovation Towards a Circular Economy' [38]. It is a project to drive garment recovery and retained value through business model and supply chain innovation and it seeks to accelerate M&S Plan A commitments around reducing waste. The outcomes of the project can be applied to textile and other industries.

2.4.2 Recycling of textile nylon

The production of nylon fabrics is generally considered to have a high environmental impact, mainly due to the involved raw materials. Even though it is possible to fabricate textile nylon with other substances, the majority of the products that are used derive from petroleum, from hexamethylenediamine, main constituent of most types of nylon fabrics. It is commonly known that petroleum is not a renewable resource, the processes require a high amount of energy and numerous waste materials are generated. Plenty of water is employed for the cooling of the fibers and this water often conveys pollutants into the environment around production sites. In the production of adipic acid, which is the secondary constituent of most types of nylon fabrics, nitrous oxide is released into the atmosphere, and this is considered worse for the environment than CO2.

While other fabrics, such as cotton, can biodegrade relatively fast, nylon (which is entirely synthetic and non-biodegradable) remains in the environment for years. Fortunately, these fabrics, in some forms, are recyclable. In fact, being almost unfeasible to limit the environmental impact during their production, the only way to make these fabrics more sustainable is to properly dispose them. As far as nylon is concerned, physical and chemical methods are generally exploited. Moreover, fiber recycling results less achievable than polymer and monomer recycling.

2.4.2.1 Physical recycling of nylon

Among all the techniques to deal with plastics waste, the one that is considered the most cost efficient and effective and deemed to be consistent enough for being implemented by the plastic’s industry is the physical recycling. It is the process of collecting plastic debris, washing, melting and having the waste transformed into raw material for a new productive process of plastic transformation.

Q-NOVA is an environmentally friendly recycled nylon 6.6 fiber developed by Fulgar [39]. To produce it, Fulgar uses mostly post-industrial nylon waste coming from its yarn production cycle, that could not have been reused in any other way and would have otherwise been disposed of as external waste. Q-NOVA production occurs through the MCS process, a locally based mechanical regeneration system that doesn't require chemicals: discarded materials are melted down, regenerated, and restored into polymers, without the use of chemicals, and then integrated into further processing stages.

Apart from the more traditional mechanical recycling processes of melting and re-extrusion, also chemical recycling ones have great potential. Nonetheless, each process is applicable for specific plastic waste and combinations could be created for a more general usage [40].

2.4.2.2 Chemical recycling of nylon

Chemical recycling involves breaking down the molecular structure of the polymer, using chemical reactions. This is called depolymerization. The products of the reactions, then, can be purified and used again to produce either the same or a related polymer. In a depolymerization reactor, PA6 fibers are treated with superheated steam in the presence of a catalyst to produce a distillate containing caprolactam, nylon monomer. The crude caprolactam is distilled and repolymerized to form PA6. The obtained caprolactam is comparable to virgin caprolactam in purity. The main approaches for PA6 depolymerization are presented in [41]. Shukla et al. [42] experimented depolymerization of nylon waste fibers through dissolution in various acids and then through the heating of the solution under reflux for different times.

A very efficient regeneration and recycling process of PA 6 waste collected from various resources has been developed by the internationally renowned Aquafil group through the ECONYL® project [43]. This group has developed a three-step system to produce recycled PA6 (R-Nylon-6) from 100% regenerated waste materials, which includes fishing nets abandoned in the oceans and aquaculture, as well as scraps from carpets and various industrial nylon products otherwise directed to landfills. The first step of the ECONYL® process consists of the collection of PA-6 waste from landfills, oceans, and all over the world. Step two develops an accurate regeneration and purification process, articulated in the depolymerization of the collected PA-6 waste (with transformation of the recycled material into caprolactam), purification of caprolactam, and re-polymerization. Such a process drives the material back to its original purity, obtaining a regenerated material, which exhibits physical and mechanical properties practically identical to those of the virgin material. Step three consists of the manufacturing of AQ R-Nylon-6 granulates to be processed for the fabrication of carpet and textile yarns or filaments, to be employed for a variety of industrial uses.

Table 7. Polyamide recycling initiatives (adapted from [27]*)*

Company	Input Stream	Product	Status
Nylon: physical recycling to polymers			
Fulgar with the MSC process	Post-industrial waste	Q-Nova®, 50/50 regenerated/virgin PA 6,6 fiber	Unknown
Nylon: chemical recycling to monomers			
Aquafil with Econyl technology (Depolymerisation to caprolactam)	Nylon 6 fishing nets, carpets, post-industrial textiles	Econyl® yarn, PA6	Commercial, Italy

2.4.2.3 Nylon blends

By blending two or more fibers together, it is possible to achieve desirable characteristics that cannot be achieved through the use of only one fiber. As far as nylon fabrics are concerned, this solution was developed due to marketing reasons: consumers found that pure nylon textiles could be uncomfortable due to lack of absorbency. They could also be itchy and tended to cling and sometimes spark as a result of static electrical charge built up by friction. Therefore, industries started to blend nylon with other existing fibers or polymers such as cotton, polyester, and spandex. The new nylon blends retained the desirable properties of nylon (elasticity, durability, ability to be dyed) and kept prices low and affordable.

Nylon and cotton blend is abbreviated as NyCo. It boasts the excellent abrasion-resistance properties of nylon and most of the performance characteristics of cotton, including comfort and moisture retention.

Nylon and polyester are both lightweight and durable synthetic fabrics that share many of the same properties, such as easy care, wrinkle resistance, stretch and shrink resistance. Their similarities make them easy to be blended. Nylon is softer than polyester but also stronger, while polyester is faster drying, easier to dye and abrasion resistant. Neither is a better fabric, though each has uniquely superior attributes that lend themselves to certain uses. In fact, not only is polyester more heat resistant with respect to nylon, but also it doesn't absorb water.

Nylon is often blended with spandex to achieve superior elasticity, the ability to regain the original shape when not in use, and comfort characteristics, that make nylon spandex the most suitable fabric for sportswear nowadays.

Recycling of blended fabrics poses a significant challenge in engineering because of the inhomogeneous nature of the materials, that causes the waste of polymer blends to be often discarded or incinerated unless the components can be economically separated. Therefore, in order for the fibers from these fabrics to be reclaimed, effective separation has to occur. Lv et al. [44] studied the recovery of cellulose from waste nylon/cotton blended fabrics through dissolution. Blends of polyamide and polyester have academic and technological interest, but there was no study considering blends of textile waste. Spandex may be removed from blended fabrics by dissolving it in solvents such as dimethylformamide (DMF), but the use of such solvents is undesirable for economic and environmental reasons. Alternative processes may consist of melt processing through mixing and molding [45] or selective degradation, involving heat treatment and washing [46].

2.4.2.4 Recycling of fishing gears

Fishing nets are made from a variety of materials: polyamide (PA), polyethylene (PE), polypropylene (PP) and other similar plastics. PA ones tend to have the highest tensile properties compared to the others. Nevertheless, it is possible to slightly change the performance of fishing gears by increasing the yarn diameter or the mesh size, leading to resulting higher breaking load, tensile strength, and drag coefficient as well as bending stiffness and breaking strength. Based on the properties of PA, it can be concluded that this material is more suitable for fishing to prevent “ghost fishing”. This expression refers to any discarded, lost, or abandoned fishing gear in the marine environment. This gear continues to fish and trap animals, entangle and potentially kill them, and deface marine environment and life. This phenomenon is one of the reasons for fishing nets to be a great source of plastic waste in oceans. The development of an effective recycling system for fishing nets may lead to a solution to this problem and, thus, it is of utmost importance. The Catalyse and Replicate Solutions Working Group of the Global Ghost Gear Initiative (GGGI) [47] provided a general overview of challenges and opportunities surrounding the collection and recycling of fishing gear, assuming that the appropriate management of end of life and recovered fishing gear will have a direct impact on the amount of gear that ends up lost or, otherwise, discarded at sea.

An example of model for logistic operations is given by Nofir AS [48], European leader at working with the fishing industry and aquaculture to collect, dismantle and recycle fishing nets and other related products. After collection, nets are cleaned by using only water, that is filtered afterwards, so that it is not wasted. Once cleaned, the equipment is disassembled and sorted by material. The nets and ropes made of nylon, polypropylene and polyethylene, as well as the other components made of steel and lead, are passed on to specialised partners for recycling.

Net-Works [49] is a program that focuses on recycling discarded fishing nets into nylon yarn. Local communities collect and clean the fishing nets. Then, they are sent to Aquafil, where the nets are turned into yarn. The yarn is then sold to Interface to make high design carpet tiles.

Depending on the material, there is a different suitability for recycling. For example, nets made from PA6 have a high value as a waste resource and are appealing for recyclers, whereas nets made from polyethylene (PE), polypropylene (PP) and other similar plastics have a lower value as recycled material and are thus less appealing due to the prohibitive costs involved and lower margins of profit. Mechanical recycling is the simplest process: it involves sorting, cleaning, granulation, drying, melting, extrusion and pelletizing. Technically, it is possible to separate most plastics into recognizable streams, but not all plastic streams are mechanically processable. However, chemical recycling is widely applied, mainly through ECONYL technology.

Plastix Global [50] is a clean-tech recycling company specialized in mechanical recycling of post-use plastics primarily from the maritime industry. Their process consists of sorting, fractioning and drying of the material, that is eventually extruded into pellets (*figure 7*).

A similar program is followed by Harbour Authority [51], even though it works on a smaller scale.

Figure 7. Pellets from Plastix Global

Mondragon et al. [52] characterized PA6 obtained from the recycled fishing nets. The results showed that the samples presented thermomechanical properties like commercial ones, meaning that the material didn’t suffer for degradation due to the marine use and that it is valuable for a variety of applications. Companies are turning recycled fishing nets into skateboards (*figure 8*), trainers (*figure 9*), sunglasses (*figure 10*), clothing and furniture (*figure 11*), with innovators even looking at opportunities to use recycled net filaments in 3D printing [53].

Figure 8. Skateboard advert from Bureo

Figure 9. Trainers from adidas x Parley

Figure 10. Sunglasses from Waterhaul

Figure 11. Chair from LifestyleGarden

2.4.2.5 Recycling of carpet waste

A typical carpet has four main layers (*figure 12*). The top layer, or face yarn, is composed of nylon fibers tufted through a primary backing, usually made of polypropylene. Other fibers such as jute, polyethylene, polyesters and rayon may also be used. Latex adhesive is applied under the primary backing in order to secure the face fiber. Finally, a secondary backing (same material as the primary backing) may optionally be added to the primary backing and bonded to it by the same adhesive. The nylon face fibers, containing dyes, soil-repellents (to improve the resistance to stains), and possibly other additives to improve the quality of the carpet, usually account for about half of the total carpet weight.

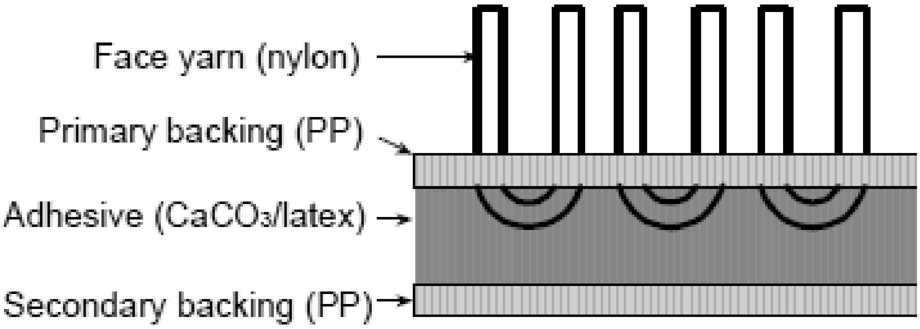


Figure 12. Typical carpet construction

During carpet manufacturing, the edges of a tufted carpet need to be trimmed and the face yarns sheared. This waste is approximately 60% edge trim and 40% shear lint. During the fitting process, the carpet is formed and cut into various irregular shapes, and waste is generated as a result. The largest amount of carpet waste, however, is from the discarded post-consumer carpet. It is estimated that about 2.3 million tons of carpet and rugs were placed in the municipal solid waste stream in 1996, of which only 1% was recovered for recycling [54]. According to the U.S. Department of Energy, about 3.5 billion lb of waste carpet are discarded each year in the United States, with about 30% of them made from PA 6. The largest supply of waste for recycling of nylons is thus obtained from used carpets. These are collected, sorted and then subjected to a mechanical shredding process before depolymerization. The face carpet fibers, consisting primarily of PA 6 and PA 6.6, represent the majority component in the carpet waste. Recent financial incentives and environmental constraints have motivated the industrial sector to develop recycling strategies for these fibers.

Mihut et al. [55] focused on the problem of carpet recycling, analysing the main adopted methods. In particular: depolymerization (with the same modalities mentioned in section Chemical recycling of nylon), extraction of polyamides (without involving the conversion into monomers), melt blending (direct melting or extrusion of the carpet). Zhang et al. (extracted from [56]), instead, obtained encouraging results from the recycle of pre-consumer and post-consumer carpet waste via injection and compression molding. Advantages that derive from the usage of these waste sources are presented by Kotliar (extracted from [56]), who achieved wood-like properties from composites and laminates made up of waste carpet material in the core and higher-modulus textile materials, such as cotton and polyester, in the outer layers, and Wang [57], who applied the fibers for reinforcement of concrete and soil.

2.4.3 Recycling of textile nylon for AM

Within the scope of circular economy, recycling processes can be inspired by the fact that textile waste contains polymers that can be converted into composites and made into 3D printable filaments. An interesting issue that has not been widely explored yet is the recycling of textile nylon for additive manufacturing, referring to the development of a complete circular economy model in which polyamide recovered from clothing becomes a secondary raw material for the creation of 3D printed objects.

Among the sources of recycled textile nylon, the easiest to be processed and, thus, the one that most favourably could be selected for 3D printing is probably fishing nets. What makes this assessment reliable is the fact that the material obtained from fishing nets recycling is already being supplied from companies in the form of either pellets or filaments, that are two common forms for 3D printing feedstock material. Opportunities may therefore exist for encouraging existing SMEs (or to stimulate start-up enterprises) to create, develop and commercialise selected 3D printed products from recycled fishing nets and ropes [58]. Currently, Fishy Filaments' [59] produces 3D printing filaments from recycled PA6 from fishing gears: Porthcurno and Longships blends, whose properties are presented in *table 8.*

Table 8. Fishy Filaments' material datasheet ([59]*)*

	Printing Temperature [°C]	**Printing speed [mm/s]**	**Printing bed temperature [°C]**	**Tensile strength (Break) [MPa]**	**Melt Flow Index [g/10min]**
Porthcurno	250-270	30-60	60-80	55	-
Longships	260-280	30-60	90-110	52	15

Farina et al. [60] employed 3D printed recycled nylon fibers, manufactured through an extrusion process of PA6 grains obtained from fishing nets, as reinforcement of cement mortars to study their flexural response, the tensile behaviour and compare them to the experimental behaviour of the unreinforced material. The results emphasize the high environmental and mechanical potential of recycled nylon fibers used as reinforcement.

FDM 3D printing offers numerous options for the reprocessing and repurposing of fishing gear polymers into valuable products. While the direct extrusion and subsequent printing of fishing gear polymers may be limited to select polymer types and those materials with the lowest levels of contamination, there exists a growing market for 3D printing filament. The most problematic option appears to be the direct printing of saleable goods using filament made from fishing gear polymers, due to the limitations of 3D printing technology, including print quality, speed and size, which reduce both the economic viability and the volume of fishing gear material able to be processed. For the fishing gear polymers unsuitable for direct 3D printing and extrusion into filament, alternatives using injection moulding hold significant potential. Prior to any of these options being implemented, however, it is important that further testings are carried out [61].

Other initiatives involve recycled textiles used in making 3D-printed shoes. It is the case of Adidas: the company recently produced a sport shoe prototype that incorporates a 3D printed midsole, made up of recycled polyester and gill nets [62]. But also Chris Margetts, founder of The Sole Theory and fashion brand Humans Are Vain, used recycled fibers from clothing, specifically nylon and polyester, to make 3D printed shoes [63].

As far as the recycling of clothing textile nylon for additive manufacturing is concerned, the specific scientific literature is poor, if not even null. To innovatively contribute to this matter is the purpose of this work.

3. DEVELOPMENT OF A RECYCLING PROCESS FOR TEXTILE NYLON

The objective of this work is to develop a brief, inexpensive and low environmental impact process chain for the recycling of an end-of-life textile nylon product that shows potential for reuse and reintroduction in a production process, with the aim of successively employing the recovered material in the field of additive manufacturing.

In this chapter, the sequence of processes for the mechanical recycling and the involved equipment as well as the behaviour of the material throughout the processes are discussed.

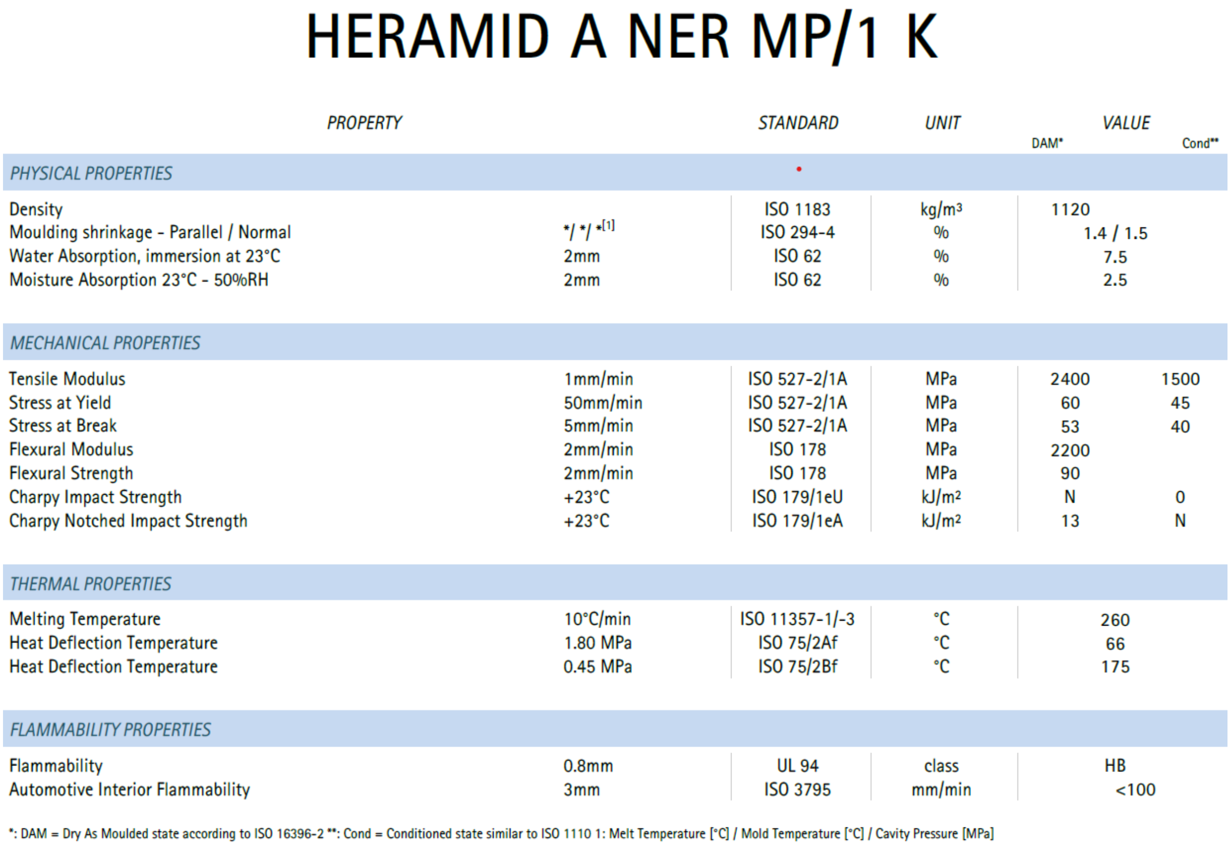
3.1 MATERIALS

For the recycling process, pielleitalia supplied textile nylon, in particular post-consumer nylon t-shirts (*figure 13*), made of 100% PA66, including the thread used to sew buttons and labels. This nylon presents green colour, and its properties are not far from the ones obtainable from similar post-industrial recovery materials, as the company assessed.

Figure 13. Post-consumer nylon t-shirts

As reference for the properties of PA66, the datasheet of a pelletized PA66 recycled from industrial scraps is provided in *table 9*.

Table 9. Datasheet of reference PA66



HERAMID A NER MP/1 K

PROPERTY		STANDARD	UNIT	VALUE DAM*	VALUE Cond**
PHYSICAL PROPERTIES					
Density		ISO 1183	kg/m³	1120	
Moulding shrinkage - Parallel / Normal	*/ */ *[1]	ISO 294-4	%	1.4 / 1.5	
Water Absorption, immersion at 23°C	2mm	ISO 62	%	7.5	
Moisture Absorption 23°C - 50%RH	2mm	ISO 62	%	2.5	
MECHANICAL PROPERTIES					
Tensile Modulus	1mm/min	ISO 527-2/1A	MPa	2400	1500
Stress at Yield	50mm/min	ISO 527-2/1A	MPa	60	45
Stress at Break	5mm/min	ISO 527-2/1A	MPa	53	40
Flexural Modulus	2mm/min	ISO 178	MPa	2200	
Flexural Strength	2mm/min	ISO 178	MPa	90	
Charpy Impact Strength	+23°C	ISO 179/1eU	kJ/m²	N	0
Charpy Notched Impact Strength	+23°C	ISO 179/1eA	kJ/m²	13	N
THERMAL PROPERTIES					
Melting Temperature	10°C/min	ISO 11357-1/-3	°C	260	
Heat Deflection Temperature	1.80 MPa	ISO 75/2Af	°C	66	
Heat Deflection Temperature	0.45 MPa	ISO 75/2Bf	°C	175	
FLAMMABILITY PROPERTIES					
Flammability	0.8mm	UL 94	class	HB	
Automotive Interior Flammability	3mm	ISO 3795	mm/min	<100	

*: DAM = Dry As Moulded state according to ISO 16396-2 **: Cond = Conditioned state similar to ISO 1110 1: Melt Temperature [°C] / Mold Temperature [°C] / Cavity Pressure [MPa]

3.2 PROCEDURE

In this section, the process chain to recover the material from the polyamide t-shirts is discussed. In particular, nylon is present inside the t-shirts in form of textile fibers, and therefore it should be processed in such a way that makes it usable for other applications. In this case, the purpose is to feed an extrusion-based additive manufacturing machine, EFeSTO, which is fed by feedstock material in form of pellets. Thus, the complete route starts from t-shirts and must end with pellets.

It was decided that the recycling would consist of a mechanical procedure, based on breaking down the fabrics and then thermally process them, and not a chemical procedure, which would involve the use of chemical solvents. The decision depended on the fact that mechanical recycling is considered the most effective approach, in terms of time, economic cost and environmental impact, and, thus, it is perfectly in line with the objective of the project.

First of all, t-shirts should lose their form and the fabric should be cut and shredded so to obtain frayed nylon fibers. After that, the fibers should be subjected to a melting process in order to be turned into a plastic solid structure material. Plasticization is the most critical step, since it requires the choice of thermal parameters, that for plastics are not trivially adjustable. Eventually pellet shape should be obtained.

Before thermal processes are performed, being nylon hygroscopic, drying process is fundamental to remove most of the absorbed moisture due to ambient exposure. In fact, at high temperature, water content is responsible for defects such as burns and voids formation due to boiling, that generally affect the output of thermal processes in terms of worse mechanical and physical properties.

Figure 14 summarizes the process chain. The main steps to follow are shredding or grinding of the fabric, plasticization of the fibers and shaping of the pellets.

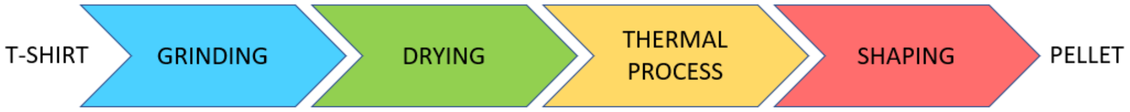


Figure 14. Process chain

Preliminary material testing was performed for each step of the process and for each employed machine to understand and quantify whether the treatment could be suitable for the purpose of the recycling process.

The complete recycling process was eventually executed on 1 kg of t-shirts.

3.3 RECYCLING PROCESS

3.3.1 Preparation of the t-shirts

Firstly, from the t-shirts all the buttons and labels were removed, so that these elements could not be mixed with nylon fibers and contaminate them.

Moreover, it was initially supposed that the dimensions of a t-shirt could not allow to put it inside the grinding machine as an entire piece. Therefore, apart from one t-shirt only, all the others were cut with scissors into chunks of non-precise dimensions, about 20cmx20cm (*figure 15*), so that they could be easily inserted into the cutting mill. The whole t-shirt would be used to make an attempt to verify whether the supposition was correct.

Figure 15. Preparation of the t-shirts

3.3.2 Grinding operations

At first, the TRA200 shredder (*figure 16*) was employed for grinding operations. It is a machine designed to shred long and coiled metal swarf. Nevertheless, this shredder turned out to be unsuitable for the process. In fact, for the functioning, the material had to fall due to gravity between the teeth of the machine, but since it was lightweight it could not be caught, and it didn't work.

Figure 16. TRA200 shredder

Eventually, the machine used for grinding operations was the Cutting Mill SM 300 from Retsch, available in the CIRC-eV Laboratory at Politecnico di Milano. Cutting mills are suitable for the grinding of soft, medium-hard, tough, elastic, fibrous, and heterogeneous mixes of products. As it can be seen from *figure 17*, the machine presents a feeding channel that conveys the material to a bladed rotor knife. Under the rotor chamber, a bottom sieve is inserted. It separates the chamber from the suction duct through which the processed material flows and reaches a bucket, where it is collected.

Figure 17. Cutting Mill SM 300 from Retsch

The bottom sieve was available in different sizes. The purpose was to obtain disassembled fibers, almost like powder, that could be then properly employed for the successive thermal process. For this reason, the choice was either 1 mm or 4 mm, the two minor holes dimensions.

Some of the pieces of cloth were used for a test to compare the results. *Figure 18* and *figure 19* show the differences respectively between 1 mm and 4 mm sizes. Clearly, the value of the holes dimension represents an estimation of the dimensions of the pieces that would be collected in the bucket after passing through the bottom sieve.

This mill is adaptable to application requirements by variable speed from 100 to 3000 rpm. In all the activations, rotor speed was set to 3000 rpm.

Figure 18. Result of 1 mm holes grating

Figure 19. Result of 4 mm holes grating

The obtained samples were examined under the microscope to understand how the grinding operation affected the fibers structure. The adopted microscope was the continuous zoom Stereo Microscope SM 500 from echoLAB.

It was observed that this mechanical process only shortened the length, exactly as it was macroscopically, whereas nothing happened to the section diameter nor to the shape of the fibers. In *figure 20*, fibers from a scrap of the original fabric are visible. Their diameter was measured through the specific function of the software associated to the microscope and it resulted to be 12 μm long. In *figure 21*, fibers from 1 mm sample are visible. Also in this case, the measured diameter was 12 μm long. Moreover, the main difference is the compactness of the fibers in the two samples: while in the first one the fibers are easily distinguishable, in the second one they are closer the one to the other, and this is due to the fact that they arranged differently in the space, accordingly to their length. However, no difference in the structure is noticeable.

Fibers from 4 mm sample presented same common characteristics and the appearance was intermediate between the two previous cases.

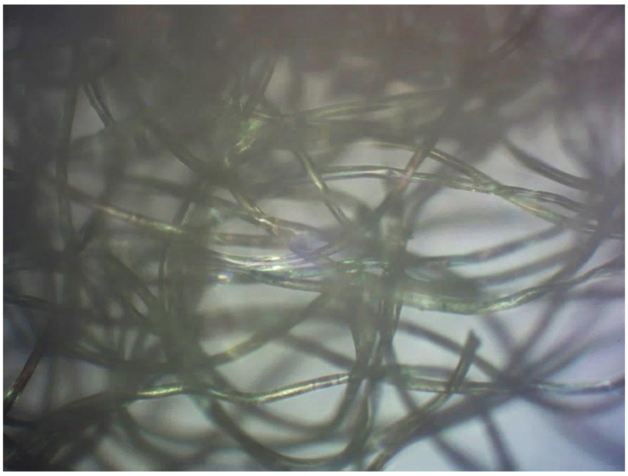


Figure 20. Fibers from a scrap of the original material under the microscope

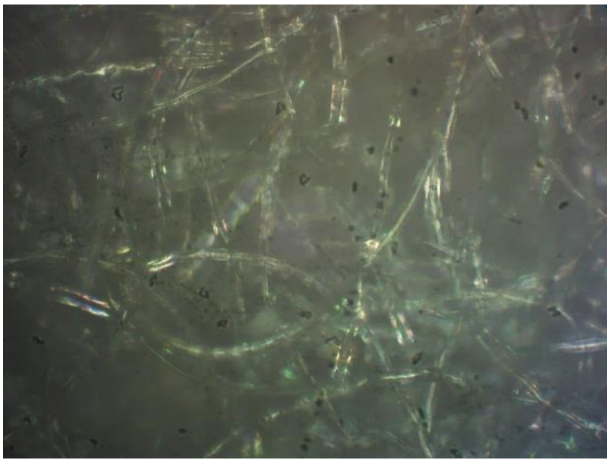


Figure 21. Fibers from 1 mm sample under the microscope

Finally, the chosen bottom sieve was the one with 4 mm holes dimensions. The reason for this choice mainly lies on a practical matter: it was easier to take this sample from the bucket of the cutting mill rather than it was to take the 1 mm sample, since this last one tended to spread in the surrounding environment more than the first one. Moreover, 4 mm had already been supposed to be a sufficiently small size for the successive steps of the process.

In *figure 22*, the final appearance of the whole material after grinding is shown. It was noticed that the texture was fluffy and voluminous.

Figure 22. Grinded nylon fibers

As previously mentioned, it was supposed that one whole t-shirt could not enter the rotor chamber due to its excessive dimensions. However, the attempt was made, and it proved unsuccessful. In fact, the fabric jammed all around the rotor and in the bottom sieve, causing the rotor to suddenly stop.

In the end, it could be stated that the employed cutting mill was a suitable machine for grinding operations, because the process was feasible, and the desired results were easily achieved. However, bigger dimensions of the chamber and of the rotor would improve the productivity of the process, since it would be possible to insert the t-shirts inside the machine with no need to cut them preliminarily.

3.3.3 Drying operations

Drying of the grinded nylon fibers was performed through a Nabertherm N250/85-HA oven (*figure 23*) with forced air circulation, available at MUSP Laboratory in Piacenza. Time and temperature were respectively set to 24h and 80°C, with a heating rate of 50°C/h. Input and output air vents were open in order to allow air exchange. The material was placed inside a cotton sack and closed with a metallic thread to ensure good transpiration. The sack was kept hanged in the middle of the oven in contact with the regulation thermocouple.

Figure 23. Nabertherm N250/85-HA oven

At the end of the treatment, the material was extracted and, still hot, it was packed and vacuum sealed (*figure 24*).

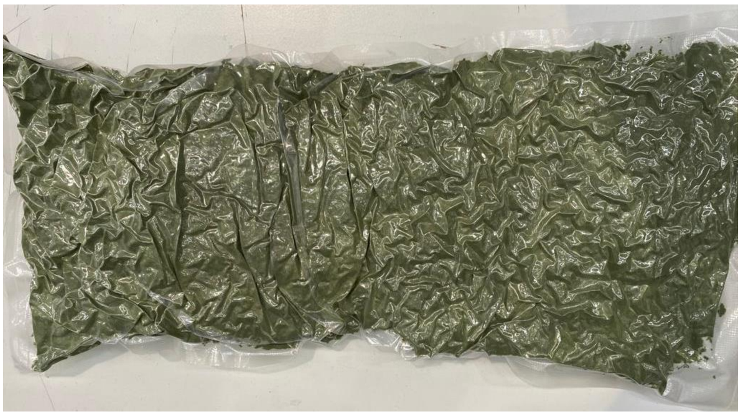


Figure 24. Vacuum sealed grinded and dried nylon fibers

3.3.4 Nylon plasticisation (failed attempts)

The next step of the recycling process aimed at turning the frayed fibers into a material of solid plastic consistency. In order to do it, the best option was to perform a melting process: when plasticisation occurs, the structure of the fibers is changed, but the polymer molecules that make up the fibers remain intact.

Different attempts were made in order to assess the proper machine for the purpose, to be chosen according to the availability and to the feasibility of the process. The attempts and the correspondent obtained results are presented below.

- Hot mounting press

The first attempt was made using a hot mounting press.

Only the lateral surface of the mold of the press could be heated, at a temperature of 200°C. The result, visible in *figure 25,* was a cylindrical block of pressed material whose external lateral surface was the only plasticized part, which presented smooth texture and darker colour. The bases and the inner volume were still soft to the touch and had the appearance of the grinded fibers, indicating that plasticisation did not occur.

This attempt was considered a failure because the outcome was not the desired one, and therefore the machine turned out to be unsuitable.

Figure 25. Result of hot mounting process

- <u>Pellet Extruder</u>

In this case, a pellet extruder from Direct3D was employed. This machine combines a pellet melter and a pushing mechanism, single screw extruder, in one device. In *figure 26*, it is possible to see the configuration of the feeding hopper, where material was inserted, and the screw.

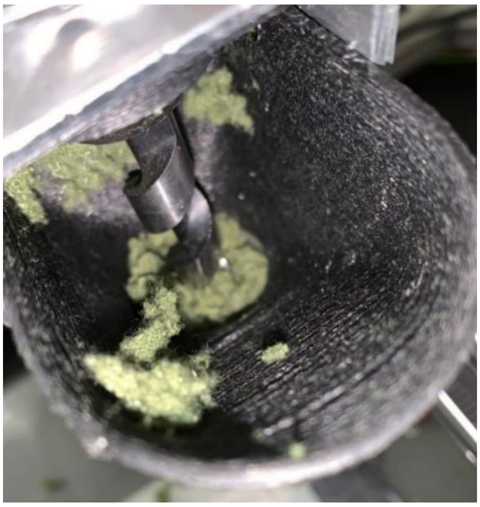


Figure 26. Hopper and screw of the pellet extruder

Also this attempt was a failure, because the screw did not manage to funnel the material through the channel and hence, instead of obtaining a filament of plasticized material, only some irregularly shaped fragments were produced (*figure 27*).

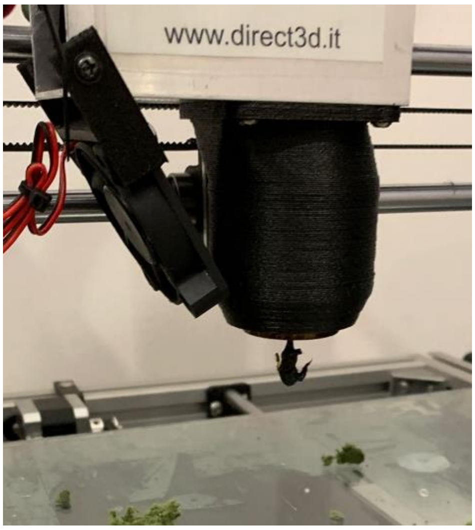


Figure 27. Irregularly shaped fragments exiting the nozzle

- <u>SACMI PH150 Press</u>

Another option was to use SACMI PH150 Press, available at MUSP Laboratory. It is a hydraulic press equipped with a mould for powder compaction (*figure 28*). The maximum allowed vertical load is 1500 kN and the maximum vertical stroke is 200 mm. Hot pressing can be performed at a temperature of maximum 600°C. Both the mould and the punches can be heated. The pressing compartment is cylindrical and has a diameter of 60 mm and a height of 200 mm.

Figure 28. SACMI PH150 Press

With this machine, thirteen samples were produced. Each sample was made inserting about 10g of material inside the mould and setting different combinations of temperature, oil pressure, processing time. Apart from the first one, all the samples were disks with diameter of 60 mm and height ranging between 4 mm and 8 mm. In *figure 29*, the obtained samples are shown. The order is the same as the trials and the evolution of the process is clearly visible.

Figure 29. Samples resulting from hot pressing

Table 10 collects the data of the corresponding samples. For all the procedure, parameters were varied based on the observations made after a sample was produced: if the new sample did not appear as if material had plasticized, it meant that temperature, oil pressure and/or time had to be changed, most of the times they were increased. The disks became harder, more solid and plastic each time, apparently reaching the point of full plasticisation with sample E.

Samples from 1 to 8 were produced with no previous drying, whereas samples from A to E were either vacuum dried or dried in oven. Sample 1 is the result of a too high temperature set: material was liquefied, and it was scattered on the mould. Data about sample 5 are not to be taken into consideration as some technical issues arose during the process.

The large number of samples is due to the difficulty with finding the right parameters for plasticisation: as it was previously mentioned, this aspect was critical and crucial. Moreover, it can be said that pressure was not as relevant as temperature and time. In fact, when only pressure was drastically changed between a sample and the next one, no apparent difference was noticeable in the results. Longer processing time positively affected the outcome, but temperature was even more important for sure. However, the factor that was responsible for obtaining the best results was the drying process before hot pressing.

For all the samples except number 1, density was computed as ratio between mass and volume, and the obtained values are in *table 10*. These values are estimations, since the samples were not perfect cylinders, and their height was irregular.

Table 10. Data of the samples obtained from hot pressing

Sample	T [°C]	p (oil) [bar]	t [s]	Further information	Density [g/cm3]
1	250	11	60		/
2	180	11	60		0,494
3	200	11	60		0,675
4	200	15	180		0,706
5	209	15	180	Distorted (technical issues)	0,779
6	218	15	180		0,761
7	227	15	180		0,683
8	227	50	180		0,748
A	227	15	180	Vacuum drying 48h	0,812
B	235	15	180	Vacuum drying 48h	0,775
C	235	15	600	Vacuum drying 48h	0,800
D	235	15	600	Drying in oven at 90°C for 4h	0,859
E	240	15	180	Vacuum drying 48h	0,688

Figure 30 plots the behaviour of the measured densities and the employed temperatures and times for each sample. Pressure was not plotted since it was the least relevant variable. Density of the reference recycled PA66 (datasheet in section 3.1) is equal to 1.12 g/cm^3. Notice that, compared to the reference density, the computed values are all lower. The explanation for this could be that, even though fibers were pressed, they were not fully compacted, and air could still be present inside the volume.

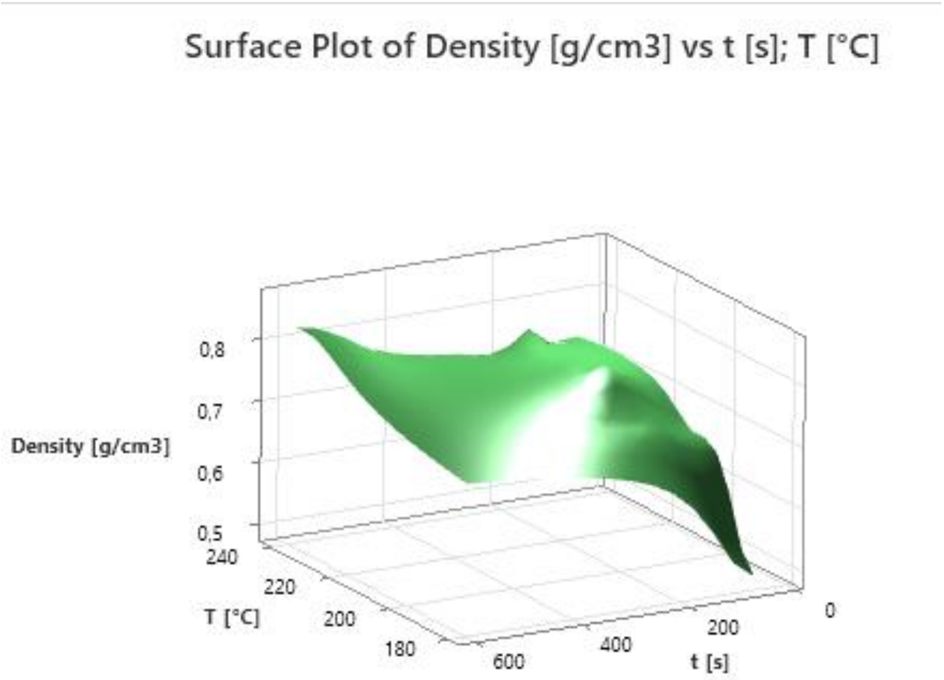


Figure 30. Behaviour of data of the samples from hot pressing

Some of the obtained samples, in particular samples 3, 6 and E, were examined under the microscope to understand how the thermal process affected the fibers structure.

Sample 3 macroscopically was a soft and flexible light-coloured disk, while sample 6 had some darker spots on the surface 6. In both cases, it did not seem plasticisation had occurred. *Figure 31* and *figure 32* show respectively sample 3 and 6 examined under the microscope. It is clearly visible that the material still had a fibrous structure, in which fibers had been compacted but had still been preserved. The difference between these two samples is that in the second one the fibers are more ordered.

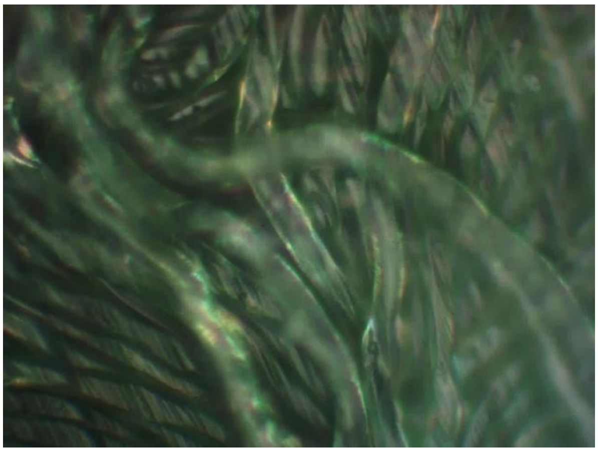


Figure 31. Sample 3 under the microscope

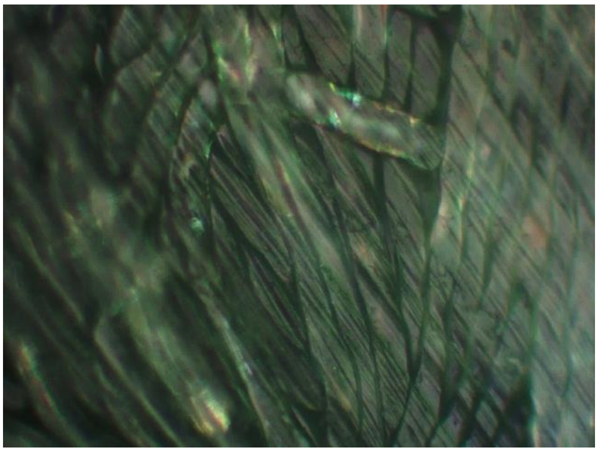


Figure 32. Sample 6 under the microscope

Differently from the previous two, sample E appeared dark and solid on sight, and it seemed that material had plasticized, even though it was not perfectly homogeneous. The sample was sectioned, and the section was examined under the microscope.

From *figure 33* it is possible to see that the hot-pressing process performed on sample E allowed plasticisation of the material. In fact, fibers are not visible anymore. The structure is instead solid and plastic, not only macroscopically.

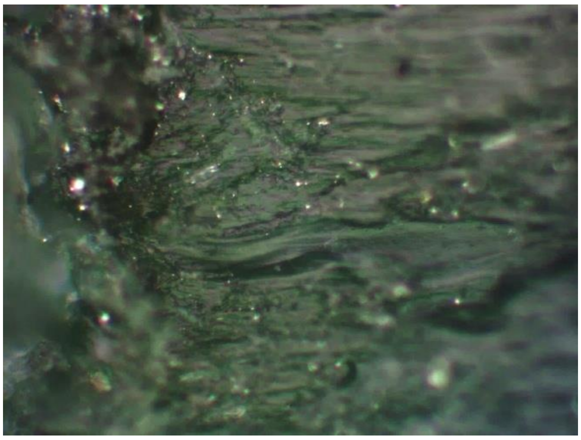


Figure 33. Sectioned sample E under the microscope

Even though this attempt led to positive results, as the target of nylon plasticisation was apparently achieved, the process turned out to be unfeasible either for the difficulty with the parameters setting and for the fact that it is not possible to perform it continuously. As far as the first reason is concerned, it must be noted that little uncertainties can lead to divergent results: as an example, for sample 1 and sample E all the parameters were different, but the most important one had close values, that is only 10°C of temperature difference, and yet sample 1 was a disastrous outcome while sample E was the best one. Moreover, hot pressing was not a continuous process since it allowed to produce one piece at a time and the waiting times in between were quite long. Therefore, it was decided that an alternative process had to be found.

3.3.5 Brabender Plasti-Corder

Among all the considered options, the most appropriate machine for the purpose turned out to be the Brabender Plasti-Corder (figure 34), available at the AMATECH Laboratory of Politecnico di Milano. The machine is a single screw extruder with torque rheometer and temperature controls. It is equipped with four thermocouples which measure the temperature in four zones of the extrusion group: the first zone is close to the feeding hopper and the last zone is in correspondence of the nozzle. Moreover, a system of levers measures the total torque required at a given rotational speed during the operations.

Figure 34. Brabender Plasti-Corder

Firstly, the machine was started up and temperatures were set at, in order from zone 1 to zone 4, that is along the screw up to the nozzle, 200°C, 210°C, 225°C, 240°C (*figure 35*). This set was chosen in order to keep a temperature gradient along the screw, considering that 240°C as highest temperature together with the action of the screw would be suitable factors for the melting of the material.

Figure 35. Initial temperature set

After some time for the warming, the motor was started, and the speed was increased manually up to 50 rpm, that is the general working condition for this machine.

Material was inserted in the hopper (*figure 36*), but since it was fluffy and lightweight it could not go down and enter the extrusion chamber. Thus, it was necessary to push it until it reached the screw using a piston manufactured ad hoc (*figure 37*). In addition, feeding had to be done with limited quantities of material at a time, otherwise the push would not be effective.

Figure 36. Grinded fibers inside the hopper

Figure 37. Piston manufactured ad hoc

Filaments exited the nozzle continuously, as it can be seen in *figure 38*. They were plastic and dark-coloured, as targeted, and after cooling down they were stiff and easily breakable. However, it was noted that extrusion was irregular, and filaments presented rough surface, slightly variable colour and different levels of opacity (*figure 39*).

Figure 38. Filaments exiting the nozzle

Figure 39. Irregular filaments from initial parameters set

Parameters were changed. Temperatures were increased close to the feeding zone in order to facilitate the melting process and they were tuned at 240°C, 230°C, 230°C, 240°C, in the same order as before. Speed was reduced and set equal to 40 rpm, so to allow a better filament formation.

Extrusion resulted still continuous, but it looked definitely more stable (*figure 40*). Also, the surface of the filaments was smooth, their diameter was constant, and it was more difficult to break them, as they became less brittle. They are shown in *figure 41*.

Figure 40. Filaments exiting the nozzle after parameters change

Figure 41. Regular filaments after parameters change

Brabender Plasti-Corder has proved to be the best available option for the process, in terms of both results and feasibility. The only difficulty was with the feeding part, even though the expedient of the piston was applied, and the problem solved.

A possible solution, that would make the mixing and plasticisation even more feasible, would be to employ a twin-screw extruder (*figure 42*) with wider feeding zone, so that material could be better funnelled through the extrusion chamber, with no need of external action. Unfortunately, this machine was not available, thus no testing could be done to verify whether it could have been the optimal procedure, and the operations were completed using the single screw extruder.

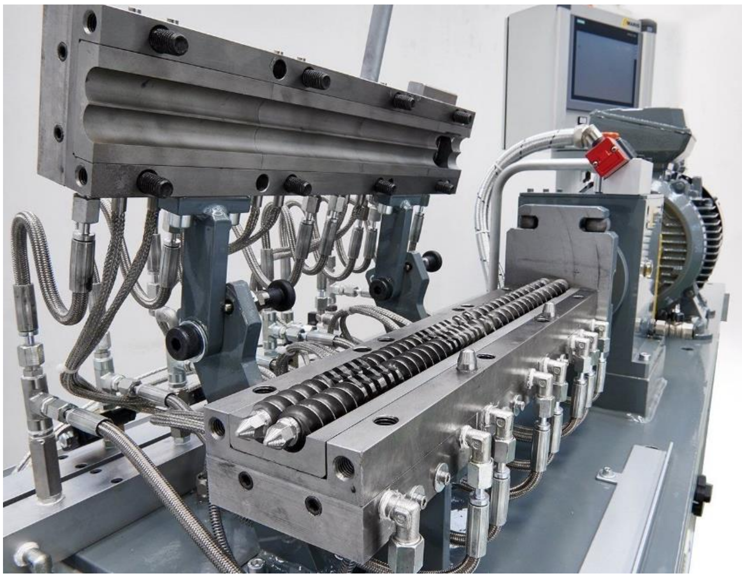


Figure 42. Twin-screw extruder

3.3.6 Shaping of the pellets

Once the filaments were extruded and nylon fibers plasticization was obtained, the next step was to break the filaments into pieces, so to obtain pellets. This was necessary as the machine to be used for the EAM process required pellet form feedstock material.

Since a granulator was not available, this process was carried out manually using pincers and work shears and about 1 kg of nylon pellets were cut. Pellets are shown in *figure 43*.

Figure 43. Nylon pellets

The difficulty of this step laid in the fact that, when cut, the filaments were subjected to brittle fracture and thus the pieces were randomly shot in the surrounding environment. The adopted expedient to avoid this consisted of cutting the pieces inside a plastic bag, so that they could be collected at once.

A more automated and more suitable for industrial applications solution would be to use a front granulator (as the one in *figure 44*) in cascade with the extruder: it has a blade that rotates and chops the hot filament as soon as it exits the extruder.

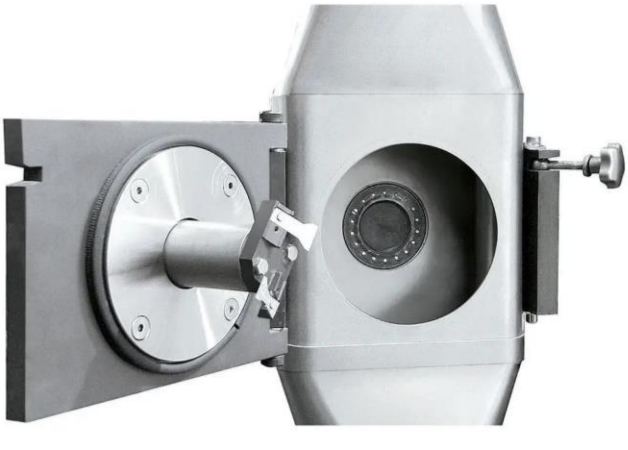


Figure 44. Front granulator for pellet production

3.4 CHARACTERIZATION OF RECYCLED TEXTILE NYLON

Characterization of recycled textile nylon was carried out to determine some of its relevant properties. In particular, in this section, the variability of density and colour of the pellets are presented. In addition, DSC analysis was performed both on the pellets and on the fibers of the original t-shirts. In the next chapter, the results of the DSC analysis on the material after print and an overall comparison will be presented.

3.4.1 Density

From datasheet in section 3.1, the reference value of density of recycled PA66 is 1.12 g/cm3. An estimation of density was done for the obtained pellets, in order to compare the result with the reference value.

Twenty samples of pellets were randomly selected for the computation. They were weighted and, for each one, diameter and length of the sample were measured with the microscope using the proper function. Density was eventually obtained through ratio between mass and volume. *Table 11* shows the results of the computation. *Figure 45* shows the histogram of frequency of density and the correspondent Gaussian distribution.

Table 11. Density of samples of pellets

Sample	Diameter [mm]	Length [mm]	Mass [g]	Density [g/cm³]
1	2,709	3,276	0,02100	1,1122
2	2,529	5,704	0,03339	1,1653
3	2,000	3,320	0,01184	1,1352
4	2,713	3,569	0,02539	1,2306
5	2,569	2,893	0,01666	1,1109
6	2,614	5,000	0,03082	1,1486
7	2,881	2,679	0,02148	1,2299
8	2,849	4,110	0,03086	1,1778
9	2,845	4,564	0,03316	1,1429
10	2,691	2,970	0,01995	1,1811
11	2,506	4,095	0,02276	1,1269
12	2,586	3,490	0,02134	1,1642
13	2,773	5,643	0,03859	1,1323
14	2,720	4,757	0,03153	1,1407
15	2,738	6,803	0,04490	1,1210
16	2,909	6,417	0,04921	1,1538
17	2,866	6,397	0,04736	1,1476
18	2,675	4,598	0,02871	1,1110
19	2,677	4,778	0,03142	1,1684
20	2,972	4,226	0,03423	1,1676

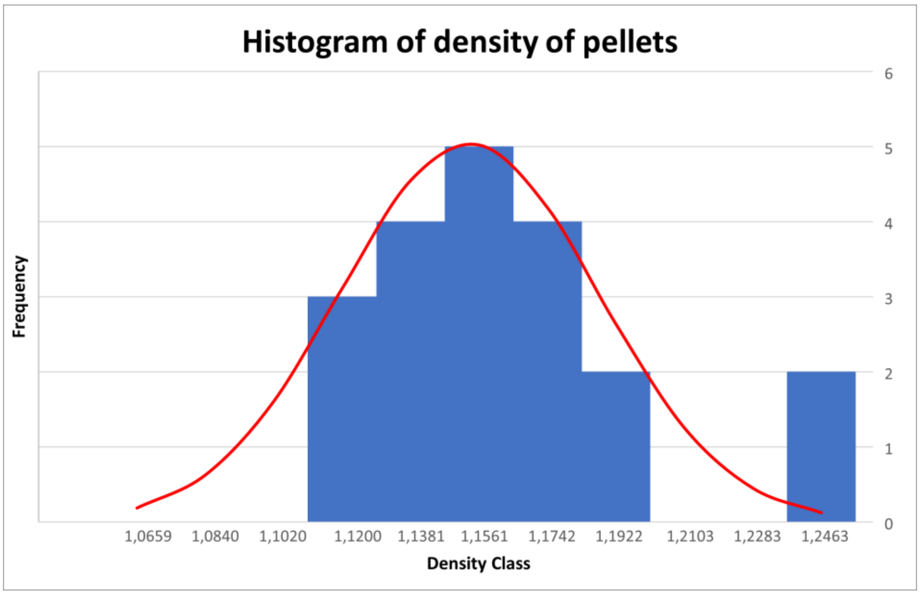


Figure 45. Histogram of frequency of density of pellets

The average value of density is equal to 1.1534 g/cm^3 and the standard deviation is 0.0340 g/cm^3. Notice that these values are estimations. However, the resulting value of density of the pellets is very close to the reference one. Thus, the recycling process starting from the t-shirts led to the targeted pellets whose density can be considered as valid and acceptable.

3.4.2 Variability of the colour

It was noticed that the obtained pellets were not uniform in colours. *Figure 46* shows the main six types found.

Figure 46. Pellets of different colours

Three colours could be distinguished, respectively blue, green and grey. For each colour, there were both shiny and matte pellets. In order to analyse them, RGB codes were detected and collected in the ternary plot in *figure 47*. Also the RGB code of the colour of the t-shirt fibers was detected and the correspondent point on the plot is the closest to the Red-Green side. It can be seen that the colour changed after thermal processing, mostly passing from green to blue.

The great majority of the pellets were blue, shiny and matte. Green pellets were the fewest. The differences in colour were probably due to the fact that the extrusion process was not homogenous. For instance, green pellets were the results of a lower degree of plasticisation, while the grey ones were slightly degraded.

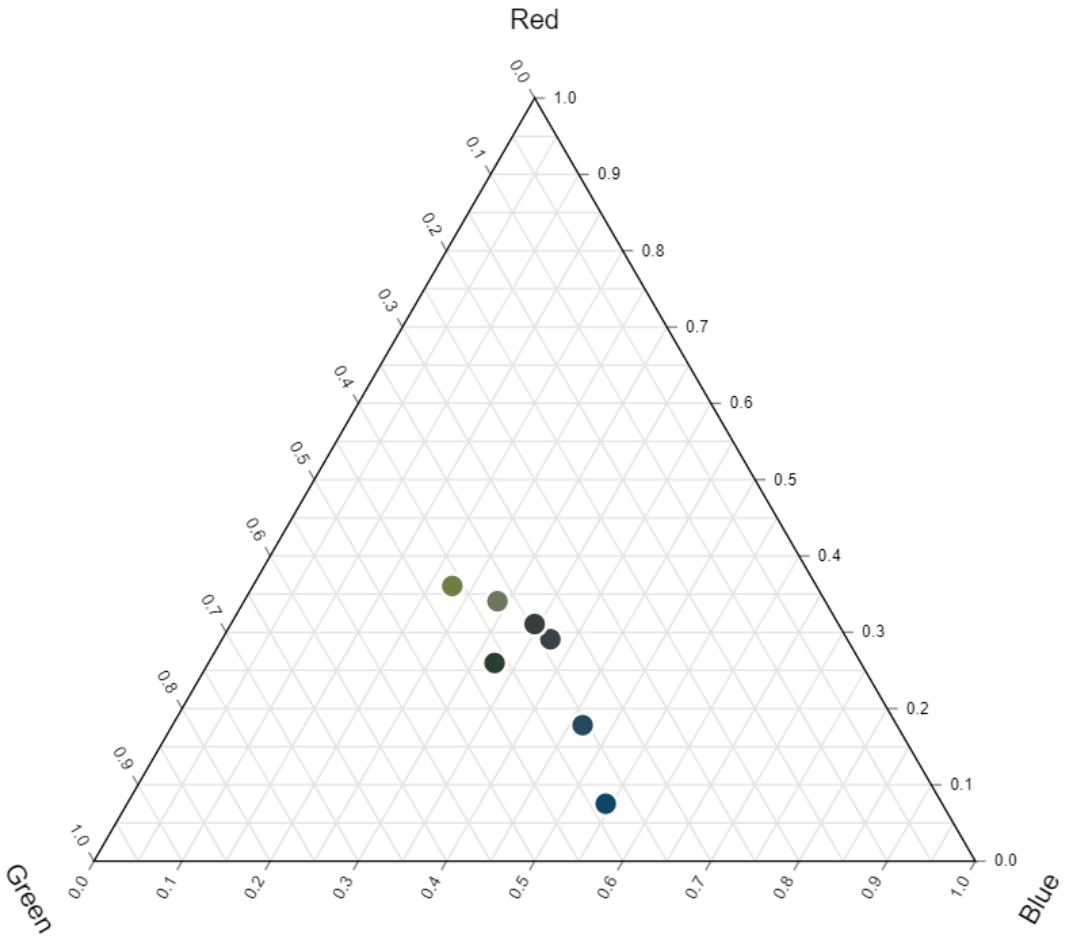


Figure 47. Ternary plot of RGB codes of detected colours

3.4.3 DSC analysis

DSC (Differential Scanning Calorimetry) is an experimental analysis in which a sample and a reference material are heated or cooled with a specific "temperature - time" program. During the analysis, the difference of thermal power needed to maintain two materials at the same temperature is measured. The environment is thermally insulated, and the atmosphere is made inert through Argon or Nitrogen.

The DSC analyses are generally used to determine:

- Temperature and enthalpy of crystallization, melting and phase change in materials
- Glass transition and melting temperature in polymeric materials
- Presence of possible degradation phenomena or cross-linking reactions in a determined temperature range

In *figure 48* and *figure 49*, the DSC curves related to respectively the fibers and the pellets are presented. In both curves, the lower line corresponds to the heating of the sample, while the upper line corresponds to the cooling.

In the curve of the fibers, the peak at 253,38°C represents melting phase and the peak at 226,56°C represents crystallization. Moreover, there is a wide peak at about 100°C that indicates the presence of absorbed humidity in the analysed sample.

In the curve of the pellets, instead, melting occurs at 257,88°C and crystallization occurs at 225,55°C.

The most noticeable difference between these two curves is given by the variation of heat flow in correspondence of the melting phase. In fact, for the fibers it is much bigger than the variation for the pellet. This difference denotes that the material of the pellet is degraded with respect to the fibers. It means that degradation occurred during the thermal process.

The curves will be employed also in section 4.2.6.1, where the results of DSC analysis on the material after printing will be presented. A comparison will be made in order to analyse the evolution of the material characteristics after a second thermal process.

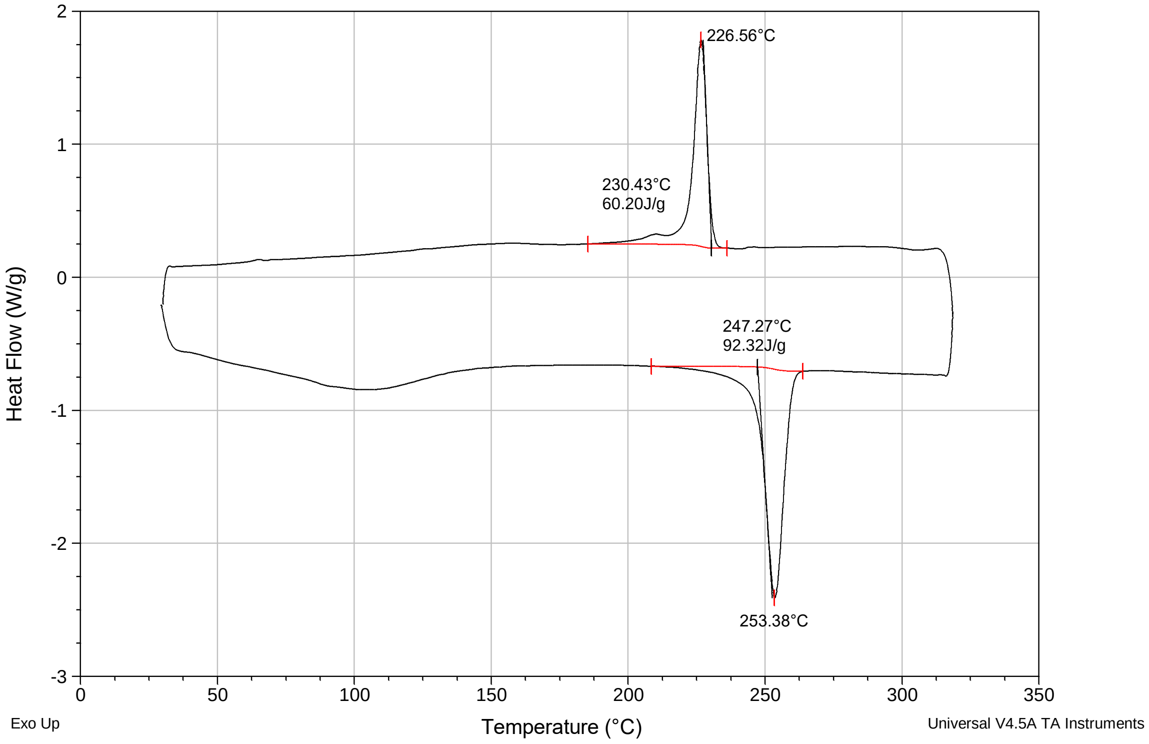


Figure 48. DSC curve of nylon fibers

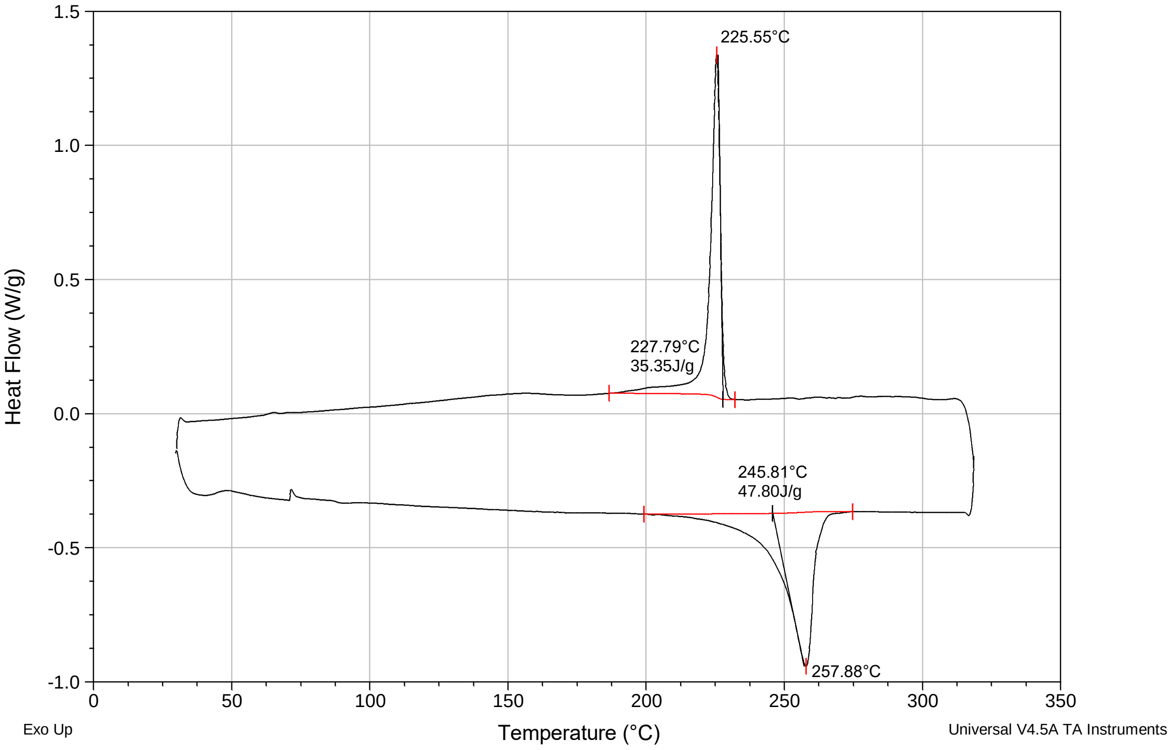


Figure 49. DSC curves of recycled nylon pellets

4. EXTRUSION ADDITIVE MANUFACTURING

Additive manufacturing includes a variety of processes united by the common idea of manufacturing objects by a selective and iterative layer by layer addition of material.

The most commercially diffused is Extrusion Additive Manufacturing (EAM), also called FDM, in which the material is heated and melted at a temperature slightly above the melting point, and then extruded through a nozzle, moved in space through PLC driven motors. A software slices the digital model of the geometry, and a code is generated to define the paths in space for the nozzle. In *figure 50*, the scheme of EAM process is shown.

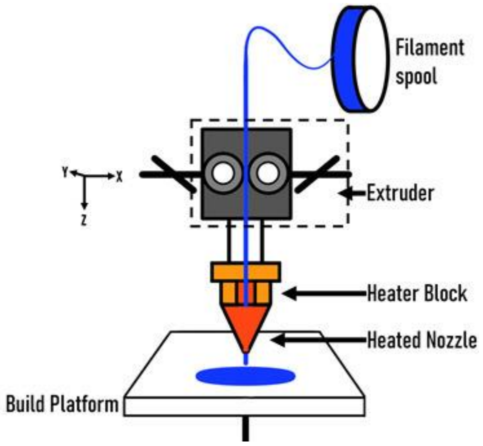


Figure 50. Extrusion Additive Manufacturing

EAM can be mainly performed with polymers, but also with metals, alloys and ceramics. Usually, materials are in the form of filaments or pellets. The FDM process has several process parameters. Among the main ones are extrusion temperature, print speed, layer thickness, nozzle diameter, deposition pattern.

Being EAM a thermal technology, many problems are present related to an excess or shortage of heat flux through the piece. Among the problems there are:

- Overheating: this problem is caused by to poor substrate stability, due to the excessively molten state of the material.
- Impossibility of making overhangs: when material is deposited in overhang condition it tends to fall due to gravity.

- Heat Creep: heat goes up through the extrusion head where it's not supposed to, it can result in clogs or damages of the machine.
- Warping: colder layers tend to shrink, while hot layers are expanded, and some thermal stresses arise. These generate deformations, and corners tend to curl.
- Delamination: when the temperature of the previous layer is too low with respect to the next one and there is no bonding, resulting in detached layers.

4.1 EFeSTO

The second part of this thesis is about the study of the printability of recycled textile nylon. The adopted technique was Extrusion Additive Manufacturing, and the operations were carried out on the project EFeSTO (Extrusion of Feedstock for manufacturing of Sintered Tiny Objects), innovative machine developed at Politecnico di Milano since 2014.

EFeSTO (*figure 51*) is made up of a modified Metal Injection Molding deposition head combined with a parallel kinematic build plate. The extrusion head is relatively powerful and heavy, so it is fixed in space while the motion along the three axes (X, Y and Z) is given to the build plate.

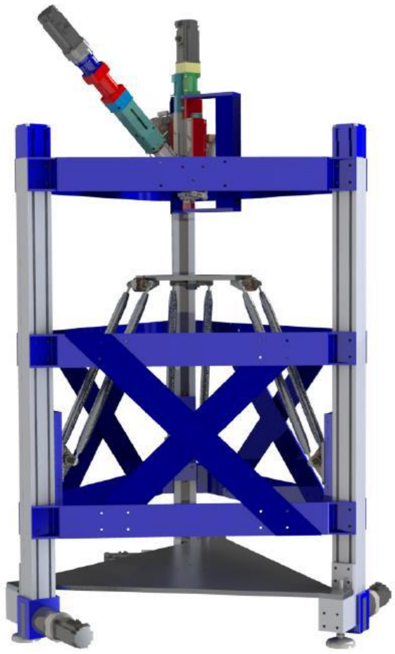


Figure 51. EFeSTO machine

The printing head is mainly composed by a feeder, where the pellets of feedstock are placed, and two pistons, a plasticizer and an injector. Material in form of flakes or pellets is inserted in the hopper and falls by gravity in a first chamber, the loader. It is pushed by the piston through some metal spheres to increase the shear stress and allow plasticisation. Then it enters a second chamber, the extruder, where the viscous fluid is kept at a given temperature and is pushed by the piston out of the nozzle. Pistons are driven by brushless motors.

Both the chambers are heated. Three resistances provide heat to the material, and four thermocouples are used for PID temperature control. The resistances are placed in the nozzle, in the extruder and in the loader, each with a thermocouple. The fourth thermocouple is present in the thermal cut-off zone, to control the temperature and to protect the piston of the loader, motors and electronics.

The two-phase loading procedure allows a decoupling of the plasticization phase, which needs to be done at constant speed and pressure, and the printing phase, which can have a variable speed depending on the mould geometry.

The kinematic system consists of a parallel kinematic machine (PKM) which drives the build surface in space through the linear movement of three vertical sliders. It is a 3-axis Linear Delta configuration that allows the motion of the workplane along X, Y, Z directions.

The control terminal (*figure 52*) includes a PC, directly connected through USB to a PLC, Motion Control Unit, Temperature Control Unit and Human Machine Interface.

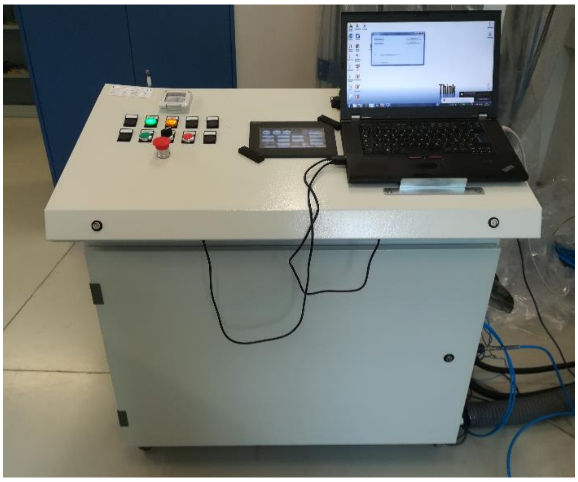


Figure 52. EFeSTO Contol Terminal

The control of the machine is performed through brushless motors. The position and speed of the motors are controlled through a PID control. The Temperature Control Unit is used for a PID control of the three resistances, based on the measurements from the thermocouples.

The HMI (*figure* 53) is a touch screen display with a visual interface. It was used to activate motors, heaters and temperature control, bring the delta structure, the extruder and the loader to home position, control the extruder and the loader when loading material or purging and cleaning the chambers. The temperature of the bed surface and fan speed were controlled externally and not with the HMI.

Figure 53. Human Machine Interface

The digital chain of the 3D printing are the passages which allow to pass from the idea of a three-dimensional object designed on CAD software to the real object. In Efesto, the steps are:

1. The component to be printed is drawn using a CAD software and the file is saved in STL format. Fusion 360 software was used in this work.
2. The STL file is used to generate a G-code through a slicing software. PrusaSlicer software was used here.
3. The G-code is used as starting point for generating print trajectories in the workspace. It is given to a Matlab compiled program, which converts the G-code in CAM instructions for the machine.
4. Another software transmits the data created in the previous step to the machine during printing, through online communication.
5. The motion CPU of the system uses the data coming from the PC to generate the trajectories of the axes of the machine and to print the object.

4.2 EXPERIMENTAL CAMPAIGN

In this section, an experimental procedure to study the printability of recycled textile nylon is discussed, in particular the target was to understand whether the material previously recovered from t-shirts could be effectively employed for Extrusion Additive Manufacturing applications. To have a reference, prints were done with virgin nylon alone. Also the effects of blending the recycled material with virgin nylon are evaluated. The experimental campaign was carried out with EFeSTO machine.

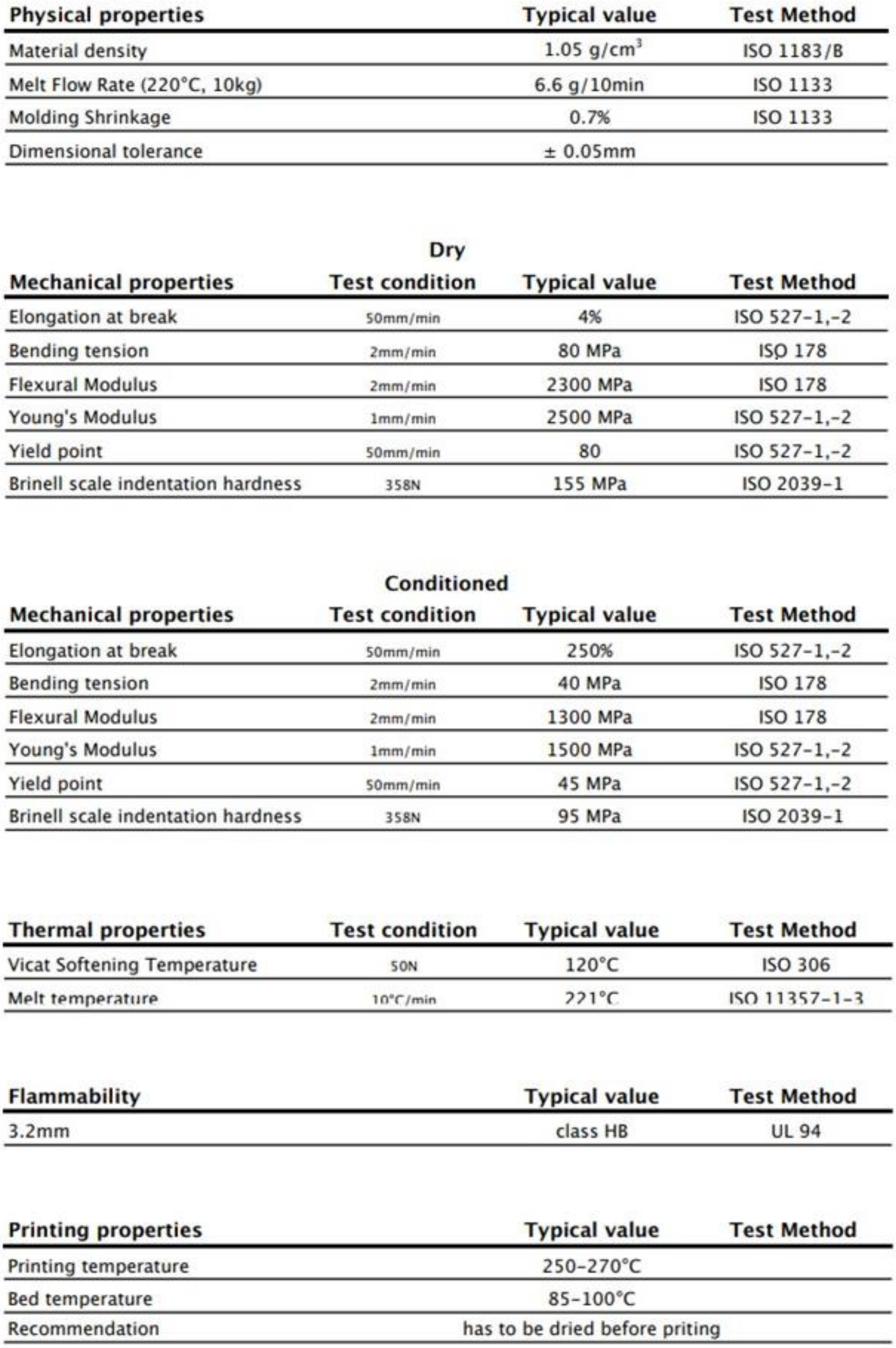
4.2.1 Materials

In the experimental campaign, the recycled PA66 resulting from the recycling process presented in chapter 3 is the main protagonist. Nylon pellets were obtained because the feedstock material for EFeSTO machine must be in pellet form.

Apart from the recycled PA66, a second material was acquired for the campaign. It is Spectrum Nylon PA6 Low Warp Filament from 3DJake. In *table 12* the datasheet of the material is presented. This nylon had an auxiliary role in the campaign, since it was used to make a blend with percentage in mass of 30% of recycled nylon.

Notice that density of PA6 is slightly smaller than the density of PA66. Moreover, while PA66 melting temperature is about 260°C, melt temperature of PA6 is 221°C, but its printing temperature is between 250 and 270 °C. Generally, PA6 and PA66 are considered two similar materials and copolymers PA6/66 exist that are employed for additive manufacturing applications.

Table 12. Spectrum Nylon PA6 Low Warp Filament datasheet



Physical properties	Typical value	Test Method
Material density	1.05 g/cm^3	ISO 1183/B
Melt Flow Rate (220°C, 10kg)	6.6 g/10min	ISO 1133
Molding Shrinkage	0.7%	ISO 1133
Dimensional tolerance	± 0.05mm	

Mechanical properties	Dry Test condition	Typical value	Test Method
Elongation at break	50mm/min	4%	ISO 527-1,-2
Bending tension	2mm/min	80 MPa	ISO 178
Flexural Modulus	2mm/min	2300 MPa	ISO 178
Young's Modulus	1mm/min	2500 MPa	ISO 527-1,-2
Yield point	50mm/min	80	ISO 527-1,-2
Brinell scale indentation hardness	358N	155 MPa	ISO 2039-1

Mechanical properties	Conditioned Test condition	Typical value	Test Method
Elongation at break	50mm/min	250%	ISO 527-1,-2
Bending tension	2mm/min	40 MPa	ISO 178
Flexural Modulus	2mm/min	1300 MPa	ISO 178
Young's Modulus	1mm/min	1500 MPa	ISO 527-1,-2
Yield point	50mm/min	45 MPa	ISO 527-1,-2
Brinell scale indentation hardness	358N	95 MPa	ISO 2039-1

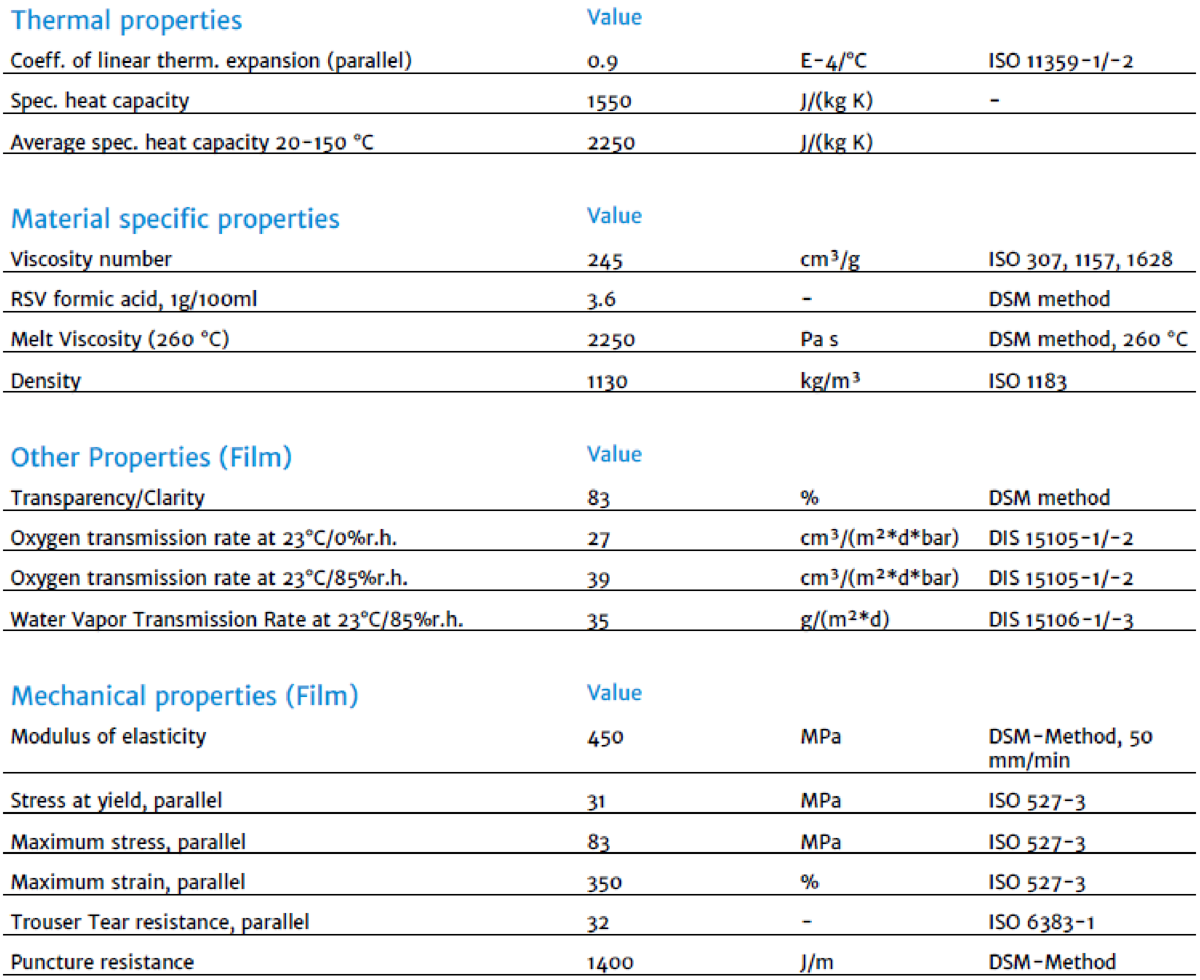
Thermal properties	Test condition	Typical value	Test Method
Vicat Softening Temperature	50N	120°C	ISO 306
Melt temperature	10°C/min	221°C	ISO 11357-1-3

Flammability	Typical value	Test Method
3.2mm	class HB	UL 94

Printing properties	Typical value	Test Method
Printing temperature	250-270°C	
Bed temperature	85-100°C	
Recommendation	has to be dried before priting	

In addition, pellets of Akulon F136-C1 PA6 (*table 13*) from ReprapWorld were employed for comparison with the behaviour of virgin nylon.

Table 13. Akulon F136-C1 PA6 datasheet



Thermal properties	Value		
Coeff. of linear therm. expansion (parallel)	0.9	E-4/°C	ISO 11359-1/-2
Spec. heat capacity	1550	J/(kg K)	-
Average spec. heat capacity 20-150 °C	2250	J/(kg K)	
Material specific properties	**Value**		
Viscosity number	245	cm^3/g	ISO 307, 1157, 1628
RSV formic acid, 1g/100ml	3.6	-	DSM method
Melt Viscosity (260 °C)	2250	Pa s	DSM method, 260 °C
Density	1130	kg/m^3	ISO 1183
Other Properties (Film)	**Value**		
Transparency/Clarity	83	%	DSM method
Oxygen transmission rate at 23°C/0%r.h.	27	$cm^3/(m^2*d*bar)$	DIS 15105-1/-2
Oxygen transmission rate at 23°C/85%r.h.	39	$cm^3/(m^2*d*bar)$	DIS 15105-1/-2
Water Vapor Transmission Rate at 23°C/85%r.h.	35	$g/(m^2*d)$	DIS 15106-1/-3
Mechanical properties (Film)	**Value**		
Modulus of elasticity	450	MPa	DSM-Method, 50 mm/min
Stress at yield, parallel	31	MPa	ISO 527-3
Maximum stress, parallel	83	MPa	ISO 527-3
Maximum strain, parallel	350	%	ISO 527-3
Trouser Tear resistance, parallel	32	-	ISO 6383-1
Puncture resistance	1400	J/m	DSM-Method

4.2.2 Dryer

Since the printing process is based on extrusion and thermal processing of the material, also in this part of the project, drying of the material was necessary for the same reasons mentioned previously.

AIRID Polymer Dryer from 3Devo was employed. This dryer is designed to eliminate any moisture complication that may occur within a polymer. Additionally, within the dryer, a stirring rotator guarantees evenly dried materials across all surface areas.

For nylon the suggested cycle time is equal to 4 h at a temperature of 80°C.

4.2.3 Materials for bed adhesion

First-layer adhesion is critical to ensure 3D print success. If bed adhesion is not guaranteed, corners unstick from the 3D printer's build surface, warping occurs, and ultimately parts fail. Moreover, adhesion problems can be caused by a number of factors or any combination of issues, including bed levelling, bed temperature, extruder temperature, build plate deficiencies, slicer settings.

Two different products were employed: Dimafix Spray and Magigoo HT.

Dimafix Spray is a specific fixing spray for 3D printing with heated surfaces. It allows the seal of the prints with the surface temperature above 70°C giving maximum performance at 100°C. It is applied to a cold flatbed printer, then it is heated, and, at the end of the printing, the piece is removable as soon as the temperature of the workplate drops below 45°C.

In the case of 100% recycled nylon, it was necessary to set the bed temperature above 100°C, and therefore this spray was not as performing as needed, since the first layers of the prints tended to detach from the surface. Magigoo HT was applied in substitution. Magigoo HT improves bed adhesion for higher temperatures. The spreading on the build surface was harder than the spray, but it was observed that the objects remained adherent to the surface for all the printing time.

4.2.4 3D Models

Since the experimental campaign was carried out with the purpose of evaluating the printability of the materials, a demonstrative specimen was created, using Fusion 360 CAD software, taking into considerations the geometrical features that cause the most frequent issues when objects are printed.

The model (*figure 54*) was obtained starting from a square base, with 20 mm side length, that was revolutionized around a separate axis for 45°. A through hole with diameter of 8 mm was obtained along the vertical axis. Eventually, one of the lateral surfaces was cut along a slanting plane, with a slope of 20° with respect to the vertical direction.

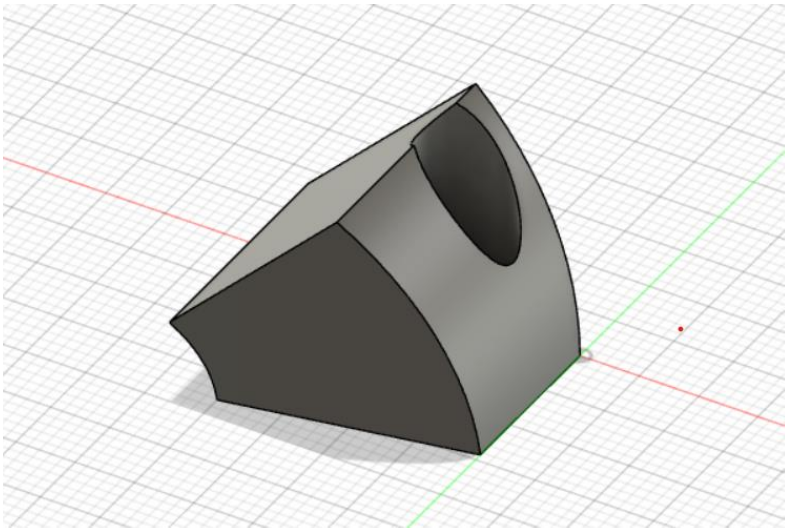


Figure 54. 3D Model

The complexity of the geometry lies in the presence of slanted and curved surfaces, developed both overhanging and on the upper part of the block, and of a hole. In fact, overhangs are needed to test if an angled surface can be printed without falling due to gravity. Moreover, with this model also the surface quality and the staircase effect can be checked.

The evaluations about printability refer to the observed behaviour of the print when some parameters are varied. In particular, the greatest attention was paid to body and nozzle temperature, layer fan speed and bed temperature.

4.2.5 Printer settings

The settings of the printer are reported below in *figure 55*, *figure 56* and *figure 57*.

Layer height

Layer height: 0.25 mm

First layer height: 0.5 mm or %

Figure 55. Layer settings

Speed for print moves

Perimeters: 60 mm/s

Small perimeters: 60 mm/s or %

External perimeters: 60 mm/s or %

Infill: 60 mm/s

Solid infill: 60 mm/s or %

Top solid infill: 60 mm/s or %

Support material: 60 mm/s

Support material interface: 100% mm/s or %

Bridges: 60 mm/s

Gap fill: 60 mm/s

Ironing: 15 mm/s

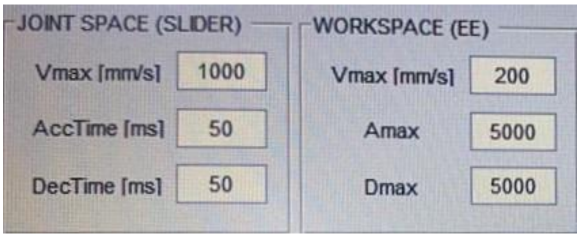
Speed for non-print moves

Travel: 90 mm/s

Modifiers

First layer speed: 15 mm/s or %

Figure 56. Speed settings



JOINT SPACE (SLIDER)

Vmax [mm/s] 1000

AccTime [ms] 50

DecTime [ms] 50

WORKSPACE (EE)

Vmax [mm/s] 200

Amax 5000

Dmax 5000

Figure 57. Linear Delta speed settings

4.2.6 100% recycled nylon

At the beginning of the experimentation, some preliminary samples of the model were printed, varying different parameters to find some basic working conditions. Body and nozzle temperatures, layer fan and bed temperature were varied based on the aspect and consistency of the extruded filament. Below, the parameters and the corresponding results are shown.

1.

Table 14. Parameters for sample 1

Body Temperature [°C]	**Nozzle Temperature [°C]**	**Bed Temperature [°C]**	**Layer Fan Speed**	**Adhesive - adhesion**
255	260	110	0%	Dimafix - no

Nozzle temperature was chosen equal to the melting temperature from PA66 datasheet. Body temperature was chosen slightly lower in order to have higher viscosity in the extruder. No layer fan was activated. Bed temperature was relatively high, and even though spray fixer was applied to the workplate, during the print process there was loss of adhesion and the sample detached.

In *figure 58*, it can be seen that the sample was not completed, because the print was interrupted after the detachment. Moreover, it resulted that the filament was matte and fragmented, meaning that body and nozzle temperatures were probably low.

Figure 58. Printed sample 1

2.

Table 15. Parameters for sample 2

Body Temperature [°C]	Nozzle Temperature [°C]	Bed Temperature [°C]	Layer Fan Speed	Adhesive - adhesion
260	260	110	0%	Dimafix - no

In this case, body temperature was increased. All the other conditions were the same as the previous print.

Figure 59 shows that the filament was more fluid and shinier, that were better conditions with respect to before, but it was affected by overheating problem and bad road stability, resulting in poor quality of the printed object.

Again, detachment occurred, and the piece was not completed.

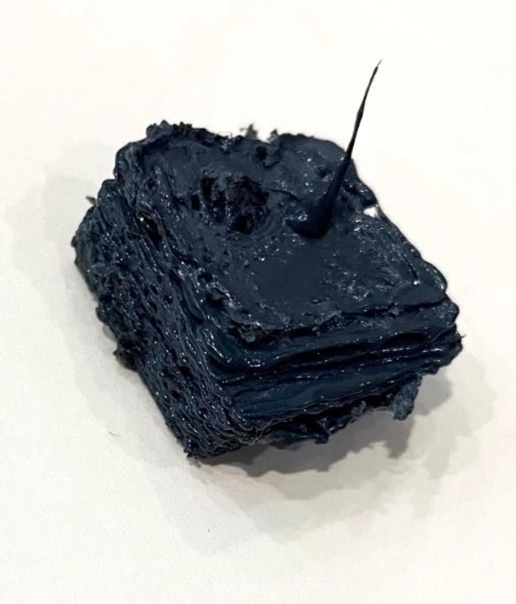


Figure 59. Printed sample 2

3.

Table 16. Parameters for sample 3

Body Temperature [°C]	**Nozzle Temperature [°C]**	**Bed Temperature [°C]**	**Layer Fan Speed**	**Adhesive - adhesion**
230	270	190	100%	Dimafix - no

Nozzle temperature was increased, and body temperature was decreased, trying to find a combination of temperatures that could improve filament consistency.

Higher bed temperature was set in order to improve bed adhesion, but still there was detachment and the print remained uncomplete.

Layer fan was activated at the maximum speed, because temperatures at the nozzle and at the bed were considerably high, and thus the fan would have been necessary to avoid overheating. As it can be seen in *figure 60*, not only overheating was still present, in smaller amount, but also delamination occurred.

Figure 60. Printed sample 3

4.

Table 17. Parameters for sample 4

Body Temperature [°C]	**Nozzle Temperature [°C]**	**Bed Temperature [°C]**	**Layer Fan Speed**	**Adhesive - adhesion**
230	270	200	60%	Magigoo - yes

Body and nozzle temperatures were kept the same and bed temperature was slightly increased.

Sample 4 (*figure 61*) was the only one to be completed, since bed adhesion was achieved with a different adhesive.

Layer fan was lowered to 60% and still overheating and delamination were present.

Figure 61. Printed sample 4

5.

Table 18. Parameters for sample 5

Body Temperature [°C]	**Nozzle Temperature [°C]**	**Bed Temperature [°C]**	**Layer Fan Speed**	**Adhesive - adhesion**
230	270	200	35%	Magigoo - no

Temperatures were not changed. Layer fan was decreased to try to avoid delamination. From *figure 62*, it is possible to see that delamination was not present, but due to overheating, the material was too liquid, and the structure could not support it.

Unexpectedly, there was loss of adhesion even though bed temperature and adhesive were the same as sample 4 case.

Figure 62. Printed sample 5

In *table 19*, the parameters of the five preliminary prints are collected.

Table 19. Preliminary prints parameters

Sample	Body Temperature [°C]	Nozzle Temperature [°C]	Bed Temperature [°C]	Layer Fan Speed	Adhesive - adhesion
1	255	260	110	0%	Dimafix - no
2	260	260	110	0%	Dimafix - no
3	230	270	190	100%	Dimafix - no
4	230	270	200	60%	Magigoo-yes
5	230	270	200	35%	Magigoo - no

The preliminary prints brought to light the fact that the recycled material behaves inconsistently and no choice of the parameters for successive prints could be made, since the collected data did not provide useful and sufficient information.

It was evident that material was not homogeneous, and it tended to lose consistency during extrusion, so that no parameter setting could improve the situation during the deposition of the filament.

In addition, no more than five trials could be realized, in order to collect more data, because material behaviour was so critical that it caused malfunctioning of the EFeSTO machine. In fact, loading and extrusion could not be performed continuously and properly for all the printing time.

Apparently, degradation of nylon took place during the process resulting in clogs inside the machine, both in the loader and the extruder sides. In fact, degradation is a time and temperature dependent phenomenon, meaning that the more the material remained inside a hot environment, the more and the faster it was subjected to it.

The first sign of degradation was the change in the colour of the material: from dark blue-green it started becoming dark grey at first and eventually it became pale brown. In *figure 63* some material that remained stuck between the nozzle and the outside of the machine is shown. The different colours are clearly visible.

Figure 63. Colour change after degradation

Figure 64 shows some degraded material that caused a clog in the nozzle.

Figure 64. Clogging material inside the nozzle

Another reason to think that material was being subjected to degradation is that its consistency varied in different moments, even though the temperature settings were kept the same. In *figure 65*, it is possible to see a filament of dense blue-green material next to some liquefied brown material, both produced when body and nozzle temperature were set equal to 250°C.

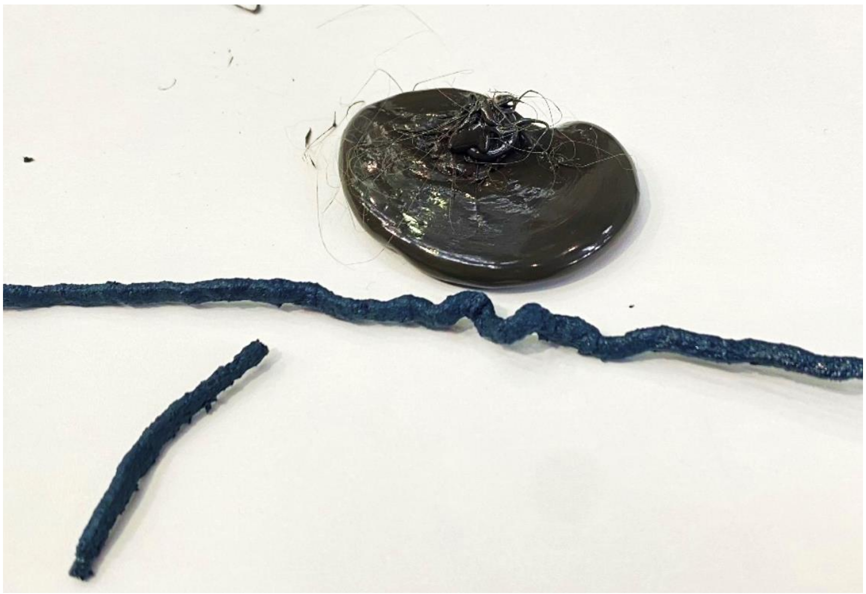


Figure 65. Difference in consistency of the material

4.2.6.1 DSC analysis

As mentioned in paragraph 3.4, DSC analysis was performed on the printed material for a comparison with the previous results.

In *figure 66*, the three overlapped curves are shown.

It is possible to observe a reduction in the temperature at the beginning of melting, from fibers (247°C) to pellet (245°C) to printed material (237°C). This is consistent with the advancement of level of thermal degradation.

During heating, the highest heat flow peak in the curve of the original fiber is coherent with the initial state of the material and with the spinning process, that promotes crystallization. The lowest peak is in the curve of the pellet and it is consistent with degradation and with a high cooling speed. While the peak of the printed material is slightly higher than the pellet one since cooling speed was lower.

The fact that crystallization temperature becomes lower from fiber to pellet and then to printed material could be linked to the progressive degradation, that causes greater difficulty in crystallizing, and that is pointed out by both lower temperature and lower heat flow. Partially, these effects could be also due to the different cooling speed.

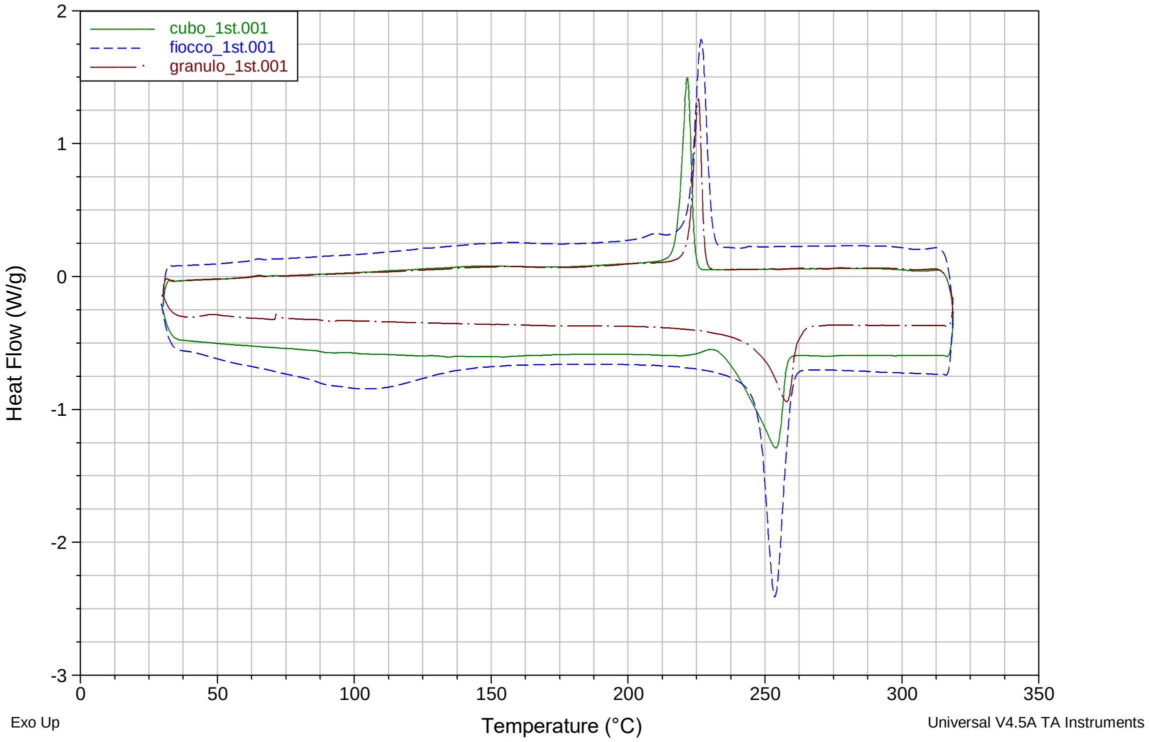


Figure 66. Comparison of DSC curves

Overall, the curves confirm that, after being subjected the second thermal process, the material shows a further level of degradation. This justifies the inconsistency of behaviour of the material observed during the prints.

4.2.7 100% virgin PA6

Before proceeding with the prints of the blended material, the behaviour of virgin PA6 in the EFeSTO machine was analysed. Again, the varied parameters were body and nozzle temperatures, layer fan and bed temperature.

a.

Table 20. Parameters for sample a

Body Temperature [°C]	**Nozzle Temperature [°C]**	**Bed Temperature [°C]**	**Layer Fan Speed**	**Adhesive - adhesion**
225	250	120	0%	Dimafix - no

The first print (*figure 67*) was performed setting lower temperatures both in the body and at the nozzle. Material showed good consistency. However, warping and detachment occurred.

Figure 67. Printed sample a

b.

Table 21. Parameters for sample b

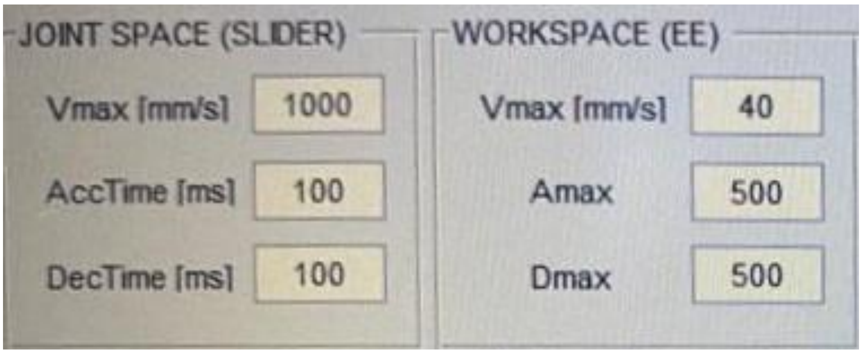
Body Temperature [°C]	**Nozzle Temperature [°C]**	**Bed Temperature [°C]**	**Layer Fan Speed**	**Adhesive - adhesion**
225	250	120	30%	Magigoo-yes

Adhesion was obtained by applying Magigoo. Thanks to 30% of layer fan speed overheating was limited.

The print (*figure 68*) was not completed since the machine went overload, probably due to high velocity and accelerations settings.

Figure 68. Printed sample b

c. Printer settings were adjusted, and velocity and accelerations values were reduced, according to *figure 69*. All the other parameters were kept the same as the previous print.



JOINT SPACE (SLIDER)

Vmax [mm/s] 1000

AccTime [ms] 100

DecTime [ms] 100

WORKSPACE (EE)

Vmax [mm/s] 40

Amax 500

Dmax 500

Figure 69. Adjusted printer settings

In *figure 70*, sample c is shown. In this case, slight delamination was present.

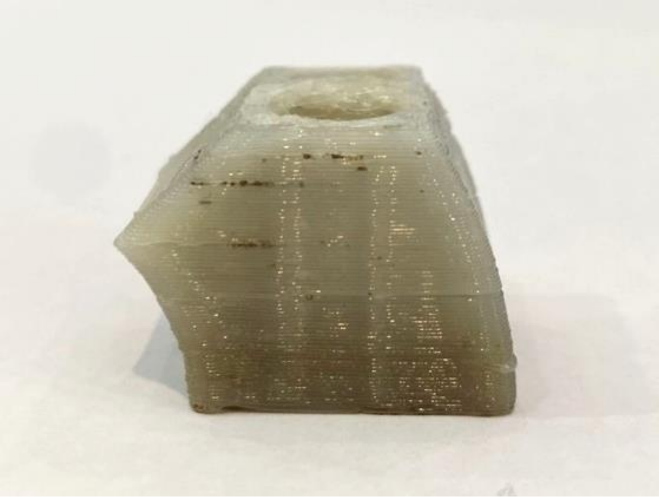


Figure 70. Printed sample c

d.

Table 22. Parameters for sample d

Body Temperature [°C]	**Nozzle Temperature [°C]**	**Bed Temperature [°C]**	**Layer Fan Speed**	**Adhesive - adhesion**
225	250	120	20%	Magigoo-yes

Last print was successfully completed. Lower fan speed eliminated the problem of delamination.

Moreover, sample d (*figure 71*) was apparently good enough to define the starting parameters for the next step, that is for the print of 30% recycled nylon blend.

Figure 71. Printed sample d

4.2.8 30% recycled nylon blend

PA6 filament was grinded with the same cutting mill used in section 3.3.2. After, it was combined with recycled nylon pellets, so to obtain a blend with percentage of 30% in mass of recycled nylon.

Usually, polymer blending procedure is done in a melting-mixing process using an extruder. However, this process affects the properties of the materials, especially because thermal degradation occurs.

Since two extrusion cycles were already included in the material history, one in the recycling process and one in the additive manufacturing procedure, blending was not carried out through an additional one, in order not to subject the material to excessive degradation. Moreover, extrusion with EFeSTO would have contributed, at least partially, to the mixing of the two materials.

The parameters for the print were the same used for sample d, in section 4.3.7.

Even though virgin material was employed to improve the printability of recycled nylon, the results showed that the process is critical: also in this case, fast degradation when nylon was exposed to hot environment occurred. Again, the machine got clogged and the pistons couldn't move.

For sure, the fact that the mixture was not homogeneous was a problem.

The attempt could be done to perform an extrusion cycle with the Brabender Plasti-Corder before EFeSTO, in order to try to print a more homogeneous blend. Moreover, better results could be obtained if the percentage of recycled nylon in the blend was lower than 30%.

5. CONCLUSIONS

In this thesis, the objective to develop a brief, inexpensive and low environmental impact process chain for the recycling of an end-of-life textile nylon product was pursued and the recovered material was printed via extrusion additive manufacturing.

The experimental study was divided in two parts. In the first one, a purely mechanical procedure to recover textile nylon from nylon t-shirts was presented and the sequence of the performed mechanical processes was described. Before each process, the testing of material behaviour was analysed to define the most proper machine to be employed. Firstly, to grind the fabrics a cutting mill was a better option than a swarf shredder. Then, material had to be plasticized. Among the tested machines there were a hot mounting press, a pellet extruder, a press, a single-screw extruder. The last one turned out to be the best available option. Drying of the material before thermal processing was fundamental. The textile fibers were extruded, and plastic filaments were generated. Eventually, filaments were cut, and recycled nylon pellets were obtained.

Characterization of the recycled nylon was carried out. Density of the pellets was measured, and it was compared to a reference, observing great similarity in the values. Since the appearance of the pellets was not uniform, analysis of the colour variability was made. Variations consisted of three colour shades, according to the level of degradation of the material, and of different opacity. Moreover, DSC analysis was made. Temperature and enthalpy of crystallization, melting and phase change were defined. The presence of possible degradation phenomena was detected.

In the second part, extrusion additive manufacturing was performed with the EFeSTO machine to understand whether the recycled material had good prospects of being 3D printed. The study of printability was carried out by varying some relevant parameters according to the quality of the prints output. When 100% recycled nylon was printed, the material tended to behave critically and no choice of the parameters for successive prints could be made. The printed samples presented poor quality, due to signs of overheating and delamination. It was evident that material was not homogeneous, and it tended to lose consistency during extrusion, so that no parameter setting could improve the situation during the deposition of the filament. Degradation of the material had occurred inside the machine, causing change in colours and consistency in the material and clogs and malfunctioning in the machine. 100% virgin nylon, instead, was printable. After some trials, it was possible to define the parameters for the printing settings, that were body and nozzle temperatures, layer fan and bed temperature, velocity and accelerations of the workplate during printing. Eventually, the blend with percentage of 30% in mass of recycled nylon was made, combining it with virgin nylon, without melting-mixing process. The mixture was not homogeneous and also in this case, complications arose, due to degradation phenomena.

Future developments could involve the employment of a blend with lower percentage in mass of recycled material, for instance 10% or 15%. Higher presence of printable virgin material could improve the properties of the recycled one and could lead to successful trials when printing with EFeSTO.

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