U.Porto Journal of Engineering, 9:3 (2023) 91-101
ISSN 2183-6493
DOI: 10.24840/2183-6493_009-003_001845

Received: 29 September, 2022
Accepted: 23 January, 2023
Published: 28 April, 2023

Recycling Potential of Onyx Composite for Additive Manufacturing

M. E. M. Mergulhão[1], S. G. Magalhães[2], J. M. Costa[3]

[1]Department of Metallurgical and Materials Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 PORTO, Portugal, and Department of Materials Engineering, São Carlos School of Engineering of the University of São Paulo, Avenida Doutor Arnaldo, 715, 01246904 São Carlos, SP, Brazil (marina.mergulhao@usp.br) ORCID 0000-0002-7749-3160

[2]Department of Metallurgical and Materials Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 PORTO, Portugal (up201705665@edu.fe.up.pt)

[3]Department of Metallurgical and Materials Engineering, Faculty of Engineering, University of Porto, and LAETA/INEGI - Institute of Science and Innovation in Mechanical and Industrial Engineering, Rua Dr. Roberto Frias, 4200-465 PORTO, Portugal (jose.costa@fe.up.pt) ORCID 0000-0002-1714-4671

Abstract

The evaluation of product cycles has allowed companies to transition from linear to circular production and reuse collected material. However, recycling is only sometimes straightforward and involves the material history of thermal cycles, the recycled content, and other characteristics. Therefore, recycling processes' adversities and products need to be studied. Thus, this study aims to obtain a recycled Onyx filament, a micro carbon fiber-filled nylon, and evaluate its recycling potential to produce 3D printed samples. Tensile tests, optical microscopy, and evaluation of the quality of 3D printed samples and filaments were conducted. Under the studied conditions, the recycled Onyx filament did not present a satisfactory performance for 3D Printing, leading to nozzle clogs and precluding the 3D printed samples from being completed. These problems have been related to previous work. Therefore, it is necessary to investigate Onyx recycling under other conditions, such as recycling conditions or adding virgin material during recycling.

Author Keywords. Circular Economy, Onyx, Extrusion, Additive Manufacturing, 3D Printing.

Type: Research Article

1. Introduction

Fused Filament Fabrication is a 3D Printing technology based on filament extrusion, which is pushed into the printer head, melted, and passes through a nozzle producing an even thinner filament to deposit and build the part layer by layer (Das, Etemadi et al. 2021, Al-Mazrouei, Al-Marzouqi et al. 2022). Poor interlayer bonding between layers reflects mechanical properties, so reinforcement is added to the neat polymer and can improve stiffness and strength (Das, Etemadi et al. 2021). Modern 3D printers can print composites, like Onyx, that are usually heterogeneous materials composed of a rigid reinforcement and a jointing material, that is, carbon nanofiber and Nylon, respectively for Onyx (Bárnik, Vaško et al. 2019).

Markforged Onyx consists of nylon reinforced with chopped micro carbon fiber and stands out due to its good appearance and for standing up to industrial requirements (Hetrick, Sanei et al. 2021). Few materials have the versatility of Onyx. When printed alone, it offers precise parts with an almost perfect surface finish, high strength, toughness, and chemical resistance. Pieces printed in Onyx warp less than the equivalents in Nylon. It can provide parts with stiffness equal to or greater than any pure thermoplastic for 3D Printing and can also be reinforced with continuous fibers (Bárnik, Vaško et al. 2019, Markforged 2022).

Reverse logistics consists of managing the product cycle, considering that the discarded material returns to the process and remains in the value chain along multiple lifecycles (Gomes, Cadete et al. 2022). In addition to being positive for the environment, this practice also brings financial, image, and social returns for the companies that practice it (Liva, Pontelo et al. 2018). Hence, reverse logistics has a close relationship with recycling once it facilitates the return of the product to industries, allowing it to be used as raw material.

In this context, primary mechanical recycling consists of reusing discarded uncontaminated material. This type of material has the advantage of not demanding high costs for material selection and knowing the history and tracking of the material. For good homogenization and mixing, it is necessary to grind the pieces, which often involves the processes of shredding, crushing, and milling (Ignatyev, Thielemans et al. 2014).

However, recycling is a thermo-mechanical process and can cause the degradation of properties due to high temperatures and shear rates, exacerbating most thermoplastic oxidative processes. This can change the polymers' chain lengths and alternate the materials' processability, properties and quality. Therefore, it is common to reinforce the recycled material to obtain better mechanical properties or new functionality. It is also relevant that the number of lifecycles or processes that a material is submitted influences the level of degradation and, thus, limits the circular flow in the supply chain and the applications of the recycled product (Gomes, Cadete et al. 2022). For this reason, recycling a material is not simple and demands tests and research.

Recycling filament for 3D Printing offers economic and environmental benefits. However, literature reports limitations. First, there is a problem with reducing the molecular weight after successive recycling cycles at elevated temperatures. Studies with PLA showed that due to the chain scission, recycled filaments reduced adhesion strength between the beads of the polymer (Zhao, Hwang et al. 2018). In addition, there are risks when recycled filaments are used due to nozzle clogs, mechanical properties degradation and increased particle release. However, there is a need to investigate those problems, once in many cases, it can be solved with the investigation and minimizing sample contamination with the use of larger nozzles or with higher forming temperatures (Anderson 2017). Another adversity is water, since Onyx tends to absorb water from the environment up to 8% of its weight, leading to the creation of bubbles and voids in the deposited filament (Pascual-González, Iragi et al. 2020).

Thus, it is interesting to study the feasibility of recycling the Onyx composite to implement reverse logistics. For the first moment, the recycling of pre-consumer materials, that is, primary recycling, is attractive because it does not involve variables such as waste separation and collection, and the contamination is exiguous. Thus, this study proposes the Recycling of Onyx to produce filament and 3D printed samples to evaluate the potential of this process for Onyx, within the tested conditions, by analyzing the mechanical properties of the filament in the tensile test, by optical microscopy and by the quality of the printed sample.

2. Materials and Methods

Markforged is an American company founded in 2013 focused on additive manufacturing. Among its products are included 3D printers, software and materials. Regarding materials, the main composite base material of Markforged is Onyx, which is produced in Billerica, Massachusetts, United States of America (Markforged, 2022). As mentioned above, Onyx has high strength and toughness, providing an impressive surface finish on the parts produced. Table 1 shows the properties of the Onyx material supplied by Markforged (Markforged 2022).

The study started by preparing Onyx for extrusion. Improperly stored filaments and parts that had a manufacturing defect by 3D Printing were gathered and then sliced to facilitate the following processes. These materials are shown in Figure 1. Thus, these pieces were inserted into a mill (Figure 2) to be crushed and reduced in size. The process was repeated until the granules were about 2 mm thick or less, what was controlled by visual inspection and the largest granules were collected and measured to verify their thickness with a ruler. It is noteworthy that there was difficulty with the grinding due to the high rigidity of the material, which often blocked the grinding wheel. Finally, about 0.5 kg of material was obtained, which was enough to continue the subsequent steps. Then, these granules were taken to the oven to remove moisture for one day at 60 °C,. This was made following Markforged recommendation since these materials are commonly hygroscopic, and could not be taken measurements in storage to avoid humidity in material.

Properties	
Density	1.2 g/cm3
Tensile Strength	36 MPa
Tensile Modulus	1.4 GPa
Flexural Strength	81 MPa
Flexural Modulus	3.6 GPa
Heat Deflection Temperature	125 °C

Table 1: Onyx properties (Markforged 2022).

Figure 1: Diverse Onyx pieces that were used for recycling.

Figure 2: Mill Equipment.

The extrusion machine is a filament maker from the Dutch company 3DEVO, based in Utrecht, and is shown in Figure 3 and was used to conduct the extrusion. This equipment is a specialized machine oriented towards industrial quality results. It has an integrated control panel with easily accessible settings, standard material pre-sets, and customizable material profiles. It also has a hopper with an optical sensor to check the material level where the crushed material is introduced. Then, the extruder has four heating zones, reaching a temperature of up to 400 °C, with a nitride tempered steel extruder screw. The cooling system consists of two fans with adjustable angles for uniform air distribution; fan speed is customizable. The sensor accurately measures the extruded filament diameter and optimal placement to ensure filament roundness. The filament passes through the positioner and is wound onto the spool (3devo 2022).

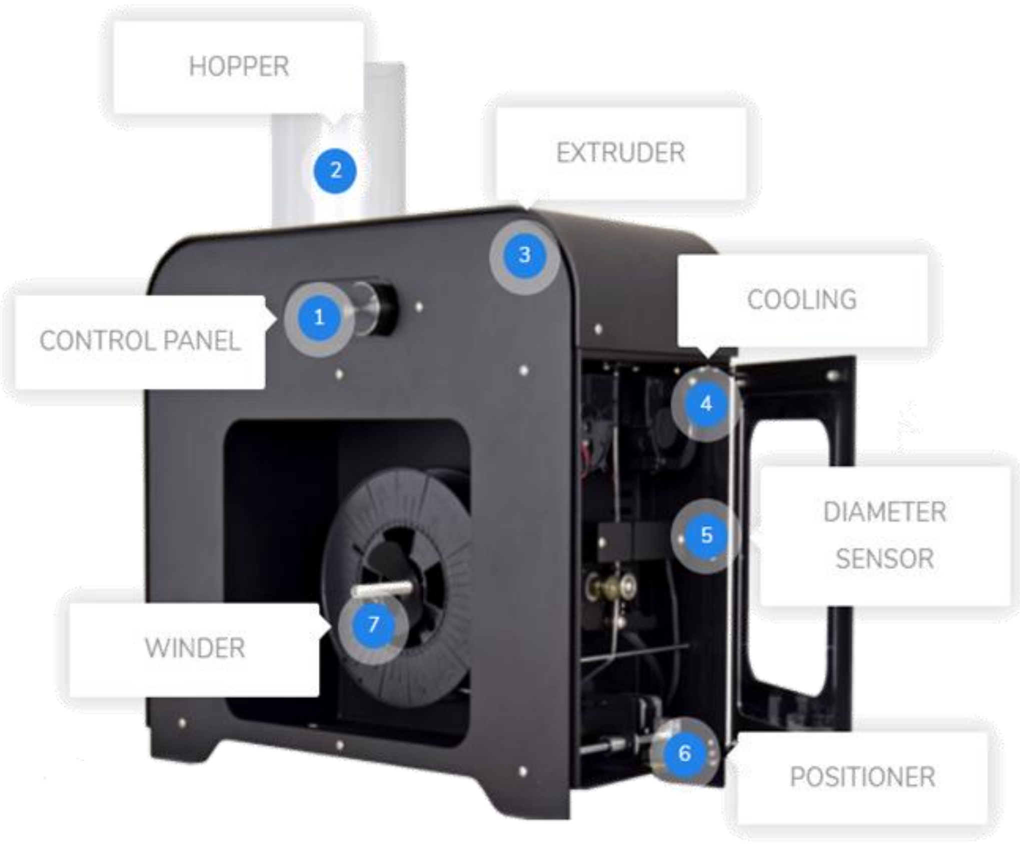

Figure 3: 3DEVO extruder machine.

Therefore, the filament was extruded with the milled granules of Onyx. This was performed initially on an ENDER-3 printer, from 3D lab. It has a limitation of 260°C and a nozzle of 0.4 mm (Figure 4) was used. Other conditions were determined experimentally and will be detailed in the next section. After successfully obtaining Onyx filaments, 3D Printing was carried out. The ENDER-3 parts are shown in Figure 4. It has an integrated display screen with easily accessible settings, a base frame, the hotbed can be heated to 100 °C in 5 minutes, it has filament holder, and it also comes with a spatula to help us remove the printed object. However, for this material, the 3D Printing presented difficulties. The hypothesis raised was that the ideal temperature for recycled Onyx Printing was not being reached with the equipment or that the machine was not working properly, so different 3D printers were used, including an ENDER-5 and a Norcan, which is used for Onyx that Markforged made available. In all cases the pieces' Printing was precluded, and parts were not entirely completed. Therefore, it was not possible to print an Onyx specimen in the traditional shape for tensile test, although initially there was an intention of performing the test.

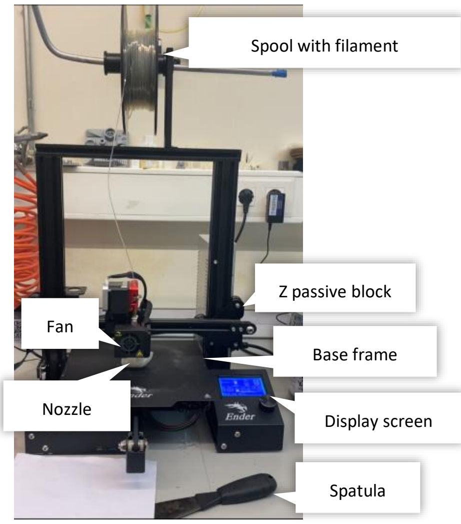

Figure 4: Ender 3 3D printer

Regarding the tensile test, although it was initially planned to print the specimens in the traditional format for tensile testing conducted according to NP EN 10002-1 standard with an EZ-SX Short Model, due to the impossibility to obtain an acceptable Printing, it was decided that the extruded filament would be studied, as will be discussed in the next section. So, to understand the materials properties in this step and what caused the problems during 3D Printing, the filament was studied. For comparative purposes, the tensile test was performed with three tests for each material studied: the original Onyx and recycled. The samples consisted of cylindrical filaments with 1.75 mm of diameter and 190 mm in length.

Microstructural analysis of the filaments was conducted. Filaments were assembled, both horizontally and vertically, from the filaments produced at FEUP and from the original filaments supplied by Markforged. Then the samples were polished and observed under an optical microscope.

3. Discussion

3.1. Onyx Extrusion

During the extrusion it was possible to control the temperatures of the four heaters, screw speed, the diameter of the extruded material and the intensity of the cooling speed. Several attempts were made with different scenarios to acquire the best filament as possible, and they are shown in Table 2.

For the first attempt, the heaters were placed at about 20 °C above the melting temperature. So, as the Onyx's melting temperature is around 192 °C (Papa, Silvestri et al. 2021), the heaters were set to 210 °C, leaving the intensity of the cooling speed at 70% and screw speed at 5 rpm. During all the experiment the set diameter was held at 1.75 mm. This attempt was not successful, as the extruded filament was fragile and thin. For the second attempt, as PLA already has a 3DEVO configuration, the same cycle was used, increasing only 10 °C to each heater, as the melting point of Onyx is 10 °C higher than that of PLA. This attempt did not work because the material is fragile and looks whitish when it was broken. From then on, the temperatures, screw speed and cooling speed were changed. It took several attempts to obtain a suitable filament. However, it was noticeable that at higher temperatures (as in attempt 21) and, consequently, a higher cooling rate, it was possible to obtain a hard and homogeneous filament.

Thus, in the 21st attempt, it was possible to obtain the best filament, which was later chosen to perform 3D Printing. Trials 18 and 23 also provided good filaments, but they were thinner and not-so-regular when compared to attempt 21.

Attempts	**Heaters**				**Screw Speed (rpm)**	**Diameter (mm)**	**Cooling Speed (%)**
	4	***3***	***2***	***1***			
1	210	210	210	210	5	1.75	70
3	180	195	200	180	5	1.75	70
4	180	195	200	180	6.5	1.75	70
5	180	195	200	190	6.5	1.75	70
6	180	195	200	180	6.5	1.75	70
7	180	195	200	180	6.5	1.75	80
8	180	195	200	180	6.5	1.75	70
9	190	205	210	190	5	1.75	70
10	190	205	210	200	5	1.75	70
11	180	195	200	180	8.5	1.75	70
12	180	195	200	190	6.5	1.75	70
13	195	210	215	215	6.5	1.75	70
14	180	200	205	195	8.5	1.75	70
15	195	210	210	200	6.5	1.75	70
16	200	210	210	200	8	1.75	70
17	195	195	200	205	6.5	1.75	70
18	195	195	200	200	6.5	1.75	70
19	200	200	200	200	6.5	1.75	90
20	195	195	200	200	6.5	1.75	90
21	200	200	195	195	6.5	1.75	90
22	230	230	230	230	6.5	1.75	90
23	220	220	220	220	6.5	1.75	90

Table 2: Scenarios for Onyx extrusion

3.2. Onyx 3D Printing

As mentioned above, 3D Printing is usually performed at about 50 °C above the fusing temperature. Onyx's fusing temperature is 192 °C and the Printing was performed at 260 °C (Papa, Silvestri et al. 2021). This choice is suitable based on the Printing temperatures of other materials and in literature, where virgin Onyx Printing temperatures have been reported between 220 °C and 280 °C (Pascual-González, Iragi et al. 2020, Das, Etemadi et al. 2021). So, it was conducted about 70 °C above the fusing temperature with both ENDER-3 and ENDER-5 printers. With this, printing the part of the intended object was possible, but the machines stopped Printing. The print could not be completed due to the interruption of the 3D Printing machine. Other temperatures were also evaluated but the best result was obtained at 260 °C, which is the maximum temperature that the 3D printers could reach.

These interruptions were already reported in literature and can be related to nozzle clogging or presence of water. In the first case, a higher temperature for Printing recycled Onyx or larger a nozzle would be demanded, but the 3D printers used are limited to 260 °C (Anderson 2017). Also, nozzle clogging can be related to heterogeneity of the filament, which had flatter parts and with slight variations in the diameter. Attempts were made to change other parameters like the bed temperature, but they were unsuccessful. Initially, it was believed that it was a machine error, but when a filament of another material was placed, it was successfully printed. Thus, it was concluded that it was impossible to conduct the 3D Printing of the recycled Onyx filament due to a limitation of the equipment, as it cannot achieve temperatures above 285 °C. The problem can also be related to the presence of water. Although the material was dried and stored properly, it is possible that during the many trials of the experiment it has absorbed water, since Onyx has this tendency. That can create bubbles and voids, weakening interlayer bonding (Pascual-González, Iragi et al. 2020).

The Printing of the recycled Onyx filament used a Norcam machine provided by Markforged, in the same conditions that the company uses to print virgin Onyx. However, the same interruption happened, and it was not possible to finish Printing of a cube, although the result of this was better than the Printing at laboratory.

The results are shown in Figure 5, where it is possible to notice that the piece printed with virgin filament (Figure 5A) presented great details, precision and did not stop printing until it received that command. In contrast to this successful printing, during the production of the object with recycled filament the process was imprecise, the release of the material often started with delay and in wrong points, leading to unsuccess to bind layers until it suddenly stopped releasing material. The results are shown in Figure 5B.

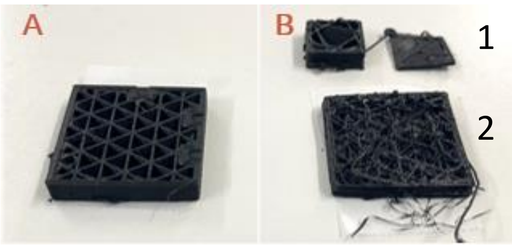

Figure 5: Onyx parts from 3D Printing: (A) from original Onyx; (B) from recycled Onyx (1 indicates samples printed in the laboratory, and 2 is the one that was printed with Markforged 3D printer).

3.3. Tensile Test

Once the recycled filament did not allow to print complete pieces, probes could not be manufactured in the geometry used in traditional tensile test. For comparative purposes, the tensile test was performed using the filaments, as shown in 6.

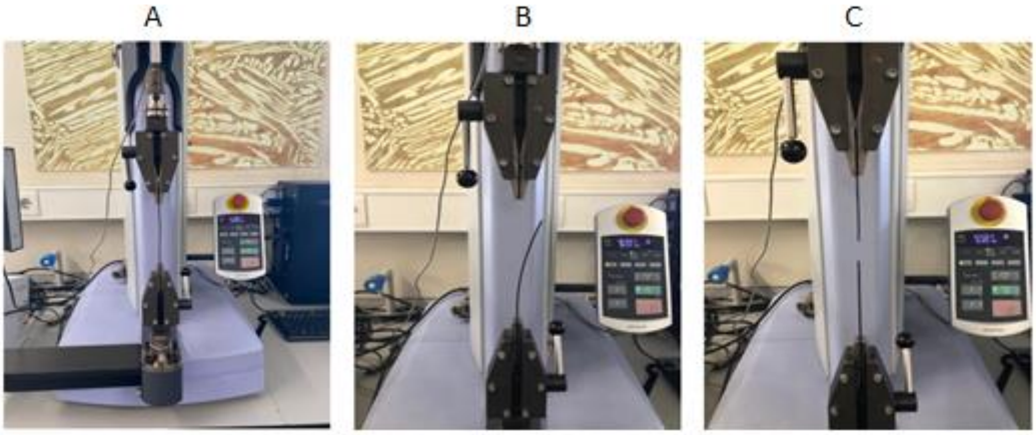

Figure 6: Tensile test of Onyx (a) before the test; (b) after the test of original Onyx filament; (c) after the test of recycled Onyx.

For both original and recycled filaments, the samples used were selected among all considering the best quality and avoiding imperfections and its dimensions are detailed in "Materials and Methods." A result was predicted that all the filaments would break at the attachment point, as this is where the tension would be concentrated. All samples of recycled

Onyx broke in the center, while those of Onyx obtained from the original filament broke in the grip. A possible fact for this is related with utilization of polymers already extruded to filament before, which allows the degradation of polymers, and as consequence changes initial properties of material. Figures 6b and c. shows de difference between original and recycled filament.

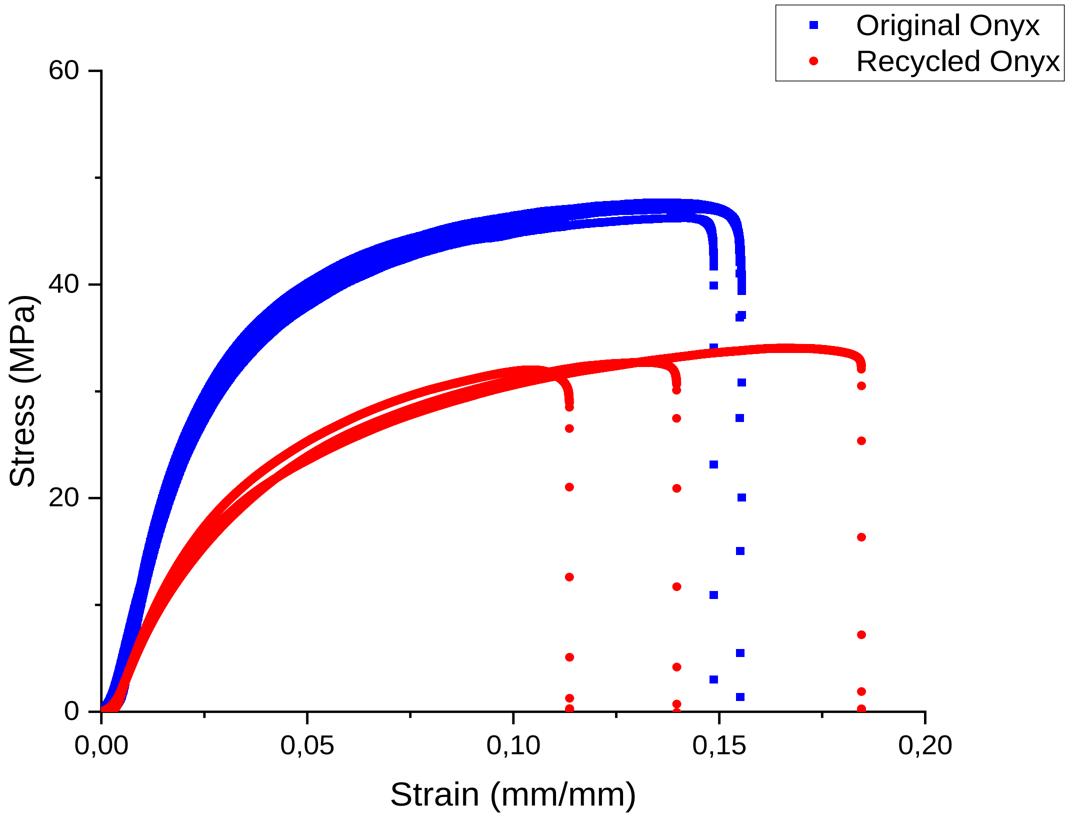

Figure 7: Tensile strength results, stress versus strain curve

The stress-strain curves obtained, and shown in Figure 7 shows that the original Onyx presented greater rigidity, and the results were much more homogeneous than the recycled ones. Note that comparing the tensile strength of 36 Pa from the data provided in Table 1 with the results of the tensile test of the present research, the values obtained with the original composite were more accurate than those from the recycled samples, which were reduced due to degradation of molecular structure and chain scission (Zhao, Hwang et al. 2018). Also, the fracture occurred in a narrow range of values of strain when the original filament was studied, while the recycled varied. The rupture in the test of the virgin Onyx happened in the grips due to the stresses that were concentrated in the ties, as expected. However, the different location of the rupture that happened with the recycled composite is probably related to imperfections along the filament, which are also tension concentrators and were the weakness and were probably the cause for the rupture of these materials.

3.4. Microstructural Analysis

After observing the samples under an optical microscope, it was possible to report that the differences between the microstructures were discreet. The filament produced by Markforged is like the filament extruded at the laboratory through recycling. For better observation of the microstructures, it would be interesting to perform in a scanning electron microscope. However, it is possible to see carbon fiber in a nylon matrix with a randomly oriented length and direction. The microstructures are shown in Figure 8.

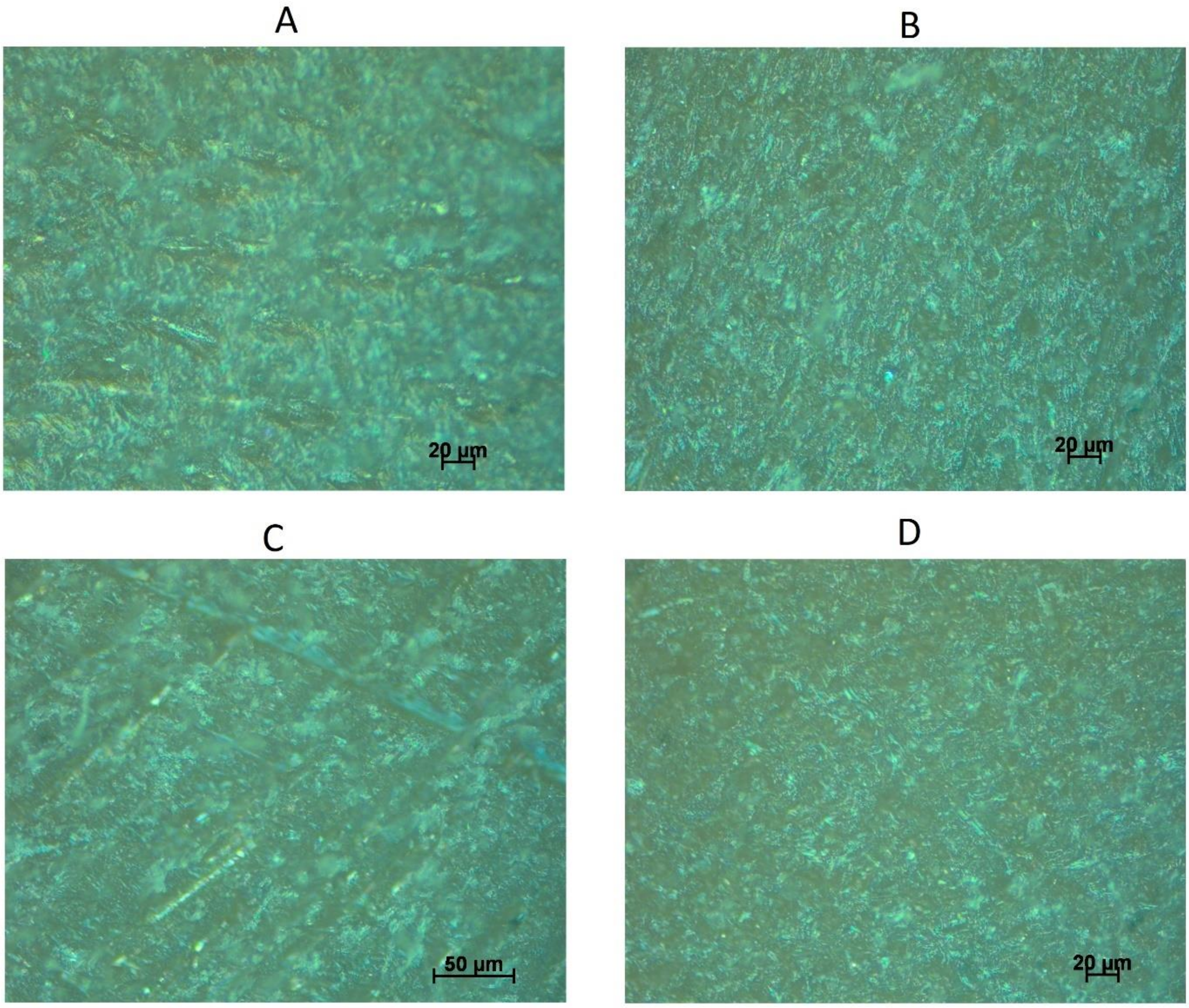

Figure 8: Onyx microstructure: (A) Virgin filament (horizontal cut); (B) virgin filament (vertical cut); (C) recycled filament (horizontal cut); (d) recycled filament (Vertical cut).

4. Conclusions

Onyx is a material of great interest regarding its surface finishing, high strength, toughness, chemical resistance and stiffness. The extrusion of Onyx is an exciting strategy in terms of properties and reuse of parts, evolving in terms of sustainability and circular economy, with beneficial aspects for manufacturing, recycling and environment. However, in the conditions performed in this study, recycled Onyx filaments presented inferior properties to original Onyx filaments due to factors such as chain scission because of recycling, presence of moisture and stress concentration because of the inhomogeneity of the filament.

For future work, it is suggested to study the recycling of Onyx considering the addition of different percentages of original Onyx to the recycled material before extrusion. The addition of other thermoplastics could also lead to interesting results. These attempts may allow acquiring a material that guarantees better filament quality. Furthermore, it is needed to use different nozzle sizes and use 3D printer that support higher temperatures to investigate as an attempt to solve the Printing clogging. Thus, developing an appropriate specimen for tensile testing and assessing material properties according to existing standards would be possible.

5. Future work

This is an introductory work. In the future it is intended to continue study, and have deeper analysis and characterization.

References

“About 3devo - Inventive and High-Tech Startup in the Netherlands | 3devo.” n.d. Accessed February 23, 2023. https://www.3devo.com/about-3devo.

Al-Mazrouei, Noura, Ali H. Al-Marzouqi, and Waleed Ahmed. 2022. “Characterization and Sustainability Potential of Recycling 3D-Printed Nylon Composite Wastes.” Sustainability 14 (17): 10458. https://doi.org/10.3390/su141710458.

Anderson, Isabelle. 2017. “Mechanical Properties of Specimens 3D Printed with Virgin and Recycled Polylactic Acid.” 3D Printing and Additive Manufacturing 4 (2): 110–15. https://doi.org/10.1089/3dp.2016.0054.

Bárnik, František, Milan Vaško, Milan Sága, Marián Handrik, and Alžbeta Sapietová. 2019. “Mechanical Properties of Structures Produced by 3D Printing from Composite Materials.” Edited by I. Malujda, M. Dudziak, P. Krawiec, K. Talaśka, D. Wilczyński, M. Berdychowski, J. Górecki, Ł. Warguła, and D. Wojtkowiak. MATEC Web of Conferences 254: 01018. https://doi.org/10.1051/matecconf/201925401018.

Das, Arit, Martin Etemadi, Bradley A. Davis, Steven H. McKnight, Christopher B. Williams, Scott W. Case, and Michael J. Bortner. 2021. “Rheological Investigation of Nylon-carbon Fiber Composites Fabricated Using Material Extrusion-based Additive Manufacturing.” Polymer Composites 42 (11): 6010–24. https://doi.org/10.1002/pc.26281.

Gomes, Tiago EP, Mylene S. Cadete, João Dias-de-Oliveira, and Victor Neto. 2022. “Controlling the Properties of Parts 3D Printed from Recycled Thermoplastics: A Review of Current Practices.” Polymer Degradation and Stability 196 (February): 109850. https://doi.org/10.1016/j.polymdegradstab.2022.109850.

Hetrick, Dakota R, Seyed Hamid Reza Sanei, Charles E Bakis, and Omar Ashour. 2021. “Evaluating the Effect of Variable Fiber Content on Mechanical Properties of Additively Manufactured Continuous Carbon Fiber Composites.” Journal of Reinforced Plastics and Composites 40 (9–10): 365–77. https://doi.org/10.1177/0731684420963217.

Ignatyev, Igor A., Wim Thielemans, and Bob Vander Beke. 2014. “Recycling of Polymers: A Review.” ChemSusChem 7 (6): 1579–93. https://doi.org/10.1002/cssc.201300898.

Liva, P., et al. (2018). "Logística Reversa - I." Journal of Chemical Information and Modeling: 1-10. https://pubs.acs.org/toc/jcisd8/58/1.

Markforged (2022). "Company." Retrieved January 2023, from https://markforged.com/about/company.

Markforged (2022). "Onyx." Retrieved December 2022, from https://markforged.com/materials/plastics/onyx.

“Meet the Composer and Precision - Desktop Filament Makers | 3devo.” n.d. Accessed February 23, 2023. https://www.3devo.com/filament-makers.

Papa, Ilaria, Alessia Teresa Silvestri, Maria Rosaria Ricciardi, Valentina Lopresto, and Antonino Squillace. 2021. “Effect of Fibre Orientation on Novel Continuous 3D-Printed Fibre-

Reinforced Composites." Polymers 13 (15): 2524. https://doi.org/10.3390/polym13152524.

Pascual-González, C., M. Iragi, A. Fernández, J.P. Fernández-Blázquez, L. Aretxabaleta, and C.S. Lopes. 2020. "An Approach to Analyse the Factors behind the Micromechanical Response of 3D-Printed Composites." Composites Part B: Engineering 186 (April): 107820. https://doi.org/10.1016/j.compositesb.2020.107820.

Zhao, Xing Guan, Kyung-Jun Hwang, Dongoh Lee, Taemin Kim, and Namsu Kim. 2018. "Enhanced Mechanical Properties of Self-Polymerized Polydopamine-Coated Recycled PLA Filament Used in 3D Printing." Applied Surface Science 441 (May): 381–87. https://doi.org/10.1016/j.apsusc.2018.01.257.

Acknowledgments

The authors appreciate the support from Norcam, Engenharia e Design Industrial (website: www.norcam.pt) since they supported the investigation regarding material and 3D Printing of components using both new and recycled Onyx.