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Recycling in Polymer Additive Manufacturing

A review of recycling methods and their impact on thermomechanical properties of polymers

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Polymer material production is increasing yearly, and improvements for polymer waste management are required. Polymer additive manufacturing uses thermoplastic materials, which means that they can be obtained through the common recycling methods for polymers. Recycling supports circular economy, and economical and ecological advantages can be found by using recycled feedstock in additive manufacturing instead of using raw materials. In this thesis, a literature review was conducted to present ways to recycle polymer waste into feedstock for polymer additive manufacturing.

Polymer recycling processes are mechanical, thermal, and chemical. Mechanical recycling is cheaper and easy to implement, but it is unable to remove impurities from the polymer waste. Chemical and thermo-chemical recycling is able to remove impurities, but it is generally more expensive and energy-consuming to use when compared to mechanical. Recycling generally decreases thermomechanical properties of polymers, which can cause problems in both the mechanical properties of the printed parts, and the printability of the recycled polymer feedstock.

There are available solutions to decrease the thermomechanical degradation of the recycled polymer, which increases the usability of the recycled feedstock in additive manufacturing. For example, virgin polymer material can be added to the recycled polymer before the re-extrusion, which is a relatively cheap way to increase the thermomechanical properties. It is suggested that large-format additive manufacturing should be considered when using recycled feedstock. The large-format additive manufacturing printing process is less likely to fail due to small inconsistencies in the feedstock, and a larger printing area allows the printing layer to cool down more before another layer is added, which increases the interlayer fusion. A need for standardization of recycling was found in additively manufactured polymer parts, such as already exists with polymer parts made with conventional manufacturing methods.

Key words: Additive manufacturing, recycling, polymer.

Polymeerintuotanto kasvaa vuosittain, minkä vuoksi parannuksille polymeerijätteen käsittelyssä on kasvava tarve. Polymeeria käyttävä lisäävä valmistus käyttää lämpömuovattavia polymeereja raaka-aineena, joten raaka-ainetta voidaan saada polymeerin kierrätysmekanismeja hyödyntämällä. Kierrättäminen kannattaa kiertotaloutta, minkä lisäksi kierrätetyn materiaalin käyttö uuden raaka-aineen sijaan antaa muita ekologisia sekä taloudellisia etuja. Tämä tutkielma on kirjallisuuskatsaus, joka esittää tapoja yhdistää kierrättäminen ja lisäävä valmistus ja polymeerin kierrätyksen vaikutuksesta tulostettavuuteen.

Polymeerin kierrätyskeinot voidaan jakaa mekaanisiin, lämpö-, kemikaalikierrätystekniikoihin. Mekaaninen kierrätys on edullisin keino, mutta sen avulla ei pystytä poistamaan epäpuhtauksia muovijätteestä. Lämpö- ja kemikaalikierrätys on tyypillisesti kalliimpaa ja energiaintensiivisempää, mutta molemmilla tavoilla pystytään poistamaan epäpuhtauksia polymeeristä. Kierrätyksen huonoja puolia ovat kuitenkin sen vaikutukset polymeerimateriaalin ja siitä tuotetun kappaleen termomekaanisiin ominaisuuksiin, huonontaen samalla sen 3D-tulostettavuutta.

Termomekaanisten ominaisuuksien huononemista voidaan estää tai vähentää erilaisin keinoin, esimerkiksi lisäämällä uutta raaka-ainetta kierrätetyn materiaalin sekaan. Suuren tulostusalueen lisäävää valmistusta pidetään myös hyvänä tapana pienentää tulostettavuusongelmia kierrätetyn polymeerin tilanteessa. Suurempi tulostin on vähemmän herkkä materiaalin pieniin epäjatkuvuuskohtiin, ja suurempi tulostusalue antaa enemmän kerroksen jäähtymiselle ennen uuden kerroksen lisäämistä, kasvattaen kerrostenvälistä fuusiota. Lisäävän valmistuksen tuotteiden kierrätysmerkinnöille on tarve standardisoinnille, jota löytyy tavanomaisesti valmistetuista polymeerituotteista.

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1 Introduction

1.1 Plastic materials

Plastics, or polymers, are popular materials in manufacturing because they have relatively low production costs, corrosion resilience and relatively low weight compared to durability and strength [1], [2]. Annual polymer production has already surpassed the amount of most common steels, and has been continuously increasing during the last six decades [2]. Global production in 2018 was 359 million tons [1], and is predicted to increase up to 850 million tons by 2050 [3]. A staggering amount of used polymers end up in landfill as waste, which poses a need for solutions for more sustainable waste management. [1], [3]. Plastic waste management can be for example in energy collection or recycling. Recycling is by far the preferable choice, as it reduces the need for new raw polymer materials [1].

Studies show that about 90 % of produced plastics could be recycled [1], but only about 30 % of plastics were effectively recycled globally in 2020 [4]. Altogether, roughly 80 % of produced plastics has ended up in landfills globally [5]. The result is quite poor, and action needs to be taken in order to create incentive for better waste management. Packaging was by far the largest source of polymer waste in 2015, which is problematic in the sustainability viewpoint, as packaging has a relatively low lifespan [6]. Increased understanding of change in material properties of recycled polymers and finding further uses for recycled plastics could reduce the amount of non-recycled plastic waste, and thus the amount of plastic ending up in landfills [7], [8].

Concept of circular economy (CE) focuses on rethinking production and utilizing already existing storages of resources and energy [4]. Through reusing the plastic waste for new production, the amount of waste ending up in landfills, and economical costs for production can both be decreased while simultaneously reducing the demand for raw polymer materials [4]. The European Union (EU) Waste Directives press for taxes regarding the landfill amounts in order to increase the incentive for recycling [9]. The EU has also set CE goals for the next decade, stating for example that the amount of plastic waste ending up to landfills should be reduced to a maximum of 10 % by 2030, whereas 24.9 % was still landfilled in the EU in 2020 [1].

Some of currently recycled polymers for plastic AM include Polylactic Acid (PLA), Acrylonitrile Butadiene Styrene (ABS), Polycarbonate (PC), and Polyethylene Terephthalate (PET) [1], [4].

1.2 Polymer Additive Manufacturing (AM)

Manufacturing three-dimensional (3D) objects by adding layers of build material on top of each other is considered AM. Plastic (or polymer) AM is a fast-growing manufacturing method, and it is especially practical for quick tooling, prototyping, and manufacturing complex structures in smaller scale production [1],[5],[8].

However, polymer AM creates a notable amount of plastic waste, for example in forms of failed or end-of-life parts, unusable prototypes, and support structures needed for printing the product [1],[7]. The amount of waste generated is approximately 34 % of the printed polymer material [10]. This amount can pose great social, environmental, and economic issues when considering AM [4], [11]. On the other hand, moving the production of plastic parts to or closer to the end user decreases the pollution and energy usage caused by logistics of moving products from centralized production plants to end user [12]. Other improvements provided by AM include the amount of energy consumption of the processing, topology optimization and reduced weight of the products [10]. Environmental impact of AM processes have not been satisfactorily realized yet, but it is thought, that polymer AM could give a positive push towards a more environmentally sustainable production [13].

The most popular polymer AM method is fused deposition modelling (FDM), also known as fused filament fabrication (FFF). Survey conducted in 2023 showed that industrially over 50 % of polymer AM consisted of FDM methods [5]. The processes consist of extruding and positioning of melted thermoplastic materials through a nozzle in order to create desired shapes, which categorizes FDM as a material extrusion method [4], [5], [13]. In FDM, filaments made of thermoplastic materials are used as feedstock, and extruded through a nozzle in order to fabricate 3D-products, as illustrated in Figure 1. [4], [12], [13]. It is crucial for FDM, that the printable filament material has a constant diameter and a good surface quality [14]. Advantages in using FDM as an AM process are relatively low operational costs, small equipment size, ease of use, wide range of usable materials and low process temperatures [7], [13]. Disadvantages include poor surface quality of printed products (layer lines in the printed product, roughness of the surface), lower strength of printed products, requirement of supporting structures, and limitations caused by for example nozzle radius [13]. Widely used thermoplastics in FFF or FDM are for example polylactic acid (PLA) and Acrylonitrile Butadiene styrene (ABS) [12].

Large-format AM (LFAM) means that the printing volume of the printer is equal to or over a cubic meter (m^3) [7]. Conventional LFAM uses pellet feedstock for a larger quantity deposition of thermoplastic material, in stead of a filament which is used in most FDM processes [4], [7].

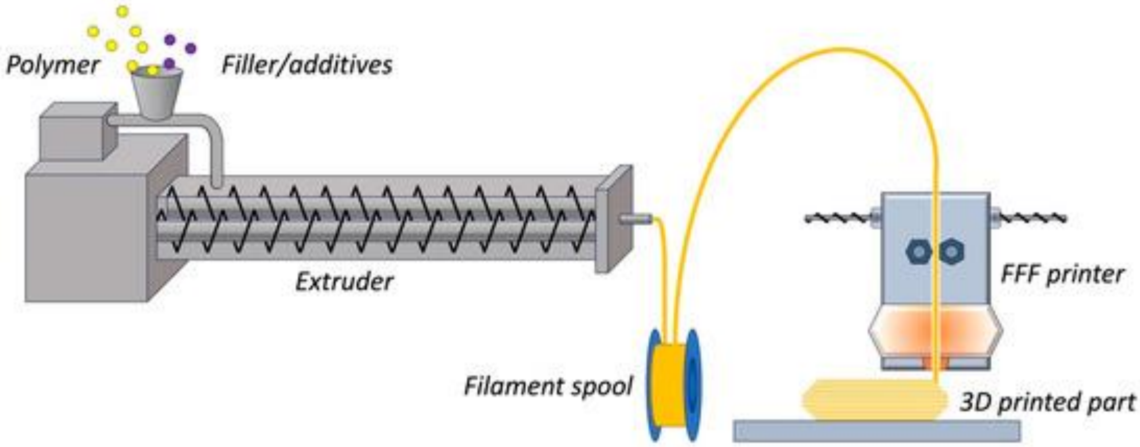

Figure 1. Basic principles of extrusion and fused filament fabrication (FFF) -process. Filament is created when polymer is fed to a twin-screw extruder. The filament can then be used as feedstock for a polymer 3D printer. Figure from Sola and Trinchi (2023) [5].

Environmental impacts of polymer AM have not yet been fully realized. They could be documented for example as energy consumption, product life cycle, waste management, and air pollution [13].

1.3 Recycling in polymer AM

Plastic AM also offers a partial solution for plastic recycling. It can reduce the economical and environmental impacts of both plastic material and plastic product transportation [12]. Waste management in AM can be divided into using recycled filaments in AM, and recycling 3D-printed parts (support structures, or other end-of-life products) [3], [13].

A filament for AM can be 5 – 10 times more expensive to produce compared to raw plastic [15], [16]. This by itself gives an incentive to find some economical savings in producing the filament, for example through recycling. Study by Mikula et al. (2021) [1] for example found financial savings of up to 80 % in acquisition of filaments, if a grinder (mechanical recycling) is used to acquire recycled feedstock for plastic printers in stead of using virgin filaments.

There are existing methods for recycling thermoplastic waste into a usable filament for plastic AM, such as shown in Figure 1 [1], [8]. Polymer AM products and by-products can be recycled as they are made from thermoplastic materials [5]. But according to Mikula et al. (2021) [1], commercially available off-the-shelf recycled filaments were not much cheaper to buy than a “virgin” (non-used) filament in 2021 [1]. In study by Sola and Trinchi (2023) [5], it was referred however that the cost of recycling polylactic acid (PLA) and turning it into feedstock for FDM was less than 1 $/kg, while virgin PLA feedstock price was around 17 – 18 $/kg. In the case of polymer composites, such as carbon fibre filled ABS (CF-ABS), it was estimated, that a pound (lb) of recycled polymer composite could be produced for a fifth or even a sixth of the price compared to buying virgin CF-ABS feedstock [7]. Composites in general are also more environmentally harmful to produce compared to conventional polymers [5], so recycling of composite polymers for reuse can have a great effect on reducing environmental impact of polymer AM as well. This suggests that by recycling, substantial economical savings in the costs of materials can be achieved [5], [7].

CE can be implemented to polymer AM to upcycle plastic waste into valuable products, while simultaneously reducing the environmental and economical impacts of plastic production [8]. Figure 2. shows a CE model for AM proposed by Al Rashid and Koç (2023) [8]. The model included five steps as follows: first was obtaining the material (preferably recycled), second was producing feedstock for AM from the recycled material, third was creating functional parts via AM, fourth was using the parts, and lastly the fifth step was evaluation and recycling of the end-of-life AM part.

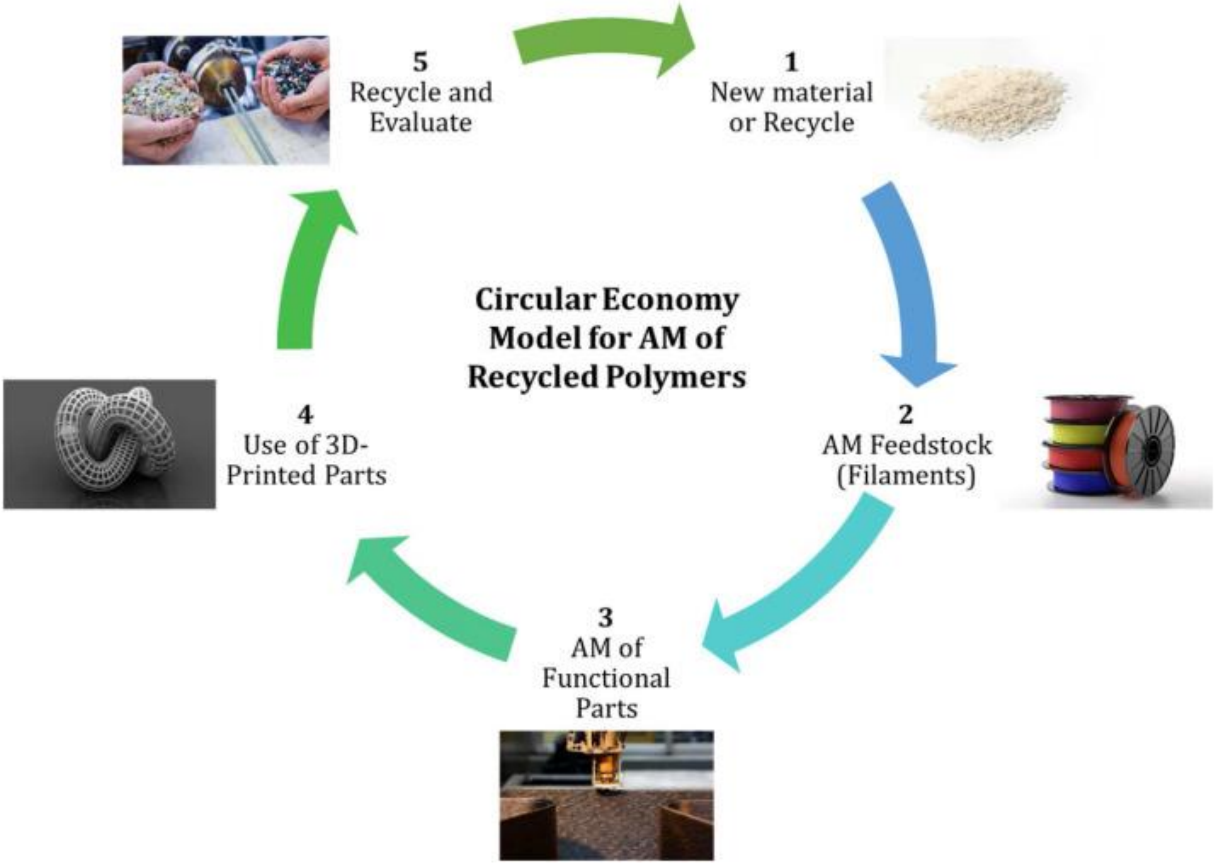

Figure 2. Circular economy (CE) model for polymer AM. The figure shows a circular economy model, where a loop can be created for AM. First new or recycled material (1) is used for creating feedstock (filaments or pellets) for additive manufacturing (2), then a part is manufactured using AM (3), the part is used (4), and finally the used part is recycled for reuse in feedstock creation (5). Figure from Al Rashid and Koç (2023) [8].

Even though recycling polymers to feedstock for AM is found to decrease thermomechanical properties of filaments, some existing solutions are available to counter these problems, for example sieving shredded polymer to increase homogeneousness of the feedstock, and altering the printing parameters to counter the loss of viscosity and molecular weight which occur after recycling [1], [4].

Recycling includes some additional costs due to for example logistics of collecting, sorting and separation of the plastic materials, and processing costs of pre-treatments, washing, shredding, storing (drying), and pelletizing [5], [11]. Another problem in the collection step of recycled polymers for AM is the lack of standards in the recycling of products made with AM. There are no standardized markings in products, like there are on conventional commercial plastic products, indicating the correct way to recycle the product at the end of its life cycle. The end user might be confused or unaware of what material the AM product is made out of, thus complicating the collection process [5]. A need exists for better standardization in AM products, for example in the form of recycling symbols [16].

Traditional, centralized recycling has been found to be ineffective [12]. In stead of a centralized collecting and processing of plastic waste, that creates low-value recycled plastics, the recycling process could be distributed among the manufacturers or individuals utilizing plastic AM [1]. Generally, sorting of different polymers can pose major issues during the recycling process, but in the case of AM in a closed loop of manufacturing and recycling, these issues could be removed [5], [8].

Distributed Recycling in AM (DRAM) is a concept, where the producer collects its own plastic waste and upcycles it to a filament for AM, and then to valuable products [1], [5]. DRAM has already been commercially utilized for smaller FDM or FFF printers, for example with usage of a recyclebot [15]. A recyclebot can create usable thermoplastic filaments for polymer AM through shredding and re-extrusion (filamentation) of the recycled material [12], [15], [16]. Applications, such as a recyclebot, can reduce the cost of producing filaments, as well as pollution and energy consumption caused by logistics, affecting both economical and environmental factors of production [15], [16]. Savings of up to 90 % in embodied energy of logistics, processing, and usage of natural resources, can be realized [16].

DRAM in LFAM shows even greater promise compared to smaller FDM printers [12], [15], [16]. Novel LFAM can directly use granulate feedstock in fused granular fabrication (FGF), or fused particle fabrication (FPF) processes, so the material degradation during recycling occurs less compared to smaller-scale traditional FDM [4], [7], [16]. This is due to FGF and FPF processes not needing the additional reprocessing step for filamentation of the recycled polymer, which is required for conventional FDM [4], [7], [12], [16]. Additionally, the filamentation step is a time- and energy-consuming step in the production of polymer feedstock, which further highlights the ecological and economical efficiency of FGF or FPF compared to traditional FDM [12], [16]. It should be noted however, that especially when considering larger plastic parts (products made with LFAM), the recycling process itself can become more challenging [13]. Then the excessive amount of plastic waste could preferably be dealt with before the production phase by better design of the product, for example in decreased need of supporting structures [13].

Utilization of DRAM reduces the pollution of logistics in recycling and can shorten the overall length of supply chains in polymer manufacturing [12]. It is more environmentally friendly, but it can also be operationally important. For example, if the production is located in a remote place (military operations, space, arctic areas), where the supply of production materials can be challenging [12].

There are some challenges currently in DRAM. As the recycling is executed locally, it is important to be able to assess the quality of the recycled feedstock. Decontamination of the feedstock is important in matters of health risks as well as material properties. Sorting of the recyclable plastic must needs be done to acquire polymers that are suitable for the printing process. Sorting and washing processes are required locally, and the technology available should then be made locally feasible in order to utilize DRAM properly. [12]

There are some research gaps in the utilization of DRAM: collecting, sorting, and washing processes before the filamentation, and quality assessment for the recycled feedstock (granular or filament). [12]

In “The perpetual Plastic Project”, the event organizers demonstrated the process of filament creation from waste plastic. The steps included washing, drying, and shredding the waste material, and finally re-extrusion and 3D printing. The whole process from waste to printing took about 30 minutes, which encourages feasibility for recycled filament processing in industry as well. [1]

2 Recycling mechanisms

Thermoplastics can be recycled using common polymer recycling methods [5]. Polymer recycling technologies are for example mechanical, chemical, and thermo-chemical processes [8]. As polymer AM uses thermoplastics, recycling can be implemented to polymer AM products, and the recycled thermoplastic can again be used as feedstock for polymer AM [4], [5].

Recycling for AM involves several activities: selective material separation, decontamination and purification, (washing), grinding, re-melting and re-extrusion to a filament [1]. Contamination of the recycled feedstock can cause problems in each mentioned recycling method, so washing steps might have to be done if the plastic is for example from food industry [8]. Washing involves corrosive chemicals and water, which can cause degradation of the polymer [8]. However, contamination of the recycled polymer can also increase degradation [12]. The degradation caused due to washing of the polymer can be decreased through drying of the polymer after washing [2]. It was noted in the study by Sola and Trinchi (2023) [5], that especially closed loop recycling, or DRAM, might have problems with the scalability of the recycling volumes. For a single cycle, and in a large scale, the drying process could lead to a need of additional storage space for the polymer, and altogether slow the recycling process down [2].

Recycling steps generally decrease thermomechanical properties of plastic materials [1], [4], [11], [12], which have to be assessed in order to consider recycled material’s usability in plastic AM. Mikula et al. (2021) [1] proposed a use of additives to the feedstock before extrusion, in order to enhance the otherwise decreased mechanical properties of the filament. As described by Khosravani and Reinicke (2020) [13], a recycled filament containing up to 95 % of recycled thermoplastics could be produced, and an addition of virgin polymer feedstock can be done to counter the excessive loss of thermomechanical properties.

2.1 Mechanical recycling

The mechanical recycling process includes segregation, washing, and shredding or granulation of collected recycled plastic material [1], [2], [12]. It is an optimal way to end the life cycle of a plastic product, for example from food packages or failed or non-usable plastic AM parts [11].

In recycling of polymers, mechanical recycling seems to be mostly downcycling, for example in case of PET getting downcycled only once from a plastic bottle to a textile [17].

Mechanical recycling causes a reduction in the molecular weight, or chain length, of the polymer, as the chain links of the polymer are broken [18]. Mechanical recycling is also unable to remove additives or contaminations from the recycled polymer during the recycling, which can increase degradation and decrease thermomechanical properties [17], [19]. This also means, that the sorting of polymer waste is a very important step when considering mechanical recycling, whereas chemical or thermo-chemical recycling industry is capable of removing impurities and therefore the separation step is not as crucial [17].

Shredding of the recycled plastic is done using a shredder and a granulator [1], [7]. In the study by Romani et al. (2024) [4], the shredding was done multiple times to increase homogeneousness of the granulated polymer. It is also suggested that the material is dried after the shredding, as it can decrease the loss of molecular weight during recycling [2]. The shredded granulate needs to be further extruded into pellets or filaments when using conventional LFAM, or similarily FFF, due to the inhomogenousness of the granulated material, as illustrated in Figure 3 [4], [7]. It is especially impactful for smaller scale FFF AM technologies, since the inconsistencies in the filament can more easily cause clogging or jamming of the smaller nozzle or barrel of the desktop-size 3D-printer [7]. An extruder is typically a screw, which heats and mixes the granulates into a homogenous matter, then transports the polymer through a die [8]. Extrusion creates a homogenous filament with constant geometry dependent on the nozzle diameter [1]. Studies suggest, that an extra process step could be skipped when using FGF LFAM, due to bigger sizes of the nozzle [4], [7]. This way, the inconsistencies of the granular feedstock would not matter as much, and skipping the extra processing step of pelletizing the granulate feedstock would reduce the unwanted loss of mechanical properties [4], [7], [1].

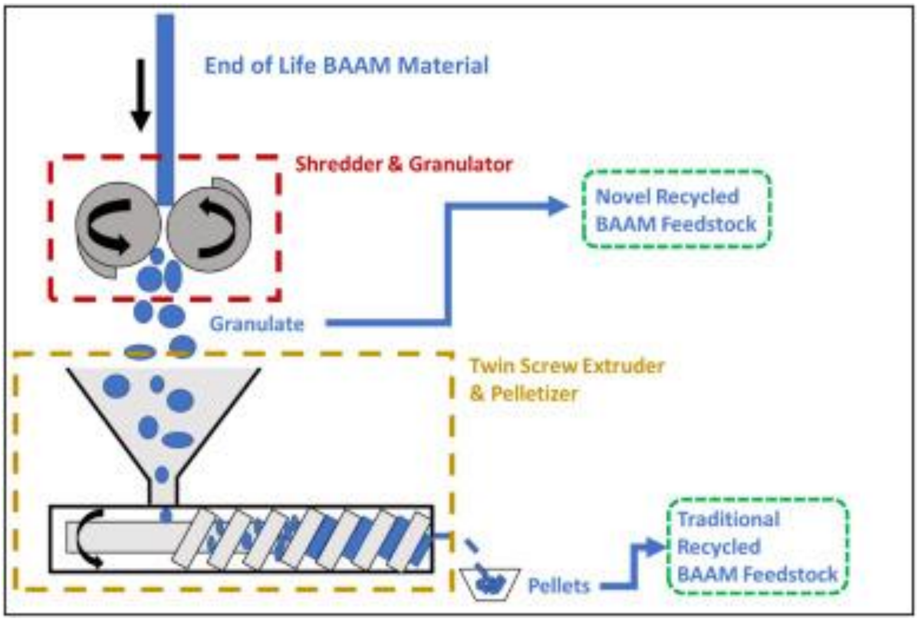

Figure 3. Advantages of using novel Fused Particle Fabrication Big Area AM (FPF BAAM) compared to traditional AM. By utilizing novel FPF BAAM technology, which can directly use shredded and granulated polymer material, an extra thermomechanical processing step of pelletizing/filamentation of the recycled polymer can be skipped. This decreases the thermomechanical degradation the polymer suffers during the recycling and printing process. Figure from Korey et al. (2023) [7].

2.2 Chemical and Thermo-chemical recycling

Chemical and thermo-chemical recycling is a process which breaks down the polymer material to monomers with a combination chemicals and heat energy, after which polymerization can be done to manufacture new polymer materials. The chemical recycling process for polymers can commonly be divided into three steps: depolymerization, purification and re-polymerization [1], [2], [8], [18], [19].

In depolymerization step, the polymer is turned into monomers through for example pyrolysis, gasification, or solvolysis [8], [18]. Pyrolysis turns the polymer to a liquid and gaseous forms through a thermo-chemical process, and as the components of the polymer are separated, impurities and additives are removed from the monomers [6], [19]. Gasification turns the solid recycled matter to gas and separates different chemicals by using different temperatures in the gasifier (where gasification reactions happen) during the process [20]. Solvolysis breaks the bonds of the polymers with a solvent like water or alcohol [18].

After depolymerization, the monomers are purified with using for example chromatography or distillation [8]. Re-polymerization is done to the purified monomers through polymerization methods like condensation or addition [8].

Chemical recycling should be considered, when the polymer in question is difficult to recycle using mechanical or thermal recycling [8]. Chemical recycling helps to remove impurities and additives from the polymer, which mechanical recycling is unable to perform [18]. In case of polymer composites for example, chemical recycling should be considered, at least after the composite has undergone the first few mechanical recycling cycles [7].

Challenges with chemical and thermo-chemical recycling are relatively high energy consumption, high costs especially in smaller scales, usage of dangerous chemicals, and presence of impurities and degradation to the chemically recycled polymer [8].

3 Effects on materials

Recycling process alters the mechanical properties of polymers. Washing weakens the polymer chain structure, shredding and high temperatures are shown to reduce molecular weight, which is believed to lead to poorer mechanical, thermal, and viscosity properties [1], [4], [10], [11]. The properties affect the printability of the polymer material, as well as the quality of the printed parts made with AM [1], [12].

Mechanical properties of the recycled polymer are analysed, as they provide a good estimation of the degradation during the extrusion processes and the printability of a product made from the recycled feedstock [12]. Many different methods exist for assessing thermal or mechanical properties for materials. Thermogravimetric analysis (TGA) studies mass change in a heated polymer sample [1]. It can be used to assess thermal stability, and degradation temperature [1], [11]. Other suggested methods for measuring material degradation were thermal analysis with differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), Fourier-transform infrared spectroscopy (FT-IR), and thermal conductivity tests [1],[11]. Colorimetric analysis, tensile tests with printed specimens, gel permeation chromatography (for molecular weight analysis) (GPC), DSC, rheological testing (for viscosity characterization), and visual assessment of demonstration products were also considered in [4]. Morphological analysis is particularly useful for composite AM feedstocks, because it can be used to determine the distribution of composite particles in the polymer matrix [12]. Particle size distribution can be used for example to determine average molecular weights and in FGF it is used to determine quality of the feedstock [12].

After the mechanical shredding process, sieving can be done in order to characterize the polymer feedstock. Different size meshes can be used to sort a limited amount of the shredded feedstock to calculate the proportional particle sizes [4]. Printability can suffer with too large particle sizes and variation, so sieving also helps by filtering out the biggest particles and thus helps to maintain the printability of the recycled material [16].

A loss of mechanical properties and printability, caused by thermomechanical recycling and extrusion, limits the amount of recycling cycles to about five in many polymer materials, to keep the material usable for AM, without the usage of additives such as virgin polymer material [15], [16]. Blending virgin feedstock to the recycled feedstock could decrease the degradation that the recycling process applies on the polymer feedstock in a relatively cost-effective way without including composite materials to the feedstock [12]. Melt flow index (MFI) has been used for specifying the quality of recycled polymer composite feedstock it is linked to printability, as it gives information for example about a change in viscosity before and after recycling. The MFI value should ideally be close to that of commercially available feedstocks, so the printability would not be drastically affected [12].

3.1 Polylactic Acid

Polylactic acid (PLA) is good choice for plastic AM, because it is easy to process and it has relatively good mechanical properties [4],[11]. It is also an environmentally preferred plastic material because it has less harmful effects on nature, as PLA is a bio-based, biodegradable and bio-compatible material [1], [11]. Recycled PLA is easily and commercially accessible, as it can be collected for example from used food containers or bottles [1]. Drawbacks compared to other polymers are decreased durability and temperature sensitivity (already in under 200 °C), which causes thermomechanical degradation to occur faster [1], [11].

One of the recycling methods for PLA is direct recycling, as described by Mikula et al. (2021) [1]. Direct recycling means the grounding up of collected PLA and re-extruding it to a uniform filament. It was found that the directly recycled PLA filament had similar diameter and surface properties compared to a virgin filament, but a loss in mechanical properties could be measured.

Direct recycling reduces viscosity, which is problematic during the printing process. Products printed from recycled PLA filament showed increase of unwanted pinholes (internal air bubbles), which can cause a printed part to fail unpredictably. Intrinsic viscosity slightly decreases in reprocessing of recycled PLA (about 5 %) due to reduction of chain length [11], and significantly more if the recycled PLA is washed [1],[11]. This happens due to high temperatures and shear stresses during thermal reprocessing of PLA [1], [11]. As described by Beltrán et. al (2018), the intrinsic viscosity losses were considered to have only limited effects on mechanical properties of the plastics, but tests conducted by Romani et. al (2024) [4] on the other hand found a decrease of 50 % in zero-shear viscosity after four cycles of extrusion, going further down 90 % after six cycles, making the material unprintable.

Reduced viscosity was found to increase elastic modulus of the recycled PLA, while at the same time reducing other mechanical properties like tensile strength and strain at break [8]. These changes could be decreased by the addition of virgin PLA to the recycled PLA before re-extrusion, improving the viscosity and other thermomechanical properties of the filament and the printed parts [1], [8].

Recycling reduces the chain length of PLA [1],[11]. Shorter chain length, or reduced molecular weight in other words, increases the ability of the polymer chains to move and reorganize into more ordered crystal structures [4],[11]. This was found to increase the MFI, which can cause problems in printability and quality of the part [1]. Shortened chain length was also linked to decreased mechanical properties like strain at break, reducing the mechanical strength of the recycled plastic AM products [1], [4], [11]. In measurements conducted by Romani et al. (2024) [4], the molecular weight was half of the original (virgin feedstock) average molecular weight after five recycling processes (six extrusions).

A general increase of cold crystallization was found after two or more recycling cycles for PLA [1], [4], [11]. This was deducted from the increase of enthalpy of fusion in the feedstock samples [4]. Clear multiple peaks of melting points were found after five recycling steps, indicating the presence of multiple different crystalline structures of PLA due to many melting, crystallization, and remelting cycles [4]. Heating of PLA, which happens for example during the re-extrusion process, lowers the cold crystallization temperature also increasing crystallization [1]. Thermomechanical processing itself can also cause uncontrolled crystallization in the polymer [5]. Increased crystallization makes the printed PLA more stiff and brittle [5].

Tensile test measurements conducted by Romani et al. (2024) [4] found no notable decrease in strain at break after 1–3 recycling cycles of PLA, but a more significant decrease could be found after 4 recycling cycles. A decrease in ultimate tensile strength was also found, but it was only notably bigger after the third re-extrusion step. Generally, the ultimate tensile strength further decreases after more recycling cycles [4]. Woern et al. (2018) [16] found similar results, a loss of tensile strength of barely 2.5 % after the first few recycling cycles. The average decrease after six re-extrusions was not drastic, only -15.7 %, though deviation of the results among samples increased, suggesting an increase of heterogeneousness of the feedstock after multiple recycling cycles [4]. Study by Mikula et al. (2021) [1] found degradation of tensile strength to be about 30 % after 3 injection cycles, and 60 % after 7 cycles.

According to the DCS tests conducted by Romani et al. (2024), the loss of thermal properties, like melting temperature, was relatively small even after multiple recycling cycles [4]. The result was supported in other studies as well [1], [11].

FGF LFAM with recycled PLA feedstock was tested by Romani et al. (2024) [4]. FGF process is less detrimental to PLA feedstock, since it skips the extrusion step for making the filament out of the recycled PLA, thus decreasing the amount of thermomechanical processing and degradation [1], [11]. Feedstock was found to be usable after up to 5 cycles of recycling. Proof-of-concept parts were created for furniture uses after 3 recycling cycles. The printing speeds were kept close to normal (as used with virgin pellets), to show that the using of recycled feedstock would be industrially feasible [4].

The decrease in mechanical properties could be decreased with the introduction of protective coating, like Polydopamine, which increases adhesion and tensile strength of the feedstock. The coating substance is added to the polymer before re-extrusion. [1]

Another aspect in printability and quality of the printed part could be dimensional accuracy. Dimensional accuracy assessment with a maximum overhang of 30° was done in by Romani et al. (2024) [4]. Using the same printing parameters as with the virgin feedstock, some issues were found. Problems occurred for example with sharp corners or peak overhangs, resulting in local collapses of the printed product. These problems could be countered by lowering the printing speed from original 20 mm/s down to 8 mm/s, allowing the cooling time for the recycled feedstock in the printed part. The same result could be obtained through designing AM products with bigger cross-sectional areas, such as LFAM is capable of producing. [4]

Colour degradation is a visual aspect in the quality of a printed polymer part, and it is connected with thermal degradation and loss of molecular weight. Colorimetric analysis conducted by Romani et al. (2024) [4] found a notable colour variation between the virgin and re-extruded feedstocks, with virgin pellets producing a more translucent and neutral colour, and the recycled feedstocks (with more thermomechanical degradation) producing increasingly more yellower and darker colours [4]. To decrease colour degradation, for example virgin polymer can be added to the recycled feedstock [8].

3.2 Polyethylene Terephthalate

PET is the industrially the most recycled polymer, and the most used material for example in food packaging industry, making it an easily accessible in the material acquisition viewpoint [9]. PET unfortunately has some disadvantages as a material for recycling in AM.Virgin PET shows a drastic loss of mechanical properties already after the second recycling process [9]. Recycled PET has been found to be problematic during the printing process, because of its high fusion temperature, crystallinity, water absorption and contaminants causing further degradation in the material [12].

3.3 Glycol-modified Polyethylene Terephthalate

Glycol-modified PET (PETG) on the other hand, shows great promise for usage as a recycled filament for AM [9]. PETG can either be recovered by recycling products made of PETG, or glycol can be used as an additive to a PET feedstock. In addition to other superior mechanical properties, PETG has better printability compared to PET, which makes it a preferable material for FDM. PETG is usable after up to six cycles of recycling, before it is unprintable. After the fourth cycle though, some significant degradation can be observed, and the printability starts to suffer due to changes for example in viscosity.

The decrease of quality and thermomechanical properties happens due to degradation in the material during the recycling process of shredding and re-extrusion. Mechanical, thermal, and morphological properties were studied to assess the degradation of the material. TGA, DSC, scanning electron microscopy and Raman spectroscopy were used to analyse the results.

PETG was shredded, dried for 24 hours in 80 °C, pelletized, extruded to a 1.75 mm filament and dried again. This process was replicated six times for the material, and the results were analysed.

Tensile tests were conducted with the D638-02a ASTM type-V specimen. The loss of mechanical properties was found to be relatively small after up to six recycling processes. Tensile strength after the first recycling was 39.8 MPa, and after the sixth step it was down to 33.3 MPa (with a higher deviation of 5.53 MPa). The highest value for tensile strength was 46.1 MPa after three cycles. This is an increase of about 15.8 % compared to virgin PETG. Modulus of elasticity was 189.1 MPa, 237.5 MPa and 183.3 MPa after the first, third and sixth recycling cycles respectively. The highest value was after the fourth recycling cycle, with an increase of about 30.7 % compared to virgin PETG. It was noted that there were both cases, supporting and against, an increase in tensile strength found in literature, so the results are debatable. The test results showed however, that there is a trend of increased stiffness until third or fourth recycling steps, after which the material turns more ductile again.

TGA and DSC were used to find the changes in critical degradation and glass transition temperatures of the material after specific recycling cycles. After the first and sixth recycling processes, the critical degradation temperature, where rapid degradation of PETG starts to occur, was found to be similar at about 380 °C. Glass transition temperatures were 66 °C, 68 °C, and 69 °C, after the first, third and sixth recycling processes respectively.

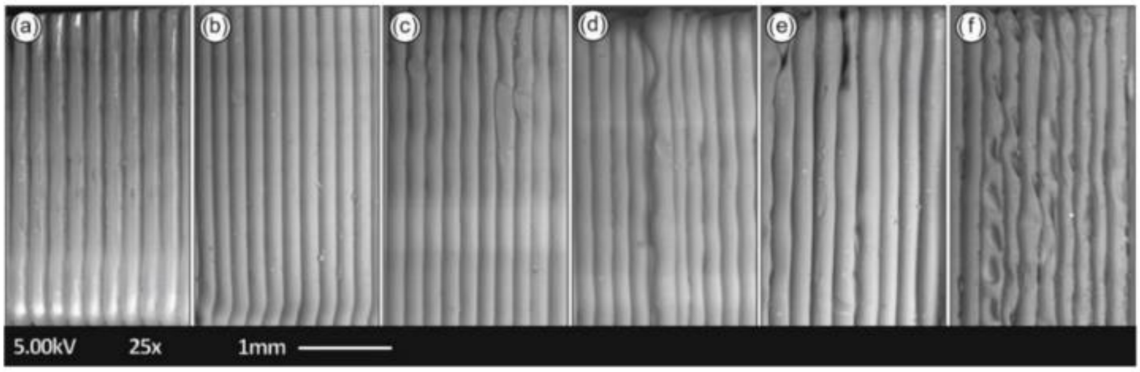

Figure 4. Deformities between the printing layers after 1–6 recycling cycles for PETG. The pictures were taken with Scanning Electron Microscopy. The labels a)–f) illustrate the changes between printing layers after 1–6 recycling cycles respectively. After the fourth cycle, some larger deformities are noticeable, and after the fifth cycle, gaps and deformities start to increase. Figure from Vidakis et al. (2021) [9].

After the fifth and sixth recycling cycles, a noticeable increase in deformities and gaps between the printing layers can be observed, as seen in pictures e) and f) in Figure 4. It was thought to be probably due to crosslinking of the polymer chains and decreased viscosity after multiple cycles of recycling. This can decrease the mechanical properties of the printed part and lead to an overall lower quality product. But as seen from pictures a)–d) in Figure 4., the adhesion between the printing layers remains quite good for up to four cycles of recycling, meaning that the produced part has good mechanical performance and quality after the PETG feedstock has been recycled four times. [9]

3.4 Acrylonitrile Butadiene Styrene

ABS is a widely used material for polymer AM, and it is known to degrade during recycling [10], [14]. Conventional recycling of ABS causes for example chemical degradation, and a decrease in decomposition temperature and stress and strain at fracture. Cress et al. (2021) [10] conducted tests to find the effects of up to three cycles of recycling on ABS feedstock.

Recycling increased porosity (cavities inside the material) of the ABS by up to about 55 %. Pores in the structure of 3D printed ABS can cause brittleness and unexpected failures, so the increase of porosity can be problematic. Cress et al. (2021) suggested an optimization of printing parameters, and for example inclusion of vibration during printing, to counter the number of pores in the structure.

Elastic modulus did not change notably during three cycles of recycling. Tensile strength decreased by about 10 %, strain at tensile strength by 13 %, and stress at facture by 3–7 % after three cycles. Strain at fracture decreased about 8 % per cycle of recycling down to -25 % after three cycles, and toughness was reduced 37 % by the third cycle. The changes of tensile strength between virgin and recycled ABS filaments were negligible, but a difference was notable in the printed products. It was deducted, that the most degradation happens during the FDM printing process rather than the recycling process of the ABS feedstock [10].

D’Amico and Peterson (2020) [14] studied the thermal properties for ABS in small-scale FDM and BAAM. It was found that a print made by smaller scale FDM cools down much faster than one made by BAAM. In BAAM, the mass of the object is much bigger, which is why the cooling also takes longer. This can lead to positive results in the thermomechanical properties of the printed part, like interlayer diffusion and weld formation between layers, but also problems like slumping or sagging of the larger and heavier printed part. Lowered glass transition temperature can lead to a tendency for delamination of the print. The glass transition temperature lowers during the recycling of the polymer, increasing the possibility for the problems to occur, especially with BAAM where the printing layers are allowed to cool down for a longer period of time before another printing layer is added. [14]

Mohammed et al. (2020) [3] described the effects of a single mechanical recycling on 100% recycled ABS feedstock [3]. The ABS was shredded and crushed, and larger particles were sieved out in order to decrease the distribution of particle sizes. Some changes in mechanical properties of parts made from 100 % recycled ABS compared to virgin ABS feedstock were noticed. A change in viscosity of the recycled feedstock required a lowering of printing speeds to avoid under-extrusion (noticeable gaps in the printed structure). It was lowered from 60 mm/s to 50 mm/s, which is about 17 %. The study compared produced filament diameters between pelletized virgin ABS and recycled ABS and found that the same filament diameter could be observed with temperatures of 205 °C and 200 °C for virgin and recycled ABS respectively. This would mean a drop of about 2.5 % in temperature, which indicates some thermal degradation due to recycling. Ultimate tensile strength was also reduced by 13–49 % depending on the printing direction, and stiffness reduced by 17–28 % in a similar manner. Surface quality suffered only minor decreases compared to virgin ABS, as average roughness was increased from 2.08 micrometres to 2.16 micrometres, which is about 3.8 %.

3.5 PC

Reich et al. (2019) [15] described the effects of recycling in polymer AM with polycarbonate (PC) as a feedstock material. PC is a high-performance polymer, which means that it has high mechanical strength and heat resistance. Three cases were considered for recycled waste PC: moulding for lower melting point polymers, high temperature, and high-strength applications. In this study, a Gigabot X Fused Particle Fabrication (FPF) machine was used. FPF is similar to FGF, as it uses particles as feedstock rather than a filament, which is used by traditional FDM or FFF technologies. [15]

The Gigabot X could print with pellet sizes below 22 mm^2. However, there were issues with larger particle sizes that stopped the extruder from working. The reliability of the printing could be improved by sieving the larger particles out through a sifter which had 5.5 mm diameter holes. [15]

The printing speed was set to 5 mm/s, which produced a volumetric deposition rate of 5 mm^3/s with the FPF Gigabot X. The result was good when compared to conventional FFF, which averaged 0.4 mm^3/s with 0.2 mm layer height and a 0.4 mm nozzle, which suggests that the use of recycled PC was feasible. [15]

Ultimate tensile strengths (UTS) tests were conducted using ASTM D638 Type 4 standard tensile bar geometry. Gigabot X (FPF) produced an average UTS of 64.9 MPa, and FFF averaged a UTS of 62.2 MPa with a TAZ printer and 66.3 MPa with an FFF-based Gigabot. The test results were comparable to printed parts made from filaments of virgin PC, meaning that the mechanical performance of the recycled PC was good enough to replace virgin PC in high performance applications of polymer AM. [15]

Along the results of UTS tests, the relatively good printing speed supported the feasibility of the usage of recycled PC as feedstock for FFF-printers and FPF-printers, with a note that the Gigabot X was not capable of printing accurate small shapes because of the larger nozzle diameter it had. With about 2.5 % of the cost compared to printing with virgin PC feedstock, substantial economic advantages can be gained by using recycled PC compared to virgin PC. [15]

3.6 Composites

Polymer composites are a blend of polymers and other reinforcing materials, such as carbon fibre [7],[5],[8]. Composites have better mechanical properties compared to weight or density, than some commercial metals [7]. For this reason, polymer composite feedstock should be considered, when manufacturing load-bearing products or parts in AM [5].

Use of recycled carbon fibre filled ABS (CF-ABS) in AM was studied by Korey et al. (2023) [7]. CF-ABS is used for example in LFAM to make printed moulds used for concrete production. The CF-ABS moulds are considered waste after several uses, and they could be recycled afterwards. CF-ABS, like other polymer composites, is a relatively high-cost material for AM, which is why study for the effects of recycling needs to be conducted, making it more industrially feasible and less environmentally harmful to use composites for AM [7].

Carbon fibre -reinforced PLA (CF-PLA) is a composite application that can be easily used in FDM. Due to the more environmentally friendly profile of PLA compared to other thermoplastics, PLA composites can also generally be considered relatively green. It should be noted however, that inclusion of a composite component in a polymer feedstock requires an additional processing step, which produces additional emissions. Usage of carbon fibre enhances mechanical properties, like stiffness, of PLA. [5]

Composites, like polymers in general, lose mechanical properties during the recycling process [7]. In the recycling process of composite polymers, two types of degradation occur: loss of reinforcing material as the smaller shredded CF does not get through the separator after the shredding, and loss of mechanical properties for the polymer in a similar way described for PLA during the recycling [7]. In the case of recycling CF-ABS material, the carbon fibre (the reinforcing material) loses quality, and fibre length and size, among other parameters, hindering the mechanical performance. Loss in fibre length of CF especially decreases the mechanical performance. Tests conducted by Korey et al. (2023) [7] found a 39 % reduction in fibre length after one recycling process of CF-ABS. This was most likely thought to be due to the fibres breaking in shredding and re-extrusion, and high temperatures cause the polymer material around the fibres to melt, creating some significant shear stresses to the fibres [7]. Sola and Trinchi (2023) [5] mentioned that the strength of printed parts made of recycled composite feedstock would retain mechanical strength typically after the first and second cycles of recycling, but after that a decreasing trend was to be expected. In contradiction, some studies have aimed to increase the homogeneity of the feedstock by implementing multiple mechanical shredding and extrusion steps for composites [5]. This would lead to further loss of mechanical properties for the composites, even though the recycled feedstock becomes more homogeneous [5], [7].

The recycling process used by Korey et al. (2023), [7] consisted of shredding and granulating the AM product, and using the granulate directly in 3D-printing of another similar product. There was a noticeable increase in granulate particle size compared to virgin CF-ABS granulate, and the deviation of particle sizes was larger. The deviation was higher because of the sieving process done after shredding. There was a certain dimension of particles, that would pass as granulates. Some parts would make through as feedstock after less cycles of shredding than others. The material that had to go through more cycles of shredding, would generate more mechanical degradation of the composite part, and smaller average particle sizes compared to virgin pellets. [7]

The recycled feedstock posed no problems in clogging of the nozzle of the FDM printer and achieved the same layer thickness in the printed products compared to the virgin feedstock. Surface quality was however noticeably poorer with the recycled feedstock. [7]

A loss of density between printed products made out of virgin and recycled CF-ABS feedstock was found. This was thought to be due to loss of molecular weight and, in case of using granulate without re-pelletizing, the irregularity in shapes and sizes of the granulate material, which can cause cavities during particle packing in the extruder of the printer. [7]

No drastic loss of strength of the recycled feedstock was found in the study by Korey et al. (2023) [7], but a downward trend in the mechanical properties could be noted. The weakest direction in strength of the printed part was between the printing layers due to adhesion being lower than the cohesion inside a single layer. [7]

After one mechanical recycling process done to a composite polymer, it was suggested that another recycling method (chemical or thermal) should be used in order to retain the mechanical properties of the composite component, as thermos-chemical recycling does not degrade the composite part as much as shredding. [7]

3.7 Additives

Usage of additives was suggested to counter or reduce the colour or thermomechanical degradation of the feedstock caused by the recycling process [1], [2], [5], [8]. Additives can for example increase molecular weight (as chain extenders), tensile stiffness and strength of the additively manufactured products [1], [5].

Even though additives, or fillers, are considered as a solution to a problem, they can also bring challenges to the AM process. Fillers can for example increase nucleation and therefore crystallization, or even increase degradation through hydrolysis or thermolysis [5]. Additives can also make the recycling altogether more complicated, if for example the additive material is non-recyclable [8]. The mechanical recycling process can not remove the additives from the feedstock, so chemical or thermo-chemical recycling has to be used, which increases the energy consumption and overall costs of the recycling after additives have been added to the polymer feedstock [8], [17], [19]. Thermomechanical properties of additives are also hindered during the recycling process. Some additives may for example have poorer thermal stability than polymers, or be more susceptible to chemicals used during recycling [5]. Studies found an example loss of strength in glass fibres to be up to 80–90 % after recycling [5].

One example of an additive is a fibre. Carbon and glass fibres improve the bending strength of polymer material and improves the material recovery rate in the recycling process [1]. Biocarbon was found to increase mechanical properties (tensile strength + 32 %) in PET feedstock made from recycled bottles, and stiffness of PLA feedstock was improved by about 8 % [1].

Like fibres, reinforcing particles can also be used as additives. A particle filler can be for example a metal particle. Usage of metal particles was found to increase thermal stability and mechanical properties such as yield strength [12]. Nanofillers are relatively small, and substantially enhance the mechanical properties of the polymer feedstock [5]. As they are small, they will not cause clogging in the nozzle of the 3D printer [5]. The drawbacks are currently in safety of their usage. Nanofillers are highly toxic, and can easily be inhaled by humans, affecting for example the respiratory systems [5]. While they are in the polymer matrix structure, they are harmless, but nanofillers can spread to the environment especially during the addition to the polymer feedstock, and when the nanofiller-enhanced polymer is recycled again or ends up as waste in the environment [5].

Another suggested solution for countering thermomechanical degradation for recycled feedstock was the usage of protective coating. For example, Polydopamine was used to improve adhesion in polymers. Polydopamine works well as protective coating due to its ability to easily absorb to the surface of recycled polymer. [1]

Sola and Trinchi (2023) [5] listed a number of different recycled fillers from different industries that could be used as reinforcement for polymer feedstock in FFF. Usage of recycled fillers was encouraged in order to reduce the economical and environmental impacts of additive usage, since they are both expensive to manufacture and environmentally harmful to dispose [5]. Other way to be more environmentally friendly is to use bio-based fillers or additives. Use of bio-based lignin (found for example from different plants) with recycled PLA feedstock was considered. It was found to improve Young’s modulus by 6 % and tensile strength by 18 % compared to pure PLA feedstock [1]. Lots of other bio-based additives have been considered, such as vegetable fillers [5]. Bio-additives bring a problem to the extrusion, since they can bring water into the re-extrusion process [5]. Inclusion of water could possibly lead to reduction in molecular weight, which would hinder the mechanical properties of the polymer. Bio-based additives might therefore need additional drying, chemical, or mechanical treatments before application [5]. Animal-based additives are also similarly used in FDM. They can be obtained from by-products of food production, so usage of such additives can be considered as recycling [5].

4 Conclusions

For this thesis, a literature review was conducted to give an overview of the current state of recycling in additive manufacturing. The recycling methods for polymers were presented, and their effects on polymer material degradation were assessed. Existing solutions to counter the thermomechanical degradation happening due to recycling were presented. This thesis considered a few common polymer materials that are currently used in additive manufacturing: Polylactic Acid (PLA), Acrylonitrile Butadiene Styrene (ABS), Polyethylene Terephthalate (PET) (and Glycol-modified Polyethylene Terephthalate (PETG)), Polycarbonate (PC) and polymer composites, like Carbon Fiber -reinforced ABS and PLA.

The recycling process generally degrades the thermomechanical properties of polymers. The degradation causes problems in both the mechanical performance of the printed parts, and the printability of the recycled feedstock. For most common polymers, the printability can be maintained for up to five cycles of recycling.

Polymer recycling methods can be divided into mechanical, thermal, and chemical processes. Mechanical recycling or shredding is a cheaper way to process the polymer into granulate, which can be either used as it is with novel Fused Particle Fabrication or Fused Granulate Fabrication (FGF) AM technologies, or it can be pelletized and filamented into feedstock for conventional Fused Deposition Modeling (FDM) technologies. Advantages in using novel technologies is less thermomechanical degradation, as the thermal processing step for turning the granulated material to a pellet or a filament can be skipped. Chemical and thermal recycling methods have disadvantages compared to mechanical recycling, as they are typically more expensive and energy consuming, and include the use of hazardous chemicals. On the other hand, mechanical recycling is unable to remove additives or impurities from the recycled polymer, which can be done by using thermal and chemical recycling processes. For composite materials, thermo-chemical recycling is suggested after the first 1–2 cycles of recycling to avoid excessive degradation of the composite. There are other existing solutions for countering the problems caused by the thermomechanical degradation which occurs due to recycling, for example the use of additives before re-extrusion of the recycled feedstock and changing the printing parameters like the printing speed or the usage of large-format additive manufacturing instead of using conventional FDM technologies.

Recycling in AM is already realizable, and significant economical, and ecological advantages can be obtained through usage of recycled feedstock in stead of using raw virgin polymer as feedstock. An interesting concept for recycling in AM is Distributed Recycling in AM (DRAM), where the whole recycling process is localized, and the recycled material can be locally upcycled to valuable printed polymer parts. A good exhibition about the usefulness of DRAM was “The perpetual Plastic Project”, where the amount of time from receiving polymer waste to printing of the recycled polymer was down to only 30 minutes.

Large-format AM shows great promise when considering recycled polymer feedstock. FGF large-format AM is especially interesting, as it can directly use shredded and sieved polymer waste for printing. The large-format printing process is less likely to fail due to inconsistencies of the recycled feedstock, and the bigger area of the printing layer allows the layer to cool down for a longer period of time before another layer is added. The large-format printing increases the fusion between the printing layers, which improves the mechanical performance and the quality of the printed part. Sagging of the printed part can cause problems, for example in big overhangs of the part, which happen more easily due to changes in the thermomechanical properties of the recycled polymer.

Further improvements are needed to increase the recycling in polymer additive manufacturing, such as standardization for recycling of printed polymer parts. A lack of markings indicating the material and recycling instructions on the printed parts makes it harder for an end user to recycle the part at the end of its’ life cycle.

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