Additive manufacturing with varying material properties of thermosetting reactive polymers
A framework and comparison of different modes for implementing material transitions

Pajonk, Adam; Luna-Navarro, Alessandra; Knaack, Ulrich; Blum, Ulrich

DOI
10.1080/00038628.2024.2348141

Publication date
2024

Document Version
Final published version

Published in
Architectural Science Review

ARCHITECTURAL SCIENCE REVIEW
https://doi.org/10.1080/00038628.2024.2348141

Additive manufacturing with varying material properties of thermosetting reactive polymers: a framework and comparison of different modes for implementing material transitions

Adam Pajonk [a,b], Alessandra Luna-Navarro [a], Ulrich Knaack [a] and Ulrich Blum [b]

[a]Department of Architectural Engineering + Technology, Delft University of Technology, Delft, Netherlands; [b]Department of Digital Design and Construction, Muenster University of Applied Sciences, Muenster, Germany

ABSTRACT

Additive Manufacturing with Varying Material Properties enables controlled spatial variation of material properties in 3D-printed components, facilitating custom-tailored characteristics, added functionalities and reduced assembly processes. To promote this approach in building façade applications, this paper presents a novel framework for Additive Manufacturing with varying material properties using a thermosetting reactive polymer, specifically polyurethane. By dynamically changing the polyurethane's chemical composition, the material properties can be precisely controlled. The framework's individual aspects, including the material, hardware setup and computational system, are described in detail. Additionally, the research explores the implementation of material transitions with this framework, highlighting three different modes (horizontal, vertical and multi plane) and their impact on print time and material consumption. The paper concludes by discussing the potential of this approach for building façade applications, addressing current challenges and outlining future research directions.

ARTICLE HISTORY
Received 21 March 2023
Accepted 19 April 2024

KEYWORDS
Varying property additive manufacturing; thermoset reactive polymers; reactive extrusion additive manufacturing; robotic 3D-Printing; heterogeneous materials; polyurethane

1. Introduction

Additive Manufacturing (AM), also referred to as 3D-printing, has become a significant research field in architecture and construction (Camacho et al. 2018; Labonnote et al. 2016; Paolini, Kollmannsberger, and Rank 2019). One of AM's most promising features is its ability to fabricate components with spatially varying material properties, by combining different materials or material mixtures in a single object – an aspect recognized as critical for future research in this domain (Camacho et al. 2018; Grigoriadis 2015; Labonnote et al. 2016; Pajonk et al. 2022; Wiscombe 2012).

Traditional assembly procedures often undermine the efficiency of the construction process as they require the assembling of multiple parts and the careful fitting of individual components to each other (Cremers 2016; Wiscombe 2012). In contrast, the capability to incorporate varying material properties in a single AM process introduces new design possibilities (Gibson, Rosen, and Stucker 2010), that could potentially bypass traditional assembly or construction procedures (Excell 2013; Keating 2014).

The building façade, in particular, presents a high potential to benefit from this approach, since the façade is generally required to fulfil several functions at the same time and has to coordinate different environmental and user-related conditions (Knaack et al. 2014; Herzog, Krippner, and Lang 2017). As a result, the façade typically consists of several individual layers and components which often need to be fitted or modified to interface properly with one another or the overall building structure (Herzog, Krippner, and Lang 2017; Knaack et al. 2014).

Yet, most AM research in architecture and construction has focused on processing a single, homogeneous material in a layer-wise sequence (Camacho et al. 2018; Labonnote et al. 2016; Paolini, Kollmannsberger, and Rank 2019). Research exploring the use of multiple materials or varying material mixtures remain relatively scarce, and only a few approaches can be considered suitable for building façade applications (Pajonk et al. 2022).

1.1. Methodology overview

To address this gap, this research leverages the versatility of thermosetting reactive polymers. These polymers can change their specific material properties by altering their chemical composition. Specifically, this research focuses on polyurethane, exploiting its capacity to modify tensile strength and shore hardness by varying the components of its mixture. This feature is than implemented into an AM process.

1.2. Aim and objectives

The aim of this research is to explore AM with varying material properties as a novel approach for the fabrication of building façade components. The objectives include:

(1) Developing a framework for AM with thermosetting reactive polymers that utilizes the ability of such polymers to change

CONTACT Adam Pajonk A.M.Pajonk@tudelft.nl Faculty of Architecture and the Built Environment, Department of Architectural Engineering + Technology, Delft University of Technology, Julianalaan 134, 2628BL Delft, Netherlands

the resulting material properties during the 3D-printing process.

(2) Explore different modes for implementing material transitions with the AM process, and comparing these in terms of material usage and time consumption.

1.3. Paper structure

First, this paper reviews previous work on AM with varying material properties for the building façade (Section 2). Following this, a framework for manufacturing components with varying mechanical properties using polyurethane is presented (Section 3). The paper then shows initial results and explores the frameworks inherent modes for implementing material transitions in a 3D-printing and compares them in terms of material and time expenditure (Section 4). Section 5 discusses the key findings and the potential of the framework for building facade applications. The conclusions and future research directions are summarized in Section 6.

2. Additive manufacturing with varying material properties in the building façade

2.1. Potentials and opportunities

AM with varying material properties introduces unique advantages that hold the potential to advance the application of AM in the building industry, and in particular in façade construction. A primary advantage is its capability to integrate multiple functions into a single component, thereby eliminating the need for assembly after manufacturing (Grigoriadis 2015; Strauß 2013; Wiscombe 2012). This capability presents an innovative approach, challenging the traditional segmentation of construction processes, that could potentially be applied on different scales on the building façade, ranging from individual components which need to be custom fitted during installation, up to the whole façade construction.

Additionally, AM's ability to create customized components unlocks opportunities for optimization strategies and mass-customization within building facades (Herrmann and Sobek 2016). This supports the production of facades and its individual components tailored to specific building locations, environmental conditions, usage needs and performance expectations.

Hence, by fostering a more tailored and contiguous approach to façade construction, AM with varying material properties holds substantial potential to enhance building facades and the construction process.

2.2. State-of-the-art Review

To achieve a varying composition of material properties in a 3D-printed component, multiple materials or varying material mixtures are employed in a single AM process (Gebhardt, Kessler, and Laura 2019; Gibson, Rosen, and Stucker 2010). However, the implementation of this approach in architecture and construction faces challenges, predominantly related to material compatibility and fabrication constraints such as print size and speed (Labonnote et al. 2016; Pajonk et al. 2022; Strauß 2013).

Previous research has explored both concrete and polymer materials for this approach. Concrete based research has focused on the variation of concrete mixtures, enabling modifications to the concrete's properties throughout the volume of the 3D-printed component. This ability introduced opportunities for optimization, such as reducing material consumption and component weight (Herrmann and Sobek 2016; Oxman, Keating, and Tsai 2011; Tay et al. 2022). Other studies combined the load-bearing capabilities of concrete material with thermal insulation properties by incorporating lightweight filler materials in the AM process (Ahmed et al. 2020; Craveiro et al. 2020; Dielemans et al. 2021; Duballet, Gosselin, and Roux 2015). However, the results of these studies are limited to concrete use in solid wall construction, and thus only provide a solution to a limited range of functions for a building façade.

Polymer-based AM research has focused on varying the material properties within thermosetting reactive polymers like silicon and polyurethane (Oxman, Keating, and Tsai 2011). However, these concepts are still in their early stage and require further development (Oxman, Tsai, and Firstenberg 2012).

Recent studies, on the other hand, have introduced novel techniques for AM with thermosetting polymers. These methods utilize polymers that avoid the need for subsequent UV-light curing, thereby broadening their potential application (Rios et al. 2018; Uitz et al. 2021). Furthermore, subsequent research by Uitz et al. demonstrated the capacity to integrate functional particles – specifically iron oxide – in a functionally graded manner thereby introducing shape memory properties into 3D-printed components (Uitz et al. 2023).

Alternative approaches that utilize thermoplastic polymers in Fused Filament Fabrication (FFF) have been investigated by Correa et al. and Teoh et al. (Correa et al. 2015; Teoh et al. 2017). Their research demonstrates the potential of AM with variable material properties for creating responsive components, such as sun shading devices for building facades. These examples show the benefits of component simplification and assembly reduction through the use of AM methods with varying material properties (Tibbits et al. 2014).

AM using biopolymers is another research focus (Duro-Royo et al. 2017). However, the relevance of these bio-based materials to building facades remains limited. Furthermore, persistent challenges in layering additional print layers further limit the application of this approach (Lee et al. 2020).

Research on Multimode AM offers a different approach, combining AM methods with manual assembly or additional manufacturing steps like milling (Bar-Sinai, Shaked, and Sprecher 2021; Mostafavi, Kemper, and Du 2019). This approach facilitates the combination of different materials, such as a raw material for the AM and preprocessed materials, thereby enabling the combination of materials and components that differ greatly from one another. However, the need for manual interventions and synchronization of multiple fabrication steps distinguishes this approach from the AM with varying material properties.

The state-of-the-art review reveals a currently limited range of materials suitable for use in AM with varying material properties, particularly in building façade applications. While early research into thermosetting reactive polymers shows promise, it requires further exploration. Nevertheless, new AM processes, such as the AM with thermosetting reactive polymers, present unprecedented opportunities for advancing this approach. Ultimately, these innovations could pave the way for broader adoption of AM with varying material properties in various construction applications, including building facades.

3. Framework for additive manufacturing with varying mixtures of thermosetting reactive polymers

To address the limitations discussed previously, this section presents a framework for the additive manufacturing with varying mixtures of thermosetting reactive polymers. This includes the material selection, hardware setup, and computational workflow that is essential for this process.

3.1. Material

The focus within this research was set on polyurethane, a thermosetting reactive polymer that can be tailored to a wide range of material properties through changing its chemical composition (Sonnenschein 2021; Uhlig 2006). This allows polyurethanes to be used in various facade applications including insulation panels when used as foamed plastic (Defonseka 2019, Hegger et al. 2006, Uhlig 2006), sealants and adhesives to seal and bond façade elements while providing a durable and weather-resistant seal (Hegger et al. 2006; Uhlig 2006), coatings for façade surfaces to enhance their durability and protect against UV radiation, weathering and corrosion (Hegger et al. 2006; Uhlig 2006,), expansion joints to facilitate movement of individual elements while maintaining a durable and weather-resistant joint (Hegger et al. 2006; Uhlig 2006), and also as structural elements such as window frames when combined with glass-fibres (Covestro 2021a; Cremers 2016).

Thermosetting reactive polymers are commonly used as two-component systems, where the chemical reaction is achieved by mixing the two basic components, typically referred to as component-A and component-B (Defonseka 2019). In this research, a two-component polyurethane system was used, comprising an isocyanate component (Covestro 2021b) and a polyol component (Covestro 2021c). In contrast to existing research (Rios et al. 2018; Uitz et al. 2021; Uitz et al. 2023), the framework developed in this research features the ability to change the chemical composition of the polyurethane and thus its material properties, by altering between differing polyol components of the polyurethane system.

The polyol components that were employed are Desmophen VP LS 2328 and Desmophen VP LS 2249/1. When combined with the isocyanate component, the use of each individual polyol results in different mechanical properties of the polyurethane. The use of Desmophen VP LS 2328 (flexible-cured polyurethane) results in a lower shore hardness of A60 with a lower tensile strength of 3.8 N/mm⊃2, while the use of Desmophen VP LS 2249/1 (hard-cured polyurethane) achieves a shore hardness of D70 with a higher tensile strength of 22.6 N/mm⊃2. As a consequence, their deformation behaviours differ significantly. The polyurethane based on VP LS 2328 demonstrates a greater ability to deform under applied forces, making it suitable for applications where spring-like characteristics are desired. On the other hand, the polyurethane based on VP LS 2249/1 exhibits higher resistance to deformation. Additionally, the employed polyurethane demonstrates high resistance to chemicals, weathering and UV radiation (Covestro 2021b).

To better distinguish the different polyurethane mixtures in a 3D-print, Desmophen VP LS 2328 was coloured pink and Desmophen VP LS 2249/1 was coloured blue. A more detailed description of the mechanical properties of the used polyurethanes can be found in Table 1. The values provided are based on the material data sheet for each respective polyurethane formulation provided by Covestro.

As previously reported on additive manufacturing with reactive polymers, fumed silica was added to the polyurethane stock components to increase the material's rheology for additive manufacturing (Lindahl et al. 2018; Uitz et al. 2021). For this, 7 wt% of Aerosil R812s was added to both, the isocyanate and polyol components.

The Shore hardness of the 3D-printed specimen was measured across the area of the specimen using a Shore-Durometer Type A and Type D. The measurements were conducted in reference to the EN ISO 868:2003 with the remark that the 3D-printed specimen did not fully meet the requirement of a completely flat surface area due to the inevitable resulting carvings on the top surface through the path-like routing of the 3D-printing method.

3.2. Hardware setup

The process of AM with thermosetting reactive polymers, also referred to as reactive extrusion additive manufacturing (Uitz et al. 2021), forms the starting point of the hardware setup. In this process, a thermosetting reactive two-component system is mixed and deposited using an extrusion head, capable of processing both components. Upon deposition, the mixture undergoes a chemical reaction to form the thermoset polymer, allowing for the addition of subsequent layers on the 3D-printed component (Rios et al. 2018; Uitz et al. 2021).

In this framework, an additional material metering unit has been implemented alongside the existing units. This introduced the ability to switch between different polyol components of the polyurethane mixture. As a result, this setup allows for the dynamic adjustment of the supplied polyol components during 3D-printing, and consequently, to change the chemical composition of the extruded polyurethane (Figure 1).

Table 1. Polyurethane materials and its properties used by the AM process.

Type	Trade name	Color	Tensile strength (N/mm⊃2)	Elongation at Break (%)	Tear strength (N/mm)	Shore hardness
Isocyanate	Desmodur N3600	Pink	3.8	78	5.6	Shore 60 A
Polyol	Desmophen VP LS 2328					
Isocyanate	Desmodur N3600	Blue	22.6	57	98.0	Shore 70 D
Polyol	Desmophen VP LS 2249/1					

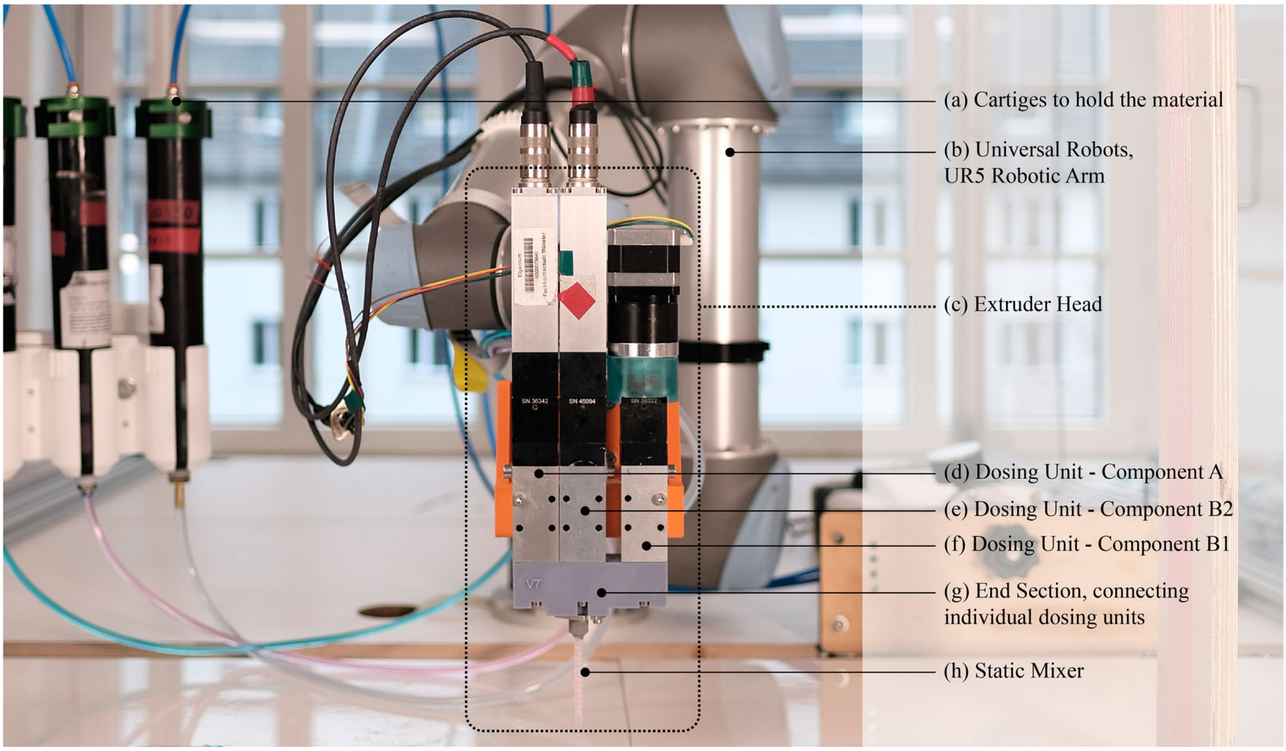

Figure 1. Image of the AM setup. The UR5 robotic arm (b), equipped with the modified extrusion head for thermoset reactive polymers (c), serves as a positioning platform for the additive manufacturing process, as it controls the movement of the extrusion head. The used materials are stored in cartages (a), next to the UR5 robotic arm.

An initial version of this setup was presented by the authors at the Built Environment Additive Manufacturing Symposium in 2021 (Pajonk 2021). Furthermore, a comparable concept for the additive manufacturing of reactive polymers was recently presented by Uitz et al. for the use of an epoxy resin with the ability to gradually introduce iron oxide to the mixture (Uitz et al. 2023).

The developed setup is based on a Viscotec vipro HEAD 5/5, an extrusion head (h. in Figure 2) that is capable of processing two-component thermosetting reactive polymers, such as epoxy resins, acrylate, silicone and polyurethanes. Unlike the original extrusion head, the modified version in this research featured three dosing units, with two of them merged into a single outlet for the polyol component of the two-component system (i. in Figure 2). The dosing units accurately metre out the required amount of material for each component which were then mixed together by a static mixer right before extrusion. The output speed of each dosing unit can be adjusted to control the mixing ratio between the individual components (k., l. and m. in Figure 2).

The individual components of the polyurethane system were stored in 360 cc cartridges, housed in metal sleeves that transported the material to the dosing units using pressurized air (e., f. and g. in Figure 2).

The extrusion head was attached to the end effector of a 6-axis Universal Robots UR5 robot arm (n. in Figure 2), providing precise control over the extrusion head's movement and enabling the creation of 3D-components.

The individual dosing units were controlled using the Arduino microcontroller, a small computer commonly used for prototyping projects. Three stepper motor drivers, which control the movement of the motors of the dosing units, were utilized in conjunction with one Arduino microcontroller each. The combination of these components formed the secondary controller (c. in Figure 2).

Commands for the robot arm movement, extrusion process and material dosing were combined in a single robot program written in the UR Script programming language. The main controller of the robot arm (b. in Figure 2) received the program commands and forwarded them to the robot arm and to the secondary controller using digital output commands. The secondary controller received the commands through its digital inputs, allowing for control of the individual dosing units. This setup ensures precise synchronization between the robot arm movement and the extrusion process.

3.3. Computational system

The construction of a 3D-component by additive manufacturing is done layer-by-layer. Therefore, the component to be printed must be described in layer-by-layer, which means that the 3D-model of the component (Figure 3a) is decomposed into several slices (Figure 3c) that reassemble the same 3D-shape. These slices are then translated in the printing path (Figure 3d) that the extruder has to follow to print the whole shape in a layer-by-layer fashion. As a result of this procedure, a material transition can be implemented by assigning different material information to each single printing path.

To accommodate the ability to fabricate components with varying material compositions, a computational system was developed in the Computer-Aided Design (CAD) software Rhino-3D in conjunction with the graphic algorithm editor Grasshopper. The system was designed to translate CAD geometries that

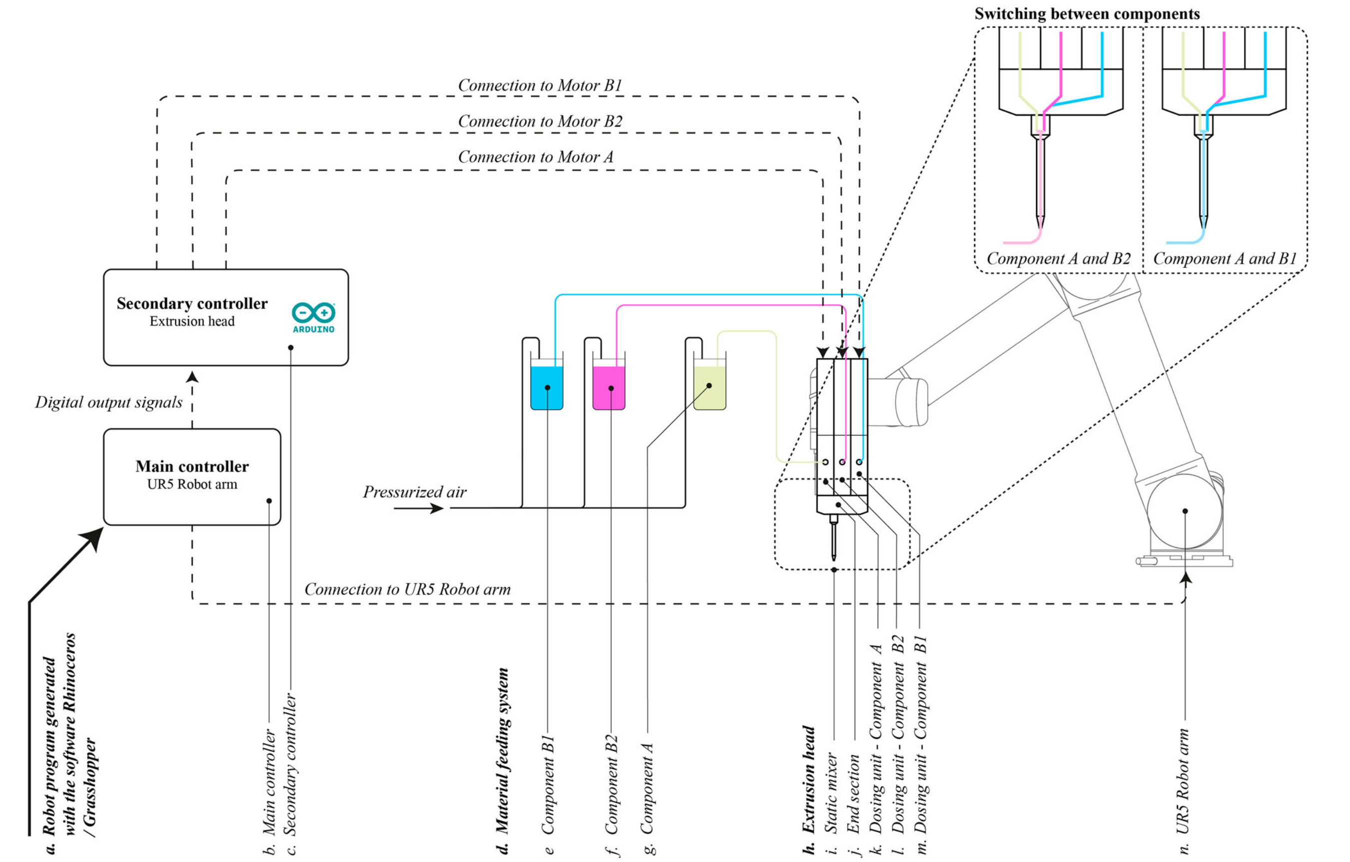

Figure 2. Schematic diagram of a setup for AM with varying material properties utilizing three dosing units (k–m) that can be switched individually. The robot programme (a), written in the UR script language, provides fabrication instructions for the UR5 robotic arm controller (b) which controls the robot arm movement along with instructions for the extrusion head (h). The controllers communicate via digital input/output signals, which are transmitted from the main controller (b) to the secondary controller (c). The secondary controller (c), regulates the motors of the dosing units. The individual cartridges (e–g) hold the materials, which are fed through pressurized air to the extrusion head (h).

reassemble the to be printed 3D-component into a printing path for the extrusion head that also contains material information. The geometries were prior designed in a CAD environment and represent a contiguous 3D-component consisting of several individual surfaces or poly-surfaces (multiple surfaces that are connected) (Figure 3a). Furthermore, the individual surface elements are representative of individual material properties within the overall component (Figure 3b).

The input surface geometries were sliced into layers for additive manufacturing, with each surface geometry corresponding to an individual printing path within a respective layer (Figure 3c). Hereby, each surface geometry is rendered into a single printing path that defines the 3D-printed segment within a single layer (Figure 3d). The printing path itself defines the waypoints for the robotic arm. A waypoint is a specific position in space that the robot arm is programmed to move to. Multiple waypoints can be used to form a path for the robot arm to follow. The generated waypoints included, the start and end point of the segment and if necessary additional points that are located in between to further reflect the intended geometry. Furthermore, waypoints that are elevated from the start and end points were added to allow for the travel of the extrusion head without potential collision with already 3D-printed parts. In addition to the waypoints, a command for material feed which defines the specific material mixture was added for each printing path, in combination with a command for the extrusion start and stop. Finally, the resulting printing paths for each layer were sorted, according to their individual material mixture, so that all paths of a specific mixture can be printed one after the other.

After generating the printing paths, the program was compiled into UR Script language using the Scorpion Grasshopper plug-in. The robot program was sent to the robot arm's main controller over a local area network via an Ethernet interface.

4. Results

4.1. Fabricating components with varying material properties

Following the framework outlined in the previous section, an initial specimen was fabricated using both polyurethane mixtures. The resulting specimen had the dimensions of 120 mm x 70 mm x 4.5 mm, and was created from a series of parallel surfaces spaced at a distance of 1.9 mm from each other. A total of five layers were deposited, each with a layer height of 0.9 mm.

The transition from the hard-cured polyurethane to the flexible-cured polyurethane was initiated after a first segment of the specimen which corresponds to a path length of 864.7 mm for each layer and was 3D-printed with the hard-cured polyurethane. The remaining path length of 1669.4 mm of each layer was used for the transition from the hard-cured polyurethane to the flexible-cured polyurethane and for a segment where the flexible-cured polyurethane was applied. This

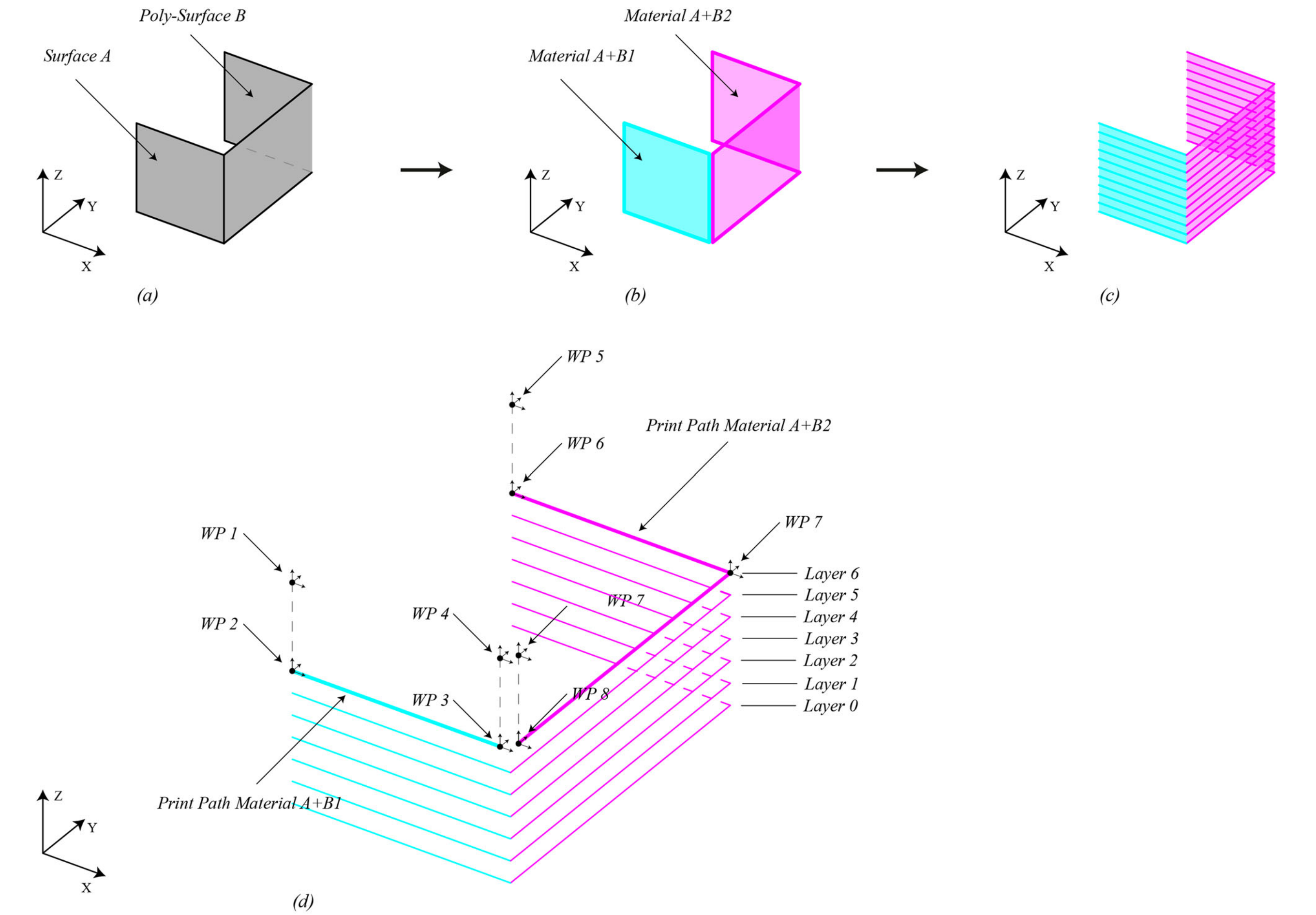

Figure 3. Diagram showing the orientation of a 3D-model in *x, y* and *z*, and the steps required to generate the printing path: (a) the 3D-model, (b) material allocation to the individual surface elements (c) the sliced model into multiple layers and (d) the printing paths of one layer with its waypoints for the robot arm movement: (WP1) elevated start point of printing path material A + B1; (WP2) start point of printing path and command for starting the extrusion; (WP3) end point of printing path and command for stopping the extrusion; (WP4) elevated end point of printing path material A + B1; (WP5) elevated start point of printing path material A + B2; (WP6) start point of printing path and command for starting the extrusion; (WP7) additional waypoint, (WP8) end point and command for stopping the extrusion (WP9), elevated end point of printing path material A + B2.

Table 2. Process parameters used for creating functionally graded polyurethane.

Process variable	Value	Unit
Print Speed	11	mm/s
Travel Speed	300	mm/s
Acceleration	100	mm/s⊃2
Nozzle Diameter	0.8	mm
Layer Height	0.9	mm
Material Flow Rate Hard	1.20	ml/min

procedure was repeated for each layer of the 3D-printed component. The process parameters used to fabricate the specimen are documented in Table 2, the used material mixtures and their mechanical properties are documented in Table 1.

Figure 4 shows the differing shore-hardness properties measured from the 3D-printed specimen. The area where Desmophen 2328 polyol was applied resulted in an average Shore A hardness of 73.6 A. The area where Desmophen 2249/1 was applied resulted in an average Shore D hardness of 67.9 D. Due to the relatively short transition between both polyol components, no shore hardness measurements could be made in this zone.

As already reported by Oxman, Tsai, and Firstenberg (2012) and Uitz et al. (2023) the use of a static mixer inevitably causes a lag in the switched material mixture, from the moment a change in the material mixture is triggered to the extrusion of the altered material. This delay results from the fact that the new material must first displace the material still present in the inlets to the static mixer and the static mixer nozzle.

Furthermore, the 3D-printed specimen shows that the change between the two polyol components takes place in a gradual manner along the print path. It is important to note that the different polyol components that were used require different mixing ratios of the polyol component and the isocyanate component. As a result, to avoid insufficient reaction between the components of the polyurethane system due to an inaccurate mixing ration it is necessary to displace the prior mixture and introduce a sharp transition between individual mixtures. Ultimately leading to a sharp interface between the different polyurethane mixtures.

4.2. Material change procedure

To further refine the AM process and enable sharp transitions between different polyurethane mixtures, it was crucial to understand the discharge process in detail. This led to a test,

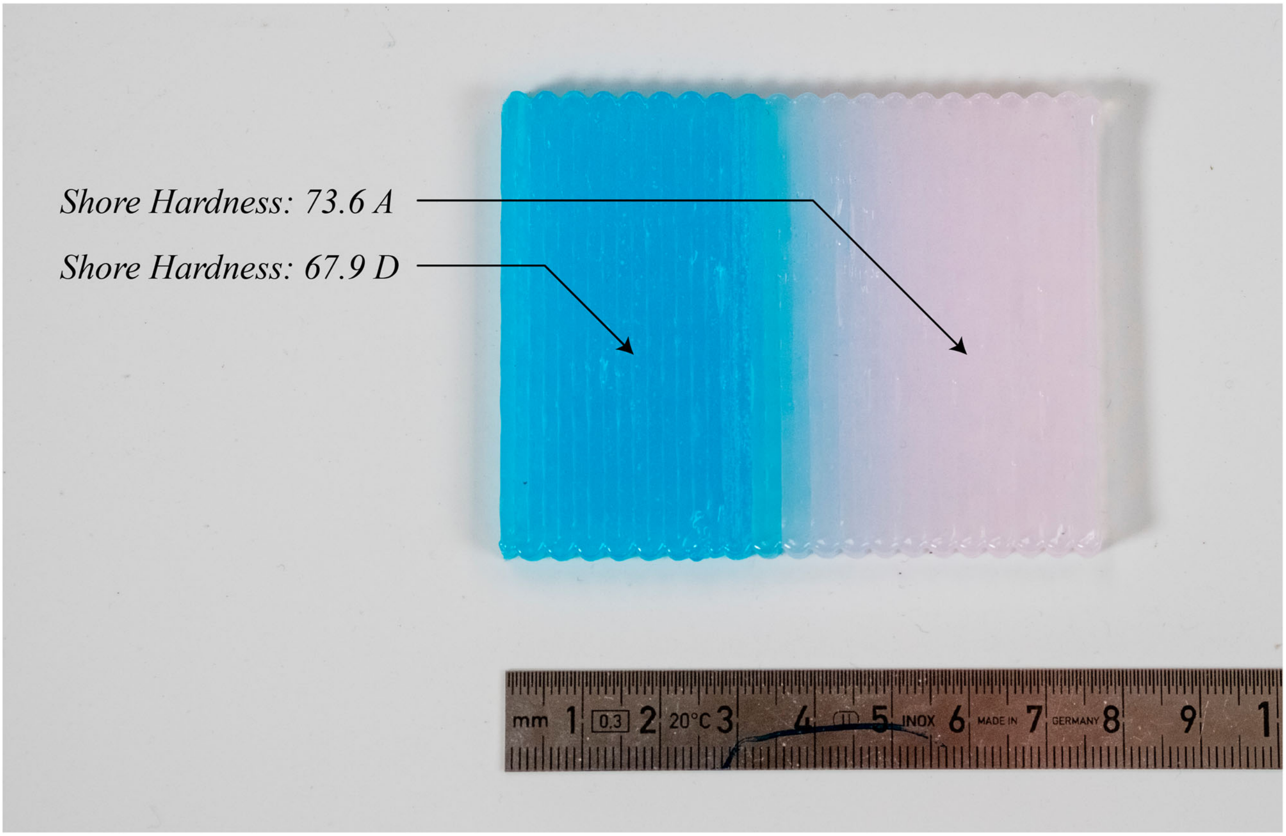

Figure 4. Image of a 3D-printed geometry exhibiting both polyurethane mixtures. The hard-cured polyurethane had a Shore Hardness of 67.9 D and the flexible-cured polyurethane a Shore Hardness of 73.6 A.

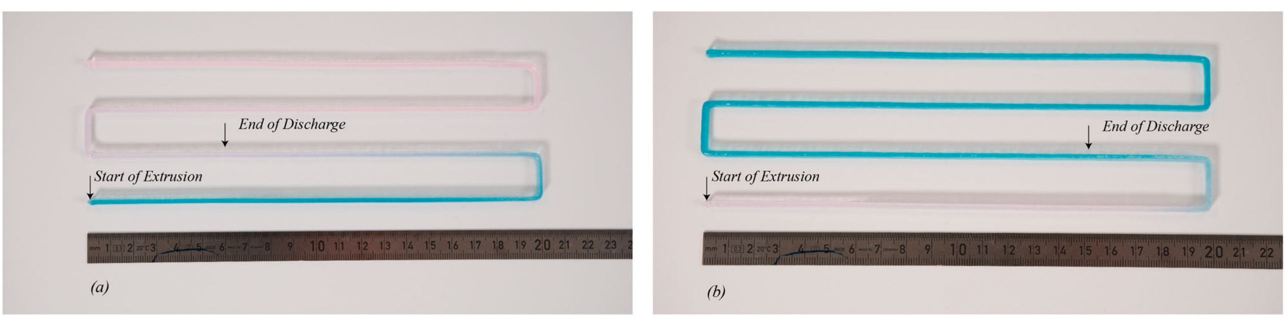

Figure 5. Image of the 3D-printed line for determining the amount of discharge needed: (a) transition from the hard-cured polyol to the flexible-cured polyol, (b) transition from the flexible-cured polyol to the hard-cured polyol.

conducted to measure the total amount of material that needed to be discharged. This test was carried out by printing a single line with a material transition along the printing path (Figure 5). Before starting the 3D-printing, the extruder head and mixer nozzle was prefilled with the hard-cured polyol and isocyanate components. The signal to initiate the material change to the flexible-cured polyol was set at the start of the printing path, enabling to measure the distance from the start of the 3D-print to the point where the material transition was visually completed. Throughout the transition period, the mixing ratio for the hard-cured polyol was maintained. The same procedure was repeated with the flexible-cured polyol and its relating mixing ratio. Based on the measured distance, the estimated discharge time and amount of discharge material was calculated.

The process parameters used for these tests are documented in Table 2. Table 3 shows the measured distances, the resulting amount of material that is required to be discharged and the resulting time expenditure that is required for the discharge process. Based on the determined results of material quantity and time expenditure for the discharge process, utilizing different material compositions in a single 3D-print is expected to have a negative effect on the overall 3D-printing time and amount of waste material that is generated.

Table 3. Determined material quantity and time expenditure for the discharge procedure of the polyurethane mixtures.

Discharge procedure	Length for discharge (mm)	Discharge material (g)	Discharge time (s)
Desmophen 2249/1 to 2328	360	0.74	33
Desmophen 2328 to 2249/1	270	0.55	25

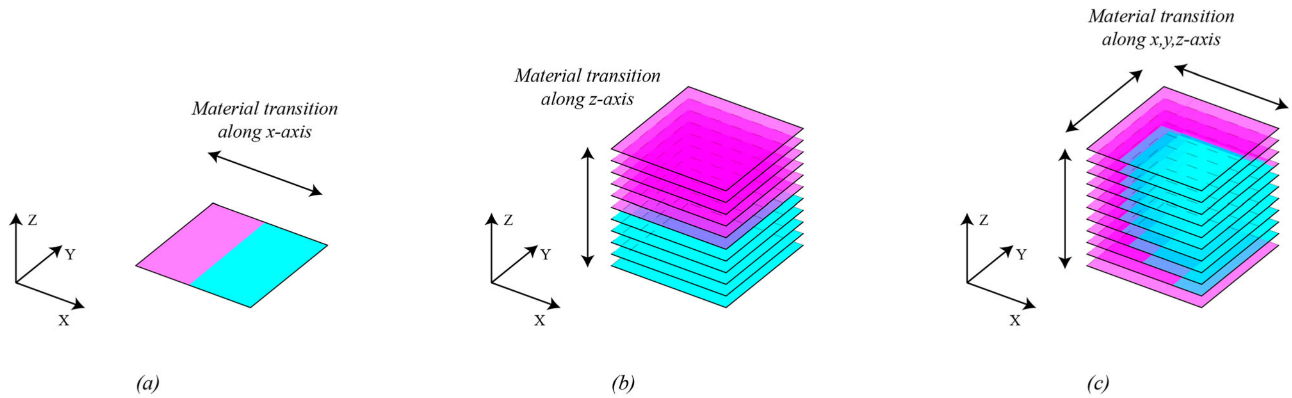

Figure 6. Diagram of material transition modes: (a) horizontal, (b) vertical, (c) multi-plane.

4.3. Comparison between different modes for material transition

To further explore the ability to incorporating material transitions, this research investigated different modes of transitions in a 3D-printed component.

In the developed computational system, different material mixtures were represented by individual surface geometries from which individual printing paths with their respective material information originated. This process allows for creating material transitions by placing surface geometries representing different materials next to each other. As a result, three different modes for material transitions could be employed in the 3D-printed component: horizontal transitions, vertical transitions and multi-plane transitions.

Figure 6 shows a schematic representing the different modes in which material transitions can be defined and the respective surface models employed in this research. In the horizontal mode, a material transition occurs within a single layer across multiple printing paths in the x-y plane (Figure 6a). The vertical mode, on the other hand, involves a material transition between individual print layers in the z-direction (Figure 6b). The third mode, multi-plane, combines both horizontal and vertical approaches (Figure 6c).

To demonstrate the modes and evaluate the resulting material waste and time expenditure, three specimens were fabricated, each representing a different mode. Each specimen followed the same geometry, but differed in how different materials were assigned to the geometry. The geometry and their parameters are documented in Figure 7a. The 3D-printed specimen and their respective printing paths are documented in Figure 7b–e. The material discharged for each specimen was collected and measured after the 3D-printing. The printing time was measured through an implemented function in the secondary controller. Regardless of whether the flexible-cured polyurethane was changed to the hard-cured polyurethane or vice versa, the discharge time was set to 33 s, which is the time relevant for the discharge of the hard-cured polyurethane to the flexible-cured. In addition to the three models, a reference model of the same geometry was produced from only one material mixture.

Table 4 summaries the results of the printed specimen and illustrates the relationship between the number of material transitions and the additional time expenditure and material discharge. The results clarify that the way in which different materials are arranged in the component in relation to the layer direction of the 3D-printing had an influence on the frequency of the material transitions and thus the discharged material quantity and time expenditure. However, it should be noted that the expected time expenditure can be reduced by further optimizing the applied discharge speed. The discharged material quantity on the other hand, is bound to the size of the static mixer and material inlets. Based on the results an average discharge time of 46 s for each discharge and an average discharge amount of 0.74 g was measured.

For testing purposes, this effect was scaled down to a small sized object, however the results can be extrapolated to larger objects. It should also be noted that scaling the to be printed component will also alter the ratio of printed material to discharged material as well as the ratio of printing time to time spend for the material discharge procedure.

To further illustrate the effect a specific mode can have in regard to the total print time and waste material, a simplified profile geometry with a total length of 1000 mm and a cross-section that is composed of both polyurethane mixtures was introduced. This example serves as a theoretical and illustrative case, to further enlighten the potential implications of different modes on both aspects, especially when scaled to larger components.

The amount of material discharge and time for this geometry was estimated in both, a horizontal, and vertical orientation of the geometry. As a result, the vertical orientation resulted in a total of 1111 layers with a layer height of 0.9 each. Furthermore, in this orientation a material transition takes place in each single layer, resulting in a total number of 2221 of discharge procedures. In contrast to this, the horizontal orientation resulted in a total layer count of 67 layers with a similar layer height. In this orientation however, a material transition only takes place once. In comparison, the 3D-print of this component in a vertical orientation would require an estimated addition print time of 28 h 22 min 46 s over 46 s for the horizontal orientation. In terms of discharged material, the vertical orientation would require an additional amount of 1643.53 g of material, compared to 0.74 g for the horizontal orientation. Figure 8 illustrates the investigated geometry, its parameters and displays both orientations.

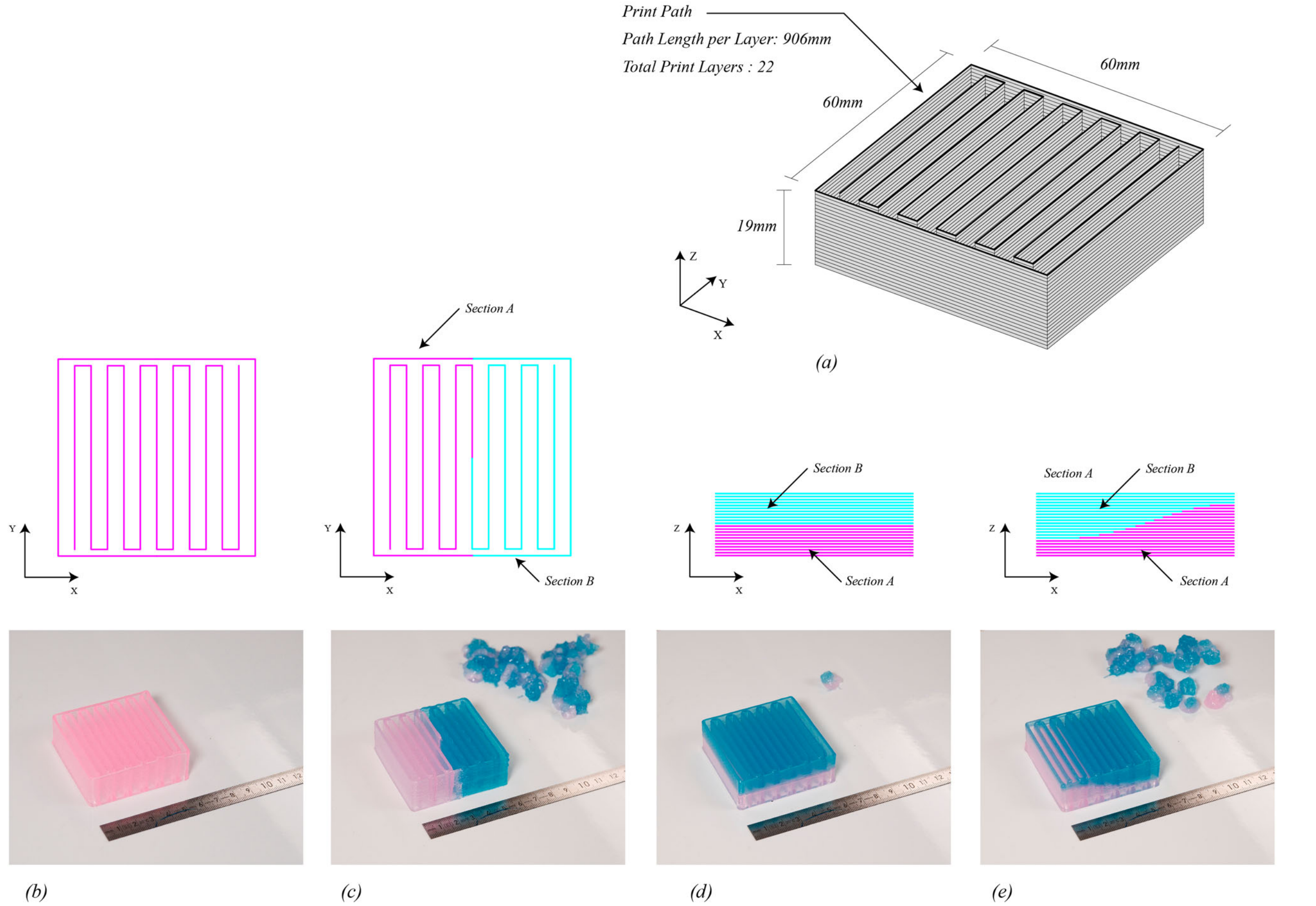

Figure 7. Image and diagram of the 3D-printed specimen. (a) displays the overall geometry and their parameters, (b) no transition, (c) horizontal transition, (d) vertical transition, (e) multi-plane transition.

Table 4. Measured material quantity and time expenditure for the discharge procedure for different transition modes.

Transition mode	Specimen weight (g)	Number of material discharges	Print time (s)	Discharge material (G)	Estimated discharge time (s)
Horizontal	39.9	43	4139	30.9	2090
Vertical	39.2	1	2094	0,7	45
Multi plane	39.7	25	3186	18.7	1137
No transition	39.6	0	2049	0	0

5. Discussion

Our research introduces a comprehensive framework for the AM with variable mixtures of a thermosetting reactive polymer, specifically a polyurethane. This approach offers promising solutions to the existing challenges in the realm of AM by combining the ability to manipulate the material properties of a thermosetting reactive polymer with the process of AM. In this discussion, we will further explore the potential of this approach in terms of its applicability to facades and scaling for façade construction.

5.1. Material, properties and potential applications

The ability of thermosetting reactive polymers to change their material properties through changing their chemical composition is a key feature utilized in this research. Based on the specified material properties of the employed polyurethane system (see Section 3.1 – Material), the presented approach can be used to create components that exhibit both, areas of flexibility and areas that exhibit a high tensile strength and resistance to deformation. Leveraging these distinct material properties, this approach allows for the production of tailored designs that integrate flexibility and tensile strength in a single component. In contrast to prior research (see section 2) this approach introduces thermoset reactive polymers, particularly polyurethane, to the AM with varying material properties.

Within the context of building façades, material transitions between both material properties can be used to incorporate various elements directly into components such as frames, profiles and single or multi-wall sheets. For instance, gaskets and weather-resistant sealings can be incorporated by transitioning from the hard-cured to the flexible-cured polyurethane at the component's interfaces. Similarly, expansion joints, designed as segments 3D-printed with the flexible-cured polyurethane, can be embedded into larger components to mitigate thermal expansion. Additionally, these transitions facilitate the

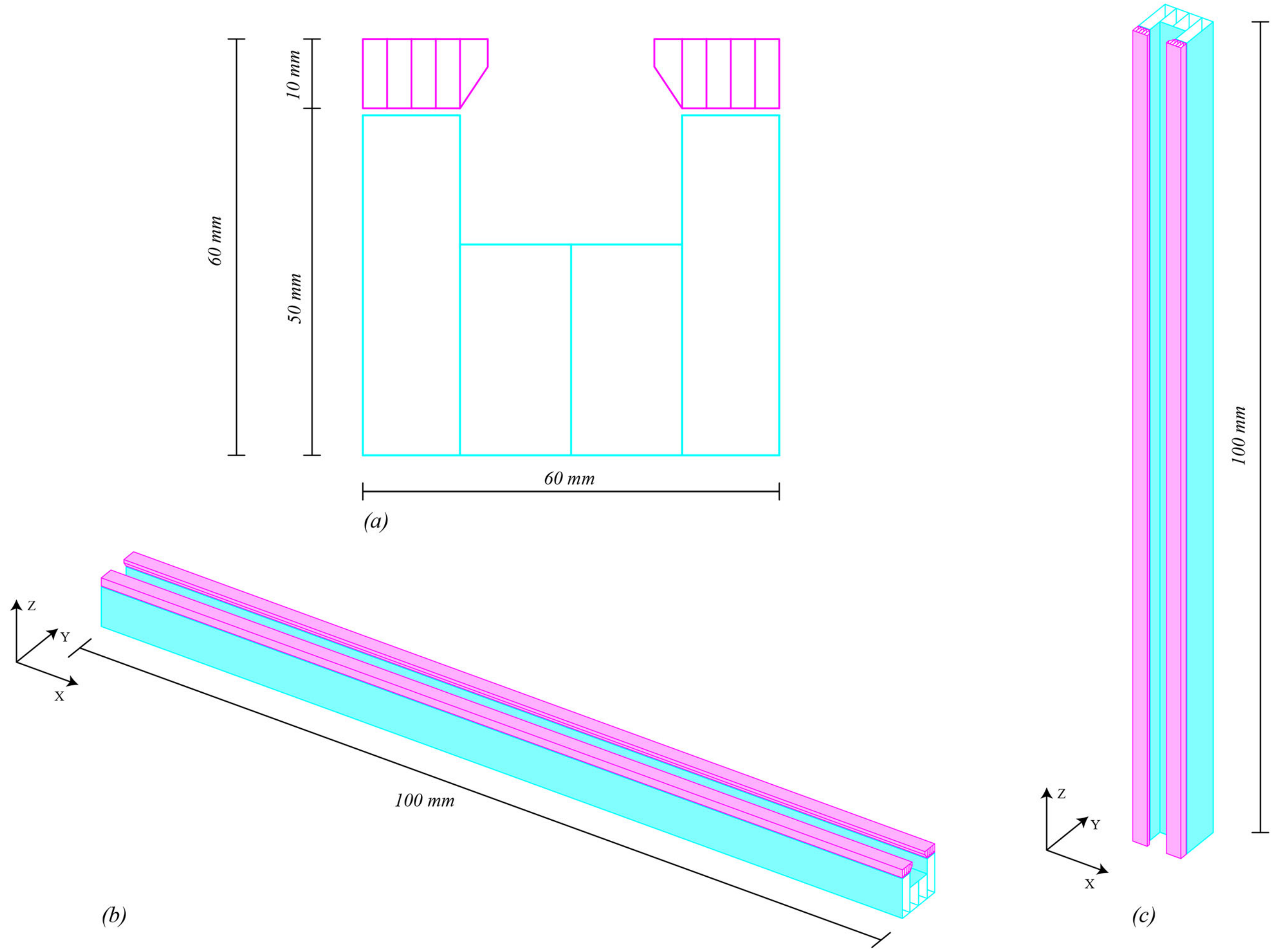

Figure 8. Diagram of the profile geometry used for illustrating the effect of material discharge. (a) diagram of the simplified profile geometry, (b) horizontal orientation of the profile geometry, (c) vertical orientation of the profile geometry.

introduction of intricate designs, from integrated spring-like mechanisms to acoustic decoupling connections, simplifying installation and removal procedures or enhancing the acoustic insulation of façade components.

However, it should be noted that the polyurethane used in this research has a lower tensile strength than comparable materials, such as polyvinyl chloride (PVC), which typically has a tensile strength of 41–65 N/mm⊃2 (Ashby 2021). Despite this, implementing additional measures – like using a greater wall thickness during fabrication – could allow for the production of more demanding structural components, such as window frames. Additionally, to fully exploit the potential of this technology, future research could focus on enhancing the chemical formulation of the polyurethane to increase its tensile strength. Furthermore, this research only focused on altering the tensile strength and shore hardness of the polyurethane. Future research could also focus on other material properties such as the density of the polyurethane. Ultimately, expanding further the range of obtainable material properties with this approach.

Furthermore, thermoset reactive polymers, including polyurethane, are often viewed as challenging to recycle. While recent advances have ushered in industrial-scale recycling processes for polyurethane, these methods have still limitations in terms of material compatibility and energy consumption (Fonseca et al. 2023; Sabu et al. 2018; Simón et al. 2018; Zia, Bhatti, and Bhatti 2007). Biodegradation offers a promising alternative to address polyurethane waste concerns. The ongoing advancements in creating recyclable polyurethanes offer a positive perspective on future waste management strategies (Cregut et al. 2013; Tai et al. 2021). Furthermore, given polyurethane's widespread use across multiple industries, there is a compelling incentive to accelerate developments in its recycling ability and waste management. While acknowledging the challenges surrounding the recyclability of polyurethanes, its unique material characteristics, as demonstrated in this research, offers distinct advantages for AM.

5.2. Build volume

In the domain of building facades, the capacity to manufacture components of relevant size is a significant determinant of a technology's applicability. The framework presented in this research is independent of the scale of fabrication, with the achievable size of components being determined by the manipulator used to control the AM process. One advantage of this AM process is its flexibility, as it does not require any specific build platform or build chamber. This opens up the possibility to employ larger manipulators, such as gantry systems or robotic arms, capable of operating in larger build spaces. In the setup utilized in this research, a robotic arm with an 850 mm reach was employed. Furthermore, previous research on AM with thermoset reactive polymers has shown even larger-scale implementations, such as using a robotic arm with a horizontal reach of 2000 mm (Uitz et al. 2023).

5.3. 3D-Printing time and material waste

Efficiency in terms of time and material usage is an important aspect in any manufacturing process, even more so when it comes to the manufacturing of large components for the building facade. The duration of 3D-printing a component can be influenced by adjusting the factors of layer height and printing speed.

The setup used in this research employed a layer height of 0.9 mm and a material flow rate of 1.2 ml/min. In contrast, comparable research by Uitz et al. utilized a larger layer height of 2.5 mm and a significantly higher flow rate of 102 ml/min (Uitz et al. 2021). This comparison illustrates the potential range for adjusting these parameters in the AM process to reduce printing time. However, increasing layer heights may compromise the level of detail in the printed component, making it unsuitable in certain cases.

The speed of 3D-printing is constrained by both the maximum speed of the manipulator in use and the corresponding material flow rate that can be sustained. The movement speed for our printing process was set to 11 mm/s while the maximum speed of a UR5 robot can go up to 1000 mm/s. The extruder head was adjusted to a material flow rate of 1.20 ml/min, but each individual dosing unit of the extruder head could theoretically achieve up to 6 ml/min. More impressively, Uitz et al. demonstrated the feasibility of achieving material flow rates as high as 102 ml/min with a different setup. However, this research did not focus on optimizing the print speed but rather provides a basis for further enhancements. Therefore, future research should focus on increasing the movement speed of the manipulator and optimizing the corresponding material flow rates in order to make this approach more feasible for application in building façades.

For reference, Taseva et al. (2020) demonstrated the successful use of the Fused Filament Fabrication AM process to manufacture façade panels with homogeneous material properties, showcasing the potential for application of these AM processes in the building façade domain. They achieved the printing of a façade panel with a height of 3000 mm and a width of 1300 mm using a layer height of 1 mm and a print speed of up to 25 mm/s.

5.4. Material transition modes in building façades

The research presented in this paper underlines the significant role of material transition strategies in the process of 3D-printing components with varying material properties. It presents three different modes for introducing a material transition and the specific impact each of these modes can have on print time and material consumption. While these transitions are integral to the presented framework, they do introduce an additional expenditure of time and material, posing a challenge for efficiency and sustainability.

Furthermore, the design and/or orientation of a 3D-printed component thus influences the overall printing speed and degree of material waste. By carefully considering how different material properties are utilized in a design, as well as the orientation of the component in the 3D-print, the effects of these transitions can be mitigated. This awareness forms a critical guideline for designers working with the framework presented in this research. Despite this constraint, optimizing the material discharge procedure will reduce the time required for each transition, lessening the impact on the overall 3D-printing time. While each transition mode has its implications for printing efficiency, their capability to transition between differing material properties brings unique advantages to the design of a façade component.

5.4.1. Horizontal transitions

Horizontal Transitions offer the capability of merging adjacent functional layers in façade component. This allows architects and façade builders to address varied façade requirements through a single manufacturing process. Specifically, the investigated framework enables the combination of a rigid structure alongside more flexible areas. Such a configuration can meet the specific aesthetic or tactile demands of a building façade (Hegger et al. 2006; Herrmann et al. 2015). Another potential application is the inclusion of flexible-cured polyurethane sections within predominantly rigid components, such as single or multi-wall sheets. This could potentially ease the high thermal expansion of such components in building facades (Knippers et al. 2011).

While the utilized polyurethane materials offer considerable versatility, broadening the spectrum of material properties might expand this approach to even more façade functionalities.

The conducted printing test demonstrated that a sharp transition between two material properties could be achieved in an additive manufacturing setting. However, one key observation was the necessity for frequent material discharge due to the use of both material properties in each print layer (refer to section 4.3 for details). This makes horizontal transitions particularly suitable for components with a large cross-section. In this case, the additional material and time expenditure for the required material discharge, remain relatively minimal in contrast to the entire printing process.

5.4.2. Vertical transitions

Vertical transitions allow adaptability by varying materials from one layer to the next. This mode enables a vertical alteration in a façade component's material properties. While it shares similarities to horizontal transitions in enabling flexible sections, the orientation here is vertical. A key advantage of vertical transitions lies in their ability to produce an uninterrupted and smooth interface at the component's final layers, made with a differing material to the preceding layers. Transitioning from a hard-cured polyurethane to a flexible-cured polyurethane might enable to integrate a sealing interface. This capability can enhance a component's compatibility with other façade elements, which is a frequent design task in polymer sheet cladding design (Knippers et al. 2011).

The conducted printing test confirmed the feasibility of achieving a sharp transition between both material properties, in a vertical orientation. A notable observation was the necessity for just a single material discharge, minimizing the discharge process's impact (refer to section 4.3 for details).

5.4.3. Multi-plane transitions

Multi-plane transitions leverage the full potential of 3D-printing by enabling spatial variation in material properties across all dimensions of a component. By incorporating features of both horizontal and vertical transitions, this mode offers an increased degree of design freedom.

These transitions not only pave the way for intricate designs and the creation of complex geometries with varied material properties, but also presents promising applications for building façades. A key potential lies in integrating non-assembly mechanisms (Lussenburg, Sakes, and Breedveld 2021). These mechanisms have to potential to reduce assembly efforts during manufacturing and construction by integrating or enhancing connection mechanisms.

Preliminary findings, presented by the authors at the BE-AM Symposium, have showcased the potential of multi-plane transitions. These findings include the creation of a series of non-assembly mechanism using multi-plane transitions between a hard-cured and a flexible-cured polyurethane (Pajonk et al. 2022).

The printing test successfully demonstrated material transition across multiple planes, encompassing both vertical and horizontal variations. However, it is important to note that the extend of additional print time and material usage depends on the specifics of each 3D-print and its number of required discharges. Furthermore, as exemplified with the illustrative case of a simplified profile geometry, not only the design and therewith the implementation of material transitions, but also the components orientation during the 3D-print can have a significant effect on print time and additional material usage.

While these tests highlight the capability to modify material properties along various axes, the applicability of this mode in façade components will become clearer through specific use-case implementations.

6. Conclusion

This research has presented a comprehensive framework for AM with varying material properties using a thermosetting reactive polymer, specifically polyurethane. The focus was set on the variation in tensile strength and shore hardness of the employed polyurethane. This approach enables the fabrication of components with varying material properties throughout the components volume, exhibiting areas of flexibility and rigidity.

However, the research also identifies that incorporating multiple material mixtures in a single 3D-print tends to increase both the printing time and the amount of waste material, due to the need for discharging residual material.

A secondary focus of this research was exploring different modes for material transitions, namely horizontal, vertical and multi-plane transitions. The findings reveal that the chosen mode of transition influences the frequency of material changes, and ultimately impacts waste and time expenditure.

Future research should aim to enhance the range of obtainable material properties, improve overall printing speed and optimize the discharge procedure. Since this research could only implement sharp transitions between individual mixtures, future research should also explore achieving stepwise transitions.

Beyond these technical improvements, future research should also investigate practical applications of this method. Establishing tangible use cases, especially in the context of façade construction, is essential to comprehend the real-world implications and potential of this novel approach.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This paper is part of an ongoing PhD research project, funded through the University of Applied Sciences Muenster (FH Muenster) and developed within the Architectural Facades & Products Research Group (AF&P) of the Department of Architectural Engineering + Technology, Delft University of Technology (TU Delft) and the Department of Digital Design and Construction, Muenster University of Applied Sciences (FH Muenster).

Data availability statement

The data that supports the findings of this study are available from the corresponding author, A.P., upon reasonable request.

ORCID

Adam Pajonk http://orcid.org/0000-0002-4182-0414
Alessandra Luna-Navarro http://orcid.org/0000-0003-0183-0199
Ulrich Knaack http://orcid.org/0000-0001-9998-6428
Ulrich Blum http://orcid.org/0000-0003-1005-593X

References

Ahmed, Z. Y., F. P. Bos, M. C. A. J. Van Brunschot, and T. A. Salet. 2020. "On-demand Additive Manufacturing of Functionally Graded Concrete." *Virtual and Physical Prototyping* 15 (2): 194–210. https://doi.org/10.1080/17452759.2019.1709009.

Ashby, Mike. 2021. "Material Property Data for Engineering Materials." Accessed 4 August 2023. https://www.ansys.com/academic/educators/education-resources/booklet-material-property-data-for-engineering-materials.

Bar-Sinai, K. L., T. Shaked, and A. Sprecher. 2021. "Robotic Tools, Native Matter: Workflow and Methods for Geomaterial Reconstitution Using Additive Manufacturing." *Architectural Science Review* 64 (6): 490–503. https://doi.org/10.1080/00038628.2021.1898324.

Camacho, D., P. Clayton, W. O'Brien, C. Seepersad, M. Juenger, R. Ferron, and S. Salamone. 2018. "Applications of Additive Manufacturing in the Construction Industry - A Forward-Looking Review." *Automation in Construction* 89 (2018): 110–119. https://doi.org/10.1016/j.autcon.2017.12.031.

Correa, D., A. Papadopoulou, C. Guberan, N. Jhaveri, S. Reichert, A. Menges, and S. Tibbits. 2015. "3D-Printed Wood: Programming Hygroscopic Material Transformations." *3D Printing and Additive Manufacturing* 2 (3): 106–116. https://doi.org/10.1089/3dp.2015.0022.

Covestro, A. G. 2021a. "Innovative PU Resins for Pultrusion Enable High Productivity For Composite Parts." Accessed 4 August 2023. https://solutions.covestro.com/en/highlights/articles/theme/processing-technology/pupultrusiontechnology.

Covestro, A. G. 2021b. "Desmodur: For Quality Coatings, Adhesives and PU Foams." Accessed 30 January 2023. https://solutions.covestro.com/en/brands/desmodur.

Covestro, A. G. 2021c. "Desmophen: Versatile Polyols for Wide Array of PU Coatings, Adhesives and Foams." Accessed 30 January .2023. https://solutions.covestro.com/en/brands/desmophen.

Craveiro, F., S. Nazarian, H. Bartolo, P. Bartolo, and J. Duarte. 2020. "An Automated System for 3D Printing Functionally Graded Concrete-Based Materials." *Additive Manufacturing* 33 (2020), https://doi.org/10.1016/j.addma.2020.101146.

Cregut, M., M. Bedas, M.-J. Durand, and G. Thouand. 2013. "New Insights Into Polyurethane Biodegradation and Realistic Prospects for the Development of a Sustainable Waste Recycling Process." *Biotechnology Advances* 31 (8): 1634–1647. https://doi.org/10.1016/j.biotechadv.2013.08.011.

Cremers, J. 2016. *Building Openings Construction Manual*. Munich: Detail.

Defonseka, C. 2019. *Two-Coponent Polyurethane Systems*. Berlin: Walter de Gruyter GmbH.

Dielemans, G., D. Briels, F. Jaugstetter, K. Henke, and K. Dörfler. 2021. "Additive Manufacturing of Thermally Enhanced Lightweight Concrete Wall Elements with Closed Cellular Structures." *Journal of Façade Design and Engineering* 9 (1): 59–72. https://doi.org/10.7480/jfde.2021.1.5418.

Duballet, R., C. Gosselin, and P. Roux. 2015. "Additive Manufacturing and Multi-Objective Optimization of Graded Polystyrene Aggregate Concrete Structures." In *Modelling Behaviour*, edited by M. Thomsen, M. Tamke, C. Gengnagel, B. Faircloth, and F. Scheurer, 225–235. Cham: Springer. https://doi.org/10.1007/978-3-319-24208-8_19

Duro-Royo, J., J. Van Zak, Y. J. Tai, A. S. Ling, and N. Oxman. 2017. "Parametric Chemistry Reverse Engineering Biomaterial Composites for Additive Manufacturing of bio-Cement Structures Across Scales." *Challenges for Technology Innovation* 217 (223): 217–223. https://doi.org/10.1089/3dp.2015.0022.

Excell, J. 2013. "The Rise of Multi-Material 3D Printing." Accessed 11 October 2022. https://www.theengineer.co.uk/the-rise-of-multi-material-3d-printing/.

Fonseca, L. P., A. Duval, E. Luna, M. Ximenis, S. de Meester, L. Avérous, and H. Sardon. 2023. "Reducing the Carbon Footprint of Polyurethanes by Chemical and Biological Depolymerization: Fact or Fiction?" *Current Opinion in Green and Sustainaible Chemistry* 41 (2023), https://doi.org/10.1016/j.cogsc.2023.100802.

Gebhardt, A., J. Kessler, and T. Laura. 2019. *3D Printing: Understanding Additive Manufacturing*. Munich: Carl Hanser Verlag.

Gibson, I., D. Rosen, and B. Stucker. 2010. *Additive Manufacturing Technologies, Rapid Prototyping to Direct Digital Manufacturing*. New York: Springer.

Grigoriadis, K. 2015. "Material Fusion: A Research Into the Simulated Blending of Materials Using Particle Systems." *International Journal of Architectural Computing* 3 + 4 (13): 335–352. https://doi.org/10.1260/1478-0771.13.3-4.335.

Hegger, M., V. Auch-Schwelk, M. Fuchs, and T. Rosenkranz. 2006. *Construction Materials Manual*. Munich: Detail.

Herrmann, E. M., M. Krammer, J. Sturm, and S. Wartzeck. 2015. *Enclose | Build*. Basel: Birkhäuser.

Herrmann, M., and W. Sobek. 2016. "Functionally Graded Concrete: Numerical Design Methods and Experimental Tests of Mass-Optimized Structural Components." *Structural Concrete* 18 (1): 54–66. https://doi.org/10.1002/suco.201600011.

Herzog, T., R. Krippner, and W. Lang. 2017. *Facade Construction Manual*. Munich: Detail.

Keating, S. 2014. "Beyond 3D Printing: The New Dimensions of Additive Fabrication." In *Designing for Emerging Technologies: UX for Genomics, Robotics, and the Internet of Things*, edited by J. Follett, 379–405. O'Reilly Media.

Knaack, U., T. Klein, M. Bilow, and T. Auer. 2014. *Facades Principles of Construction*. Basel: Birkhäuser Verlag.

Knippers, J., J. Cremers, M. Gabler, and J. Lienhard. 2011. *Construction Manual for Polymers + Membranes*. Munich: Detail.

Labonnote, N., A. Rønnquist, B. Manum, and P. Rüther. 2016. "Additive Construction: State-of-the-art, Challenges and Opportunities." *Automation in Construction* 72 (2016): 347–366. https://doi.org/10.1016/j.autcon.2016.08.026.

Lee, N. A., R. E. Weber, J. H. Kennedy, J. J. Van Zak, M. Smith, J. Duro-Royo, and N. Oxman. 2020. "Sequential Multimaterial Additive Manufacturing of Functionally Graded Biopolymer Composites." *3D Printing and Additive Manufacturing* 7 (5), https://doi.org/10.1089/3dp.2020.0171.

Lindahl, J., A. A. Hassen, S. Romberg, B. Hedger, P. Hedger, M. Walch, T. Deluca, et al. 2018. "Large-Scale Additive Manufacturing with Reactive Polymers." *CMAX Conference Proceedings*, Dallas, TX, USA.

Lussenburg, K., A. Sakes, and P. Breedveld. 2021. "Design of non-Assembly Mechanisms: A State-of-the-art Review." *Additive Manufacturing* 39 (2021): 101846. https://doi.org/10.1016/j.addma.2021.101846.

Mostafavi, S., B. N. Kemper, and C. Du. 2019. "Materializing Hybridity in Architecture: Design to Robotic Production of Multi-Materiality in Multiple Scales." *Architectural Science Review* 62 (5): 424–437. https://doi.org/10.1080/00038628.2019.1653819.

Oxman, N., S. Keating, and E. Tsai. 2011. "Functionally Graded Rapid Prototyping." *Proceedings of VRAP: Advanced Research in Virtual and Rapid Prototyping*, 483–489.

Oxman, N., E. Tsai, and M. Firstenberg. 2012. "Digital Anisotropy: A Variable Elasticity Rapid Prototyping Platform." *Virtual and Physical Prototyping* 7 (4): 261–274. https://doi.org/10.1080/17452759.2012.731369.

Pajonk, A. 2021. "Structured Materials By Additive Manufacturing". *BE-AM Built Environment Additive Manufacturing* 2021. Darmstadt.

Pajonk, A., A. Prieto, U. Blum, and U. Knaack. 2022. "Multi-material Additive Manufacturing in Architecture and Construction: A Review." *Journal of Building Engineering* 45), https://doi.org/10.1016/j.jobe.2021.103603.

Paolini, A., S. Kollmannsberger, and E. Rank. 2019. "Additive Manufacturing in Construction: A Review on Processes, Applications, and Digital Planning Methods." *Additive Manufacturing* 30 (2019), https://doi.org/10.1016/j.addma.2019.100894.

Rios, O., W. Carter, B. Post, P. Lloyd, D. Fenn, C. Kutchko, R. Rock, K. Olson, and B. Compton. 2018. "3D Printing via Ambient Reactive Extrusion." *Materials Today Communications* 15: 333–336. https://doi.org/10.1016/j.mtcomm.2018.02.031.

Sabu, T., K. Krishnan, G. T. Martin, V. R. Ajay, and V. K. Abitha. 2018. *Recycling of Polyurethane Foams*. Oxford: Elsevier. https://doi.org/10.1016/C2016-0-01054-9

Simón, D., A. M. Borreguero, A. de Lucas, and J. F. Rodríguez. 2018. "Recycling of Polyurethanes from Laboratory to Industry, a Journey Towards the Sustainability." *Waste Management* 76 (2018): 147–171. https://doi.org/10.1016/j.wasman.2018.03.041.

Sonnenschein, M. F. 2021. *Polyurethanes Science, Technology, Markets, and Trends*. Hoboken, NJ: John Wiley & Sons, Inc.

Strauß, H. 2013. *AM Envelope – The Potential of Additive Manufacturing for Façade Construction, Faculty of Architecture*. Delft University of Technology.

Tai, N. L., M. Ghasemlou, R. Adhikari, and B. Adhikari. 2021. "Starch-based Isocyanate- and Non-isocyanate Polyurethane Hybrids: A Review on Synthesis, Performance and Biodegradation." *Cabrohydrate Polymers* 265 (2021), https://doi.org/10.1016/j.carbpol.2021.118029.

Taseva, Yoana, Eftekhar Nik, Kwon Hyunchul, Leschok Matthias, and Dillenburger Benjamin. 2020. "Large-Scale 3D Printing for Functionally-Graded Facade." CAADRIA 2020.

Tay, Y. W. D., J. H. Lim, M. Lin, and M. J. Tan. 2022. "Creating Functionally Graded Concrete Materials with Varying 3D Printing Parameters." *Virtual and Physical Prototyping* 17 (3): 662–681. https://doi.org/10.1080/17452759.2022.2048521.

Teoh, J. E. M., C. K. Chua, Y. Liu, and J. An. 2017. "4D Printing of Customised Smart Sunshade: A Conceptual Study." In *Challenges for Technology Innovation: An Agenda for the Future*, edited by C. Rijo, S. Gracio, and S. Antunes, 105–113. https://doi.org/10.1201/9781315198101-24

Tibbits, S., C. McKnelly, C. Olguin, D. Dikovsky, and S. Hirsch. 2014. "4D Printing and Universal Transformation." In *Proceedings of the Association for Computer Aided Design in Architecture 2014*, 539–548. Los Angeles, CA.

Uhlig, K. 2006. *Polyurethan Taschenbuch*. Munich: Carl Hanser Verlag.

Uitz, O., P. Koirala, M. Tehrani, and C. C. Seepersad. 2021. "Fast, low-Energy Additive Manufacturing of Isotropic Parts via Reactive Extrusion." *Additive Manufacturing* 41), https://doi.org/10.1016/j.addma.2021.101919.

Uitz, O., R. Leng, T. Pan, X. Zhao, A. Oridate, C. Seepersad, Z. Ounaies, and M. Frecker. 2023. "Reactive Extrusion Additive Manufacturing (REAM) of Functionally Graded, Magneto-Active Thermoset Composites." *Additive Manufacturing* 67), https://doi.org/10.1016/j.addma.2023.103486.

Wiscombe, T. 2012. "Beyond Assemblies: System Convergence and Multi-Materiality." *Bioinspiration & Biomimetics* 7 (2012), https://doi.org/10.1088/1748-3182/7/1/015001.

Zia, K. M., H. N. Bhatti, and I. A. Bhatti. 2007. "Methods for Polyurethane and Polyurethane Composites, Recycling and Recovery: A Review." *Reactive and Functional Polymers* 67 (8): 675–692. https://doi.org/10.1016/j.reactfunctpolym.2007.05.004.