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Investigation of additively manufactured lost cores for the production of hollow bodies by silicone casting

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Abstract

Lost cores have been used for many years in the industry for fibre composites, injection molded and die-cast components. The lost cores are generally used to support the later component material or temporarily fill cavities during the respective manufacturing process. Afterwards the dissolution process begins and the core material is removed from the manufactured part. The core is removed, for example, on contact with water, through increased temperature or mechanically. This process creates a cavity inside of the component that could not be produced in any other way using direct manufacturing processes.

In industrial applications, this process is used for large-area components where the opening size of the component and thus the contact surface of the solvent with the core plays a minor role. The aim of this publication is to investigate various additively manufactured lost cores that are used to manufacture smaller silicone cast components. The aim is to keep the opening in the silicone casting component as small as possible so that it can be closed after the dissolution process of the additively manufactured part, thus creating a completely closed cavity in the component. This can otherwise only be achieved using a double-shell concept.

To achieve the goal of making the opening as small as possible, various methods for dissolving the additively manufactured lost core are being investigated. These include dissolving in liquids, melting under the influence of temperature and mechanical removal of the core. All core materials are manufactured using different additive manufacturing processes. This publication concludes with an outlook on future tasks and its industrial relevance.

Keywords Lost core · Silicone casting · Additive Manufacturing · Hollow space · Soluble support

1. Introduction and motivation

In the production of hollow silicone cast components, various processes are used, such as the tumbling process, a direct manufacturing like Liquid Additive Manufacturing (LAM) and the production using additively manufactured lost cores. This publication takes a closer look at the process with additively manufactured lost cores. This means that the lost cores, which are located inside of the silicone body during the casting process, are subsequently removed using material-specific processes.

When producing additively manufactured components, they can be divided into rapid prototyping, rapid tooling or rapid manufacturing depending on the area of application [1]. The components are subject to different processes, but all are built element-wise or layer-wise as described in VDI 3405 [2]. Depending on the manufacturing process, the selected material and the associated process, the layer upon layer production leads to rough surfaces and anisotropic mechanical properties [3]. To take advantage of one of the major benefits of additive manufacturing, the ability to produce individual parts regardless of anisotropic material properties, the option of silicone casting with additively manufactured lost cores is getting more and more important and has a lot of advantages. One of the biggest advantages is the production of complex geometries inside the component, which cannot be produced in one piece using conventional manufacturing processes. This allows innovative designs to be created. The freedom of geometry also enables high casting and molding accuracy. Another advantage is the possibility of material diversity in production and a cost-efficient production process.

To illustrate the advantages, the production process for silicone cast components is described in more detail. First, the outer molds (cavities) are additively manufactured as a master mold [4]. The space between the two cavities is then filled using 2-component room temperature vulcanizing (RTV) silicones (two-component silicones that crosslink at room temperature) before the silicone hardens [5]. To avoid air inclusions or to fill thin-walled components better, the process can be used with vacuum as vacuum casting [6]. In this way, the individually produced mold is cast as a negative onto the component. In this way, individual bodies can be produced that do not have a layered structure. A serious disadvantage of the silicone casting or vacuum casting process is the production of hollow spaces inside of the silicon component. As the silicone fills any volume, planned cavities in the component are also filled with material. To produce cavities, as in an injection mold, cores must be inserted into the component where the silicone should not flow during the filling process. The production of cavities automatically leads to undercuts that are difficult or impossible to remove, as a collision between the component and the core would occur when demolding the core [7]. In some cases, it may be possible to remove the silicone part from the core with small undercuts, but there are limits which can lead to an impossible removal or to a destruction of the parts.

For this reason, this publication examines various options for additive manufacturing of the core material from a soluble, meltable or mechanically removable material. This is done in the industry, among other things, with wax in the investment casting process [8]. The technical term for this process is described by lost cores [9]. The process for producing silicone cast components is described in Figure 1. First, the lost cores and the cavities are additively manufactured to produce a unique silicone part. Silicone is then filled into the cavities through the opening provided and, depending on the material recipe, the silicone hardens at room temperature after a defined time. Depending on the material or removal method, the additively manufactured lost cores and the shaping cavities are removed. This results in the finished molded part with a hollow space inside.

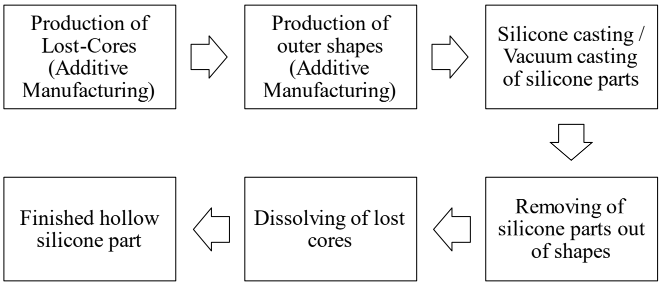


Figure 1: Process flow of component production with additively manufactured lost cores

Lost cores are usually used in the production of fiber composite, injection-molded or die-cast components to temporarily support the component and then create cavities inside the component [10]. Additive manufacturing has opened further design options for lost cores, which are highlighted in various publications. Both, the manufacturing processes, and the post-processing processes, for example sand cores, meltable wax cores and water-soluble Polyvinyl alcohol (PVA) cores produced using binder jetting (BJT-SSt/P [11]), are examined in Wang et al., Gawronova et al., Piangsuk et al. and Goyanes et al [12-15].

The aim of this publication is to investigate the different options for additive manufacturing of lost cores for a silicone cast component with a very small opening (≤ 6 mm). Compared to die-cast components, silicones have a significantly higher heat resistance temperature (HRT), which means that other types of lost cores are possible in this application. These should form a cavity inside the silicone casting and have the smallest possible contact surface with the solvent or the environment. The reason for this is that the opening in the silicone casting should be completely closed again to create a closed cavity, which would otherwise only be possible with connected shell elements.

2. Definitions

This publication examines various options for the production of additively manufactured lost cores and their subsequent removal with the smallest possible diameter (in this publication 5.6 mm) in the silicone castings. Figure 2 shows three different material properties for removing these lost cores. The first option are washable cores. This means that the additively manufactured cores are dissolved by contact with water or acids. The prerequisite for this is that the silicone is resistant to the chemicals used and the core material is not. A major advantage in the production of silicone components is that they have good resistance to a wide variety of chemicals [16]. Another possibility is that the core can be molten out. The melting temperature of the lost core should have a temperature delta as large as possible to the heat resistance temperature of the silicone. Depending on the type of silicone used, the heat resistance temperature is in the range of 250 °C to 300 °C [17, 18]. A third option is to investigate the mechanical removal by a subtractive process such as milling or turning.

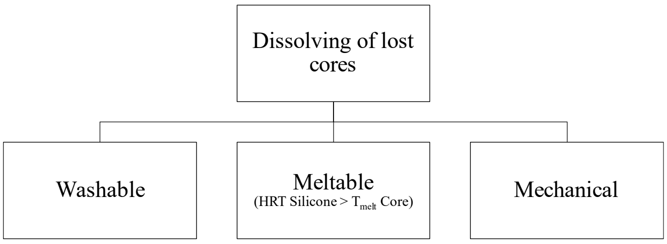


Figure 2: Various material properties for removing lost cores for silicone casting process

For the different dissolving possibilities there are different advantages and disadvantages. These are shown in Table 1.

Table 1: Advantages and disadvantages of the various options for removing the lost cores [19-23]

	Advantages	**Disadvantages**
Washable (Water)	• No special security gear • No special attention because of handling with acids or mechanical removed parts • No interaction between silicone and water	• Less water soluble materials on the market • More time consuming process than others • Hygroscopy of materials
Washable (Chemical)	• Wider choice of material compared water soluble • Faster solving process than with water	• Special security gear • Potential interaction with silicone • Deduction system needed
Meltable	• Very fast solving of part • Material gets melted • Silicone has a high Heat Resistance Temperature	• External heating necessary
Mechanical	• No special acids necessary	• Damage of silicone part possible • Limitations because of big equipment and small diameter in silicone part

Based on the advantages and disadvantages listed in the Table 1, various options for the process chain are investigated in this publication. These different options are described on the following pages.

2.1. Production of silicone casting parts

As mentioned in the introduction, the silicone will be injected through a hole in the upper part of the cavity with a syringe. In Figure 3 the cavity with the upper part, the lower part and one core which is made of PVA is shown. The O-ring is used as an axial sealing between the two cavity parts and keeps the silicone inside of the cavity. After the curing time of the silicone the cavity can be opened and the silicone part can be removed with the lost core inside. As the last step the lost core will be dissolved, depending on the core-material.

Figure 3: Additively manufactured cavity with additively manufactured PVA core before silicone casting process

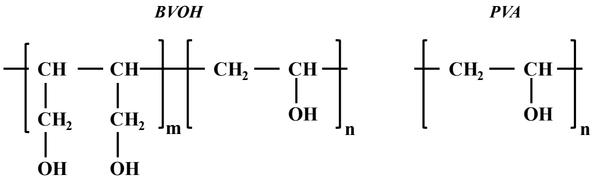
The different removing possibilities will be explained in detail in chapter 2.2.

2.2. Investigated core materials

Washable core (Water)

Various polymers are being investigated for water-soluble, additively manufactured materials. Two of the most used soluble core materials are examined in this publication. PVA is a water-soluble support material which is often used in Fused Layer Modeling (material extrusion process, MEX-TRB/P [11], FLM) to generate a support structure for overhangs that can be removed afterwards without mechanical work [19]. Contact or storage in water causes dissolution (hydrolysis), which in turn leads to separation and decomposition of the material. It is a polymer with remaining vinyl-alcohol parts. For the tests the material “PVA175N05” from eSUN is used.

Another material being investigated here is a Butenediol-Vinyl Alcohol Copolymer (BVOH). The “Natural BVOH” from Formfutura (melt flow rate 7.5 g/10min) which is described as an experienced water-soluble support material is used in the tests. It is a copolymer with Vinyl-Alcohol and Butenediol and has another chemical structure than PVA. The difference is shown in Figure 4. These two materials are tested because they are easy to obtain and widely used.



$$-\left[CH(CH_2OH)-CH(CH_2OH)\right]_m-\left[CH_2-CH(OH)\right]_n- \qquad -\left[CH_2-CH(OH)\right]_n-$$

Figure 4: Chemical structure of BVOH (left) and PVA (right)

The process sequence can be seen schematically in Figure 5. After a material and process-specific time in the water bath, the lost core dissolves and is more or less removed from the silicone part.

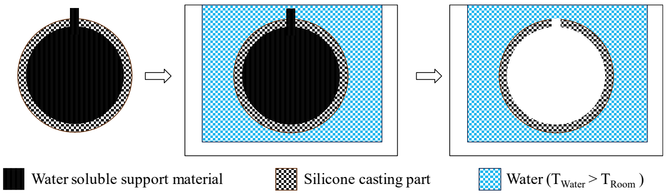


Figure 5: Schematic process flow of water soluble core

A water-soluble PVA core is shown in Figure 6. To increase the surface area, which is in contact with water, this part contains holes in the core, which are compared with cores without holes in this research work. Increasing the surface area shortens the time to complete decomposition. This can be seen in the publication in an extensive study on the dissolution of PVA in an Acrylonitrile-Butadiene-Styrene copolymer (ABS) body by Duran et al. [19]. The core geometry investigated was chosen as a cylindrical shape with a dome in order to recognize geometric influences due to edges, radii or curves.

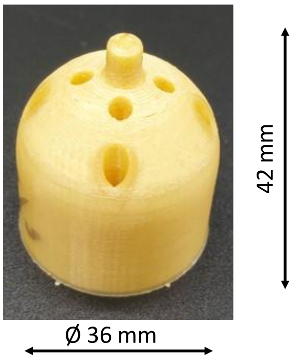


Figure 6: Additively manufactured water soluble PVA core

In an initial fundamental investigation, different infill densities, surfaces in contact with water as well as different water temperatures are taken into account for the dissolution of the water-soluble materials. The reason for this is that different studies have determined different values for the solubility of the material. While Duran et al. recommend a temperature as high as possible close to the boiling temperature of water as the most promising temperature, Rosales et al. state 40 °C as the optimum decomposition temperature for PVA [19, 20]. Table 2 shows the different processing parameters of the additively manufactured PVA cores. The changed parameter in each case compared to the previous test is highlighted in gray. The parameters of the other direct additively manufactured core materials BVOH and high-impact Polystyrene (HIPS) can also be seen in the table.

Table 2: Parameters of the basic tests with PVA, BVOH and HIPS core

Parametersetting	Holey - 30% Infill - 40 °C	Holey - 0% Infill - 40 °C	Holey - 5% Infill - 40 °C	Holey - 5% Infill - 75 °C	Holey - 5% Infill - 90 °C	Holey - 5% Infill - 25 °C	5% Infill - 90 °C - 8 g	6% - 90°C - 13g	BVOH - 5% - 90 °C	HIPS - 5% - Limonene
Nozzletemp. [°C]	200								***230***	230
Bedtemp. [°C]	60								***70***	***60***
Layer Height [mm]	0,2									
Infill Density [%]	30	***0***	***5***	5	5	5	5	***6***	5	5
Infill Geometry	Gyroid									
Wall lines [n]	3	3	3	3	3	3	3	***6***	3	3
Print Speed [mm/s]	100									
Infill Speed [mm/s]	70									
Wall Speed [mm/s]	70									
Top / Bottom Speed [mm/s]	40									
Stirrertemp. [°C]	40	40	40	***75***	***90***	***25***	***90***	90	90	/
Stirrer Speed [1/n]	500									/
Nozzle diameter [mm]	0,4									
Material	PVA								***BVOH***	***HIPS***

Washable core (Chemical)

In principle, all materials with poorer chemical resistance than silicones are possible within the scope of solubility through chemical contact. But of course, not every polymer can be produced in additive manufacturing. As an easy-to-handle option, HIPS is processed in the FLM process and can be dissolved by the chemical "Limonene", a terpene substance which is made from the peels of oranges or lemons [21]. The dissolving process is shown schematically in Figure 7. The chemical has an extremely sweet odor, should be used with an air extraction system and must be handled with appropriate protective equipment. The temperature of the solvent should be at room temperature. Goh et al. investigated the dissolving HIPS with Limonene in the production of microchannels [22].

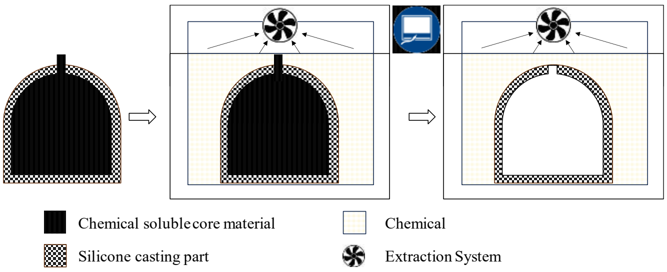


Figure 7: Schematic process flow of chemical soluble core

Meltable core (Temperature)

In the area of additively manufactured, meltable materials, substances are being investigated which have a significantly lower melting point compared to the HRT of silicone, liquefy due to a temperature rising and are thus removed from the cavity. The cast components including the core are suspended in a device to melt out the core by the temperature and gravity. This is shown in Figure 8.

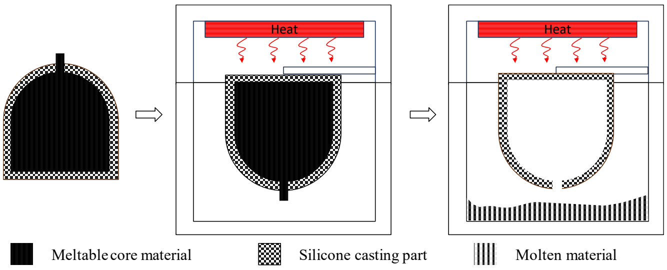


Figure 8: Schematic process flow of temperature meltable support material

Two different concepts are being investigated as meltable materials. Firstly, a core is casted from a paraffine wax, which is commonly used in the manufacture of candles and has a significant lower melting temperature (55 °C to 59 °C) than the HRT of Silicone. In this case, the paraffin wax pastilles are first melted in a pot in a hot water bath and then poured into an additively manufactured cavity to produce the lost core. In the same principle, the material Polycaprolactone (PCL), colloquially known as Polymorph, can be heated and liquefied at a temperature of about 60 °C. The melting temperature of the material is 56-65 °C and much lower than the heat resistance temperature of Silicone [23]. The materials are heated up to 90 °C.

The production of the thermally soluble cores is not done, like the other soluble materials, by FLM process. The materials, which are in pellet form, are first heated and melted in a water bath. The temperature of the water bath is at 90 °C. This temperature is above the melting temperatures of the materials and at the same time within the recommended melting temperatures, which should not exceed 100 °C for Polycaprolactone. Subsequently, the liquefied materials are poured into a previously additively manufactured mold. After the materials have cooled and hardened, they are removed from the mold. After demolding, the test procedure described at the beginning can be carried out.

<u>Mechanically removable core</u>

Another potential process being investigated is the mechanical removal of a hard support structure. In this case, the lost core is made of Polylactide (PLA), since this is easily machinable, easy to process and not expensive to procure. The material gets removed by mechanical processing such as drilling, turning or milling. The challenge is the removal of the lost core parts, which are not located in a direct axis to the machine. This is also illustrated in Figure 9, where every angle must be covered by the drill/mill.

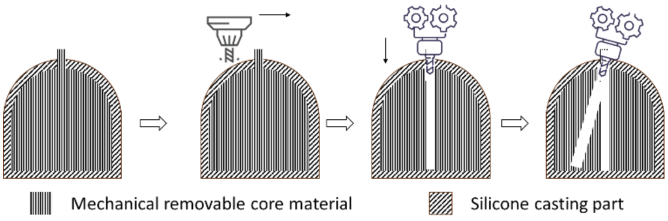


Figure 9: Schematic sequence of a mechanically removable core

<u>Casting silicones</u>

The commercially available TFC Baseline 100 cast silicone from TFC Trollfactory is used to manufacture the silicone components. Due to its low viscosity of 3500 mPa*s, it has good flowability and can reproduce geometries well.

2.3. Used machines

<u>FLM process</u>

Since some core materials are in the shape of filaments, these are processed using a Creality Ender 3. The filaments of the water-soluble materials have very strong hygroscopicity. They should be kept dry before processing, for example with using silica gels and storage boxes. The filament is then fed to the heating nozzle by the motor and friction rollers and gets melted. Subsequently, the components are built up layer upon layer [2].

<u>Scale for weight reduction</u>

To investigate the weight loss over time of the various materials, the weight of the lost cores is measured at defined time intervals using a commercially available precision scale (+/- 0,01 g).

<u>Universal heating oven</u>

A Memmert UF55 universal heating oven is used to melt the thermal meltable materials. Depending on the test procedure, the oven is heated to the respective temperature and thus liquefies the materials.

<u>Magnet stirrer</u>

A commercially available magnetic stirrer from Anzeser is used for the dissolution tests of PVA and BVOH in water.

3. Results

3.1. Preliminary examination of the various dissolvable materials

To make a preliminary selection of possible materials, the cores will first be examined for their weight reduction over time without silicone casting. The aim is to make an initial preselection to investigate the favored core materials as a carrier for a silicone casting component in the further publication.

To investigate the weight loss of the different materials over time, the weight of the lost cores is measured in a defined time interval with smaller steps in the beginning and bigger ones during the ongoing process. To avoid any measurement errors in the results, three cores with the same parameters are produced and measured in each material and process specification. This is represented by the standard deviation in the diagrams.

Influence of filling density for PVA cores

The first investigation in this publication shows the influence of the filling density in relation to the time required for dissolution. The dissolving PVA core is weighed at defined measuring points. Figure 10 shows a sequence of pictures how the core decomposes after a time until it has completely dissolved. The core initially increases significantly in weight because, as already mentioned, the material is strongly hygroscopic and is initially saturated with water. After initial saturation, the weight starts to decrease until the cores are completely dissolved in water.

Figure 10: Image sequence of a dissolving PVA core on the precision weight scale

Figure 11 shows the weight reduction over time of three different fill densities with the same fill structure. The solid line describes a fill density of 30 %, while the dashed and dotted lines show a much lower fill level of 5 % and 0 %. This can also be seen in the initial weight at the time of 0 minutes, as the higher density already has a significantly higher weight (17.40 g compared with 11.58 g and 10.15 g). For all materials, the effect of water absorption is seen at a similar relative level. While saturation is already reached after five to ten minutes for the lower fill densities, the weight continues to increase at 30 % fill density to the measured value at 15 minutes. Subsequently, all samples decrease afterwards in weight. While the samples with an infill density of 5 % and 0 % have completely dissolved after 90 minutes, the component with 30 % infill density needs about 150 minutes. All tests are carried out at a constant water temperature of 40 °C. Three repetitions of each test series are carried out.

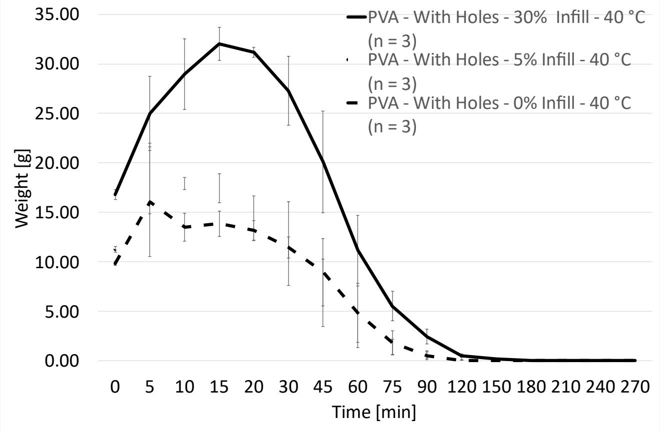


Figure 11: Graphical representation of weight loss over time of PVA cores with different infill at a water temperature of 40 °C

Influence of the water temperature for dissolving of PVA cores

After the investigation of the infill density, the infill density is kept constant at 5 % in further tests for a better comparison (to be seen in Figure 12). In the following test, the water bath temperatures for dissolving the PVA cores of 25 °C (solid line), 40 °C (dotted line), 75 °C (dashed line) and 90 °C (framed line) are investigated. The higher temperatures of 75 °C and 90 °C are significantly faster in dissolving the core compared to the lower temperatures. At a water temperature of 90 °C, the core is completely dissolved after only 30 minutes, while at 40 °C (approx. 120 minutes) and 25 °C (approx. 270 minutes) significantly more time is required. Three repetitions of each test series are carried out.

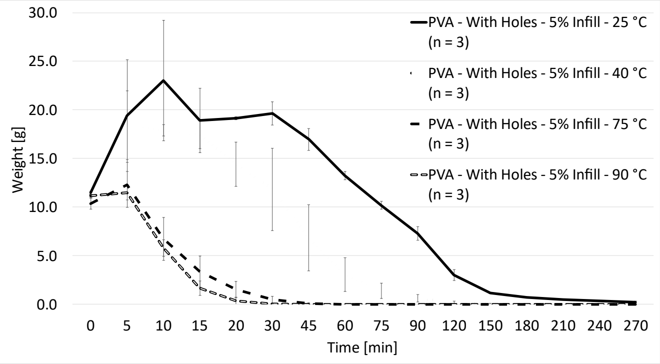


Figure 12: Graphical representation of weight loss over time of PVA cores with constant infill density and different water temperatures

Influence of the surface area between Water and PVA cores

By inserting the holes into the geometry, the surface area in contact with water increases by approx. 55 %. Despite the recesses, the weight also increases due to the higher number of wall lines. For weight comparability, the weight of the undrilled body is therefore also increased to the same weight of 13 g (due to the increase in the wall lines). The results of the dissolution can be seen in Figure 13. The unperforated variant with a weight of 13 g (solid line) takes significantly longer than the holey variant (dotted line) to decompose completely. Three repetitions of each test series are carried out.

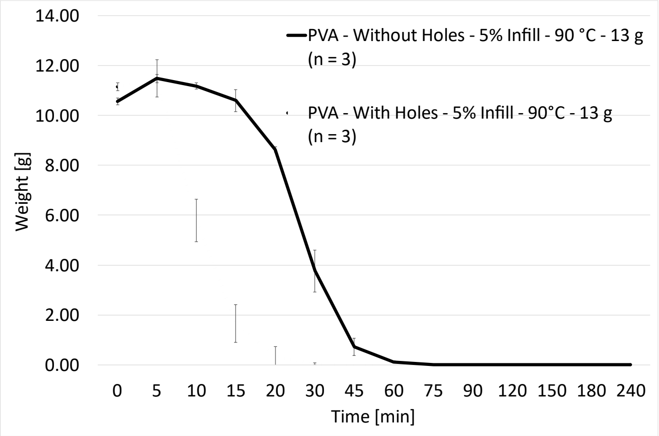


Figure 13: Graphical representation of weight loss over time of PVA cores with different surfaces at 90 °C

Influence of different water-soluble materials

Based on the results already presented, the variant with the shortest dissolution time of the PVA tests is used for a direct material comparison. This is the hole variant with an infill density of 5 % and a dissolution temperature of 90 °C. In comparison, a series of tests with the material BVOH is carried out with the same boundary conditions. The results are shown in Figure 14. Three repetitions of each test series are carried out.

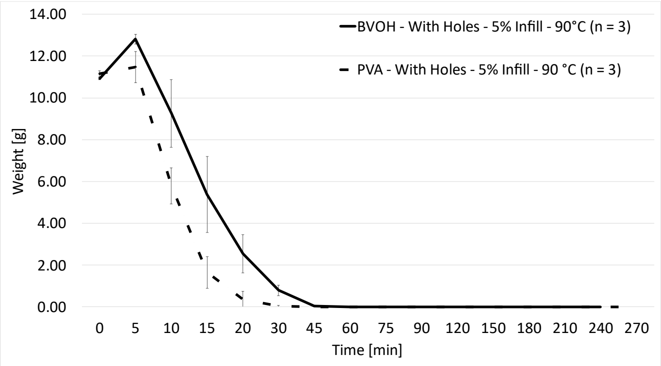


Figure 14: Graphical representation of weight loss over time of PVA cores and BVOH cores at 90 °C

This shows that BVOH has a longer dissolution time than PVA. While the PVA core dissolves at the time of about 30 minutes, the BVOH core needs about 45 minutes. For this reason, the PVA material (infill density 5 %, water temperature 90 °C) is selected as the preferred variant for the water-soluble core materials.

3.2. Preliminary examination of chemical solving lost core materials

The HIPS cores dissolved in Limonene have a significantly longer dissolution time than most of the PVA cores in water. Figure 15 shows the graph of the decrease in weight of a HIPS core in Limonene (solid line) compared to a PVA core in water at 90 °C (dashed line). The HIPS cores also initially increase in weight due to component saturation before the dissolution process starts. The dissolution process begins after around 20 minutes of saturation. While the PVA core has already completely dissolved after approx. 30 to 35 minutes, a large part of the HIPS core is still in an undissolved state. Complete decomposition of the core takes place after a period of around 210 minutes. Three repetitions of each test series are carried out.

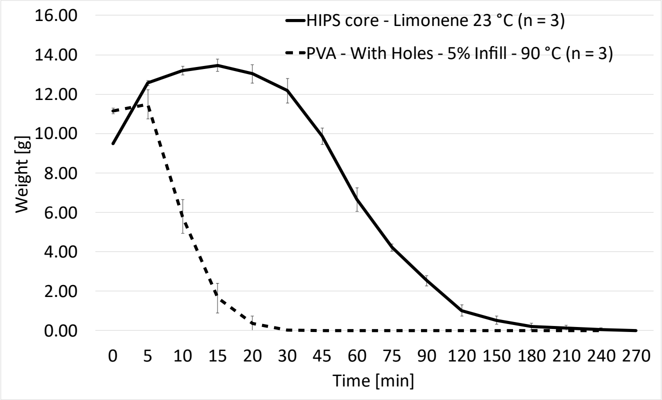


Figure 15: Graphical representation of weight loss over time of HIPS core in Limonene a PVA core in a 90 °C water bath

3.3. Preliminary examination of thermal solving lost core materials

The first insight into the different melting behavior can already be determined during the production of the cores. While paraffine wax is completely liquefied by the heating process in the water bath and can be poured in entirely, polycaprolactone only becomes liquid at a temperature significantly above the melting temperature and must be introduced into the mold with a spoon. This can be seen in Figure 16.

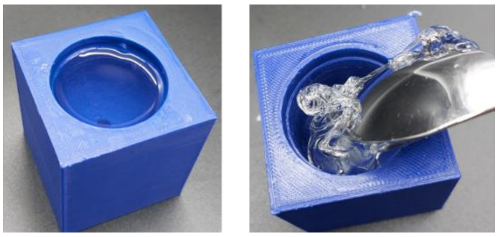


Figure 16: left: casted paraffin wax in mold, right: molten polycaprolactone which is placed in mold with spoon

On the left side, the already poured-in paraffine wax is in the liquid state in the mold, while on the right side, the molten polycaprolactone is brought into the mold with the help of a spoon. The dimensions of the cavity are 45 mm x 45 mm x 60 mm.

The findings from the casting tests are also confirmed in the dissolution tests of the cores. This can be seen in Figure 17. While the paraffine wax cores (solid line) begin to liquefy after only 5 minutes and the dissolution process already starts here, the weight of the polycaprolactone cores remains constant in the first 25 to 30 minutes, because only a melting of the surface can be observed. At this time, 2/3 of the wax core has already been molten, until complete decomposition occurs after about 45 minutes. The polycaprolactone core continues to liquefy very slowly, but then remains at about the same weight level, so that no further measurable weight reduction can be seen in the graph and the measurement is stopped. Three repetitions of each test series are carried out.

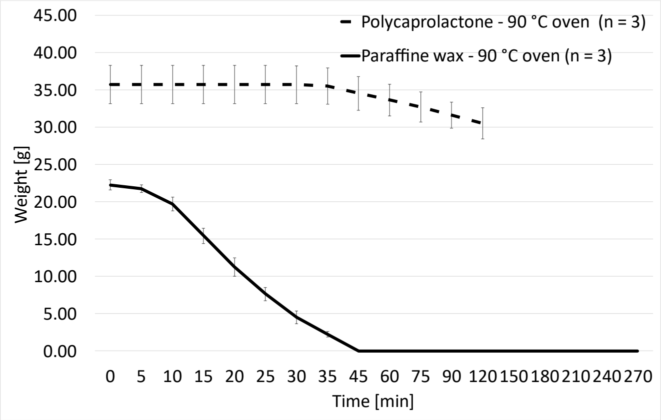


Figure 17: Graphical representation of weight loss over time of molten wax and polycaprolcatone cores at 90 °C

3.4. Silicone Casting parts

The silicone cast hollow parts are manufactured using the favored concepts from the previous chapters. The favoured settings are shown in Table 3.

Table 3: Favored settings for the lost cores of silicone casting parts

Material	Infill-Density [%]	Dissolving temperature [°C]
PVA	5	90 (Water bath)
Paraffine Wax	Solid	90 (Oven)

For the washable materials this means a PVA core with an infill-density of 5 % and a water temperature of 90 °C. For the meltable materials, the paraffine wax cores are melted out at a temperature of 90 °C.

The uncovered part at the upper end of the translucent silicone molded part is used as positioning in the cavity and now represents the only contact surface of the core with the environment. The dissolution process is started via this surface in the experiment. When this nipple is removed, the water can flow on the inside of the cavity. The PVA core with a silicone cover can be seen on the left-hand side and on the right-hand side before the silicone casting process in Figure 18.

Figure 18: left: Silicone casted part with PVA core, right: PVA core before casting process

There are major differences in the decomposition time with and without a silicone coating. While the pure paraffine wax core is completely decomposed after a dissolution time of 45 minutes, it takes longer with a silicone coating. After approx. 120 to 150 minutes, the unsolved volume settles down to a residual small weight, hence small residues remain. As this value is not 0 g, small residues remain inside the silicone castings during this process, which can be removed by a washing process, for example. Three repetitions of each test series are carried out. This can be seen in Figure 19.

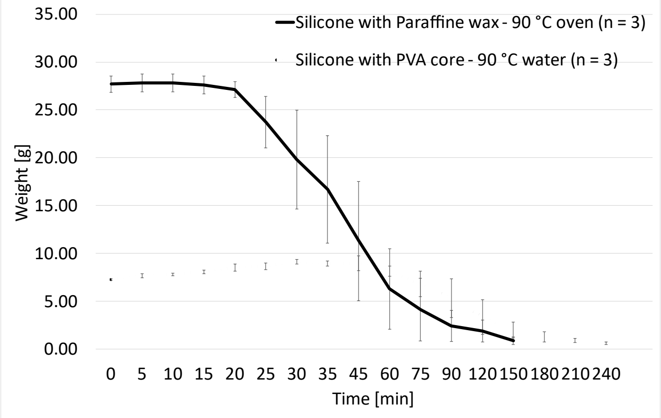


Figure 19: Graphical representation of weight loss over time of silicone casted body with paraffine wax in a 90 °C oven and PVA core in a 90 °C water bath

With PVA cores, the decomposition time is also significantly longer than without a silicone part. A time of approximately 240 minutes is required for almost complete decomposition. The hygroscopicity of the material leads to an increase in weight of up to 60 minutes. In Figure 20 a silicone casted hollow body can be seen after the decomposition process of a PVA core.

Figure 20: Top view on silicone casting body with hole after decomposition of PVA core in water

The PLA cores, which are removed mechanically using a milling machine and drill, cannot be removed cleanly through the small opening due to the accessibility problem which is illustrated in Figure 9. This problem cannot be solved for undercuts, in the hollow space of a part, which cannot be reached by a mechanical tool. Because of that, this process will no longer be pursued.

4. Discussion of results

4.1. Pre tests

4.1.1. Water soluble materials

Influence of infill density

As seen in Figure 11, the infill density has a high influence on the dissolution time. The 30 % infill density requires about 60 minutes longer for a complete decomposition than the significantly less filled samples with 5 % infill density and 0 % infill density. This primarily confirms the hypothesis that a higher infill density leads to a higher volume to be dissolved and thus also to a higher dissolution time. However, the 0 % infill density has a slightly higher dissolution time than the 5 % infill density, which can be explained by a potentially different dissolution behavior because of another decay of the material. The results of these two diagrams are comparable within the standard deviations. For almost every application at Fused Layer Modeling at least a filling density of 5 % is necessary to support the printing structures. With the help of these findings a filling density of 5 % can be used for all further experiments with PVA cores in this publication.

Influence of water temperature

The influence of the water temperature can be seen in Figure 12. As already described in the publication by Duran et al., a higher water temperature leads to a significantly faster decomposition of the lost core. The faster decomposition due to higher temperatures can be explained on the one hand by more strongly moving polymer chains in the PVA core, and on the other hand, the water temperature allows the water molecules to move more energetically efficient, which favors the breaking of the hydrogen bonds and leads to a faster dissolution.

Influence of surface area

As described in the publication by Duran et al., a larger surface area leads to faster decomposition of the material [19]. This could not be proven initially due to the difference in weight, but by correcting the component weight and thus isolating the influence of the surface area, the result from the publication can be confirmed. Also, for the selected core geometry, a significantly faster dissolution can be observed by increasing the surface area. This can be explained based on the surface in contact with water. The larger the surface area, the more sites start chemical decomposition at the same time and thus the largest possible contact surface leads to faster decomposition. Because of the selected core geometry for the silicone casting body, there are no holes possible inside the geometry. This leads to the result, that the favourite geometry for the upcoming tests is without holes.

Influence of the core material

Due to the two different investigated polymers PVA and BVOH, different dissolution times are also shown at the same water temperature. The differences in the dissolution times may result from the varying chemical structure, different molecular weights, but also from manufacturing process optimized materials for the decomposition process. As a copolymer, BVOH is a mixture of Butenediol and vinyl alcohol, while PVA is a vinyl alcohol. Due to the repeating OH groups, water is drawn and a hydrogen bond is formed with the water molecules. As a result, bound molecules are dissociated and thus PVA cores decompose faster than BVOH.

4.1.2. Chemical soluble materials

Compared to the PVA cores in water, HIPS dissolves much more slowly in limonene. Since the decomposition of the substances depends not only on the chemical structure of the polymers, but also on the polarity and temperature of the solvent, this is where the differences for the various dissolution times arise. Since the PVA studies also show serious differences in the tests between room temperature and 90 °C, a similar conclusion can be drawn for limonene. Due to the flash point of limonene of about 45 °C, it can only be dissolved at room temperature, which leads to significantly higher dissolution times.

4.1.3. Thermal soluble materials

As seen in Figure 17 there are different weight reductions over time between the two investigated materials. This can be explained by various characteristics of the materials. In addition to the lower melting point of paraffine wax compared to polycaprolactone, the molecular structure and the thermal conductivity also plays a significant role. While paraffine wax consists of alkanes, polycaprolactone is a polymer that only becomes melt shaped at these temperatures due to its chemical structure. Also, the higher thermal conductivity of paraffine wax (approx. 0.40 W/mK depending on the type [24]) compared to polycaprolactone (0.20 W/mK [25]) allows the complete core to heat up faster and thus also accelerates the liquefaction of the whole core. Another very important thing is the difference of the standard deviation of the cores. While the standard deviation of the wax cores is very low, it is very high at the shaped Polycaprolactone core. The reason for that is the aggregate state at the production process of the cores (wax is liquid, Polycaprolactone is plasticized). For these reasons, there is a clear advantage to using paraffine wax than Polycaprolactone for melting out in hollow bodies, not only because of the dissolution time but also because of the aggregate state of the molten material. Although the wax cores have a higher dissolution time compared to the best results of the PVA cores, the initial weights (approx. 22.5 g versus 11 g) are also different, since the PVA cores are not solid bodies (5% infill density).

4.2. Silicone casting tests

The differences between the decomposition of the additively manufactured cores with and without silicone cover have various reasons depending on the decomposition process. Firstly, the thermally dissolvable paraffine wax core is considered in this paragraph. As silicone has a strong insulating effect, it takes considerably longer for the oven to heat the wax core completely and for the wax to liquefy. This can also be seen in the graph, which initially falls slowly until a steeper drop occurs. There are also large differences in the PVA cores dissolved in water, as the surface area of the material in contact with water is reduced to a minimum here. This once again confirms the results from the surface tests. Due to the lower surface area, there is a much longer decomposition than without a silicone coating. The insulating effect intensifies the slowdown of the dissolving process for the PVA cores too.

5. Conclusion and outlook

In the context of this publication, various soluble, additive manufacturable support materials were investigated to qualify for the production of hollow silicone castings and also as a use case for support materials of additive manufacturing. In addition to water-soluble materials (PVA and BVOH), the material HIPS was dissolved in Limonene as a representative of chemically soluble materials. The best results provided PVA as a representative of the liquid-soluble materials, and paraffine wax for the thermal soluble materials. In preliminary tests, these showed the shortest dissolution time and are used to produce the hollow space casting components. Here, paraffine wax showed a much shorter dissolution time, which can be explained by the different dissolution behavior and a shorter liquefying process.

Even though the current results are very promising, the current and further work should be examined as a residue-free dissolution and a smaller opening of the paraffine wax as well as the possibility of a faster dissolution method for PVA cores. Likewise, various real applications of silicone castings are to be investigated to determine whether there is an advantage to be gained from the possibilities offered by the soluble cores.

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7. Contributions

The findings presented in this publication generate added value for various areas. The detailed investigation of additively manufactured support materials not only create a basis for silicone casting or other cavity components, it also provides a guideline for the use of non-mechanically removable support materials. Furthermore, the two decomposition temperatures mentioned in the literature for the dissolution of PVA cores are examined once again. Another important finding is the enormous difference in decomposition with and without a coating (in this case silicone). The results can be used as a basis for any choice of support material for additively manufactured parts or the production of hollow casting processes.

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