Processing of In-Plant Mechanically Recycled PA-12

Tino Meyer, Paul Sherratt, Andy Harland, and Barry Haworth, Loughborough University, UK
Chris Holmes and Tim Lucas, adidas AG, Germany

Abstract

The increasing public awareness and demand for a more sustainable handling of the earth's resources has led to the idea/ concept of a circular economy. Within this concept materials will be re-used in a closed loop system rather than being down-cycled or inappropriately managed (disposed via landfill) at the end of their life-cycle. Based on previous research, Polyamide 12 (PA-12) is a promising material candidate in the sports and leisure sector and its ability for being reprocessed via injection molding has been investigated. While other PAs tend to show a decrease in impact properties on mechanical recycling, PA-12 is shown to be able to overcome these problems when reprocessed at a higher melt temperature, yielding samples with improved impact properties compared to the primary material.

Introduction

To satisfy the increased global demand for more sustainable products and a continuous reduction in carbon dioxide emission, there is an ongoing need to design lighter structures. In order to achieve this target there is a focus on avoiding over-dimensioning by applying modern tools and simulation technology in combination with lightweight, innovative materials. If these materials are also re-processable, the idea of a circular economy comes into life. Since the process of injection molding is one of the most widely employed methods for manufacturing an extremely diverse range of polymeric parts of varying size and complexity, successful research within that field, aligning both industry and market needs, will facilitate future developments in technology and sustainability requirements.

Injection molded materials can be reprocessed in different ways depending on the material type and possible reinforcements/ additives used. While crosslinked thermosets can only be recycled by incorporating them in other materials and therefore downgrading them to the role of fillers, thermoplastics like PAs can be recycled in a closed melt processing loop, i.e., for the same application for which virgin material is used, providing that the effects of degradation from service and the recycling process are known and can be overcome. Recycling can be done either mechanically or chemically and while the mechanical techniques include separation, washing, grinding re-melting and processing of the material, chemical recovery restarts at the monomer level according to the reaction mechanism involved [1]. However apart from the cost, chemical recycling may cause safety and environmental concerns, due to the handling and use of large amount of solvents required [2] and is therefore arguably less desirable.

With focus on PAs, previous work on mechanically recycled materials suggests a problem of decreasing physical properties especially within the category of impact resistance, leading up to embrittlement in some cases after being recycled multiple times. Several publications on the reprocessing of pure PA-6 [3]–[5] all highlight the reduction in impact resistance while making contradictory statements regarding the fundamental reason for property changes. The origin is from a change in molecular weight (MW) due to different degradation processes but different interpretations have emerged. Crespo et al. [3] and Su et al. [4] have observed a reduction in MW and viscosity, explored via Rheometer and Differential Scanning Calorimetry (DSC), whilst Lozano-González et al. [5] report an increase in MW based on GPC correlating with decrease in the Melt Flow Index (MFI) as the number of reprocessing cycles increased. Either way, due to the documented loss in properties, chemical recycling seems to be a preferred approach within the industry for PA-6, with companies like Aquafil and their Econyl® material, which is already commercially used [6]. Essential further work has been conducted on recycled PA-66 [7], the other PA currently in high demand, with focus on the thermo-oxidative ageing sensitivity of reprocessed parts, which is important for any final life estimations of a product. With regards to PA-12, the work by Mägi et al. [8] is just one example of the numerous publications within the 3D printing sector looking into the use of powder left overs from previous productions rather than the actual recycling of the final products. Of interest to the current research, the authors show a decrease of tensile properties for micro injection molded reused powder compared to virgin material, with the highest offset recorded for elongation at break.

This paper examines the mechanical recycling of injection molded PA-12 and its prospects to be used as a material within a circular economy. Based on previous research [9], which showed the possibility of modifying certain material properties for PAs by altering applied process parameters during the injection molding process, one possible approach of preventing a decrease in impact properties might be an increase in the applied melt temperature during reprocessing. This theory is based on earlier findings [10] where PA-12 showed an increase of MW when injection molded at higher temperatures, in contrast to the other standard PA grades. This unique behavior could make PA-12 an interesting material for possible applications under the circular economy umbrella and explains the interest in further research to understand its re-processability.

Materials

The investigated material is a semi-crystalline heat and light stabilized (5 %) PA-12 grade which has a suggested melt temperature window of 220-290°C and is known for its superior impact properties.

Experimental

Virgin PA-12 pellets were injection molded, tested and characterized or reprocessed after granulation. The influence of an increased melt temperature during the reprocessing is investigated by injecting samples at the standard recommended 240°C and at an increased melt temperature of 270°C. The material properties were tested with regards to the quasi-static tensile behavior, while melt flow and thermal properties are characterized by MFI and DSC.

Sample Preparation

All PA-12 pellets were dried at 80°C using a Genlab air oven (OV/150/F) for 16 hours prior to processing. BS EN ISO 527-2 5A tensile specimens were injection molded using an Arburg Allrounder 270S with an external cooling unit by ICS (i-Temp ci90e). Besides the two different melt temperature settings, the key process parameters were kept as follows:

- 80°C mold temperature
- 20 sec cooling time
- 40 cm^3/s flow rate during injection
- 70 MPa holding pressure
- 5 sec holding time

Conditions were adopted for the processing of both raw material types, virgin and 100 % recycled PA-12 respectively. Previously injected samples at 240°C were recycled using a Cumberland 1520 granulator (3026-C) for the reprocessing trials.

Rheological Properties

Melt Flow Index investigations were conducted on the virgin as well as recycled material to provide an accurate assessment of shear flow property changes. Material pellets were loaded into the Tinius Olsen MP600 melt indexer and the flow rate was analyzed under a load of 5 kg at 240°C. The results were compared to injection pressure data collected during the injection molding process.

Mechanical Properties

Quasi-static tensile tests were carried out 24 hours after processing the samples, with no further conditioning, using an Instron 5569 tensile test machine at ambient laboratory conditions. The upper clamp was operated at a speed of 50 mm min^{-1}, with an initial clamp distance of 55 mm. The data were collected using a 1 kN load cell. To eliminate incorrect modulus calculations caused by unwanted onset or machine inertia effects, a preload of 5 N was applied. Each test on the standard type 5A 2 mm thick samples was performed until the test specimen failed by separation and test data were collected and analyzed using Bluehill 2.0 software by Instron. In addition to the measurement of modulus, and conventional stress-strain data, energy absorption data was established using MatLab software. An accurate 'tensile toughness' parameter was calculated from the integrated stress and strain plots derived directly by using the implemented trapezoidal function:

$$\int_a^b f(x)\,dx \approx \frac{1}{2}\sum_{n=1}^{N}(x_{n+1}-x_n)\,[f(x_n)+\ f(x_{n+1}] \qquad (1)$$

Where $(x_{n+1} - x_n)$ represents the spacing between each consecutive pair of points within the investigated curve.

Material Characterization

To investigate different endothermic melting and crystallization responses in the stages of the molded PA-12, a DSC Q2000 thermal analysis device combined with a RCS 90 cooling system (both from TA Instruments Inc.) was used. Nitrogen was employed as the purge gas with a flow rate of 50 ml min^{-1}. A standard heat/cool/heat procedure was chosen at heating/ cooling rates of 10°C min^{-1}. Sample weight was 5.2 mg ± 0.2 mg, aligned with the current standard procedure (BS EN ISO 11357-1).

Results

The following data was obtained for a single reprocessing cycle to prove the concept of using injection molded PA-12 within a circular economy.

Rheological Properties

The collected MFI information and pressure values obtained during the injection molding process are shown in Table 1.

Table 1. Rheological properties for material processed at 240°C: Melt Flow Index vs. In-Situ Injection Molding.

Pellet Type	Viscosity	Injection Molding Pressure
Virgin	1516 Pa/s	120 MPa
Recycled	1513 Pa/s	111 MPa

While the viscosity results obtained via MFI yielded no difference between the virgin and the recycled material, the in-situ injection pressure showed a slight viscosity decrease during the second processing of the material. ‘Viscosity’ data from the MFI analysis provided an accurate comparative indication of flow behavior at low shear stress but did not represent in-process performance. In contrast, the real-time data from the injection unit provided more meaningful comparisons, in response to the set temperature and volumetric flow rate.

For recycled material reprocessed at 270°C melt temperature, the measured injection pressure was found at 97 MPa.

Mechanical Properties

The final properties of a PA-12 injection molded part are influenced when injected from recycled rather than virgin raw material at the same process conditions. A comprehensive overview, highlighting the differences in tensile properties for samples produced from virgin as well as recycled material, is given in Figure 1.

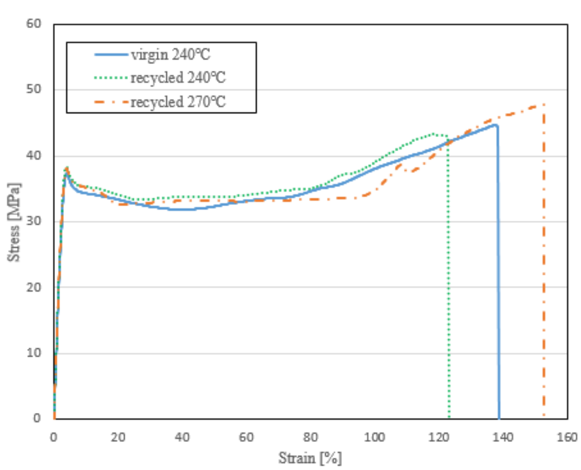

Figure 1. Raw data for tensile testing of PA-12: effect of raw material and melt temperature

The stress-strain data shows a stabile yielding followed by necking, cold drawing and strain hardening for all three sample types. The obtained results from the quasi-static tensile test experiments are shown in Table 2 for the virgin and recycled samples processed at 240°C.

Table 2. Mechanical properties for virgin and recycled material processed at 240°C.

Tensile Properties	Virgin	Recycled
Modulus [MPa]	1028 ± 1.2 %	986 ± 1.8 %
Yield Stress [MPa]	37.0 ± 0.5 %	38.1 ± 0.7 %
Yield strain [%]	4.07 ± 0.1 %	3.94 ± 0.8 %
Stress at break [MPa]	43.4 ± 4.5 %	42.2 ± 2.7 %
Strain at break [%]	137 ± 7.3 %	121 ± 4.7 %
Toughness [J]	21. 2 ± 8.9 %	18.9 ± 5.7 %

While the modulus was found to decline after reprocessing, the yield stress increased slightly. The most influenced parameters were the strain at break with a decline of 11.5 % and similar the calculated overall tensile toughness with 11.2 %.

When reprocessed at a higher melt temperature, 270°C respectively, samples showed superior properties even compared to the virgin findings, especially with regards to the tensile toughness. The obtained data is presented in Table 3.

Table 3. Mechanical properties for reprocessed material at increased melt temperature (270°C).

Tensile Properties	270°C melt
Modulus [MPa]	1038 ± 2.0 %
Yield Stress [MPa]	38.0 ± 1.2 %
Yield strain [%]	3.99 ± 0.8 %
Stress at break [MPa]	47.2 ± 5.3 %
Strain at break [%]	150 ± 12 %
Toughness [J]	23.9 ± 17 %

The melt temperature increase led to similar results for modulus and the yield instability region in PA-12, while the stress and strain at break increased by 9.0 % and 9.9 % compared to samples produced at 240°C from virgin material and by 11.9 % and 24.2 % in case of samples from recycled material. The calculated tensile toughness increased by 12.7 % and 26.9 % respectively.

In contrast to the samples processed from virgin PA-12 material, both sets of reprocessed samples (240°C and 270°C) showed post-yield stress whitening, an indicator for a change regarding the intrinsic failure behavior under load.

Material Characterization

The change in mechanical properties aligns with findings regarding the thermal characteristics. While Figure 2 shows the initial heating curves for samples produced either from virgin or from recycled material, highlighting an offset with regards to the detected melting peak temperature, Figure 3 shows a delayed re-crystallization of the tested material due to a higher applied temperature.

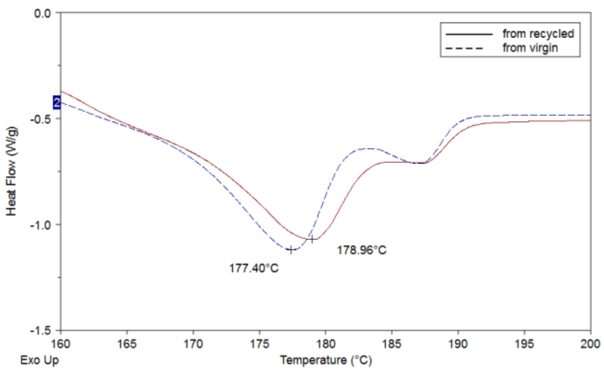

Figure 2. DSC initial heating curve: samples produced from virgin and recycled material.

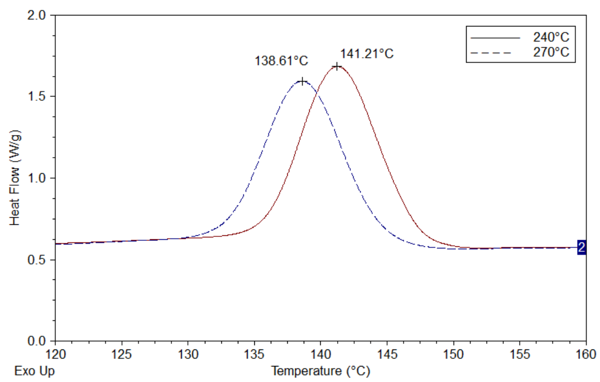

Figure 3. DSC cooling curve virgin PA-12 pellets: different applied peak temperature.

Both findings could be explained by a difference in the molecular structure of the respective samples. The delayed re-crystallization for higher melt temperatures applied, detected while testing the material pellets, is assumed to be caused by a MW increase due to an occurring combination of melt state polycondensation and cross-linking during the heating phase [10]. The higher peak temperature observed for samples produced from recycled materials indicate an increased size and perfection of crystallites, which could be attributed to reduced chain length.

Discussion

As previously described for PA-6 [3]–[5], the processing of recycled PA-12 material at identical parameters led to a change in some mechanical properties, above all with regards to their tensile toughness behavior. This is assumed to be caused by a reduction of chain length due to an increased degree of material degradation.

Prior to reprocessing, the virgin and recycled material granulate showed no difference in viscosity (via MFI) and comparable thermal characteristics (via DSC). However, the real-time pressure measurements observed on injection molding indicate structural changes reflecting a change in shear viscosity at high flow rates during reprocessing.

Increasing the melt temperature during reprocessing to overcome the reduction in toughness properties appears to be effective, albeit for a single reprocessing cycle. Further research is essential to explore other variables, such as residence time variations at high temperatures, or different thermo-mechanical history during injection. Also, studies on post-consumer materials would be required to ensure that the property increase is not archived by reducing part capabilities in any other way, e.g. the physical/ chemical ageing sensitivity.

Since the PA-12 was mechanically recycled, contamination during the granulation needs to be considered as another possible factor, when accounting for the reduction in toughness properties. This is considered as a low risk in the current research, due to the overall levels of consistency involved, especially in post-yield response to tensile stress.

Besides the occurring stress whitening post-yield, the recycled samples also showed a slight discoloration (more opaque) assumed to be caused by the change in underlying crystalline morphology and heat increased yellowing of the stabilizer within the material, which could be an issue if their semi-transparency is important for the final application.

Conclusions

This research presents a first step towards the investigation of PA-12 as a possible material for injection molded products in a circular economy. Test results for a single reprocessing cycle confirm previous outcomes suggesting that a loss in mechanical properties in PA-12 can be compensated by increasing the applied melt temperature. A 30°C rise, from 240°C to 270°C, during the reprocessing of mechanical recycled material led to samples with superior tensile properties, even compared to raw material/ virgin samples. These findings form the basis for further investigations in which the material is recycled and re-processed numerous times (to achieve high process residence times) and tested in more depth regarding other possible structure/ property changes due to the different reprocessing. Subsequently, the laboratory scale and controlled processing environment could be extended towards a more realistic scenario to investigate the recycling of postconsumer goods.

Overall this paper serves as a proof of concept and forms a basis on which to stimulate further research interest in injection molded PA-12, given its excellent balance of mechanical properties and prominence in some important industrial sectors.

Acknowledgment

The presented results are part of an industrial funded PhD at Loughborough University (UK).

References

[1] K. Hamad, M. Kaseem, and F. Deri, *Polymer Degradation and Stability*, **98**, pp. 2801–2812 (2013).

[2] A. Bernasconi, P. Davoli, D. Rossin, and C. Armanni, *Composites - Part A: Applied Science and Manufacturing*, **38**, pp. 710–718 (2007).

[3] J.E. Crespo, F. Parres, M.A. Peydró and R. Navarro, *Polymer Engineering and Science*, **53**, pp. 679–688 (2013).

[4] K. H. Su, J. H. Lin, and C. C. Lin, *Journal of Material Processing Technology*, **192–193**, pp. 532–538 (2007).

[5] M. J. Lozano-González, M. T. Rodriguez-Hernandez, E. A. Gonzalez-De Los Santos, and J. Villalpando-Olmos, *Journal of Applied Polymer Science*, **76**, pp. 851–858 (2000).

[6] EPD International, *Enviromental Product Declaration for Econyl Yarn* (2014).

[7] P. -A. Eriksson, P. Boydell, K. Eriksson, J. -A. E. Månson, and A.-C. Albertsson, *Journal of Applied Polymer Science*, **65**, pp. 1619–1630 (1997).

[8] P. Mägi, A. Krumme, and M. Pohlak, *Key Engineering Materials*, **674**, pp. 9–14 (2016).

[9] T. Meyer, P. Sherratt, A. Harland, B. Haworth, and C. Holmes, T.Lucas, *14th International Conference on Manufacturing Research*, pp. 43–48 (2016).

[10] T. Meyer, A. Harland, B. Haworth, C. Holmes, T. Lucas, and P. Sherratt, *International Polymer Processing*, (in press)