Development, Construction and Testing of a 3D-Printing-System for Additive Manufacturing of Carbon Black filled Rubber Compounds

3D-Printing · Additive Manufacturing · Rapid Prototyping · Process Chain · Carbon Black filled elastomer · Hot Air Vulcanization

Additive manufacturing of carbon black filled elastomers provides unique opportunities for polymers. The process is based on Fused Filament Fabrication (FFF). The system explained in this paper, consists of a commercially available 3D-printer for processing thermoplastic filaments and has been expanded to implement a twin-screw extruder for simultaneous processing of rubber compounds. Furthermore, the process chain beginning with the construction file and ending with the vulcanized elastomer is described. The results of preliminary investigations of the extrusion process, with the twin screw extruder are presented. It can be seen that the generated measurement setup offers promising possibilities for the additive manufacturing of carbon black filled elastomer parts.

Entwicklung, Aufbau und Erprobung einer Anlagentechnik zur Verarbeitung von rußgefüllten Kautschukmischungen mittels additiver Fertigung

3D-Druck · Additive Fertigung · Rapid Prototyping · Prozesskette · rußgefüllte Elastomere · Heißluftvulkanisation

Durch den entwickelten Messaufbau wird die vielseitig einsetzbare Werkstoffgruppe der Elastomere für die additive Fertigung von rußgefüllten Elastomerbauteilen zugänglich. Als Grundlage dient das Fused-Filament-Fabrication-Verfahren (FFF). Der Aufbau der Anlage besteht aus einem handelsüblichen Thermoplast 3D-Drucker, der um einen Doppelschneckenextruder zur Verarbeitung der Kautschukmischungen erweitert wurde. Die notwendige Prozesskette vom Erstellen der Konstruktionsdatei bis zum vollständig vulkanisierten Elastomer wird beschrieben. Die Ergebnisse von Voruntersuchungen zur Extrusion der Kautschukmischungen mittels Doppelschneckenextruder werden dargestellt. Der generierte Messaufbau bietet vielversprechende Möglichkeiten für die additive Fertigung von rußgefüllten Elastomerbauteilen.

Figures and Tables:
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1. Introduction

Additive manufacturing of thermoplastics or metals is a well approved process to obtain rapidly precise and highly individual technical components, which are applied for aerospace, machinery, medical products or motor vehicles. [1] Rubber is a versatile material with a wide application in the field of dampers [2], sealings [3] and tires [4]. Except for crosslinked silicone rubber [5] or thermoplastic elastomers (TPEs) [6], there is no current way for additive manufacturing of elastomeric materials in particular carbon black filled rubber parts in a stable economically viable process. Silicone rubber compounds show a strong temperature dependent chemical resistance and mechanical behavior. For that reason, the possible applications are restricted compared to conventional carbon black filled cured rubber materials. [7] One approach can be the additive manufacturing of colloidal rubber latex using an inkjet process. [8] Recently reported was also the 3D-printing of styrene-butadiene rubber latex in an adapted stereo lithographic procedure, providing elastomeric rubber parts. [9] By micro-architected design of siloxane-based ink materials, elastomeric behavior could be imitated in part, in this way an improvement of flexibility and negative stiffness was achieved. [10] All mentioned approaches underline the scientific interest to create a promising stable additive manufacturing process for rubber parts with elastomeric behavior. The high viscosity of rubber during processing compared to conventional thermoplastics and the plastic flow behavior of uncured rubber [11] are challenging for the additive manufacturing of elastomers of carbon black filled rubber.

Based on the principle of the *Additive Manufacturing of Elastomers* (AME) – process, proposed 2019 *by Wittek et al.* [12], we now report first results of the used 3D-printing system, which allows simultaneous processing of thermoplastics and rubber materials. The printing and crosslinking of the rubber is separated in two steps: First the printing is realized by the extrusion of uncured rubber (conventionally prepared in an internal mixer) with a small twin screw extruder, working according to a derived *Fused-Filament-Fabrication* (FFF) principle, patented by Stratasys in 1992 [13] and first called *Fused Deposition-Modeling* (FDM) in 1996 [14], in which conventional thermoplastic filaments are molten and extruded through a nozzle and placed in a defined geometric manner, so that the component is built up in layers. [15] In the second step of the AME –process the component is vulcanized in a high pressure hot-air autoclave. Due to the plastic flow behavior of non-crosslinked rubber materials, the FFF has to be adapted to keep the extruded material in shape depending on the height of the target component. Therefore, a surrounding thermoplastic shell is required to keep the geometry and position of the extruded rubber in shape. One layer of thermoplastic shell and one layer of rubber is printed alternatingly until the component is finished. In this way the additive manufactured binary component is placed in the autoclave to obtain the

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elastomer after the curing process, which needs to be separated finally from the thermoplastic shell. The shell can be reused or recycled by melting (depending on the thermoplastic material used). This material can be introduced into the process again (circulation process).

2. Experimental

2.1 Extruder specifications

The rubber extruder is a co-rotating 9 mm twin screw extruder with a conveying screw design without kneading elements of *Three-Tec GmbH* providing a maximum torque of 13 Nm. The slope of the screws is 9 and the relation L/D is 20. Different rotational speeds can be adjusted from 0-200 rpm. The temperature can be controlled in three zones separately up to 200 °C. Experiments were carried out with a conical nozzle of 1 mm diameter.

2.2 Additive manufacturing unit for thermoplastics

The basic 3D-printer is a former CNC milling machine, converted to a FFF-Printer (Modell *M3-3D* of *BZT Maschinenbau GmbH*). The 3D-printer has two high-temperature print heads for thermoplastic material that can be heated up to 400 °C. The size of the printing area is 500 mm x 500 mm x 250 mm. The repeatability in the printing process is 0.03 mm. The printing bed is a carbon printing plate, which can be heated up to 120 °C in a closed construction space. Consequently, the construction space can be heated by the plate. For a better adhesion between the printed components and the printing plate, the printing plate is coated with Kapton®-tape.

2.3 Microscopy

The pictures of cryo sections were made with a *Keyence VHX-600*. To prepare the cross-section samples, the 3D printed rubber strips were cooled down in liquid nitrogen below T_g before cutting, to prevent a deformation.

2.4 Materials

The natural rubber based recipe used in this study is for windshield wiper blades applications. The formula is based on a "SVR CV 50" natural rubber with a Mooney viscosity ML (1+4) at 100 °C of 50 MU ± 5. "Corax N 550" with a STSA of 39 m^2/g and an OAN of 121 ml/100 g (values from official data sheet, "Orion Engineered Carbons GmbH") is used as semi active filler. The carbon black content is 40 phr. Additional additives and a sulphur-accelerator (combination of CBS "Vulkacit CZ" and DPG "Vulkacit D/EGC") based curing system including ZnO and stearic acid complete the formula. The Mooney viscosity of the rubber compound is determined to Mooney ML (1+4) at 100 °C by means of a Monsanto "MV 2000 E" viscometer to 45 MU. It was measured with the large rotor, at a preheating time of 1 min and a testing time of 4 min.

3. Results and Discussion.

3.1 Setup for the AME-process

The AME-process for the manufacturing of rubber based carbon black filled elastomers consists of two steps. First the component is printed, and second the component is cured. Consequently, the process requires a 3D-printer and an autoclave for external vulcanization. [12]

The 3D-printer is a commercially available FFF-3D-printer which was extended to print rubber by an implementation of the extrusion unit. The 3D-printer has a heatable carbon based printing bed. After each printed layer, the print heads move up by one unit of length, thus the table of this 3D-printer model is stationary.

Since the rubber viscosity is too high even when heated, direct printing via the integrated print heads for thermoplastic materials is not possible. Therefore, the 3D printer has to be modified for the AME-process. For this purpose, a twin screw extruder is integrated into the existing 3D printer. The extruder has a sufficiently high torque to extrudate and print the rubber. The extruder is assembled directly on the traversing unit of the 3D-printer as shown in Figure 1.

Since the extruder is significantly heavier (approximately 12 kg) than the two original thermoplastic print heads of the 3D-printer, the extruder was assembled as close as possible to the balance point of the traversing unit to minimize the tilting moment, to prevent vibrations during the printing process which might cause a loss of the printing resolution. The extruder is directly connected to the movement of the 3D-printer. Only the feeding of the rubber has to be controlled separately. The original thermoplastic print heads were finally assembled in front of the extruder. Since the printer control system only has two assignments for the printing units, one original print head was shut down. However, one print head is sufficient to combine the additive manufacturing process of the rubber compound and its thermoplastic shell. Whether the print head for the thermoplastic material or the extruder for the rubber is selected to run, is managed by the control unit of the 3D-printer. Though, the controller does not directly give the order for printing to the extruder, however activates it via the extruder's additionally post-implemented control unit. An additional touch panel on the control unit of the extruder enables the controlling of the feed rate, by adjusting the rotational speed of the screws. In general, the speed values are fixed before the printing process starts, so that the control unit of the extruder only receives the order to start or to stop printing.

To ensure a continuous material feeding of the extruder, a freely rotating wheel is installed above the extrusion

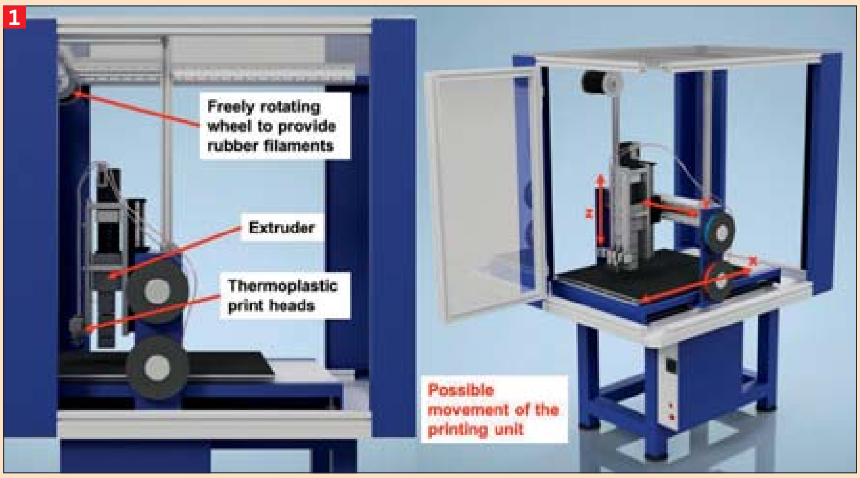

Figure 1: Setup of the new additive manufacturing plant for the AME process

unit which is able to follow the movement of the 3D-printing unit in x-direction. The roller is wrapped with rubber filament before printing. While printing, the material is fed by the extruder and continuously processed. Only a continuous material feed ensures a continuous material flow, which is required for a constant printing speed and a printed layer with constant volume and stable geometry.

3.2 The process chain

To manufacture a designed part from rubber by additive manufacturing, several steps must be carried out which are presented in Figure **2**.

First of all, the rubber part has to be built using Computer Aided Design (CAD) and converted into the STL-format. This file format has established itself for additive manufacturing. Afterwards, the part needs a thermoplastic shell which ensures the geometry stabilization during printing, preventing the plastic flow of the rubber [7] until scorch effects are starting, during the vulcanization process, depending on the vulcanization kinetics of the rubber material used.

The shell is generated with the *Autodesk Netfabb Premium 2019 software* using the „*Generate Shell*" tool. In this way the printed rubber part is enlarged by a shell thickness that can be individually selected. Afterwards the rubber part is removed using the „*Boolean Operation*" function, providing finally the shell as an independent layer separated from the rubber part as original layer. This shell is also converted to the STL format.

The two virtual parts are imported into the open source software *Slic3r* to generate the printable G-code. The virtual component must be shifted in all directions of the thickness of the shell, because all components are automatically loaded into the origin of the coordinate system. After moving the part in all directions the component is placed exactly inside its virtual shell. In the slicing software the two components can be selected separately and assigned to the respective print heads. In the case of the AME-3D-printer, the shell is assigned to the print head for the thermoplastic material and the rubber part itself to the twin screw extruder. In addition, the off-set, that means the mounting distances between the two print heads in the x- and y-direction, must be considered as well. Then the G-code is generated correctly and the rubber part is printed precisely in its shell. The nozzle diameter of the print heads, the print speed, the temperature settings and the generated height for each printed layer depending on the positioning distance between nozzle outlet and the print bed have to be selected before the process is carried out. After all settings are made, the final G-code is generated.

The software uses a travel optimized, so-called "*ABBA*-strategy" for generating the G-code. This means that first the shell (A) is printed in one layer, then the core (B) in the same layer, and in the next layer first the core (B) followed the shell (A) and so on. Since this printing behavior would result in possibly non-geometrically stable rubber layers being printed in every second printing step before the thermoplastic, this printing strategy is not suitable for the AME-process. For this reason, the project has developed a sorting algorithm for the generated G-code that transforms the *ABBA*-strategy into an *ABAB*-strategy, thus ensuring that in each printing step the thermoplastic layer is printed first followed by the rubber layer. This is then processed directly by the 3D printer.

It is also possible to print the shell in a higher resolution than the rubber part, which should be favorably done, to minimize imprints of the layer structures covered by the rubber surface, due to flowability of the rubber material until the vulcanization process has stabilized the geometry. It should be noted that the resolution of the thermoplastic shell must be a fraction of the resolution of the rubber component so that the layers are always completed after the rubber has been printed. On the other hand, a higher resolution results in an increased printing time. For a rubber resolution of 0.6 mm, either a resolution of 0.2 mm or 0.15 mm of the shell would be possible. An even finer resolution is also conceivable, if the 3D-printer used permits this technically. Consequently, a printing strategy of the type *x*A→B→*x*A→B would be applied, whereby the *x* represents the number of layers of the thermoplastic material to be printed. To achieve a better adhesion to the printing table, the use of a so-called "*brim*" is recommended. This enlarges the first printing layer, which results in a larger contact surface between the shell and the printing table. [16] The exact size of the brim is set in *Slic3r*.

After printing, the rubber part is vulcanized in its shell. The vulcanization step and the parameters used are not content of this publication. After vulcanization, the cured stable rubber part cools down in its shell and is released and cleaned afterwards from thermoplastic residues.

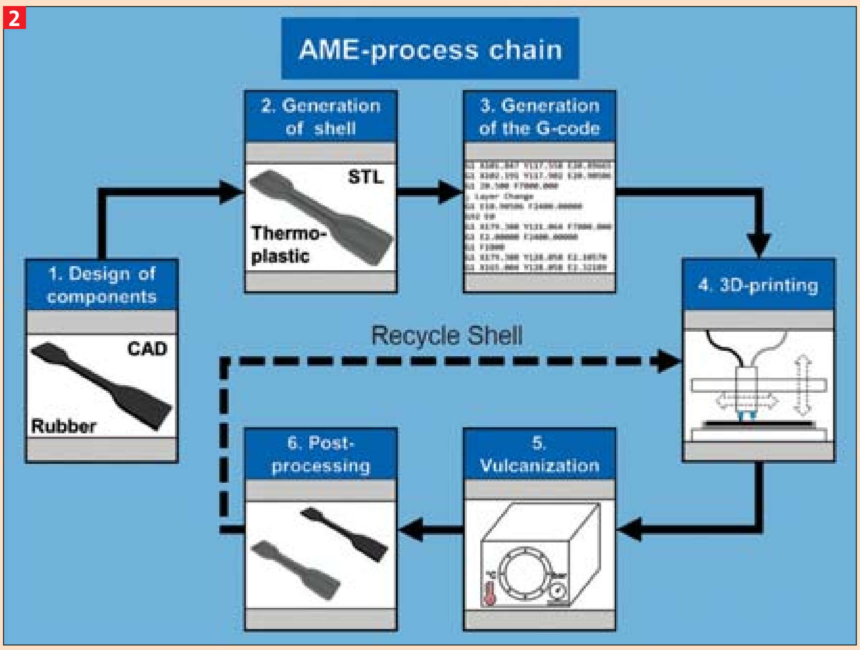

Figure 2: Process chain of the AME process

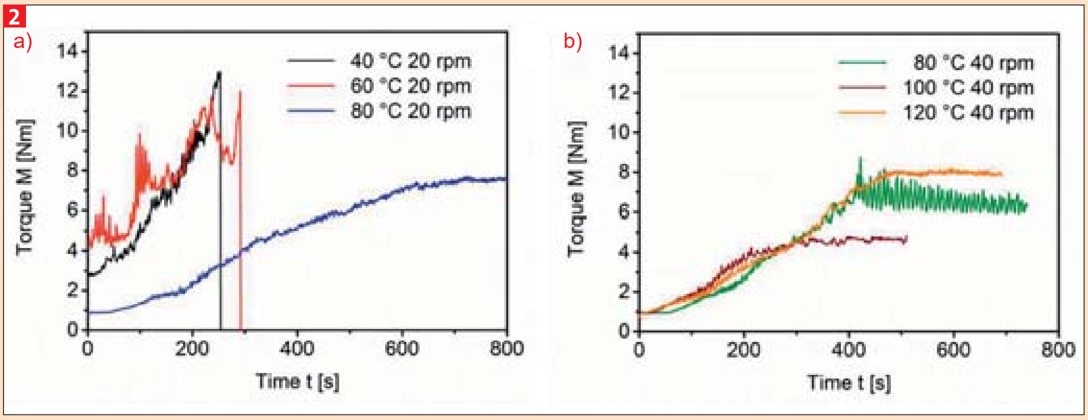

Figure 3: Torque curve while extrusion with different rotational speeds and temperatures of the rubber mixture a) Temperatures from 40 °C to 80 °C and rotational speed of 20 rpm b) Temperatures from 80 °C to 120 °C and rotational speed of 40 rpm.

3.3 Processing behavior of the rubber

To synchronize the rotational speed of the extruder with the pre-adjusted mass throughput of the slicing software a constant material feeding is required, because the twin screw extruders throughput is dependent of the feeding rate if the extruder is underfeeded. [17] To achieve a constant material flow rubber strips with a diameter of 2.38 mm were produced in advance and wrapped around the freely rotating material storage, as can be deduced from Figure **1**. The strips were dusted with talc powder to avoid adhesion among each other. The diameter of the feeding strips has to be larger than the thickness of the printed layers, to make sure that the screw flights are constantly filled with material to ensure that more material can be drawn in from the extruder when necessary than printed through the nozzle. In that way a constant material throughput during the additive manufacturing is enabled. In a first step the printing velocity range of the system has to be pre-estimated and the printing temperature has to be set. Therefore, different extrusion experiments with different temperatures and rotational speeds were carried out.

The torque curves of different rotational speeds at different temperatures of the extruder are shown in Figure **3**.

The extruder is started empty and is fed with rubber strands until a constant torque is observed. From Figure **3a)** could be deduced that the maximum of the torque level of 13 Nm is exceeded, when the material is extruded at temperatures of 40 °C or 60 °C with 20 rpm, which leads to a shutdown of the servo motor (black and red curve respectively). At 80 °C a constant torque level can be observed after 600 s extrusion time (blue curve). To achieve more application-related printing velocities, the extrusion´s rotational speed was increased to 40 rpm. In Figure **3b)** is shown how the torque level is developing when 40 rpm are used. A temperature of 80 °C is probably too low to process the material with 40 rpm, due to the lack of additional shear induced warming of the material (green curve), so that the torque varies between 6 and 8 Nm. At 100 °C the torque decreased in the steady state after 300 s to approximately 4.3 Nm (brown curve). When the temperature is further increased to 120 °C, the torque level increased again to approximately 8 Nm, because the temperature and the additional shear induced heating of the material during the extrusion leads to scorch of the material (orange curve). The processability of the material is proved, regardless of its high viscosity, which is ensured via the implemented twin screw extruder. The extrusion velocity of the material was determined at 80 °C, 100 °C and 120 °C using 40 rpm °C, to synchronize the extruder speed with the traversing speed of the 3D-printer. The extrusion velocities are shown in Table **1**.

The maximum of the extrusion velocity of the material used in this study is observed at 100 °C: In case of using a lower temperature of 80 °C the materials viscosity is still too high to provide a sufficient throughput. As well as at 120 °C the throughout is lowered, which could be an indication for a scorching behavior of the material in the extruder.

1 Extrusion velocities at different temperatures

Temperature	80 °C	100 °C	120 °C
Extrusion velocity [mm/s]	8.2	19.8	17.6

The following experiments were carried out at 100 °C and 40 rpm. To synchronize the extruder´s rotational speed and the traversing speed of the printer, the printing velocity in the slicing software was adjusted to 19.8 mm/s.

3.6 Microscopy

Additive manufactured components and separately extruded strips were investigated by light microscopy, to characterize the surface properties of the additive manufactured uncured rubber strips. The rotational speed was 40 rpm and the temperature 100 °C. The images are shown in Figure **4**.

The surface of the mixture is smooth and homogenous at 100 °C processing temperature. In contrast the picture of the strips at 80 °C shows some slight surfaces defects and roughness due to an insufficient homogenization of the mixture in the extruder. The strip extruded at 120 °C shows the poorest surface properties. Here, the extruded strip is not even in cylindrical shape, rather providing a rough wavy surface due to a probable scorching behavior.

3.4 Printing of rubber strips on the printing bed

After the synchronization of the extrusion and traversing speed, first printing experiments could be carried out. The initial contact adhesion of the rubber strip after passing the nozzle and getting in touch with the Kapton® tape coated printing bed was turned out to be insufficient, so that the rubber strips had to be pressed manually to the printing bed at the beginning of the printing process. In this case further studies have to be done to improve the contact adhesion between the rubber and the surface material used for the printing bed.

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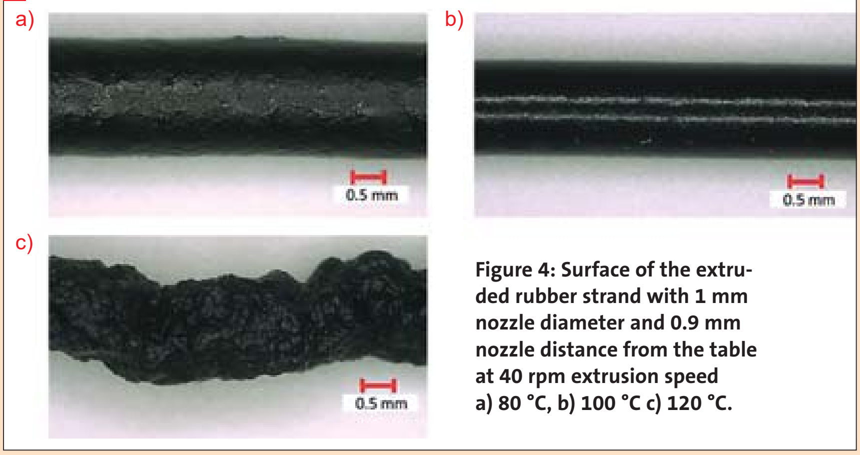

Figure 4: Surface of the extruded rubber strand with 1 mm nozzle diameter and 0.9 mm nozzle distance from the table at 40 rpm extrusion speed a) 80 °C, b) 100 °C c) 120 °C.

The printed strip is shown in Figure 5. A printing velocity of 19.8 mm/s was used as determined in 3.5. The nozzle distance was chosen to 0.9 mm, which is smaller than the diameter of the used rubber strips for feeding, to ensure a sufficient contact to the printing bed regardless to a geometrical deformation in first step.

3.7 Influence of the distance between nozzle and printing bed

To investigate the influence of the nozzle distance from the printing bed on the geometry of the 3D-printed rubber layers, different rubber strips has been printed with a constant extrusion velocity of 40 rpm at 100 °C extrusion temperature. Starting from 0.7 mm, the distances were increased up to 2.1 mm in 0.2 mm steps at a printing velocity of 19.8 mm/s.

The shape of the strips compared in Figure 6.

The extruded rubber strips show a larger diameter than the nozzle itself, due to the entropy elasticity of the polymer die swell, which allows the polymer to return to the state of maximum disorder by performing the relaxation process while cooling down in the environmental unstressed atmosphere. [18] Starting with a nozzle distance of 2.1 mm to prevent the nearly cylindrical shape of the strips, the width and the height are increased to 40 % and 31 % respectively (Figure 6a), compared to the nozzle diameter of 1 mm. The initiated back pressure while printing flattens the printed strip and might lead to a slight broadening as well. The width of the strips is up to 3.7 times broader than the nozzle diameter, when the nozzle distance is only 0.7 mm (Figure 6h). It is obvious, that the cylindrical shape is more broadened when the distance of the nozzle from the printing bed is decreased. Thinner layers show an increased specific surface, which should improve the bonding behavior between the layers. This may influence the layer structure and the stress resilience of the finally vulcanized rubber component. However the printing resolution in one dimension is reduced, so that an acceptable compromise between layer adhesion and resolution has to be chosen. Decreasing the nozzle distances leads step by step to a broadening of the strips, however the broadening using 0.7 mm nozzle distance is strongly increased. A distance of 0.9 mm seems in that way reasonable for further experiments. The values of the geometrical dimensions of the strips are listed in Table 2.

4. Conclusion

This paper deals with the development, construction and testing of a 3D-printing-system for additive manufacturing of rubber parts. The practicability of the AME-process (Additive Manufacturing of Elastomers) could be proven so that future studies will directly focus on the manufacturing process of first carbon black filled rubber parts with subsequent hot air vulcanization. The build-on system is based on a 3D-printer for the manufacturing of thermoplastics from *BZT Maschinenbau GmbH*. Additionally, a 9 mm twin screw extruder from *Three-Tec GmbH* is implemented to allow the rubber printing. The rubber strips are continuously fed. The 3D-printer enables the additive manufacturing of rubber compounds and thermoplastic materials in a serial process by alternative printing of thin layers to build up a designed part especially of rubber materials.

The used material was a carbon black filled natural rubber based compound to investigate different material dependent process parameters. The process chain of the AME procedure is a six-step process: (i) The required rubber part has to be designed and converted into the STL format,

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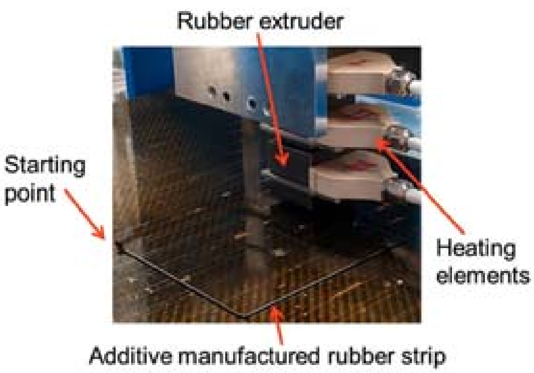

Figure 5: Printed rubber strip at 100 °C, 40 rpm, nozzle diameter 1 mm and nozzle distance to the table 0.9 mm.

2 Geometrical dimensions and deformation of the extruded rubber strips

Nozzle distance	Width [mm]	Height [mm]	Ratio Height/ Width
2.1	1.4	1.3	0.94
1.9	1.8	1.5	0.87
1.7	1.8	1.5	0.86
1.5	1.9	1.5	0.82
1.3	2.3	1.4	0.63
1.1	2.5	1.2	0.49
0.9	2.8	1.0	0.37
0.7	3.7	0.9	0.25

(ii) then the thermoplastic shell is computer aided automatically generated, (iii) the printable G-code of the part and its shell is generated, (iv) the G-code has to be sorted by a program in a way that first the thermoplastic and then the rubber is printed in each layer, (v) the printing and subsequent vulcanization of the part in its shell is then carried out in an external autoclave process, (vi) the rubber part is removed from its shell and a post-processing could be initiated if necessary.

To achieve a steady material flow the feeding has to be constant as well. The most practical solution seems to be a continuous process providing strips from a freely rotating wheel as material reservoir. The strips are fed between the screw segments of the extruder while the printing process is carried out. A processing temperature of 100 °C at 40 rpm for the extruder seems to be reasonable for 3D-printing of rubber layers using the NR-based compound in this study. The distance of 0.9 mm between nozzle and printing bed was beneficial, because a higher specific surface is generated in that manner, which might lead to a better strip adhesion among each other for in the future entirely printed rubber parts.

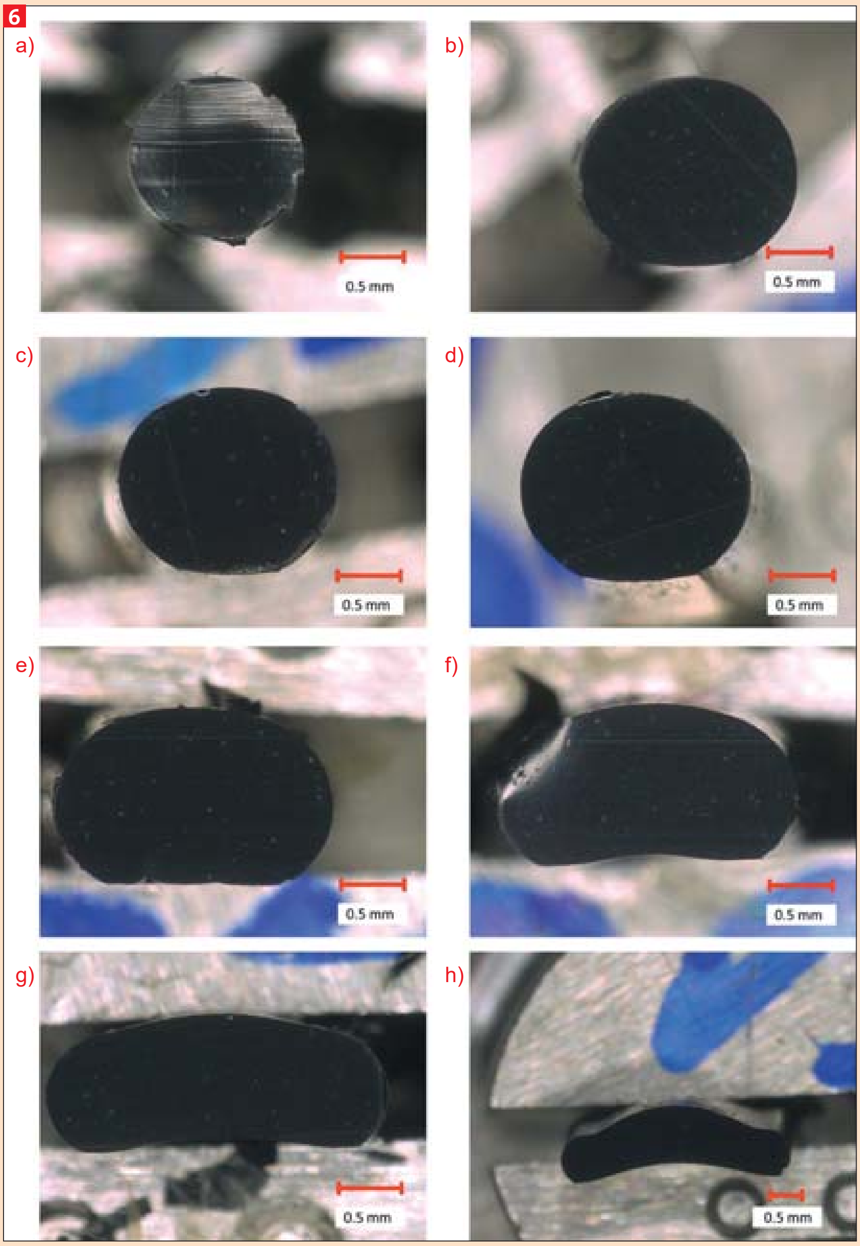

Figure 6: Influence of the nozzle distance from the printing bed a) 2.1 mm b) 1.9 mm c) 1.7 mm d) 1.5 mm e) 1.3 mm f) 1.1 mm g) 0.9 mm h) 0.7 mm.

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