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INFLUENCE OF COOLING CONDITIONS DURING 3D PRINTING ON THE SWITCHING TEMPERATURE OF A TPU WITH SME

Lang, Anette [a]; Boca, Marius-Andrei [b] and Sover, Alexandru [c]

[a] *Ansbach University of Applied Sciences, Germany (anette.lang@hs-ansbach.de)*
[b] *Ansbach University of Applied Sciences,* Germany *(marius-andrei.boca@hs-ansbach.de)*
[c] *Ansbach University of Applied Sciences,* Germany *(a.sover@hs-ansbach.de)*

ABSTRACT: Shape memory polymers (SMP) are materials with a special structure, designed to react to a certain stimulus. Using such SMPs with 3D printing technology opens up further fields of application thus providing for the so-called 4D printing. After such a printing process it is mandatory for the SMP to still be able to form a crystalline structure, maintaining its own shape memory effects (SME). The crystalline portion or the hard section of polymers is strongly influenced by the cooling rate during the printing process. In order to evaluate the influence of the cooling on the formation of the segments, thermal measurements using Differential Scanning Calorimetry (DSC) were carried out. The test shows that the cold crystallization was evident in each case in the first heating run, but the cooling rate in the FFF (Fused Filament Fabrication) technology could not be reduced to such a level that the switching temperature changed. In order to have an influence on the melt peak, the cooling rate must be increased further. This was demonstrated in the 2nd heating run of the DSC measurements.

KEYWORDS: *Shape memory polymers, 3D printing, Differential Scanning Calorimetry, Cold crystallization, Melting point*

1. INTRODUCTION

The use of smart materials, such as shape memory polymers (SMP), has opened new ways in many areas of life. The application areas include for example automotive, aerospace and medicine implicating traditional applications such as heat-shrinkable tapes and tubes

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but also, for example, in the medical field, biodegradable sutures, actuators, catheters and smart stents. Other interesting examples in the technical field include information storage, which allows for thermally reversible recording, but also temperature sensors and actuators. Due to their structure, SMPs have the ability to change their shape after a certain stimulus is reached. Depending on the polymer, the external stimulus can be e.g. temperature, radiation, pH and many others (Mater, 2007).

Using such materials, a conversion from classical 3D printing to a programmable 4D printing is possible and enhanced. The obtained products can be exposed to a predetermined external stimulus resulting in a self-transforming or self-assembling new object with new forms or functions.

Thermoplastic polyurethanes can exhibit shape memory effects (SME) due to their structural configuration and consequently belong to the group of SMPs (Sahoo NG,2007). The SME in this TPU is based on the fact that shape memory polymers have a network structure and the crossing of a phase transition is associated with a significant change in mechanical properties. The hard segments of the TPU, which consist of the polyurethane groups, form the phase with the highest transition temperature. This temperature is exceeded when the material is fully melted and injection moulded or extruded to give it its permanent shape. The soft segments of the TPU, which consist of long-chain polyester regions, form another phase with a much lower transition temperature. If only the soft segments are melted, a temporary shape can be imposed on the component and this can be physically crosslinked by crystallisation of the soft segments and stabilized in this way. Subsequent melting of the soft segment crystallites then triggers the SME (Thakur and Hu, 2017).

During the last decades, both equipments and materials related to additive manufacturing have evolved rapidly. Those changes gain the attention of researchers and companies. Linking such SMPs with 3D printing technology, for example FFF-technology, opens up further fields of application due to the simple adaptation to new conditions. Even though nowadays, most 4D prints are made using Polyjet 3D printing technology (Ly S. T., 2017), technologies such as FFF are increasingly being implemented, due to their price-related advantages and their user-friendly characteristics.

In any case, for the SME of this SMP, it is important that the crystalline phase and thus the hard segment can form well after processing. The crystalline portion of polymers is always formed as a function of the time and therefore of the cooling rate. These two factors can be strongly influenced by the printing settings in the FFF technology and as a consequence can have an effect on the mechanical properties, but also on the SME itself. In order to be able to evaluate the influence of the cooling on the formation of the segments, thermal measurements were carried out through/using Differential Scanning

Calorimetry (DSC). The main focus was on the cold crystallisation and the melting temperature of the soft segment.

2. EQUIPMENT AND EXPERIMENTAL WORK

For the following experimental research, material Desmopan® 2795A-SMP in the form of granules was used. The TPU based polymer, from Covestro AG, Leverkusen-Germany, has a density of approx. 1.2 g/cm^3 and a switching temperature of approx. 40 ºC. Prior to use, SMPs pellets were dehumidified using AIRID Polymer Dryer, from 3devo B.V., Atoomweg- Netherlands. The device uses heated air and a stirring rotator to obtain dried materials across all surface areas. Based on the material manufacturer's recommendation, the drying process has to be done at 110 ºC for 4 h and with a rotation speed of the mixing device of 15 rpm, followed by a slow cooling in the covered hopper. Subsequently, the granular material is transformed into a 2,85 mm filament using Composer 350 filament maker, from 3devo B.V.. The temperatures used for the four zones of the desktop extruder are 195 ºC/ 205 ºC/ 210 ºC/ 195 ºC and the automatic screw rotation is about 5 rpm. At this stage, the cooling of the filament is extremely important and it is performed with the help of two fans directing the cold air into the outlet area of the hot filament from the nozzle. Using inadequate cooling can lead to an ovalisation of the filament in the guiding area and during winding on the coil or to a varying diameter of the filament due to rapid uncontrolled shrinkage.

The Ultimaker 3 professional desktop printer was used to further create the DSC samples. Because this is the last stage of the material processing, cooling during printing can affect the shape-changing properties of the finished product. Inadequate rapid cooling at this stage is also associated with the effect of physical aging of the material and further post- or cold-crystallisation which lead to an increased degree of crystallisation and a lower melting point of the new lamelar formation (Weeks, 1963). The main considered printing parameters that can affect the shape memory properties are printing and build plate temperatures, printing speed and cooling percentage. Table 1 summarizes the printing conditions for the sample preparation:

Table 1: Printing conditions for the samples

Printing conditions	**Sample**		
	1	2	3
Layer height [mm]	0.2	0.2	0.2
Printing temperature [°C]	230	230	230
Build plate temperature [°C]	**40**	**40**	**24** (RT)
Printing speed [mm/s]	20	20	20
Cooling of fan [%]	**30**	**100**	**100**

The DSC measurements were done with the DSC822 from Mettler Toledo. One measurement comprised several heating and cooling runs, which allows to differentiate between the sample history and the material properties. The temperature range in which the measurement was carried out was always between -100 °C and 230 °C. This temperature range ensured that both the hard and soft segments are melted. The heating rate was constant at 10 K/ min each time, only the cooling rate was changed for each run. The following cooling rates were represented by the experiment: -16 K/min, -8 K/min and -4 K/min.

3. RESULTS

Printing the sample with a 3D printer ensures an optimal contact surface on the aluminum crucible and thus optimal heat transfer into the TPU. As a result, the sample receives a specific prehistory, which can be seen in the first heating run. The following figure shows the whole DSC measurement of the printed TPU sample 1 with the described test sequence (see Figure 1). It was printed under the conditions described in Table 1.

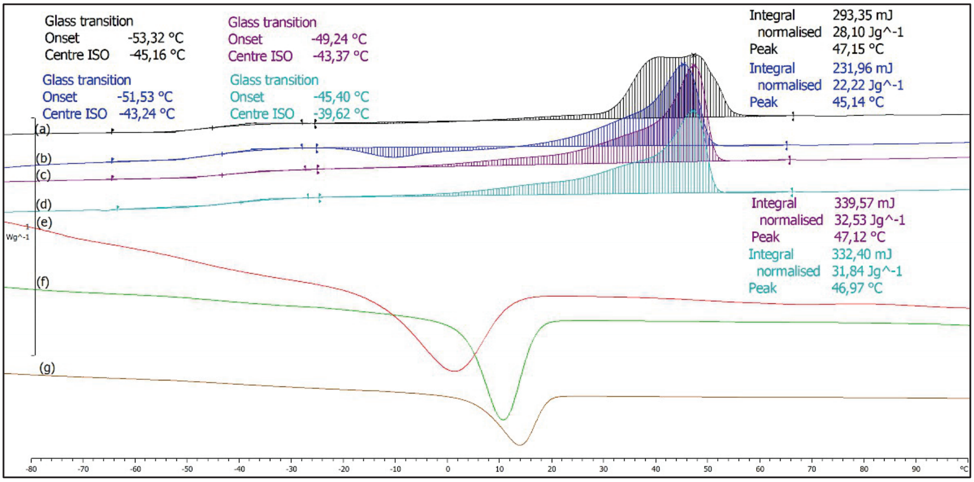

Figure 1. DSC measurement of sample 1 [(a) 1st heating run, (b) 2nd heating run, (c) 3rd heating run, (d) 4th heating run, (e) 1st cooling rung, (f) 2nd cooling run, (g) 3rd cooling run]

In the first heating run of sample 1, the glass transition temperature was -45.16 °C, cold crystallisation was observed and the melt peak of the soft segment is 47.15 °C. Cold cristallization is also established in the 2nd heating run, since the preceding cooling rate was very high, at -16 K. From a cooling rate of -8 K, cold crystallisation no longer occurs. It can be concluded from this that the hard segment has formed completely and also the cristalline phase of the soft segment.

When the melt peaks of the soft segment in the individual heating runs are compared with each other, the melt peak of the 2nd heating run stands out. This differs from the others by approx. 2 K. However, it can be concluded for 3D printing that the current printing conditions (plate temperature 40°C, cooling 30%) have no effect on the melt peak and thus on the switching temperature.

Since only the temperature range between -70 °C and 80 °C is of interest for the current investigations, the results for samples 2 and 3 are only shown in this temperature range (see Figure 2 and Figure 3)

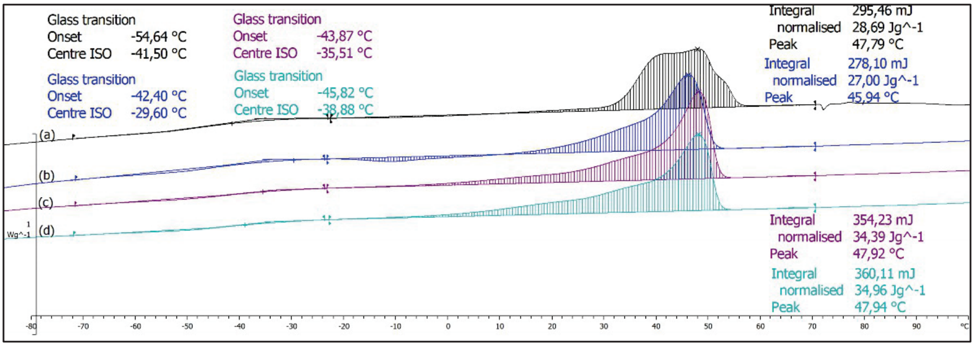

Figure 2. DSC measurement of sample 2 [(a) 1st heating run, (b) 2nd heating run, (c) 3rd heating run, (d) 4th heating run]

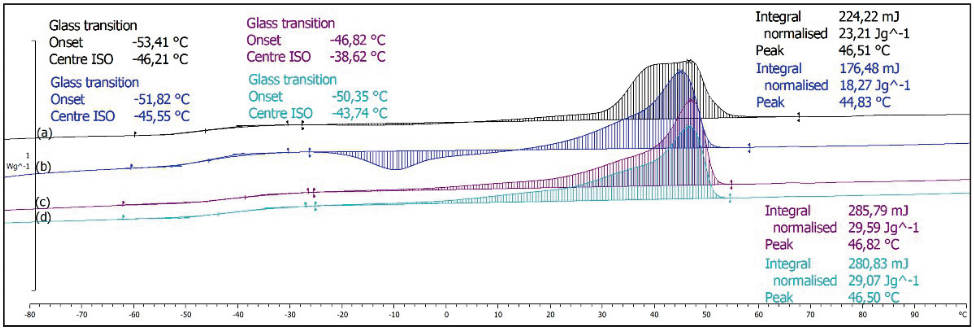

Figure 3. DSC measurement of sample 3 [(a) 1st heating run, (b) 2nd heating run, (c) 3rd heating run, (d) 4th heating run]

A similar picture is obtained for the samples 2 and 3. The glass transition temperatures in the first heating run are about -46°C for both samples. The melt peak in the first heating run is also at the same temperatures as in the 3rd and 4th heating run. Thus, the printing settings used have no influence on the switching temperature of the SMP. In order to have an influence on the switching temperature, the cooling would have to be even faster. This is evident from the second heating run. Because at a cooling rate of -16 K, the melt peak shifts slightly to lower temperatures which could be observed in all three samples. As a result, the crystallisation and therefore the structure of the two segments - the hard one and the soft one - can be influenced.

4. CONCLUSION

The switching temperature is essential for the application of SMPs. It is possible to influence this switching temperature through the manufacturing process if the polymer is not given the opportunity to form its crystalline regions correctly. The cooling rate in the 3D printing application with FFF technology using the Ultimaker 3 could not be reduced to such a level that the switching temperature changed. Nevertheless, cold crystallisation was evident in each case in the first heating run, indicating that a higher degree of crystallisation of the TPU would be possible. Further investigations can determine the influence on the SME. It is also interesting to note that in each case in the first heating run, the melt peak encloses a different area. The extent to which an SME is already stored by the 3D printing must be clarified by further investigations.

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AUTHOR CONTRIBUTIONS

A.L. conceived, designed, performed experiments, analysed the results, wrote the manuscript. M.A.B prepared the samples, analysed the results, wrote the manuscript. A.S. analysed the experiments, technical proof of results, and review of the manuscript. All authors have read and agreed to the published version of the manuscript.

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