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Life Cycle Assessment of Composites Additive Manufacturing Using Recycled Materials

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Abstract: Additive manufacturing (AM) of composite materials is promising to create customizable products with enhanced properties, utilizing materials like carbon fibers (CFs). To increase their circularity, composite recycling has been proposed to re-introduce the recovered components in AM. A careful evaluation of recycling is necessary, considering the sustainability and functionality (i.e., mechanical properties) of the recovered components. Thus, Life Cycle Assessment (LCA) is applied to estimate the environmental impacts of AM via Fused Filament Fabrication (FFF), using virgin or recycled CFs via solvolysis at a laboratory scale. This study aims to provide a detailed Life Cycle Inventory (LCI) of FFF and evaluate the sustainability of using recycled CFs in AM. For both virgin CF manufacturing and CF recycling, electricity consumption was the main contributor to environmental impacts. CF recovery via solvolysis resulted in lower impacts across most impact categories compared to AM with virgin CFs. Different scenarios were examined to account for the mechanical properties of recycled CFs. AM with 75% recycled CFs, compared to 100% virgin CFs undergoing landfilling, resulted in over 22% reduction in climate change potential, even after a 50% loss of recycled CF functionality. Overall, this study offers insights into the LCI of FFF and shows that CF recycling from composites is worth pursuing.

Keywords: additive manufacturing; life cycle assessment; carbon fiber; recycled materials; solvolysis

Citation: Chatzipanagiotou, K.-R.; Antypa, D.; Petrakli, F.; Karatza, A.; Pikoń, K.; Bogacka, M.; Poranek, N.; Werle, S.; Amanatides, E.; Mataras, D.; et al. Life Cycle Assessment of Composites Additive Manufacturing Using Recycled Materials. *Sustainability* **2023**, *15*, 12843. https://doi.org/10.3390/su151712843

Academic Editors: Wei Wen, Kui Wang and Said Ahzi

Received: 16 June 2023
Revised: 15 August 2023
Accepted: 16 August 2023
Published: 24 August 2023

1. Introduction

Additive manufacturing (AM) technology, in which objects are created by layering materials, has gained significant attention in recent years, as it allows unique opportunities for design flexibility and customization. Compared to conventional subtractive manufacturing, AM has lower material requirements and generates less waste, as only a small amount of the material used may need to be removed during the final machining of the manufactured product [1]. Composite materials, for example, fiber-reinforced plastics, are commonly used in AM [2]. Composite materials allow a high degree of tailoring and achieve the desired physical and chemical attributes in the final product by combining materials with different properties. Fiber-reinforced composites are currently used in several industrial sectors, including the manufacturing of wind turbine blades, aircrafts, and naval and automotive components [3]. Consequently, large waste volumes are generated at the end of the lifecycle of these components, estimated to reach 23,360 tons per year by 2035 for the aircraft sector if left unrecycled [4].

While several attempts have been made in Europe to increase the recycling of reinforced waste materials, a significant percentage of manufacturing and End-of-Life (EoL) waste is still currently landfilled, with reports of as high as 90% for glass-fiber reinforced polymers [3]. The existing recycling approaches for reinforced composites face different challenges and limitations, including the inability to recover all components of the original material (e.g., plastic resin and glass fibers in the case of pyrolysis), the high energy demand for some processes (i.e., up to 91 MJ/kg for chemical recycling and 30 MJ/kg for pyrolysis), or loss of structural value of mechanically recycled materials compared to the virgin component [3]. Among the recycling methods proposed for reinforced composites, solvolysis is a promising approach, as it can be used to recover both fractions of the composite material (i.e., resin and fibers) with high yield (i.e., up to 98% fiber recovery and selective decomposition of the nylon resin to ε-caprolactam [5], which can be recovered from the liquid phase and polymerized into nylon-6 [6] in a secondary process). Several innovations can further improve the environmental impact of solvolysis, such as the use of supercritical water as a reaction medium, which eliminates the need for a catalyst during the reaction [7], or the use of plasma, which is expected to enhance oxidation and assist the dissolution of the resin.

To determine whether recycling reinforced composite materials, compared to the conventional disposal method of landfilling, is advantageous, a detailed investigation of the environmental impacts is necessary, considering several impact categories throughout the entire lifecycle of AM products, from raw material extraction to the EoL phase. Such a systematic and holistic approach would prevent problem-shifting during decision making. One approach to systematically investigate the environmental impacts while designing waste valorization steps is Life Cycle Assessment (LCA), an internationally standardized (ISO 14040 and ISO 14044 [8,9]), widely recognized, holistic methodology to quantify the potential environmental impacts of a process or a product throughout its entire lifecycle. Several previous scientific reports highlight the importance of applying an LCA approach to investigate AM using reinforced composite materials in order to compare process alternatives [10,11], identify hotspots of environmental impacts along the lifecycle of the investigated technologies [12], analyze different scenarios to identify the impact of different process options [13,14], and thus help drive innovation towards more promising alternatives and highlight process steps that require further improvements in terms of environmental performance.

The study presented in this manuscript has been conducted in the framework of the European-funded project EuReComp, which aims to apply an R-6 strategy (Reuse, Repair, Refurbish, Remanufacture, Repurpose, and Recycle) for composite materials from various industries (e.g., aerospace, aeronautics, automotive, and wind energy). The project investigates a holistic, interdisciplinary approach for closed-loop and open-loop recycling over multiple scales (lab, pilot, and demonstrator scale). The present study focuses on laboratory-scale processes and applies LCA with the aim to investigate the environmental impacts of a composite product along its entire lifecycle with closed-loop recycling. The investigated product is a testing coupon, manufactured using Fused Filament Fabrication (FFF) AM, with carbon fiber (CF)-reinforced thermoplastic material as an input (15% weight percentage of chopped CFs). Different scenarios are investigated related to the origin of the CFs (i.e., 100% virgin, 50% virgin, and 25% virgin CFs) and the EoL treatment of the composite material (i.e., landfilling, supercritical solvolysis, and plasma-enhanced solvolysis). Furthermore, three different scenarios are examined in terms of the properties of the recovered CFs (i.e., the same functionality between virgin and recovered fibers, 25% loss of functionality, and 50% loss of functionality after solvolysis).

Previous LCA studies on composite materials focused on specific life cycle stages [12,14], whereas others investigated the entire lifecycle of composite products/materials [10,11,13,15], which was also performed in the current study. The majority of

LCA studies either do not define the EoL process [10,11], or focus on more established and commonly applied EoL processes, such as landfilling, incineration, and pyrolysis [13,16], whereas solvolysis (particularly supercritical water solvolysis) has only been considered in a limited number of reports [14,15]. To our knowledge, this is the first study to consider plasma-enhanced solvolysis. Among the previously performed assessments that include an EoL process to recover composite components, a recovery factor or functionality loss percentage is often not included [10,11,13–16]. This study assumed a 90% recovery factor of CFs after solvolysis, which is within the range or lower than the values typically reported from laboratory experiments with supercritical solvolysis [5]. Different scenarios related to the quality of the recovered products (up to 50% loss in functionality) were considered in order to avoid overestimating the added value of recycled components compared to virgin CFs. A significant improvement in the environmental impacts in most impact categories was found for solvolysis compared to landfilling and to virgin CF manufacture, and for the cradle-to-grave assessment of a product containing recovered CFs, compared to virgin CFs. Therefore, it is concluded that the recovery of CFs at the EoL stage of composite materials via solvolysis is a promising alternative to conventional landfilling and virgin CF manufacturing.

2. Materials and Methods

LCA was performed according to standardized procedures [8,9] and consisted of four stages: (1) goal and scope definition, (2) inventory analysis, (3) impact assessment, and (4) interpretation.

2.1. Goal and Scope of the Study

The present study focuses on the manufacture (via FFF) and EoL treatment of a 3D-printed coupon, which consists of nylon (PA6 or PA12) and chopped CFs (15% wt.). The goal was to compare products containing 100% virgin CF, which were disposed of in a landfill at the end of their lifecycle, and products that consisted of a mixture of virgin and recycled CFs (with 50% or 75% recycled CF content), the latter being recovered from the composite material via solvolysis (supercritical water solvolysis or plasma-enhanced solvolysis). A cradle-to-grave approach was used, from raw material extraction to the EoL of the products. The use phase could not be defined for the 3D-printed testing coupon being investigated; therefore, this life stage was excluded. The processes included in the system boundaries are shown in Figure 1, and vary among the different scenarios, as further explained in the next paragraph.

The functional unit used for this analysis was a coupon with a total weight of 9 g. While the testing coupon does not have a defined service life, in order to allow the investigation of scenarios related to the functionality and thus durability of the coupon, a certain lifetime and desired service life were selected here. Specifically, the coupon was assumed to be used for 10 years before being disposed of in a landfill. A lifetime of 5 years was assumed for the coupon consisting of virgin fibers or recovered fibers when no loss of CF functionality occurred during solvolysis; thus, at least two rounds of 3D printing were included in the proposed functional unit. For the baseline scenario, the product was manufactured twice from virgin materials, and each time it was disposed of in a landfill. For the scenarios including recycling of fibers, a product was initially manufactured with virgin fibers, and recycled after 5 years, recovering 90% of the CFs. A second product was manufactured with a certain percentage of the recovered CFs, which had a lifetime of 5 years and was eventually disposed of in a landfill. For scenarios that included loss of functionality for the recovered CFs, the second product had a lifetime of less than 5 years. Therefore, an additional solvolysis step and 3D printing step were included to reach the 10 years of functionality determined by the functional unit. After 10 years, the product was landfilled. The value chains and system boundaries for the different scenarios are shown schematically in Figure 1.

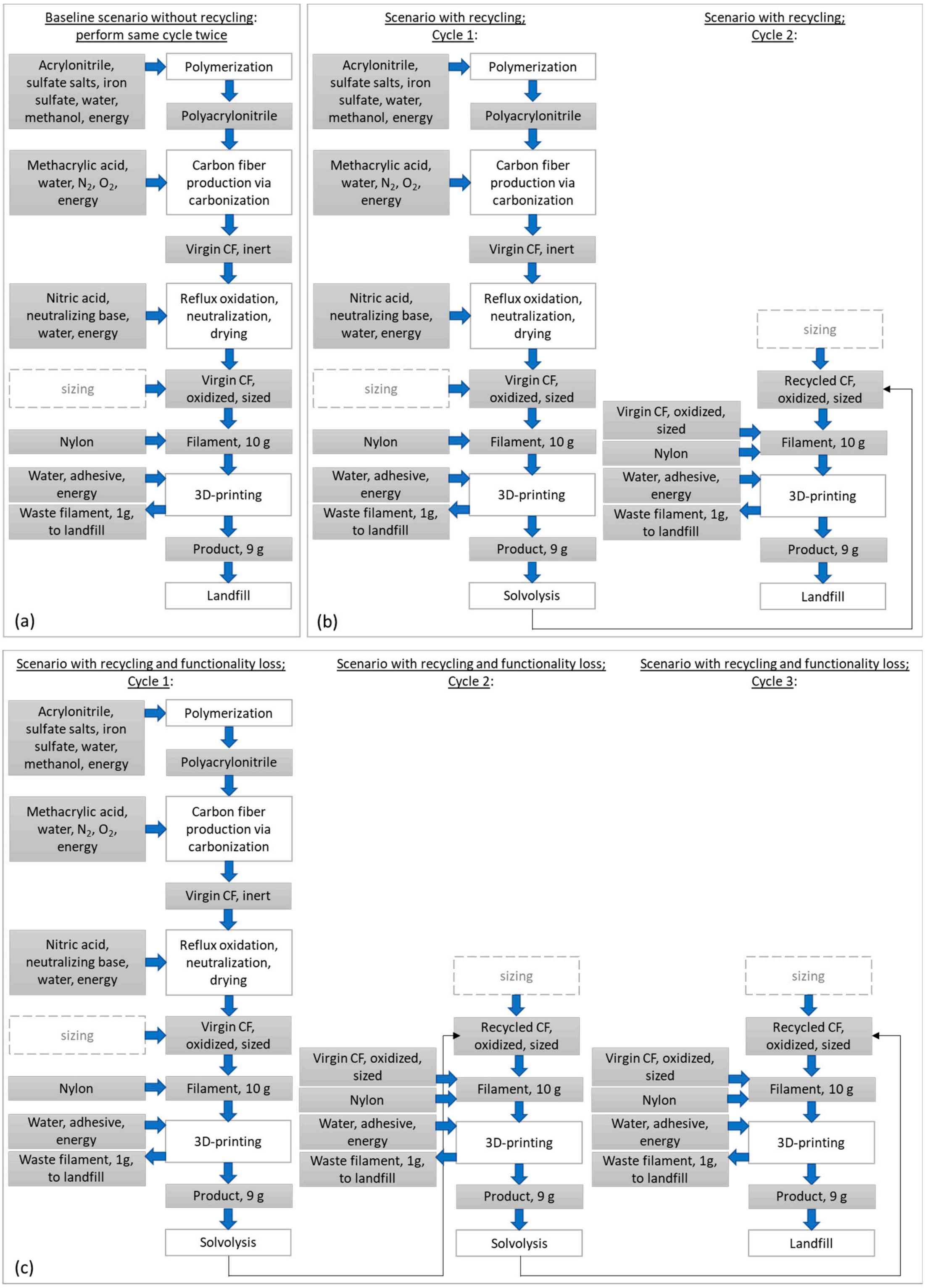

Figure 1. System boundaries of different scenarios: (**a**) without recycling; (**b**) recycling without functionality loss; (**c**) recycling with functionality loss. Dashed lines indicate processes excluded from LCA.

2.2. Inventory Analysis

The Life Cycle Inventory (LCI) refers to the collection and calculation of data on material, energy, waste, and emissions related to the processes within the system boundaries. Primary data were collected from the manufacturer (FFF process) and included the electricity consumption, input material requirements, and amount of waste generated during 3D printing of an ASTM D638 Type I testing coupon with a Modix Big40 3D printer model (Table 1). The print volume of the model Modix Big40 3D printer corresponded to 400 × 400 × 800 mm, and it was equipped with a E3D Volcano 1.75 mm print head. Two separate power-supplying units were used during 3D printing: a Meanwell 24 V 280 W Power Supply Unit for the electronics, and a Heat Bed AC powered heater of 1370 Watt for the build plate. Further information regarding the components and operation of the printer can be found on the provider's website [17] and the corresponding technical specification webpage [18]. A schematic and a photograph of the resulting 3D-printed coupon are shown in Figure 2. For the 3D printing experiments described in Table 1, a commercially available filament was used (PA6 CF15, Spectrum FILAMENTS). The settings used for 3D printing were the following: extrusion multiplier: 1; extrusion width: 0.6 mm; heat bed temperature: 90.00 °C; nozzle diameter: 0.6 mm; nozzle temperature: 230.00 °C; layer height: 0.300 mm; infill: 100%; infill angle: 90°; shells: 2; printing speed: 8 mm/s. The electricity consumption reported in Table 1 was measured during printing using a UNI-T® power socket (model UT230B-EU Power Socket). A flowchart of the 3D printing process is shown in Figure 3.

Table 1. Electricity, material inputs, and outputs for 3D printing of 1 product coupon or 5 product coupons using a Modix Big40 device. Optimal use of equipment corresponds to printing 5 coupons per day. n.a.: not applicable.

Process Steps of AM with Description	Electricity Input Amount and Unit (Individual Process Steps)	Amount and Unit (Cumulative)	Ecoinvent Entry
Warm-up of printer build plate to 100 °C for 20 min	540 Watt per coupon or per 5 coupons at optimal equipment use	184.2 Wh per coupon or per 5 coupons at optimal equipment use	Electricity, medium voltage {Europe without Switzerland} | market group | cut-off, S
Stand-by idle operation of printer for 20 min during warm-up	12.6 Watt per coupon or per 5 coupons at optimal equipment use		
Maintaining temperature of build plate during printing (59 min per coupon)	Fluctuating electricity use (30–530 Watt), total measured consumption 230 Wh	353.0 Wh per coupon	
Printing 1 coupon, for 59 min	Fluctuating electricity use over multiple process steps, total measured consumption 123 Wh		
Material Input Description	**Amount and Unit (Individual Processes)**	**Amount and Unit (Cumulative)**	**Ecoinvent Entry**
Total amount of filament loaded in printer, sufficient for 5 coupons, can be stored and used later if not fully used	50 g (for 5 coupons) 10 g (for 1 coupon)	n.a.	For polymer (85% wt.): Nylon 6-6 or Nylon 6 {RER} | production | cut-off, S For CF (15% wt.): Manually created process for virgin CF synthesis (see Figure 1)

Table 1. *Cont.*

Adhesive added as thin coating on build plate to ensure sufficient attachment of coupon	<1 g per coupon	Round up as 1 g per coupon	Polyurethane adhesive {GLO} | polyurethane adhesive production | cut-off, S
Water needed to clean adhesive after printing	1 L per coupon	Assume 1 kg/L for density, model the input as 1 kg per coupon	Tap water {Europe without Switzerland} | tap water production, conventional treatment | cut-off, S
Material Output Description	**Amount and Unit (Individual Processes)**	**Amount and Unit (Cumulative)**	**Ecoinvent Entry**
Printed coupon	1 coupon or 5 coupons at optimal equipment use	n.a.	Manually created process
Wastewater from washing adhesive	1 L per coupon	n.a.	Wastewater, average {Europe without Switzerland} | treatment of wastewater, average, capacity 1E9l/year | cut-off, S
Waste filament for 3D printing skirt and correcting imperfections on-spot in the levelling of the print bed	0.75 g per coupon or per 5 coupons at optimal equipment use	n.a.	Waste plastic, mixture {CH} | treatment of sanitary landfill | cut-off, S With default material/waste type: Nylon 6-6 or Nylon 6 {RER} | production | cut-off, S
Waste filament from loading and unloading filament in the 3D printer	0.25 g per coupon or per 5 coupons at optimal equipment use	n.a.	

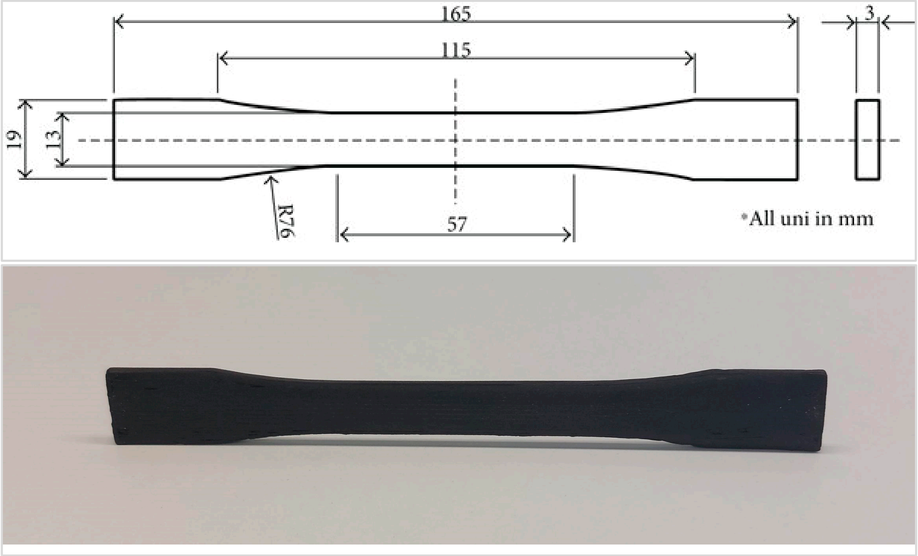

Figure 2. Above: schematic of 3D printed coupon ASTM D638 Type I. **Below**: photograph of the printed coupon described in this manuscript.

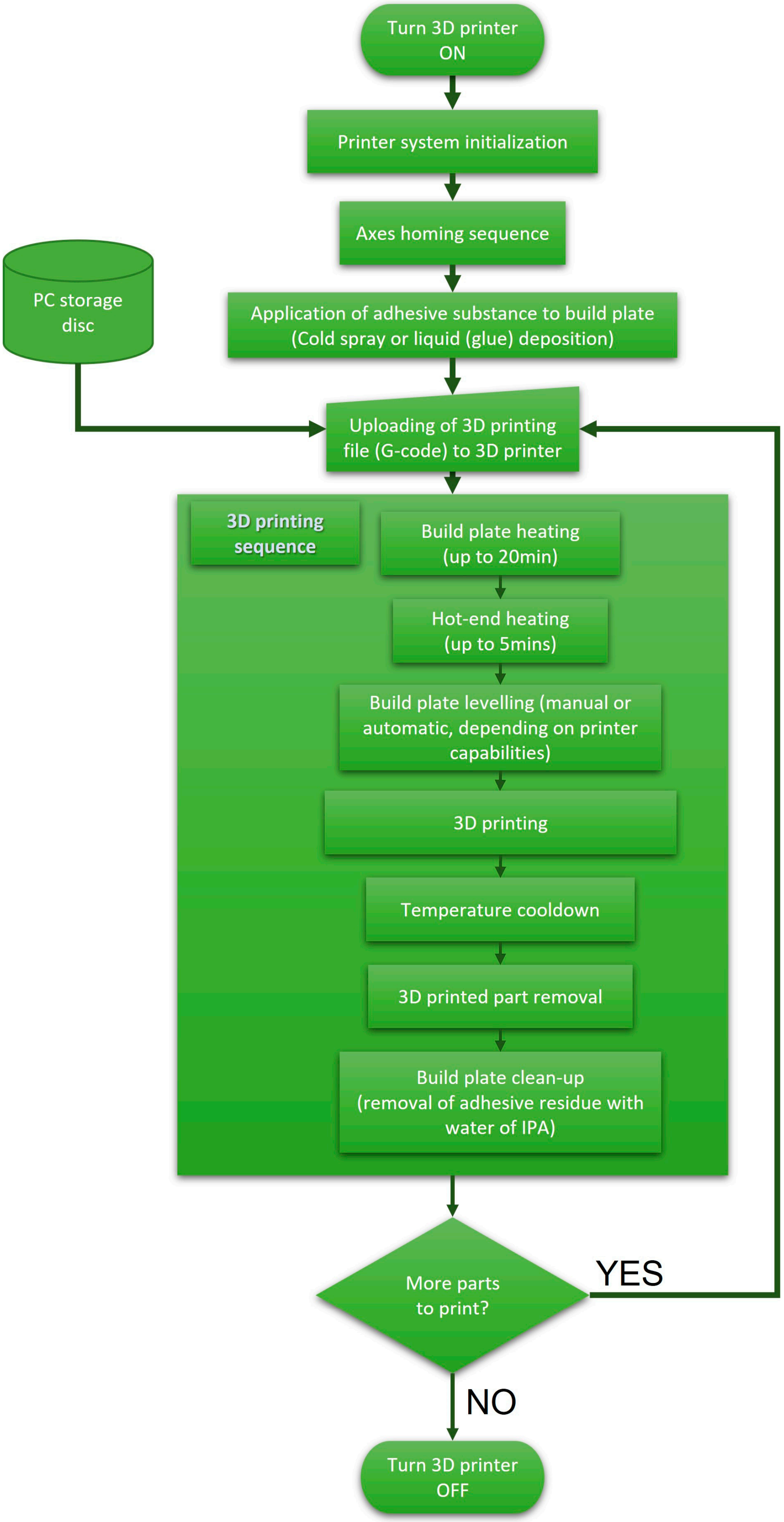

Figure 3. 3D printing process flowchart.

Manufacture of virgin CF: Polyacrylonitrile (PAN)-based CFs were selected in this research, considering that PAN is the predominant precursor for CFs [19]. PAN synthesis via polymerization of acrylonitrile was modelled based on the laboratory-scale protocol reported by El-Newehy and co-workers [20]. The production of CFs from PAN was modelled based on previously published protocols [19,21], assuming a yield of 1 kg CFs per 5.64 kg polymer [21] and a ratio of 90% PAN and 10% methacrylic acid as the added co-monomer [19]. After the synthesis of inert CFs, reflux oxidation for 1.5 h in concentrated nitric acid was modelled, followed by neutralization of the acidic solution, washing the fibers with demineralized water until neutral effluent pH, vacuum filtering to recover the fibers, and overnight drying in a laboratory oven, as has been previously reported [22]. The sizing of the oxidized CFs was excluded because a sufficiently detailed protocol to model this process was not available. The electricity consumption for the equipment used in the aforementioned procedures was calculated based on data retrieved from laboratory equipment providers (i.e., Cole-Parmer Instrument Co. Europe; Bioevopeak Co., Ltd., China; Beckman Coulter Inc., Brea, CA, USA; VACUUBRAND GmbH + Co. KG, Germany), assuming the optimal utilization of the equipment (i.e., based on the production volume compared to the total capacity of the devices). In order to model the manufacture of CFs independently of the country of origin, global (GLO), Rest-of-World (ROW) and Rest-of-Europe (RER) electricity (medium voltage), processes (e.g., wastewater treatment), and input materials were selected from the Ecoinvent database. Considering that the country of origin was unknown, transportation was excluded from our analysis.

Filament as input for 3D printing: A total of 10 g of filament (8.5 g nylon; 1.5 g CFs) was modelled as input for FFF, with a product output of 9 g and waste filament material of 1 g (i.e., 3D printing skirt, the amount lost when loading and unloading the filament in the device, or correcting any imperfections on-spot in the levelling of the print bed). A landfill waste treatment process ("Waste plastic, mixture {CH} | treatment of, sanitary landfill | Cut-off, S" entry from Ecoinvent) was assumed for this waste filament material. No process was modelled for reinforcing the nylon with the CFs. Two types of nylon were considered as follows: PA6 (using the "Nylon 6 {RER} production" entry from the Ecoinvent database) and PA12 (using the "Nylon 6-6 {RER} production" entry as a proxy).

End-of-Life processes (i.e., landfilling and recycling): For the baseline scenario (i.e., without recycling) and the final treatment process (i.e., landfilling) applied after 10 years in all scenarios, the same landfill process from Ecoinvent was considered, as described in the previous paragraph for the waste filament material from the 3D printing process. While both solvolysis processes modelled have the potential to recover both the CFs and the polymer from the treated coupon, only the recovery of CFs was modelled here, whereas the monomers/oligomers from the polymer were modelled as waste products, undergoing wastewater treatment while dissolved in the solvent. Supercritical water solvolysis of the product was modelled based on the laboratory-scale protocol reported by Chaabani and co-workers [5], scaled up for the treatment of 100 g of reinforced polymer in one batch at 400 °C and 25 MPa pressure for 15 min under continuous ventilation, using a high-pressure tube furnace (modelled based on compatible equipment from the laboratory equipment provider MTI Corporation, KJ Group). After the solvolysis step, the polymer dissolved in water was separated from the recovered fibers via vacuum filtering and disposed of via a wastewater treatment process. The recovered fibers were further purified with a 10 min ultrasonication step and oven-dried overnight. A schematic of this process is shown in Figure 4. The plasma-enhanced solvolysis of the 3D printed product was modelled based on unpublished information provided by the practitioners as a batch treatment process for 100 g of reinforced polymer. Briefly, the process consisted of two 5 min treatment steps, using compressed air as input at ambient conditions, with the first step performed in a plasma-enhanced acidic solution (modelled as 34% nitric acid), and the second step in a plasma-enhanced organic solvent (modelled as acetone). The electricity consumption of the plasma generator was modelled based on the measurements reported by Aileni and co-workers [23]. The polymer-covered fibers recovered after the first step were separated from the bulk acidic solution via centrifugation and oven-dried. A total of 90% of the acidic solution was reused, and 10% was disposed of in a wastewater treatment process after neutralization. The fibers underwent a second treatment step, wherein they were completely separated from the polymer, purified via vacuum filtering, and dried under ventilation. The organic solvent was recovered via distillation, and energy consumption was calculated based on the specific heat capacity and boiling point of acetone. As was also the case for the manufacturing process of virgin CFs, additional equipment energy consumption data were acquired from equipment suppliers and modelled considering the optimal use of equipment in terms of capacity. Given that the recycling activities take place within Europe, the European average (i.e., Europe without Switzerland or RER) of medium voltage electricity and processes (e.g., for wastewater treatment) were selected, when possible, from the Ecoinvent database for the two solvolysis processes. A schematic of this process is shown in Figure 5.

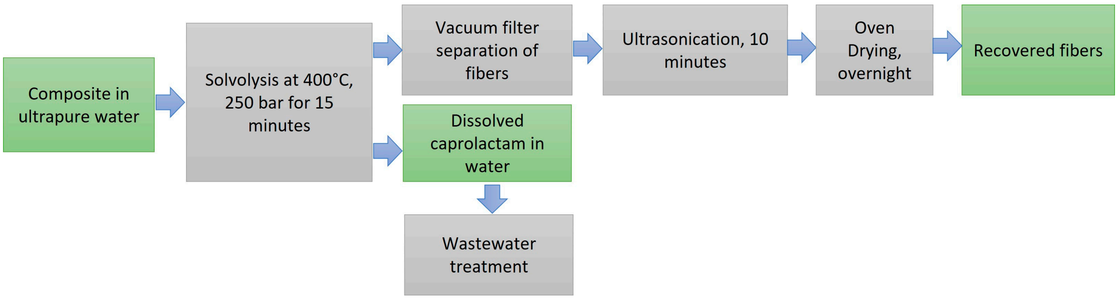

Figure 4. Schematic representation of supercritical water solvolysis. Wastewater treatment of water with dissolved caprolactam is modelled with the Ecoinvent process "Wastewater from anaerobic digestion of whey {RoW} | treatment of, capacity 1E9l/year | Cut-off, S".

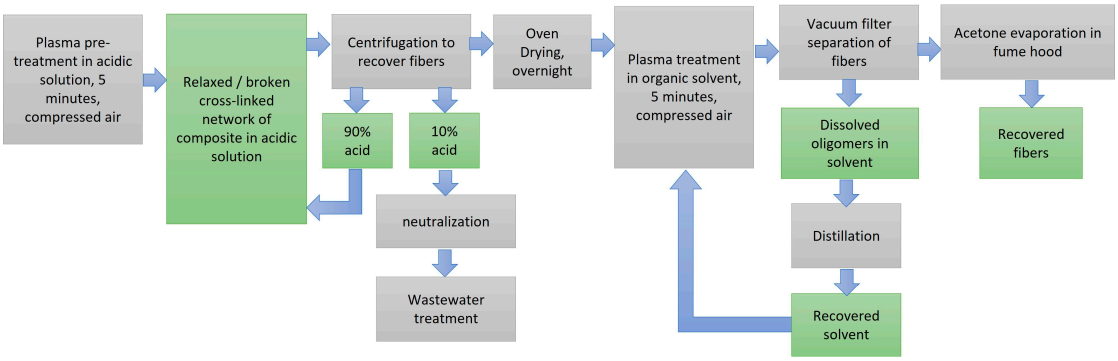

Figure 5. Schematic representation of plasma-enhanced solvolysis. Wastewater treatment of neutralized solvent is modelled with the Ecoinvent process "Wastewater from anaerobic digestion of whey {RoW} | treatment of, capacity 1E9l/year | Cut-off, S".

2.3. Impact Assessment

The Life Cycle Impact Assessment (LCIA) was performed using SimaPro (version 9.4.0.2) commercial software and the Ecoinvent 3.8 database. The impact assessment method used was the Environmental Footprint (EF) 3.0 (version 1.03). In this method, the environmental impacts were calculated and reported over 16 midpoint impact categories as follows: climate change (in kg CO_2 eq.); ozone depletion (in kg CFC11 eq.); ionizing radiation (in kBq U-235 eq.); photochemical ozone formation (in kg NMVOC eq.); particulate matter (as disease inc.); human toxicity, non-cancer (in CTUh); human toxicity, cancer (in CTUh); acidification (in mol H^+ eq.); eutrophication, freshwater (in kg P eq.); eutrophication, marine (in kg N eq.); eutrophication, terrestrial (in mol N eq.); ecotoxicity, freshwater (in CTUe); land use (in Pt); water use (in m^3 depriv.); resource use, fossils (in MJ); and resource use, minerals and metals (in kg Sb eq.). All LCIA results presented in Section 3 stem from the characterization step of the EF 3.0 method, whereas no normalization or weighing was performed on the LCIA results.

3. Results and Discussion

3.1. Gate-to-Gate Impact Assessment of Solvolysis Processes

The two solvolysis processes can be compared to landfilling, as alternative EoL treatment processes, or to the primary manufacture of virgin CFs, as secondary processes that yield CFs [14]. The two comparisons are shown in Figure 6a,b. The environmental impacts were calculated per kg of composite material undergoing EoL treatment (Figure 6a) or per kg of CFs produced (or recovered, Figure 6b). For each impact category, the contribution of the processes under investigation is expressed as a percentage, compared to the process contributing to the highest (or lowest negative) impact, which is set to 100% (or negative 100%, in the case of negative environmental impacts).

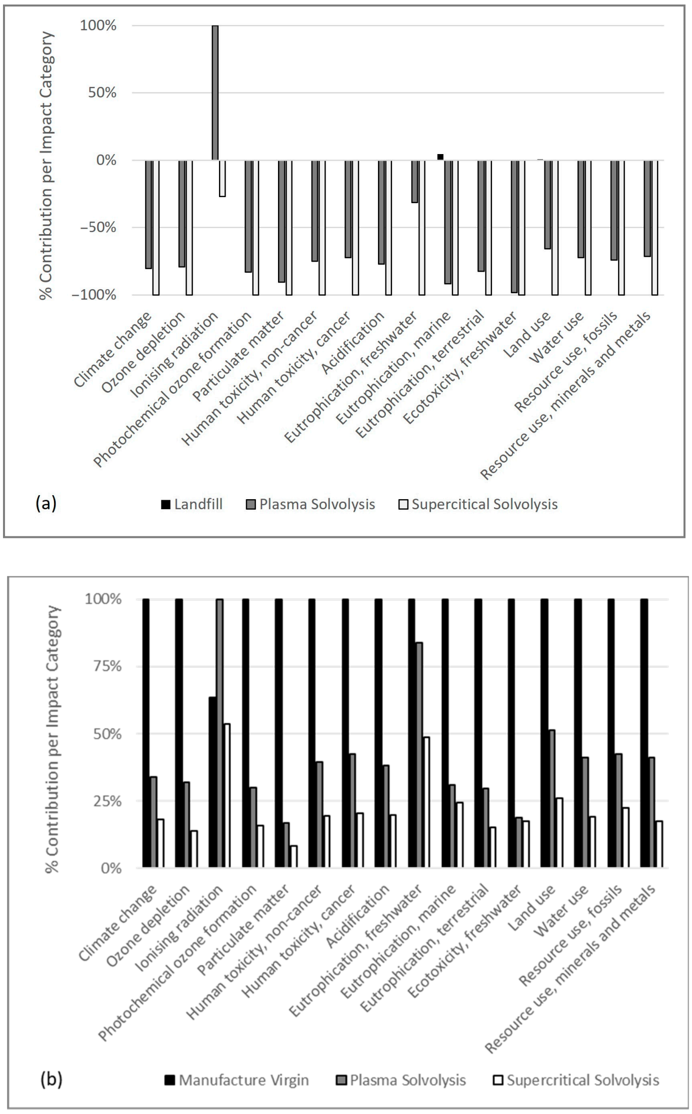

Figure 6. (**a**) Comparative impact assessment of EoL treatment processes (landfilling, black bars; plasma-enhanced solvolysis, grey bars; supercritical water solvolysis, white bars), with negative impacts for solvolysis processes due to avoided products, assuming 90% recovery of CFs and no functionality loss. (**b**) Comparative impact assessment of cradle-to-gate virgin CF manufacture (black bars), and gate-to-gate recovery of CFs via plasma-enhanced (grey bars) and supercritical water solvolysis (white bars), assuming 90% recovery of CFs with no functionality loss after solvolysis.

As EoL processes (Figure 6a), both solvolysis treatments result in negative environmental impacts across most impact categories, given that the recovered product (i.e., CFs) can be credited as an avoided product (i.e., avoided production of virgin CFs). Specifically, considering the climate change potential (expressed as kg of CO_2 equivalents) and based on the investigated lab-scale processes, landfilling of 1 kg of composite material resulted in emissions of 0.11 kg of CO_2 eq., whereas recovering CFs from 1 kg of composite material resulted in avoided emissions of −37.4 kg and −46.5 kg of CO_2 eq. for the plasma-enhanced and supercritical water solvolysis, respectively. In Figure 6b, the cradle-to-gate manufacture of virgin CFs (i.e., excluding EoL) is compared to the gate-to-gate recovery of CFs via solvolysis. A gate-to-gate system boundary was selected for solvolysis, given that the input material was a waste product, and thus no impact was credited from its manufacture to its EoL treatment, while also no benefit (i.e., avoided virgin CF production) was credited to it [14]. As can be observed, a significant decrease in environmental impacts in most impact categories was calculated for the two solvolysis processes, compared to the manufacture of virgin CFs (resulting in 420 kg CO_2 eq. emissions per kg of virgin CF manufacture), with up to 82% and 66% decrease in climate change potential for supercritical water solvolysis (corresponding to 75.7 kg CO_2 eq. per kg of recovered CFs) and plasma-enhanced solvolysis (corresponding to 143 kg CO_2 eq. per kg of recovered CFs), respectively, assuming that the recovered CFs undergo no functionality loss during solvolysis. Interestingly, even with an assumed 50% loss of functionality, the two solvolysis processes tested had a lower impact across most impact categories considered compared to the cradle-to-gate impact of virgin CF manufacture, with up to 64% lower climate change potential for CFs recovered via supercritical water solvolysis and a 50% loss of functionality (corresponding to 151 kg CO_2 eq. per kg of recovered CFs, not shown in Figure 6b).

For both comparisons shown in Figure 6, the product undergoing solvolysis contained 100% virgin CFs, and the solvolysis process resulted in 90% recovery of CFs with no functionality loss. A similar trend can be observed in both figures: supercritical solvolysis has the lowest impact across all impact categories, whereas plasma-enhanced solvolysis has a lower impact compared to conventional processes (i.e., landfilling, virgin CF manufacture) in all impact categories except for ionizing radiation. The primary contributor to the ionizing radiation potential is the electricity consumption associated with plasma generation. While optimization of the plasma-enhanced solvolysis process is required (i.e., via upscaling or using a device with lower power consumption) to render it competitive over other solvolysis methods, these results indicate that CF recovery via both solvolysis processes is a promising approach to improve the environmental performance of composite materials. For example, Aileni and co-workers [24] reported the use of plasma equipment with a power consumption of 1.2 kW, which, assuming 10 min of total plasma treatment, would result in 20 times lower electricity consumption, compared to the values used in the present work. Nevertheless, as plasma-enhanced solvolysis experiments are still ongoing and the actual electricity consumption values are unknown, this study will refrain from analyzing different electricity consumption scenarios and will report data based on supercritical solvolysis for the remainder of the Section 3.

3.2. Cradle-to-Grave Impact Assessment of AM with Virgin or Recycled CF

The entire lifecycle of products manufactured with nylon PA6 or PA12, based on different scenarios for the EoL treatment (i.e., landfilling and supercritical water solvolysis), percentage of recovered CFs in the product (0%, 50%, and 75%), and percentage of functionality loss of recovered CFs after solvolysis (0%, 25%, and 50%) were analyzed, and the findings are shown in Figure 7a (for PA6) and Figure 7b (for PA12).

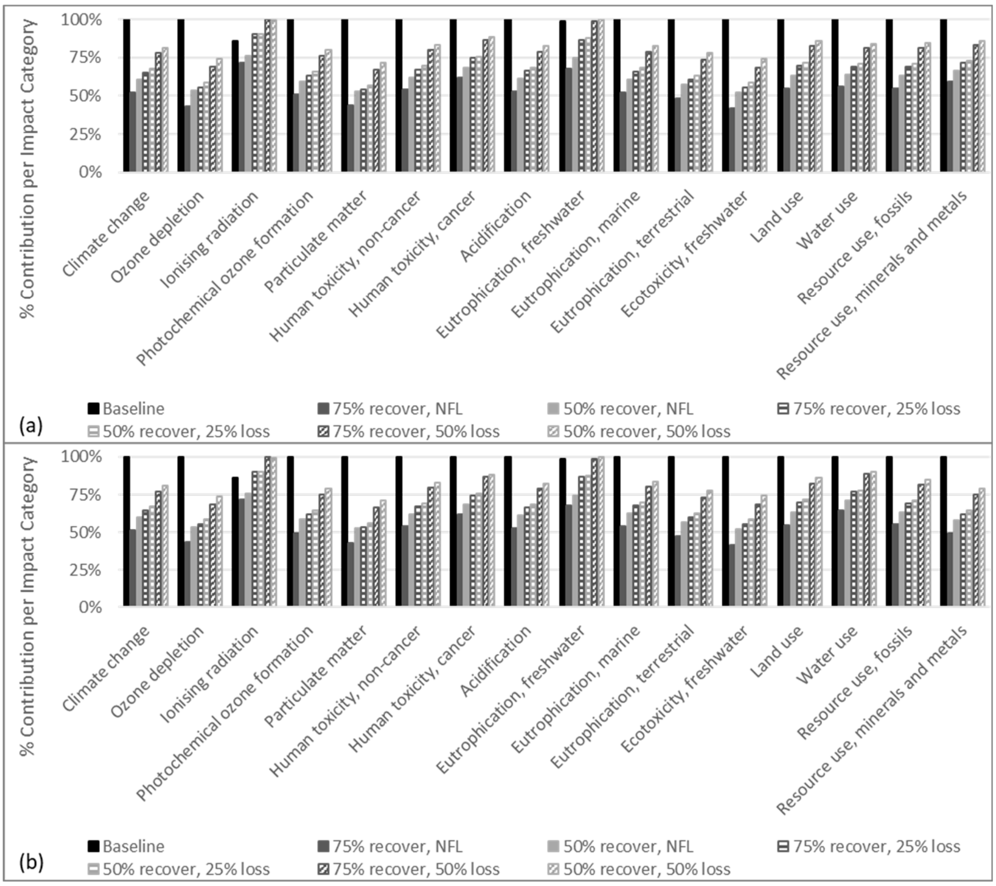

Figure 7. Comparative cradle-to-grave impact assessment of products manufactured with nylon PA6 (**a**) and PA12 (**b**) under different scenarios. NFL: no functionality loss.

Among the impact categories examined, products with PA6 undergoing solvolysis and re-introducing recycled fibers in their manufacture had a lower environmental impact, even when fibers lost 50% of their functionality after solvolysis, compared to the baseline scenario (i.e., products manufactured with virgin CFs and being disposed of in a landfill at the end of its lifecycle). For example, a 3D printed product with PA6 that contained 75% recycled fibers, compared to a product with 100% virgin fibers, resulted in up to a 48% decrease in climate change potential (i.e., from 1.87 kg CO_2 eq. to 0.98 kg CO_2 eq. per coupon of 9 g), assuming 90% fiber recovery after solvolysis and no functionality loss for the recovered fibers. Even in the worst-case scenario of 50% functionality loss, products with 75% recovered fibers resulted in a decrease of over 22% (i.e., from 1.87 kg CO_2 eq. to 1.45 kg CO_2 eq. per coupon of 9 g) of climate change potential compared to a product with 100% virgin fibers. One exception was the freshwater eutrophication category, for which the baseline scenario had a slightly lower impact (1%) compared to the product consisting of 50% recycled CFs and undergoing 50% functionality loss after solvolysis, whereas all other scenarios exhibited a lower impact than the baseline. The impact category most heavily affected by recycling is ionizing radiation, for which recycling had a better environmental performance than landfilling only when no functionality loss occurred during solvolysis, whereas even a 25% decrease in functionality of the recovered CFs resulted in higher environmental impacts compared to the conventional scenario. For all four scenarios with a higher ionizing radiation impact than the baseline scenario (i.e., 75% or 50% recycled fibers with 25% or 50% functionality loss), the main contributor to this impact category was electricity use, resulting primarily from the additional 3D printing process needed to reach the 10 years of a lifetime for the printed coupon. For example, for a product with 75% recycled CFs and 50% functionality loss, the electricity consumption for 3D printing accounted for 63% of the ionizing radiation impact over the entire lifecycle.

The substance emission responsible for this trend was Radon-222, originating from nuclear power production included in the Ecoinvent market group for medium-voltage electricity within the geography "Europe without Switzerland" [25]. Similar trends can also be observed for products manufactured with nylon PA12 (Figure 7b).

3.3. Fused Filament Fabrication: Life Cycle Inventory and Equipment Use Optimization

The product lifecycles presented in Section 3.2 were modelled assuming that one product (i.e., coupon) is printed at a time, and therefore all impacts of printing are fully credited to the product being printed. However, the environmental impact can be improved by printing multiple products in a row, thus decreasing the electricity consumption allocated to each product during the warm-up phase of the equipment and resulting in lower filament loss per product (e.g., one skirt needs to be printed for several products). In Figure 8a, the contribution of each input and output during 3D printing is shown for each impact category, assuming that one coupon is printed at a time. Instead, Figure 8b shows a comparative impact assessment of the 3D printing process, assuming either that only one product is printed at a time or that five products are printed in a row. Both assessments use virgin CFs (15% wt.) and nylon PA6 as the filament input. As can be observed in Figure 8b, using the 3D printer at a higher capacity results in lower environmental impacts per product across all impact categories, with, for example, up to a 12% decrease in climate change potential, from 0.93 kg CO_2 eq. to 0.82 kg CO_2 eq. per one coupon of 9 g. More specifically, when considering only the filament waste generation for printing one coupon or five coupons in a row (as described in Table 1), an 8% decrease in all impact categories is calculated. When considering only the energy consumption optimization (as described in Table 1), the environmental impact decreases by over 27% across all impact categories. A similar finding was reported in previous LCA studies on AM using 3D printing, wherein maximizing the use of equipment (24 h per day, 7 days per week) resulted in nearly ten times lower environmental impacts compared to low utilization (one printing job per week, with machines being powered down or set to idle mode when not printing) [10]. The most notable improvement for the overall process corresponds to the ionizing radiation (Figure 8b), which decreases by 20% when equipment is used at a higher capacity. Such an improvement is particularly significant, considering that the ionizing radiation associated with the 3D printing process results in substantially higher impacts when the functionality of CFs decreases during the solvolysis process, as discussed in Section 3.2. These results indicate that the environmental footprint of composite materials using recycled CFs can be further optimized by optimizing the use of equipment during their lifecycle.

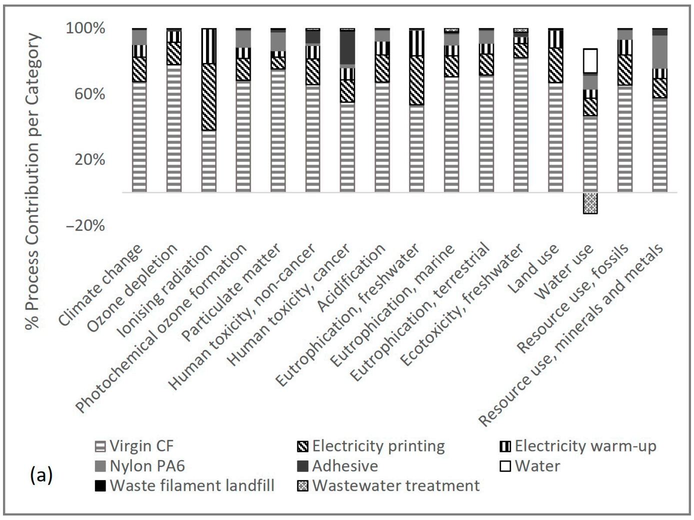

Figure 8. *Cont.*

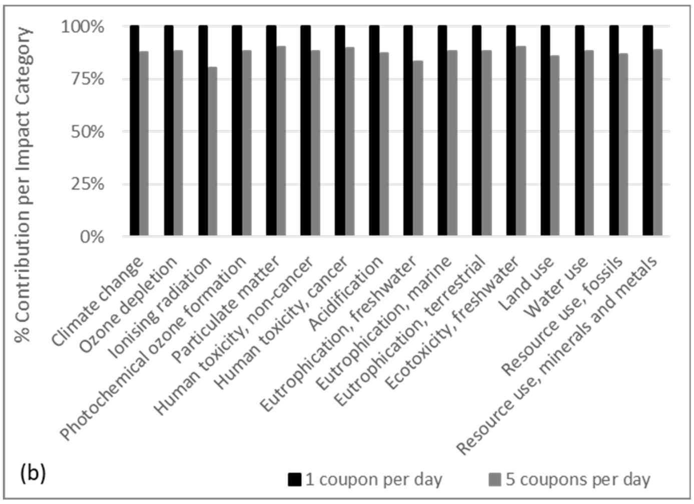

Figure 8. Contribution per impact category of individual 3D printing inputs and outputs (**a**). Comparative impact assessment of coupon manufacture per coupon, assuming that one coupon is printed at a time (black bars), or that five coupons are printed in a row (grey bars, (**b**)). Data shown for nylon PA6.

3.4. Functionality Loss and Impact Assessment from a Practical Perspective: Filament Composition and Protocol Adaptations

In this study, the environmental impacts of the manufacture of a testing coupon (ASTM D638 Type I) have been presented, using either a reinforced nylon-based filament with virgin chopped CFs or a filament containing recycled CFs, via two solvolysis processes. For the recycled CFs, different scenarios were analyzed related to the properties of the recovered components (i.e., loss of functionality), which were directly correlated to the expected durability and thus the lifetime of the printed coupon. While the loss of functionality cannot be further defined at this stage, since the examined solvolysis processes are still under development and optimization, previous findings from the literature on CF recovery could help explain the properties of the recovered CFs that may degrade upon recycling. For example, Chaabani and co-workers [5] reported a minor decrease in the average tensile strength of CFs after supercritical water solvolysis under the same conditions as reported here (i.e., 400 °C for 15 min), which was, however, not statistically significant considering the standard deviation for virgin (4931.29 ± 530 MPa) and recycled (4575.03 ± 940 MPa) CFs. However, the loss of tensile strength depends on the exact conditions tested, with, for example, up to 38% loss reported by Bai and co-workers for CF recovery via supercritical water oxidation [26]. Both authors reported changes in the surface roughness and oxygen groups on the surface of the CFs after recovery. Chaabani and co-workers [5] further reported a decrease in the Weibull parameter after supercritical solvolysis, compared to virgin CFs, which likely indicates structural defects in the graphitic structure after solvolysis. While Scanning Electron Microscopy did not reveal any visible cracks on the surface of the recovered CFs, Raman spectroscopy revealed alterations in the nanostructure of the fibers, with partial loss of the graphitic structure [5]. Based on these findings, it is reasonable to expect a possible mild loss of mechanical strength for CFs after solvolysis within the range of the functionality loss scenarios tested here (i.e., from 0 to 50%).

Upon optimization of the two solvolysis processes examined here, an additional analysis of the environmental impacts, as well as a technical assessment, should be performed for a more thorough evaluation of these technologies with results from laboratory experiments and pilot-scale applications. Furthermore, a benchmarking analysis of the two solvolysis processes addressed here and other innovative treatment methods for composite wastes could be performed, considering the technical and sustainability aspects, to help steer research and development towards the most promising approaches for the treatment and valorization of composite waste. Finally, an economic assessment and benchmarking of the proposed processes, compared to conventional virgin CF manufacturing and landfilling, should be performed in order to evaluate the opportunities and limitations of the two solvolysis processes upon upscaling. While such an economic assessment is outside the scope of this work, several reports from the literature show the promising prospects of CF recycling from an economic standpoint. For example, Prinçaud and co-workers [15] previously reported on a market analysis for recycled CFs and concluded that recycling via solvolysis can be economically feasible, provided that the prices of recovered fibers do not exceed 70–80% of the price for virgin CFs. Dong and co-workers [27] performed a thorough economic and environmental assessment of recovery and disposal strategies for CF-reinforced polymer waste with different technologies. Recovery via supercritical water resulted in higher operational costs and higher average unit cost per mass unit waste, compared to microwave-assisted or pyrolysis techniques, especially considering that the data used in the analysis were retrieved from bench- and pilot-scale applications. Nevertheless, the authors reported the advantages of this method to retain the mechanical properties of the fibers and concluded that it can be economically competitive with a fiber recovery rate of 80% or higher. La Rosa and co-workers [28] reported a detailed environmental, economic, and technological assessment of recycling via solvolysis and remanufacture of dog bone specimens (ASTM D638 type), similar to the coupons investigated in the present study, composed of CF-reinforced thermoset material with virgin or recovered CFs based on lab-scale experiments. The authors reported a significant decrease in both environmental impacts (i.e., CO_2 eq.) as well as costs (from 288 to 2.91EUR per kg material recycled during one solvolysis recycling batch, equal to 35.5 kg). Based on these results, it is evident that CF recycling via solvolysis can be very promising in terms of environmental impacts and costs, particularly with further technology development and upscaling.

In addition to the loss of mechanical strength for the recovered fibers, other processes and properties may also differ between virgin and recycled fibers, and consequently, the filament and resulting composite printed products. For example, differences in the graphitic structure and surface oxidation of recovered CFs may require adaptations to the sizing or filament molding process. In this study, the processes of sizing and manufacturing the reinforced filament were excluded, as a sufficiently detailed inventory could not be retrieved from the literature to model these processes. A previous study by Ballout and co-workers on composite materials using recovered CFs revealed a mild loss of mechanical properties for the resulting composite of up to 7% as a result of the lower adhesion between the fresh epoxy resin and recycled CFs due to the absence of sizing, which was partly compensated by the good interface between the fresh epoxy and the residual cured epoxy that remains on the recovered fibers [29]. Furthermore, the authors did not report any required adaptations to the vacuum-assisted resin transfer molding process used to prepare the composite material [29]. Based on these findings, it is reasonable to assume that the exclusion of sizing and composite fabrication process in this study should not result in significant differences in the comparative LCA between coupons with virgin and recycled CFs. Furthermore, the reported loss of mechanical properties of up to 7% for composites with recovered CFs is well within the range of the functionality loss scenario tested here (0–50%). Additional research should be performed to determine the mechanical properties of the recovered fibers with the solvolysis processes investigated here, as well as the potential required adaptations to the process of sizing and composite manufacturing, as a result of these altered properties.

Defining the loss of functionality for recovered CFs as a loss of lifetime for the final printed product was selected here in order to provide a preliminary proof-of-principle regarding the sustainability of processes and products under investigation. A more accurate definition of a functional unit is not possible for a product without a specific function, such as a testing coupon. Instead, at more mature stages of the technologies under investigation, specific products of AM with composite materials containing recovered CFs could be envisioned with specific functionalities. For example, the use of reinforced polymers with either recycled or virgin CFs as construction materials would allow a more accurate definition of the function, lifetime, and functionality loss, considering the actual properties that will be affected, such as a decrease in mechanical strength, which would require additional reinforcing structures in the building, or an increased amount of fibers in the composite materials, to overcome this loss. Nevertheless, the final product and its utilization in an actual application cannot be defined at this stage; therefore, this analysis is not included in the present manuscript.

4. Conclusions

The LCA performed in this study provides results concerning the environmental impacts during the life cycle of a testing coupon, consisting of composite carbon fiber reinforced polymers (CFRPs) and manufactured via Fused Filament Fabrication (FFF). The CFRPs examined consisted of either virgin or recovered fibers (via solvolysis).

Several scenarios were considered regarding the origin of the fibers (100% virgin; 50% recycled; 75% recycled), the End-of-Life treatment of products (landfilling, plasma-enhanced solvolysis, and supercritical water solvolysis), and the retained functionality of the recovered fibers (100%, 75% or 50% retained functionality after solvolysis). Importantly, this is the first study to report on the process of plasma-enhanced solvolysis for carbon fiber recovery from composites, and one of the few studies to provide a detailed inventory of the materials, waste, and energy requirements of FFF.

The results showed that recycling the composite materials led to evident environmental benefits along the lifecycle of the products. Assuming a worst-case scenario of 50% functionality loss after solvolysis, recycling and re-using carbon fibers resulted in a lower environmental impact for most impact categories than the manufacturing and landfilling of virgin fibers. Higher ionizing radiation potential in some scenarios was linked to the Ecoinvent electricity production process used for modelling recycling and FFF. The present study includes laboratory-scale results. However, it is expected that electricity consumption and, therefore, the overall environmental impact, will decrease upon potential scale-up.

Overall, the findings presented show that recycling composite materials at the end of their lifecycle results in an evident improvement in the environmental impact, and at the same time, solvolysis is a promising End-of-Life treatment option for composite materials. The development of sustainable recycling processes for composite materials is an important step towards the European targets to decrease the volume of waste currently diverted to landfills, and to promote circular economy models for composite materials. In particular, considering the European ambition for decreasing CO_2 emissions, recycling of composite materials via solvolysis could have a significant contribution in meeting the envisioned targets, as it can lead to over 48% decrease in global warming potential along a product's lifecycle.

Author Contributions: Conceptualization, K.-R.C., D.A., F.P., A.K. and E.P.K.; Methodology, K.-R.C., D.A., F.P., A.K. and E.P.K.; formal analysis, K.-R.C. and D.A.; investigation, K.-R.C., D.A., F.P., K.P., E.A. and D.M.; resources, K.-R.C., D.A., M.B., E.A., D.M., N.P., S.W. and E.P.K.; writing—original draft preparation, K.-R.C., F.P., N.P. and D.A.; writing—review and editing, all authors; visualization, K.-R.C., N.P., S.W. and D.A.; supervision, D.A., F.P. and E.P.K.; project administration, A.K., and E.P.K.; funding acquisition, A.K., and E.P.K. All authors have read and agreed to the published version of the manuscript.

Funding: This study was funded by the European Union within the HORIZON-CL4-2021-RESILIENCE-01 project "European recycling and circularity in large composite components (EuReComp)", call "A Digitized, Resource-Efficient and Resilient Industry 2021", HORIZON Research and Innovation Actions, Contract Number 101058089. However, the views and opinions expressed are those of the author(s) only and do not necessarily reflect those of the European Union or HADEA. Neither the European Union nor the HADEA can be held responsible for them.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Detailed life cycle inventory data are available upon request.

Conflicts of Interest: The authors declare no conflict of interest.

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