



Additive Manufacturing of Recyclable Multiple-Materials

Master Thesis

Ardhito Jehian Naindraputra

Additive Manufacturing of Recyclable Multiple-Materials

Master Thesis

by

Ardhito Jehian Naindraputra

Student Name	Student Number
Ardhito Jehian Naindraputra	5767075

Instructor: S. Abrahami
Project Duration: January, 2024 - April, 2025
Faculty: Faculty of Mechanical Engineering, Delft

Cover: Black and Silver Industry Machine by Kadir Celep
Style: TU Delft Report Style, with modifications by Daan Zwaneveld

Abstract

This study investigates the effect of repeated recycling processes on the properties of PLA matrix 3D printed filaments mixed with 20 wt.% Fe_3O_4 magnetic particles. The recycling process of the composite was simulated by using extrusion and manual cutting to achieve multiple closed-loop recycling processes. The research studied the 1st, 3rd, 5th, and 6th cycles, while the initial batch virgin materials (0 cycles) was used as a baseline.

Visual observations revealed that surface defects increase with each cycle, along with diameter inconsistencies and brittleness. The analysis showed that the 5th cycle had the highest diameter variation (range = 2.37 mm, standard deviation = 0.44 mm). The 6th cycle was unusable filament with a disoriented shape and chaotic flow behavior, which made it impossible to inject or print into the 3D printing machine. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDS) analysis indicated significant morphological changes, agglomeration of magnetic particles, and content reduction along cycles. GPC analysis confirmed that the molecular weight of the PLA decreased, and that the polydispersity increased, while NMR identified the absence of dichloromethane as a solvent, confirming that the degradation which indicated by PLA molecular weight reduction was solely caused by thermomechanical reprocessing effects.

The findings suggest that PLA/ Fe_3O_4 filaments can be processed up to five times, but the practical usability of the reprocessed filament is limited due to surface defects and poor filament diameter consistency. During the first cycle, the filament frequently stuck in the 3D printer feeder due to diameter inconsistencies, and by the third cycle, attempts to print resulted in improperly shaped parts, highlighting significant processing challenges. Additionally, repeated processing cycles lead to loss of magnetic particles, significantly affecting the filament's functionality. The characterization of using the Vibrating Sample Magnetometer (VSM) demonstrates a reduction in magnetic properties, with a 28.62% decrease in Cycle 3, a 51.41% decrease in Cycle 5, and a 73.91% decrease in Cycle 6 compared to Cycle 1. Moreover, thermal stability of PLA is also compromised, as evidenced by the decrease in degradation temperature recorded in the Thermogravimetric Analysis (TGA), highlighting the declining performance of the filament after multiple recycling cycles. Further improvements in processing methods, material quality, and testing are recommended to enhance recyclability and ensure consistent print results in future applications.

Acknowledgement

I would like to sincerely thank the following individuals who have played a key role in the successful completion of my master's thesis:

Shoshan, Ava, and Mehrshad : I want to sincerely thank my thesis supervisors, Shoshan, Ava, and Mehrshad, for their incredible support and dedication throughout my thesis journey. Your commitment to my academic progress has meant so much to me. I truly appreciate the time you've devoted to our meetings, offering thoughtful feedback and guidance. Your constant enthusiasm for my work has been a great source of motivation, encouraging me to push the limits of my research. I look forward to the possibility of working together again in the future. Thank you once again!

LPDP : I would like to extend my heartfelt gratitude to LPDP for their generous scholarship support. This financial assistance has been instrumental in allowing me to fully dedicate myself to my master's program and complete this thesis. I am committed to applying the knowledge and skills I've gained throughout my studies to contribute to the sustainable development of Indonesia. Thank you for making this journey possible.

KTB BAJGN : Nael, Jahns, Grendy, and Benaya. Our decade-long friendship has been an incredible source of joy and strength in my life. Your unwavering support, valuable feedback, and all the fun moments since high school have truly enriched my journey in ways I can't fully express. Thank you for being such an important part of my life.

Chrizia : I want to thank my best friend, even though we're miles apart—me in Indonesia and you in the Netherlands. Our long-distance friendship has been a huge support for me during this journey. You've always been there when I needed to talk, offering advice and encouragement, no matter the time or distance. I truly appreciate our connection, and I'm grateful for the bond we've maintained, despite the miles between us.

Papa, Mama, Abel, Bimo : Keluarga Naindra, I want to express my deepest gratitude for your unwavering support, love, and guidance throughout my journey. Your constant prayers, the wisdom you've shared, and the sacrifices you've made have been the foundation of everything I've achieved. Your belief in me and your endless encouragement have been my driving force, both academically and personally. I am truly thankful for everything you've done, and I will forever be grateful for your presence in my life.

Suster-suster Dadakan : I would like to extend my heartfelt thanks to my friends (especially Fakhri, Tita, Puti, Daoni, Petra) who stepped in as temporary nurses during my leg surgery and took such great care of me in CAMELOT. Your kindness, patience, and dedication during that challenging time meant more than words can express. You not only provided physical care but also emotional support, making the recovery process more bearable. I am incredibly grateful for your selflessness and the way you all went above and beyond to ensure I was comfortable and well taken care of. Thank you for being there when I needed you most.

APCH Friends : I would like to express my sincere gratitude to my Indonesian friend from the APCH Christian community. Your support, kindness, and companionship have been a great blessing to me. Through your faith and friendship, you've helped me find strength during both good times and challenges. Your prayers, encouragement, and the moments of fellowship we've shared have been a true source of comfort. I am thankful for your presence in my life and for the meaningful bond we've formed through our shared values and faith.

William : I want to thank my little brother, William, for offering me a place to stay during my time in the Netherlands while working on my sample making. Your hospitality, generosity, and the warm welcome you gave me made the whole experience so much easier and more enjoyable. I'm also grateful for the

countless stories and laughter we shared—it truly made those moments unforgettable. Thank you for being there for me, and for being such an amazing friend throughout it all.

Finally, I would like to express my gratitude to everyone whose names I may have unintentionally left out, but who have still played a part in my academic journey. Your contributions, no matter how small, have not gone unnoticed.

This thesis is the result of the collective efforts and support from all these individuals and institutions. Any mistakes or shortcomings in this work are solely my own. Thank you all for being such an important part of my academic path.

Thank you,

Ardhito Jehian Naindraputra

Delft, 16 May 2025

Contents

Abstract	i
Acknowledgement	ii
1 Introduction	1
1.1 Background	1
1.2 Research Question	3
2 Literature Review	4
2.1 Additive Manufacturing	4
2.1.1 Benefits and Challenges of Additive Manufacturing	4
2.1.2 Additive Manufacturing for Polymer Matrix Composite (PMC)	5
2.2 Application of the PLA/Fe ₃ O ₄ Composites	7
2.2.1 Polylactic Acid (PLA)	8
2.3 Polymer Recycling	9
2.3.1 Recycling in Additive Manufacturing : Processing Parameters	10
2.3.2 Recycled Polymers : A Review of Performance After Multiple Cycles	11
2.3.3 Recycling Impact Towards Composites Properties	17
3 Material Preparation and Characterization	23
3.1 Material Preparation	23
3.1.1 Material	23
3.1.2 Preparation Process	24
3.1.3 Shredding and Sieving	25
3.1.4 3Devo Filament Maker	26
3.1.5 Filament Production Parameters	27
3.1.6 Filament Production Process	27
3.2 Characterization	28
3.2.1 SEM and EDS	28
3.2.2 Vibrating Sample Magnetometer (VSM)	29
3.2.3 Thermogravimetric analysis (TGA)	29
3.2.4 Gel Permeation Chromatography (GPC)	29
3.2.5 Nuclear Magnetic Resonance (NMR) Spectroscopy	30
4 Result and Discussion	31
4.1 Filament Production	31
4.2 Characterization Result	34
4.2.1 SEM & EDS	34
4.2.2 TGA	37
4.2.3 VSM	40
4.2.4 GPC	41
4.2.5 NMR	42
5 Conclusion and Recommendation	44
5.1 Conclusion	44
5.2 Recommendation	45
References	47

Introduction

1.1. Background

The use of bio-polymers has increased in the global polymer industry. Recent market research by Dammer et al. [1] shows about 1-2% growth of biopolymer in the total polymer production in the Netherlands, Europe, and worldwide. Figure 1 illustrates the increase in bio-based polymers' production capacities in the Netherlands from 2011 to 2020. This indicates an ascending trend caused by the increased application of biopolymers in broad industry sectors such as textiles, automotive, packaging, and biomedical industries. The advantages of biopolymers include their biodegradability, biocompatibility, and low carbon production, making them appealing to multiple applications. Moreover, bio-polymers can be explicitly designed to meet specific requirements such as biocompatibility and easy availability [2].

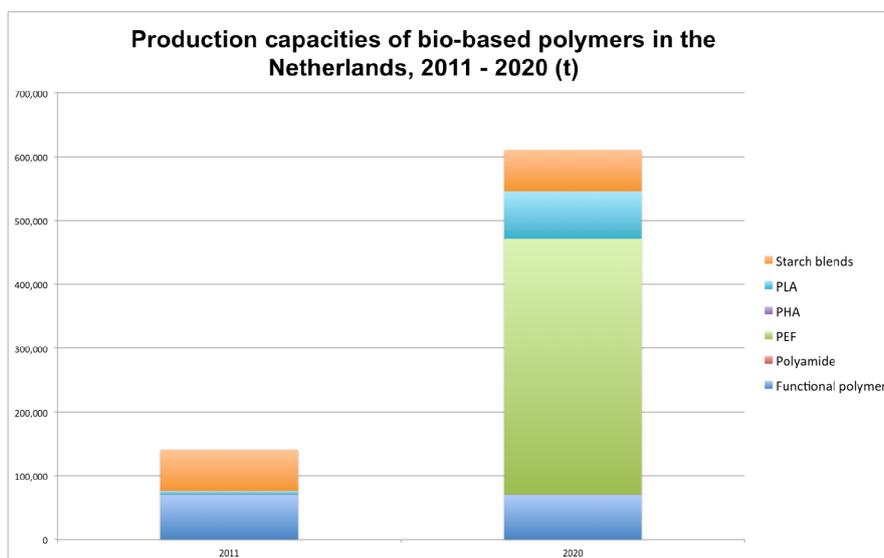


Figure 1: Production capacities of bio-based polymers in the Netherlands, 2011 and 2020 [1]

One of the bio-polymer advancements was the discovery of lactic acid by hydrolyzing ammonium lactate in the 1850s. In the 1930s, a chemist from DuPont first synthesized high molecular weight polylactic acid (PLA) with direct polymerization of lactic acid, which marked the first PLA ever produced [3]. Due to its versatility, PLA has gained interest across various industries because of its superior properties to other polymers used in additive manufacturing, especially in the application of the 3D printing sector. PLA is used as a feedstock because of its characteristics such as low melting point (150–160 °C), ease of the process, and favorable mechanical properties such as superiority in tensile, flexural strength, and

Young's modulus compared to other polymers (PS, PP, and PE) [4]. Furthermore, PLA's biocompatibility makes PLA widely used in biomedical sectors, including surgery equipment, customized anatomical models, bioprinting, controlled drug delivery systems, and frames for tissue engineering frameworks [5].

Along with the progress of the times, several technologies of additive manufacturing (AM) have been developed, including stereolithography, inkjet printing, selective laser sintering, laminate object manufacturing, and also fused deposition modeling (FDM) and fused filament fabrication (FFF) [6]. The most commonly used FDM and FFF technique uses a thermoplastic filament, with the plastic being continuously fed into the printer, heated, melted, and then extruded through the heating nozzle and deposited on the printing platform, creating the desired object layer by layer. Even though 3D printing is stated to be a more sustainable manufacturing method due to its ability to reduce raw and waste materials by reducing defect and post-processing steps by engineering the optimal process condition (such as nozzle temperature, printing velocity, and thickness of each layer), it still has a potential environmental impact because it still generates significant material waste, especially from the use of support structures required for complex prints [7]. 3D printing affects the environment by producing a significant number of waste [8]. Many filament materials could be thrown away during production for various reasons, including printing failure, snapped parts, unused support structures, and nozzle testing [9].

One of the uses of PLA as a 3D printing parts material is using it as soft robot parts. Soft robots can perform translation movement (e.g., a simplified grabbing action) and have contact with their surroundings without significant damage [10]. The shape and design of the soft robots are inspired by highly functional parts of living creatures' body parts (such as fish fins, elephant trunks, reptile fingers, and gecko feet) to produce flexible, functional, and durable robots [11]. Soft robots that can be controlled by magnetic fields are made using magnetic polymer composites (MPC). MPC uses external magnetic sources such as permanent magnets or electromagnets. This ability can remove the need for a built-in continuous power supply, like batteries, so the robot can be used as long as the external magnetic source is turned on [12]. Recent studies show that miniaturized soft robot designs can move in complex motion. These robots are suitable for medical fields because magnetic fields are safer for the human body [13].

Recycling PLA waste into new ready-to-use filaments can lower production costs. One study found that using recycled PLA filaments reduced expenses by 40% compared to using virgin PLA [14]. Utilizing recycled PLA also aligns with environmental goals by reducing plastic waste and reducing reliance on fossil fuels. This closed-loop recycling approach may contribute to a more sustainable lifecycle for PLA products. While PLA offers the possibility of closing the loop of 3D printing waste recycling, challenges remain when using recycled PLA materials in 3D printed parts. A study by Marec et al. [15] highlighted that different processing conditions (such as mixing time and temperature) have a critical role in the degradation of PLA during fabrication. The heat caused by friction between viscous material and extruder also accelerates this degradation.

While these findings contribute valuable insights, further investigation is still needed, particularly into the mechanical, thermal, and magnetic properties of PLA-based Magnetic Polymer Composite (MPC) after multiple recycling cycles. Although previous findings have indicated that the material waste can be reduced using Additive Manufacturing (AM) [16], the long-term feasibility of using recycled PLA-based MPC remains underexplored, specifically for applications like soft robots. This research tries to fill this gap by investigating how multiple reprocessing cycles can affect the mechanical, thermal, and magnetic properties of PLA-based MPC filaments. Through experiments that involve shredding and re-extruding recycled PLA-based MPC, this study aims to provide an understanding of the potential of using recycled PLA filaments for 3D printing soft robots, also addressing an essential gap in the literature on the recyclability and performance of PLA-based composites.

1.2. Research Question

These are the research questions that are sought to be answered in this study:

- What is the recyclability limit of PLA/Fe₃O₄ composites before significant degradation occurs, defined as the point at which the material exhibits excessive fluidity and can no longer be reliably extruded and printed as a filament?
- How do multiple recycling cycles affect the degradation behavior and magnetic properties of PLA/Fe₃O₄?

2

Literature Review

2.1. Additive Manufacturing

Additive manufacturing (AM) or 3D printing has become a resourceful technology in model making and prototyping using computer-assisted design (CAD). By using AM, manufacturers can produce customized parts from metal, ceramics, and polymers without using molds or post-processing, such as machining in subtractive manufacturing. Meanwhile, usual fabrication is limited by processing constraints caused by industrial mass production demand [17].

AM allows 3D structure fabrication with high complexity. Figure 2 shows the basic concept of 3D printing to help understand the basic concept of AM. In the beginning, a virtual object is made using CAD Figure 2a. Figure 2b shows a floating object (coffee mug handle) that is sketched to use temporary support to avoid structure collapse during the printing process. The virtual object has a coordinate that will be used to move motors, which move the position of the nozzle or the 3D-disperser orifice, which is illustrated by Figure 2c. This computer-aided manufacturing (CAM) method usually prints the material layer by layer with a thickness from 15 to 500 μm . In the case of a very thin thickness (below 50 μm , the naked eye can not see the stair structure, which is caused by the layered manufacturing process. Meantime, thicker layers normally demand post-processing application to remove support structures and enhance the surface properties.

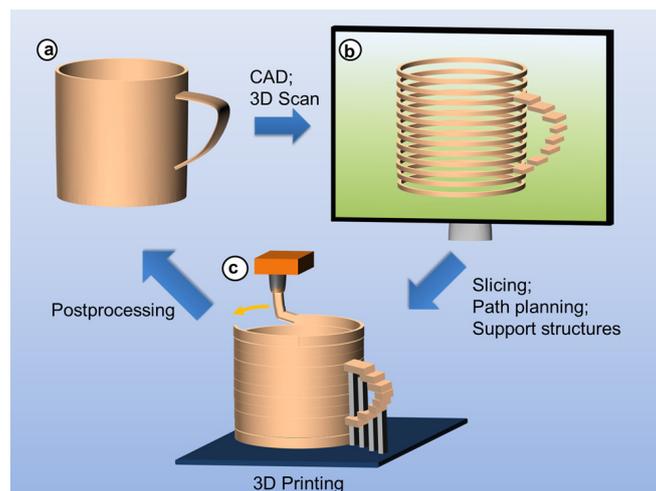


Figure 2: Basic principles of additive manufacturing (a) CAD sketch; (b)processing virtual model; (c)printing [17]

2.1.1. Benefits and Challenges of Additive Manufacturing

Additive manufacturing offers various significant advantages. One of the most common superiority is its freedom complexity design. With additive manufacturing, people can produce complex shape geometry

with complicated internal support, which could not be achieved using the conventional manufacturing process [18]. Also, additive manufacturing can make lightweight but superior mechanical properties, which is beneficial for particular sectors like aerospace and automotive engineering.

The next advantage of additive manufacturing is its sustainability through material efficiency [18]. Compared with subtractive manufacturing, which removes materials to make a component, additive manufacturing builds the component step by step by adding one layer on top of another. This method uses the material only when it's needed, without causing too much waste on the material. This approach can reduce waste and also production costs, which supports the sustainability of the industry. Besides that, potential on-demand production can decrease the need for storage and inventory space, which leads to resource efficiency.

However, additive manufacturing also has several challenges. One of the main challenges is the limitation on the material that can be used [18]. Even though additive manufacturing has been developed, achieving mechanical properties similar to conventional methods remains difficult. Porosity, residual stresses, and inconsistent printed parts could affect the mechanical properties of the product, which hinder its function as a load-bearing component. Furthermore, AM is difficult to mass produce due to slow production speed, which makes AM less suitable for high-volume production.

In addition, printing inconsistency will become a challenge which can reduce the structural integrity of AM components. Few factors like non-optimal processing parameters, material properties, and environmental condition causing weak spots [19]. These spots are caused by defects from lack of fusion or cracking within the solidified region during the manufacturing process. These defects can pose challenges in applying the repeatability and reliability of the AM process, which are important for fulfilling industry requirements.

2.1.2. Additive Manufacturing for Polymer Matrix Composite (PMC)

Polymer matrix composite uses multi-material printing techniques. These methods provide a precise and accurate deposition using different raw materials to fulfill certain requirements and design [20]. Moreover, pre-blended composite feedstock usage, which contains various types of fillers to improve the properties of the printed object, also increased [21]. The choice of composite design is mainly affected by which printing method system will be used. Nevertheless, this approach is good at infusing additional materials with distinct properties into the main matrix [22]. The field of PMC additive manufacturing combines advanced technologies and materials, imparting significant potential, cost reduction, simplicity, and other benefits [23]. Below are some examples of additive manufacturing techniques that can make PMC

Selective Laser Sintering (SLS)

Selective laser sintering is an additive manufacturing process that uses polymer powder particles then fused together using laser power. The basic principle of SLS is to fuse the polymer powder selectively by using a laser at targeted locations for each layer according to the design [24]. The condition of the final products is affected by processing conditions, particularly the power of the laser and the scan speed. Schimid et al. [25] stated that SLS is able to use various types of polymer powder as a raw material. In addition, SLS is also able to accommodate not only blended polymers but also polymer matrix composites [26].

Stereolithography

Stereolithography can be distinct from other additive manufacturing techniques due to its ability to fabricate mechanically stable and watertight polymeric channels by using a liquid photo-curable resin as a raw material [27]. SLA can be used for a wide area of industrial fields, including aerospace, automotive, biomedical, construction, and even fashion, as noted by Bartolo et al. [28]. The advantages of using SLA are its production speed, stability, mask-less operation, and layer-by-layer additive process that can create three-dimensional and lightweight structures effectively. SLA can utilize both natural and synthetic polymers, which makes SLA a promising potential method for biomedical applications [29] because of its ability to maintain the degradability and mechanical properties of the polymer.

Laminated Object Manufacturing

The laminated object manufacturing (LOM) technique build prototypes using laminate and laser cut to process the material such as polymeric films, foils, and metal laminates. LOM able to enhance the mechanical properties of these materials by transforming them into solid blocks [30]. LMO utilize the combination of adhesion joining, ultrasonic welding, and clamping methods to improve the materials.

Layers of sheet or foil are bonded to the block using heat and pressure which come from a heated roller. When the materials are fed from the side of the machine to the other side as shown by Figure 3, the platforms move down with the thickness of each new layer (ranging from 0,07-0,2mm). Shaping process involves laser (typically CO laser with 25 W or 50 W power) or knife to cut the post-layer deposition according to the determined design [31].

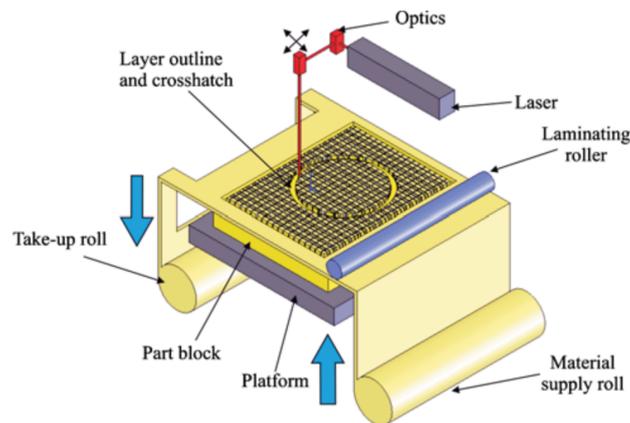


Figure 3: Laminated object manufacturing [31]

LOM superiority compared to other methods is its ability to remove the need for external support structures. Supportive material is needed during the manufacturing process to hold the geometry of the product from deformation. Nonetheless, it is very challenging to remove the supporting structure and needs manual hand work to reduce the damage to the sensitive parts. Especially for the parts with hollow or small passages that are very difficult to reach and clean.

One of the disadvantages of LOM technology is that it is costly due to its principle of using material temporarily. The materials are not included as the end products and will become waste after building, particularly when the manufacturer uses expensive materials. However, LOM is a unique AM method due to its basic principle of production, which cuts the material to form layers, instead of other prototyping methods, which build layer by layer [32]. As a result, the mechanical properties of the prototypes may vary throughout the production due to the increasing layers of material and adhesive. LOM is a precise method because of its ability to process very thin sheets that can lead to very good detail in prototyping. LOM can work with various materials, including composites, metals, and polymers, but PVC films and paper sheets are the most widely used materials.

Inkjet

Inkjet typically processes two-dimensional materials such as organic color inks. However, there is a rapid growth in inkjet technology usage for non-graphical purposes especially in micro-engineering fields. The basic principle of inkjet printing is the printer deposits the materials selectively in a precise manner [33]. The inkjet printing technology evolved eventually, making the printer able to deploy smaller droplets up to a few pico liters. The inkjet printer function has been enhanced due to this technological advancement, which enables the fabrication of more complex shapes with micrometer-scale features by utilizing computational topology design (CTD).

The most common function of inkjet in the industrial field is the manufacture of electronic components such as light-emitting diodes (LEDs) and thin film transistors (TFT) due to its versatility, simplicity, and cost-effectiveness [34]. Additionally, inkjet has been adjusted for biomedical applications as a consequence of the requirement of precise microscale patterning from biological molecules such as proteins, peptides, and DNA [35]. Three-dimensional printing for inkjet methods has been achieved by utilizing

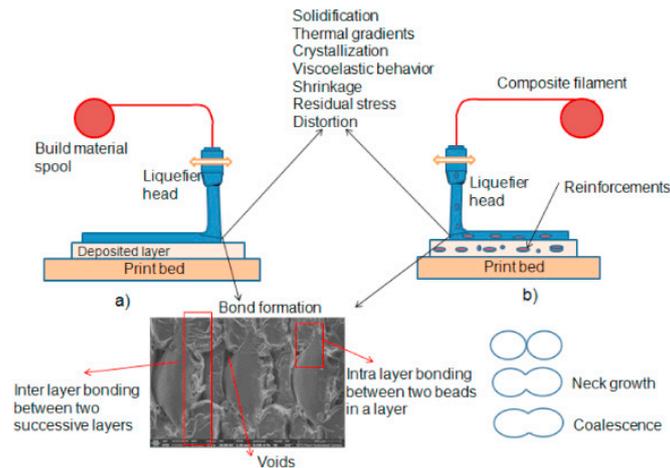


Figure 4: Schematic and illustration of different physical phenomena during FDM process: a) printing of neat polymer b) printing of polymer reinforced with particle fillers or short fibers. [38]

polymer ink as a feedstock. The combination of polymeric materials feedstock with inkjet technologies unlocks new opportunities for 3D printing, which allows for the creation of a wide range of structures. In spite of all these benefits, Yun et al. [36] stated that inkjet printing is still limited by various factors such as polymer concentration, polymer ink composition, and solvent type.

Fused Deposition Modeling (FDM)

Fused deposition modeling (FDM) is one of the most commonly used techniques worldwide and has become a broad research subject. Parandoush et al. [37] highlighted that FDM is responsible for 41,5% of the market sales, with up to 15.000 units sold in 2010. Basically, FDM operates by using the extrusion principle. FDM used to be only compatible with pure thermoplastics, but due to technological advancement, FDM is able to handle reinforced feedstocks. FDM popularity also increased because of its traits, which are cost-effective and able to produce various types of materials. As time goes by, FDM has been used to fabricate products using extensive types of materials such as plastics, ceramics, metal powders, and composites through various sectors such as aerospace, medical field, automotive, and mold design [38]. In FDM, filament materials are sent through a heated nozzle and deposited layer by layer in a semi-solid state. As illustrated in Figure 4, the setup of FDM includes platform building, a printer bed, a liquefier head, and a spool of build materials. Further details regarding the technology, materials, and application will be elaborated further in this section.

The product quality of the printed parts is affected by numerous physical events during the process of printing, as illustrated in Figure 4. The unity and properties of the printed parts are notably influenced by the quality of the bonds. The bond formation process that connects two layers implies surface contact, molecular diffusion, and neck growth [39]. These bonding happened between consecutive layers (inter-layers) and also within a single layer (inter-layer). The limited time for solidification will lead to incomplete neck growth and partial blending. As a result, void formation will appear between layers, as shown by Gurralla et al. [40] during the bonding process analysis. The occurrence of these voids causes a reduction in the strength properties of FDM parts compared to parts manufactured by other methods, such as injection molding. Moreover, temperature changes between each layer during solidification can cause the printed part to shrink, develop internal stress, and become distorted. The build chamber temperature has an important role during the FDM process. Additional thermal stresses and 3D-printed part warping are caused by the temperature difference between the filament and the build chamber. These stresses can be reduced by frequently heating the build chamber to a high temperature.

2.2. Application of the PLA/Fe₃O₄ Composites

This study aims to learn more about the recycling of waste from the production of 3D printing filaments mixed with magnetic particles. In the past study, these filaments were utilized for soft robot manufactur-

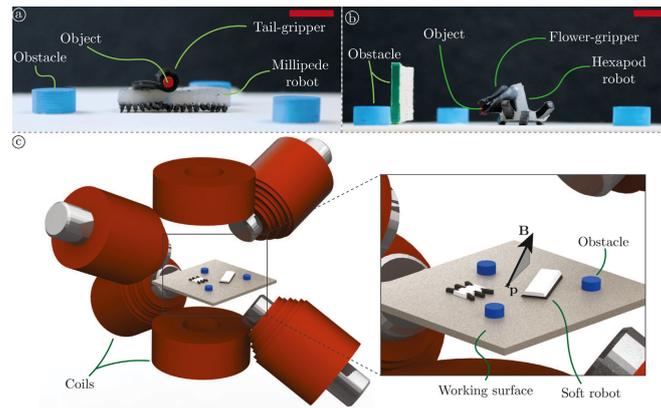


Figure 5: Small-scale magnetic soft robots capable of tandem actuation of grasping and locomotion. a) 'Millipede robot' with a 'Tail gripper' carrying a cylindrical object and b) 'Hexapod robot' with 'Flower gripper' carrying a spherical object. Scale bar is 10 mm. c) The actuation of the soft robots is achieved using BigMag: an array of six movable electromagnetic coils, capable of generating a magnetic field (B) at any point (p) within the workspace. [10]

ing. This section provides a general explanation of how soft robots will perform for real-life applications based on Venkiteswaran et al. study [10]. In this study, the soft robots was designed based on a bio-inspired multi-legged with grasping manipulators as shown in Figure 5. The robots consist of two parts: the locomotion and the grippers that wireless function utilizing electromagnets phenomenon. The robots and grippers are made using MPC and magnetized in certain patters in purpose to make them able to move untethered. The basic principle for soft robot movement is that it has multiple legs that produce variable displacement through the geometric biasing of magnetic dipoles inside the robot body. As a result, these robots perform a repeatable motion, including consistent steering accuracy. Meanwhile, the grippers are designed to grab and release objects when triggered and hold the designated objects during the robots' movement. The robot designer has engineered the robots and the grippers so they will not interfere with each other.

2.2.1. Polylactic Acid (PLA)

Various polymers are used as matrix materials in the 3D printing process. Each polymer has its own characteristics and mechanical properties. Table 2.1 compares the mechanical properties of various polymers, which are typically used as a material in the 3D printing processes, such as PVC, PP, PS, and nylon. PS has the highest tensile modulus, showing that PS is the stiffest material among all. PLA has a relatively high tensile modulus, indicating it is also quite stiff, followed by Nylon. On the other hand, nylon has the highest yield strength, which makes it the strongest material before reaching deformation. PLA and PS have the same value and are stronger than PVC and PP. From the flexural strength point of view, Nylon exhibits the highest value, which means it has great resistance to bending. PVC and PS also have higher flexural strengths than PLA, showing their performance in applications requiring bending resistance. PP is the most ductile material because it has the highest elongation percentage and can stretch before breaking. PLA and PS have the same value but at a relatively low rate, indicating they have less ductile properties. In comparison with all polymers in the table, nylon stands out as the material with the highest overall mechanical properties, flexural strength, and yield strength, making nylon suitable for objects requiring high strength and flexibility. Besides that, PLA has a good tensile modulus and yield strength but is less ductile compared to PP and Nylon and also has moderate flexural strength.

Due to its innate biodegradability characteristics, biopolymers receive more recognition as 3D printing materials [41]. Different biopolymers have been used as matrix materials combined with various reinforcements in order to manufacture biocomposites. Among other polymers, PLA was favored because of its compatibility with different natural reinforcements and promising mechanical and physical properties [42]. PLA has biocompatibility, biodegradability, and non-toxic properties, making it appealing to be used as material in structural components and as a functional polymer [43]. For example, in paper materials, PLA can be used as an additive, adhesive, coating, thickening agent, concrete agent, and flocculant. PLA only need simple conventional process with less energy and time cost cause PLA has

cheaper and more available polymer, PLA also can be easily designed in various shape and using various fabrication techniques such as extrusion and injection molding.

Table 2.1: Comparison of properties between PLA and other polymers [44]

Polymer	Properties			
	Tensile Modulus (GPa)	Yield Strength (MPa)	Flexural Strength (MPa)	Elongation (%)
Polylactic Acid (PLA)	3.2	49	70	2.5
Polyvinyl chloride (PVC)	2.6	35	90	3
Polypropylene (PP)	1.4	35	49	1
Polystyrene (PS)	3.4	49	80	2.5
Nylon	2.9	71	95	5

2.3. Polymer Recycling

Plastic production has increased from 1.5 tonnes in 1950 to 359 million tonnes in 2018, which caused a significant increase in plastic waste [45]. Based on the data from the European Parliament, in Europe, one-third of plastic waste is recycled, while energy recovery using incineration is the most common disposal method, with 25% of plastic waste still landfilled. Due to limited local processing capacity, a large portion of plastic waste collected for recycling is exported to non-EU countries such as India, Egypt, and Turkey. Low recycling rates in EU cause economic and environmental losses, as example 95% of plastic packaging material's value is dropped after single-use cycle. In 2019, plastic production and incineration contributed to over 850 million tonnes of global greenhouse gases. It is predicted that there will be a rise of the gases to 2,8 billion tonnes by 2050 if there are no improved recycling efforts.

To tackle this problem, countries in the EU have made an effort, which is shown by the recycling rate from data in Eurostat. From Figure 6, we can see that the highest recycling rate is Belgium 80%, followed by Netherlands and Slovakia in the range between 70-80%. Plastic waste management has emerged and become an important global issue, while recycling comes out as a key strategy to reduce environmental damage caused by waste and also can improve resource sustainability. Among the various recycling methods, mechanical and chemical recycling are two well-known approaches that are used to process plastic waste. Mechanical recycling is a method that focuses on processing plastics without altering any chemical structure, while chemical recycling offers a more advanced way of breaking down polymers into their basic molecular components.

Mechanical Recycling

Mechanical recycling is a process of transforming plastic waste into raw materials or products without altering the chemical structure of the waste material [46]. Plastic waste that has been sorted will be washed and undergo flotation separation and drying. The plastic flakes will undergo further processing into granulates or plastic pellets. The main focus of recycling is on thermoplastics because of their ability to be re-melted and re-processed into the final products by using techniques like injection molding or extrusion. Examples of plastics which commonly recycled are polypropylene (PP), polyethylene (PE), and polyethylene terephthalate (PET).

Sorting is an important first step in the mechanical recycling process. The plastic waste is contaminated, often consisting of various types of materials (e.g., composites, blends, and multilayer films) with different colors, shapes, and sizes. The plastic waste is initially brought to a sorting facility to be separated according to its material type. Proper material identification is needed to obtain maximum purity in the recycled product. Therefore, various technologies such as near-infrared (NIR), laser, or x-ray are used. The challenge in achieving 100% separation is the presence of blended or laminated products, which are very hard to be separated into individual materials. At the end of the process, the material will be recovered through smelting and granulation. In this process, high temperature and

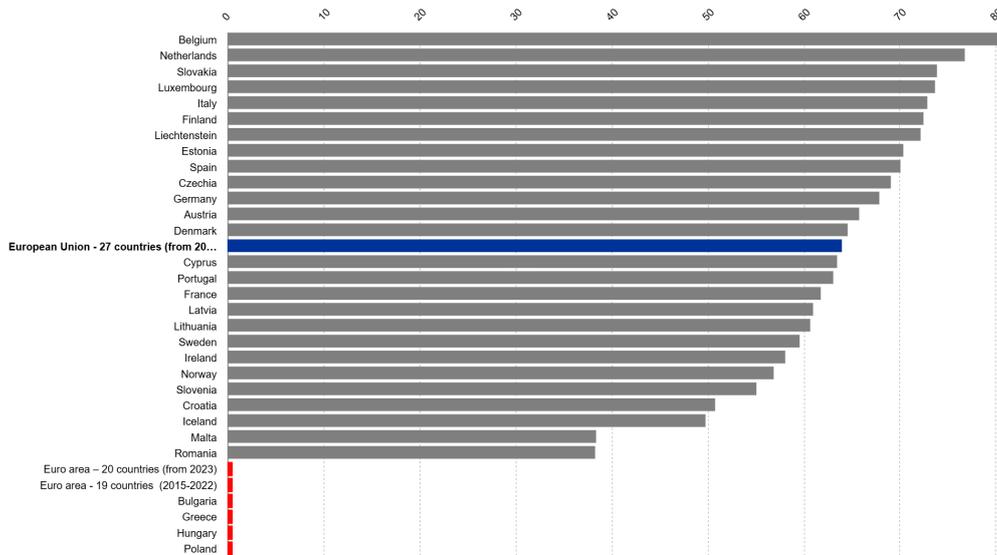


Figure 6: Recycling rate in EU countries (2021)

shear force cause thermomechanical degradation to occur, which affects the chain length and distribution and has an impact on material properties such as crystallinity and mechanical strength [47]. Too much contamination will cause the products to not meet the specifications of virgin materials, leading to a decrease in material value (down-cycling).

Chemical Recycling

Chemical recycling is a method of recycling that processes polymeric waste by altering its chemical structure and returning it into a substance that can be used as a raw material again [48]. The basic principle behind chemical recycling is breaking the plastic waste down into its constituent molecular parts so that the waste can be reconstituted into original raw materials again.

Chemical recycling has a wide scope, based on its technologies, it divided into three distinct categories according to the output position of the plastic [49]. First is dissolution, where in this process additives are removed from the polymer by immersing the waste in a solvent. The plastic then will dissolve and revert to its polymer stage. The polymer stage will be used by reformulating it into new recycled plastic. Second is depolymerization which involves a solvent and heat to break the polymer down into smaller molecules or monomers. The monomer then later serves as a feedstock for plastic production as secondary raw materials. The third is conversion, which is the principle of utilizing a catalyst to help break down plastic waste into either liquid, gas, or oil-like feedstocks like hydrocarbons.

2.3.1. Recycling in Additive Manufacturing : Processing Parameters

Most polymers that are recycled are thermoplastic because of their characteristic to become soft when heated. A previous study by Hemmati et al. [50] found that factors can affect the blend's morphology. These are the components' mass ratio (composition of the blends), the blending sequence, material properties, and the process parameters. In this study, we will only focus on the process parameters. The extrusion process is commonly used to reprocess the plastic pellets. Plastic materials have to be plasticized and mixed, which is done by using a screw extruder machine. The extruder works by generating pressure and shear force to push or press the polymer material by utilizing the rotation of the processing screw [51]. As a result, the polymer undergoes full plasticization and uniform mixing to make products in the desired shape.

The extruder has three zones: the feed or solid conveying zone, the compression or melting zone, and the metering or melt pumping zone. The feed zone has a function as a place to feed raw materials by utilizing the principle of drag flow (relative motion between the material and the screw or barrel walls). The polymer solid particles are going to be compacted together in the screw channel to form a solid layer of material [52]. The temperature in the feed zone could not be too high because it can

cause the material to get stuck on the screw or barrel walls which causes solid conveying instabilities. In the melting zone, the plasticization process occurs where the material undergoes a transition from solid state to molten state. Therefore, strict temperature control is required. When the temperature is too low, the viscosity will become too high, which causes the material's flow capacity to weaken. Consequently, it will reduce the plasticizing effect and leave unmelted material in the product. However, if the temperature is too high, the degradation will occur and reduce the product quality. In the melting zone, the material is expected to be in the molten state. It is required to set the specific temperature to avoid premature curing during processing [53]. The process parameters which can affect the recycling product that is going to be discussed in this study are the effects of screw speed and barrel temperature on the screw extruder machine.

Barrel Temperature

In their study, Shokoohi et al. [54] found that there was an effect of barrel temperature on material properties. Shokoohi found that Young's Modulus of polymer blend that was processed at temperature 240 °C was better than the one processed at temperature 220 °C. This is related to the reduction in interfacial tension between phases due to the increase in temperature, which reduces the size of the equilibrium particle. Subsequently, it increases the degree of dispersion of the minor phase and leads to the improvement in Young's Modulus [50]. Reducing interfacial tension also causes an increase in interfacial adhesion that can enhance the tensile properties of polymer blends by decreasing the generation of voids and defects [55]. However, there is also a finding by Capone et al. [56] who discovered in their study that the effect of high temperature can accelerate the degradation process of the polymer in the barrel, causing local burning, especially in the local hot spot of the extruder barrel.

Screw Speed

Besides barrel temperature, screw speed is also one of the keys parameter in the extruder machine. The rotational motion generated by the screw gives the extruder the power to push the material forward, and changing the screw speed will cause a change in the rate of extrusion material. The higher the speed, the faster the extrusion rate and it will become more efficient in terms of process energy [57]. If the screw speed is too slow, the shear effect on the material will become smaller and causing the material to get stuck inside the barrel so that the barrel transfer more heat to the material. However, if the screw speed is too high, the material will be extruded too fast from the barrel and causing uneven material melting and leading to a poor plasticizing effect. Moreover, if the extrusion speed is too high, poor extrusion stability will occur and cause residual thermal stress to form inside the products, negatively affecting the product quality [58].

In his study, Shokoohi et al. [54] observed there were changes in the tensile properties of the polymer blend of polypropylene (PP) with polyamide6 (PA6), which was influenced not only by the barrel set temperature but also screw speed. Initially, the Young's modulus and yield stress decreased; then, after the rotational speed was raised, the Young's modulus and yield stress increased. When the screw speed increased from 90 to 120 rpm, the tensile properties decreased because of the influence of thermomechanical polymer chain fracture caused by high shear force generated by raising the screw speed that produce high shear viscous heat generation. However, when the speed increased to 150 rpm, the PA6 polymer particles changed into fibrous rods within the matrix. This phenomenon led to an increase in yield stress and Young's modulus. According to their study, Jazani et al. [59] found that increasing the screw speed stimulates the breakage process in the minor phase inside the matrix, which prevents agglomeration and increases the degree of dispersion and results in tensile properties improvement.

2.3.2. Recycled Polymers : A Review of Performance After Multiple Cycles

The consumption of polymers, especially plastics, has significantly increased in the past few years due to the growing demand for plastic production. Recycling become a promising strategy to solve the environmental issues caused by high polymeric waste. Recycling polymeric waste aims to preserve the natural resources because most polymers materials are made from oil and gas, hopefully recycling can close the production loop to reduce the usage of raw materials [60]. In this subsection, several recycling efforts will be discussed, as well as the effect of recycling, especially the degradation effects of several kinds of polymers.

Polyethylene (PE)

PE experiences the degradation effect after the recycling process. Jin et al. [61] reported the effect of mechanical recycling on rheological and thermal properties during low-density polyethylene (LDPE) recycling projects. LDPE samples go through numerous extrusion cycles, up to 100 cycles. Figure 7a indicate the result of complex viscosity increased a long with the number of extrusion cycles. Samples are tested using a low test frequency, 0,628 rad/s. This phenomenon is caused by the crosslinking reaction, which occurs due to the presence of reactive radicals carbon throughout LDPE chains during the recycling process [62]. A similar tendency was observed in the melt flow index (MFI) measurements shown by Figure 7b, where there was a decrease in the MFI value aligned with the increase in the number of extrusion cycles. This study showed that the processability of LDPE was significantly affected after 40 times extrusion cycles. Moreover, Kartalis et al. [63] found that recycling the LDPE showed significant processing stability even after five consecutive extrusion cycles if LDPE mixed with medium-density polyethylene (MDPE). Meanwhile, Valim et al. [64] are able to recycle high-density polyethylene (HDPE) waste using virgin polyamide (PA6) by using a twin-screw extruder. The result of their studies was the improvisation of prepared blend mechanical properties and thermal stability caused by size domain reduction of the recycled HDPE.

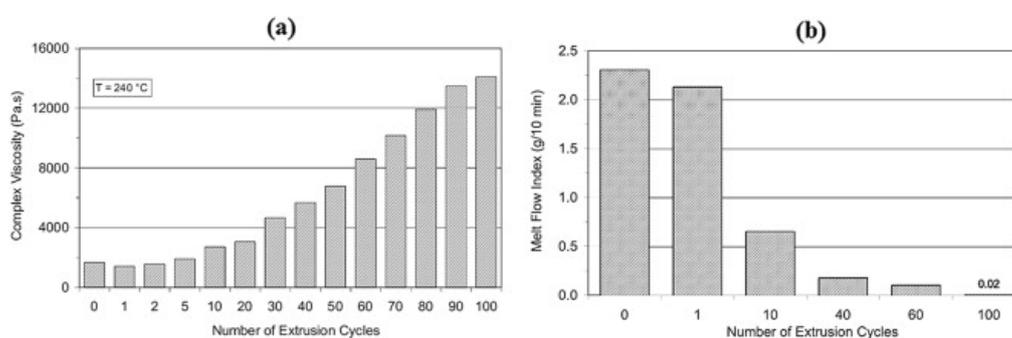


Figure 7: Complex viscosity and MFI of LDPE after extrusion cycles [61]

Polypropylene (PP)

Aurrekoetxea et al. [65] inspected the morphology and properties of polypropylene (PP) samples that were treated with multiple injection cycles. The study stated that PP melt viscosity decreased after processing because of the molecular weight reduction caused by reprocessing. In addition, the recycled PP revealed a higher crystallization rate, greater crystallinity, and an increase in equilibrium melting temperature in comparison to virgin PP. There were also changes in mechanical properties, Young's modulus, and yield stress increase along with the number of injection cycles. This event attributed to the enhanced crystallinity of PP after processing, on the other hand reduction of PP molecular weight cause the decline in elongation at break and also fracture toughness.

Phuong et al. [66] conducted research about the recyclability of polypropylene and other organophilic-modified layered silicate nanocomposites with a twin-screw for over ten cycles at various temperatures. Phuong investigated the changes in mechanical properties and rheological of PP after each cycle. The result showed that with the increase in the number of extrusion cycles, the melt flow index (MFI) also increased. This behavior is already observed in several studies on PP recycling and its stability which is caused by the role of thermal degradation during extrusion [67]. Results from mechanical testing showed that recycled PP tensile strength declined with the increasing number of extrusion cycles, but the impact strength remained unchanged, as shown in Figure 8. Some other studies found that recycling by preparing the PP composites using extrusion had an effect on the rigidity of PP. The outcome showed that the rigidity of composites was still almost unchanged after several processing cycles, which was caused by effective stabilization of the fiber aspect ratio after recycling.

Another recyclability of PP composites was also studied by Bahlouli et al. [68] who investigated another type of PP composites recyclability, specifically ethylene propylene diene monomer (EPDM)/PP and talc/PP utilizing extrusion process. This study focused on the mechanical, rheological, and structural properties of PP composites after being treated with numerous extrusion cycles. The results showed

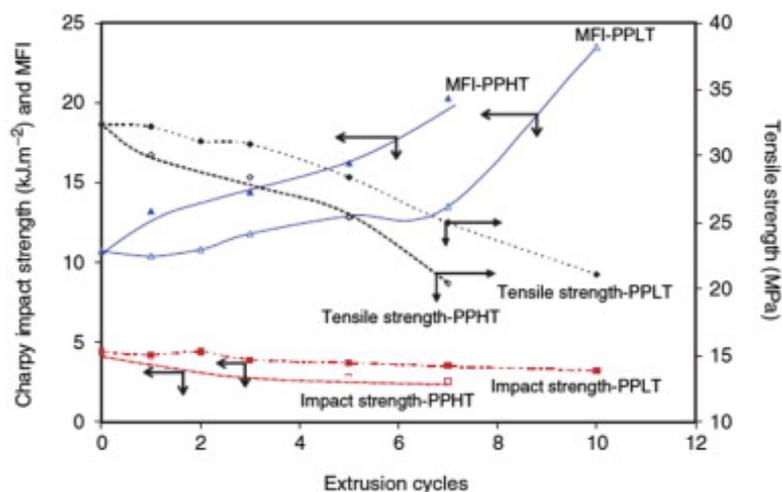


Figure 8: Effect of the extrusion cycle on the mechanical properties and MFI of polypropylene/organophilic modified layered silicates nanocomposites [66]

that with the increase in the number of processes, the melt viscosity of the composites also decreased. Similar behavior was also observed when using pure PP [69]. Moreover, the mechanical properties of the composites also experience a decrease along with the number of processing cycles. The reason behind these changes in the composite's properties was the alterations in the structural properties during the recycling process. The discoveries from this study are important for increasing the quality of the recycling process and also improving the utilization of recycled materials in component design.

Polystyrene (PS)

Studies about the effect of recycling acrylonitrile butadiene styrene (ABS), impact polystyrene (HIPS), and a blend of ABS and HIPS waste were conducted by Brennan et al. [70]. The mechanical and thermal properties of both virgin and recycled ABS and HIPS were investigated and compared in this study. The result was the recycling process has an insignificant effect on the tensile strength and tensile modulus for both ABS and HIPS, which contain a small amount of the two components (ABS and HIPS) shown in Figure 9 a and b. Nonetheless, the impact strength and also the strain at the break of the polymer blend were highly impacted compared to the virgin and pure components Figure 9 c and d. These findings reveal that adding a small amount of ABS or HIPS is able to increase the tensile strength and modulus of the polymer blend after recycling.

Elmaghor et al. [71] used poly(ethylene-co-vinyl acetate) and poly(styrene-b-ethylene/butylenes-b-styrene) as compatibilizers in a ternary polymer mix made from waste polymers, including polystyrene (PS), high-density polyethylene (HDPE), and polyvinyl chloride (PVC) by using a single-screw extruder. The extruded materials were subjected to gamma radiation in order to enhance the compatibility of the mixed components. The outcome presented was notable, which showed that compatibilizers and gamma irradiation greatly improved the mechanical properties of the blend. Also, highly enhanced its impact strength and ductility with a small improvement in its tensile strength.

The impact of reprocessing cycles on properties and structure of PS nanocomposites which contain 5wt.% organophilic clay, marketed as Cloisite 15 A, was studied by Remili et al. [72]. This study analyzed the rheological, mechanical, and structural properties of the composites after being subjected to reprocessing cycles and compared them with pure PS samples. As shown in Figure 10, the PS/Cloisite 15A composites had better recyclability and reprocessability compared to pure PS. This difference was caused by an increase in the molecular weights of the composites after experiencing eight processing cycles, and then crosslinking occurred [73]. Meanwhile, the molecular weight of pure PS decreased to around 49% after eight cycles.

Acrylonitrile-butadiene-styrene copolymer (ABS)

Boronoa et al. [74] researched the impact of reprocessing cycle conditions on the properties of acrylonitrile butadiene styrene (ABS), especially its shear rate and temperature. Two grades of ABS were

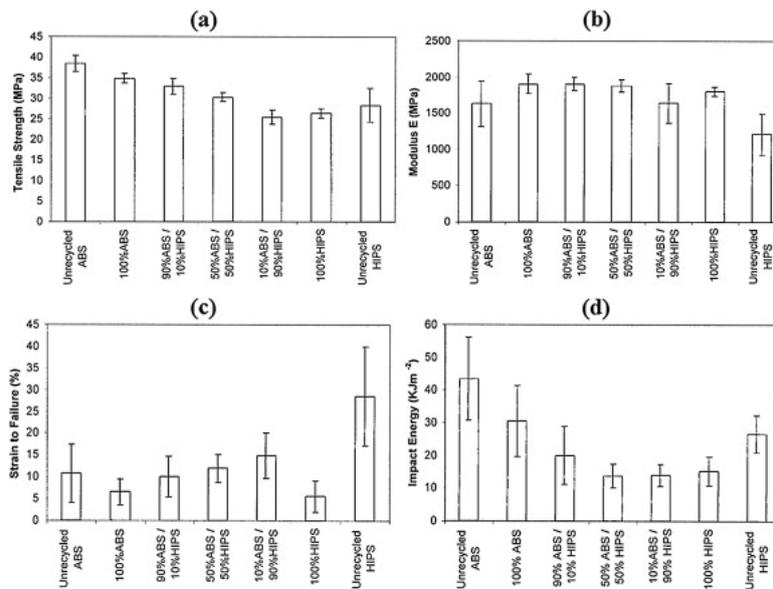


Figure 9: Mechanical properties recycled ABS and recycled HIPS blend [70]

used in this experiment, one with high viscosity and the other with low viscosity. The results showed there was a distinct behavior between each grade. The high viscosity grade exhibited an increase in melt viscosity when the number of processing cycles increased. On the other hand, the low viscosity grade showed a reduction in viscosity as the number of processing cycles increased.

Perez et al [75] investigated the effect of reprocessing towards the mechanical, thermal, and rheological properties of ABS. The results indicated that melt viscosity and tensile strength were insignificantly affected by the number of processing cycles. This suggested that ABS performed a good mechanical recyclability; moreover, adding toughness agents could improve the impact strength after recycling. The results of this study were aligned with Karahaliou and Tarantili [76], who studied the stability of ABS that had experienced five extrusion cycles. In their study, ABS was able to demonstrate good mechanical and rheological stability during the processing cycles.

Another effort to process ABS waste was made by using ABS waste as an additive, and the effect of additive content on the mechanical properties of the blend was analyzed [77]. The results showed that adding ABS waste had an insignificant effect on mechanical properties such as tensile strength, elongation at yield, flexural strength, flexural modulus, and impact strength. Even so, adding more waste content led to higher values of hardness, melt flow index, and glass transition temperature in the blend.

Similar research was done by Scaffaro et al. [78], who studied the effect of ABS waste content in the mixing of virgin and recycled ABS. They also examined the impact of reprocessing cycles on the mechanical properties of mixed blends. The result showed that the viscosity of the blend was not highly affected by increasing the content of recycled ABS. However, the viscosity of the blends decreased with increasing the number of processing cycles which shown by Figure 11a. The mechanical properties were also affected, which was shown by the decrease of tensile strength, tensile modulus, elongation at break, and impact strength, along with the number of processing cycles. In addition, Figure 11b illustrated the small decline in the mechanical properties along with adding more ABS content.

Yeh et al. [79] studied the comparison between ABS/wood composites and composites made with virgin ABS by utilizing ABS waste as an additive in the ABS/wood composites. A twin-screw extruder was used to make composites containing 50% wood and also a coupling agent, and characterized the mechanical properties. The result of the study showed a significant contrast in impact strength and ductility between recycled polymer and virgin materials. However, the composite properties only showed slight differences.

Bai et al. [80] investigated the effect of reprocessing on the mechanical properties of ABS/CaCO₃ com-

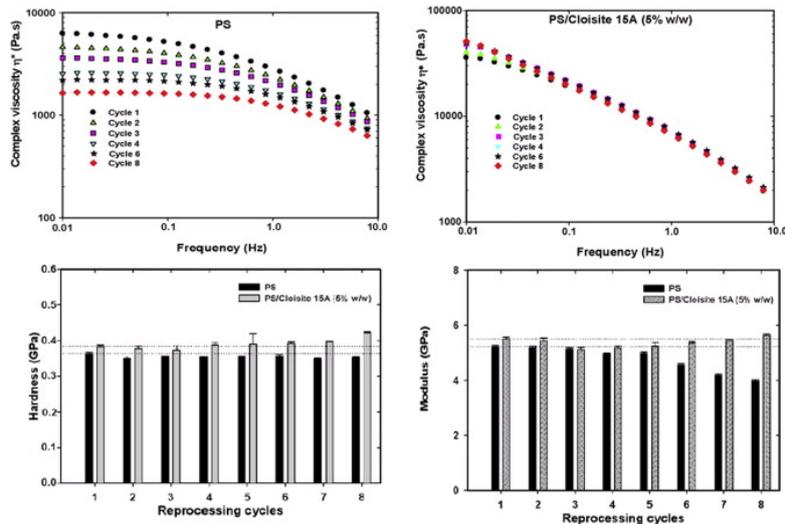


Figure 10: Effect of recycling on the melt viscosity and mechanical properties of PS and PS/Cloisite 15 A nano composite [72]

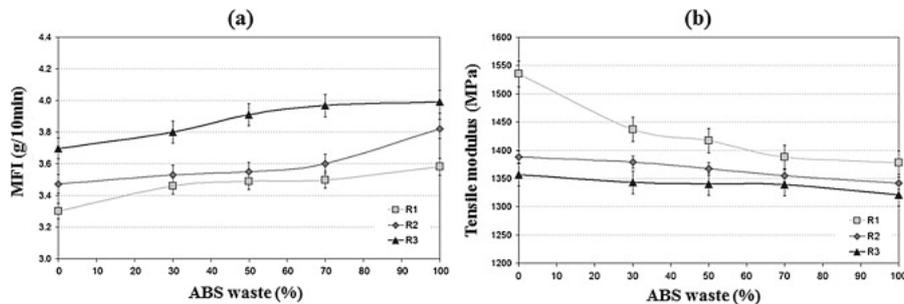


Figure 11: Effect of the recycled ABS content and number of extrusion cycle (R1, R2 and R3) on (a) MFI and (b) tensile strength of virgin ABS [78]

posites. The outcome of the study was in low CaCO₃ content conditions (less than 10%); increasing the number of processing cycles caused a decrease in the impact strength of the composites due to thermal gradation from the rubber phase inside ABS. Nevertheless, in high CaCO₃ conditions (greater than 15%), the impact strength of the composites increased aligned with the number of processing cycles.

Poly(lactic Acid (PLA))

Biodegradable polymers, such as PLA, will undergo a thermos-mechanical recycling process during reprocessing. Thermos-mechanical recycling using reprocessing and reusing PLA material is predicted could reduce the production energy and also closed the loop of production, as stated in Papong et al [81] research, compared to recycling method that use incineration and chemical recycling. It is recently considered as a new end-of-life framework for this variant of polymer. A previous study by Pilin et al. [82] was able to recycle PLA seven times, including the injection molding process, and detected a decrease in glass transition temperature from 66 to 57 °C. Additionally, the molecular weight also dropped to 50% after three recycling cycles and the viscosity decreased from 3960 Pa.s to 25 Pa.s after seven cycles, also the crystallinity increased surpassing 50%. Badia et al. [83] stated that with the increase of crystallization enthalpy, the chain scission occurs, but the cold crystallization reduced around 10 °C. Moreover, in this research, PLA remains in the amorphous stage during recycling, and there are no noticeable changes in the functional group, which is observed by FTIR.

Brüster et al. [84] found that PLA able to withstand up to 5 successive reprocessing cycles which include extrusion and compression molding. Furthermore, it was also found that there was considerable embrittlement of PLA due to a significant decline in its tensile and impact properties. It was found that the reason behind PLA degradation was chain scission. This process implied the breaking of the

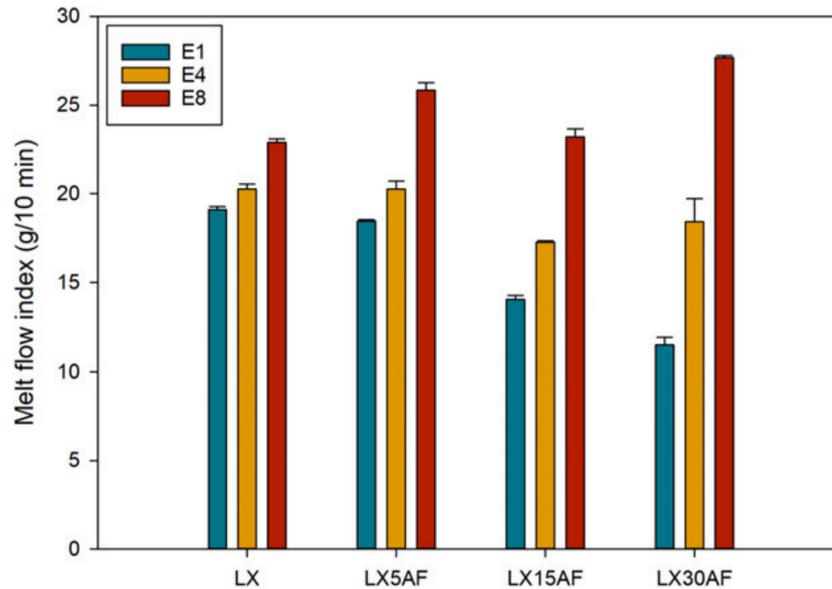


Figure 12: Melt flow index of PLA and its biocomposites subjected to different reprocessing cycle [86]

polymer chain into shorter chains. The chain breakage found happened randomly along the polymer chain. When PLA was reprocessed, it undergoes thermal and mechanical stress which stimulate the breakdown of polymer chains and also lead to a decrease in the molecular weight [85] that can affect the PLA mechanical properties. Moreover, during elevated temperatures, the thermal energy can snap the covalent bonds within the polymer chain. This type of degradation commonly occurred on extrusion or injection molding.

Ramos-Hernandez et al [86] studied the effect of mechanical recycling of PLA that mixed with agave fiber bio composites. The biocomposites were used and mixed by using extrusion with 5, 15, and 30 wt%, and also it was reprocessed eight times. The result of this study indicated that the dimensions of the fibers were reduced significantly when reprocessing. The most notable reduction happened after the initial reprocessing cycles, followed by a more gradual decline with each cycle. Figure 12 shows the result from the melt flow index (MFI) for the PLA and its fiber biocomposites. For plain PLA, the MFI increased 22%, from 18.7 g/10 min to 22.9 g/10 min after 8 extrusion cycles. This increase was caused by chain scission from mechanical forces during extrusion, which led to PLA viscosity reduction. On the contrary, by adding 5, 15, and 30 wt% of fiber in the first cycle caused the MFI to decrease 3%, 26%, and 40% respectively. This decline was linked to the higher viscosity of bio composites along with increase in the fiber content [87]. After 8 extrusion cycles, the MFI of bio-composites with 5, 15, and 30 wt% of AF increases by 40%, 65%, and 140%. The presence of the fiber was enhancing the shear forces during extrusion, was lead to a greater degradation in bio composites with higher fiber concentrations [88]. Even though the PLA degraded with its fiber during reprocessing cycles, Zenkiewicz et al. [89] found that the MFI of PLA increased by 194% after 10 extrusion cycles. These studies indicated that the degradation of PLA and its fiber biocomposites were limited to around 8 to 10 cycles.

The twin-extrusion process is typically used for blending polymers and additives or other components such as fibers. It utilized heat and shear stresses which caused molecular changes in bio polymers like PLA [86]. Not only the extrusion process but also external factors such as humidity, light, and interactions with chemical substances also contributed to PLA degradation. These factors generated chain scissions and the formation of terminal group like hydroxyl and carboxyl groups which caused depolymerization [86]. This phenomenon reduces the molecular weight until the material loses its properties during reprocessing. Amarin et al [90] studied another way in PLA degradation which was caused by both radical and non-radical, as a result lactide groups were produced as the final products.

Agbakoba et al. [91] studied the effect of the mechanical recycling from PLA waste that contained bio-composite filaments of nanocellulose fibers collected from rejected products of 3D printing operations.

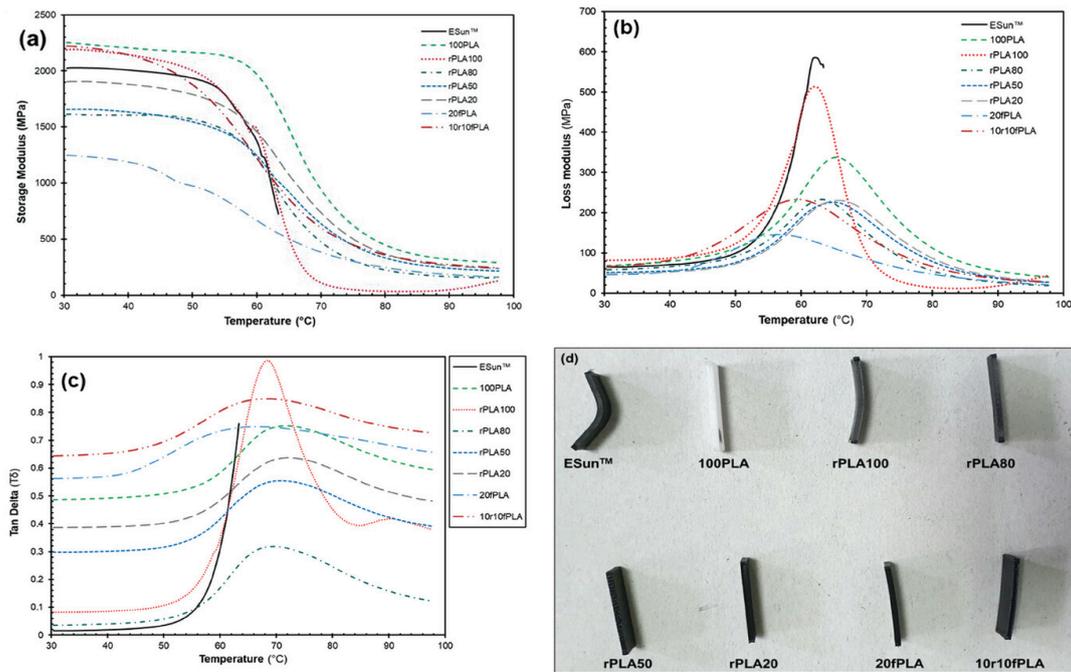


Figure 13: Temperature sweep analysis showing a) the evolution of Storage modulus (MPa), b) Loss modulus, c) Tan δ , and d) shape recovery of each sample at the end of the experiment. [91]

The specimens were printed using a desktop Fused Filament Fabrication (FFF) 3D printer. Figure 13 showed the changes in dynamic storage modulus (E'), loss modulus (E''), and tan delta ($\tan \delta$) of the 3D printed specimens. This study compared the mechanical results between recycled PLA and commercially available PLA. During the onset (around 30°C), the recycled filament PLA showed a higher storage modulus (E') of 2189.7 MPa, compared to 2025.6 MPa for commercial PLA. This slight increase in storage modulus was caused by restricted molecular chain motions, which were initiated by the higher crystallinity in recycled PLA [91]. From Figure 13 showed that the commercial PLA yields at 64°C . This yield showed the failure of mechanical strength due to material softening at 64°C .

It was also shown from figure 13 that the E' decreased for the virgin PLA and recycled PLA blend samples. E' reduction was attributed to a drop in molecular weight due to polymer chain scission. E' indicates the material's ability to save energy and resist any deformation, so that any reduction in polymer chain length disturbs the uniform transfer of applied energy, which makes the material more susceptible to deformation [91]. When the temperature was increased, the storage modulus (E') of all samples were decreased, as shown in Figure 13a. The E' was gradually decreasing until the glass transition (T_g) occurred and caused an abrupt drop in E' . The T_g is correlated with the onset of molecular and segmental mobility in the amorphous region. The T_g is marked by the inflection point of the E' onset, peak E'' , and also $\tan \delta$. The T_g values derived from E' and E'' curves showed an increase in segmental and molecular mobilities [91].

2.3.3. Recycling Impact Towards Composites Properties

Decreasing Filler Content Across Recycling Cycles

Multiple extrusion or recycling cycles have a negative impact on the PLA/ Fe_3O_4 composite, which is a gradual loss of magnetite filler content in the PLA matrix. Previous studies found several mechanisms on how the filler could be lost during reprocessing.

Mechanical Loss and Detachment

Every reprocessing cycle will give high shear and heat to the composite, which can degrade the polymer and the polymer-filler interface. Fe_3O_4 particles could detach from the PLA matrix and be physically lost if the interfacial adhesion weakens. Detached particles may stuck inside the barrel or even fall out during the handling. During their study on the re-extrusion of clay-filled polypropylene, Delva et al.

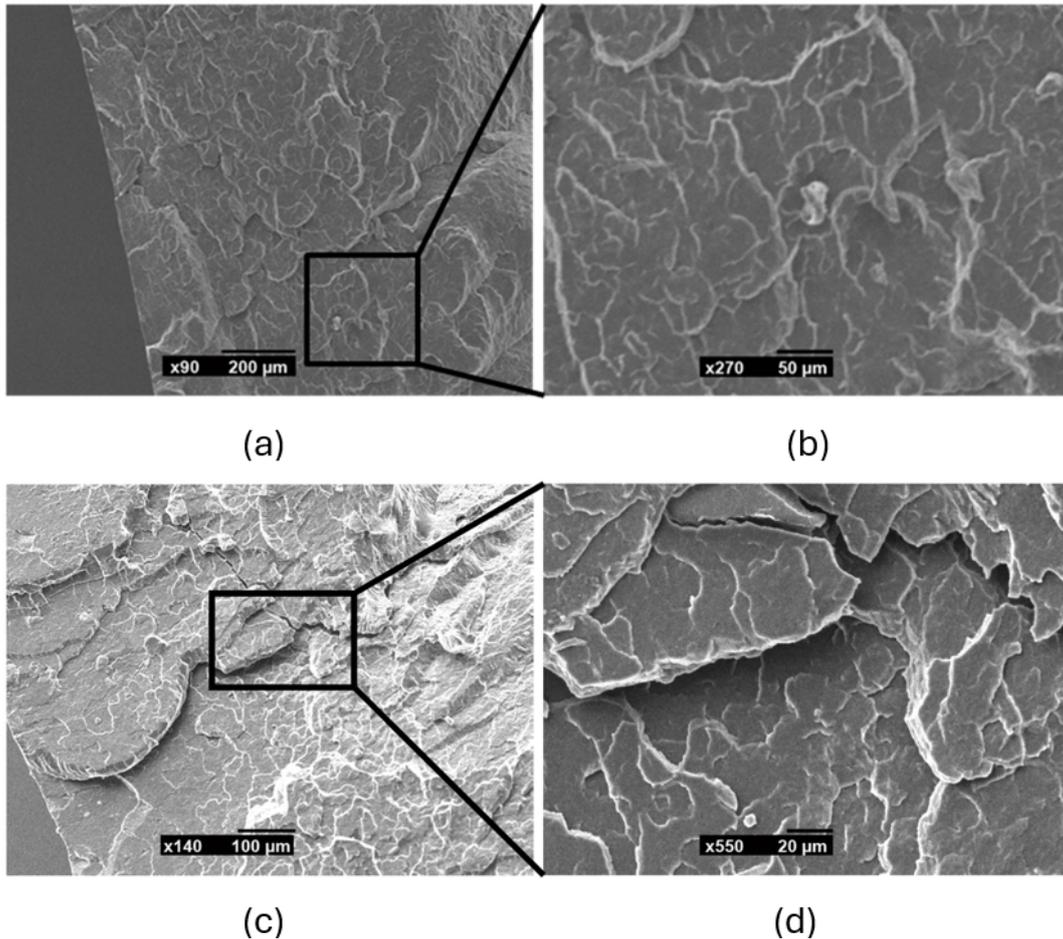


Figure 14: SEM micrographs of freeze-fractured surfaces of PP-MMT samples after a single extrusion cycle shown at magnifications of (a) $\times 90$ and (b) $\times 270$ and after 11 extrusion cycle magnifications of (c) $\times 90$ and (d) $\times 270$ [92]

[92] observed that the filler began to detach from the matrix after many reprocessing cycles. Figure 14 shows the differences between PP/clay composite for one extrusion cycle and after 11 extrusion cycles. After 11 cycles, the presence of a large amount of delamination and also matrix fracture fissures become clearer, which enhances the detachment process of the filler particles. In the same condition, magnetite particles from Fe_3O_4 composite also can slough off. Additionally, when the extruded filament is cut or shredded, any weak interfacial bond Fe_3O_4 could separate as dust. After several reprocessing cycles, these small losses may accumulate, leading to the reduction of Fe content. Overall, recycling can carry away a bit of filler particle each repeated cycle, either left behind inside the equipment or lost as waste, which results in a lower Fe_3O_4 fraction for the next batch of production.

Agglomeration and Sedimentation

A repeated extrusion cycle can make the nano/micro-particles agglomerate. Fe_3O_4 particles tend to pull each other (due to magnetic force and Van der Waals force) and form larger clusters, particularly when the polymer matrix viscosity drops (due to thermal degradation of PLA). Larger agglomerates are more difficult to keep suspended in the molten PLA matrix. A previous study by Samal et al. [93] reported that large or concentrated particles may precipitate to the bottom of the polymer melt, which becomes a sedimentation of the filler phase. In the context of recycling, if magnetite agglomerates settle down in the hopper or at the bottom of an extrusion flow, the sample taken out may have depleted filler particles. This phase separation leads to a difference in the Fe_3O_4 content along the filament than originally present because, in each cycle, a fraction of filler is lost progressively. Agglomeration also means that a part of Fe_3O_4 is tucked into clumps that might stick in the machinery or not be dispersed into the new melt, which contributes to filler particle loss. Heavy fillers Fe_3O_4 can segregated during

the production process if the matrix can't hold the well, leading to potential fraction drop and uneven distribution in the recycled materials.

Thermal Degradation of PLA and Interface

The degradation behavior of PLA during recycling has been widely explored, particularly due to temperature effects. Several studies emphasize that PLA exhibits relatively stable behavior when processed below approximately 200 °C. Previous study reported that PLA processed at 180 °C in a twin-screw extruder maintained molecular weight and viscosity values comparable to those of the virgin material, indicating minimal chain scission [94]. However, as processing temperatures increase beyond this point, significant degradation becomes more visible. At 220 °C, a decline in zero-shear viscosity was observed, while at 260 °C, all PLA grades exhibited a dramatic loss in viscosity, showing molecular weight reduction [94]. This is consistent with other findings in the literature, where researchers such as Khankruea et al. noted that PLA is especially vulnerable to thermal degradation above 200 °C, with substantial chain scission occurring in the 220–250 °C range if stabilizers are not used [95]. Processing time also plays a critical role, PLA may endure short exposures at moderately high temperatures, but prolonged residence times even at 190 °C can lead to significant molecular breakdown, which is shown by a 35% viscosity drop after one hour [96].

While temperature plays an important role in PLA degradation, recent research indicates that thermal effects alone do not fully explain the degradation mechanisms observed during recycling. Mechanical forces generated by shear flow within extruders have been shown to contribute to polymer breakdown. Velghe et al. [97] highlighted that shear and prolonged stresses in the molten state can directly cause chain scission in PLA, in addition to generating heat through viscous dissipation, a phenomenon known as shear heating. These findings suggest that the degradation process is caused not only by thermal but rather by thermomechanical forces, where both heat and mechanical stress act together to accelerate molecular degradation.

This thermomechanical perspective is further supported by studies that investigated the role of shear stress under various processing conditions. Cuadri et al. [98] showed that PLA subjected to high shear and elevated temperature in an oxidative environment degraded more rapidly compared to samples processed under milder conditions or inert atmospheres. Moreover, extrusion studies involving PLA 3D printing filaments found that faster draw speeds, which increase elongational strain which resulted in lower final molecular weights, implying that mechanical stress can enhance chain scission even at moderate temperatures [99]. These results show degradation mechanisms in PLA and highlight the importance of considering both thermal and mechanical parameters when evaluating the recyclability and long-term performance of PLA-based composites.

Moreover, repeated reprocessing cycles could reduce the PLA's ability to encapsulate and retain the filler particles. In addition, any surfactant or surface modifier Fe_3O_4 (if used to aid dispersion) may degrade at elevated temperatures. As a result, adhesion between the polymer and the filler particles will decrease after several reprocessing cycles. In the previous study, reprocessing composite material may lose the interfacial agents or polymer breakdown, which leads to filler loss in the matrix [92]. Even though Fe_3O_4 is thermally stable and will not decompose at PLA processing temperature, the polymer around it may degrade or form volatile substances that potentially carry away tiny Fe_3O_4 particles. Thermal degradation also introduces micro-voids or cracks in the PLA during reprocessing, causing the Fe_3O_4 particles near these cracks to be lost. Thus, repeated thermal cycles indirectly cause the filler particle loss by degrading the matrix material.

Effect of Fe_3O_4 Fillers Toward Polymer Properties

Not only multiple extrusion cycles but the Fe_3O_4 particles itself has negatively impacted the polymer matrix. The addition of Fe_3O_4 into the PLA matrix would alter the thermal degradation profile of the composite. Earlier research reports that Fe_3O_4 -filled PLA has slightly lower thermal stability, which is shown by the earlier degradation process, compared to pure PLA. Yu et al. [100] observed that PLA's decomposition temperatures decreased as Fe_3O_4 increased. In their TGA data, the weight of pure PLA began to decline significantly around 330 - 331 °C (5% weight loss point), while PLA + 5% Fe_3O_4 composite began to degrade at 298 °C. In addition, the temperature at 50% weight loss and the maximum degradation temperature also decreased. This trend indicates a decline in the thermal stability properties of PLA with Fe_3O_4 . The main reason is that Fe_3O_4 acts as a depolymerization

catalyst, which can accelerate PLA degradation. The surface of filler particles may carry adsorbed moistures or hydroxyl groups, also iron oxides can destabilize ester linkages. Yu et al. [100] note that “active sites on Fe_3O_4 surface could act as depolymerization catalysts to accelerate the degradation of PLA. Basically, Fe_3O_4 provides a surface for the PLA chain to break more easily, leading to faster earlier thermal degradation from the polymer matrix.

Moreover, heat conduction effects also contribute to polymer matrix degradation. Fe_3O_4 has higher thermal conductivity compared to PLA. When dispersed in the polymer matrix, these particles can conduct heat into the material's interior faster. This causes the composite to heat more evenly and slightly faster during TGA characterization, which makes the weight reduction happen earlier compared to pure PLA, which may retain more heat on the material's surface. A recent study on hybrid CNT/ Fe_3O_4 showed that even though carbon nanotubes are able to increase material's thermal stability at lower loadings, at higher loadings, the thermal conductivity of the fillers accelerates the decomposition process due to the heat that was carried into the inside part of the material and reduce the thermal stability [101].

Fe_3O_4 filler particles also affect the thermal transitions of PLA. Some studies found that adding Fe_3O_4 nanoparticles can increase the glass transition temperature (T_g) of PLA-based blend by a few degrees, indicating that the polymer chain's mobility was restricted due to the presence of rigid particle [102]. The cited work noted that with Fe_3O_4 nanoparticles added, the T_g is 65°C , slightly higher than pure PLA around $55 - 60^\circ\text{C}$. The stiffening effect is not always significant but shows Fe_3O_4 role as a filler by inhibiting the polymer chain movement. Fe_3O_4 also affecting the crystallization process which was studied by Yu et al. [100], observed that Fe_3O_4 particles hindered the cold crystallization of PLA leading to a lower degree of crystallinity.

Impact on Magnetic Properties of Material

Magnetic properties of PLA/ Fe_3O_4 composites tend to decrease when exposed to thermomechanical processes during reprocessing. In the first few cycles, the magnetic properties will not be decreased significantly only if the filler is still intact well inside the matrix. After the the matrix around the filler is damaged, researchers observe a drop in saturation magnetization after each subsequent cycle [103]. This decline is caused by previously mentioned factors, such as particle agglomeration and potential loss of magnetite content. In addition, Fe_3O_4 it can also catalyze the PLA degradation process according to a previous study by Yu et al. [100] which mentioned that adding 5-15% of iron powder increases the initial PLA decomposition temperature for $33 - 70^\circ\text{C}$. This finding suggests that PLA, which has Fe_3O_4 filler particles, may experience property changes faster than pure PLA.

In previous research, the studies found that the magnetic properties of Fe_3O_4 particles may change after several thermal or mechanical processes. Oxidation has been discovered as one of the reasons. Magnetite nanoparticles (~ 10 nm) can oxidize to maghemite even at ambient temperature over time, while bulk magnetite begins the oxidation around 220°C [104]. During the extrusion process, which happened typically at $180 - 220^\circ\text{C}$ for PLA, the oxidation process may occur slowly per cycle but accumulate across multiple heat histories. Researchers have studied that saturation magnetization decreases due to oxidation caused by annealing or heating process [105]. This phenomenon also potentially happen to the magnetite particles which can lead to measurable drop in magnetic saturation in PLA composite, even the magnetite particles can be oxidized into hematite [106].

In composites, after the recycling process, the presence of oxygen can lessen the magnetic potency of Fe_3O_4 particles. Moreover, if polymer degradation produces a bypass product such as peroxide, radicals, or even acids, it can further oxidize or corrode the Fe ions in magnetite. Another evidence of magnetite oxidation due to reprocessing was also found in other polymers that are used Fe_3O_4 as a filler. Bukowska et al. [107] in their research tried to encapsulate the Fe_3O_4 particles with protective shell coating, but later found a portion of magnetite still oxidized into maghemite despite hydrophobic coating, which was indicated by using spectroscopy and observing a color change, represented by Figure 15.

Impact on Mechanical Properties

Recycling PLA-based composite commonly degrades the material properties as the number of cycles increases. Mechanically, pure PLA can endure reprocessing cycles without significantly degrading.

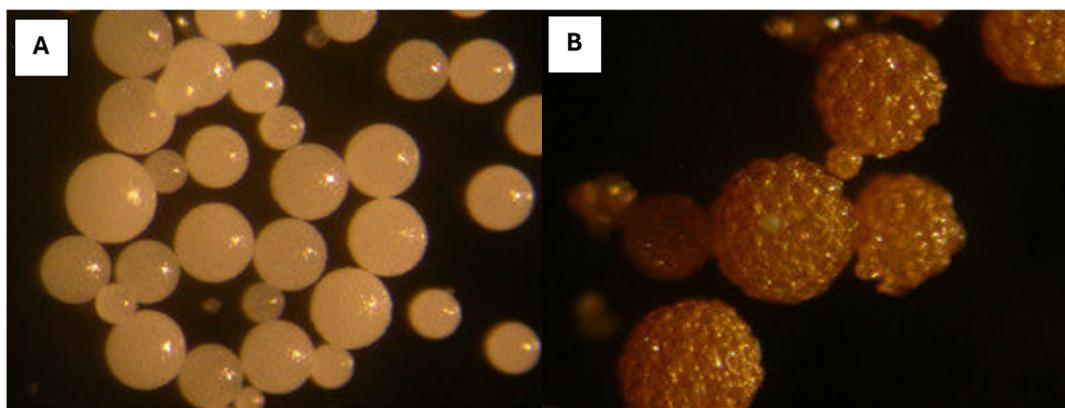


Figure 15: Microphotographs picture of GMA-based polymer microparticles (A) without Fe_3O_4 and (B) with Fe_3O_4 [107]

Aguero et al. [108], in their study, found that PLA can handle up to 3 cycles of extrusion/injection with relatively similar tensile strength and modulus. However, by the 4th cycle or 5th cycle, the material becomes more brittle. Aguero et al. also found that after four cycle loops, PLA impact toughness was lost over 50%. Recycled PLA often reduces thermal stability due to accumulated chain scission and the formation of lower molecular polymer fraction. It was also found that PLA is sensitive to hydrolysis and thermal cleavage, which means that after each reprocessing cycle, the polymer chain is shortened. It was evidenced by the melt flow index value increase and decreased viscosity in recycled PLA represented in Figure 16. Higher MFI value negatively impacts the filament-making and 3D printing process because it makes the material have a more liquid state and hinders a smooth production process. Chain shortening also leads to the incline of crystallinity upon cooling because shorter chains are easier to move and pack more easily into ordered crystals. In addition, increased crystallinity also makes the recycled PLA become more brittle, which is an undesired condition during the filament-making process in additive manufacturing.

Entrapped Solvent

During batch making, there is possibility that the solvent may be entrapped inside the polymer matrix. One of the reasons is the insufficient drying process, either drying duration or drying temperature. Using a drying temperature below the solvent boiling point may cause incomplete solvent drying and make the solvent stay inside the material. Another reason is the high viscosity when mixing the solvent and polymer pellets. Tamnanlo et al. [109] found that the mixture becomes very viscous when PLA is dissolved using DCM (dichloromethane) with high concentration and adding filler particles. This thick solution slows the diffusion process of the solvent and leads to the formation of glassy skin, which can entrap the DCM inside. The outer layer of PLA solidifies before the DCM escapes and encapsulates the remaining solvent inside the matrix. Entrapped DCM contributes to the final result of the material properties. Phaechamud and Chitrattha et al. [110] demonstrated that DCM initiates the liquid-liquid phase separation, a primary mechanism of pore formation during PLA film making. These porous structures negatively impact the final PLA matrix's morphological features and mechanical properties. To prevent residual solvent entrapment, it is crucial to implement a thorough drying process during the batch making process.

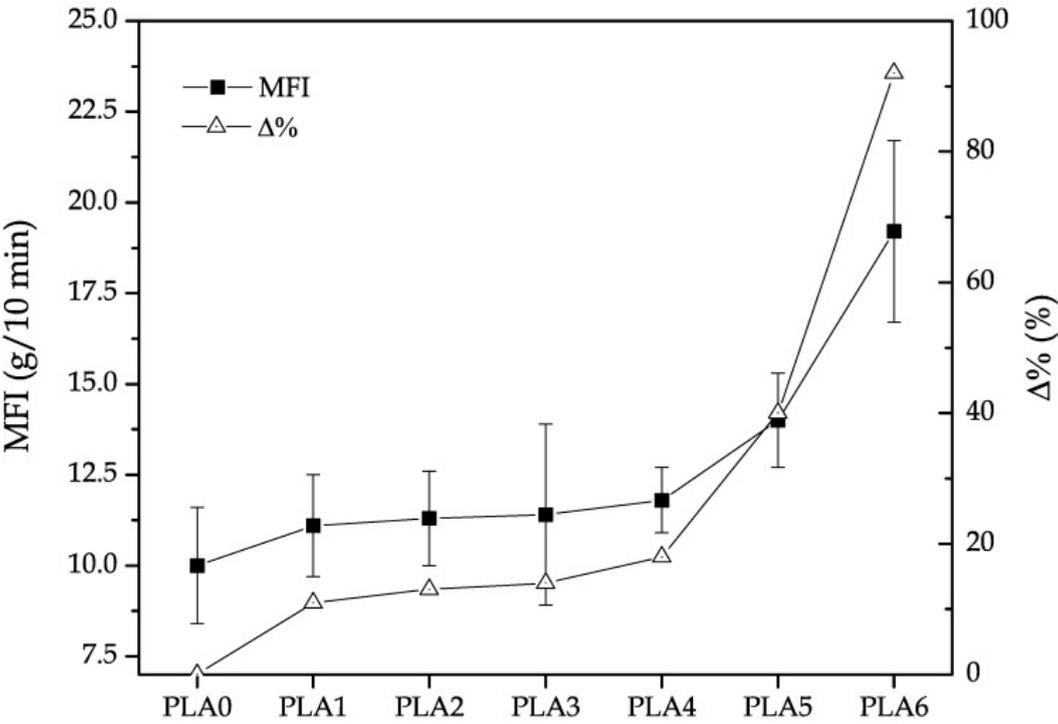


Figure 16: Melt Flow Index (MFI) results from different reprocessing cycles of PLA [108]

3

Material Preparation and Characterization

3.1. Material Preparation

The samples used in this research are new smart filaments combining polylactic acid (PLA) with magnetic particles (Fe_3O_4) and multiple recycling cycles. The intended ratio of magnetic particles is 20 wt.%. A linear production flow is shown in Figure 17. The flow consists of material preparation, filament making, 3D printing, and characterization.

The material-making process begins with material preparation. The chemical process is used to mix magnetic particles with PLA. Second, a filament maker machine is used to make the filament for 3D printing. Due to the extruded result, the filament will not be 3D printed in this research. The recycling step is performed by cutting the filament into small pieces and feeding them into the filament maker machine to make the next batch of filament, simulating the industrial thermomechanical recycling process. Finally, material characterization is evaluated.

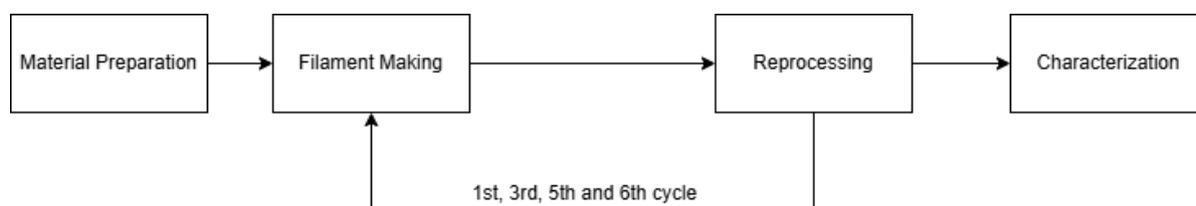


Figure 17: Research Flow

3.1.1. Material

PLA pellets (commercial grade: Ingeo-4043D) from 3Devo (Utrecht, NL) are used in this experiment. Magnetic particles and dichloromethane are obtained from Sigma-Aldrich (Saint Louis, MO, USA). The key properties of these materials are shown in Table 3.1. The supplier has provided this information.

Material preparation follows a chemical process. PLA is dissolved using DCM solvent to form a viscous liquid; the magnetite particles are then poured and mixed. For the solvent, dichloromethane (DCM) is chosen because of its excellent solubility for PLA and low boiling point, which minimizes the combustion risk [114]. Next, the mixture is dried directly inside the mixing vessel (beaker glass) to avoid the need for pouring and residual mixture that sticks to the wall of the vessel. This method slows the drying process due to the reduced surface area for solvent evaporation, so the mixture is heated several degrees above DCM's boiling point at 60°C for 48 hours in a vacuum oven to ensure the complete removal of residual DCM. After the solvent is evaporated, solid $\text{PLA}/\text{Fe}_3\text{O}_4$ is formed. Solid $\text{PLA}/\text{Fe}_3\text{O}_4$ is pulled out of the vessel and shredded to obtain a 4 mm pellet size, the recommended pellet size from the

PLA	
Density [(g/cm ³)]	1.24
Young's Modulus [MPa]	3.6
Tensile Strength [GPa]	60
Melting Temperature [°C]	145 - 160
Glass Transition Temperature [°C]	55 - 60
Magnetite	
Particle size μm	< 5
Residual flux density [T]	0.5 - 1.0
DCM	
Density [(g/cm ³)]	1.24
Boiling Point [°C]	40

Table 3.1: Material Properties PLA, magnetite, and DCM [111], [112], [113]

3Devo filament maker machine [115]. Besides the recommendation from the 3Devo Filament Maker manufacturer, a pellet size of 4 mm is also chosen based on the research by Engelen et al. [116], as it has been found to produce high-quality filament output after extrusion. Following this study, the shredded material is sieved to ensure that the particle size is approximately 4 mm. Any significant deviation from this size may lead to inconsistent material flow and extrusion issues.

3.1.2. Preparation Process

First, the volume of dichloromethane (DCM) is calculated based on the weight of PLA. It can be determined by using a relation in Equation 3.1, which divides the weight of DCM with its weight percentage and multiplies the weight percentage of PLA. In Equation 3.1, m_{pla} is the weight required of PLA (grams), V_{dcm} represents the volume of DCM (milliliters), ρ_{dcm} is the density of DCM (g/cm³), and $wt\%_{pla}$ is the PLA weight percentage that is used in this experiment, which is 20 wt%. A total of 66 g of PLA pellet is used, and based on the calculation, 200 ml of DCM is needed for each batch. For the purposes of this thesis, two batches are used to make the filament samples.

$$m_{pla} = V_{dcm} \rho_{dcm} \frac{wt.\%_{pla}}{1 - wt.\%_{pla}} \quad (3.1)$$

The fume hood is used to provide safety while using DCM solvent. The required amount of DCM is measured inside the fume hood using a glass beaker. The beaker is clamped and placed on the heating plate for stabilizing purposes. A mechanical mixer is used with a cap attached to the shaft. The mixer is set to a certain speed to create a slight vortex.

Next, half of the PLA is gradually added to ensure the mixture does not agglomerate. The speed of the mechanical stirrer is adjusted to prevent the PLA pellets from sticking together. Pellet adhesion can hinder the dissolution process by reducing the surface area of particles in contact with the solvent. The first half of PLA will be dissolved in around three hours. During the mixing process, the surface of the beaker is closed to minimize solvent evaporation.

Once all the PLA has dissolved, the speed of the mechanical mixing is increased to recreate a vortex, while the remaining PLA is gradually added in order to prevent agglomeration. The complete dissolution process takes approximately three hours. After the PLA has fully dissolved, the required amount of magnetite is measured using a calculation that divides the weight of PLA by one minus the desired magnetite weight percentage, then multiplies the result by the target weight percentage of magnetite. This relationship is shown in Equation 3.2, which m_{mag} represents the required weight of magnetite (grams), m_{pla} is the weight of PLA (grams), and $wt.\%$ describe the desired magnetite content, which is 20wt%.

$$m_{mag} = m_{pla} \frac{wt.\%_{mag}}{1 - wt.\%_{mag}} \quad (3.2)$$

Then the magnetite is slowly added to the PLA mixture during the mixing process. The mixture is stirred for approximately one hour to ensure the material is evenly distributed, but excessive mixing is avoided because it can cause magnetite agglomeration [117]. Once mixing is complete, the beaker glass is uncovered, and the mixing shaft is removed from the mixer; the shaft is placed above the beaker to allow the remaining mixture to drip back. The heating plate is turned on and set to 60°C to evaporate the solvent. The mixture will shrink and detach naturally from the beaker after the solvent evaporates. Not only solvent, drying process is also important to prevent any moisture from entering the barrel because water can transform into vapor, leading to bubbles in the filament and reducing the filament quality [116]. This heating process takes approximately 48 hours.

After evaporation, the solidified PLA/ Fe_3O_4 composite is removed from the beaker glass and put inside the vacuum oven for an additional 8 hours at 60°C to eradicate any residual DCM. The oven used for this step should be equipped with ventilation to the outside. From Figure 18, we can see a schematic representation of material preparation process.

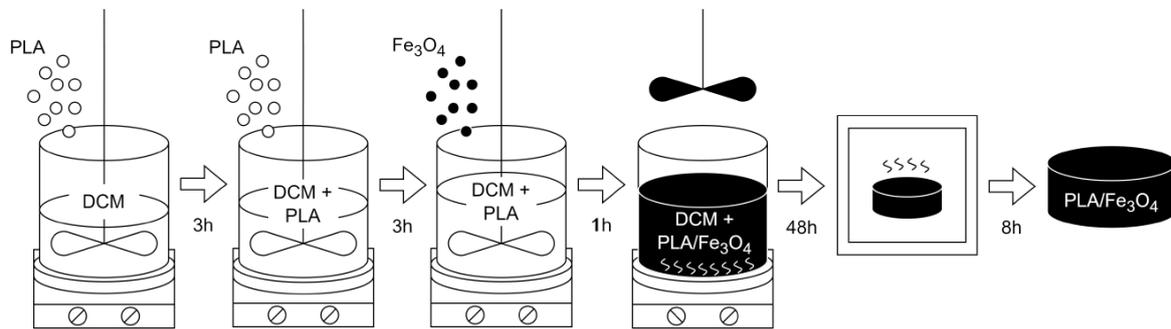


Figure 18: Schematic overview of PLA/ Fe_3O_4 composite material preparation [116]

3.1.3. Shredding and Sieving

The R25 Granulator, which is shown in Figure 19, is an industrial-grade machine designed for plastic recycling. R25 Granulator can process various materials, including PP, ABS, LDP, and PLA. First, the solid bulk PLA/ Fe_3O_4 from the previous batch-making process is shredded to achieve 4 mm pellet size. The first step of the shredding process is loading the solid bulk PLA/ Fe_3O_4 into the hopper on the top of the machine. These materials are fed to the cutting chamber, where static and rotating blades reduce the material size. After the material is small enough, it passes through a mesh filter and is collected in the collection bin.

Second, sieving is conducted. This process is required to ensure the smoothness of the filament-making process due to the requirement of a 3Devo Filament maker, which recommends a 4 mm minimum pellet size [115]. In this research, the sieving process is carried out using a Retsch AS 200 basic machine, as shown in Figure 19. The sieving is conducted in stages using sieve sizes of 2 mm, 1 mm, 710 μm , and 500 μm . The initial weight of shredded PLA/ Fe_3O_4 is 103 grams, with a plastic bag weight of 6.4 grams. The results of the sieving process are as follows: 69.4 grams for the 2 mm sieve, 22.7 grams for the 1 mm sieve, 2.3 grams for the 710 μm sieve, 1 gram for the 500 μm sieve, and 0.9 grams for particles smaller than 500 μm .

The virgin filament produced in this study, referred to as Batch 0, is made by shredding the bulk material obtained from the batch-making process. The shredded material is then sieved to acquire approximate material size with a minimum size of 4 mm. These particles are subsequently put into the 3Devo filament maker feeder to produce the initial filament. For the following recycling cycles (first, second, third, fourth, and so on), the method for shredding and sieving is no longer being used. To avoid unnecessary material loss and to obtain uniform pellet size, the recycled filament is manually cut into pieces, as shown in Figure 20. This method made it possible to get material pellets with 4 mm length to ensure consistent feeding into the filament maker without the risk of irregular particle sizes caused by the mechanical shredder. The manual cutting method could also help minimize material waste during reprocessing due to the limited amount of material available. However, the main drawback of this method is that it is highly time-consuming, especially when preparing material for multiple recycling



Figure 19: R25 Granulator (left) and Retsch AS 200 Basic Sieving Machine (right)

cycles, because each filament must be cut individually by hand.



Figure 20: Manual cutting of recycled filament

3.1.4. 3Devo Filament Maker

This research uses the 3Devo Composer 450 filament maker for filament production, as shown in Figure 21, which illustrates the extrusion system consisting of several essential parts for processing the material, such as the extruder, heating chamber, and nozzle. The process starts with loading the material into the hopper, which should be filled with enough capacity to ensure sufficient pressure on the pellets. From the hopper, the material moves into the extrusion screw, which drives the material into the barrel. The screw's inner diameter is gradually increasing towards the nozzle end, causing a reduction of the cross-sectional area and thereby increasing the internal pressure. Inside the barrel, four heaters are responsible for melting the material, and each heater can be adjusted independently according to the required temperature. Once it melts, the material will be extruded through the nozzle due to the accumulated pressure. The nozzle has 4 mm diameter, ensuring a consistent filament output.

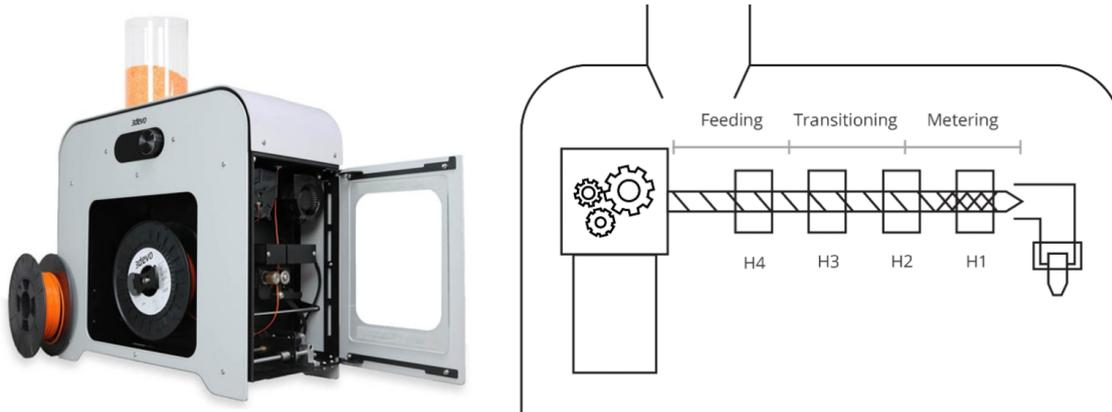


Figure 21: 3Devo Filament Maker and the extrusion elements of the filament maker [116]

3.1.5. Filament Production Parameters

The filament extruder has several adjustable settings that can affect the filament production process significantly. One of the most crucial parameters is the temperature of the heaters. The final heater is set to have a lower temperature to increase the viscosity of the material. If the material melts too quickly, molten material will push against other molten material, resulting in extrusion instability. If the temperature is set too high, the material will become too fluid, leading to excessive stretching due to its own weight or difficulties in maintaining uniform filament dimensions. Another condition is when the material is too cold, the clogging phenomenon may occur, or partially solidified material could be included in the extrusion, reducing the filament quality.

Besides the heater temperature, the extrusion speed can also be adjusted by modifying the screw's RPM. The speed impacts the rate at which material enters the barrel, passes through the heaters, and is extruded. Using a higher extrusion speed results in a shorter heating and cooling duration. Therefore, when the RPM is increased, corresponding changes must be applied to the heater and the cooling system to maintain process stability.

Another important parameter is the fan speed, which can control the intensity of the cooling airflow. Too much airflow can cause the filament to solidify too quickly, hindering proper stretching and making the filament unstable. Insufficient cooling may result in deformation due to the force from the puller wheels. This will affect the accuracy of the measurement and produce an ovalized filament that can impact its usability in 3D printing applications. Additional settings are available in the filament extruder, but these primary factors mentioned before play a crucial role in determining the final product quality.

A default preset for PLA from 3Devo Filament maker is chosen. At the same time, custom parameters for heaters temperature, screw's RPM, and fan speed are manually adjusted. The temperatures for heaters 1 through 4 are set at 170 °C, 190 °C, 185 °C, and 170 °C, respectively. These temperature settings have been chosen based on the research conducted by Engelen et al. [116], which demonstrated that these specific temperatures optimize the extrusion process for high-quality PLA filament production. The extruder rotation speed (RPM) is set to 3.5, which has been shown to provide optimal material flow and consistency in the same study. Additionally, the fan operates at 70% capacity to ensure sufficient cooling without compromising the extrusion process, as Engelen et al. [116] recommended for producing high-quality filament.

3.1.6. Filament Production Process

Sieved samples that have the correct size specifications are then fed into the feeder of the 3Devo filament maker, which has preset configurations for common materials used for 3D printer filaments, like PLA and ABS. Standard PLA is used initially to stabilize the extrusion process. Before switching to PLA/Fe₃O₄ composite material, a regular PLA pellet is first extruded in order to get a stabilized filament output. During the process, the shreds must be stirred occasionally with a stick or similar tool to prevent

bridging, a phenomenon where cohesive structures form and block the barrel entry. If necessary, a stick can be used to push the material to maintain the barrel's opening gently. Once the hopper is completely emptied, the PLA/Fe₃O₄ composite materials are gradually introduced.

After the material is extruded from the nozzle, it needs to be stretched to achieve the desired diameter. Initially, the extruded filaments exit the nozzle with a diameter of approximately 4mm. Two fans, which are shown by Figure 22 are positioned below the nozzle to accelerate the cooling process and solidify the material. Solidified material tends to have less diameter changing than material that comes out directly from the nozzle. The filament is then gripped by two puller wheels that control both the stretching and filament thickness.



Figure 22: The extruding side of 3Devo filament maker

Once a stable extrusion is achieved, the filament spooling process can be started. It is important to check that the first five winds are properly aligned and have a proper filament pressure and that the first two filament layers are evenly distributed on the spool. If these initial layers are correctly positioned, the machine should be able to operate smoothly for the rest of the material.

In order to ensure that there is no residue from the previous cycle that can contaminate the next cycle, a purging process is needed. The purge process is done using a combination of DevoClean and HDPE pellets. DevoClean role is to bind any materials left inside the extruder and make the extruder free from any impurities. The next step is using HDPE to ensure no DevoClean and any residues left inside the chamber. The HDPE will push all of the residue materials through the extruder to the nozzle. The filament maker uses default parameters for default HDPE material when the purging process is in progress. Because of the magnetic particles, the color of PLA/Fe₃O₄ the filament is black, while the default colors of PLA, HDPE, and DevoClean pellets are white and transparent. The purging process is considered done when the color of extruded DevoClean and HDPE is transparent white. If any black color is seen, there are still impurities and residue materials from the previous cycle, and the purging process continues.

3.2. Characterization

3.2.1. SEM and EDS

In this study, the morphologies of the sample will be observed using SEM. This characterization focuses on the morphology of filament samples produced from the PLA/Fe₃O₄ composite. The main goal of this characterization is to evaluate the distribution of Fe₃O₄ particles inside the filament and to observe any structural changes that occur due to repeated reprocessing cycles. Proper sample preparation is important to get clear and accurate imaging. The samples are prepared using a cold embedding

method to prevent further sample degradation during handling. Since the composite material is non-conductive, the samples are prepared using conductive resin during embedding to reduce the charging effect when SEM imaging. Lastly, a thin carbon coating of approximately 15 nm is deposited onto the sample surface to enhance its conductivity and improve the image quality, allowing a better observation of fine structural details.

Energy Dispersive X-ray spectroscopy (EDS) is used alongside SEM to better understand the composition of PLA/Fe₃O₄ filament composite. By using the region scanning function, EDS helps identify the main elements present in the sample, primarily carbon, oxygen, and iron, which correspond to the PLA matrix and the magnetic particle filler. The elemental mapping provides general information on how these elements are distributed across the scanned area. Quantitative results from EDS can show the iron content varied across scanned regions, suggesting that the magnetic particles are either well-distributed or agglomerated. The point scanning feature is used to get a closer look at specific areas, particularly on denser spots in the SEM images, hinting at possible agglomeration. These point scans may confirm higher iron concentrations, indicating some Fe₃O₄ particles clustering within the PLA matrix.

3.2.2. Vibrating Sample Magnetometer (VSM)

Magnetic characterization uses a magnetometer to learn the effect of thermos-mechanical reprocessing on the magnetic properties of PLA composite. Magnetic properties is important for robotic parts, due to its origin traits to move without installing built-in power source such as battery. A vibrating sample magnetometer (VSM) is used in this research to measure the magnetic hysteresis loop of a material. This method works by vibrating a magnetic sample within a coil, and the current is induced by Faraday's law.

For this research, the VSM is mainly used to evaluate the material's magnetic properties, specifically its remanence. The instrument used for this analysis is the Lake Shore Cryotronics VSM 7300 Series. The samples are taken by cutting the filament to 3,55 mm in length. Testing is conducted at room temperature. The maximum applied magnetic field is set to 1,5 T, with a field increment of 101 mT. The ramp rate is configured at 10 mT/s with 60 number of data points. Once analysis is complete, the results are shown in magnetic moments units (Am^2). The VSM analysis will use 3 samples for reproducibility.

3.2.3. Thermogravimetric analysis (TGA)

NETZCH STA Machine is used in this study. The crucible is made of ceramic or platinum. To calculate the weight differences, a counterweight or a reference sample that has almost identical weight is placed at the end of the balance. The reference sample that is used in this research is Al₂O₃. In the beginning, both the sample and reference crucible's weight will be measured. Then, the Al₂O₃ is placed inside the crucible, and the net weight is measured. Next, the sample is weighed until it has more or less the same weight as the reference and put inside the crucible. Inert gas argon is used to ensure no reaction with oxygen happens inside the chamber. As the temperature increases, the sample may lose mass because of evaporation, combustion, or decomposition. The balance records these mass changes in real time.

The temperature is increased 20 °C in every minute until it reaches 800 °C. Yang et al. [118] observed that PLA is burned off at a temperature around 500 °C, yet the temperature is targeted to 800 °C in order to achieve complete combustion of all materials during the analysis. TGA is also able to determine the weight percentage of the magnet particles in the filament after each recycling cycle by measuring the weight of residue material inside the crucible.

3.2.4. Gel Permeation Chromatography (GPC)

SHIMADZU GPC Machine is used for characterization in this research. GPC works by separating molecules based on their effective size in the mobile phase, which is usually correlated with the molecular mass. GPC is able to determine some key molecular parameters, including the number-average molecular mass (Mn), weight-average molecular mass (Mw), peak molecular mass (Mp), and polydispersity index (Mw/Mn).

In this research, dimethylformamide (DMF) is used as a solvent. The preparation included dissolving the material in a vial by soaking the sample using solvent, attaching the vial to the floater, and utilizing

the vibration of ultrasonic cleaner to accelerate the dissolving process. After making sure all the samples are dissolved, the syringe is used to pull out the sample and then inject it into the new vial using a microfilter. The microfilter is used to ensure no magnetic particles are included in the solution for GPC analysis.

3.2.5. Nuclear Magnetic Resonance (NMR) Spectroscopy

Agilent-400 MR DD2 spectrometer is used for NMR analysis to investigate the chemical profile of the PLA/Fe₃O₄ filament composite. Both proton (¹H) and carbon (¹³C) NMR spectroscopy are performed to get a more complete picture of the molecular structure. NMR characterization is conducted using Norell Select Series 5 mm NMR tubes. The samples are prepared by dissolving the filament in deuterated chloroform CDCl₃ at a ratio of 0.06 grams of filament per milliliter of solvent. NMR preparation sufficiently uses 5 ml CDCl₃ per batch to fully dissolve the material and produce a clear NMR signal. To accelerate the dissolving process, the mixture is treated with an ultrasonic vibrator. After that, the solution is passed through a microfilter to remove any magnetic particles that interfere with the NMR spectra quality. When viewed in the NMR tube, a volume of 0.7 ml, or roughly the height of three phalanges, is needed to get a well-defined NMR spectrum.

The main purpose of running NMR in this study is to check any trace amounts of solvent that might have been trapped inside the filament during processing. Residual solvents negatively impact the material's properties, so it is important to identify their presence so we can know if the main reason for degradation from the material is solely the thermomechanical process during recycling or caused by any other factors like solvent residue. By comparing the spectrum of the prepared sample with known solvent peaks, we could tell whether any unwanted residues remained from the filament production.

4

Result and Discussion

4.1. Filament Production

This study successfully produced 15 m of length filaments through five reprocessing cycles of PLA/FE₃O₄ composites. However, during the sixth cycle, filament production failed. The extruded material became too liquid, forming large, uncontrollable bulges upon exiting the nozzle. The filament had improper structural integrity, was highly fragile, and could not be consistently pulled by the system, preventing successful spooling. This behavior indicates that the material had undergone severe thermal and mechanical degradation, reaching a point where further recycling was no longer viable.

The 3D printing filament produced after the 5th reprocessing cycle displayed notable differences compared to the 1st cycle filament, as shown in Figure 23. As a result of visual inspection, the 5th cycle filament exhibits more surface defects, including pronounced bumps and irregularities along the filament's length. These defects suggest a further degradation of the polymer material caused by exposure to multiple thermal and mechanical reprocessing conditions. Compared to the 1st cycle filament, which had fewer inconsistencies, the 5th cycle filament shows more severe diameter variation. This situation will negatively impact its printability and extrusion stability during the 3D printing process.



Figure 23: 1st and 5th Cycle Filament

As the number of reprocessing cycles increased, the filament became progressively more difficult to wind properly during extrusion and spooling. The material demonstrated higher brittleness, which makes it more prone to breaking during the spooling process. During the spooling process, the machine operator needed to work more slowly and carefully to prevent material expansion near the nozzle and filament breakage, resulting in reduced production efficiency. The filament produced after the 5th reprocessing cycle showed pronounced fragility and unnatural bending, indicating a significant loss of flexibility. The spooling process also makes this issue worse because the filament faces difficulties in forming a smooth and continuous loop and instead bends sharply, causing more tension in the step turn region. These observations indicate that repeated recycling cycles affect both the surface quality and mechanical properties of the filament, highlighting the effect of multiple reprocessing iterations on the material's usability, especially for 3D printing filament. In particular, the increasing inconsistency in filament diameter caused feeding issues, such as filament jams in the printer feeder, and led to uneven printing quality during fabrication.

The effect of reprocessing on filament inconsistency is also supported by diameter measurement data for each cycle. The measurements are taken using a micrometer screw gauge, measuring 30 random points along the filament. Figure 24 presents a graph that compares the filament diameter across three cycles. At the same time, Table 4.1 provides statistical analysis of the diameter fluctuations,

which include range and standard deviation values.

Number of Cycle	Average Diameter (mm)	Diameter Range (Max-Min) (mm)	Standard Deviation
1st	1.84	0.83	0.21
3rd	1.92	1.00	0.23
5th	1.90	2.37	0.44

Table 4.1: Average Diameter, Range, and Standard Deviation of 1st, 3rd, and 5th Cycle Filament

The 1st cycle filament (red line) shows the most stable and consistent diameter with a range of 0.83 mm and a standard deviation of 0.21 mm. The most significant variation happened when measuring the diameter of the filament with big bumps. This indicates that the polymer structure remains intact during initial extrusion, which allows more uniform filament production. However, with increasing the recycling cycles, greater variations in filament diameter become more visible. The 3rd cycle filament (green line) shows more fluctuations, with a slightly higher range of 1.00 mm and a standard deviation of 0.23 mm. This event shows more inconsistencies happened in the extrusion process that the 1st cycle and degradation effects have started to impact the quality of the filament.

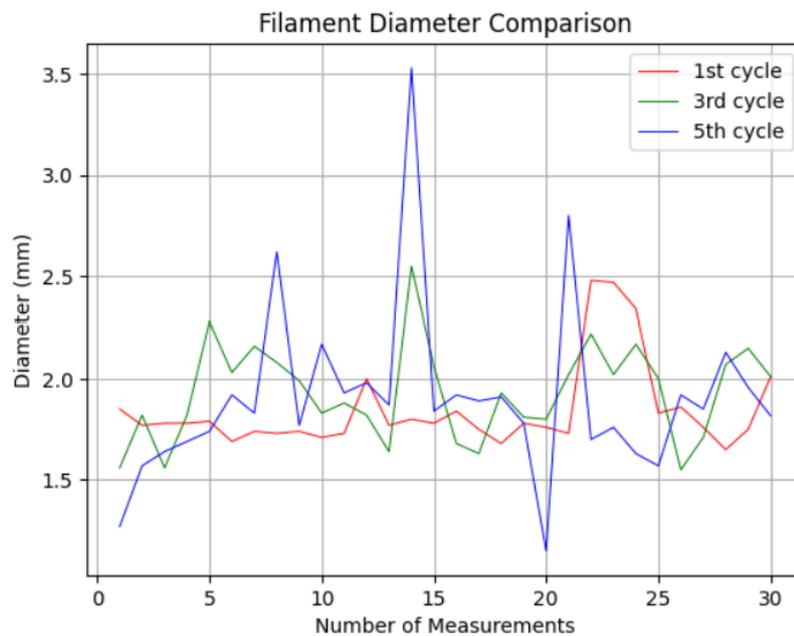


Figure 24: Comparison of Filament Diameter Between 1st, 3rd, and 5th Cycle

By the 5th cycle (blue line), the diameter variation becomes significantly uncertain with multiple sharp peaks and deviations, with the diameter increasing to 2.36 mm, which is the highest among all cycles, and having a standard deviation value 0.44 mm. These irregularities suggest that thermal and mechanical processing cause polymer degradation, which leads to unstable behavior during extrusion. This confirms that the 5th cycle filament is the most inconsistent, which aligns with the visual observations of the surface defects, brittleness, and difficulty level in the spooling process. The large diameter could lead to crucial 3D printing issues because consistent filament dimensions are important to achieve proper extrusion and layer adhesion during printing.

The filament produced after the 6th reprocessing cycle displayed severe degradation, as shown in Figure 25. The material became excessively fluid during extrusion, forming large bulges upon exiting the nozzle, and lacked sufficient structural integrity to maintain a consistent filament shape. As a result, the filament was fragile, difficult to spool, and prone to clogging and mechanical failures during processing. This stage marks the practical limit of recyclability, beyond which the material can no longer be

processed or extruded effectively. Compared to the 5th cycle filament, the 6th cycle filament demonstrated complete loss of mechanical properties due to polymer chain degradation, thermal fatigue, and embrittlement. These factors disrupted uniform flow and spooling, leading to chaotic filament formation. Thus, the 5th cycle represents the last usable stage for PLA/Fe₃O₄ filament recycling, as material processed beyond this point is no longer viable for 3D printing.

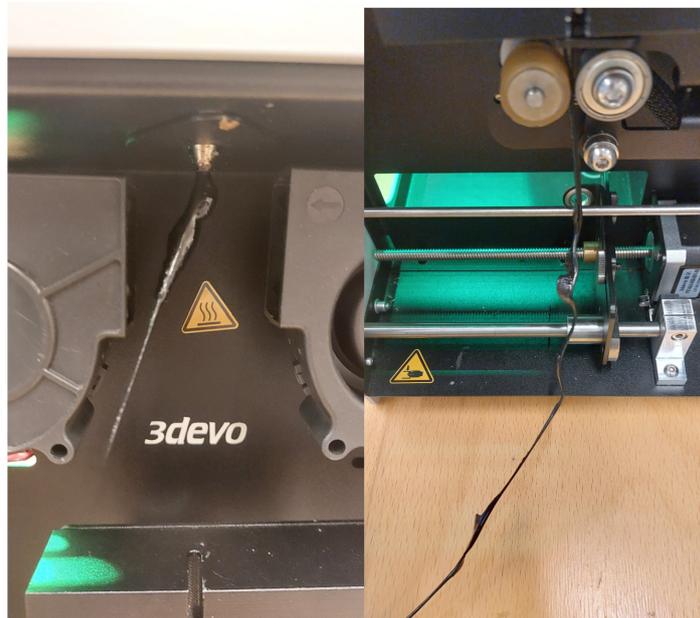


Figure 25: 6th Cycle Filament

4.2. Characterization Result

4.2.1. SEM & EDS

Scanning Electron Microscopy (SEM) is performed on the filament produced from the 1st recycling cycle to observe the surface morphology and magnetic particle distribution within the PLA matrix. For SEM and EDS analysis, cross-sections of the filament were taken from the edges of the filament, rather than from the middle section. As shown in Figure 26a, the SEM images show a relatively smooth surface with uniform dispersion of the magnetic particles, which are represented by the bright spots embedded throughout the polymer. In this 1st cycle, no significant agglomeration is observed, indicating that the initial recycling and filament extrusion process produced a well-mixed composite with relatively uniform particle distribution.

SEM analysis of the 1st cycle filament revealed good particle dispersion and the appearance of microcracks in the PLA matrix. These cracks likely formed due to localized stresses during processing steps like extrusion, cooling, or manual handling. In recycled PLA composites, it is well known that repeated exposure to heat and mechanical forces causes thermal degradation and chain scission, which reduce the molecular weight of the polymer and make it more brittle [108]. Although the microcracks observed at this stage were relatively minor, they may represent the early onset of mechanical degradation, which could worsen with further recycling and contribute to filler detachment and a gradual loss of mechanical strength.

By the 5th cycle, the filament shows much more pronounced changes in its surface morphology. As seen in Figure 26b, large clusters of Fe₃O₄ particles have formed, indicating significant agglomeration of the magnetite filler as recycling progresses. The PLA matrix surface also appears rougher and more irregular, with noticeable voids and disrupted areas suggesting mechanical and thermal degradation have taken a greater toll. Interestingly, while distinct microcracks were visible in the 1st cycle, they are no longer observed in the 5th. The increasing brittleness of the material can explain this shift. Rather than forming clean microcracks, the degraded matrix fractures more chaotically and uncontrolled, resulting in rough surfaces, voids, and particle clustering instead of well-defined crack lines.

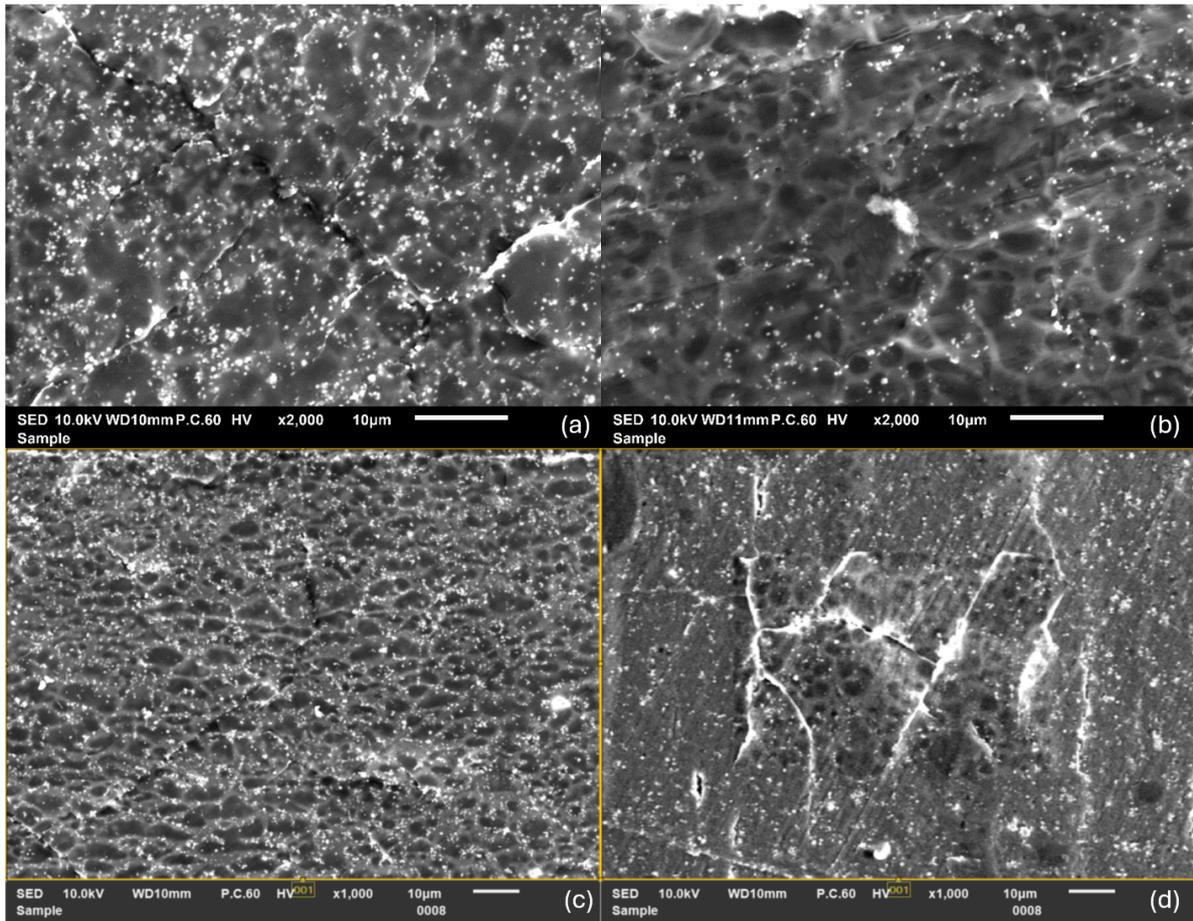


Figure 26: SEM Images (a) 1st Cycle Filament and (b) 5th Cycle Filament; EDS Images (c) 1st Cycle Filament and (d) 5th Cycle Filament

Complementing the SEM observations, Energy Dispersive X-ray Spectroscopy (EDS) analysis is also used to determine the filament's elemental composition, represented by Figure 26. The mass percentage of each element from EDS is shown in Table 4.2 which confirms the presence of carbon (C), oxygen (O), and iron (Fe), corresponding to the PLA matrix and Fe_3O_4 filler. For the filament after the first recycling cycle, the measured iron content was 20.72 wt%, indicating that a substantial amount of magnetic filler remained embedded within the polymer matrix. In contrast, after the fifth recycling cycle, the filament showed a reduced iron content of 7.85 wt%, suggesting a significant loss of Fe_3O_4 particles during repeated reprocessing. This reduction in iron content is consistent with the visible changes in the SEM images, where the dispersion of magnetic filler appears less uniform, and more areas of filler agglomeration and voids are observed. These results indicate that repeated recycling leads to filler loss, increased filler agglomeration, and surface damage, which are expected to worsen progressively with additional reprocessing cycles. SEM and EDS thus provide critical insight into the material degradation processes occurring during recycling and establish a reference point for comparing the extent of deterioration across multiple cycles.

Element	Mass Percentage		
	1st Cycle	5th Cycle	3Devo Cleaner
C	61.91	77.70	91.76
O	17.37	14.45	6.96
Fe	20.72	7.85	1.28

Table 4.2: Mass percentages of elements in different cycles and 3Devo cleaner

The changes seen in the SEM and EDS results match what has been reported in previous studies. Repeated exposure to heat, mechanical stress, and even moisture during recycling can break down the PLA structure, causing a drop in molecular weight and making the material more brittle [108]. As PLA becomes more brittle, it loses the ability to absorb mechanical stress, which can form microcracks around filler particles, similar to what was observed in the 1st cycle filament. As the recycling continues, the ongoing damage to the polymer chains worsens the material's condition, leading to more problems such as particle agglomeration, void formation, and rougher surfaces, as seen in the 5th cycle filament. Agglomerated filler particles create weak points in the matrix, making it even easier for cracks to grow and mechanical failure to occur. Overall, these degradation processes help explain why the filament quality keeps declining with each recycling cycle.

As a way to analyze the distribution of Fe_3O_4 particles and learn about how much material is lost, EDS analysis is performed on two areas of the 5th cycle filament. The first scan is done over a wide surface area and detects an overall iron content of 7.85 wt%. The result is significantly smaller than the result from the 1st cycle, which is 20.72 wt%. Reduction in iron content indicates material loss during recycling, likely caused by particle detachment during handling, extrusion, or manual cutting. This result agrees with a previous study done by Finnerty et al. [119], which reported that mechanical recycling could cause gradual filler loss, especially when particles become less embedded within the polymer matrix due to the weakening process of interfacial bonding from multiple reprocessing cycles.

A second EDS scan is focused on the large agglomeration identified in the SEM image as shown in Figure 27. The result shows 32.28 wt% in iron content, which confirms that the remaining Fe_3O_4 particles have begun to gather in localized clusters rather than evenly distributed along the matrix. Agglomerates can also act as stress concentrators, instigating micro-crack formation and making the material degradation faster with the increased reprocessing cycles.

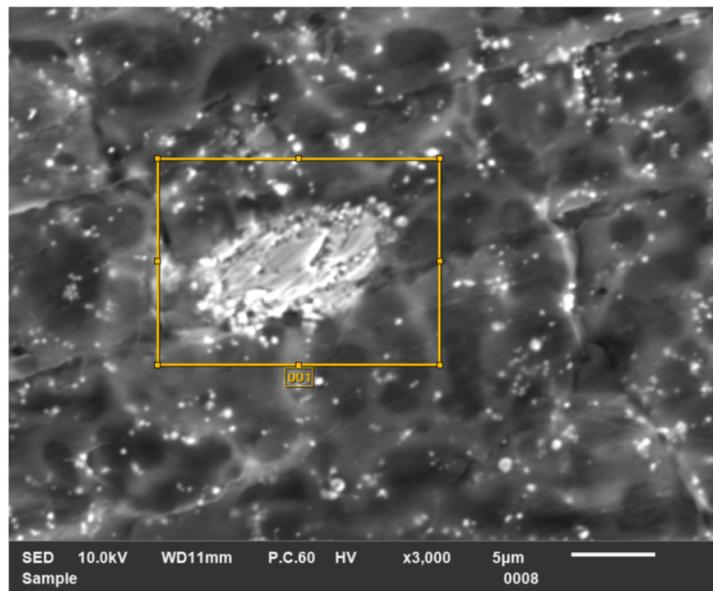


Figure 27: SEM Images of Fe Agglomeration

Figure 28a and b shows the visual of extruded filament using 3D Devo cleaner. Figure 28c shows the picture from SEM and EDS scanning area of samples obtained from the 3Devo Cleaner process. The original color of the 3Devo cleaner is transparent white, but after cleaning the PLA/ Fe_3O_4 filament making process, it becomes black. The color changes due to PLA/ Fe_3O_4 residues inside the extruder chamber that bonded to the 3Devo cleaner. The SEM and EDS sample is taken from the cross-section of the filament that is fabricated from 3Devo cleaner that is used during extruder cleaning after each reprocessing cycle. The bright white regions represent the presence of Fe particles which bound onto the surface of the 3Devo cleaner filament during the cleaning process. This observation suggests that some residues of Fe_3O_4 particles stick to the cleaner filament and are then removed from the

composite material through the nozzle. EDS result in Table 4.2 also shows a small percentage of iron content. These findings prove that magnetic particle loss during reprocessing is contributed by the extruder cleaning process using the 3Devo cleaner.

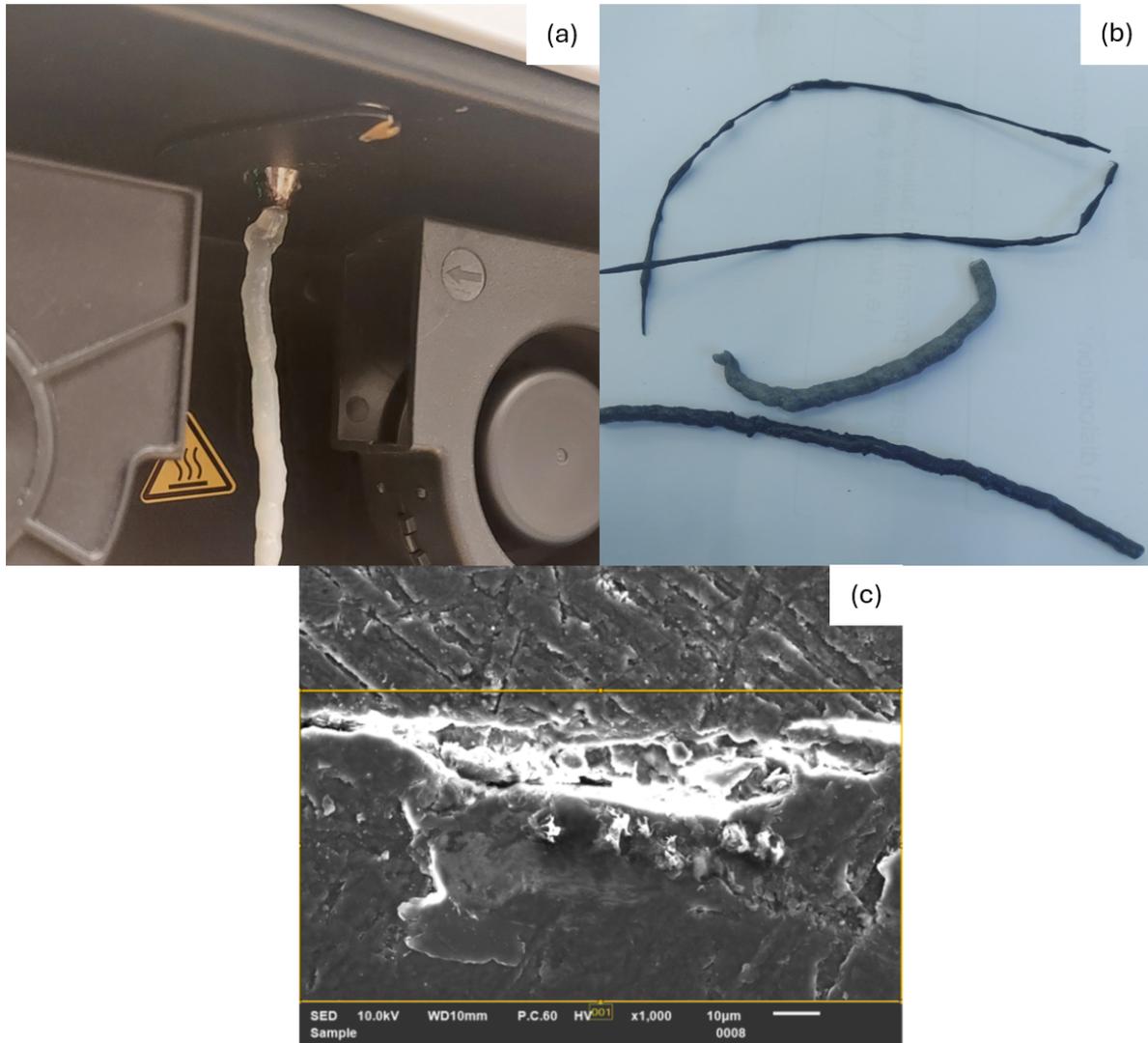


Figure 28: Visual picture of 3Devo Cleaner (a) without residual particles, (b) with residual and (c) SEM EDS image of 3Devo cleaner with residual particles

4.2.2. TGA

TGA is used for evaluating the thermal stability and decomposition of the recycled PLA/Fe₃O₄. Figure 29 represents the average of TGA curves on the 1st, 3rd, 5th, and 6th recycling cycles. This research has two types of samples based on their origins where the sample is cut along the filament. The first samples are taken from the edges of the filament, while the second type of samples are taken from the middle part. For extra information, the 6th filament is not able to form any filament spool during reprocessing, so the samples are randomly taken from the undetermined 6th filament region. Three samples are taken from each cycle for reproducibility. The data shown in this research is the average calculation from all three samples. The X-axis shows the function of temperature, while the Y-axis shows the weight loss curves.

The first type of samples, which were taken from the edge of the filaments, showed a result where there is a significant weight loss that occurs between approximately 300 °C and 400 °C that corresponds to the degradation of PLA. As the number of recycling cycles increases, the shift in thermal degradation

behavior becomes more visible. Based on Figure 29, the degradation temperatures were determined by identifying the onset of significant weight loss, which begins at temperatures around 280 °C to 400 °C. The average degradation temperature for the first cycle was 312 °C, while it decreased slightly to 307 °C for the third cycle, followed by a more significant decrease to approximately 291 °C for the fifth cycle and 290 °C for the sixth cycle.

These results suggest that the material reprocessing initially leads to a small decline in the degradation temperature, with a shift of approximately 1.5% decrease from the first to the third cycle. However, based on the calculation, a more notable change in the degradation temperature was observed starting from the fifth cycle, with a shift of approximately 6.6% decrease for the fifth cycle and 6.7% decrease for the sixth cycle compared to the first cycle. This trend shows a possible deterioration of thermal properties, likely due to the breakdown of PLA polymer chains or changes in the PLA/Fe₃O₄ interactions during repeated extrusion and reprocessing.

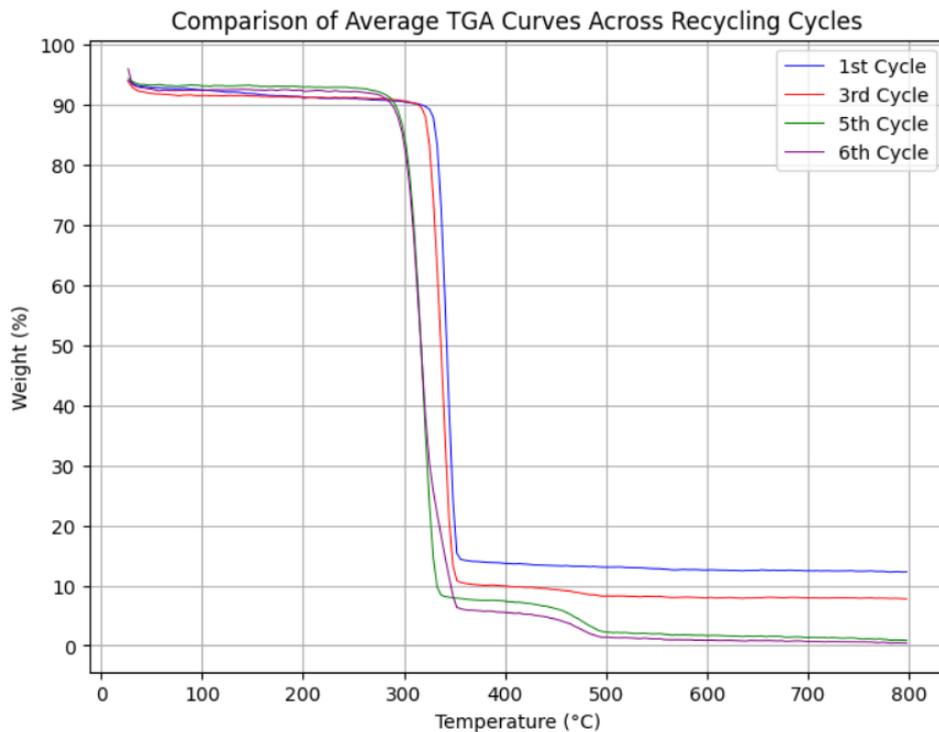


Figure 29: Comparison of Average TGA Curves Across Recycling Cycles (1st type sample)

The TGA curves show that with each additional recycling cycle, the residual weight at high temperatures decreases, which suggests that the Fe₃O₄ content in the composite material is reduced. In this study, the PLA/Fe₃O₄ composites start with 20% by weight of iron particles, but the Fe₃O₄ content in the first sample cycle, which is cut from the edges of the filament spool, is already much lower. Delva et al. [92] found something similar in their research on re-extruding clay-filled polypropylene. They observed that recycling can physically remove some of the filler material each time, either lost as waste or left behind in the equipment, which results in a decrease in Fe₃O₄ content during each cycle.

To measure the Fe₃O₄ content, we calculate the residual mass from the TGA analysis, as shown in Figure 30. The graph shows a downward trend, indicating a significant loss of Fe₃O₄ particles with each cycle. In the first cycle, the Fe₃O₄ content is around 12%, much lower than the initial 20% used in the batch preparation. This reduction continues, with the Fe₃O₄ content dropping to about 8% by the third cycle and nearly 2% by the fifth cycle. By the sixth cycle, the Fe₃O₄ content is less than 1%. This notable decrease points to the fact that the recycling process, especially during extrusion, results in a significant reduction in magnetic particles. Several factors could contribute to this, including mechanical loss, detachment, agglomeration, sedimentation, and the loss or retention of particles during reprocessing and extrusion.

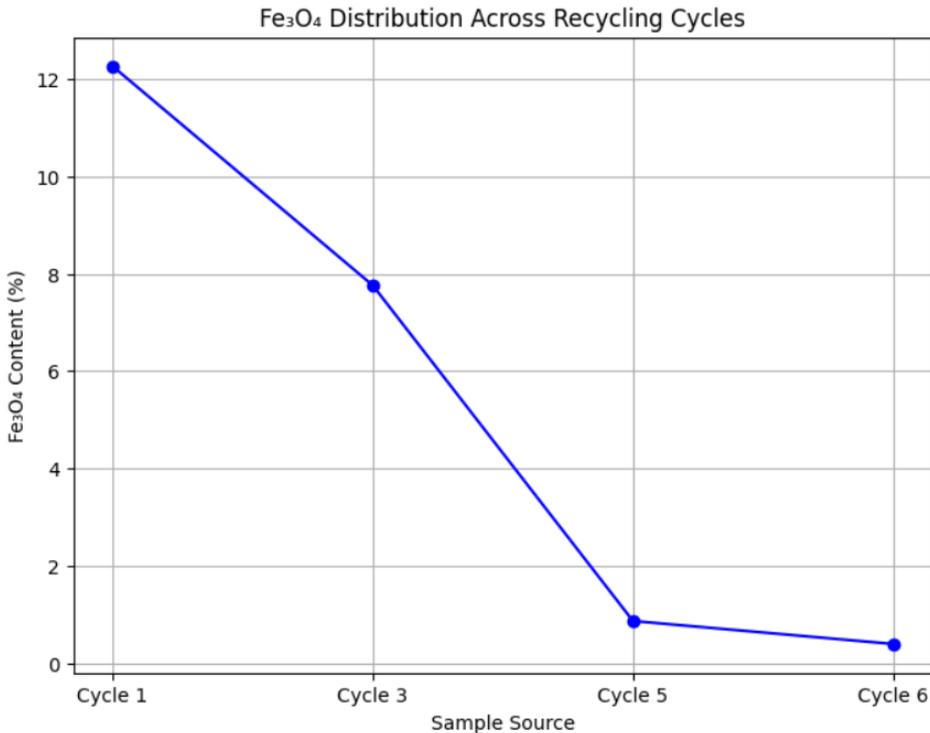


Figure 30: Fe₃O₄ Distribution Across Recycling Cycle (1st type sample)

In this research, it was observed that partial Fe₃O₄ particles were left inside the extruder. Evidence of this was found in the extruded filament from the 3Devo cleaner, which also contained magnetic particles. This was confirmed by SEM and EDS results shown in Figure28. A second TGA was performed to investigate how significantly the cleaner contributes to material loss. Figure 31 shows that the 3Devo cleaner filament had approximately 2.5% Fe₃O₄ residue remaining in the TGA crucible after cleaning. Also, the original transparent white color of the 3Devo cleaner changed to black after cleaning, likely due to Fe₃O₄ residues bonding inside the extruder chamber. These findings suggest that the cleaning process during each cycle contributes to the loss of filler particles during reprocessing.

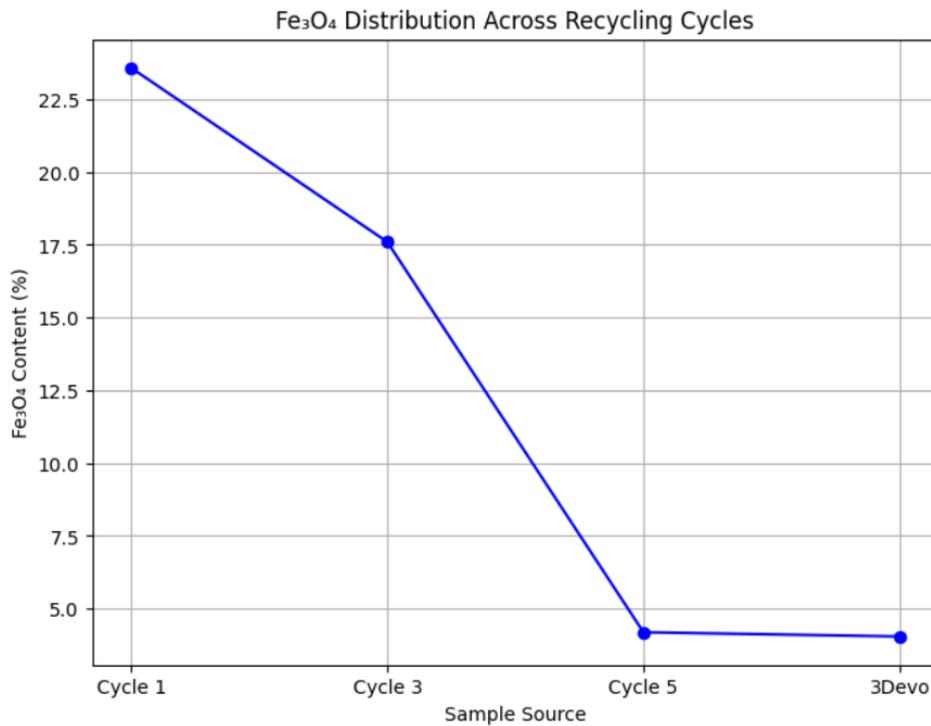


Figure 31: Fe₃O₄ Distribution Across Recycling Cycle (2nd type sample) and 3Devo Cleaner

Figure 31 also shows the differences in Fe₃O₄ particle distribution along the filament length. Compared to the first type of samples, which were taken from the beginning or the end of the filament, the second type of samples, taken from the middle part of the filament, showed a higher Fe₃O₄ content. For example, in the first cycle, the first sample had a Fe₃O₄ content of 12%, while the second sample had a higher content of 23%. By the third cycle, the first sample's Fe₃O₄ content decreased to 8%, while the second sample dropped to 17.5%. In the fifth cycle, the first sample's content was reduced to 1%, while the second sample still retained 3%. This suggests that magnetic particles appear to be more concentrated in the middle section of the filament rather than at the beginning or end. High-density fillers like magnetite ($5 \text{ (g/cm}^3\text{)}$) have a particular challenge in filament extrusion. The big difference in the density compared to the PLA matrix ($1.24 \text{ (g/cm}^3\text{)}$) makes the filler particle unevenly distributed. Heavier particles are more sensitive to settling because of gravity, especially during the extrusion process. In this research, fewer particles were found at the edges of the filament, suggesting that settling may lead to higher concentrations of magnetic particles in other areas, though further characterization and analysis is needed to identify the exact locations.

4.2.3. VSM

Vibrating Sample Magnetometry (VSM) is used to learn about the impact of recycling on the magnetic properties of PLA/Fe₃O₄ composites. The hysteresis loop that is obtained from VSM measurements is shown by Figure 32. From Figure 32, we can see there is a progressive decline in the saturation magnetization (Ms), coercivity (Hc), and remanent magnetization (Mr) as the number of recycling cycles increase. The first cycle is represented with a blue line, showing the highest saturation magnetization $16 \text{ Am}^2/\text{kg}$. Followed by the red line, which is the third cycle with $13 \text{ Am}^2/\text{kg}$. Next is the green and yellow line which represented the fifth and sixth cycle with saturation magnetization $9 \text{ Am}^2/\text{kg}$ and $7 \text{ Am}^2/\text{kg}$.

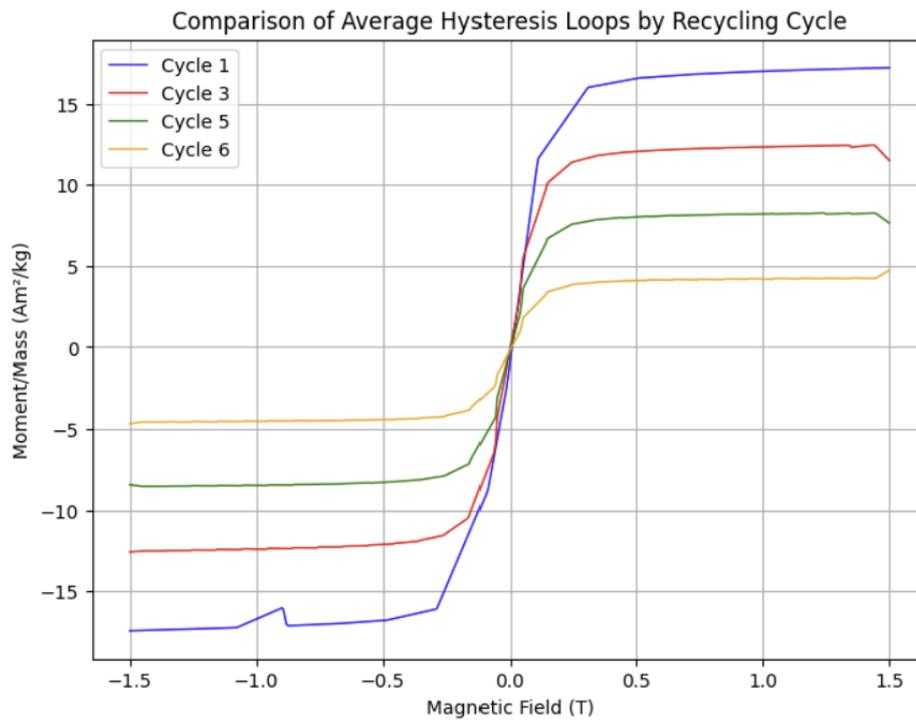


Figure 32: Comparison of Average Hysteresis Loops by Recycling Cycle

In a previous study, Mussig et al. [120] found that non-uniform filler distribution correlates with changes in magnetic properties. The area of the matrix that has fewer magnetite particles will contribute less to overall magnetization. In contrast, clustered particles might not effectively increase the composite's net magnetization. This study aligns with the results from SEM and EDS characterization which showing that repeated reprocessing can alter the dispersion of Fe_3O_4 particles inside the PLA matrix. This change in dispersion directly correlates with a decline in saturation magnetization, as observed in the VSM results, underscoring the significant impact that particle distribution has on the composite's magnetic properties.

The loss of Fe_3O_4 particles causing a significant impact on the magnetic properties. Looking at the TGA results in Figure 29, the curves show a drop in residual weight between 600 - 800 °C, which suggests a reduction in Fe_3O_4 content. This is further confirmed by the data in Figure 30. These findings align with the decrease in saturation magnetization observed in the VSM results, where a lower Fe_3O_4 content leads to reduced magnetic performance per unit mass. The trend in the hysteresis loops supports this connection as well.

4.2.4. GPC

Gel Permeation Chromatography (GPC) is used in this research to investigate changes in molecular weight distribution of the PLA/ Fe_3O_4 filaments composite through various recycling cycles. The result is presented in Table 4.3. Number-Average Molecular Weight (M_n) represents the average molecular weight of all polymer molecules, giving each molecule equal weight without concern for size. M_n reflects how many chains there are and what is their average weight. It is more sensitive to low molecular weight polymers. Meanwhile, weight-average molecular weight (M_w) represents the average molecular weight, giving heavier molecules more highlight. Next, the Polydispersity Index (M_w/M_n) is a measure of the spread of molecular weights in a polymer sample. A higher number of PDI means more heterogeneous polymer chains, possibly caused by degradation or incomplete polymerization. Lastly, M_z indicates the z-average molecular weight, which gives more importance to the very large molecules with the heaviest weight. M_z is used to analyze the tail of the molecular weight distribution because it can determine the polymer's performance [121].

The GPC results showed a reduction in both number-average (M_n) and weight-average molecular

weight (Mw) over the recycling cycles, with Mn decreasing by 26%, Mw by 52%, and Mz by 42% by the third cycle compared to the first. These reductions indicate PLA chain scission caused by repeated thermal and mechanical stress during reprocessing. Additionally, the polydispersity index (PDI) showed a gradual increase from the 1st to 6th cycle, suggesting a broader molecular weight distribution, which may indicate more diversity in polymer chain lengths. This could reflect uneven degradation behavior, though further analysis and characterization are needed to fully understand the underlying mechanisms. The decline in Mz (which decreased by 50% by the 6th cycle) suggests a reduction in the heaviest molecular weight fraction of the polymer, showing that the longest chains undergo degradation. This phenomenon implies a reduction in chain entanglement, which can negatively affect the mechanical properties and the polymer's printability. It was also observed that the behavior of the extruded filament during the filament-making process became less consistent with each recycling cycle. These findings are consistent with observations by Velghe et al. [97], who reported that thermomechanical degradation that was driven by both shear flow and thermal conditions caused direct PLA chain scission and reduced structural stability in the melt.

Cycle	Mn	Mw	Mz	Mw/Mn
1	87545	251940	334207	1343
3	64516	119951	190781	1858
5	37182	81792	172028	2200
6	29039	72770	164008	2506

Table 4.3: Measured molecular weight characteristics of PLA vs recycling cycles

Multiple recycling processes cause the PLA matrix to reduce molecular weight, affecting both filament quality and print performance. As chains get shorter, the material flows more easily, which is helpful at first for extrusion, but too much melt flow makes it hard to control, as we can see from the 6th cycle filament behavior (seen in Figure 25). The unstable behavior of the 6th filament after extruding through the nozzle corresponds to the significant reduction in molecular weight, with Mn decreasing by 66%, Mw by 71%, and Mz by 50%. This aligns with findings by Cuadri et al. [98], who reported that PLA exposed to high shear and elevated temperature undergoes accelerated molecular breakdown, making the material increasingly prone to flow instability and difficult to process.

PLA requires a sufficient molecular weight to maintain melt strength for proper filament drawing and consistent printing. Studies have shown that after about 2–3 extrusion cycles, the molecular weight can drop by over 20–30%, making the filament brittle and prone to snapping [122]. This behavior is consistent with the results observed in this study, where a significant decrease in molecular weight was noted, with Mn decreasing by 66.83%, Mw by 71.12%, and Mz by 50.93% after multiple recycling cycles. The filament becomes more difficult to handle and spool during reprocessing because of its brittle properties causing an irregular spooling shape. The decline in molecular weight also weakens printed parts, especially between layers. Higher molecular weight PLA allows better layer bonding due to more chain entanglement, while degraded PLA struggles to tie layers together, leading to delamination [123]. This delamination phenomenon also corresponds with the occurrence of material loss during processing and handling.

4.2.5. NMR

To investigate the potential presence of residual dichloromethane (DCM) inside the PLA/Fe₃O₄ composite material after reprocessing, both proton (1H) and carbon (13C) nuclear magnetic resonance (NMR) spectroscopy were conducted on samples from 1st reprocessing cycle. There are two kinds of samples that were observed in this research, the first sample is the normal processed filament, and the other with DCM intentionally added to the NMR tube, which is used as a reference. Figure 33 shows the 1H NMR spectrum of the reference sample, showing a distinct peak at 5.22 ppm [124] with a splitting pattern of CH₂ protons in DCM [125]. On the other hand, the spectrum from the normal sample doesn't have any double or split peaks, which indicates that there is no presence of DCM inside the material.

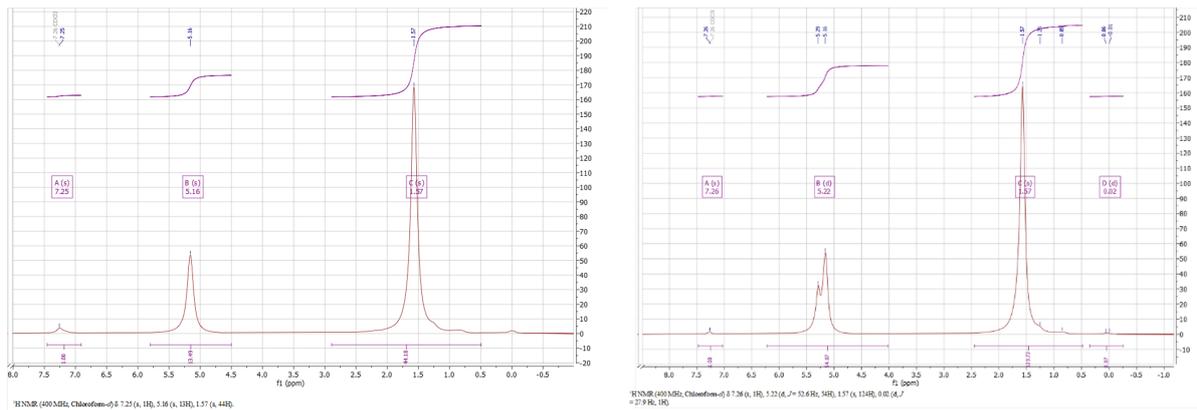


Figure 33: 1H NMR Result untreated sample (left) and treated sample (right)

Further confirmation is obtained from ^{13}C NMR spectra, which are represented by Figure 34. The treated sample showed a clear signal at 53 ppm, which corresponds with the carbon atom in CH_2Cl_2 indicating the presence of DCM solvent. Nonetheless, this peak is absent in the untreated sample, which only exhibited PLA characteristics signals at 169.7 ppm (carbonyl carbon), 69.1 ppm (the backbone of CH), and 16.7 ppm (methyl group) [126]. The absence of DCM peak in the ^1H and ^{13}C NMR spectrum in untreated samples provides strong evidence that there are no DCM residues in the composite after the making and filament fabrication process.

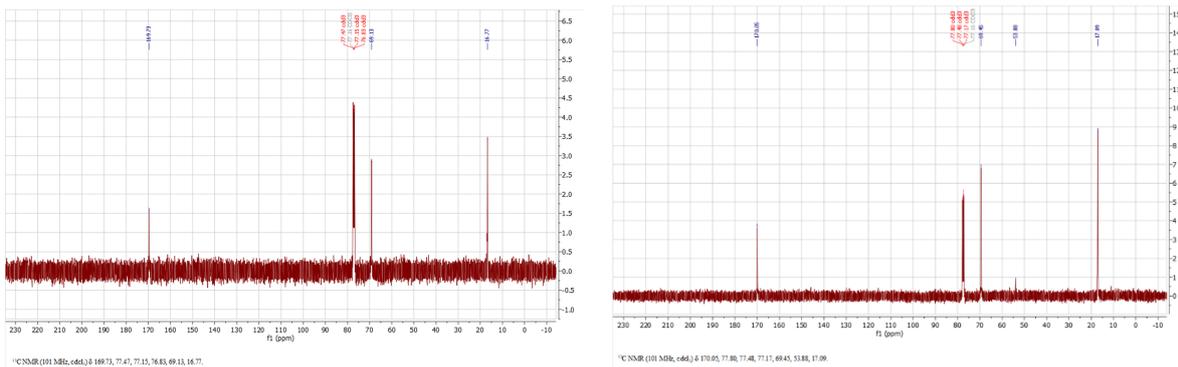


Figure 34: ^{13}C NMR Result untreated sample (left) and treated sample (right)

Based on NMR results, it can be concluded that the extrusion and drying processes used in this filament fabrication are sufficient to remove the residual DCM from PLA/ Fe_3O_4 the composite. DCM, used during the initial processing, has a low boiling point of around 40°C , and although the composite was dried at 60°C , there was some concern that traces might remain trapped in the material. However, since filament extrusion involves much higher temperatures (at least 170°C), it's reasonable to expect complete evaporation of the solvent. This expectation was confirmed by NMR analysis, which showed no detectable DCM in untreated samples. These results eliminate the possibility of DCM that acts like a plasticizer, interfering with crystallinity, or accelerating the chain scission process. Therefore, it is ensured that the observed changes in composite properties across recycling cycles are caused solely by the mechanical and thermal effects of reprocessing and not by solvent retention.

5

Conclusion and Recommendation

5.1. Conclusion

This research explored the impact of repeated recycling on a composite filament made from polylactic acid (PLA) with 20 wt% Fe_3O_4 magnetic particles. Multiple recycling cycles were done through manual cutting and to evaluate the structural integrity, magnetic properties, morphology, and thermal stability of the composite across multiple processing cycles.

The results showed that a clear degradation occurred, decreasing filament quality and composite performance as the number of recycling cycles increased. Visual analysis revealed that filament surface defects, such as bumps, uneven filament curvature, and brittleness, became more visible with each cycle. Diameter consistency worsened by the 5th cycle, with the largest diameter range (2.37 mm) and standard deviation (0.44 mm), compared to the 1st cycle, which had a diameter range of 0.83 mm and standard deviation of 0.21 mm. Meanwhile, the 6th cycle was fabricated under severe deformation conditions, indicating the material's limit of reusability. The filament produced after the 6th reprocessing cycle displayed severe degradation, with the average diameter showing an increase from 1.90 mm in the fifth cycle to an even more inconsistent and flawed extrusion, marked by excessive fluidity, loss of structural integrity, and fragility, ultimately reflecting the practical limit of recyclability, where the material could no longer be effectively processed or extruded.

SEM and EDS characterization showed that in the beginning, the Fe_3O_4 particles were uniformly dispersed and became agglomerated in later cycles. The iron content also dropped significantly, from 20.72 wt% in the 1st cycle to 7.85 wt% by the 5th cycle. It confirms that material loss through repeated handling and extrusion is also supported by detecting Fe content in the 3Devo cleaning filaments. Microstructural changes were also found in the 1st cycle. Distinct microcracks formed within the PLA matrix, likely due to localized stress, but by the 5th cycle, these were replaced by rough, irregular fractures and voids, suggesting more advanced degradation. These morphological changes contributed to the overall decline in mechanical properties.

TGA analysis supported these observations by showing a consistent reduction in Fe_3O_4 residual weight in each cycle. The 6th cycle sample exhibited the lowest thermal stability and had minimal residual mass, which implies a significant loss of magnetic filler and thermal degradation of the PLA matrix. VSM measurements also reflected this trend with the decrease in magnetization saturation from 16 Am^2/kg in the first cycle to 7 Am^2/kg in the 6th cycle, which confirms the loss of magnetic behavior caused by filler loss and poor particle dispersion.

GPC analysis showed that repeated recycling can reduce molecular weights (M_n and M_w) and increase the polydispersity index (PDI). The result implies progressive chain scission and broadening the molecular weight distribution. These molecular changes are related to the observation of filament reliability and printability during the filament fabrication process.

NMR analysis eliminated solvent retention as a contributing factor to the degradation observed during processing, as no DCM peaks were detected in the NMR spectra of untreated samples. DCM, used

during the initial processing stage, has a low boiling point of around 40 °C. Although the composite was dried at 60 °C, there was still concern about residual solvent being trapped inside the material. However, the filament extrusion process, which operates at temperatures of at least 170 °C, is sufficient to remove any remaining DCM. The absence of DCM in both ¹H and ¹³C NMR confirms that the solvent was successfully eliminated during processing. These results rule out the possibility of DCM acting as a plasticizer, altering crystallinity, or accelerating chain scission. Therefore, the degradation observed throughout the recycling cycles can be attributed to mechanical and thermal effects alone.

In conclusion, PLA/Fe₃O₄ composite filaments can be recycled until five cycles. However, with each recycling step, the material becomes increasingly brittle, which compromises its suitability for use as a functional filament. Although recycling is technically possible up to five times, practical observations, such as increased brittleness and difficulty during spooling, suggest that a maximum of three recycling cycles is more appropriate to maintain usability. Further mechanical testing is recommended to more precisely evaluate the performance limitations for recycling this composite material.

Physical changes, particularly in diameter inconsistencies and surface bumps, were observed since the first recycling cycle. Although the filament can technically be recycled up to five times, these irregularities compromise its printability from the beginning, making it increasingly unsuitable for reliable use in 3D printers. These bumps will increase the potential for the filament to get stuck in the feeder mechanism of 3D printers, which causes feeding failures or clogging. Even though the fifth cycle filament can technically be reprocessed, its functionality is unsuitable for consistent 3D printing output.

These findings highlight the practical recyclability limit of PLA/Fe₃O₄ the composite and give insights into degradation mechanisms. Further research is encouraged to optimize the recycling process, investigate the effects of additives or compatibilizers, potential magnetic particle oxidation, and explore alternative fillers and matrix materials to improve the sustainable work environment in additive manufacturing.

5.2. Recommendation

Based on the findings and limitations that have been encountered during this research, several recommendations are proposed to improve future PLA/Fe₃O₄ composite recycling:

1. Utilization of Advance Processing Equipment

It is recommended to use more updated processing technologies, which allow for direct 3D printing from shredded materials without requiring to remake the filament. This approach can significantly reduce material loss and minimize thermal and mechanical degradation of the polymer matrix, which improves the sustainability and efficiency of the recycling process.

2. Magnetic Particle Percentage Variable

The effect of the magnetic particles' presence on the PLA matrix is still unexplored. In order to deepen the understanding of how magnetic particles can contribute to PLA matrix degradation, using various magnetic percentage variables in the future is needed.

3. Improved Shredding and Cutting Method

The current manual cutting process using nail clippers may introduce contamination or moisture into the material and lead to inconsistent filament size, which can enhance the degradation of the material. It is also recommended to use mechanical shredders or filament choppers in a more controlled and less humid environment to reduce moisture exposure.

4. Phase Analysis of Magnetic Particles

In order to gain a better understanding of the impact of recycling on magnetic properties, phase identification tests such as XRD are suggested to verify if the Fe₃O₄ particles undergo oxidation during reprocessing. This oxidation process could significantly affect the magnetic properties of composites.

5. Mechanical Property Testing

Future work should include mechanical testing, particularly brittleness and tensile strength tests, to support the qualitative observation that was made in this study. Data from mechanical testing is important to determine the usability of recycled filaments for proper 3D printing parts.

6. Melt Flow Index Measurements (MFI)

It is recommended that MFI testing be conducted to evaluate how the PLA/Fe₃O₄ composite flow behaves after each cycle. MFI data can provide valuable information regarding changes in viscosity and processability during recycling, which is useful for the next 3D printing steps.

By implementing these recommendations, future research will be able to achieve a deeper understanding of how materials behave and the degradation in each recycling cycle and create a more reliable path toward sustainable magnetic composite filaments in additive manufacturing.

References

- [1] L. Dammer, M. Carus, A. Raschka, L. Scholz, and nova-Institute, "Market Developments of and Opportunities for biobased products and chemicals," Tech. Rep., 2013. [Online]. Available: https://www.eumonitor.nl/9353000/1/j4nvg5kjg27kof_j9vvik7m1c3gyxp/vjken6y2ivvo/f%3D/blg338557.pdf.
- [2] J. Mehta, K. Gupta, S. Lavania, P. Kumar, V. Chaudhary, and P. Gupta, "Inherent roadmap in synthesis and applications of sustainable materials using oil based and microbial polymers," *Materials Today Sustainability*, vol. 25, p. 100615, Mar. 2024. DOI: 10.1016/j.mtsust.2023.100615.
- [3] T. Jackson, *The origin of PLA and its importance in 3d printing*, Jun. 2023. [Online]. Available: <https://www.sunlu.com/blogs/products-knowledge/the-origin-of-pla-and-its-importance-in-3d-printing>.
- [4] E. H. Tümer and H. Y. Erbil, "Extrusion-Based 3D Printing Applications of PLA Composites: A review," *Coatings*, vol. 11, no. 4, p. 390, Mar. 2021. DOI: 10.3390/coatings11040390.
- [5] M. V. P. Van den Eyden, *Industrial Applications of Poly(lactic acid)*. Jan. 2018, vol. 282, pp. 139–158. DOI: 10.1007/978-3-319-75459-8.
- [6] Z. Liu, Q. Jiang, Y. Zhang, T. Li, and H. Zhang, "Sustainability of 3D printing: A critical review and recommendations," *Volume 2: Materials; Biomanufacturing; Properties, Applications and Systems; Sustainable Manufacturing*, Jun. 2016. DOI: 10.1115/msec2016-8618.
- [7] L. Sandanamsamy, W. S. W. Harun, I. Ishak, *et al.*, "A comprehensive review on fused deposition modelling of polylactic acid," *Progress in additive manufacturing*, vol. 8, no. 5, pp. 775–799, Oct. 2022. DOI: 10.1007/s40964-022-00356-w.
- [8] Andersonsabelle, "Mechanical Properties of Specimens 3D Printed with Virgin and Recycled Polylactic Acid," *3D printing and additive manufacturing*, vol. 4, no. 2, pp. 110–115, Jun. 2017. DOI: 10.1089/3dp.2016.0054.
- [9] T. Breški, L. Hentschel, D. Godec, and I. Đuretek, "Suitability of recycled PLA filament application in fused filament fabrication process," *Tehnički glasnik*, vol. 15, no. 4, pp. 491–497, Nov. 2021. DOI: 10.31803/tg-20210805120621.
- [10] V. K. Venkiteswaran, D. K. Tan, and S. Misra, "Tandem actuation of legged locomotion and grasping manipulation in soft robots using magnetic fields," *Extreme mechanics letters*, vol. 41, p. 101023, Nov. 2020. DOI: 10.1016/j.eml.2020.101023.
- [11] M. Wehner, R. L. Truby, D. Fitzgerald, *et al.*, "An integrated design and fabrication strategy for entirely soft, autonomous robots," *Nature*, vol. 536, no. 7617, pp. 451–455, Aug. 2016. DOI: 10.1038/nature19100.
- [12] J. Kim, S.-W. Chung, S.-E. Choi, H. Lee, J. Kim, and S. Kwon, "Programming magnetic anisotropy in polymeric microactuators," *Nature materials*, vol. 10, no. 10, pp. 747–752, Aug. 2011. DOI: 10.1038/nmat3090.
- [13] V. Nguyen, A. S. Ahmed, and R. Ramanujan, "Morphing soft magnetic composites," *Advanced materials*, vol. 24, no. 30, pp. 4041–4054, Jul. 2012. DOI: 10.1002/adma.201104994.
- [14] A. Yousaf, A. A. Rashid, R. Polat, and M. Koç, "Potential and challenges of recycled polymer plastics and natural waste materials for additive manufacturing," *Sustainable materials and technologies*, vol. 41, e01103, Sep. 2024. DOI: 10.1016/j.susmat.2024.e01103.
- [15] P. E. L. Marec, L. Ferry, J. C. Quantin, *et al.*, "Influence of melt processing conditions on poly(lactic acid) degradation: Molar mass distribution and crystallization," *Polymer degradation and stability*, vol. 110, pp. 353–363, Dec. 2014. DOI: 10.1016/j.polymdegradstab.2014.10.003. [Online]. Available: <https://doi.org/10.1016/j.polymdegradstab.2014.10.003>.

- [16] R. Solo, *Sustainability in Manufacturing: Reducing Waste with Additive Manufacturing* | Tronix3D, Sep. 2024. [Online]. Available: https://www.tronix3d.com/t3d-blog/sustainability-in-manufacturing-reducing-waste-with-additive-manufacturing?utm_source=chatgpt.com.
- [17] S. C. Ligon, R. Liska, J. Stampfl, M. Gurr, and R. Mülhaupt, "Polymers for 3D printing and customized additive manufacturing," *Chemical reviews*, vol. 117, no. 15, pp. 10 212–10 290, Jul. 2017. DOI: 10.1021/acs.chemrev.7b00074.
- [18] S. Ford and M. Despeisse, "Additive manufacturing and sustainability: an exploratory study of the advantages and challenges," *Journal of Cleaner Production*, vol. 137, pp. 1573–1587, May 2016. DOI: 10.1016/j.jclepro.2016.04.150.
- [19] A. Jamili, J. Jhabvala, S. Van Petegem, *et al.*, "Avoiding cracks in multi-material printing by combining laser powder bed fusion with metallic foils: application to Ti6Al4V-AISI12 structures," *Additive manufacturing*, p. 104 615, Dec. 2024.
- [20] S. Singh, S. Ramakrishna, and F. Berto, "3D Printing of polymer composites: A short review," *Material design processing communications*, vol. 2, no. 2, Aug. 2019. DOI: 10.1002/mdp2.97.
- [21] S. Christ, M. Schnabel, E. Vorndran, J. Groll, and U. Gbureck, "Fiber reinforcement during 3d printing," *Materials Letters*, vol. 139, pp. 165–168, 2015.
- [22] J. Wang and L. L. Shaw, "Fabrication of functionally graded materials via inkjet color printing," *Journal of the American Ceramic Society*, vol. 89, no. 10, pp. 3285–3289, 2006.
- [23] A. Winkel, R. Meszaros, S. Reinsch, *et al.*, "Sintering of 3 d-printed glass/ha p composites," *Journal of the American Ceramic Society*, vol. 95, no. 11, pp. 3387–3393, 2012.
- [24] K. S. Prakash, T. Nancharaih, and V. S. Rao, "Additive manufacturing techniques in manufacturing-an overview," *Materials Today: Proceedings*, vol. 5, no. 2, pp. 3873–3882, 2018.
- [25] M. Schmid, A. Amado, and K. Wegener, "Polymer powders for selective laser sintering (sls)," in *AIP Conference proceedings*, AIP Publishing, vol. 1664, 2015.
- [26] Y. Xia, P. Zhou, X. Cheng, *et al.*, "Selective laser sintering fabrication of nano-hydroxyapatite/poly- ϵ -caprolactone scaffolds for bone tissue engineering applications," *International journal of nanomedicine*, pp. 4197–4213, 2013.
- [27] L. Brandhoff, S. van den Driesche, F. Lucklum, and M. J. Vellekoop, "Creation of hydrophilic microfluidic devices for biomedical application through stereolithography," in *Bio-MEMS and Medical Microdevices II*, SPIE, vol. 9518, 2015, pp. 59–64.
- [28] P. J. Bártolo, *Stereolithography: materials, processes and applications*. Springer Science & Business Media, 2011.
- [29] R. J. Mondschein, A. Kanitkar, C. B. Williams, S. S. Verbridge, and T. E. Long, "Polymer structure-property requirements for stereolithographic 3d printing of soft tissue engineering scaffolds," *Biomaterials*, vol. 140, pp. 170–188, 2017.
- [30] F. W. Liou, *Rapid prototyping and engineering applications: a toolbox for prototype development*. Crc Press, 2007.
- [31] I. Gibson, D. W. Rosen, B. Stucker, *et al.*, *Additive manufacturing technologies*. Springer, 2021, vol. 17.
- [32] I. Pahole, I. Drstvensek, M. Ficko, and J. Balic, "Rapid prototyping processes give new possibilities to numerical copying techniques," *Journal of materials processing technology*, vol. 164, pp. 1416–1422, 2005.
- [33] N.-B. Cho, T.-H. Lim, Y.-M. Jeon, and M.-S. Gong, "Inkjet printing of polymeric resistance humidity sensor using uv-curable electrolyte inks," *Macromolecular Research*, vol. 16, pp. 149–154, 2008.
- [34] J. Bharathan and Y. Yang, "Polymer electroluminescent devices processed by inkjet printing: I. polymer light-emitting logo," *Applied Physics Letters*, vol. 72, no. 21, pp. 2660–2662, 1998.
- [35] J. Sumerel, J. Lewis, A. Doraiswamy, *et al.*, "Piezoelectric ink jet processing of materials for medicaland biological applications," *Biotechnology Journal: Healthcare Nutrition Technology*, vol. 1, no. 9, pp. 976–987, 2006.

- [36] Y. H. Yun, J. D. Kim, B. K. Lee, Y. W. Cho, and H. Y. Lee, "Polymer inkjet printing: Construction of three-dimensional structures at micro-scale by repeated lamination," *Macromolecular research/Macromolecular Research*, vol. 17, no. 3, pp. 197–202, Mar. 2009. [Online]. Available: <https://doi.org/10.1007/bf03218679>.
- [37] P. Parandoush and D. Lin, "A review on additive manufacturing of polymer-fiber composites," *Composite Structures*, vol. 182, pp. 36–53, 2017.
- [38] P. K. Penumakala, J. Santo, and A. Thomas, "A critical review on the fused deposition modeling of thermoplastic polymer composites," *Composites Part B: Engineering*, vol. 201, p. 108 336, 2020, ISSN: 1359-8368. DOI: <https://doi.org/10.1016/j.compositesb.2020.108336>. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1359836820333850>.
- [39] C. Bellehumeur, L. Li, Q. Sun, and P. Gu, "Modeling of bond formation between polymer filaments in the fused deposition modeling process," *Journal of manufacturing processes*, vol. 6, no. 2, pp. 170–178, 2004.
- [40] P. K. Gurralla and S. P. Regalla, "Part strength evolution with bonding between filaments in fused deposition modelling: This paper studies how coalescence of filaments contributes to the strength of final fdm part," *Virtual and Physical Prototyping*, vol. 9, no. 3, pp. 141–149, 2014.
- [41] R. B. Valapa, G. Pugazhenth, and V. Katiyar, "Effect of graphene content on the properties of poly (lactic acid) nanocomposites," *Rsc Advances*, vol. 5, no. 36, pp. 28 410–28 423, 2015.
- [42] D. S. Bajwa, S. Adhikari, J. Shojaeiarani, S. G. Bajwa, P. Pandey, and S. R. Shanmugam, "Characterization of bio-carbon and ligno-cellulosic fiber reinforced bio-composites with compatibilizer," *Construction and Building Materials*, vol. 204, pp. 193–202, 2019.
- [43] M. L. Di Lorenzo and R. Androsch, *Industrial Applications of Poly (lactic acid)*. Springer, 2018, vol. 282.
- [44] L. Ranakoti, B. Gangil, S. K. Mishra, *et al.*, "Critical review on Polylactic acid: Properties, structure, processing, biocomposites, and nanocomposites," *Materials*, vol. 15, no. 12, p. 4312, Jun. 2022. DOI: [10.3390/ma15124312](https://doi.org/10.3390/ma15124312).
- [45] V. Shanmugam, O. Das, R. E. Neisiany, *et al.*, "Polymer Recycling in Additive Manufacturing: an Opportunity for the Circular Economy," *Materials Circular Economy*, vol. 2, no. 1, Nov. 2020. DOI: [10.1007/s42824-020-00012-0](https://doi.org/10.1007/s42824-020-00012-0). [Online]. Available: <https://doi.org/10.1007/s42824-020-00012-0>.
- [46] Z. O. G. Schyns and M. P. Shaver, "Mechanical Recycling of Packaging Plastics: A review," *Macromolecular Rapid Communications*, vol. 42, no. 3, Sep. 2020. DOI: [10.1002/marc.202000415](https://doi.org/10.1002/marc.202000415). [Online]. Available: <https://doi.org/10.1002/marc.202000415>.
- [47] E. B. e.V., "MECHANICAL RECYCLING TECHNOLOGY LANDSCAPE," Tech. Rep., Jul. 2020. [Online]. Available: https://docs.european-bioplastics.org/publications/bp/EUBP_BP_Mechanical_recycling.pdf.
- [48] P. Europe, *Chemical recycling 8226; Plastics Europe*, Mar. 2024. [Online]. Available: <https://plasticseurope.org/sustainability/circularity/recycling/chemical-recycling/>.
- [49] *3D Printing Filament Market, Industry Size Growth Forecast, Trends Report, [Latest]*. [Online]. Available: <https://www.marketsandmarkets.com/Market-Reports/3d-printing-filament-market-267169690.html>.
- [50] Y. Ding, C. Abeykoon, and Y. S. Perera, "The effects of extrusion parameters and blend composition on the mechanical, rheological and thermal properties of LDPE/PS/PMMA ternary polymer blends," *Advances in Industrial and Manufacturing Engineering*, vol. 4, p. 100 067, Dec. 2021. DOI: [10.1016/j.aime.2021.100067](https://doi.org/10.1016/j.aime.2021.100067).
- [51] M. Stevens and J. A. Covas, *Extruder principles and operation*. Springer Science & Business Media, 2012.
- [52] J. Vlachopoulos and D. Strutt, "Polymer processing," *Materials Science and Technology*, vol. 19, no. 9, pp. 1161–1169, Sep. 2003. DOI: [10.1179/026708303225004738](https://doi.org/10.1179/026708303225004738).
- [53] D. Douroumis, *Hot-melt extrusion: Pharmaceutical applications*. John Wiley & Sons, 2012.

- [54] S. Shokoohi, A. Arefazar, and G. Naderi, "Compatibilized polypropylene/ethylene-propylene-diene-monomer/polyamide6 ternary blends: Effect of twin screw extruder processing parameters," *Materials & Design*, vol. 32, no. 3, pp. 1697–1703, 2011.
- [55] A. Jain, A. Nagpal, R. Singhal, and N. K. Gupta, "Effect of dynamic crosslinking on impact strength and other mechanical properties of polypropylene/ethylene-propylene-diene rubber blends," *Journal of applied polymer science*, vol. 78, no. 12, pp. 2089–2103, 2000.
- [56] C. Capone, L. Di Landro, F. Inzoli, M. Penco, and L. Sartore, "Thermal and mechanical degradation during polymer extrusion processing," *Polymer Engineering & Science*, vol. 47, no. 11, pp. 1813–1819, 2007.
- [57] C. Abeykoon, P. Pérez, and A. L. Kelly, "The effect of materials' rheology on process energy consumption and melt thermal quality in polymer extrusion," *Polymer Engineering & Science*, vol. 60, no. 6, pp. 1244–1265, 2020.
- [58] C. Abeykoon, A. McMillan, and B. K. Nguyen, "Energy efficiency in extrusion-related polymer processing: A review of state of the art and potential efficiency improvements," *Renewable and Sustainable Energy Reviews*, vol. 147, p. 111 219, 2021.
- [59] O. M. Jazani, A. Arefazar, M. Saeb, and A. Ghaemi, "Evaluation of mechanical properties of polypropylene/polycarbonate/sebs ternary polymer blends using taguchi experimental analysis," *Journal of Applied Polymer Science*, vol. 116, no. 4, pp. 2312–2319, 2010.
- [60] K. Hamad, M. Kaseem, and F. Deri, "Recycling of waste from polymer materials: An overview of the recent works," *Polymer Degradation and Stability*, vol. 98, no. 12, pp. 2801–2812, 2013, ISSN: 0141-3910. DOI: <https://doi.org/10.1016/j.polymdegradstab.2013.09.025>. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0141391013003133>.
- [61] H. Jin, J. Gonzalez-Gutierrez, P. Oblak, B. Zupančič, and I. Emri, "The effect of extensive mechanical recycling on the properties of low density polyethylene," *Polymer degradation and stability*, vol. 97, no. 11, pp. 2262–2272, 2012.
- [62] W. Waldman and M. A. De Paoli, "Thermo-mechanical degradation of polypropylene, low-density polyethylene and their 1: 1 blend," *Polymer Degradation and Stability*, vol. 60, no. 2-3, pp. 301–308, 1998.
- [63] C. Kartalis, C. Papaspyrides, and R. Pfaendner, "Recycling of post-used pe packaging film using the restabilization technique," *Polymer degradation and stability*, vol. 70, no. 2, pp. 189–197, 2000.
- [64] M. R. Vallim, J. R. Araujo, M. A. S. Spinace, and M.-A. De Paoli, "Polyamide-6/high-density polyethylene blend using recycled high-density polyethylene as compatibilizer: Morphology, mechanical properties, and thermal stability," *Polymer Engineering & Science*, vol. 49, no. 10, pp. 2005–2014, 2009.
- [65] J. Aurrekoetxea, M. Sarrionandia, I. Urrutibeascoa, and M. L. Maspoch, "Effects of recycling on the microstructure and the mechanical properties of isotactic polypropylene," *Journal of materials science*, vol. 36, pp. 2607–2613, 2001.
- [66] N. Tri Phuong, V. Gilbert, and B. Chuong, "Preparation of recycled polypropylene/organophilic modified layered silicates nanocomposites part i: The recycling process of polypropylene and the mechanical properties of recycled polypropylene/organoclay nanocomposites," *Journal of Reinforced Plastics and Composites*, vol. 27, no. 18, pp. 1983–2000, 2008.
- [67] J. Yang, J. Liang, and C. Y. Tang, "Studies on melt flow properties during capillary extrusion of pp/al (oh) 3/mg (oh) 2 flame retardant composites," *Polymer testing*, vol. 28, no. 8, pp. 907–911, 2009.
- [68] N. Bahlouli, D. Pessey, C. Raveyre, *et al.*, "Recycling effects on the rheological and thermomechanical properties of polypropylene-based composites," *Materials & Design*, vol. 33, pp. 451–458, 2012.
- [69] Z. Gao, T. Kaneko, I. Amasaki, and M. Nakada, "A kinetic study of thermal degradation of polypropylene," *Polymer Degradation and Stability*, vol. 80, no. 2, pp. 269–274, 2003.

- [70] L. Brennan, D. Isaac, and J. Arnold, "Recycling of acrylonitrile–butadiene–styrene and high-impact polystyrene from waste computer equipment," *Journal of applied polymer science*, vol. 86, no. 3, pp. 572–578, 2002.
- [71] F. Elmaghor, L. Zhang, and H. Li, "Recycling of high density polyethylene/poly (vinyl chloride)/polystyrene ternary mixture with the aid of high energy radiation and compatibilizers," *Journal of applied polymer science*, vol. 88, no. 12, pp. 2756–2762, 2003.
- [72] C. Remili, M. Kaci, A. Benhamida, S. Bruzaud, and Y. Grohens, "The effects of reprocessing cycles on the structure and properties of polystyrene/cloisite 15a nanocomposites," *Polymer Degradation and Stability*, vol. 96, no. 8, pp. 1489–1496, 2011.
- [73] L. Zaidi, M. Kaci, S. Bruzaud, A. Bourmaud, and Y. Grohens, "Effect of natural weather on the structure and properties of polylactide/cloisite 30b nanocomposites," *Polymer Degradation and Stability*, vol. 95, no. 9, pp. 1751–1758, 2010.
- [74] T. Boronat, V. Segui, M. Peydro, and M. Reig, "Influence of temperature and shear rate on the rheology and processability of reprocessed abs in injection molding process," *Journal of Materials Processing Technology*, vol. 209, no. 5, pp. 2735–2745, 2009.
- [75] J. Pérez, J. Vilas, J. Laza, *et al.*, "Effect of reprocessing and accelerated weathering on abs properties," *Journal of Polymers and the Environment*, vol. 18, pp. 71–78, 2010.
- [76] E.-K. Karahaliou and P. Tarantili, "Stability of abs compounds subjected to repeated cycles of extrusion processing," *Polymer Engineering & Science*, vol. 49, no. 11, pp. 2269–2275, 2009.
- [77] S.-C. Chen, W.-H. Liao, M.-W. Hsieh, R.-D. Chien, and S.-H. Lin, "Influence of recycled abs added to virgin polymers on the physical, mechanical properties and molding characteristics," *Polymer-Plastics Technology and Engineering*, vol. 50, no. 3, pp. 306–311, 2011.
- [78] R. Scaffaro, L. Botta, and G. Di Benedetto, "Physical properties of virgin-recycled abs blends: Effect of post-consumer content and of reprocessing cycles," *European Polymer Journal*, vol. 48, no. 3, pp. 637–648, 2012.
- [79] S.-K. Yeh, S. Agarwal, and R. K. Gupta, "Wood–plastic composites formulated with virgin and recycled abs," *Composites Science and Technology*, vol. 69, no. 13, pp. 2225–2230, 2009.
- [80] X. J. Bai, Z. Wu, and N. Feng, "Degradation of abs in abs/caco3 composites during reprocessing," *Advanced Materials Research*, vol. 455, pp. 845–850, 2012.
- [81] S. Papong, P. Malakul, R. Trungkavashirakun, *et al.*, "Comparative assessment of the environmental profile of PLA and PET drinking water bottles from a life cycle perspective," *Journal of cleaner production*, vol. 65, pp. 539–550, Feb. 2014. DOI: 10.1016/j.jclepro.2013.09.030.
- [82] I. Pillin, N. Montrelay, A. Bourmaud, and Y. Grohens, "Effect of thermo-mechanical cycles on the physico-chemical properties of poly (lactic acid)," *Polymer Degradation and Stability*, vol. 93, no. 2, pp. 321–328, 2008.
- [83] J. Badía, E. Strömberg, S. Karlsson, and A. Ribes-Greus, "Material valorisation of amorphous polylactide. Influence of thermo-mechanical degradation on the morphology, segmental dynamics, thermal and mechanical performance," *Polymer degradation and stability*, vol. 97, no. 4, pp. 670–678, Apr. 2012. DOI: 10.1016/j.polymdegradstab.2011.12.019.
- [84] B. Brüster, F. Addiego, F. Hassouna, D. Ruch, J.-M. Raquez, and P. Dubois, "Thermo-mechanical degradation of plasticized poly(lactide) after multiple reprocessing to simulate recycling: Multi-scale analysis and underlying mechanisms," *Polymer degradation and stability*, vol. 131, pp. 132–144, Sep. 2016. DOI: 10.1016/j.polymdegradstab.2016.07.017.
- [85] A. Soroudi and I. Jakubowicz, "Recycling of bioplastics, their blends and biocomposites: A review," *European Polymer Journal*, vol. 49, no. 10, pp. 2839–2858, 2013.
- [86] T. Ramos-Hernández, J. R. Robledo-Ortíz, A. S. M. Del Campo, D. Rodrigue, A. Cano, and A. A. Pérez-Fonseca, "Mechanical recycling of poly(lactic acid)/agave fiber biocomposites," *Journal of reinforced plastics and composites*, May 2024. DOI: 10.1177/07316844241253905.
- [87] N. X. Li, N. L. G. Tabil, N. S. Panigrahi, and N. W. J. Crerar, "The Influence of Fiber Content on Properties of Injection Molded Flax Fiber-HDPE Biocomposites," *Publication*, Jan. 2006. DOI: 10.13031/2013.22101.

- [88] N. Eselini, S. Tirkes, A. O. Akar, and U. Tayfun, "Production and characterization of poly (lactic acid)-based biocomposites filled with basalt fiber and flax fiber hybrid," *Journal of elastomers and plastics*, vol. 52, no. 8, pp. 701–716, Nov. 2019. DOI: 10.1177/0095244319884716.
- [89] "Characterisation of multi-extruded poly(lactic acid)," *Polymer Testing*, vol. 28, no. 4, pp. 412–418, 2009, ISSN: 0142-9418. DOI: <https://doi.org/10.1016/j.polymeresting.2009.01.012>. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0142941809000191>.
- [90] N. S. Q. S. Amorin, G. Rosa, J. F. Alves, S. P. C. Gonçalves, S. M. M. Franchetti, and G. J. M. Fechine, "Study of thermodegradation and thermostabilization of poly(lactide acid) using subsequent extrusion cycles," *Journal of applied polymer science*, vol. 131, no. 6, Oct. 2013. DOI: 10.1002/app.40023.
- [91] V. C. Agbakoba, N. Webb, E. Jegede, R. Phillips, S. P. Hlangothi, and M. J. John, "Mechanical recycling of waste PLA generated from 3D printing activities: filament production and thermo-mechanical analysis," *Macromolecular materials and engineering*, Nov. 2023. DOI: 10.1002/mame.202300276.
- [92] L. Delva, K. Ragaert, J. Degrieck, and L. Cardon, "The effect of multiple extrusions on the properties of montmorillonite filled polypropylene," *Polymers*, vol. 6, no. 12, pp. 2912–2927, Dec. 2014. DOI: 10.3390/polym6122912. [Online]. Available: <https://www.mdpi.com/2073-4360/6/12/2912#:~:text=most%20pronounced%20for%20the%20PP,clay%20in%20the%20PP%20matrix.>
- [93] S. Samal and I. Blanco, "Investigation of dispersion, interfacial adhesion of isotropic and anisotropic filler in polymer composite," *Applied Sciences*, vol. 11, no. 18, p. 8561, Sep. 2021. DOI: 10.3390/app11188561. [Online]. Available: <https://www.mdpi.com/2076-3417/11/18/8561>.
- [94] O. Mysiukiewicz, M. Barczewski, K. Skórczewska, and D. Matykiewicz, "Correlation between Processing Parameters and Degradation of Different Polylactide Grades during Twin-Screw Extrusion," *Polymers*, vol. 12, no. 6, p. 1333, Jun. 2020. DOI: 10.3390/polym12061333.
- [95] K. Akaradechakul, P. Chanthot, N. Kerddonfag, and C. Pattamaprom, "The effect of polycarbodiimide chain extender on thermal stability and mechanical properties of biobased poly(lactic acid)/natural rubber blown films," *Journal of Plastic Film Sheeting*, vol. 38, no. 3, pp. 396–415, Mar. 2022. DOI: 10.1177/87560879211058679. [Online]. Available: <https://doi.org/10.1177/87560879211058679>.
- [96] T. Instruments and K. Coasey, "Thermal stability of Bio-Derived polymer feedstock," Tech. Rep. [Online]. Available: <https://www.tainstruments.com/pdf/literature/TA456.pdf#:~:text=PLA%20can%20degrade%20during%20processing,photodegradation%20when%20exposed%20to%20UV.>
- [97] I. Velghe, B. Buffel, V. Vandeginste, W. Thielemans, and F. Desplentere, "Review on the Degradation of Poly(lactic acid) during Melt Processing," *Polymers*, vol. 15, no. 9, p. 2047, Apr. 2023. DOI: 10.3390/polym15092047. [Online]. Available: <https://pmc.ncbi.nlm.nih.gov/articles/PMC10181416/#:~:text=,temperature%20due%20to%20shear%20heating.>
- [98] A. Cuadri and J. Martín-Alfonso, "Thermal, thermo-oxidative and thermomechanical degradation of PLA: A comparative study based on rheological, chemical and thermal properties," *Polymer Degradation and Stability*, vol. 150, pp. 37–45, Feb. 2018. DOI: 10.1016/j.polymerdegradstab.2018.02.011. [Online]. Available: <https://doi.org/10.1016/j.polymerdegradstab.2018.02.011>.
- [99] P. Main, S. Petersmann, N. Wild, *et al.*, "Impact of multiple reprocessing on properties of polyhydroxybutyrate and polypropylene," *Polymers*, vol. 15, no. 20, p. 4126, Oct. 2023. DOI: 10.3390/polym15204126. [Online]. Available: <https://www.mdpi.com/2073-4360/15/20/4126>.
- [100] B. Yu, M. Wang, H. Sun, F. Zhu, J. Han, and G. Bhat, "Preparation and properties of poly (lactic acid)/magnetic Fe₃O₄ composites and nonwovens," *RSC Advances*, vol. 7, no. 66, pp. 41 929–41 935, Jan. 2017. DOI: 10.1039/c7ra06427f.
- [101] B. Wu, H. Zhu, Y. Yang, *et al.*, "Effect of different proportions of CNTs/Fe₃O₄ hybrid filler on the morphological, electrical and electromagnetic interference shielding properties of poly(lactic acid) nanocomposites," *e-Polymers*, vol. 23, no. 1, Jan. 2023. DOI: 10.1515/epoly-2023-0006.

- [102] M. A. Yousefi, D. Rahmatabadi, M. Baniassadi, M. Bodaghi, and M. Baghani, "4D Printing of Multifunctional and Biodegradable PLA/PBAT/Fe₃O₄ Nanocomposites with Supreme Mechanical and Shape Memory Properties," *Macromolecular Rapid Communications*, Oct. 2024. DOI: 10.1002/marc.202400661. [Online]. Available: <https://pmc.ncbi.nlm.nih.gov/articles/PMC11756866/#:~:text=,indicating%20improved%20thermal%20stability>.
- [103] J. O. C. De França, Q. D. S. Lima, M. M. De Melo Barbosa, *et al.*, "Sonochemical Synthesis of Magnetite/Poly(lactic acid) Nanocomposites," *Polymers*, vol. 15, no. 24, p. 4662, Dec. 2023. DOI: 10.3390/polym15244662. [Online]. Available: <https://www.mdpi.com/2073-4360/15/24/4662#:~:text=assumption%2C%20in%20turn%2C%20is%20supported,were%20completely%20oxidized%20to%20hematite>.
- [104] U. S. H. Al-Kindi, S. H. Al-Harhi, H. M. Widatallah, M. E. Elzain, M. T. Z. Myint, and H. H. Kyaw, "SN²⁺ doping: A strategy for tuning of Fe₃O₄ nanoparticles magnetization dipping Temperature/Amplitude, Irreversibility, and curie Point," *Nanoscale Research Letters*, vol. 15, no. 1, Oct. 2020. DOI: 10.1186/s11671-020-03423-9. [Online]. Available: <https://pmc.ncbi.nlm.nih.gov/articles/PMC7530164/#:~:text=since%20nanoparticles%20with%20size%20of,s%7D%20of>.
- [105] A. Jafari, S. F. Shayesteh, M. Salouti, and K. Boustani, "Effect of annealing temperature on magnetic phase transition in Fe₃O₄ nanoparticles," *Journal of Magnetism and Magnetic Materials*, vol. 379, pp. 305–312, Dec. 2014. DOI: 10.1016/j.jmmm.2014.12.050. [Online]. Available: <https://doi.org/10.1016/j.jmmm.2014.12.050>.
- [106] L. R. Khanal, M. Ahmadzadeh, J. S. McCloy, and Y. Qiang, "Relationship between nanostructure-magnetic property induced by temperature for iron oxide nanoparticles in vacuum, Ar and O₂ environments," *Journal of Magnetism and Magnetic Materials*, vol. 498, p. 166 158, Nov. 2019. DOI: 10.1016/j.jmmm.2019.166158.
- [107] A. Bukowska, K. Bester, S. Flaga, and W. Bukowski, "Reactive polymer composite microparticles based on glycidyl methacrylate and magnetite nanoparticles," *Solids*, vol. 5, no. 1, pp. 151–171, Mar. 2024. DOI: 10.3390/solids5010011. [Online]. Available: <https://www.mdpi.com/2673-6497/5/1/11#:~:text=seemed%20to%20suggest%20that%20some,of%20the%20magnetite%20particles%20added>.
- [108] A. Agüero, M. Del Carmen Morcillo, L. Quiles-Carrillo, *et al.*, "Study of the influence of the re-processing cycles on the final properties of polylactide pieces obtained by injection molding," *Polymers*, vol. 11, no. 12, p. 1908, Nov. 2019. DOI: 10.3390/polym11121908.
- [109] J. Tamnanloo and M. Tsige, "All-atom molecular dynamics simulation of solvent diffusion in unentangled polystyrene film," *Soft Matter*, vol. 20, no. 26, pp. 5195–5202, Jan. 2024. DOI: 10.1039/d4sm00641k. [Online]. Available: <https://pubs.rsc.org/en/content/articlelanding/2024/sm/d4sm00641k>.
- [110] T. Phaechamud and S. Chitrattha, "Pore formation mechanism of porous poly(dl-lactic acid) matrix membrane," *Materials Science and Engineering C*, vol. 61, pp. 744–752, Jan. 2016. DOI: 10.1016/j.msec.2016.01.014.
- [111] *Sigma-Aldrich. Safety data sheet dichloromethane 32222-m, 2022.*
- [112] *Resinex. Ingeo 4043d natureworks llc - polylactic acid, 2020.*
- [113] *Sigma-Aldrich. Safety data sheet iron(ii,iii)oxide, 2023.*
- [114] A. Amirov, A. Omelyanchik, D. Murzin, *et al.*, "3D printing of PLA/Magnetic ferrite composites: Effect of filler particles on magnetic properties of filament," *Processes*, vol. 10, no. 11, p. 2412, Nov. 2022. DOI: 10.3390/pr10112412.
- [115] *Output too low or thin.* [Online]. Available: <https://support.3devo.com/output-too-low-or-thin>.
- [116] F. H. Engelen, "Material preparation, design and production of an actuated 3d printed magnetic part," M.S. thesis, University of Twente, Department of Engineering Technology, Apr. 2024.
- [117] P. Knight, A. Johansen, H. Kristensen, T. Schæfer, and J. Seville, "An investigation of the effects on agglomeration of changing the speed of a mechanical mixer," *Powder Technology*, vol. 110, no. 3, pp. 204–209, Jun. 2000. DOI: 10.1016/s0032-5910(99)00259-4.

- [118] S.-L. Yang, Z.-H. Wu, W. Yang, and M.-B. Yang, "Thermal and mechanical properties of chemical crosslinked polylactide (PLA)," *Polymer testing*, vol. 27, no. 8, pp. 957–963, Dec. 2008. DOI: 10.1016/j.polymeresting.2008.08.009.
- [119] V. E. Bazhenov, A. V. Sannikov, E. P. Kovyshkina, *et al.*, "The influence of injection temperature and pressure on pattern wax fluidity," *Journal of Manufacturing and Materials Processing*, vol. 7, no. 4, p. 141, Aug. 2023. DOI: 10.3390/jmmp7040141.
- [120] S. Müssig, B. Kuttich, F. Fidler, *et al.*, "Reversible magnetism switching of iron oxide nanoparticle dispersions by controlled agglomeration," *Nanoscale Advances*, vol. 3, no. 10, pp. 2822–2829, Jan. 2021. DOI: 10.1039/d1na00159k.
- [121] Agilent, "Polymer molecular weight distribution and definitions of MW averages," Tech. Rep., Apr. 2015. [Online]. Available: <https://www.agilent.com/cs/library/technicaloverviews/Public/5990-7890EN.pdf>.
- [122] D. Hidalgo-Carvajal, Á. H. Muñoz, J. J. Garrido-González, R. Carrasco-Gallego, and V. A. Montero, "Recycled PLA for 3D Printing: A Comparison of Recycled PLA Filaments from Waste of Different Origins after Repeated Cycles of Extrusion," *Polymers*, vol. 15, no. 17, p. 3651, Sep. 2023. DOI: 10.3390/polym15173651. [Online]. Available: <https://www.mdpi.com/2073-4360/15/17/3651#:~:text=In%203D%20printing%2C%20viscosity%20is,Thus%2C%20the%20intrinsic%20viscosity>.
- [123] D. Lee, Y. Lee, I. Kim, K. Hwang, and N. Kim, "Thermal and mechanical degradation of recycled polylactic acid filaments for Three-Dimensional printing applications," *Polymers*, vol. 14, no. 24, p. 5385, Dec. 2022. DOI: 10.3390/polym14245385. [Online]. Available: <https://pmc.ncbi.nlm.nih.gov/articles/PMC9781530/#:~:text=is%20due%20to%20a%20reduction,polymer%20materials%2C%20which%20can%20be>.
- [124] *Dichloromethane(75-09-2) 1H NMR spectrum*. [Online]. Available: https://www.chemicalbook.com/SpectrumEN_75-09-2_1HNMR.htm.
- [125] G. Ye, Q. Yong, L. Hu, *et al.*, "Molecular engineering of nanocellulose-poly(lactic acid) bio-nanocomposite interface by reactive surface grafting from copolymerization," *International Journal of Biological Macromolecules*, vol. 306, p. 141 371, Feb. 2025. DOI: 10.1016/j.ijbiomac.2025.141371.
- [126] *Dichloromethane(75-09-2) 13C NMR spectrum*. [Online]. Available: https://www.chemicalbook.com/SpectrumEN_75-09-2_13CNMR.htm.