# RECYCLED PA 12 EXCLUDED FROM PROCESSING BY ADDITIVE TECHNOLOGIES

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The ecological and economical treatment of derivatives from non-renewable sources is a current trend in the development of polymer systems, which supports global activities leading towards a sustainable environment. This article, therefore, deals with the effective management of powdered waste material (PA 12), which is no longer usable for additive technologies. Throughout recycling process, the material was modified and optimised for injection moulding technology, and transformed into pellets in the next step. The resulting thermoplastic material has a wide application potential, especially with regard to its very good mechanical and physical properties, which are evaluated in this contribution. The advantages of the resulting polymer are based, among other things, on the economic aspect, whereby a material with the nature of a structural plastic will be more available compared to plastics from an analogous category.

**KEYWORDS**

Plastic recycling, nylon 12, additive technology, waste management, MJF, SLS

## 1 INTRODUCTION

The production and consumption of plastics increases by approximately 5% every year. [Geyer 2019] However, the accumulation of plastic waste is a major problem and a potential threat to the environment in the long term. Plastic products of daily consumption with a very short service life are the greatest problem. Much of this plastic waste ends up in landfills without further use. Sustainable development is based on efficient and economical waste management, ideally so that it becomes a part of the circular economy. For plastics, this trend is mainly represented by recycling, which can partially cover the growing demand for plastic materials and at the same time it has the potential to significantly reduce the amount of unused plastic waste. [Chow 2017]

## 2 PLASTIC RECYCLING

Plastics are very tough, durable, and their processing is relatively easy. These advantages have contributed to their very rapid expansion, but they are also the reason for difficulties in dealing with plastic waste. More than 50% of plastic products end up in landfills at the end of their service life, where they decompose on average for 500 to 1000 years, and substances from their decomposition can further pollute groundwater and the surrounding area, including flora and fauna. [Helm 2022, Rigamonti 2014] Therefore, it is very important to increase the amount of plastic that is recycled. At present, four methods of recycling are available within the framework of plastic waste management. These methods are also referred to as material, chemical, and energy recycling. Primary recycling is a method of material recycling, where a similar product is created from the original product at the end of its service life (plastics are modified with additives and returned to the production chain in a form that can be processed by standard production technologies). Secondary recycling is also a part of material recycling, where a completely different product is created from the original product (for example, PET bottles are processed into fibres that can be further used for completely different applications). Tertiary recycling refers to chemical recycling, where basic chemicals and fuels are produced from separated plastic waste. The last option is quaternary recycling, where energy is obtained from plastic waste in the form of heat by incineration, which is then transformed into steam, electricity, etc. [Siddiqui 2013, Rigamonti 2014, Horodytska 2019] Considering the costs (necessary equipment, preparation of plastics, energy consumption, etc.) that the individual types of recycling require, material recycling is the most advantageous. For primary recycling, it is very important to monitor the quality of the input material. The material must not be contaminated with another type of immiscible plastic or any substance that would adversely affect both the recycling process itself and the resulting quality of the recycled plastic. In addition, the material at the input of the recycling process can also be degraded to a large extent, which will again adversely affect the quality of the output recycled material. [Pan 2020, Lazarevic 2010, Alhazmi 2021]

## 3 ADDITIVE TECHNOLOGIES SLS AND MJF

Selective laser sintering (SLS) and multi jet fusion (MJF) technologies belong to a group of additive technologies called powder bed fusion. In general, these technologies are based on melting a thin layer of material that is processed in the form of a powder. The molten material in individual layers is fused into one monolithic volume and the resulting product is gradually formed layer by layer. The unmelted powder forms the supporting structure of the final product (the bed), in which the product is laid during production. By their nature, both of the mentioned technologies are very similar. The basic principle for both of them is to quickly heat and melt the processed material (mainly thermoplastics). They mainly differ in the heat source they use. [Cai 2021, Zeng 2012]

SLS is based on melting the material under the action of a $CO_2$ laser, which selectively heats a defined zone, creating a compact layer of molten material which results in the gradual building of the desired product. [Ruth 2003, Sanjay 2003]

MJF uses fusing lamps to heat defined zones. The entire build area is intensively heated to a temperature approximately 5 °C lower than the melting point of the processed material. In addition to these fusing lamps, the print head is equipped with injectors that apply two reagents to a thin layer of powder. The first is a fusing agent, which promotes an increase in the temperature of the material locally above the melting point under the influence of heat from the fusing lamp. The second is a detailing agent, which forms the exact contour of the product in the current building plane, whereby defining the volume of the material that will be melted, without melting the surrounding material adjacent to the melting zone. [Morales-Planas 2018, Sosswald 2021, Xu 2019]

## 4 POLYAMIDE 12

Polyamide 12 (PA 12) is a tough material that provides a high degree of adhesion between individual layers and is therefore widely processed by powder bed fusion technologies. In general, PA 12 is classified among technical thermoplastics, which are characterised by their high strength, but at the same time sufficient flexibility. Other advantages include chemical resistance, very good processability, and usability for a wide range of applications. Its self-supporting nature and the possibility of supplying it in the form of a very fine powder are the main advantages for powder bed fusion technology. This material also has certain limitations and disadvantages. Due to its polar nature, PA 12 is highly prone to moisture absorption and degrades under prolonged exposure to higher temperatures. [Drummer 2014, Feng 2019, Weinmann 2020]

During exposure to elevated temperatures, material used in the case of the SLS technology is protected against oxidation by an inert gas atmosphere, while the MJF technology works in the atmosphere of standard air and all the material in the building unit is exposed to a temperature of around 165 ˚C (slightly below the melting point) during the entire production period. Therefore, after repeated exposure to these conditions and with the simultaneous action of the above-mentioned agents, degradation and oxidation of the material occur. A change in the colour of the powder from the original white to yellow and brown is a concomitant phenomenon to the degradation process. However, many more factors contribute to its overall degradation. In addition to the oxidising atmosphere with MJF technology, the main factor is the total time when elevated temperatures act on the material (duration and progression of the cooling process, number of heating cycles, etc.). The gradual deterioration of the powder quality causes lower mechanical properties of the material and worsens the quality of the surface of the part etc. This is eliminated by the continuous mixing of a new material, most often in a ratio of 70% reused material and 30% of virgin material, or 80:20. For the SLS technology, this ratio is 50:50. [Feng 2019, Tiwari 2015, Xu 2019]

## 5 MATERIALS AND METHODS

PA 12 waste material was obtained from production on HP Jet Fusion 4200 machines. This waste had undergone at least eight work cycles and was removed from the production based on a visual evaluation. To optimise the resulting mechanical properties of the recycled material, the compatibilising agent Lashan AR-1 (Lushan, China) was mixed with the base matrix, which improves the toughness of the polyamide matrix and ensures higher homogeneity of the system when mixing the powder wastes from different batches and with different degrees of degradation and contamination. Furthermore, a thermal stabiliser (GUARD DOG™ UV360 Light Absorber) was mixed into the base matrix in the amount of 2 wt. %, with a UV stabiliser (VIBATAN NY UV MASTER 00732) represented by 4 wt. % and black pigments (SA Black 007) represented by 4 wt. %.

Recycling and modification of the waste material took place on a Collin ZK 25E twin-screw extruder with an ECON EWA 10 granulation unit, working on the principle of hot granulation technology. The temperature profile of the extruder was set to 175 to 190 °C with regard to the thermal and rheological properties of the PA 12 and the additives. Other parameters of the extrusion process were the speed of the extruder (150 rpm) and the operating output (10 kg/hour). The parameters of the granulation unit were optimised to obtain a high quality granulate. The valve temperature was 195 °C and the temperature of die plate was 205 °C. The speed of the knife head was 2800 rpm. The temperature of the cooling water was maintained at 20 °C using an external cooling system. Before extrusion, the PA 12 was dried in a Venticell 222 device at the temperature of 80 °C for 12 hours to a residual moisture level below 0.1%. During extrusion, the polyamide matrix was further modified with a Lushan AR-1 compatibiliser in concentrations of 3 and 6 wt. %. From the produced pellets of recycled material, test specimens were further produced by injection moulding for subsequent analyses of the mechanical properties. Before the injection process, the pellets were vacuum dried in a Maguire LPD 100 device at the temperature of 80 °C for 2 hours and a vacuum of 0.8 bar. The specimens were produced using an Aurburg 270 S 400-100 injection moulding machine according to the ISO 294-1 and ISO 16396-2 standards. The optimised technological parameters are listed in Table 1.

| | | |
|---|---|---|
| **Temperature zone 1** | 40 | °C |
| **Temperature zone 2** | 200 | °C |
| **Temperature zone 3** | 215 | °C |
| **Temperature zone 4** | 220 | °C |
| **Nozzle temperature** | 225 | °C |
| **Mould temperature** | 60 | °C |
| **Injection velocity** | 25 | $cm^3/s$ |
| **Holding pressure** | 300 | bar |
| **Holding pressure time** | 40 | s |
| **Cycle time** | 60 | s |
| **Back pressure** | 20 | bar |

**Table 1.** Optimised technological parameters for injection moulding of the specimens

All the mechanical properties were determined at ambient temperature (23 °C). After injection moulding, the specimens were stored in a climatic chamber at a temperature of 70 °C and relative humidity of 62% for 7 days before testing according to the ISO 1110 standard. Tensile strength ($\sigma_m$) was determined by the ISO 527/1A/50 method and tensile modulus ($E_t$) by the ISO 527 /1A/1 method. Measurements were performed on a TiraTest 2300 device (Labortech, Czech Republic) with an Epsilon Model 3542 axial extensometer (Epsilon Technology Co., USA).

Flexural tests revealed the flexural strength and flexural modulus of elasticity according to the ISO 178 standard (three-point bending). Characteristics were measured on specimens with dimensions 80 x 10 x 4 mm using a Hounsfield H10KT device with the range of the sensor head up to 500 N. The testing speed was 2 mm/min.

Measurement of the Charpy impact strength was performed under standard conditions according to the ISO 179-1 / 1eA standard (impact on the narrower side of the notched specimen) using the Ceast Resil 5.5 testing device. The specimens had dimensions of 80 x 8 x 4 mm. To determine the impact strength of the specimens, a hammer with a nominal energy of 0.5 J was used.

Flow properties were determined by measuring the melt volume flow rate (MVR) at the temperature of 250 °C and load of 2.16 kg using a Ceast melt flow tester (Torino, Italy) according to the ISO 1133 standard. Before measurement, the material was dried in a Binder VD53 vacuum oven (Binder, Tuttlingen, Germany) to a residual moisture content of less than 0.01%. Residual moisture was controlled on an HX204 halogen analyser (Mettler Toledo, Greifensee, Switzerland) at 130 °C.

## 6 RESULTS AND DISCUSSION

In the first step, the quality of waste PA 12 in the form of powder was evaluated at the input to the recycling process. The melt flow index according to the ISO 1133 standard was the primary evaluation parameter. Before testing the rheological behaviour of the waste powder, the material was dried for 4 hours at the temperature of 80 °C to achieve a residual moisture below 0.1%. The measured values ranged from 12 to 19 $cm^3$/10 min at a temperature of 250 °C and load of 2.16 kg, depending on the final degree of degradation and contamination. After the recycling and modification of the waste, the produced pellets were dried again for at least 4 hours at a temperature of 80 °C, and then the recycled PA 12 was used for the production of test specimens. These injected parts were further conditioned and used for the analysis of selected properties. The measured values are clearly showed in Table 2.

The measured data were classified on two levels. The first level focused on evaluating test specimens printed from PA 12 using the MJF technology, for which the powder material is primarily intended. The recycled material from the waste powder was then compared with these basic data on the second level, where the effect of the presence of the compatibilising agent was mainly monitored. As premised, the best mechanical properties were identified within the analysed range for specimens produced by the MJF technology from the original material without the presence of an over-limit amount of reused material. From the tensile and flexural properties, structural characteristics such as tensile and flexural strength and modulus of elasticity were evaluated and compared. The drop in the tensile modulus of the recycled material represented more than 33% (at 3 wt.% compatibiliser), or almost 28% for the variant with 6 wt. % compatibiliser compared to the maximum achieved by printed bodies. However, such differences were not recorded for the ultimate strength. Recycled material with 6 wt. % compatibiliser reached a similar strength limit as the printed bodies, and the lower strength limit was measured only for the less modified recycled material (by approximately 3.5%). Similar trends were recorded in the analysis of bending properties. The modulus of elasticity decreased for the variant with 3 wt. % compatibiliser by more than 20%, while with a higher representation of the compatibiliser, the decrease was only approximately 11% compared to the values measured for the printed bodies. The differences in strength were again not so outstanding, but they were more significant than those recorded in the framework of the tensile loading. The decrease was almost 6% (with 6 wt. % of compatibiliser), and 11% when adding 3 wt. % compatibiliser. Another analysed characteristic was the notched impact. The original material processed by the MJF technology also demonstrated a relatively high degree of impact resistance, which is typical for PA 12. For the recycled material, a drop in impact resistivity by more than 25% was recorded for the variant with 3 wt. % of compatibiliser and by almost 37% with a higher proportion of the compatibiliser. The rheological behaviour of the compared systems shows an increase in the fluidity of the recycled material by up to 30% compared to the behaviour of the original powder. A higher compatibiliser presence reduced this difference to approximately 18%.

| Production method | Comp. | Tensile test ISO 527 | | Value | St. dev. |
|---|---|---|---|---|---|
| Injection moulding | 3 wt. % | Tensile modulus | $E_t$ [MPa] | 1284 | 20 |
| | 3 wt. % | Tensile strength | $σ_m$ [MPa] | 48.8 | 1.6 |
| | 6 wt. % | Tensile modulus | $E_t$ [MPa] | 1403 | 83 |
| | 6 wt. % | Tensile strength | $σ_m$ [MPa] | 50.8 | 1.2 |
| 3D printing | X | Tensile modulus | $E_t$ [MPa] | 1941 | 94 |
| | X | Tensile strength | $σ_m$ [MPa] | 50.6 | 1.8 |
| **Production method** | **Comp.** | **Flexural test ISO 178** | | **Value** | **St. dev.** |
| Injection moulding | 3 wt. % | Flexural modulus | E [MPa] | 1146 | 37 |
| | 3 wt. % | Flexural strength | $σ_{fM}$ [MPa] | 53.1 | 0.2 |
| | 6 wt. % | Flexural modulus | E [MPa] | 1284 | 21 |
| | 6 wt. % | Flexural strength | $σ_{fM}$ [MPa] | 56.2 | 0.8 |
| 3D printing | X | Flexural modulus | E [MPa] | 1447 | 102 |
| | X | Flexural strength | $σ_{fM}$ [MPa] | 59.7 | 1.7 |
| **Production method** | **Comp.** | **Charpy notched impact test ISO 179-1** | | **Value** | **St. dev.** |
| Injection moulding | 3 wt. % | Notched impact strength | $a_{cA}$ [kJ/mm²] | 5.3 | 0.9 |
| | 6 wt. % | Notched impact strength | $a_{cA}$ [kJ/mm²] | 4.5 | 0.6 |
| 3D printing | X | Notched impact strength | $a_{cA}$ [kJ/mm²] | 7.1 | 1.3 |
| **Material form** | **Comp.** | **Melt flow test ISO 1133** | | **Value** | **St. dev.** |
| Pellets | 3 wt. % | Melt volume flow rate | MVR [$cm^3$/10 min] | 35.2 | 1.8 |
| | 6 wt. % | Melt volume flow rate | MVR [$cm^3$/10 min] | 31.9 | 1.1 |
| Fresh powder | X | Melt volume flow rate | MVR [$cm^3$/10 min] | 27.1 | 2.4 |

**Table 2**. Analyses of chosen mechanical propertie (comp. = compatibilisers)

## 7 CONCLUSIONS

This article is focused on the possibility of the further utilisation of PA 12 in the form of waste powder from powder bed fusion technology. This material, which is no longer usable by additive technologies, was recycled into the form of pellets, which is intended for processing by injection moulding or extrusion. For this purpose, the basic waste material that entered the recycling process was modified with standard additives (UV stabiliser, heat stabiliser and pigments); however, this study was primarily focused on the effect of the presence of the compatibiliser at a volume of 3 wt. % and 6 wt. %. Tensile, flexural, and impact properties were analysed in this study. The targeted level of the selected mechanical properties was determined on test specimens printed with the MJF technology, for which PA 12 in the form of powder is primarily optimised and therefore can demonstrate the best potential of it. In a mutual comparison with the prepared recycled material from which the test specimens were subsequently produced by injection moulding, a clear trend was that the mechanical properties decreased, particularly the modulus of elasticity in tension and bending (decrease by 34% and 22%, respectively). This decrease was lower when the compatibiliser was increased to 6 wt. % (decrease by 28% and 11%, respectively). The decrease in the tensile and flexural strength due to material degradation was also recorded; however, to a lesser extent (maximum decrease of 4% and 11%, respectively). On the other hand, in the case of the variant with 6 wt. % of compatibiliser there was no difference in the tensile strength compared to the printed bodies. The recycled material also showed much lower impact strength (decrease of up to 37%). The presence of the compatibiliser caused an overall increase in the strength characteristics of the recycled material, which was also reflected in an increase in the resulting brittleness of the test specimens. According to the observed trends, the presence of the compatibiliser also slightly reduced the fluidity of the analysed systems. The resulting price of the recycled material is approximately 4 EUR/kg, while the virgin material is available for approximately 6 EUR/kg.

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