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EXTRUSION OF THERMOPLASTIC ELASTOMER FILAMENTS FOR THE DESIGN OF MULTI-POLYMER STRUCTURES BY 3D PRINTING

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TÍTULO: EXTRUSION OF THERMOPLASTIC ELASTOMER FILAMENTS FOR THE DESIGN OF MULTI-POLYMER STRUCTURES BY 3D PRINTING

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RESUMEN:

El objetivo del proyecto es crear un objeto impreso en 3D mediante FDM (Modelado por Deposición Fundida) con una parte suave y una parte dura combinando sus propiedades y el diseño del objeto. Diseñar un filamento de material blando con buena compatibilidad con un termoplástico, poli (ácido láctico) (PLA) usando diferentes (co)polímeros comerciales para el proceso de extrusión e impresión y por último elegir un método para evaluar la adhesión del filamento diseñado con el filamento de PLA. En este informe se estudia la extrusión y la posibilidad de impresión de diferentes TPE (elastómeros termoplásticos). Primero, se incluye un fondo bibliográfico que presenta el estudio. En segundo lugar, se recopila una lista de los materiales y métodos utilizados para este estudio. Y finalmente, se presentan los resultados obtenidos en este estudio, así como las perspectivas de conclusión.

PALABRAS CLAVE:

Polímeros, termoplásticos elastómeros, extrusión, impresión 3D, Poliuretano termoplástico

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ABREVIATIONS AND ACRONYMS

Table 1. Detail table

ABREVIATIONS/ACRONYMS	DETAILS
ABS	Acrylonitrile Butadiene Styrene
COPE/TPC	Thermoplastic copolyester
EPDM	Ethylene Propylene Diene Monomers
FDM	Fused Deposition Modeling
PLA	Poly (lactic acid)
PP	Polypropylene
SBS	Poly (styrene-butadiene-styrene)
SEBS	Poly (styrene-ethylene-butylene-styrene)
TP	Thermoplastic
TPA	Thermoplastic polyamides
TPE	Thermoplastic elastomer
TPO	Thermoplastic polyolefinelastomers
TPS	Styrenic block copolymers
TPU	Thermoplastic polyurethanes
TPV	Thermoplastic Vulcanizates

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INTRODUCTION

Several properties render FDM as a highly flexible AM method. Firstly, it allows for processing of many different material systems including thermoplastic polymers blended with functional agents. Secondly, it offers a straight forward multi-material configuration where dissimilar materials can be extruded from multiple different nozzles and can be composited in complex configurations. These unique aspects of FDM have been attracting significant attention of both low-level users and researchers towards realizing new functional products. There is substantial room for research on design and synthesis of new functional material systems that can be processed with FDM, understanding of material property FDM process parameters manufactured product properties for different materials of interest and new functional composites enabled by multi-material capabilities of FDM. [1]

Due to the multi-material manufacturing capabilities of the FDM, the fact of studying the possibility of manufacturing a piece with a soft and a hard part, formed by a TP (in this case, Poly (lactic acid)) and a TPE (TPU, because it is the most compatible with PLA).

This is of great interest because it allows to print pieces that combine the properties of the TPE with the properties of the TP in the same element. This will be useful in many fields, but this study may have a great interest in the field of biomedicine, for the use of prostheses or orthopedic elements. In addition, both the PLA and the TPU are biocompatible elements.

Thermoplastic polyurethane (TPU) is a highly elastic linear polymer composed of soft segments, usually flexible polyester or polyethers, and hard segments, usually diisocyanates with benzyl structure. TPU exhibits good biocompatibility, and also excellent mechanical properties such as good abrasion resistance, high elongation, and moderate tensile and compression strength. [2] These properties enable TPU to be widely applied in many fields including coatings, foaming, adhesives and tissue engineering. However, TPU does have several drawbacks including poor shape fixity and low mechanical strength. [3] Poly (lactic acid) (PLA), on the other hand, derived from renewable resources instead of petroleum have a high biocompatibility and biodegradability. PLA is mechanically strong and rigid, but very brittle with low flexibility and impact resistance.

The objective of the project is make a 3D printed object by FDM (Fused Deposition Modeling) with a soft part and a hard part combining their properties and the object's design.

- Design a filament from soft material with good compatibility with a thermoplastic, Poly (lactic acid) (PLA), and to adjust if possible the softness.
- Use of different commercial (co)polymers for the extrusion and printing process.
- Choose a method to evaluate the adhesion of the designed filament with PLA.

In this report the extrusion and the possibility of printing of different TPE (thermoplastic elastomers) are studied.

First, a bibliographic background (1) is included, which introduces the study. Secondly, a list of the materials and methods (2) used for this study is collected. And finally, the results (3) obtained in this study are presented, as well as the perspectives of conclusion (4).

1. BIBLIOGRAPHIC BACKGROUND

1.1. TPE

1.1.1. Definitions and structure

Thermoplastics are plastics that soften under the action of heat and harden by reversibly cooling. Most of the plastics used in the packaging are thermoplastics, which allows them to be recycled. Polyethylene (PE), high density polyethylene (HDPE), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS) or polyamide (PA) are thermoplastics whose employment is very widespread. Figure 1

An **elastomer** is a polymer that returns rapidly and approximately to its original shape and size after the cessation of a low stress that has produced significant deformation. Figure 2**¡Error! No se encuentra el origen de la referencia.**

Thermoplastic elastomers (TPE) combine the elastomer characteristic to be stretched to moderate extensions and, after the elimination of the effort, to return approximately to its original form with the recyclability and processing advantages of thermoplastics. These advantages over conventional rubbers make them highly competitive in all applications that do not require high elasticity or high heat resistance. TPEs have in the same macromolecule of flexible segments and rigid segments. These arrange themselves in rigid domains constituting the reversible "nodes" of a physical network, for example styrene-butadiene-styrene or SBS. The physical bonds of the rigid domains relax and then disappear when the temperature increases, allowing the shaping according to the techniques used for the thermoplastics. The elasticity is given by the flexible segments that alternate with the rigid segments. [4]

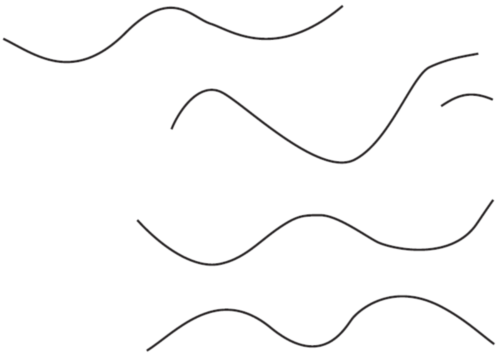


Figure 1. Thermoplastic structure

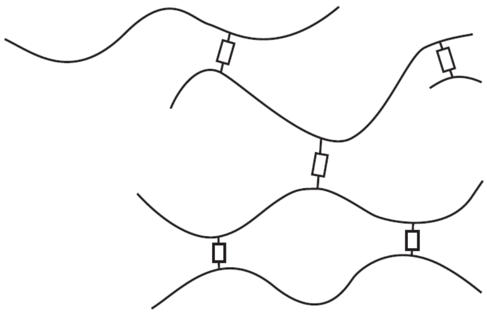


Figure 2. Elastomer structure

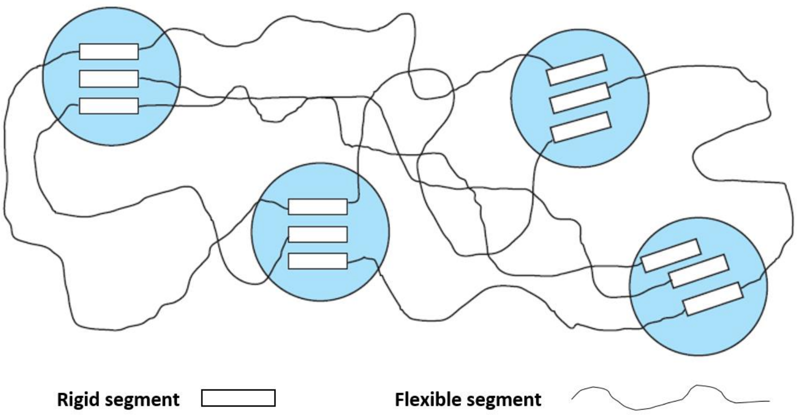


Figure 3. TPE structure

In short, TPEs are a family of rubber like materials that combine the characteristics of rubber with the recyclability and processing advantages of plastics.

Like thermoplastics, when heated and with the application of shear force, TPEs become free-flowing and when cooled regain their original structure and stability. Unlike the chemical cross-linking which occurs in thermoset rubbers, TPE involves purely physical cross-linking, which can be reversed via the further application of heat, this makes it possible to re-use all production waste and end of life products can be easily reprocessed. [5]

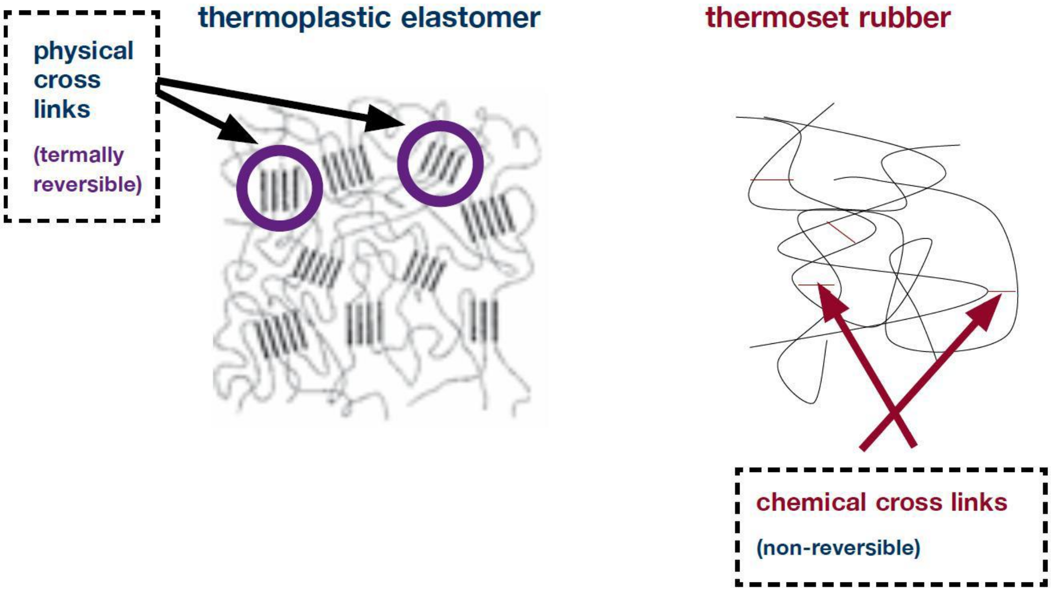


Figure 4. The cross-linking structure of a thermoplastic elastomer shows that there are no chemical cross-links unlike thermoset elastomers. [6]

1.1.2. Categories of TPE

TPE can be divided into 2 categories:

1) Blend

Mechanical mixture of semi-crystalline and amorphous polymers. [7] It can be seen in Figure 5.

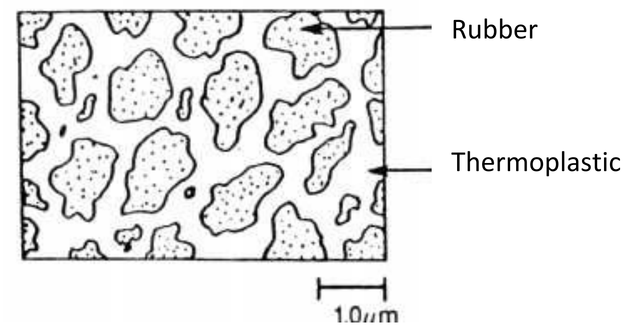


Figure 5. Blend

Polyolefins (TPO or TPE-O)

The most common TPO compounds are resin blends of polypropylene (PP) and un-crosslinked EPDM (Ethylene Propylene Diene Monomers) rubber and polyethylene. They are characterised by high impact resistance, low density and good chemical resistance.

They are small amount of finely dispersed regularly shaped rubber particles in a thermoplastic matrix, as shown in Figure 6.

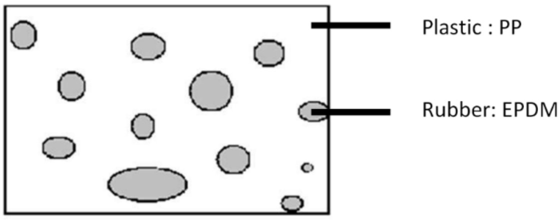


Figure 6. Small amount of finely dispersed regularly shaped EPDM particles in a PP matrix. [7]

They are used in applications where there is a requirement for increased toughness and durability over the conventional PP copolymers, such as automotive bumpers and dashboards. The properties are restricted to the high end of the hardness scale, typically >80 Shore A and with limited elastomeric properties. TPOs can be easily processed by injection moulding, extrusion or blow moulding.

Thermoplastic vulcanisates (TPV or TPE-V)

TPV compounds are the next step up in performance from TPO. Coming to the previous example of PP and EPDM rubber, but TPV are dynamically vulcanised during the compounding step. Vulcanization is a chemical process for the conversion of rubber or related polymers into more durable materials through the addition of sulfur or other "curative" equivalents. These additives modify the polymer by forming cross-links (bridges) between the different polymer chains.

These are large amount of less spherical, cross-linked rubber domains in a continuous PP matrix, as shown in Figure 7.

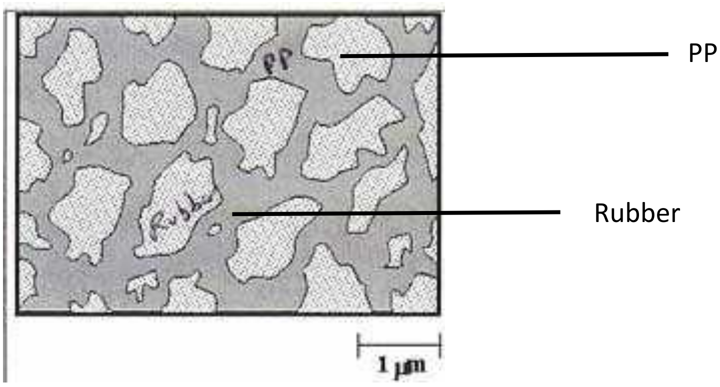


Figure 7. Rubber domains in a PP matrix. [8]

Its main properties are high temperature resistance, wide range of hardnesses, resistance to chemicals and weathering, low compression set, flex fatigue resistance, lightweight and good colourability.

2) Block Copolymer

Composed of discrete blocks of crystalline and amorphous domains within the same polymer chain, as shown in *Figure 8*.

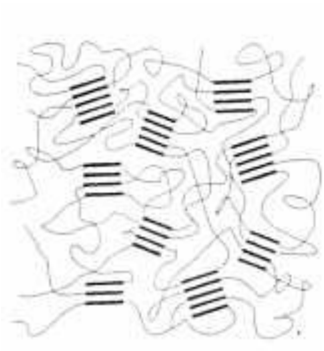


Figure 8. Block Copolymer

Styrenic Block Copolymers (TPS or TPE-S)

Thermoplastic elastomers described as TPS are compounds based on SBS.

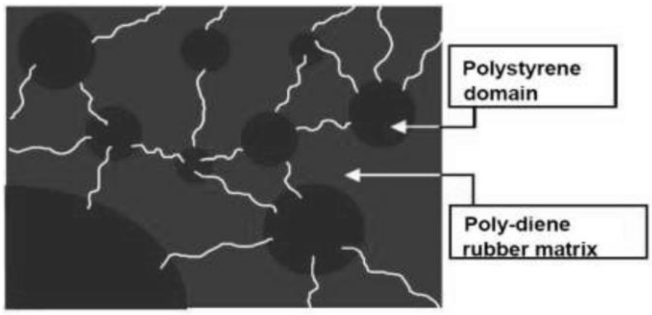
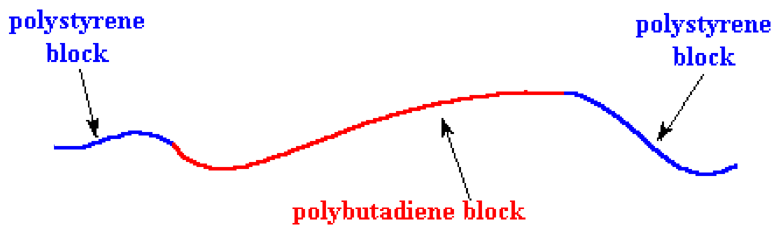


Figure 9. Styrenic Block Copolymer

SBS (styrene-butadiene-styrene) is based on two-phase block copolymers with hard and soft segments, as shown in Figure 9. The styrene end blocks provide the thermoplastic properties and the Butadiene mid-blocks provide the elastomeric properties. [5]

a)



b)

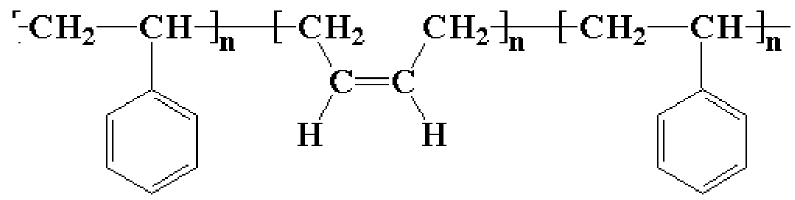


Figure 10. a) SBS structure; b) Poly (styrene-butadiene-styrene), otherwise known as SBS rubber

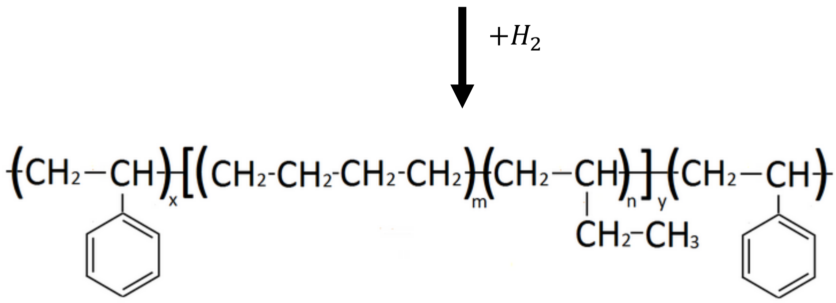


Figure 11. Poly (styrene-ethylene-butylene-styrene)

Thermoplastic Polyurethane (TPU)

TPU is a multi-phase block copolymer that is created when three basic raw materials are combined together in a specific way. The individual components required to produce a TPU are a polyol or long-chain diol, a chain extender or short-chain diol and a diisocyanate.

The soft block, built out of a polyol and an isocyanate, is responsible for the flexibility and elastomeric character of a TPU. The hard block, constructed from a chain extender and isocyanate, gives a TPU its toughness and physical performance properties. Figure 12.

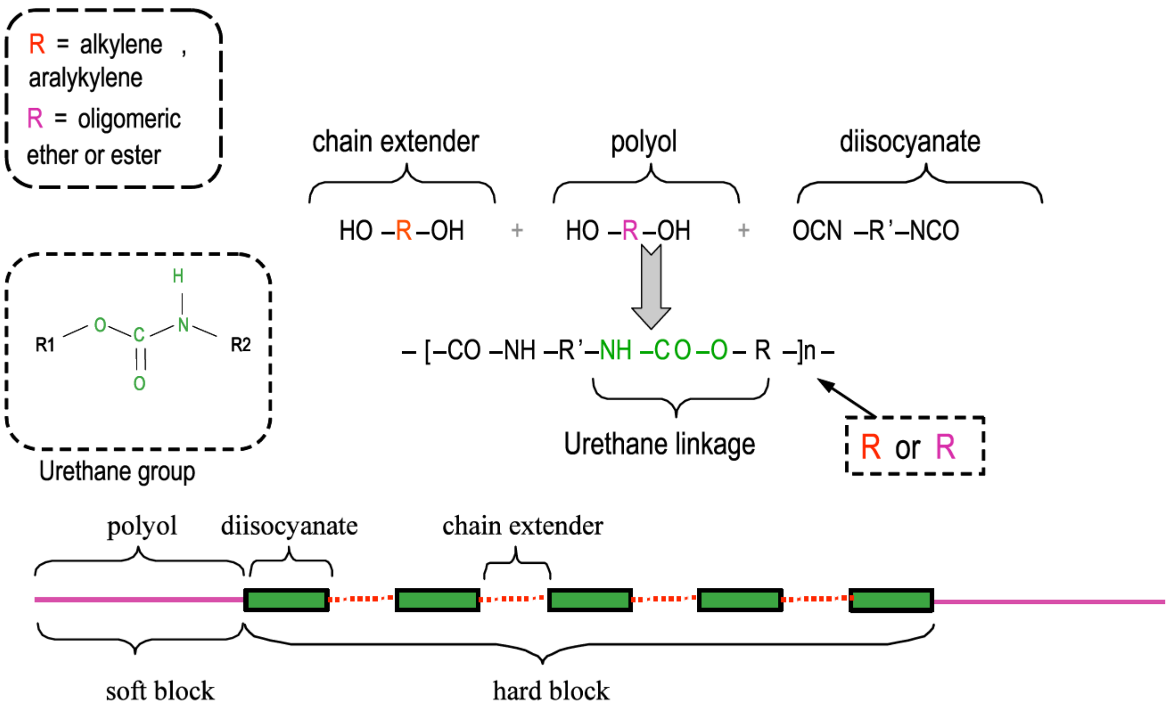


Figure 12. Basic chemistry of TPU.

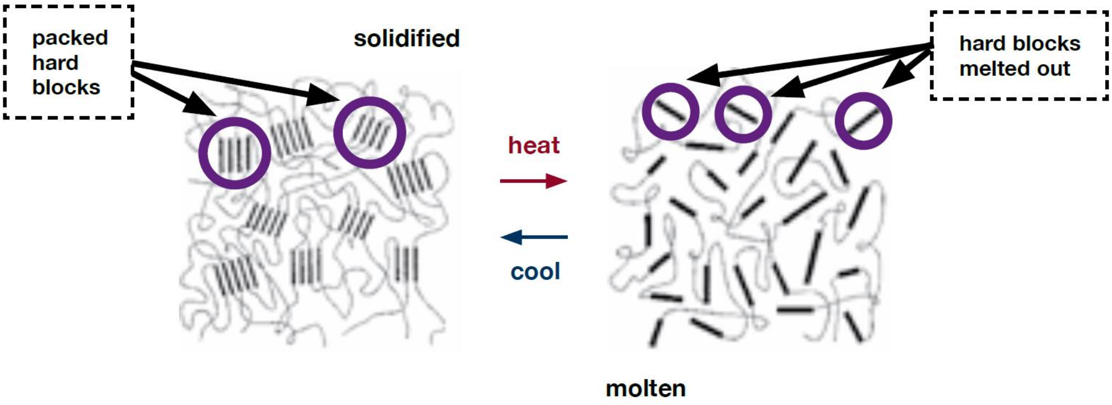


Figure 13. Graphic illustration of the morphology of a TPU. It shows how physical cross-links melt out under heat and repack when the material is cooled.

The typical properties are a high elongation and tensile strength, an excellent abrasion resistance, a low-temperature performance, ones excellent mechanical properties, combined with a rubber-like elasticity, a hhigh transparency and good oil and grease resistance.

The most important applications can be seen in Figure 14.

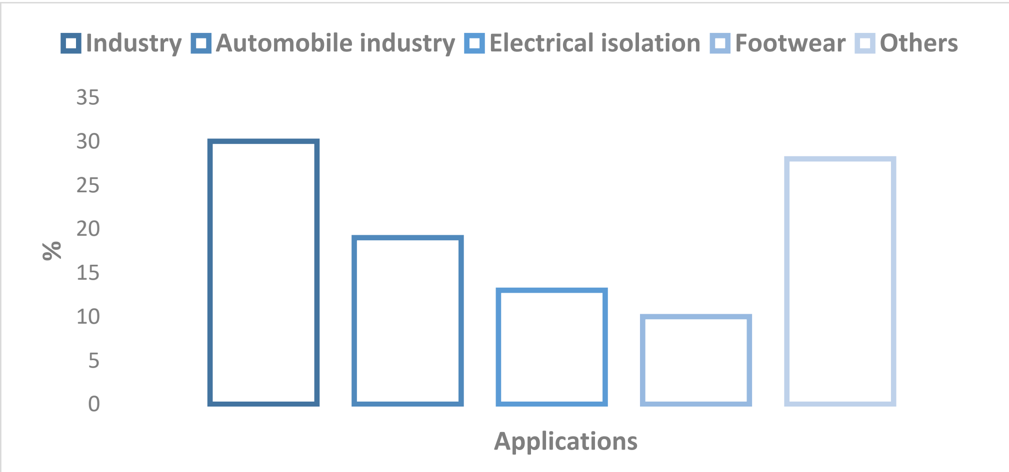


Figure 14. TPU applications [4]

Thermoplastic Copolyester Elastomers (TPE-E or COPE)

Thermoplastic copolyesters (TPE-Es) are block copolymers that have a generalised formula of (-A-B-). Typically, they are copolyether esters with alternating, random-length sequences of either long-chain or short-chain glycols connected by ester linkages. TPE-Es are similar in macromolecular structure to polyurethanes and polyamide elastomers. TPE-Es are composed of hard and soft segments; hard segments are typically multiple short-chain ester units, like tetramethylene terephthalate, whereas soft segments are usually aliphatic polyether and polyester glycols.

TPE-E has a biphasic structure, with one phase remaining soft at room temperature and the other remaining hard at room temperature. The soft segments are amorphous while the hard segments are crystalline, and both the segments are immiscible. The hard segment becomes fluidic when heated and imparts a thermoplastic nature to the polymer, while the soft segment imparts an elastomeric nature. The hard segments form noncovalent networks that are thermally reversible, relying on intramolecular interactions for their stability. A simple TPE-E copolymer structure comprises of alternating A-B-A blocks, where A is the hard phase, and B is the soft phase. The hard and soft phases are randomly joined head-to-tail, yielding the copolymers. The general structure of TPE-E copolymers is as follows: [9]

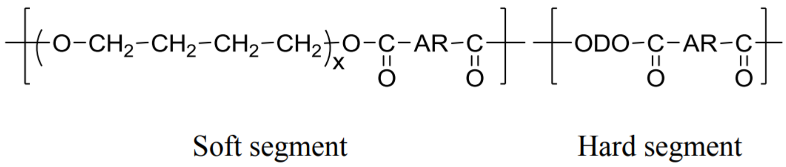


Figure 15. General structure of TPE-E copolymers

Where AR is the aromatic moiety of the dicarboxylate; D is the alkylene portion of a short-chain diol; and x = the number of tetramethylene ether units in the polytetramethylene glycol (PTMG)

One typical example of poly (ether ester) consists of poly (butylene terephthalate) (PBT) as the hard (rigid) and short segment connected by ester group with long and flexible (soft) poly (tetramethylene oxide) segment.

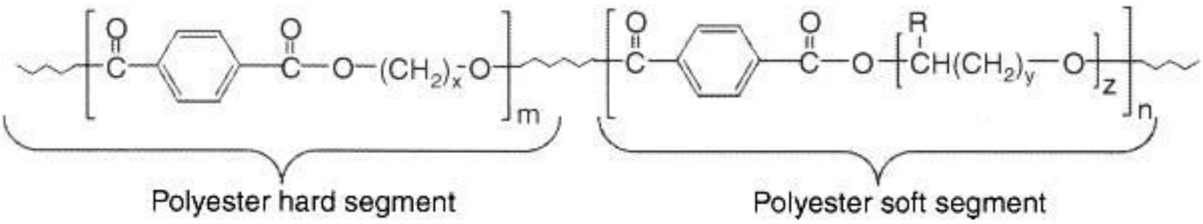


Figure 16. Chemical structure of poly (ether ester); x = 2, 3, 4; R: -CH_3 (y = 1) or -H (y = 1-3); the average degree of polymerization of polyether z = 14 - 60.

The typical properties are a low density, a chemical resistance, high strength and hardness, resilience, ones excellent properties at low temperatures, very good dynamic properties and a good thermal stability.

The most important applications can be seen in Figure 17.

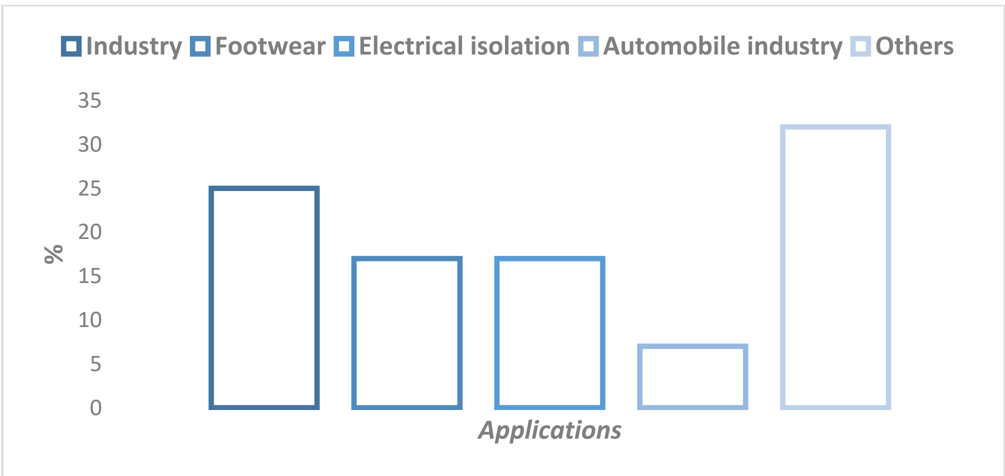


Figure 17. COPE applications [4]

1.2. Extrusion

Basically, the extrusion process involves heating a thermoplastic above its melting temperature and forcing it through the die. The extruder is a heating and pressurizing device involves one or more screws operating in a heated barrel. The key determinant of an extruder's performance is the screw. It has three main functions to perform: feeding and conveying the raw material feed; melting, compressing and homogenizing the material; and metering and pumping it through the extrusion die at a constant rate. The raw thermoplastic elastomer pellets are fed into the barrel of the extruder and comes into contact with the screw. As a melt delivery device, the rotating screw forces the polymer forward into barrel which is heated at a desired temperature to form a filament. [10] The extruded plastic can be drawn from the die to determine the final diameter of the filament. The die is shaped to form the extruded plastic into the desired cross-section. [11] The tension on the filament, or how quickly it is pulled out of the extruder directly have an effect on the size and shape of the filament strand. This can be manipulated by adjusting the speed of which the filament comes out of the machine. [12] An extruder can be seen in Figure 18.

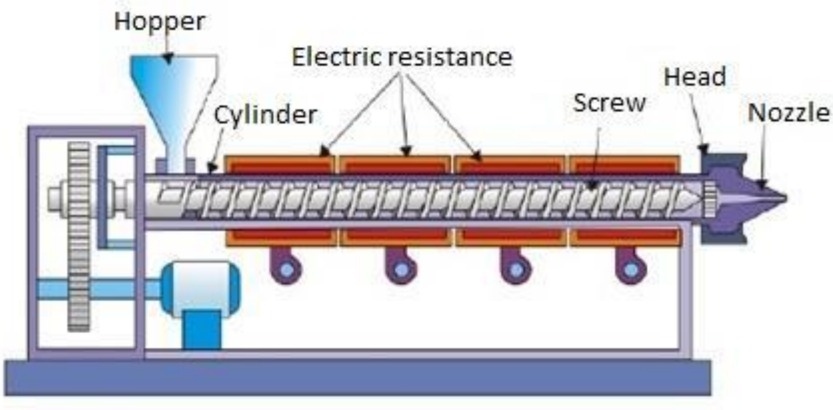


Figure 18. Extruder

1.2.1. Materials for extrusion

Producing 3D printing filament follows a specific set of conditions to have the process be successful. Using a system of machinery, the plastic resin is treated through four primary zones and extruded into spools of wire. [12] Below is shown an example of typical TPE extruder temperature profile in Table 2.

Table 2. Typical TPE extruder temperature profile [8]

°C	TPO/TPV 45 to 73 Shore A	SEBS 72 Shore A	TPU	COPE 38 to 74 Shore D
Feed	175-180	80-100	160-180	
Barrel Zone 1	175-180	220-232	160-180	205-260
Barrel Zone 1	180-190	220-232	170-190	205-260
Barrel Zone 1	180-190	220-232	180-210	205-260
Head	190-200	220-232	180-210	205-260
Die	200-205	220-235	180-220	205-260
Melt	195-200	190-232	185-220	185-221

1.2.2. TPE Extrusion Problems

Extrusion problems can occur in diverse ways and these can have several reasons. Typical problems in the extrusion of TPE as shown in Figure 19.

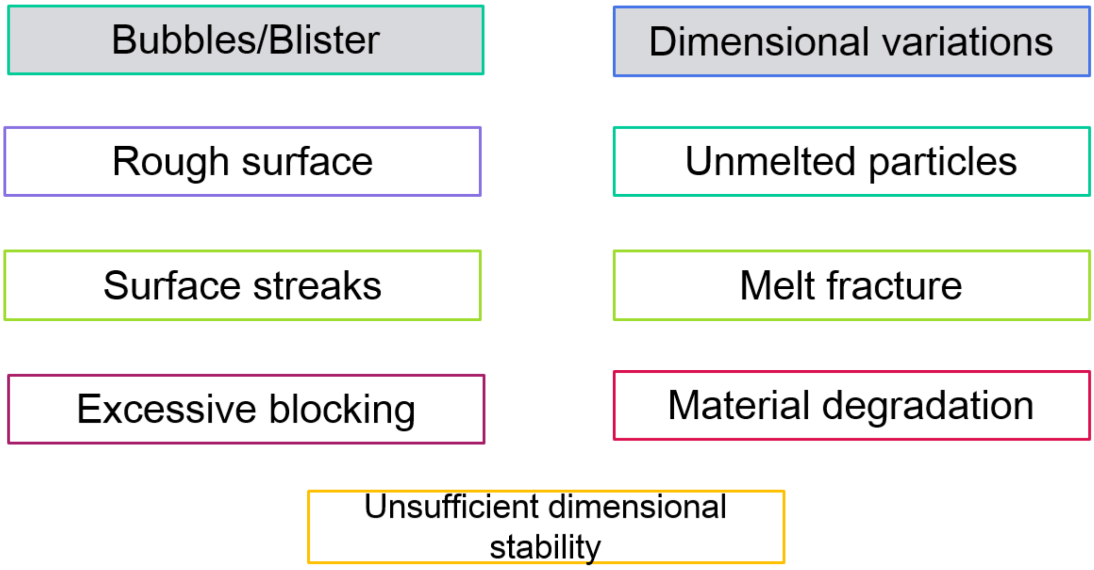


Figure 19. Typical problems in TPE extrusion. [13]

1.2.3. How to improve extrusion

In order to get rid of the extrusion problems a few things can be done.

Table 3. Tips to improve the extrusion of TPE. [13]

BUBBLES/BLISTER	DIMENSIONAL VARIATIONS
Reduce screw temperature	Remove moisture
Reduce die temperature	Variate: Die temperature Screw speed Homogenization
Increase screw speed	
Remove moisture	

1.3. 3D Printing-FDM

In Fused Deposition Modeling process, a plastic or wax material is extruded through a nozzle that traces the part of the cross-sectional geometry layer by layer. The build material is usually supplied in filament form. The nozzle contains resistive heaters that keep the plastic at a temperature just above its melting point so that it flows easily through the nozzle and forms the layer. The plastic hardens immediately after flowing from the nozzle and bonds to the layer below. Once a layer is built, the platform lowers, and the extrusion nozzle deposits another layer. [14]

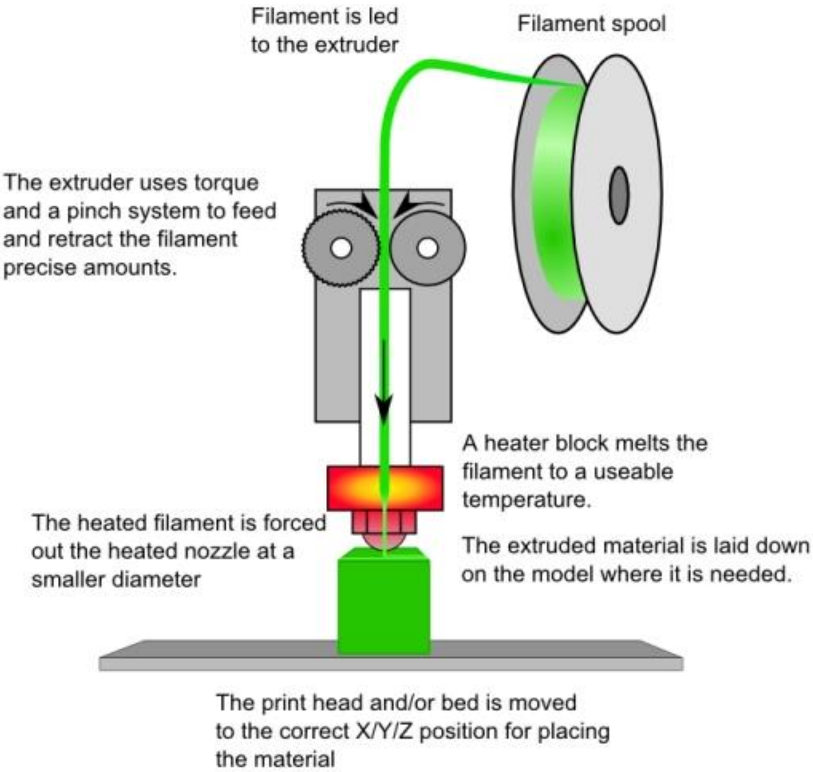


Figure 20. FDM Technology

1.3.1. Commercial TPE Filaments

In Table 4 are the principal commercial TPE filaments for FDM and its mechanical characteristics and in Table 5. TPE filament printing guidelines. Table 5 there are the printing parameters recommended by producers.

Table 4. TPE filaments

Brands	FilaFlex	NinjaFlex	TPC Flex	FlexiSMART	FlexiFil	Python Flex
Reference	[15]	[16]	[17]	[18]	[19] [20]	[21]
Material	TPU + additives.	TPU	COPE	TPU	COPE	TPU
Shore Hardness	70A, 82A, 95A	85A	45D	97A	45D	98A
Diameter (mm)	1.75 and 2.85	1.75 and 3	1.75 and 2.85	1.75 and 3	1.75 and 2.85	1.75 and 2.85
Elasticity (% Elongation)	700	660	530	600	530	450
Young modulus (MPa)	48	12	95	--	95	150
Traction resistance (Mpa)	54	26	--	--	24	50

Brands	PrimaSelect	Arnitel	Taulman	Tefablock	Tefablock	Tefablock
Reference	[22]					
Material	COPE	COPE	PCTPE	TPS-TPO	TPS-TPO	TPS-TPO
Shore Hardness	45 D	34 D	--	60A	70A	90A
Diameter (mm)	1.75 and 2.85	1.75 and 2.85	1.75 and 3	--	--	--
Elasticity (% Elongation)	530	350	497	440	250	340
Young modulus (MPa)	95	29	76	--	--	--
Traction resistance (Mpa)	24	8	35	3	3	3

Table 5. TPE filament printing guidelines.

Brands	FilaFlex	NinjaFlex	TPC Flex	FlexiSMART	FlexiFil
Reference	[15]	[16]	[17]	[18]	[19] [20]
Printing temperature (°C)	240–245	225–235	220-260	195-220	220-260
Print Speed (mm/s)	20	10-35	20	20-60	--
Heated bed (°C)	Not required	40	± 100	>18/ Not required	90-110

Brands	Python Flex	Arnitel	Taulman	Primaselect
Reference	[21]	[22]		
Printing temperature (°C)	220-250	240–250	220-230	220-260
Print Speed (mm/s)	--	20-50	--	--
Heated bed (°C)	--	30	30-60	90-100

1.3.2. Existing studies combining TP and TPE in the same piece

Regarding the bibliographical research, only one study has been found bout a 3D printed piece with both TP and TPE filaments. In that study, used multi-material FDM to print composites consisting of FilaFlex and PCL, in which outer shells of the structures are printed from FilaFlex (TPE) whereas their infills are printed from Polycaprolactone (TP). [1]

Moreover, two studies about a 3D printed pieces with compounded filaments were found. In the first study, ABS and SEBS pellets were mixed in different proportions and were put it in a twin screw extruder. [23] In the second study, TPU, PLA and Graphene Oxide were dissolved separately in dimethylformamide and then were been put in together and the result precipitate was extruded. [24]

No report is adapted to the review that is want to make in this research, so it is even more interesting to study.

1.4. Adhesion

Below are some adhesion tests that will be studied. It will be chosen among the test the most suitable to evaluate the adhesion between the thermoplastic elastomer and the thermoplastic (PLA for example).

Then, the chosen test or the chosen tests will be adapted to the conditions that are to be measured and determined.

1.4.1. Lap Shear Test

Two substrates are joint and pulled in opposing directions to provide shear loading as shown in the Figure 21. Normally there is an adhesive between the two substrates.

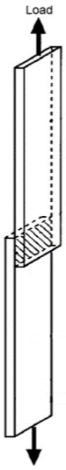


Figure 21. Lap shear test scheme. Adapted from

"Due to the increased use of adhesive-bonded plastics because of the inherent advantages afforded by bonded rather than mechanically fastened joints, particularly the alleviation of stress raisers and stress cracking, there is a need for standard tests by which joints of various plastic substrates and adhesives can be compared. This test method is intended to meet such a need". [25]

Equipment

Conforming to the requirements and having the capabilities of the machine in Practices E4 [26] with self-aligning grips capable of securely grasping the specimen throughout the test without allowing the specimen to slip. [27]

Specimen and procedure

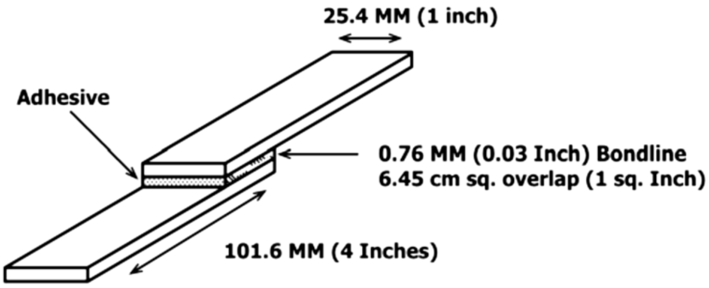


Figure 22. Dimensions of the specimen use in Lap shear test.

Height: 2.5 mm
Width: 25.4 mm
Length: 101.6 mm
Contact surface: 6.45 cm^2
[28]

It can be noted that in the ASTM Standard, adhesive between two substrates is considered; in that case, the height of the adhesive is 0.76 mm.

In ASTM D5868 the specimen loading rate is 13 mm/min (0.5 in/min) but a rate of 5 mm/min is reported in different works that use thermoplastic and thermoplastic elastomers as substrates [29] [30]

1.4.2. Peel test

This test method covers the determination of the comparative peel or stripping characteristics of adhesive bonds when tested on standard-sized specimens and under defined conditions of pre-treatment, temperature, and testing machine speed. [31]

It is this test that will determine the compatibility between the tape adhesive and the material (s).

There are different conditions of peeling:

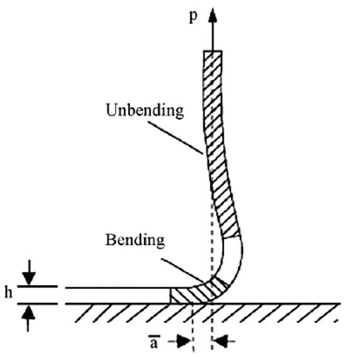


Figure 23. Schematic of 90° peel test. P, h and a represent the applied shear force, beam depth and beam length respectively

90° Peel: This test method consists of testing laminated or bonded adherends, where one adherend is rigid and the other adherend is flexible, by peeling of the flexible adherend from the rigid adherend at a 90-degree angle of peel. [32] [27]

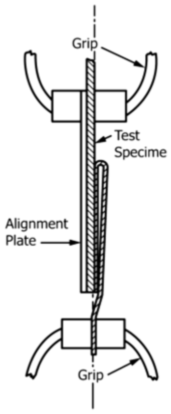


Figure 24. Schematic 180° Peel test

180° Peel: This test was commonly used to determine the adhesion strength of a tape to a substrate prior to the 90° peel test. [31]

T- Peeling: This test method gives a measure of a key property of hook and loop touch fasteners which is of interest to users of such devices. This is a means of determining the resistance to separation when forces are applied normal to the line of separation of the fastener. [33]

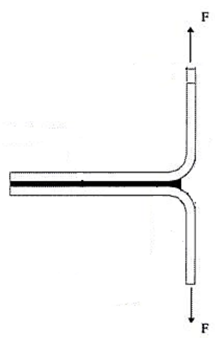


Figure 25. T Peel test scheme.

Equipment

90° Peel: It shall have the capability of constant Rate of Extension (CRE) with a crosshead speed range of 12 mm/min (0.5 in./min) to 250 mm/min (10 in./min). The testing machine shall have an adequate pen or computer response to record the force-extension curve. Self-aligning grips shall be used to hold the flexible adherent. The breaking load shall fall between 15 and 85 % of the full-scale load range. The grips need to engage the outer 25 mm (1 in.) of the flexible adherent firmly and, when load is applied, the direction of the applied force needs to be through the centre line of the grip assembly. [32]

180° Peel: A power-driven machine, with a constant rate-of-jaw separation or of the inclination balance or pendulum type, which fulfils the following requirements:

The applied tension as measured and recorded is accurate within 61 %. Hold specimens in the testing machine by grips which clamp firmly and prevent slipping always. The rate of travel of the power-actuated grip is 305mm (12 in)/min. This rate which provides a separation of 152 mm (6 in)/min is to be uniform throughout the tests. The machine is autographic giving a chart having the inches of separation as one axis and applied tension as the other axis of coordinates. The capacity of the machine is such that the maximum applied tension during test does not exceed 85 % nor be less than 15 % of the rated capacity. [31]

T- Peeling: A constant rate of extension (CRE) tensile tester shall be used. The tester shall have two clamps with centres in the same plane, parallel to the direction of the motion of the stressing clamp, and so aligned that they will hold the specimen ends wholly in the same plane; a means of moving the stressing clamp at a uniform rate of 12.0 ± 0.5 in./min (305 ± 13 mm/min), an autographic device for recording the load; and provided with an integrator if the integrator average is to be used. [33]

Specimen and procedure

90° Peel: Insert the test specimen into the peel test fixture with the unbonded end of the flexible adherend gripped in the test machine jaw. Peel the specimen at a constant crosshead speed of 254 mm/min (10 in/min). Other crosshead speeds may be used as required by a test specification or at a speed agreed upon by the manufacturer. If the backup plate bends or is distorted during the test, it is recommended that the specimen be redesigned with a backup member stiff enough to ensure even peel.

During the resistance-to-peel test, make an autographic recording of load versus head movement (load versus distance peeled).

Record the load over at least a 76 mm (3 in) separation length of the bond line or as agreed to by the adhesive manufacturer and the end user, disregarding the first 25 mm (1 in) of peel. [32]

180° Peel: Separate the free end of the 25-mm (1-in.) wide flexible member by hand from the other member for about 1 in. Place the specimen in the testing machine by clamping the free end of the 8-in. long member in one grip, turning back the free end of the flexible member and clamping it in the other grip as shown in Figure 24. Attach the separated end of the specimen, with all separate parts except the one under test securely gripped, to the recording head by means of a clamp using care to adjust it symmetrically in order that the tension is distributed uniformly. Maintain the specimen during the test approximately in the plane of the clamps. This may be done either by attaching the minimum weight required to the free end of the specimen or by holding the specimen against an alignment plate (Figure 24) attached to the stationary clamp. In either case, consider the added weight in determining the load causing separation. Grip the 1-in. wide flexible member symmetrically and firmly without twisting in the power-actuated clamp. Adjust the autographic mechanism and chart to zero and start the machine. Strip the separating member from the specimen approximately at an angle of 180° and continue the separation for a sufficient distance to indicate the peel or stripping value. Peel at least one half of the bonded area, even though a peel or stripping value may be indicated before this point.

T- Peeling: Hook and loop material for this test shall be in the width as supplied, not to exceed 1 in. (25.4 mm) in width. For materials greater than 1 in. (25.4 mm), a 1 in. (25.4 mm) specimen shall be slit from the centre of the sample. If material less than 1 in. (25.4 mm) wide is tested, test results will not be directly proportional to those obtained with the 1 in. (25.4 mm) wide material. Remove the outer layer of each roll before selecting the required number of strips, hook and loop, 8 in ± 1⁄4 in (203 ± 6 mm) long.

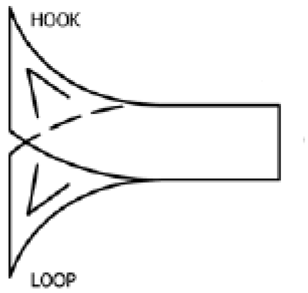


Figure 26 . T Peel test specimen

Use a clamp separation speed of 12.0 ± 0.5 in./min (305 ± 13 mm/min). [33]

1.4.3. Scratch test

The scratch test is closely related to the nanoindentation test, and for simplicity, the two will be considered together. In both cases adhesion is assessed using a fine tip that is dragged across the samples surface under an increasing load, resulting in an indentation. Indentation and scratch tests are well suited to the investigation of thin films and coatings, generally producing definitive results.

Nanoindentation has been used to investigate surface properties such as hardness and coating delamination force for polymers. Failure mechanisms for polymer systems have also used in scratch tests to explain surface condition. [27]

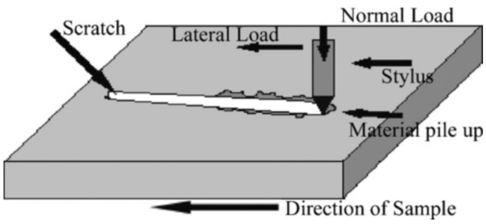


Figure 27. Scratch test

Equipment

Balanced Beam, Scrape Adhesion Tester consisting of a balanced beam to which is secured a platform for supporting weights, and a rod at an angle of 45° that holds the scraping loop. The rod shall be set so that the scraping loop contacts test surfaces directly below the weights. The loop shall be 1.6 mm (1⁄16 in) diameter rod, bent into a "U" shape with an outside radius of 3.25 ± 0.05 mm (0.128 ± 0.002 in.) and hardened to Rockwell HRC 56 to 58, and shall be a smooth finish. The loop can be either chromium plated, nickel plated, or heat treated polished steel, as agreed upon between the purchaser and the supplier. These testers are adjustable to accommodate flat, metallic, and non-metallic specimens to 12 mm (0.5 in.) thick and 100 to 400 mm (4 to 16 in.) wide and long.

Specimen and procedure

The specimen should be at least 12 mm (1/2 in) wide.

Condition the test panels for at least 48 h at 23 ± 2°C and 50 ± 5 % relative humidity, and test in the same environment, or immediately on removal there from, unless otherwise specified or agreed by the seller and the purchaser. Test at least two replicate specimens of each material.

Carefully lower the beam until the loop rests on the uncoated portion of the test specimen and the full load is applied, then slowly (1 to 2 s/in.) push the sliding platform away from the operator for a distance of at least 75 mm (3 in.). If the coating is removed, continue the testing, using successively smaller loads (0.5-kg increments) until the coating is not removed. If the coating is not removed by the initial scrape, continue the testing, using successively larger loads (0.5-kg increments) until the coating is removed or until the maximum load of 10 kg has been applied.

1.4.4. Probe track

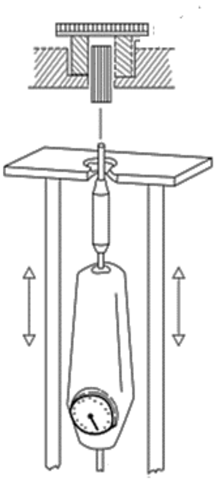


Figure 28. Sample Position in Probe Tack Apparatus

The Probe Tack is used for the measurement of the pressure sensitive tack of adhesives. Tack is typically measured as the force required to separate an adhesive and the adherent shortly after having been brought into contact under a defined load of known duration at a specified temperature. [34]

Equipment

A mechanical system for bringing the adhesive into contact with the probe, automatically controlling the dwell time during which the adhesive and probe are in contact under pressure, and subsequently pulling the adhesive away from the probe. The machine is calibrated in compliance with Practices E4 requirements.

Specimen and procedure

The recommended dry adhesive thickness is 0.025 mm. Adhesives already on some supporting material are examined as they exist.

The specimen of supported adhesive should be place, sticky side down, on the annular ring weight and width should be a specimen large enough to cover the hole in the weight without slippage during the test and small enough so that it does not adhere to the carrier supporting the weight.

At a speed of 10 mm/s, bring the probe into contact with the adhesive. After a dwell time of 1.0 s separate the probe from the adhesive at 10 mm/s.

Record the tack as the maximum force in newtons required to separate the probe from the adhesive. [35]

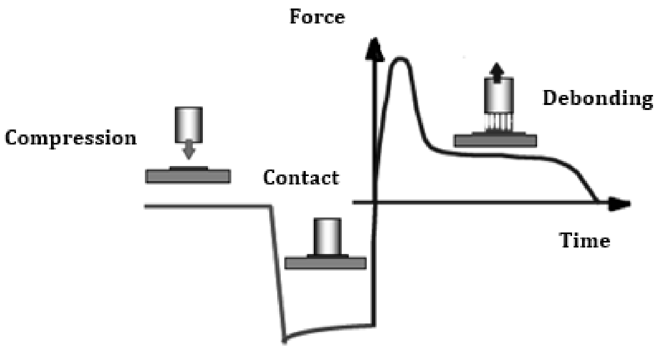


Figure 29. Schematic diagram of a probe-tack

1.4.5. Pull-off

This test method covers a procedure for evaluating the pull-off strength (adhesion) of a coating system from metal substrates. [36]

This test method consists in exerting a tensile force in the direction perpendicular to the bonding surface and opposite to bonding. [37]

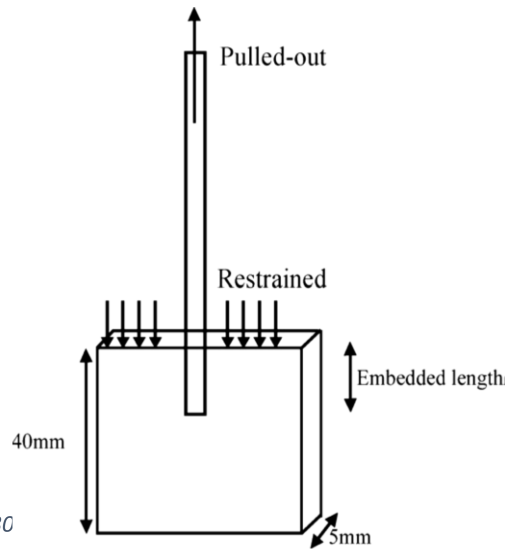


Figure 30

Equipment

This is a fixed-alignment portable tester. The tester is comprised of detachable aluminium loading fixtures having a flat conic base that is 20 mm in diameter on one end for securing to the coating, and a circular T-bolt head on the other end, a central grip for engaging the loading fixture that is forced away from a tripod base by the interaction of a hand wheel (or nut), and a coaxial bolt connected through a series of Belleville washers, or springs in later models, that acts as both a torsion relief and a spring that displaces a dragging indicator with respect to a scale.

Specimen and procedure

The force is indicated by measuring the maximum spring displacement when loaded. Care should be taken to see that substrate bending does not influence its final position or the actual force delivered by the spring arrangement.

The adherend samples must be thin, as a sufficient thickness of adhesive is required around the embedded sample. As the thickness of the adhesive increases, preparation of the adhesive block becomes more difficult. In general, there is a high degree of scatter with inelastic behaviour occurring at the point of interface failure. Also, shear stress at the interface does not seem to correlate with failure. Intense stress concentrations occur near the exit point of the shim (stress near the exit of the adherend is ~3 times the stress along the centre of the adherend. The extensive inelastic deformation of the adherend and the resulting complexity of the interfacial stress distribution lead to problems in the interpretation of results from this test.

2. MATERIALS AND METHODS

2.1. Extrusion

2.1.1. Equipment

A twin-screw extruder equipped with a single-screw volumetric feeder was used for all experiments. The extruder was equipped with eight controllable temperature zones (including the die zone).

The first extruder used is Thermo Scientific Pharma 11 by Thermo Fisher Scientific. In the Table 6 there are the characteristic of the extruder used which can be seen in the Figure 31. It will be identified as "small extruder".

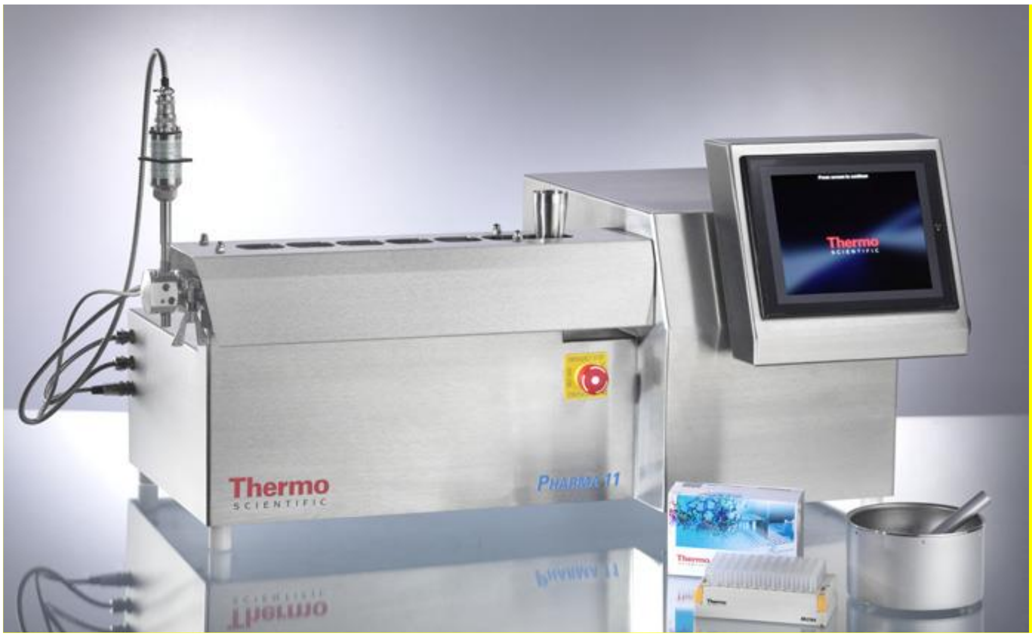


Figure 31. First extruder used. Extruder 1

Table 6. Extruder Technical Data [38]

Speed	Variable speed drive system (10 to 1000 rpm)
Temperature	10°C to 280°C
Heating zones	7 x 5 L/D heat/cool zones, +1 heating zone for die
Feed zone	Permanent liquid cooled feeding port
Die	Rod die 2 mm, Optional exchangeable die nozzles
Torque	6 Nm per shaft, constant torque, safety monitored
Pressure	100 bar, safety monitored
Power supply	230 V single phase, 16 Amps
Size (L x W x H)	90 x 50 x 41 cm
Weight	55 kg
Material	Pharma grade stainless steel

The second extruder used is HAAKE Rheomex PTW 24 OS by Thermo Fisher Scientific. In the Figure 32 there are the characteristic of the extruder used which can be seen in the Table 7. It will be identified as “big extruder”.

Figure 32. Second extruder used. Extruder 2

Table 7. Extruder Technical Data [39]

Speed	Variable
Temperature	Max. 350°C (opt. 400/450°C)
Heating zones	10
Feed zone	Cooled
Die	-
Torque	Max. speed 180 Nm
Pressure	100 bar
Power supply	230V +/-10 % ; 50 - 60Hz
Size (L x W x H)	57x 113 x 720 cm
Weight	165 kg
Material	-

2.1.2. Procedure

The raw plastic pellets are gravity-fed from the hopper into the twin-screw. Inside the pipe the molten plastic is forced through a die at the end of the pipe to form a filament. Before starting, the feed flow rate, screw speed, the temperature in each extruder zone and the temperature in the die zone were adjusted. The basic mechanism is comprised of a twin-screw that transports raw plastic pellets from a hopper through a heating zone in a metal pipe where the plastic is melted. The extruded plastic can be drawn from the die to determine the final diameter of the filament. The extruder profiles can be chosen and the mixing zones can be increased or decreased. The die is shaped to form the extruded plastic into the desired cross-section.

2.1.3. Materials

It has been chosen to print TPU for this study because its good printing properties are known by FDM, as can be seen in several studies and in the wide range of commercial flexible filaments. In addition, the TPUs are chosen for this project due to its compatibility with the PLA thermoplastic. Several studies independently indicated that thermoplastic polyurethane (TPU) showed good compatibility with PLA because of its hydrogen bonding. [40] [41] [42] [43]

Lactic acid is made by converting sugar or starch obtained from vegetable sources using a fermentation process. There are four unique groups attached to the central carbon atom; lactic acid is a chiral molecule.

PLA is fairly rigid material that shows little to none elastic behavior, and its inherent brittleness and low toughness restricts its application in which good flexible properties are required. [44] [45]

TPU is a linear segmented block copolymer derived from the reaction of diisocyanates, oligomeric diols, and low molecular weight diols (called chain extenders). TPU morphology can be visualized as a coherent soft segments (SS) matrix with a dispersed phase of separated hard segment (HS) domains. At room temperature, low Tg SS sequences are quite mobile and mostly they present in an amorphous conformation. In contrast, high Tm HS sequences are quite polar and fixed by intermolecular bonding. Consequently, HS domains act as fillers as well as ‘‘physical crosslinks’’ for the soft segment matrix, giving high elasticity and strength to the resulting TPU. They are tough, biocompatible, and hemocompatible. They can be strong elastomer or rigid plastic, and they can be processed by using extrusion, injection molding, film blowing, solution dipping, and two-part liquid molding. [46] [47] Polyurethanes can be used in certain conditions where other materials do not work. Polyurethane is one of the most versatile construction materials that can be formulated.

The TPU which have been considered for this project are the following. Actually, there have been already tried to extrude Pellethane 2102-65D, Tecoflex EG-100A and Pellethane 2102-90A, which can be seen in Table 8.

Table 8. TPE considered

	Pellethane		**Tecoflex**	**Isothane**	**Desmopan**
	[48]		[49]		[50]
Brand	DOW		LUBRIZOL	GRECO	BAYER
Type	TPU		TPU	TPU	TPU
Reference	2102-65D	2102-90A	EG-100A	3080A	3695AU
Shore Hardness	65D	94A	94A	80A	96A
Melt temperature (°C)	210-221	204-221	176-194	--	215-235
Elasticity (% Elongation)	390	440	370	620	400
Traction resistance (Mpa)	44.1	44.8	56	34	59

The commercial TPU pellets are shown in Figure 33, Figure 34 and Figure 35

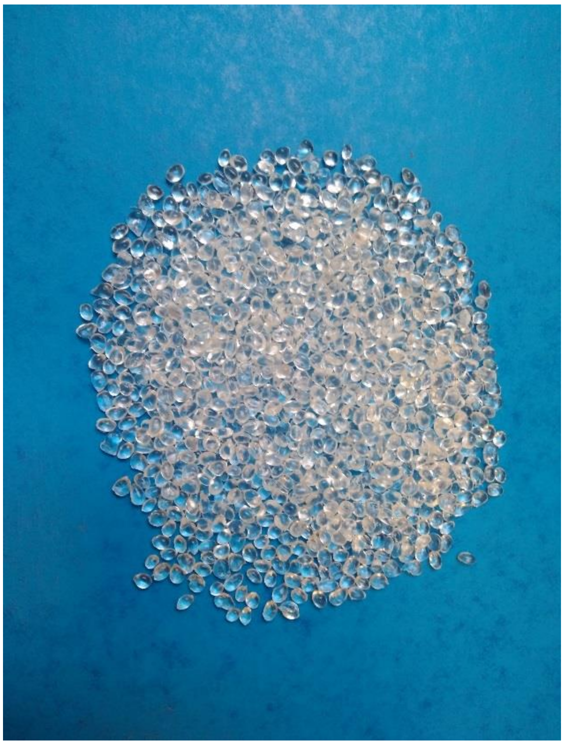


Figure 33. Pellehane 2102-90A by DOW

Figure 34. Pellehane 2102-65D by DOW

Figure 35. Tecoflex EG-100A by LUBRIZOL

2.2. 3D Printing

2.2.1. Equipment

The printer used is the Mondrian 3.0 which is an open source, RepRap style printer. In the Table 9 there are the characteristic of the 3D printer used which can be seen in the Figure 36.

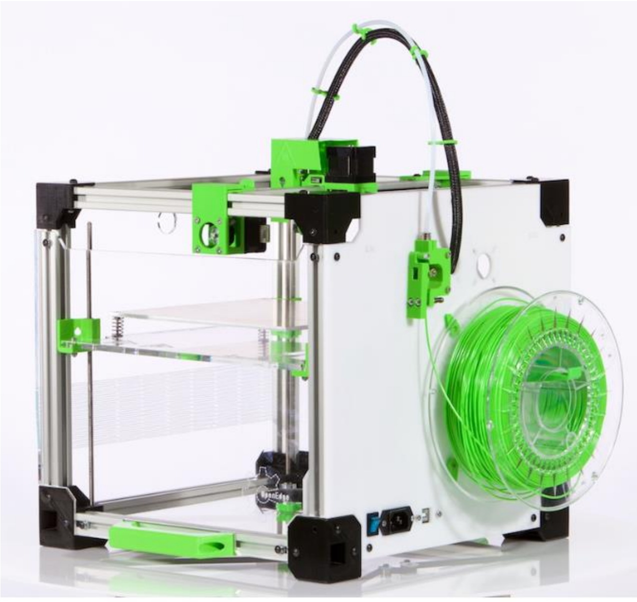


Figure 36. 3D printer used

Table 9. 3D Printer description [51]

Device	
Type	RepRap – replicating rapid prototype (partially built with 3D-printed parts)
Technique	FFF – fused filament fabrication
Heating bed	
Printing parameters	
Filament	Ø 1.75 mm
Nozzle	Ø 0.5 mm
Speed	between 10 and 60 mm/sec.
Positioning precision	XY = 0.0125 mm | Z = 0.00025 mm
Object resolution	+/- 0.05 mm
Layer height	high = 0.30 mm | medium = 0.20 mm | low = 0.10 mm
Heating temperatures	
Bed	≤ 85 °C
Head	≤ 260 °C

The software that is used for the design is **Slic3r** (version 1.2.9), which convert a digital 3D model into printing instructions for the 3D printer and the software with which the pieces are printed is **Printrun** 1.6.0.

2.2.2. Procedure

Se introduce el filamento que ha sido extruido anteriormente y se elige la pieza a imprimir. Extruder temperature, bed temperature and print speed were adjusted. The bed should be calibrated to be straight.

2.3. Adhesion

A tensile machine is available for the adhesion measure test. Considering this limitation and the materials that will be used, the different test presented previously were evaluated.

Scratch test was discarded because of the necessary equipment for its implementation. Pull off and probe task test are not applicable for the kind of material that is going to be use. Peel test can be applicated considering the material, but there are complications when using the machine due to certain parameters that can't be controlled properly and could produce wrong results. In lap shear test case, the machine is adequate, and the test could be executed.

The result obtained by the test would be the bond strength between, in this case, a thermoplastic (PLA) and a thermoplastic elastomer (TPU); so, to know how strong the bond is, it is appropriate to compare other polymers whose adhesion is considered good under the same conditions (including PLA-PLA union).

As shown in the Figure 37, there are defined geometry for the specimen that should be used in this method, however, the specimen that will be used in this work has a slight difference, there is not an adhesive between the substrates. Adapted from [28].

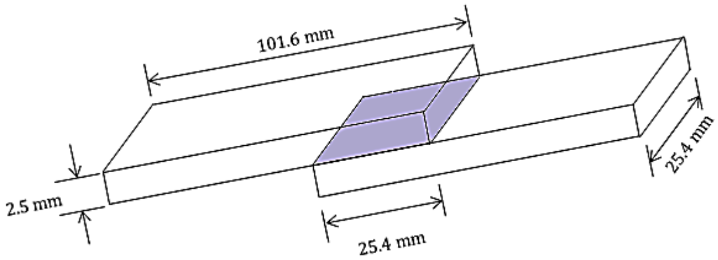


Figure 37. Geometry and dimension of the proposed specimen for Lap shear test.

Standard ASTM 5868 [28] recommends a speed of 13 mm/min for the test, but different adhesion measure studies between polymers [29] [30] recommends 5 mm/min.

Is recommended to evaluate 5 specimens to have a more accurate value.

The report of the results must be presented at least with the following information:

- Complete identification of the substrates used and method of surface preparation to bonding them.
- Individual peak load values, psi (kPa) and averages by maximum and minimum values.
- Test temperature and conditions.
- Type of failure observed.

3. RESULTS

3.1. Extrusion

It has been possible to make the filament with Pellethane of two different hardnesses, but the Tecoflex has not yet been possible to extrude it.

Flow rate determination for the small extruder

Three trials were made at each opening % of the extruder power supply in periods of one minute. The amount of pellet was collected, and it was weighed, thereby obtaining the flow rate for each % of the extruder en g/min. It can be seen in ANNEX A. Flow rate determination.

3.1.1. Tecoflex EG100A extrusion trial

Table 10. Tecoflex extrusion trials

T100A	Drying	Screw temperature (°C)	Die temperature (°C)	Screw speed (RPM)	Torque (%)	Flow rate (g/min)
E1T100A-Small extruder	No	200	200	70	40	11.73
	No	200	200	70	51	2.10
E2T100A-Small extruder	3h/90°C	180	180	70	82	4.07

In the first trial it was extruded Tecoflex by LUBRIZOL which hardness are 94A in the small extruder. It did not succeed. There were many bubbles and low consistency.

For the next trial with Tecoflex, which was dried, there was use a vacuum pump in zone 5 and there was use the screw profile in which there have just one mixing zone. The results were that there were less bubbles, but the diameter was irregular and there was a low consistency.

3.1.2. Pellethane 2102-65D extrusion trial

In this try Pellethane 2102-65D by DOW was extruded. The conditions of the best extrusion are shown in the table Table 11.

E1P65D-Small extruder

Table 11. Better extrusion conditions-E1P65D

EXTRUSION CONDITIONS	
Screw temperature (°C)	210
Die temperature (°C)	205
Screw speed (RPM)	90
Flow rate (g/min)	9.2

There are observing in the Figure 38 and Figure 39 that the filaments have two important defects. First the whole filament doesn't have the same diameter and second, there are bubbles inside it.

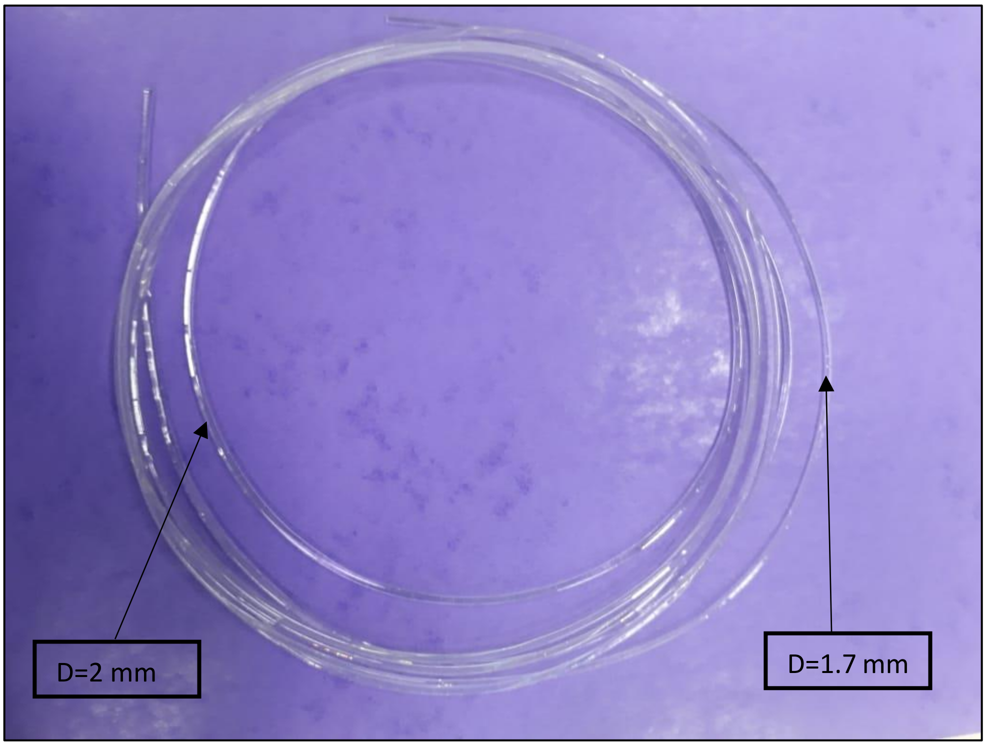


Figure 38. Pellethane 2102-65D filament (E1P65D)

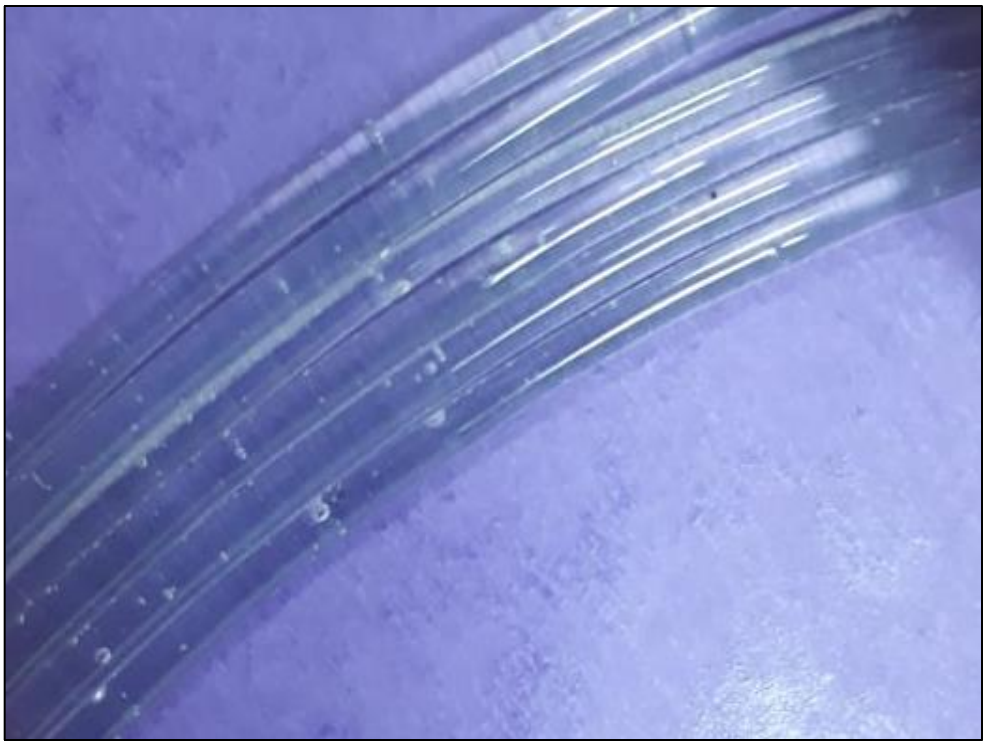


Figure 39. Detail of the Pellethane 2102-65D filament (E1P65D)

E2P65D-Small extruder

Then, a second extrusion *trial* was made, the result of which was worse. These can be seen in the Table 12. *So,* the changes that could be made to improve the results were considered.

Table 12. E2P65D trial

E2P65D	Drying	Screw temperature (°C)	Die temperature (°C)	Screw speed (RPM)	Flow rate (g/min)	Torque (%)	Observations
1	No	200	200	70	4.8	90	Many bubbles
2		200	200	70	4.8	40	
3		200	200	50	3.4	67	
4		200	200	70	5.8	90	
5		200	200	70	6.9	66	
6		200	200	70	4.8	86	Less bubbles
7		200	200	70	6.9	90	Diameter too small
8		**200**	**200**	**70**	**6.9**	**90**	
			Change of die to a bigger one.				
9		210	200	70	6.9	90	Worst
10		210	190	150	8.1	90	
11		200	190	150	8.1	90	
12		200	190	50	8.1	90	

How to improve the extrusion?

To improve the extrusion, a series of viable solutions were considered and implemented, which can be observed in the Figure 40.

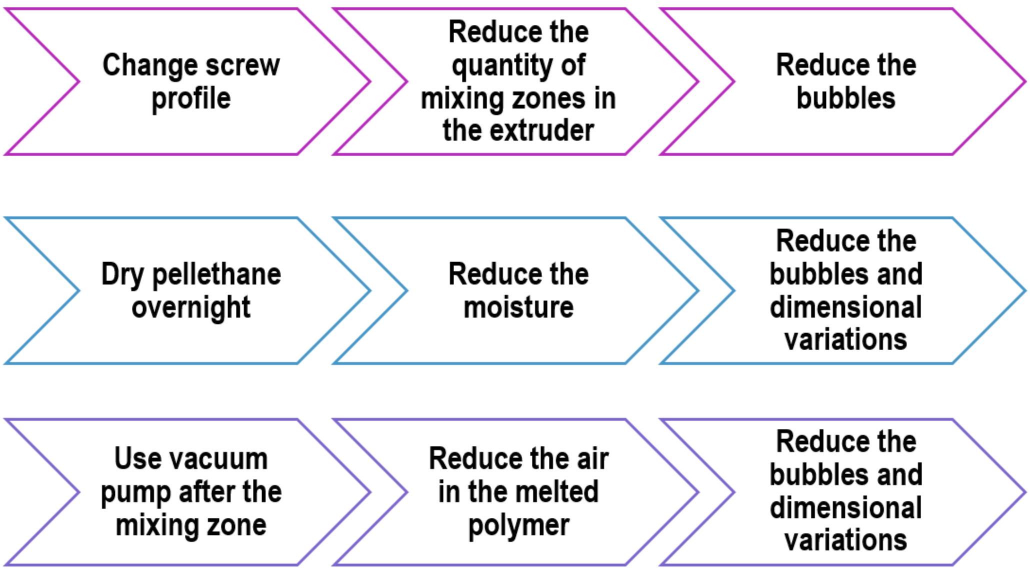


Figure 40. Improvements implemented.

E3P65D-Small extruder

For the third extrusion of Pellethane 2102-65D the large extruder was used, but the results were not satisfactory either.

Table 13. E3P65D trial

E3P65D	Drying	Screw temperature (°C)	Die temperature (°C)	n (1/min)	P (bar)	Screw speed (RPM)	Torque (%)	Flow rate (g/min)	Observations
1	90°C	200	200	45	21	70	130	13	
2		200	200	45	21	50	120	13	
3		200	200	100	21	50	109	13	
4		200	200	150	15	50	81	13	
5		200	200	100	9.13	50	68.5	13	
6		200	200	75	12.3	70	85.2	13	
7		200	200	100	7	70	83.7	13	
8		200	200	80	13.3	70	98	13	
9		**200**	**200**	**80**	**15.5**	**60**	**99**	**13**	**Diameter too small**
10		**200**	**205**	**80**	**13.2**	**70**	**102**	**13**	**Diameter too small**
11		205	200	90	20	70	90	13	
12		195	195	110	9.8	70	78	13	Bubbles
13		205	200	115	5.6	100	42.7	13	
14		205	205	60	13	70	91	13	

The filament obtained in both attempts 9 and 10 had very good conditions, but the diameter was too thick.

3.1.3. Pellethane 2102-90A extrusion trial

E1P90A-Small extruder

The Pellethane 2102-90A by DOW was extruded, which has a hardness of 94A. The Pellethane was not dried before extrusion. It was use the small extruser with the improvements applied.

There was use a vacuum pump in zone 5 and there was use the screw profile in which there have just one mixing zone. The results were better than Tecoflex and Pellethane 65D, because of there were less bubbles and the better dimensional stability.

Table 14. Better extrusion conditions E1P90A

EXTRUSION CONDITIONS	
Screw temperature (°C)	**200**
Die temperature (°C)	**190**
Screw speed (RPM)	**110**
Flow rate (g/min)	**5**

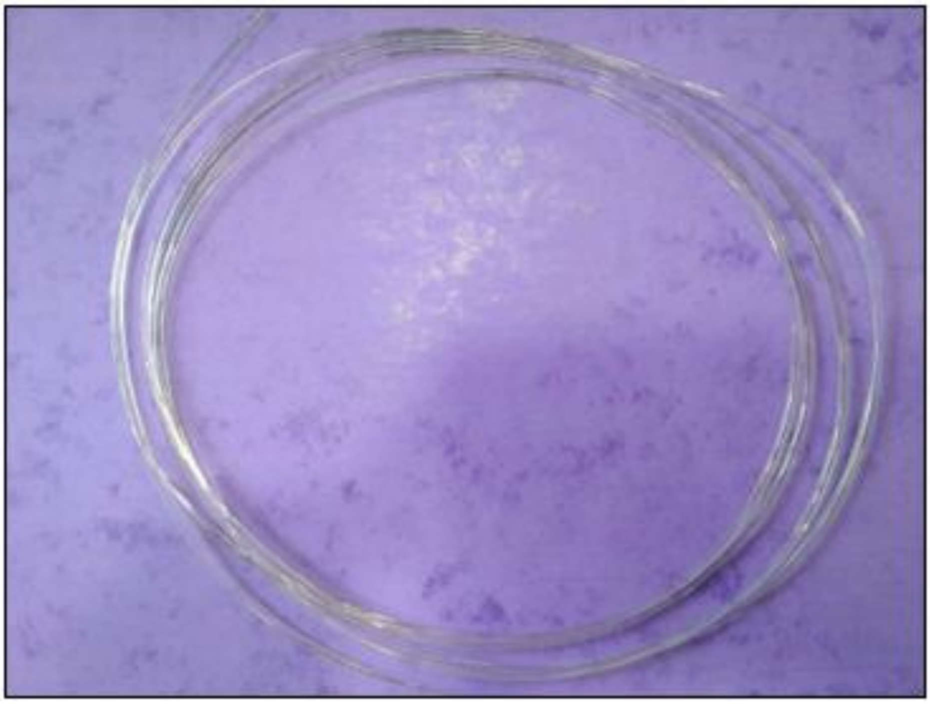


Figure 41. Pellethane 2102-90A filament (E1P90A)

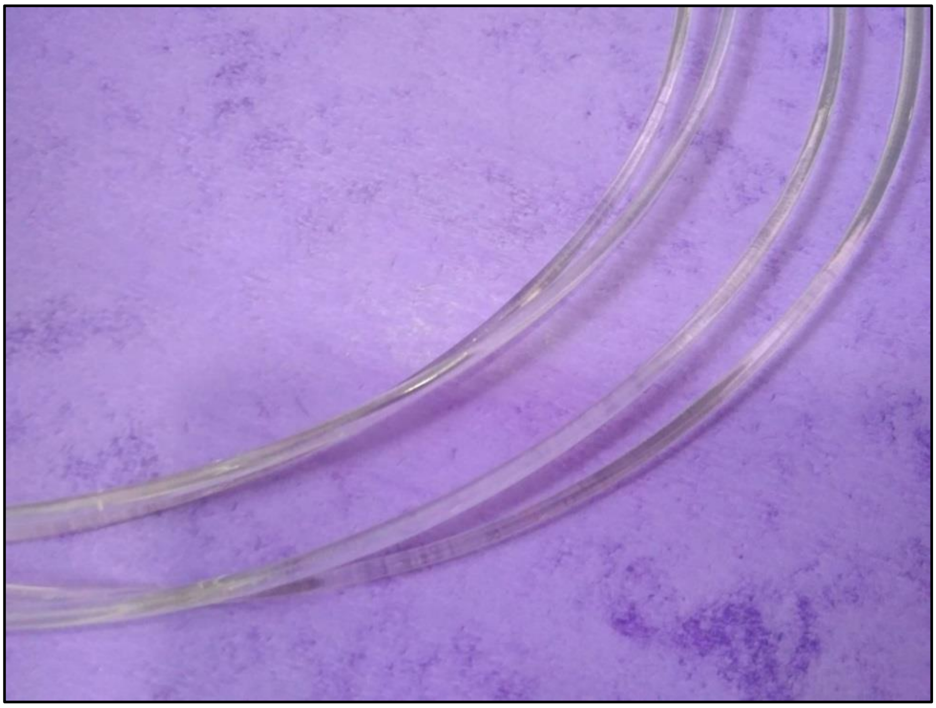


Figure 42. Detail of the Pellethane 2102-90A filament (E1P90A)

E2P90A-Big extruder

For the second extrusion of Pellethane 2102-90A the big extruder was used. The extrusion conditions can be observed in Table 15 and the result in Figure 43 and Figure 44.

Table 15. E2P90A

E2P90A	Drying	Screw temperature (°C)	Die temperature (°C)	n (1/min)	P (bar)	Flow rate (g/min)	Observations
1	90°C	190	190	100	-	-	Diameter too thick.
2				70	-	-	Diameter too thick.
3				50	-	-	Diameter too thick.
4				**45**	**15**	**13**	**OK**

Figure 43. Pellethane 2102-90A filament (E2P90A)

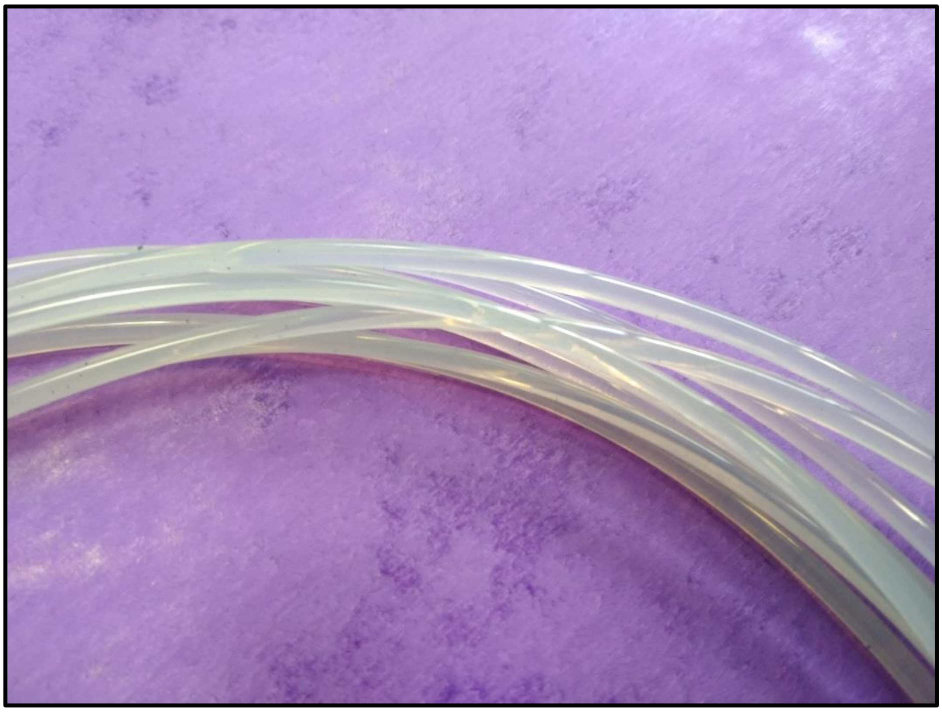


Figure 44. Detail of the Pellethane 2102-90A filament (E2P90A)

In the filament there is no presence of bubbles, but irregularities in the filament dimensions can be observed, probably due to the picking up of the filament in the coil.

The printer stops printing because the dimensions of the filament are too irregular.

3.2. 3D Printing

3.2.1. FMD trial of extruded Pellethane 2102-65D (E1P65D)

In the Figure 45 can be observed the first 3D printed piece with the extruded Pellethane 2102-65D filaments. The printing conditions can be seen in the

Table 16.

Table 16. Printed conditions

PRINTING CONDITIONS	
Head temperature (°C)	**195**
Bed temperature (°C)	**65**
Print speed (mm/min)	**30**

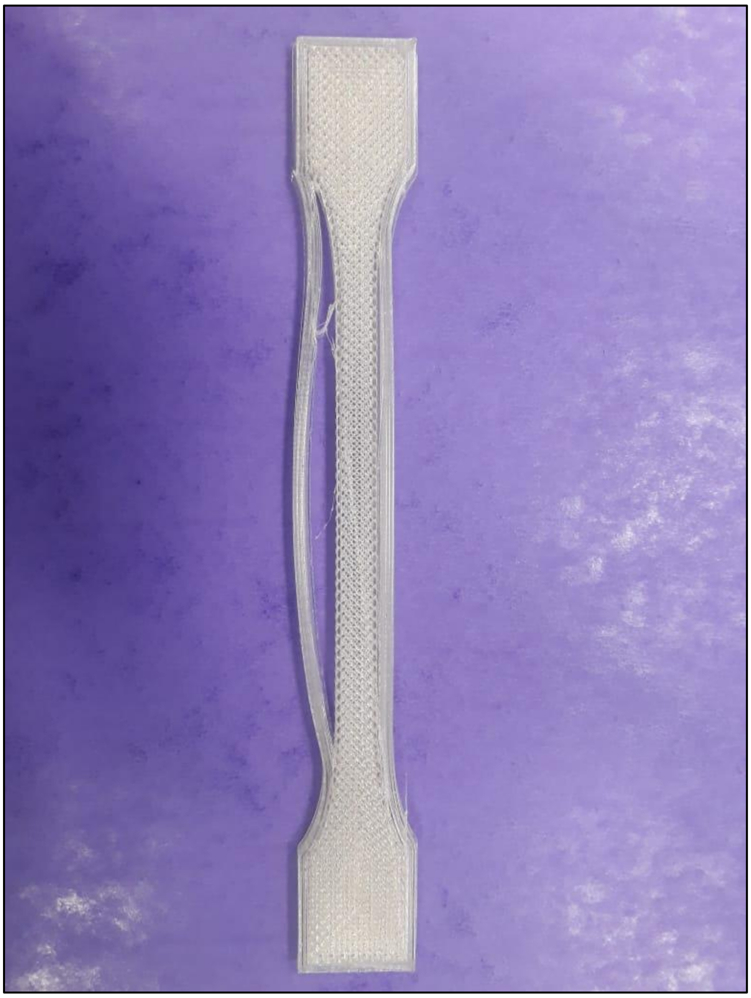


Figure 45. 3D printed piece with the extruded Pellethane 2102-65D filaments

3.2.2. FMD trial of extruded Pellethane 2102-90A (E1P90A)

First trial E1P90A

In the Figure 46 can be observed the first 3D printed piece with the extruded Pellethane 2102-90A filaments with the conditions observed in the

Table 17.

Table 17. Printed conditions

PRINTING CONDITIONS	
Head temperature (°C)	**200**
Bed temperature (°C)	**100**
Print speed (mm/min)	**12**
Print speed (%)	**62**
Print set (%)	**162**

Figure 46. First 3D printed piece with the extruded Pellethane 2102-90A filaments

Second trial E1P90A

The second 3D printed piece with this material can be observed in Figure 47. It was extruder with the conditions observed in the Table 18.

Table 18. Printed conditions

PRINTING CONDITIONS	
Head temperature (°C)	**200**
Bed temperature (°C)	**90**
Print speed (mm/min)	**12**
Print speed (%)	**40**
Print set (%)	**100**

Figure 47. Second 3D printed piece with the extruded Pellethane 2102-90A filaments

Printing with this filament gives many problems due to the flexibility of the filament, which becomes entangled before reaching the extruder of the printer. There was a moment in which the polymer wasn't going out of the head.

Third trial E1P90A

The third 3D printed piece with this material can be observed in Figure 48. It was extruder with the conditions observed in the Table 19.

Table 19. Printed conditions

PRINTING CONDITIONS	
Head temperature (°C)	**200**
Bed temperature (°C)	**80**
Print speed (mm/min)	**12**
Print speed (%)	**50**
Print set (%)	**50**

Figure 48. Third 3D printed piece with the extruded Pellethane 2102-90A filaments

Fourth trial E1P90A

The fourth 3D printed piece with this material can be observed in Figure 49. It was extruder with the conditions observed in the Table 20.

Table 20. Printed conditions

PRINTING CONDITIONS	
Head temperature (°C)	**200**
Bed temperature (°C)	**90**
Print speed (mm/min)	**12**
Print speed (%)	**50**
Print set (%)	**60**

Figure 49. Fourth 3D printed piece with the extruded Pellethane 2102-90A filaments

Fifth trial E1P90A

The fifth 3D printed piece with this material can be observed in Figure 50Figure 48. It was extruder with the conditions observed in the Table 21.

Table 21. Printed conditions

PRINTING CONDITIONS	
Head temperature (°C)	**200**
Bed temperature (°C)	**90**
Print speed (mm/min)	**12**
Print speed (%)	**40**
Print set (%)	**60**

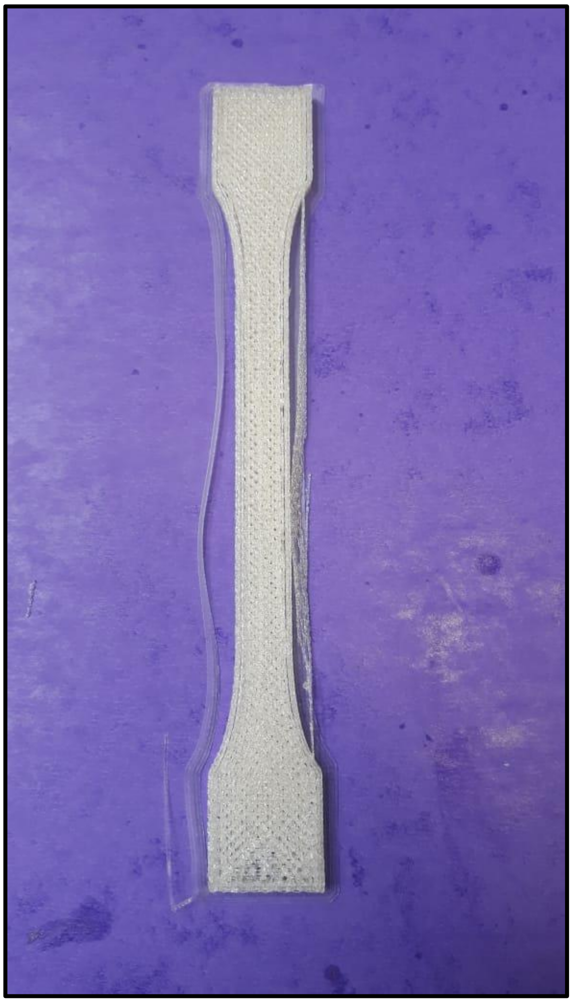


Figure 50. Fifth 3D printed piece with the extruded Pellethane 2102-90A filaments

The best impression so far of Pellethane 2102-90A has been the fifth.

4. CONCLUSION PROSPECTS

The filament with the best conditions so far has been the one that has been extruded with Pellethane 2102-90A by DOW, which has a hardness of 94A: E1P90A-Small extruder.

Regarding 3D printing the printing piece with best conditions so far has been the one that has been printed with Pellethane 2102-65D by LUBRIZOL, which has a hardness of 65D and it printed with a filament extruded (E1P65D) in the small extruder.

The following steps to perform are listed below:

- Choose a definitive TPE: The material with which the best conditions are obtained in the sum of the extrusion, the impression and the adhesion with the thermoplastic.
- Improve the extrusion conditions of this TPE: an extrusion without bubbles has already been achieved. It is necessary to extrude a filament with homogeneous dimensions along the entire filament, improving for this the system of collecting in the coil.
- Improve the 3D printing conditions of the TPE filament
- Design the evaluation test of adhesion: it is appropriate to compare other polymers whose adhesion is considered good under the same conditions.
- Improve adhesion between the thermoplastic elastomer and the thermoplastic.

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ANNEXES

ANNEX A. Flow rate determination

The determination of the flow for the Pellethane is shown, but the same was done with the rest of the materials.

The Table 22 shows the results of weigh the samples and the average of the three trials, for each opening%. In the graphs that are observed in the Figure 51 and Figure 52 it is observed how linear approximation can be done with great accuracy. With the obtained equation, we can calculate the flow rate in g / min for each opening% that is read in the extruder.

Table 22. Pellet weight for each%.

% FEEDER	1	2	3	AVERAGE
0	0	0	0	0
1	1,3	1,3	1,1	1,2
2	1,9	2,5	3,0	2,5
3	3,4	3,5	3,4	3,4
4	4,8	4,5	5,1	4,8
5	6,0	5,5	5,9	5,8
6	7,3	6,5	7,0	6,9
7	8,1	8,5	7,8	8,1
8	8,8	9,5	9,2	9,2
9	10,6	10,2	9,7	10,2
10	11,9	11,1	11,5	11,5
11	11,3	11,5	12,0	11,6
12	12,9	11,8	12,7	12,5
13	13,1	14,2	13,5	13,6
14	14,5	14,8	15,0	14,8
15	17,6	16,8	16,1	16,8
20	22,1	21,8	21,4	21,8
30	32,6	31,5	29,5	31,2
40	41,6	40,5	40,6	40,9
50	52,3	50,5	49,0	50,6
60	59,4	58,8	56,4	58,2
70	66,9	68,9	66,4	67,4
80	76,2	77,0	76,3	76,5
90	86,0	86,4	84,8	85,7
100	95,3	92,4	92,1	93,3

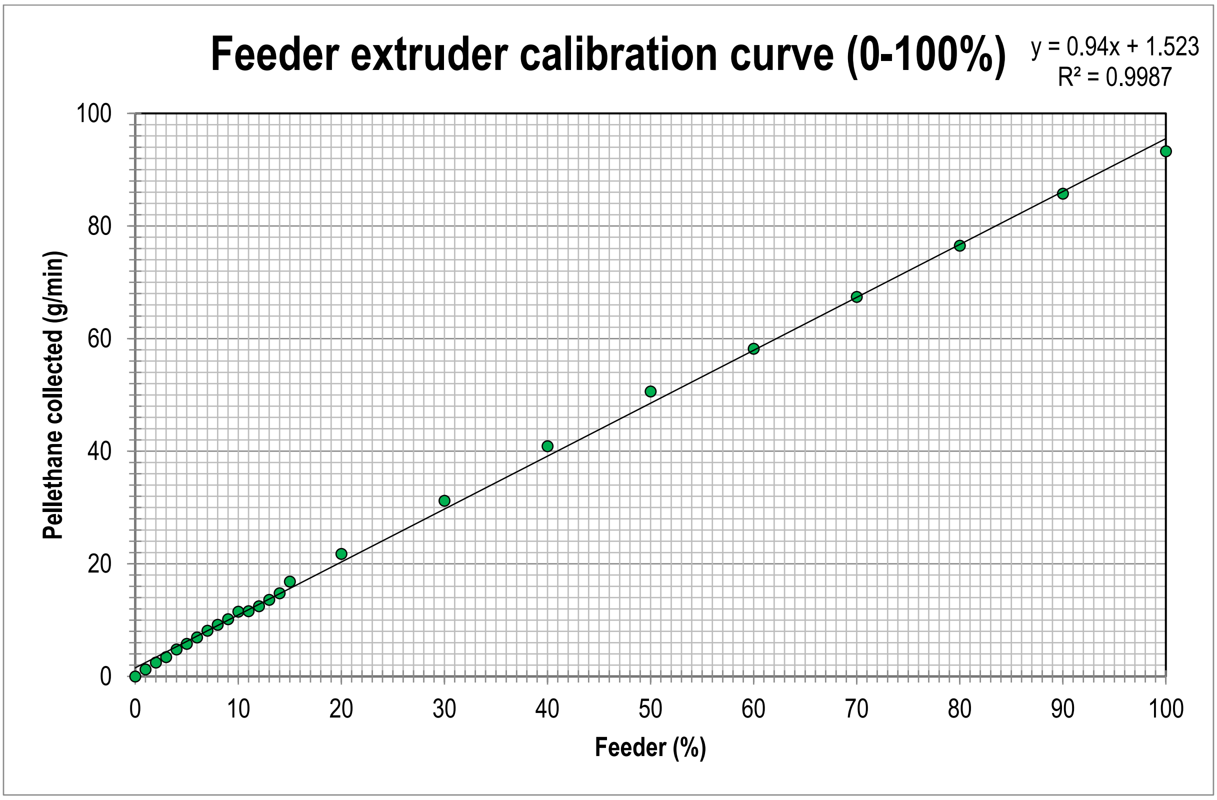

Figure 51. Pellet weight for each% 1-100

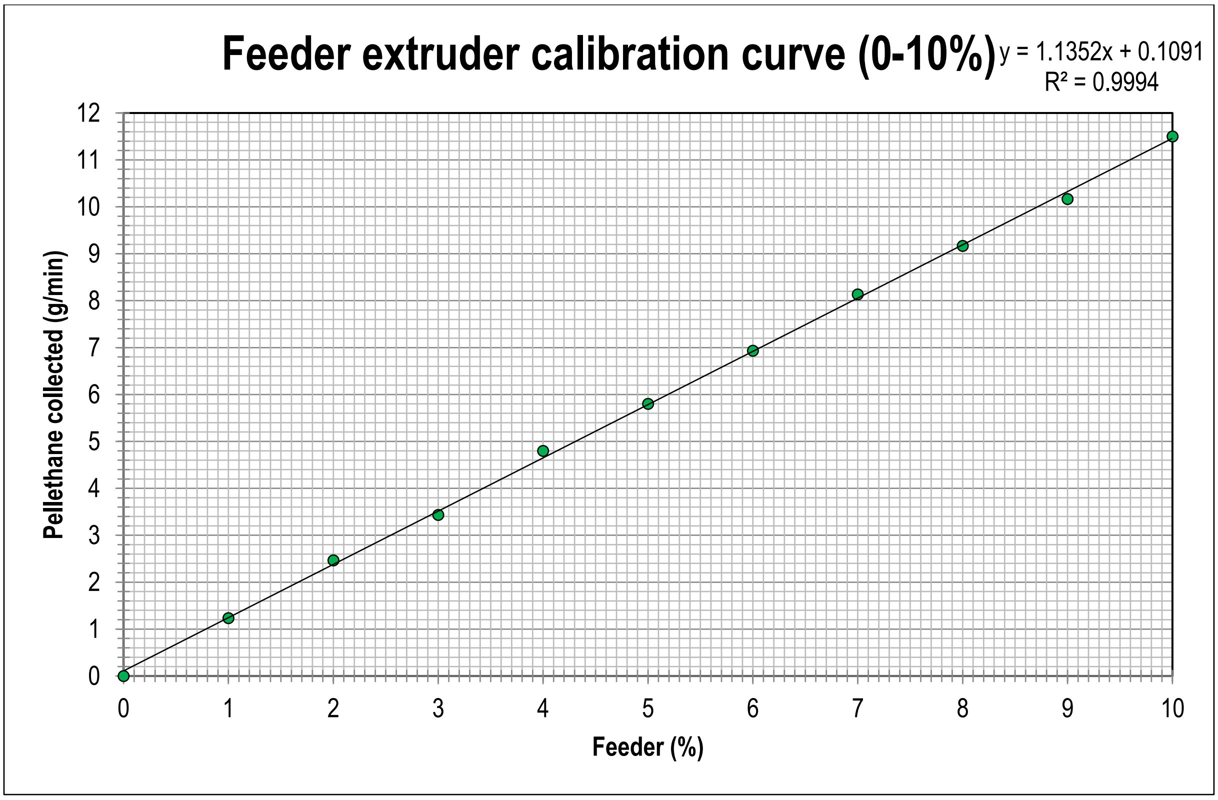

Figure 52. Pellet weight for each% 1-10