Suitability of recycled PP for 3D printing filament

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Abstract: This thesis investigates the possibility of manufacturing 3D printer filament from CIRCO® recycled polypropylene (rPP), provided by Fortum Waste Solutions Oy. Nowadays, ABS and PLA are two dominant thermoplastics used in filament form for 3D printing. The literature study therefore focuses on finding out why PP, being one of the most used plastics in the world with a multitude of appreciated properties and consequently applications, has not yet landed in 3D printing. The empirical part of the work is primarily aimed at finding out the feasibility of producing a good quality rPP filament suitable for 3D printing. The other methods used are tensile testing to analyse mechanical properties of rPP and melt flow index measurement, which is conducted for obtained rPP filament and ABS and PLA commercial filaments to compare the materials on this count.
According to the literature research, PP undergoes heavy warping and has poor layer adhesion during printing. Only very few printers currently manage to print with it given that special equipment setup is arranged. As the empirical study showed, it is not feasible to produce rPP filament of satisfactory quality, at least with the available equipment. The best possible results with respect to the quality of the filament can be achieved by using the water bath as a cooling method so that the temperature of the cooling water would be much higher than the room temperature as well as the extrusion temperatures should also be high enough. Additionally, it is experimentally established that when using virgin PP as a cleaning material prior to extrusion of rPP, the quality of the produced filament is considerably better. However, it is still unsatisfactory to use it in a 3D printer. It has relatively large diameter variations of around ±0.30 mm while the acceptable deviation is ideally ±0.05 mm. The produced filament does not have perfectly round shape, but rather elliptical.
As for the testing of material properties, CIRCO® rPP has better flow properties than virgin PP and no significant difference in mechanical properties is noted. The obtained rPP filament has also significantly higher MFI values than both ABS and PLA commercial filaments and in terms of this parameter is not comparable to two most dominant 3D printing materials.
All in all, rPP seems to have a potential of successful conversion to 3D printer filament. It will need some further research on how to get around the main issues, which are the filament roundness and diameter deviations across the entire length of the filament.

Keywords:	Recycled materials, recycled polypropylene, PP, 3D printing filament, fused deposition modeling, 3D printing
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ABBREVIATIONS

ABS	Acrylonitrile butadiene styrene
AM	Additive manufacturing
FDM	Fused deposition modelling
MFI	Melt flow index
MW	Molecular weight
MWD	Molecular weight distribution
PET	Polyethylene terephthalate
PLA	Polylactic acid
PMMA	Polymethyl methacrylate
PP	Polypropylene
rPP	Recycled polypropylene
RP	Rapid prototyping
SLA	Stereolithography
SLS	Selective laser sintering

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Helsinki, October 2017
Elina Iunolainen

1 INTRODUCTION

1.1 Background

3D printing is a strong-growing technology that can create from raw material anything a computer tells it. It has been around for quite a while now, but still might sound like something futuristic. [1]

The basic principle of 3D printing, which is also known as additive manufacturing (AM), is that 3D printers can directly fabricate a three-dimensional tangible object by slowly putting one layer of material on top of another. [2] The desired object is initially created on a computer using Computer Aided Design (CAD) software [3, pp. 1-2].

At the present time, there is an extended range of available materials for printing, from plastics to various metals and ceramics. Although, the most commonly used ”building materials” are plastics, such as acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), or nylon (PA), which altogether in terms of volume accounted for almost a half of the global 3D printing materials market in 2013 [4]. Such high demand for plastics in the 3D printing market can be attributed to their durability, flexibility, and availability in a wide range of colours. Whatever plastic material is used in printing, it is normally delivered to a print head as a solid, thin strand or *”filament”* that is then heated into a molten state [5].

As 3D printing grows with plastic being still the leading material used in the industry, therefore has naturally emerged the necessity to make the industry more environmentally friendly. It is common knowledge that plastic is rarely good news when it comes to the environment, no matter which manufacturing process was involved in creating a product. Scientists estimate that around 100 million tons of plastic waste is floating in the world's oceans, while each piece can take up to 1,000 years to decompose [6].
Hence, there is a necessity of making the 3D printing technology even more environmentally friendly manufacturing process. This can be achieved by among other things using 3D printer filament made from recycled plastic as an alternative to filament made from virgin raw plastic. After years of extensive research and testing, many companies have

already successfully converted plastic waste into 3D printing filament of good quality. There are currently a number of manufacturers producing reclaimed ABS, PLA and PET filaments [7].

While ABS and PLA are the most popular thermoplastics in the 3D printing industry, Polypropylene (PP) being one of the most used plastics in the world with a wide range of industrial and consumer applications, is barely used for 3D printing at present. Although, it has a multitude of appreciated properties, like high chemical resistance, including resistance to acids and organic solvents, along with remarkable mechanical properties [8]. Yet, PP has not yet been embedded in 3D printing as firmly as ABS and PLA.
PP is also one of the most common types of plastic in the household waste stream [9]. Therefore, turning it into PP filament for subsequent usage in 3D printing would be extremely good since it will be quite a while before we run out of this kind of plastic waste. [10]

This work therefore focuses on an attempt to answer the posed questions concerning PP in the 3D printing industry and investigates the possibility of manufacturing 3D printing filament from recycled PP.

1.2 Aims and objectives

The principle aim of this work is to find out suitability of recycled PP for 3D printing filament. The attainability of this will be discussed after approaching five main objectives of this work:

- Find requirements and material properties of the most popular plastic materials used to manufacture 3D printing filament.
- Compare the material properties of the most common plastics for filament production with those of PP and provided CIRCO® rPP and find out why PP is not yet used extensively in 3D printing.
- Find experimentally the possibility of manufacturing 3D printing filament from CIRCO® recycled PP.
- Measure and assess the properties of provided CIRCO® recycled PP; mechanical properties from tensile testing and flow properties by melt flow index test.
- Measure MFI values of commercial ABS and PLA filaments and find out how they correlate to rPP filament on this count.

2 LITERATURE REVIEW

Firstly, the section gives essential theory regarding the 3D printing process and the most common plastic materials used for production of 3D printing filament. Secondly, relevant information about the material in concern of this work, which is PP, is also reviewed. Additionally, an overview of the manufacturing method involved in production of the filament is presented as well as some relevant theoretical data on the other methods used during experimental study.

2.1 3D printing

2.1.1 Overview of the course of 3D printing history

Additive Manufacturing (AM) or 3D printing is a strong-growing technology that has been around in the world of manufacturing for about 30 years now, since the late 1980s. When this layer-based technology emerged, it was actually known as Rapid Prototyping (RP) first, since it was all about fabrication of sticky and brittle parts. Those parts were intended to be used only as prototypes for new product designs before committing them to production, what allowed to save a significant amount of time and money [2].
In 1984, Charles Hull invents the first printing method called *stereolithography* that enables a tangible 3D object to be fabricated from digital data. Two years later, in 1986, the first patent was issued to Charles Hull for stereolithography apparatus (SLA). Stereolithography was not the only RP technique developed at that time. In 1989, for example, Scott Crump invented Fused Deposition Modelling (FDM) technology, which is still the most popular printing technique that consumer 3D printers utilise. The FDM printers use filament that is first heated and melted and then deposited in successive layers to form a 3D printed part. In the following years, many other RP techniques were also emerging, such as the Selective Laser Sintering (SLS), which is currently one of the three most widely used 3D printing methods along with SLA and FDM [1, pp. 10-13].
In addition to development of printing methods, more and more extended range of materials has become qualified for AM applications in the course of time. Today virtually all

classes of materials can be processed using 3D printers: from plastics, metals, and ceramics to more unusual ones, such as food, concrete, and human tissue [2].
In the early 2000s, the focus of manufacturers as well as of the users finally changed from just prototyping to manufacturing end-use products using 3D printers because of improved accuracy, materials, software, and the overall quality of the output. Nowadays, 3D printers have a broad spectrum of applications with a nearly limitless potential. Apart from prototyping being still the largest application of 3D printing, other fields include tooling and casting, medical and dental sector, the AM technologies are also extensively utilised in the aerospace and automotive industry [5].

2.1.2 3D printing process

The concept behind 3D printing process is basically the same as that of 2D printing technologies, presented by inkjet or laser printers, which are used in offices and homes today. In a similar fashion, 3D printing refers to any manufacturing process, which layer-by-layer turns virtual solid model data into tangible 3D output. The predetermined geometry of the part is thus precisely copied in the AM machine without adjustments for manufacturing processes, like undercuts, draft angles or other features. [3, pp. 3-5]
To 3D print an object, a virtual model first needs to be created in a computer. This may be achieved using a computer aided design (CAD) application or some other 3D modelling software, or a digital model may be even captured by scanning a real object with a 3D scanner. Regardless of how this is done, after a digital part is ready for production it needs to be run through a “slicing software” that will break it down into a number of layers that are normally about 0.1 mm thick. These digital data is then sent to a 3D printer that fabricates a complete 3D printed product. [5, 11]

2.1.3 FDM printing method

As it has already been stated, three most common 3D printing technologies today are FDM, SLA and SLS. Both SLA and SLS machines use lasers to produce their prints, and are usually for industrial usage.

The printing technique that is of a greater concern for this work is Fused Deposition Modelling (FDM), since most widespread desktop consumer 3D printers use this printing method as their work concept. [1, p. 12]
The FDM technology is an extrusion-based process with plastics being the most widely extruded materials. Figure 1 provides an illustration of material extrusion. The FDM printing works by melting plastic filament via a heated extruder head onto the 3D printer's "build platform", a layer at a time, which hardens and bonds to the previous one. The whole process is run according to the 3D data supplied to the printer. [5]

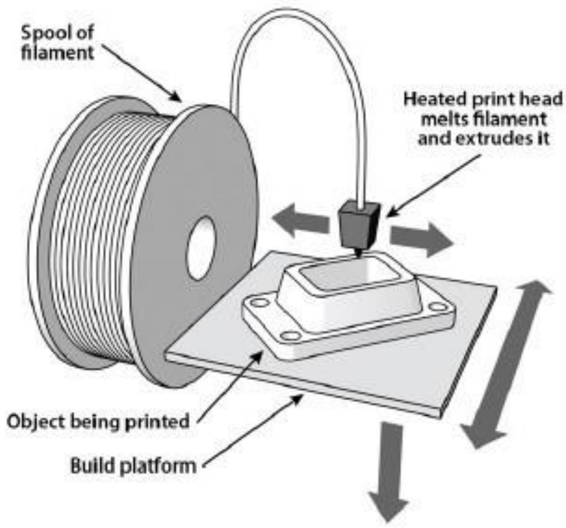

Figure 1. Schematic of extrusion 3D printing [5, p. 25]

2.2 3D printing materials

As it has been previously mentioned, 3D printing processes have currently a multitude of available materials, including plastics, metals, resins, composites, and much more, which can be used in various states (filament, powder, pellets). However, the most popular materials for AM processing have from the outset been plastics or polymers, which have long ago become virtually indispensable to modern society due to a great variety of applications they are used in. [5]
When it comes to FDM printing process, the two most common polymer materials are PLA and ABS in filament form. Other popular types of plastic used for commercial 3D

printer filament include biodegradable Polyvinyl Alcohol (PVA) and High Impact Polystyrene (HIPS), strong and flexible Polyethylene Terephthalate (PET) and nylon (PA). [12]

For the sake of relevance to this work, more detailed theory regarding only plastic materials and particularly two dominant ones, ABS and PLA, is set forth in the next chapter.

2.2.1 Plastics

All plastics can be divided into two groups, called thermoplastics and thermosets. *Thermoplastics* are solids at room temperature and can be heated to become soft and flexible, placed into a mould or other shaping device, and after cooling down, they acquire the desired shape. The distinctive characteristic of all thermoplastics is that they can be reshaped many times if desired by reheating the part. This unique feature is what sets thermoplastics apart from *thermosets*, which cannot be remoulded upon cooling. An explanation of this lies in the crosslinking of polymer chains of thermosets in addition to normal covalent bonds that join the atoms, as shown in Fig. 2. While in the mould, thermosetting plastics undergo also a crosslinking reaction that takes longer than the cooling of thermoplastics, meaning that such crosslinked materials cannot be fully remelted after they are once shaped [13, pp. 63-65].

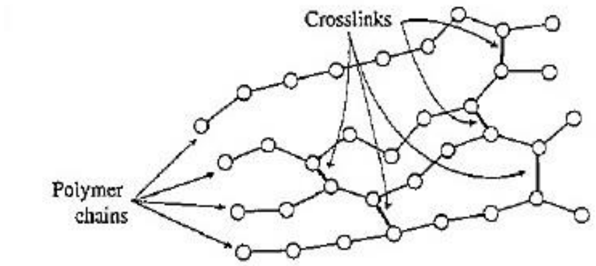

Figure 2. Crosslinks between polymer chains in thermosets [13, p. 63]

Both ABS and PLA, being the two leading polymers for 3D printing, and PP, as the material of the research concern, are identified as *thermoplastic materials*. [5]

Thermoplastics can also be classified into two groups according to their morphology (the way in which the molecules are organised). Depending on the degree of the intermolecular interactions that occurs between the polymer chains, two different types of structure may be formed in the solid state of polymeric materials: *amorphous* or *crystalline* structures. [14]

Amorphous polymers have the molecules randomly coiled about each other with entanglement, very much as wet spaghetti would be twisted together (Fig. 3b). Polymers with the crystalline type of structure have molecules packed together into regular, repeating structural patterns, as pictured in Figure 3a. Although, polymers cannot be totally crystalline, they still have some amorphous regions. Those with high concentrations of crystalline zones (maximum 80% degree of crystallinity) are considered to be crystalline or, to put it more accurately, *semi-crystalline* [13, pp. 75-77].

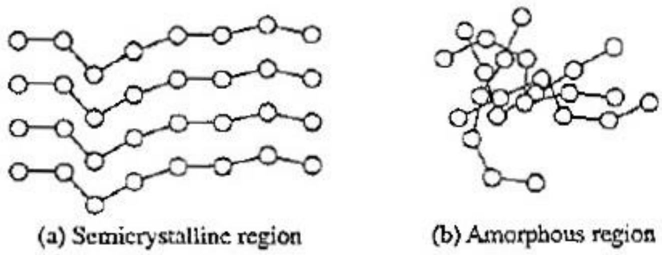

Figure 3. Amorphous and semi-crystalline regions in a polymer structure [13, p. 76]

The degree of crystallinity has much influence on many properties of a polymer. In turn, other characteristics and processes affect the degree of crystallinity. Highly branched polymers have a tendency to have lower degree of crystallinity, as is easily seen in the difference between branched low-density polyethylene (LDPE) and the more crystalline high-density polyethylene (HDPE). LDPE is more flexible, less dense and more transparent than HDPE. This is a great example that the same polymer can have different degrees of crystallinity [15, p. 14].

Examples of common *amorphous thermoplastics* include ABS, polycarbonate (PC), acrylic (PMMA), and polystyrene (PS). [16]

Semi-crystalline thermoplastics include, for instance, the polyethylene family (LDPE, HDPE), polypropylene (PP), nylon, and polyester thermoplastic PLA [16].

Most important characteristics and properties of both types of thermoplastics are summarised in Table 1 below.

Table 1. Common characteristics of semi-crystalline and amorphous plastics [13, 16-17]

Semi-crystalline polymers (PP, PLA, nylon, etc.)	**Amorphous polymers (ABS, PC, PS, etc.)**
Predominantly opaque	Predominantly transparent
Better chemical resistance and resistance to stress-cracking and fatigue	Prone to stress-cracking and poor fatigue resistance
Difficult to bond	Easier to bond
Average impact resistance	Better impact resistance
Sharper melting point	Soften over a range of temperatures
More challenging to process due to higher shrinkage upon cooling	Lower shrinkage upon cooling, easier to process

2.2.1.1 Acrylonitrile butadiene styrene (ABS)

ABS is an extensively used engineering polymer. It is an opaque and amorphous thermoplastic composed of three kinds of monomers – acrylonitrile, 1,3-butadiene, and styrene. ABS was created to combine rigidity, hardness and good chemical resistance acquired from a continuous phase of styrene-acrylonitrile copolymer (SAN), with the impact strength over a wide range of temperatures through addition of a rubber component, polybutadiene (Fig. 4) [18].

"ABS is usually made in the compositional ratio of 21 to 27% acrylonitrile, 12 to 25% butadiene, and 54 to 63% styrene on average." [16, p. 102] ABS can easily be modified both by the addition of additives and by variation of the ratio of the three monomers, hence there are a multitude of grades available for various applications. [18]

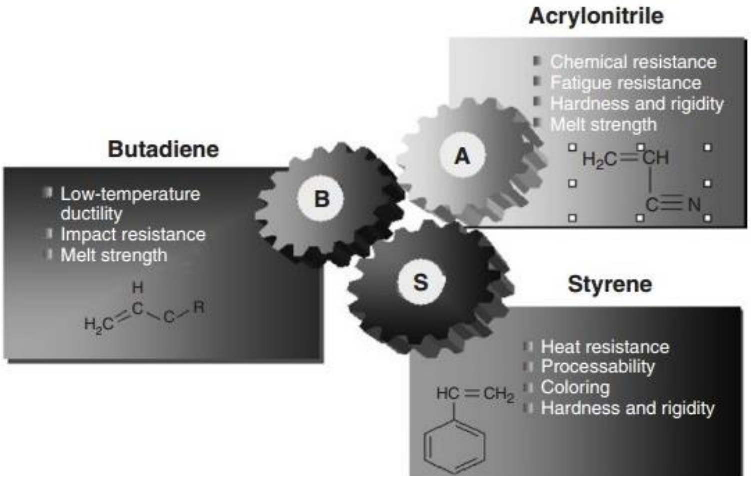

Figure 4. ABS and its functionality [18, p. 102]

ABS has outstanding impact strength and high mechanical strength making it well suitable for tough consumer products. Additionally, ABS has good dimensional stability and is particularly simple to be injection moulded into a great many things, for example, keys on a computer keyboard, electronic housings, Lego toys, or cycle helmets. It can also be processed with normal processing techniques of extrusion, blow moulding, and thermoforming. [15, pp. 21-22]
Since ABS is mechanically strong and able to withstand high temperatures, it makes it the material of choice for the FDM filament when a product of high durability and ability to withstand high temperatures needs to be printed. ABS spools are also available in a large range of colours and ABS 3D printed product can be easily painted to any colour.

2.2.1.2 Polylactic acid (PLA)

PLA is a rigid biodegradable thermoplastic polymer that can be semi-crystalline or totally amorphous, depending on the stereopurity of the polymer backbone. It can be produced by direct condensation polymerisation from its basic building block *lactic acid* derived by fermentation of sugars from renewable resources, such as corn, sugarcane, or tapioca (Fig. 5) [19, pp. 3-4].

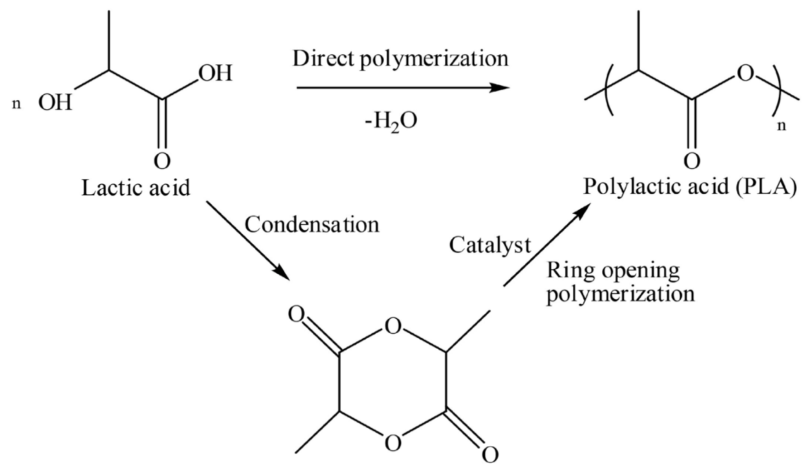

Figure 5. Synthesis of poly (lactic) acid (PLA) [40]

PLA has physical properties comparable to those of petroleum-based polyethylene terephthalate. Although, the huge benefit of PLA compared to conventional oil-based plastics is that it naturally degrades when exposed to the environment. Due to its excellent biocompatibility, biodegradability, nontoxicity, and mechanical strength, outside of 3D printing PLA is largely applied in biomedical applications, such as in tissue engineering for scaffolds, surgical implants, or drug delivery system. [19, p. 4] [20] It also shows great organoleptic characteristics and is excellent for food packaging applications.

As for PLA 3D printing filament, it is easier and safer to print with than ABS due to a lower printing temperature and organic nature of PLA. Besides, when heated PLA smells slightly sweet in contrast to unpleasant fumes often given off by ABS. [1, p. 16]

However, ABS filament has superior mechanical properties, such as higher flexural strength and improved ductility, making it suitable for high impact applications. Moreover, PLA features a fairly low glass transition temperature and melting point than ABS, meaning that PLA printed parts are unsuitable for high-temperature applications, since it can cause warping, cracking, or melting of the part. [5]

2.2.2 Polypropylene (PP)

Polypropylene (PP) is a thermoplastic polymer that is produced by polymerising propylene molecules, the monomer units (Fig. 6), into long polymer chains. The polymerised propene molecule can be formed into three basic chain structures. The structure is determined by the arrangement of the methyl groups, which are attached to every second carbon atom in the chain. If all the methyl groups are on the same side of the macromolecular backbone, as illustrated in Fig. 7, the product is referred to as *isotactic* PP [21].

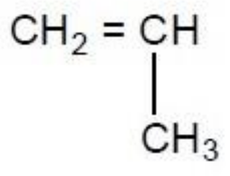

Figure 6. Propylene monomer [21, p. 1]

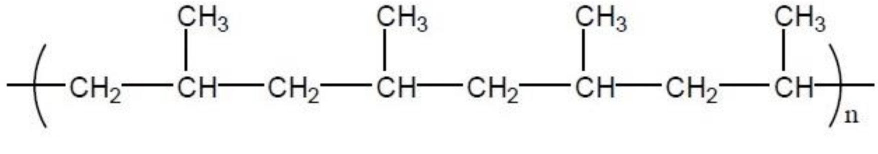

Figure 7. Isotactic polypropylene [21, p. 1]

In the second PP chain structure, methyl groups are attached to the backbone chain in an alternating manner, while the third structure has methyl groups located randomly along the chain. The above two structures are referred to as “syndiotactic” and “atactic”, respectively. However, only *isotactic* arrangement has molecules packed tightly into crystalline structure what allows the isotactic material to be more rigid and strong than both syndiotactic and atactic. Hence, the most commercially important form of PP is isotactic, since only highly crystallized PP has the properties required for a useful plastic material. [13, p. 239] Such PP is made by Ziegler-Natta catalysis with catalysts that produce crystallisable polymer chains, meaning a polymer that is semicrystalline with good physical, mechanical, and thermal properties in the solid state. [13, pp. 239-240]

All in all, the properties of polypropylene depend on the tacticity, molecular weight (MW) and molecular weight distribution (MWD), degree of crystallinity, type and proportion of comonomer (if used) [15, p. 17].

PP offers good chemical resistance over a wide range of chemicals (acids, alkalis and organic solvents), good fatigue resistance, good environmental stress cracking resistance, good detergent resistance, and ease of machining, together with the unique ability to be manufactured by any standard processing methods such as injection moulding, extrusion, blow moulding, and thermoforming [15, p. 17].

Thanks to all those properties, PP is among the three most used plastics in the world after PE and PVC with a multitude of industrial and consumer applications. [21, p. 6] PP can be referred to as both commodity and engineering plastic. Examples of numerous applications of PP include household goods (bottles, buckets), packaging, automotive industry (bumpers, wheel covers), building construction, pipes and fittings, fibres, furniture, etc. PP is also used to replace engineering plastics, such as polyethylene terephthalate (PET), polycarbonate (PC) and ABS in kitchen and domestic appliances. [21, 22]

As for PP application in 3D printing, it is notorious for being difficult to print due to serious warping and bad layer adhesion, only very few printers manage to print with PP now. If not for this, PP would likely compete with PLA in 3D printing thanks to its excellent mechanical and chemical properties. [23]

The typical physical and mechanical properties of unmodified PP are compared with the two most popular materials for 3D printer filaments, ABS and PLA, in Table 2 below.

Table 2. Typical material properties of ABS, PLA and isotactic PP

Material Property	PP	ABS	PLA	Ref.
Density	0.90-0.91 g/cm3	1.0-1.4 g/cm^3	1.3 g/cm^3	[15]
Glass Transition Temperature (Tg)	-20 – 20 °C	-85 – 105 °C	60-65 °C	[24]
Melting Point (Tm)	160-165 °C	Amorphous	150-160 °C	[24]
Processing Temperature	200-230 °C	210-230 °C	160-220 °C	[15]
Heat deflection temperature (HDT) at 0.46 MPa.	100 °C	98 °C	50 °C	[20], [22]
Tensile Strength at yield	26 MPa	34 MPa	60 MPa	[25], [26], [27]
Young's Modulus	1.3-1.5 GPa	1.7 -2.8 GPa	2-3.5 GPa	[25], [26], [27]
Flexural Modulus	1.5-2 GPa	1.5-2.7 GPa	2.4-4 GPa	[25], [26], [27]
Impact Strength (Notched Izod impact at 23°C)	150 J/m	250 J/m	47 J/m	[26], [27], [28]

It can be seen from the table that in terms of stiffness and strength, which are defined as the Flexural and Young's Moduli, PLA shows the highest values. The reason PP is low on Flexural Modulus is due to its ability to elongate. PP is considerably more elastic then PLA. This is why it's problematic to print living hinges for lids with PLA, which is brittle, and always tends to break rather than bend. [29] As for the impact resistance, PP has a significantly higher amount of impact strength than PLA. However, ABS has the highest impact resistance among these three. On the basis of Heat Distortion Temperature (HDT) values, PLA is considerably lower than PP; at the same time, PP value of HDT is comparable to ABS.

2.2.2.1 CIRCO® recycled PP

The material provided for the purpose of this research is CIRCO® recycled PP refined by Fortum (formerly known as Ekokem).

> *Fortum is a clean-energy company that delivers electricity, heating and cooling as well as has its own Recycling and Waste Solutions unit to enhance resource efficiency.* [30]
>
> *Fortum has a Circular Economy Village in Riihimäki, Finland. Materials taken from municipal waste are heading to recycling through the Plastic Refinery and the Bio Refinery. The Plastic Refinery deals with plastics collected separately from industry and the retail sector and redirects them back into the cycle to replace virgin raw materials.* [31]

The main physical and mechanical properties of CIRCO® recycled PP provided by Fortum can be seen in Table 3 below.

Table 3. Some properties of the provided rPP (Fortum CIRCO® Polypropen Material Datasheet [32])

Property	Value
Density at 23°C	905 kg/m^3
MFI 230°C/2.16 kg	11 g/10min
Tensile strength at break MD	21.4 MPa
Elongation at yield MD	7.2 %
Tensile strength at yield MD	26 MPa
Tensile Modulus	1.3 GPa
Impact strength	60
Flexural Modulus	1.3 GPa

2.2.2.2 Recycling of polypropylene

Nowadays, polypropylene represents one of the main sources of plastic waste. [33] The first step in the successful recycling process is to ensure that polypropylene is separated from any other plastic polymers. The plastic type of a product can easily be recognised using the resin identification coding system, which was established by the Society of the Plastic Industry (SPI) [34]. The 'code' is normally printed on the bottom of a product which is using that particular plastic. These codes are used for recycling operations, so that different polymer types can be recycled separately without contamination of the recyclable mix. [35] Items made from PP have the universal identification number '5' within the recycling triangle (Fig. 8).

Figure 8. The resin identification code for PP [34]

In practice, PP is often blended with PET to produce plastic products such as beverage bottles. In this case, identification of plastic type can be achieved by 'sink/float' method, which works on the principal that PP has a unique specific density and as a result will float when other polymers will go down. As PP has a specific density of 0.93-0.95g/cm^3 and PET has a specific density of 1.43-1.45 g/cm^3, PP will float on water and PET will sink, what will provide separation of the polymers. [35]

If possible, the PP should also be sorted by colour before processing. Most plastic factories will also separate the different grades of PP before processing; this creates a product of better quality. When the plastic is homogenous, it is shredded into 'flakes', which can be resold as recycled goods. The recycled PP may also be further processed by extrusion to produce denser plastic pellets. [35]

The major difficulties in the recycling of homogeneous PP arise from the easy degradability of this polymer during processing and recycling operations. [36] Polypropylene is eventually affected by thermal degradation, the bonds between hydrogen and carbon weaken. However, the moment when this occurs is dependent on the use of PP, it is generally considered that PP can be recycled in a 'closed loop' four times before the thermal degradation has a negative effect on PP. [35] Besides, mechanical stress and ultraviolet radiation also strongly alter the structure and the morphology of PP. Elongation at break and impact strength are most influenced properties by degradation. Since PP has the tertiary carbon in the chain, the impact of thermal and mechanical degradation on PP is even more dramatic than on other polymeric materials. [36]

2.3 Filament requirements

The degree of success while 3D printing is primarily defined by the quality of the filament, which in turn depends upon several aspects. The most important quality in a good filament is its *diameter tolerance*, which describes the variation in diameter the filament has. In an ideal world, a filament should maintain an absolutely constant diameter across the whole spool. Spools of filament are typically either 1.75 or 3 mm in diameter. Between the two, 1.75mm is more common and offers better extruding and flow of plastic. The gold standard for diameter tolerance is 0.05 mm across the industry. Serious issues can arise when using filament of irregular diameter. For instance, gross diameter deviations can lead to the condition where the extruder fails and no plastic goes to the hot end. The other risk is when the extruder motor is not strong enough to push filament through or it does not fit into the hot end opening if it is too wide. [37]

Another important characteristic for a successful 3D print is constant *filament roundness* across the full length of a spool. This is because filament that does not have a good circular shape can cause serious extruder failure just in the same way that irregular filament diameter does. [37]

Impurities is the third major issue when producing or selecting a 3D printer filament. Chemical impurities will lead to poor melted plastic viscocity with debris blocking the extruder nozzle. This can be a costly experience in terms of both money and time. [12]

2.4 Filament processing and testing

In this section, some essential theory pertinent to filament processing and testing methods is presented.

2.4.1 Extrusion

Extrusion is one of the most prevalent manufacturing processes in the plastic industry. It is a continuous process, in which raw plastic is converted into a product of uniform cross-

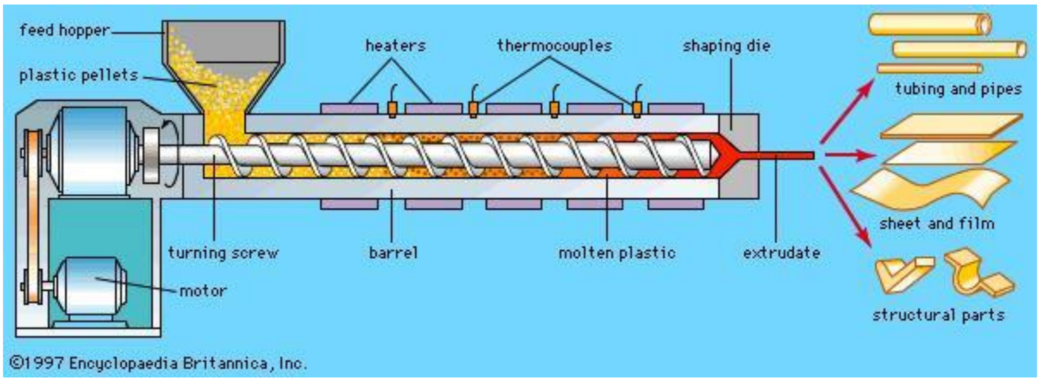

Figure 9. A schematic of a screw extruder (Source: Encyclopedia Britannica)

section by pushing it through a die under controlled conditions. Extruder is common equipment in the manufacture of tubing and pipes, different profiles used in constructions like windows, doors and frames, and aircraft parts and structures. Thermoplastics are the most common plastics to be used in the extrusion process; they include PE, PP, polyamides, PS, PVC, and ABS. [13] [15, p. 100]

Essential components of an extruder include hopper, barrel, screw, heater bands, and die. [13, p. 368] In usual plastics extrusion, a plastic in a form of granules, pellets, or powders, is fed into a hopper. From the hopper the material comes onto the rotating screw inside the barrel, which transports the plastic forward into a closed heated zone where the plastic is melted by mechanical energy from the screw rotation and by heating elements arranged along the barrel. The screw conveys the molten plastic forward until it reaches a die where it exits through a hole. The die is what gives the final product its shape. After exiting the die, the plastic stream solidifies; this is usually achieved by pulling the extrudate through the cooling system. [13, 15]

Auxiliary equipment such as puller with adjustable speed is placed after the cooling system and is used to move the extrudate away from the extruder and through the cooling system at the proper rate. If the product is not properly pulled from the extruder, the melt would flow down onto the floor after leaving the die. Other auxiliary equipment may include a cutting device to cut the extrudate to the appropriate length and package it for shipment by coiling or by stacking. [13, pp. 363-365] [15, pp. 87-90] A schematic of a typical screw extruder with major components is pictured in Fig. 9.

2.4.1.1 Screw

The extruder screw is a crucial component of the machine. Screw design plays an important role and along with optimum processing parameters, such as screw speed and feed rate, is a key aspect in attaining excellent product quality. Schematics of two types of single screws designed to optimize extrusion performance of two thermoplastics, PE and nylon, are illustrated in Fig. 10. Extruder screws have several functional zones or sections. They are feed section, compression section, and metering section. [13, pp. 371-372]

- *Feed section (also solid conveying zone)*

The feed zone is located directly under the feed throat and feeds the resin into the extruder, it is normally 3 to 10 turns of the flight. The purpose of this zone is to preheat and convey solid materials further into the die compression section where materials are melted. [13, p. 373]

- *Compression section (also melting zone)*

The melting or compression section is the place where most of the polymer is melted. It can be characterised by gradual increase in the diameter root and progressive decrease of the channel depth along the length of the zone. [13, p. 374]

- *Metering section (also melt conveying zone)*

The following section is called metering zone. The root diameter is constant and channel depths are very shallow and also constant throughout this zone. Here, the last particles are melted, final mixing and thermal uniformity is ensured, and a homogeneous melt is conveyed to a die. [13, p. 375] [15, pp. 101-102]

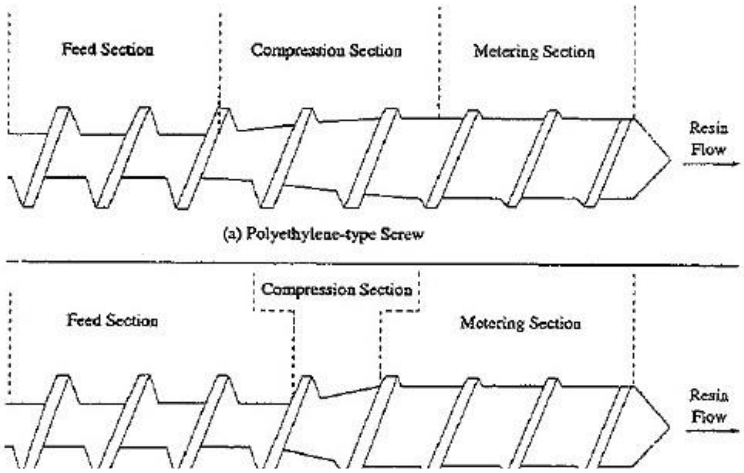

Figure 10. Functional zones of screws [13, p. 373]

2.4.1.2 Die

The die is another key component that is mounted on the end of the extruder. The purpose of the die is to impart a shape to the molten material so that after exiting the die it can be solidified into the dimensions created in the die. There are different die types used in plastics extrusion, such as sheet dies, blown-film dies, tubing dies, etc. used according to desired final products. [13, p. 376] [15, pp. 95-96]

2.4.1.3 Extrudate swell

One of the most important phenomena in the polymer extrusion is the swell of the extrudate as it leaves the die. Plastic melt is very viscous during processing and extrusion of a hot melt through a cooler die region significantly expands the swell of some thermoplastics. In extrusion, extrudate swelling depends upon shear history and rate, polymer molecular weight distribution (MWD), the length to diameter (L/D) ratio of the screw, and the difference in the diameters between the extrusion reservoir and die orifice. The polymer swelling is one of the most important considerations for the design of the extrusion process. [15, pp. 97-98]

2.4.1.4 Cooling

After leaving the die, the hot extrudate must be cooled down to harden into the desired dimensions. The most common way of cooling is to introduce the extrudate into a cooling water bath in which water is circulated or is sprayed onto the product. Temperature of the water varies according to the needs for cooling the particular material; it can be room temperature or cooled. The extrudate can also be cured with air or a combination of these systems can be used for cooling, this is dependent on the polymer in question. [13, p. 378]

2.4.2 Melt Flow Rate Testing

Melt flow index (MFI) or *rate* (MFR) is an analysis method to determine the flow properties of a melted plastic by characterising how many grams of a polymer flow through the die in 10 minutes. MFR is one of the most important parameters specified when describing a polymer. The method is described in the standards ASTM D1238 and ISO 1133, and is conducted using a melt flow indexer (typical device is shown in Fig. 11). The sample of several grams of the polymer material is heated (the temperature depends on the type of polymer and is specified in the test method) and forced to flow through a capillary using a weighted piston (the weight specified by the test method for each type of polymer). The weight of the material extruded through the capillary in the allotted time is the melt flow rate, expressed in grams per 10 minutes. [13, pp. 105-107]

In general, if MFR is a large number, meaning high flow, the material has short chains and, therefore, low molecular weight. Hence, a high melt index indicates a low molecular weight, while a low melt index means a high molecular weight. The obtained MFI number also shows the viscosity of a polymer in such a way that a higher MFI, meaning the polymer flows quickly through the test apparatus, corresponds to a lower material viscosity. Polymers with a low MFI flow slowly and have a high viscosity. Hence, high MFI numbers of a polymer show ease of melting, lower energy input required, and easy processing. [13, pp. 105-107]

Although the melt flow index is a prevalent method in the plastic industry to determine important flow characteristics of polymers due to low cost of the indexer and ease of use, it is only an approximation of the melting conditions for the polymer during actual processing. Consequently, MFI test is not a totally accurate method to provide a measure of actual viscosity. To obtain more accurate viscosity data, some companies execute, for example, in-mould rheology tests using actual manufacturing moulds. [13, pp. 105-107] [38, pp. 20-21]

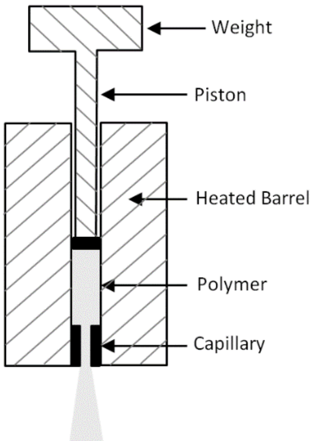

Figure 11. Melt flow indexer (Source: polymerdatabase.com, retrieved 2.5.17)

2.4.3 Tensile Testing

A tensile test of materials is the most fundamental mechanical test performed to obtain information about the mechanical behaviour of the material. In particular, the test provides very important quantitative measurements, such as tensile strength, yield strength and ductility of the material (elongation defined as the strain at or after the point of fracture). [39]

The basic idea of a tensile test is to first place a test sample of a material between two grips, which hold the material, and then to apply an ever-increasing load or force to the sample up to the point of failure. The material has known dimensions, such as length and cross-sectional area. The result of this test is a graph, often called a stress/strain curve, which shows how the material behaves throughout the test. [13, pp. 121-122]

A typical tensile specimen, also referred to as a dumbbell sample, used for the tensile test is illustrated in Fig. 12. It has enlarged ends or shoulders for gripping. The gage length is the area over which measurements are made and is centred within the reduced gage section. The distances between the ends of the gage section and the shoulders need to be large enough so that the bigger ends do not cause deformation within the gage section. The gage length should be large compared with its diameter. [39]

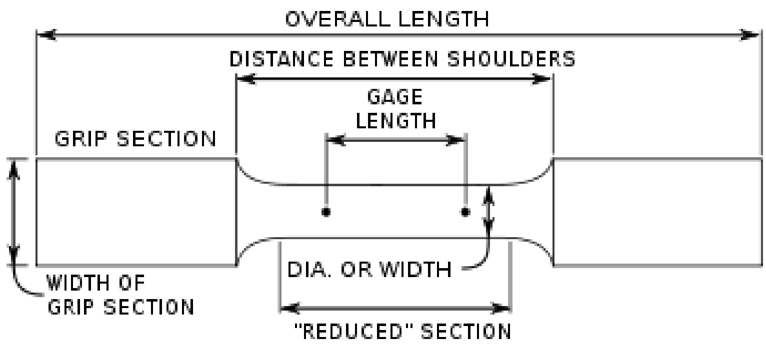

Figure 12. Typical tensile specimen (Source: wikipedia.org, retrieved 24.6.17)

3 METHODS

The empirical part was executed using the following methods:

I. Filament extrusion
II. Melt flow index measurement
III. Production of dumbbell samples by injection moulding and tensile testing

3.1 Materials

Apart from the CIRCO® recycled PP, provided by Fortum Waste Solutions Oy in pellet form, virgin violet Sabic PP 505P was also used in the testing (MFI and tensile tests). This was done in order to be able to analyse mechanical and flow properties of rPP in relation to virgin PP. Sabic PP was also used as a cleaning material during extrusion.

Figure 13. Pellets of virgin Sabic PP and CIRCO® recycled PP

3.2 Equipment

The following equipment available at the Arcada's production laboratory was used to conduct the above-mentioned empirical part of this work:

1. KFM Eco Ex Extruder for filament production
2. Mitaten MEP 2/PC Extrusion plastometer for MFI measurement

3. ENGEL ES 200/25HL CC88 Injection moulding machine for manufacture of dumbbell samples
4. Testometric M 350-5CT Material testing machine for testing mechanical properties

3.3 Filament extrusion

3.3.1 Extrusion equipment

The filament was produced using KFM Eco Ex extruder, shown in the figure below.

Figure 14. KFM extruder (Arcada plastics laboratory, March 2017)

The extruder screw possesses six temperature zones (Fig. 15). Zones 1 and 2 function as the feed section or solid conveying section, zones 3 and 4 can be identified as the compression or melting section, whereas the last two zones, 5 and 6, function as the melt conveying section leading to the die. The filament die (FD) was utilised throughout the work. Besides, during extrusion several cooling systems were tried out such as cold-air gun (Fig. 16) and cooling water bath equipped with the heating element and thermostat (Fig. 17). Other auxiliary equipment used while extruding included also a pulling device (Fig. 18), which pulls the filament at a specific steady speed.

Figure 15. Temperature zones

Figure 16. Cold-air gun

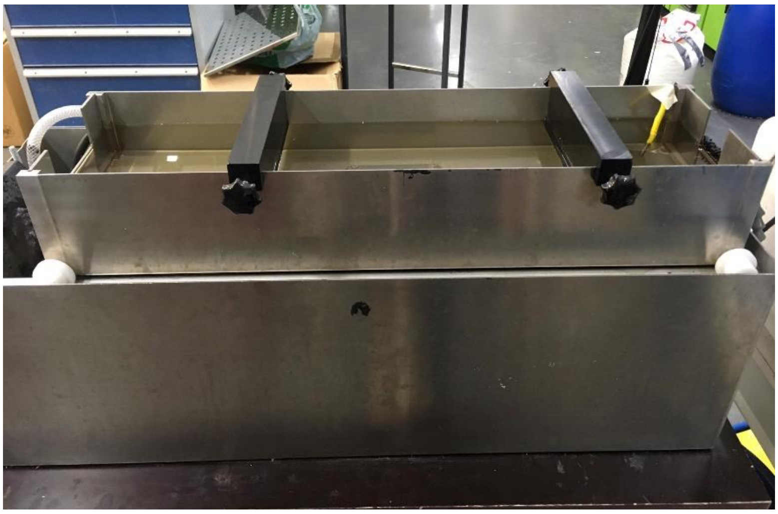

Figure 17. Cooling water bath

Figure 18. Puller

3.3.2 Extrusion optimization

A number of test runs was made to optimise the extrusion process in order to produce a filament as good in quality as possible. Ideally, the filament should be a consistently round-shaped thread that has a constant diameter of 1.75 mm without sharp deviations and smooth surface without impurities across the full length of the filament.

The pulling speed was every time set in accordance with the extrusion speed.

Experiment 1

In the first experiment, for filament pressurized air cooling system was used. The values for the extrusion temperature and speed were set as shown in Table 4 in the section "Results". Exactly these temperature values were used earlier while extruding filament from virgin Sabic PP.

Experiment 2

In the second testing, to cool down the extruded filament cooling water bath fitted with the heating element and thermostat was utilised instead of a cold-air gun.

Additionally, several other parameters adjustments were made in comparison to the first experiment. Such as an increase of the extrusion temperature to a higher one in an attempt to obtain more smooth surface and get rid of the many swelled, not fully melted parts across the filament length.

The exact values for the main production parameters are listed in Table 4 in the section "Results".

Experiment 3

In the third experiment, further adjustment of some parameters was made. Such as the water temperature in the cooling bath was increased to try reaching even more roundness of the filament.

Moreover, it was decided to clean the extruder not with the previously used Asaclean UP Grade purging compound, normally used in the Arcada's plastics laboratory as a cleaning material, but instead with violet Sabic PP. The reason behind this decision was the prediction that particles of UP compound remaining inside the extruder after cleaning are causing contamination of the filament.

The obtained results from implemented experiments as well as the main production parameters are summarised in Table 4 in the section "Results".

The diameter was measured twice at one point as dimensions of length "a" and "b" at an interval of 1 m with a digital calliper. Using Excel, some diameter parameters, such as average diameter and diameter deviation, max and min diameter, were calculated. The values from this measurement are presented in Table 5 in the section "Results".

3.4 Testing

3.4.1 Melt Flow Index measurement

As it was stated in the literature part, MFI test is conducted to determine the flow properties of a melted plastic by characterising how many grams of a polymer flow through the die in 10 minutes; the units for MFI therefore are g/10 min.

Extrusion plastometer depicted in Fig. 19 was utilised in order to perform the test for virgin Sabic PP and CIRCO® recycled PP to compare their flow properties as well as for produced rPP filament and ABS and PLA commercial filaments to see if the materials correlate at least on this count.

The test was done according to ISO 1133:2005 Standard for PP, ABS and PLA.

For virgin PP and rPP, initially the extrusion plastometer was heated to 230°C; in case with ABS this temperature was 220°C, for testing PLA – 210°C. Then 5 grams of all tested materials were placed inside the barrel with piston being inserted afterwards. Then the material was preheated for 5 minutes at the pre-set initial temperature. After the pre-heating the load of 2.16 kg (only in case with ABS the load was 10kg according to the standard) was applied onto the piston to push down the molten plastic through a die. The cut-off time interval was set to 5 seconds; when testing PLA filament the cut-off interval was 10 sec. 10 samples of molten plastic were taken and individually weighed to get the average mass of the cut-offs. The following formula was used to compute the MFI (g/10min):

$$MFI\ (230°C/2.16\ kg)\ = \frac{600m}{t}$$

Where m is the average mass of the cut-offs (g) and t is the cut-off time interval (s).
MFI test with all test materials (virgin PP, recycled PP, obtained rPP filament, ABS and PLA commercial filaments) was successively run 3 times each to obtain mean values of MFI.

Figure 19. Extrusion plastometer

3.4.2 Tensile testing

First, Engel injection moulding machine (Fig. 20) was utilised in order to manufacture dumbbell samples for further tensile testing. Samples were produced from both virgin PP and rPP.

Figure 20. ENGEL injection moulding machine

PP pellets were introduced into the machine through a hopper, from where they entered the heated barrel. In the barrel, the material was melted by both frictional action of a reciprocating screw and thermal energy from the heaters. The molten material was then moved forward through the nozzle into a mould cavity where it cooled down and solidified. The mould was then opened and the part ejected by ejector pins.
The obtained tensile test specimens are pictured in Fig. 21.

Figure 21. Violet PP and rPP tensile test specimen

In order to obtain mechanical properties of rPP and virgin PP, such as tensile strength, elongation at yield, Young's modulus etc., and to be able to compare the mechanical data of rPP in relation to virgin PP, tensile testing was implemented. This was done according to the explanation in chapter 2.4.3 using Testometric material testing machine with wedge grips. The test was successively run for 3 test specimens of each material in order to find average values. The tests were conducted at a testing speed of 2.5 mm/min in accordance with ASTM Standard D638. Dimensions of one test specimen are 33 x 5.45 x 1.6 mm. Figure 22 shows tensile testing of t rPP test sample. The obtained results are presented in chapter 4.3.

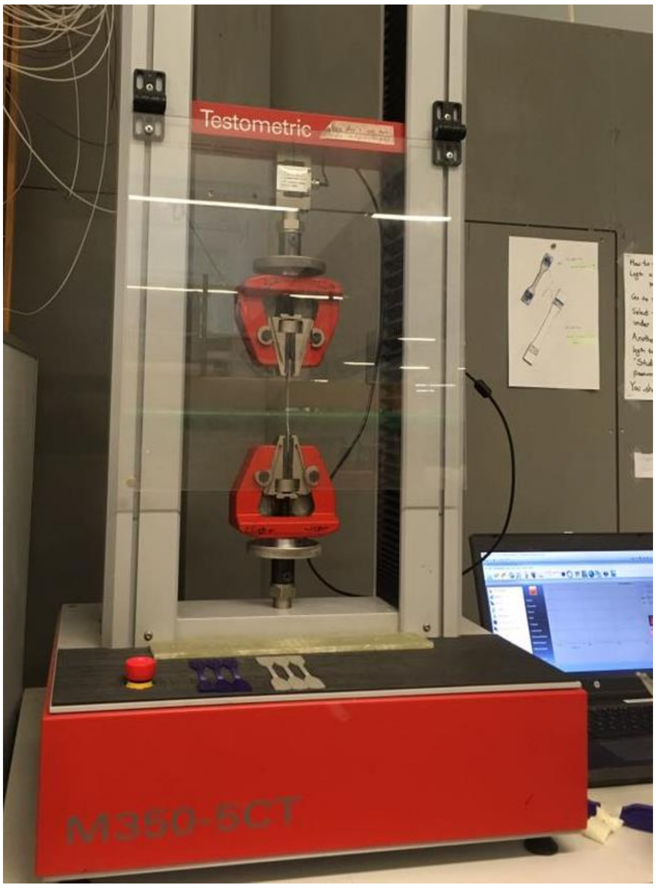

Figure 22. Tensile testing of the rPP test specimen

4 RESULTS

4.1 Filament extrusion

Table 4. Extrusion parameters and results

	Experiment 1	Experiment 2	Experiment 3
Extrusion T (zones 5 to 1 respectively)	200-205-200-195-190 [˚C]	225-225-215-215-210 [˚C]	225-225-215-215-210 [˚C]
Extrusion speed	5-25 rpm	25 rpm	25 rpm
Cooling method	Cold-air gun	Water bath	Water bath
Water T in the water bath	–	40 ˚C	50 ˚C
Cleaning material	UP resin	UP resin	Violet Sabic PP
Outcome	The filament did not have enough time to cool down and solidify with the current air-cooling setup – it collapsed under its own weight irrespective of the used extrusion speed.	• Moderately rough surface with impurities across the entire filament length • Sharp deviations in diameter • Not round-shaped, noticeably ellipse-shaped	• Less rough surface with almost no contaminated areas • Big diameter variations • Not perfectly round-shaped, rather elliptical

The third experiment was admitted the most successful out of the 3. It showed the best possible results with respect to the quality of the produced filament from provided Circo rPP. However, the manufactured filament, shown in Fig. 23, is still far from ideal concerning quality, what makes it unsuitable for the direct use in a 3D printer. The surface is not entirely smooth as well as deviations in diameter are still quite substantial.

Figure 23. Produced filament from provided rPP

Table 5 below shows diameter values for the produced rPP filament.

Table 5. Diameter values for the filament produced from provided rPP

	a	**b**
Average ø [mm]	1,729	1,925
Average Deviation ø [mm]	0,07	0,09
The % of average deviation from average	4,05	4,67
Max ø [mm]	1,88	2,05
Min ø [mm]	1,59	1,74
Max difference in ø [mm]	0,29	0,31
The % of the max difference from the average	16,77	16,1
max |a-b|	0,35	
min |a-b|	0,05	
Total length [mm]	40000	

4.2 Melt Flow Index

Table 6 shows MFI values for Sabic PP, rPP, obtained rPP filament, ABS and PLA commercial filaments found during MFI testing:

Table 6. Results of MFI test

Sabic PP 230°C/2.16 kg [g/10min]	**rPP 230°C/2.16 kg [g/10min]**	**rPP filament 230°C/2.16 kg [g/10min]**	**ABS commercial filament 220°C/10 kg [g/10min]**	**PLA commercial filament 210°C/2.16 kg [g/10min]**
7,2	14,4	16,4	6,4	7,8

4.3 Tensile Testing

Table 7 shows values for tensile strength, Young's modulus and strain at yield obtained during tensile testing:

Table 7. Results of tensile testing

	Stress at Yield (MPa)	**Young's Modulus (MPa)**	**Strain at Yield (%)**
CIRCO® recycled PP	25.18	594.32	9.83
Sabic virgin PP	31.65	677.1	10.81

5 DISCUSSION

This section reviews the results obtained during the empirical part of the study.

5.1 Filament extrusion

During filament extrusion a number of test trials was made before obtaining the potentially maximum good quality filament from provided recycled PP. Various available cooling systems were tried out. In the first attempt, the pressurised air cooling system was used but the filament did not have enough time to solidify and started to hang down under its own weight. Thus, the use of the cold-air gun was admitted unsuitable for cooling rPP filament. Throughout further extrusion tests, the water bath equipped with the heating element was utilised for cooling.

In the second attempt, the extrusion temperature was raised to obviate the problem of considerable surface roughness and contamination across the filament length. Besides, the cooling water temperature was also increased from room temperature up to 40°C in an attempt to reach more round-shaped filament. The outcome was still unsatisfactory: the extruded filament had contaminated areas and quite rough surface across the entire length, the shape was noticeably elliptical.

In the third attempt, it was decided to use violet Sabic PP instead of previously used Asaclean UP Grade purging compound to clean the extruder prior to rPP extrusion. The prediction that U resin particles remaining inside the extruder lead to contamination of the filament proved correct and the extruded filament had almost no impurities this time. The increase of the cooling water temperature up to 50°C also resulted in a more round-shaped outcome, although still not perfectly. Given the available equipment, these extrusion parameters proved to be the best amongst all experiments and gave the best possible result with respect to the quality of the produced filament from provided recycled PP. However, the obtained filament is not suitable to directly use it in a 3D printer.

The filament diameter measurement showed 1,729mm average diameter for “a” dimension and 1,925mm for “b” dimension, meaning that the filament is somewhat oval-shaped. In addition, the obtained rPP filament has sharp variations in diameter, maximum values for “a” and “b” dimension are 1,88mm and 2,05mm respectively, while the minimum value is 1,59mm for “a” dimension and 1,74mm for “b”.

Diameter tolerance and filament roundness are the main characteristics for a good quality filament. If the filament has sharp deviations in its diameter or does not have a constant circular shape, it can result not only in a poor quality print but also cause serious printer failure. That is why the acceptable diameter tolerance of the 3D printer filament across the industry is considered to be ±0.05 mm.

5.2 Testing of material properties

5.2.1 Flow properties

The MFI test was conducted for CIRCO® recycled PP and Sabic virgin PP to analyse the flow properties of provided rPP in relation to virgin PP. The test was also performed for produced rPP filament and ABS and PLA commercial filaments to compare flow properties of rPP and two most popular 3D printing materials. The tested MFI value of virgin PP gives 7,2 g/10min and recycled PP gives 14,4 g/10min, indicating an increase of 50% in MFI value of provided rPP. The obtained MFI values of rPP filament is 16,4 g/10min while ABS and PLA commercial filaments have 6,4 g/10min and 7,8 g/10min respectively. This clearly shows significant difference for this value between rPP filament and two dominant commercial filaments, meaning that rPP filament has considerably lower material viscosity and molecular weight than both ABS and PLA.

5.2.2 Mechanical properties

The tensile testing was conducted for CIRCO® recycled PP and Sabic virgin PP to analyse the mechanical properties of provided rPP in relation to virgin PP. Recycled PP gives an average value of 25,18 MPa and virgin PP gives an average value of 31,65 MPa for stress at yield. The value of tensile strength of rPP is observed to significantly decrease with respect to virgin PP, by 20,5%.
Young’s modulus value of the tested virgin PP is 677,1 MPa whereas rPP shows an average value of 594,32 MPa indicating the decrease of 82,78 MPa, which is 12,3%.

The difference in the yield strain value between virgin PP and recycled PP is 1%, having 10,81% and 9,83% respectively. This corresponds to the decrease of 9,1% of strain at yield for rPP in relation to virgin PP.

Overall lower mechanical performance of provided rPP with respect to virgin PP can be linked to the fact that CIRCO® rPP may contain different plastic grades. Besides, low tensile strength values of rPP may also be the result of degradation occurred during recycling operations.

6 CONCLUSION

FDM is one of the 3 main techniques of the dramatically and constantly developing 3D printing technology. Nowadays, FDM printing method is employed for manufacturing extensive spectrum of end-use products. However, the range of materials used for creating 3D printed products by FDM process have been limited to utilizing primarily acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA) based filaments. Further expansion of material range for FDM printing is therefore needed to fulfil the full potential of 3D printing industry.

PP, being one of the most widespread plastics with a large number of valuable physical and chemical properties in the solid state and consequently applications, has not yet landed in 3D printing and very little research was done concerning PP as a 3D printing material. The findings in the literature research showed that the reason behind unpopularity of PP as a 3D printing material lies primarily in its crystalline structure. PP as opposed to ABS is a semi-crystalline polymer and is difficult to print with due to serious warping and poor layer adhesion during printing.

This work investigated primarily the feasibility of manufacturing good quality 3D printer filament from provided CIRCO® recycled PP.

The empirical research of this work covered the attempt to find optimal extrusion parameters for manufacturing rPP filament.

After parameters optimisation during filament production, the ultimate result is still unsatisfactory in terms of the quality. The produced rPP filament has quite large diameter variations as well as it is not perfectly round-shaped, but rather elliptical.

MFI values comparison of the produced rPP filament with the two prevalent commercial filaments ABS and PLA was also made to see how the materials correlate on this score. The recycled PP showed considerably higher flow than both ABS and PLA, and at least with respect to this parameter, CIRCO® rPP is not comparable to them.

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